ASSOCIATION FOR PROMOTION OF HOLISTIC APPROACH TO ENVIRONMENT

in cooperation with

CENTRE OF EXCELLENCE FOR INTEGRATIVE BIOETHICS

BALKAN ENVIRONMENTAL ASSOCIATION

UNIVERSITY OF APPLIED SCIENCES VELIKA GORICA

1st INTERNATIONAL CONFERENCE

THE HOLISTIC APPROACH TO ENVIRONMENT

PROCEEDINGS BOOK



SEPTEMBER 13th - 14th, 2018

SISAK, REPUBLIC OF CROATIA

PROCEEDINGS BOOK OF THE 1st INTERNATIONAL CONFERENCE THE HOLISTIC APPROACH TO ENVIRONMENT

PUBLISHER

Association for Promotion of Holistic Approach to Environment

Buzetska 25

44000 Sisak

Republic of Croatia

www.cpo.hr

EDITORS

Anita Štrkalj

Zoran Glavaš

Sanja Kalambura

ISSUE

150 copies

ISSN 2623-677X

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in cooperation with

Centre of Excellence for Integrative Bioethics

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University of Applied Sciences Velika Gorica

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Ministry of Environment and Energy

Croatian Environment and Nature Agency

Escola Superior de Tecnologia da Saúde de Coimbra

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City of Sisak

MEDIA COVERAGE

Radio Quirinus

Internet portal www.sisak.info.hr

New Sisak's weekly newspaper

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1st INTERNATIONAL CONFERENCE
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Croatia, Sisak, September 13th-14th, 2018

RESULTS FROM AN APPROACH FOR ADAPTING AGRICULTURAL LAND MANAGEMENT TO CLIMATE CHANGE IN A PROTECTED AREA

Alma Ahmeti*, Spiro Grazhdani*, Adriana Zyfi*

* Agricultural University of Tirana, Faculty of Forestry Sciences, Tirana, Albania

corresponding author: Alma Ahmeti, e-mail: aahmeti@yahoo.com

Original scientific paper

ABSTRACT

The objective of this study was to use a modelling framework to analyse the sensitivity of indicators of four important agricultural functions (crop yield, soil nutrient leaching and water use), to a wide range of agricultural practices for current and future climate conditions. To this end, relevant drivers that explain high proportions of variance of productivity, erosion, and leaching are first identified. Then, impacts of climate change on the indicators are assessed. The method relies on the integration of the crop model CropSyst within a spatial optimization routine. First, CropSyst has been calibrated for case study conditions. Second, CropSyst has been coupled with empirical functions to account for livestock production in terms of fodder consumption, nutrient loads and water intake. Third, by integrating these models into a multi-objective spatial optimization routine, a series of optimum trade-off scenarios for regional adaptation strategies were produced by varying weights of each indicator.

***Keywords**: agricultural land management, climate change adaptation, CropSyst model, multi-objective optimization*

1. INTRODUCTION

In many regions of the world, climate change is expected to have severe impacts on agricultural systems. As many previous impact studies suggest, yields could decrease, water resources may decline, and erosion risk could increase.

Agriculture is an economic sector that is sensitive to climate change. In temperate regions of Europe, increased air temperature is expected to first have positive effects on agriculture through higher crop productivity and expansion of suitable areas for crop cultivation [1]. Changes in temperature and in precipitation pattern may lead to the emergence of new or aggravate existing water-related issues in agricultural production [2, 3] including

competition for land and water resources [4]. Climate change is also expected to aggravate environmental impacts, such as higher erosion rates [5], faster decomposition of soil organic matter and increased nitrogen (N) leaching [6]. Changes in land management are one way to adapt to future climatic conditions, including declining water resources. Consequently, there is a need for adaptation of agricultural land management to reduce the sensitivity of cropping systems to cope with the expected change in climatic conditions. This may include adjustments of crop rotations by shifting from high to low water demanding crops, changing fertilization intensity, use of conservation soil management such as direct seeding, or changing livestock stocking density. To maintain agricultural productivity and preserve finite natural resources, adaptation measures need to be developed at different decision levels, and scientists need to assist planers and decision makers in this process [7].

In previous studies, possibilities for adaptation with respect to one or multiple objectives have mostly been explored by testing alternative scenarios. Systematic explorations of land management possibilities using optimization approaches were so far mainly restricted to studies of land and resource management under constant climatic conditions.

In this study, is bridged this gap and exploit the benefits of multi-objective regional optimization for identifying optimum land management adaptations to climate change. More specifically, this study addresses the following research questions: (i) How can a crop model be calibrated in data-limited situation for climate impact studies?; (ii) Which agricultural practices have the greatest potential for adaptation of multifunctional agriculture?; (iii) What are the trade-offs resulting from adaptation?; (iv) What are the benefits of regional adaptation compared to the status-quo scenario?; (v) Which guidelines can be provided based on this work for adapting agricultural land management in the Prespa Park catchment around 2050?

The method relies on the use of the generic crop model CropSyst [8]. After CropSyst calibration, it was coupled with empirical functions to represent livestock production (i.e. fodder consumption, water intake, and nutrient loads). The model was then integrated within a spatial optimization routine, and applied in combination with climate scenarios to investigate other questions.

2. EXPERIMENTAL

2.1. Case study

The study region is the Lakes Prespa watershed, which is located on the borders between eastern Albania, Greece and Macedonia, in south-eastern Europe and covers an area of about 1,218.1 km^2. It is a high-altitude basin, which includes two inter-linked lakes, the Macro Prespa (259.4 km^2) and the Micro Prespa (47.4 km^2) at approximately 850 meters above sea level [9]. Agriculture is by far the most important sector for employment in Park Prespa. Of the total employed labour pool in the Prespa Basin, approximately seventy-five percent are engaged in agriculture. Land use is dominated by cropland in the flat areas, while permanent grassland dominates areas at elevations above 700 a.m.s.l. Major crops are winter wheat, silage/grain maize, dry beans, and potato [10].

Lakes Prespa area is prone to erosion due to steep slopes and widespread use of conventional tillage. N-leaching had been and is still a concern and is expected to become a more important issue with enhanced mineralization of soil organic matter in a warmer climate.

2.2. Management options

To solve the optimization problem, we considered the following management options (table 1): land use type, crop rotation, intensity, irrigation, and soil management. These management options have important impacts on agricultural productivity, erosion and N leaching and offer great room for adaptation in the study area if well adjusted. The most important factor for controlling erosion was found to be soil management, but crop sequence plays also a very important role, i.e. the fallow time during autumn/winter when highest precipitation amounts occur. N-leaching depends more on soil type than management, but the crop sequence has a significant impact on soil N availability and, thus, on N losses.

Two irrigation options were considered: rainfed and supplemental (automatic) irrigation. In CropSyst, supplemental irrigation is triggered when soil moisture falls under a crop specific threshold and is refilled to a user-defined level.

50 different 5-year rotations for croplands were generated based on rules provided by Vullioud [11], with regard to (i) feasibility of crop sequences and (ii) recommended maximum proportions of crops. In addition to those crop rotations, permanent grasslands and pastures were included in the simulations.

Table 1. Management options used as decision variables in the spatial optimization

Management option		Levels
Land use		cropland, permanent grassland, pasture
Crop sequence		50 crop rotations generated stochastically
Intensity	• N fertilization (all); • clipping (grassland); • stocking density (pasture)	recommended: average N fertilization needs (in kgN), 5 cuts yr^{-1}, 3 LSU[a] ha^{-1} reduced: N fertilization needs -25%, 4 cuts yr^{-1}, 2 LSU ha^{-1} low: N fertilization needs -50%, 3 cuts yr^{-1}, 1 LSU ha^{-1}
Irrigation		rainfed or supplemental (automatic)
Soil management	• tillage operation • residue management	conventional: regular tillage & harvest residues removed conservation: reduced tillage & harvest residues retained

[a] LSU: Livestock Unit (1 LSU = 1 dairy cow)

Management intensity was defined by (i) the total amount of N fertilizer (in kg), (ii) the number of grassland clippings, and (iii) the stocking density.

Two types of soil management were investigated for croplands: conventional (regular tillage and removal of residues) and conservational (no tillage and residues retained). Tillage consisted of plowing 10 days prior to sowing and harrowing one day before sowing. When residues were removed, a loss coefficient of 10 % was used.

2.3. Methods

In this section of the paper is provided an overview of the main steps involved the identification of optimum management schemes with regard to agricultural productivity (crop yields in t ha^{-1} yr^{-1}), minimum irrigation amounts (m^3 ha^{-1} yr^{-1}), minimum erosion (t ha^{-1} yr^{-1}) and minimum N-leaching (kg N ha^{-1} yr^{-1}).

Simulation results for all combinations of agricultural practices and local conditions were computed prior to the optimization for the two climate scenarios and stored in a lookup table. Then, outputs of interest (crop yield *P*, irrigation *I*, erosion *E*, N-leaching *L*) were

passed to an optimization routine to identify in each pixel the best management scheme with regard to a performance criterion.

The optimization routine was repeated several times by modifying the priority given to the different objectives. Results (i.e. objective values and optimized management) were aggregated at the regional level. Of all generated solutions, 16 clusters were defined. For each cluster, the most representative solution was extracted. At last, a set of restrictions was applied (e.g. maximum irrigation, minimum productivity) to identify compromise solutions, which were then analysed in detail in terms of the underlying land use and land management.

2.3.1. Crop model

CropSyst process-based model was integrated for simulating a wide range of management options. In CropSyst, biomass accumulation is calculated as a function of crop potential transpiration and intercepted radiation, corrected by factors reflecting water and N limitations. Final crop yield is the total biomass accumulated over the growing season multiplied by a harvest index.

Annual soil loss due to water erosion is calculated using the Revised Universal Soil Loss Equation (RUSLE) by Renard et al. [12] as:

$$E = R \times K \times L \times S \times P \times C \quad (1)$$

where: *R*: rainfall energy intensity factor; *K*: soil erodibility factor; *L* and *S*: slope length and steepness factors; *P*: soil conservation practice factor; *C*: represents the effect of land management on erosion, which depends on surface residue cover, incorporated residues, crop cover and soil moisture.

*E*was first calculated in CropSyst with reference L_{ref} and S_{ref}. Then, soil loss was adjusted a posteriori in the optimization routine dividing *E* by the reference factors and multiplying it by local *L* and *S* factors based on the slope map. This increased substantially the computation efficiency as CropSyst had to run only once with L_{ref} and S_{ref} for every combination of soil, weather and management.

The components of the simulated N balance include N transport, N transformations, ammonium sorption, and crop N uptake. N transport associated with infiltration is determined on the basis of a so-called bypass coefficient. N transformations developed for CropSyst include net mineralization, nitrification and denitrification. Ammonium in the soil is either absorbed into the soil in solid phase or dissolved in soil water. Crop N uptake is determined as the minimum of crop N demand and potential N uptake. Crop N demand is the amount of N the crop needs for potential growth, plus the difference between the crop maximum and actual N concentration before new growth. Potential N uptake is proportional to maximum N uptake per unit length of root, root length, N availability, and to square of a soil water availability factor.

CropSyst was calibrated following Klein et al. [13] for the most important crops in Lakes Prespa, i.e. winter wheat, maize, potato, and dry beans. CropSyst calibration for grassland was also done.

2.3.2. Livestock production

To account for the lack of animal production in CropSyst, empirical functions were used to estimate daily grazing needs and N excretion on the fields. For the 3 livestock types

considered (dairy/nurse cow, cattle fattening/breeding, calf fattening), daily grazing needs were computed as a function of fodder requirements per Livestock Unit (LSU), the proportion of the time on pastures and the stocking density (optimized number of LSU ha^{-1}). Daily grazing requirements (kg dry matter) were then used in CropSyst to simulate grazing as a clipping management with the calibration for grasslands.

Similarly to the grazing needs, N excretions by animals on pastures were computed as a function of total N excreted in a day by one LSU, the proportion of the time on pastures and the stocking density. In CropSyst, N excretions returning directly to the field were simulated as organic N applications.

2.3.3. Spatial optimization routine

Since neighbourhood effects were not relevant in this study, local optimization could be applied to minimize the computational effort [14]. This means that the optimization problem was solved individually for every pixel.

Simulations were repeated with different sets of management options for each pixel. Optimal solutions determined with respect to the objective function J (eq. 2) were selected. Individual objectives were scaled from 0 to 1 (P', E', L', I') based on regional maximum and minimum values for current climate (for instance $E' = \frac{E - Emin}{Emax - Emin}$). P' was the arithmetic mean of crop yields over the rotation, scaled with regional maximum and minimum values. For croplands, each individual yield in the rotation was scaled separately with crop-specific values. P' for pastures was based on total grazed biomass by animals.

In our approach, J was calculated with all N possible combinations of management ($\{f_k\}_{K=1}^{N}$), separately for the ETH (J^E) and SMHI (J^S) climate scenarios to account for climate projection uncertainties and identify robust optimum solutions. This means in practice that, for every k, the minimum between J^E and J^S was selected to make a new series J^* which was maximized for every pixel.

$$J = \max \{W_p P' + W_i (1-I') + W_e (1-E') + W_l (1-L') \quad (2)$$

where

$$W \in [0; 1] \text{ with an increment of } 0.1 \text{ and } \sum W = 1 \quad (3)$$

In eq. 2, individual weights W were varied systematically to produce a wide range of potential adaptation options with different priorities and to identify possible trade-offs between objectives. Each weight was varied from 0 to 1 with an increment of 0.1 with the constraint that the sum of all weights equals 1. This led to a total of 258 weight combinations representing the same number of adaptation options. The optimization was subject to two further constraints. First, the maximum slope for crop cultivation and use of heavy machinery was set to 33 % based on expert judgment. Second, groundwater protected zones were considered to account for legal management restrictions regarding the spreading of liquid manure and the use of irrigation. Preliminary tests of the optimization routine showed that, if economic values of livestock are not considered, pastures do not appear in the optimal solutions, unless animal production was prescribed. Hence, the number of animals was used as constraint and variables which were optimized were the spatial distribution of pastures for each livestock type and the stocking density. In the optimization routine, pastures were first

distributed across pixels where differences in the objective function values with and without pastures were the highest. Then, croplands were allocated to the remaining units.

2.3.4. Selection of compromise solutions

A subset of compromise solutions was selected for further analysis based on the following criteria:

- agricultural productivity is maintained or improved compared to the reference level;
- monthly irrigation needs are below the maximum amount of water that on average can be extracted from lakes water in the watershed;
- better performances with regard to soil loss and N-leaching than the reference under climate change without adaptation.

3. RESULTS AND DISCUSSION

3.1. How can a crop model be calibrated in data-limited situation for climate impact studies?

Default crop parameter values usually result in poor predictive power of crop models [15] and, for this reason, calibration is indispensable to improve the quality and reliability of simulations in climate impact studies [16]. Arguably the best references for crop model calibration are experimental data [17] but the availability of such data is limited as field experiments are time-consuming and expensive [18]. In this study, a calibration procedure that can be applied to any location covered by an available database is used. The present method consists of three successive steps: (i) the extraction of reference data from the dataset, (ii) a parameter screening to identify sensitive parameters based on the Morris method [19] and (iii) an automatic parameter estimation relying on a genetic algorithm [20].

Besides being widely applicable, the calibration procedure has proved to be feasible at low computation costs thanks to the combination of the Morris method [19] with a genetic algorithm. Repeating the procedure multiple times allows obtaining several reliable parameter sets, which is crucial to estimate effects of parametrization uncertainties in climate impact studies. Parameter sets that perform equally well under present conditions can produce large deviations under future climate, an effect that is even more pronounced when applying the model to other site conditions, even for locations that are in geographic terms relatively close to each other. This suggests that the predictive power of crop models declines substantially when used with conditions that differ significantly from those that are representative for the calibration. This is opposed to the belief that the validity of dynamic crop models is beyond the conditions for which they have been calibrated [18]. This is particularly problematic for climate impact assessments as current climate is not representative for future conditions, which further emphasizes the need to consider parameter uncertainties.

3.2. Which agricultural practices have the greatest potential for adaptation of multifunctional agriculture?

In the simulations presented here, a tendency for productivity to decrease by 2 – 3 % is found, for erosion to increase by 25 – 30 % due to shorter crop growth cycles and increased rainfall intensity in fall/winter, and for N-leaching to increase by 43 – 52 % as a consequence of higher mineralization rates in a warmer and sufficiently wet climate. Crop yields and erosion are highly variable not only with climate scenarios, but also across cropping practices and soil types, suggesting that negative impacts of climate change can be reduced through an adequate choice of management. In contrast, leaching is primarily driven by soil texture and does not depend much on the management scheme, which is in line with a long-term experiment by Askegaard et al. [21].

The variability of crop yields induced by the choice of cropping practices depends exclusively on the crop rotation choice, the intensity level (fertilization and frequency of grass clipping) and the soil management type (tillage operations and residue management), each option explaining about one third of the total variance. A strong correlation between productivity and total N uptake suggests that nutrient management is critically important to maintain productivity, which is in line with the finding by Mueller et al. [22] that the yield gap can be closed with appropriate nutrient management. Simulations indicate that a management scheme that maintains high soil temperature and sufficient humidity enabling high mineralization and nitrification rates would be most beneficial for productivity. This can best be obtained with heavily fertilized rotations involving crops such as sugar beet in combination with conventional soil management, i.e. soil tillage and residue removal. High fertilization has two beneficial effects, a direct one by increasing soluble N in the soil, and an indirect effect by decreasing the C/N ratio of dead materials, which enhances residue nitrogen net mineralization and reduces N immobilization. Conventional soil management increases soil temperature leading to higher mineralization and nitrification rates in turn. However, in the longer run, this option decreases soil organic matter and hence soil fertility.

The combination of practices that can sustain high productivity in the future is expected to be the same as under current climatic conditions. The relative importance of different cropping practices is also expected to remain unchanged under future climatic conditions, with few exceptions. Soil management explains a lower fraction of variance under climate change because higher temperatures lead to higher mineralization rates, increasing N availability and, hence, reducing the effect of soil management on soil temperature. Conversely, the importance of crop rotation slightly increases, and irrigation becomes a relevant option in particular on coarser soils because of their lower water retention capacity.

Erosion is also very sensitive to agricultural practices. Soil losses are mainly controlled by soil management (70 % of variance explained) and to some extent by the crop rotation choice (~10 % of variance explained). Conservation soil management is the most effective practice to reduce erosion. Rotations with short fallow periods thanks to the use of catch crop or cropped grassland and the exclusion of root crops (e.g. potato) have also proved to offer good protection against erosive winter rainfall. Unlike productivity, erosion rates depend on local conditions; erosion is on average 50 % higher on loamy soils than on sandy loam soils because of lower infiltration rates and higher runoff.

Although leaching is not very sensitive to management, the rotation choice can contribute to some extent to reduced leaching, with the establishment of a catch crop or the use of cropped grassland to ensure N uptake in autumn/early winter when temperatures are still sufficient to enable organic matter mineralization. The importance of catch crops to reduce leaching has been widely suggested in the literature, either based on modelling studies [23 - 25], or field experiments [21, 24]. Results show also that leaching is the lowest when a

winter crop follows maize (e.g. winter wheat) to deplete soil N and keep fallow periods to a minimum.

3.3. What are the trade-offs resulting from adaptation?

In agreement with most previous studies [26], a trade-off exists between agricultural productivity and environmental impacts. From the results of this study, it can be anticipated that the trade-offs between agricultural productivity, soil erosion and N-leaching are likely to aggravate with climate change. However, results show that there are possibilities for synergies between the different agricultural functions. Soil management and crop rotation have been found to be the most relevant practices to reduce soil loss and N-leaching, respectively, while productivity also depends greatly on the two latter practices. Note that it may be simpler to identify synergies on loamy soil as N-leaching is not an issue; moreover, it is not advisable to focus on minimizing the latter on this particular soil type because it results in low productivity and high erosion.

For the study region, the use of cropped grasslands in combination with conservation soil management appears to be the most judicious choice to maintain productivity and avoid trade-offs with erosion and N-leaching. Rotations including a grass/legume crop can be beneficial for productivity as grassland serves well as a good pre-crop and a high proportion of grassland also reduces erosion and helps to reduce N-leaching. Conservation soil management is very efficient to prevent excessive soil erosion and soil organic matter loss maintaining soil fertility in the long run. Moreover, conservation soil management improves clean water provision. Indeed, N-leaching is substantially reduced on sandy loam soil due to reduced mineralization, while the decrease in runoff and thus increase in permeability due to this management type has low effects on a soil that is already very permeable and prone to leaching. As a downside of conservation soil management, productivity is decreased by ~ 40 % on average under current climatic conditions due to reduced mineralization.

However, under climate change this effect is reduced (~-20 %), which indicates that the synergistic effects of conservation soil management could increase in the future. Trade-offs can also be envisaged from the time scale perspective. A positive impact of residues removal on productivity has been suggested, which is in contrast to the view that management decisions such as no-till and returning crop residue to the field increase soil organic matter content, improve infiltration and soil water retention, and thus help to maintain soil fertility in the long run and increase the resilience of cropping systems to climate change [27]. However, the positive effect of conventional soil management is short-lived as CropSyst simulates a decline in soil fertility in the longer term.

3.4. What are the benefits of regional adaptation compared to the status-quo scenario?

Without changes in agricultural land management, mean regional productivity of crops in the Prespa Park catchment will decrease by 0 – 12 % on the time horizon 2050, in parallel with an increase in water needs by 15 - 45 %. In contrast to those moderate changes in productivity, impacts of climate change on erosion and leaching are expected to be largely negative (increase by 25 – 40 % for leaching and 20 – 30 % for erosion). These results emphasize that, in order to cope with increasing environmental pressure, adaptation is needed, either through adjustment of agricultural practices (e.g. crop rotations, tillage operations), or redistribution of agricultural land uses.

Results show that a wide range of different adaptation options is possible depending on the goals to achieve. If productivity is the only objective, then nearly all grasslands of the region should be converted to croplands with high shares of irrigated maize and potato. In those conditions, crop yields would increase by 35 % compared to the current level, which is more than the 10 – 15 % yield adaptation benefits suggested by Lotze-Campen and Schellnhuber [28]. However, consequences on the environment would be disastrous, leading to an increase of erosion by 45 – 54 % and leaching by 64 - 77 % compared to the current situation. Furthermore, irrigation would have to be 2-4 times higher, exceeding systematically average surface water availability during summer months. In contrast, if the main objective is to reduce environmental impacts, then crop yields would decrease by up to 23 %.

3.5. Which guidelines can be provided based on this work for adapting agricultural land management in the Prespa Park catchment around 2050?

Adaptation of agricultural land management to climate change in the Prespa Park catchment will be necessary for the time horizon 2050, mostly to limit increasing environmental impacts. In order to cope with changing climate conditions and maintain productivity while minimizing environmental impacts, general recommendations to be undertaken have been identified:

- maintaining recommended intensity level. Today's recommended intensity level is and will be best as it has a positive effect on productivity, which in turn has an influence on erosion (i.e. the more biomass the better the soil protection) without leading to high N leaching rates;
- increased use of conservation soil management. Reduced tillage and retaining harvest residues are known to improve soil organic matter and conserve soil fertility [29], while increasing soil surface protection and reducing runoff [30, 31]. In addition, it has been shown that impacts on soil temperature and N mineralization become less important as air temperature increases. However, conventional soil management can still be applied on flat areas that are not subject to erosion;
- decrease in share of irrigated spring crops. Water-stress sensitive crops (e.g. potato) should be partly replaced by winter rapeseed. Winter rapeseed is an eco-friendly crop that can serve as a catch crop to reduce N-leaching during the autumn-winter period thanks to its high capacity to take up nitrate from the soil [32]. In addition, winter rapeseed has been found to limit soil loss [33] and to perform well under climate change [34];
- relocation of pastures around villages (medium elevation). Very steep slopes are found in the region around villages and locating pastures in those areas allows to drastically reducing erosion;
- irrigation applied in priority on coarse soils. Optimal irrigation patterns do not differ significantly from current irrigated areas as irrigation is and will be worthwhile only in the lowlands of the Prespa Park. However, it would be preferable to apply water extracted from the Lakes Prespa on coarse soils that are more distant from them as opposed to the current practice where irrigation is mostly applied on soils located close to the lakes with high water retention capacity.

4. CONCLUSION

In this study are identified optimum options for adaptation of agricultural land management to climate change for a small watershed where adaptation will be necessary on the horizon 2050, mostly to limit increasing environmental impacts. To this end, is applied a modelling approach, relying on a crop and a livestock model which were integrated within a spatial multi-objective optimization routine. The multifunctional role of agriculture was examined by including four of the most important aspects of Albanian agriculture for future adaptation, namely agricultural productivity, water saving, soil preservation and clean water provision.

The method presented here allowed identifying several acceptable solutions. Are identified the following general recommendations to be taken to cope with climate change around 2050 in the Prespa Park watershed:

- conservation soil management should be more widely used at the expense of conventional soil management, except in flat areas;
- high elevation grasslands should be converted to croplands under climate change, as those areas become favourable for crop cultivation in a warmer climate; however, grasslands should remain at high elevations on coarse soils;
- shares of irrigated spring crops should decrease, while shares of early harvested winter crops (i.e. rapeseed and barley) should increase;
- pastures should be located on steeper slopes in the region (medium elevation) to avoid severe soil losses.

The taken results are encouraging and could provide a useful basis for discussion with regional planners about the strategies to be implemented for achieving the most desirable solution(s).

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Acknowledgments

The research work reported in this paper was supported by grants from the Albanian Ministry of Education and Research in the framework of the Program ''Research for Development" and Agricultural University of Tirana. Their kindly providing the field data for this study is greatly appreciated.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

POTENTIAL OF ARTEMISIA ABSINTHIUM FOR PHYTOREMEDIATION OF SOILS CONTAMINATED WITH HEAVY METALS

Violina Angelova*, Marija Ihtjarova*

*Agricultural University-Plovdiv, Plovdiv, Bulgaria

corresponding author: Violina Angelova, e-mail: vileriz@abv.bg

Original scientific paper

ABSTRACT

A field study was conducted to evaluate the efficacy of wormwood (*Artemisia absinthium*) for phytoremediation of contaminated soils. The experiment was performed on an agricultural fields contaminated by the Non-Ferous Metal Works near Plovdiv, Bulgaria. The content of heavy metals in different parts of wormwood (roots, stems, leaves and flowering tops) was determined by ICP. Wormwood is a plant which is tolerant to heavy metals and can be grown on contaminated soils. Based on the obtained results and using the most common criteria, wormwood can be classified as Pb and Cd hyperaccumulator and Zn accumulator, therefore, this plant has suitable potential for the phytoremediation of heavy metal contaminated soils. Favourable is also the fact that heavy metals do not influence the development of the wormwood, as well as on the quality and quantity of the essential oil. The possibility of further industrial processing will make wormwood an economically interesting crop for farmers of phytoextraction technology.

***Keywords**: contaminated soils, heavy metals, phytoremediation, wormwood*

1. INTRODUCTION

Phytoremediation is an inexpensive and environmental-friendly method used for cleaning up heavy metal contaminated soils [1]. Up to now, more than 400 plant species belonging to 45 families with extremely high capacity for accumulation of heavy metals have been known [2 - 5]. These plants are classified as hyperaccumulators. Generally, these plants are characterized by low biomass and are not suitable for effective phytoremediation [6]. The demand and identification of plants with large biomass and capacity to absorb significant amounts of metals are of growing interest.

It has been found that the medicinal plants can accumulate larger amounts of heavy metals such as Cd, As, Pb and Hg compared to other plants [7]. It is known that plants of the Artemisia family can accumulate metals from soils [8 - 11]. The plants of the Artemisia genus

are also widespread in Bulgaria and have a large biomass production capacity. However, there are no studies on the possibilities of heavy metals accumulation in wormwood when grown on contaminated soils.

Artemisia absinthium L. is a perennial shrub of the genus Artemisia and occurs as a weed in North Africa, Asia, Europe and New Zealand [12, 13]. The plant is known with different names such as wormwood (in English), grand absinthe (in French) and wermut (in German) [14]. It is a perennial silver grey herbaceous plant, covered with a multitude of hairs with a pleasant aroma and a bitter taste. The stem is 40 - 120 cm high, branched at the top and woody at the base [12]. Leaves on both sides are covered with silvery silk hairs. The flowers are tubular, yellow, without petioles, placed on a hairy torus. Wormwood blooms from July to September [15].

Wormwood has been known to humans as a spice and healing plant since ancient times. These properties are due to content of essential oils, tannins, resins, flavonoids, fatty acids, vitamins (C, B6), and minerals (K, Ca, P, Fe, Na) [16 - 18]. Wormwood contains 0.1 - 1.5 % of oil [19 - 21]. The main components of oil are oxygen derivatives of bicyclic terpenes - the alcohol thiol and the ketone thujone, which are considered to be the characteristic ingredients for the wormwood oil [22]. The etheric oil also contains compounds such as monocyclic terpene phellandrene, bicyclic sesquiterpene cadinene and azulene sesquiterpene chamazulenogen, which is oxidized in the air to chamazulene. It has been proven that the bitter substances contained in the plant (absinthin) stimulate muscles of digestive organs, increase secretion of digestive juices and improve digestion [17]. The ingredients contained in the essential oil (thujone, thiol, etc.) excite the central nervous system and have a beneficial effect on neurological diseases [23]. Chamazulene has an anti-inflammatory effect and the ability to remove spasms of the smooth muscle organs (stomach, bronchi, etc.). Wormwood is used to treat gastritis and other inflammations of the stomach, liver and bile diseases [24].

The purpose of this work is to undertake a comparative study, which allows us to determine the quantities and the deposits for accumulation of Pb, Zn and Cd in the vegetative organs of wormwood, as well as the possibilities to use the plant for phytoremediation of heavy metal contaminated soils.

2. EXPERIMENTAL

The experiment was performed on an agricultural fields contaminated by Zn, Pb and Cd, situated at different distances (0.5, and 15.0 km) from the source of pollution, the Non-Ferrous-Metal Works (NFMW) near Plovdiv, Bulgaria.

Characteristics of soils are shown in table 1. The soils were neutral to slightly calcaric, with moderate content of organic matter and essential nutrients (N, P and K) (Table I). The psedo-total content of Zn, Pb and Cd is high and exceeds the maximum permissible concentrations (MPC) in soil 1 (from 0.5 km from the NFMW) (table 1).

The study included wormwood grown on areas located at different distances from the source of contamination NFMW Plovdiv (0.5 km and 1 km). Wormwood is grown according to conventional technology. Five plants of each of the areas were used for the analysis. Upon reaching the stage of flowering, wormwood was harvested and the content of Pb, Zn and Cd in different parts - roots, stems, leaves and flowering tops was determined. Before the analyses root samples were thoroughly washed by distilled water to remove all adhering soil particles. Samples were oven dried to constant weights at 105 °C. Each dried sample was ground to powder using a blender. One gram of each sample was used for analysis. Pseudo-total content of metals in soils was determined in accordance with [25]. The available

(mobile) heavy metals contents were extracted by a solution of DTPA (1 M NH_4HCO_3 and 0.005 M DTPA, pH 7.8) [26]. The contents of heavy metals (Pb, Zn and Cd) in the plant material (roots, stems, leaves and flowering tops) were determined by the method of the microwave mineralization. The quantitative measures were carried out by ICP method (Jobin Yvon Emission - JY 38 S, France).

Table 1. Characterization of the soils

Parameter	pH	EC, dS/m	Organic C,%	N Kjeldal,%	P, mg/kg	K, mg/kg	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg
Soil 1(S1) 0.5 km	7.4	0.15	2.2	0.34	625.6	6960	2509.1	2423.9	64.3
Soil 2 (S2) 15 km	7.5	0.15	1.54	0.12	387.3	6780	49.4	172.7	1.0

MPC (pH 6.0 - 7.4) – Pb -100 mg/kg, Cd - 2.0 mg.kg, Zn -3 20 mg/kg
MPC (pH > 7.4) – Pb – 100 mg/kg, Cd – 3.0 mg/kg, Zn - 400 mg/kg

Digestion and analytical efficiency of ICP was validated using a standard reference material of apple leaves (SRM 1515, National Institute of Standards and Technology, NIST). The Bioconcentration factor (BCF) and Translocation factor (TF) were calculated. BCF root is a ratio of the content of heavy metals in plant roots to soil content (BCFroots = [Metal] roots/[Available metal] soils).

BCF shoot is defined as the ratio of the metal concentration in the above-ground mass of the plant and in the soil (BCFshoots = [Metal] shoots / [Available metal] soils).

The Translocation Factor (TF) a ratio of the content of heavy metals in plant shoots to plant roots (TF = [Metal] shoots / [Metal] roots).

3. RESULTS AND DISCUSSION

3.1. Soils

The results presented in tables 1 and 2 shows that in the soil samples S1 (taken from the area situated at the distance of 0.5 km from NFMW), the reported values for Pb were exceeding MPC approved for Bulgaria and reached to 2509.1 mg/kg. In the area located at a distance of 15 km, the contents of Pb significantly reduce to 49.4 mg/kg. Similar results were obtained for Cd and Zn. The results for the mobile forms of the metals extracted by DTPA show that the mobile forms of Cd in the contaminated soils are the most significant portion of its total content and reached to 57.2 %, followed by Pb with 33.8 % and Zn with 9.8 %.

In the soil located at a distance of 15 km from KCM the mobile forms of Cd are the most significant part of its and reach up to 70 %, followed by Pb - 43.5 % and Zn -22.5 %.

Table 2. DTPA-extractable Pb, Zn and Cd (mg/kg) in soils sampled from NFMW

Soils	Pb		Cd		Zn	
	mg/kg	%*	mg/kg	%	mg/kg	%
S1	849.1	33.8	36.8	57.2	236.8	9.8
S2	21.5	43.5	0.7	70	38.9	22.5

*DTPA -extractable / total content

3.2. Content of heavy metals in wormwood

The soil conditions and the type of plants affect the uptake of heavy metals by plants and their accumulation in the different parts of plants depends on their content in the soil. Plants grown on contaminated soils accumulate heavy metals in the vegetative organs, mostly in the roots, as they are in contact with contaminated soil. In some plants, however, the substantial content of the heavy metals is accumulated in the above-ground mass [27].

To clarify the issues of absorption, accumulation and distribution of heavy metals in the vegetative organs of wormwood, samples of roots, stems, leaves and flowering tops were analysed. Table 3 presents the results obtained for the content of heavy metals in the organs of studied essential oils crop. Substantial differences were discovered in the content of the elements in different parts of the wormwood. Most of them (Pb, Cd and Zn) are accumulated in the aboveground parts of the wormwood (the leaves and flowering tops).The content of Pb in the roots of the wormwood grown at 0.5 km from NFMW reaches up to 1913.0 mg/kg, Zn – 172.1 mg/kg and Cd – 102.7 mg/kg. The obtained values for the heavy metals (Cd, Pb and Zn) in the roots are much higher than the values considered by Orav et al. [19] as toxic for the plants (0.1 mg/kg Cd, 30 mg/kg Pb, 100 mg/kg Zn).

Table 3. Content of Pb, Cd and Zn (mg/kg) in wormwood

Element	Distance, km	Roots, x ± sd	Stems, x ± sd	Leaves, x ± sd	Flowering tops, x ± sd	Oil, x ± sd
Pb	0.5 km	1913.0±8.7	123.5±2.3	4414.9±10.8	1223.3±6.8	0.11+0.01
	15 km	3.3±0.5	1.1±0.3	7.2±0.8	4.0±0.5	0.02±0.01
Cd	0.5 km	102.6±2.1	33.5±0.7	225.1±3.5	163.9±2.4	nd
	15 km	0.5±0.05	0.3±0.05	0.7±0.05	0.3±0.05	nd
Zn	0.5 km	1724.1±7.5	117.2±3.6	2461.8±9.7	871.6±6.9	0.44±0.05
	15 km	55±0.8	25.3±0.5	114.0±3.4	67.7±1.0	0.14±0.02

x- average value(mg/kg) from 5 repetitions; sd - mean standard deviation, nd- non detected

The studies of Rachieru et al. [18] lead to the conclusion that wormwood accumulates heavy metals primarily in the aboveground parts. The roots are the main plant organ which is in contact with the contaminated soil and capable to accumulates heavy metals. Wormwood has fibrous roots. It has short rhizomes with many branches that are covered with silky hairs like the above-ground parts of the plant [28]. The major portion of the roots is located in the soil layer from 30 to 50 cm. Probably this is the reason why wormwood accumulates significant amount of heavy metals in the roots.

The content of heavy metals in the above-ground mass is greater than that of the root system. A significant accumulation of Pb is found in the leaves and stems of the wormwood. The content of this element reaches up to 123.5 mg/kg in stems, and 4414.9 mg/kg in leaves of the wormwood grown at a distance of 0.5 km from NFMW. Probably a portion of the accumulated heavy metals in the above-ground mass of the wormwood is also due to aerosol pollution, which can be explained by the anatomical and morphological characteristics of the crop. The greater accumulation of Pb in the above-ground mass is probably due to the fact that the leaves and stems of the plant are covered with fine silky hairs, which favours the attachment of the aerosols and their accumulation therein. The content of Cd in the stems and leaves of the wormwood grown at a distance of 0.5 km from NFMW reaches up to 33.5 mg/kg and 225 mg/kg, respectively, values considered to be toxic to plants. According to

Kabata Pendias and Pendias [7] 5.0 mg/kg is considered to be a toxic value for the plants. Our results show the ability of the wormwood to accumulate Cd in the above-ground mass.

The content of Zn in the stems and leaves of the wormwood grown at a distance of 0.3 km from NFMW reaches up to 117.2 mg/kg, and 2461.8 mg/kg, as these values are also higher than the critical values for plants – 100 - 400 mg/kg.

The content of heavy metals in the stems and leaves of thewormwood grown at 15 km from NFMW reaches up to 1.1 mg/kg and 7.2 mg/kg (Pb), 0.3 mg/kg and 0.7 mg/kg (Cd) and 25.3 mg/kg and 114.0 mg/kg (Zn).

The results obtained show that significant quantities of heavy metals are accumulated in the above ground part of wormwood, with their values significantly exceeding the widely accepted critical toxic levels [29, 30], but none of the symptoms of heavy metal toxicity have been detected. This shows that common wormwood has high tolerance to heavy metals. The results we obtained are in line with the finding of Alirzayeva et al. [10], that in the Artemisia species studied, larger amounts of Zn are accumulated in their above ground parts. Zn concentrations vary from 600 to 900 mg/kg in the above ground mass, and from 100 to 330 mg/kg in the roots. The results we obtained are much higher than the results of Badea [11] and Fischer et al. [31] (5.37 - 14.42 mg/kg in herbs), 0.118 - 0.434 mg/kg Cd and 0.005 - 0.012 mg/kg Hg, as well as the results of Chizola [32] and Steff et al. [33] (0 - 0.5 mg/kg Cd, 0 - 2.25mg/kg Pb, and 41.3 - 41.9 mg/kg Zn).

According to Rachieru et al.[18], *Artemisia absinthium* L. has the ability to accumulate heavy metals mainly in the above ground parts (stems and leaves), when grown on a landfill. According to the authors, the high values of heavy metals in the above ground parts cannot be explained only by the soil absorption, but are also due to the adsorption of heavy metal aerosols from the air. Similar results were found by Imelouane et al. [34], according to whom significant amounts of Pb and Cd in wormwood leaves are due to road traffic (Pb - 1036.1 mg/kg, Cd - 20.6 mg/kg, Zn - 798.1 mg/kg).

The heavy metal content in the flowering tops is considerably lower in comparison to the root system and the above-ground mass of the plants. The contents of Pb, Zn and Cdi n the flowering tops of the wormwood grown at a distance of 0.5 km from NFMW reaches up to 1223.3 mg/kg, 871.6 mg/kg and 163.0 mg/kg, respectively. With increasing the distance from NFMW a clear trend is seen towards reducing the content of heavy metals in the inflorescences of the studied crop. Significantly lower is the content of heavy metals in the flowering tops of the wormwood grown at 15 km from NFMW. The content of Pb in the flowering tops reaches up to 4.0 mg/kg, Zn- up to 67.7 mg/kg and Cd – up to 0.3 mg/kg. Probably a portion of the accumulated heavy metals in the flowering tops of the wormwood is due to the aerosol pollution.

The heavy metal content in the essential oil from wormwood was also determined. The results obtained show that the majority of the heavy metals contained in the flowering tops of the wormwood do not pass into the oil during the distillation, therefore their content in the oil are much lower. Pb content in the essential oil of wormwood reaches up to 0.11 mg kg, Zn up to 0.44 mg/kg, while the content of Cd is below the limits of the quantitative measurement of the method used. Significantly lower are the results in the essential oil of wormwood grown at a distance of 15 km from NFMW – 0.02 mg/kg Pb and 0.14 mg/kg Zn. The results obtained show that the content of heavy metals in the essential oils is much lower compared to the flowering tops of the wormwood, and the amounts of Pb, Zn and Cd in the oil of wormwood are lower than the accepted maximum values and meet the requirements of an environmentally friendly product (0.1 mg/kg Pb, 0.05 mg/kg Cd). The results confirms the ones reported by Angelova et al. [35] and Zheljazkov et al. [36], which found that the heavy metal content in the essential oil is very low and is not affected by the level of soil contamination with heavy metals. Essential oils contain only traces of heavy metals in

distilled oils because these types of molecules are too heavy and large to be volatilized under distillation process.

The distribution of heavy metals in the organs of the wormwood has a selective nature, which decreases in the following order: leaves> roots> stems> flowering tops (figure1).

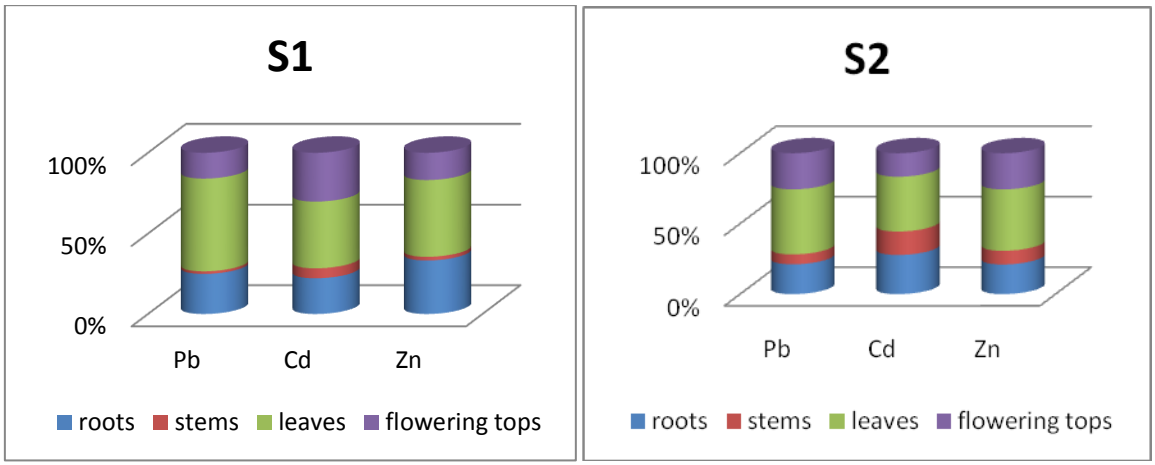


Figure 1. Distribution of heavy metals in wormwood grown in contaminated (S1) and uncontaminated (S2) soils

There is a distinct feature in the accumulation of heavy metals in the vegetative organs of the wormwood. The wormwood accumulates heavy metals through its root system, a significant portion of the heavy metals are retained by the roots, and most of them move and accumulate in the above-ground parts (stems, leaves and flowering tops). The results obtained show that the wormwood can be successfully grown in the areas exposed to the heavy metals pollution. On the one hand, that may reduce the risk of the use of these areas for growing food crops. On the other hand, the selective accumulation of Pb, Zn and Cd in stems, leaves and flowers makes the wormwood a very lucrative for the purposes of phytoremediation.

To determine the extent to which wormwood accumulates heavy metals and to which group of plants it can be assigned (hyperaccumulators or accumulators) we used the existing criteria for determination of heavy metal accumulation in plants. Plants have the ability to accumulate metals, and some of them in large quantities (100 times more than other plants under the same conditions, without showing any adverse effects). Plants that have the ability to tolerate and accumulate heavy metals in quantities greater than the toxic levels are known as hyperaccumulators. In recent years, the number of studies on the use of hyperaccumulators for remediation of contaminated areas, owing to their capacity of these plants to absorb heavy metals from contaminated soil and accumulate them in their aboveground biomass, has been steadily increasing.

The classification of plants as hyperaccumulators, accumulators, indicators and non-accumulator species is based on precise and clear criteria [37]. Plants that contain high quantities of heavy metals in their root biomass but whose aboveground biomass/root biomass ratio is less than 1, belong to the non-accumulator species. According to Baker and Walker [38], indicator species are those whose heavy metal content is proportionate to the heavy metal content in the soil. Plants can be classified as hyperaccumulators if they meet the following criteria: (a) have an aboveground biomass/root biomass ratio > 1; (b) have an extraction ratio (the ratio of the heavy metal content in the above ground biomass to the heavy metal content in the soil) > 1; (c) have a heavy metal content which is 10 - 500 times higher than that of plants grown in non-contaminated soils; and (d) contain more than 1000 mg/kg of

copper, lead, nickel, chromium; more than 100 mg/kg of cadmium or more than10,000 mg/kg of zinc [39].

The values obtained for BCF and TF, are the most important test that can be used to assess the potential of the plants for phytoremediation. Our results indicate that in the wormwood both factors BCF shoot and TF are higher than 1 and by this indicator it can also be classified as an accumulator in terms of Pb, Zn and Cd (table 4).

Table 4. Uptake of heavy metals from wormwood

Element	TF		BCF root		BCF shoot	
	0.5 km	15 km	0.5 km	15 km	0.5 km	15 km
Pb	2.4	2.5	2.3	0.15	5.3	0.4
Cd	2.1	2.0	3.3	0.7	7.0	0.4
Zn	1.5	2.5	7.3	1.4	10.9	3.6

BCF roots=[Metal]roots/[Available metal]soils, TF=[Metal]shoots/[Metal]roots),
BCFshoots=[Metal]shoots /[Available metal]soils

Similar results have been obtained by Alirzayeva et al.[10], according to whom various types of Artemisia collected at a distance of 10 m from the source of contamination have been found to have the highest bioaccumulative factors: Zn (14.9), Cd (13.4), Cu (1.9), Pb (12.1) and Ni (0.4).The results obtained on Zn, Cd, and Pb bioaccumulation factors are much higher than 1, suggesting that wormwood has significant potential of wormwood for phytoextraction. The bioaccumulation factor (BCF) in metal hyperaccumulators is always higher than 1 [40]. It decreases with the increasing levels of total heavy metals in the soil [41], which contradicts to our results.

Comparing the criteria shows that in terms of Pb and Cd all criteria necessary for referral of the wormwood to the hyperaccumulatorsare covered. In terms of Zn only 1 of the criteria is not covered - sufficient accumulation of Zn in the above-ground mass (less than 10000 mg/kg Zn) and movement of Zn from the soil to the above-ground mass. Therefore, the wormwood can be attributed to the group of accumulators of Zn.

Although phytoremediation is a new technology, in recent years many studies have been conducted in an attempt to determine how plants absorb metals, the mechanisms of movement of translocation of metals from the roots to the above-ground mass, the storage and their detoxification. One of the main principles of phytoremediation is to find suitable plant species that can be grown on contaminated soils. Our results strongly suggest that the wormwood is a crop that is tolerant to heavy metals and can be grown on heavy metals polluted soils. It can be attributed to hyperaccumulators of Pb and Cd and to accumulators of Zn and can be successfully used for phytoremediation of soils contaminated with Pb, Zn and Cd.

4. CONCLUSION

Based on the obtained results, the following conclusions can be made:

- there is a clear distinction in the accumulation of heavy metals in vegetative organs of wormwood. Wormwood accumulates heavy metals through its root system, a significant portion of the heavy metals is retained by the roots, but most of the heavy

metals move and are being accumulated in the above-ground parts (stems, leaves and flowering tops),

- wormwood is a crop tolerant to heavy metals; it can be attributed to hyperaccumulators of Pb and Cd and accumulators of Zn, and can be successfully used in phytoremediation of heavy metal polluted soils,
- the concentrations of Pb, Zn and Cd in the wormwood oil are lower than the accepted maximum values and meet the requirements of an environmentally friendly product. Processing of the flowering tops to oil and the use of the obtained oil in perfumery will significantly reduce the cost of phytoremediation.

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Acknowledgements

The financial support by the Bulgarian National Science Fund Project DFNI H04/9 is greatly appreciated.

SISTEMATIZACIJA I UPOREDNI PREGLED ZAKONSKE REGULATIVE EVROPSKE UNIJE I REPUBLIKE SRBIJE U OBLASTI UPRAVLJANJA PROCEDNIM VODAMA KOMUNALNIH DEPONIJA ČVRSTOG OTPADA

SYSTEMATIZATION AND COMPARATIVE OVERVIEW OF THE EUROPEAN UNION AND THE REPUBLIC OF SERBIA LEGISLATION IN THE AREA OF MUNICIPAL SOLID WASTE LANDFILL LEACHATE MANAGEMENT

Katarina Antić*, Dragan Adamović*, Maja Turk Sekulić*, Jelena Radonić*

*Univerzitet u Novom Sadu, Fakultet tehničkih nauka, Republika Srbija

autor za korespondenciju: Katarina Antić, e-mail: antickatarinaa@gmail.com

Pregledni rad

SAŽETAK

Zakonska regulativa Evropske Unije i Republike Srbije u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada nije strogo definisana. Sistematizacija zakonske regulative u navedenoj oblasti ostvarena je usvajanjem integrativnog pristupa. Primenom relevantne zakonske regultaive iz oblasti upravljanja otpadom i upravljanja vodama formirana je celovita slika upravljanja procednim vodama. Nakon izvršene sistematizacije, pristupljeno je pregledu i isticanju korelativnosti zakonske regulative na nivou Evropske Unije i Republike Srbije u navedenoj oblasti. Naposletku, istaknute su prednosti implementacije formiranog pristupa u navedenoj oblasti, kako na nivou Evropske Unije, tako i na nivou Republike Srbije. Priemenom referentnih zakonskih akata omogućiće se uspostavljanje efektivnog sistema monitoringa u periodu nakon zatvaranja deponijskih lokaliteta, prikupljanje podataka sa aspekta kvalitativnog i kvantitativnog sastava procednih voda, čime se značajno doprinosi uvidu i razumevanju procesa generisanja i morfologije procednih voda u navedenom periodu, kao i sagledavanje tehničko-tehnoloških poteškoća prilikom dostizanja strogih graničnih vrednosti za ispuštanje tretiranih procednih voda u vodoprijemnike.

***Ključne riječi**: zakonska regulativa, Evropska Unija, Republika Srbija, upravljanje procednim vodama, upravljanje otpadom, upravljanje vodama*

ABSTRACT

The legislation of the EU and the Republic of Serbia in the area of municipal solid waste landfill leachate management is not strictly defined. It was systematized through an integrative approach. A complete picture of leachate management was formed by applying relevant legislation in waste management and water management. After completing systematization, the correlation of EU and Serbian legislation was reviewed and accentuated. Finally, advantages of implementing the formed approach were highlighted, at the level of both the EU and the Republic of Serbia. The application of relevant legal documents will allow the establishment of an efficient monitoring system in the period after closing landfill sites, data collecting from the aspect of qualitative and quantitative leachate composition, thereby contributing to the perception of generation and morphology of leachate in this period, and the consideration of technical-technological difficulties in reaching strict limit values for discharging treated leachate into water recipients.

***Keywords**: legislation, the European Union, the Republic of Serbia, leachate management, waste management, water management*

1. UVOD

Procedne vode predstavljaju entitet na koji utiče kompleks činilaca, kako unutar samog tela deponije (starost deponije, morfološki sastav otpada, temperatura i sadržaj vlage, migracioni tok tečnosti, tehnologije tretmana otpada pre odlaganja, debljina tela deponije, faze dekompozicije otpada), tako i van nje (meteorološki parametri, sa akcentom na godišnje količine padavina, smena godišnjih doba). Proces formiranja deponijskog filtrata obuhvata rastvaranje čvrstih supstanci u vodi koja se procеđuje kroz telo deponije i izdvajanje rastvorenih ili suspendovanih materija nastalih biološkim i hemijskim procesima koji se neminovno odigravaju unutar tela deponije [1]. Proces generisanja procednih voda predstavlja integralni deo ciklusa kretanja vode na deponiji. Početak ciklusa odlikuje se procеđivanjem prispelih atmosferskih padavina kroz aktivne slojeve deponovanog otpada. U okviru navedenog procesa vrši se rastvaranje organskih, neorganskih i ksenobiotičkih organskih supstituenata, teških metala i potencijalnih hazardnih supstanci prisutnih u aktivnim slojevima deponovanog otpada, kao i proces spajanja procеđenih atmosferilija sa vlagom procеđenom iz aktivnih slojeva deponovanog otpada čime se formira optimalan medijum za transport polutanata. Izvestan deo formiranog filtrata otiče sa deponije, deo se vraća u atmosferu isparavanjem sa gornje površine deponije ili vegetacije (transpiracija), dok se preostali udeo formiranog filtrata zadržava u gornjem sloju deponije, pri čemu dolazi do povećanja vlage u otpadu, te i obezbeđenja uslova za kontinualnu produkciju novih količina procednih voda.
Osnovni ciljevi uspostavljanja i integracije sistema upravljanja procednim vodama sa sistemom za upravljanje otpadom su sledeći [2]:

- smanjenje potencijalnog oticanja procednih voda preko bokova ili baze deponijskog tela usled iskorišćenja, neadekvatne izrade slojeva deponiskog tela ili oticanjem kroz matriks deponijskog tela,
- prevencija i kontrola nivoa deponijskog filtrata na deponijama u cilju izbegavanja prelivanja i nekontrolisane kontaminacije okolnih kanala, odvoda i izvorišta,
- kontrola procesa formiranja deponijskog gasa, praćenjem formiranja procednih voda, kao i postizanje hemijske i biološke stabilizacije unutar deponijskog tela,

- smanjenje interakcije između procednih voda i funkcionalnih slojeva deponijskog tela,
- Osiguranje stabilnosti otpada koji se odlaže, u slučaju nadzemnih deponija.

Kompleksan hemijski sastav i kontinualna produkcija procednih voda tokom životnog veka deponija, kao i nakon zatvaranja istih, zahtevaju implementaciju optimalnog sistema upravljanja procednim vodama. Konstitutivne elemente sistema za upravljanje procednim vodama predstavljaju sistem za sakupljanje i uklanjanje procednih voda i rezervoar za skladištenje procedne vode. Kompleksan sistem za sakupljanje i uklanjanje procednih voda iz tela komunalne deponije sastoji se od sledećih elemenata [2]:

- drenažni sloj (pokrov) - sastav navedenog sloja može varirati od prirodnih granulisanih materijala, kao što su pesak i šljunak, do sintetičkih drenažnih materijala, kao što su geonet ili geokompozit. Primena navedenih sintetičkih drenažnih materijala moguća je i pri oblaganju bočnih zidova deponijskih ćelija, u slučaju nemogućnosti primene prirodnih granulisanih materijala,
- zaštitni filtarski sloj – primena navedenog sloja vrši se kao preventivna mera u cilju sprečavanja fizičkog nakupljanja materijala na gornjoj površini drenažnog sloja, čime se ostvaruju optimalni uslovi za funkcionisanje istog. Zaštitni filtarski sloj najčešće se izrađuje od finih granulisanih materijala,
- perforirane cevi za prikupljanje procednih voda – perforirane cevi se u značajnom broju slučajeva izrađuju od materijala kao što su polietilen ili polipropilen velike gustine, čineći mrežu perforiranih cevi izuzetno fragilnim elementom sistema za sakupljanje i uklanjanje procednih voda. Međutim, upravo odabir materijala doprinosi neophodnoj izdržljivosti mreže perforiranih cevi izloženoj složenim hemijskim uticajima procednih voda koje se transportuju istim. Drenažni sloj predstavlja značajni činilac sa dvojakom zaštitnom ulogom u pravilnom funkcionisanju perforiranih cevi za prikupljanje procednih voda. Usled filtriranja i proceđivanja kroz drenažni sloj, deponijski filtrat dotiče u perforirane cevi postavljene unutar drenažnog sloja, delimično prečišćen u odnosnu na kvalitet filtrata prilikom proceđivanja kroz aktivne slojeve deponovanog otpada. Takođe, drenažni sloj štiti perforirane cevi od mehaničkih oštećenja usled kretanja teške mehanizacije i neplaniranih dodatnih opterećenja,
- pristupne tačke za monitoring procednih voda,
- šahtovi za prikupljanje procednih voda ili glavni odvodni sistem cevi pomoću kojeg procedne vode mogu biti uklonjene iz deponije.

Rezervoari sa skladištenje procedne vode, u zavisnosti od plana i načina upravljanja procednim vodama, mogu biti cementni rezervoari projektovani u skladu sa BS 8007 (Britanskim standardom za projektovanje cementnih struktura za skladištenje tečnih materija), montažne jedinice, objekti ojačani geosintetičkim materijalima ili lagune za skladištenje procednih voda [2]. Prilikom projektovanja građevinskih konstrukcija za skladištenje procednih voda neophodno je voditi računa o usklađivanju proračunatog inteziteta generisanja procednih voda posmatranog deponijskog lokaliteta sa veličinama projektovanih konstrukcija za skladištenje, u cilju sprečavanja prelivanja i potencijalne kontaminacije životne sredine i ugrožavanja zdravlja ljudi u okolini projektovane jedinice. Obezbeđenje optimalnog funkcionisanja laguna za skladištenje procednih voda sprovodi se implementacijom adekvatne konstrukcije, pri čemu se akcenat stavlja na kompozitnu oblogu, odnosno bazu konstrukcije, koja se sastoji iz sledećih elemenata [2]:

- gornjeg sloja kompozitne obloge – tehnički zahtevi u pogledu sastava gornjeg sloja kompozitne obloge ogledaju se u primeni fleksibilnog membranskog sloja čija je izvedba moguća uz pomoć polietilenskog materijala minimalne debljine 2 mm ili ekvivalentnog felksibilnog membranskog materijala,
- donjeg sloja kompozitne obloge – donji sloj kompozitne obloge može se izvesti na dva načina. Prvi način obuhvata formiranje sloja sabijenog zemljišta debljine 1 m čija je hidraulička konduktivnost manja ili jednaka vrednosti od 1 x 10^{-9} m s^{-1}, odnosno nasipanjem i sabijanjem slojeva se konstruiše serija slojeva krajnje debljine 1 m, pri čemu debljina pojedinačnog sloja ne sme da prelazi 250 mm. Drugi način se takođe sastoji u konstrukciji serije slojeva, maksimalne debljine pojedinačnog sloja 250 mm, pri čemu se ugrađuje dodatni sloj zemljišta debiljene 0,5 m ekvivalentne hidrauličke konduktivnosti kao i u prvom navedenom slučaju u cilju postizanja optimalnog zaštitnog efekta.

Nakon konstrukcije kompozitne obloge neophodno je proveriti integrisanost konstitutivnih slojeva istraživanjem curenja ili uz pomoć testa za zadržavanje tečnosti. U praksi, širu primenu našla su istraživanja za detekciju curenja, koja se tokom operativnog veka laguna moraju ponavljati u cilju sprečavanja curenja i potencijalnog zagađenja životne sredine.

Dodatni element sistema za sakupljanje i uklanjanje procednih voda predstavljaju obodni kanali. Izgradnja i primena navedenog elementa u okviru sistema za upravljanje procednim vodama je potpuno proizvoljna i određena definisanim načinom i planom upravljanja procednim vodama određenog deponijskog lokaliteta. Funkcionisanje obodnih kanala, kao elementa sistema za sakupljanje i uklanjanje procednih voda, zasniva se na sakupljanju atmosferskih padavina i njihovom zasebnom transportu, putem kolektora, do bazena za atmosferske vode, odakle se obavlja njihovo upuštanje u sistem za preradu i recirkulaciju [3]. Rezultat primene navedenog elementa je smanjenje kvantitativnog udela produkcije deponijskog filtrata, kao i očuvanje kvaliteta atmosferilija prispelih na određeni deponijski lokalitet smanjenjem kontakta sa procednim vodama. Kapitalni troškovi izgradnje obodnih kanala su veoma niski, pri čemu se dugoročno smanjuju i potrebna ekonomska ulaganja u pogledu kvantitativnog udela procednih voda koje je neophodno podvrgnuti različitim tehnologijama tretmana.

U odnosu na način kanalisanja u okviru sanitarnih komunalnih deponija čvrstog otpada, razlikuju se sledeće metode zbrinjavanja procednih voda: mokra polja, recirkulacija i uporedni tretman procednih voda ispuštanjem u komunalne kanalizacione sisteme. Navedene metode odlikuju se niskim kapitalnim ulaganjima, sa aspekta troškova implementacije, rada i održavanja, međutim njihova efikasnost značajno varira u zavisnosti od kvalitativnog i kvantitativnog sastava procednih voda. Najefikasniju, ali i kapitalno najzahtevniju metodu zbrinjavanja procednih voda u okviru sanitarnih komunalnih deponija čvrstog otpada, predstavlja obrada u postrojenjima za tretman procednih voda. Primenom različitih tehnologija tretmana, u zavisnosti od varijacija u kvalitativnom i kvantitativnom sastavu procednih voda određenog deponijskog lokaliteta, postiže se mogućnost dostizanja propisima zahtevanih graničnih vrednosti emisije tretirane vode pre ispuštanja u određeni vodoprijemnik.

Uspostavljanje optimalnog sistema upravljanja procednim vodama komunalnih deponija čvrstog otpada, pored kontrole procednih voda unutar tela deponije, doprinosi i ispunjenju jednog od tri glavna cilja upravljanja otpadom, odnosno postizanju očuvanja zdravlja ljudi i životne sredine. Benefit uspostavljanja navedenog sistema predstavlja i smanjenje potencijalne kontaminacije podzemnih i površinskih voda, preduzimanjem

adekvatnih mera u cilju postizanja propisanih emisionih standarda za ispuštanje prečišćenih procednih voda u vodoprijemnike.

Osnovni instrument za ostvarivanje aspiracija u pogledu dostizanja emisionih standarda za ispuštanje prečišćenih procednih voda u vodoprijemnike, zaštitu životne sredine i zdravlja ljudi predstavlja adekvatna zakonska regulativa u oblasti upravljanja procednim vodama. U okviru zakonske regulative uspostavljene su optimalne mere, standardi i propisi usled čijeg pridržavanja je moguće postići zadovoljavajući status u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada.

2. SISTEMATIZACIJA I UPOREDNI PREGLED ZAKONSKE REGULATIVE EU I REPUBLIKE SRBIJE U OBLASTI UPRAVLJANJA PROCEDNIM VODAMA KOMUNALNIH DEPONIJA ČVRSTOG OTPADA

2.1. Zakonska regultaiva EU u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada

Zakonska regulativa Evropske Unije u oblasti upravljanja procednim vodama komunalnih deponija nije strogo definisana, već se odlikuje integrativnim pristupom. Primenom zakonske regulative iz oblasti upravljanja otpadom i upravljanja vodama formira se celovita slika upravljanja procednim vodama. Relevantna zakonska regulativa u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada obuhvata sledeće zakonske akte:

- Okvirnu direktivu o otpadu (2008/98/EC),
- Direktivu o deponijama (1999/31/EC),
- Okvirnu direktivu o vodama (2000/60/EC),
- Direktivu o prečišćavanju komunalnih otpadnih voda (91/271/EEC),
- Direktivu o dopunama Direktive (91/271/EEC) na određene zahteve uspostavljene u njenom Aneksu I,
- Direktiva o prikupljanju podataka, formiranju BAT referentnih dokumenata i obezbeđenju njihovog kvaliteta (2012/119/EC).

Okvirna direktiva o otpadu (2008/98/EC) i Direktiva o deponijama (1991/31/EC) su značajno uticale na oblast upravljanja procednim vodama komunalnih deponija čvrstog otpada.

Tačkom 2 Ankesa I Direktive o deponijama (1999/31/EC) koji se odnosi na generalne zahteve za sve klase deponija, uspostavljeni su opšti zahtevi u oblasti kontrole voda i upravljanja procednim vodama. U skladu sa karakteristikama deponijskog lokaliteta i meteorološkim uslovima neophodno je preduzeti adekvatne mere kako bi se ispunili sledeći zahtevi [4]:

- kontrola atmosferskih padavina koje se proceđuju kroz telo deponije;
- sprečavanje prodiranja površinskih i/ili podzemnih voda unutar deponovanog otpada;
- prikupljanje kontraminiranih voda i deponijskog filtrata; ukoliko procena zasnovana na lokalitetu deponije i karakteristikama deponovanog otpada pokaže da ne postoji potencijalni rizik za kontaminaciju životne sredine, nadležne vlasti mogu

doneti odluku o razrešavanju menadžmenta deponijskog lokaliteta od primene navedene mere;
- Tretman sakupljenih kontaminiranih voda i deponijskog filtrata sa deponije u cilju ispunjenja odgovarajućih standarda za ispuštanje u vodoprijemnik.

Tačkom 3.3 Aneksa I pomenute Direktive regulisani su tehnički propisi koje je neophodno zadovoljiti prilikom projektovanja sistema za sakupljanje i uklanjanje procednih voda [4]. U okviru navedene tačke nalaže se obezbeđenje i dodatna zaštita deponijskog dna u cilju sprečavanja migracije procedne vode u podtlo deponijskog tela i to na sledeći način prikazan u tabeli 1.

Tabela 1. Mere dodatne zaštite deponijskog dna [4]

Klasa deponije	Za neopasan otpad	Za opasan otpad
Veštačka zaptivna obloga - folija	zahteva se	zahteva se
Drenažni sloj ≥ 0,5 m	zahteva se	zahteva se

Ukoliko, nakon razmatranja potencijalnog rizika po životnu sredinu, nadležne vlasti ustanove da je primena mera zaštite u cilju sprečavanja migracije procednih voda neophodna, propisuje se implementacija veštačke zaptivne obloge. Preporuke za implementaciju veštačke zaptivne obloge, kao integralnog dela deponijskog dna, prikazane su u tabeli 2.

Tabela 2. Preporuke za način projektovanja deponijskog dna u slučaju kada postoji rizik od kontaminacije životne sredine uzrokovan generisanjem procednih voda [4]

Klasa deponije	Za neopasan otpad	Za opasan otpad
Sloj za drenažu deponijskog gasa	zahteva se	ne zahteva se
Veštačka zaptivna obloga	ne zahteva se	zahteva se
Nepropustan mineralni sloj	zahteva se	zahteva se
Drenažni sloj > 0,5 m	zahteva se	zahteva se
Pokrovni sloj zemlje > 1 m	zahteva se	zahteva se

Tačkom 3 Aneksa III pomenute Direktive, koji se odnosi na procedure kontrole i monitoring u okviru operativne faze i faze nakon zatvaranja deponije, data su upustva za adekvatno sprovođenje monitoringa procednih voda komunalnih deponija čvrstog otpada. Navedenom odredbom nalaže se sprovođenje monitoringa procedne vode na reprezentativnom broju uzoraka na svakoj tački na kojoj se tečnost kontrolisano odvodi sa lokacije. Merenje zapremine i sastava procedne vode vrši se jednom mesečno u toku ekspolatacije deponije. Navedena merenja se vrše i po prestanku eksploatacije deponije svakih šest meseci prvih pet godina, a zatim jednom godišnje do odumiranja deponije. Tabelom 3 prikazan je plan monitoringa procednih voda u toku i po prestanku eksploatacije deponije.

Tabela 3. Plan monitoringa procednih voda u toku i po prestanku eksploatacije deponije [4]

	Aktivna faza	Pasivna faza[3]
Zapremina procedne vode	Mesečno[1][3]	Svakih šest meseci
Sastav procedne vode[2]	Kvartalno[3]	Svakih šest meseci
Zapremina i sastav površinske vode[4]	Kvartalno[3]	Svakih šest meseci

[1] Učestalost uzorkovanja se može prilagoditi na osnovu morfološkog sastava, a određuje se dozvolom.
[2] Parametri za merenje koji se analiziraju variraju u zavisnosti od sastava deponovanog otpada, određuju se dozvolom.
[3] Ukoliko procena podataka ukazuje da su duži intervali jednako efikasni, merenja mogu da se vrše u tim intervalima, ali obavezno jednom godišnje.
[4] Na osnovu karakteristika lokacije deponije, nadležna institucija koja daje uslove može utvrditi da ova merenja nisu potrebna i o tome obavestiti nadležni organ.
[1] i [2] primenjuju se samo kod klase deponije na kojoj se vrši sakupljanje procedne vode.

U okviru Direktive o deponijama (1991/31/EC) postavljeni su ciljevi koji se odnose na smanjenje količine biorazgradivog otpada koji se deponuje. Kao referentna godina (za zemlje EU-15) uzeta je 1995. godina, dok krajnji rok za dostizanje ciljeva predstavlja 2016. godina. Konkretno, ciljevi za postepeno smanjenje količine deponovanog biorazgradivog otpada su sledeći [4]:

- do kraja 2006. godine količina biorazgradivog komunalnog otpada koja se deponuje mora biti smanjena najmanje na 75 % od ukupne količine biorazgradivog komunalnog otpada koji je generisan 1995. godine,
- do kraja 2009. godine količina biorazgradivog komunalnog otpada koja se deponuje mora biti smanjena najmanje na 50 % od ukupne količine biorazgradivog komunalnog otpada koji je generisan 1995. godine,
- do kraja 2016. godine količina biorazgradivog komunalnog otpada koja se deponuje mora biti smanjena najmanje na 35 % od ukupne količine biorazgradivog komunalnog otpada koji je generisan 1995. godine.

Implementacija navedenih ciljeva Direktive o deponijama (1991/31/EC) značajno je uticala kako na sektor upravljanja otpadom, tako i na sektor upravljanja procednim vodama komunalnih deponija čvrstog otpada.

Smanjenje udela biorazgradivog otpada koji se odlaže na deponije značajno je uticao na ukupnu količinu i morfološki sastav otpada koji se deponuje. Rezultat takve prakse predstavljaju značajne promene kvalitativnog sastava, pre svega sa aspekta parametara kao što je HPK, BPK_5 i NH_4-N, kao i kvantitativnog udela procednih voda koje se generišu u okviru deponija [5]. Promene u okviru kvalitativnog sastava i kvantitativnog udela procednih voda generisanih na deponijama direktno utiču na tehničko-tehnološke promene u okviru sistema za sakupljanje i uklanjanje procednih voda. Prema tome, usvajanjem i sprovođenjem navedenog propisa Direktive o deponijama (1991/31/EC), ostvaruje se indirektan uticaj na oblast upravljanja procednim vodama, čime se potvrđuje činjenica da oblast upravljanja otpadom i upravljanja procednim vodama predstavljaju integrativnu celinu.

Pored toga što je problematika deponovanja pojednih frakcija otpada određenog kvalitativnog i kvantitativnog sastava određena donošenjem i primenom odgovarajućih propisa Direktive o deponijama (1991/31/EC), problematika odgovornosti i postupanja nakon

zatvaranja deponije, kao i odgovarajući referentni periodi upravljanja deponijama i kontrole nakon zatvaranja, određeni su propisima Okvirne direktive o otpadu (2008/98/EC). Odredbe navedene Direktive nalažu kontrolu deponijskih lokaliteta od 30 do 60 godina nakon zatvaranja. Međutim, sprovedena istraživanja sugerišu nove rokove za kontrolu deponijskih lokaliteta nakon zatvaranja, koji se kreću u rasponu od 200 godina za nesanitarne deponije komunalnog čvrstog otpada, do 75 godina za sanitarne deponije komunalnog čvrstog otpada, sa prethodno optimalno uspostavljenim i primenjivanim sistemom za upravljanje otpadom u toku operativnog veka deponije [5]. Uvođenje navedenih rokova od izuzetnog je značaja za oblast upravljanja procednim vodama komunalnih deponija sa naučno-istraživačkog aspekta. Sprovođenjem sistema monitoringa u cilju vršenja kontrole u navedenim periodima nakon zatvaranja deponijskih lokaliteta, omogućeno je prikupljanje podataka sa aspekta kvalitativnog i kvantitativnog sastava procednih voda, čime se značajno doprinosi uvidu i razumevanju procesa generisanja i morfologije procednih voda u navedenom periodu.

Sa druge strane, odredbama u oblasti upravljanja vodama uspostavljenim usvajanjem Okvirne direktive o vodama (2000/60/EC) i Direktive o prečišćavanju komunalnih otpadnih voda (91/271/EEC), strogo su definisani i pooštreni kriterijumi i limiti za ispuštanje voda iz postrojenja za prečišćavanje otpadnih voda u vodoprijemnike [6 - 8]. Usled navedenog, u praksi na nivou Evropske Unije prisutne su strepnje u pogledu dostizanja referentnih graničnih vrednosti emisije u vodoprijemnike procednih voda koje se tretiraju u postrojenjima za prečišćavanje. Razlog takvog stava predstavljaju učestale varijacije kvalitativnog sastava procednih voda, kao i varijacije u efikasnosti uspostavljenih tretmana, naročito sa aspekta uklanjanja NH_4-N, fosfora i ukupnog ugljenika [9]. Stoga je, na nivou Evropske Unije, još uvek široko rasprostranjena praksa uporednog tretmana procednih voda komunalnih deponija čvrstog otpada sa komunalnim vodama iz domaćinstava, u postrojenjima za tretman komunalnih otpadnih voda. Primena ovakvog tretmana procednih voda zasniva se na hidrauličkom opterećenju influenta u postrojenje za tretman komunalnih otpadnih voda, uz preporuku da zapremina procednih voda koja se prima ne sme da premašuje procenat ukupnog godišnjeg opterećenja postrojenja u kojem se vrši tretman.

Dugoročni efekti primene navedenih odredbi referentne zakonske regulative još uvek nisu poznati, ali izvesno je da će promene u kvalitativnom sastavu procednih voda, zajedno sa strogim graničnim vrednostima za ispuštanje tretiranih procednih voda u vodoprijemnike, zahtevati integrativni pristup delovanja u cilju uspešnog upravljanja procednim vodama komunalnih deponija čvrstog otpada.

2.2. Zakonska regulativa Republike Srbije u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada

Kao i u slučaju Evropske Unije, zakonska regulativa Republike Srbije u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada nije strogo definisana, već je zasnovana na integrativnom pristupu. Sistematizacija zakonske regulative u navedenoj oblasti postiže se primenom relevantnih zakonskih akata iz oblasti upravljanja otpadom i iz oblasti upravljanja vodama:

- Zakon o zaštiti životne sredine (“Sl. glasnik RS”, br. 135/2004, 36/2009,36/2009 – dr. zakon, 72/2009 – dr.zakon, 43/2011- odluka US i 14/2016),
- Zakon o upravljanju otpadom (“Sl. glasnik RS”, br. 36/2009, 88/2010 i 14/2016),
- Uredba o odlaganju otpada na deponije (“Sl. glasnik RS”, br. 92/2010),
- Zakon o vodama (“Sl. glasnik RS”, br. 30/2010),

- Zakon o integrisanom sprečavanju i kontroli zagađivanja životne sredine ("Sl. glasnik RS", br. 135/2004),
- Uredba o graničnim vrednostima emisije zagađujućih materija u vode i rokovima za njihovo dostizanje ("Sl. glasnik RS", br. 67/2011, 48/2012 i 1/2016),
- Uredba o graničnim vrednostima prioritetnih i prioritetnih hazardnih supstanci koje zagađuju površinske vode i rokovi za njihovo dostizanje ("Sl. glasnik RS", br. 35/2011).

Zakonska regulativa Republike Srbije u oblastima upravljanja otpadom i upravljanja vodama u potpunosti je usklađena sa relevantnom zakonskom regulativom Evropske Unije u pomenutim oblastima. S obzirom na to, odredbe vezane za upravljanje procednim vodama komunalnih deponija čvrstog otpada navedene u poglavlju 2.1. sadržane su u Uredbi o odlaganju otpada na deponije, Zakonu o vodama i Uredbi o graničnim vrednostima emisije zagađujućih materija u vode i rokovima za njihovo dostizanje [10 - 12].

Odredbe o obezbeđenju i dodatnoj zaštiti deponijskog dna u cilju sprečavanja migracije procednih voda u podtlo deponije sadržane su u okviru tačke 2, priloga 2 Uredbe o odlaganju otpada na deponije [10]. Dodatna zaštita dna depoonije realizuje se na načine prikazane u tabeli 4.

Tabela 4. Zahtevi sa aspekta dodatne zaštite dne deponije u cilju sprečavanja migracije procedne vode u podtlo deponije [10]

Klasa deponije	Za neopasan otpad	Za opasan otpad
Veštačka zaptivna obloga – folija	zahteva se	zahteva se
Drenažni sloj ≥ 0.5 m	zahteva se	zahteva se

Zaptivanje deponijskog dna i bočnih strana deponije moguće je realizovati primenom drugih metoda i tehnika, kojima se obezbeđuju uslovi iz priložene tabele 4. Na osnovu proračuna bilansa voda izrađuje se projekat drenažnog sloja, drenažnih cevi i odvodnih kanala sa ciljem obezbeđivanja optimalnog delovanja sistema za dreniranje i prečišćavanje procedne vode, kao i uspostavljanja kontrole rada i održavanja deponije. Primenom optimalnih tehničkih rešenja, sprečava se prodiranje otpada u drenažni sistem. Za održavanje i kontrolu drenažnih cevi za prikupljanje procedne vode neophodna je izgradnja dovoljnog broja šahtova koji moraju biti stabilni i oslonjeni na podtlo. Bezebedno privremeno zadržavanje procedne vode koja se prikupi iz tela deponije ostvaruje se posstavljanjem sabirnog šahta, otpornog na hemijske uticaje, obezbeđenog na eksploziju i emisiju neprijatnih mirisa. Sakupljena procedna voda pre ispuštanja u prijemnik obrađuje se, odnosno prečišćava u skladu sa posebnim propisima kojima se uređuje zaštita voda [10].

Uslovi u pogledu deponijskog dna i procednih voda ne primenjuju se na deponije inertanog otpad, jer proces raspada inertnog otpada ne utiče na životnu sredinu, odnosno oticanje procednih voda sa navedenih deponija nema negativnih efekata na kvalitet zemljišta, podzemnih i površinskih voda [10].

U okviru deponija opasnog i neopasnog otpada nužno je obezbediti poseban sistem za sakupljanje i odvođenje procedne vode kroz drenažni sloj, u okviru kojeg su položene drenažne cevi za odvođenje iste u projektovani sistem za njen tretman [10].

Parametri na osnovu kojih se realizuje kontrola nastajanja i kvaliteta procednih i prečišćenih tečnosti na deponiji sadržani su u okviru priloga 5 Uredbe o odlaganju otpada na deponije i predstavljaju ih [10]:

- temperatura na ulazu u projektovani objekat i temperatura okolnog vazduha,

- vrednost parametra pH deponijskog filtrata na ulazu i prečišćene tečnosti na izlazu iz projektovanog objekta,
- potrošnja permanganata,
- BPK (biološka potrošnja kiseonika).

Odredbe vezane za plan monitoringa procednih voda u toku i po prestanku eksploatacije deponije sadržane su u okviru tačaka 3 i priloga 6 Uredbe o odlaganju otpada na deponije [10]. Monitoring procednih voda realizuje se na reprezentativnom borju uzoraka, na svakoj tački na kojoj se tečnost kontrolisano odvodi sa lokacije. Merenje i kontrola kvalitativnih i kvantitativnih karakteristika procedne vode ostvaruje se jednom mesečno u toku eksploatacije deponije. Navdena merenja realizuju se i nakon zatvaranja deponijskih lokaliteta, svakih šest mesesci prvih pet godina, a zatim jednom godišnje do odumiranja deponije [10].

Republika Srbija, kao država koja prolazi kroz proces tranzicije, odlikuje se niskom vrednošću bruto domaćeg proizvoda po glavi stanovnika, u iznosu od 5.544.394 US $, što je svrstava na devedeseto mesto na Svestkoj listi zemalja u odnosu na projektovanu vrednost BDP po glavi stanovnika za 2017. godinu [13,14]. Navedena vrednost za 2008. godinu, iznosila je 5.509.06 US $, odnosno 6,1 %, od čega je 0,35% BDP utrošeno na oblast zaštite životne sredine iz budžeta.

Finansijska podrška za 15 projekata u oblasti životne sredine u 2008. godini iz Nacionalnog investicionog plana iznosila je 455 miliona dinara, od toga je za 6 projekata regionalnih deponija izdvojeno 270 miliona dinara, odnosno 60 %. Na osnovu predstavljene vrednosti BDP, Republika Srbija se svrstava u države sa višim-srednjim prihodima regiona Evrope i Centralne Azije (ECA), za koje je propračunata vrednost ulaganja u sistem upravljanja komunalnim čvrstim otpadom za 2010. godinu iznosila 24,5 biliona US $, dok projekcije za 2025. godinu ukazuju na neophodnost još viših eknomskih ulaganja u iznosu od 63,5 biliona US $ [15]. Predstavljajući deo integralne celine formirane sa sistemom upravljanja komunalnim čvrstim otpadom, uspostavljanje i optimizacija sistema upravljanja procednim vodama zahtevaju 20 - 30 % finansijskih sredstava od ukupnih ulaganja u sistem upravljanja komunalnim čvrstim otpadom [15]. Činjenica da je od dvadeset i četiri predviđenih regionalnih centara za upravljanje komunalnim čvrstim otpadom na teritoriji Republike Srbije, do 2017. godine formirano samo osam, ukazuje na nedovoljna ekonomska ulaganja u okviru oblasti upravljanja otpadom, te samim tim i u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada.

U skladu sa postepenim razvojem oblasti upravljanja otpadom, zasnovanim na minimalnim finansijskim ulaganjima, rokovi za dostizanje ciljeva postepenog smanjenja deponovanja biorazgradivog otpada, predstavljeni u okviru Uredbe o odlaganju otpada na deponije, modifikovani su u odnosu na zahteve postavljene u okviru Direktive o deponijama (1999/31/EC) [10].

U okviru člana 10 stav 3 Uredbe o odlaganju otpada na deponije, definisane su sledeće stope smanjenja odlaganja biorazgradivog otpada u cilju uspostavljanja sistema kontrolisanog odlaganja [10]:

- u periodu od 2012. do 2016. godine – najmanje 25 % od ukupne količine (po težini) biorazgradivog komunalnog otpada,
- u periodu od 2017. do 2019. godine – najmanje 50 % od ukupne količine (po težini) biorazgradivog komunalnog otpada,
- u periodu od 2020. do 2026. godine – najmanje 65 % od ukupne količine (po težini) biorazgradivog komunalnog otpada.

Postepeno smanjenje odlaganja biorazgradive frakcije na deponije uzrokovaće izvesne promene u okviru kvalitativnog i kvantitativnog sastava procednih voda generisanih u okviru komunalnih deponija čvrstog otpada. Navedene promene u oblasti procednih voda zajedno sa minimalnim ekonomskim ulaganjima, dovešće do formiranja značajnih izazova za dostizanje uspostavljenih graničnih vrednosti emisija za vode sa deponija i postrojenja za biološki tretman otpada, uz zahtev implementacije optimalnih tehničko-tehnoloških rešenja sa minimalnim kapitalnim ulaganjima.

2.3. Kontrola zagađenja voda u Republici Srbiji

Kontrola zagađenja voda u Republici Srbiji do 2011. godine zasnivala se na primeni imisionih standarda. Međutim, donošenjem Uredbe o graničnim vrednostima emisije zagađujućih materija u vode i rokovima za njihovo dostizanje, od 2011. godine kontrola zagađenja vode temelji se na primeni emisionih standarda, odnosno graničnih vrednosti emisije [12]. Uredba o graničnim vrednostima emisije zagađujućih materija u vode i rokovima za njihovo dostizanje se odnosi na emisije za određene grupe ili kategorije zagađujućih supstanci u tehnološkim otpadnim vodama pre njihovog ispuštanja u kanalizaciju, tehnološkim i drugim otpadnim vodama koje se neposredno ispuštaju u recipijent, vodama koje se posle prečišćavanja ispuštaju iz sistema javne kanalizacije u recipijent i otpadnim vodama koje se iz septičkih i sabirnih jama ispuštaju u recipijent, odnosno na regulisanje ispuštanja komunalnih i industrijskih otpadnih voda u prijemnike. Granične vrednosti emisije (GVE) određene za 49 sektora, zasnovane su na primeni najboljih dostupnih tehnika (BAT). Rok za dostizanje graničnih vrednosti emisije propisan Uredbom je do 31. decembra 2030. godine, dok nova postrojenja moraju odmah zadovoljiti GVE. Izuzetak od navedenog roka predstavljaju postrojenja za prečišćavanje otpadnih voda iz aglomeracija sa opterećenjem većim od 2.000 ekvivalentnih stanovnika koja svoje komunalne otpadne vode ispuštaju u recipijent. Propisani rok za dostizanje graničnih vrednosti emisije za navedenu grupu predstavlja 31. decembar 2045. godine. Komunalne otpadne vode koje se ispuštaju iz aglomeracija sa opterećenjem manjim od 2.000 ekvivalentnih stanovnika imaju obavezu da svoje granične vrednosti emisija zagađujućih materija postignu u skladu sa planom upravljanja vodama.

Neophodno je da svi obveznici Uredbe donesu akcione planove za dostizanje graničnih vrednosti emisije i njima utvrde rokove za postepeno dostizanje graničnih vrednosti emisije zagađujućih materija, u skladu sa planom zaštite voda od zagađivanja na osnovu zakona kojim se uređuju vode, u roku od šest meseci od donošenja ovog plana [12].
Obveznici Uredbe dužni su da Ministarstvima nadležnim za poslove zaštite životne sredine i vodoprivrede podnose izveštaj o sprovođenju akcionog plana, svake tri godine od dana donošenja pomenutog plana [12].

U okviru Uredbe o graničnim vrednostima emisije zagađujućih materija u vode i rokovima za njihovo dostizanje, tačkom 42, stav 1, tačkom 44, stav 1, tačkom 2, stav 2 i tačkom 2a, stav 2 definisane su granične vrednosti emisije otpadnih voda od odlaganja otpada na površinu, kao i za tehnologije tretmana otpada pre deponovanja. Implementacijom navedenih propisa ostvaruje se mogućnost celovite kontrole vrednosti emisija otpadnih voda, sa primarnim akcentom na procedne vode, na mestu ispuštanja u površinske vode, kao i pri mešanju sa ostalim otpadnim vodama na nivou pogona, te samim tim i sprovođenje odredbi propisanih Uredbom u okviru celokupnog sistema upravljanja otpadom [12].

3. ZAKLJUČAK

Sistematizacija zakonske regulative u oblasti procednih voda komunalnih deponija čvrstog otpada integracijom relevantnih zakonskih akata iz oblasti upravljanja otpadom i upravljanja vodama omogućuje temeljan i strategijski pristup delovanja u navedenoj oblasti. Relevantni zakonski okvir u oblasti upravljanja procednim vodama na nivou EU i Republike Srbije u potpunosti je usklađen. Neophodnu stavku na nivou Republike Srbije predstavlja aktivna i optimizovana implementacija zahteva propisanih regulatornim okvirom.

Primena sistematizovane zakonske regulative u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada na nivou Evropske Unije povlači sa sobom konsekvence, kao što su:

- značajne promene u kvantitativnom i kvalitativnom sastavu procednih voda,
- neophodne modifikacije procedura kontrole i monitoringa procednih voda u okviru operativne faze i faze nakon zatvaranja komunalnih deponija čvrstog otpada,
- unapređenje tehničko-tehnoloških operacija tretmana procednih voda sa ciljem dostizanja strogih graničnih vrednosti za ispuštanje tretiraih procednih voda u vodoprijemnike.

Kontinualno praćenje kvantitativnog i kvalitativnog statusa procednih voda, te samim tim i transparentan uvid u navedene podatke, razumevanje procesa generisanja i morfologije procednih voda zavisno od implementacije nastalih izmena na nivou zakonske regulative, neophodnost unapređenja procedura i plana kontrole i monitoringa, kao i mogućnost inovativnog pristupa u okviru rešavanja tehničko-tehnoloških poteškoća tretmana procednih voda komunalnih deponija čvrstog otpada predstavljaju benefite primene sistematizovane zakonske regulative i značajnu šansu ka ostvarivanju unapređenja u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada.

Primena sistematizovane zakonske regulative u oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada na nivou Republike Srbije, u odnosu na Evropsku Uniju, nosi sa sobom gotovo iste prednosti i mane. Otežavajuću okolnost predstavlja finansijski aspekat, odnosno postojeća minimalna ulaganja u odnosu na aspiraciju za uspostavljanjem optimalnog sistema upravljanja procednim vodama komunalnih deponija čvrstog otpada, prevashodno sa aspekta zadovoljenja relevantne zakonske regulative. Ostvarenje navedene aspiracije zahteva postepen, sistematičan i strategijski pristup pojedinačnim segmentima integrativnih konstituenata oblasti upravljanja procednim vodama komunalnih deponija čvrstog otpada, odnosno oblastima upravljanja otpadom i upravljanja vodama. Takođe, značajan aspekat čitave celine predstavlja odvikavanje od ustaljene prakse zbrinjavanja procednih voda komunalnih deponija čvrstog otpada, odnosno recirkulacije, i makar partitativno savladavanje tehničko-tehnoloških poteškoća, odnosno prilagođavanje procedura tretmana procednih voda minimalnim kapitalnim troškovima uz mogućnost dostizanja strogih graničnih vrednosti za ispuštanje tretiranih procednih voda u vodoprijemnike od strane celokupnog sistema.

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ANALIZA TEHNOLOŠKIH INDIKATORA RAZLIČITIH PROIZVODNIH ENERGETSKIH JEDINICA SPREGNUTIH SA SEKTOROM PROMETA

ASSESSMENT OF TECHNOLOGICAL INDICATORS OF DIFFERENT GENERATION TECHNOLOGIES COUPLED WITH TRANSPORTATION SECTOR

Dražen Balić*, Tomislav Čop*, Bruno Židov*

* Energetski institut Hrvoje Požar, Zagreb, Hrvatska

autor za korespondenciju: Dražen Balić, e-mail: dbalic@eihp.hr

Stručni članak

SAŽETAK

Suvremeni energetski sustav velikim dijelom uvjetovan je intermitentnim obnovljivim izvorima energije. Obnovljivi izvori energije jedan su od ključnih čimbenika pri tranziciji energetskog sustava s fosilnih goriva na tzv. zelena i okolišno prihvatljivija goriva. Međutim, integracija većeg udjela obnovljivih izvora energije postavlja i određene dodatne zahtjeve pri upravljanju elektroenergetskim sustavom kako bi se osigurala stabilnost i pouzdanost opskrbe. Za ispunjenje tih zahtjeva pružaju se različite mogućnosti, kao što su primjerice konvencionalne elektroenergetske jedinice (na fosilna goriva ili biomasu) ili flota električnih automobila. Konvencionalne proizvodne elektroenergetske jedinice, kao i električna vozila, uspoređivana su u ekonomskom, društvenom i tehnološkom kontekstu. Pokazano je kako integracija električnih vozila i njihov utjecaj na energetski sustav može polučiti slične efekte kao i konvencionalna postrojenja s povoljnijim utjecajem na društvo.

***Ključne riječi**: fleksibilnost elektroenergetskog sustava, e-mobilnost, konvencionalni izvori fleksibilnosti*

ABSTRACT

Contemporary energy sector is highly influenced with intermittent renewable energy sources. The renewable energy sources are one of the key factors in transition from fossil based energy system to the green and environmental friendly system. However, integration of higher shares of intermittent renewable energy sources require certain forms of support in

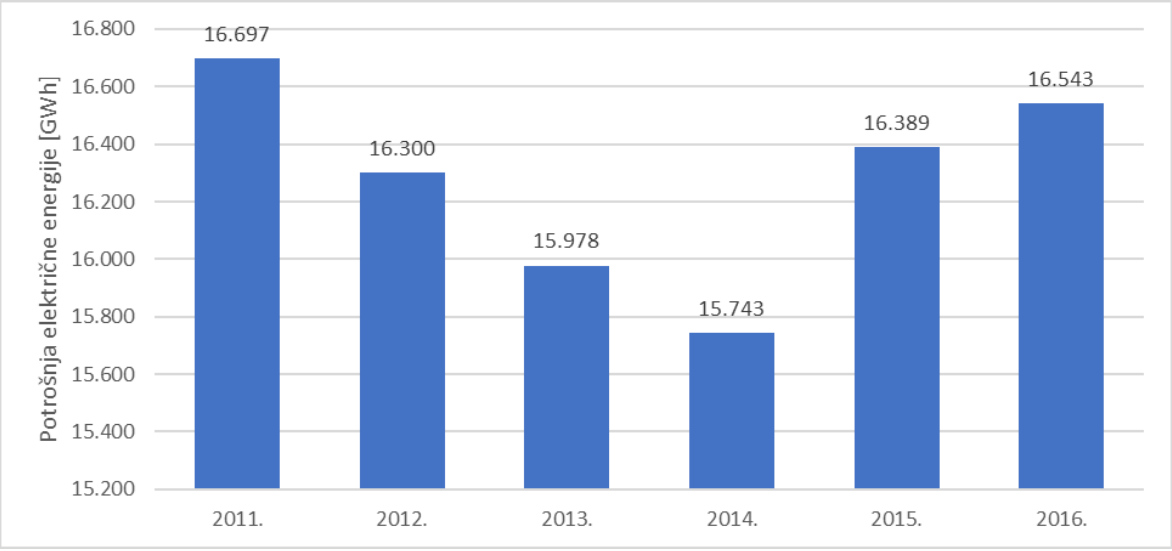
order to maintain power grid stability. This support can be provided by various sources. Some of them are conventional generation units (based on fossil fuels and biomass) and electric vehicles, which are in the focus of this research. The conventional power generation units as well as fleet of electric vehicles were compared in economic, societal and technological point of view. It is shown that integration of electric vehicles and its impact on power grid can provide the similar effects as conventional generation units with more beneficial impact on society.

***Keywords**: flexibility of power system, e-mobility, conventional sources of flexibility*

1. UVOD

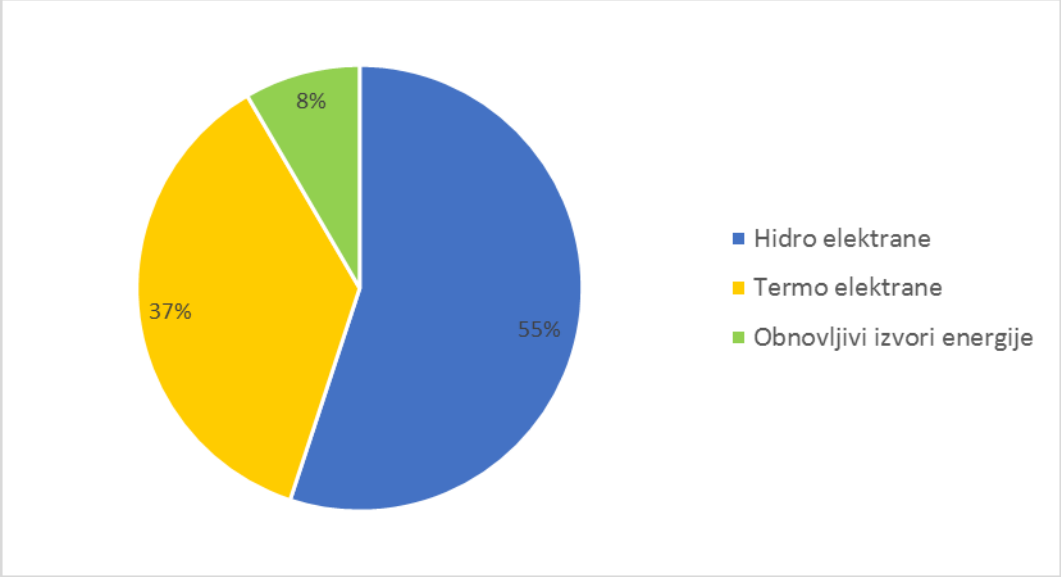
Energetska politika Europske Unije u zadnjih 20-tak godina uvjetovala je postavljanje određenih ciljeva. Pritom se prvenstveno misli na porast udjela obnovljivih izvora energije, pored povećanja energetske učinkovitosti i smanjenja emisija stakleničkih plinova [1]. Navedeni ciljevi, implicirali su izgradnju i integraciju značajnijih kapaciteta za proizvodnju električne energije čiji karakter proizvodnje odlikuje intermitentnost. Kao najznačajniji predstavnici takvih proizvodnih postrojenja su vjetro i fotonaponske elektrane. Izazovi koji takva postrojenja nameću posljedica su specifičnosti električne energije, tj. elektroenergetskog sustava, čije normalno i stabilno funkcioniranje nalaže kontinuiranu ravnotežu između proizvedene električne energije te količine električne energije za kojom postoji potreba na strani krajnjih korisnika. Ukoliko je ta ravnoteža narušena, stabilnost cjelokupnog elektroenergetskog sustava također je narušena što može rezultirati devijacijom nazivnih vrijednosti ključnih fizikalnih veličina (napon, frekvencija) te u konačnici raspadom cjelokupnog sustava.

Ukoliko se analizira trend potrošnje električne energije u Republici Hrvatskoj, može se zamijetiti kako je u razdoblju od 2011. do 2014. godine potrošnja električne energije u padu, dok se u 2015. i 2016. godine bilježi ponovni porast potrošnje električne energije, kako je prikazano slikom 1.



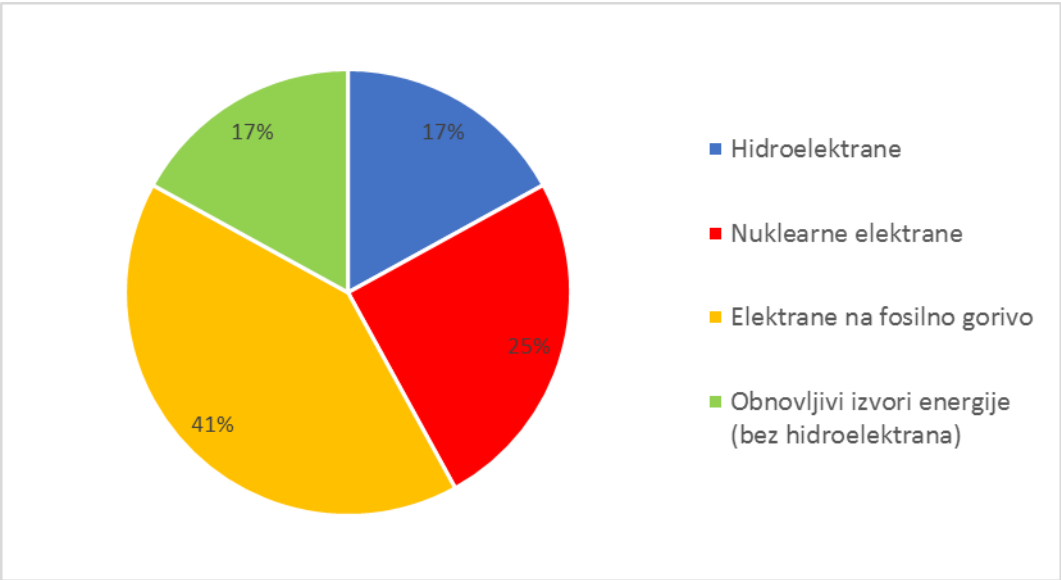
Slika 1. Potrošnja električne energije u Republici Hrvatskoj u razdoblju od 2011. do 2016. godine [2]

Ako se pak pogleda udio obnovljivih izvora u proizvodnji električne energije može se konstatirati kako su u Republici Hrvatskoj u 2016. godini intermitentni proizvodni kapaciteti fotonaponskih i vjetroelektrana doprinosili s ukupnim udjelom u proizvedenoj električnoj energiji od 8% (slika 2).



Slika 2. Struktura proizvodnje električne energije u Republici Hrvatskoj u 2016. godini [2]

Ukoliko se razmotri stanje u Europskoj Uniji, tj. na području koje pokriva europsko udruženje operatera prijenosnih sustava ENTSO-E, može se konstatirati kako je udio proizvedene električne energije iz obnovljivih izvora energije na razini od 17 %, kako je prikazano slikom 3.



Slika 3. Struktura proizvodnje električne energije na ENTSO-E području u 2015. godini [3]

Sukladno [4] očekuje se kako će udio u električne energije proizveden iz intermitentnih obnovljivih izvora energije postizati udjele od 22,9 % u 2025. godini te 26,6 % u 2030. godini.

Imajući to na umu, za očekivati je kako će budući elektroenergetski sustav imati povećane zahtjeve za fleksibilnošću u cilju očuvanja stabilnog i pouzdanog rada cjelokupnog sustava. Kako bi se odgovorilo na buduće izazove, razvijaju se različiti pristupi i modeli. U sklopu ovog rada analizirat će se usporedba fleksibilnih konvencionalnih elektroenergetskih proizvodnih postrojenja, čija strategija vođenja se može prilagoditi budućih zahtjevima u sustavu, sa sektorom elektromobilnosti, koji predstavlja jedan od načina za pohranu viškova električne energije proizvedenih iz intermitentnih obnovljivih izvora električne energije.

2. KONVENCIONALNI IZVORI FLEKSIBILNOSTI

Stabilnost elektroenergetskog sastava, kako je prethodno bilo napomenuto, počiva na ravnoteži između proizvodnje i potrošnje električne energije u svakom vremenskom trenutku. U suprotnom dolazi do devijacije frekvencije i napona od nazivnih vrijednosti, što može rezultirati negativnim ishodom. Navedena fleksibilnost pruža se odgovarajućim tehničkim rješenjima i svako djelovanje u smislu očuvanja stabilnosti elektroenergetskog sustava može se smatrati pružanjem usluga elektroenergetskom sustavu u cilju očuvanja stabilnosti.

U Republici Hrvatskoj, sukladno važećim Mrežnim pravilima prijenosnog sustava [5], proizvodna termoenergetska postrojenja nazivne snage preko 30 MW_e, te hidroenergetska postrojenja nazivne snage preko 10 MW_e dužna su pružati tzv. primarnu regulaciju, tj. sekundni odziv u isporučenoj snazi u cilju očuvanja stabilnosti sustava.

Dominantni izvori fleksibilnosti u postojećem elektroenergetskom sustavu dolaze od velikih centraliziranih postrojenja hidroelektrana i termoelektrana. Međutim, s tehnološkim razvojem počinju se javljati i drugi izvori i koncepti za pružanje fleksibilnosti. Mala proizvodna postrojenja također imaju takve tehničke karakteristike koje omogućavaju, uz određene uvjete, pružanje fleksibilnosti. Generalno se može konstatirati kako integracija većeg udjela intermitentnih obnovljivih izvora energije zahtijeva fleksibilnost sustava koja može biti ostvarena na nekoliko sljedećih načina:

- Pojačanje infrastrukture, tj. povećanje interkonekcijskih vodova kako bi se veće količine električne energije mogle transportirati na veće udaljenosti i na taj način osigurati fleksibilnost sustava. Dakako, takav pristup je kapitalno intenzivan.
- Integracija fleksibilnih proizvodnih jedinica manjih snaga, primjerice motora s unutarnjim izgaranjem pogonjenih prirodnim plinom. Navedena postrojenja imaju odlične dinamičke performanse i nizak kapitalni trošak.
- Upravljanje potrošnjom (*Demand Side Management*) – koncept kojim krajnji korisnici doprinose ravnoteži između proizvodnje i potrošnje električne energije promjenom svojih navika.
- Spremnici energije – suvremeni izvor fleksibilnosti od kojeg postoje velika očekivanja, ali su još uvijek opterećeni relativno visokim kapitalnim troškom. Kada se govori o spremnicima energije potrebno je istaknuti ako postoji različiti tipovi spremnika energije, tj. spremnika koji pohranjuju različite oblike energije – električnu, toplinsku, kemijsku i sl. Autori u [6] obrađuju problematiku implementacije različitih tipova spremnika energije s tehničke i ekonomske strane. Ustanovljeno je, kako s aspekta vođenje elektroenergetskog sustava, tehnički je najpovoljniji spremnik električne energije. Međutim, takvi spremnici još uvijek su opterećeni relativno intenzivnim kapitalnim investicijama. Međutim, mogu se pronaći i primjeri gdje je ustanovljeno kako i spremnici toplinske energije, koje odlikuje značajno niži

investicijski trošak, mogu imati pozitivan utjecaj na vođenje elektroenergetskog sustava, na distribucijskoj razini [7]

Pored navedenih mogućih izvora fleksibilnosti, potrebno je napomenuti kako su trenutno termoenergetska postrojenja bazirana na tehnologiji plinskih turbina te hidroenergetska postrojenja najznačajniji izvori fleksibilnosti. Navedena postrojenja predstavljaju dokaznu i provjerenu tehnologiju koja će i u budućnosti imati ključnu ulogu u očuvanju stabilnosti elektroenergetskog sustava.

3. SCENARIJ DUGOROČNE POTROŠNJE ENERGIJE U SEKTORU PROMETA U REPUBLICI HRVATSKOJ

Uvažavajući izrazitu kompleksnost energetskog sustava (u kojem električna vozila predstavljaju sponu između elektroenergetskog i prometnog sustava), koji je u pozitivnoj korelaciji s ekonomskim i ekološkim sustavom pojedine države, odnosno zemljopisnog područja, planiranje potrošnje energije i posljedičnih, potencijalnih emisija onečišćujućih tvari u zrak, zahtijeva primjenu matematičkih modela za analizu potrošnje energije i izračun emisija.

Polaznu platformu u korištenom modelu predstavlja rekonstrukcija potrošnje energije u referentnoj godini. To zahtijeva prikupljanje i kompiliranje potrebnih podataka iz različitih izvora te provođenje određenih kalkulacija iz kojih proizlaze ulazni parametri, koji se zatim dodatno podešavaju, a sve sa konačnim ciljem uspostave vjerodostojne bilance potrošnje energije u referentnoj godini. Ovaj inicijalni korak je nužan i provodi se u svrhu kalibracije modela specifičnostima Republike Hrvatske.

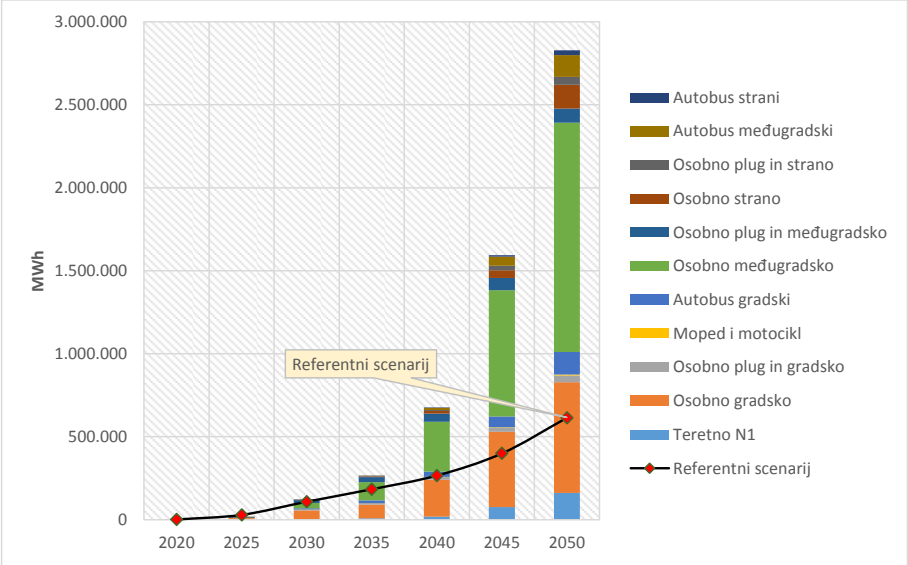
Predviđanje budućih energetskih potreba temelji se na scenarijskom pristupu, pri čemu svaki od scenarija predstavlja zaseban skup pretpostavljenog razvoja odrednica potrošnje. Funkcionalna veza osnovnih odrednica potrošnje energije i finalne potrošnje energije je simulacijska, a ista se utvrđuje strukturnom analizom, pri čemu je funkcionalna veza ostvarena linearnim jednadžbama. U načelu, definirani scenarij ovisi o fundamentalnim karakteristikama socijalnog i ekonomskog razvoja zemlje, kao i o tehnološkim faktorima koji podrazumijevaju energetsku učinkovitost i prodor alternativnih oblika energije na tržište.
Metodološki pristup podrazumijeva primjenu svojstvene jednadžbe za kalkulaciju energetskih potreba u budućnosti. Ista podrazumijeva primjenu scenarijski utvrđene odrednice potrošnje iz budućnosti na referentnu specifičnu potrošnju energije, korigiranu koeficijentom očekivane evolucije kroz utvrđeno vremensko razdoblje.

Energetske potrebe u sektoru prometa izračunate su u formi finalne potrošnje kao funkcija ukupnih potreba putničkog prometa, teretnog prometa, energetskih potreba pojedinih transportnih oblika te specifičnih energetskih potrošnji i faktora opterećenja svakog elementarnog transportnog oblika.

Promatrani vremenski horizont u analizi energetske potrošnje, do 2050. godine, jednak je obuhvaćenom vremenskom razdoblju koje iznosi strateški dokument Europske unije [8], a koji definira temeljne smjernice za prijelaz na konkurentno nisko-ugljično gospodarstvo do 2050. godine. S obzirom na relativnu dugotrajnost promatranog razdoblja, prilikom predviđanja potrošnje energije u budućnosti, potrebno je uvažiti niz faktora koji se, između ostaloga, u najvećoj mjeri odnose na gospodarske prilike, tehnološki razvoj te način gospodarenja energijom. Posebna nepoznanica je tehnološki razvitak i dinamika privođenja novih tehnologija komercijalnom korištenju, a čiji će stupanj prodora na tržište u najznačajnijoj mjeri ovisiti o mnoštvu međusobno povezanih čimbenika, koji između ostaloga

uključuju štetno djelovanje postojećih energetskih tehnologija, spremnost građana da plate više za čistu energiju, energetske krize uvjetovane ekonomskim (mogućnost utjecaja na cijenu nafte od strane zemalja OPEC-a), geopolitičkim (promjena političkog nazora u zemljama izvoznicama energije) ili čisto fizičkim razlozima (smanjenje ili povećanje rezervi), stupnju razvitka novih tehnologija, spremnosti Vlada da podržavaju istraživanja i demonstraciju novih tehnologija te uključivanju velikih industrija i financijskih institucija (automobilska industrija, banke, osiguranja, investicijski fondovi, komunikacije, itd.). Širok spektar utjecajnih faktora osnovni je razlog scenarijskom pristupu predviđanja finalne energetske potrošnje u sektoru prometa u RH, a isti je između ostalih rezultirao i scenarijem snažne penetracije električnih vozila, prihvatljivim iz perspektive načelnih ciljeva smanjenja CO_2 emisije do 2050. godine.

Sukladno modelskim pretpostavkama, potrošnja cestovnih vozila s pogonom na električnu energiju mogla bi iznositi oko 2 830 GWh električne energije u 2050. godini (slika 4). Udio predmetne potrošnje u ukupnoj potrošnji električne energije mogao bi biti veći od 10 posto u 2050. godini te iz toga proizlazi činjenica da električna vozila mogu voditi važnu ulogu u konceptu uravnoteženja elektroenergetske mreže i upravljanja potrošnjom.



Slika 4. Scenarij očekivane potrošnje električne energije cestovnih vozila
*pretpostavke uključuju politički okvir koji favorizira elektrifikaciju voznog parka u što većoj mjeri

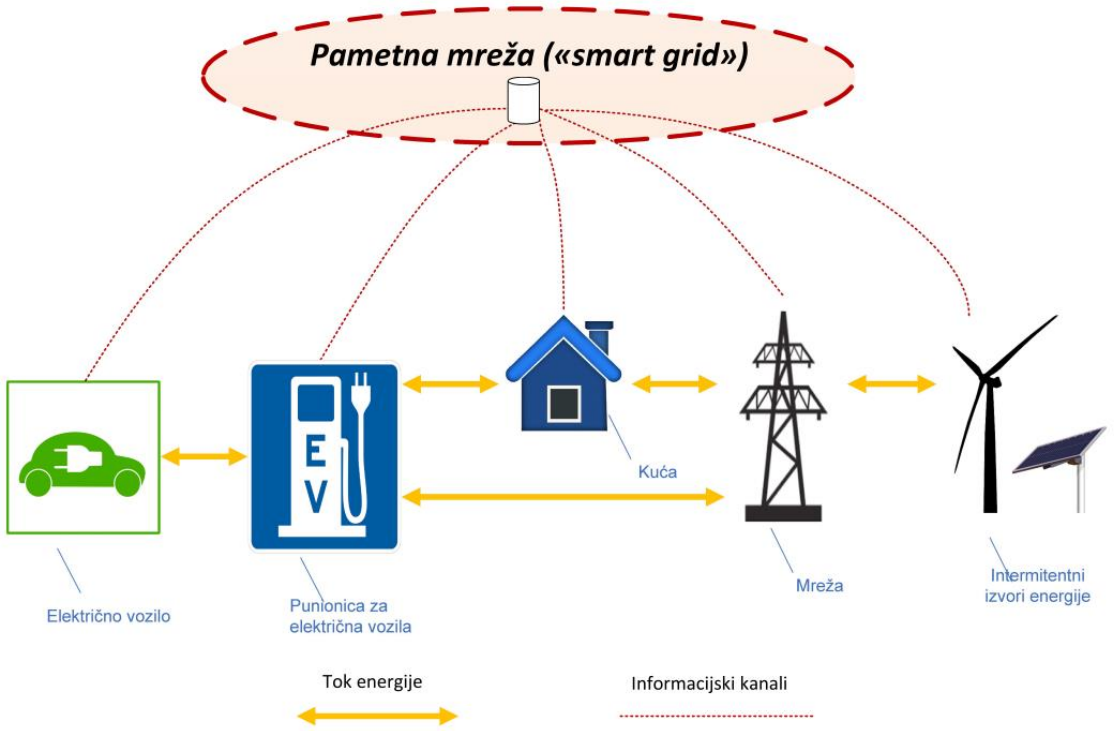
4. MOGUĆNOSTI SEKTORA PROMETA U PRUŽANJU FLEKSIBILNOSTI ELEKTROENERGETSKOM SUSTAVU

Elektromobilnost (skraćeno „e-mobilnost“) ne predstavlja samo pojam koji označava vozila s električnim pogonskim sustavom, već novu paradigmu te redefiniranje prometa i mobilnosti. Koncept e-mobilnosti, temeljen na električnoj energiji kao alternativnom gorivu, otvorio je prostor za razvoj i uvođenje niza novih tehnoloških rješenja, stvaranje novih poslovnih modela, napredak u integraciji obnovljivih izvora energije u elektroenergetski sustav, inovativna rješenja u planiranju mobilnosti kao i prostor za rad akademske zajednice na ovom području. U konačnici, sve to omogućuje put ka ispunjenju međunarodnih i nacionalnih ciljeva u pogledu smanjenja lokalnih i globalnih štetnih emisija te poboljšanja kvalitete života. Unatoč brojnim izazovima i preprekama, proces razvoja e-mobilnosti ostvaruje značajne pomake u recentnom uz izuzetno pozitivne izglede u narednom vremenu.

Mogućnost pružanja usluge fleksibilnosti elektroenergetskom sustavu jedan je od ključnih aspekata e-mobilnosti, obzirom na već dobro poznate izazove troškovno učinkovitog upravljanja vršnim opterećenjem uz integraciju obnovljivih izvora energije. Osim elektroprivreda, postoje još mnogi dionici s različitim interesima i motivacijama za sudjelovanjem u ovom procesu, kao što su proizvođači električnih vozila, proizvođači baterijskih sustava za električna vozila, vlasnici električnih vozila, vlasnici infrastrukture za punjenje električnih vozila, regulatorne institucije, itd.

Za funkcioniranje sustava u kojem električna vozila predstavljaju distribuirani spremnik energije za intermitentne izvore energije, a zatim i potencijal za pružanje usluge fleksibilnosti, potrebo je ispunjavanje određenih preduvjeta koji se mogu podijeliti na (i) tehničke, (ii) pravno-regulatorne te (iii) ekonomske.

U tehničkom pogledu, osnovni preduvjet za pružanje fleksibilnosti je postojanje infrastrukture, vozila i ostalih dijelova sustava koji podržavaju dvosmjerni protok električne energije te razmjenu podataka, pri čemu su svi elementi objedinjeni u koncept pametne mreže (engl. *smart grid*, slika 5).



Slika 5. Koncept povezanosti elemenata e-mobilnosti i elektroenergetskog sustava objedinjen sustavom pametnih mreža

Iz pravno-regulatornog pogleda, potrebno je prepoznavanje elemenata koncepta e-mobilnosti u smislu pružanja novih usluga, između ostalih i mogućnosti pružanja fleksibilnosti elektroenergetskom sustavu, te njihovo definiranje u sklopu pravnog okvira.

Na koncu, potreba za upravljanjem cijelim procesom pružanja usluga fleksibilnosti otvara prostor za stvaranje novih poslovnih modela u kojima će razni dionici pronaći svoje interese, pri čemu je jedan od osnovnih uvjeta postojanje dovoljnog broja električnih automobila i odgovarajuće infrastrukture za ekonomsku opravdanost takvih procesa.

5. KOMPARATIVNA ANALIZA

U Republici Hrvatskoj usluge fleksibilnosti, tj. pružanje sekundarne i tercijarne regulacije osigurano je od strane proizvodnih elektroenergetskih jedinica unutar portfelja HEP Proizvodnje d.o.o. Pritom, kao najznačajniji izvori fleksibilnosti mogu se navesti hidroelektrane (HE Vinodol, HE Zakučac; HE Senj, RHE Velebit, HE Dubrovnik, HE Orlovac te hidroelektrane na rijeci Dravi) [9]. Može se konstatirati kako je u Republici Hrvatskoj ukupno angažirano ±83 MW za potrebe sekundarne regulacije te +256/-51 MW za potrebe tercijarne regulacije [10]. Sukladno podacima od strane HEP Proizvodnje d.o.o. u 2015. godini od osigurane rezerve snage za sekundarnu regulaciju proizvedeno je 159,71 GWh električne energije za potrebe pozitivne sekundarne regulacije, odnosno 109,99 GWh električne energije za potrebe negativne regulacije. Ako se razmatra tercijarna regulacija, onda se može konstatirati kako je u 2015. godini proizvedeno 131,86 GWh električne energije za potrebe pozitivne tercijarne regulacije, odnosno 132,50 GWh električne energije za potrebe negativne regulacije [11].

Energetski potencijal voznog parka u Republici Hrvatskoj za pružanje usluga fleksibilnosti u određenom trenutku funkcija je ukupnog broja električnih vozila, udjela konektiranih vozila s elektroenergetskim sustavom u tom trenutku, stanja napunjenosti baterije te zadanih postavki vlasnika vozila. Uz pretpostavke da broj vozila odgovara prethodno modeliranoj očekivanoj potrošnji električne energije, da prosječan kapacitet baterije u 2050. godini iznosi 50 kWh po osobnom vozilu, da vozilo sudjeluje u procesu ukoliko stanje napunjenosti baterije iznosi preko 60 posto kapaciteta te da privola vlasnika vozila za sudjelovanjem u procesu iznosi 90 posto, tada ukupni raspoloživi kapacitet osobnih vozila registriranih u RH u 2050. godini, u skladu s modelskim pretpostavkama, iznosi od 13 GWh do 24 GWh, ovisno radi li se o dnevnom ili noćnom režimu punjenja.

6. ZAKLJUČAK

Temeljem modelskih rezultata uočen je izraziti ekološki i ekonomski potencijal koji može postati realnost u slučaju ostvarenja tržišta u kojem dominanti udio voznog parka čine električna vozila. Kao i kod većine relativno novih tehnologija na putu masovne implementacije stoji niz prepreka, a u načelu se iste grupiraju u regulatorne, ekonomske i tehničke. Iako je u kontekstu europske politike smanjenja emisije stakleničkih plinova ostvarenje scenarija široke rasprostranjenosti električnih vozila zapravo nužnost, trenutno u Republici Hrvatskoj ne postoji dokument koji definira sveobuhvatne karakteristike tržišta te svakako postoji potreba za izradom strategije koja će imati za cilj definirati uvjete, aktere, legislativne podloge i infrastrukturne lokacije s planiranom dinamikom investicija. Ovdje se može spomenuti činjenica da na tržištu električne mobilnosti u Hrvatskoj dominira entropija, gdje krajnji korisnici u većini slučajeva električnu energiju na javnim punionicama dobivaju besplatno (model naplate, niti bilo kakav tarifni sustav nije definiran).

Izvjesna proliferacija električne mobilnosti pozicionira električna vozila u aktivne sudionike u funkcioniranju elektroenergetskog sustava, što osim tehničkih i komunikacijskih zahtjeva, postavlja i zahtjeve pred legislativu. Direktiva o uspostavi infrastrukture za alternativna goriva zahtijeva od Republike Hrvatske implementaciju prikladnog broja punionica za električna vozila, a isto tako i zahtjeva mogućnost *ad hoc* punjenja na svakoj od punionica, bez da korisnici pritom moraju sklopiti ugovor s operatorom punionice ili dobavljačem energije. Prema tome, opravdano se postavlja veliki broj pitanja koja su vezana uz koncept električne mobilnosti u Republici Hrvatskoj, a u načelu ista se svode primarno

(trenutno) na dvojbe spojivosti s maloprodajnim tržištem energije, vlasništva utičnica, naplaćivanja usluga punjenja, povezanosti između operatera punjenja i vlasnika vozila te regulacije tržišta. Paralelno s navedenim izazovima valjalo bi promišljati o izglednosti tzv. *vehicle to grid* koncepta, implementacijom kojeg bi se omogućio dvosmjeran tok električne energije, od mreže prema vozilu, odnosno bateriji te obrnuto, od vozila prema distribucijskoj mreži, na zahtjev operatora. Pogodnost ovakvog punjenja proizlazi iz činjenice da operator može upravljati dijagramom opterećenja sustava i primjerice tijekom velikih opterećenja ili u kriznim situacijama visokih cijena ili loših naponskih prilika u distribucijskoj mreži koristiti energiju pohranjenu u baterijama električnih vozila. Za očekivati je da će takav koncept punjenja zaživjeti u odmakloj fazi razvoja tržišta električnih vozila, tek nakon što se distribucijska mreža funkcionalno pripremi za prihvat takvih novih korisnika.

Iz svega navedenog može se konstatirati kako vozni park električnih vozila, s određenim pretpostavkama, može doprinositi očuvanju stabilnosti elektroenergetskog sustava. Dakako, korištenje navedenog potencijala, u smislu potencijalno raspoložive energije za uravnoteženje elektroenergetskog sustava, predstavlja jedan od izazova u budućem energetskom sustavu. Pritom je potrebno analizirani potencijal gledati u širem kontekst, tj. kao samo jedan od mogućih izvora fleksibilnosti čiji stvarni potencijal može biti iskorišten ukoliko se energetski sustav promatra i planira holistički. Za takav pristup potrebna je promjena paradigme cjelokupnog sustava i upravo se to može smatrati jednim od najvećih izazova u budućem razvoju energetike.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

APPLICATION OF MATHEMATICAL MODELLING IN ANAEROBIC DIGESTION OF BIODEGRADABLE ORGANIC MATTER

Robert Bedoić*, Boris Ćosić, Tomislav Pukšec**, Neven Duić****

* SDEWES Centre, Zagreb, Croatia
** Faculty of Mechanical Engineering and Naval Architecture, Zagreb, Croatia

corresponding author: Robert Bedoić, e-mail: robert.bedoic@gmail.com

Original scientific paper

ABSTRACT

Anaerobic digestion is the acceptable technology of energy recovery from organic biodegradable waste that results in the production of biogas and digestate. Biogas is composed mainly of methane and carbon dioxide, while other components like hydrogen sulphide, oxygen, ammonia and nitrogen can be found in traces. The application of Anaerobic Digestion Model No. 1 implemented in process simulator AQUASIM on anaerobic co-digestion process has been investigated. The feedstock in the biogas power plant is primarily composed of maize silage and animal slurry. The average temperature of the process is about 39 °C that defines the mesophilic conditions in fermenters. Model predicts the following components in biogas: methane, carbon dioxide and hydrogen. The results of the conducted simulations are comparable to data from the biogas plant, as well with the data from the early conducted investigations by other authors. Therefore, the model could be used for a predictive study on anaerobic digestion process in a full-scale biogas plant.

***Keywords**: anaerobic digestion, modelling, simulator, biogas*

1. INTRODUCTION

Anaerobic digestion (AD) is the acceptable technology of energy recovery from organic biodegradable waste. Output materials in AD process are in gaseous form (biogas) and liquid-solid form (digestate) [1]. The most common substrates in the AD are cattle and swine manure [2] and energy crops. One of widely used energy crops for biogas production is maize, whether as grains or silage [3]. Authors in the paper [4] have investigated the antagonistic and synergistic effects on biogas and methane production from anaerobic co-digestion of cattle and pig slurries with grass silage in a batch process. Besides substrates like agricultural residues, energy crops and animal excreta, there are also some substrates used in an AD that has a potentially dangerous effect on the environment. One of them is

slaughterhouse by-products and waste streams that have been studied as cosubstrates at the biogas power plant in [5]. Another substrate generated in food value chain that could be used as a source of energy is rotten food. Authors in [6] have studied problems according to mono-digestion of rotten food. Anaerobic co-digestion of rotten food could be integrated with existing AD facilities with the production of value-added products.

There are many parameters that affect the AD process, either to control the process or to ensure proper biodegradation of substrate. Parameters of the process are interconnected, for example, the substrate composition defines the initial pH in the fermenters, the biogas yield and biogas composition [7]. Hydraulic Retention Time (HRT) defines the average period of time that substrate retains in a fermenter, with a defined volume of fermenter [8]. As the temperature in fermenters increases (psychrophilic < mesophilic < thermophilic), the HRT decreases and the process is less stable. In order to ensure proper biodegradation of substrates and to get significant biogas yield, HRT should be long (between 30 and 40 days for mesophilic conditions in fermenters) which makes the anaerobic digestion time-consuming method of energy recovery.

Mathematical modelling of anaerobic digestion of biodegradable matter describes the interactions between physical and biological mechanisms [9]. In general, there are two types of models: mechanistically inspired models – include the knowledge of the physical and chemical reactions occurring and black box models − the input data are directly linked to the output without including any prior knowledge as in mechanistically inspired models. Anaerobic Digestion Model No. 1 (ADM1) describes the reactions occurring in anaerobic digestion, by assuming a perfect mixture. The components are expressed in terms of their Chemical Oxygen Demand (COD) [$kgO_2\ m^{-3}$] or in molar concentrations [$kmol/m^3$]. Recent investigations on modelling of anaerobic digestion by using ADM1 have been applied on several substrates: animal dung and rotten vegetable [10], grass silage [11], a mixture of municipal waste and grease [12], microalgae [13] and many others. The ADM1 is available in Matlab and Simulink and in water related simulation softwares like WEST, BioWin and AQUASIM.

The main goal of this research is to study the application of mathematical model on the anaerobic digestion of biodegradable organic matter composed from maize silage and animal slurry. Results of the model have been compared to experimental data and investigations conducted so far in this area. The aim is to apply the examined mathematical model for the estimation of biogas production and stability of the continuous process at a real biogas plant operating under mesophilic conditions.

2. EXPERIMENTAL

Modelling of anaerobic co-digestion has been performed by the use of Anaerobic Digestion Model No. 1 (ADM1) implemented in open source software AQUASIM, Version 2.0.

2.1. Anaerobic Digestion Model No. 1 (ADM1)

ADM1 is introduced by IWA Task Group [14] with the aim to develop a general model of anaerobic digestion. The model includes several steps in which biochemical and physico-chemical processes occur. Algebraic and differential equations are implemented in ADM1 to describe mass balance in each step. Following variables are involved: 26 static state

variables, 32 dynamic state variables and 8 implicit state algebraic variables for reactor description. Generated biogas in the model is composed of following components: methane, carbon dioxide and hydrogen. Figure 1 presents the one-stage reactor with inlet and outlet streams [14].

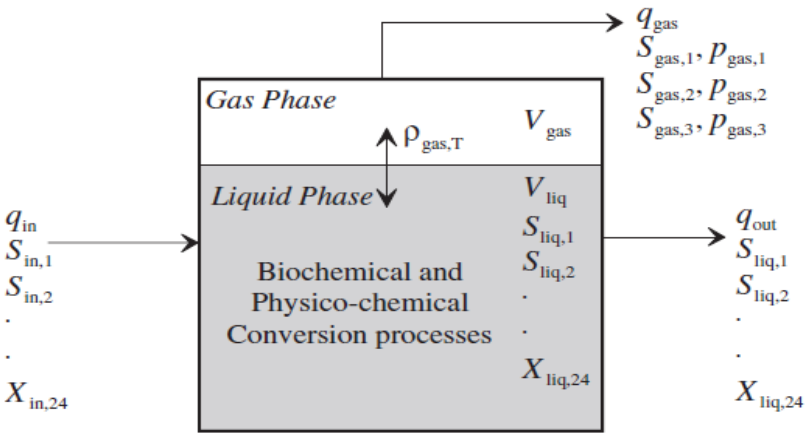


Figure 1. Characteristics of inlet and outlet streams described by the ADM1 in one-stage reactor [14]

Notations shown in figure 1 have the following meaning:

- ρ, rate of process [$kgO_2/(m^3d)$]
- p, partial pressure [m^3/h]
- q, volume flow rate [m^3/d]
- S, concentration of soluble component [kgO_2/m^3]
- X, concentration of particulate component [kgO_2/m^3]
- V, volume [m^3]
- *in*, inlet
- *out*, outlet
- *gas*, gas
- *liq*, liquid
- *T*, transfer (from liquid to gas phase)

Expressions of reaction rates and stoichiometric coefficients are taken from [15]. Mass balance in the liquid phase (for both soluble and particulate components), a gas transfer from liquid to gas phase and mass balance for components in gas phase present the base of the modelling of anaerobic digestion.

2.2. AQUASIM

AQUASIM software is designed for identification and simulation of aquatic systems in the laboratory, industrial processes and in nature [16]. The programme is based on four subsystems: variables, processes, compartments and links as shown in figure 2.

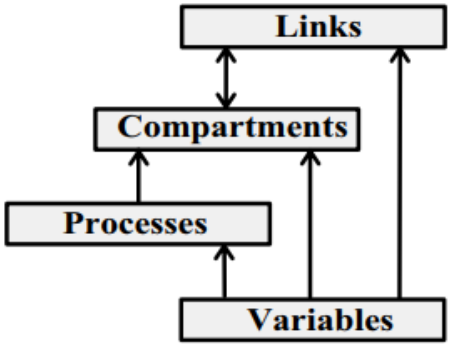


Figure 2. Subsystems of the AQUASIM structure [16]

Variables are objects of the model that assume specific numerical values. There are 6 types of variables in the AQUASIM [16]:

- *"State Variables are used to describe properties of water or a surface in contact with water to be calculated by the model.*
- *Program Variables present auxiliary quantities used in the program available to the system of variables.*
- *Constant Variables are used as model parameters in sensitivity analysis and parameter estimation.*
- *Real list Variables provide measured quantities for use in the system of variables.*
- *Formula Variables are used to build functional relations out of other variables.*
- *Probe Variables make the values of variables evaluated at a given location in a compartment globally available."*

Processes are divided into dynamic and equilibrium. Dynamic processes describe mass transformation or mass transport. They are characterized by the rate of the process and individual stoichiometric coefficients. Equilibrium processes are described by the use of algebraic equations due to higher process rates compared to dynamic processes.

Compartments are introduced in the AQUASIM in order to divide the reactor space into segments for easier examination of the processes. There are many structures in Compartment subsystem of AQUASIM that can be used to study the natural phenomena. In this study the Mixed Reactor Compartment has been used in order to describe the AD process, as it is shown in figure 3 [16]. Reactor type of Mixed Reactor Compartment has been selected as ″constant volume″ due to the fact that fermenters have defined and known volume. In this study three segments of Mixed Reactor Compartment have been introduced: liquid reactor, headspace and effluent. Liquid reactor has been used to examine the conversion processes that occur in the liquid phase. Headspace segment has been used to calculate the flow rate of biogas and its composition. Effluent segment has been used to describe the flow of the outlet stream of reactor. Explanation of other types of Compartments, as well as more detailed view of the used Compartment type can be find in the literature [16].

The last subsystems are Links. They are used to describe the flow of matter from one Compartment segment into another. There are two types of Links, diffusive and advective.

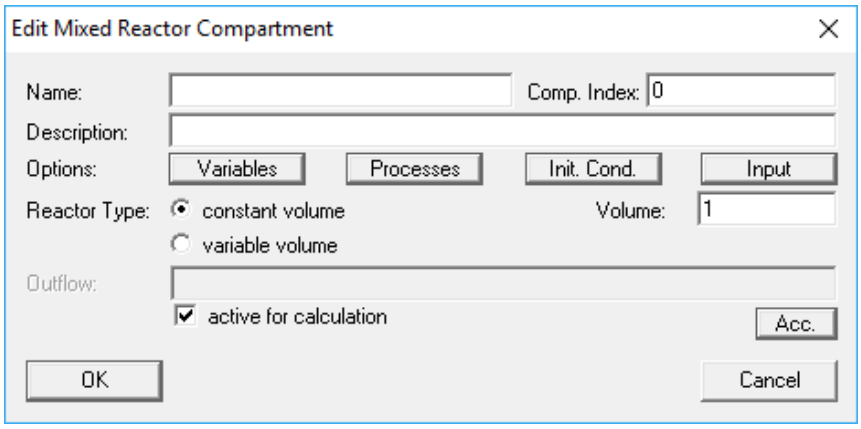


Figure 3. Mixed Reactor Compartment in AQUASIM [16]

2.3. Simulation

Numerical values of variables are adopted from Batstone [14]. The temperature of the anaerobic digestion process in the biogas plant is 39.0 ± 0.1 °C. The raw feedstock enters the first fermenter F1 where the degradation of organic matter starts. After some time, the reactive mixture is transported from fermenter F1 into the second fermenter F2. The volume of the first fermenter (F1) is 3,000 m^3, and the volume of the second fermenter (F2) is 3,820 m^3. Headspace volume is set to 1,000 m^3. Iteration step in time is set to 0.1 day and the number of steps is 350. The volume of biogas given by the model is normalised to 0 °C and 101,325 Pa, according to International Union for Pure and Applied Chemistry (IUPAC) [17].

3. RESULTS AND DISCUSSION

Results contain the experimental measurements and model predicted results for a continuous process. Below every Figure, there is a discussion of results given by the model and experimental data given by the biogas power plant. Also, the results have been compared with the results of previous investigations by other authors of the examined topic.

Figure 4 shows the measured data of pH values (circles and triangles) and model predicted data (lines) in fermenter F1 and fermenter F2, in time (*t*).

Optimal pH value of a mixture of maize silage and the animal slurry is between 7 and 8 [18, 19]. The model predicts values of pH slightly above neutral, whether measured values in both fermenters are much closer to pH=8. In fermenter F1, measured pH values are in the range of 7.70 up to 7.90, while model predicts pH values from 6.95 up to 7.20. Measured data on pH in fermenter F2 varies from 7.80 up to 7.90 and model predicted data varies from 7.05 up to 7.20. By comparing model results and measured values, it can be stated that significant set-off exists.

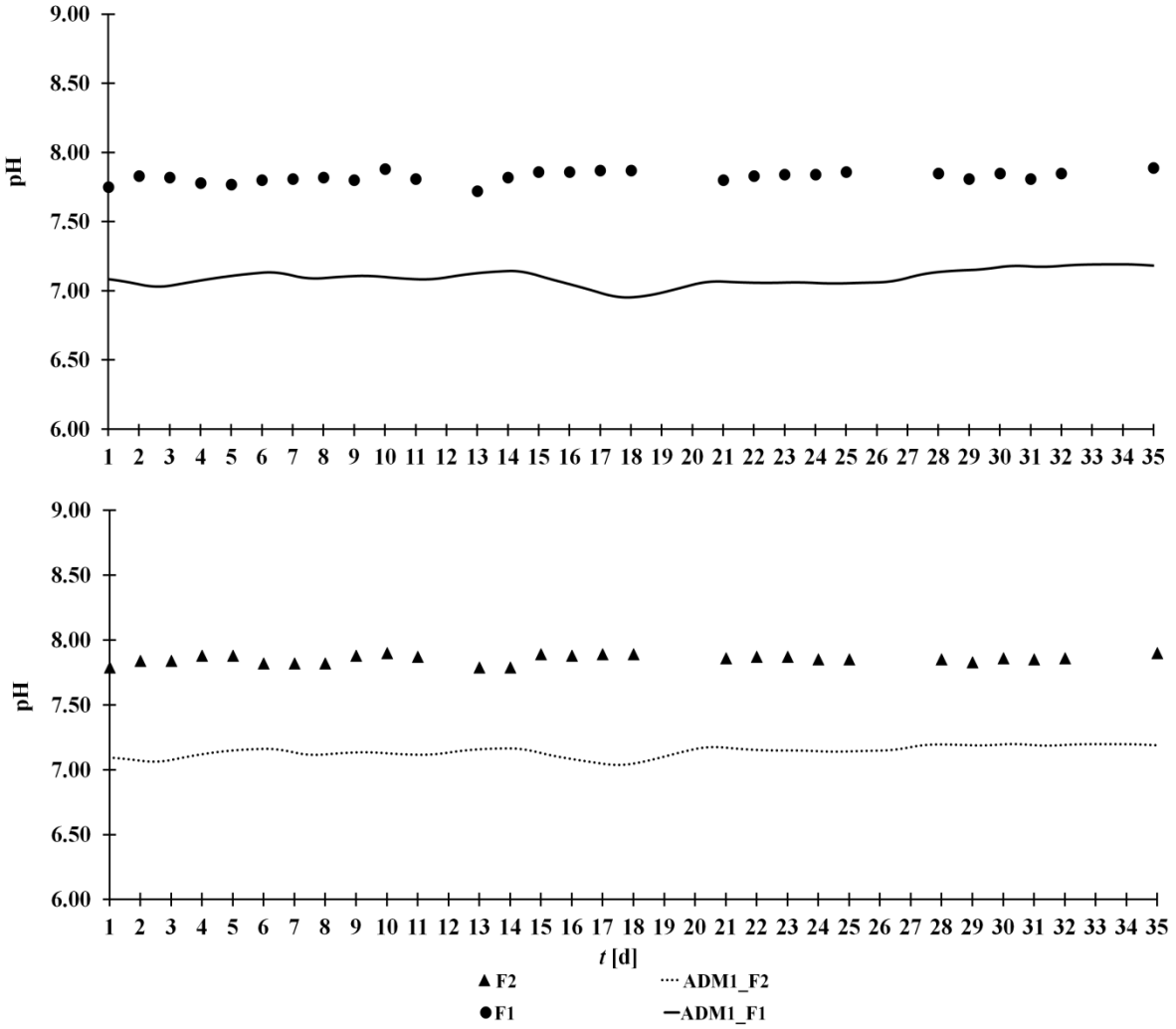


Figure 4. Measured pH data in fermenters F1 (circle) and F2 (triangle) and modelled data in fermenters F1 (solid line) and F2 (dashed line)

Figure 5 shows the measured data of process stability indicator, ratio of concentration of volatile fatty acids (VFA) and concentration of inorganic carbon, total alkalinity (TA). VFA/TA values (circles and triangles) and model predicted data (lines) in fermenter F1 and fermenter F2.

The ratio of VFA concentration and TA concentration is an indicator of process stability on biogas plant [20]. If the ratio is between 0.30 and 0.40 then the biogas production is at maximum and process is stable. When the ratio is below 0.20 then a load of feedstock is too low. If the ratio exceeds 0.60 the fermenter is overloaded. Results in Figure 5 show that both fermenters operate under acceptable load rate of feedstock (fermenter F1 ─ 0.23÷0.28; fermenter F2 ─ 0.24÷0.31). The model predicts higher values of VFA/TA for fermenter F1, from ca. 0.20 up to ca. 0.80. As it is mentioned in subsection Simulation, the raw feedstock first enters the fermenter F1. Therefore, higher loads of maize silage have caused significant increasement of VFA/TA ratio predicted by the model in fermenter F1 in the period between 15th and 21st day. On the other hand, such intensive increasement of VFA/TA ratio is not assumed by the ADM1 for fermenter F2. The reason is in the fact that after the organic matter is partially degradated in fermenter F1 and it enters the fermenter F2, with lower quantities. Therefore, the VFA/TA ratio estimated by the model shows less deviation to experimental data when fermenter F2 is analysed.

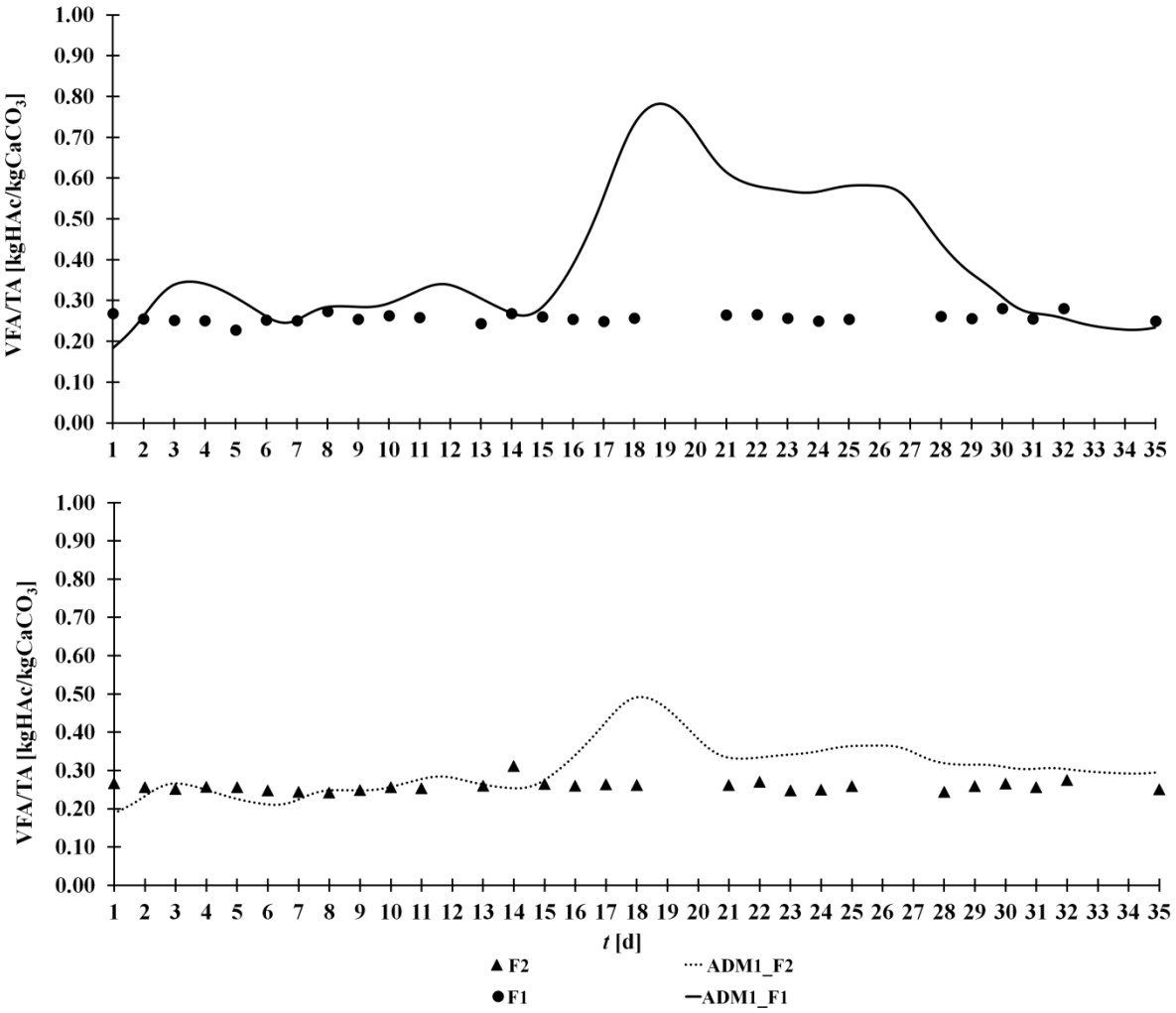


Figure 5. Measured VFA/TA data in fermenters F1 (circle) and F2 (triangle) and modelled data in fermenters F1 (solid line) and F2 (dashed line)

Figure 6 presents measured data of methane presence ($\varphi(CH_4)$) in biogas values (circles and triangles) and model predicted data (lines) in fermenter F1 and fermenter F2.

Measured methane share in fermenter F1 varies between 57.50 % and 60.73 % and in the same time fermenter F2, operates with methane share between 56.74 % and 60.32 %. The model predicts a slightly wider range of methane percentage in biogas. In fermenter F1 model estimates methane share between 55.61 % and 65.12 % and in fermenter F2 between 58.24 % and 65.16 %. It can be stated that model shows the acceptable accuracy of methane share in generated biogas. Current investigations on the AD of a mixture of maize silage and animal slurry showed that the share of methane in biogas varies between 50 % and 75 % [21 - 23].

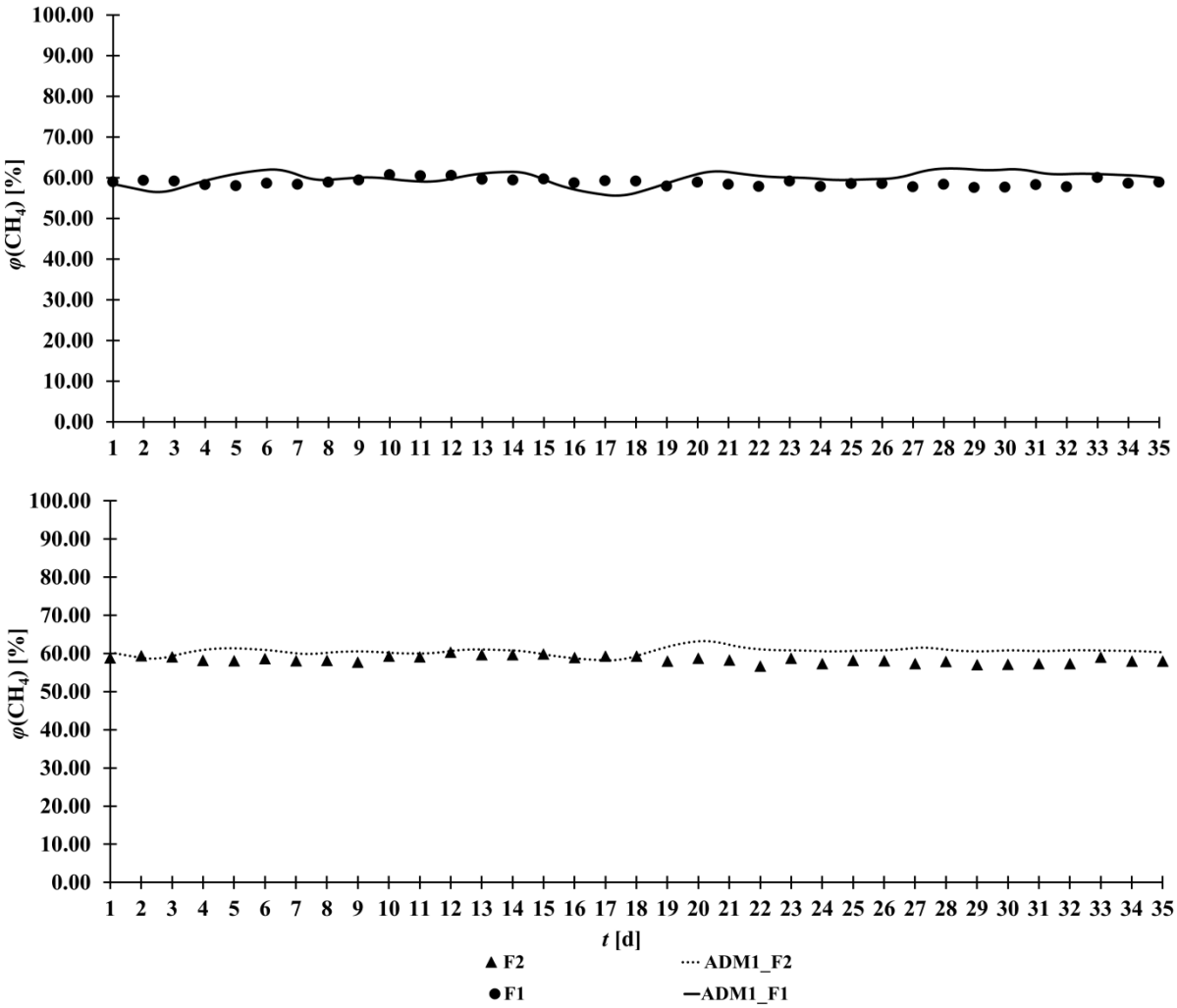


Figure 6. Measured data on methane share in biogas in fermenters F1 (circle) and F2 (triangle) and modelled data in fermenters F1 (solid line) and F2 (dashed line)

The accumulated volume of biogas (V(biogas)) predicted by the model with respect to cumulative input mass of feedstock (m(feedstock)) in fermenters is presented on figure 7. Using the linear regression in MS Excel the biogas yield in the examined system has been determined.

The model predicts the biogas yield of around 0.135 Nm^3 per kilogram of feedstock. In the analysed period, the average feedstock composition has been following: three-quarters of maize silage and one-quarter of the animal slurry. Authors in [24, 25] stated that between 0.155 Nm^3 and 0.220 Nm^3 of biogas is generated over a kilogram of maize silage. In [24] authors also stated that between 0.015 Nm^3 and 0.025 Nm^3 of biogas is generated over the kilogram of the animal slurry. The model predicted data on biogas yield compete with previously conducted investigations in this area.

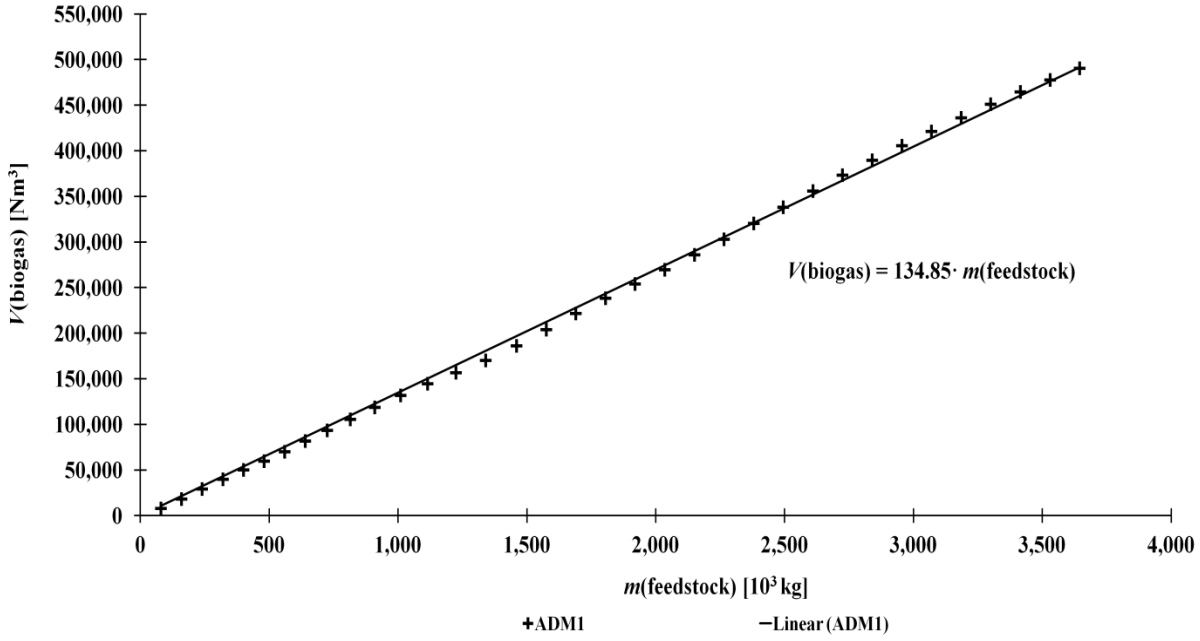


Figure 7. Cumulative biogas volume estimated by the model as a function of cumulative input feedstock mass

4. CONCLUSION

The model successfully describes the gas phase compared to available measured data on methane presence in biogas. In addition, results of biogas yield per kilogram of feedstock match the data found in the literature for analysed substrates [24, 25]. There are some minor deviations of model compare to experimental data on gas phase. On the other hand, model data do not compete with measured data for the liquid phase. There is relatively high deviation of model data compared to measured data for VFA/TA ratio, and as well as in fermenter pH. In order to describe the liquid phase in more detail, extended versions of ADM1 or even more complex models should be taken for observation. Future investigations in this field will be oriented to use of more complex mechanistically inspired models and on the experimental tests of AD process, in both laboratory and industrial scale. Furthermore, the use of some alternative energy crops like grass silage will be the topic of future studies.

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Acknowledgements

This work has been financially supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No: 690142-2 (AgroCycle project).
We gratefully acknowledge assistance in data providing from the biogas power plant Bioplinara Organica Kalnik 1 Ltd. and director Aleksandar Sandić.

ADSORPTION OF NAPROXEN FROM AQUEOUS SOLUTION USING ACTIVATED CARBON HYDRODARCO C

Veselin Bezanovic*, Mladenka Novakovic*, Miodrag Zivancev*, Dusan Milovanovic*, Ivana Mihajlovic*

* University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia

corresponding author: Veselin Bezanovic,e-mail: veselinbezanovic@uns.ac.rs

Original scientific paper

ABSTRACT

Presence of the pharmaceuticals oddment in surface and groundwater, after wastewater treatment, presents emerging environmental issue. The adsorption process is generally known as effective and complementary to conventional treatments in the removal of pharmaceuticals compounds. In this study, the adsorption of a pharmaceutically active compound, naproxen, onto powdery activated carbon has been studied. Several adsorption parameters including the adsorbent dosage, pH, the initial naproxen concentration and contact time were studied. The adsorption isotherm was analysed by different isotherm models. Results show that commercial activated carbon, as an adsorbent, is able to remove the pharmaceutical compound from the aqueous medium. The maximum removal efficiency, over 80 %, was obtained on pH value 5 with the contact time of 30 minutes. The present study indicates that the commercial activated carbon can be used as an adsorbent for removing pharmaceuticals from water and as a tertiary treatment option in wastewater treatment systems.

***Keywords**: naproxen, adsorption, activated carbon, isotherm models*

1. INTRODUCTION

Recently water availability is threatened due to increased anthropogenic pollutants from industrial and non-industrial sectors [1]. About 2 million tons of sewage is being discharged into fresh water every day and in annual report, UN estimated that about 1500 km^3 of wastewater is generated on average level, mark that current amount is about six times higher than existing river waters in the world [1, 2]. The development of civilization has contributed to the enormous technological advancement in many areas of our lives as well as a global problem, which is the impairment of the quality of drinking water and aquatic ecosystem [3]. The current cognition about the contamination levels of water resources with anthropogenic organic pollutants alerts for the necessary development of efficient and

economically and environmentally sustainable remediation methods [4]. Widely used pharmaceuticals and one of the most significant groups of environmental pollutants, mainly due to their resistance and persistence in aquatic ecosystems are non-steroidal anti-inflammatory drugs (NSAIDs) [4, 5]. Among the most commonly used drugs in the pharmacotherapy of pain, NSAIDs are sometimes referred as nonnarcotic - analgesics, which do not cause euphoria and their use does not lead to addiction [3]. One of the NSAID frequently used as over-the-counter drugs in most countries is naproxen. Naproxen is a member of the arylacetic acid group of non-steroidal anti-inflammatory drugs used for treating diseases and alleviating pain. In treated wastewater systems, reported concentration of naproxen was in range of 0.1 – 2.6 gL^{-1} and in surface waters in range of 0.01 – 0.1 gL^{-1} [6]. Simple procurement of naproxen, without any recipe is directly cause of very fast and uncontrolled manner, causing water and soil pollutions and the reason why the appearance of certain pharmaceuticals in irrigation water using fro crops are reported [1]. During the last decade, significant number of research explains that some process such as flocculation, filtration, activated sludge and chlorination is not effective in the elimination of these compounds from wastewaters [7]. Of all treatment methods that have been developed, the process which copious different advantages such as: simple to operate and to design, handling, vigorous continuous and batch processes, toxicity removal, low investment cost and probability of adsorbent reuse and regeneration is adsorption on activated carbon, as one of the most pertinent and promising method for removing organic and inorganic micro pollutants [1, 8, 9]. Activated carbon (AC) is defined as a carbonaceous solid with high micropores volume, well developed surface area and high adsorptive capacity as an efficient adsorbent for water treatment and air pollution control [10, 11]. Activated carbon has been widely applied for several purposes, such as, for the removal of colour, odour, taste and other undesirable organic and inorganic pollutants from drinking water; for solvent recovery; and for the purification of air and pharmaceutical products. Activated carbons (AC) are the most commonly used adsorbents which can be either in granular or powdered form (GAC or PAC, respectively). PAC is usually more efficient with faster adsorption kinetics (due to smaller particle size) and GAC has the main advantage of regeneration/reuse after saturation [4]. The aim of this study was to comprehensively evaluate the adsorption of naproxen onto commercial activated carbon Hydrodarco C, produced by steam activation of lignite coal. In order to optimize processes of adsorption, influence of operational parameters was investigated. The operational parameters such as adsorbent dosage, pH value, contact time and initial concentration were changed in different experiments.

2. EXPERIMENTAL

2.1. Materials and methods

Naproxen (linear formula $CH_3OC_{10}H_6CH(CH_3)CO_2H$, MW = 230.26 $gmol^{-1}$, purity ≥ 98.0 %) is supplied by Sigma Aldrich, Germany, figure 1. represents chemical structure of naproxen.

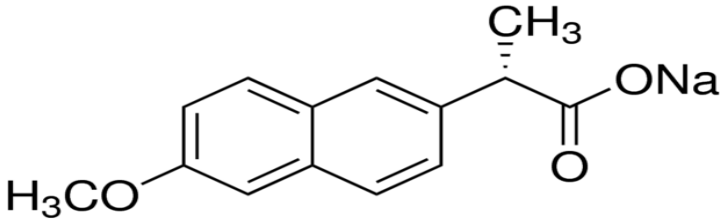


Figure 1. Chemical structure of naproxen [12]

Acetonitrile and acetic acid (HPLC grade) were also obtained from Sigma Aldrich. The powdered activated carbon Hydrodarco C was obtained from CABOT Company, Latvia. The stock solution was prepared by dissolving 5 mg of analytical standard in 25 ml of acetonitrile (final concentration of 200 mgL^{-1}) and the working solutions were obtained by diluting the stock solution with distilled water. As an aqueous matrix, distilled water was used. For pH adjustment, solution of 0.1 % HCl and 1 % of NaOH were used. All chemicals used in experiments were of analytical grade. For determination of remaining pharmaceutical residues, HPLC with diode array detector (Agilent 1260 series) was applied. Chromatography separation was performed at reverse stationary phase Eclipse XDB-C18 (150 x 4.6, particle size 5μm) at flow rate of 0.2 ml min^{-1} and injection volume of 10 μL at room temperature. Mobile phases were consisted of: A – 0.1 acetic acid and B – acetonitrile. The maximum absorbance for observed pharmaceutical is 230 nm.

2.2. Adsorption experiments

Adsorption assays were performed in batch mode at room temperature (25 °C). In order to analyse the influence of pH value, five different pH values were used (3, 5, 7, 9 and 10). The initial concentration of naproxen was 5 mgL^{-1}, prepared in 50 mL Erlenmeyer flasks. After pH adjustment, samples were agitated at mechanic shaker at 140 rpm. The contact time between adsorbent and pharmaceutical was 30 minutes. After stirring, all samples were filtered through filter paper in order to remove activated carbon from solution. After the performed experiment, 1 mL of samples were transferred into 2 mL vials [13].

The influence of mass dosage on adsorption processes was performed in 50 mL aqueous solution of naproxen with different masses of adsorbent (1, 3, 5, 7 and 10 mg). Kinetic studies were investigated at different time intervals (5 - 60 minutes). The initial concentration of naproxen was 5 mgL^{-1}. The influence of initial concentration on adsorption of naproxen was studied with six different concentrations of naproxen (2 – 10 mgL^{-1}), prepared in 50 mL of standard solution.

3. RESULTS AND DISCUSSION

3.1. Influence of pH value

The pH value represents one of the crucial parameters which have the influence on adsorption capacity. Changes in the pH affect the ionization degree and the solubility of the solute as well as the surface charge of the adsorbent. Figure 2 shows the effect of pH value on naproxen adsorption.

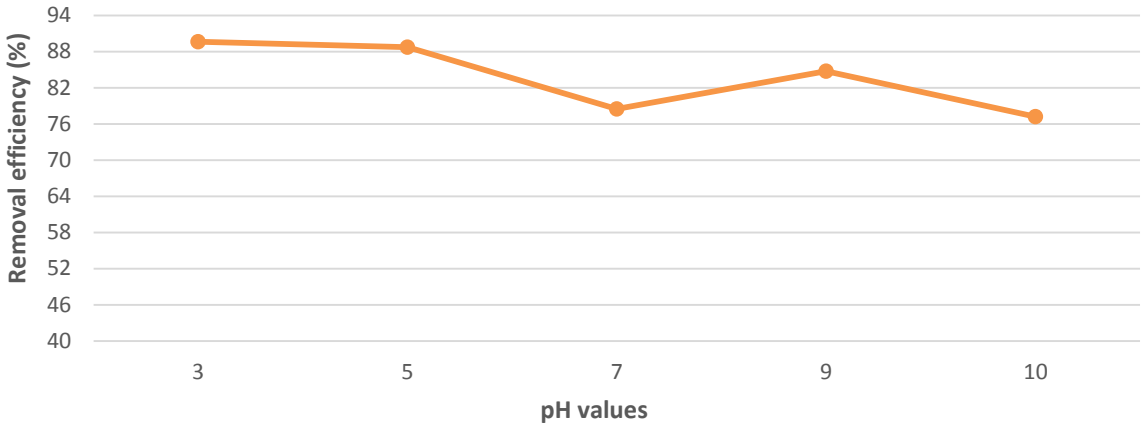


Figure 2. The effect of pH value on adsorption of naproxen

The intensity of interactions remains almost constant at acid conditions. Although naproxen molecule acts like neutral component, according to obtained results, the maximum removal efficiency (88 %) was achieved in acid medium, at pH 3 and 5. After performed the first set of experiments, pH 5 was adopted as optimal.

3.2. Influence of mass dosage

It is necessary to investigate what is the optimal mass of activated carbon in order to achieve satisfactory removal efficiency. By increasing the amount of activated carbon, the number of available sorption sites on its surface area will increase causing the increase in removal efficiency. Figure 3 shows the impact of activated carbon dosage on naproxen adsorption.

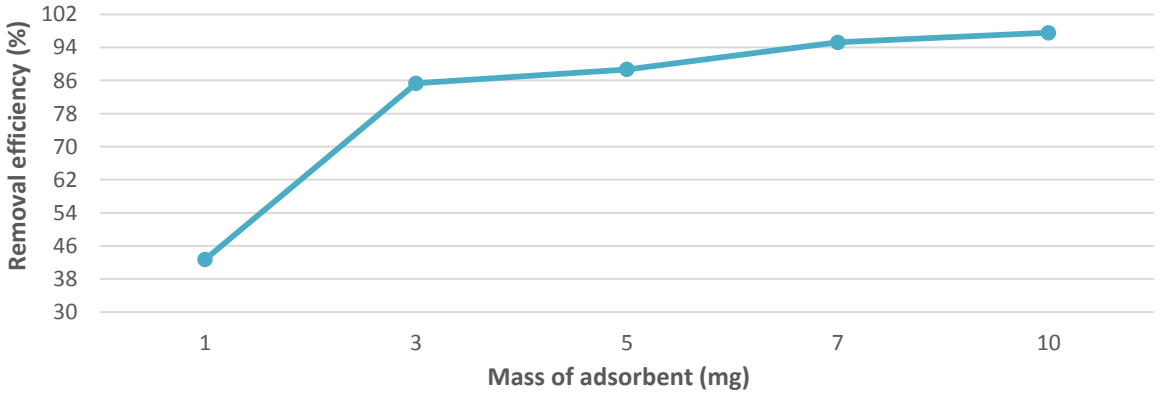


Figure 3. The influence of activated carbon mass

According to figure 3 the maximum removal efficiency was archived at 10 mg dosage (≥ 95 %). However, the difference in efficacy from 5 to 10 mg is not higher than 8 %, so in further research, with economic viability and sustainability, 5 mg of activated carbon was used as optimal mass, where efficiency is around 89 %.

3.3. Influence of contact time

The time in which activated carbon and target pollutant are in contact is essential for the theoretical modelling which can explain the nature of the adsorption process. Figure 4 shows the effect of contact time on naproxen adsorption. The contact time of 30 min was used as optimal for adsorption of naproxen on AC.

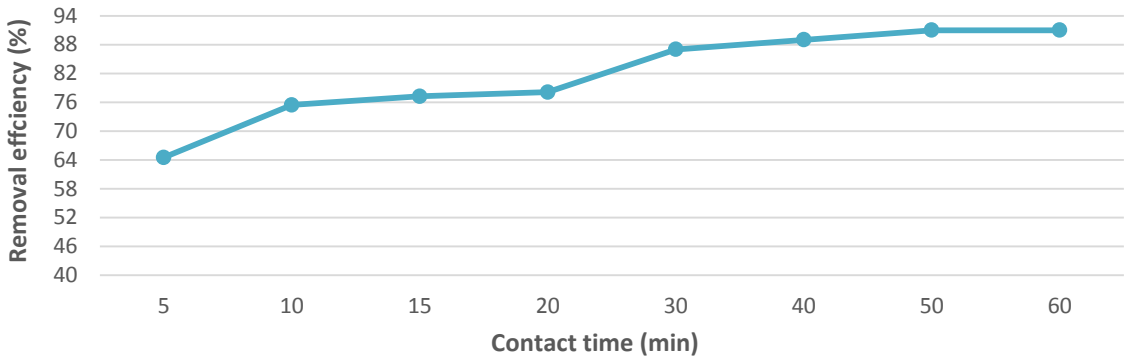


Figure 4. The influence of contact time

From the attached graphics it can be concluded that after 30 minutes the adsorption process is stabilized, where larger amounts of pollutants are removed and further need for mixing and additional power consumption that ultimately requires higher operating costs are unnecessary.

3.4. Influence of initial concentration

The effect of initial concentration of naproxen is very important for the determination of adsorption equilibrium state. Figure 5 shows that by increasing the concentration of naproxen the removal efficiency slightly decreases.

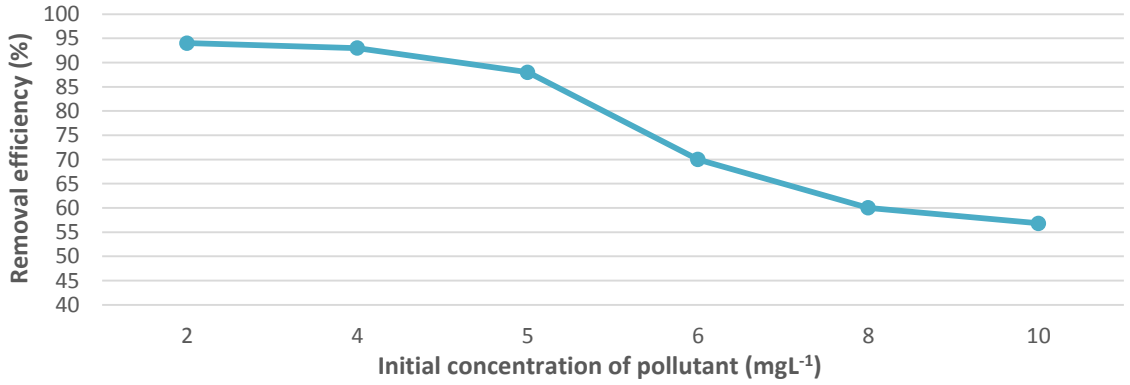


Figure 5. The influence of initial concentration

3.5. Adsorption kinetics

In order to evaluate the kinetics of adsorption, pseudo-first and pseudo-second order kinetic models were used. The pseudo-first order is defined by following linear equation:

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad (1)$$

where q_e is the amount of adsorbate (mgg^{-1}) adsorbed at equilibrium, q_t is the amount of adsorbate (mgg^{-1}) adsorbed at time t (min), and k_1 is the pseudo - first order rate constant ($Lmin^{-1}$).

The pseudo-second order model can be defined by next equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (2)$$

where k_2 is the pseudo-second order rate constant (g/mg min), which is determined from the plots of t/q_t versus t.

According to correlation coefficient provided from statistical data, the nature of adsorption process is best described by pseudo second order model with high correlation coefficient (R^2 = 0.998) (figure 6.).

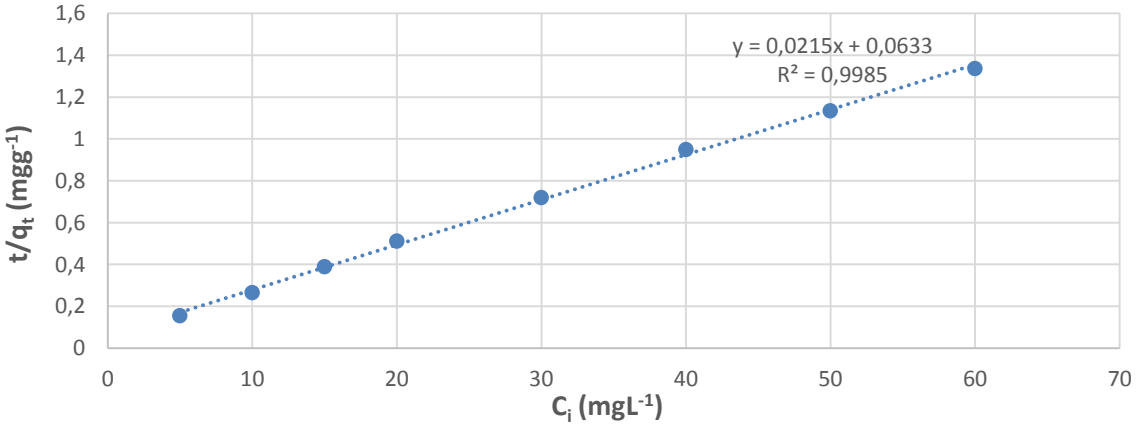


Figure 6. The pseudo second order model

3.6. Equilibrium isotherms

Equilibrium state as a result of dynamic-adsorption processes is commonly represented by so called adsorption isotherms. Adsorption isotherms are presented as the amount of solute retained by mass of solid adsorbent vs. the equilibrium concentration of solute in the liquid phase at the constant temperature. Three types of adsorption isotherms were evaluated: Freundlich, Langmuir and Temkin's isotherms. The Freundlich isotherm assumes that surface of adsorbent is characterized by heterogeneous nature. The linear form of Freundlich isotherms is expressed by the following expression:

$$lnq_e = lnk_f + \frac{1}{n} lnC_e \quad (3)$$

where k_F is the Freundlich constant and n is the adsorption intensity (dimensionless).

The Langmuir isotherm is based on assumption that the surface of adsorbents is consisting of homogeneous binding sites and there is no interaction with adsorbed molecules. The linear form of Langmuir isotherm is presented by the following expression:

$$\ldots\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m + K_L} \tag{4}$$

where c_e (mgL^{-1}) is the equilibrium concentration, q_m is maximum adsorption capacity (mgg^{-1}) and K_L (Lmg^{-1}) is the Langmuir isotherm constant. The Temkin isotherm assumes that heat of adsorption decreases linearly as the extent of adsorption increases.

The linear form of Temkin isotherm is:

$$\ldots q_e = \frac{RT}{b_t} lna_t + \frac{RT}{b_t} lnc_e \tag{5}$$

where R is universal gas constant (8.314 Jmol^{-1}K^{-1}), T (K) - absolute temperature of adsorption process and a_t (Lg^{-1}), b_t (Jmol^{-1}) are Temkin isotherm constants.

According to statistical analysis, on figure 7, the best fit with experimental data is obtained with Langmuir isotherm (correlation coefficient 0.978).

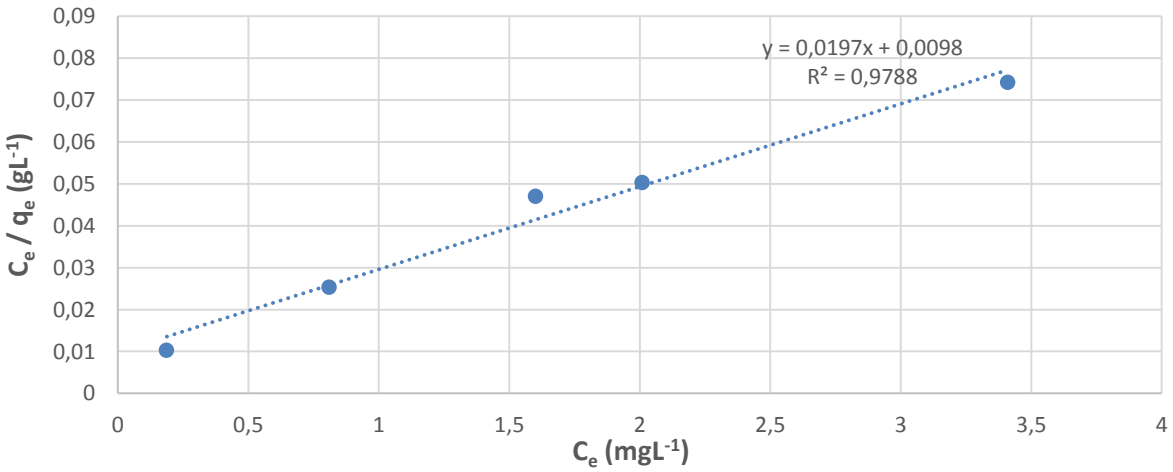


Figure 7. The Langmuir isotherm

4. CONCLUSION

The possibility of applying the adsorption for removal of nonsteroidal anti-inflammatory drug (NSAID), used for used to treat pain or inflammation caused by conditions such as arthritis, ankylosing spondylitis, tendinitis, bursitis, gout, or menstrual cramps, naproxen, in water matrices, was investigated. The obtained results revealed that adsorption onto the commercially available activated carbon Hydrodarco C are effective for the removal of naproxen from the water. According to provided experiments, pH value of 5, mass of 5 mg, contact time of 30 minutes are the most suitable for efficient naproxen removal. The pseudo second order adsorption kinetics is the most suitable for explanation of naproxen adsorption mechanism. The naproxen adsorption is explained by chemisorption which involves chemical

reaction between surface and adsorbate. Langmuir isotherm indicates that separation of naproxen is followed by monolayer adsorption.

Pharmaceutical products and their degradation products are increasingly detected in the environment and still their fate and transformation pathways are largely unknown. After determining the individual capacities of the active carbon and its possible use in the adsorption process for wastewater treatment, it is necessary to approach the researches in which the possibility of removing more pollutants from the same matrix is examined. This approach is much closer to real conditions which occur in our midst. The further development of effective methods for removal of pharmaceuticals, in wastewater and surface water, that are economically viable and sustainable, will be a great challenge.

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Acknowledgements

This study was financially supported by the Project III46009 „Improvement and development of hygienic and technological procedures in the production of foodstuffs of animal origin in order to obtain quality and safe products that are competitive on the world market“.

UTJECAJ DODATKA KOMPLEKSIRAJUĆEG AGENSA U KISELO TLO NA SADRŽAJ CINKA, NIKLA I KROMA U POJEDINIM BILJKAMA

INFLUENCE OF ADDING A COMPLEXING AGENT IN ACIDIC SOIL ON THE CONTENT OF ZINC, NICKEL AND CHROMIUM IN CERTAIN PLANTS

Farzet Bikić*, Amira Pašalić**

* Univerzitet u Zenici, Metalurško-tehnološki fakultet, Zenica, BiH
** Univerzitet u Zenici, Metalurški institut „Kemal Kapetanović", Zenica, BiH

autor za korespondenciju: Farzet Bikić, e-mail: farzet_bikic@yahoo.com

Izvorni znanstveni rad

SAŽETAK

U ovom radu je ispitivan utjecaj dodatka kompleksirajućeg agensa u kiselu podlogu tla na sadržaj cinka, nikla i kroma u pojedinim biljkama. Tlo koje je korišteno za ovaj eksperiment, uzeto je s površina uz saobraćajnicu u neposrednoj blizini Željezare u Zenici. Kompleksiranje tla je izvršeno s otopinom dinatrijeve soli etilendiaminotetraoctene kiseline, Na_2H_2Y, a obaranje pH vrijednosti tla s otopinom aluminij sulfata, $Al_2(SO_4)_3$. Biljke koje su korištene za navedena ispitivanja su: zelena salata (*lat. Lactaca sativa capitata*), mješavina trava, djetelina (*lat. Trifolium repens*), kukuruz (*lat. Zea mays*) i kopriva (*lat. Urtica dioica*). Određivanje sadržaja navedenih metala u pripremljenom tlu i biljkama rađeno je spektrometrijskom metodom ICP-OES, na uređaju atomski emisioni spektrometar. Rezultati provedenih ispitivanja pokazuju da kompleksiranje kisele podloge tla dovodi do povećanja akumulacije cinka, nikla i kroma iz tla u nadzemmne dijelove ispitivanih biljaka.

***Ključne riječi**: cink, nikal, krom, biljke, tlo, kompleksiranje.*

ABSTRACT

This paper examines the effect of addition of complexing agent in acidic soil substrate on the content of zinc, nickel and chromium in certain plants. The soil used for this experiment was taken from the road surfaces, near the Steelworks in Zenica. The soil was complexed with a solution of ethylenediaminetetraacetic acid disodium salt, Na_2H_2Y, while reduction of pH of soil was done with solution of aluminium sulfate, $Al_2(SO_4)_3$. The plants

used for the above-mentioned tests were: lettuce (*lat. Lactaca sativa capitata*), mixture of grass, clover (*lat. Trifolium repens*), maize (*lat. Zea mays*) and nettle (*lat. Urtica dioica*). Determination the content of the specified metals in the prepared soil and plants was done by using spectrometric method ICP-AES, on the device atomic emission spectrometer. The results of the research indicated that the complexation of the acidic soil substrate had led to increased accumulation of zinc, nickel and chromium in the soil and the aboveground parts of the tested plants.

***Keywords**: zinc, nickel, chromium, plants, soil, complexation*

1. UVOD

Teški metali su u okolišu prisutni još od samog nastanka Zemlje, međutim njihov štetni utjecaj se primjećuje tek sa intenzivnijim tehnološkim i industrijskim razvojem i posebno je izražen u urbano-industrijskim sredinama kao što je i zenički region. Biopristupačnost i bioakumulacija teških metala u biljkama izravno je vezana za njihov sadržaj i mobilnost u tlu [1]. Sadržaj teških metala u tlu predstavlja rezultat inputa metala iz matičnog supstrata, atmosferskih depozicija, saobraćaja, đubriva i pesticida [2]. Najveći dio teških metala u tlo dospijeva atmosferskim depozicijama, te se oko industrijskih postrojenja tlo može kontaminirati od 15 - 40 km u smjeru dominantnih vjetrova, pa čak i šire [2]. U tlu su teški metali prisutni zahvaljujući tome što su vezani u kemijske spojeve (okside, sulfide, sulfate, karbonate) koji su u vodi praktično netopljivi. Topljivost pojedinih komponenti tla, najčešće se povećava porastom kiselosti. Zato pH reakcija tla predstavlja jedan od ključnih faktora unosa teških metala u biljke. Smanjenjem pH za jednu jedinicu, topljivost, a samim tim i mobilnost u tlu teških metala kao što su cink, kadmij i nikal povećava se za dva puta [3]. Promjenom pH vrijednosti mijenja se topljivost navedenih metala, bilo da se talože (obično kod povećanja pH) ili otapaju iz slabo topljivih oksida ili hidroksida, pri čemu nastaju neorganski i organski kompleksi u tlu. Biljke teške metale usvajaju iz tla preko korijenovog sistema te taj način učestvuju u ciklusu kruženja tvari u prirodi. One predstavljaju "međurezervoar" kroz koji se teški metali iz tla i dijelom iz zraka djelimično kreću kroz lanac ishrane prema čovjeku. Da bi korijen biljke usvojio teški metal, potrebno je prvo da se metal otopi u vodi, jer su veoma često metali u tlu u netopljivom obliku vezani za organske ili anorganske čestice u podlozi [4]. Biljke ih usvajaju u obliku iona ili organskih kompleksa, u većoj ili manjoj količini, iz hranljive otopine, odnosno iz tla za koje su vezane korijenovim sistemom. Apsorpcija metala koje biljke vrše iz tla, vrlo je kompleksna i zavisi od koncentracije, mobilnosti, kemijskih osobina i topljivih formi kemijskih elemenata (koje mogu biti ionske, neionske i kompleksirane).

Osnovni cilj ovog rada je bio da se istraži i potvrdi utjecaj dodatka kompleksirajućeg agensa u kiselo tlo na ekstrakciju pojedinih teških metala iz kontaminiranog tla u određene biljne vrste. Etilendiaminotetraoctena kiselina (EDTA) je jedan od glavnih kemijskih reagensa korištenih za izdvajanje tragova elemenata iz uzoraka tla kako bi se predvidjela njihova biodostupnost ili mobilnost [5]. EDTA se već dugi niz godina upotrebljava kao helatizirajući agens za opskrbu mikronutrientnih kationa za biljke. S druge strane, EDTA je jedan od najčešće korištenih industrijskih agenasa za kompleksiranje (fotografska industrija, tekstilna i metalna industrija, proizvodnja papira, industrijsko čišćenje) te je stoga i ozbiljan polutant u rijekama i podzemnim vodama.

2. EKSPERIMENTALNI DIO

Eksperimentalni dio ovog rada se sastoji iz:

- analize cinka, nikla i kroma u tlu i određivanja pH vrijednosti suspenzije uzorka tla, nulto stanje,
- pripreme tla za zasijavanje odabranog bilja,
- zasijavanje sjemena i njegovanje do postizanja odgovarajućeg rasta,
- obrada biljnog materijala i njegova kemijska analiza na sadržaj cinka, nikla i kroma.

Tlo koje je korišteno za ovaj eksperiment uzeto je s površina uz saobraćajnicu u neposrednoj blizini Željezare u Zenici, prenijeto u laboratorij, te je miješanjem u rotacionom bubnju homogenizirano. Homogenizirano tlo je raspoređeno u deset posuda od po 12 dm^3. Određivanje sadržaja ispitivanih teških metala (Zn, Ni i Cr) u pripremljenom tlu rađeno je prema standardu ISO 11 466, 1995. Koncentracije ispitivanih metala (Zn, Ni i Cr) mjerene su iz ekstrakata tla spektrometrijskom metodom ICP-AES, na uređaju atomski emisioni spektrometar, PERKIN ELMER 7000DV. Vrijednost pH reakcije tla je određena u vodenoj suspenziji, čime se dobije aktivna kiselost, i suspenziji tla u 1M otopini KCl, čime se dobije potencijalna kiselost. Za ispitivanje utjecaja dodatka kompleksirajućeg agensa na sadržaj ispitivanih teških metala u pojedinim biljkama pripremljene su dvije podloge tla: kisela (K) i kisela kompleksirajuća (KK). Biljke koje su korištene za navedena ispitivanja su: zelena salata (*lat. Lactaca sativa capitata*), mješavina trava, djetelina (*lat. Trifolium repens*), kukuruz (*lat. Zea mays*) i kopriva (*lat. Urtica dioica*). Priprema tla za sijanje i rast biljaka se odvijala u zatvorenom prostoru, kako bi se izbjeglo dodatno unošenje teških metala iz atmosfere preko nadzemnih dijelova biljaka. Nakon navedenih radnji, pristupilo se zasijavanju pomenutih biljnih vrsta. Posude sa zasađenim biljkama su smještene u prostoriju na mjestu koje je omogućavalo odgovarajuću osvijetljenost. Nakon što je završila vegetacija, nadzemni dijelovi biljaka su sječenjem, neposredno iznad korijena, uzeti iz posuda u kojima su bile zasađene, osušeni na zraku, zatim u sušioniku na 105 ^oC i usitnjeni drobljenjem, a na kraju u ahatnom tarioniku. Za određivanje sadržaja ispitivanih metala u biljkama, odvagano je po 1,000 g biljnog materijala i preneseno u platinskom lončiću u kojem je pažljivo spaljen bez pojave plamena. Ugljenisani ostatak je spaljen u žarnoj peći, držan je oko 15 minuta na temperaturi 750 ^oC. Nakon toga, u lončić je dodano 5 cm^3 vode i 2 cm^3 HNO_3 i, uz blago zagrijavanje, sadržaj u lončiću je preveden u otopinu. Dobivena otopina je kvantitativno prenesena u odmjernu tikvicu od 25 cm^3, koja je nakon hlađenja na sobnu temperaturu, dopunjena vodom do marke. Koncentracija ispitivanih teških metala u biljnom materijalu je također određivana metodom ICP-AES, na uređaju atomski emisioni spektrometar, PERKIN ELMER 7000DV. Ponovljivost rezultata svih analiza ispitivanih teških metala (u tlu i biljnom materijalu) provjerena je na način da je za svaki uzorak vršena analiza na tri replike, pri čemu preračunata vrijednost relativne standardne devijacije niti jednog analiziranog uzorka (%RSD) nije prelazila 5 %. Za pripremu svih otopina korištenih u provedenom eksperimentu korištene su super čiste kemikalije (Merck, Njemačka) i redestilovana voda. Cijeli eksperiment, priprema podloge, zasijavanje i uzgajanje eksperimentalnih biljaka, kemijska analiza tla, analiza sadržaja ispitivanih metala u tlu i biljkama, rađen je u kemijskom laboratoriju Metalurškog instituta "Kemal Kapetanović" u Zenici.

3. REZULTATI I DISKUSIJA

Vrijednosti sadržaja ispitivanih teških metala u tlu predstavljene su u tablici 1. Granične vrijednosti sadržaja Zn, Ni i Cr u tlu prikazane su u tablici 2. Uspoređivanjem dobijenih rezultata određivanja sadržaja Zn, Ni i Cr u tlu korištenom za ovaj eksperiment, sa propisanim graničnim vrijednostima jasno se uočava da koncentracije ispitivanih teških metala prelaze propisane granične vrijednosti. Na osnovu kemijske analize tla na sadržaj ispitivanih teških metala, bilo je jasno da odabrane teške metale nije potrebno dodatno unositi u tlo. Na ovaj način su uslovi rasta biljaka u laboratoriju bili vrlo slični onim u prirodi. Naime, ukoliko bi se metali dodavali „vještačkim“ putem, to bi bilo uglavnom dodavanje u otopini, odnosno putem topljivih soli, što se u prirodi mnogo manje susreće.

Tablica 1. Sadržaj ispitivanih teških metala u tlu (nulto stanje)

Sadržaj teških metala u tlu ($mg/kg_{s.m.}$)		
Zn	Ni	Cr
440	170	80

Tablica 2. Granične vrijednosti sadržaja Zn, Ni i Cr u tlu [6]

Teški metal	Pjeskovito tlo ($mg/kg_{s.m.}$)	Praškasto-ilovasto tlo($mg/kg_{s.m.}$)
Zn	100	150
Ni	30	40
Cr	50	80

Izmjerena vrijednost pH reakcija tla u vodenoj suspenziji, aktivna kiselost, iznosila je 7,8 dok je izmjerena vrijednost pH reakcija tla u suspenziji tla u 1M otopini KCl, potencijalna kiselost, iznosila 6,9. S obzirom da su rezultati pokazali da je tlo za zasijavanje biljaka alkalno, u svih deset posuda sa tlom se pristupilo njegovom zakišeljavanju (K podloga). Zakišeljavanje tla je vršeno dodavanjem 200 cm^3 otopine aluminij sulfata, $Al_2(SO_4)_3$, koncentracije 50 gdm^{-3} na 13 kg tla. Zatim je u 5 posuda sa K - podlogom dodata otopina dinatrijeve soli etilendiaminotetraoctene kiseline, Na_2H_2Y, te je na taj način pripremljena i kisela kompleksirajuća podloga (KK). Kompleksiranje tla je vršeno dodavanjem 200 cm^3 0,1 M otopine Na_2H_2Y, na 13 kg tla. Nakon pripreme podloga za zasijavanje ponovno je određena pH vrijednost tla u vodenoj suspenziji i suspenziji tla u 1M otopini KCl, te su izmjerene vrijednosti predstavljene u tablici 3.

Tablica 3. pH tla pripremljenog za sijanje

Vrsta podloge tla	pH (u H_2O)	pH (u 1M KCl)
K	6,3	5,7
K-K	5,9	5,3

U tablici 4 su dati rezultati sadržaja Zn, Ni i Cr u pojedinim biljkama.

Tablica 4. Sadržaj ispitivanih teških metala u pojedinim biljkama

Metal	Tip podloge	Koncentracija metala u pojedinim vrstama biljki (mg/kg$_{s.m.}$)				
		Zelena salata	Djetelina	Mješavina trava	Kukuruz	Kopriva
Zn	K	68,8	39,1	72,2	66,5	24,0
	KK	72,8	82,8	183,5	148,6	103,6
Ni	K	18,1	6,0	7,6	2,1	6,0
	KK	28,4	65,5	68,0	6,0	44,0
Cr	K	4,0	9,3	6,1	6,0	5,1
	KK	4,2	12,4	18,3	7,0	3,5

Rezultati iz tablice 4 pokazuju da je koncentracija sva tri ispitivana teška metala veća u gotovo svim biljkama gajenim u kiselom kompleksirajućem tlu u odnosu na kiselu podlogu tla koja nije kompleksirana. Izuzetak od navedene konstatacije je jedino sadržaj kroma u koprivi.

Sadržaj cinka u eksperimentalnim biljkama je bio znatno veći u odnosu na ostale ispitivane metale, što se moglo i očekivati s obzirom da se cink može smatrati i kao esencijalni element za biljke**.** Naime, cink je neophodan za sintezu indoloctene kiseline i hormona rasta – auksina, za metabolizam dušika, sintezu škroba itd. Sadržaj cinka u kiselom tlu (K-podloga) se kretao od od 24,0 mg/kg$_{s.m.}$ u koprivi do 72,2 mg/kg$_{s.m.}$ u mješavini trava. Kopleksiranjem kiselog tla (KK -podloga) dolazi do povećanja sadržaja cinka u svim ispitivanim biljkama. Najveće povećanje akumulacije ovog metala je bilo kod koprive gdje se sadržaj cinka povećao više od 5 puta i to sa 24,0 na 103,6 mg/kg$_{s.m.}$, zatim kod mješavine trava sa 72,2 na 183,5mg/kg$_{s.m.}$. Ovi rezultati zapravo pokazuju da je cink sklon stvaranju kompleksa. Kelatni agensi, bilo prirodni ili sintetski, igraju važnu ulogu u mobilnosti cinka u tlima. Smatra se da prisutnost EDTA u suspenziji tla može smanjiti sorpciju cinka u tlu. Vezujući cink u komplekse EDTA održava većinu Zn u mobilnom obliku [7].

Sadržaj nikla u kiselom tlu (K-podloga) se kretao od od 2,1 mg/kg$_{s.m.}$ u kukuruzu do 18,1 mg/kg$_{s.m.}$ u zelenoj salati. Kopleksiranjem kiselog tla (KK -podloga) dolazi do povećanja sadržaja nikla u svim ispitivanim biljkama. Sadržaj nikla, kompleksiranjem kiselog tla (KK-podloga), varirao je zavisno od vrste biljke i kretao se od najniže od 6,0 mg/kg$_{s.m.}$u kukuruzu do 68,0 mg/kg$_{s.m.}$ u mješavini trava. Najveće povećanje akumulacije nikla je bilo kod djeteline, više od 10 puta (sa 6,0 na 65,5 mg/kg$_{s.m.}$), zatim kod mješavine trava, skoro devet puta (sa 7,6 na 68,0 mg/kg$_{s.m.}$). Navedeni rezultati pokazuju da je i nikl sklon stvaranju kompleksa. Nikl je esencijalni nutrijent za biljke i životinje i sastavni je dio ureaze, metil koenzim M reduktaze, hidrogenaze i karbonmonoksid dehidrogenaze [8].

Sadržaj kroma u kiselom tlu (K-podloga) se kretao od od 4,0 mg/kg$_{s.m.}$ u zelenoj salati do 9,3 mg/kg$_{s.m.}$ u djetelini. Kopleksiranjem kiselog tla (KK -podloga) dolazi do povećanja sadržaja kroma u gotovo svim ispitivanim biljkama, izuzetak je kopriva. Registrovane vrijednosti, izuzme li se kopriva, su se kretale od 4,2 mg/kg$_{s.m.}$u salati do 18,3 mg/kg$_{s.m.}$ u mješavini trava. Najveće povećanje akumulacije kroma je zabilježeno kod mješavine trava (tri puta) i to sa 6,1 na 18,3 mg/kg$_{s.m.}$ Koncentracija pristupačnog kroma za biljke u većini podloga tla je niska, pa se u biljkama zbog toga i nalaze manje koncentracije kroma.

4. ZAKLJUČAK

Kompleksiranje kisele podloge tla s otopinom dinatrijeve soli etilendiaminotetraoctene kiseline, Na_2H_2Y dovodi do povećanja akumulacije cinka, nikla i kroma iz tla u nadzemmne dijelove ispitivanih biljaka, a to su: zelena salata, mješavina trava, djetelina, kukuruz i kopriva. Izuzetak je jedino sadržaj kroma u koprivi gdje nije došlo do povećanja akumulacije navedenim postupkom kompleksiranja. Povećana mobilnost kompleksiranjem kisele podloge tla je izraženija kod cinka i nikla a manje izražena kod kroma. Razlog tome može biti to što se cink i nikl mogu smatrati esencijalnim elementima za biljke kao i elementima koji imaju povećan afinitet u stvaranju kompleksa s EDTA.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

QUANTIFICATION OF POLYBROMINATED DIPHENYL ETHERS IN BOTTOM SEDIMENT OF DANUBE RIVER IN THE VICINITY OF NOVI SAD

Maja Brborić*, Branislav Vrana, Jelena Radonić*, Tijana Marinković*, Maja Turk Sekulić***

* University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia
** Masaryk University, Faculty of Sciences, Research Centre for Toxic Compounds in the Environment RECETOX, Brno, Czech Republic

corresponding author: Maja Brborić, e-mail: majastupavski@uns.ac.rs

Original scientific paper

ABSTRACT

Polybrominated diphenyl ethers (PBDEs), belonging to the group of brominated flame retardants are widely used in various commercial products. PBDEs have attracted increasing attention due to their toxicity and bioaccumulation potential. In this article, ten PBDE congeners were analysed in three bottom sediment samples collected from the Danube River in the vicinity of Novi Sad. All ten PBDE congeners were detected in sediments with the with total concentrations range from 0.01 to 3.44 ng/g (Begeč), 0.003 to 0.49 ng/g (Ratno Ostrvo), 0.01 to 7.92 ng/g (Šangaj) and the mean levels of 0.36, 0.05 and 1.17 ng/g (respectively). Penta- and deca- BDE were more frequently detected than others. Obtained concentration levels are higher or similar when compared with previously conducted researches, and are likely associated with anthropogenic activities in their surrounding area, which has experienced a fast industrial growth in the last decade. The article provides new and useful information on PBDEs concentration levels in the Danube River.

***Keywords**: polybrominated diphenyl ethers, sediment, Danube River*

1. INTRODUCTION

A specific chemical analysis of some environmental matrices can lead to an unambiguous clarification of their pollution status. For aquatic systems, both the stream water and bottom sediments act as important sinks of different contaminants in the freshwater system [1 – 3]. The surface water quality is very important for specific area and reflects the activities going on around the catchment of the surface water [4]. Small streams may carry not contaminated water for most parts of the year whereas, during the rainy season, the water may

transport a moderate amount of dirt, organic debris, and suspended materials [5]. As streams move closer to inhabited or dumpsite areas, water quality can undergo various forms and levels of deterioration capable of eroding the availability of water for humans and ecosystems and even decrease species diversity within a given ecosystem [6].

Polluted riverine sediments may serve as a secondary source of downstream contamination during sediment remobilization, especially in high flow periods, floods or in the case of riverbed remediation and management. Such remobilization may transport polluted sediments further downstream or to a wider watercourse area. It is very important to understand the contribution of sediments as a secondary source of persistent and emerging organic pollutants, especially in large river systems such as Danube, with many different types of water usage. Also, it is essential to understand the relationship between trace contaminants and riverine sediments and then it is possible to better recognise the fate and effects of these compounds in aquatic ecosystems.

Flame retardants and their degradation products block a burning process by stopping the exothermic process that occurs in the flame. Thus, the system is cooled, reducing the amount of combustible gas, and, finally, burning process will be inhibited. The importance of flame retardants is reflected in the extension of time causing large flames and time of absolute combustion of certain materials to 30 minutes, which allows people safer evacuation. Brominated flame retardants (BFRs) are the substances that added to industrial products in order to inhibit or slow down the propagation of fire [7, 8]. BFRs, including polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD), have been detected in environmental and biotic matrices on a global scale. With their increasing temporal concentration trends, concern for long-term effects on human health has been raised [9]. Among the ten new persistent organic pollutants, tetra-BDE and penta-BDE have been listed in the Stockholm Convention on Persistent Organic Pollutants in 2009 [10], while BDE 47, 99, 100, 153, 154, 198, 209, based on the NORMAN list (*Network of Reference Laboratories for Monitoring of Emerging Environmental Pollutants*), have been designated as emerging contaminants [11]. BFRs are released into the environment through a variety of routes, such as volatilization or dust formation during the use of treated products in homes, car interiors and workplaces, emissions during manufacture and ensuing waste disposal, as well as during recycling of PBDE-containing products. Hepta-PBDEs have been detected in soil and the scalp hair of Chinese populations residing around electronic waste disassembly sites [12], while concentrations of deca-BDPE have been reported in air and dust from an electronic recycling facility, homes, offices, cars and hotels [13 - 16].

The aim of this study was to compare the concentrations of ten PBDE congeners in the Danube River sediments of the three different locations in the vicinity of Novi Sad. We have also studied the relationships between the levels of PBDEs and the contents of organic carbon in the sediments.

2. EXPERIMENTAL

2.1. Sample collection

The sampling of sediment was performed in October 2012. Within this study, three samples of bottom sediment from different sites of Danube River in the vicinity of Novi Sad were collected using a grab sampler Begeč, D1 (1,275 km of Danube), Ratno Ostrvo, D2 (1,257 km of Danube) and Šangaj, D3 (1,250 km of Danube) (figure 1). Samples were

transported to the laboratory in the ice cooler, where they were weighed and sealed to avoid contamination. All sediment samples were analysed in the laboratory of Research Centre for Toxic Compounds in the Environment - *RECETOX* (Brno, Czech Republic). Before analysis, wet sediment samples were sieved though 2 mm sieve to remove leaves, stoned and roots.

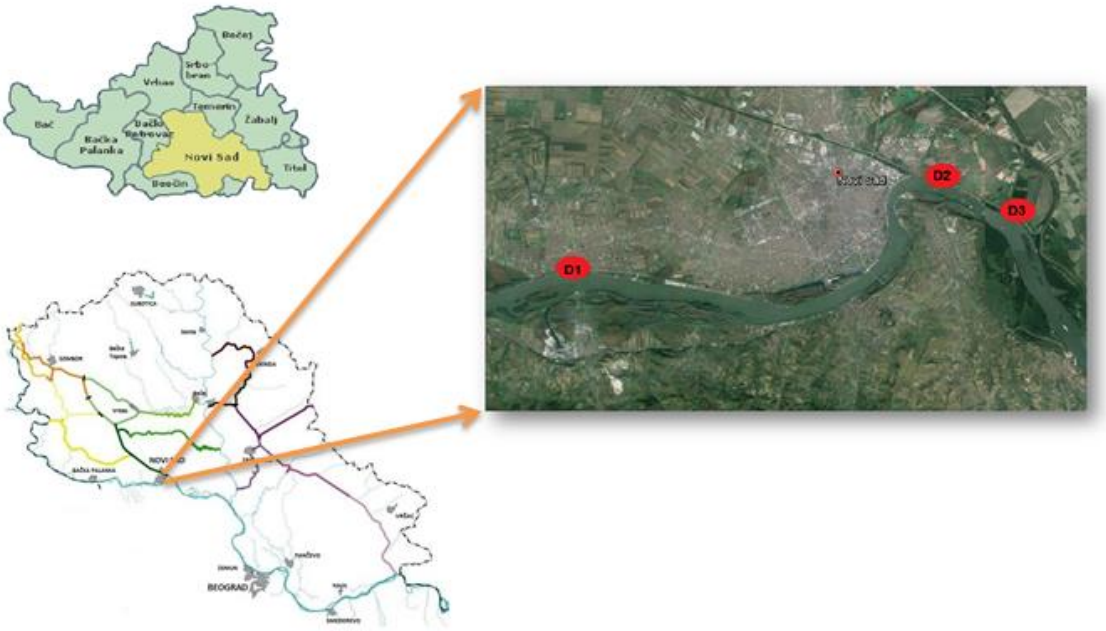


Figure 1. Danube River sampling sites in the vicinity of Novi Sad

2.2. Sediment analysis

Sediment samples were extracted in a Soxhlet extractor (60 minutes warm Soxhlet followed by 30 minutes of solvent rinsing) with toluene in a B-811 extraction unit (Büchi, Switzerland). Prior to extraction, the samples were spiked with 13C BDEs (28, 47, 66, 85, 99, 100, 153, 154, 183, 209). The concentrated extracts were cleaned-up on a sulphuric acid modified silica gel (30 % w/w), eluted with 40 ml DCM/n-hexane mixture (1:1). Fractionation was achieved in a micro column (6 mm i.d) containing from bottom to top: 50 mg silica gel, 70 mg charcoal/silica gel (1:40) and 50 mg of silica gel. The column was pre-washed with 5 ml of toluene, followed by 5 ml of DCM/cyclohexane mixture (30 %). Then, the sample was applied and eluted with 9 ml DCM/cyclohexane mixture. Samples were concentrated using the stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into an insert in a vial. The syringe standards (13C BDEs 77 and 138) were added to all samples and the final volume was 50 µl. PBDEs were analysed using 7890A gas chromatography–mass spectrometry (Agilent, USA), equipped with a 15m x 0.25 mm x 0.10 um DB5 column (Agilent J&W, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK).

In this study, Pearson correlation analysis was performed to obtain information about the interrelationships between PBDEs and TOC.

3. RESULTS AND DISCUSSION

Figure 2 shows total concentration of 10 PBDEs (BDE 28, 47, 66, 85, 99, 100, 153, 154, 183, 209) (a) and carbon content (%) (b) in sediments of the Danube River. Concentration levels of PBDEs (ng/g dry weight (d.w.)) in the sampling sites Begeč, Ratno Ostrvo and Šangaj were in the range from $1.05 \cdot 10^{-3}$ to 3.42 ng/g d.w., from $0.26 \cdot 10^{-3}$ to 0.49 ng/g d.w. and from $1.37 \cdot 10^{-3}$ to 0.56 ng/g d.w., with the sum of total concentration of 3.65 ng/g d.w., 0.52 ng/g d.w. and 11.70 ng/g d.w., respectively. These are much higher values than those previously reported for other aquatic sediment [17, 18]. The percentage of deca-BDE indicates absolute dominance in all tested sediment samples and was over 94 % for sites D1 and D2. At the site D3, the contribution of BDE 183 (hepta-BDE) was 67.7 % of all investigated pollutants (figure 3).

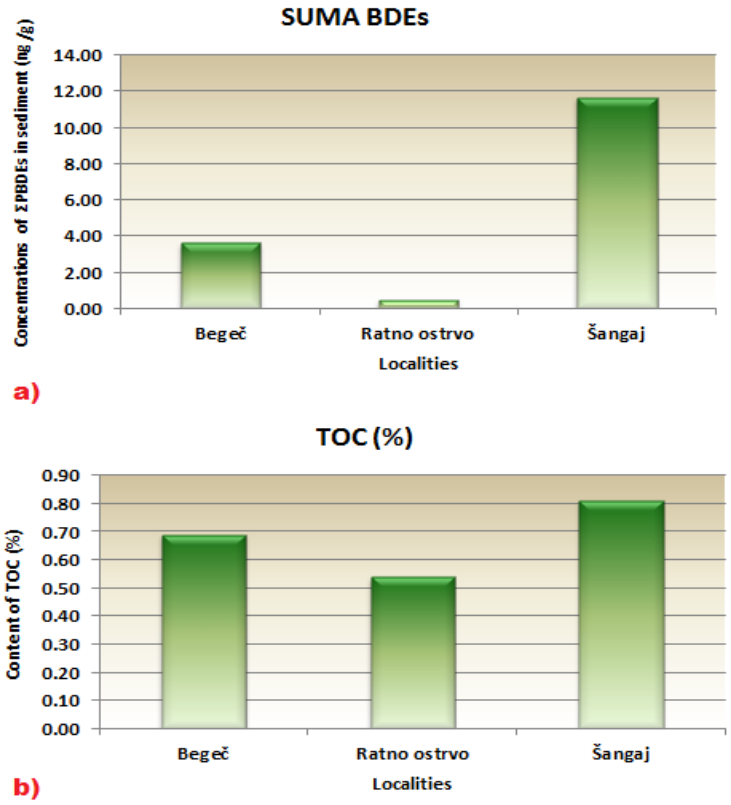


Figure 2. ΣPBDEs total concentration (a) and TOC contents (b) in Danube sediment

The TOC contents in sediment samples were 0.69 %, 0.54 % and 0.81 % for localities D1, D2 and D3, respectively (figure 2b). In our study, correlation analysis was performed to obtain information about the interrelationships between concentration levels of PBDEs and TOC contents in sediments. There was a positive, significant linear correlation between PBDEs concentrations and TOC contents in the sediments of Danube River ($r = 0.95$; $p < 0.01$). Also, significant correlation was observed between the content of organic matter and individual PBDEs concentrations, ranging from $r = 0.74$ (for PBDE 28) to $r = 0.99$ (for PBDE 118) (table 1). These results suggested that the organic matter in the sediment may play significant role in the PBDEs levels.

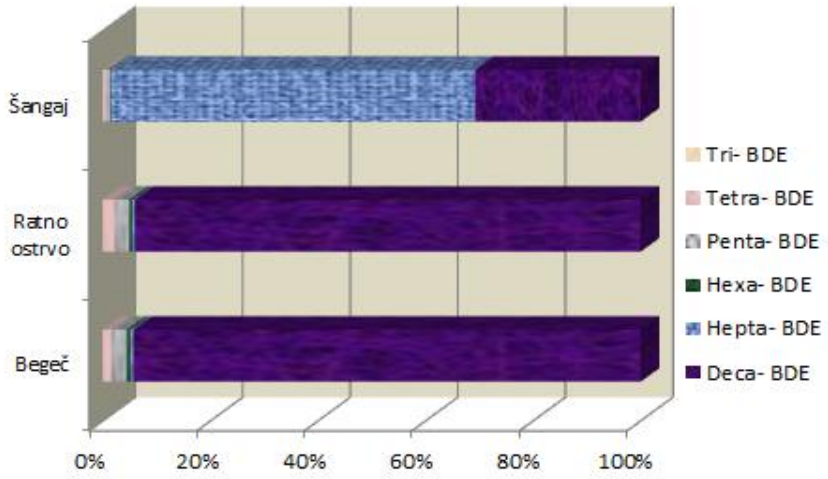


Figure 3. The composition of PBDE congeners at the selected sites

Table 1. Pearson correlations between the content of TOC and PBDE congeners in sediment samples

	Proximity Matrix										
	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209	TOC (%)
BDE 28	1.000	0.968	0.912	0.955	0.940	0.824	0.876	0.831	0.746	0.963	0.990
BDE 47		1.000	0.986	0.999	0.995	0.940	0.969	0.944	0.556	1.000	0.923
BDE 66			1.000	0.993	0.997	0.984	0.997	0.986	0.408	0.989	0.845
BDE 85				1.000	0.999	0.955	0.979	0.959	0.515	1.000	0.903
BDE 99					1.000	0.968	0.988	0.971	0.474	0.997	0.882
BDE 100						1.000	0.995	1.000	0.238	0.946	0.735
BDE 153							1.000	0.996	0.332	0.973	0.798
BDE 154								1.000	0.250	0.950	0.744
BDE 183									1.000	0.541	0.833
BDE 209										1.000	0.916
TOC (%)											1.000
This is a similarity matrix											

4. CONCLUSION

In conducted study we are presented the concentration levels of ten PBDE congeners in the Danube sediment at 3 locations in the vicinity of Novi Sad (D1-Begeč, D2-Ratno ostrvo and D3-Šangaj). The highest level of PBDEs was recorded at the locality D3, while the lowest at the locality D1. The results obtained within our study suggest the dominance of the deca-BDE congener at localities Begeč and Ratno ostrvo and hepta-BDE at locality Šangaj, as well as the significant correlation of presence of all examined pollutants with the values of TOC in sediment.

Despite the extensive investigations that have been done globally on persistent organic pollutants, there is a lack of information about BFRs in the Serbian environment. This study addresses a knowledge gap by providing the data on contamination status of aquatic body by PBDEs, which is an important contribution regarding environmental matters on new emerging contaminants. A more comprehensive understanding would be achieved by further studies on

the dynamic pollution mechanism and the status of aquatic biota in this region. Systematic ecological and ecotoxicological effects of BFRs and associated contaminants on aquatic biota would provide a significant indication of the bioavailability of these new emerging contaminants.

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Acknowledgements

This research was supported by Ministry of Education, Science and Technological Development, Republic of Serbia (III46009).

SIMULTANEOUS EXTRACTION AND CHROMATOGRAPHIC DETERMINATION OF VETERINARY PHARMACEUTICALS THAT AFFECT OUR ECOSYSTEM

Dijana Ceric*, Danijela Asperger, Ivona Kaselj**, Sabina Prasnicki****

* BergmanLabora, Karlsrovägen 2D, Danderyd, Sweden
* Faculty of chemical engineering and technology, Zagreb, Croatia

corresponding author: Dijana Ceric, e-mail: dijana.dijanaceric@gmail.com

Original scientific paper

ABSTRACT

The extraction and analysis of eight veterinary pharmaceuticals in sediment sample by ultrasound solvent extraction and matrix solid phase dispersion followed by high performance liquid chromatography with diode array detector were presented. Chosen pharmaceuticals were tylosine (macrolide antibiotic), albendazole, febantel and levamisole (antihelmintics), lidocaine and procaine (anesthetics), hydrocortisone and dexamethasone (steroidal hormones). After chromatographic analysis both methods were validated and the optimal parameters were determined for ultrasound solvent extraction (solvent, extraction duration, power and temperature of ultrasonic bath) and matrix solid phase dispersion (sorbent, solvent, solvent volume, sediment/sorbent mass ratio). Recoveries of selected pharmaceuticals from spiked sediment samples were generally higher than 50 %. However, dexamethasone and hydrocortisone showed lower recoveries due to their significantly different molecule structure. The results showed the ability to simultaneously extract investigated pharmaceuticals from complex sediment sample by two different extraction methods followed by simple and sensitive high performance liquid chromatography method.

Keywords: *sediment, veterinary pharmaceuticals, ultrasound solvent extraction, matrix solid phase dispersion, high performance liquid chromatography*

1. INTRODUCTION

Pharmaceuticals are biologically active substances used in small amounts to treat various human and animal diseases. Due to their excessive use, today pharmaceuticals represent a threat to our environment and are therefore classified as potential environmental pollutants.

Modern way of living, population growth and industrialisation has led to occurrence of pharmaceuticals in water, ground, soil and sediment. Although the concentrations of pharmaceuticals in environment are small, in range from ng/L to μg/L, their long-term presence may lead to negative consequences, most commonly seen after several years. Pharmaceutical industry is one of the fastest growing industries and that is why pharmaceuticals availability is growing from day to day. The biggest source of pharmaceuticals is coming from the waste water treatment plants since the respective physicochemical processes are not enough to remove all present pharmaceuticals. Ozonisation and nanofiltration are novel techniques for removal of pharmaceuticals but they also cannot remove hundred percent of all present pharmaceuticals.

Excessive usage of pharmaceuticals generates non-wanted side effects such as today`s one of the biggest health problem-antibiotic resistance. When an antibiotic has no longer effect on certain bacteria, the bacteria is antibiotic resistant. Metabolites and degradation products also represent big concern since they can be even more toxic than the parent compound [1, 2].

Given that the presence of pharmaceuticals has only started to be actively monitored for the last few decades, ecotoxicological properties and their hazard assessment are still not known as their maximum allowable concentrations in the environment are not yet defined. Concentrations of pharmaceuticals in meat, fruit, honey are defined but the maximum allowable concentrations in water, soil and sediment are not yet under legislation. The reason for that is the lack of standardized methods and to the recent, lack of more sensitive analytical methods that can detect small concentrations of pharmaceuticals in different samples and enable their safe and reliable detection. Due to this fact pharmaceuticals are nowadays called "new pollutants" next to the Pharmaceuticals and Personal Care Products (PPCP), hormones, brominated flame retardants, fuel additives etc. Their common characteristic is that they are highly soluble and highly persistent [3, 4].

The importance of pharmaceuticals determination in environmental samples, especially in less examined sediment, provides a source of information needed to be able to predict the human health and ecological risk assessment.

Pharmaceuticals can be easily emitted to drinking water reservoirs through the sediment. How and in which amount pharmaceuticals will be released depends on pharmaceuticals characteristics and sediment. Sediment is a potential receiver for many hazardous substances including pharmaceuticals and that is why it is used as a direct indicator of environmental pollution. Sediment can be characterized through its texture, amount of water, pH, soil adsorption capacity, amount of humus and carbonate content. Pharmaceuticals characteristics can be described through K_d, K_{oc}, K_{ow} and pK_a parameters. Distribution coefficient (K_d) is defined as the ratio of solid phase to solute concentrations indicating the adsorption of the pharmaceuticals onto sediment. Since the organic carbon content varies a lot in environment it is recommended to use organic carbon-normalised partition coefficient parameter (K_{oc}) instead. The higher the K_{oc} parameter is, the pharmaceuticals are more hydrophobic and tend to absorb more onto organic phase of the sediment. K_{oc} values are often estimated from octanol-water partition coefficient (K_{ow}) which describes lipophilic and hydrophobic properties of the pharmaceuticals. The higher the logK_{ow} value is, the pharmaceuticals are more soluble in non-polar organic solvents. Ionisation property of pharmaceuticals (pK_a) shows the strength of the acid or base in a solution and thus enables the setting of the right pH value. To successfully apply the liquid chromatography method, as one of the most used methods for this type of analysis, the pK_a value is of great help. Dissociation of the pharmaceuticals depends on pH of the mobile phase and chromatographic retention therefore depends on pH of the mobile phase [5, 6].

Conventionally used extraction method of pharmaceuticals from solid samples is traditional Soxhlet extraction or mixing the solid with some organic solvent. Many articles describe the usage of solid phase extraction (SPE) with additional clean-up step, especially when it comes to extraction from environmental matrices. Mechanical shaking and ultrasound extraction (USE) also belong to traditional extraction methods that combine simplicity, shortened extraction time and no need for expensive instrumentation. Recently described extraction methods were PLE (pressurized liquid extraction), MAE (microwave assisted extraction), MSPD (matrix solid phase dispersion), LLE (liquid liquid extraction) and supercritical fluid extraction (SFE). Advantages obtained by using MAE and PLE are higher reproducibility, lower solvent consumption and reduced time for sample preparation. MSPD extraction represents a selective and sensitive method of separating an analyte from a complex sediment matrix. Also, the method is simple, relatively fast method and doesn`t require expensive equipment [1, 6, 7].

The most commonly used method for analysis of pharmaceuticals from environmental samples were liquid chromatography (LC) with diode array detection (DAD), fluorescence detection (FLD), mass spectrometry (MS) or tandem mass spectrometry (MS/MS). LC-MS/MS method is already routinely used method for determination of compounds from environmental samples, offering high sensitivity and selectivity. Anyway, HPLC-UV and HPLC-DAD methods are still used because of their accessibility and low operating costs. Gas chromatography is not so often applied due to the physicochemical properties of the pharmaceuticals and thus the need for additional derivatisation step [8 - 10].

Scientific articles describing determination of pharmaceuticals in solid samples available today are focusing on antibiotics and/or hormones only. In this work, several different pharmaceutical groups (macrolide antibiotic, anthelmintics, anesthetics, steroidal hormones) were determined at the same time in sediment sample. The simultaneous determination of several different groups of pharmaceuticals is besides its challenging side, of great ecological importance since large groups of pharmaceuticals are nowadays present in our environment.

2. EXPERIMENTAL

2.1. Chemicals and materials

Chosen pharmaceuticals were tylosine (TYL), albendazole (ABZ), febantel (FEBA), levamisole (LEV), lidocaine (LID), procaine (PROC), hydrocortisone (HYD), dexamethasone (DEXA), purchased from Veterina (Kalinovica, Croatia).

Used chemicals were Milipore ultrapure water (H_2O), methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), acetone (ACO), acetonitrile (ACN), complexone III (K III), dichloromethane (DKM), ethyl-acetate (EtOAc), toluene (TOL), dioxane (DIO), *n*-hexane (HEXA), oxalic acid ($C_2H_2O_4$), all *pro-analysis* or HPLC grade purity. Solvent mixtures were prepared in terms of volume ratios.

Stock solution was prepared in methanol by dissolving powdered pharmaceutical standards so that the mass concentration of each pharmaceutical was 50 mg/L. Working standards solutions were prepared from stock solution by serial dilution with MeOH. All prepared solutions are stored in a refrigerator for up to 2 weeks, at 4 °C, protected from light with aluminium foil.

2.2. Sediment

Sediment sample was collected from Kupirovo in Ličko-senjska County, Croatia. Blank test showed no previous contamination of sediment by target pharmaceuticals.

2.3. Sample preparation

After collection and upon arrival in laboratory, sediment was dried for 7 days, crushed in a mortar and sieved through 2 mm pore size. 20 g of sediment was weight and spiked with 20 mL of standard solution. 15 mL of MeOH was also added for better homogenisation. The mixture was gently mixed in circular motions and left in a dark for 24 h until all MeOH evaporated.

2.4. Extraction methods

USE and MSPD were optimized regarding different characteristic parameters. All samples were analysed in triplicate plus blank.

2.5. Optimization of use

USE was optimized according to the sediment mass, solvent, extraction time, power and the temperature of the ultrasound bath. Extraction of pharmaceuticals in sediment was done in ultrasound bath Bandelin, Sonorex Digital 10 P, Berlin, Germany. Chosen solvents were: MeOH, EtOH, H_2O, 1-PrOH, ACO, DKM, DIO and ACN. For optimization of sediment mass 1 g and 5 g were used. Other parameters such as solvent volume, extraction duration, temperature and the power of ultrasound bath were set according to literature review as follows: 15 mL of solvent, 30 min, 30 °C and 600 W. The power of ultrasound bath of 1200 W was also examined. Extraction duration was optimized by performing the experiments in duration of 30 min and 60 min. To improve extraction efficiency few solvent mixtures were also examined: MeOH:CAN =50:50, MeOH:ACN=30:70, MeOH:ACN=70:30, MeOH:H_2O=50:50, MeOH:H_2O=30:70, MeOH:ACO=50:50, MeOH:ACO=30:70, MeOH:ACO=70:30, MeOH:ACO:ACN=35:35:30, MeOH:ACO:H_2O=35:35:30, MeOH:ACO:H_2O=35:35:30, MeOH:ACN:H_2O=35:35:30, H_2O (pH = 2; 6; 10) and MeOH:DIO=50:50. Extraction temperature was optimized by performing the experiments at 30 °C and 50 °C. Prior the injection into HPLC-DAD system supernatants were evaporated to dryness at 40 °C and the dry residue was dissolved in 1 mL of MeOH.

2.6. Optimization OF MSPD

Optimization of MSPD extraction was done according to sorbent type, extraction solvent, solvent volume and sediment/sorbent mass ratio. Experiments were performed by using extraction unit Visiprep^{TM} 24, Supelco with the flow rate of 1 mL/min. Used sorbents were egg shells, C18 and Florisil. C18 sorbent is chosen according to literature data as one of the best sorbents when performing MSPD extraction.

Chosen solvents were MeOH, EtOH, 1-PrOH, 2-PrOH, ACO, ACN, DKM, HEXA, TOL, EtOAc and H_2O (pH = 2; 4; 6, 8; 10). Also following solvent mixtures were examined:

MeOH:1-PrOH=50:50, MeOH:1-PrOH=30:70, MeOH:1-PrOH=70:30, MeOH:2-PrOH=50:50, MeOH:2-PrOH=30:70, MeOH:2-PrOH=70:30, EtOH:1-PrOH =50:50, EtOH:1-PrOH =70:30, EtOH:1-PrOH=30:70, EtOH:2-PrOH=50:50, EtOH:2-PrOH=70:30, EtOH:2-PrOH=30:70, MeOH:ACO=80:20, MeOH:ACO=50:50, MeOH:ACO=20:80, MeOH:ACO=60:40, MeOH:ACO=40:60, MeOH:H_2O=70:30, MeOH:H_2O=50:50, MeOH:H_2O=30:70, MeOH:H_2O=80:20, MeOH:H_2O=90:10, 5 % C2H2O4, K III, ACN:H_2O=60:40, ACN:5 % C2H2O4=60:40, MeOH:H_2O =60:40, MeOH:H_2O=40:60, MeOH:H_2O=50:50, EtOH:H_2O=60:40, EtOH:H_2O=40:60, EtOH:H_2O=50:50, 1-PrOH:H_2O=60:40, 1-PrOH:H_2O=40:60, 1-PrOH:H_2O=50:50, 2-PrOH:H_2O=60:40, 2-PrOH:H_2O=40:60, 2-PrOH:H_2O=50:50, ACN:H_2O=60:40, ACN:H_2O=40:60, ACN:H_2O=50:50, ACO:H_2O=60:40, ACO:H_2O=40:60, ACO:H_2O=50:50. Examined solvent volumes were 5 mL, 6 mL and 9 mL. Regarding the sediment/sorbent ratios first the change of sediment mass in 0.05 g steps was examined when using egg shells (0.10 g sorbent + 0.05 g sediment, 0.10 g sorbent + 0.10 g sediment, 0.10 g sorbent + 0.15 g sediment). Next the change in sorbent mass of 0.10 g with the same sediment mass was examined (0.10 g sorbent + 0.05 g sediment, 0.20 g sorbent + 0.05 g sediment, 0.30 g sorbent + 0.05 g sediment). When using C18, the mass of sorbent was constantly 10 g and the sediment mass was changed in values of 0.05, 0.10 and 0.15 g. In following experiments, the sediment mass was 0.05 g and the sorbent mass was changed in values of 0.10 g, 0.20 g and 0.30 g.

2.7. HPLC-DAD analysis

All samples were analysed by high performance liquid chromatography using Varian ProStar 500 (Walnut Creek, CA, USA) equipped with Varian 410 autosampler, Varian 330 diode array detector, Varian 230 solvent pump, bottles for mobile phase and waste and personal computer for collecting and processing the data. Injection volume was 30 μL and each sample was analysed in triplicate.

The separation of the pharmaceuticals was carried out on an InertSustain™ C18 column (250 mm × 4.6 mm i.d., 5 μm), supplied by GL Sciences Inc., Japan at a flow rate of 0.5 mL/min. The column was thermostated at 30 °C. Mobile phase was a binary system: A (0.01 % formic acid in water) and B (0.01 % formic acid in acetonitrile) with gradient elution with following gradient profile: (1) 0, 100 % A (2) 2.30 min, 92 % A, (3), 6 min, 90 % A, (4) 11 min, 70 % A, (5) 15 min, 40 % A, (6) 18 min, 5 % A, (7) 28 min, 5 % A, (8) 28.10 min, 100 % A, (9) 30 min, 100 % A. Separations were monitored at wavelengths at which each pharmaceutical have its highest response: 210 nm (ABZ, FEBA, LID), 254 nm (DEXA, HYD), 285 nm (TYL) and 295 nm (PROC).

2.8. Method validation

First, the chromatographic method for pharmaceuticals detection and quantification was validated. HPLC-DAD system was validated in terms of linearity, sensitivity, LOD, LOQ, repeatability and reproducibility using the pharmaceuticals standard solutions of following concentrations: 0.5, 1, 3, 5, 10, 30, 50 mg/L. Blanks were also prepared for quality control reason but they were not included in regression analysis. LODs and LOQs were determined by serial dilutions of standard solution and based on signal to noise (S/N) value of 3 and 10, respectively. Performance characteristics of USE-HPLC-DAD method was established by validation with spiked sediment sample in three replicates at three concentrations 5-10-50 mg/L and for the MSPD-HPLC-DAD method at fifteen concentrations

0.03, 0.05, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 10, 20, 30, 40, 50 mg/L. Evaluated validation parameters were selectivity, specificity, linearity, sensitivity, MDL, MQL, repeatability, recovery in the assessment of trueness and stability of a standard solution as the parameter of the robustness. The external standard and matrix matched calibration methods were used to ensure reliable quantification of the samples and to correct the expected matrix effect.

3. RESULTS AND DISCUSSION

3.1. Sediment characterization

The sediment was characterized as a sandy loam, neutral to basic character, with high percentage base saturation of the adsorption complex and with high sum of exchangeable bases. Sediment contains significant amount of carbonates, which is also the key characteristic of the basic sediments (pH > 7).

3.2. Chromatographic analysis

Qualitative analysis was performed according to spectrums and retention times for each pharmaceutical: t_R(ABZ) = 22.893 min, t_R(DEXA) = 22.413 min, t_R(FEBA) = 25.507 min, t_R(HYD) = 21.560 min, t_R(LEV) = 18.591 min, t_R(LID) = 18.947 min, t_R(PROC) = 17.560 min, t_R(TYL) = 22.022 min. Chromatographic areas for each pharmaceutical were read at its optimal wavelengths as described in Chapter 2.7.

3.3. Optimization of use-HPLC-DAD and MSPD-HPLC-DAD

Optimal conditions for the USE-HPLC-DAD method were achieved by using 1 g of sediment and MeOH:ACO=50:50 mixture, at temperature of 30 °C for 60 min and 600 W for ultrasound bath power. Obtained recoveries were as follows: ABZ 60.56 %; DEXA 11.08 %; FEBA 61.25 %; HYD 8.58 %; LEVA 45.00 %; LID 66.48 %; PROC 44.28 %; TYL 72.19 %. Recoveries obtained for DEXA and HYD are lower than 20 % when using organic solvents. When water was used in combination with ACO and MeOH, recovery for DEXA is higher (27.96 %) as well as for HYD when using water with MeOH (14.12 %). This leads to conclusion of slightly improved DEXA and HYD solubility when adding water to organic compound. Generally, for other pharmaceuticals except DEXA and HYD obtained results in water media are low despite changing the pH value from acidic to basic.

MSPD-HPLC-DAD was optimised using the egg shells, C18 and Florisil as extraction sorbents. Egg shells are natural material, easy accessible and environmental friendly. It is used as a novel sorbent in extraction of pharmaceuticals from different samples. Porous structure of egg shells main component calcite is what makes them a good sorbent [11]. C18 or octadecyl derivatized silica is sorbent which enables reversed phase bonding of hydrophobic components such as pharmaceuticals. Bigger, polar part of the C18 sorbent makes octadecyl group while silanol residues makes polar part which has good bonding density. C18 sorbent enables good mixing with a sample which is than uniformly distributed over the C18 chain [12, 13]. Florisil is very polar sorbent why it is used in extraction of lipids, pharmaceuticals, pesticides etc. It is often used in MSPD extraction next to alumina and C18. In comparison to C18, Florisil has bigger particles and sharper structure which enables very

good flow of solvent and good abrasion of the sample [12, 14]. When using egg shells the optimal conditions were achieved with 5 mL of MeOH:H_2O=80:20 mixture and sediment/sorbent ratio 0.15 g/0.10 g. Obtained recoveries were as follows: ABZ 99.82 %; DEXA 25.71 %; FEBA 71.42 %; HYD 20.78 %; LEVA 93.51 %; LID 115.09 %; PROC 86.98 %; TYL 40.64 %. The obtained results show the lowest recovery for DEKSA and HIDRO. LID achieved recovery higher than 100 % meaning that some new compounds have been formed or something from the sample matrix has been dissolved. When the C18 was used the optimal conditions were achieved with 1-PrOH:H_2O=40:60 mixture and the sorbent/sediment ratio 0.10 g/0.10 g. Obtained recoveries are: ABZ 82.32 %; DEXA 9.43 %; FEBA 84.23 %; HYD 32.26 %; LEVA 59.35 %; LID 83.40 %; PROC 62.72 %; TYL 86.13 %. The lowest obtained recoveries are again recorded for pharmaceuticals DEXA and HYD. When using Florisil the optimal conditions were achieved by using 5 mL of EtOH and the sorbent/sediment ratio 0.10 g/0.10 g. Obtained recoveries were as follows: ABZ 80.79 %; DEXA 11.23 %; FEBA 67.04 %; HYD 21.37 %; LEVA 60.85 %; LID 86.89 %; PROC 63.01 %; TYL 46.04 %. Again, the biggest challenge was to extract the DEXA and HYD in higher recoveries. The highest recovery for DEXA was obtained when using egg shells and for the HYD when using C18 sorbent. Obtained recovery for TYL is similar when using egg shells which is lower comparing to recovery obtained with C18 sorbent.

3.4. Validation of HPLC-DAD, use-HPLC-DAD and MSPD-HPLC-DAD

Linearity of HPLC-DAD method was obtained by determining the coefficient of correlation (r^2) which was higher than 0.9991 for all pharmaceuticals except for ABZ (0.9987), FEBA (0.9981) and LID (0.9987). Linearity of each pharmaceutical was in concentration range 0.019-50 mg/L for ABZ, 0.017-50 mg/L for DEXA, 0.073-50 mg/L for FEBA, 0.070-50 mg/L for HYD, 0.588-50 mg/L for LEV, 0.780-50 mg/L for LID, 1.535-50 mg/L for PROC and 0.136-50 mg/L for TYL.

Obtained LOD values were relative low (0.005-0.460 mg/L) as well as LOQ values (0.017-1.535 mg/L).

Sensitivity of the HPLC-DAD method is evaluated through the slope of calibration curve obtained by plotting the response against the pharmaceutical mass concentration. The method showed to be sensitive enough and small pharmaceutical concentrations can be differentiated easily.

Repeatability of HPLC-DAD method was examined by analysing five replicates of a 10 mg/L standard solution during the same day. Expressed in RSD, repeatability was less than 5 % except for LEV (14.04 %) and PROC (24.51 %) which indicates the presence of an error that is most likely caused by the preparation of the solution or due to the loss of sensitivity of the deuterium lamp.

Reproducibility was measured over a period of nine days (measurements were performed 1st, 2nd and 9th day) for concentrations of 5 mg/L and 50 mg /L. As expected, RSD values for 5 mg/L were generally higher than for 50 mg/L. When analysing 5 mg/L solution during first two days RSD values were less than 20 % for all pharmaceuticals except for PROC (34.92; 35.44 %) while RSD values obtained on the last 9th day were quite high for all pharmaceuticals, now lowest for PROC (32.28 %) and for other pharmaceuticals in range 48.43-71.88 %. For 50 mg/L during whole period RSD values were less than 20 % for all pharmaceuticals except for PROC. Despite deviations in results for LEV and PROC we can conclude that HPLC-DAD method indicates good measurement repeatability, with RSD values less than 5 %.

Significant deviations occurred the last day, as the solution get older at the concentration of 5 mg/L. Despite that deviation and deviation for PROC during first two days of tested period, we can say that HPLC-DAD method indicates good measurement reproducibility.

After the HPLC-DAD method was validated, validation of USE-HPLC-DAD and MSPD-HPLC-DAD methods was performed as described in Chapter 2.8.

The selectivity or specificity of the method is the possibility of a method to determine the analyte in the analysed matrix despite the presence of interferences from matrix components. Selectivity was demonstrated by comparing the chromatogram of blank, chromatogram of extracted targeted pharmaceuticals and chromatogram of a pharmaceuticals standard solution. Non-contaminated blank and characteristic chromatograms of pharmaceutical extracts indicate that the USE-HPLC-DAD and MSPD-HPLC-DAD methods are selective.

When evaluating the linearity of the USE-HPLC-DAD method the obtained r^2 values were in range 0.9856-0.9996. For the MPSD-HPLC-DAD method obtained r^2 values were in range 0.9123-0.9996 when using egg shells, 0.9769-0.9999 when using C18 and in range 0.9699-0.9999 when using Florisil sorbent.

Sensitivity of USE-HPLC-DAD and MSPD-HPLC-DAD methods was evaluated by plotting the calibration curves of pharmaceutical extracts vs. calibration curve of pharmaceuticals standard solution. Small differences in curve slopes for ABZ and LID indicate the good sensitivity of the USE-HPLC-DAD method for named pharmaceuticals. DEXA and HYD recorded the greatest loss of sensitivity due to the large difference in the slope of the pharmaceutical standard solution and the obtained extracts. This is also directly related to their lowest obtained recoveries (less than 20 %). Slight loss of sensitivity is recorded for the FEBA, LEV, PROC and TYL, especially at higher concentrations.

Matrix effect can also be expressed when evaluating sensitivity through comparison of calibration curve slopes. If the slope of the extract is lower than the slope of the standard there is matrix suppression present. If the slope of the extract is higher than matrix enhancement is present. For the USE-HPLC-DAD method it was observed that slopes of all pharmaceutical extracts were lower than the slopes of pharmaceuticals standard solution.

When it comes to MSPD-HPLC-DAD method, the small difference in slopes of calibration curves are observed why we can conclude that the MSPD-HPLC-DAD when using all three sorbents is very sensitive method. When egg shells are used, for the pharmaceutical DEXA slightly higher standard extraction slope is observed. A small drop in sensitivity was observed for PROC at a concentration of 50 mg/L, while for the TYL at 50 mg/L the slope of the standard was lower than the slope of the extract indicating a decrease in sensitivity at that concentration. When sorbent C18 was used, the smallest difference in slopes is observed for DEXA while PROC sensitivity dropped at a concentration of 50 mg/L. Loss of sensitivity was recorded when Florisil sorbent was used for DEXA, PROC and TYL throughout the whole concentration range.

The matrix effect was the biggest for DEXA when using all three sorbents and for the PROC and TYL when Florisil is used. Florisil sorbent consists of larger particles compared to egg shells and C18 sorbents why the sample destroying is simply stronger. Bigger matrix effect results thus in easy adsorption of Florisil components when performing pharmaceuticals extraction.

Obtained MDL for USE-HPLC-DAD method were 0.073-1.815 mg/L and MQL values 0.244-6.051 mg/L. For the MSPD-HPLC-DAD method when using egg shells, the obtained MDL were in range 0,066-3,948 mg/L and MQL in range of 0.220-11.660 mg/L. When using C18 sorbent the obtained MDL were between 0.056-17.759 mg/L and MQL

0.187-59.20 mg/L. When using Florisil the obtained MDL were 0.020-12.789 mg/L and respectively MQL values in range of 0.067-42.630 mg/L.

Repeatability of USE-HPLC-DAD and MSPD-HPLC-DAD was performed by analysing three replicates of an extract at concentrations 10 mg/L in the same day. The MeOH:ACN=50:50 is used as extraction solvent for the USE-HPLC-DAD method. Obtained RSD values are in the range between 1.29 and 9.07 % except for TYL (25.51 %). Repeatability of MSPD-HPLC-DAD method was determined using optimal solvents: MeOH:H_2O=80:20 (egg shells), 1-PrOH (C18) and EtOH (Florisil). When using egg shells obtained values are in range from 0.85 to 7.09 % except for TYL which recorded the highest deviation (12.47 %). The lowest RSD showed LEV (0.85 %). When sorbent C18 was used the repeatability ranged from 0.17 to 6.54 %. When using Florisil sorbent obtained repeatability is in range 0.19 to 3.79 % which is also the best result compared to the previous two sorbents.
Recovery (%) was obtained by the ratio of the peak areas of the pharmaceutical extracts and the pharmaceuticals standard at 50 mg/L in three replicates.

When performing USE-HPLC-DAD method the highest recovery is obtained for the LID with value of 69.95 %, while the lowest recovery was recorded for HYD with value of 9.75 %.

The obtained recoveries when the egg shells are used are in range from 77.37 to 94.69 % where the lowest recovery was obtained for PROC (77.37 %) and the highest for ABZ (94.69 %). Pharmaceuticals DEXA and TYL recorded recoveries greater than 100 % which indicates possible extraction of other components during their determination. When C18 is used as a sorbent, the recoveries are in range from 73.27 to 94.74 %, where only DEXA has the value of 100.51 %. Recoveries obtained when Florisil was used ranged from 70.64 to 97.84 %.

The stability of the standard solution is one of the typical parameters of the method robustness. Stability is determined as the measure of the resistance of the analytical procedure to the small changes in working conditions of the method, expressed through RSD. The purpose of validating the stability of the standard solution was to get the information about its stability over the period in which the USE-HPLC-DAD and MSPD-HPLC-DAD methods were performed. DEXA, FEBA, HYD, LEV and TYL recorded the highest stability in the standard solution with the RSO values less than 10 % when the USE-HPLC-DAD method was performed. Values above 10 % were obtained for pharmaceuticals ABZ (15.53 %) and LID (12.58 %). The highest RSD value was obtained for PROC (53.03 %). When performed MSPD-HPLC-DAD method using egg shells the RSD of the standard solution is less than 20 % for most pharmaceuticals except for PROC that has a value of 25.20 %, while TYL records the highest RSD value of 35.46 %. When sorbent C18 was used the RSD`s were lower than 10 % for most pharmaceuticals except for PROC (29.05 %). When Florisil was used, the RSD values were lower than 10 % for all pharmaceuticals except LEV (11.86 %) and PROC (32.69 %).

4. CONCLUSION

Use-HPLC-DAD and MSPD-HPLC-DAD methods were optimised and validated for simultaneous extraction of eight veterinary pharmaceuticals (ABZ, DEXA, FEBA, HYD, LEV, LID, PROC, TYL) from sediment sample.

Final results showed very good recovery for the macrolide antibiotic TYL, higher than 50 %, when extracted with USE-HPLC-DAD and MSPD-HPLC-DAD using C18 sorbent. According to its logK_{ow} value less than 2, it was also expected that the TYL will be less

mobile and relatively easy to extract from the sediment. For the group of anthelmintics (ABZ, FEBA, LEV) better method proved to be MSPD-HPLC-DAD with all three sorbents. Here only FEBA has logK_{ow} value less than 2 why its good recovery could be expected. That was confirmed in all experiments where its obtained recoveries were higher than 50 %. ABZ and LEVA showed higher recoveries than expected according to their logK_{ow} values. When extracting anaesthetics (LID and PROC), both methods showed good recoveries except when using egg shells in MSPD-HPLC-DAD method where the obtained recovery for LID was higher than 100 %. The extraction of steroide hormones (DEXA and HYD) presented a big problem and they showed the lowest obtained recoveries for both methods. DEXA and HYD are widely used in veterinary and human medicine and have high ecotoxicological risk so the major challenge in development of USE-HPLC-DAD and MPSD-HPLC-DAD was their simultaneous extraction with other selected pharmaceuticals. The reason for their low recoveries is in their significantly different structure comparing to other pharmaceuticals. Their physico-chemical properties are also not known which makes it difficult to select their optimal separation method from the complex sediment sample. More efficient method for their extraction showed to be MSPD-HPLC-DAD where the highest recovery for DEXA was obtained when using egg shells and for the HYD when using C18 sorbent. These recoveries were obtained with omit solvents MeOH:H_2O=80:20 (egg shells) and 1-PrOH:H_2O=40:60 (C18) and it can be concluded that that the certain amount of water contributes to their extraction.

Both methods proved to be selectable which means they are suitable for the determination of the tested pharmaceuticals in the sediment sample, despite the presence of interferences. The better linearity showed USE-HPLC-DAD method with r^2 values between 0.9856 and 0.9996 mg/L. The biggest matrix effect is recorded when performing MSPD-HPLC-DAD method when using C18 for the DEXA and when using Florisil for the DEXA, PROC and TYL pharmaceuticals. The pharmaceuticals DEXA and HYD showed the biggest loss in sensitivity when performing both methods. The lowest MDL (0.020 mg/L) and MQL (0.067 mg/L) was achieved for FEBA when performing MSPD-HPLC-DAD method with Florisil sorbent. The best repeatability (0.19-3.79 %) is showed when using Florisil sorbent in MSPD-HPLC-DAD method.

For routine analysis USE-HPLC-DAD method showed to be more efficient. This method is also simple, cheap and achieves relatively good recoveries. MSPD-HPLC-DAD method can also be used for routine analysis but omit the higher matrix effect.

Both investigated methods managed to compromise compounds with different physicochemical properties. Methods showed the possibility for simultaneous determination of pharmaceuticals of different structure groups in complex sediment sample. Analysis of investigated samples was conducted with HPLC-DAD with satisfactory detection and quantification for investigated compounds. The advantage of these analytical methods is that they are simple and affordable.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

FINDING BIOCOMFORT AREAS IN URBAN PLANNING STUDIES FOR LANDSCAPE AND MANAGEMENT

Mehmet Cetin*

*Kastamonu University, Faculty of Engineering and Architecture, Kastamonu, Turkey

corresponding author: Mehmet Cetin, e-mail: mcetin@kastamonu.edu.tr

Original scientific paper

ABSTRACT

The purpose of this study was to determine the appropriate areas of Amasra province for biocomfort based on the meteorological data of the city. In the study, data were obtained from the meteorological stations of Amasra province. The average temperature, relative humidity and wind values for these stations have been transferred to the Geographic Information Systems (GIS) using ArcView GIS ™ 10 software. Climate maps were created from the data transferred to the GIS and appropriate areas for biocomfort were determined. These maps have been obtained with the help of the map of bioclimatic comfort conditions, taking into account the annual sensed temperature and bioclimatic comfort zone for the region. Amasra's classified zones have been identified on the maps. The resulting maps of the study can be the basis for sustainable urban planning studies for Amasra city. In conclusion, Amasra's residential areas, where many of the terms of bioclimatic comfort in the more remote areas of the central region, have been shown to be suitable if there are suitable areas.

***Keywords**: biocomfort, urban planning, landscape plan*

1. INTRODUCTION

Climate is an important influence in shaping the geographical environment and fulfilling the requirements of human life. Throughout the years, we have tried to adapt to environmental conditions by producing shelter, producing food, and obtaining energy. The needs and productions of people depend directly on climate and seasons. The global scale change of climate, which is an important factor for human comfort, also has a regional effect. Altered climatic conditions cause adverse environmental impacts. This affects bioclimatic comfort. From this point of view, it is necessary to take more consideration of the bioclimatic comfort situation in the physical plans made considering the use of climate for reaching people, plants, animals and environment and for human comfort [1 - 10].

In urban planning, the importance of climate has been recognized as an effective factor for many years. The urban climate not only affects the regional and global climate, but also a very important factor for urban liveability [5 - 9, 11 - 13].

The scenarios on climate change have begun to influence planning and design decisions, especially in urban areas, and have become a part of ecological life, such as green, infrastructure, transportation, the trend has also increased. The roads within the urban space affect water surfaces, open spaces, green spaces, building surfaces, urban climate and human comfort. For this reason, it is a necessity to know these qualities which will give design direction for people to live in more comfortable places. This has accelerated biomedical comfort studies in recent years [8 - 10, 14 - 17].

Climate change and global warming are factors that directly affect living things. The characteristics of the atmosphere itself (wind, humidity, precipitation and temperature) are related to the instantaneous state of the air and are also called climate elements. Among the properties belonging to the air, the most effective properties on human activities are the properties of the atmosphere itself. Although these characteristics vary from place to place, the average for many years in a given area and season does not change much and forms the climatic characteristics of the spot. As a result; most scientific studies reveal natural phenomena that cause significant changes in the ecological structure and the recent loss of life and economic loss due to the gradual warming of the world, the rise of glaciers, the rise of sea levels, and the change of precipitation rates, the severity and frequency of extreme weather events [4 - 10].

The accepted definition of bioclimatic comfort in recent years; It is the climatic conditions in which people generally adapt to their surroundings by consuming the least amount of energy and feel themselves extremely healthy and dynamic. From this point of view, it is aimed to reveal the bioclimatic comfort situation positively. With this result obtained, it is aimed to provide substation data which can be used for bioclimatic comfort situation in physical plans directed to. In order to determine the bioclimatic comfort situation in one place, the temperature, relative humidity, and wind conditions must first be determined and evaluated. Besides these basic factors; the number of hot days, rainfall conditions, air pollution and air pollution due to weather events, and the amount of oxygen in the atmosphere also affect human comfort. Bioclimatic comfort can be determined by considering all these effects all together [5 - 10, 15 - 18].

Bioclimatic comfort is described as the adaptation of the climatic conditions in the environment by consuming the least amount of energy. When high temperatures and high relative humidity conditions coexist in the same time zone, an environment that affects human comfort in a negative way arises and overwhelming thermal conditions arise. For human comfort, factors such as temperature, humidity and wind have certain values. These values, which are most appropriate for the physiology of humans, are set forth in the light of previous scientific studies. Bioclimatic comfort values will be determined according to the climate parameters, taking into account the values set out. By comparing the determined values with the climatic values of Amasra, it is aimed to determine the regions which are suitable for the bioclimatic comfort of the province. Thus, in the plans to be made for the province, these values obtained in terms of providing bioclimatic comfort will have a guiding quality.

The maps produced within the context of this study, which enables bioclimatic comfort status to be determined locally due to the climatic characteristics of Amasra province, can be used as a basis for the physical planning processes of the basin. In the traditional planning approach, bioclimatic comfort is not created or ignored because climate data is used only as input. From these requirements, as a base data which can be used in the physical plans to be created with; It is aimed to reveal bioclimatic comfort situation of Amasra Province locally.

2. EXPERIMENTAL

The work was conducted in Amasra province. The aim of the study was to identify the natural and cultural domain of the study and to understand its historical and cultural structure. Field studies in the field, the existing building uses in the area, the formation of maps that guide the work of the conditions, such as their qualities, and the introduction of suggestions afterwards.

Within the scope of the field studies, data were collected in the direction of the data obtained from the field observations, photo shoots and meteorological stations. Then, using GIS, meteorological data, natural and cultural data were processed in digital environment, data transformations were realized and thematic maps were produced in GIS environment. In this context, numerical elevation model, slope, view etc. are obtained by using temperature, humidity, wind and precipitation values in the current meteorological data of the area and the inventories were evaluated.

Throughout the research, it was tried to determine how the data about the area was digitized in the GIS environment and transformed into biocomfort maps and shaped the characters of Amasra. Thus, in bioclimatic comfort zones, areas where appropriate values for biocompatibility are determined for each climate element.

The study material is Amasra. The natural and cultural rich area of Amasra has geographical positions between 41 ° 44' 49 'North latitudes and 32 ° 23' 7' East longitude coordinates. The geographical position of Amasra is as shown in figure 1 [18, 19].

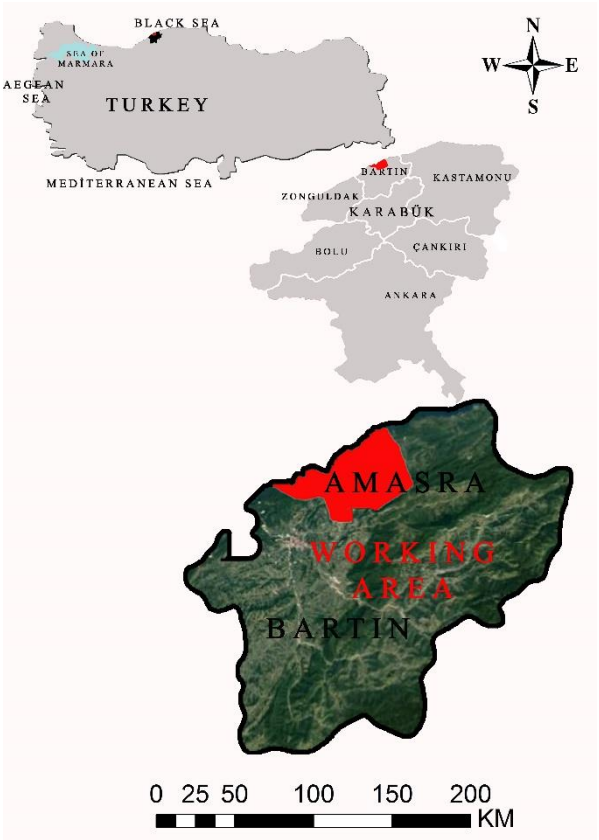


Figure 1. Location of study area

The method of the study is the temperature, relative humidity, wind speed data prepared in the analysis stage. Point data obtained from these maps are calculated according to Physiological Equivalent Temperature (PET) indices, which show the bioclimatic comfort

structure of the field area and are widely used today. During these calculations, RayMan1.2 program was used. The obtained values were spread to the surface using interpolation techniques in ArcMap 10 program in GIS environment. Thus, regions of the Amasra province with bioclimatic comfort are mapped. At the last stage, the results and suggestions obtained from all these analyses are presented.

Bioclimatic affecting comfort is physical and physiological characteristics of the body and environmental factors [5 - 10]. For bioclimatic comfort analysis, PET calculation is performed using the RayMan model. Based on a model known as Physiological Equivalent Temperature, it has been developed especially for outdoor environments [5-10]. The environmental factors of the space where comfort values are calculated; Temperature: Tmrt = Ta = ° C, Wind Speed: v = 0,1 m/s, Relative Humidity: RH = %, Radiation: W/m², Steam Pressure: VP = 12,0 hPa, Cloudiness: N = Oktas.

In the atmospheric environment, meteorological parameters such as air temperature, mean reflection radiation temperature, wind speed, relative humidity, cloudiness or radiation are used to prove and maintain human bioclimatic comfort in planning and evaluating human bioclimatic comfort [20 - 22]. PET also adds heat transfer resistance and metabolic heat production to the apparel. The environmental characteristics of the imaginary interior calculated by the comfort values are: Tmrt = Ta, v = 0,1 m / s, VP = 12,0 hPa.

Tmrt, average reflection radiation temperature; Ta, the temperature of the air; V, wind speed and VP are the vapor pressure. The comfort ranges used to find the ranges of PET index values that define human bioclimatic comfort are given in table 1. The most comfortable range is 18.1 to 23.0 °C [5 - 10, 20].

Table 1. Thermal stress categories of PET index [20]

PET (°C)	Human Feeling	Thermal Stress Level
< 4	Very cold	Extreme cold stress
4.1 - 8.0	Cold	Strong cold stress
8.1 - 13.0	Cool	Moderate cold stress
13.1 - 18.0	Slightly cool	Light cold stress
18.1 - 23.0	Comfortable	No thermal stress
23.1 - 29.0	Light temperate	Light Hot Stress
29.1 - 35.0	moderate	Medium Hot stress
35.1 - 41.0	hot	Strong Hot stress
> 41.0	Very hot	Excessive Hot Stress

The details of the environmental factors are set with the obtained PET maps of the bioclimatic comfort analyses. Thermal Band Analysis is used to calculate physical factors, which is another factor. In Thermal Band Analysis (TBA), surface temperature distribution of Landsat satellite images can be determined by using thermal bands. Surface temperature according to Streutker [23], surface energy balance (equilibrium), atmospheric conditions and thermal properties of the surface, physical factors and so on. Many variables are connected. The surface temperature data of the satellite image can be obtained by using the thermal band (10.45 - 12.42 μm) data of the Lansat TM satellite image [5, 6, 8 - 10].

The thermal images of the thermal band 6 are converted to spectral radians (Lλ) and calculated by formula (1) [5, 24]. The results are converted to sensor temperature values (T_B) of the spectral radians (Lλ) value and calculated by the formula (2) [5, 25].To obtain accurate temperature values, the spectral emissivity (ε) values of the study area are needed [5, 26]. Emissivity values can be obtained using the Normalized Plant Index (NDVI) value [5, 27].

Using NDVI values and Emissivity (ε) values, the resultant temperature values are calculated with formula (3) [5, 6, 8 - 10, 28].

$$L_\lambda = \left(\frac{Lmax_\lambda}{Qcalmax} - \frac{Lmix_\lambda}{Qcalmin}\right)(Q_{calmax} - Q_{calmin}) + Lmix_\lambda \quad (1)$$

$$T_B = \frac{K_2}{\ln(+\frac{K_1}{L_\lambda})} \quad (2)$$

$$T = \frac{T_B}{1+(\lambda+\frac{T_B}{\alpha})X \ln \varepsilon} \quad (3)$$

3. RESULTS AND DISCUSSION

In the study, the average temperature, humidity and wind data for the long years (1965/2017) taken from 7 meteorological stations in Amasra province were used. A three-month average temperature map was produced based on the temperature values of the stations obtained from the meteorological directorate. According to the obtained map, the average temperature values of the research area over the long years vary from -12 °C to 32 °C. Annual average temperature values are decreasing from the south of the area to the north (due to the increase in elevation). According to the relative humidity values of the stations, a 3 month average relative humidity map was produced. According to the obtained map, the relative humidity values of the study area vary between 38 – 75 %. Relative humidity status% increases to the south of the area due to the presence of a dam.

A 3-month average wind speed map was obtained based on the wind speed values of the stations. According to the obtained map, mean wind speed values of the survey area vary between 1.42 - 3.37 m/sec. The average wind speed values are increasing towards the north and inner parts of the area. With the PET maps obtained, details of the environmental factors are put in place. In the calculation of the physical factors, appropriate areas in terms of comfort in terms of Amasra bioclimatic comfort were determined by using Thermal Band Analysis. In recent studies, studies such as Kutahya, Kastamonu and Aydin show that the importance of bioclimatic comfort assessment of landscaping is important. Areas where bioclimatic comfort values are most appropriate are often found to be more appropriate in regions close to water [5, 6, 8 – 10]. The evaluation of all the analyses made in Amasra has been determined to be below the comfort value in most regions in general, but it has been observed that the comfort values are reached in the regions close to the water element, which should be considered. The bioclimatic comfort maps for Amasra is shown figure 2.

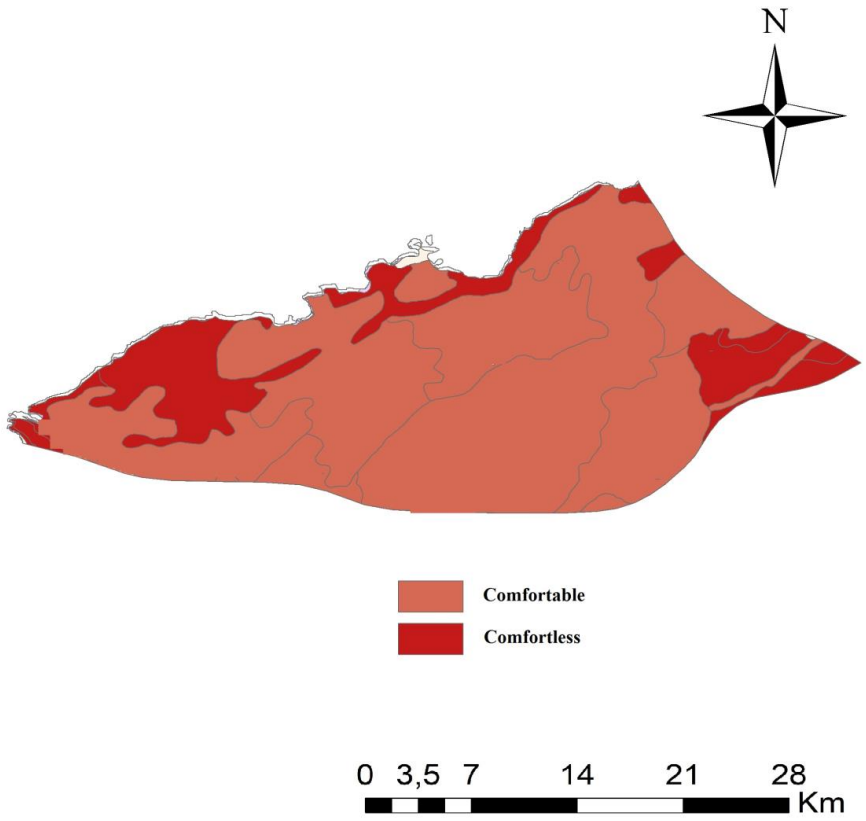


Figure 2. Showing of bioclimatic area for Amasra

4. CONCLUSION

When the results of the study were evaluated, it was determined that the overall duration of the bioclimatic comfort in Amasra was highest in the central areas with high altitudes, especially at altitudes of 300-500 m and high altitudes. When the monthly FES index between Amasra was examined according to the thermal comfort category, light cool, comfortable and milder thermal sensations were determined between June and August.

With this study, Remote Sensing and Geographical Information Systems are aimed to achieve more accurately and quickly by using more effectively in the determination of bioclimatic comfort situation. In study and physical planning, it became important to integrate climate data only into the planning by putting more emphasis on the bioclimatic comfort situation. Taking into account the bioclimatic comfort situation in planning, the heat will be caused by the knowing of heat islands or adverse conditions.

As a result of the study, the usage areas and decisions about the area within the scope of bioclimatic comfort for Amasra have been established and the landscape design proposal has been developed in line with these decisions. The biocomfort - mental principles that are intended to be identified are important both for the current use of natural and cultural characters and for playing the most important role in shaping future landscape planning. Before arriving at the design stage, GIS data collection, storage and updating features were used to collect data on the area and the recommendations mentioned in the previous sections were developed within these data. As a result, the most suitable land use decisions were taken for Amasra.

It is considered that the study will contribute significantly to land use decisions in the case of Amasra in assessing the natural and cultural values of the biocomfort. As a result of the study, it is possible that the desired results can be achieved as well as the dissemination of similar works especially in touristic areas and play an active role in the field usage decisions.

Landscape architecture and planning can be improved by the application of bioclimatic comfort conditions principles and design criteria. Planning in the wrong conditions and designing bio-climatic comfort can create extremely negative conditions because natural vegetation cannot become suitable for bioclimatic comfort in hot and cold stressed areas and intense natural conditions. Significant energy loss has been detected in the construction of the new zoning plan in our country. At the same time, this study may be important in terms of energy conservation by arranging old plans.

Perhaps the most important influence of the results of this study is that it is the most important guide in future landscape planning. Planning to bring bioclimatic comfort to the highest level will also help to identify new settlement areas in the Amasra region.

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METODOLOGIJA MODELIRANJA PROCESA KAO DOPRINOS CJELOVITOM PRISTUPU OKOLIŠU

METODOLOGY OF MODELLING PROCESSES AS CONTRIBUTION TO HOLISTIC APPROACH TO THE ENVIRONMENT

Mirjana Čurlin*, Virgjina Lipoveci*

* Sveučilište u Zagrebu, Prehrambeno biotehnološki fakultet, Zagreb, Hrvatska

autor za korespondenciju: Mirjana Čurlin, e-mail: mcurlin@pbf.hr

Pregledni rad

SAŽETAK

Rutinski nadzor kvalitete ekoloških sustava kao i uspješno vođenje eko procesa zahtjeva provedbu brojnih laboratorijskih analiza kako bi se odredili hidrološki, biološki te fizikalno kemijski parametri propisani pravilnicima. Provedba analiza osim generiranja otpadnih tvari rezultira i velikom bazom kompleksnih višedimenzionalnih podataka. Za analizu, interpretaciju te međusobne korelacije pojedinih pokazatelja kvalitete potreban je sustavski pristup analizi eksperimentalnih podataka primjenom statističke metodologije i metodologije modeliranja procesa. Osnovna zadaća ovog pristupa je sinteza mnogobrojnih hidroloških, bioloških i fizikalno-kemijskih podataka u statistički značajne informacije. Informacije dobivene primjenom linearne multivarijantne metodologije te linearnih i nelinearnih predikcijskih modela omogućit će prostornu i vremensku raspodjelu pokazatelja onečišćenja kao i uspješno vođenje eko procesa i na taj način dati doprinos cjelovitom pristupu okolišu.

***Ključne riječi**: statistička metodologija, metodologija modeliranja, sustavski pristup, cjeloviti pristup.*

ABSTRACT

The routine monitoring of the quality of ecological systems and the successful control of the eco process requires the numerous laboratory analyses for determination of the hydrological, biological and physico-chemical parameters, prescribed by the regulations. The laboratory analysis, apart from the generation of waste materials, results in a large base of complex multidimensional data. The analysis, interpretation and correlation of some quality

indicators requires a system approach to the analysis of experimental data using statistical and modelling methodology. The basic task of this approach is the synthesis of many hydrological, biological and physico-chemical data in statistically significant information. Information obtained through the use of linear multivariate methodology and linear and nonlinear prediction models will allow spatial and temporal distribution of pollution indicators as well as successful eco-process control and thereby contribute to a holistic approach to the environment.

***Keywords**: statistical methodology, modelling methodology, system approach, holistic approach.*

1. UVOD

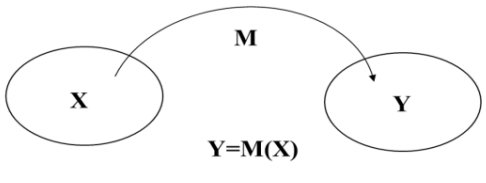
Okoliš je opće dobro te je osobitog značaja za državu i njene stanovnike te kao takav mora imati i posebnu zaštitu. Svi zahvati u okoliš ne smiju utjecati na kvalitetu življenja, na zdravlje ljudi i održivi razvoj prirode. Stoga se upravljanje okolišem provodi pod uvjetima i na način propisan zakonima. Zaštita okoliša kao općeg dobra predstavlja skup aktivnosti i mjera za sprječavanje opasnosti za okoliš, nastanka šteta i/ili onečišćivanja okoliša, smanjivanja i/ili otklanjanja šteta nanesenih okolišu te povrata okoliša u stanje prije nastanka štete [1].

Sastavnice okoliša moraju biti zaštićene od onečišćenja pojedinačno i u okviru ostalih sastavnica okoliša, uzimajući u obzir njihove međusobne odnose i među utjecaje. Zaštita od onečišćenja i očuvanje pojedine sastavnice okoliša ureduju se Zakonom, posebnim zakonima, i propisima donesenim na temelju tih zakona a oni uključuju: zaštitu tla i zemljine kamene kore, zaštitu šumskog područja, zaštitu zraka, voda, mora i obalnog područja, zaštitu prirode, zaštitu od štetnog utjecaja genetski modificiranih organizama, zaštitu od buke, zaštitu od ionizirajućih zračenja i nuklearnu sigurnost, zaštitu od štetnog utjecaja kemikalija, od svjetlosnog onečišćenja te gospodarenje otpadom. Za potpunu brigu o okolišu i cjeloviti pristup nisu dovoljni samo propisani zakoni i njihovo provođenje nego je izuzetno važno razvijanje ekološke svijesti stanovništva neke države kao i ekološke svijesti u cjelini. Ekološka svijest predstavlja dio šire filozofije društvenog pokreta usmjerenog na očuvanje i unaprjeđenje prirodnog okruženja, kako u interesu pojedinca, tako i u interesu civilizacije i njenog opstanka u cjelini [2].

Kontinuirano i sustavno praćenje stanja okoliša generira skup podataka koji nam daju informacije o statusu i promjenjivim trendovima u kvaliteti okoliša. Informacije kao takve moraju biti dostupne javnosti te su neophodne za učinkovitiju implementaciju sprječavanja onečišćenja okoliša i porasta ekološke svijesti, jer znanje počiva na informacijama i stvara se iz informacija. Za porast ekološke svijesti potrebna je slobodna razmjena informacija te slobodan pristup informacijama, a da bi se to omogućilo potrebno je sigurno pohranjivanje informacija, jer svaka informacija koja nije na raspolaganju onome kome bi trebala biti je izgubljena prilika za stvaranje novog znanja odnosno iznalaženja rješenja. Sustavnim praćenjem okoliša formiraju se velike baze kompleksnih višedimenzionalnih podataka. Za analizu, interpretaciju te međusobne korelacije pojedinih pokazatelja kvalitete potreban je sustavski pristup analizi eksperimentalnih podataka primjenom statističke metodologije i metodologije modeliranja procesa. U ovom radu opisat će se i naglasiti važnost pojedinih matematičko statističkih alata kojima je moguće definirati linearne i nelinearne odnose i međuodnose pokazatelja onečišćenja okoliša, te prostorne i vremenske raspodjele, kao doprinos cjelovitom pristupu okolišu.

2. MODELIRANJE PROCESA

Modeliranje procesa općenito, a posebice eko procesa, započinje definiranjem procesnog prostora u kojem se odvija proces. Svi procesi u našem okolišu su zapravo fizikalni, kemijski i biološki procesi složene prirode, od molekularne pa do makroskopske razine. Osnova pristupa matematičkog modeliranja je sažimanje i prikazivanje istraživanih procesa na način da se, na određenoj razini modela, za istraživani procesni prostor definiraju dva osnovna skupa veličina modela i njihova zavisnost (slika 1). Potrebno je definirati skup ulaznih veličina (X) i skup izlaznih veličina (Y) te odnos nezavisnih veličina (X) koje su uzrok promjena i zavisnih veličina (Y), koje su posljedica tih promjena. Definiranje skupova ulaznih i izlaznih veličina nije jedinstveno. Veličine procesnog prostora moguće je na različite načine pridružiti ulazno-izlaznim skupovima, i tako definirati modele različite složenosti, od vrlo jednostavnih do vrlo složenih, kao i modele s različitom svrhom i vrlo širokim spektrom moguće primjene matematičko statističkih korelacija kao i dostupne računalne podrške.

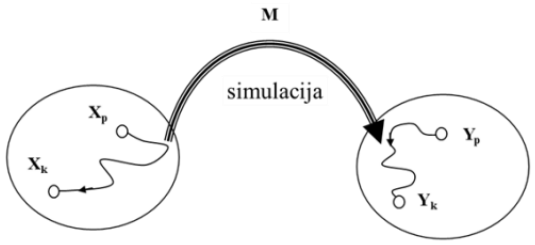


Slika 1. Shematski prikaz modela (M) kao međuodnosa skupa ulaznih X (nezavisnih) i skupa izlaznih Y (zavisnih) veličina [3]

Zadaća modeliranja u okolišu odnosi se na: i) opis prirodnih pojava za bolje razumijevanje i planiranje nadzora, ii) predviđanje vrijednosti fizikalnih, kemijskih i bioloških parametara, iii) predviđanje ponašanja sustava u cjelini koji se odnosi na projektiranje uređaja i postrojenja za obradu, ispitivanje postojećih uređaja i optimizaciju rada te upravljanje procesima i kontrolu neželjenih događaja. Metodologija modeliranja i struktura matematičkog modela može biti vrlo različita i najčešće je određena prirodom istraživanog sustava, njegove svrhovitosti i zadaće matematičkog modeliranja. Postupak izrade matematičkog modela sastoji se od nekoliko koraka i iterativne je prirode. Kao prvi korak nameće se definiranje svrhe modela, potrebnih podataka i preciznosti s kojom model mora biti izrađen. Nadalje slijedi izrada strukture modela (prikupljanje podataka, provjera kvalitete podataka te planiranje provedbe dodatnih laboratorijskih analiza). Struktura modela i procjena parametara modela je slijedeći korak, te kalibracija i validacija modela kao najznačajniji korak nakon kojeg možemo prihvatiti postavljeni model ili se vratiti na bilo koji prethodni korak sa zadaćom poboljšanja modela. Nakon svih ovih koraka slijedi simulacija modela i interpretacija rezultata. Osnovni metodološki postupak istraživanja primjenom modela naziva se simuliranje procesa ili sustava koji se temelji na istraživanju prostora skupa ulaznih veličina i posljedica tih promjena u skupu izlaznih veličina (slika 2). Simulacija modelom je podržana adekvatnom računalnom podrškom uz pomoć koje je moguće učinkovito računanje vrijednosti izlaznih veličina, prikladan grafički prikaz i statistička analiza rezultata simulacije.

Zavisno od matematičke strukture na kojoj se model zasniva postoje različite razine složenosti modela. Najjednostavnija matematička struktura svakako je jednadžba regresijskog pravca na kojoj se temelje multivarijabilni linearni regresijski modeli, autoregresijski linearni modeli te regresijski modeli glavnih komponenata. Složenija matematička struktura u obliku običnih i parcijalnih diferencijalnih jednadžbi sastavni je dio nestrukturnih modela za čiju je izradu potrebno dobro poznavanje procesa. Napredne metode modeliranja i složenije strukture

modela temelje su na primjeni neuronskih mreža (eng. *neural network*) i neizrazite logike (eng. *fuzzy logic*).



Slika 2. Shematski prikaz simulacije procesa kojom se istražuje prostor skupa ulaznih veličina X od početne Xp za t = 0 do konačne vrijednosti X_k za t = t_k i posljedice ovih promjena u skupu izlaznih veličina Y od početne Yp za t = 0 do konačne Y_k za t = t_k [3]

3. NESTRUKTURNI MODELI

Ako procese u okolišu prikazujemo kao klasične inženjerske procese koji se baziraju na bilancama mase i energije i kao takvi služe za opis fizikalnih procesa prijenosa tvari i topline te kemijskih i bioloških procesa koji se odvijaju u zadanom procesnom prostoru, onda govorimo o nestrukturnim modelima. Matematička struktura takvih modela je jedna ili više običnih ili parcijalnih diferencijalnih jednadžbi zavisno od promatranog prostora (cjelokupnog ili djelomičnog). Ovim tipom modela opisuje se dinamičko vladanje procesa kao promjena pojedine varijable stanja u zavisnosti od vremena trajanja procesa. Uz dobro poznavanje procesa i primjenu adekvatne računalne podrške omogućuje se primjena modela za simulaciju eko procesa. Najpoznatiji primjeri ove vrste modela primjenjuju se u procesima obrade otpadne vode i aerobne razgradnje, poznati pod nazivnom modeli aktivnog mulja (eng. *Activated Sludge Model*, ASM) i modeli procesa anaerobne razgradnje (eng. *Anaerobic Digestion Models,* ADM). *Activate Sludge Model* (ASM) je najčešće primjenjivan model ovog tipa, a postoji u nekoliko oblika složenosti (ASM1, ASM2, ASM3) [4]. Ti modeli uključuju velik broj mjernih veličina, a opisuju dvije najvažnije faze postupka: biološku oksidaciju i naknadno taloženje. Glavni nedostaci ovih modela baziraju se na složenosti modela, primjenjivi su posebice za modeliranje procesa obrade komunalnih otpadnih voda te nedovoljan opis dinamike procesa obrade. Modeli procesa anaerobne razgradnje, ADM, temelje se na četiri faze razgradnje: hidrolizu, acidogenezu, acetogenezu i metanogenezu, a u model je uključeno 19 procesa i 26 procesnih veličina [5].

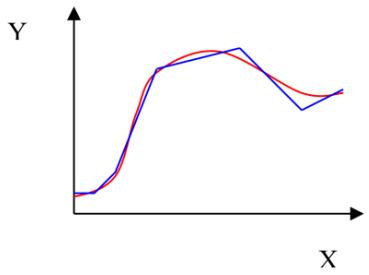
4. EMPIRIJSKI MODELI

Pri izradi empirijskih modela nije potrebno poznavanje procesa jer se model isključivo oslanja na odnos ulaznih i izlaznih varijabli i na predikciju budućih stanja dobivenu na osnovi prethodnih stanja. Za izradu ovih modela potrebna je velika baza podataka dobivena mjerenjem parametara kroz duže vremensko razdoblje. Izrada modela ne ovisi o poznavanju procesa i o definiranju pojedinih fizikalno, kemijsko bioloških procesa u okolišu nego se ovaj

tip modela zasniva na statističkoj analizi baze podataka, kojom se utvrđuje zavisnost odnosno među zavisnost pojedinih varijabli.

4.1. Modeli zavisnosti varijabli

Utvrđena zavisnost ulaznih i izlaznih veličina prikazuje se funkcijom (jednadžbom modela), a ovisno o prirodi funkcije kojom se opisuje zavisnost varijabli mogu biti linearni i nelinearni. Linearni empirijski modeli primjenjuju se za opisivanje linearnih, ali i nelinearnih procesa, poput složenih procesa u okolišu. Njihova se primjena pritom temelji na pretpostavci da se i nelinearni procesi mogu lokalno aproksimirati linearnom funkcijom [6]. Aproksimacija nelinearne funkcije uz pomoć više linearnih funkcija prikazana je na slici 3.



Slika 3. Grafički prikaz aproksimacije nelinearne funkcije (krivulja označena crvenom bojom) pomoću nekoliko linearnih funkcija (pravci označeni plavom bojom).

Izrada linearnih modela temelji se na primjeni tehnika modeliranja poput viševarijantne linearne regresije (engl. *Multiple Linear Regression*, MLR) ili metode djelomičnih (parcijalnih projekcija) najmanjih kvadrata (engl. *Partial Least Squares*, PLS). Kada je broj utjecajnih varijabli (regresora) malen i kad one nisu međusobno kolinearne, te imaju razumljiv utjecaj na ponašanje sustava ili promatranu zavisnu veličinu, MLR modeli mogu prilično dobro opisivati složene nelinearne procese [7].

Međutim, u praksi je pred analitičara često postavljen velik skup varijabli od kojih mnoge nemaju jasan utjecaj na ponašanje sustava. Kako je ranije naglašeno ovaj tip modela nužno ne zahtjeva znanje o procesu, ali poznavanje procesa u ovom slučaju može doprinijeti točnosti modela i smanjenjem koraka izrade modela. Prethodna obrada podataka kojom se nastoji smanjiti broj promatranih varijabli, uvelike olakšava izradu modela i pojednostavljuje ga. Eksperimentalni podaci također često sadrže šumove, kao posljedicu netočnih mjerenja, pa se može dogoditi da se za izradu modela izdvoje varijable koje se slučajno poklapaju, a odbace inače važne varijable, što naravno umanjuje točnost modela.

U nelinearnim empirijskim modelima proces se nastoji aproksimirati nekom od uobičajenih nelinearnih funkcija poput logaritamske, eksponencijalne, kvadratne, itd. Obično ovakvi modeli eko procesa, koji su uglavnom i nelinearni po prirodi, daju bolje rezultate od linearnih, što je i razumljivo. Drugim riječima, model mora vjerno reproducirati vladanje realnog procesa u područje njegove primjene. Navedeni empirijski modeli primjenjivi su za promatranje i upravljanje procesom, a temelje se na analizi zavisnosti ulaznih i izlaznih varijabli kojima se opisuje proces.

4.2. Modeli međuzavisnosti varijabli

Za razliku od prethodno opisanih modela za analizu provedbe procesa u empirijske modele spadaju i modeli koji se temelje samo na međuzavisnosti varijabli, tzv. multivarijatni pristup analizi, u ovom slučaju informacija o stanju okoliša. Cjeloviti pristup okolišu očituje se u tome da pojedini parametar stanja okoliša u kombinaciji s nekim drugim parametrom može imati različito značenje za okoliš kao cjelinu pa stoga i različit doprinos opisu stanja okoliša. Stoga se u ovoj skupini modela, kojoj su glavni predstavnici faktorska analiza (eng. *Factor Analysis*, FA) i analiza glavnih sastavnica (eng. *Principal Component Analysis*, PCA), proučava i analizira međusobni odnos više varijabli istovremeno. Osnovica za provedbu ovog tipa analiza i izrade modela je postavljanje korelacijske matrice koja sadrži koeficijente (Pearsonove ili Spermanove) jednostavne linearne korelacije. Na ovaj način moguće je podijeliti parametre po skupinama, te prikazati prostornu i vremensku raspodjelu parametara uzimajući u obzir varijable lokacije i vremena provedbe analize.

5. ZAKLJUČAK

Skupovi podataka dobiveni kontinuiranim praćenjem stanja okoliša daju nam informacije o pojedinim parametrima, nalaze se na različitim mjestima i u različitim oblicima te su stoga, iako dostupni, najčešće nerazumljivi u smislu međuzavisnosti pojedinih parametara onečišćenja i pojedinih parametara djelovanja i razvoja društva u cjelini. Postavlja se pitanje njihove maksimalne iskoristivosti za dobrobit i cjeloviti pristup okolišu. Za analizu, interpretaciju te međusobne korelacije pojedinih pokazatelja kvalitete potreban je sustavski pristup analizi eksperimentalnih podataka primjenom statističke metodologije i metodologije modeliranja procesa. Otvoreni pristup bazama podataka "Open Access" koji se danas zagovara u pojedinim znanstvenim krugovima i primjena suvremene računalne tehnologije koja omogućava analizu velikih skupova podataka "Big Data Analysis" metodologijom modeliranja omogućili bi maksimalnu iskoristivost i pomogli u pronalaženju "skrivenih" na prvi pogled ne vidljivih međuodnosa koji bi zasigurno pridonijeli cjelovitom pristupu okolišu.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

USING ANN MODEL AS AN EFFICIENT METHOD TO PREDICT THE AIR POLLUTION CONCENTRATIONS

Frederik Dara*, Ariola Devolli**

* University of Tirana, Faculty of Natural Sciences, Albania
** Agricultural University of Tirana, Faculty of Biotechnology and Food, Albania

corresponding author: Frederik Dara, e-mail: frederik.dara@fshn.edu.al

Original scientific paper

ABSTRACT

Air pollution is one of the most important environmental problems. Sulphur dioxide (SO_2) and Suspended Particles (PM_{10}) are considered the most important atmospheric pollutants. The preliminary prediction of air pollutant concentrations would allow us to take preventive measures to reduce the pollutant emission. This work illustrates the use of Artificial Neural Networks (ANNs) to predict the air pollution concentrations in Tirana city, Albania. The different parameters (SO_2, NO_2, CO, O_3, PM_{10}) are measured in different sites in Tirana city for a period of time. The Multi-Layer Perceptron ANNs are applied to predict the air pollutant concentrations in urban areas. Observed versus predicted data are compared to test the efficacy of ANNs. Results confirm ANNs as an improvement of classical models and show the utility of ANNs for prediction. The performance estimation is determined using the Root Mean Square Error (RMSE) and Mean Absolute Error (MAE).

***Keywords**: neural networks, prediction, air pollutant, PM_{10}*

1. INTRODUCTION

Air pollution is an important environmental problem. It is influences on human health and activities [1]. There are more deaths from non good air quality than from automobile accident [2]. There are many different chemical substances that contribute to air quality. These chemical components come from natural sources (forest fires, wind erosion, pollen dispersal, evaporation of organic compounds, etc.) and from also the human industrial activity. Nitrogen oxides, sulphur oxides, carbon monoxides, ozone and organic compounds are among the types of air pollutants. The particulate matter under 10 microns (PM_{10}) and ground-level ozone (O_3) are the most pollutants that influence directly or indirectly in human death [3, 4].

The preliminary air quality prediction would allow us to take preventive measures to reduce the pollutant emission. It is important for planning, providing proper actions and controlling strategies, so that to minimize the negative effects. Artificial Neural Networks are a suitable model for many purposes, provided that efficient architectures are available. An ANN is a computing system that is made up of several simple and highly interconnected processing elements, which process information by their dynamic state response to inputs. Recently, Artificial Neural Networks have been widely used in modelling, control, pattern recognition, signal processing, prediction purposes and so on [5 - 8]. They are becoming an alternative to "classical" statistical tools for the capabilities of handling non-linear problems and, more than this, for their generalization capabilities [9].

It is well-known that ANNs are proven to be universal approximates [10] and forecasting techniques based on ANNs are appropriate means for prediction of the state of the environment [11] from previously collected data [6]. The ANNs can be used to evaluate the predictive performance [12, 13], and gives a better performance comparable to other models. Unlike other predicting techniques, ANNs make no prior assumptions to data distribution. The ANNs are capable to define the linear and non-linear relationships between the variables and complex patterns in data sets [10]. They can be trained accurately when feed with a new data set.

In this work we present an application of feed-forward neural network modelling air quality data prediction, where historical data collected over the four month time period are used to "train" the model.

2. EXPERIMENTAL

Study Area In this study, four air monitoring stations in Tirana city were selected, located within the city area with high population density and known as the most polluted area. Three of these sites are monitored by mobile stations.

Figure 1 and table 1 illustrate the air-quality monitoring area and the description of sampling stations. The daily traffic density is classified as moderate to high and the peak periods found during morning and evening.

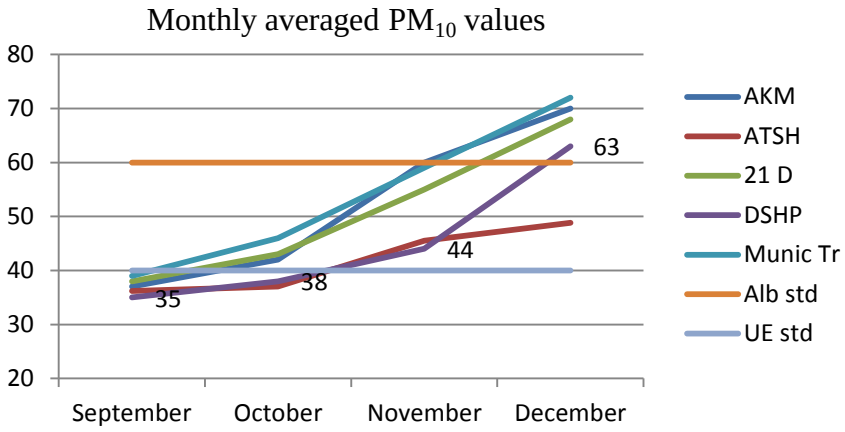


Figure 1. Monthly averaged values recorded in 5sites of Tirana city

Data Sets The data sets used in this study consist of hourly mean concentrations of air pollutant concentrations of SO_2, NO_2, CO, O_3, PM_{10} and meteorological parameters of air

temperature and rainfall recorded at four different urban sites from September to December during 2017 in Tirana city (figure 1). The input data are provided by the National Environmental Agency and by Institute of GeoSciences, Energy, Water and Environment.

Table 1. Monitoring sites

No.	Place	Type
1	Near AKM building	automatic station
2	Ministry of Environment Building (Near ATSH)	automatic station
3.	21 Dhjetori crossroad	mobile station
4.	DSHP Building	mobile station
5.	Municipality of Tirana	mobile station

Based on the average monitored data for the 4-month period, it is noted that they are higher than the EU annual rate. Thus, at the ATSH station (Ministry of Environment), the average monitored value is 41.88 μg/m³ compared to the annual rate of 40 μg/m³ and thus exceeds 1.81 μg/m³ while at the ATSH station the monitored average value is 52.25 μg/m³ and compared to the annual rate we have exceeded 12.25 μg/m³. Even at other points we have an exceeded average values from 5 to 14 μg/m³.

2.1. ANN Model

One of the most common examples of architectures used is the multilayer perceptron [9]. The ANN architecture we adopt is MLP perceptron model with 3-layer as shown in figure 2. The first layer, input layer, contains seven input variables (linear neurons) SO_2, NO_2, CO, O_3, and PM_{10} (five pollutant variables) and T_{air}, $R_{ainfall}$ (two comfort variables). There is one hidden layer and different numbers of its neurons were chosen to optimize the ANN performance. Every neurons of the hidden layer is non-linear and is connected with every neuron from the previous layer by weighted links. They are activated by hyperbolic tangent sigmoid function [9, 14]. The third layer is the output layer. It consists of the target of prediction model, PM_{10}. Its neuron uses the pure linear activation function. The input and target values were normalized into interval [-1, 1] in the pre-processing phase. The weights and biases were adjusted based on Levenberge-Marquardt (LM) in the training phase [15]. To avoid overfitting of network the method of early stopping was used [16]. The dataset was divided randomly into three sets, which is learning set for ANN training (70 %), validation set (20%) for ANN validating of the model and testing set (10%) to verify the efficiency and correctness of the developed model.

Software For development of the air quality prediction model, MATLAB Neural Network Toolbox [17] was used because its capabilities.

Network Error Calculation The predicted values of ANN models were compared with observed ones. The Root Mean Square Error (RMSE) and Mean Absolute Error (MAE) were chosen as the statistical criteria for measuring of the network performance:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(x_i - y_i\right)^2} \tag{1}$$

$$MAE = \frac{1}{n}\sum_{i=1}^{n}\left|x_i - y_i\right| \tag{2}$$

where x_i and y_i denote the observed and the predicted data, respectively, and n is the number of testing dataset observations. The RMSE represents the sample standard deviation of the differences between predicted values and observed values and MAE is the average absolute difference between y_i and x_i.

The lower of RMSE and MAE (RMSE, MAE ~ 0) and the highest of R^2 (R^2 ~ 1), the more accurate the prediction is and is expected to be the best model for forecasting.

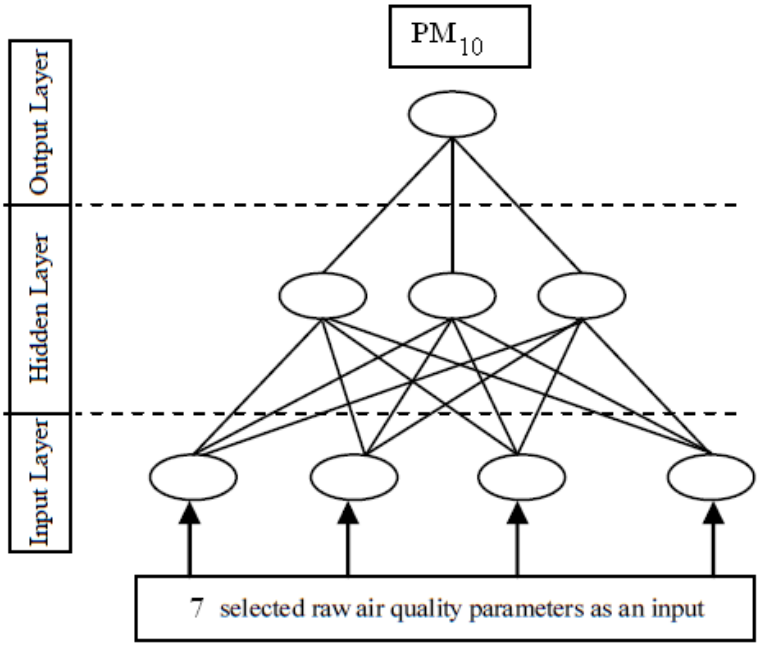


Figure 2. ANN architecture of Multi-layer Perceptron (MLP) with one hidden layer

3. RESULTS AND DISCUSSION

This work presents the possibilities of using ANNs as nowcasting (short term: 1 or 3 hours) and forecasting (medium/long term) the system's evolution.

The database of hourly time series (with 2900 values) allowed preliminary broad statistical analysis. The mean, standard deviation, variance, median of the data are some of very important of statistical properties of the dataset used for data analysis and processing (see table 2).

Table 2. Statistical properties of data set

Parameter	Statistical Property		
	Mean	Std. Dev.	Median
SO_2	7.1	2.34	7.8
NO_2	35.64	7.75	35.72
CO	0.94	0.25	0.915
O_3	38.66	45.16	32.68
PM_{10}	48.82	118.13	44.76

The structure of ANN model was varied with different numbers of its hidden neurons to optimize the ANN performance. The best structures, with their parameters, are displayed in table 3.

Table 3. The ANN parameters

Models	Model A	Model B	Model C
Inputs	SO_2, NO_2, CO, O_3, PM_{10}		
ANN Structure	7-6-1	7-10-1	7-15-1
Activation Functions	Tansig/purelin	Tansig/purelin	Tansig/purelin
Learning Rate	0.12	0.11	0.12
No. of Epochs	6000	4500	5200
SSE	0.1e-4	0.1e-4	0.1e-4
Output	PM_{10}	PM_{10}	PM_{10}

The models' performance in terms of R^2 and RMSE has been shown in table 4.

Table 4. Neural networks performance

	R^2			RMSE		
Model	Training	Validation	Testing	Training	Validation	Testing
A	0.962	0.812	0.7496	0.0192	0.0989	0.1342
B	0.973	0.854	0.8147	0.0136	0.0758	0.0985
C	0.9.68	0.836	0.7515	0.0161	0.0857	0.1331

The values obtained for the individual MLPs indicate that the model B is the best MLP of the training/validating and testing phases. Considering the experiments performed here, the our best MLP approach led to an average improvement in RMSE of 5.67 % over the other models were used. So, the ANN model implemented in this work was able to explain more than 80% of the variance of the environmental phenomena.

4. CONCLUSION

In this paper, the study was carried out for short-term predictions of PM_{10} air pollutant using ANN models. MLP perceptron, which was used for hourly predictions, came up as the best tool for forecasting. The results shown here are indications that the ANN techniques are useful tools of air quality management and prediction. The models studied in this paper are easily implemented, and they can be easily applied for real time predictions. These models can behave very well with noisily and uncertainty input data.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

THE PALYNOMORPHOLOGICAL DATA OF *CENTAUREA JACEA L.* IN ALBANIA

Anxhela Dauti*, Gezim Kapidani, Blerina Pupuleku*, Nikoleta Kallajxhiu*, Admir Jançe*, Silvana Turku***

* University "A. Xhuvani", Faculty of Natural Sciences, Elbasan, Albania
** Faculty of Natural Sciences, University of Tirana, Tirana, Albania

corresponding author: Anxhela Dauti, e-mail: dauti.anxhela@yahoo.com

Original scientific paper

ABSTRACT

In this paper are presented the palynological data of the pollen grains of *Centaurea jacea L.* in Albania. Also in the paper is presented the comparison of the palynological features of the *Centaurea jacea* pollen grains with *Centaurea cyanus* and *Centaurea solstitialis* pollen grains.

From the observation, with the light microscope, of pollen grains of *Centaurea jacea* results that they are tricolporate. The outline shape of pollen grains is spheroide. The exine is thick and with a scabrate (microechinate) sculpture.

By the comparison between the palynological features of the pollen grains of *Centaurea jacea* with those of *Centaurea cyanus* and *Centaurea solstitialis* we can notice that there are similarities and differences between them.

***Keywords**: Centaurea jacea, pollen grains, tricolporate, exine, scabrate (microechinate).*

1. INTRODUCTION

The genus *Centaurea L.* is one of the largest genera in the Asteraceae family. The number of species involved in this genus varies from 200 to 700 species depending on the classification [1 - 3]. This genus is mostly found in the Mediterranean region and in Western Asia [4]. In Albania, the genus *Centaurea* is represented by 35 species, spread mainly in rocky areas, high altitude areas of Northern Albania, undeveloped soils, grasslands, roadsides, etc. [5].

Centaurea species are important medicinal plants taking into consideration the biologically active metabolites like lignan [6 - 7]. In folk medicine, aerial flowering parts of some *Centaurea* species have been used to facilitate a wide range of symptoms [8 - 9].

The genus *Centaurea* presents nomenclatural and taxonomic problems. Palynological studies along with the latest molecular and cariological approaches are very useful in solving these problems [10, 11].

There have been several studies to estimate the morphology of the pollen grains of *Centaurea* [10 - 33]. According to morphological features of pollen grains, they are classified and recognized eight types of *Centaurea* pollen grains [12]. *Jacea* type of pollen grains is more advanced among other types [11].

In Albania, the morphological features of the pollen grains of two *Centaurea* species: *Centaurea cyanus* and *Centaurea solstitialis* [34, 35] have been studied.

The aim of this study is to present the morphological features of the pollen grains of *Centaurea jacea*, to give a helping to palynological literature of our country. Also, this study presents the comparison of the palynomorphological features of *Centaurea jacea* with those of *Centaurea cyanus* and *Centaurea solstitialis* obtained from the albanian literature.

2. EXPERIMENTAL

The material for the study was obtained in National Herbarium in Tirana. In order to realize the study of morphological characteristics of pollen grains a variety of processing methods can be used, but the most common for light microscopy studies are the following methods which are also used by us during the processing of pollen material:

Acetolysis of Erdtman method [36],
Acetolysis of Avetisjan method [37],
Basic fuchsine method [38].

The method of acetolysis according to Erdtman

The flower or leaf-bud is developed in an alcohol 96° in order to separate the other parts of the flower which can be separated inside distilled water. The bags of pollen grains with their pollen grains are dried in a thermostat, and then wetted with an acetolysis mixture (anhydrite acetic and sulfuric acid concentration and with pure chemicals in a 9:1 ratio), which is done every time in a repeating way. The test-tubes together with pollen grains and acetolysis mixture are placed in bathroom at a temperature 70 - 80 °C. The length-time of pollen grains staying in bathroom varies from different kinds. Then, the test-tubes are centrifuged where as they are cleaned several times with distilled water. Pollen grains are placed on slide and are observed with a microscope by dropping one dot from glycerine solution and water in a ratio 1:1. If the pollen grains are darken a lot then the material is separated in a test-tube by adding 1 - 2 sodium chloride 1 - 2 concentration sulfuric acid drops until the material becomes lighter. Then, it is done the second shower with distilled water. Through separation and centrifugation the material is taken and it is ready to become a preparation.

The simplified method of acetolysis according to Avetisjan

Pollen grains are placed in slide. Then, we dropped some ethyl alcohol (96%) drops on the slide composite. All fat substances of pollen grains created after the alcohol actions are cleaned with blotting-paper. The mixture of acetolysis is prepared every time frequently.

The slide composite is treated with 1 - 2 acetolysis solution drops and then it is warmed up in a thermostat or on the alcoholic lamp flames. The composite is controlled with a microscope continuously during the warming phase so it cannot get darker more than what is allowed. After the desired colour is reached the wash-up with alcohol (70 %) is done. Then the composite is washed from all other remains and then sealed with glycerine gelatine prepared according to Kisser method [39].

The coloured method of basic fuchsine according to Smoljaninov, Gollubkov

Pollen grains are placed on the lama and then we add some alcoholic concentrated drops. In case the alcohol evaporates quickly we add an extra drop again. After that, we observe that the fat composite of pollen grains is spreader from alcohol toward the slide side. This fatness composite is taken away from the slide with blotting paper. After the slide is washed away from remains with blotting paper we add to it the coloured solution of basic fuchsine which is prepared in two variants listed below:

1) Basic fuchsine, alcohol 75 % and phenol in this ratio 1:700:100
2) Basic fuchsine, ethyl alcohol 96 % and xylol in the ratio 1:600:800

Phenol and xylol are used in the transparency growth of markers and are necessary as antiseptic. After the color materials are fixed with gelatine glycerine which is prepared according to Kisser method [39].

For the study of pollen grains of *Centaurea jacea* are prepared 3-6 microscope slides with the methods above. In order to accomplish the quantitative analysis of palynomorphological features, 31 pollen grains are taken in consideration. The study of palynomorphological features and the pollen grains photos are realized with light microscope Digital Microscope / Camera Software, Motic Images Plus 2.0 ML, B1 Series. The microscopic photos of pollen grains of *Centaurea jacea* are made in polar and equatorial view with magnification 1000X, taken by DAUTI Anxhela.

The terminology is based on that recommended by [40], [41] and [42].

3. RESULTS AND DISCUSSION

Morphological description of pollen grains

Centaurea jacea L., Sp. Pl. 914(1753) (C. amara L. pro parte)

Hemicryptophytes. Perennial plants. It grows in meadows and open woodland. It blooms in june – july. Honey plants [5].

The pollen grains of *Centaurea jacea* are tricolporate. Their polar axis varies from 24 - 28 (26.3) μm, while the equatorial diameter varies from 25 - 28 (27) μm. In polar view, the pollen grains have circular shape to triangular, while in equatorial view they have elliptic shape to spheroidal. From the outline the shape is spheroidal (P/E = 0.96 - 1.04). Exine is thick and with scabrate (microechinate) sculpture. The thickness of exine varies from 3 - 4.5 μm. Ectexine is thicker than endexine. Ectexine varies from 2 - 3.5 μm, while the endexine is about 1 μm. The pores appear with circular outline. Their diameter vary from 3 - 5 (4.4) μm. The length of the colpi vary from 17 - 21 (19.4) μm, while the width of the colpi vary from 4 - 6 (5.27) μm. Mesocolpium varies from 17 - 21 (18.3) μm (figures 1 – 15).

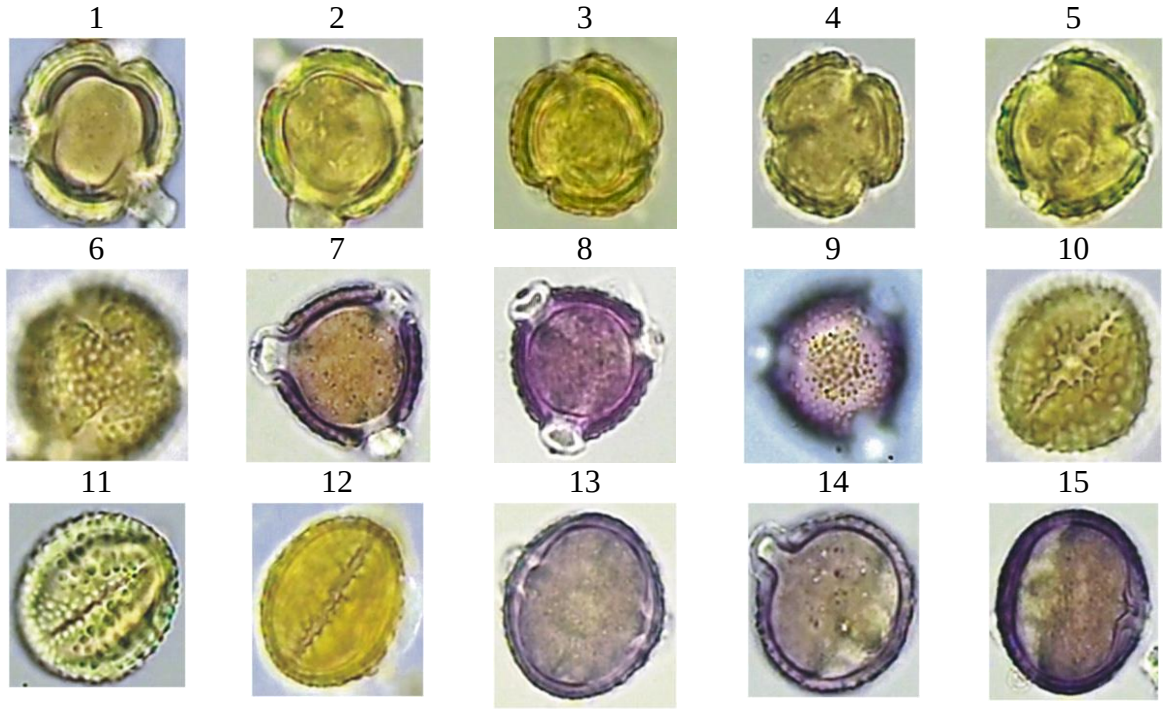


Figure 1 - 15. Pollen grains of *Centaurea jacea*, polar view (figure 1 - 9) and equatorial view (figure 10 - 15) (1000 X)

In the table 1 are presented the morphological features of the *Centaurea jacea* pollen grains and the palynomorphological features of *Centaurea cyanus* and *Centaurea solstitialis* taken from the literature of our country [34, 35]. Based on the data from table 1 and figure 16, it is noticed that between the pollen grains of the three *Centaurea* species there are similarities and differences in the studied palynomorphological features.

Table 1. Comparative table of morphological features of *Centaurea* pollen grains

Palynological features	*Centaurea cyanus* (Kallajxhiu, 2011)	*Centaurea jacea*	*Centaurea solstitialis* (Dauti, 2016)
The polar axis (P), µm	31- 36.72 (34.75)	24- 28 (26.3)	25- 30 (28.33)
The equatorial diameter (E), µm	26.92- 30.19 (28.63)	25- 28 (27)	25.5- 31.5 (28.6)
The thickness of exine**,** µm	4.19	3- 4.5 (3.7)	5- 6 (5.76)
The length of pores, µm	4.94	3- 5 (4.4)	9.3
The width of pores, µm	7.65	3-5 (4.4)	6.9
The length of colpi, µm	34.17	17- 21 (19.4)	25.06
The width of colpi, µm	4.25	4-6 (5.27)	9.6
The sculpture of exine	psilate	Scabrate (microechinate)	Scabrate (microechinate)
The shape of pollen grains (P/E)	subspheroidal	spheroidal	spheroidal

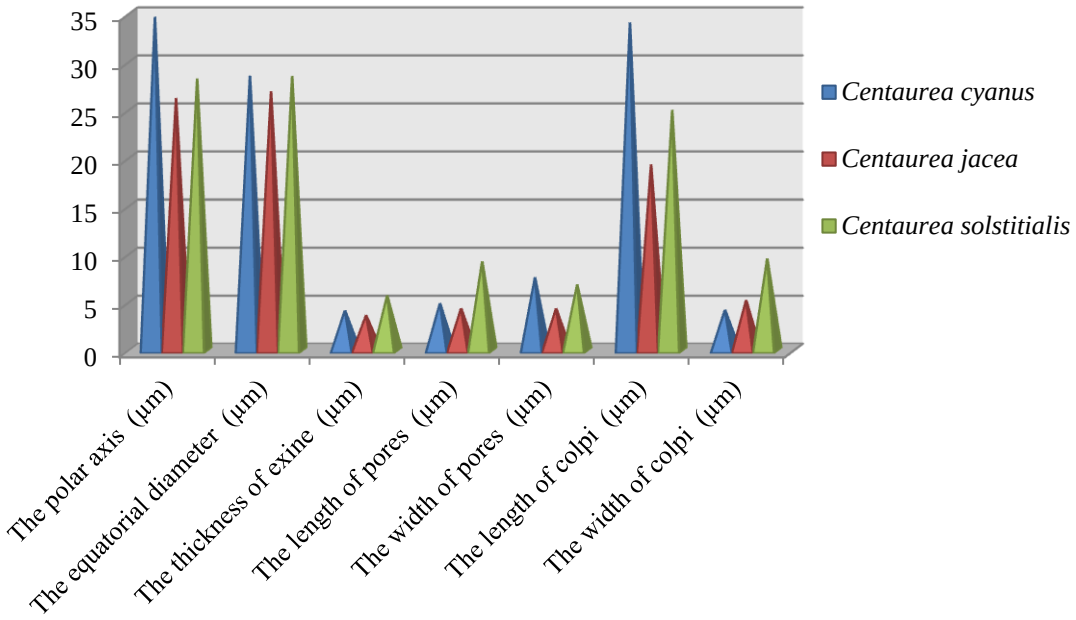


Figure 16. Chart of the average dimensions of *Centaurea* pollen grains

Regarding the polar axis of the pollen grains, the *Centaurea cyanus* pollen grains are bigger than the pollen grains of the other two species. If we see the equatorial diameter of the pollen grains, there are some similarities between *Centaurea cyanus* and *Centaurea solstitialis*. The shape of the pollen grains, according to the outline (P\E) is subspheroidal in *Centaurea cyanus* while at *Centaurea jacea* and *Centaurea solstitialis* it is spheroidal. The exine is thick in three *Centaurea* species, but it is more thicker in the pollen grains of *Centaurea solstitialis*. The sculpture of the exine is different in *Centaurea* species. In *Centaurea cyanus* pollen grains, it is psilate, while in the other two species it is scabrate (microechinate). The pores of pollen grains of *Centaurea cyanus* and *Centaurea solstitialis* species are prolonged, while at the *Centaurea jacea* pollen grains appear almost circular. The length of the pores is bigger in the *Centaurea solstitialis* pollen grains, while the width of the porea is bigger in *Centaurea cyanus* pollen grains. The length of colpi appears different in the three *Centaurea* species. The biggest length of colpi is noticed at *Centaurea cyanus* pollen grains. Even the width of the colpus appears different in the three *Centaurea* species, but the biggest is noticed at the *Centaurea solstitialis* pollen grains.

4. CONCLUSION

- from the analysis of the palynomorphological features of *Centaurea jacea* and their comparison with those of *Centaurea cyanus* and *Centaurea solstitialis* results that they are tricolporate,
- *Centaurea jacea* pollen grains are smaller than the other two species,
- the shape of the pollen grains varies from spheroidal to subspheroidal,
- the exine appears thinner at the *Centaurea jacea* pollen grains,
- the sculpture of exine varies from psilate to scabrate (microechinate),
- the pores vary from circular to prolonged and they are smaller at *Centaurea jacea* pollen grains,

- the pollen grains of *Centaurea* species have different length and width of colpi, where the length of colpi is smaller at *Centaurea jacea*, while the width of colpi is smaller at *Centaurea cyanus*.

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Acknowledgements

We thank Edmond Dauti for helping to edit the manuscript.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

ASSESSMENT OF SURFACE WATERS QUALITY AND THE DETERMINATION OF MAIN POLLUTANTS

Ariola Devolli*, Frederik Dara, Arta Kodra*****

* Agricultural University of Tirana, Faculty of Biotechnology and Food, Albania
** University of Tirana, Faculty of Natural Sciences, Albania
*** National Environment Agency of Albania, Tirana, Albania

corresponding author: Ariola Devolli, e-mail: adevolli@ubt.edu.al

Original scientific paper

ABSTRACT

Discharges into surface waters are a phenomenon which progressively has affected to the decrease of rivers water quality, and the environment in general. The purpose of this study is the assessment of surface waters quality and the determination of main pollutants.

This study evaluates water quality of Ishëm and Erzen rivers based on the results of physical-chemical parameters. Sampling, measures and assessment of river water quality is performed according to the recommended standards.

Results of Ishem River shows that nitrate, dissolved oxygen, biological oxygen demand are at high levels compared with the recommended values. Results taken from monitoring of the waters of Erzen river indicate bad quality with high values of total phosphorus, ammonia, as well as with dissolved oxygen values in the range 2 - 4 mg/l O_2. The collected data were subject to statistical analysis (ANOVA) using the SPSS software. Based on average values Ishëm river waters are of a bad quality due to high urban pressure.

***Keywords**: water river quality, physical-chemical analysis, assessment*

1. INTRODUCTION

Surface water pollution could threaten human, animal and ecosystem [1]. During recent years, there has been increasing awareness of, and concern about, surface water pollution all over the world [2]. People on globe are under tremendous threat due to undesired changes in the physical, chemical and biological characteristics of air, water and soil. Water is one of the vital needs of all living beings [3]. Waste materials including liquid are the by-products of human activities which may be treated or untreated before being disposed off. Waste generally has assumed exponential increases and as a result of rapid growth of

population and development in the urban centres where large volume of waste are generated due to multiple productions of goods in the industrial and agricultural sectors [4].

Industrial development (either new or existing industry expansion) results in the generation of industrial effluents [5]. Liquid urban, industrial and agricultural discharges into surface waters are a phenomenon which affects the ecology of the aquatic environment. In an industrial district where wastes are continuously generated and discharged into the environment without adequate disposal methods, the aquatic system eventually receives the bulk of the contaminants. Effluents discharged into rivers may have effects on aquatic fauna and flora either directly or indirectly [6]. The major concern is the decrease of rivers water quality, and the environment in general [7]. Surface water can be impacted through inputs from industrial, domestic, agricultural activities, sewage discharge, and groundwater leaching and run off [8].

Domestic waste discharge into the surface water may accumulate large quantity of nutrients enrichment and stimulates eutrophication process and bioaccumulation of organic and inorganic compounds. Further, it may result in alteration and interaction among both aquatic flora and fauna. Eutrophication refers to the excessive accumulation of micro and macro flora in water bodies which is closely associated with increase in human activities in the catchment area [9].

Agricultural activities is both cause and at the same time victim of water pollution. It is a cause through discharge of pollutants and sediments to the surface water and it is a victim through the use of waste water which contaminates crops and transmits diseases to consumers and farm workers. Normally, agricultural water pollutants are transported to aboveground or underground receiving streams by periodic storm water [8].

Pesticides, herbicides and insecticides are used to kills agricultural pest; these chemicals may enter and contaminate water through direct application, run-off and atmospheric addition [1]. In this context takes importance the evaluation of surface water quality and definition of main pollutants discharged into them, with the aim of environmental protection and rehabilitation and the establishment of data base for an integrated and sustainable management of water resources.

High levels of pollutants in river water systems increase content of biological oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus, ammonium and nitrate and hence make such water unsuitable for drinking, irrigation and aquatic life [10].

Water pollution is a major global problem which requires on going evaluation and revision of water resource policy at all levels [11].

Albania is rich in water resources like lakes, rivers, springs, lagoons, with a high quantity of available water. The Albanian territory covers about 65 % of a total watershed area [12].

Environmental problems related to industrial pollution and poor natural resource management in Albania are considered as severe. Erzeni and Ishem are the most important rivers in Albania country.

Some branches of these rivers are close to the industrial area of Tirana and Durres City. Most of the factories and manufactures industries discharge their effluents into a branch of river or directly into the river [13]. These effluent from industries have a great deal of influence on the pollution of the water body, they can alter the physical, chemical and biological nature of the receiving water body [14]. Physicochemical parameters such as turbidity, pH, temperature, nitrate and others with respect to water quality are widely accepted as water quality parameters [3].

The present paper aims to evaluate water quality of Ishëm and Erzen rivers based on the results of physical-chemical parameters such as: pH, temperature, ammonia, nitrates, total phosphorus, chemical oxygen demand, dissolved oxygen, biological oxygen demand.

Assessment of river water quality is performed according to EC Water Framework Directives [15].

2. EXPERIMENTAL

Study Area: Ishëm River lies in the western part of Albania country and flow to the north area of Tirana, Albanian capital city. It flows into the Adriatic Sea near the town Ishëm. The length of the watercourse is recorded in different sources as between 74 and 79 km. The drainage basin of the Ishëm covers a total area of 673 km^2. The average discharge at the mouth of the river is 20.9 m^3/s.

The Erzeni River lies on southern area of Tirana city and eastern area of Durres city in central Albania. This river flows also to the Adriatic Sea. The length of Erzeni watercourse is 109 km while the catchment area is 760 km^2 [16].

The determination of sampling location in rivers is based on hydrodynamic theory of aquatic environments. The sampling location usually is assigned in those parts of the aquatic environment, where the mixture of water is better and its movement is almost laminar.
For both rivers it is necessary to have three sampling sites, based on their expansion and on their composition [17].

Sample collection: The water to be sampled should be representative of river's water. Sampling plays particular importance in water quality assessment. Water samples were collected from both rivers in six different sites during 2015. The samples were collected from the surface water of the river in 1-liter pre-cleaned polyethylene bottles. These sample bottles were closed and placed in thermo-box to avoid any contamination until they arrived at laboratory and were analysed within twenty-four hours of collection. Sample collections were carried out based on techniques used by EPA Region 8 Laboratory staff [18].

Six different sites were selected for the collection of water samples (figure 1). The sites present various levels of human and industrial impact, from the upper, middle and downstream flow of rivers.



Figure 1. Map of rivers sampling sites (in red) [19]

Water samples of Ishem River are taken in three different sites of its tributaries: Brari (I1) in the upper stream, Lana (I2) in the middle stream and Ishmi (I3) in the downstream flow. Water samples of Erzeni River are taken in three different sites of its tributaries: Ibe (E1) in the upper stream, Ndroq (E2) in the middle stream and Sallmonaj (E3) in the downstream flow.

Determination of Physicochemical Parameters: The collected samples were tested at both Laboratory of Chemistry Department and Laboratory of Agro-environment and Ecology,

Agricultural University of Tirana. All analytical methods used are standard ones, recommended by APHA. The procedure for analysis followed Standard Methods of Analysis of Water and Wastewater (APHA) [20].

Water samples were tested for different physicochemical parameters. Water pH and temperature were determined in situ by using calibrate digital pH meter and a mercury thermometer, respectively.

DO was measured by Winkler method. The BOD_5 measurement was performed with the dilution method for five days. Dissolved oxygen was measured initially and after incubation, and the BOD is computed from the difference between initial and final DO according to standard method 5210 B. The COD concentration in the river's water was determined with dichromate methods by close refluxing according to the standard method 5220D with an accuracy of 0.1 mg COD per Liter. All nutrients were determined according to standard methods by using UV-VIS Spectrophotometer (APHA) [21].

3. RESULTS AND DISCUSSION

Water analyses were conducted with 3 replications. The collected data were subject to statistical analysis (ANOVA) using the SPSS software (significance level at 0.05). Graphs were performed by using Graph Pad Prism 6 software.

Assessment of river waters quality is based on EU Water Framework Directives for "Quality of fresh waters supporting fish life". According it, natural freshwater objects can be classified on five quality status, from very good status (class 1) to very bad status (class 5) [22].

The pH of the aquatic systems is an important indicator of water quality and the extent of pollution in the studied areas. Unpolluted rivers normally show near neutral or slightly alkaline pH. The pH of both rivers' water varied from 6.34 to 8.56 during the studding period (table 1).

Table 1. Result of pH and temperature values of water samples

River	Ishem			Erzen		
Sites	I.1	I.2	I.3	E.1	E.2	E.3
PH	7.2±0.63	7.3±0.68	7.16±0.68	7.28±0.56	7.35±0.58	7.28±0.6
Temp (^{0}C)	12.5 - 18.5			13 - 19.3		

Tables 1 shows that values of temperatures varied from 12.5 to 19.3 ^{0}C depends on sampling period, which not exceed the maximum permitted level for surface water (30 - 35°C).

Based on WFD there is no problem concerning pH values in those rivers: all data are between 6.5 and 8.5 (figure 2). Relying on pH values and according to NIVA classification this water can be classified as good quality [23, 24].

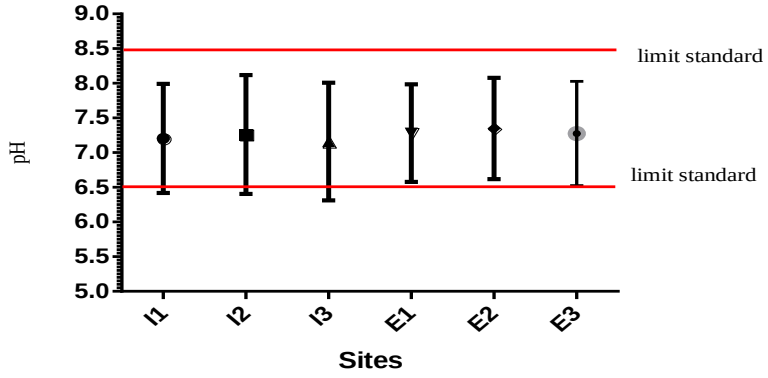


Figure 2. pH values of water samples

Mean values of dissolved oxygen (DO) ranged between 3.4 - 7.8 mg/L (table 2). The lowest values of DO measured were 1.4 mg/L and 2.5 encountered at site (I3) and (E2) respectively. The higher value of dissolved oxygen indicates good aquatic life.

The figure 3 shows that the content of dissolved oxygen in Ishëm and Erzeni rivers is almost higher than minimum permitted level (3 mg/L). Most of the samples contain DO between 3mg/L to 7 mg/L limit values for good quality status. According to WFD directives and standards of Albanian National Environment Agency sites I3 and E2 are classified as very bad and bad status based on DO levels. Water samples of sites I1 and E1 can be classified as good quality. Most of the analysed waters did not meet the normal permitted level of DO (> 7mg/L), so they are considered as bad to good quality.

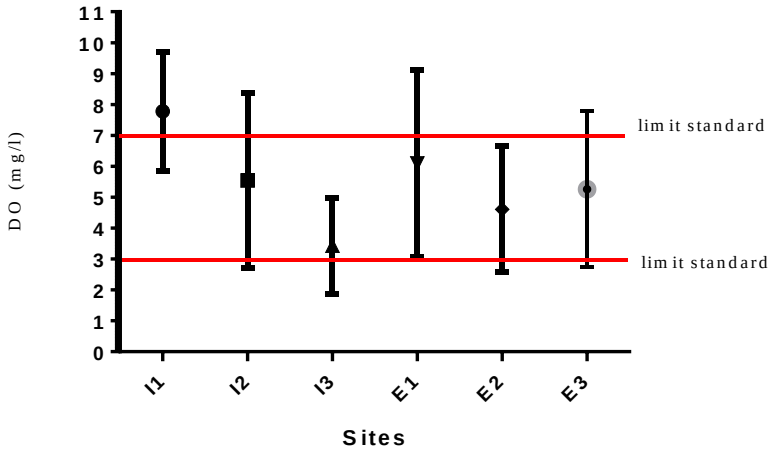


Figure 3. Dissolved oxygen content in water samples

The Chemical Oxygen Demand (COD) indicates the organic matter which is present in water sample. This organic matter can be oxidized by a strong oxidant such as dichromate. This parameter is used widely used to measure the amount of organic matter in urban and industrial discharge water [25].

Table 2 show that COD values range from 40 mg/L to 100mg/L (minimum and maximum COD measured values are 15.5 mg/L and 165 mg/L respectively).

Table 2**.** Results of physicochemical parameters of water samples

Parameters	Ishem River			Erzen River		
Sites	I.1	I.2	I.3	E.1	E.2	E.3
DO (mg/L)	7.78±1.68	5.54±2.49	3.43±1.36	6.09±2.66	4.61±1.78	5.26±2.21
COD (mg/L)	41.4±10.63	91.4±20.78	97.96±38.73	38.74±19.57	82.16±12.95	60.86±18.89
BOD (mg/L)	21.94±8.05	47.2±13.35	51.34±20.93	21.62±12.59	45.62±9.53	28.82±9.83
$N\text{-}NH_4^+$(mg/L)	1±1.12	6.9±4.61	8.48±6.29	1.7±1.24	11.04±5.43	8.05±4.79
P- total (mg/L)	0.08±0.024	0.94±0.54	1.76±1.21	0.056±0.032	0.54±0.36	0.34±0.34
$N\text{-}NO_3$ (mg/L)	0.36±0.12	0.92±0.38	1.11±0.48	0.5±0.2	0.85±0.19	1.26±0.41
$N\text{-}NO_2$ (mg/L)	0.018 - 0.09			0.025 - 0.1		

The biochemical oxygen demand may be defined as the oxygen required for the microorganism to performed biological decomposition of dissolved solids or organic matter in the wastewater under aerobic conditions [26].

The biochemical oxygen demand reported from water samples at Ishem and Erzeni River was ranged between 22 mg/L to 60 mg/L (table 2). The highest recorded BOD level in those rivers was 87 mg/L (site I3), due to the amount of wastes generated by human and industrial activities.

Figures 4 and 5 show that Ishëm River has higher amounts of COD and BOD than Erzeni River. According to standards (WFD) the maximum permitted level of COD and BOD are < 20 mg/L and < 10 mg/L respectively. Refer to this all analysed samples exceed those levels (Figure 4-5).

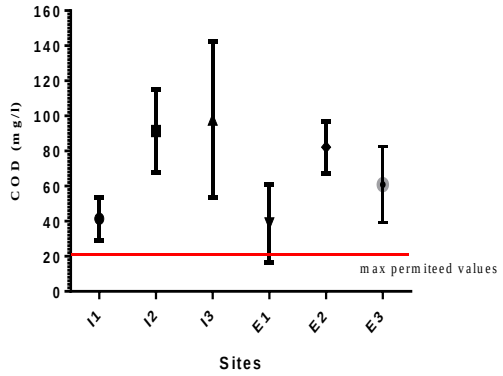


Figure 4. COD content of water samples

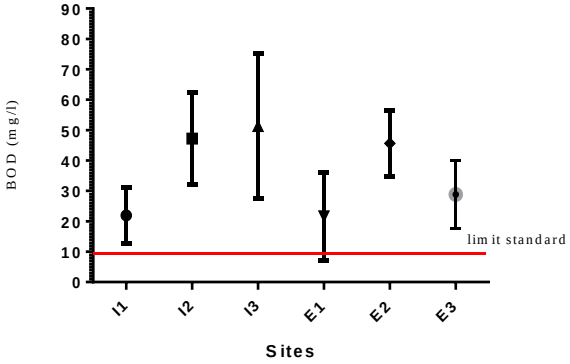


Figure 5. BOD content of water samples

Tables 2 shows that ammonium mean values of all analysed samples ranged from 1 - 11 mg/L. Figure 6 noticed that ammonium content is higher than maximum permitted level allowed by EC directives (<1.5 mg/L). The main contribution to this situation belongs to sites (I2 and I3) of Ishëm River and sites (E2 and E3) of Erzeni River. Those tributaries respectively collect urban and industrial effluents including untreated sewage discharges [17]. It is well-known that levels as much as 1 to 5 mg N/L when converted to ammonia may be very toxic to fish and other river fauna. This is the case of sites mentioned above.

Nitrates are contributes to freshwater through discharge of sewage and industrial wastes and run off from agricultural fields [27].

The amount of nitrate recorded in the water of Ishëm and Erzeni rivers ranged from 0.5 -1.3mg/L $N\text{-}NO_3$. Much better situation is for sites I1 and E1 showing nitrate levels lower

than 0.8 mg/L. Figure 7 shows that all sites are almost within the allowed standard values of nitrates content.

High levels resulted especially in three sampling sites (I2, I3 and E2) of Ishëm and Erzeni River, caused from sewage discharges of big habitant centers.

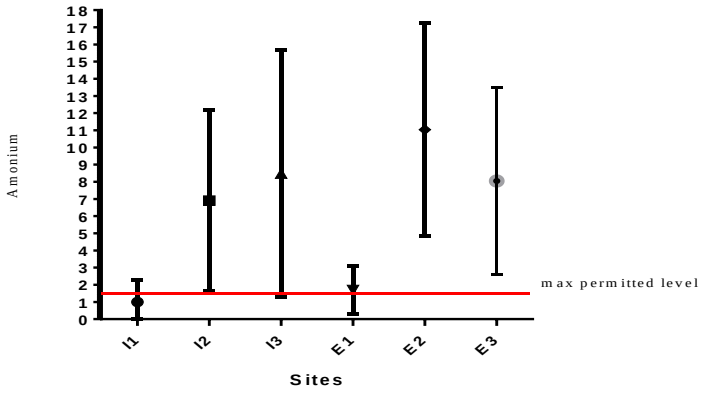


Figure 6. Ammonium (N-NH_4 mg/L) content of water samples.

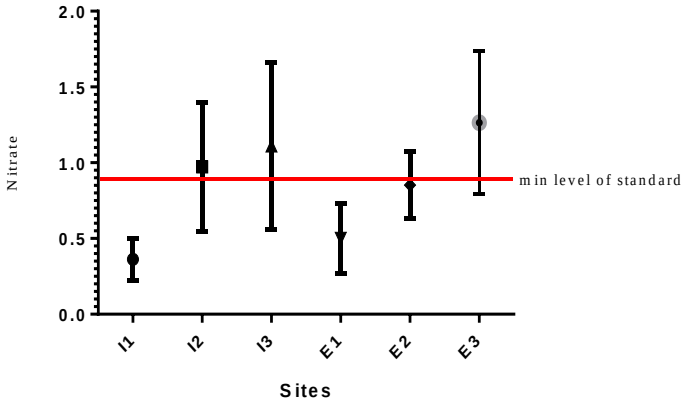


Figure 7. Nitrate (N-NO_3 mg/L) content of water samples

Presence of nitrite is an indicator of sewage pollution of waters. The concentration of nitrites in our water samples ranged 0.02 - 0.1 mg/L N-NO_2^- (table 2).

The total phosphorus content varied from 0.02 - 3.9 mg/L (table 2). The figure 8 shows that total phosphorus content is higher in sites I2 and I3. The reasons for that deviation are urban discharges that are rich with solution detergents containing phosphorus.

Based on analytical results and according to EC directives most of samples shows low content of total phosphorus than maximum permitted level.

Quality assessment and classification of rivers tributaries given in table 3 was carried out based on analytical results of physicochemical parameter of rivers according to WFD directives of EC and based on reports of National Environment Agency of Albania [15, 22].

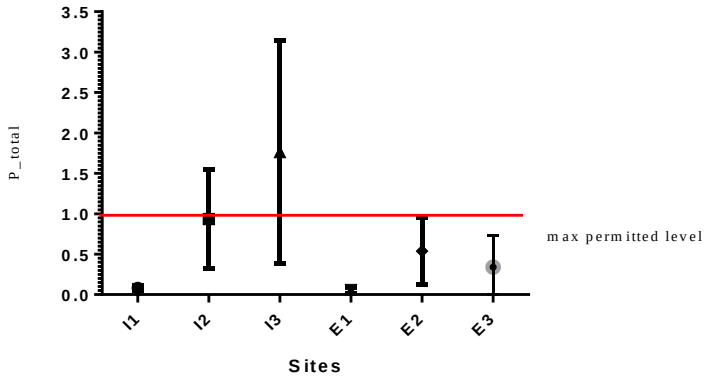


Figure 8. Total phosphorus (P-total mg/L) content of water samples

Table 3. Quality evaluation and classification of rivers tributaries

Sites	pH	DO	COD	BOD	$N\text{-}NH_4$	$N\text{-}NO_3$	P-total
I1	I	I	V	V	IV	I	I
I2	I	III – IV	V	V	V	I - II	IV
I3	I	V	V	V	V	II	V
E1	I	V	V	V	III - IV	I	I
E2	I	V	V	V	V	II	II
E3	I	V	V	V	V	II	II

4. CONCLUSION

Based on all above we can say that Ishem River has higher levels of pollution compared to Erzeni River. It has high levels of pollution due to the great impact of urban and industrial discharges.

The content of COD and BOD in all sites results in high levels compared with the standards. Sites I1 and E1 presents lower level of pollution compared with other sites included in this study.

Ammonium content of all analysed samples was found to be higher than standards due to urban sewage discharges.

In conclusion results of physicochemical parameters show clearly that both rivers are polluted and are considered as bad quality water (or classified to class IV - V).

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Acknowledgements

Authors are grateful to chemists and laboratory technicians of Albanian National Environmental Agency for their collaboration in this study.

PROSTORNA I VREMENSKA RASPODJELA TROFIČKOG (TRIX) INDEKSA KAO POKAZATELJA EKOLOŠKOG STANJA MORA U UVALI TELAŠČICA

SPATIAL AND TEMPORAL CLASSIFICATION OF TROPHIC (TRIX) INDEKS AS A INDICATOR OF ECOLOGICAL STATE OF THE COASTAL WATERS OF TELAŠČICA

Vito Dujmović*, Goran Olujić, Marija Bralić*, Mirjana Čurlin*****

* University of Split, Faculty of Chemistry and Technology, Split, Croatia
** Hydrographic Institute of the Republic of Croatia, Split, Croatia
*** University of Zagreb, Faculty of Food Technology and Biotechnology, Zagreb, Croatia

autor za korespondenciju: Marija Bralić, e-mail: bralic@ktf.hr

Izvorni znanstveni rad

SAŽETAK

U ovom radu provedena je statistička multivarijantna analiza rezultata određivanja trofičkog indeksa (TRIX) kao ekološkog pokazatelja stanja mora u prirodnom parku Telaščica. Analiza je provedena na rezultatima dobivenim na 6 lokacija kroz 4 godišnja doba. Zadaća rada bila je prostorna i vremenska raspodjela trofičkog indeksa TRIX-a kako bi se definirao ekološki status promatranog područja s obzirom na eutrofikaciju izazvanu prirodnim mehanizmom ili antropogenim utjecajima. U antropogene utjecaje najčešće ubrajamo ispuste komunalnih otpadnih voda koji narušavaju ekološku ravnotežu povećanjem koncentracija dušikovih i fosfornih spojeva. Dobiveni rezultati koristi će se za procjenu stupnja eutrofikacije i ekološkoga stanja mora koji su od osobite važnosti za planiranje i upravljanje prostorom u priobalnom području. Upravljanje priobalnim područjem odnosi se na izbor pogodnog sustava za ispuštanje otpadnih voda u more, predlaganje mjera sanacije već onečišćenog područja ili općenito očuvanje ekološke ravnoteže u moru.

Ključne riječi: *trofički indeks, eutrofikacija, upravljanje priobalnim područjem, vremenska i prostorna klasifikacija.*

ABSTRACT

In this paper statistical multivariate analysis of the trophic index (TRIX) as an ecological indicator of the coastal waters of the Telaščica natural park was performed. The analysis was carried out on results of trophic index obtained at 6 locations over 4 seasons. The aim was the spatial and temporal distribution of trophic index to define the ecological status of the observed area with regard to eutrophication caused by a natural mechanism or anthropogenic influences. Anthropogenic impact, most usually, include discharge of municipal wastewater that disturbs the ecological balance by increasing the concentration of nitrogen and phosphorus compounds. The obtained results will be used to evaluate the degree of eutrophication and ecological status of the sea, which are importance for the planning and management of the coastal area. Coastal area management refers to the choice of a suitable sewage disposal system in the sea, proposing process of the remediation for the already contaminated area, or generally preserving the ecological balance in the sea.

***Keywords**: trophic index, eutrophication, coastal area management, temporal and spatial classifications*

1. UVOD

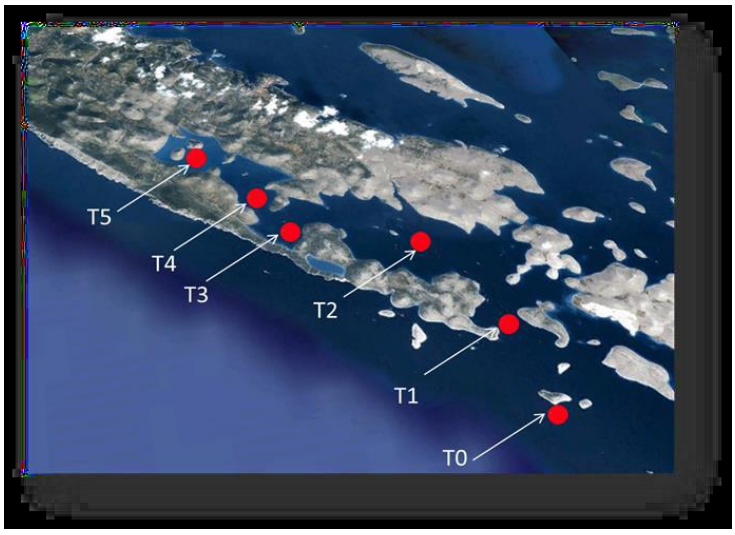
Eutrofikacija (grč. εύτροφία: dobro hranjenje) je,prema službenoj definiciji europske agencije za zaštitu okoliša (EEA),*promjena u ekosustavu uzrokovana prekomjernom brzinom stvaranja organske tvari, odnosno njenim vanjskim donosom.* U pojedinom ekosustavu može ju uzrokovati unos zagađivala, suspendiranih tvari, hranjivih soli i biorazgradivih organskih tvari iz točkastih i difuznih izvora. Prirodna eutrofikacija koja dovodi do povećanja bioloških resursa pozitivna je za ekosustav,a negativne pojave su veoma rijetke. Eutrofikacija uzrokovana antropogenim utjecajem može narušiti ekološku ravnotežu i veoma je nepovoljna za ekosustav te izaziva neželjene posljedice [1] Antropogeni utjecaj na priobalna područja čine dotoci rijeka kao i ispusti komunalnih i industrijskih otpadnih voda. Dotoci rijeka zbog povišenih koncentracija hranjivih soli, teških metala i pesticida često predstavljaju veći pritisak na ekološko stanje priobalnih područja od unosa ovih zagađivala putem komunalnih i industrijskih otpadnih voda. Veliki utjecaj na rijeke predstavljaju oborinske i procjedne otpadne vode čiji sastav ovisi o mjestu i načinu nastajanja, a mogu biti, uslijed ispiranja poljoprivrednih zemljišta, opterećene hranjivim tvarima i pesticidima. Danas se uz ubrzani tehnološki razvoj sve više pridaje pozornost primjeni zelenih tehnologija kojima bi se antropogeni utjecaji mogli smanjiti, ali se i sve više pozornosti pridaje definiranju ekološkog stanja pojedinih sustava, definiranjem različitih indeksa kvalitete. Za razvoj pogodnih indeksa za opisivanje ekološkog stanja morskog okoliša potrebno je intenzivno proučavanje kompleksnih odnosa stanja sustava, pojedinog utjecaja na sustav kao i odgovora ekosustava na tu promjenu. Radi se o složenom dinamičkom sustavu pa je potrebno u određivanje indeksa uključiti kako velik broj parametara tako i definiranje međusobnih utjecaja, a od osobite važnosti je i raspodjela indeksa kvalitete, kako prostorna tako i vremenska. Procjena stupnja eutrofikacije i ekološkoga stanja mora važna za planiranje i upravljanje prostorom u priobalnom području te za očuvanje ekološke ravnoteže u moru. Trofički indeks(TRIX)jedan je od općih pokazatelja stupnja eutrofikacije određenog morskog područja. U uvjetima niske eutrofikacije (oligotrofni uvjeti) more je bistro i prozirno, fitoplanktonska biomasa niska, koncentracije otopljenog kisika visoke. U uvjetima visoke eutrofikacije (eutrofni uvjeti) biološka potrošnja kisika raste (bakterijska razgradnja organske tvari), koncentracije kisika

opadaju. Dolazi do pojava hipoksije i anoksije. Područja priobalnih voda mogu se podijeliti na: i) hipertrofno područje – područje izrazito visoke produktivnosti, ii) eutrofno područje - područje visoke produktivnosti, iii) mezotrofno područje - područje umjerene produktivnosti i iv) oligotrofno područje - područje niske produktivnosti [1, 2]. Trofički uvjeti europskih mora variraju i razlikuju se po pojedinim regijama. Trofički indeks predložen od strane Vollenweider i suradnika 1998. godine temeljen na četiri parametra (klorofilu *a*, saturaciji kisika, ukupnom dušiku i ukupnom fosforu) koristi se za područje Mediterana [3]. Službeno je uvršten u talijansko zakonodavstvu i koristi se za rutinske procjene trofičkog stanja Jadranskog mora. Osim Italije ovaj indeks koriste i ostale mediteranske države , Albanija, Alžir, Turska, Španjolska, kao i Republika Hrvatska. Na osnovi trofičkog indeksa možemo odrediti tri tipa kategorizacije trofičkog stanja. Indeks klasificira tri raspona vrijednosti koji predstavljaju oligotrofno (2 - 4), mezotrofno (4 - 5) i eutrofno (5 - 6) trofičko stanje vodene mase, zavisno od izmjerenih, odnosno izračunatih koncentracija hranjivih tvari i biomase fitoplanktona.

Određivanje stupnja eutrofikacije i općenito ekološkog stanja od osnovne je važnosti kod planiranja i upravljanja prostorom u priobalnom području. Na osnovi dosadašnjeg iskustva razrađeni su specifični kriteriji za Jadransko more, temeljeni na usporedbi izmjerenih podataka s izabranim rasponima vrijednosti glavnih pokazatelja koji se smatraju tipičnim za različite stupnjeve eutrofikacije, odnosno ekološkog stanja. Korištene su metode obrade i prikazivanja podataka koje su, koliko je god to moguće u ovom trenutku, u skladu s Okvirnom direktivom [4] o vodama Europske Unije, međutim za sada ne postoji uredba kojom bi se klasificiralo more prema svom ekološkom i kemijskom stanju. Obzirom da je određivanje stupnja eutrofikacije i općenito ekološko stanje od osnovne važnosti za neko područje, u ovom radu naglasak je na prostornoj i vremenskoj raspodjeli određenog trofičkog indeksa za priobalno područje akvatorija Telašćice.

2. EKSPERIMANTALNI DIO

Uzorci morske vode za određivanje trofičkog stanja priobalnih voda uzeti su na području parka prirode Telaščica. Lokacije uzorkovanja označene su oznakama od T_0 do T_5 i prikazane su na slici 1.



Slika 1. Ispitivano područje i lokacije uzorkovanja morske vode u uvali Telaščica

Uzorci morske vode uzimani su mjesečno u razdoblju od listopada 2011. godine do rujna 2012. godine sa standardnih oceanografskih dubina (0, 10, 20, 50, 75 m) Nansen –ovim crpcima. Otopljeni kisik određen je po Winkleru, a zasićenost morske vode kisikom izračunata je na osnovi podataka o temperaturi, salinitetu i sadržaju otopljenog kisika. Mjerenje temperature i saliniteta (konduktiviteta) provedeno je sondom SEABIRD 25, prikazanoj na slici 2. Salinitet je određen standardnim odnosom iz izmjerene električne provodnosti morske vode. Uzorci su odmah po uzorkovanju analizirani na sadržaj otopljenog kisika, a poduzorci za određivanje koncentracija klorofil *a* i hranjivih soli su zamrznuti (-24 ^{0}C). Koncentracije ukupno otopljenog anorganskog dušika i ukupnog fosfora određene su prema standardnim metodama [5, 6] spektrofotometrijski korištenjem SUPERSCAN 3 spektrofotometar (Shimatzu UV-1601) sa sljedećim karakteristikama: raspon valne duljine 190 - 900 nm; raspon Abs 0.140 - 3.000 Abs; točnost optičkog sustava 0.2 nm; elektronski čitač valnih duljina. Klorofil *a* u uzorcima morske vode određen je fluorimetrijskom metodom uz TD 700 Laboratory Fluorometer [5].



Slika 2. Sonda „SEABIRD 25“[1]

Trofički indeks TRIX za prikazane priobalne postaje određen je prema [3] za površinski dio vodenog stupca od 0 do 10 m dubine. Trofički indeks TRIX izračunat je za svih 6 lokacija uzorkovanja T0 do T5) za svako godišnje doba koristeći podatke po oceanografskim dubinama prema jednadžbi (1).

$$TRIX = \frac{log(\Delta O_2 \cdot Chl_a \cdot TN \cdot TP) + f_1}{f_2} \quad (1)$$

gdje je:
ΔO_2 – apsolutna razlika mjerenog i teorijskog (maksimalnog) zasićenja vodenog stupca kisikom,
$Chl_{(a)}$ – koncentracija klorofila izražena u µg/L,
TN – koncentracija ukupnog anorganskog dušika izražena u µg/L,
TP – koncentracija ukupnog fosfora izražena u µg/L,
f_1 – korekcijski faktor iznosa 1,5,
f_2 – korekcijski faktor iznosa 1,2.

Korekcijski faktori u jednadžbi (1) uvode se zbog donje granice vrijednosti indeksa trofičke skale koja sadrži od 0 do 10 TRIX jedinica određenog područja. Trofička skala od 0

do 10 je rezultat matematičke jednadžbe TRIX indeksa, te pomoću iznosa, dobivenog decimalnog broja, određujemo trofički stupanj ispitivanog područja [3, 7].

Određivanje prostorne i vremenske klasifikacije TRIX-a na promatranom području provedeno je primjenom statističke multivarijantne klaster analize. Obzirom da je zadaća klaster analize grupirati slične objekte, prvi korak u provođenju ove analize je izbor mjerila sličnosti odnosno udaljenosti. Osnovna mjerila udaljenosti između pojedinih objekata su Euklidne udaljenosti (engl. *Euclidean Distances*), odnosno kvadrat Euklidne udaljenosti (engl. *Squared Euclidean Distances*) koje se najčešće koriste u ovakvim analizama. Sve analize provedene su u programskom sustavu Statistica 10. (StatSoft., 2010) određivanjem euklidnih udaljenosti za pojedinu lokaciju i za svako godišnje doba. Rezultat je dendrogramkao prikaz postupnog kombiniranja objekata u klastere na kojem se uočavaju udaljenosti između pojedinih razina, temeljeni na jakoj matematičkoj podlozi.

3. REZULTATI I DISKUSIJA

Uzorci za analizu uzimani su prema proceduri sa standardnih oceanografskih dubina od 0, 10, 20, 50 i 75 m i za sve uzorke provedeno je mjerenje ključnih parametara ΔO_2, Chl(a), TP i TN iz kojih je računat trofički indeks (TRIX). U ovom radu za provedbu prostorne i vremenske klasifikacije trofičkog indeksa na ispitivanom području korišteni su rezultati srednjih vrijednosti za sve oceanografske dubine. Prostorna klasifikacija određena je s obzirom na mjerne postaje označene s T_0 – T_5, prikazane na slici 1, a vremenska klasifikacija obuhvaćala je vrijednosti parametara trofičkog indeksa po pojedinim godišnjim dobima, pri čemu je vrijednost za pojedino godišnje doba dobivena kao srednja vrijednost parametara za pojedino vremensko razdoblje (3 mjeseca) koje obuhvaća to godišnje doba. Rezultati pojedinih analiza za ispitivane parametre (ΔO_2, Chl(a), TP i TN) dio su provedbe standardnog monitoringa stanja mora i kao takvi korišteni su za određivanje trofičkog indeksa. Rezultati trofičkog indeksa za pojedine postaje prikazani su u tablici 1.

Tablica 1. Srednje vrijednosti trofičkog indeksa (TRIX) na promatranom području po lokacijama uzorkovanja

Lokacija	T_0	T_1	T_2	T_3	T_4	T_5
TRIX	1,45	1,4	1,78	1,37	1,22	1,28

Fosfor je kritična hranjiva sol u odnosu na primarnu produkciju u Jadranu, a u morskom okolišu uglavnom dolazi unosom preko otpadnih voda, dotokom iz Sredozemlja i protokom kroz sediment. Promatrano područje odlikuje se niskim vrijednostima ortofosfata. Na prostornu raspodjelu dušika u vodenom stupcu znatno utječe gustoća populacije fitoplanktona koji mogu u nekim slučajevima ukloniti sav otopljeni dušik. Na ispitivanom području uočene su niske vrijednosti ukupnog anorganskog dušika kao i male vrijednosti Chl(a). Niska koncentracija hranjivih tvari uz relativno visoke vrijednosti otopljenog kisika ukazuje da ovo područje spada u oligotrofno područje. Izračunate vrijednosti trofičkog indeksa koje su u rasponu od 1,2 do 1,8 također ukazuju da se radi o području primarne produktivnosti organske tvari. Jadransko more u cjelini slabo je produktivno, oligotrofno more, produktivnije uz obalu i u području kanala. Niska razina organske produkcije posljedica je male količine hranjivih soli u vodi, posebno fosfora i dušika. Kako je ranije navedeno glavni nedostatak trofičkog indeksa je mali broj parametara na osnovi kojih se određuje indeks te stoga daje nepotpune informacije o utjecaju ostalih parametara na stanje mora. Kao

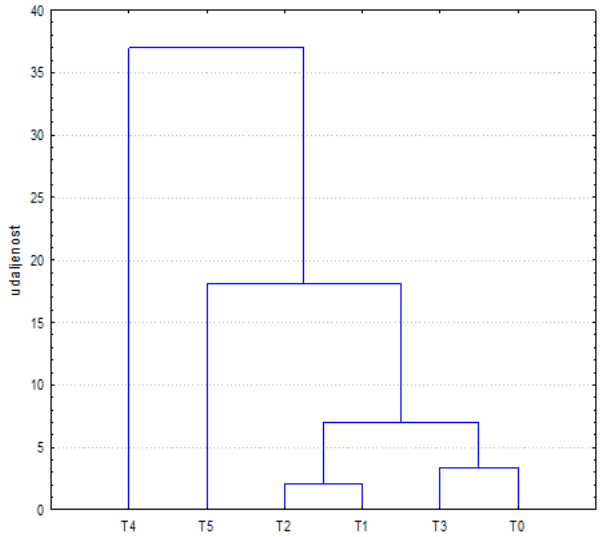
multimetrički indeks, TRIX ne može utvrditi koje varijable (parametri) igraju važniju ulogu u svrstavanju u određenu razinu trofičnosti, niti može ukazati na to koliko vanjski utjecaji utječu na trofičko stanje bez provedbe detaljnije analize svake varijable pojedinačno. Stoga je daljnjom analizom utvrđena međusobna linearna zavisnost pojedinih parametara na svim lokacijama određivanjem Spearmanovih koeficijenata korelacije. Rezultati provedene analiza prikazani su u tablici 2.

Tablica 2. Spearmanovi koeficijenti korelacije za pojedine parametre

Parametar	O_2	TN	TP	Chl(a)	TRIX
O_2	1				
TN	0,1	1			
TP	-0,314	-0,5	1		
Chl(a)	-0,142	0,37	-0,02	1	
TRIX	0,771	0,04	-0,68	0,34	1

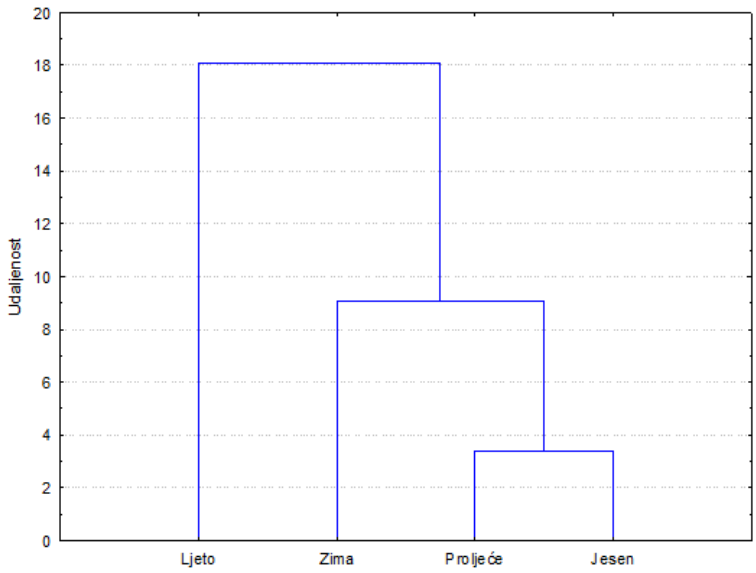
Izračunati koeficijenti korelacije pokazuju jaku linearnu zavisnost trofičkog indeksa s tri promatrana parametra: zasićenosti kisikom, ukupnim fosforom i koncentracijom klorofila. Sadržaj kisika u morima povezan je s procesima difuzije iz zraka kao i kisika nastalog fotosintezom primarnih proizvođača u moru. Oba procesa ograničena su na površinske slojeve koji su onda bogatiji kisikom. Nastali kisik iz procesa fotosinteze primarnih proizvođača glavni je indikator biološke aktivnosti mora. Visoke vrijednosti zasićenosti kisikom promatranog područja ukazuju na niski intenzitet antropogenog utjecaja na svim postajama te nemaju značajniji utjecaj na ekološko stanje promatranog područja.

Kako je Jadransko more u cjelini slabo produktivno, oligotrofno more s nešto produktivnijim zonama uz obalu i u područjima kanala daljnjom multivarijabilnom analizom provedeno je grupiranje ispitivanog područje kako bi se odredila područja s istim/različitim oligortrofnim svojstvima te vremenska raspodjela koja bi ukazala na veću/manju aktivnost zavisno po godišnjim dobima. Rezultati provedene analize prikazani su u obliku Ward-ov dijagrama (slika 3) na kojima je vidljivo grupiranje pojedinih lokacija na kojima se mogu uočiti sličnosti/razlike u oligotrofnosti. Ovdje treba napomenuti da je cijelo područje izrazito oligotrofno i da su ove razlike samo mali utjecaj pojedine lokacije.



Slika 3. Dendogram klaster analize za pojedina mjesta uzorkovanja, lokacije

Možemo uočiti pripadnost istoj razini odnosno veoma male razlike za postaje T_0 i T_3 te za postaje T_1 i T_2, što i odgovara njihovom geografskom položaju. Postaje T_4 i T_5 izdvojene su u zasebne skupine što pokazuje njihovu različitost u odnosu na prethodne 4 postaje i ukazuje na različitost u trofičnosti tog područja. Iako je ranije naglašen veoma mali antropogeni utjecaj na čitavo područje, rezultati ovih analiza i položaj lokacija na karti ukazuju na nešto veći antropogeni utjecaj na ovom području. Na ovaj način dobivena je prostorna raspodjela trofičkog indeksa i veze pojedinih lokacija na kojima se onda može trofički indeks povezati s ostalim karakteristikama same lokacije i pridonijeti jasnijem definiranju pojedinog područja. Rezultati provedene analize za utvrđivanje vremenske raspodjele prikazani su na slici 4.



Slika 4. Dendogram klaster analize uz prikaz Euklidnih udaljenosti po godišnjim dobima

Dobivena vremenska raspodjela ukazuje na značajnost perioda promatranja trofičkog indeksa gdje je vidljivo da se stanje priobalnog područja može zajedno promatrati za vremensko razdoblje jesen – proljeće, dok je zimski i ljetni period izdvojen zasebno što znači da su u ovom vremenskom periodu značajne razlike u stanju mora. Već ranije je naglašen utjecaj temperature koji posredno utječe na ostale parametre za izračun TRIX-a, a ovdje svakako treba uzeti u obzir i strujanje mora koje će imati značajan utjecaj na raspodjelu kisika, kao i na transport eventualno prisutnih antropogenih zagađivala. Iz ove analize nije vidljiv pojedini utjecaj navedenih parametra, ali je jasno pokazana razlika za pojedini period godine.

4. ZAKLJUČAK

Promatrano priobalno područje Telaščice, prema vrijednostima trofičkog indeksa i skale raspodjele, spada u oligotrofno područje. Trofički indeks se unatoč navedenim nedostatcima ipak može koristiti kao pokazatelj prikaza trenda trofičkog stanja. Pri tome je važno provesti detaljnu multivarijantnu statističku analizu kako bi se pokazale sličnosti/razlike na prostornoj i vremenskoj razini. Prikaz na ovaj način daje detaljnije

informacije o kvaliteti okoliša i kao takav se može koristiti za potrebe upravljanja pojedinim ekološkim područjem. TRIX je jednostavan i razumljiv format te je stoga lako primjenjiv na različitim nivoima upravljanja okolišem.

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ODRŽIVOST TEORIJE I PRAKSE ODRŽIVOG RAZVOJA: NOVI KONCEPT INŽENJERSKOG OBRAZOVANJA

SUSTAINABILITY OF THE THEORY AND PRACTICE OF SUSTAINABLE DEVELOPMENT: NEW CONCEPT OF ENGINEERING EDUCATION

Petar Đukić*, Slaviša Đukanović**

* Univerzitet u Beogradu, Tehnološko-Metalurški fakultet, Beograd, Srbija
** Visoka poslovna škola strukovnih studija, Novi Sad, Srbija

autor za korespondenciju: Petar Đukić, e-mail: djukic@tmf.bg.ac.rs

Pregledni rad

SAŽETAK

Najbitnija odrednica održivog razvoja proističe iz objedinjavanja principa zaštite okoliša, socijalne efikasnosti i međugeneracijske pravde, kao i njihove primjene na kvalitet ekonomskog i tehnološkog razvoja. Koncept se probijao iz oblasti društveno-ekonomskog i biološkog poimanja ka inženjerskim i prirodnim naukama. Danas nema područja života, od privrede itehnologija, preko, javnog zdravlja, do kulture i umjetnosti, u kome se ne traga za održivošću.

"Održivi razvoj" prema prvobitnoj zamisli nije uspio. I sama zamisao djelomice kontroverzna, ponekad se dovodi u pitanje teorijski, kao i praktičnim postupcima. Veći dio današnjeg svijeta ne bi se mogao pohvaliti održivom implementacijom održivog razvoja. Aktuelna orijentacija ka klimatskim promjenama i održivoj energetici,samo je faza u redefinisanju održivosti, koja se nastavlja, a najvažniji učinak evolucije održivog razvoja jeste njegova interdisciplinarnost i otvorenost. Za moderno obrazovanje inženjera, od sve veće važnosti je prihvatanje integralnog poimanja i operacionalizacije održivog razvoja, u sklopu procesa usaglašavanja tehnologije sa odrednicama opšte zaštite prirode, društva i okoliša.

Ključne riječi: *održivi razvoj, zaštita okoliša, ravnoteža razvojnih ciljeva, harmonizacija, klimatske promjene, ekološka obnova*

ABSTRACT

The most important definition of sustainability is derived from merging of the principles of the environmental protection, the social efficiency and the intergeneration justice, as well as their implementation to the quality of economic and technological development. The concept progressed, from the area of societal and economic, as well as biological understanding, to the engineering and natural sciences. Today there is no area of living, economy, agriculture, technologies, arts and culture or social life sector without search for sustainability.

Sustainable development has not succeeded in its original concept. As slightly fluid and controversial notion by its own, it was questionably treated by many pragmatic actions and strategies. Most part of the today world could hardly be proud by the sustainable implementation of the sustainability concept. Current orientation to the climate changes or to the sustainable energy is only one phase of sustainable development redefinition. The most important effect of previous evolutions of sustainable development is its interdisciplinary treatment and openness. For the solid fundamental education of engineers in modern sense, the integral acceptance of sustainable development is necessary. That concept could basically harmonise technology development, with coordinates of the protecting of environment, societal/economic and natural system.

***Keywords**: sustainable development, environmental protection, balance of developmental goals, harmonisation, climate changes, environmental renewal*

1. UVODNE NAPOMJENE

Održivi razvoj (OR) je otpočeo kao razumijevanje mogućnosti čovječanstva da se izbori sa kontroverzama na relaciji: ekonomski rast - resursi- okolina - pad kvaliteta života i porast rizika. Izvještaj, još uvijek djelujućeg Rimskog kluba nezavisnih eksperata (1972) naznačio je mnoštvo problema i tada aktuelnih razvojnih kontroverzi, dok je dokument *Our Common Future*, Brundtland komisije UN (1987.) trebao da predoči jednu optimističku viziju i mogući koncept, koji bi pomirio kontroverzne zahtjeve čovječanstva na kratak i dugi rok, na globalnoj i na lokalnoj razini. Tako postavljena zamisao, razumije se da nije mogla biti ni perfektna niti potpuna [1].

Njena institucionalna evolucija, tekla je samo djelom u skladu sa novim naučnim saznanjima, a mnogo više u ovisnosti od redefinicije ekonomskih ciljeva i njihovog političkog usaglašavanja. Početno filozofsko uvjerenje o prioritetu zaštite Zemlje kao "pramajke" (izvora života), pomjerilo se ka pragmatičnim ciljevima i interesima ljudi. Tehnološko usavršavanje sa ciljem održivosti kao da je prevagnulo u odnosu na opšte principe "međugeneracijske pravde", participativnosti i suradnje svih sektora, ili pak "kategoričke"ekološke zapovjedi, poput: "zagađivač plaća", "sačuvaj, obnovi, recikliraj, smanji, popravi"[2]. Današnji svijet, sve više je opterećen esakalacijom klimatskih promjena, ekstremizmom, nacionalizmom-populizmom, terorizmom... Pored svega, nije se dovoljno ozbiljno u obzir uzimala činjenica o tome da porast svih vrsta nejednakosti, registrovan tokom posljednje tri decenije, dodatno uvećava socijalne, tehničke i druge rizike po održivost [3].

Dobija se utisak da je globalno partnerstvo, odnosno široka participacija u razumijevanju i primjeni principa i mjera ključna odrednica uspjeha održivog razvoja. Svijet se ubrzano mijenja, tako da se redefiniranje postojećih razvojnih koncepata dešava i prije no što su ostvareni ciljevi prethodnih. U svakom slučaju, bez obzira na izazove koji stoje pred

vladajućim modelom globalne ekonomije, ostaje dominantna teza većine ekonomista da je "najbolji način da se ostvari napredak stanja životne sredine u većini zemalja njihovo sopstveno bogaćenje“ [4].[1]

2. KRITIKE KONCEPTA ODRŽIVOG RAZVOJA

Kritika je, bez sumnje, dobra pretpostavka za usavršavanje i održivost svake zamisli pa i koncepta održivog razvoja. Nametnula se usled praktičkih, ekonomsko-političkih i djelomice teorijskih kontroverzi, koje su pratile primjenu održivog razvoja. Od samog nastanka, opće teorijsko-metodološke kritičke primjedbe bile su usmjerene na „održivost“, kao pojam koji podrazumijeva kontinuitet i ravnotežu, dok „razvoj“, prema ovim nalazima, predstavlja dinamizam i promjene. Pristup "ekologa" je, navodno, bliži traganju za aspektom „održivosti“, dok vlade i privreda daju prednost „razvoju“, pri čemu kao parametar razvoja podrazumijevaju rast bruto domaćeg proizvoda [2].

Od onih ideološki obojenih kritika, valja napomenuti kritički otklon "s desna" i "s lijeva": Prvi ovdje pomenuti kritički diskurs, onaj sa pozicije ultra-liberalne (tržišne) desnice, najbolje predstavlja argumentacija paradigmatičnog Vaclava Klausa o tome da je OR, za razliku od liberalnog tržišta, suviše statičan koncept, koji sputava slobode, umanjuje pozitivno djelovanje tržišta i inicijativu, kao i šanse nedovoljno razvijenih zemalja da se razviju. Međutim, ni Klaus nije odolio ideološkim izazovima, već potrže "argument" po kome je zaštita Zemlje samo nametanje gotovih modela, što, poput marksističke koncepcije i retorike, vodi ka "zelenom totalitarizmu" i "planeti u okovima"[5].

A prema ponašanju današnjih zagovornika zaustavljanja akcije za klimu, koje, na primjer personifikuje aktuelni predsednik SAD Donald Trump, ovakva i slične argumentacije uveliko se (zlo)upotrebljavaju da bi se zaustavili globalni napori i mjere u okviru Pariskog klimatskog sporazuma [6][2]. Može se reći da su na globalnoj sceni nove nepovoljne determinante "akcije za klimu". Tako se na ključnim pozicijama odgovornim za pitanja zaštite okoliša i održivi razvoj, ovisno od volje čelnika izvršne vlasti, pojavljuju osobe krajnje problematičnih ličnih stavova i vrijednosti koje, po logici političke subordinacije, i ne baš samo struke, prihvataju nove stavove generalne politike, pa tako i Scott Pruitt[3] na mjestu direktora čuvene i veoma kompetentne američke Agencije za zaštitu okoliša (EPA) .

Da ne bi njihova "argumentacija" ostala bez potpunije teorijske podrške, valja naglasiti da je ideja klimatskih promjena, kao djela normalnih geofizičkih procesa i dugoročnih ciklusa prilično stara, a da je na njoj najviše traga ostavio matematičar Milutin Milanković, objašnjavajući, između ostalog velike i srednje cikluse klimatskih promjena geofizičkim i kozmičkim činjenicama, popularno izloženim u djelu *Nebeska mehanika* [7].[4] Ne ulazeći u relativni značaj Milankovićevih ciklusa na današnje stanje klime na Zemlji, valja napomenuti samo to da Milanković svojevremeno nije mjerio doprinos antropogenog faktora na promjene

[1]Beckermann, prema: Samuelson, Nordhaus, *Ekonomija* XVIII izdanje, op. cit. str. 364.

[2]Trump nastupa veoma uporno sa tezom "Americafirst", povremeno varirajući staru tezu kako navodno nije dokazano da klimatske promjene postoje...

[3]Scott Pruitt, novi direktor American Environment Protection Agency (EPA) izjavljuje da je "globalno zagrijevanje možda dobra stvar za čovječanstvo", bez imalo rezervi ili bar relativizacije u balansiranju loših i povoljnih posljedica.

[4]Naime, kolebanja temperataure Zemlje, koja se odvijaju tokom dugih razdoblja, Milanković je objasnio promjenama osunčanosti pri njenom složenom kretanju oko Sunca, usljed promjena položaja najbliže točke prema Suncu i nagiba ose Zemljine rotacije.Videti u: Ajdačić Vladimir (1998): *Nauka kao bajka*, Zlatna knjiga, Beograd, str. 94

klime, nemajući, naravno ni priliku usporedbe rezultata istraživanja klimatologa koja su danas dostupna u izvještaju međunarodnog Panela za klimatske promjene (IPPC).

Drugi kritički pristup, koji uslovno može da se nazove kritika sa "lijeve pozicije", upražnjavaju uglavnom sociolozi. U tome se posebno ističe britanski autor Anthony Giddens [8], koji na sebi svojstven način prihvata kao mjerodavan pojam "održivosti", ali smatra nepodobnom kategoriju "razvoja", s obrazloženjem da svaki razvoj vodi u "prekomjernost". Pod prekomjernim razvojem Giddens podrazumijeva rast radi samog rasta (koji degradira okoliš i prirodne resurse) o čemu su se već mnogo prije njega negativno odredili brojni socijalni i ekonomski teoretičari, pa i neoklasični i institucionalni ekonomisti i inženjeri[5]. Neki kritičari održivog razvoja posebno apostrofiraju elemente „tautologije u njegovoj definiciji“[6], „suštinsku nejasnoću“, u smislu koji bi podrazumijevala sintagma: „imati i jare i pare“. Zapravo, prema mišljenju tih autora, značenja dva osnovna izraza „održivost“ i „razvoj“ donekle su proturječna.[7]

Usprkos svim kritičkim stavovima, održivi razvoj kao politički koncept i teorijski model, nije propao. I dalje privlači pažnju mnogih koji su orijentisani na percepciju budućnosti sa stanovišta međugenaracijske pravde, pa se može reći da je za OR najvažnije: "usmjerenost ka jačanju ljudske dobrobiti, zadovoljavanju osnovnih potreba, zaštiti životne sredine, sudbini budućih generacija, ostvarivanju pravednog odnosa bogatih i siromašnih, kao i šire učešće u procesu odlučivanja“ (Villiam Rafferty i Jammes Meadowcroft) [8].

Prema mišljenju djela kritičara, upravo tako širok spisak ciljeva lišava održivi razvoj njegove suštine i pokazuje da je ovaj pojam suviše širok da bi mogao biti od „bilo kakve analitičke koristi“.[8] Primjedbe na koje se oslanja i Giddens, mogle bi se ustanoviti i u kritičkoj teoriji ekonomskog razvoja uopće, sve od ranih sedamdesetih godina XX. veka, otkad je indijski ekonomist i nobelovac Amartya Sen otpočeo promišljanje i kritiku tzv. ekonomije blagostanja, teorije društvenog izbora, ekonomske i socijalne pravde sa stanovišta kvalitativne analize ekonomskog rasta i razvoja, o čemu danas postoji obimna ekonomska literatura. Ključna odrednica ovih autora za pojam ekonomskog razvoja, nije stanje dohotka po stanovniku, već stopa smanjenja siromaštva i stupanj slobode koji razvoj omogućava pojedincima [8].

Očigledno je da se većina ovih primjedbi fokusira na socijalne pritivrečnosti, poput dubinskog ili endemskog siromaštva, kao i suviše niskog dohotka ili nezaposlenosti, socijalne patologije uzrokovane siromaštvom, slabim obrazovanjem, lošim instituicijama i destimulativnom kulturom [9]. Međutim, ne treba zaboraviti problem neposrijedne veze niskog dohotka i ekološkog stanja, kao i relativne nerazvijenosti sa slabim obrazovanjem. Opet, da bi se ostvarilo kvalitetnije i masovnije obrazovanje, neophodan je viši dohodak. Tako se, u razvojnom smislu, formira jedan *circulus vitiosus* siromaštva, ekonomske nerazvijenosti, kulturne i tehnološke zaostalosti i lošeg stanja okoliša, što bi sve zajedno moglo da glasi: loša perspektiva u pogledu održivog razvoja. Neposredna konzekvenca koja iz prethodnog proističe jeste da je potrebna operativna redefinicija održivog razvoja [10].

[5]Ranu filozofsku kritiku ideologije ekonomskog rasta, sa stanovišta ekologije, dali su najprije novoljevičari, među kojima posebno austrijski filozof Andre Gorz, britanski ekonomist Edward Mishan, američki ekonomist KennethBoulding i drugi. Detaljnije o tome [2].

[6]Naime, održivi razvoj je definisan kao “razvoj koji…”. To znači da kategorija definiše delom tautološki, odnosno jedan pojam koji u sebi sadrži riječ “razvoj”, definira istom rječju.

[7]William Baue, “ Rio+10 Serias”, *SustainableInvestment News*, 23. avgust 2002. prema Anthony Giddens, op. cit. str. 79.

[8]William Baue, “ Rio+10 Serias”, *Sustainable Investment News*, 23. avgust 2002. prema Anthony Giddens, op. cit. str. 79.

3. REDEFINICIJA KONCEPTA I REKONFIGURACIJA CILJEVA

Ekonomski posmatrano, od početka je u fokusu ciljeva bio *kvalitetan i permanentan* ekonomski rast. Dalje objedinjavanje pojmova ka još složenijoj sintagmi "pametan, inkluzivan i održiv rast" [9][11], svodilo je razvoj na rast ekonomske aktivnosti u dugom roku, pod određenim uslovima: tako da se ne dovodi u pitanje uravnoteženo pozitivno djelovanje na sva tri "stuba": privredu, društvo, okoliš.

Evolucija razumijevanja OR je, dakle, tekla redukcionistički, od nedovoljno precizirane kategorije "razvoj", ka svojevrsnom povratku na konkretniji i merljivi "ekonomski rast", sa novododatim epitetima, kao što su inkluzivan, "zeleni", "pametni" ili održiv. Da li je pri tome došlo do "zamora" u preciziranju dodatnih kvalitativnih pretpostavki razvoja nije baš izvjesno, mada sve djeluje pomalo konfuzno. Nakon ustanovljene institucije periodičnih konferencijskih pretresanja stanja i mjera održivog razvoja, konkretizacija na kojoj se insistiralo širom svijeta, prema Organizaciji UN, bila je stvar lokalnih ili regionalnih razvojnih politika i strategija. Organizacija ujedinjenih naroda otpočela sa periodičnim globalnim konferencijama o održivom razvoju na svakih 10 godina (od Rija 1992, preko Johanezburga 2002, do Rija + 20, 2012). Na svakom od tih, indikativnih globalnih samita, dešavale su se značajne stvari koje su utjecale i na sam koncept.

3.1. Redefinicije ciljeva

U Riju 1992, usvojena Deklaracija o razvoju i zaštiti životne sredine, jedan zaista krucijalan i još neprevaziđeni bazni dokument, osnova je institucionalne evolucije održivog razvoja. Mada se u naslovu "održivi razvoj" ne pominje, već samo "razvoj", on se eksplicite ili indirektno nalazi u okviru svih 27 principa Deklaracije. Ključna načela ovog dokumenta, zasnivaju se na odlučujućoj ulozi ljudi u razvojnom modelu. Pri tome zemlje ostaju suverene u održivom raspolaganju resursima, sa pravom na ekonomski razvoj i međugeneracijsku odgovornost. Okoliš se postavlja u središte svih sektorskih politika. Eksterni troškovi se internalizuju, saglasno principu: "zagađivač plaća". Posebno se inzistira na primjeni načela participativnosti, predostrožnosti, ulozi žena i mladih, a pominju se zaštita ljudi od ugnjetavanja, veza između mira, slobode, razvoja, itd.. Ovde nema potrebe da se vrši analiza svih 27 pomenutih principa, ali sve ukazuje na to da je u samom startu došlo da veoma široke operacionalizacije održivog razvoja, tako da čitav koncept nije bio lako primjenljiv.

U Johanezburgu, 2002. godine, po prvi put je ostvareno okupljanje velikog broja poslovnih ljudi, koji su, zajedno sa političarima i naučnicima, podržali ideje i praksu održivosti. Konačno, Konferencija Rio + 20, iznedrila je snažnu demonstraciju volje za usmeravanjem koncepta održivog razvoja u što većoj mjeri ka "zelenoj ekonomiji"[12].

Kad je riječ o konkretnim ciljevima održivosti, na globalnom nivou pojavljuju se ozbiljne kontroverze, posebno u prilikama koje ovise od finansiranja. Uočljiva je orijentacija da se,od apstraktne ideje "spasa Planete", preko zaštite biodiverziteta i pojedinih ekosistema, te održivog gospodarenja prirodnim resursima, pređe na uređivanje održivog privređivanja, kao i socijalnog sistema. Ovo posljednje posebno je otjelotvoreno kroz tzv. *Milenijumske ciljeve,* koje su OUN oktobra 2000. godine zacrtale kao zadatak čitavom svijetu do 2015. godine. To su:

- iskorijenjivanje ekstremnog siromaštva i gladi,

[9]Slučaj Evropske unije u dokumentu *Europe 2020*. Strategy, https://ec.europa.eu/info/business-economy-euro/economic-and-fiscal-policy-coordination/eu-economic-governance-monitoring-prevention-correction/european-semester/framework/europe-2020-strategy_

- ostvarivanje univerzalnog osnovnog obrazovanja,
- ostvarivanje ravnopravnosti polova i jačanje položaja žena,
- smanjenje smrtnosti djece,
- poboljšanje zdravlja majki,
- borbu protiv HIV-a, malarije i drugih bolesti,
- ekološku stabilnost,
- izgradnju globalnog partnerstva za razvoj, itd.

Međutim, ovo što je u prethodnim alinejama navedeno, a ozvaničeno krajem drugog milenijuma, odnosi se na opće razvojne ciljeve, dok se održivi razvoj u svom operativnom značenju, kad god bi se govorilo o konkretnim mjerama, po pravilu odnosio na nešto što ima neposredne veze sa zaštitom okoliša.

To je jedna od prvih kontroverzi u samoj primjeni OR. Da li je održivi razvoj svaki kvalitetan razvoj, koji integriše sve društvene (dakle ne samo ekonomske) ciljeve, ili pak samo jedan aspekt društveno-ekonomskog i tehnološkog razvoja? Na ta pitanja faktički još uvijek nema odgovora, kako u teorijskom, tako i u institucionalnom pogledu.

Iako Milenijumski ciljevi suštinski, a pogotovo kvantitativno, nisu ostvareni, to nije utjecalo da se na nivou OUN, nakon 2016. već promovišu novih 17 ciljeva održivog razvoja, sa perspektivom do 2030. Na osnovu ovih ciljeva, nešto bolje se sagledava pomjeranje fokusa i globalnog razumjevanja održivog razvoja ka kompleksu klimatskih promjena i energetici [13].

3.2. Teorijske dileme u redefiniranju razvojnih ciljeva

Sa stanovišta ekonomike životne sredine [14], između obilja i oskudice mala je razlika, jer obilje jedne vrste dobara, kao što su saobraćajna infrastruktura, industrija, gradovi, kuće i stanovi, automobili, podrazumijeva veoma često oskudicu drugih pretpostavki obilja, kao što su prostor, bezbednost, biodiverzitet, zdrave šume i čista mora i okeani, dovoljno kvalitetne vode. Proizvodnja jedne vrste dobra i zalihe tih dobara ne garantuje da će se obilje održati ili podići na višu razinu. Ljudske potrebe su, po definiciji, neograničene i promijenljive, tako da se i pojam obilja mijenja. Pojam slobode ključni je za razumijevanje samog pojma obilja i resursa, jer bez slobode nema ni stvaranja novih tehnologija i potreba, dakle nema razvoja. Oskudica također proističe iz slobode da zahtijevamo i biramo.

Sve veći broj ciljeva OR odnose na sektorske aspekte održivosti: resurse, klimu, energetiku, vode, šume i ekosisteme... Organizacija ujedinjenih naroda je tokom 2016. usvojila novi program koji obuhvata čak "sedamnaest ciljeva da bi se preobrazio naš svijet"[10]. U dokumentaciji se podvlači kako "zemlje treba da primjene novu agendu održivog razvoja kao i globalnog sporazuma za klimu". U cjelu stvar se umiješao "Svjetski biznis savet za održivi razvoj", koji svojim programom pokazuje da se trend, otpočet 2002. godine u Johanezburgu i nastavljen 2012. na Konferenciji Rio+20, održava. To znači da se održivim razvojem danas ne bave više samo države, nevladine, prevashodno ekološke organizacije, već i sindikati, kulturne institucije i poslodavci, a naročito velike kompanije. Tzv. društveno odgovorno poslovanje poprima svojstva standarda, koji čine deo korpusa održivog razvoja [2].

Bez obzira na mnoštvo kritičkih primjedbi koje pogađaju konzistentnost kategorije i preciznost definicije: "održivi razvoj", zahvaljujući prije svega institucionalnoj podršci OR opstaje kao koncept, podjednako prihvatljiv kako za najrazvijenija postindustrijska društva,

[10]https://sustainabledevelopment.un.org/content/documents/975GSDR%20Executive%20Summary.pdf

tako i za zemlje u razvoju, odnosno one koje su manje ili više ugrožene klimatskim promjenama, zagađenjem i odgovorima Planete na neprirodne i violentne ljudske aktivnosti.

4. REKONCEPTUALIZACIJA I STRATEŠKA ADAPTACIJA CILJEVA I PRINCIPA ODRŽIVOG RAZVOJA - JUČER, DANAS, SUTRA

4.1. Stubovi i domeni održivosti; zašto ih ne bi bilo pet ili šest?

Današnjem društvu prijeti jedna više-manje oduvijek prisutna opasnost: da se dobro zamišljeni teorijski koncepti (pa i OR) pretvore u ispraznu ljušturu ili da se simplifikuju, imajući u vidu loše institucionalnu formalizaciju i sprovođenje, odnosno ponašanje ljudi. U ovom razmatranju, sama od sebe, nameće se jedna dilema. Da li je umesto prethodne većinske predstave o OR kao modelu tri "preklapajuća područja" ili "stuba" možda bolje danas definirati pet ili šest takvih područja, ili možda bolje rečeno oblasti. Zadržaćemo u upotrebi za ovu priliku oba izraza, jer bi pojam "sektor" možda više podrazumijevao nešto što je grana ili oblast privrede (gde možda ne bi spadale i oblasti javnog zdravlja, institucija, kulture, itd).
Evo prijedloga za takve oblasti: ekonomija, socijalni sistem, okruženje, institucije, tehnologija i resursi. Da li je tehnologija po definiciji ekonomska činjenica? Današnji svet pokazuje da nije više tako. Tehnologija zabave, zdravlja, kulture ima ekonomsku dimenziju kao i sve ostalo. Sistem koristi i troškova prati također i društvene odnose, instutucije, okoliš, kulturu, mada su oni nešto više od obične privredne aktivnosti.

4.2. Šta je sve novo u konceptu i praksi održivog razvoja?

Odlično zamišljen, ali nemogući koncept - to je otprilike deo kritičkog razumijevanja održivog razvoja u djelu poslovnog i političkog sveta današnjice, mada se to tako nigdje eksplicite ne navodi. A šta se uglavnom čini?

To je sprovođenje pojedinačng, tzv. nacionalnog ili kompanijskog interesa, koji podrazumijeva prioritizaciju ciljeva kratkog roka. Po neki "ukras" učini se u gestovima ekološki ili socijalno odgovornog poslovanja. Nema jedinstvenog akcionog plana ni dogovorenih, nesporno prihvatljivih koordinata održivog razvoja. To je glavni problem sprovođenja koncepta koji će se održavati još dugi period. Takozvana tri suba održivosti teško mogu da funkcionišu i dalje. U svakom od njih mogli bi se smjestiti pojedini ciljevi, a opet mnogi pripadaju negdje drugdje. U novim dokumentima, sve veći broj ciljeva odnosi se na sektorsku održivost u pogledu: klime, resursa, voda, energetike, šuma i ekosistema... Ujedinjeni narodi su tek 2016. usvojili inovirani program čak "sedamnaest ciljeva da bi se preobrazio naš svijet"[11].

To je urađeno sa obrazloženjem da je potrebna "nova agenda održivog razvoja kao i globalnog sporazuma za klimu". Nova globalna instutucija "Svjetski poslovni savjet za održivi razvoj" pokušava da dokaže kako se trend koji je otpočeo 2002. godine u Johanezburgu, a nastavljen 2012. na Konferenciji Rio+20, produžuje. Ako je tako, to bi moglo da znači da se održivim razvojem danas bave ne samo države, nevladine, prevashodno ekološke i stručne organizacije, kulturne institucije, već i poslodavci, sindikati, a naročito velike kompanije. Davno promovisano društveno odgovorno poslovanje bi, u tom smislu, moglo da poprimi svojstva standarda održivosti.

[11]https://sustainabledevelopment.un.org/content/documents/975GSDR%20Executive%20Summary.pdf

Međutim, to su, pre svega zvanični stavovi OUN i njenih specijalizovanih ustanova. Na drugoj strani, prijeteće akcije pojedinih velikih učesnika u globalnoj ekonomiji i politici zabrinjavaju upravo najviše na području održivog razvoja. Zato preostaje da se pozabavimo bliže inoviranim ciljevima. Pokušaj sistematizacije koji sledi pokazaće da bi se 17 ciljeva OR mogli svrstati čak u pet ili šest posebnih celina. U našem slučaju određene su sledeće oblasti-područja: ekonomska, socijalna, ekološka, institucionalna, tehnološka i resursna, oblast javnog zdravlja i humaniteta. Pod takvom pretpostavkom svih 17 navedenih novih ciljeva OR svrstani su u pomenutih 5 područja (tablica 1).

Tablica 1. Novi ciljevi i sadržaji održivog razvoja prema OUN 2016.

Svrstavanje oblasti i područja u prvobitne "stubove" OR	Definisane **oblasti - područja OR** prema upotpunjenim ciljevima (17 ciljeva OR - OUN 2016)	Ciljevi OR redefinisani 2016.
I. Stub: ekonomija	**Gospodarska oblast**	iskorjenjivanje siromaštva, inkluzivan i održiv rast, promocija blagostanja, održiva industrijalizacija, dostojanstven rad, održiva potrošnja i proizvodnja
II. stub: socijetet	**Socijalna oblast**	eliminacija gladi, inkluzivno i kvalitetno obrazovanje, mogućnosti cjeloživotnog obrazovanja, inkluzivna, bezbjedna i održiva naselja i gradovi
I. i II. stub	**Javno zdravlje i humanitet**	zdravlje i humanitarne potrebe, zdrav život, bezbjedna hrana i unapređenje ishrane, sanitacija, pristup pijaćoj vodi, položaj žena i unapređenje okoliša za žene i djevojčice.
III. stub: životna sredina	**Životna sredina**	hitna akcija za klimu, zaštita oceana i mora, bilje, zaštita biodiverziteta, prevencija deforestizacije.
I. stub: ekonomija (?)	**Područje tehnologije i energetike**	izgradnja i adaptacija infrastrukture, pristup i ostvarenje modern (ekološke) energetike,
II. stub - društvo (?)	**Institucije**	pravda za sve, izgradnja inkluzivnih i ostvarljivih institucija, eliminiranje neopravdanih nejednakosti i smanjivanje nejednakosti među zemljama, izgradnja miroljubivog i inkluzivnog socijeteta za održivi razvoj, obnova globalnog partnerstva za održivi razvoj .

Tablica 1, kreirana od strane autora radi boljeg pregleda sektora i ciljeva održivog razvoja, pokazuje da su okolnosti koje su uslovile redefinisanje ciljeva OR istovremeno

nasleđene i možda malo drugačije tretirane tendencije i problemi iz XX vijeka. Međutim, neki od njih su u fokus analize, u praktičnom smislu (klimatske akcije), izbili tokom XXI stoljeća.

Struktura i relacije ciljeva svrstnih u 6 oblasti ili područja pokazuju sljedeće:

- uslovno određenih 6 oblasti-područja mogu se samo djelomice svrstati u tri "stuba" održivosti,
- neke oblasti mogle bi se naći u okviru dva, ili čak sva tri stuba OR (javno zdravlja i humanitet),
- veliki dio posebnih ciljeva (od ukupno 17), morali bi se naći u više različitih oblasti i područja, (primjer: akcija za klimu, industrijalizacija, vodosnabdijevanje, obrazovanje, eliminiranje siromaštva...),
- pojedini ciljevi teško se uklapaju kako u oblasti, ili područja, pa čak i u prvobitno redukcionistički definisane "stubove" održivosti (iskorjenjivanje siromaštva, inkluzivne institucije, smanjenje nejednakosti),
- najveći dio ciljeva OR (od ukupno 17), pripada ekonomskom stubu, što pokazuje bazni nalaz da se svaki, ili bar većina problema neodrživosti, konačno ispostavlja kao ekonomski problem u dugom roku,
- pojedini ciljevi (iz novog spiska od 17), pripadaju istovrijemeno različitim područjima ili oblastima, odnosno faktički mogu pripasti svakom od područja i stubova.

Održivi razvoj se, potvrđuje kao integralan koncept. Analiza pokazuje da preostaje dalji rad na sistematizaciji i preciziranju onoga što predstavlja pojam održivi razvoj, kao i na posebnim operativnim ciljevima OR, čiji spisak definitivno nije okončan. Jedan od uzroka ovakvog stanja, nakon više od tri decenije duge evolucije institucionalizovane teorije i prakse OR (računajući kao početak 1987), vjerojatno je fluidnost i nedovoljna polazna određenost održivog razvoja, kao nečega što nije. Naime, početna operativna određenja na nivou OUN (u okviru dokumenta *Naša zajednička budućnost*) odnosila su se uglavnom na to šta OR ne bi smio da uzrokuje i do čega da dovede. Daleko prije "održivosti" bila je definirana "neodrživost", uglavnom kao narušavanje prirodnih ravnoteža, socijalne strukture i poretka, kao i ekonomske aktivnosti usred dugoročno štetnih i perspektivno opasnih trendova. Prostije rječeno, pošlo se od toga što se evidentno pokazalo kao neodrživo, da bi se tek kroz primjenu tragalo ka sadržajima održivosti [12].

Pri tome su humanitarna, socijalna i demografska oblast, svakim danom postajale sve neuralgičnije. One i dalje zahtijevaju sve brže redefinicije održivosti, naročito u narednom periodu, koji donosi nove i kompleksnije rizike, poput klimatskih, geo-političkih, a posebno onih visoko-tehnoloških. Dodatni razlog neuređenosti i redefiniranja je taj što se proturječnosti se multiplikuju, a problemi nagomilavaju, prelazeći iz oblasti u oblast[12].

[12]Ilustracije radi, brz rast nejednakosti između bogatih i siromašnih pokazuje da raspodela globalnih dobara i bogatstva u svijetu postaje jedan od ključnih rizika. Dostupni podaci govore je 8 najbogatijih ljudi na svetu raspolaže vrednošću kao i 3,2 milijarde najsiromašnijih ljudi sveta, što je blizu jedne polovice. Ta činjenica vodi ka novim konfliktima, koji bi mogli da podstaknu desni i populistički ekstremizam, ili pak da vode ka socijalnoj revoluciji.

5. KLIMATSKI IZAZOVI I RIZICI ZA ODRŽIVI RAZVOJ

Povrijemeni pomaci u okviru akcija UN po pitanju klimatskih promena, veoma često se dovode u vezu sa praktičkim odstupanjem od zvaničnih opredijeljenja i stavljenih potpisa na međunarodne sporazume. U takvim okolnostima, postavlja se pitanje: ima li uopće smisla razmatrati strateška pitanja OR i njegove operacionalizacije u globalnom svijetu, kao i na regionalnoj i lokalnoj razini? Da li će se sadržaji održivog razvoja tumačiti u budućnosti slično kao što se to dešava danas? Što će donijeti promjena kulture, obrazovanja i tzv. četvrta industrijska revolucija u pogledu sadržaja i ciljeva održivosti? Da li će pragmatičke i kratkoročne prepreke preovladati?

Na ta pitanja teško je dati pouzdane odgovore, izuzev u okviru koridora dosadašnjih pravaca promjena. Ekstrapolacija prethodnih trendova, međutim, nikada nije bila dobar saveznik "čitačima budućnosti", kakvi su uvijek bar djelom, i promoteri održivog razvoja.

5.1. Emisije GHG i rizici klimatskih promena

Postoji opasnost od redukcionističkog razumijevanja održivog razvoja kao aktivnosti ljudi koje su isključivo usmjerene ka ublažavanju dejstva (mitigacija) ili spriječavanju mogućih posljedica (prevencija) djela klimatskih promjena.

Tablica 2 proistekla je na osnovu preuzimanja podataka najizraženijih rizika za svijet od 2013-2017. U njoj su svi tipovi rizika nijansirani različito, u zavisnosti od toga da li pripadaju nekoj od tipičnih kategorija. Uočljivo je, da se prvih pet globalno vrednovanih rizika po verovatnoći dešavanja, veoma često ponavljaju ali sa različitim redosljedom.

Podjeljeni u pet kategorija, ovdje su grubo razvrstani u sledeće grupe:

- *ekološki* - ukupno 10, sa trendom povećanja,
- *ekonomski* - ukupno 5, sa trendom održanja,
- *geopolitički* - ukupno 5,
- *socijalni* - ukupno 5, sa trendom povećanja nakon 2015,
- *tehnološki* - ukupno 2; sa trendom povećanja.

Tablica 2. Redosljed rizika po godinama (2013-2017), prema anketama koje je širom svijeta sproveo Svjetski ekonomski forum, WEF [15]

Rizik /rang	2013.	2014.	2015.	2016.	2017.
1.	Oštre dohodovne razlike	Nejednakosti dohotka	Međudrž. i regionnalni konfl.	Masovne nevoljne migracije	Ekstremne vremenske neprilike
2.	Hron. fisk. neravnoteža	Vremenski ekstremi	Vremenske neprilike	Ekstremne vremenske nepogode	Široke nevoljne migracije
3.	Rast gasova staklene bašte	Nezaposlenost i nedov. zaposl.	Greške nacionalnih vl.	Greške u politici za klimu	Velike prirodne nesreće
4.	Kriza vodosnabdije-vanja	Klimatske promjene	Kriza ili kolaps države	Međudržavni i region. konflikti	Masovni teroristički napadi
5.	Nekontrolisano starenje stanovništva	Sajber napadi	Visoka strukt. nezaposlenost	Velike prirodne katastrofe	Masovna manipulacija sa podacima

Analiza prioritetnih uzroka prema utjecaju pokazuje da se redosled globalnih rizika razlikuje u ovisnosti da li se procjenjuje intenzitet djelovanja, ili verovatnoća ostvarenja. Vodeći rizici po godinama, na osnovu procene intenziteta, odnosno uticaja, prikazani su u tablici 3.

Tablica 3. Prioritetni rizici po godinama prema oceni ispitanika iz cjelog svijeta [15]

Rizici WEF	*Prioritetni rizici prema utjecaju*
2013	veliki sistemski finansijski promašaji
2014	fiskalna kriza
2015	kriza vodosnabdijevanja
2016	program mjera za klimu
2017	oružje za masovno uništenje

Najutjecajniji rizici koji su tretirani, pokazuju da sve veći broj rizika zabrinjava ispitanike na globalnom planu. Oni ugrožavaju život ljudi i njegov kvalitet. To je trajni trend, koji je uslovljen opštim ekološkim kapacitetom Zemlje, trendovima porasta populacije, strukture privredne aktivnosti i potrebama ljudi prema materijalnim dobrima, energiji i uslugama.

5.2. Rizici emisije GSB malih i velikih ekonomija

Sa stanovišta interesa malih zemalja i svjetske zajednice, to bi mogao biti jedan od izazova da se male ekonomije dalje integrišu u akciji za prevenciju rizika. Možda najvažniji ili bar trenutno najaktualniji problem emisija gasova staklene bašte (GSB)prikazan je na osnovu komparacije stanja u nekoliko balkanskih zemalja, zajedno sa usporedivim podacima iz SAD, Kine i Indije (tablica 4).

Kina, prema podacima svjetskog Instituta za resurse, emitira više GSB (CO_2 ekv) po stanovniku, od svih u tabeli prikazanih zemalja. SAD po kupovnoj moći BDP, imaju skoro 4 puta viši dohodak po stanovniku, ali emituju jedva nešto više CO_2 po stanovniku od Srbije, a ta emisija je skoro na nivou Slovenije, koja je prema procenjenom dohotku od 31 hiljadu dolara (ppp), na nivou od oko 60 % u odnosu na SAD.

Vjerojatno uskoro najmnogoljudnija zemlja na svetu, Indija koja je prema dohotku po stanovniku na polovici razine današnje Srbije, emitira po stanovniku više CO_2 ekv, od svih balkanskih zemalja. Međutim, za ovu analizu je bitno i to da je u Kini i Indiji cijena električne energije na nivou Srbije i Crne Gore (bar u vrijeme koje prikazuju podaci) a daleko niža nego u odnosu na ostale balkanske nacije. Energetski intenzitet (potrošnja energije po jedinici ostvarenog novčanog proizvoda, najviša je bez sumnje u Kini (0,13 kWh) po dolaru, ali su Crna Gora i Srbija odmah za njom sa 0,1 kWh/USD. Emisija GSB po stanovniku najveća je u Kini oko 0,6 tona ekv. ugljenika po stanovniku, ali je Srbija odmah za njom sa 0,5 tona[13].

[13]Ovdje su u pitanju problemi strukture energetike i njenog naslijeđa. Srbija je od bivše Jugoslavije nasljedila elektroenergetski sektor baziran na uglju, a nije mnogo učinila da tu strukturu izmjeni. Kina još uvek svoj dinamičan razvoj i rekordni rast zasniva na najvećoj potrošnji uglja u svijetu.

Tablica 4. Veliki i mali emiteri - poređenje emisije GSB po stanovniku, 2012 [16]

	BDP per. cap.ppp USD	En. Inten-en/$ kWh/USD	Cijena el. ener. za domać. /USD/kWh	Gubici el. en. u distrib. %	Emisija CO_2/per.cap. tona	Rast emisije GSB %
USA	55837	0.09	0.22	6.2	0.35	*-1*
Kina	14239	0.13	0.08	6.2	0.6	8.4
Indija	6089	0.09	0.08	*19.7*	0.32	*6.1*
Slovenija	31122	0.09	0.22	6.3	0.24	0.3
Hrvatska	21880	0.08	0.18	11.2	0.22	-0.2
Cr. Gora	15485	0.1	0.08	15.1	0.32	1.5
Albanija	11305	0.08	0.12	21	0.16	*2.2*
Srbija	13482	0.1	0.08	15.9	*0.5*	0.6

Veoma su indikativni gubici električne energije u distribuciji i prenosu. Oni zavise, sa jedne strane od nasleđa, niskog realnog dohotka i populističke politike kao i od zakona i loših institucija. Tako se iz tabele 4 može uočiti da su najviši gubici u današnjoj Albaniji (21 %) zatim u Indiji (19,7 %) dok su najveći gubici bivše Jugoslavije u Srbiji 15,9 % i Crnoj Gori (15,1 %) .

Konačno, veoma su indikativni trendovi rasta emisije GSB u kompariranim zemljama. Ubjedljivo najviši trend rasta emisije u periodu 2013 - 2015 imale su Kina (8 %) i Indija, (6,1 %), dok su na Balkanu najbrži porast štetne emisije imale Albanija (2,2 %) i Crna Gora (1,5 %). Negativan priraštaj ili opadanje ostvarile su SAD (-1 %) i u našem okruženju Hrvatska (-0,1 %). Sudeći po trendovima, ispada da je model obrnute "U krive", kao metafore za relaciju ekonomski razvoj- zagađenje, još uvijek veoma aktualan. To znači da bi za zemlje Balkana bilo neophodno dostizanje razine srednjeg višeg dohotka od oko 20000 $ per capita, da bi se počela smanjivati emisija GHG.

6. ZAKLJUČAK: ŠTO SA ODRŽIVOŠĆU ODRŽIVOG RAZVOJA?

Današnja globalna scena obiluje proturječnostima i sukobima razvojnih motiva: globalni-lokalni, društveni – individualni - kompanijski, regionalni-nacionalni, kratkoročni-dugoročni, egzistencijalni - kulturni.

6.1. Današnje kontroverze u praksi

Svijet se formalno zalaže za toleranciju, razvoj suradnje i razumijevanje, multikulturalnost, a praktički sprovodi projekte izolacionizma, ekstremizma, netolerancije. Umjesto doskora neprikosnovene globalizacije, nalazimo se u svijetu antiglobalizma. Umjesto suradnje i razumijevanja svih nacija i država, na osnovu povelje Ujedinjenih naroda o pravima čovjeka, imamo sve više demonstraciju dominacije i zloupotrijebu sukoba malih nacija koje je još Frojd nazvao "narcizmom malih razlika". Umjesto međunarodne globalne

suradnje u akciji za klimu, protiv terorizma i za mir i saradnju u svijetu, kao i radi zaštite Zemlje kao jedinog našeg doma, danas se sve više ispoljavaju netolerancija i geostrateške konfrontacije, sa stanovišta sebičnih ili tzv. viših nacionalnih interesa. Održivi razvoj fundamentalno počiva na ljudskim slobodama [17], kao i na intergeneracijskoj pravdi, toleranciji, demokratskoj javnosti i širokoj participaciji društvenih snaga i njegovom kreiranju i sprovođenju. Zato je često na udaru nacionalnih geo-strategijskih i geopolitičkih faktora usmjerenih na preraspodjelu globalnih resursa, kao i na kontrolu zemaljskih privrednih tokova.

6.2. Principi nove percepcije održivog razvoja

Klimatska politika ozbiljno je dovedena u pitanje, kao i primena Pariskog sporazuma. Uz to, posebno zabrinjavaju protekcionistoičke mere koje se šire po svijetu, kao i oružane vojne intervencije. Međutim, sa druge strane, energetska efikasnost, zelena gradnja, antiugljenična industrija, pametni saobraćaj i komunikacije, zelena i cirkularna ekonomija zasnovana na znanju, ostaju temeljne odrednice za primjenu održivosti. Inženjerstvo i tehnologije će morati da nude sve novija i po prirodu prijateljska praktička rješenja u ovim sektorima. Sve današnje inovacije, bilo na planu tehnoloških rješenja, gospodarstva, zdravstva, kulture i duhovnosti, uglavnom se zasnivaju na načelu održivosti, popravljanja stanja ekosistema i okoliša. Ekonomska nauka nije u manjoj mjeri ekološki orijentisana u odnosu na inženjerstvo ili hemiju, medicinu ili geografiju. Što više, teorija eksternalija već skoro čitavo stoljeće unazad, pokazuje da se svaki, pa i ekološki trošak mora adresirati ka počiniocu, u skladu sa načelom "zagađivač - korisnik plaća".

Nije dovoljna suradnja ekonomije i inženjerstva na konkretnim razvojnim projektima kako bi se ispunili standardi održivosti tih projekata. Održivost se danas mora preispitivati, dograđivati u skladu sa novim teorijskim istraživanjima i dostignućima nauke, kulture, prava i praktičkih iskustava, uglavnom u skladu sa principima predostrožnosti, participativnosti, integrisanja zaštite životne sredine u sektorske politike, posebno u obrazovanje. Klasičnom disciplinarnom obrazovanju za "struku", davno je odzvonilo. Novi svijet za život, sa svim izazovima promjene klime i novih globalnih rizika, zahtijeva *novi sustav obrazovanja za održivi razvoj*. To bi mogla da bude i tema sledećeg Simpozijuma za koji je priređen ovaj tekst.

6.3. Održivost suradnje u regionalnim okvirima

Za zemlje regiona Jugoistočne Evrope, karakteristična je visoka ranjivost na klimatske promjene i vrlo nizak nivo međusobne suradnje na području održivog razvoja.
Što se može odmah učiniti da bi stanje bilo povoljnije, a izgledi za buduće generacije bolji?

6.3.1. *Redefinisanja praktičkih ciljeva održivog razvoja i suradnje. Neophodna je fleksibilizacija pojedinih ciljeva*. Vjerovatno će se proces smanjenja broja životnih vrsta na zemlji nastaviti. Čovjek svojom akcijom ne može spasti sve vrste insekata, bilja i ptica, pa i sisara. Međutim, praksa je pokazala da se može zaštititi od propadanja dobar dio ribljeg fonda i bogatstva ribljih vrsta (uzgajanje brancina u Jadranskom moru, spas ohridske pastrmke u Makedoniji, spasavanje mladice na Drini od strane entuzijasta i biologa Srbije).

6.3.2. *Princip zagađivač plaća*. Neophodno je njegovo dosljedno sprovođenje u daleko većoj mjeri, kako bi se preventivno očuvali resursi i zahvatanjem troškova negativnih

eksternalija, djelovalo pozitivnim eksternalijama. *Održiva proizvodnja i potrošnja* kao princip podrazumijeva daleko veći utjecaj organizovanog društva na proizvodnju, trgovinu i potrošnju, kako u pogledu kvaliteta, bezbjednosti, zdravlja, tako i utjecaja na životnu sredinu.[14]

6.3.3. *Princip lokalne suradnje* u mjerama za klimu i vremenskim nepogodama. Ne treba zaboraviti da su poplave 2014. pokazale kako je moguća solidarnost i suradnja između pogođenih srednje-balkanskih nacija Srbije, BiH i Hrvatske. Veliki poplavni talas pogodio je ove zemlje bez ekonomskog presedana. Po računici Svjetske banke, štete od poplava u Srbiji iznosile su 1,6 milijardi evra a u BiH čak 1,8 milijardi. To znači da je udio tih šteta u Srbiji bio 5,3% BDP, u BIH čak oko 8% BDP[15]. Nakon toga poplave se periodično ponavljaju sad u jednoj sad u nekoj drugoj zemlji Balkana, ali su najveći troškovi izazvani sušama (štete u poljoprivredi i požari). Biće neophodno da se djeluje zajednički, kako na istraživanju i razvoju, tako i na monitoringu, procenama i prevenciji. Tehnički i finansijski, kao i ljudski potencijali nisu mali, ukoliko su udruženi.

6.3.4. *Solidarne u usaglašene strategije* malih zemalja. Pouke nesreća su utoliko veće ukoliko je riječ o *malim i nerezvijenim ekonomijama,* jer su pod uticajem slabe organizacije, loših tehnologija i minornih fondova, naročito osiguranja. Ti mali subjekti morali bi da poprave svoje izglede kroz zajedničke akcije. Energetika, poljoprivreda, turizam, saobraćaj, predstavljaju najočiglednije sektore pod najvećim rizikom održivosti a na udaru klimatskih promjena. U slučaju balkanskih nacija, neophodno je redefinirati ciljeve održivog razvoja u regionalnim akcijama. Skoro sve zemlje našeg regiona imaju slične razvojne probleme: nelikvidnost, visok javni dug, debalans javnih finansija, deficit međunarodne trgovine, niska produktivnost, slabi učinci poljoprivrede, prljava i neefikasna energetika. Zato su u daleko većoj mjeri izložene rizicima klimatskih promjena i njihovih uvećanih posljedica. Neophodno je da uspostave preventivne zajedničke fondove, da se koncentrišu na tehnički i ljudski potencijal za hitna reagovanja. Takođe je veoma bitno da svoj potencijal zajednički usmjere u istraživanja i naučnu suradnju sa ciljem zaštite prirode i klime. Posebno su važne lokalne i regionalne institucije i projekti koji se tiču klimatskih akcija najvišeg prioriteta: vodna infrastuktura, regulacija vodotokova, prevencija poplava, navodnjavaje, zajednički vodozahvati, regulacija kanala i jezera, brane i hidroelektrane.

Sledeće je "pametni" saobraćaj, "" infrastruktura, bolja gradska i ruralna suradnja, zajednički projekti energetske efikasnosti, stabilnost i interkonekcije enektrosnabdevanja, bezbednost hrane kao i izgradnja zajednički brendova hrane i pića "made in Balkan".

6.3.5. *Zelena ekonomija* i fondovi. Redefinicija fondova je mjera koju je neophodno sprovesti na širem planu od puke zelene održivosti. Zelena ekonomija se mora tretirati kao sistem koji je tržišno zasnovan, a ipak vodi ka održivom razvoju, bilo u smislu ekološke ili socijalne efikasnosti, bilo kroz smanjenje emisije GHG ili upotrebljene energije po jedinici ostvarenog BDP. Najveće mogućnosti prostiru se u domenu energetike. Mnoge teme i kontroverze potresaće još uvek svijet na sličan način i sredinom tekućeg veka. Niskokarbonska energetika biće i dalje najvjerovatnije prioritet održive energetike. Mnogo

[14]Dobra vijest, u trenutku dovršavanja ovog teksta glasi: "zabrana prometa i upotrebe tankih najlon kesa u Srbiji". Hrvatska je dobrim primerom stimulativne separacije i otkupa, već pre više od osam godina riješila problem zagađenja PET ambalažom. Slovenija je impresionirala svojim primerom insineracije otpada u Ljubljani kao i u većem dijelu zemlje.

[15]Najveća prethodno procenjena šteta jedne katastrofe pogodila je Japan 2011 (Fukušima Daići). Šteta je iznosila 4,2% japanskog BDP.

više izazova predstavljaće odgovor na pitanja novih vidova ugrožavanja životne sredine i prirode uopšte.

Najveća ulaganja treba da budu u novu infrastrukturu, koja bi zemljama Balkana mogla da donese daleko viši nivo ekološke bezbednosti, energetske efikasnosti i podsticaja za zelene tehnologije i nova zelena radna mesta. Ukupna održiva infrastruktura budućnosti treba da bude ne samo ekološka, u smislu da pogoduje zaštiti okoliša, već i održiva u svakom pogledu (najpre ekonomski, onda u socijalnom, bezbednosnom i psihološkom smislu). Tako na primjer elektromreža i povezani elektrosistemi, kao i (pametni) saobraćaj, putevi, zgrade, moraju da budu rezultat odličnog regionalnog umreženja, kojim se štedi energija, smanjuju rizici i postižu socijalno prihvatljivi ciljevi. Prirodne pretpostavke balkanskih zemalja pružaju priliku za ustanovljenje kvalitetne zdravstveno bezbedne hrane i pića . Organska hrana kao brend treba da bude povezana sa kvalitetnom i koordiniranom poljoprivredom, "ekološkom energetikom" [18] i održivim turizmom [19], za šta već ima dovoljno literarnih i praktičnih pretpostavki.

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Zahvala

Ovaj rad rađen je u okviru projekta "Modeliranje razvoja i integracije Srbije u svetske tokove u svetlu ekonomskih, društvenih i političkih gibanja", evidencioni broj 179038, koji finansira Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

ENERGY AND NUTRIENT RECOVERY OF SEWAGE SLUDGE FROM WASTEWATER TREATMENT PLANT WITHIN CIRCULAR ECONOMY

Dinko Đurđević*, Vitomir Komen**

* Energy Institute Hrvoje Požar, Zagreb, Croatia
** Faculty of Engineering, University of Rijeka, Croatia

corresponding author: Dinko Đurđević, e-mail: ddurdevic@eihp.hr

Review paper

ABSTRACT

Circular economy is a new business model that is expected to lead to sustainable development and harmonious society. Although circular economy is often identified with recycling, it is not applicable for every situation. Regarding wastewater and wastewater sludge, recovery principle needs to be implemented for the amounts of waste that cannot be recycled, in order to reduce the amounts of generated waste. Conventional energy recovery from wastewater sludge takes place in anaerobic digestion processes (biogas utilization) and through incineration. However, these processes lead to loss of valuable nutrients that are contained in the wastewater sludge. Advanced processes of energy and nutrient recovery, such as pyrolysis and gasification are becoming appropriate options for wastewater sludge management, which will be presented in this paper. Other processes will also be presented, that are harmonized with sustainable wastewater sludge management, through recovery of energy and nutrients that it contains.

***Keywords**: circular economy, wastewater sludge, energy recovery, nutrients*

1. INTRODUCTION

Population growth and urbanization lead to significant increase in amounts of generated wastewater sludge. The annual increase in wastewater sludge generation has constantly been present and the trend will continue in the future. Progressive reduction of wastewater sludge utilization in agriculture, mainly because of environmental standards that concern pathogens and heavy metals, require finding alternative methods of sludge management. In that context, thermochemical treatment of sludge becomes more significant [1].

Several factors contribute to the existing trend of waste generation, and they include economic activities, demographic changes, technological innovations, lifestyle and pattern of production and consumption. All these factors need to be taken into account, in order to achieve optimal waste management. Dry matter (DM) from wastewater sludge produced in primary, secondary and tertiary treatment in EU amount to ca. 90 g per day per capita. Problems related to wastewater sludge management are related to two factors:

- Increase in sludge volume that is generated in wastewater treatment plants (WWTP)
- Decrease of biodegradable waste that is landfilled.

Main methods of sludge management in EU are: landfilling, application on soils and incineration, which represent almost 90 % of generated wastewater sludge. Emission to oceans and seas (after treatment, mostly only grate pre-treatment) and landfilling are practices that trying to be abandoned, even though 35 - 40 % of sludge in Europe is managed in this manner. Legal framework related to wastewater sludge management utilization on soils is becoming stricter, in order to prevent health risks caused by the potential presence of toxic elements, such as heavy metals, pathogens, and organic pollutants. EU data from 2012 [2, 3] show that significant amounts of wastewater sludge were utilized in agriculture. Sludge is a valuable agricultural product because it contains valuable nutrients, such as nitrogen (N), phosphorus (P) and potassium (K) and can contribute to the quality of unproductive soils and recover degrade soils with nutrients increase that are necessary for plant growth.

However, sludge is generated during the whole year, while soils are fertilised only once or twice per year. Therefore, sludge requires appropriate storage until utilization, which causes significant environmental problems. Moreover, sludge from WWTPs has a negative connotation as a fertiliser with farmers. Because of these problems, its utilization in agriculture is reduced in European countries, such as Finland, Slovenia, Sweden, Netherlands, Greece and Belgium, during last several years [4].

Wastewater sludge management requires designing in coherence with waste management hierarchy, introduced by Waste Framework Directive [5]. Directive presents a preferable order of actions for reduction and waste management, i.e. prevention, minimisation, reuse, recycling, energy recovery and landfilling, as the last and undesirable option. Amount of landfilled sludge is planned to be significantly reduced because the Landfill Directive [6] bounds member states to reduce the quantities of biodegradable waste sent to landfills to 35 %, in comparison to levels in 1995. This implies the reduction of waste collection and landfilling in EU27 by 2020 [7].

Transition to circular economy (CE) brings many possibilities and opportunities for Europe and its citizens. It is an important part of modernization and transformation of the European economy, leading it towards a sustainable way of thinking. The objective of CE is reduction of lost resources in circular materials cycle, in order to make the system function in an optimal way – figure 1. The main advantage of CE system is in the containment of added value of products as long as possible and elimination of waste production.

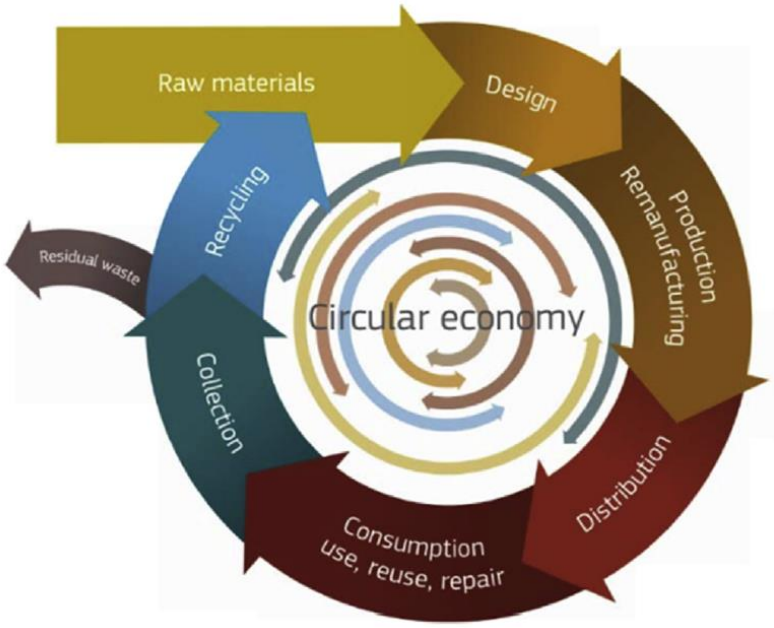


Figure 1. Circular economy strategy [8]

Wastewater sludge is considered a renewable biomass, which is why it is categorized as carbon-neutral fuel. An example of utilization of sludge for energy production is process of pyrolysis, which is becoming more popular for production of gases and biochar [9]. However, there are other methods, which will be described in the following sections.

2. PRODUCTION OF SEWAGE SLUDGE

Wastewater sludge is a complex heterogeneous mixture of microorganisms, undigested organic matter such as paper, plant residues and faeces, inorganic material and moisture that occurs during wastewater treatment in WWTPs [10].

The first step in wastewater treatment is the pre-treatment process which consists of grate treatment, which removes large solid matter. In the next step, wastewater passes through primary treatment which includes thinners and sedimentation reactor, in order to settle the particles in wastewater. During this treatment, 40 – 50 % of suspended particles and 30-40% of chemical oxygen demand (COD) is removed and the resulting sludge is mostly organic matter pervious to further degradation. Furthermore, wastewater is treated in the secondary treatment which involves aerobic microorganisms, with the purpose of removal the remaining COD and suspended particles. The remaining effluent from this treatment passes through secondary thinner, which produces sludge with organic matter content of 90 %. Mixed primary and secondary sludges pass through additional treatment which includes gravity thickening or flotation, thereby removing as much water as possible and reduces the volume of raw sludge to half of its initial volume. The process is shown in figure 2.

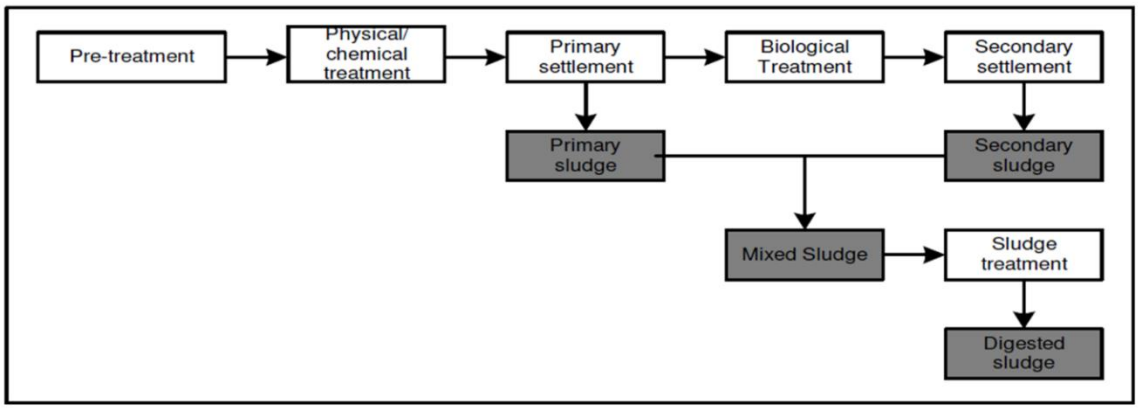


Figure 2. Conventional wastewater treatment plant [11]

Although sludge amounts to only 1 - 2 % of treated wastewater volume, its management is very complex and treating costs are 20 - 60 % of total operational costs of WWTP. Besides economics, location is very important because sludge treatment is often occurring outside the WWTP's border.

Sustainable wastewater sludge management presents a problem for WWTP due to increase in urban population and stricter legal framework for conventional sludge management methods. Sludge management in EU remains an open question, considering that Council Directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC) is still in force, which is old and undefined, and it is expected that the amount of wastewater sludge in Europe will rise up to 13 million tons DM until 2020.

In order to solve this problem, many EU countries implemented various primary, secondary and tertiary processes for wastewater treatment and are intensively developing new process technologies for sludge management, to close the cycle of waste in an energy (heat and/or electricity production), environmentally, economically and materially (valuable nutrients) sustainable way.

3. TECHNOLOGIES FOR SEWAGE SLUDGE TREATMENT AND ENERGY RECOVERY

Wastewater sludge management systems are generally composed of thickening, dewatering and several various alternative main treatments, such as anaerobic digestion (AD), composting, incineration or melting. The main by-product of AD is biogas, which consists of methane and carbon dioxide (CO_2). Composted sludge can be used as a soil conditioner in agriculture because it returns carbon (C), nitrogen (N), phosphorus (P) and essential elements back to the soil. However, pathogens and heavy metals that it contains can prevent the utilization of this method. Incineration and melting are methods for solving the problem of waste where high temperatures are present (800 - 1800 °C, depending on the used method). The main problem of sludge incineration is the generation of significant amounts of dioxins, furans and fly ash, that can severely pollute the environment and human health. Fly ash contains toxic metals such as lead, cadmium, copper and zinc, but also dioxins and furans [12]. Although there are several filter types that are used in incineration processes for dioxins and heavy metals removal, complete removal is not possible, especially due to their cost.

Table 1 shows value limits for heavy metals concentrations in sludge when it is utilized as soil amendment.

Table 1. Heavy metal concentrations in wastewater sludge used for agricultural soils (mg/kg DM) [11]

	Range in EU [13]	Directive limit values [14]	Concentration in WWTP [15]
Cadmium	0.4 – 3.8	20 – 40	1.38 ± 0.35
Chromium	16 – 275	-	79.12 ± 15.99
Copper	39 – 641	1,000 – 1,750	193.19 ± 43.17
Mercury	0.3 – 3	16 – 25	1.43 ± 0.01
Nickel	9 – 90	300 – 400	29.24 ± 8.80
Lead	13 – 221	750 – 1,200	334.05 ± 48.37
Zinc	142 – 2,000	2,500 – 4,000	1,521 ± 57

The main method for sludge management is storage and utilization in agriculture. However, it is possible to transform large quantities of sludge into useful energy by using thermal processes. Processes of thermal treatment can be developed and utilized on existing plants (power plants, thermal plants, cement kilns) or constructed on new plants. Prior to thermal processes, it is necessary to include dewatering and drying processes. With thermal treatment, it is possible to obtain significant reduction in amounts and volume of wastewater sludge. Thermal treatment of sludge is determined by its characteristics, such as calorific value and composition, which will be considered in the following sections. The calorific value of raw sludge is 17 MJ/kg, active sludge around 15 MJ/kg and stabilised sludge around 11 MJ/kg. However, energy required for dewatering of raw wastewater sludge should be taken into account, due to its effect on the final energy balance of thermal processes. Most used technologies for wastewater management in EU are shown in figure 3.

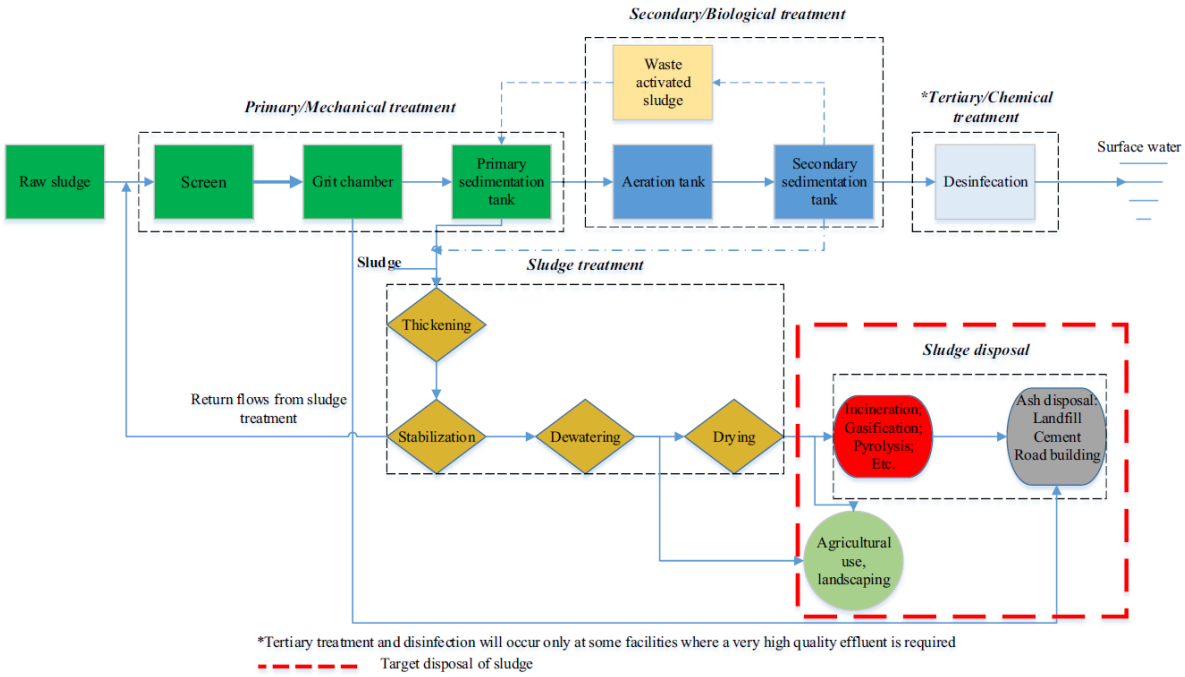


Figure 3. Main technologies for wastewater treatment and wastewater sludge management in EU [16]

3.1. Incineration

Incineration is one of the main methods of energy recovery during sludge treatment, which is applied in a large number of developed countries. Incineration can accomplish stabilization, volume reduction and energy recovery from sludge. The main goal of sludge incineration is a complete oxidation of organic compounds during high temperatures. During the process, biological solid substances are incinerated in kilns with excess air (oxygen), in order to form mainly N and water, producing inert material (ash) as a by-product. Wastewater sludge incineration is different from traditional fuel incineration due to a large amount of present water. Sludge has to contain around 28 - 33 wt.% of solid fraction so it can burn autothermically and should not require additional fuel for incineration process [3].

The process cannot be considered as a final option for sludge treatment because ash is produced, which contains inorganic matter that did not react during the oxidation process. Generated ash needs to be managed and can be used as a material for the production of construction materials [10]. Ash characteristics are presented in various literature [3] and show that most common elements in ash are silicon, aluminium, calcium, iron and phosphorus. Crystal formations that remain in the ash are silicon oxide (SiO_2), calcium phosphate ($Ca_3(PO_4)_2$) and iron oxide (Fe_2O_3).

During incineration, besides ash, other residues are generated: fly ash and slag. Fly ash particles are generally smaller than 100 μm. Based on current studies, fly ash can be utilized in road building and in concrete manufacturing. In case fly ash contains higher concentrations of heavy metals, it is necessary to treat it before landfilling. In this case, solidification process is applied, i.e. mixing with cement and water, to obtain blocks hard enough that will secure chemical stability.

3.2. Pyrolysis

Pyrolysis is a process of chemical molecules degradation under impact of high temperatures (300 – 900 °C) in anaerobic conditions [9, 17]. Main products groups that are developed during sludge pyrolysis are:

- Gas fraction, which mostly contains hydrogen, methane and carbon dioxide, with trace gases: calorific value of pyrolysis gas is around 15 MJ/m^3,
- Solid fraction (pyrolysis coke, with over 90 % of carbon); also includes inert compounds and dust with significant amount of heavy metals,
- Liquid fraction, which contains mostly oils, water, tar and organic compounds,

Pyrolysis components ratio depend mainly on process temperature and pressure and reactor turbulence, but also many other factors. Technology sludge-to-oil is based on pyrolysis. Process is occurring by pyrolysis of wastewater sludge (with 95 % DM) at temperature 450 °C and atmospheric pressure, during > 30 min. As a result, solid hydrocarbons and carbonized products (e.g. pyrolytic coke) are formed. Products can be used as a raw material in many industries (e.g. petrochemical industry). One of the most important pyrolysis processes of wastewater sludge treatment is Carver-Greenfield (C-R), which produces refuse-derived fuel (RDF) [18]. This process provides possibilities of simultaneous sludge drying before its incineration or gasification. The essence of the process is in mixing of raw sludge with oil refuse (e.g. used motor oil). Pyrolysis of sludge produces oil that has similar characteristics and element content as diesel (table 2).

Table 2. Pyrolysis and diesel oil characteristics comparison [19]

Component	Pyrolysis oil	Diesel oil
C (mas.%)	86.57	86.07
H (mas.%)	13.51	12.80
O (mas.%)	Negligible	0.86
N (mas.%)	0.08	0.05
S (mas.%)	0.22	0.22
Ash (mas.%)	0.01	0.02
Specific weight at 15,6 °C	0.83	0.85
Incineration heat (kJ/g)	46.18	45.89

Prepared mixture is passed through evaporation system to remove all the water. After drying, sludge is passed through centrifuge to separate liquid fraction from solid particles. The result is a solid waste and liquid fraction which is returned to the plant for utilization as a fuel. This process reduces the necessity for flue gases treatment. Sludge is stabilized (drying) and because of lack of oxygen there is no NO_x emissions.

3.3. Gasification

Gasification is a process similar to pyrolysis, however the process produces only one flammable gas, which can be utilized locally. Capital and operational costs are similar and the difference between two processes is only in the generated products. Gasification produces surplus energy and requires additional energy only during process start. Produced gas contains CO, H_2, CH_4 and hydrocarbons in traces, such as ethane and ethene, water, N_2 and various pollutants (carbon particles, ash, tar and oil). If air is used as a gasification medium, gas is produced with calorific value of 5 MJ/m^3 and N content of 50 -60 % [20].

Gasification efficiency is higher than incineration process because the produced gas can be directly used for energy production. The disadvantage of this method is high concentration of tar and dust during synthetic gas (syngas) production.

Variation of the gasification process is plasma gasification. It is an advanced technology that is ecologically acceptable. It is a thermal process which does not include incineration, but uses high temperatures in anaerobic environment, to degrade waste inputs to simple molecules [21]. The main products are syngas, which can be used for energy production, and vitreous material (slag). Moreover, the process emissions are much lower, compared to competitive technologies, such as incineration [22].

3.4. Liquefaction

Liquefaction is a conversion process which occurs in liquid phase, at low temperatures and high pressures, with addition of high hydrogen partial pressure and catalyst to improve the reaction [20]. Reaction parameters are following:

- Temperatures up to 350 °C;
- Pressures up to 300 bars;
- Low heating level in combination with relatively long retention period in the reactor;
- Possible addition of hydrogen, CO and/or catalyst.

The main product is oil with low oxygen concentration and calorific value of 35-40 MJ/kg and is appropriate for energy production. This calorific value is higher than that obtained through pyrolysis process (generally 25 MJ/kg). However, liquefaction process is expensive and there are several problems concerning biomass input during high pressure, separation of products from solvent and utilization of hydrogen during high pressure.

3.5. Hydrothermal carbonization (HTC)

HTC process is a thermochemical process for conversion of organic raw material into valuable products at high temperatures (180 - 350 °C) and pressures (2 - 10 MPa), in the presence of water, during several hours [23]. Obtained product is called hydrochar and has composition similar to biochar, which is obtained in different process parameters. Reaction mechanisms of this process are similar to pyrolysis process and include hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization.

Generally, biochar is produced in dry carbonization processes, pyrolysis or gasification of biomass, while hydrochar is produced in HTC from sludge in water, under pressure. Biochar and hydrochar have considerably different chemical and physical properties.

HTC of organic matter and production of new chemicals and fuel has significantly increased the interest of researches in the last 10 years, considering that yields of products are in following ratios: 50 - 80 % dry fraction, 5 - 20 % liquid fraction and 2 - 5 % gas fraction. However, this ratio is dependent on type of raw material and reaction conditions (temperature, retention time, DM content), which is proved to be a problem, since it is almost impossible to determine and predict the composition of sludge from WWTPs.

4. NUTRIENTS RECOVERY IN CIRCULAR ECONOMY

One of the advantages of wastewater and wastewater sludge utilization is their nutrients content. Even after treatment, wastewater contains organic matter and high concentrations of valuable nutrients that are contained in any fertiliser, and which can be recycled. Biological solid matter (sludge and faeces) contain various micro-nutrients, such as cobalt, copper, iron, manganese, molybdenum and zinc, which are critical for optimal plant growth. It is estimated that 1000 m^3 of municipal wastewater used for irrigation of one hectare of agricultural land can contribute with 16 - 62 kg total N, 4 - 24 kg P and 2 - 69 kg P [24]. That is why it is possible to replace chemical fertilisers, i.e. enable available plant nutrients to poor farmers.

In recent years, there were several technologies developed for P recycling from wastewater sludge ash, including pyrolytic and other wet processes. In pyrolytic processes, metals are partially removed ash and P remains in form of insoluble apatite [25], which is not available for plants and has a low value as fertiliser. In wet processes, ash from wastewater sludge is treated with acid or base, to dissolve P, which can then be recovered through precipitation as ammonium-, calcium-, sodium-, iron- or aluminium phosphate, whose forms are almost identical to the ones that are present in mineral phosphate fertilisers.

Ash generated during incineration process can also be sustainably utilized in construction sector. Potential advantages in construction industry and construction material production industry are immobilization of heavy metals in the matrix of new material through incineration, oxidation of organic matter and destruction of pathogens during incineration. It

should be noted that ash utilized in construction industry needs to fulfil all standards and criteria related with construction materials. This requires technology design for ash stabilization by utilization of appropriate reactants, which provide necessary strength and simultaneously do not present a treat to the environment [26].

All the above-mentioned processes require a sustainable component, such as recovery and reuse of nutrients. A good example for reuse in CE is a process developed during the project SUSAN (Sustainable and Safe Re-use of Municipal Sewage Sludge for Nutrient Recovery) [27] – a thermochemical process which removes heavy metals and significantly increases the solubility of P. The principle of the process is shown in figure 4.

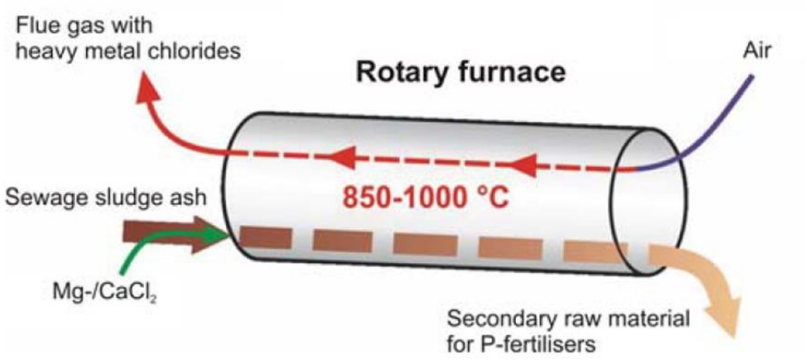


Figure 4. Thermochemical process developed in project SUSAN [27]

It consists of two steps: first is mono-incineration of wastewater sludge for energy recovery and destruction of organic pollutants. The second step removes heavy metals and nutrients (P) are transformed in a form available for plants. This step is conducted at 850-1000 °C. Thermochemically treated ash contains around 20 % P_2O_5 in biologically available form and is commercially acceptable for production of fertilisers, such as P-, PK- or NPK fertilisers. Nutrients (P, Ca, Mg and K) that were present in wastewater sludge are transferred to fertiliser through ash and can be recovered with this technology.

5. CONCLUSION

WWTPs aim to achieve sustainable wastewater sludge management strategies due to legal frameworks which prohibit management methods such as landfilling. However, because of increased growth in population number, there is a increase in amounts of generated sludge. This leads to overflowing of WWTPs capacities to hold the generated sludge, which requires expansion and upgrades to bear the load that is expected in the near future. Two components in wastewater sludge are technically and economically cost-effective for recycling: nutrients (mainly N, P, K) and energy.

Wastewater sludge composition, which includes a wide range of organic and inorganic compounds that affect the environment, determines its technological and utilization options. However, it is almost impossible to construct a universal facility which can treat every type of wastewater sludge, due to various contents of wastewater sludge characteristics.

Considering the fact that landfilling and utilization of wastewater sludge as soil amendment will in the near future no longer be acceptable, it is necessary to find a feasible solution to manage growing amounts of wastewater sludge.

This paper described some of the currently available thermal treatment technologies that are present on the market. It can be concluded that technologies that combine efficient mass and volume reduction of wastewater sludge with production of marketable products present preferable solutions, especially in the framework of circular economy, which requires the closure of energy and nutrients cycle. Development and selection of optimal treatment for wastewater sludge requires customization, which can maximize the benefits of wastewater sludge management and utilization. This can especially be applicable in decentralized wastewater treatment plants that have more controlled input stream. Moreover, it requires development of operational systems adjusted to local terms. That is why it is necessary to implement legal framework suitable for local conditions, which enables long-term service of technology utilization for wastewater sludge treatment.

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ADSORPCIJA OCTENE KISELINE NA OTPADU IZ METALURŠKE PROIZVODNJE

ADSORPTION OF ACETIC ACID ON THE WASTE FROM METALLURGICAL PRODUCTION

Zoran Glavaš*, Anita Štrkalj*

* Sveučilište u Zagrebu, Metalurški fakultet, Sisak, Hrvatska

autor za korespondenciju: Zoran Glavaš, e-mail: glavaszo@simet.hr

Izvorni znanstveni rad

SAŽETAK

U ovom radu određivana su adsorpcijska svojstva otpada iz metalurške proizvodnje. Kao adsorbensi su korišteni otpadna kalupna mješavina i anodna prašina, a kao adsorbat octena kiselina. Dobiveni rezultati ukazuju na to da otpadna kalupna mješavina ima veći kapacitet adsorpcije u odnosu na anodnu prašinu. Ravnotežni eksperimentalni podaci su obrađeni Freundlichovom i Langmuirovom izotermom. Kinetika procesa opisana je s Lagergrenovim i Ho i McKey modelima. Dobiveni rezultati su pokazali da se adsorpcija octene kiseline na otpadnoj kalupnoj mješavini odvijala prema Freundlichovom i Lagergrenovom modelu, a adsorpcija octene kiseline na anodnoj prašini prema Langmuirovom i Ho i McKey modelu.

***Ključne riječi**: otpadna kalupna mješavina, anodna prašina, octena kiselina, adsorpcija, kinetika, ravnoteža*

ABSTRACT

In this paper, adsorption properties of waste from metallurgical production were investigated. Waste foundry moulding sand and anode dust were used as adsorbents. Acetic acid was used as adsorbate. The obtained results show that the waste foundry moulding sand has a higher adsorption capacity than anode dust. The equilibrium experimental data were processed using Freundlich and Langmuir isotherms. The kinetics of the process was described by Lagergren and Ho and McKey models. The obtained results show that the adsorption of acetic acid on waste foundry moulding sand takes place according to

Freundilich and Lagergrenovom model. Adsorption of acetic acid on the anode dust takes place according to Langmuir and Ho and McKey model.

***Keywords**: waste foundry moulding sand, anode dust, acetic acid, adsorption, kinetic, equilibrium*

1. UVOD

Intenzivna upotreba organskih tvari u svakodnevnom životu uzrokuje velike probleme u okolišu [1]. Industrije poput kemijske, tekstilne, prehrambene i sl. u svojim proizvodnim procesima, ali i gotovim proizvodima imaju organske tvari. Uslijed proizvodnog procesa znatnija količina organskih tvari odlazi u otpadne vode. Octena kiselina je jedan od takvih zagađivača. Koristi se u proizvodnji gnojiva, proizvodnji bezalkoholnih pića, praška za pecivo, itd. [2]. Povećana koncentracija ove kiseline u vodama ima štetan utjecaj na biljni i životinjski svijet [3].

Procesi uklanjanja štetnih primjesa iz otpadnih voda vrlo dobro su istraženi. Međutim istraživanja se provode i dalje radi smanjenja troškova pročišćavanja. Jedan od često primjenjivanih procesa je adsorpcija. To je relativno jednostavan, efikasan i često primjenjivan postupak pročišćavanja otpadnih voda. Na ovaj način se najčešće uklanjaju teški metali, ali i organske tvari [4 – 7]. Kao adsorbens se obično koristi aktivni ugljen [8, 9]. Cijena aktivnog ugljena je relativno visoka te se zbog toga, unatoč njegovim izvrsnim adsorpcijskim svojstvima, istražuju i drugi jeftiniji materijali. U novije vrijeme raste interes za otpadnim produktima ili nusproduktima različitih grana industrije.

Metalurška industrija je jedna od industrija u kojima nastaju znatne količine otpadnih produkata, poput troske, otpadne kalupne mješavine, mulja, različitih vrsta prašine itd. U dosadašnjim istraživanjima pokazalo se da su otpadna kalupna mješavina i anodna prašina dobri adsorbensi [10 – 12]. Anodna prašina je otpad koji nastaje pri proizvodnji ugljičnih anoda koje se koriste u proizvodnji aluminija. Osnova te prašine je ugljik (> 90 %) uz manju prisutnost pratećih elemenata (Si, Al, S, Fe itd.). Zbog neodgovarajućeg kemijskog i granulometrijskog sastava, prašina se ne vraća u proces dobivanja anoda ili iskorištava u bilo kojem drugom koraku proizvodnje aluminija te se odlaže na odgovarajućim odlagalištima [13, 14]. Kalupna mješavina upotrebljava se za izradu kalupa u koje se lijeva tekući metal radi proizvodnje odljevaka. Sastoji se od ljevaoničkog pijeska (> 90 %), vode, bentonita (gline) i male količine aditiva (ugljena prašina, žitarice i sl.). Tijekom proizvodnog procesa gubi na kvaliteti i nakon određenog broja ciklusa upotrebe postaje otpad [15].

U ovom radu korišteni su anodna prašina i otpadna kalupna mješavina kao adsorbensi za uklanjanje octene kiseline iz vodene otopine. U radu je praćen utjecaj prirode adsorbensa, početne koncentracije kiseline i vremena kontakta adsorbens/adsorbat. Eksperimentalni podaci opisani su s dvije najčešće korištene izoterme (Langmuir i Freundlich) i dva najčešće korištena kinetička modela (za reakcije pseudo prvog i pseudo drugog reda).

2. EKSPERIMENTALNI DIO

Uzorci koji su korišteni u ovom radu predstavljaju otpadni materijal koji nastaje u postupku proizvodnje anoda namijenjenih za proizvodnju aluminija, te proizvodnji odljevaka.

Uzorci su nakon procesa uzorkovanja homogenizirani i sušeni na 105°C do konstantne mase. Nakon toga provedeno je određivanje kemijskog sastava klasičnom kemijskom analizom i spektrometrijskom metodom.

„*Batch*“ eksperiment proveden je tako da je 1 g anodne prašine stavljen u kontakt sa 100 mL octene kiseline početnih koncentracija 0,875; 1,75; 2,625; 5,25 i 7,69 mol/L na 20 °C. Sustav adsorbens/adsorbat bio je u kontaktu 5, 10, 15, 20 i 30 minuta kod konstantnog pH. Nakon 30 minuta provedena je filtracija preko filtar papira plava vrpca. Koncentracija kiseline u filtratu određena je titracijom sa 0,5 mol/L NaOH uz fenolftalein kao indikator. Na isti način je proveden eksperiment s otpadnom kalupnom mješavinom kao adsorbensom.

Tri paralelna mjerenja provedena su za svaki eksperiment i rezultati su prikazani kao srednja vrijednost.

Kapacitet adsorpcije octene kiseline na otpadnoj kalupnoj mješavini, odnosno anodnoj prašini određen je pomoću jednadžbe (1):

$$q_e = \frac{c_0 - c_e}{m} \cdot V \tag{1}$$

ghje je:

q_e – ravnotežni kapacitet adsorpcije octene kiseline na korištenim adsorbensima (mol/g),
c_0 - početna koncentracija octene kiseline (mol/L),
c_e - ravnotežna koncentracija octene kiseline (mol/L),
m - masa adsorbensa (g),
V - volumen octene kiseline (L).

Eksperimentalni podaci obrađeni su pomoću dva najčešća modela izotermi (Langmuir i Freundlich). Opći oblik Langmmuirove izoterme prikazan je jednadžbom (2), a Freundlichove izoterme jednadžbom (3):

$$q_e = \frac{q_m \cdot K_L \cdot c_e}{1 + K_L \cdot c_e} \tag{2}$$

gdje je:
q_m- maksimalni adsorpcijski kapacitet octene kiseline na korištenim adsorbensima (mol/g),
K_L- Langmuirova konstanta (L/mol).

$$q_e = K_F \cdot c_e^{1/n} \tag{3}$$

gdje su:
K_F i n – Freundlichove konstante.

Kinetika adsorpcije opisana je Lagergrenovim i Ho i McKay kinetičkim modelima. Lagergrenov model prikazan je jednadžbom (4), a Hoov i McKayev model jednadžbom (5):

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \tag{4}$$

gdje je:
q_t- adsorpcijski kapacitet octene kiseline na korištenim adsorbensima u vremenu t (mol/g),
t – vrijeme (min),
k_1 – konstanta brzine reakcije prvog reda (1/min).

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (5)$$

gdje je:
k_2 – konstanta brzine reakcije drugog reda (g/(mol·min).

Za određivanje parametara adsorpcijskih izotermi i kinetičkih konstanti korištena je linearna regresijska analiza.

3. REZULTATI I DISKUSIJA

3.1. Utjecaj prirode adsorbensa

Kemijski sastavi otpadne kalupne mješavine i anodne prašine prikazani su u tablicama 1 i 2.

Tablica 1. Kemijski sastav otpadne kalupne mješavine

Kemijski sastav otpadne kalupne mješavine	SiO_2	Fe	Al_2O_3	Ca	C	Mg	Cr	Mn
Udio, mas.%	96,1	2,57	0,85	0,31	0,12	0,03	0,009	0,01

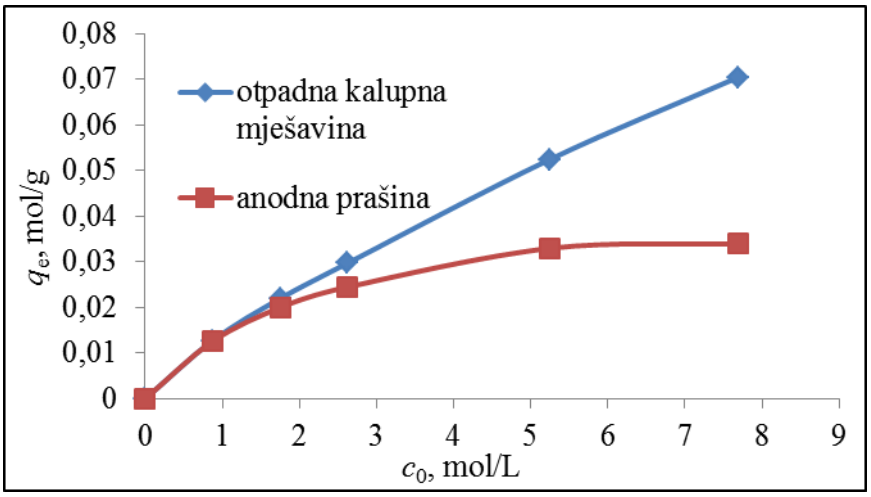
Tablica 2. Kemijski sastav anodne prašine

Kemijski sastav anodne prašine	C	Si	Al	S	Fe	Na	V	Ca
Udio, mas.%	94,54	1,73	1,69	1,50	0,34	0,089	0,072	0,044

Iz tablica 1 i 2 vidljivo je da se otpadna kalupna mješavina uglavnom sastoji od SiO_2 što je i očekivano budući da je osnovni sastojak kalupne mješavine kvarcni pijesak (SiO_2). Anodna prašina u svom sastavu sadrži najviše ugljika (94,54 %) što je također očekivano budući da je anodna prašina otpad pri proizvodnji ugljičnih anoda. U oba slučaja uz osnovnu komponentu u ispitivanim adsorbensima nalazi se i mala količina pratećih elemenata. Prateći elementi su u otpadnu kalupnu mješavinu došli tijekom procesa proizvodnje odljevaka (lijevanja i skrućivanja metala kao i rušenja kalupa). Za vrijeme proizvodnje odljevaka talina reagira s kisikom iz zraka tvoreći oksidi sloj na površini odljevka koji prilikom rušenja kalupa u određenoj mjeri otpada s odljevka i ostaje u mješavini. Ostali elementi u otpadnoj kalupnoj mješavini mogu biti sastavni dio pijeska ili potječu iz taline ulivene u kalup koja je reagirala s kalupnom mješavinom ili prodrla u nju. Prateći elementi u anodnoj prašini sastavni su dio koksa od kojeg se izrađuju anode.

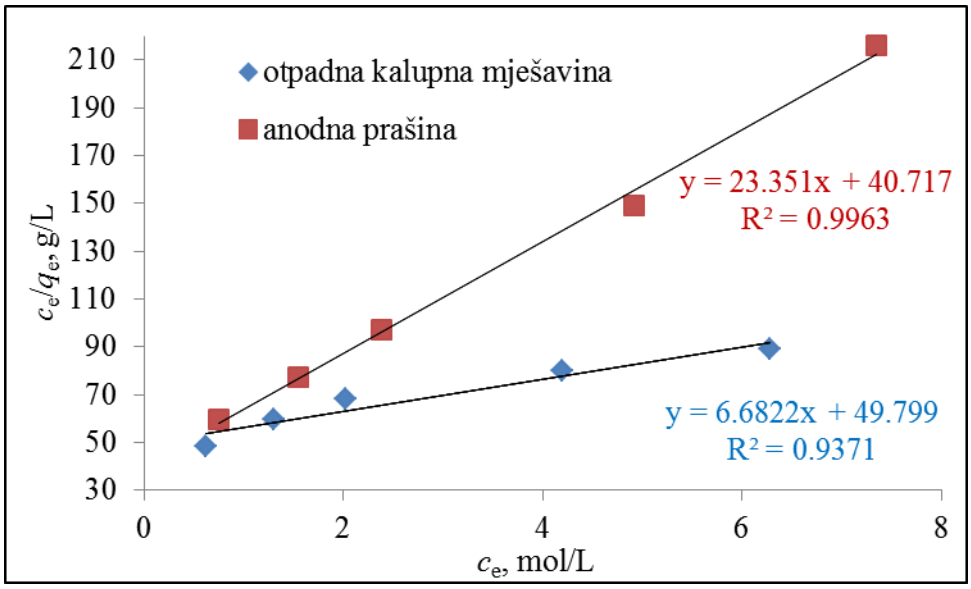
3.2. Utjecaj početne koncentracije octene kiseline

Utjecaj početne koncentracije octene kiseline na ravnotežni kapacitet adsorpcije (q_e) prikazan je na slici 1.

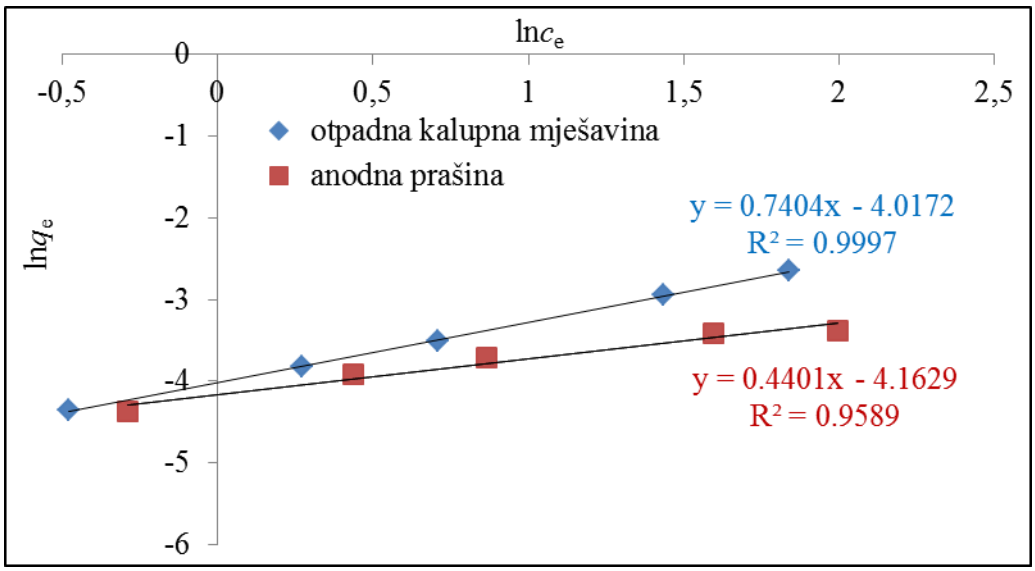


Slika 1. Utjecaj početne koncentracije octene kiseline na ravnotežni kapacitet adsorpcije (q_e)

Iz slike 1 vidljivo je da kapacitet adsorpcije otpadne kalupne mješavine raste s porastom koncentracije octene kiseline. Povećanjem koncentracije otopine octene kiseline povećava se i broj molekula kiseline u otopini te je veća mogućnost vezanja spomenutih molekula. Kapacitet adsorpcije vjerojatno raste sve dok ima dovoljno slobodnih mjesta na površini adsorbensa. Kapacitet adsorpcije anodne prašine raste s porastom početne koncentracije octene kiseline. Međutim, daljnjim porastom koncentracije kiseline kapacitet stagnira. Razlog za to je vjerojatno popunjavanje praznih mjesta na površini anodne prašine. Također se može primijetiti da je kapacitet adsorpcije otpadne kalupne mješavine veći od kapaciteta adsorpcije anodne prašine. Do ove pojave vjerojatno dolazi i zbog prirode adsorbensa. Naime otpadna kalupna mješavina u svom sastavu sadrži pijesak (SiO_2), nešto bentonita (gline) i ugljene prašine. Poznato je da su sve navedene komponente dobri adsorbensi [7, 9, 16]. Ravnotežni eksperimentalni podaci opisani su s Langmuirovom i Freundlichovom izotermom (slike 2 i 3). Karakteristične konstante navedenih izotermi, kao i koeficijenti determinacije dobiveni iz jednadžbi pravaca, prikazani su u tablici 3.



Slika 2. Langmuirova adsorpcijska izoterma za adsorpciju octene kiseline na otpadnoj kalupnoj mješavini i anodnoj prašini



Slika 3. Freundlichova adsorpcijska izoterma za adsorpciju octene kiseline na otpadnoj kalupnoj mješavini i anodnoj prašini

Tablica 3. Adsorpcijske konstante i koeficijenti determinacije za adsorpciju octene kiseline na otpadnoj kalupnoj mješavini i anodnoj prašini

	Langmuir			Freundlich		
Adsorbens	q_m, mol/g	K_L, L/mol	R^2	n	K_F	R^2
Otpadna kalupna mješavina	0,149	0,135	0,9371	1,35	0,0180	0,9997
Anodna prašina	0,043	0,571	0,9963	2,27	0,0161	0,9589

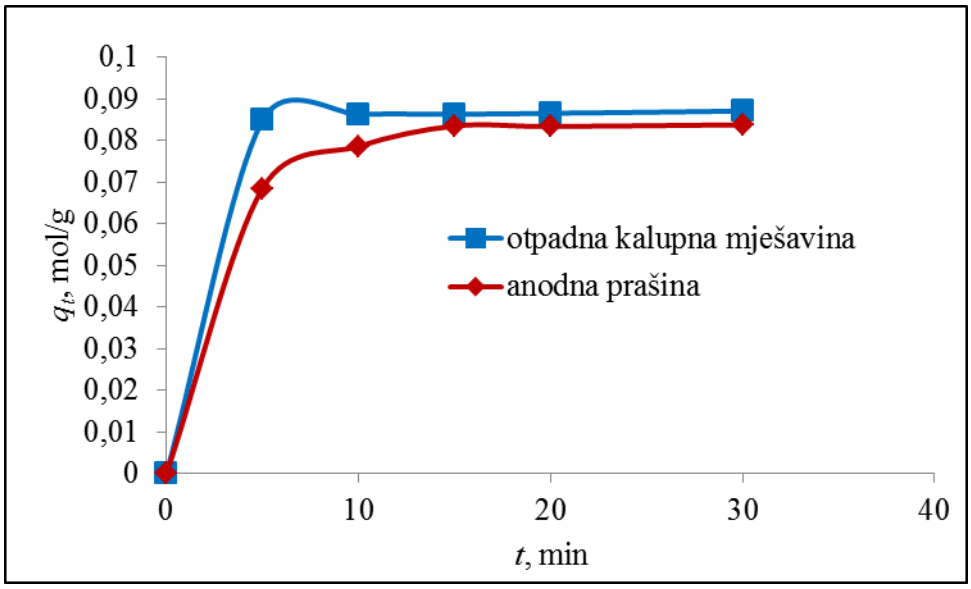
Prema podacima u literaturi koeficijent determinacije pokazuje koji adsorpcijski model je reprezentativniji za opis adsorpcijskog procesa [17]. Ukoliko se adsorpcija opisuje Langmuirovim modelom vjerojatno se odvija kemisorpcija, a Freundlichov model ukazuje na fizikalnu adsorpciju [18]. Usporedbom koeficijenata determinacije ispitivanih sustava (slike 2 i 3 i tablica 3) vidljivo je da je navedeni koeficijent veći za adsorpciju octene kiseline na otpadnoj kalupnoj mješavini prema Freundlichvom modelu dok je za adsorpciju octene kiseline na anodnoj prašini veći za Langmuirov model. Ti podaci ukazuju na to da je adsorpcija octene kiseline na otpadnoj kalupnoj mješavini fizikalni proces, dok se adsorpcija octene kiseline na anodnoj prašini odvija kao kemisorpcija. Ovu činjenicu potkrjepljuju i rezultati dobiveni prilikom praćenja utjecaja koncentracije kiseline na adsorpciju. Naime, kapacitet adsorpcije sustava otpadna kalupna mješavina / octena kiselina raste s porastom koncentracije kiseline. Općenito, tijekom fizikalne adsorpcije uslijed slabih fizikalnih sila između adsorbiranih tvari i površine adsorbensa dolazi do istovremene adsorpcije i desorpcije adsorbata, što je i ovdje slučaj [18]. Vjerojatno se veći dio molekula (iona kiseline) adsorbira, a manji desorbira i pri tome dolazi do blagog porasta kapaciteta adsorpcije. Kod sustava anodna prašina / octena kiselina prisutna je kemisorpcije pri čemu se molekule octene kiseline (odnosno njihovi ioni) vežu kemijski, čvrstim vezama. U tom slučaju ne dolazi do desorpcije, slobodna mjesta na površini anodne prašine su popunjena i nije moguće daljnje vezanje adsorbata [19].

Prema literaturi [20] adsorpcijski proces će se odvijati prema Langmuirovom modelu ako su mala odstupanja u kapacitetima adsorpcije koji su određeni eksperimentalno i teorijski (iz jednadžbe pravca). U slučaju sustava otpadna kalupna mješavina /octena kiselina teorijski kapacitet iznosi 0,149 mol/g dok je eksperimentalno određeni kapacitet 0,071 mol/g. Za sustav anodna prašina/octena kiselina teorijski kapacitet iznosi 0,043 mol/g, dok je eksperimentalno određeni kapacitet 0,034 mol/g. Vidljivo je da se za sustav otpadna kalupna mješavina /octena kiselina teorijski i eksperimentalni kapaciteti dosta razlikuju dok su za sustav anodna prašina /octena kiselina razlike između spomenutih kapaciteta male te bi se na osnovi toga kao i na osnovi podataka iz literature moglo zaključiti da se samo u sustavu anodna prašina /octena kiselina adsorpcija odvija prema Langmuirovom modelu.

3.3. Utjecaj vremena kontakta adsorbens/adsorbat

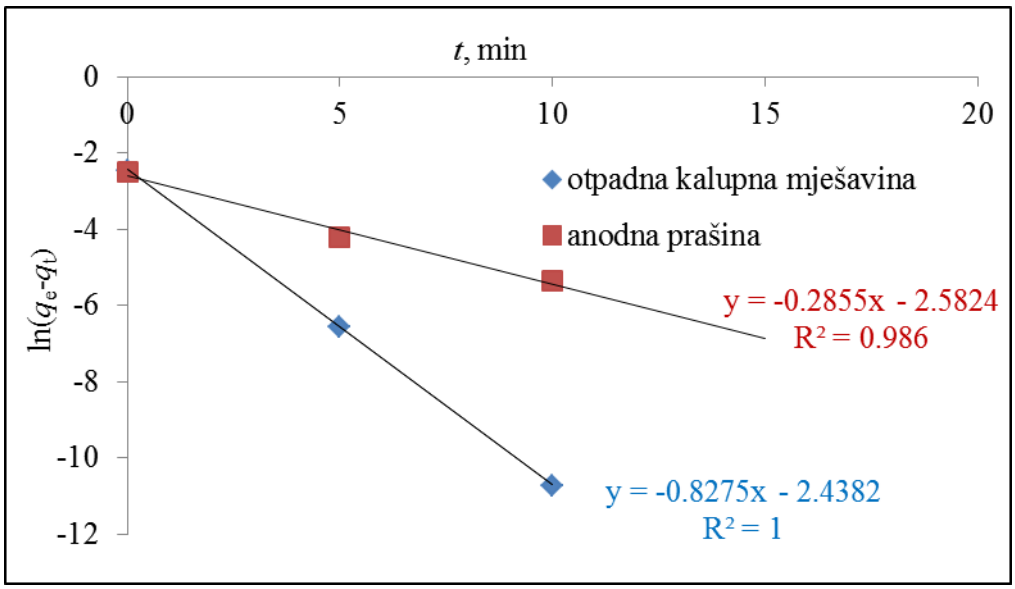
Na slici 4 prikazan je utjecaj vremena kontakta na adsorpciju octene kiseline na otpadnoj kalupnoj mješavini i anodnoj prašini.

Iz slike 4 je vidljivo da adsorpcija octene kiseline na oba ispitivana adsorbensa raste s porastom vremena kontakta u prvih 15 minuta za početnu koncentraciju octene kiseline od 0,875 mol/L. Također se može zaključiti da se adsorpcija odvija relativno brzo uz uspostavljanje ravnoteže za svega 15 minuta. Nakon toga kapacitet blago opada. Ti rezultati su u skladu s rezultatima drugih istraživača [21] prema kojima je nakon određenog vremena kontakta preostali broj slobodnih mjesta na adsorbensu teško dostupan ili odbojan za adsorbat, te iz tog razloga dolazi do stagniranja ili blagog pada kapaciteta.

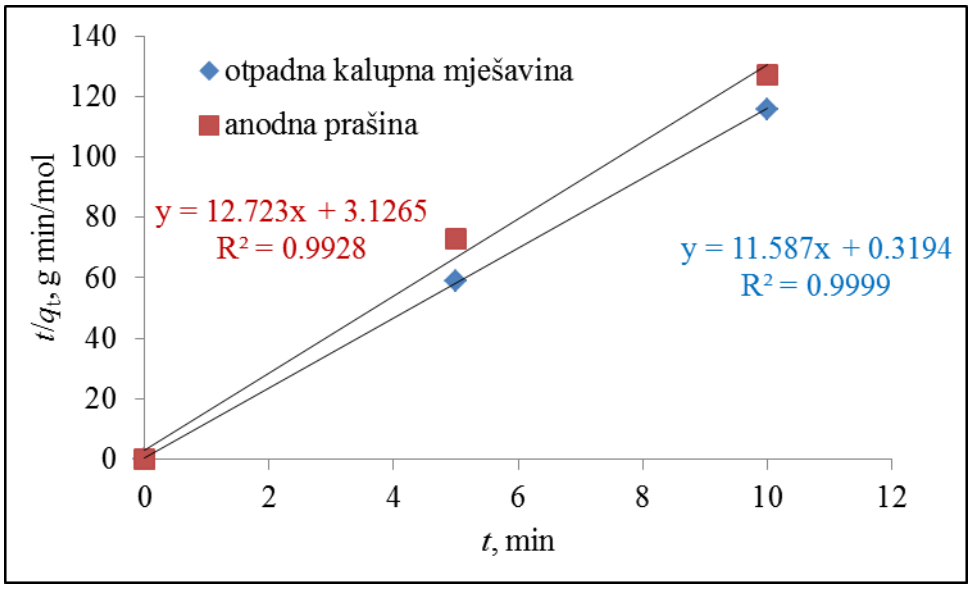


Slika 4. Utjecaj vremena kontakta na adsorpciju octene kiseline na otpadnoj kalupnoj mješavini i anodnoj prašini pri početnoj koncentraciji od 0,875 mol/L

Eksperimentalni podaci testirani su na dva najčešće korištena kinetička modela, a rezultati slaganja modela s eksperimentalnim podacima prikazani su na slikama 5 i 6.



Slika 5. Lagergrenov kinetički model za sustave otpadna kalupna mješavina / octena kiselina i anodna prašina / octena kiselina



Slika 6. Ho i McKayev kinetički model za sustave otpadna kalupna mješavina / octena kiselina i anodna prašina / octena kiselina

U tablici 4 prikazane su karakteristične kinetičke konstante za ispitivane modele. Prema tablici 4 vidljivo je da su koeficijenti determinacije oba kinetička modela za ispitivane sustave vrlo slični. Prema literaturi [22] veličina koeficijenta determinacije govori o jakosti veze među promatranim varijablama. Prema tome je Lagergrenov model reprezentativniji za opis kinetike sustava otpadna kalupna mješavina / octena kiselina jer ima veću vrijednost koeficijenta determinacije dok Ho i McKayev model bolje opisuje sustav anodna prašina / octena kiselina. Prema literaturi adsorpcija u sustavima koji se bolje opisuju Lagergrenovim modelom obično je fizikalne, a prema Ho i McKayevom modelu kemijske prirode [18, 23, 24]. Dobiveni rezultati istraživanih sustava u ovom radu u skladu su s literaturnim podacima kao i ranije navedenim tvrdnjama.

Tablica 4. Karakteristične kinetičke konstante za sustave otpadna kalupna mješavina / octena kiselina i anodna prašina / octena kiselina

	Lagergrenov model			Ho i McKayev model		
Adsorbens	$q_{e,}$ mol/g	$k_{1,}$ 1/min	R^2	$q_{e,}$ mol/g	k_2, g/(mol·min)	R^2
Otpadna kalupna mješavina	0,087	0,8275	1	0,086	0,023	0,9999
Anodna prašina	0,076	0,2855	0,9860	0,079	0,020	0,9928

4. ZAKLJUČAK

Ispitivanja provedena na sustavima otpadna kalupna mješavina / octena kiselina i anodna prašina / octena kiselina ukazuju da adsorpcija ovisi o prirodi adsorbensa, početnoj koncentraciji kiseline i vremenu kontakta. Dobiveni rezultati prikazuju da otpadna kalupna mješavina ima veći kapacitet adsorpcije za octenu kiselinu od anodne prašine. Povećanje koncentracije octene kiseline u intervalu od 0,875 do 7,69 mol/L rezultira povećanjem kapaciteta adsorpcije otpadne kalupne mješavine, dok kapacitet adsorpcije anodne prašine stagnira pri višim koncentracijama kiseline. Sustav otpadna kalupna mješavina / octena kiselina bolje se opisuje Freundlichovom, a sustav anodna prašina / octena kiselina Langmuirovom izotermom. Lagergrenov kinetički model bolje opisuje sustav otpadna kalupna mješavina / octena kiselina dok Ho i McKeyev model bolje opisuje sustav anodna prašina / octena kiselina.

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AN EMPIRICAL APPROACH FOR MEASURING THE IMPACT OF ACCESS TO CURBSIDE RECYCLING ON QUANTITY RECYCLED IN PRESPA PARK WATERSHED

Dorina Grazhdani*

* Agricultural University of Tirana, Faculty of Economy & Agribusiness, Tirana, Albania

corresponding author: Dorina Grazhdani, e-mail: d.grazhdani@yahoo.com

Original scientific paper

ABSTRACT

In this study is developed and employed an empirical approach to measure the extent to which curbside access affects quantity recycled. The empirical analysis is based on the quarterly informations derived from Prespa Park administration recycling data during 2010 - 2015. Data are used to distinguish between curbside recycling and material diverted from other recycling modes. Fixed-effects linear regressions of curbside beverage container return quantities on the percent of the population served by curbside programs and other covariates are used. Results suggest marginal increases in curbside availability increase returns at the curb, but have very small impacts on total recycled quantities of beverage containers. Specifically, a one percent increase in the percent of a village's population served by curbside programs increases total beverage container recycling returns by only 1.04 % for plastic, 0.62 % for glass, and 0.76 % for aluminum. The proposed approach can provide comprehensive information on waste management, enabling decision makers to develop integrated polices and measures for waste management over a longer period of time.

***Keywords**: curbside recycling, empirical investigation, fixed-effects linear regressions, Prespa Park*

1. INTRODUCTION

There are a broad empirical literature that examined the change in waste and recycling behavior as a function of policy variables and socioeconomic characteristics [1 - 11]. Using cross-sectional survey data, Hong et al. [12] and Hong and Adams [13] found that an increase in waste disposal fees increased curbside recycling participation and quantities recycled, but did not generate large reductions in trash. Rechovsky and Stone [14] used similar data and found that curbside programs increased total recycling rates if implemented in conjunction with mandatory recycling and unit-based waste pricing. Fullerton and Kinnaman [15] directly

measured household waste generation, and their results suggested that garbage unit pricing increased curbside recycling, volumetric compacting, and illegal dumping significantly. Callan and Thomas [16] and Kinnaman and Fullerton [17] used geographically diverse cross-sectional community level data and further examined the effects of unit pricing and recycling. An important contribution of Kinnaman and Fullerton [17] was illustrating the potential endogeneity of curbside program implementation.

Jenkins et al. [18]'s important analysis used household survey data to demonstrate that the presence of a curbside program for a given material increased the probability that over 95 percent of an average household's material would be recycled by between 25 to 50 percent. Jenkins et al. [18] further investigated the marginal effect of replacing a recycling center with a curbside program on households' propensity to recycle.

Our study differs in that it examines curbside recycling in the presence of alternatives, such as drop-off recycling depots, using a panel of aluminum, glass, and plastic beverage container returns data from Prespa Park administration. The study focused on recyclables that can be returned for refund such as beverage containers, and aimed at measuring the impact of access to curbside recycling on quantities returned to the curb, total quantities returned, and quantities returned to drop-off recycling centers.

2. EXPERIMENTAL

2.1. Case study: Prespa Park

Prespa Park is the first transboundary protected area in the Balkans established February 2nd 2000. The area contains three National Parks located in Albania, Greece, and the Republic of Macedonia, respectively (figure 1). In 2014, the Ohrid Prespa Transboundary Reserve between Albania and Macedonia was added to UNESCO's World Network of Biosphere Reserve.

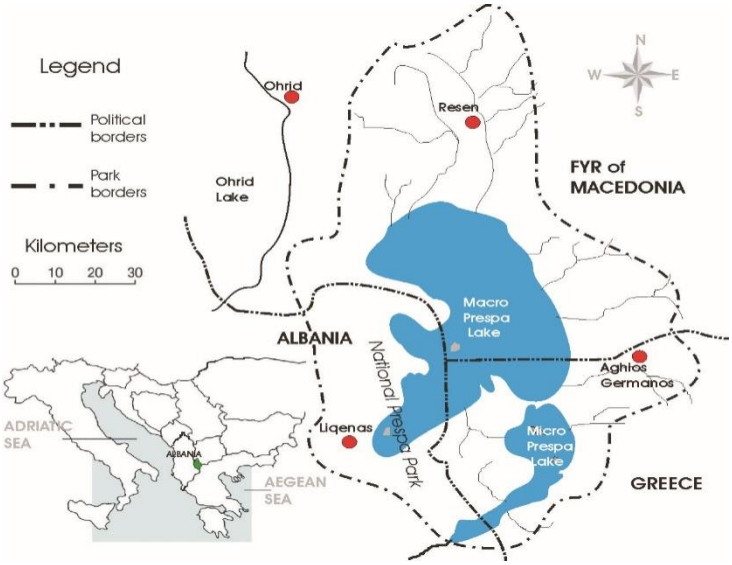


Figure 1. Prespa Park region

The Prespa Park has a population of about 24,000 inhabitants, an area of 1218.1 km^2. The distribution of villages and people located around the two Prespa lakes shows that the

latest census has counted 5634 inhabitants living in 12 villages on the Albanian side, 1569 from 13 villages on the Greek side and 16,825 inhabitants in one town (Resen with 8,748 inhabitants) and 43 villages in Macedonia [1].

The area in Prespa Park has not been covered with a sufficient waste collection system. There is an urgent need for development of functional solid waste structures, because the actual situation can have a serious impact on the environment and the agriculture in the region.

Our sample of Prespa Park administration recycling data consists of quarterly observations for the six year period 2010 - 2015. Time series variation in our data allows us to exploit panel techniques to control for unobserved heterogeneity while accounting for potential program endogeneity. This particular period is promising for exploration because curbside programs were expanding, there were no major changes to the bottle bill or its associated redemption values, and data were readily available.

The results taken by this study can enable decision makers to develop integrated policies and measures for waste management in the area over the long term.

2.2. Analysis conceptual framework

The conceptual framework used in this study shares features of the models in Kinnaman and Fullerton [17] and Jenkins et al. [18], but differs by emphasizing choices between recycling modes.

In a first stage allocation decision, the agent maximizes a weakly separable utility function over the consumption of beverages, other goods, and waste disposal services. Optimization is subject to a time/money budget constraint.

The solution to this first stage problem yields waste disposal service expenditures W and material-specific beverage container expenditures E_i. Assuming fixed prices, E_i implies beverage container quantities B_i. Assume that B_i and W are exogenous to a second stage within-group optimization over the choice of disposal method. For each material type i, total beverage quantities B_i can be recycled at the curb (CS_i), recycled at drop-off recycling centers (RC_i), or not recycled (NR_i). The latter option incorporates trash, illegal dumping, etc. Preferences among disposal methods may depend upon household characteristics α.

In this framework, subutility is maximized over disposal methods subject to a subgroup expenditure constraint and a quantity adding up constraint:

$$\begin{aligned} &\max\ (CS_i, RC_i, NR_i, \alpha) \\ &\text{s.t. } p_{CSi}\, CS + p_{RCi}\, RC + p_{NRi}\, NR \le W \\ &CS_i + RC_i + NR_i = B_i \end{aligned} \tag{1}$$

Solving the representative consumer's choice problem (1) yields a system of estimable conditional demands for each material i:

$$\begin{aligned} CS_i &= f(p_{CSi}, p_{RCi}, p_{NRi}, B_i, W, \alpha) \\ RC_i &= f(p_{CSi}, p_{RCi}, p_{NRi}, B_i, W, \alpha) \\ NR_i &= f(p_{CSi}, p_{RCi}, p_{NRi}, B_i, W, \alpha) \end{aligned} \tag{2}$$

A reduced-form version of the system of equations in (2) serves as the basis for our empirical estimation. Since we do not have data on non-recycled beverage containers, we follow Kinnaman and Fullerton [17] and estimate each material-specific system as a series of

demand equations. Since the independent variables in each equation are the same, there is no bias from estimating the system as separate equations.

2.3. Variables

To examine the impact of curbside recycling on quantities returned at the curb, total recycling quantities, and recycling center quantities, were constructed variables consistent with the conceptual framework developed above. Our key dependent variables were material-specific per capita recycled quantities of beverage containers. For example, were considered per capita kg of aluminum beverage containers recycled at the curb, recycled in total, and recycled at drop-off recycling centers.

Important explanatory variables include those that represent the time and money prices of recycling modes in (2). In this vein, the key explanatory variable was the percent of a village's population served by curbside programs. This serves as a proxy for the price of curbside recycling. Were also included recycling centers per square kilometer and two measures of recycling center hours open as proxies for the price of drop-off recycling centers.

Other independent variables included total quarterly per capita consumption of each material at the park-level, since our conceptual framework indicates that quantities recycled are a function of total beverages consumed. Were also included quarterly dummies and year dummies to account for seasonality and broad trends in the real price of beverages, beverage consumption, and the propensity to recycle.

Finally, were exploited the panel structure of the data by including fixed effects. This captures systematic differences across counties and serves as a proxy for α in our conceptual framework. Fixed-effects may represent village-specific factors such as size, location, density, and demographic characteristics like education and income.

2.4. Regression model

In short, the basic regression model for each material can be written $y_{it} = X_{it}\beta + \alpha_i + \varepsilon_{it}$, where *i* indexes the unit of observation (village) and *t* indexes time (quarters). α_i captures time invariant village-level fixed effects and ε_{it} represents the usual idiosyncratic error term. The columns of the matrix *X* include all of the preceding subsection's explanatory variables. As previously noted, the most important of these is the share of a village's population served by curbside in that period.

The regression model has three noteworthy features. First, the dependent variables are material-specific. This is important because materials vary considerably by weight and bulk, which affect the ease of recycling. Second, the dependent variables measure beverage container recycling quantities. Third, the endogeneity controls afforded by the fixed effects α_i are novel relative to the previously cited literature.

3. RESULTS AND DISCUSSION

3.1. Empirical results

3.1.1. The effect of curbside access on curbside returns

In this sub-sectionare presented results considering the most immediate impact of curbside access: to what extent does increasing curbside coverage increase the quantity of material recycled at the curb?

Results from fixed-effects linear regressions of curbside beverage container return quantities on the percent of the population served by curbside programs and other covariates are presented in table 1 (Part 1). Reschovsky and Stone [14] fail to reject the hypothesis that curbside recycling programs alone do not yield an increase in the propensity to recycle.

Results in table 1 (Part 1) indicate that the estimated impact of increasing curbside access on curbside beverage container returns is positive and statistically significant for all materials. For example, a one percent increase in the percent of a village's population served by curbside results in a 0.0023, 0.0245, and 0.0037 kg per capita increase in the quantity of aluminum, glass, and plastic beverage containers collected at the curb. For aluminum, this coefficient translates into 2.54 % of mean curbside quantity. In other words, a one percent increase in the percent of the population served by aluminum curbside programs translates roughly into a 2.54 % increase in returns of aluminum beverage containers to the curb. For glass, a one percent increase in the population served by glass curbside programs yields a 1.84 % increase in mean curbside quantity. Forplastic, the coefficient translates into a 3.41 % increase.It is important to note that all results should be interpreted as changes on the margin, conditional on average villagelevel institutions and covariates. Beatty et al. [19] also reported that access on curbside beverage container returns is positive and significant.

Table 1. Results from fixed-effects linear regressions

Variable description	Part 1: Quantity recycled at the curb			Part 2: Quantity recycled in total			Part 3: Quantity recycled at recycling centers		
	Aluminium	Glass	Plastic	Aluminium	Glass	Plastic	Aluminium	Glass	Plastic
Percent of the population served by curbside	0.0023*** (2.56)	0.0245*** (3.89)	0.0037*** (2.87)	0.0031* (1.52)	0.0389* (2.93)	0.0209*** (2.54)	0.0004 (0.02)	-0.0187*** (-2.87)	-0.0008** (-1.37)
Number of recycling centers per area	-0.4532 (-1.54)	-9.0547*** (3.78)	-2.2189*** (-3.97)	3.8794*** (3.07)	27.5487*** (5.66)	0.4285 (0.67)	4.0986*** (3.89)	36.5647*** (7.98)	2.5683*** (3.65)
Village average number of recycling centers hours open	0.0019** (2.21)	0.0357*** (3.65)	0.0004 (0.44)	0.0005 (0.08)	0.0789*** (0.08)	0.0091** (1.98)	-0.0018 (-0.28)	0.0654*** (3.07)	0.0058** (1.83)
Average temperature	0.0002 (0.45)	-0.0007 (1.08)	-0.0003*** (-2.21)	0.0002*** (5.54)	-0.0006 (-0.78)	-0.0002 (-0.67)	0.0018*** (6.05)	0.0002 (1.57)	0.0002 (1.85)
Second quarter dummy	-0.0387* (-2.07)	0.0659 (0.56)	0.0287* (2.07)	-0.1187 (-1.56)	0.3552 (1.12)	0.0465* (1.63)	-0.0892 (-0.89)	0.2387 (0.89)	0.008 (0.65)
Third quarter dummy	-0.026 (-0.78)	0.2367 (1.37)	0.0644*** (3.77)	0.0964 (0.88)	0.9873*** (3.09)	0.1089*** (4.08)	0.0965 (1.54)	0.7329*** (2.21)	0.0657** (2.26)
Fourth quarter dummy	-0.0032 (-0.65)	-0.007 (-0.08)	0.0267** (2.08)	0.0634* (1.55)	0.0786 (0.54)	0.0881*** (4.96)	0.0667** (2.32)	0.0821 (0.62)	0.0567*** (4.02)
2010 year dummy	-0.0052 (-1.23)	0.0987 (-1.56)	-0.0044 (-0.64)	-0.18599*** (-4.78)	-0.3377** (-2.89)	0.0896*** (4.07)	-0.23178*** (-4.08)	-0.3217** (-2.55)	-0.06521*** (5.02)
2011 year dummy	0.0021 (0.52)	-0.1458* (-2.13)	0.0087 (0.75)	-0.1937*** (-4.55)	-0.5632*** (-3.87)	0.0990*** (6.85)	-0.2579*** (-5.08)	-0.3587*** (-3.08)	0.0885*** (6.23)
2012 year dummy	0.0054 (0.77)	-0.1865** (-2.65)	0.0005 (0.06)	-0.2168*** (-6.08)	-0.689*** (-5.07)	0.0965*** (7.02)	-0.2369*** (-5.54)	-0.4561*** (-4.14)	0.0960*** (7.07)
2013 year dummy	0.0264** (2.65)	-0.0108 (-0.18)	0.0398*** (3.07)	-0.2088*** (-3.99)	-0.321 (-1.64)	0.1155*** (8.77)	-0.2037*** (-4.51)	-0.3254 (-1.96)	0.0990*** (8.06)
2014 year dummy	0.0446*** (5.02)	0.6633*** (2.04))	0.0891 (1.76)	-0.3336*** (-5.96)	0.7563* (1.9)	-0.0463 (-0.45)	-0.3388*** (-6.66)	0.0789 (0.28)	-0.1109* (-2.04)
Per capita total quantity sold	0.0657** (3.07)	0.0311 (0.87)	0.0496 (1.65)	0.3309** (2.33)	0.265 (1.11)	0.1753*** (4.88)	0.2098 (1.32)	0.1032 (1.32)	0.1366*** (4.67)
Constant	-0.0963 (-1.32)	1.2318* (2.05)	0.3561*** (3.28)	0.0655 (0.66)	4.5631*** (4.01)	0.0896 (0.74)	0.2361 (0.65)	2.9988*** (4.88)	-0.3210*** (-3.08)
Fixed Effects	68 village-specific fixed effects			68 village-specific fixed effects			68 village-specific fixed effects		
R-squared	0.87	0.91	0.85	0.94	0.85	0.91	0.92	0.93	0.87

,, and * indicate statistical significance at the 1 % , 5 %, and 10 % levels of significance. In parentheses appear the *t*-statistics.

Increasing the number of recycling centers per area has a negative and significant effect on curbside returns for both glass and plastic beverage containers. This intuitive result provides some preliminary evidence that curbside and recycling center programs may be substitutes. Similarly, an increase in the variability of hours open is significantly negatively associated with aluminum, glass, and plastic curbside returns. However, an increase in the average number of drop-off center hours open is positively associated with curbside returns for aluminum and glass. Perhaps center hours induce spillover effects from increased recycling awareness. All other explanatory variables have the anticipated signs. Increases in total beverage container sales are associated with increased curbside quantities, and significantly so for aluminum. This corresponds well with the findings of Beatty et al. [19].

Curbside returns are seasonal and tend to increase over time for all materials, although non-linearly.

3.1.2. The effect of curbside access on total recycling returns

Results of the preceding sub-section indicated that, on the margin, increased curbside access is associated with increased beverage container returns at the curb. However, for policymakers a more relevant question is whether curbside programs increase total beverage container recycling.

Results from fixed-effects linear regressions of total beverage container return quantities on the percent of the population served by curbside programs and other covariates are presented in table 1 (Part 2).

Results in table 1 (Part 2) indicate that the estimated impact of increasing curbside access on total beverage container returns is positive, but small. The result is not consistent with Jenkins et al. [18], who detect no significant impact of curbside access on total recycling returns. Beatty et al. [19] also found that increasing curbside access has a positive, but a small effect on total recycling return. Meanwhile, Kinnaman and Fullerton [17], Blaine et al. [20], Dahlen et. al. [21] and Woodard et. al. [22], found that curbside recycling programs have a positive and significant effect on total recycling returns. In fact, we fail to reject a null hypothesis of no relationship between increased curbside access and total returns. For plastic, the coefficient translates into 1.04 % of mean total quantity. In other words, a one percent increase in the percent of the population served by plastic curbside programs translates roughly into a 1.04 % increase in total returns of plastic beverage containers. The aluminum and glass coefficients are translated into 0.62 % and 0.76 % increases in total returns, respectively.

In contrast to the results for a marginal expansion of curbside, table 1 (Part 2) indicates that the effects of recycling center characteristics on total recycling are substantial. For example, recycled quantities increase significantly with the average number of open hours for both glass and plastic beverage containers. Further, increasing the density of recycling centers has a large and significant impact on aluminum and glass returns.

3.1.3. The effect of curbside access on recycling center returns

Results from fixed-effect linear regressions of recycling center beverage container return quantities on the percent of the population served by curbside programs and other covariates are presented in table 1 (Part 3). Results in table 1 (Part 3) indicate that the estimated impact of expanding curbside access on drop-off recycling center returns is negative for glass and plastic beverage containers. Results are economically and statistically

significant for glass, and perhaps economically significant for plastic. This finding is also consistent with previous findings [19, 20].

Table 1 (Part 3) also indicates that the effects of recycling center characteristics on recycling center returns are substantial. For example, drop-off returns of all materials increase significantly when the density of recycling centers increases. Drop-off quantities of glass and plastic also increase considerably when the average number of open hours increases on the margin.

Note also that the collective outcomes of tables 1 satisfy an important adding-up identity. For each material, the marginal total impact of expanded curbside access is equal to the marginal increase in curbside returns less any marginal diversion from drop off recycling centers. This result is similar to that presented in Beatty et al. [19] and Harderet al. [23].

The adding-up conditions allow us to further interpret our diversion results. Most notably, approximately 72 % of incremental glass curbside quantities are cannibalized from existing drop-off recycling centers. This corresponds well with the opinion of Beatty et al. [19]. Despite the fact that increasing curbside access for glass recyclables does increase glass beverage container curbside returns, the majority of incremental quantities come from materials previously recycled at recycling centers. Net recycling gains are small. Further, approximately 24 % of incremental curbside plastic beverage containers are cannibalized from existing recycling centers.

3.2. Further exploration

The analyses of the preceding sub-sections presented evidence that cannibalization between recycling modes is occurring, with economically significant effects for glass and plastic. In this section, is extended our analysis to study the impact of structural and demographic characteristics on the diversion response. To this end, in this section are augmented the diversion regressions (summarized in table 2) with time variant village-level socioeconomic variables, such as the median family income, unemployment, and population density in a given village. For each material, are included these regressors directly and interacted with the curbside access variables.

Results from fixed-effects linear regressions of recycling center beverage container return quantities on the percent of the population served by curbside programs, socioeconomic interactions, and other covariates are presented in table 2. Note that identification still comes from village-specific variation over time, since are retained fixed-effects. Computed standard errors are heteroskedastic-consistent and *t*-statistics appear in parentheses.

The interpretation of the results in table 2 is begun by considering the coefficients on the uninteracted curbside access variables. Holding median family income, unemployment, and population at zero, the marginal effect of an increase in the percent of the population served by curbside on drop-off recycling center beverage container returns is negative for every material. The results are statistically significant for aluminum and plastic and similar in magnitude to the significant results in table 1 (Part 3) for glass. Similar results are obtained and by Beatty et al. [19]. While too much emphasis should not be placed on interpreting outcomes conditioned on zeroed socioeconomic variables, results are at least suggestive that economically significant cannibalization between recycling streams is robust across specifications.

Results in table 2 also show that the interaction between population density and curbside access is significant for plastic. This result confirms that revealed by Beatty et al. [19] and Blaine et al. [20]. An intuitive interpretation of the positive coefficient is that the diversionary response becomes stronger (more negative) as density decreases. In other words,

consumers are more likely to forego redemption payments in exchange for convenience, particularly for bulky items like plastic containers, when population density decreases.

Table 2. Socioeconomic regressions results of drop-off center quantities

Variable description	Aluminium	Glass	Plastic
Percent of the population served by curbside	-0.0264** (-2.56)	-0.0285 (-1.99)	-0.0065** (-2.78)
Density * Percent served by curbside	-0.0015 (-1.09)	0.0089 (-1.63)	0.0034*** (2.67)
Unemployment * Percent served by curbside	0.0002 (0.62)	0.0033*** (2. 18)	0.0002 (1.32)
Mean family income * Percent served by curbside	0.0007** (2.07)	-0.0007** (-2.58)	0.0003 (0.66)
Density	0.1563 (0.44)	-0.9321 (-0.87)	0.589*** (3.54)
Unemployment	-0.0108 (-1.82)	-0.0664*** (-4.02)	-0.0088* (-2.23)
Median family income	-0.0455 (-1.96)	-0.0256 (-0.65)	-0.0099* (-2.04)
Number of recycling centers per area	4.9861*** (3.99)	21.5631*** (3.65))	5.0289*** (4.94)
County average number of recycling centers hours open	-0.0007 (-0.22)	0.0563*** (3.04)	0.0066** (2.07)
Standard deviation of recycling centers hours open	0.0077 (1.37)	-0.0108 (-0.77)	-0.0073 (-0.44)
Average temperature	0.0024*** (5.54)	0.0004 (0.04)	0.0004 (1.28)
Second quarter dummy	-0.0964 (-1.11)	0.2087 (0.96)	0.0099 (0.66)
Third quarter dummy	0.1056 (1.65)	0.7866*** (3.07)	0.0589* (2.32)
Fourth quarter dummy	0.0608* (1.99)	0.0564 (0.55)	0.0486*** (3.01)
2010 year dummy	-0.1456*** (-4.44)	-0.2314** (-2.88)	0.0657*** (4.56)
2011 year dummy	-0.1667*** (-4.55)	-0.4267*** (-3.02)	0.0826*** (6.66)
2012 year dummy	-0.2657*** (-4.98)	-0.5632*** (-2.96)	0.0996*** (5.02)
2013 year dummy	-0.3214*** (-4.11)	-0.1891 (-1.55)	0.0988*** (6.88)
2014 year dummy	-0.4789*** (-6.02)	0.1057 (0.53)	-0.2564** (-2.56)
Per capita total quantity sold	0.2645 (2.01)	0.1054 (1.88)	0.1456*** (6.02)
Constant	0.9654 (1.07)	5.896** (2.99)	-0.1035*** (-3.05)
Fixed effects	68 village-specific fixed effects		
R-squared	0.94	0.91	0.85

***,**, and * indicate statistical significance at the 1 % , 5 %, and 10 % levels of significance.

Table 2 further indicates that the interaction between unemployment and curbside access is significant for glass. An intuitive interpretation of the positive coefficient here is that the diversionary response becomes stronger (more negative) as employment increases. In other words, consumers are more likely to forego redemption payments in exchange for convenience, particularly for heavy items like glass containers, when employment increases.

The results in table 2 on the interaction between median family income and curbside access are mixed. For glass, an intuitive interpretation of the significant negative coefficient is that the diversionary response becomes stronger (more negative) as median family income increases. In other words, consumers are more likely to forego redemption payments in exchange for convenience when income increases. For aluminum, however, the interaction coefficient is significant and positive. The results of this study do not differ much from those observed by Beatty et al. [19].

3.3. Quantity comparisons

To further put our results in perspective, are conducted some simple quantity comparisons that incorporate our empirical results. It was first considered the efficacy of expanding curbside access relative to expanding recycling center hours of operation. For glass, a one percent increase in the percent of the population served by curbside generates 10.2 times less total recycled quantity than expanding recycling center hours by one hour per week. In other words, the same increase in total glass beverage recycling is obtained by increasing the percent of the population with access to curbside by one percent or by expanding recycling center hours of operation by as little as 6 minutes per week (60 minutes/10). Extensive diversion from recycling centers simply implies that incremental changes in curbside programs do not result in large incremental changes in total glass beverage container recycling.

For plastic, a one percent increase in curbside access generates 2.9 times less total recycled quantity than expanding recycling center hours by one hour per week. In other words, the same increase in total plastic beverage recycling is obtained by increasing the percent of the population with access to curbside by one percent or by expanding recycling center hours of operation by approximately 20 minutes per week (60 minutes/3). For aluminum, point estimates suggest that a one percent increase in the percent of the population served by curbside generates 5.1 times more total recycled quantity than opening recycling centers an additional one hour per week. Here, recycling centers would have to expand hours of operation by approximately 300 minutes per week in order to bring in as much additional aluminum as increasing the percent of the population with curbside access by one percent.

Next was compared the efficacy of expanding curbside access relative to expanding the number of recycling centers. For glass, a one percent increase in curbside access generates 6.4 times less total recycled quantity than adding one recycling center per county. In other words, the same increase in total glass is obtained by expanding the number of recycling centers per village by one or by increasing the percent of the population with access to curbside by 5.8 %. For aluminum, a one percent increase in the percent of the population served by curbside generates 2.9 times less total recycled quantity than expanding the number of recycling centers by one per county. For plastic, point estimates suggest a one percent increase in the percent of the population served by curbside generates 5.2 times more total recycled quantity than an additional center per village.

4. CONCLUSION

This paper analysed the impact of curbside recycling when other recycling modes are present, because curbside recycling rarely exists in isolation. We considered the impact of access to curbside recycling on quantities returned to the curb, total quantities returned, and quantities returned to drop-off recycling centers.

The extent to which curbside access affects quantity recycled was measured. It was found that the impact of incrementally expanding curbside programs on total quantities of beverage containers recycled was small. A large reason for the small net gains from incrementally expanding curbside programs is cannibalization from existing recycling streams, particularly for heavier and bulkier materials.

Finally, our calculations indicated incremental curbside access expansion may not be the least cost option for increasing beverage container recycling returns. Recall that these are marginal results, and curbside programs are already prominent in many areas. Specifically, our results indicate that household time cost differences would need to be large for the marginal costs of recycling center availability to outweigh the marginal costs of curbside expansion.

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RESULTS FROM A CONTINGENT VALUATION SURVEY FOR ASSESSING THE WILLINGNESS-TO-PAY FOR ECOSYSTEM SERVICES RESTORATION

Dorina Grazhdani*

* Agricultural University of Tirana, Kamëz, Tirana, Albania

corresponding author: Dorina Grazhdani, e-mail: d.grazhdani@yahoo.com

Professional paper

ABSTRACT

The contingent valuation method (CVM) is one of the standard techniques for eliciting the willingness-to-pay (WTP) for the ecosystem services restoration. We developed a CVM statistical model based on the outcome of surveys conducted among households in Prespa Park (shared between Albania, Greece and Macedonia). The surveys were set to determine both the WTP of residents and factors that affect WTP for the ecosystem restoration. Results from 345 surveys indicated that households are willing to pay a monthly average of €2.84. Education, marital status, occupation, and family size were not the major factors affecting residents' WTP for ecosystem services restoration. It was also found that age was negatively correlated to WTP, while females had a higher WTP than males, and younger are willing to pay more than older residents. The results suggested that there is a strong public demand for environmental improvement on urbanized coastal watershed of Prespa Park.

***Keywords**: ecosystem services, contingent valuation method, Prespa Park, urbanized coastal watershed, willingness-to-pay*

1. INTRODUCTION

With over 50 % of the world's population living within 60 to 100 kilometres of the coastline [1], coastal ecosystems worldwide are experiencing the effects of urbanization. The changes in land-use required to support an increasing human population often have deleterious effects on ecosystems, as urban and suburban infrastructure replaces native land cover.

The conversion from unaltered to altered landforms can affect water quality, mostly through point-source and non-point source pollution, reductions in habitat for native biota, a loss of functioning soils, and reduced opportunities for recreational activities [2].

Conversion of unaltered landforms (forests, grasslands, wetlands) to agriculture, urban, and suburban development reduces the amount of suitable habitat available to native populations of plants and wildlife, leading to population fragmentation and decreases in population abundance [2, 3]. Recreational activities, such as fishing and swimming, have also been impacted as fish abundances have decreased and bathing sites have closed due to water quality concerns. It is worth noting that most of these services are intertwined; conversion of unaltered land can lead to soil instability and erosion, which increases sediment loads to receiving water bodies, decreasing water quality and thereby reducing fish survivability and reproduction, resulting in less fish for recreational fishers to pursue.

Ecosystem services valuation is the process of determining the monetary value of an ecosystem and is crucial in providing information to determine the necessary actions and economic support needed to maintain and restore ecosystem services [4]. The process integrates ecological concerns with economic considerations in order to calculate the costs and benefits of restoration.

Ecosystem restoration and its associated costs are not easily determined. The goal of ecosystem valuation relies heavily on determining the current state and benefits of a specific ecosystem and comparing that state to a historic state, or to the greatest potential benefits of the ecosystem to society. Based on the comparisons, the steps needed to be taken to repair or restore an ecosystem can be mapped out and suggested as potential policies.

Through the usage of contingent valuation studies and ecosystem evaluation, researchers have been able to reduce the controversy in the debates over the price of restoration. Using this method, spending on environments can be rationalized by placing "price tags" on ecosystems [5]. In addition, contingent valuation surveys account for many factors when determining the WTP for such restorations. By using this method, money is able to be distributed among the many services in need of restoration which is determined by the public.

However, because of the complex nature of ecosystems, there are many problems in determining objective measures of ecosystem value [6]. Within any ecosystem there is a vast number of abiotic and biotic factors, making it difficult to evaluate a single ecosystem service because they are all interdependent. Furthermore, studies often result in contradicting results, so it is inaccurate to draw conclusions based on isolated case studies.

Another area of controversy is the interpretation of variables within a study caused by variables such as tourism and animal migrations that indirectly affect the health of an ecosystem [6]. Accounting for every factor and modelling their effects is nearly impossible. The different methods that are used to value ecosystems and their services can also be debated, since many ecosystems have been evaluated using various methods.

Restoring ecosystem services not only improves the environmental conditions of an area, but also has economic benefits. If water quality is restored, fish populations may rebound and commercial fishermen may benefit from an increased catch. Improved water quality would also have a beneficial effect on a variety of fish habitats, which would lead to an improvement in the overall health of the ecosystem [7]. This would also help with tourism. For example, if fish habitats are mended, then more fish will live in the bay's waters. Thus, more recreational fishermen will visit the watershed and perhaps pay, fund, or support for further improvement of the bay. This will increase the economic support for restoring and maintaining the bay.

Ecosystem services have values based on their current condition and the services they provide. The perceived value of each service can be calculated in a variety of ways to quantitatively highlight the importance of one ecosystem valuation compared to another.

Marketing ecosystem services requires a different approach because they are not tangible and benefit the community instead of an individual, so it is difficult to put a “price

tag" on a service [5]. However, the monetary cost of these ecosystem services is ultimately repaid for by the benefits they bring about, such as the restorations of the services that include conserving natural and cultural diversity, improving land management and development, water purification, and increased recycling.

2. EXPERIMENTAL

2.1. Study area background

The Prespa Park is an urbanized watershed located in south-western Balkan. The entire watershed area takes up 1,218.1 km^2, and is a home to many important biological resources essential to the inhabitants of the area including fisheries, birds, and wildlife. These biological resources include many different areas within the watershed, shrub complexes, submerged aquatic vegetation, and upland forests. Unfortunately, human influence in the bay has reduced the quality of the habitat in which these native species thrive [8]. Erosion also poses a danger to animals nesting on the beach [8]. Increasing number of human inhabitants, commercial industries, and recreational industries has put a strain on the other species as well. Constant urban development throughout the region continuously increases and alters the Prespa landscape. With all these issues arising in the Prespa region, the environment is threatened continuously by more than one factor [8, 9]. Eventually, the condition of the area could deteriorate to a state that is inhabitable. Since all of these issues exist in the Prespa, they must be taken into account alongside various other factors that affect the process of restoration. Since the Prespa has been found to be a eutrophic ecosystem, it is a prime example of how various other coastal watershed ecosystems much like itself have been affected by coastal urbanization.

Based on the current degraded state of the watershed, a local umbrella non-governmental organization the Society for the Protection of Prespa (SPP) has developed several plans of restoration. These proposed plans have been carefully developed to repair and restore each aspect of the ecosystem services determined to be important in the watershed system. Four ecosystem services were chosen by the SPP [10] to be included in our survey. These included soil retention, habitat provisioning, water quality, and recreational use. Soil retention is the amount of water the soil can retain and is a key component of the hydrological cycle in the area, while habitat provisioning is the protection of the habitats of the various species of the Prespa. Water quality is mainly assessed by investigating the nutrient and contaminant contents in the water. Recreational activity is also a large part of the Prespa and maintaining it relies on keeping water quality and wildlife at desirable levels.

2.2. Ecosystem valuation models

There are several methods that scientists use to valuate ecosystems. Willingness to Pay (WTP) is a general framework with several methods to figure out the amount of money people decide to spend in order to use, restore or improve a beneficial ecosystem service. WTP can be determined indirectly by analysing the travel costs people are willing to pay in order to participate in recreational activities at the specified ecosystem [11, 12]. This Travel Cost Method (TCM) measures what people actually pay to use ecosystem services, and not what they claim they are willing to pay [13].

Another method of determining WTP is contingent valuation method (CVM). Ciriacy-Wantrup [14] first proposed the contingent valuation method to estimate the values of non-market goods [15]. Later, Davis [16] implemented the contingent valuation method to measure the benefits of a recreational area in Maine (USA). In the 1970s, many researchers and economists used the CV method to measure the value of different recreational areas. Thereafter, the CV method was developed and improved and was popularly used in various environmental economic studies. However, the CV method was subject to debate by economists and other researchers regarding whether it was a reliable method to estimate the value of environmental goods.

In this method, the value of an ecosystem is determined by asking people how much they would be willing to pay in a hypothetical situation to restore or maintain specific ecosystem services [17, 18]. Demographic questions are used to create a formula to predict the WTP of households given their responses; this also provides a profile of a person who would be more willing to pay than the average respondent. CVM uses a simulated market where consumers are exposed to staged information and make decisions to observe their response to a new idea [6]. The main issue with this method is whether people are actually willing to pay what they claim they will for the ecosystem services. A panel of experts was convened by the National Oceanic and Atmospheric Administration (NOAA) to determine if the CVM method was reliable enough to be used in environmental studies [19]. The panel concluded that "… well conducted CVM studies can produce estimates reliable enough to be the starting point of a judicial process of damage assessment, including lost passive values" [19].

The usefulness of responses to surveys on hypothetical referenda, in particular, standard contingent valuation surveys, has long been debated [20 - 24]. Nevertheless, opponents of CVM argue that the approach taken may not reflect the true WTP of the respondent. It is important to note, however, that these issues have been addressed by Carson [20] in his meta-analysis of CVM studies. The results of his analysis suggest that when comparing CVM estimates to estimates based on revealed-preference studies, the CVM estimates were on average slightly lower.

With the stamp-of-approval from some of the most prominent economists in the world and the continued research on its effectiveness and accuracy, the CVM has gained acceptance as a useful tool to assess the value of goods not sold in traditional markets. As such, the amount of CVM literature published has grown to be approximately 500 papers per year [25].

2.3. Survey design and distribution

The survey was designed to test the hypothesis that a correlation could be found between a person's WTP to restore ecosystem services, and their level of education. Along with additional demographic questions, the survey included opinion-based questions relating to the Prespa Park. These questions asked the participant their opinion on the quality of the Prespa Park and its various services. To ensure all respondents had an equal opportunity to understand issues facing the region, a short informational paragraph was included to give all participants some background knowledge of the Prespa Park, the current state of the ecosystem services, the proposed policy, and the expected future state of the ecosystem services before answering any questions (table 1).

Table 1. Information provided in the survey on ecosystem services restoration

Ecosystem Services	Current State	Proposed Restoration	Restored State*
Water Quality	Urbanization of the watershed has drastically decreased the supply and quality of water of the bay. These issues are related to storm water runoff, impairment of groundwater retention, leaking septic systems, and increasing amounts of fertilizer and other toxins entering the water systems.	Watershed planners suggest the retrofitting of retention/detention storm water basins. These are expected to increase infiltration and recharge groundwater. Additionally, it is recommended that a comprehensive water supply plan is developed for the entire watershed that guides water supply development, use, and reuse, through the year 2040.	Water quality is expected to improve significantly. Management of toxins entering the water will allow for maintenance and monitoring of these toxins at key points. Plant, vertebrate, and invertebrate populations should also improve significantly through adaptive management.
Soil Retention	Increasing erosion brought on by rising development and shore-use has created an unstable shoreline in many coastal areas of Lakes Prespa. Due to lack of vegetation, plants are unable to grow which, in turn, has created more erosion.	To reduce erosion, planners suggest restoring native plants along public spaces, riparian zones and other waterways.	By increasing the amount of vegetation along the shoreline and riparian zones, the rate of soil erosion will decrease while habitat and the rate of natural toxin filtration will increase
Habitat Provisioning	Due to poor water quality and erosion, many ecosystems have been disturbed. Because of human development and urbanization in the bay, habitats in forests have been destroyed with human disturbance. Populations have decreased and there is loss of wildlife.	To maintain intact large blocks of pinelands habitat within state parks and forests and other publicly owned lands. Save fire-prone regions (in the uplands of the watershed) to maintain the natural fire cycle and allow for improved habitat. Coordinate and integrate management of federal lands for natural habitat values and watch over federal owned lands to ensure continued ecological integrity of the watershed.	Establishing habitat corridors, reserves, and fire management of pinelands will decrease the current system of fragmentation and maintain and restore ecological conditions to help support terrestrial and aquatic life.
Recreational Use	Over the last 20 years, recreational activities in the Lakes Prespa have increased at the cost of the Lakes Prespa's natural ecological structure. Some recreational fisheries have declined and there have been significant declines in water quality which have resulted in beach closings.	Protect and improve vegetated buffer zones adjacent to coastal wetlands to maintain continuous riparian corridors for low-impact recreational pursuits. Establishing riparian corridors allows for canoeing and other low-impact recreation.	Promoting low-impact recreational use is expected to better maintain coastal wetlands which better protect against resource decline.

* after 15 – 30 years.

2.4. Formatting of demographic survey questions

The surveys included three types of questions: multiple choice, written values (i.e. distance in m, number of years), and yes/no questions. A yes or no approach was used in

gathering information about each recipient's environmental awareness. Personal questions were used to help determine the demographics, or a general profile, for people who were more willing to pay. These were questions asking about age, sex, relationship status, political party, degree of education, distance in m from the bay.

2.5. Focus groups and pilot groups

Throughout the survey, were considered several questions that would help determine the reasons people might be more willing to pay money to support future restoration including marital status, education, distance of residence to the lakes and political affiliation. Additional questions regarding personal information (education, marital status, etc.) were also asked to gain an understanding of the demographic of the survey participants. A pilot survey was given to a group of 30 Prespa Park residents. The pilot group was used to proofread the surveys for errors and provide feedback on the effectiveness and clarity of each question. After the focus group revisions were made to the survey, the survey was sent to 1,000 randomly selected watershed residents.

2.6. Formatting of WTP question

Most important to our study was determining WTP. The WTP question, as written on the survey, follows: "*If the restoration fund was on the ballot in the next election and it would cost your household €"X" each month extra added to your water bill, would you vote in favour or against*?"

_____ I would vote Yes
_____ I would vote No

in which "X" represents the bid amount (in €). This question has been designed using a proven method that enables a calculation of the average WTP by asking if one would be willing the pay for euro amount "X". Based on the pilot groups and literature review, the euro amounts selected were as follows: €0.5, €1, €2, €3, €4, €5, €6, €8, €10, €15, and €20. Each survey contained one randomly selected euro amount which were evenly distributed over the 1000 surveys. Participants responded if they would be willing to pay the selected amount or not for the restoration projects listed (table 2).

Table 2. Descriptive statistics of bid amount responses

Bid (in €)	0.5	1	2	3	4	5	6	8	10	15	20
Yes	42	39	31	23	19	16	14	10	6	5	2
No	2	13	2	8	4	11	9	18	24	21	26
Percent Yes	95 %	75 %	94 %	74 %	83 %	60 %	61 %	36 %	20 %	19 %	7 %

Each column shows how many households agreed and disagreed to pay each bid amount. The bottom row shows the percentage of respondents which agreed for each bid amount.

2.7. Statistical model of WTP

2.7.1. Probability and demographics of WTP

A logistic model best estimates the probability that a household will pay a given euro amount because they respond with only a 'yes' or 'no' answer [26, 27]. The model is of the form:

$$\text{Prob (Yes)} = 1 - \{1 + \exp [B_0 - B_1 (€X) + B_2 (Y) + B_3 \ldots]\}^{-1} \quad (1)$$

In which each *B* is a coefficient estimated using a logistic regression. €X is the euro amount the household was asked to pay. Other variables may include responses to attitude questions and the respondent's demographic information [27].

2.7.2. Calculating the mean WTP

The formula to calculate expected WTP based on given coefficients is:

$$\text{Mean WTP} = (1/B_1) * \ln [1 + \exp (B_0)] \quad (2)$$

in which B_1 is the estimated coefficient of the bid amount and B_0 is the grand constant, the sum of the estimated constant plus the product of the other independent values times their means [26].

2.8. Survey administration

A total of 1,000 surveys were mailed out to residents of the Prespa Park watershed area using a random number generator created using Python, a free software program. Each survey, including a cover page, basic background on each service to be restored, and the attached questionnaire, was three pages long, with information on the front and back of each page. Each portion of the survey was similar in length. The background pages were about half of the total survey, the other half being the questionnaire itself. The surveys were created in a way such that each recipient could complete it in 10 - 15 minutes, so people would be more likely to send back their completed surveys. This is vital in order to acquire a sufficient net sample to support the study.

Only 41.6 % of the recipients responded and only 34.5 % of the 1,000 surveys could be used as our net sample since the remaining 7.1 % included incomplete surveys.

3. RESULTS AND DISCUSSION

A statistical model including all environmental awareness/attitude and demographic variables was generated. No attitude variables were relevant and the demographic variables such as education, marital status, occupation, and household size were found to be insignificant. This stands in contrast to Loomis et al. [27], which found attitude values to be a significant predictor of WTP for restoration. The final logistical model was:

$$[(\log (yes)/(1\text{-}yes)] = B_0 - B_1(bid) - B_2(income) - B_3(age) - B_4(gender) - B_5(education) - B_6(occupation) - B_7(family\ size) - B_8(marital\ status) - B_9(environmental\ awareness) \quad (3)$$

in which 'yes' is the dependent variable, defined as whether or not the respondent was willing to pay the bid amount. 1 indicates a yes vote, while a 0 indicates a no vote. The bid amount is the amount of money the person was asked to pay in the form of an increased water bill. Yearly income is specified in the income groups > €5000, €3000 – €4000, €2000 – €3000, €1000 – €2000, €600 – €1000, < €600) and age in the age groups 18 - 25, 26 - 35, 36 - 45, 46 - 55, 56 - 65, and 65+. Gender is 0 if the respondent is female and 1 if the respondent is male.

For data analysis, was employed SPSS 16.0 [28]. Table 3 shows the logistic model determined using SPSS analytic software for finding the probability that a household will agree to pay a given amount of money to restore the specified ecosystem services of Prespa Park.

Income and bid amount was shown to be correlated to the probability of a 'yes' response at the 0.01 level, while age and gender are significant at the 0.05 level. Respondents who were younger, female, and had lower bid amounts had a higher WTP than older respondents, male respondents, and those with higher bid amounts.

Table 3. Summary statistics of the logistic model

Variable	Coefficient	SE Coef.	z	P value	Odss ratio	95 % CI	
						Lower	Upper
Bid amount	- 1.430938**	0.185332	-1.27	0.008	0.56	0.22	1.57
Income	2.567408**	0.547892	4.67	0.009	0.71	0.54	3.89
Age	- 1.390562*	0.271049	-1.46	0.043	0.82	0.42	2.38
Gender	- 2.390481*	0.492547	-0.82	0.487	0.59	0.29	1.68
Education	0.925618	0.241892	2.46	0.012	0.61	1.12	4.62
Marital status	-0.745919	0.325261	-1.37	0.182	0.45	0.15	1.38
Family size	0.263568	0.180147	1.13	0.307	1.34	0.86	1.78
Occupation	0.165377	0.0751669	1.68	0.087	1.53	0.87	1.34
Environmental awareness	0.659843	0.021487	1.08	0.175	1.22	0.78	1.65

Log-likelihood = -1986.842

Test that all slopes are zero: G = 54.620, df= 10, P value = 0.00

* Significant at the 0.05 level; ** Significant at the 0.01 level

A negative coefficient shows that a higher bid amount correlates to a lower chance of the respondent agreeing to pay the bid amount for restoration of ecosystem services. The independent variable of age also has a negative coefficient. Younger respondents were significantly more willing to pay the bid amount except for the 36 - 45 age group, which, along with older groups, were less willing to pay. For gender, the coefficient was negative, indicating that women were significantly more likely to pay to restore ecosystem services than men. These results confirm those of Nicosia et al. [29].

One hypothesis stated was that married couples would be less willing to pay compared to single residents because they feel that it is more important to save money for their family; therefore, they have a lower WTP. However, the relationship status of the surveyor has little impact on WTP, as both single and married people were willing to pay at different bid amounts. Another hypothesis was that people living closer to the coast would be more aware of the ecosystems' damaged conditions and thus would be willing to pay more. However, the

data collected shows that people living off the coast were willing to pay as much as people living near the lakes. These results do not differ much from those observed by Mueller [30].

The level of education of the people (options ranging from a high school degree to a PhD) has been shown also to have little or no effect on WTP, and thus is not factored into the overall WTP. It is intriguing that this variable has no correlation to WTP. A reason for this could be that different areas of education could manifest different opinions in people. Also, the hypothesis which stated that "environmentally aware citizens would pay more than those who are not as environmentally involved" was also rejected by the data, because there was no correlation between environmental awareness and WTP. These findings are not consistent with previous findings [31].

4. CONCLUSION

The purpose of this study was to understand the economic value for restoration of an urbanized coastal watershed and the value that residents place on a guaranteed source of ecosystem services to support a healthy Prespa Park ecosystem.

The results of this study suggest that residents are willing-to-pay in order to guarantee and maintain a healthy Prespa Park ecosystem, with just about 60 % willing-to-pay the amount proposed to them. The mean monthly WTP of Prespa residents to restore four ecosystem services of the Prespa Watershed (soil retention, water quality, habitat provisioning, and recreational services) was calculated to be €2.84.

The significant factors contributing to the probability that a respondent would be willing to pay to guarantee a healthy Prespa Park ecosystem include income, age and gender. Results shows that respondents with higher incomes, greater environmental values. Age was negatively correlated to WTP, while females had a higher WTP than males.

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OTPAD KAO ALTERNATIVNA ENERGIJA

WASTE AS AN ALTERNATIVE ENERGY

Tomislav Grizelj*

* GRIZELJ d.o.o., Sarajevo, Bosna i Hercegovina

autor za korespondenciju: Tomislav Grizelj, e-mail: grizelj@grizelj.com

Pregledni rad

SAŽETAK

Obzirom na ograničenost fosilnih goriva od količina, transporta, skladištenja, sigurnosnih mjera u transportu i lagerovanja do visokih i nepredvidivih cijena (uvjetovano višim silama i ratom), čovječanstvo se postepeno ali sigurno okreće prema alternativnim energentima, lokalnog (nacionalnog) karaktera ili podneblja. Danas su prisutne nove tehnologije i tehnike u termičkom tretmanu "otpada" sa korektnom emisijom polutanata bez boje, okusa, mirisa i lebdećih čestica.

Opisivanje i iskorištavanje različitih vrsta otpada kao alternativne energije svakako je jedan od glavnih ciljeva ovog rada. Također cilj je i da se kroz europske smjernice čitaocu predstavi važnost otpada kao alternativne energije.

Vrste biootpada promatrane kao eko energent u: rinfuzi, briketu, peletu sa visokom energijskom moći, najbolje mehanički i/ili biološki obrađivati na mjestu nastanka a konzumirati na potrebnim lokacijama korisnika u namjenskim kotlovima.

Ključne riječi: *alternativna energija, biootpad, otpad*

ABSTRACT

Given the limited volume of fossil fuels, transportation, warehousing, transport safety and handling at high and unpredictable prices (conditioned by higher forces and war), humanity gradually but surely turns to alternative energy, local (national) character or clime. Today, there are new technologies and techniques in thermal treatment of "waste" with the correct emission of pollutants without: colour, taste, odder, floating particles.

Describing and exploiting different types of waste as alternative energy is certainly one of the main goals of this paper. It also aims to show the importance of waste as an alternative energy through the European guidelines to the reader.

The types of bio-waste observed as eco – energies in: bulk, briquettes, pellets with high energy power, best mechanically and/or biologically processed at the site of production and consumed in the necessary user locations in the dedicated boilers.

Keywords: *alternative energy, bio-waste, waste*

1. UVOD

Kombinacije, radi konkurentnosti proizvoda, koje se danas rade na tržištu su različite i sve više omogućavaju korištenje alternativnih izvora energije u cilju održivog razvoja, kako bi se postojeći prirodni resursi racionalno koristili i tržišno prilagođavali. Pregledom različite literature da se zaključiti da se u alternativne izvore energije često ubrajaju:

- balega – izmet;
- drvo (tradicionalna biomasa);
- biomasa;
- biogoriva: bioetanol, biodizel, bioplin, bio – ETBE[1],
- biovodik;
- hidroenergija;
- energija vjetra;
- sunčeva energija: toplinska, fotonaponska;
- geotermalna energija;
- energija mora: energija plime i oseke, energija valova, toplinska energija.

Otpad je novac, reciklant, repro materijal, energent. Zbog svog štetnog utjecaja na okolinu i na osnovu EU Direktiva otpad se neobrađen više ne smije odlagati na odlagališta. Mora biti usklađeno sa svim suvremenim (europskim) standardima i zahtjevima, sa svrhom da se maksimalno izbjegne ili smanji nastajanje otpada, kao i njegov utjecaj na ljudsko zdravlje, okoliš i klimu, odnosno, da se cjelokupno gospodarenje komunalnim otpadom uskladi sa načelima održivog razvoja.

Dio "otpada" koji se može iskoristiti kao alternativna goriva je svugdje oko nas i to je nešto što se koristi ili se koristilo i više ne treba, ali daleko od toga da to ne treba nekome drugom. Stoga, sav otpad se može iskoristiti kroz reciklante, energente ili neke druge načine i ne smije biti ostavljen budućim generacijama.

Adekvatno zbrinjavanje otpada ali i njegovo iskorištavanje u svrhu dobivanja energije, postalo je nužnost suvremenog razvijenog svijeta, jer ako se ne štiti priroda, zdravlje ili će ljudi biti bolesni ili će se zaraziti, ali i negativno utjecati na klimatske promjene.

Neiskorišteni su otpad od autoguma, biomasa, procijedni mulj, mulj iz drvene, papirne, tekstilno – kožarske industrije, animalni otpad – konfiskat, stajnjak, izmet koka sa i bez prostirke, medicinski, anatomsko – patološki otpad, infektivni i opasni otpad te humani otpad. Otpad koji nastaje od klaoničkog do bolničkog može da se iskoristi i može biti izuzetno kvalitetan energent.

[1] ETBE – Etil terc – butil eter

2. OTPAD KROZ EUROPSKE SMJERNICE

Nazivi i definicije koje se odnose na materijal otpada kao i gospodarenje istim je prožeto i detaljno objašnjeno kroz Europske norme EN ISO/IEC 13965 – 1 : 2008 i EN ISO 13965 – 2 : 2008.

EN ISO/IEC 13965 – 1 : 2008 Karakterizacija otpada – Poglavlje 1. dio: Nazivi i definicije koji se odnose na materijal

Ova norma je izrađena da bi pomogla onim tijelima koja se aktivno bave različitim područjima i načinima gospodarenja otpadom. Zamišljeno je da bude osnova i zajednički jezik u suradnji tih tijela. Ona je dio niza europskih normi od kojih svaka obuhvaća dio naziva koji se odnose na otpad. Norma obuhvaća nazive koji se odnose na različite vrste otpada. Ona daje skup izabranih i aktualnih naziva i definicija koje upotrebljavaju proizvođači, industrija koja se bavi otpadom i zakonodavac u području gospodarenja otpadom te je usklađena sa aktualnim rječnikom koji se upotrebljava u gospodarenju otpadom u zakonskim propisima [1].

EN ISO 13965 – 2 : 2008 Karakterizacija otpada – Poglavlje 2. dio: Nazivi i definicije koji se odnose na gospodarenje otpadom

Ova norma je napisana da bi pomogla onim tijelima koja se aktivno bave različitim područjima i načinima gospodarenja otpadom. Zamišljeno je da bude osnova i zajednički jezik u suradnji tih tijela. Ova bi se norma trebala uvijek upotrebljavati da bi se postigao odgovarajući cilj, bilo to ispunjenje zakonskih odredbi ili ugovaranje između strana koje se bave gospodarenjem otpadom. Ona je dio europskih normi od kojih svaka obuhvaća dio naziva o otpadu. Usklađena je sa aktualnim rječnikom koji se upotrebljava u gospodarenju otpadom te u propisima; ona uključuje, uz upućivanje na druge norme, nacionalne nazive i definicije tamo gdje su takve potrebe izražene [1].

Otpad se klasificira kao opasni i neopasni otpad, ovisno o njegovim karakteristikama. Europski popis opasnog otpada, uspostavljen Odlukom 2000/532/EZ, a nadopunjen Odlukom Vijeća 2001/573/EZ, koristi se za klasificiranje otpada u okviru izvještavanja o opasnom otpadu. Trenutačno je Europski popis otpada u postupku revizije.

Direktiva 2014/94/EU Europskog parlamenta i Vijeća od 22. listopada 2014.o uspostavi infrastrukture za alternativna goriva

Alternativna goriva u smislu Direktive definiraju se kao goriva ili izvori energije koji služe, barem djelomično, kao nadomjestak za izvore fosilnih goriva u opskrbi prometa energijom i koji imaju potencijal doprinijeti dekarbonizaciji prometnog sustava te poboljšati okolišnu učinkovitost prometnog sektora, a između ostalog uključuju:

- električnu energiju,
- vodik,
- bio – goriva,
- sintetička i parafinska goriva,
- prirodni plin (stlačeni – SPP – CNG i ukapljeni – UPP – LNG).

3. POSTUPANJE S OTPADOM

Kako bi se sačuvala vrijednost "otpada, reciklanta, frakcije – agregata" od nastanka, odlaganja u kućnu kantu za selektirani otpad, kontejnera za prihvat selektiranog otpada, kamionskog prijevoza do sabirnog centra sve treba biti zatvoreni prostor.

Preporuka je da se selekcija, prihvat, tretman i lagerovanje obavlja u zatvorenom prostoru kako bi se "otpad, reciklant, frakcija – agregat" sačuvao od negativnih atmosferskih utjecaja: sunce, kiša, snijeg, led, vjetar, a priroda i okoliš od negativnog utjecaja "otpada, reciklanta, frakcije – agregata" od estetike do kontaminacije. Selektirani otpad od mjesta nastanka (*in site*) postaje reciklant, za isti se treba dobiti naknada (povrat kaucije) kod predaje operateru.

Cijeli proces termičkog tretmana sa pratećim funkcijama odvija se preko programa ENERGETIS^{ITG} koji ima integralni interaktivni program i multivarijabilni PLC (*interface touch screen*) sistem: master – kontroler – monitor koji osigurava upravljanje, kontrolu, vizualizaciju i nadzor nad tehnološkim procesom po zadanom receptu termo tretman/obrada podržanim senzorima, transmiterima i PID regulatorima sa PC za back up, trajni elektronski zapis rada uređaja i online konekciju prema centralnom SKADA sistemu. Emisija polutanata nadzire se termo senzorima, O_2 i lambda sondama.

Da bi proces tretmana otpada bio ekološki podoban koristi se reaktor za koincineraciju dimnih plinova iz incineratora opravdavajući svoju funkciju i utrošak plina, s radnom temperaturom višom od 1000 °C daje garanciju korektnog postupanja u zaštiti prirode i okoliša, emisija polutanata bez boje, okusa, mirisa, lebdećih čestica.

Reaktor za koincineraciju s obaveznom retencijom više od 2 sek. dimnih plinova iz incineratora radi:

- dezodorizacije – odstranjivanje i neutralizacija neugodnom mirisa;
- dehidracije – sušenje dimnih plinova i korištenje vodene pare kao energenta;
- detoksikacije – toksini (furani i dioksini) se neutraliziraju;
- dekontaminacije – dimni plinovi koji mogu biti kontaminirani u reaktoru se vrši dekontaminacija;
- karbonizacije – pretvaranje lebdeće materije u pepeo;
- dekarbonizacije – smanjenje štetne emisije u dimnim plinovima.

Da bi korištenje "otpada" kao energenta bilo učinkovito koristi se kontinuirani sistem praćenja emisija (continuous emision monitoring system – CEMS) kako bi se postigla niža emisija Low NO_X, CO_2, CO kod referentnog 0_2 Vol. 3 %.

Postupanje sa otpadom obuhvaća:

- Najstrožije bio i eko standarde i norme;
- Najbolje raspoložive tehnologije (BAT);
- Najbolju raspoloživu praksu (BAP);
- Bio i eko proizvode;
- Vodu, zrak, tlo i hranu;
- Energijsku učinkovitost i obnovljive izvore energije;
- Plasman energije (EKO);
- Burzu otpada;
- Efektivno i efikasno – profit;
- Zaštita čovjeka i okoline – benefit;
- Odlaganje – deponije (divlje, javne, "sanitarne").

U novije vrijeme se već duže naslućuju plazma tehnologije, iako se smatra da će se morati još sačekati zbog problema izolacionih materijala i elektroda.

4. DOBIJANJE ENERGIJE IZ OTPADA (*WASTE TO ENERGY*)

Pretvaranje otpada u energiju (*Waste to energy*) ili dobivanje energije iz otpada (*Energy from waste*) moguće je kroz selekciju prema vrsti, određivanje kvantiteta i kvaliteta materijala, a opravdanost se ogleda kroz strateški izbor tehnologija koja će zadovoljiti ekološke, energetske i ekonomske parametre.

Selekcija otpada na reciklante i/ili RDF/SRF. RDF je gorivo dobiveno iz krutog neopasnog komunalnog otpada dok je SRF gorivo ujednačene kvalitete dobiveno iz krutog neopasnog komunalnog otpada kao proizvoda. EN 15357 : 2011 Terminologija, definicije i opisi, EN 15359: 2012 – Kruta oporavljena goriva – Specifikacije i klase SRF [2].

Ako se postavlja pitanje zbog čega upotreba SRF kao vrste goriva odgovor bi bio zato što uz malo više rada može se postići veća cijena koja je financijski opravdana. Razlika između RDF i SRF je u tome da se na RDF ne primjenjuje klasifikacija prema normi – zadržava se status otpada.

Energent iz komunalnog otpada, poslije izdvojenih reciklanata ostaje kompozit koji se treba usitniti i dehidrirati na 20 % vlage kako bismo ga mogli deklarirati kao RDF energent. Izdvajanjem žice iz starih auto guma dobiva se materija koja se šredira da bi se dobio TDF kao energent ili repromaterijal za proizvodnju SNG (*Synthetic natural gas*).

4.1. Biootpad; Biomasa – Bioenergija, Agroenergija

Biomasa je biorazgradivi dio proizvoda, otpada i ostataka poljoprivredne proizvodnje (biljnog i životinjskog porijekla), šumarske i srodnih industrija. Energija iz biomase dolazi u čvrstom, tekućem (npr. biodizel, bioetanol, biometanol) i plinovitom stanju (npr. bioplin, plin iz rasplinjavanja biomase i deponijski plin).

Obilni potencijali su jedna od glavnih prednosti u korištenju biomase kao izvora, ne samo u svrhu zasađene biljne kulture već i otpadni materijali u poljoprivrednoj i prehrambenoj industriji. Za proizvodnju energije se također mogu koristiti plinovi koji nastaju korištenjem biomase. Prednost biomase u odnosu na fosilna goriva je i neusporedivo manja emisija štetnih plinova i otpadnih tvari.

Jako je važno korektno i učinkovito zbrinuti biomasu kako bi se dobio resurs: peletirano đubrivo ili energent (ovisi o specifičnosti) ili briketiran energent. Sadržaj vlage mora biti manji od 15 %, a veličina frakcija manja od 5 mm.

5. KOREKTNO POSTUPANJE S OTPADOM

Reciklaža i tretiranje otpada predstavlja prvi veliki korak u promjeni načina razmišljanja privrednika i cjelokupne kulturne orijentacije društva. Linearna ekonomija dobila je svoj suparnički koncept u kojem se, umjesto kretanja materije ravno (slika 1), zastupa kružno kretanje energije i materije (slika 2). Takav koncept je poznat pod nazivom *cirkularna ekonomija (CE)*. Ukratko cirkularna ekonomija podrazumijeva kruženje materije i njegovu

ponovnu upotrebu, čime se istovremeno koristi drastično manje energije i vode (u nekim slučajevima i do 90 %).



Slika 1. Prikaz modela linearne ekonomije [3]



Slika 2. Prikaz modela cirkularne ekonomije [3]

Cirkularna ekonomija predstavlja „instrument“ za realizaciju ciljeva održivog razvoja i podrazumijeva dugoročno ulaganje i sirovinsku i energetsku učinkovitost, uz smanjenje štetnih emisija, zamjenu fosilnih goriva obnovljivim izvorima i proizvodnju i trgovinu održivim proizvodima, čime se zatvara krug „proizvod – otpad – proizvod“.

Cirkularna ekonomija nudi novi model „proizvod – otpad – proizvod“. Osnovni izvor ekonomskog rasta jeste što veća ponovna upotreba materijala iz proizvoda koji su završili svoj „životni ciklus“ i što manje korištenje novih resursa. Poruka koju ovaj model promovira je: „ZERO WASTE“.

“*Zero waste*” (koncept bez otpada) je strategija oponašanja prirode koja ne poznaje smeće – sve se reciklira u kružnom toku materije i energije.

Cilj “*zero waste*” strategije je stvoriti uvjete u kojima sve što se proizvodi i troši ima minimalni utjecaj na okoliš i čovjeka koji u njemu živi. Zadatak je proizvodnja takvih proizvoda koji su dugovječni, a na kraju njihove upotrebe mogu biti popravljeni, ponovo korišteni ili reciklirani.

Osnovni ciljevi „*Zero Waste*“ koncepta [4]:

- bez otpada (smanjenje količine otpada, ponovna upotreba, recikliranje),
- bez štetnih emisija (u tlo, atmosferu ili vodu),
- bez otpada u životnom ciklusu proizvoda (prijevoz, potrošnja, odlaganje),
- bez upotrebe toksičnih tvari (u procesu proizvodnje i u samim proizvodima).

Sa energetske točke gledišta „*Zero Waste*“ smanjuje emisije proizvodnjom zahvaljujući povratku većine hranjivih tvari i resursa u prirodni ciklus – tla ili tehnički ciklus – razvrstavanje i recikliranje.

Načela ispravnog i efektnog postupanja sa otpadom su [4]:

- smanji,

- ponovo upotrijebi,
- recikliraj,
- energetski koristi,
- sanitarno odloži nekorisno.

6. ZAKLJUČAK

Kako bi se sačuvala vrijednost "otpada, reciklanta, frakcije – agregata" preporuka je da se selekcija, tretman i lagerovanje obavlja u zatvorenom prostoru radi negativnih atmosferskih utjecaja; sunce, kiša, snijeg, led, vjetar i negativnih utjecaja otpada na prirodu i okoliš od estetike do kontaminacije. Svijest da industrija i pojedinac zagađuju okolinu i stvaraju otpad postoji. Određene količine otpada moraju nastati jer je situacija bez otpada posljedica nultog obima proizvodnje. Količinu otpada treba svesti na optimalnu.

Nastalu količinu otpada treba tretirati kao resurs jer predstavlja alternativni izvor energije. U ovaj proces treba uključiti pojam energetske i ekonomske učinkovitosti i održivosti.

Prilikom zbrinjavanja otpada kao i njegovog tretiranja kao alternativnog izvora energije treba da bude zadovoljeno načelo 7E – edukacija, etika, ekologija, estetika, energijska učinkovitost, energija, ekonomija.

U konačnici otpad treba promatrati kroz izraz *(za)štiti okoliš i (za)radi*.

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PROCIJEDNI MULJ - OBNOVLJIVI IZVOR ENERGIJE

SLUDGE – RENAWABLE ENERGY SOURCE

Tomislav Grizelj*

* GRIZELJ d.o.o., Sarajevo, Bosna i Hercegovina

autor za korespondenciju: Tomislav Grizelj, e-mail: grizelj@grizelj.com

Pregledni rad

SAŽETAK

Muljevi su po svom sastavu, količini, obradi i konačnom odlaganju veliki ekološki, tehnološki i ekonomski problem svakog javnog sistema odvodnje. Procijedni mulj se mora korektno inaktivirati iz ambijenta, ali treba ga promatrati kao fertilizator tla i/ili obnovljivi izvor energije i kroz poštivanje metoda energetske efikasnosti potrebno ga je tretirati (iskoristiti), termovalorizirati a ne odlagati – deponirati.

Procijedni mulj kao ostatak nakon obrade otpadnih, komunalnih ili industrijskih voda, koje su podvrgnute mehaničkim i biološkim postupcima, sadrži i vrijedne organske tvari (do 70 %) i na taj način je pogodan za korištenje kao fertilizator tla za namjene kao što su hortikultura, šumarstvo ako je biološki i kemijski podoban. Pored navedenog, energetska vrijednost koju posjeduje procijedni mulj može se iskorištavati konvertiranjem za proizvodnju toplinske i rashladne energije.

Cilj rada je bio da se prikažu pogodnosti iskorištavanja energetske vrijednosti procijednog mulja korištenjem eko naprednih tehnologija kao i uloga procijednog mulja kao građevinske frakcije i fertilizatora tla.

Ključne riječi: *procijedni mulj, obnovljivi izvor energije, energent, fertilizator tla*

ABSTRACT

Sludges are in their composition, quantity, processing and final disposal, a major technological and economic problem of any public drainage system. The precipitation sludge must be properly deactivated from the environment but should be considered as a renewable source of energy and by respecting the energy efficiency method it is necessary to treat it to make a waste – to – energy and not to deposit.

Sludge as a residue after treatment of waste, utility or industrial waters, which are subjected to biological processes, also contain valuable organic substances (about 70 %) and

it is thus suitable for use in agricultural purposes or as soil fertilizers for uses such as horticulture, forestry. In addition to the above mentioned energy values, the transient sludge can be used in power generation combustion units.

The aim of the paper was to present the benefits of exploiting the energy value of the sludge by using eco-advanced technologies as well as the role of the sludge as a construction fraction and soil fertilizer.

Keywords: *sludge, renewable source of energy, energy, soil fertilizers*

1. UVOD

Korištenjem procijednih muljeva iz kanalizacijskih sistema, septičkih (crnih) jama, industrijskih separatora itd. može se vršiti eksploatacija kroz energetski, ekološki i ekonomski benefit uz zadovoljenje osnovnih načela humanosti i etike. S ciljem korištenja mulja kao obnovljivog izvora energije (OIE), koji je resurs i ima svoju energetsku vrijednost koju treba racionalno i efikasno iskoristiti, dolazi do primjene novih naprednih eko tehnologija Advanced €co Technology (A€T®) kroz istraživanje i razvoj procesnih tehnologija i tehnika.
Energijska vrijednost mulja može se iskoristiti u toku obrade, primjerice pri proizvodnji bioplina kod anaerobne stabilizacije ili iskorištavanjem energijskog potencijala pri termičkoj stabilizaciji. Procijedni kanalizacijski mulj sadrži i određenu količinu hranjivih tvari koje se mogu iskoristiti (dušik, fosfor, kalij) [1].

2. ŠTA JE PROCIJEDNI KANALIZACIJSKI MULJ?

U postupku pročišćavanja otpadnih voda kao nusprodukt se javlja mulj. Vodeni procijedni mulj u bilo kojem obliku treba promatrati kao materiju koja nije otpad već repromaterijal, sirovina, energent i ukoliko se želi zaštititi priroda i okoliš, mulj treba koristiti kao energent. Mulj iz komunalnih otpadnih voda nije bezvrijedan otpad. Sadrži oko 70 % organske tvari čija se energetska vrijednost može iskoristiti. Mulj sadrži i hranjive tvari koje se također mogu iskoristiti. Ogrjevna moć suhe organske tvari u zavisnosti je od vrste mulja te srednja vrijednost iznosi oko 25.000 kJ/kg kod neobrađenog mulja, te do 12.000 kJ/kg kod anaerobno stabiliziranog mulja. Za usporedbu, toplotna moć smeđeg ugljena iznosi 8.400 – 11.300 KJ/kg [2].

Zbog sadržaja teških metala i drugih štetnih materija, zbrinjavanje ovog mulja predstavlja poseban problem jer zbog svog kemijskog sastava i karaktera zabranjeno je da se odlaže na deponije komunalnog otpada. Često ovakav mulj ima i štetne efekte. Ovakav mulj se mora kontrolirano zbrinjavati jer predstavlja čak i veći problem od same otpadne vode. Razlog tome je što je utjecaj otpadnih voda manje vidljiv ako se ispuštaju u vodotoke ili velike akumulacije.

Kanalizacijski mulj se sada najčešće odlaže sa i bez stabilizacije vapnom što je neprihvatljivo.

Kako bi se sačuvala energetska vrijednost procijednog mulja potrebno ga je čim prije iskoristiti na mjestu nastanka (*in site*), inaktiviranje radi zaštite negativnog utjecaja prirode na mulj i mulja na okoliš i prirodu.

Na odlagalištima otpada je zabranjen prihvat, između ostalog i "komunalnog otpada ukoliko mu masa biorazgradive komponente premašuje 35 % od ukupne mase". Biološki

stabilizirani mulj sadrži uvijek više od 35 % biorazgradive tvari. Također je kao kriterij za odlaganje otpada na odlagališta neopasnog otpada, kao granična vrijednost za ukupni organski ugljik TOC[1], određeno najviše 5% od mase suhe tvari, a stabilizirani mulj ima više od 5 % TOC – a. Prema tome, muljevi sa uređaja za prečišćavanja komunalnih otpadnih voda se ne bi smjeli odlagati na odlagališta neopasnog otpada [3].

Muljevi su po svom sastavu, količini, obradi i konačnom odlaganju veliki tehnološki i ekonomski problem svakog javnog sistema odvodnje. Procijedni mulj od pročišćavanja otpadnih voda mora se korektno inaktivirati iz ambijenta, ali treba ga promatrati kao obnovljivi izvor energije i kroz poštivanje metoda energetske efikasnosti potrebno ga je tretirati (iskoristiti), termovalorizirati a ne odlagati – deponirati. Odlaganje mulja ili deponiranje nije prihvatljivo i privremena rješenja kod nadležnih organa bit će opravdana još vrlo kratak period. U vremenu naprednih i inovativnih tehnologija takvo rješenje je nedopustivo i zbog energetske neiskoristivosti a samim tim i ekonomske neprofitabilnosti. Mulj od pročišćavanja komunalnih otpadnih voda treba promatrati kao energent koji ima relativno visoku toplotnu moć 12 – 29 MJ/kg i koji se može koristiti kao energent, a preostali pepeo kao agregat – frakcija u građevinarstvu. Inertni pepeo dobiven iz procijednog mulja može se koristiti kao građevinska frakcija – agregat ili odlagati na javnim deponijima kao nasipni materijal.

3. TRETMAN PROCIJEDNOG MULJA KROZ EUROPSKE SMJERNICE

Kako bi se sačuvao okoliš doneseni su odgovarajući zakonski propisi i direktive kojih se treba nužno pridržavati prije donošenja odluka o načinu obrade i konačnog odlaganja mulja. Zakoni o korištenju obnovljivih izvora energije i efikasne kogeneracije također je stvorio obaveznost korištenja procijednog mulja kao energenta kroz zadovoljenje EU Direktive 2009/28/EC[2] poznate kao 20 – 20 – 20 do 2020. godine i EU Direktive 2012/27/EC[3] [4, 5].

Mulj od pročišćavanja svih procijednih otpadnih voda treba promatrati kao obnovljivi izvor energije i kroz energetsku učinkovitost potrebno je tretirati (iskoristiti), a ne odlagati – deponirati, što nalažu i EU Direktive 86/278/EEC[4], 91/271/EEC[5], Uredba EZ 305/11[6] [6] i lokalni zakoni, odluke i pravilnici čime se treba direktno štititi zrak, vode, tlo, hrana, biosfera uz maksimalno iskorištenje postrojenja, energetsku učinkovitost i ekonomsku profitabilnost čime se stvaraju uvjeti za održivi razvoj.

DWA tehničke smjernice za korektno i efikasno iskorištenje procijednog mulja [7]:

DWA – M 379/2004 Dehidracija mulja;

DWA – M 386/2011 Termički tretman mulja – monoincineracija;

[1] TOC – Total Organic Carbon

[2] Direktiva 2009/28/EC Europskog parlamenta i vijeća od 23. travnja 2009. o promicanju uporabe energije iz obnovljivih izvora te o izmjeni i kasnijem stavljanju izvan snage direktiva 2001/77/EZ i 2003/30/EZ

[3] Direktiva 2012/27/EC Europskog parlamenta i vijeća od 25. listopada 2012. o energetskoj učinkovitosti, izmjeni direktiva 2009/125/EZ i 2010/30/EU i stavljanju izvan snage direktiva 2004/8/EZ i 2006/32/EZ

[4] Direktiva Vijeća 86/278/EEC od 12. juna 1986. godine o zaštiti okoliša, posebno tla, kod upotrebe mulja iz uređaja za pročišćavanje otpadnih voda u poljoprivredi

[5] Direktiva Vijeća od 21. svibnja 1991. o pročišćavanju komunalnih otpadnih voda (91/271/EEC) je usmjerena na zaštitu okoliša od štetnog djelovanja ispusta otpadnih voda

[6] UREDBA (EU) br. 305/2011 EUROPSKOG PARLAMENTA I VIJEĆA od 9. ožujka 2011. o utvrđivanju usklađenih uvjeta za stavljanje na tržište građevnih proizvoda i stavljanju izvan snage Direktive Vijeća 89/106/EEZ

DWA – M 387/2012 Termički tretman kanalizacionog mulja – incineracija u termoelektranama;
DWA – M 387E/2014 Termički tretman u elektranama – koincineracija.
Incineracija i koincineracija u navedenim procedurama zahtijevaju predkalcinaciju i sušenje na 85 % ST[7].

4. ANALIZA MULJA

Kako bi se moglo opredijeliti o načinu postupanja sa procijednim muljem potrebno je redovno vršiti laboratorijske analize i donositi odluke o tome kako korektno koristiti mulj. U slučaju kad mulj treba efikasno koristiti kao fertilizator tla ili kao energent predlaže se dehidracija mulja na koncentraciju 75 % ST obzirom na visok sadržaj vlage u procijednom mulju i prisustvo flotata. Analiza mulja treba obuhvatiti sljedeće parametre [7]:

- sadržaj suhe tvari, sadržaj organske tvari;
- pH;
- sadržaj dušika i fosfora;
- sadržaj kadmija, bakra, nikla, olova, cinka, žive i kroma.

Ukoliko su izmjerene vrijednosti u dozvoljenim veličinama iz mulja se može proizvoditi eko pelet kao fertilizator tla.

Treba voditi računa da se tretmanom jedne vrste otpada ne smije ugroziti okoliš, priroda ili druga vrsta otpada.

5. ISKORIŠTAVANJE ENERGETSKE VRIJEDNOSTI MULJA KROZ NOVE EKO NAPREDNE TEHNOLOGIJE

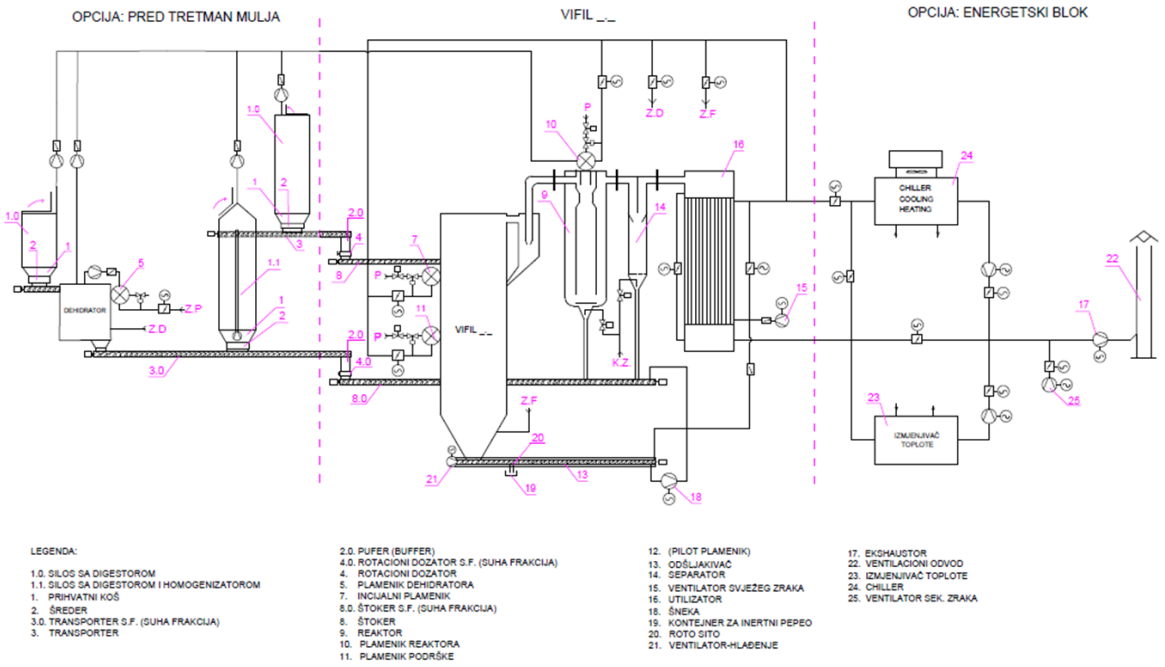
Novi pristup tretmanu/obradi procijednog mulja uz primjenu namjenski – znanstvenih razvijenih tehnologija kroz primjenu Advanced €CO Technology – Postrojenje Energetski Termički – Tretman Otpadnog Mulja, A€T® – PET – TOM, procesom dehidracije, ekstrakcije (gasifier – bioplin), incineracije, koincineracije osigurano je kroz model IDEIK-I-M/ZG, u 8 veličina kapaciteta 50 kg/h – 2500 kg/h. Odnos regulacije je 1:5 (tj. 100:500 kg/h) čime se postiže optimum eksploatacije postrojenja u kontinuitetu od 8760 h/a. Funkcionalna shema takvog uređaja je prikazana na slici 1.

Procesom ekstrakcije odstranjuje se nepoželjan i neugodan miris, a u gasifier – u izdvojen bioplin koristi se u procesu dehidracije čime se povećava energetska učinkovitost za više od 30 %, tj. smanjuje se učešće zemnog plina (primarnog energenta) za 40 % u procesu dehidracije.

Procijedni mulj potrebno je privremeno lagerovati u zatvoreni silos ili bazen (radi inaktiviranja) sa digestorom kako bi se bio plin koristio kao energent u koincineratoru, dehidracija, dezodorizacija, dekontaminacija, detoksikacija i dekarbonizacija se odvija integralno u komori za incineraciju i koincineraciju postrojenja VIFIL[8]. Optimalno korektan, kvalitetan i efektan eko tretman otpadnog mulja sa pročistača otpadnih voda vrši se termičkim postupkom u dehidratoru, turbo incineratoru, pri temperaturi > od 860 - 1000 °C (1200 °C)

[7] ST – Suha tvar
[8] VIFIL - Vrtložna incineracija i fluidizirani sloj u integralnom ložištu

uz obaveznu retenciju > 2" u turbo koincineratoru svih emisija iz turbo incineratora na temperaturi 1000 - 1200 °C (1250 °C), radi uništenja patogenih mikroorganizama i toksina, a bez reverzibilne reakcije.



Slika 1. Funkcionalna shema modela IDEIK-I- M/ZG [8]

Eko postrojenje se sastoji od zatvorenog silosa ili bazena za prihvat mulja, mlina (šredera) za usitnjavanje, transportnog puža (štokera) koji usitnjenu frakciju mulja transportira do dehidratora gdje se vrši termički tretman/obrada, zatim turbo incineratora i finalni tretman/obrada emisija polutanata u reaktoru turbo koincineratora.

Komora turbo incineratora je od INOX – a W.Nr. 1.4841 termo izolirana i u mehaničkoj zaštiti. Komora reaktora turbo koincineratora izolirana je keramičkom opekom (1600 °C), a plašt u mehaničkoj zaštiti je od INOX-a W.Nr. 1.4841, kako bi se osigurala emisija polutanata bez boje, okusa, mirisa, lebdećih čestica.

U IDEIK-I-M/ZG postrojenju modularne izvedbe uz tretman/obrada procijednog vodenog mulja mogu se inkorporirati moduli za termički tretman/obrada komplementarnog "otpada" kao što je animalni ili kompozitni "otpad" u različitim vremenskim terminima.

Toplinska energija dobivena u procesu termovalorizacije kombiniranog grijanja i hlađenja CHC[9], može se koristiti za tehnološke svrhe grijanja, za proizvodnju električne energije kogeneracijom kao i za hlađenje trigeneracijom CHCP[10] preko apsorbera koji koristi toplinsku energiju kao energent i poligeneraciju inertni pepeo ISSA[11].

Cijelim procesom termičkog tretmana otpadnog mulja upravlja se sa PLC master – kontrolerom i monitor sustavom, sa elektronskim zapisom procesa i mogućnošću on–line konekcije.

[9] CHC – engl. *Combined heat, cooling*
[10] CHCP – engl. *Combined heat, cooling, and power production*
[11] ISSA – engl. *Incinerated sewage sludge ash*

Primarni energent u termičkom tretmanu "otpada" za IDEIK-I-M/ZG modularno postrojenje preporučuje se zemni plin ili LPG/UNP[12], a njegovo učešće je 12 – 15 % po toni "otpada" uz primijenjeni turbo sistem rekuperacije.

Energetska vrijednost mulja sa pročistača otpadnih voda kreće se od 14 – 29 MJ/kg ovisno o vrsti (sirovi, aktivni) i agregatnom stanju (suhi, mokri).

Procesom dehidracije procijednog mulja sa 25 % ST na 85 % ST oslobađa se bioplin i vodena para koja sa sobom nose i neugodan miris. Tehnologijama i tehnikama DETIK-I vrši se dezodorizacija, dekontaminacija i detoksikacija izdvojenog bioplina i vodene pare u namjenskim plameniku koji se koristi u procesu dehidracije mulj.

Iz dehidrirane frakcije procijednog mulja procesom peletiranja proizvodi se eko pelet – energent.

Također postoji mogućnost da se u procesu tehnikama DETIK-I koristi i dehidrirani mulj eko pelet – energent na namjenskom plameniku u procesu dehidracije sa emisijom polutanata bez; boje, okusa, mirisa, lebdećih čestica.

5.1. Tehnički opis VIFIL__M

U postrojenju VIFIL__M kao konvertoru mulja u energiju CSP[13] postoji mogućnost korištenja:

- MOF mehanički obrađene frakcije;
- BOF biološki obrađene frakcije;
- HOF kemijski obrađene frakcije;
- TOF termički obrađene frakcije.

Opcije maksimalnog iskorištenja postrojenja čine sveobuhvatnim, bez stvaranja novih otpadnih materija "0" otpada, Zero Waste.

Prijem mulja u prihvatnom košu ili silosu sa digestorom, u procesno – tehnološkom termičkom tretmanu PET–TOM instalacije gdje odmah počinje proces korektnog zbrinjavanja i iskorištavanja mulja kao energenta.

Kod starta temperature u primarnoj komori, vrtložnom incineratoru, mora biti viša od 960 °C a u sekundarnoj komori, koincineratoru, viša od 1000 °C čime se ostvaruje korektna emisija i racionalno korištenje energenta. Unos energenta može se vršiti samo kad je radna temperatura u primarnoj komori viša od 860 °C sa masom raspoređenom za kontinuirano doziranje za kapacitet komore po satu.

Primjer 1000 kg/h : 60 min = 16,7 kg/min.

Nije dozvoljeno kumulativno – šaržno unos energenta u toku eksploatacije.

Konvertiranje mulja u energiju odvija se u primarnoj komori, modulu postrojenja za termički eko tretman. Energija iz koincineratora koristi se u utilizatoru koji je sekundarni dio postrojenja VIFIL__M za rekuperaciju sa svježim zrakom koji zagrijavamo na 500 °C i koristimo u incineratoru, koincineratoru i u fluidiziranom sloju turbo sistemom. Dimnim plinovima se oduzima toplinska energija i vraća u proces kroz zagrijavanje zraka za sagorijevanje, čime se direktno ostvaruje značajna energetska učinkovitost iz obnovljivih izvora energije pri prihvatu procijednog mulja sa 25 % ST.

Energetska frakcija vlage preko 50 % dozira se u VIFIL__M u vrtložnu komoru, a energetska frakcija ispod 50 % vlage dozira se u fluidiziranom sloju, kako bi se postiglo optimalno iskorištenje frakcije procijednog mulja.

[12] LPG/UNP – engl. Liquefied petroleum gas/Ukapljeni naftni plin
[13] CSP – engl. *Converter Sludge Power*

6. PROCIJEDNI KANALIZACIONI MULJ ENERGENT – GRAĐEVINSKA FRAKCIJA I FERTILIZATOR TLA

Poslije efektnog energetskog iskorištavanja procijednog mulja, finalni produkt termičkog tretmana/obrade dobije se inertni ohlađeni pepeo, koji je 95 % volumetrijski manji od ulazne komponente (iz 1000 kg dobije se 40 – 50 kg pepela). Ohlađeni pepeo se može koristiti kao frakcija u građevinarstvu, nasipni materijal kao pokrov u zaštiti biosfere na odlagalištima otpada, prije humanizacije. Ako u pepelu postoji vjerojatnoća ili se kroz tehnološki proces ulazne komponente utvrdi prisutnost toksične materije i teških metala takav se pepeo sistemom "utiskivanja" trajno odlaže u namjenske istraživačke napuštene bušotine ili napuštena rudnička okna, čime je sigurno zaštićena okolina (problem žive i fluora).

Pouzdanost i izvedivost metode utiskivanja dokazana je njenom originalnom primjenom u zbrinjavanju "otpada" u naftnoj industriji. U naftnoj industriji se koristi kao reverzibilni proces pri čemu je riječ i o opasnom otpadu poput otrovnih solida i teških metala. Pepeo se utiskuje u obliku kaše koja se priprema miješanjem otpada sa odgovarajućim fluidima. Utiskivanje se vrši visokotlačnim pumpama do 100 bara – otpadna smiješa se sa prirodnim slojem fluida i vremenom kemijski sjedini. Tako otpadni pepeo trajno ostaje zarobljen (zbrinut) u dubokom podzemlju. Bušotine i donji horizonti napuštenih rudničkih oceana su dubine do par stotina metara ispod razine nivoa mora a naftne bušotine do 5000 m najdublja nalazišta u geološkim slojevima, tzv. akviferima, koji su dubine do najviše 800 metara, a pitka voda za komunalne izvore crpi se sa dubine od 100 do 300 m iznad nadmorske visine.

Eko korektno zbrinjavanje otpadnog pepela u pogodne geološke formacije zasad je jedina znanstveno ispravna metoda, koja otpad na siguran i trajan način uklanja iz biosfere.

Jedan od načina iskorištavanja kanalizacijskog mulja je proizvodnja komposta kao hranjiva za biljke odnosno kao fertilizator tla. Smatra se da mulj kao nusprodukt obrade komunalnih otpadnih voda ima više korisnih nego štetnih svojstava, jer sadrži vrijedne hranjive tvari koje pospješuju rast poljoprivrednih kultura, a sadržaj hranjivih tvari u odnosu na klasična gnojiva je prikazana u tablici 1 [9 - 11].

Tablica 1. Usporedba hranjivih tvari u mineralnim gnojivima i mulja u postocima [9]

Proizvod	Dušik	Fosfor	Kalij
Mineralno gnojivo	5	10	10
Stabilizirani mulj (ST)	3,3	2,3	0,3

Dugoročno održivo korištenje mulja u poljoprivredi potiče i Europski savez nacionalnih udruženja pružatelja usluga vodoopskrbe i odvodnje [12]:

- muljem treba gospodariti kao resursom (npr. fosfor i ostale hranjive tvari te kao fertilizator tla) što je u skladu sa aktualnim razmišljanjem EU ugrađenim u razne politike, kao što je inicijativa o učinkovitom korištenju resursa u sklopu strategije EU 2020.,
- održivo korištenje mulja zahtijeva povećanu proizvodnju bioplina. To je u skladu sa energetskim ciljevima EU u sklopu strategije EU 2020.,
- u sklopu politike o otpadu, ukidanje statusa otpada je mogućnost da kompostirani mulj bude prepoznat kao korisno gnojivo.

7. ZAKLJUČAK

Probleme dispozicije procijednog mulja u posljednje vrijeme postaje sve veći. Na osnovnu toga, izboru najboljeg rješenja u zbrinjavanju i ponovnom iskorištavanju ovakvog mulja se treba pridati veća važnost.

Termički tretman otpadnog mulja programom ENERGETIS^{ITG} ima i socijalni aspekt jer ne poskupljuje naknadu za odvodnju otpadne vode već štiti prirodu i okoliš uz pretpostavku ostvarenja ekonomskih benefita.

Kako bi se cijeli program tretmana otpadnih voda i mulja korektno realizirao i postao inherentan proces potrebno je uvesti zakonski: premije za korektno postupanje sa muljem ili kaznene penale i penalizaciju za nepoštivanje i ekološke takse za nekorektno postupanje sa muljem.

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EKOLOŠKA KRIZA IZMEĐU KULTURE I PRIRODE

ECOLOGICAL CRISIS BETWEEN CULTURE AND NATURE

Josip Guć*

* Sveučilište u Splitu, Filozofski fakultet, Split, Hrvatska

autor za korespondenciju: Josip Guć, e-mail: jguc@ffst.hr

Prethodno priopćenje

SAŽETAK

Ovaj rad pokušava propitati neka od izvorišta ekološke krize polazeći od određenih konceptualnih problema, a riječ je prije svega o određenju pojmova prirode i kulture. Rad pokazuje kako se načini čovjekova posredovanja prirode, koji sačinjavaju različite aspekte kulture, sve više svode na onaj tehnološki, a takva redukcija pogubna je kako za čovjeka, tako i za prirodu. Suvremeni problemi u odnosu kulturnog i prirodnog otvaraju široki prostor za etička promišljanja, među kojima je osobito zanimljivo pitanje o tome treba li nas ekološka kriza potaknuti na zaštitu okoliša ili na zaštitu prirode. Konačno, rad ističe okvir integrativne bioetike kao najadekvatniji za razrješavanje čitavog sklopa ovdje razmatranih problema.

***Ključne riječi**: priroda, kultura, ekološka kriza, okoliš, tehnologija, bioetika*

ABSTRACT

This paper tries to examine some of the sources of the ecological crisis, starting from certain conceptual problems, primarily from the determination of notions nature and culture. The paper shows how the ways of man's mediation of nature, which constitute different aspects of culture, are increasingly being reduced to the technological one. Such a reduction is pernicious to both man and nature. Contemporary problems concerning the relationship between the cultural and the natural are opening wide fields for ethical reflections. In that perspective, an interesting question is whether the ecological crisis should initiate environment protection or nature protection. Finally, the paper highlights the framework of integrative bioethics as the most appropriate for solving the entire set of problems that are discussed here.

***Keywords**: nature, culture, ecological crisis, environment, technology, bioethics*

1. UVOD

Priroda i kultura sačinjavaju dvije osnovne sfere ljudske egzistencije. Način na koji su ti pojmovi definirani ili na koji se razumijevaju bitno utječe na čovjekovo samorazumijevanje i razumijevanje onoga s čime on ulazi u odnos. Da je ovdje riječ samo o razumijevanju, a ne i o djelovanju koje se usko veže uz njega, ova bi tema vjerojatno bila tek jedna od onih koje služe »gimnastici uma«. No imajući u vidu razorni čovjekov odnos prema njegovu prirodnom (materijalnom) okolišu, ova se tema nadaje kao neizostavna u poimanju suvremene situacije te putova kojima bismo trebali krenuti u svrhu prevladavanja ekološke krize.

Pored rasprave o određenju i važnosti određenja pojmova prirode i kulture, rad će se osvrnuti na ulogu tehnologije u ovom kontekstu, kao i na način na koji bioetika može doskočiti nekima od problema unutar napetog odnosa prirodnog i kulturnog. Kako je ovdje riječ o refleksiji nad problemima koji izviru iz ekološke krize, rad će se posebno osvrnuti na alternativu između zaštite prirode i zaštite okoliša. Njegova pretenzija ne prelazi okvire ocrta navedene problematike i nabačaja nekih određenja koja bi mogla biti od pomoći na putu njenog razrješavanja.

2. POIMANJE I ZNAČAJ POIMANJA PRIRODNOG I KULTURNOG

Potrebno je odmah naglasiti da pri početnom pristupu pojmovima 'priroda' i 'kultura' nailazimo na mnoga određenja u različitim razdobljima i sredinama, koja su, stoga, rezultirala različitim odnosima jednoga i drugoga. To je već očito na primjerima odnosa pojedinih kultura spram ljudske prirodnosti, tjelesnosti, seksualnosti itd. Naravno, tu je svakako riječ i o očitim razlikama u njihovoj nastrojenosti spram izvanljudske prirode. Međutim, ovdje nećemo ulaziti u ta različita poimanja pojedinih kultura, nego ćemo kulturu pokušati pojmiti na generičkoj razini, dakle, ne kao zbir duhovnih posebnosti određene grupe, nego kao čovjeku specifičan način bivstvovanja, reflektirajući ga u njegovu odnosu spram prirode. No ipak ćemo veću pažnju posvetiti načinu na koji su se sadržaji kulture razvili na Zapadu, gdje je kultura pokazala svoje najrazornije potencijale.

Čini se da je jasnije određenje pojmova prirode i kulture nužna pretpostavka racionalnog diskursa o problemima koji su proizašli iz ekološke krize. Naime, neke od suvremenih stramputica nastaju upravo zahvaljujući odveć samorazumljivom poimanju kulturnog i prirodnog, a one su možda više izražene u međuljudskim odnosima, negoli u čovjekovu odnosu spram ne-ljudskih živih bića i anorganske materije. Velika važnost određenja ovih dvaju pojmova proizlazi i iz toga što oni čine okosnicu našega promišljanja mnogih drugih pojmova i fenomena. Ako nam njihovo precizno određenje stalno izmiče te ako je ono, zapravo, nedostižno, tada bismo barem trebali uvidjeti načine na koje se ti pojmovi definiraju, a što nam nerijetko puno govori o načinu na koji sebi posredujemo ono što nas okružuje. U tom se svjetlu ova tema nameće kao osobito važna u ispitivanju geneze našeg nezdravog odnosa prema okolišu, kao i promišljanju mogućih alternativa.

Kao što je donekle naznačeno, određenje ovih pojmova igra ključnu ulogu u čovjekovu samoodređenju i određenju onoga što ga okružuje, a što se onda očituje u njegovu konkretnom djelovanju. Već običan, »zdravi razum«, odnosno svakodnevni jezik, često barata s pojmom prirodnoga kao poželjnoga. Ne treba posebno naglašavati da ovo gledište previđa da ono sâmo, kao jezik kojim je izrečeno i vrijednosni sustav iz kojega proizlazi, nastaje u okviru kulture, koja se izdiže nad prirodom. Čini se bespotrebnim ukazivati i na to da prirodno stanje podrazumijeva neke odnose koji su neprihvatljivi unutar kulturne zajednice (ili bi to barem trebali biti).

Ovakva razumijevanja zanemaruju posredničku »prirodu« kulture. Tu prisutan koncept prirodnosti bitno je kulturno određen, tj. kulturno posredovan, pa ovdje možemo izvrnuti konstrukciju kojom prethodna rečenica završava, nazivajući ovaj fenomen »kulturom prirode«. Međutim, već ovi konstrukti odaju bitnu isprepletenost koja stoji barem u začecima i etimologiji određenja kulture. Imajući u vidu etimologiju (lat. *colere* = gajiti, oplemenjivati), kultura je: »u najširem smislu: preradba i usavršavanje nečega, neke građe, nekog materijala za određenu svrhu. U tom se smislu i govori npr. o kulturi tla, kulturi bilja (agrikulturi) i sl. I u tom smislu već ta riječ znači zapravo oplemenjivanje« [1]. Ovakva odredba vodi k ideji, odnosno proizlazi iz ideje čovjeka kao bića čije djelovanje izvodi prirodu iz zaostalosti u plemenito postojanje, čije djelovanje time ima veću vrijednost od onog puko prirodnog. Konačno, sam taj djelatnik sebe (u generičkom smislu) postavlja kao vrjednijeg od onoga nad čime djeluje. Vidjet ćemo, iako se to već dade nazrijeti, kako oplemenjivanje i nije samorazumljiv atribut kulture. Ali ono što već kod ove definicije valja primijetiti jest da kultura uvijek stoji naspram nečega. To ne znači da ona samim time ne ovisi o tome nečemu, a ne znači niti to da ne ulazi u blisku vezu sa svojom suprotnošću.

U jednom obuhvatnom smislu kultura bi se mogla odrediti i na sljedeći način (u definiciji koja slijedi uzimamo u obzir i duhovnu i materijalnu kulturu): »U užem smislu kultura znači ostvarivanje humanih vrednota u čovjeku i njegovim djelima koja, za razliku od djela civilizacije (koju nazivamo materijalnom kulturom!), nose svoje vrednote same u sebi. Ona znači u isti mah i akt, stvaralački proces i ono što je tim procesom stvoreno. To bi bili npr. moralni čini, umjetničko stvaralaštvo, ali i ostvarena djela, za razliku od tvorevina tehnike koja služe svrhama izvan sebe. No i kulturne tvorevine (kulturna dobra!) mogu se nasljedovati i prenositi samo svojom vanjštinom, bez unutrašnjih vrednota koje su temeljne za ostvarenje kulturnih dobara. Ova vanjština kulture tvori zajedno s tehnikom ono što nazivamo civilizacijom« [2]. Iako postoji više kultura u sadržajnom smislu, radi se o jednoj kulturi po pitanju same forme. Ona se, u tom pogledu, može promatrati kao specifični modus čovjekova bivstvovanja (uz onaj prirodni) ili kao specifični način čovjekova posredovanja postojećeg – ali i mjesto na kojem se rađa moguće i buduće, što je jasno prisutno u moralitetu i stvaralaštvu, koji opet nužno podrazumijevaju neki odnos spram postojećeg, tj. posredovanje postojećeg.

Kulturi nasuprot stojeći pojam 'priroda' također je bremenit različitim značenjima koja su mu pridavana u različitim historijskim momentima. Možda je samo pitanje o određenju pojma prirode, kako navodi Branko Pavlović, lišeno kognitivnog smisla. Čini se da je određivanje nečega kao prirodnog samoevidentno, naprosto putem njegova suprotstavljanja onome što je načinjeno od strane čovjeka, iako suvremeni razvoj tehnologije unosi pomutnju u tu jednostavnu točku razdvajanja [3]. To bi se prije svega moglo pripisati čovjekovoj intervenciji u intimnu, genetičku strukturu žive prirode, ali i njegovoj progresivnoj zamjeni izvorne prirode tehnostrukturom. Izgleda da je time tradicionalni pojam prirode kao onoga čovjeku izvanjskoga »izgubio neka od svojih određenja i to utoliko što su tradicionalne suprotnosti – dakle priroda *versus* tehnika, postavljanje, kultura – ublažene mogućnošću tehničke reprodukcije prirode. Time što se bavimo tijelom kao prirodom, koja mi sami jesmo, razvija se obzirom na tradiciju posve novo viđenje i koncepcija prirode. (...) Povod formulaciji, da tijelo predstavlja prirodu koja jest sam čovjek, predstavlja činjenica da danas čovjek, i to svaki ponaosob, na vlastitu tijelu osjeća posljedice društvenog djelovanja spram prirode« [4].

Ovime pak pojam prirode ostaje neodređen, a nemogućnost njegova preliminarnog određenja prvenstveno proizlazi iz naše ukotvljenosti u kulturu i nemogućnosti da bez kulturnog posredovanja mišljenjem uopće pristupimo onome što držimo za prirodu. Usprkos samoevidentnosti postojanja prirodnog posredstvom naše tjelesnosti, ali i uvidom u postojanje ne-kulturnog, nečega što bivstvuje neovisno od ljudske kulture, sama se ta evidentnost ne bi

dala na ovoj razini osvijestiti bez kulturnog posredovanja. Kada bismo bili potpuno u prirodi, tada to naprosto ne bismo mogli poimati. Usporedbom s određenim ne-kulturnim bićima uviđamo da jesmo priroda jer smo životinja, ali u isti mah, kako kaže Hegel, prestajemo biti životinjom, [5] isto kao što zadobivanjem samosvijesti postajemo bitno drugačije biće, iako u biološkom smislu ostajemo homo sapiens. Promatrano iz naše perspektive, a iz svoje spoznajne, djelatne i stvaralačke »kože« ne možemo izaći, kultura i priroda stoje u nerazdruživom odnosu – jedna, naprosto, ovisi o drugoj. Kad bi se i inzistiralo na poimanju prirode kao sveukupnosti bića, nemoguće bi bilo unutar njega ne uspostaviti određene kvalitativne razlike. Stoga bi takvo određenje izgubilo svu eksplanatornu moć. Ništa bolje ne bi bilo ni s krajnje idealističkim svođenjem sveukupnosti bića na kulturu.

U situaciju u kojoj prirodu nije moguće naprosto preliminarno odrediti, jedino što možemo je izvesti jedan historijski pregled načina odnosa spram nje, u kojem se vrši i njena refleksija. Naravno, ovdje nije mjesto za izvođenje takvog pregleda, ali svako je potrebno ukazati na neke ključne točke razvijanja načina na koje kultura posreduje prirodu, naročito posredovanja prirode kakvo danas upražnjavamo.

2.1. Tehnološko posredovanje

Kultura se odnosi spram prirode na puno dublji način nego što su to mnogi spremni priznati. Naše poimanje prirode bitno utječe na naš odnos spram nje i njezinih pojedinačnih entiteta, pa čak i na naš odnos spram drugog čovjeka. Tako se danas lako može opaziti pogubnost mehanicističkog svjetonazora kakvog je, među ostalima, inaugurirao Descartes razumijevanjem prirode kao puke *res extensae* i tijela kao stroja, kojem se pridružila također pogubna Baconova preobrazba znanja u moć podvrgavanja prirode. O mehanicističkom se svjetonazoru u izvjesnom smislu može govoriti još od početaka ljudske kulture, [6] ali on se eksplicitno otkriva tek od začetaka moderne znanosti te zadobiva oblik koji u velikoj mjeri nasljedujemo i danas.

Uzmimo tek terminologiju i značenja koja ona nosi unutar biologije u posljednjih stotinu godina. Jezik biologije stalno poprima termine, a zajedno s njima i poimanja vladajuće tehnologije (upravo kao slike svijeta, a ne tek sredstva). To zorno prikazuje Jeremy Rifkin, ukazujući na prevladavajući utjecaj strojarskih idioma u pedesetim godinama 20. st. (tako je, primjerice, 'performansa' djelomično stupila na mjesto 'ponašanja'), a potom i na suvremenu tendenciju u kojoj biologija sve više postaje informatička znanost. To se ponajprije očituje u bliskoj vezi genetike i informacijske tehnologije, gena i računala, koja u biotehnološkom stoljeću svoj uzlet dobiva zahvaljujući projektu kartiranja i sekvencioniranja ljudskog genoma, na što se nadovezuje i genetička izmjena živog svijeta, koja vodi u smjeru komercijalnih dobitaka [7]. Treba imati na umu da je integracija biologije, informatike i ekonomije, zajedno s ostalim znanostima koje dolaze s ovima u vezu (a uglavnom potaknutima posljednjom), integracija reduktivnog tipa. Na djelu nije pokušaj svestranog pogleda na problem, u kojem bi više perspektiva moglo pružati svoje vrijedne uvide, nego o reduciranju znanosti na primjenjivo znanje, koje ima služiti tehnološkoj mašineriji, a najčešće u svrhu profita.

Rifkin uz to ističe da svaki novi koncept prirode služi opravdanju neizbježnosti načina na koji ljudi organiziraju svijet. Za to daje primjer u Darwinovu tumačenju prirodne evolucije, koja legitimira pretpostavke industrijskog društva Engleske njegova vremena, što se ponajprije ogleda u postavljanju stjecanja i nasljednosti kao osnovnih načina opstanka. Stoga nije tako, kako se često misli, da je socijalni darvinizam primjena neutralne teorije o prirodi na društvo, nego se upravo društvena situacija projektira na onu prirodnu [8]. Ako je Rifkin na ovom mjestu u pravu, ako se ovdje ne radi o pretjeranom sociologiziranju (a može se reći i:

u mjeri u kojoj se ne radi o tome), naša mogućnost zauzimanja jedne meta-pozicije spram ovakvih načina tumačenja prirode otvara izvjestan prostor neovisnosti, što opet ne znači da smo potpuno odriješeni od naših ne-znanstvenih sredstava i svrha. Čini se da je takva vrsta ovisnosti, ipak, neizbježna, međutim ona ne treba označavati slabost. Naprotiv, znanstveno rasuđivanje radi znanosti same gubi svoj *raison d'etre*. Nova situacija otvara potencijalnu normativnu dimenziju unutar onog dijela našeg znanja za koji smo često držali da je isključivo deskriptivan. Ako naše tumačenje prirode nosi sa sobom određene svrhe i namjere te ako mi iste možemo osvijestiti, tada je ono barem indirektno moralno relevantno.

Zanimljiv je suvremeni scenarij ove tendencije koji Rifkin ističe. Prema njegovu mišljenju, današnja razmišljanja o evoluciji postaju sukladna novom trgovinskom i gospodarskom uređenju. U tržišnom nadmetanju veliku vrijednost zadobiva mogućnost predviđanja i brzog snalaženja u stalno promjenjivom komercijalnom okolišu, za što je od iznimne važnosti sposobnost upravljanja podacima i stvaranja operativnih mreža. Kada taj koncept prebacimo u područje biologijskih tumačenja, tada našu želju da genetički prepravljamo organizme pravdamo time da se organizmi u prirodi ionako sami prepravljaju, pri čemu evolucija nije, kako se to mislilo, spor proces, nego se osnovne biološke promjene zbivaju brzo i iznenadno. Tu racionalizaciju prati i umrtvljenje empatičke veze spram predmeta manipulacije (prirode), kako bi se on lakše eksploatirao. Tako živa bića postaju tek »snopovi genetičkih podataka«, a kartezijansku predstavu o njihovoj bezdušnoj, mehaniziranoj prirodi zamjenjuje ideja o životu kao podacima [9]. U kontekstu primarne motivacije, prije se radi o zamjeni naglasaka, jer odnos spram živih bića kao pukih predmeta ljudske uporabe ostaje nepromijenjen. Promijenjena je samo mogućnost intervencije u njihov život unutar istog, puko instrumentalnog odnosa, iako posljedice te promijene nose jednu kvalitativno novu opasnost.

»Problem je, još jednom, u tome da u našim kozmologijama napuhujemo sićušne vidove prirodne stvarnosti koje u jednom trenutku uvodimo u univerzalnu kozmologiju pa zatim tvrdimo da čitava priroda djeluje na isti način koji se slaže s našim djelovanjem. Mi stalno prepravljamo prirodu kako bi odgovarala našim vlastitim potrebama, a zatim zaključujemo da tehnološki postupci kojima se sada služimo moraju biti slični postupcima korištenima u prvobitnom stvaranju« [10].

Naše promatranje prirode, stoga, nikako nije pogled »nevinog oka«, nego je bitno posredovano našim svrhama. To svakako postaje očitije onda kada sagledamo eksperimentalni ideal moderne znanosti koji jedan od svojih najeksplicitnijih izvora ima kod Bacona. On ne samo da otvoreno postavlja znanje kao moć, nego i eksplicitno postavlja umjetnu ljudsku konstrukciju kao onu koja najadekvatnije otkriva suštinu prirode, kad kaže da se »priroda stvari više otkriva u mučenju umijećem nego u vlastitoj slobodi« [11]. S obzirom na navedeno, ne čini se iznenađujućim što se u mislima koje uspostavljaju modernu znanost već nalaze pogubni elementi koji su se danas bjelodano aktualizirali na uštrb ne-ljudskih živih bića, ali koji sadržavaju i potencijale za napad na samo ljudsko biće. »Priroda se naime pobjeđuje samo pokoravajući joj se«, [12] jedna je od ključnih Baconovih rečenica koja je odredila put novovjekovne znanosti i upravo oslikala našu sadašnjost. Ako se priroda shvaća kao instrument ljudske moći ili puko sredstvo i ako se čovjek prirodi mora podrediti ukoliko je želi pokoriti, tada čovjek mora postati sluga svog sredstva. Fenomen čovjeka kao održavatelja stroja ili tehnologije, koji danas jasno uočavamo, rezultat je izvođenja samog duhovnog zadatka novovjekovlja.

Kako tvrde Max Horkheimer i Theodor Adorno, povećanje moći nad prirodom čovjek plaća otuđenjem od onoga što je u njegovoj moći. Stvar se, naime, priznaje samo manipuliranjem, što jasno vodi ukidanju svakog afiniteta između subjekta koji pripisuje smisao i objekta koji je tek puki nosioc značenja, a sam u sebi besmislen [13]. Čovjek je danas stekao toliku moć nad prirodom da je pokušava potpuno negirati, ali priroda mu isti

slijepi nesvrhoviti mehanizam koju je on u nju ugradio uzvraća kao osvetu. U tome leži čovjekovo prokletstvo izrastanja iz *stvaratelja* u *stvoritelja* (ili *Tvorca* kao božanske figure). Smisao koji karakterizira čovjeka stvaratelja potpuno se gubi u čovjeku stvoritelju, koji u tim okvirima gubi sposobnost osmišljavanja i određenja sebe samog. To je svakako mogao dok je stajao »naspram nečega/drugoga«, gdje su i njegova kultura (kao uzvišena pozicija) i nasuprot stojeća priroda (kao osnova za kulturu i predmet čuđenja) imale specifični smisao i vrijednost, dok se sada u odnosu spram svojeg besmislenog svijeta može odrediti samo kao formalan i obesmišljen stvoritelj. Intervencija u genetičku strukturu živih bića u izvjesnom je smislu čovjeka učinila stvoriteljem, ali takvim koji stvara po diktatu svojih sredstava: tehnologije i profita.

Tehnološko posredovanje prirode, stoga, obesmišljava čovjekovo djelovanje na više razina. Prije svega, čovjeka podvodi pod svoj diktat, čime ozbiljno ugrožava njegovu autonomiju. U tom pogledu, ono istiskuje druge moduse kulture, što se primjerice očituje u »moralnoj ucjeni« koja često prati tehnološki napredak kao samosvrhu. Sačinjavajući od prirodne okoline tehnostrukturu, tehnološko posredovanje stvara lažni privid svijeta koji ima udovoljavati čovjekovim svrhama, dok se ono, zapravo, kao osamostaljeno kreće prema svojoj unutrašnjoj logici. Tehnologija kao samosvrha postala je najinvanzivniji način na koji kultura posreduje prirodu, ali čini se da to posredovanje istovremeno postaje i za čovjeka pogubno posredovanje sama sebe i same kulture iz koje je izniklo.

3. BIOETIČKI PUTOVI K RJEŠENJU

Pokušamo li bioetički pristupiti navedenim problemima, tada prije svega samom poimanju kulture i prirode treba prići onako kako to navodi Sergio Belardinelli: »Ali pošto nijedan od ovih pojmova ne dolazi u 'čistoj' formi, jedna bioetika koja želi biti stvarno primjerena realnosti mora ove interpretirati na 'relacijski' način te pritom izbjeći Scilu oštrog razdvajanja prirode i kulture, kao i Haribdu redukcije jednog pojma na drugi« [14].

Čini se da je postojanje prirode kao nasuprot stojeće čovjeku i kulturi nužno ako bismo potonjem pridavali vrijednost. Štoviše, izvjesno odvajanje kulturnog i prirodnog nužno je kako bi se očuvala sama mogućnost pridavanja vrijednosti, koja se gubi poricanjem umnoga (bilo da ono konstruira, bilo da prepoznaje vrijednosti) kao kulturnog (homo sapiensi izvan kulture ne mogu razviti umnost), a svakako i svođenjem jednoga i drugoga na istu ravan. Pridavanje vrijednosti i prirodi i kulturi moguće je samo putem svojevrsne dijalektičke napetosti između dvoga, koje rezultira djelomičnim prožimanjem, a nikako putem strogo dualističkog međusobnog isključivanja. »Ovu povezanost se mora jasno uvidjeti da bi se primijetilo kako se epohalno značenje integrativno-bioetičkih pitanja našega vremena sastoji upravo u tome da postanemo svjesni diskrepancije između 'prve' i 'druge' prirode, dakle, da metodički objektivirane slike prirode više ne držimo za prirodnu prirodu. A ujedno nanovo primjećujemo kao da mi samo kao bića 'stršimo' u sferi prve prirode, da tu sferu ujedno nama svojstveno razumijevamo, štoviše, da je znamo u 'normativnom' smislu cijeniti« [15]. Naše stršenje iznad prve prirode na izvjestan način omogućava refleksiju nad njom, a praktički (normativni) aspekt te refleksije počinje se osvještavati onda kada smo zadobili dovoljno veliku moć da bitno utječemo na prirodu. Naime, kako naglašava Jonas, priroda je uslijed tehnološkog razvoja postala povredljiva. Može se svakako govoriti o kvalitativno novom tipu ljudskog djelovanja, a samim time i novom predmetu moralne odgovornosti [16]. »Osim fizičkih predispozicija i tehničkih sposobnosti, čovjek ima i moralne dužnosti koje se ne mogu ograničiti samo na jedno područje njegova činjenja, nego moraju 'pokrivati' čitavo područje njegove moći« [17].

Na takvim se određenjima, naime, ne iscrpljuje normativno posredovano poimanje prirode. Naime, ako bismo se ovdje poslužili Jonasovom filozofijom biologije prema kojoj i najrudimentarnije organsko (metabolizam) sadrži nagovještaje duhovnog (slobode), uvidjeli bismo da naš odnos prema ne-ljudskim živim bićima ne smije poprimati izgled odnosa spram pukih stvari. Bitak organskog stalno se afirmira pred prijetnjom ne-bitka, tj. život se afirmira pred prijetnjom smrti, pri čemu se ona u njemu utjelovljuje. Tako je život u svojoj biti relacija, što uključuje stalno transcendiranje samoga sebe [18]. Tu se svakako radi o poimanju koje se bitno protivi oštroj dualističkoj podjeli na deterministički kauzalitet prirode i na kauzalitet slobode. Međutim, upravo je pojam slobode nešto što u ovom Jonasovu konceptu može izazvati probleme, s obzirom na to da je teško govoriti o slobodi bez korelacije s moralnom odgovornošću. Ako bismo ovdje uvjetno i govorili o slobodi, očito je da je ona sloboda vezana uz mogućnost odgovornosti kvalitativno drugačija i bogatija od one koja to nije. Stoga bi, umjesto slobode, spomenuto afirmiranje živih bića bilo prikladnije označiti kao *samoostvarivanje*. U tom bi kontekstu pojam slobode označavao specifičnu formu ljudskog samoostvarivanja. Etiku koja se oslanja na pojam samoostvarivanja, a posredstvom pojma slobode, opširnije ćemo predstaviti u nekim drugim radovima. Naglasimo još samo to da pojam samoostvarivanja također bitno približava kulturu i prirodu, ovdje ne samo u međusobnom konstituiranju prirode i kulture, nego i u nalaženju čovjeku i ne-ljudskim bićima zajedničkog moralno relevantnog elementa. Ovakvo bi (bio)etičko usmjerenje s jedne strane proizlazilo iz približavanja prirode i kulture, a s druge ga strane dodatno osnaživalo, tj. doprinijelo bi odricanju njihove binarno-opozicionalne postavljenosti.

3.1. Zaštita okoliša i zaštita prirode

Ovakvo etičko usmjerenje u direktni moralni obzir ne uključuje materijalni okoliš u obliku anorganske materije upravo iz razloga nemogućnosti njenog samoostvarivanja. To nikako ne znači da ona ni u kom pogledu nije predmet moralnog djelovanja. Naime, kako mnoga živa bića bitno ovise o okolišnim uvjetima, njihovo je zanemarivanje u agresivnoj intervenciji u prirodu rezultat moralno pogrešne nastrojenosti volje.

Stoga se može govoriti o zaštiti okoliša kao o etičkoj temi, ali imajući u vidu gore izneseno, ne bismo se mogli zaustaviti samo na ljudskom okolišu, nego bismo imali dužnost štititi okoliš svakog onog bića koje se samoostvaruje, tj. svakog živog bića. U tom pogledu Nikola Visković zahtijeva »načelno poštivanje svakog života i odustajanje Homo sapiensa od njegovog dosadašnjeg pretjeranog, pljačkaškog i nepoštenog odnosa prema prirodi, a što znači i priznanje da se imperativ očuvanja *prirodne okoline čovjeka* mora uravnotežiti s imperativom očuvanja *prirodnih okolina medvjeda, kita, slona, ptice i leptira, šumskih, močvarnih i prerijskih biotopa* itd., kao samostalnih vrijednosti koje treba zaštititi koliko je god moguće, neovisno o njihovoj ljudskoj upotrebljivosti« [19]. Ako se ovdje navedeni biotopi ne gledaju kao vrijednosti u sebi, nego kao vrijedni očuvanja radi navedenih životinja i drugih živih bića koja ih sačinjavaju, tada ova misao pogađa ono što namjeravamo iskazati.

Ovdje se može postaviti pitanje: treba li u etici govoriti o *zaštiti prirode* ili o *zaštiti okoliša*? Ako bi potonja uključivala okoline svih živih bića radi samih tih živih bića, onda bi ona bila sasvim adekvatan okvir za raspravu o sadržaju naših moralnih dužnosti na tom području ljudskog djelovanja. Međutim, kako zaštita okoliša često podrazumijeva zaštitu samo ljudskog okoliša, zaštita prirode se nametnula kao alternativa tom antropocentričnom i neopravdanom sužavanju etičkog obzora. Iako je motivacija onih koji naglašavaju potrebu zaštite prirode naspram zaštite okoliša puno češće ispravnija, čini se da i tu poziciju prate određeni problemi. Naime, ako bi zaštita prirode podrazumijevala da čitava priroda, kao cjelina ili kao zbir njenih pojedinih živih i neživih elemenata, zaslužuje izravan moralni obzir,

tada se to ne bi dalo opravdati zbog onoga što je gore izneseno. S druge strane, svođenje zaštite prirode na, jednostavno rečeno, brigu o planetu Zemlji, zanemaruje jedan drugi aspekt zaštite prirode koji bi s obzirom na čovjekovo posvemašnje odprirođenje trebalo biti na djelu, a što će biti pojašnjeno u nastavku.

Sama kultura, kao »druga priroda«, za Viskovića je »po svojoj najdubljoj biti proces *odprirođivanja*. To je posebnost onoga što čovjek čini od prirode i nadgrađuje na prirodu, mijenjajući je ili ništeći, a što modernom tehnologijom ide do neslućenih razmjera. Treba biti načisto s tim da je kultura, ma koliko bila i velebna (...), uvijek razaranje, gutanje i uništenje primarne, biljne, životinjske i anorganske prirode. Kultura je uvijek ono naše umjetno. I tu se javlja, među ostalim, silan paradoks. Čovjek najprije preoblikuje, muči i uništi prirodu, ali odmah zatim tu svoju žrtvu vrednuje, osjeća za njom nostalgiju i krivnju, strah od gubitaka, strah od vlastite ugroženosti zbog takva razaranja, pa onda na različite načine svoj odnos s prirodom pokušava etički osmisliti i prirodu barem donekle zaštititi. Tako je kultura istovremeno uništenje prirode i htijenje da se ona sačuva i obnovi« [20].

Ono što je važno kod ovog uvida jest odmak od romantiziranog određenja kulture kao oplemenjivanja. U okviru rasprave o zaštiti okoliša/prirode kultura može pokazivati više svojih lica, od moralne brige (koja, zapravo, samo iz okrilja kulture može proizaći) do bespoštednog zatiranja. Međutim, kako smo mogli vidjeti iz prethodno navedenog, to zatiranje nije tek neobazriva briga za vlastiti interes, nego upravo odraz neprijateljskog stava kulture spram prirodnog kao takvog. Stoga i kad se postavi pitanje o načinu obračuna s ekološkom krizom, čini se da se koncept održivog razvoja najčešće pokazuje kao jalov. On nastavlja prirodu promatrati kao puki resurs ili tek kao sredstvo za profit i održavanje čovjekova blagostanja. Potonje se ne bi trebalo razumjeti kao promicanje čovjekova samoostvarivanja, s obzirom na gore opisanu čovjekovu podređenost svom sredstvu, tj. s obzirom na ugrožavanje same forme tog samoostvarivanja – slobode. Onda kada tehnologija istisne ostale elemente kulture kao ljudskog posredovanja prirodnog, dogodit će se upravo gubitak refleksije o mogućnosti drugačijeg, tj. slobode same, jer ćemo biti zapleteni u slijepi kauzalitet, recimo to tako, »puke tehnološke prirode«.

Opasnost nije u samim tehničkim rješenjima za pogubne rezultate našeg nezdravog odnosa prema okolišu, nego u tome da uklanjanje tih rezultata nije zamislivo ako tehnička rješenja izostanu. Ovdje se ogleda i distopičan usud tehnologije, koja, za razliku od kulture, nema potencijal mišljenja iz bitne nedovršivosti svijeta, a što se može promatrati kao nemogućnost mišljenja i djelovanja s onu stranu principa nezaustavljivosti tehnološkog napretka. Tehnološka rješenja svakako neće moći sanirati štetu koja je iz pogubnog kulturnog odnosa prema prirodnom proizašla. Ako u pojedinim slučajevima takav pristup štiti (ljudski) okoliš, pitanje je štiti li doista prirodu? Dok on nema ni snage ni namjere da transcendira okvir koji zadaju principi tržišta i tehnološkog razvoja, ne može se potvrdno odgovoriti na to pitanje, jer ti principi obećavaju samo nastavak narušavanja čovjekove autonomije, a tako i mogućnosti da bitno promijeni svoj odnos prema prirodnome.

Stoga i zaštita okoliša i zaštita prirode u određenom tumačenju imaju svoju specifičnu važnost. Prva u smislu shvaćanja važnosti okolišnih uvjeta za samoostvarivanje svakog živog bića, a druga u pogledu zaštite prirodnosti od tehnološkog nasrtaja, prirodnosti u vidu ključnog korelativa kulture, ali i u pogledu samog samoostvarivanja živih bića. Namjesto upuštanja u prisilje izbora, valja promišljati ono što ove sintagme imaju značiti s obzirom na dosljedan etički pristup, a samim time i djelovati s obzirom na obje.

3.2. Integrativna bioetika

Promjena našeg odnosa prema prirodnom, kako onom izvanjskom (okoliš), tako i onom unutrašnjem (naša vlastita tjelesnost, animalnost) zahtijeva jedan novi stvaralački (a nikako »stvorilački«) impuls. Kako ni on ne bi upao u zastranjenje (što nije svojstveno samo onom »stvorilačkom«) potrebno je rehabilitirati pojam slobode, štoviše, misliti i živjeti slobodu. U onom pogledu u kojem on označava specifičnu formu ljudskog samoostvarivanja, otvara se prostor za racionalno utemeljenje moralnog obzira spram svih živih bića.

Međutim, u svrhu odgovornog upravljanja našeg djelovanja u smjeru konkretnog omogućavanja samoostvarivanja tih živih bića danas je, više nego ikad, potrebno ovladati širokom paletom znanja. Takvo promišljanje prije nije bilo potrebno, naprosto stoga što naša moć nije bila u stanju mijenjati uvjete života gotovo svih živih bića na planetu. Ovu promjenu uloge znanja u moralu jasno će izraziti Jonas: »U takvim okolnostima *znanje* postaje prvenstvena obaveza koja nadilazi sve što se ikad uzimalo u obzir za njegovu ulogu, i to znanje mora, po veličini, biti izjednačeno s kauzalnim razmjerom našeg djelovanja. Međutim, pošto je činjenica da ono s njim, zapravo, ne *može* biti jednako po veličini, to jest pošto predskazujuće znanje zaostaje za tehničkim znanjem koje daje moć našem djelovanju, i sama ta činjenica poprima etičko značenje. Jaz između snage prethodnog znanja i moći čina proizvodi jedan novi etički problem. Priznanje neznanja, onda, postaje obratna strana obaveze da se zna, a time dio etike koja mora da podučava onu sve neophodniju samokontrolu naše prekomjerne moći« [21]. Upravo prizvuk hereze koji odzvanja uz zahtjev za smanjenjem moći odaje našu posvemašnju porobljenost i istinsku nemoć pred onim što smo stvorili.

Posebnu odgovornost za suvremenu situaciju imaju oni koji formiraju znanje. Različite malignosti koje su proizašle iz paradigme znanja kao moći zahtijevaju potpunu promjenu paradigme znanja. Redukcionizam, koji je pogodio mnoge znanosti, jedan je od izvora suvremenih stramputica, upravo u onoj mjeri u kojoj ne može osvijestiti da je redukcionizam – pretenzija na poimanje univerzalnog iz perspektive partikularnog. Stoga nije ni čudno da mnoga zastrašujuća znanstvena dostignuća i scenariji budućnosti najčešće ne proizlaze iz laboratorija i umova zlih znanstvenika, nego upravo onih dobronamjernih ili onih koji znanje drže neutralnim. Ono što dodatno zabrinjava jest podložnost suviše specijaliziranog znanja svrhama koje su davno prestale biti ljudske, a postale samosvrhe.

Nova paradigma znanja stoga bi prije svega morala namjesto redukcionističkog postaviti pluriperspektivističko znanje. Tu ne bi trebalo biti riječi o »svaštarenju«, nego o znanju u kojem etika igra stožernu ulogu, kao ona disciplina koja postavlja formalne principe ljudskog djelovanja. Potreba za pluriperspektivističkim uvidom imanentna je upravo etičkom zahtjevu za obuhvatnijim, a time i odgovornijim uvidom u kompleksnu stvarnost s kojom se čovjekovo djelovanje susreće. Upravo paradigma odgovornog i pluriperspektivnog znanja obilježje je integrativne bioetike, jedne od silnica koje smjeraju spašavanju kulture od zapadanja u barbarstvo, koje se najbjelodanije očituje u svojim destruktivnim učincima na prirodnome.

4. ZAKLJUČAK

Milan Polić će sasvim ispravno naglasiti: »Kakva god bila, *kultura nas ljudski određuje*. Kakva god bila, *tek nas kultura ljudski omogućuje.* Stoga, kakva god bila, *kultura je čovjekova sudbina*« [22]. Mi smo »osuđeni na kulturu«, upravo u navedenom smislu. To pak ne znači da smo osuđeni na odbacivanje prirode. Naprotiv, kako smo nastojali pokazati, priroda sačinjava nužan korelativ kulture. Potonja se upravo nalazi pred ugrozom u onoj mjeri

u kojoj se nalazi i prva, a što se najbolje očituje u preobrazbi stvaralaštva u »stvorilaštvo«, kao i u samouništenju slobode podilaženjem sredstvima za zatiranje prirodnog. S druge strane, kultura u vidu filozofije, najviše forme njenog samoosvješćivanja, a naročito u vidu etike kao samoosvješćivanja njenog (čovjekova) djelovanja, nalazi različite razloge za nedopustivost zatiranja prirodnog.

Suvremeni tehnološki i ekonomski razvoj pokazali su iznimno ironičan odgovor čovjekovim nadama u oslobođenje. Upravo je na tom putu čovjek svoju kulturu progresivno svodio na onu slijepu nužnost koju je pripisivao prirodi. »Svaki pokušaj da se slomi prirodna prisila uništavanjem prirode samo se još dublje sapliće o prirodnu prisilu« [23]. Stoga je ekološka kriza kulture koliko je i kriza prirode.

Premda je kultura isključivi krivac za ekološku krizu, ona je jedina koja je, uz pretpostavku opstanka ljudi na planetu, može zaustaviti. Ona sadrži potencijale za to, a jedno od mjesta na kojima se oni pokazuju jest izgradnja ideje integrativne bioetike, koja pluriperspektivno pokušava pristupiti ključnim moralnim i povijesnim problemima sadašnjice. Pored ostalih razloga, sama odgovornost nam nalaže da se u novoj situaciji, u koju smo se neodgovorno doveli, obratimo svim područjima u kojima se ljudsko znanje formiralo, ne gubeći pritom filozofski konceptualni aparat kao branu od zapadanja u bezumnost. Upravo je bezumnost, odnosno ograničena instrumentalna razumnost, uzrok našeg ponovnog zapadanja u maloljetnost, izraženu kroz ovisnost o tehnološkoj mašineriji. Stoga se, u konačnici, ovdje postavljena pitanja javljaju upravo kao povijesna, a mogu se sažeti u jedno: hoćemo li ostati u historijskoj kolotečini neslobode, kakva je ona diktirana tehnološkim napretkom, ili ćemo iskoračiti u vlastitu povijest i izgraditi novu epohu bioetičkog obzira?

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

LEACHING STUDIES OF THE LEAD-IRON PHOSPHATE RADIOACTIVE WASTE GLASSES UNDER DIFFERENT CHEMICAL ENVIRONMENTS

Goutam Hazra*

* Kalna College, Dept. of Chemistry, West Bengal, India

corresponding author: Goutam Hazra, e-mail: goutamhazra1@gmail.com

Original scientific paper

ABSTRACT

Lead-iron phosphate (LIP) glasses are a promising new waste form for the safe immobilization of both high level defence and high level commercial radioactive waste for long term disposal. LIP glasses have several advantages such as lower aqueous corrosion rate, lower processing temperature and lower viscosity in the liquid state. From all the measurements of the leaching studies of different LIP glasses in different chemical environments it is shown that the resistance of lead iron phosphate glasses to aqueous attack varies considerably with pH of the leachate solution. The best chemical resistance is exhibited at neutral pH of around 7 and the corrosion of the LIP glasses increases very rapidly with decreasing the pH (at very low pH) of the leaching medium. This can be understood by considering the size of the migrating species at the water/glass interface. In the most acidic solutions where both modifying cations are drawn into solution, cross links in the $(PO_4)_n$ chains will be broken which will inevitably lead to a loss of phosphorus and the congruent leaching of cations and anions.

***Keywords**: nuclear waste glass, leach resistance, congruent leaching, chemical environments and glass interface.*

1. INTRODUCTION

The future development of nuclear energy depends largely on the success programmes and management of radioactive wastes generated at various stages of the nuclear fuel cycle. A nuclear (radioactive) waste is any material that contains or is contaminated with radio nuclides at concentrations greater than a certain safe (permissible) level. Radioactive wastes are generated from the various sources such as nuclear power plants, medical isotope applications, defence, communication systems and atomic industries. The fission products with the usual fuel materials viz., U, Pu, and Th contain about 35 elements with 200 different

isotopes [1 - 6]. Glass has ability to dissolve most of the elements of the periodic table. The fission product constituents thus become a part and parcel of the glass structure as compared to any other mechanical entrapment [5]. Glass can be considered as a truely '*secular*' matrix, imbibing in one melt all the elements contained in the waste. This results in a permanent and irreversible fixation of the nuclides in the various matrixes [6]. Glasses in the system of lead-iron phosphate (LIP) some of which mixed high uranyl acetate loaded with simulated nuclear waste were melted. Leaching study of these glasses up to a time period of 300 hrs. were conducted under Soxhlet distillation condition with steam distilled water. Weight losses and residual activities by 'Radiotracer technique' were followed with respect to time period of leaching. SEM of some of the selected glasses has been reported. The variation of different properties were taken into account in terms of the changes in the ionic charges and ionic radii and hence ionic potentials of the different modifier ions, the source of which being the respective modifier oxides viz., PbO, Pb_3O_3, BaO, Fe_2O_3, Al_2O_3, Y_2O_3, $CaCO_3$, CeO_2, SrO_2 and UO_2 $(CH_3COO)_2$ as for the different glass system as discussed above.

2. EXPERIMENTAL

2.1. Preparation of glass batches and melting operation

Different glass compositions based on that supplied by Nuclear Recycle Group, BARC, Trombay, Mumbai has been discussed elsewhere [5, 6] and is shown in table 1 for convenience of the readers. The glass batches were prepared from the AR grade ingredients after reviewing earlier works in reference to the corresponding ternary diagrams as shown in table 2. All the glass batches were synthesized from the respective oxides/carbonates/acetates in acetone medium and mixed repeatedly after taking them in an agate mortar and pestle. They were next dried and taken in high alumina crucibles and fired in a programmable muffle furnace in the range 750 °C – 1000 °C for soaking periods of 60 min under ambient condition. For some of the LIP glasses (LIP8 – LIP10) the batches were composed by taking uranyl acetate directly into itself. The logic behind using uranyl acetate is that U is α / β active and by measuring the net counts per sec (c.p.s.) the leaching characteristics can be traced by such 'radiotracer technique' with the help of a Geiger-Muller counter.

Table 1. Compositional details of simulated low and intermediate level radioactive liquid waste

Properties	Low level radioactive liquid waste	Intermediate level radioactive liquid waste
pH	8 - 9	9 - 13
$CsNO_3$ (mmoles/L)	6.56×10^{-6}	8.39×10^{-4}
$Sr(NO_3)_2$ (mmoles/L)	2×10^{-6}	2.4×10^{-5}
$RuCl_3$ (mmoles/L)	2×10^{-9}	2.93×10^{-7}
$NaNO_3$ (moles/L)	1×10^{-2}	2
Na_2CO_3 (moles/L)	--	5×10^{-2}
$CaCl_2$ (moles/L)	2×10^{-3}	--
NaOH (moles/L)	Traces for adjustment of pH	5×10^{-3}

Table 2. Composition of different glasses (wt.%)

Glass ID	Pb_3O_4	PbO	Fe_2O_3	P_2O_5	CeO_2	SrO_2	BaO	Uranyl acetate
LIP3	49	-	8	33	10	-	-	-
LIP4	-	52.4	7.9	33.2	6.5	-	-	-
LIP5	49	-	8	33	-	10	-	-
LIP6	49	-	8	33	5	5	-	-
LIP7	49	-	8	33	-	-	10	-
LIP8	-	52.4	7.9	33.2	-	-	-	6.5
LIP9	-	51.4	7.9	33.2	-	-	-	7.5
LIP10	-	45.8	7.0	30.2	10	-	-	7.0
LIP11	-	44.05	6.76	28.45	-	-	-	20.47

2.2. Leaching study

For leaching studies, the glass samples were crushed to 300 – 425 mesh taken in nylon net. Then 0.5 g of each sample glass was vapour distilled in Soxhlet apparatus with a round bottom flask (500 ml capacity) fitted with a condenser [3, 6]. The distillation was carried out for varying period of time up to a maximum of 300 hr. The heating was done in a heating mantle. The weight loss after each run of leaching was measured by a four-decimal electronic balance (Satorius) and was converted into % wt. loss. In order to find the leach rates, BET surface area of the U-containing LIP glasses were determined under liquid nitrogen temperature [3, 4, 6]. For LIP glasses, the leaching study was augmented by noting the cps after each interval of time from its residual activity of α and/or β with the help of a G–M counter (Nucleonix, Hyderabad, India).

The leach rates (LR) for LIP8, LIP9 and LIP10 glasses after leaching are determined from BET surface area analysis. The leach rate (LR) were measured by weight loss according to the relationship

$$\mathrm{LR} = \frac{W_i - W_f}{\mathbf{SA} \times \mathbf{t}} \quad (1)$$

where W_i and W_f are the initial and final sample weights respectively, SA is the BET surface area of the sample and t is the time exposed to the leachant.

3. RESULTS AND DISCUSSION

3.1. Leaching study of the LIP glasses in distilled water under Soxhlet condition

Leaching study of the LIP glasses not containing U (LIP3 to LIP7) was performed under Soxhlet condition up to 24 hours and the cumulative weight loss with respect to time (hrs.) observed that the total wt. loss (or % wt. loss) with respect to cumulative time varies as:

$$\mathrm{LIP6} > \mathrm{LIP4} > \mathrm{LIP5} > \mathrm{LIP3} \approx \mathrm{LIP7}$$

where the LIP3, LIP4 and LIP6 contain CeO_2 and LIP7 contain BaO and LIP5 contain SrO as modifier. For the three glasses (LIP3, LIP4 and LIP6) the CeO_2 content varies as:

LIP3 (10%) > LIP4 (6.5%) > LIP6 (5%)

and the observed wt. loss with respect to cumulative time varies as: LIP6 > LIP4 > LIP3 leading to a trend that with increasing CeO_2 content the % wt. loss decreases. Hence CeO_2 (Ce^{4+}) can function as good binder-modifier [7 - 16].

3.2. Leaching study of the uranium containing LIP glasses in distilled water under Soxhlet condition (using radio tracer technique)

The residual activity of the leachant was measured with the help of the Geiger-Muller counter and Gamma-ray Spectrometer using NaI(Tl) scintillator detector coupled with Multichannel Analyser. For U-containing glasses the wt. loss data was further accompanied from the results of "radiotracer technique" (net cps vs. cumulative time). Figure 1 shows the corresponding plots.

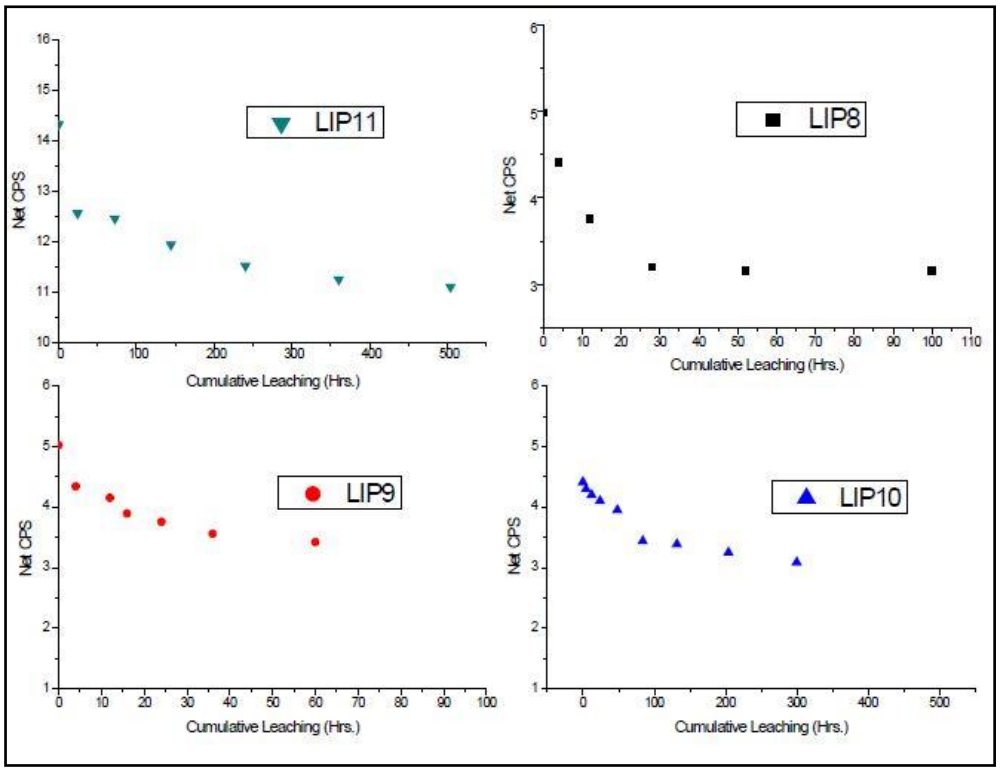


Figure 1. Plots of net c.p.s. vs. cumulative leaching time (hr.) for LIP8 to LIP11

It is observed that with increasing cumulative time, the net cps (α/β/γ) is decreasing in an exponential way signifying that with increasing leaching time, the release of uranium along with other constituents becomes slower and slower until getting stopped. Thus the glass becomes resistant to leaching and is a better choice for the disposal of nuclear waste compared [4, 7, 14]. In case of all U-containing LIP glasses, a similar type of plot is obtained. The exponential decay must not be confused with the decay of U^{238}, the present radio isotope present in the system, since its half life period is too high (~10^9 years) to be reflected in such decay. The rate decreasing the residual activity of the leachant (net c.p.s.) with respect to cumulative time is as follows:

(LIP11) > (LIP8) > (LIP9) > (LIP10)

It is further indicated that the LIP10 glass which contains CeO_2 is more leach resistant than that of the others U-containing glasses which does not contain CeO_2. Hence from the radiotracer leaching studies the role of Ce^{4+} as good binder-modifier is again established [7, 17].

The leach rates (LR) for LIP8, LIP9 and LIP10 glasses after leaching are determined from BET surface area analysis (liq. N_2 temp.). The BET surface area & Leach Rate are as follows:

$$(SA)LIP8 = 0.076\ m^2/g$$
$$(SA)LIP9 = 0.512\ m^2/g$$
$$(SA)LIP10 = 0.480\ m^2/g$$
$$[(LR)LIP8] = 4.3 \times 10^{-3}\ g.m^{-2}.hr^{-1}$$
$$[(LR)LIP9] = 8.2 \times 10^{-4}\ g.m^{-2}.hr^{-1}$$
$$[(LR)LIP10] = 1.8 \times 10^{-4}\ g.m^{-2}.hr^{-1}$$

The Leach Rate decrease in the order:

$$(LR)LIP8 > (LR)LIP9 > (LR)LIP10$$

These rates as compared to other borosilicate systems are 1000 times lower [3, 4, 6, 14] and thus LIP glasses have much improved chemical durability. This is due to Fe_2O_3 content and structural role of $Fe^{2+/3+}$, which strengthens the cross bonding between the polyphosphate chains. Percent weight loss studies show a distinct decrease in the % wt. loss value with extended period of time of leaching signifying that the extent of leaching die down with time. It is observed that the % wt. loss decreases in the order:

$$(LIP11) > (LIP\ 8) > (LIP9) > (LIP10)$$

In case of the glass LIP10, CeO_2 is present which is not present in LIP8, LIP9 and LIP11 other. Thus the role of Ce^{4+} as binder modifier is evident.

Thus the leaching rate of the LIP glasses (both with and without U) containing ceria are lower than without ceria. This is due to having higher coordination number linked with oxygen in the phosphate network. Hence the durability of the LIP glasses may be increased with the addition of CeO_2 [15, 16]. From some other point of view our observations on the U-containing LIP glasses the leach rates were found to increase with increase in the amount of U within the glass composition. This may be due to the high mass no. of the U^{238} atom being released during leaching or may be due to maximum internal dose of radiation.

3.3. Leaching characteristics at different medium

From the figure 2 and figure 3, measurements of the leaching studies of different LIP glasses in different chemical environments it is shown that the resistance of lead iron phosphate glasses to aqueous attack varies considerably with pH of the leachate solution. The best chemical resistance is exhibited at neutral pH of around 7 and the corrosion of the LIP glasses increases slowly with increasing the pH (at very high pH) of the leaching medium [16, 17].

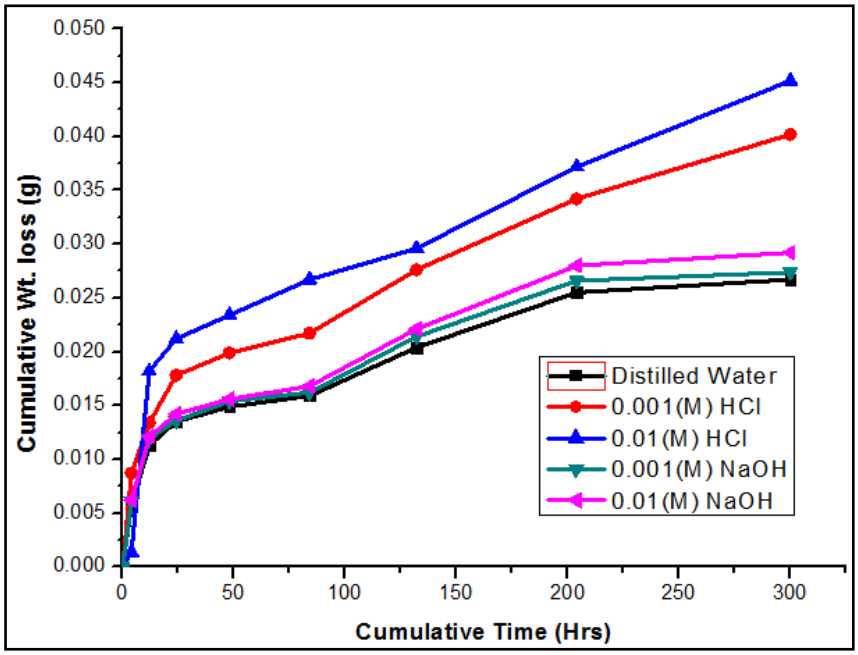


Figure 2. Leaching study of LIP10 glass in different media

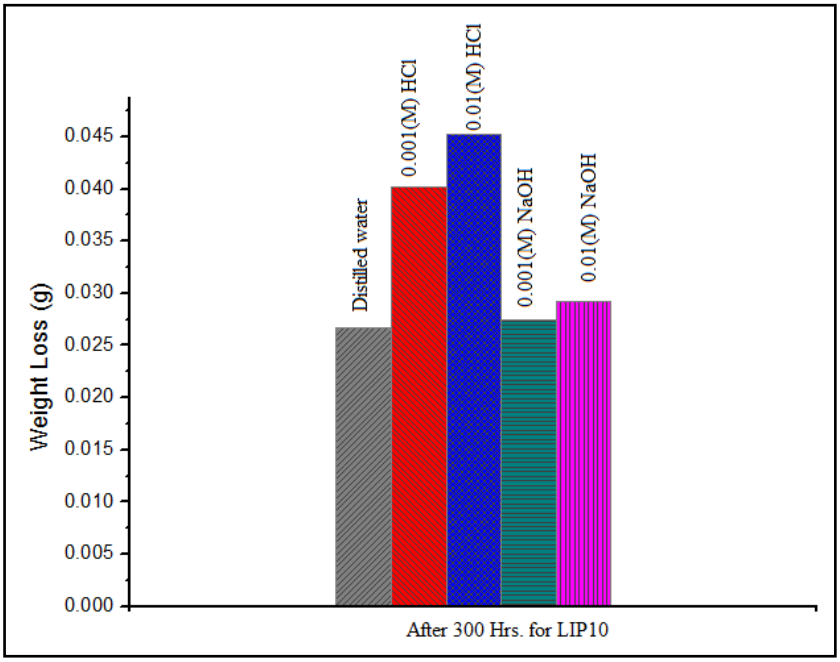


Figure 3. Bar diagram of wt. loss in different medium after 300 hours for LIP10 glass

On the other hand the corrosion of the LIP glasses increases very rapidly with decreasing the pH (at very low pH) of the leaching medium. However, the leaching of anions and cations is not always congruent [16 - 19]. This can be understood by considering the size of the migrating species at the water/glass interface. In the simplest model the modifying cations will exchange with H_3O^+ and the phosphate groups with OH^-. As Pb and hydronium are of similar size with radii of around 1 Å they should exchange readily. Ferric ions on the other hand with a radius of 0.7 Å are less well-matched and dissolve less readily [18 - 24]. In the most acidic solutions where both modifying cations are drawn into solution, cross links in

the $(PO_4)_n$ chains will be broken which will inevitably lead to a loss of phosphorus and the congruent leaching of cations and anions. At high pH, however, the scarcity of H_3O^+ will diminish cation exchange leaving anion exchange comparatively enhanced. If phosphorus is lost from chain ends, as is likely, modifying metals will not be casualties and the incongruent leaching behaviour will occur [16 - 18].

4. CONCLUSION

Chemical and physical properties of LIP glasses depend on the glass composition. The P_2O_5 is assumed to be the glass former and PbO is added to reduce the viscosity and consequently the melting point. By adding Fe_2O_3 it was possible to improve the chemical resistance and to decrease the crystallization rate. Thus improvement chemical durability is due to Fe_2O_3 content and structural role of $Fe^{2+/3+}$, which strengthens the cross bonding between the polyphosphate chains. Thus it may be concluded that a structural rearrangement occurs in the role of Fe in the glass structure from modifier to former. The structure of LIP glasses consists of Fe-O-P-O chains with Pb atoms intercalating the structure, bounded to non-bridging oxygen atoms. The cumulative wt. loss i.e. leaching or leaching rate of the simple LIP and uranium containing LIP glasses depend on the addition of modifier oxides into their compositions. It is shown that the addition of CeO_2 into LIP glass compositions decreases the leaching rate and increases the durability in aqueous solution. With increasing the amount of CeO_2 into the composition the leaching of the LIP glasses decreases. The addition of CaO, SrO and BaO into the composition of LIP glasses increase the leaching of the glass. In general addition of alkaline earth oxides increase the corrosion of the LIP glasses whereas addition of intermediated oxides decreases the corrosion of the LIP. The best chemical resistance is exhibited at neutral pH of around 7 and the corrosion of the LIP glasses increases slowly with increasing the pH (at very high pH) of the leaching medium as well as the corrosion of the LIP glasses increases very rapidly with decreasing the pH (at very low pH) of the leaching medium.

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[***This paper is dedicated to my cousin, Late Pradip Hazra who is no more with us as he had expired on 7th April, 2018 at the age of 33 years in Mumbai due to brain stroke.***]

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

IMPACT OF ANTHROPOGENIC FACTORS ON WATER QUALITY OF SHKUMBINI RIVER

Belinda Hoxha*, Marilda Osmani*, Frederik Cane*, Piro Karamelo*, Nikolin Gega*

*"A. Xhuvani" University, Faculty of Natural Sciences, Elbasan, Albania

corresponding author: Belinda Hoxha, e-mail: belindahoxha@hotmail.com

Original scientific paper

ABSTRACT

The pollution origin of surface waters might be different and anthropogenic activity is the main contributor. The purpose of this paper is the assessment of human impact on water quality of Shkumbini River in Albania regarding chemical parameters through the years. These parameters are measured in two chosen sampling points with different pollution origin and their annual averages' tendency through 2006 - 2016 is shown. Main sources of water pollution in the river are agriculture and domestic/industrial untreated wastewaters. The results show that in most cases the environmental problems in this river regard high levels of nutrients. Sampling point 2 shows higher values of nutrients than station 1 through the years. This water system belongs to the environmental class III – IV and shows a tendency of eutrophication based on annual average of nitrogen and phosphorous, indicating the continuous anthropogenic impact on it.

***Keywords**: anthropogenic impact, water standard, pollution, wastewaters, agriculture*

1. INTRODUCTION

Albania is one of the richest countries in water resources with 7 big rivers that have a total water flow of 1308 m^3/s. Shkumbini river, one of the biggest in country, originates in the villages of Pogradec and Librazhd and it flows in Adriatic sea. It passes nearby Librazhd, Elbasan, Peqin, Kavaje and Lushnje [1, 2].

The human impact on water resources is worsening every year, representing a serious risk for the environment. Some of these environmental issues are inherited from the past industrial pollution, but there are other actual pollution sources. The main source of Shkumbini River is considered the industrial activity of Metallurgical plant operating near the river flow [3]. Agricultural water flows add considerable levels of nutrients (from the fertilizers) and other chemicals (from the pesticide use). Moreover, the untreated wastewaters loadings from the inhabited areas are another important source of contamination [4].

Nevertheless, this is not the only source of contaminants and pollution of this river. Natural pollution occurs as a consequence of the sediments where the water passes, which makes the water being mineralized. The mineralization of Shkumbini River is in the range of 150 – 450 mg/l, classifying these waters with moderate mineralization. The lowest mineralization occurs during May and the highest during the summer and autumn months.

The main purpose of this paper is to evidence the human impact on water quality of Shkumbini River. This is a comparative study that takes in consideration the annual average variation of chemical parameters content such as pH, ammonia, nitrite, nitrate, phosphorous through the years in the river and with International standards of water quality. Two main stations that take pollutants from different sources are chosen from previous researches for this purpose. Station 2 has higher levels of almost all parameters, because the river in this area has accumulated pollutants from different anthropogenic sources. The trophic state index (TSI) is also used to give a general view of the trophic state of the river.

The quality assessment of water environments is based on the measurements of inorganic and organic matter in water [5]. The most important sources of organic loadings are the urban and industrial discharges. Organic matters originating from human activities are soluble, fully distributed and can be rotten consuming the water oxygen. The phosphorous content is generally lower than 25 μg/l in water systems with low human activity, and its content higher than 50 μg/l represents an indicator of anthropogenic impact [6]. The phosphorous content exceeds 500 – 1000 μg/l in heavily polluted areas. Moreover, nitrogen content over 1 mg N/L shows human impact with agricultural or urban origin. When the rivers take urban or animal farms discharges the ammonia increases and the oxygen decreases. The heavily polluted rivers have ammonium levels of 1 – 5 mg N/L, that when turning in ammonia might cause fish and other water animals' death. The OECD [7] has developed a monitoring assessment and control of water systems regarding nutrients and eutrophication [8].

Human activity causes the increase of chemical substances, especially heavy metals and organic micro pollutants in water systems, through the solid, liquid and gaseous discharges, urban, industrial, and agricultural and mine loadings. All of these represent a serious risk for the water ecosystems and even for human health [6].

2. EXPERIMENTAL

This paper considers the annual variation of chemical parameters through 2006 – 2016 in Shkumbini River. Two sampling points are considered in this study: S1 (Labinot) approximately 12 km from Elbasan with minimal human impact and S2 (Paper) with high pollutant discharges from urban/agricultural and industrial wastewaters. The measurements in 2014 and 2016 are made from the authors. Therefore, three water samples are taken periodically 30 – 50 cm of depth at each sampling point and are analysed in the laboratory for the dissolved oxygen, nitrites, nitrates, ammonia and phosphorous content. These parameters are measured using a multiparameter photometer type C99 & C200 HI 83000. The dissolved oxygen uses the Winkler method, which is based on the oxidation of manganese oxide in alkaline solution. With acidification, the manganic hydroxide produced is titrated with thiosulfate solution in presence of starch as indicator [9, 10]. Ammonia in basic solution in presence of Nessler reactive gives a yellow precipitate or colour [9, 10]. Nitrites are determined with the diazonium procedure [9, 10]. Nitrates are reduced quantitatively in nitrites and then nitrites are determined with specified reactive using a colorimetric method [10]. Phosphates are determined spectrophotochemically with the ascorbic acid method [10].

The annual averages of chemical parameters through the years are then compared with international standards; their tendency in years is evidenced.

Trophic state of a water system implies the biological response toward factors such as nutrients [11, 12]. Trophic state index (TSI) [13, 14] is one of the most used indicators in the assessment of trophic state and nutrients condition in water. The equation of Carlson and Simpson [15] are used in the paper in order to calculate the TSI based on TP:

$$TSI\ (TP) = 14.42 \ln (TP) + 4.15 \quad (1)$$

Kratzer and Brezonik [16] developed an index based on total nitrogen present in water using the formula:

$$TSI\ (TN) = 54.45 + 14.43 \ln (TN) \quad (2)$$

Annual TN and TP are then used to calculate the TSI for Shkumbini River.

3. RESULTS AND DISCUSSION

Physico-chemical parameters discussed in the paper are pH, dissolved oxygen (DO), ammonia (NH_3), nitrites (NO_2), nitrates (NO_3), phosphates (PO_4) and total phosphorous. The comparison includes the average values of the above parameters through the years 2006 [17], 2009 [4], 2010 [4], 2011 [4], 2014 and 2016. Station S1 and S2 refer to the same location in all the sampling periods.

Because it influences a wide range of biological and chemical processes within the water system, pH is a very important parameter in water quality assessment. The changes in pH values might indicate the presence of particular loadings, especially when the measurements of conductivity are taken. The daily variation of pH might be caused by the photosynthetic and respiratory algal cycles in eutrophic waters [13]. Usually, pH is measured in-situ, since a wide range of factors might influence it [13]. The average pH values range from 7.44 (in 2014) to 8.5 (in 2006) for S1 and from 7.12 (in 2014) to 8.53 (in 2006) for S2. But, it is not evidenced strong differences through the years regarding pH. pH values are within the limit according to Miho et al [18]. Moreover, its values are within the EU obligatory limits for cyprinid and salmonid waters (6 - 9) [19]. According to NIVA [5] for the pH levels Shkumbini River can be classified at the first class (very good environmental quality).

Oxygen is very important to all living forms in waters. The oxygen content may vary depending on temperature, salinity, turbulence, photosynthetic algal activity and atmospheric pressure. The dissolved oxygen measurement might be used to show the organic matter pollution, the decomposition level of organic matter and the level of water self-cleaning capacity [13]. Literature suggests that dissolved oxygen values lower than 5 mg/l influence the community functioning (USEPA limit) [20]. Moreover, values that are lower than 2 mg/l lead to fish death [21]. As it can be seen from the graph in figure 1, the average dissolved oxygen content in the river is higher than the USEPA limit [20] and then the 2 mg/l [21] in both stations during all the years. However, it can be noticed that DO levels in S2 are slightly lower than in S1, probably due to the high pollutant discharge in this area.

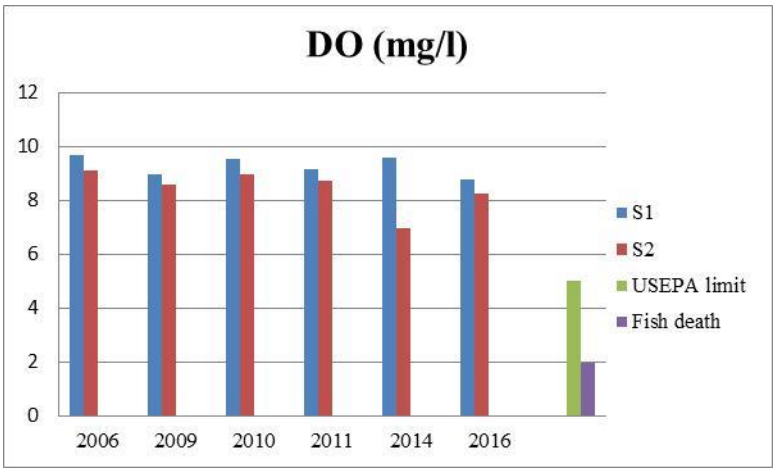


Figure 1. Dissolved oxygen in Shkumbini River through the years

Ammonia is present in water bodies as a result of decomposition of the organic and inorganic nitrogen containing matter, biota excretions, reduction of gaseous nitrogen from microorganisms and atmospheric exchange with water. High levels of ammonia are toxic for aquatic life and indicate organic pollution from untreated wastewaters, industrial wastes and agricultural loadings [13]. USEPA [22] recommends limits of 0.02 ppm as NH_3 in water bodies. NH_3 is toxic for the fish in concentrations higher than 0.03 ppm and values higher than 3 mg/l indicate organic pollution [13].

Ammonia content in Shkumbini river is generally low (figure 2), nevertheless the discharges with different origin in the river. The highest annual average belongs to 2009 (0.46 for S1 and 0.37 for S2), and the lowest in 2006 (0.05 for S1 and 0.14 for S2). Still, the ammonia content in the second station is higher than in the first one. The variations of ammonia through the years might be influenced by different factors such as climate and weather conditions, as well as the quantity of the discharges during the measurement periods. In every case, the values are slightly higher than the EC recommended value for the cyprinid waters (< 0.005 mg/l) [19], but lower than the maximum allowed concentration (MAC) for untreated and treated waters [21]

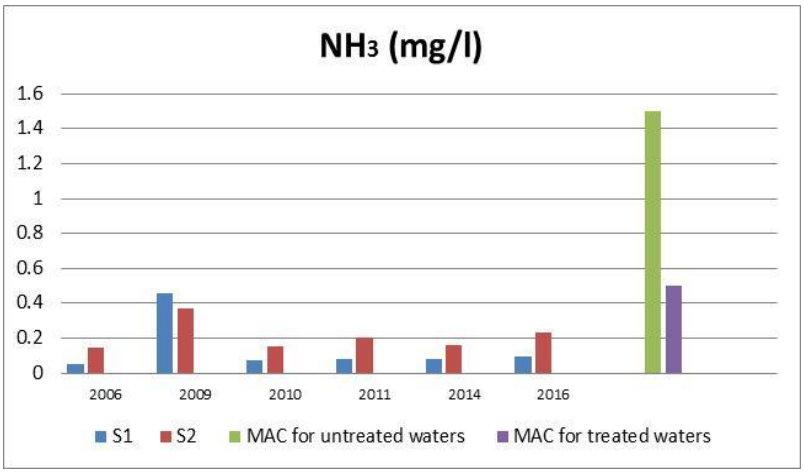


Figure 2. Ammonia content in Shkumbini River through the years

The nitrite concentrations are usually low. The presence of nitrites represents an evidence of wastewater discharges directly in the river without any treatment [13]. The

highest annual average level can be noticed in 2009 (9.3 for S1) and in 2010 (28.6 for S2), as shown in figure 3. Particularly, high levels of nitrite in the second station during all the years can be explained as a consequence of the high density of the population in the area. The nitrite levels in station 2 are higher than the EC recommended level for the salmonid waters (10 µg/l) [19] through all the years, even though there are variations of nitrite values. Meanwhile, the lowest value of nitrite is measured in station 1, 2.2 µg/l (2014).

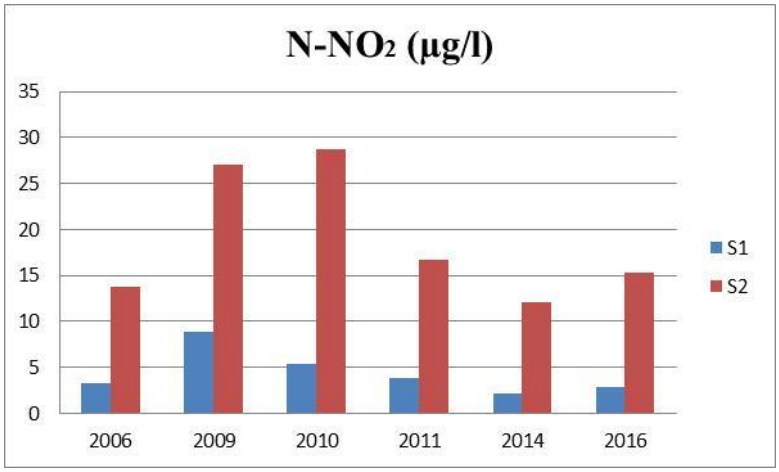


Figure 3. Nitrite content in Shkumbini River

Nitrates are the most common form of nitrogen in natural waters [13] and a very important parameter to assess the water quality. High nitrate content does not represent any risk to water organisms [23, 24]. The fertilizer use might be a considerable source of high nitrates in water. Concentrations higher than 5 mg/l indicate human or animal discharges, or agricultural spills [24]. Concentrations higher than 0.2 mg/l evidence the potential algal growth stimulation and possible eutrophication conditions [21].

Figure 4 represents the annual average values of nitrate during the 2006 - 2016 in the Shkumbini River. The average nitrate content in the River in both sampling points is lower than 5 mg/l, which indicates heavy human discharges in water. In every case, station 2 represents higher nitrate levels than the station 1, as a consequence of the high amounts of the discharge from the surrounding area. Moreover, in both cases there is enough nitrate content to stimulate the algal growth in this water system through all these years.

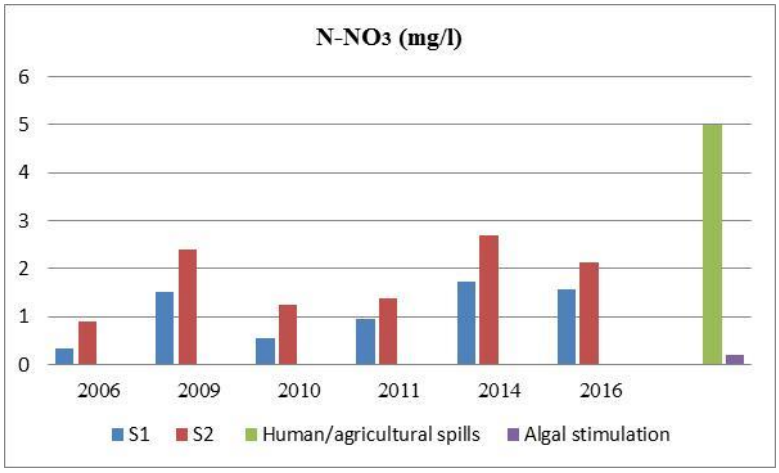


Figure 4. Nitrate content in Shkumbini River through the years

Phosphorous is rarely in high concentrations in water bodies, because it is actively taken from the plants. Phosphorous values in water bodies with little human impact are generally lower than 25 µg/l, meanwhile values higher than 50 µg/l indicate anthropogenic impact, such as wastewater discharge or agricultural loadings [6]. USEPA [22] recommends that phosphorous concentration in water should be lower than 0.082 mg/l in order to protect the underwater life. EU guideline value for surface waters that might be used as potable water sources 0.17 mg/l. Phosphorous values higher than 0.025 mg/l according the EU guidelines show eutrophication [21].

The total phosphorous (TP) annual values in figure 5 vary from 0.034 mg/l (in 2006) to 0.178 mg/l (in 2914) for the first sampling point. Meanwhile, its values have a variation from 0.0346 mg/l (in 2006) to 0.202 mg/l (in 2014) in S2, which are still higher than in S1. However, the phosphorous averages are higher than the 0.025 mg/l that shows potential eutrophication in both sampling points. The total phosphorous annual average values for S1 indicate that Shkumbini water quality belongs to class III in 2006 (18.6 µg/l), class IV in 2011 (34 µg/l) and 2016 (42 µg/l), and class V in 2014 (178 µg/l). Considering sampling point 2, its water quality varies from "moderate" (class III) to "bad/very bad" (class IV/V) [5]. The reason is the amount of water discharges in the river with high content of organic matter or agricultural spills.

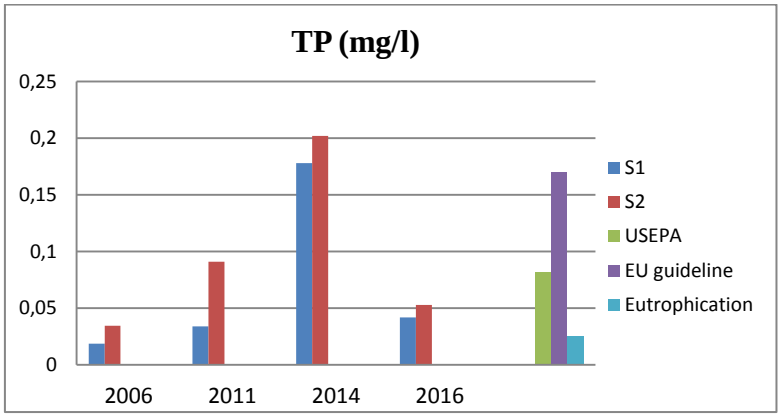


Figure 5. Phosphorous content in Shkumbini River

Table 1 represents the annual average values for phosphates in Shkumbini River during the years for both sampling stations. Phosphate contents in S2 are still higher than in S1, as it can be noticed in table 1. Phosphate concentrations are lower than obligatory level for salmonid waters [19] in both sampling points.

Table 1. Phosphate in Shkumbini River through the years

$P\text{-}PO_4$ (ug/l)		
	S1	S2
2009	19.5	18.66
2010	21	55.5
2011	21.15	36.25
2014	15.7	18.9
2016	14.3	21.7

Eutrophication and trophic state index (TSI) in Shkumbini River

Eutrophication is considered as the most dangerous water pollution type with direct effects on flora and fauna because of oxygen depletion. Eutrophic waters system tent to be foamy, turbid and appear with green colour [25]. Depending on nutrient content, water bodies might be oligotrophic, eutrophic and hypertrophic [7]. Surface waters with phosphorous content higher than 0.05 mg/l might cause eutrophic conditions [26]. Oligotrophic water systems contain less than 5 – 10 μg/l phosphorous and less than 250 – 600 μg/l nitrogen. Slightly eutrophic systems contain 10 – 30 μg/l phosphorous and 500 – 1000 μg/l nitrogen [27]. Regarding Shkumbini river, its phosphorous concentration varies from 18.6 (2006) to 178 (2014) and its respective nitrogen content varies from 0.39 mg/l (2006) to 1.98 mg/l (2010) and its trophic conditions vary from slightly eutrophic to eutrophic.

Based on TN and TP, trophic state index is calculated. As it can be seen from the table 2, Shkumbini River belongs to the class of mesotrophic (TSI 41 – 52) or eutrophic (TSI > 52) classes according to OECD [7]. The lowest value of TSI (TN) for station 1 is calculated for 2006 (41.07, mesotrophic) and the highest in 2009 (64.37, eutrophic). Meanwhile, the TSI (TN) for station 2 varies from 55.42 (in 2006, eutrophic) to 69.68 (in 2014, eutrophic), showing no amelioration through the years. Trophic conditions in sampling point 1 based on TSI (TP) vary from mesotrophic in 2006 (47.3) to eutrophic in 2014 (79.87).Whereas, the trophic water conditions remain eutrophic at the station 2, as TSI (TP) varies from 56.25 (2006) to 81.68 (2014).

Table 2. TSI based on TN and TP

	TSI (TN)		TSI (TP)	
	S1	S2	S1	S2
2006	41.07	55.42	47.30	56.25
2009	64.37	69.38		
2010	47.50	59.65		
2011	54.82	61.16	56.00	70.19
2014	62.95	69.68	79.87	81.69
2016	61.72	66.93	59.05	62.40

4. CONCLUSION

Shkumbini River is one of the most important water systems in Albania. The main sources of the pollutants evidenced are agricultural loadings and urban/industrial wastewaters. The comparison of annual values for different chemical parameters through the 2006 - 2016 in two chosen sampling stations shows that its waters belong to environmental class III – IV (moderate – bad water quality), according NIVA [5].

Nutrient annual levels (ammonia, nitrite, nitrate and phosphorous) show small variations through the years. Their annual values are higher in station 2 in all the measurements. The river in this sampling point takes high amounts of urban, agricultural and industrial wastewaters. Meanwhile, the station 1 has less influence of anthropogenic activities, with the exclusion of possible agricultural loadings from the surrounding area. Nevertheless, both sampling point show eutrophication tendency regarding nitrogen and phosphorous content and the water trophic conditions vary from mesotrophic to eutrophic.

Considering that the annual average chemical values do not show a decreasing tendency through the recent years, it can be concluded that the discharges from different origin in the river have the similar intensity during this period of time. This indicates that the anthropogenic influence still plays an important role in this area.

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HIDROMETALURŠKA PROIZVODNJA IZ PERSPEKTIVE HOLISTIČKOG ENVIRONMENTALIZMA

HYDROMETALLURGICAL PRODUCTION FROM THE PERSPECTIVE OF HOLISTIC ENVIRONMENTALISM

Damir Hršak*, Ivan Jandrlić*, Dario Mašinović*

* Sveučilištu u Zagrebu, Metalurški fakultet, Sisak, Hrvatska

autor za korespondenciju: Damir Hršak, e-mail: hrsakd@simet.hr

Stručni članak

SAŽETAK

Analiza hidrometalurške proizvodnje iz perspektive holističkog environmentalizma zahtjeva interdisciplinarni pristup jer je nužno sagledavanje ne samo tehnoloških mogućnosti provedbe određenog hidrometalurškog procesa, već i preispitivanje društvene opravdanosti gradnje ili održavanja tehnološkog postrojenja koje onečišćuje materijalni okoliš. Hidrometalurška proizvodnja iz perspektive holističkog environmentalizma promatra se dvojako: s jedne strane kao mogućnost, a s druge strane kao prijetnja. Hidrometalurška proizvodnja suvremenom čovječanstvu omogućava korištenje niza proizvoda bez kojih bi bilo nemoguće zamisliti našu tehničku civilizaciju, no ona može postati ozbiljna prijetnja ukoliko se tijekom proizvodnog procesa zanemaruje važnost očuvanja čistoće vode, zraka i tla. Za opravdanost funkcioniranja hidrometalurških postrojenja, iz pozicije holističkog environmentalizma, potrebna je socijalna odgovornost hidrometalurških poduzeća.

***Ključne riječi**: hidrometalurgija, materijalni okoliš, holistički environmentalizam*

ABSTRACT

Analysis of hydrometallurgical production from the perspective of holistic environmentalism requires an interdisciplinary approach because it is necessary to consider not only the technological possibilities of implementing a particular hydrometallurgical process, but also to re-examine the social justification of the construction and maintenance of a technological plant that contaminates the material environment. Hydrometallurgical production from the perspective of holistic environmentalism is viewed dually, on the one hand as an opportunity, and on the other hand as a threat. Hydrometallurgical production

allows modern mankind to use a series of products without which it would be impossible to imagine our technical civilization, but it can become a serious threat if during the production process the importance of preserving the purity of water, air and soil is neglected. For the justification of functioning of hydrometallurgical plants, from the position of holistic environmentalism, social responsibility of hydrometallurgical companies is needed.

***Keywords**: hydrometallurgy, material environment, holistic environmentalism*

1. UVOD

Sagledavanje hidrometalurške proizvodnje iz perspektive holističkog environmentalizma znači preispitivanje ne samo tehničke mogućnosti provedbe određenog tehnološkog procesa, već i preispitivanje smislenosti provedbe tog istog procesa. Pri tom se kao temeljna vrijednost uzima dobrobit društvene zajednice, a ne profit pojedinaca.

Prije investicije u određenu proizvodnju vlasnik sredstava za proizvodnju mora naći tehnološko rješenje provedbe proizvodnog procesa i mora ishoditi sve potrebne dozvole. Vlasnici kapitala ponajprije si postavljaju pitanje koliki će profit uspjeti izvući iz planirane proizvodnje. Investitor si može, ali i ne mora (mimo onog minimuma na koji ga propisi prisiljavaju), postavljati pitanje o kratkoročnim i dugoročnim posljedicama po materijalni i duhovni okoliš koje će njegova investicija prouzročiti. To je dužnost, zakonska i moralna, onih koji u ime društvene zajednice (grada, županije, države) izdaju potrebna dopuštenja.

Holističko environmentalistička perspektiva prvenstveno, iako ne i jedino, odnosi se na nositelje odlučivanja koji imaju mogućnost i obavezu štititi javni interes i nametnuti socijalno odgovorno poslovanje proizvodnih poduzeća. Svaka proizvodnja, pa tako i hidrometalurška, ima i svoju društvenu dimenziju.

Zadiranje u materijalni okoliš neke zemljopisne cjeline treba se kompenzirati pozitivnim doprinosom kvalitete življenja stanovnika te zemljopisne cjeline. Hidrometalurška proizvodnja, iako ne u jednakoj mjeri kao i pirometalurška, ipak ugrožava okoliš i samo poboljšavanje tehničkih značajki određenog proizvodnog procesa nije dovoljno iz perspektive holističkog environmentalizma.

Ova tema zahtjeva dugotrajna i temeljita interdisciplinarna istraživanja kako bi se mogli odgovorno izvesti konkretni i relevantni prijedlozi za poboljšanje sadašnje situacije, a ovaj rad je samo mali korak u tom smjeru. Pesimizmu nije konstruktivan jer postoje znanstvenici koji su iskreno i predano posvećeni nastojanjima uspostave što čistijih tehnologija u metalurškoj industriji [1].

2. HIDROMETALURŠKA PROIZVODNJA

Hidrometalurgiju je, između ostalih, definirao profesor Darko Maljković u prilogu za tehničku enciklopediju: „Hidrometalurgija obuhvaća postupke provođenja rude u vodenu otopinu i postupke ekstrakcije metala iz otopine bez primjene električne energije“ [2]. Kada primjenjujemo električnu energiju za ekstrakciju metala iz otopine riječ je o elektrometalurgiji. U hidrometalurgiji glavna sirovina su minerali Zemljine kore. Minerali su osnovni sastojci stijena koji izgrađuju Zemljinu litosferu. Oni imaju homogenu građu i određen kemijski sastav koji se može izraziti kemijskom formulom [3].

Hidrometalurški proizvodni procesi sastoje se od više postupaka. Prvi je priprema ili transformacija rude, zatim slijedi prevođenje korisnih sastojaka rude u otopinu, otopina se po potrebi pročisti, a nakon toga slijedi izlučivanje metala iz otopine, te rafinacija [2]. Dakle, u hidrometalurškoj proizvodnji nužno je znatno zadiranje u prirodu, narušavanje materijalnog okoliša i potrošnja znatnih količina vode. Onečišćenja zraka i tla pri tom dolaze do manjeg izražaja.

Tek kod incidentnih slučajeva, poput izlijevanja crvenog mulja na sjeveru Mađarske koje se dogodilo 05. listopada 2010., onečišćenje tla može biti pogubno. U toj katastrofi bilo je uz mnoštvo ozlijeđenih i ljudskih žrtava. Kvalitetan članak uz dojmljive fotografije o toj temi objavio je svjetski ugledan list „The Guardian“ [4].

Priprema rude za prevođenje korisnih sastojaka u otopinunije uvijek potrebna. Svrha je pripreme rude da se njeni korisni sastojci pretvore u topljivi oblik, a štetne primjese po mogućnosti u netopljivi oblik. Priprema rude može biti pirometalurška ili hidrometalurška. Kao pirometalurška priprema primjenjuje se samo prženje. Ono može biti sulfatizacijsko, oksidacijsko, redukcijsko ili kloridno. Tipično sulfatizacijsko prženje primjenjuje se prilikom hidrometalurške proizvodnje cinka pri čemu se sulfidni koncentrati prže najčešće u pećima s fluidizirajućim slojem. Oksidacijsko prženje primjenjuje se prilikom preradbe sulfidnih ruda, dok redukcijsko prženje pri elektrolitičkoj proizvodnji mangana. Kloridno prženje primjenjuje se u hidrometalurškoj pripremi rude za prevođenje netopljivih primjesa u topljive kloride koji se zatim lako mogu izluživati, primjer za to može se naći u metalurgiji kositra [2]. Priprema rude tijekom hidrometalurške proizvodnje donosi dodatno ekološko opterećenje za ekosustave u blizini postrojenja. Pri tom ekosustave definiramo kao prirodne, uravnotežene sustave koji čine međusobni odnosi organizama i njihovog okoliša [5].

3. HOLISTIČKI ENVIRONMENTALIZAM

Holistički environmetalizam definira se kao cjelovito sagledavanje materijalnog (priroda) i duhovnog (svijet) okoliša [6]. Drugim riječima, holistički environmentalizam je cjelovit pristup okolišu. Holistički environmentalizam sastavni je dio integrativne bioetike, a integrativna bioetika je znanstveno polje interdisciplinarnog područja znanosti. Dakle, holistički environmentalizam, uostalom kao i integrativna bioetika u cjelini, nije nekoherentno naklapanje o svemu i svačemu kao što to neki zlohotni redukcionisti žele prikazati jer ne razumiju ili im nije profitabilno razumjeti srž suživota bića na Zemlji. Holistički environmetalizam ima definirano interdisciplinarno područje istraživana i kroz integrativnu bioetiku svoju poziciju unutar suvremene znanosti. Interdisciplinarnost integrativne bioetike očituje se i u tome što integrativna bioetika obuhvaća kako društvene i humanističke znanosti tako i prirodne i tehničke znanosti.

Što je u stvari bioetika objašnjava Hrvoje Jurić u knjizi „Etika odgovornosti Hansa Jonasa“. “No, bioetika se ne bi smjela zadovoljiti pukim mehanički okupljanjem različitih perspektiva, različitih disciplinarnih i svjetonazorskih pogleda, nego bi trebala težiti zbiljskoj integraciji, izradi jedinstvene platforme za raspravu o etičkim problemima vezanim uz život – u cjelini i u svim kontekstualno odredivim nijansama. Integrativnost bi stoga trebala označavati zadaću (odnosno sposobnost) bioetike da sve različitosti o kojima je bilo riječi okupi u jedinstveni bioetički pogled, radije negoli u disciplinarni i disciplinirani znanstveni okvir. Prije se, dakle radi o promoviranju bioetičkog pogleda u različitim disciplinama i pristupima, negoli o utjerivanju različitih partikularnih pogleda u jedan, bioetički disciplinarni kalup. Integrativnu bioetiku bi se, u tom smislu, moglo pojmiti kao čvrsto tijelo u određenom

prostoru, čija je uloga da permanentno upija energiju, te da je isijava prema drugim tijelima u prostoru, koja su za tu energiju prijemčiva" [7].

Kada nam je polazište u holističko environmentalističkom istraživanju iz područja tehničkih ili prirodnih znanosti, kao što je u našem slučaju, tada uvijek trebamo imati na umu da svako akumulirano znanje ne donosi uvijek društveni napredak i kvalitetniji život pojedinaca, da postoji i opasno znanje. Van Rensselaer Potter je lucidno definirao opasno znanje kao ono koje se nakupilo brže nego ga je mudrost uspjela svladati. Za Pottera je svaka znanost bez mudrosti slijepa. On smatra da će opstanak svjetske civilizacije biti nemoguć ukoliko se ne donese neki dogovor o zajedničkom sustavu vrijednosti, posebno o konceptu obveza koje imamo prema budućim ljudskim generacijama [8]. Opasno znanje može se detektirati i u hidrometalurgiji.

Van Rensselaer Potter bio je američki biokemičar, dugogodišnji profesor ontologije na sveučilištu Wisconsin–Madison, dakle prirodoznanstvenik. Njegova promišljanja i zaključci posebno su bitni za nas integrativne bioetičare čija ishodišna struku nije iz područja humanističkih znanosti jer on otvara pitanja na koja ćemo trebati još dugo tražiti najbolje odgovore.

4. ZAKLJUČAK

Hidrometalurška proizvodnja iz perspektive holističkog environmentalizma sagledava se kao izazovna mogućnost i kao ozbiljna prijetnja, ovisno o tome s kojih pozicija pojedinci i različite grupacije nastupaju.

Hidrometalurška proizvodnja suvremenom čovječanstvu omogućava korištenje niza proizvoda (zlato, srebro, aluminij, cink, bakar) bez kojih bi bilo gotovo nemoguće zamisliti našu civilizaciju. U svakom slučaju bez tih proizvoda osjetno bi se smanjila kvaliteta življenja prosječnog stanovnika. Tehnološkim napretkom moguće je smanjivati, iako ne i dokinuti, onečišćenje materijalnog okoliša koje nastaje tijekom suvremene hidrometalurške proizvodnje. No, u budućnosti je moguće razvoj novih hidrometalurških tehnologija usmjeriti u pravcu onih koje okolišu nanose što manje štete.

Hidrometalurška proizvodnja može postati ozbiljna prijetnja ukoliko se tijekom proizvodnog procesa zanemaruje važnost očuvanja materijalnog okoliša te čistoća vode, zraka i tla podređuje što bržoj akumulaciji profita nastalog prodajom hidrometalurških proizvoda. Također, iz pozicije holističkog environmentalizma, prijetnja je potencijalno ekonomsko vođenje hidrometalurške proizvodnje u smjeru povećanja socijalnog raslojavanja stanovništva i posljedično tome usporavanja osobnog razvoja pojedinaca.

U svakom slučaju, kako bi se iskoristile mogućnosti, a osujetile prijetnje, iz pozicije holističkog environmentalizma preporuča se socijalno odgovorno ponašanje hidrometalurških poduzeća.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

PALYNOMORPHS DISTRIBUTION OF *BUXUS* TYPE IN ELBASANI TOWN – ALBANIA

Admir Jançe*, Anila Jançe**

* "Aleksander Xhuvani" University, Elbasan, Albania
** Sofia University "St. Kliment Ohridski", Sofia, Bulgaria

corresponding author: Admir Jançe, e-mail: adi_jance@yahoo.it

Original scientific paper

ABSTRACT

This research ensures some palynological record about the palynomorphs distribution of *Buxus* type part of Buxaceae family during New Holocene. The record about the fossil pollen given in this research, are obtained in terrestrial deposits of past XX centuries (last Quaternary or last historic period of New Holocene), in Elbasani town.

The aim of this paper is to give the link amid the deepness and spreading for the *Buxus* type palynomorphs on different time periods. Paleopalynological records for Buxus type are provided as a novelty and there not exist any corresponding survey.

As a conclusion, we can say that: the palynomorphs of Buxus type (with a total numer of 410 spores), present in all depths, growth their attendance from the depth 4 meters to 2.5 meters and in the direction of the soil face a stable presence is noted.

Keywords: *Palynomorphs, Palynological, New Holocene, Buxus type, Elbasani town*

1. INTRODUCTION

The presented study gives paleopalynological data of New Holocene deposits in Elbasan city. Fossil pollen can undoubtedly be preserved, because the outer wall of the grains is extraordinarily resistant [1, 2]. Comparison of plant spores and pollen, allows us judging the performance of primitive and specialized features of outer wall of the grains [3].

Paleopalynology is the Science which are connected to biological and geology sciences, it is the science that studies especially the fossil palynoforms, but and the acritarchs, chitinozoans, scolecodonts [4, 5].

Microfossils plants of *Buxus* type have not been studied previously from any of the localities of Elbasani town and there not exist any corresponding survey as from foreign and local researcher for the palynomorphs of this plant in Holocene deposits in Elbasani town [2, 6, 7]. This type of research provides important information about the reconstruction of

paleoflora, paleoclimate, stratygraphy of the Holocene [4, 5]. The study in New Holocene deposits provides important information about the factors which have their impact on the transformation of the flora in Elbasani town [2, 6, 8 - 10].

Observations, counting and photos of palynomorphs it was carried on using light microscopes, magnification up to 1000x. Paleopalynological data help in the discovery of traces of history on the use and cultivation of plants, feeding mode and the origin of agriculture [11]. The quantitative data of palynomorphs for *Buxus* Type part of Buxaceae Family, deposited on the ground shows the direction of evolution of this plant.

2. EXPERIMENTAL

Palynological examination of all samples showed that all contained a large amount of organic matter that appeared suitable for pollen analysis. Physical-chemical composition of the palynomorphs allows pollen anthers well saved and easily extracted from terrestrial deposits. Basically all the extraction ways, join in principle methods of physical and chemical processing of 1 gram sediment [4]. During this study we have taken 16 soil samples, starting from 4 meters of depth to 0.25 m with the 25 cm distance between the sampling.

2.1. The method of acetolysis of Erdtman

The soil sampling is based on Erdtman method [12, 13]. Erdtman acetolyze method deals on treatment of the material with an acetolyze mixture, acetic anhydride $(CH_3COO)_2$ and sulfuric acid (H_2SO_4) in a 9:1 report.

Deliberately to get better results first treat $1cm^3$ soil with 10 ml KOH (10 %). Then we cleaned it with distilled water, and then we mixed it with acetolyze ingredients, until a neutral environment is created. The acetolyze method is used in many cases in palynology because it gives clear visibility over the pollens and spores compared with the other methods used during the process of microscopic observation [5, 7, 8, 12, 13].

2.2. Fixture of prepared samples

The fixture of samples was realized with method of glue-preparations by gel-glycerine. The gel-glycerine was prepared in the Kisser method [14] by using 50 gram of gelatine, 175 ml of distillate water, 150 gram glycerine, 7 gram phenol (crystals). The final ingredient was insulated to the edges of microscope slide with paraffin and after approximately 3 days it was ready to be stored and for its use.

3. RESULTS AND DISCUSSION

On table 1 and figure 1 are presented the data about the number of palynomorphs for *Buxus* type, representative of Buxaceae family by to the depth and the total spores' number for this type.

Table 1. Spores' number according to the depth

Sample	Depth (m)	Number of spores (*Buxus* Typ - Buxaceae)
1	4	19
2	3.75	16
3	3.5	18
4	3.25	20
5	3	23
6	2.75	25
7	2.5	32
8	2.25	31
9	2	26
10	1.75	28
11	1.5	30
12	1.25	31
13	1	30
14	0.75	28
15	0.5	26
16	0.25	27
Total number of spores		410

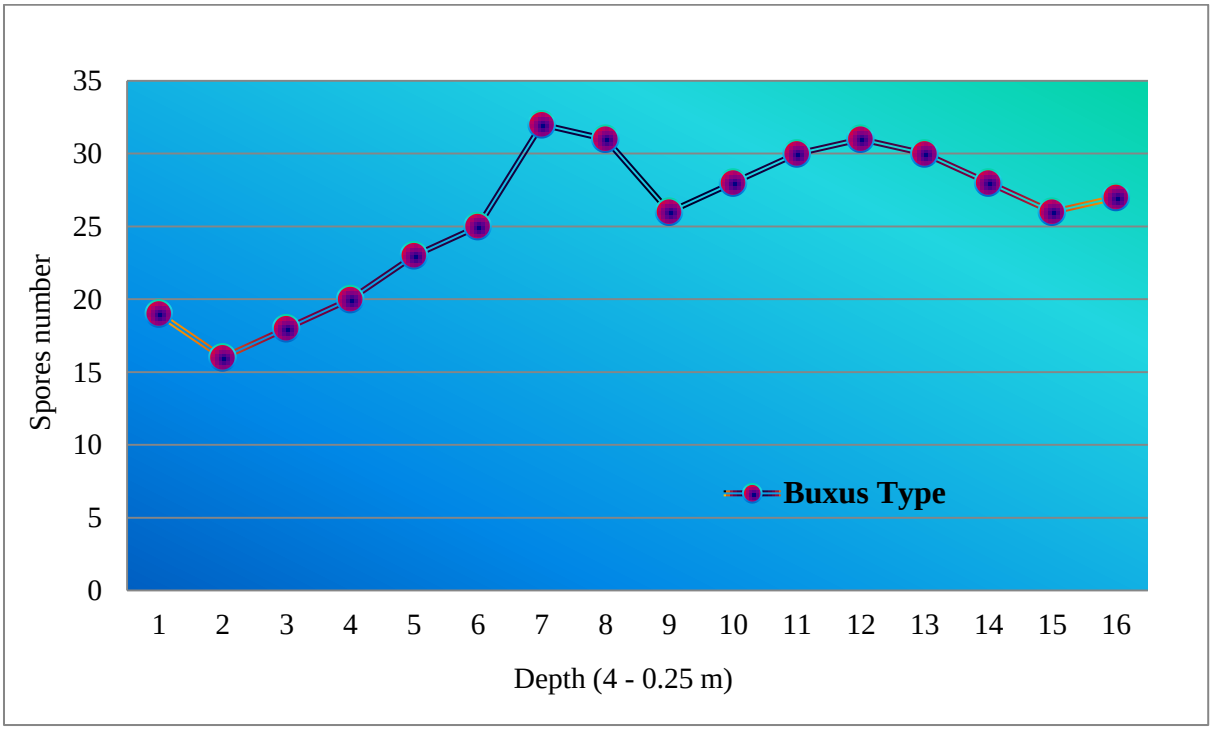


Figure 1. The palynomorphs distribution of Buxaceae family according to the depth

The minimum number (16 spores per sample) is taken exactly in 3.75 m of depth while the maximum number of spores for *Buxus* Type (32 spores) is taken in 2.5 m of depth. The basic pollen form of *Buxus* is a spheroid, zone 3-colporate grain with long extension, each of which contains 3 - 4 clearly defined, roundish, surrounded by slight nexine thickenings. Together with palaeobotanical evidence [15], these findings now allow insights

into the world-wide differentiation and possible chorogenesis of this undoubtedly quite old genus (figure 2).



Figure 2. *Buxus* type pollen *(1500x) (Source: Janҫe, 2014)*

On figure 1 is clearly shown a great increasing for the number of spores for *Buxus* Type, representative of Buxaceae family from the 4 m towards the 2.5 m of depth. Based on the data presented in table 1 the spore's total number of *Buxus* Type is 410 spores.

From the survey results of table 1 for all stations noted that, all the palynomorphs for *Buxus* Type are present at all depths, should be associated with human impact on the cultivation of the *Buxus* type plants. Also as shown in Figure 1, the Buxaceae family forms, from the 2.5 m of depth toward the surface showed the stability about their overall presence. But in this storage may have affected the ecological factors and human factors.

The Buxaceae plants are shrubs and small trees, with a cosmopolitan distribution. They are slow-growing evergreen shrubs and small trees, growing to 2 – 12 m (rarely 15 m) tall [16]. Owing to its fine grain it is a good wood for fine wood carving. The representatives of *Buxus* type is also resistant to splitting and chipping, and thus useful for decorative or storage boxes. Due to its high density and resistance to chipping, boxwood is a relatively economical material, and has been used to make parts for various stringed instruments since antiquity.

The crowns of Elbasan city today is mainly composed with fruit trees and a rich vegetation grass. The impact of human activity is the main cause during the crowns transformations of Elbasan city. The palynomorphs variety records of *Buxus* type signify the evolutionary guidance of this type.

4. CONCLUSION

- The representatives of Buxaceae family are present to all deepness.
- The palynomorphs of *Buxus* type is increasing their overall presence from the 4 m of depth to 2.5 m and then in the direction of the surface shows stability.
- Regarding to the palynomorphs presence of *Buxus* Type in all the analysed samples, we think that is closely related to the significant and inevitable impacts of the human hand for the cultivation of necessary plants during everyday life.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

THE FOSSIL POLLEN ALLOCATION OF CAPRIFOLIACEAE FAMILY OVER NEW HOLOCENE PERIOD IN ELBASAN CITY – MIDDLE ALBANIA

Admir Jançe*, Gëzim Kapidani, Peçi Naqellari*, Anila Jançe***, Nikoleta Kallajxhiu*, Blerina Pupuleku*, Anxhela Dauti*, Silvana Turku***

* "Aleksander Xhuvani" University, Elbasan, Albania
** Tirana University, Tiranë, Albania
*** Sofia University "St. Kliment Ohridski", Sofia, Bulgaria

corresponding author: Admir Jançe, e-mail: adi_jance@yahoo.it

Original scientific paper

ABSTRACT

Paleopalynological features submitted in this paper, find out in the earth depositions in Elbasan city, ancient city positioned in the Middle Albania. In this paper are provides palynological data about the spreading of Caprifoliaceae family over New Holocene period with the goal to submit the link between the dispersion and depth of Caprifoliaceae family on different time stages. Paleopalynological features for *Sambucus* type part of Caprifoliaceae family are given for the first time.

Based on the data provided, very interesting results was found, concretely the palynomorphs of Caprifoliaceae family are present in all depths (386 spores in total) and shows permanency from the bottom near to the surface, except close to the surface where there is an increase of the spore's number. We generally think that: vegetation alteration presented during the years is related to the human impact.

Keywords: *Paleopalynological, New Holocene, Sambucus type - Caprifoliaceae Family, palynomorphs, Elbasan city*

1. INTRODUCTION

The given paper presents palynological features of New Holocene deposits in Elbasan city. Palynology is an Interdisciplinary Science, connected to biological sciences and geology, particularly of botanical science, it is the science that studies the pollen and spores during the organic sediments formation, and above all this science includes the study of current and fossil palynoforms [1, 2]. Pollen and spores can undoubtedly be preserved because the outer wall of the grains is extraordinarily resistant [3, 4]. Comparison of plant spores and pollen,

allows judging the performance of primitive and specialized features of outer wall of the grains, and their evolutionary paths [5]. The fossil pollen features help in the discovery of traces of history on the use and cultivation of plants, feeding mode and the origin of agriculture [6]. In this paper are provides important data about the reconstruction of paleoflora, paleoclimate, stratygraphy of the Holocene, etc [1]. There aren't any similar studies conducted by local or foreign researchers for spore and pollen content data about this type in Holocene deposits in our country and microfossils plant of this family have not been studied previously in Elbasan city [7, 8]. In this paper the study of Holocene pocket also provides the factors which have their impact on the transformation of the flora in Elbasani town, focused on evolution of Caprifoliaceae family [7 - 11].

This study was undertaking with the goal to clarifying the correlation among the quantities data of spores and evolution over the times for this type of Caprifoliaceae family.

2. EXPERIMENTAL

Through these features we judge for the transformation of the natural environment and human impact of this transformation [12 - 14]. Paleopalynologic test are commonly used and most accurate for paleoclimates and paleoecologic studies of Quaternary period consequently and the Holocene period [15 - 17].

Physical-chemical composition of the pollen allows saved and easily extracted from soil sediments. Basically for their extraction all the used methods join in the physical and chemical processing of 1 gram earth sediment [1, 7, 8]. The fossil pollen extracted from sediments is analysed qualitatively and quantitatively.

During this study we have taken about 16 samples of soil, starting from 0.25 m to 4 meters depth with the distance between the sampling to 0.25 m. Paleopalynological test of all samples showed that all contained a large amount of organic matter that appeared suitable for pollen analysis.

2.1. The acetolysis method of Erdtman

The soil sampling is based on Erdtman method [18, 19]. In order to get better results first mix $1cm^3$ soil with 10ml KOH (10 %). Erdtman acetolyze method consists on processing the material with an acetolyze mixture, acetic anhydride $(CH_3COO)_2$ and sulfuric acid (H_2SO_4) in a 9:1 ratio. We cleaned with distilled water and mixed it with acetolyze solution, until a neutral environment is obtained. The emasculation process is followed by a centrifugal process for three minutes (3000 rotation/minute). The acetolyze method is widely used in paleopalynology; because it gives better visibility over the spores and pollen compared with the other methods used during the microscopic observation process [7, 18, 19].

2.2. Fixture of prepared composites

The fixture of prepared composites was realized by using the method of glue-preparations through gel-glycerin, which was prepared based on the Kisser method [20] by using 50 gram of gelatin, 175 ml of distillate water, 150 gram glycerin, 7 gram phenol (crystals). The composite was isolated to the edges of microscope slide with spray or paraffin and after 3 days it was ready to be used and stored.

3. RESULTS AND DISCUSSION

On table 1 are given the features about the spores' number for Caprifoliaceae family conform to the depth, and is presented also the total number of spores for this family. The maximum spores' number of Caprifoliaceae family (32 spores per sample) is taken in 2.5 m of depth while the minimum number, 19 spores, is taken in the bottom respectively 3.75 m of depth.

Table 1. Number of spores according to the depth

Sample	Depth (m)	Number of spores (Caprifoliaceae)
1	4	21
2	3.75	19
3	3.5	20
4	3.25	20
5	3	22
6	2.75	27
7	2.5	32
8	2.25	28
9	2	24
10	1.75	23
11	1.5	23
12	1.25	24
13	1	25
14	0.75	25
15	0.5	24
16	0.25	29
Total number of spores		386

On figure 1 is clearly shown the steady spores' number for Caprifoliaceae family from the bottom near to the surface, with the exception of the samples 6 and 7 where it is observed one upward trend (exactly in 2.75 - 2.5 m of depth), also is clearly shown the increasing number of spores for this family above all near to the surface. Based on the data presented in table 1 the spore's total number of Caprifoliaceae family is 386 spores. In sample 6, 7 and 16, the spores' number of Caprifoliaceae family undergoing an immediate increase (figure 2).

The data show that the increase of the representative's presence of family Caprifoliaceae near to the surface should be associated with human impact on the cultivation of this family plant, or one other reason for this increase may be related to the fact that new forms of pollen are stored better than older ones to meet the depths samples.

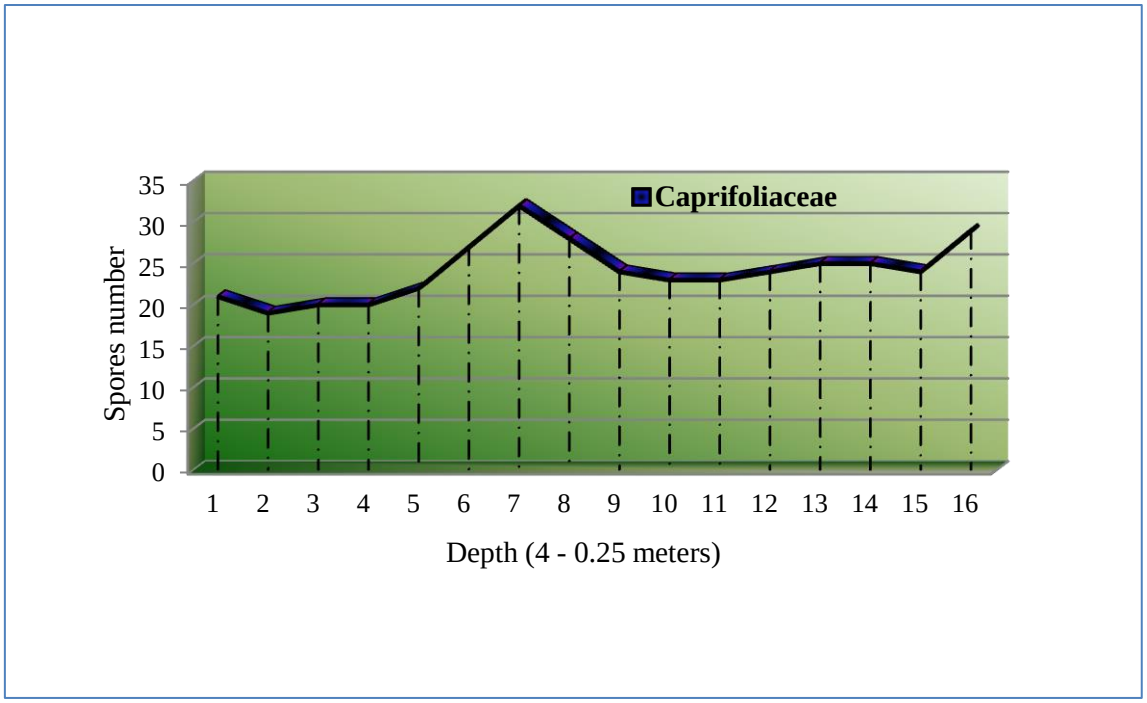


Figure 1. The spore's dispersion of Caprifoliaceae family according to the depth

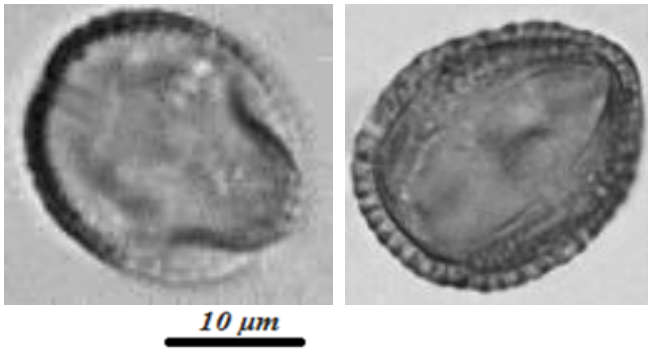


Figure 2. Caprifoliaceae family Pollen (*Sambucus* type Pollen – Photo 1)

Interesting is the fact that the samples matched depths approximately 2.75 - 2.5 m where it is observed one increasing number of spores for this family, despite the general steady trend.

Climate can cause land use changes or human societies to climate fluctuations cause complex impacts on the environment [21]. Impossible to find data on climatic factors, are supported in medieval history of Albania [22], in which it is alleged that this period was associated with wild wars of extermination of the Bulgarian and Serbian occupation where the population is greatly reduced and the town loses the economic importance.

The representatives of Caprifoliace family are mostly shrubs and vines, rarely herbs, including some ornamental garden plants in temperate regions. The various species of *Sambucus* type are commonly called elder or elderberry. The genus was formerly placed in the honeysuckle family, Caprifoliaceae, but was reclassified as Adoxaceae due to genetic and morphological comparisons to plants in the genus Adoxa [23].

The steady number of spores of Caprifoliaceae family in all depth samples maybe shows the human factor not had any impact on these plants and during these years these plants

keep the same presence, also increasing the number of spores for this family near to the surface may is connected with the cultivation of this family recent years in Elbasan city.

Many species are widely cultivated for their ornamental leaves, flowers and fruit. Ornamental varieties of *Sambucus* are grown in gardens for their showy flowers, fruits and lacy foliage. Elderberry fruit or flowers are used as dietary supplements for minor diseases such as flu, colds, constipation, and other conditions, often served as a tea, extract, or in a capsule [24]. It is not generally affected by soil type or pH level and will virtually grow anywhere sufficient sunlight is available.

Elbasani town at this time is filled with olive plantations, fruit trees and a rich vegetation grass, generally cultivated. Unquestionable is the fact of the impact of ecological and human factor to the pollen grains spreading. The quantitative pollen features of Caprifoliaceae family shows her evolution direction.

4. CONCLUSION

- The spores' number of Caprifoliaceae family shows permanency from the bottom near to the surface.
- The spore's number of *Sambucus* type increases close to the surface.
- The representatives of Caprifoliaceae family are present in all depth samples.
- Because in Elbasan city not had climate factors that have affected in the vegetation alteration, we are in thought that vegetation alteration presented during the years are most linked of the human influence.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

DATA ON THE MICROBIOLOGICAL POLLUTION OF THE AIR IN ELBASAN TOWN – ALBANIA

Anila Jançe*, Valentin Bogoev*, Admir Jançe**

* Sofia University "St. Kliment Ohridski", Sofia, Bulgaria
** "Aleksander Xhuvani" University, Elbasan, Albania

corresponding author: Anila Jançe, e-mail: adi_jance@yahoo.it

Original scientific paper

ABSTRACT

Microbiological data given in this study are taken from some stations in Elbasan city, situated in the central Albania. This study provides microbiological data for air pollution of the Elbasan town, focusing on areas with greater microbiological pollution with the goal to present the correlation between microbiological pollution of the air and the people's health. Therefore, were taken samples, collected and grown on standard culture media, concretely in M.P.A. nutrient agar (or PCA – Plate Count Agar) a microbiological growth medium for bacteria and Czapek medium (or CZA – Czapek's agar) a growth medium for propagating mosses and fungi, during a five-month period of 2016.

Emphasize that Elbasan town is dominated by a visible microbiological contamination, which is found in markets, mainly of food and industrial character. Some interesting data were found, showing distinctly the microbiological quality of bacteria and mosses.

Keywords: *Microbiological, M.P.A., Czapek, bacteria, mosses, Elbasan town - Albania*

1. INTRODUCTION

Microbiology is a branch of biology that deals with the study of microorganisms, their construction, their functioning and their impact on other living organisms [1, 2].

Van Leeuwenhoek is often cited as the first to observe microbes; Robert Hooke made his first recorded microscopic observation, of the fruiting bodies of moulds, in 1665 [3]. Air microorganisms include Aeromicrobiology which is a sub-branch of Microbiology.

Microorganisms are small, unicellular microscopic organisms invisible to the human eye. Microorganisms include bacteria, protozoa, fungus, microalgae, prokaryotes and viruses [1, 2, 4 - 6]. Many microorganisms make a major contribution to the well-being of the world's inhabitants by helping to maintain the balance of living organisms and chemical compounds in our environment.

Microorganisms interact with their environment to provide: a) energy b) electrons c) foods, that play a key role in the process called the "biogeochemical cycle". Microorganisms make it possible to transform elements such as oxygen, carbon, nitrogen, sulphur, and phosphorus into useful forms of plants and animals [2, 7 - 9].

This study provides important information about the air microorganisms in some areas of the Elbasan city during May - September 2016 period, as well as their impact on our lives. In the air there are also a large number of pathogens that cause infections in humans and animals. Parts of the pathogens are viruses that cause various diseases among which we can mention: asthma, bronchitis, allergies associated with breathing, heart disease, lung disease, etc. [4, 9].

The main causes of allergies in the air are microorganisms. Significant impact on these allergic diseases is the humidity and air temperature [10, 11].

Information on the method of collection, preservation and laboratory processing of the mosses and the bacteria were provided in this study. Our study through the analysis of the mosses and the bacteria encountered in the analysed samples in the Elbasan city tries to shed light on the potential impacts of air pollution in this area as well as on the factors that have affected this pollution.

2. EXPERIMENTAL

During the microbial analysis of air, quantitative and qualitative microbial analysis is carried out. The most common methods for microbial air analysis are: sediment method, filtration method and aspiration method. The method used for air analysis in the predetermined areas of the Elbasan city is sedimentation [12 - 14]. This method is based on sedimentation of microorganisms together with air on the terrain surface on the Petri dishes [15]. After preliminary preparation in the laboratory, sterile Petri dishes with agar, throughout the analysed period, were placed in open spaces at various points in Elbasan town. At the same time, air temperature was measured, which influenced the measurement results.

2.1. Sedimentation method

The sedimentation method is based on sedimentation of microorganisms together with the particles found in the air on the surface of the Petri dishes with agar. For analysis of microorganisms, two Petri dishes are needed with nourishing agar medium, while two plates with nourishing agar and iron sulphate are needed for anaerobes. MPA ground or PCA (plate count agar) was selected as a growth medium for bacteria. Petri dishes in Czapek or CZA – Czapek's agar are used as a growth medium for propagating mosses [16 - 18].

2.1.1. Method of work

- Petri dishes with nourishing agar, according to the type of analysis to be carried, will be transported in sterile conditions to the place where they will be analysed.
- Open the dishes in places where there is no air flow and leave open for 20-30 minutes.
- Then wrapped in paper and transported to the default location.
- The incubation takes place at a temperature of 25 - 37 ^{0}C in the period of 24 to 48 hours for bacteria and 5 – 7 days for the mosses.

2.1.2. Placement of sampling in the thermostat

Petri dishes are transported after receiving from the predefined stations in the lab by placing them in the thermostat (37 ^{0}C) and left there about 24 to 48 hours to incubate. After this the counting of the colonies is done by turning the plate with bottom from above. The colonies look like dots, with different sizes and shapes (drops, flowers, stars).

If there are over 200 colonies on Petri dishes then it is assumed that the area on which the dishes are placed has an air contaminated by microorganisms [19 - 21]. When on Petri dishes there are less than 200 colonies, then it is determined that the area on which the plate is placed has a clean air [19 - 21]. It should also be noted that at any time the temperature and humidity of the air are kept in mind [10 - 14].

3. RESULTS AND DISCUSSION

All samples taken during May - September 2016 period in the Elbasan town show that this city has microbial contamination above allowed rates. Obtained data for each of the five months (from May to September) are grouped together.

This grouping of months has been done in order to understand the performance of microbial air pollution depending on the air temperature in each of the months. The table 1 shows the number of mosses in the five months as well as the air temperature that is measured at any time. The minimum number of mosses (252) is present in morning while the maximum number (485) is present in midday.

Table 1. Number of mosses according to the analysed period (Czapek)

Date	Temp. (°C)	Morning	Temp. (°C)	Midday	Temp. (°C)	Evening
May	22	225	29	446	27	278
June	25	254	35	495	32	302
July	27	276	37	527	33	334
August	27	271	36	503	31	311
September	21	232	28	452	26	298
Average	252		485		305	
Total number of mosses	1042					

In the same way table 2 was made that present the number of bacteria in the same period together with the relevant temperature. Considering average values in the table 2 it is clearly visible that the minimum number of bacteria (319) is present in morning while the maximum number (652) is present in midday.

From the data in table 1, figure 1 was constructed. This figure shows the level of microbial contamination of air by mosses in the five months (during the three periods of the day) depending on the air temperature. It can be clearly seen a large increase for the number of mosses exactly on Midday at the time when the temperature is higher. Based on the data of table 1 and figure 1 the mosses total number is significant (1042 mosses) (figure 2).

Table 2. Number of bacteria according to the analysed period (MPA)

Date	Temp. (°C)	Morning	Temp. (°C)	Midday	Temp. (°C)	Evening
May	22	298	29	602	27	354
June	25	305	35	666	32	485
July	27	354	37	708	33	572
August	27	338	36	673	31	525
September	21	302	28	612	26	478
Average	319		652		483	
Total number of bacteria	1454					

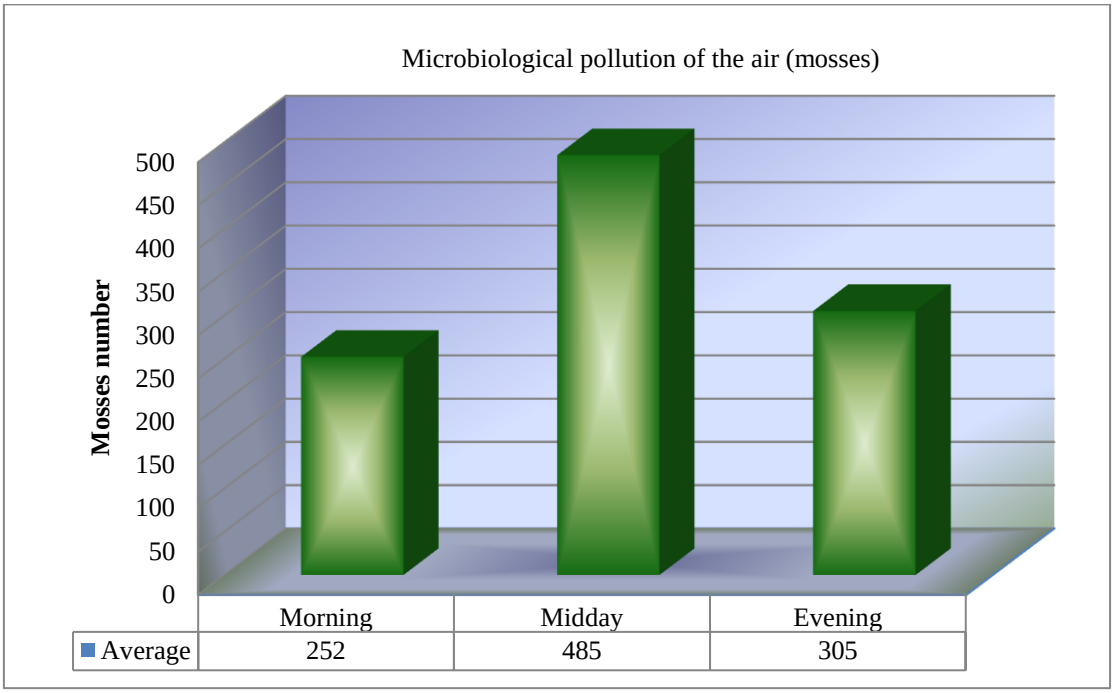


Figure 1. The level of microbial air pollution by mosses by to the analysed period (Czapek)

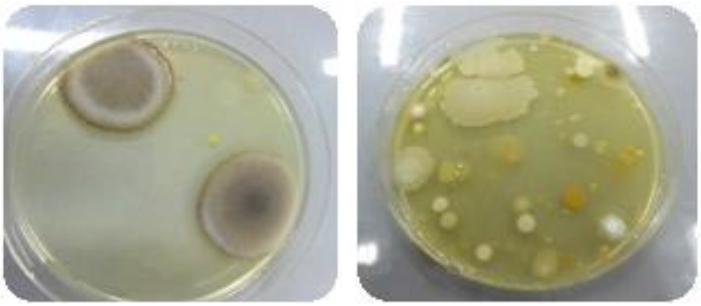


Figure 2. Mosses and Bacteria *(Source: Jançe 2016)*

In the same way from the data in table 2, figure 3 was made, which shows the level of microbial contamination of air by bacteria, presented during the three periods of the day (in the five months analysed).

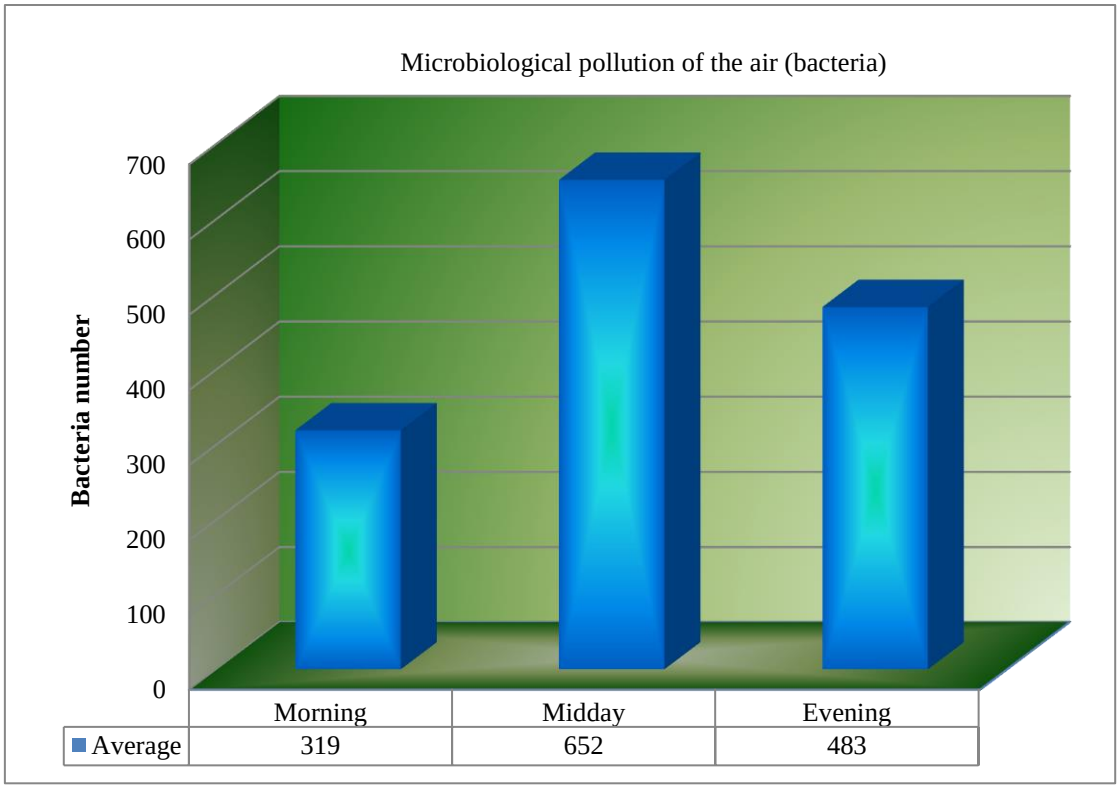


Figure 3. The level of microbial air pollution by bacteria in the analysed period (MPA)

Figure 3 clearly shows a great increase in the number of bacteria on midday when the temperatures are higher. Considering the data presented in table 2 and figure 3 the bacteria total number is approximately 1454 bacteria, higher than the number of mosses (figure 2).

Based on tables 1 and 2, the level of microbial contamination of air in the Elbasan city is increasing and as a result there is a total increase in microorganisms.

Microorganisms react differently to changes in humidity in the air, but most of them prefer high humidity. This has been one of the reasons why the level of microorganisms has grown [4, 9, 11]. Also, from the analysis of figures 1 and 3 it is visible that the level of air pollution has fluctuated during the analysis period. In midday there is an increase in the level of microorganisms and then in evening this pollution is decreases, while in the morning the level of microbial air pollution is lower. We think that the lower temperatures in the morning are the reason for it. Also human activity begins after morning.

The amount of dust measured from different sources never results under 240 mg/m^3 air and often reaches 440 mg/m^3 air, so five times higher than allowed in our country (80 mg/m^3 air) but ten times higher than the rates allowed by European Community (40 mg/m^3 air) [22]. We can say that microorganisms react differently to changes that occur during temperature changes. Great impact on this result also have small air currents that come as a result of different movements of vehicles or people, but also the marketing of various food products containing high microbial contamination. Elbasani town has been ranked among the most polluted cities in Albania for years.

The Institute of Public Health in Elbasan city has conducted a study from which it has been shown that the numbers of people affected by cancer and lung diseases are too high.

We think that the main reasons for this drastic pollution are: loaded traffic, high concentration of population, multiple buildings, lack of green areas, infrastructure, etc. Microbial air pollution has become one of the major causes of respiratory disease growth, thus decreasing the life expectancy of residents.

In conclusion: the air of the Elbasan city throughout the analysis period results to be microbiologically polluted because there are a number of bacteria above allowed limits (over 200 colonies for Petri dishes [19 - 21]).

4. CONCLUSION

- The total numbers of bacteria are greater than the total numbers of mosses.
- The minimum number of the microorganisms' representatives is present in morning while the maximum number is present in midday, both for mosses and bacteria.
- A large increase in the number of bacteria and mosses is present at midday when temperatures are higher.
- Elbasan city appears with considerable microbiological air pollution, because the level of microbial contamination of air is quite high and the numbers of microorganisms are above allowed limits.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

DESCRIPTION OF AIR CONTAMINATION FOR ELBASAN CITY – ALBANIA

Anila Jançe*, Valentin Bogoev*, Admir Jançe**

* Sofia University "St. Kliment Ohridski", Sofia, Bulgaria
** "Aleksander Xhuvani" University, Elbasan, Albania

corresponding author: Anila Jançe, e-mail: adi_jance@yahoo.it

Original scientific paper

ABSTRACT

In this paper are presented microbiological record for Elbasan town, one of the important and ancient towns situated in the Middle Albania. In this research are given microbiological data that prove the air pollution of Elbasan city with the aim to giving the evaluation of microbiological air contamination as a important parameter for a healthy lifestyle.

For this purpose, the samples were taken at three stations, contaminated with mosses grown on standard culture of Czapek (or CZA – Czapek's agar, a growth medium for mosses propagating) and bacteria M.P.A. (or PCA – Plate Count Agar, a microbiological growth medium for bacteria).

We can say that Elbasan city has been one of the most microbiologically contaminated Albanian cities. The main cause is the light and heavy industry that work without taking measures in the function of environmental protection.

Keywords: *air contamination, M.P.A., czapek, microbiological, Elbasan city - Albania*

1. INTRODUCTION

The first recorded microscope observation was of the fruiting bodies of moulds, by Robert Hooke in 1666 [1], but the father of microbiology is considered Antonie van Leeuwenhoek as he observed and experimented with microscopic organisms in 1676 [2]. Scientific microbiology developed in the 19th century through the work of Louis Pasteur [3]. The completed study belongs to the science of Microbiology that deals with the construction and the impact of microorganisms on living organisms [4, 5]. Exactly this study belongs to one sub-branch of Microbiology that is Aeromicrobiology science that deals with the study of living microbes which are suspended in the air.

Many different microorganisms can be in aerosol form in the atmosphere, including viruses, bacteria, fungi, yeasts and protozoa's [5 - 7]. In order to survive in the atmosphere, it is important that these microbes adapt to some of the harsh climatic characteristics of the exterior world, including temperature, gasses and humidity [8]. Many of the microbes that are capable of surviving harsh conditions can readily form endospores, which can withstand extreme conditions [9].

Survival rate of bioaerosols depends on a number of biotic and abiotic factors which include climatic conditions, ultraviolet (UV) light, temperature and humidity, as well as resources present within dust or clouds [10, 11]. Bioaerosols found over marine environments primarily consist of bacteria, while those found over terrestrial environments are rich in bacteria, fungi and pollen [7, 11]. The dominance of particular bacteria and their nutrient sources are subject to change according to time and location [5, 6, 12].

Micro-organism spread through air from one place to another. The micro-organisms are present everywhere in nature and the micro-organisms present in air are responsible for contamination of food or transmission of disease. The diseases such as tuberculosis, influenza, and some plant and animal fungal disease spread via air [12].

This paper provides significant data about microorganisms in the air in Elbasan town throughout a period of three months, exactly from July to September 2017. The areas selected in this case study are: "Agri-Food Market", "Train Station", and "City Park". Through our research we try to reach the assessment of microbiological pollution of air as a necessity for the safety of human health.

2. EXPERIMENTAL

The most common methods for microbial air analysis are: sediment method, aspiration method and filtration method. For the air microorganism analysis, quantitative and qualitative analysis are done. The used method for air analysis in three stations in Elbasan town is filtration. This method is based on planting that is made into liquids such as physiological water or solid substances (sodium sulphate or sugar) in the agar field with planting on the surface or pouring [13, 14].

2.1. Filtration method

The filtration method is based on the passage of a certain volume of air through a sterilized liquid (water, physiological water, diluent peptide or bujane) or through a dry substance (such as sugar or sodium sulphate) [14, 15]. Passing through these substances, air particles, including microorganisms, are suspended. Then cultivate fluids or solids with planting with a cover on the terrain surface on the Petri dishes [16].

The numbering is performed after their growth which is carried out during incubation for 48 hours and 5 - 7 days. The measurements are made for the whole amount of liquid. Knowing the amount of air that has passed through the liquid, the amount of microorganisms in 1 m^3 of air is counted.

2.2. Placement of sampling in the thermostat

MPA ground or otherwise called PCA (plate count agar) was selected as a growth medium for bacteria and Petri dishes in Czapek or CZA – Czapek's agar as a growth medium for propagating mosses [17 - 19]. The obtained material from the three stations is sent in the lab by setting them in the thermostat (37 ^{0}C) and left there for the minimum of 48 hours to incubate. After that the counting of colonies was done by turning the plate with bottom from above. The colonies have different shapes and sizes (stars, flowers, etc). Air in the analysed station was considered contaminated by microorganisms if there are more than 200 colonies on Petri dishes [20 - 22].

3. RESULTS AND DISCUSSION

Starting from the records collected during the research, the record found for each of the three months, respectively from July to September are grouped together. All specimens taken during July - September 2017 period in the Elbasan city show that this city has microbiological contamination over allowed norms.

Table 1 shows the number of mosses and bacteria in the three months for the three stations. The minimum number of mosses (42) is taken in City Park - Station while the maximum number (608) is taken in Agri-Food Market - Station.

The same thing with regard to the minimum-maximum number is noticed for bacteria. Concretely, the minimum number of 88 is present in City Park and the maximum number of 803 is present in the station of Agri-Food Market.

Table 1. Number of mosses and bacteria in the analysed period

Czapek (Mosses) - Data	1st Station Agri-Food Market	2nd Station Train Station	3rd Station City Park
July	608	384	98
August	574	322	111
September	502	264	42
MPA (Bacteria) - Data	1st Station Agri-Food Market	2nd Station Train Station	3rd Station City Park
July	795	609	92
August	803	592	88
September	689	535	95

Starting from table 1, table 2 was constructed that represents the total number of bacteria and mosses in the analysed three-month period. Considering the average values in the table 2 it is clearly visible that the minimum number of microorganisms (175) is present in City Park while the maximum number (1324) is present in Agri-Food Market.

Table 2. Total number of bacteria and mosses in the analysed period

Date	1st Station Agri-Food Market	2nd Station Train Station	3rd Station City Park
July	1403	993	190
August	1377	914	199
September	1191	799	137
Average	1324	902	175

From the record in table 2, figure 1 was made in which the microbiological contamination level of air is shown for the three months linked with the three analysed stations. Figure 1 clearly shows a large increase in the number of microorganisms in July, month with the highest temperatures. Based on the data presented in table 1, table 2 and figure 1, the mosses and bacteria total number is impressive (figure 2).

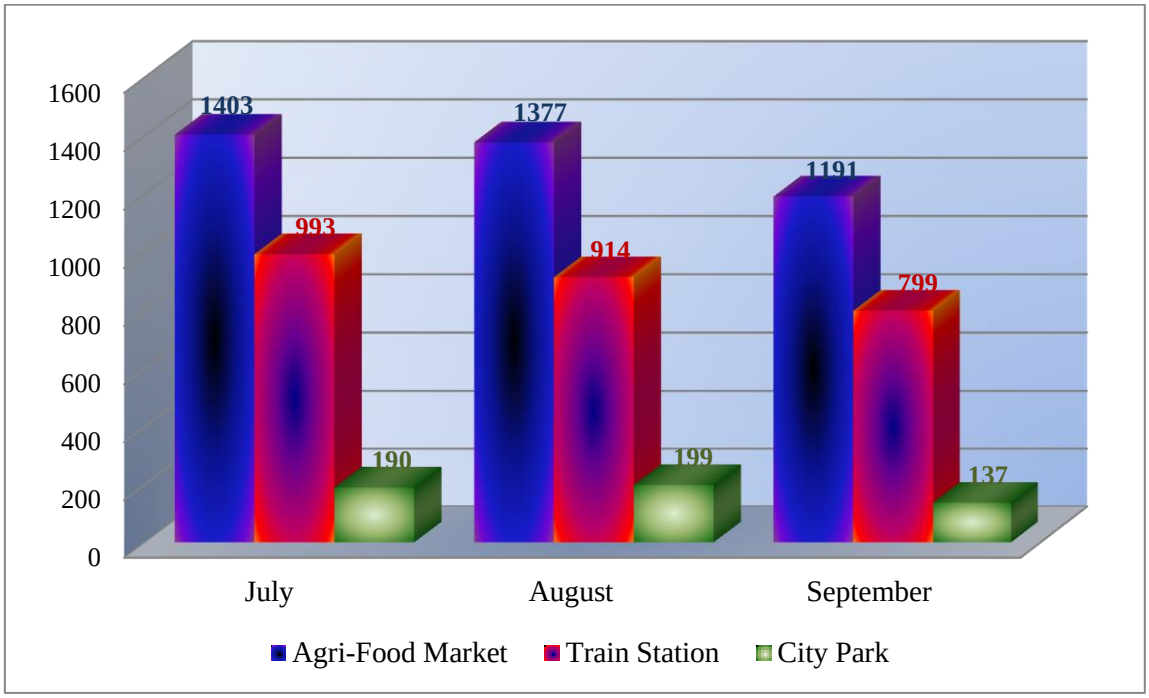


Figure 1. Level of pollution in the three analysed stations

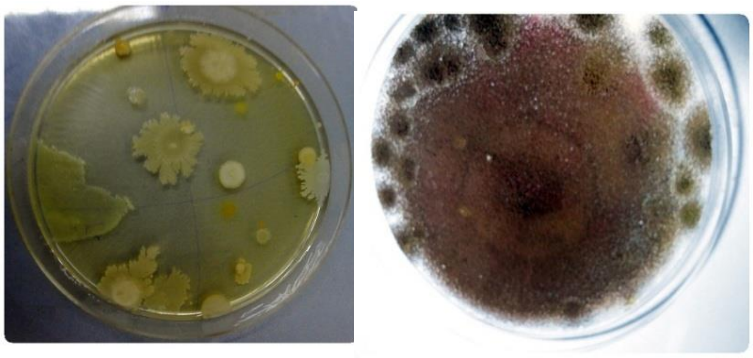


Figure 2. Bacteria and Mosses *(Source: Jançe 2017)*

Also, starting from the data in table 2, figure 3 was constructed, which shows the level of air microbial contamination by bacteria and mosses in each of the three analysed stations.

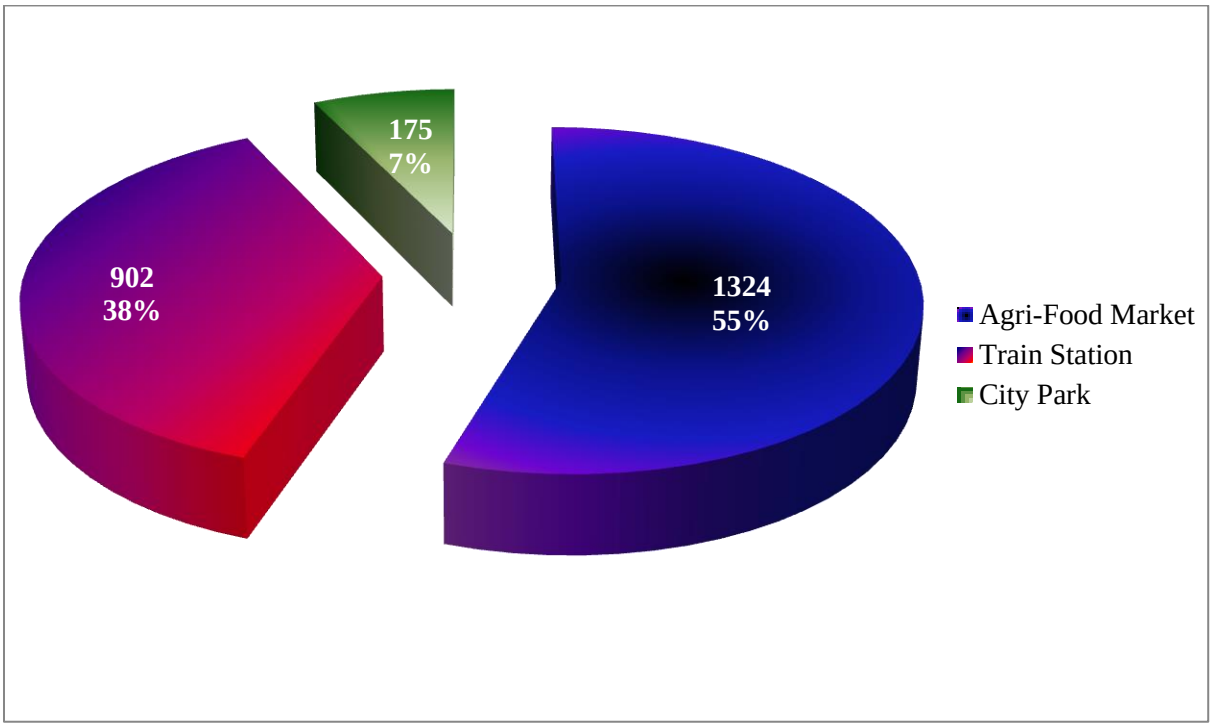


Figure 3. Microbial contamination in each of the analysed stations

Figure 3 clearly shows a great presence of microorganisms in Agri-Food Market, 55 % of the total. Considering the data shown in figure 3 the presence of microorganisms is 38 % in the Train Station and the smallest presence of microorganisms is noticed in City Park - Station with the 7 % of the total.

Based on tables 1 and 2, the level of air contamination in Elbasan town is rising, and as a result there is a total increase in microorganisms, especially in two analysed stations.

A great part of the research conducted on bioaerosols studies their effects on humans, since human disease is one of the effects of bioaerosols. Knowing what is in the air is important as human mortality rates increase with the rise of airborne particulate populations [23]. Additionally, people spend a lot of time indoors, and knowing what exists within the air they breathe is important [23, 24].

Elbasan city is one of the most polluted cities in Albania. The Institute of Public Health in Elbasani town claims that the numbers of people affected by cancer and lung diseases are too high. The main cause of these diseases is smog, which together with scrap waste and urban wastes are the main causes of environmental pollution in Elbasan city.

From the obtained data results that the area of "Agri-Food Market" has a greater number of microorganisms, while the “City Park” area has a smaller number of microorganisms.

Number of microorganisms in area "Train Station" lies between two extreme points. This station is also considered contaminated, as the number of bacteria and mosses on a Petri dish exceeds the permissible limit (over 200 colonies).

The greatest microbial contamination of the air in the "Agri-Food Market" is the result of large traffic, overcrowding, and the release of marketed products. Big impact on this result have small air streams that come as a result of different movements of cars or people, and marketing of various food products containing high microbial contamination.

The number of colonies at the “Train Station” is the lowest compared to the aforementioned station because there is no overcrowding in the station and lack of a variety of motor vehicles. But in any case the numbers of colonies is above the permissible pollution level as the “Train Station” is near waste collection site of the Elbasan city.

“City Park” area is considered pure because the above factors are missing. Lack of vehicle circulation and dense vegetation are the reason for the cleaner airspace, making this area one of the most attractive and relaxing areas for the citizens.

We conclude that the air in Elbasan city is very microbiologically polluted, because the number of microorganisms is above allowed limit (over 200 colonies for Petri dishes).
We can also say that only “City Park” has microbiologically clean air since on Petri dishes has fewer than 200 microorganisms [20 - 22].

4. CONCLUSION

- Higher presence of microorganisms is clearly shown on July, when the temperatures are higher and the smallest presence is observed in September.
- "Agri-Food Market" – Station have the greater number of microorganisms, while the “Train Station" has an intermediate number of microorganisms and “City Park” area has a smaller number of microorganisms
- "Agri-Food Market" and "Train Station" are considered contaminated, as the number of bacteria and mosses on a Petri dish exceeds the permissible limits.
- “City Park” is the only clean city area with a number of microbiological air pollutants within the allowed limits.

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HARMONIJA „SVEJEDNOTE" PRIKAZANA KAUZALNOM LINIJOM: PSIHA – OKOLIŠ – INTEGRATIVNA BIOETIKA

THE HARMONY OF „ALL-ONNENES" PRESENTED THROUGH CAUSAL LINE: PSYCHE – ENVIRONMENT – INTEGRATIVE BIOETHICS

Luka Janeš*

* Sveučilište u Zagrebu, Sveučilišni centar za integrativnu bioetiku, Zagreb, Hrvatska

autor za korespondenciju: Luka Janeš, e-mail: ljanes@unizg.hr

Prethodno priopćenje

SAŽETAK

Kroz ovaj propedeutički rad u kratkim će se crtama nastojati oslikati kauzalni suodnošaj evolutivne biotičke zajednice kozmosa, terminološki iskazane terminom svejednota, a kroz analogiju psihičkog stanja ljudi i toksikacije te destrukcije okoliša, dakle enormnog onečišćenja koje se manifestira kao posljedica potpunog gubitka odgovornosti i sebičnosti ljudske vrste. Dakako da toliko kompleksna zadaća, prikazana u kratkim crtama, potencijalno izazova primisli glede trivijalizacije sadržaja putem navedenog sažimanja, no u radu će se ukazivati na činjenicu da su zahtjevi za misaono zahvaćanje te praktično provođenje navedene težnje u velikoj mjeri jednostavni i elegantno provedivi.

Kao znanstveni metodološki smjerokaz za provođenje zadanog uvest će se disciplina integrativne bioetike, s posebnim fokusom na bioetički predmetni senzibilitet usmjeren na zaštitu svih oblika i vidova života, te metodološke smjernice pluriperspektivnosti, integrativnosti, interdisciplinarnosti i transdisciplinarnosti kao znanstveni alati za provedbu naznačene zadaće.

Ključne riječi: *psiha, okoliš, harmonija, integrativna bioetika, odgovornost*

ABSTRACT

Through this propedeutic paper, we will try to underline the causal corellation of evolutionary biotic community of the cosmos, terminologically expressed in the term of the all-onnenes, and through the analogy between the mental state of humans and the toxification and destruction of the environment. Therefore, enormous pollution is manifested as the result

of complete loss of responsibility and selfishness of the human species. Certainly, the complexity of the task, shown in the short lines, potentially provokes thoughts about the trivialization of the contents through the above-mentioned compression. Therefore, through this paper will be pointed out that demands for the massive engagement and practical implementation of these aspirations are very simple and elegantly feasible.

As a scientific methodological guideline will be introduced discipline of the integrative bioethics, with a particular focus on the bioethical subject sensibility aimed at the protection of all forms of life, as well as the methodological guidelines of pluriperspectivity, integrativity, interdisciplinarity and transdisciplinarity, that presents the scientific tools for the implementation of the indicated tasks.

Keywords: *psyche, environment, harmony, integrative bioethics, responsibility*

1. UVOD

Ljudska povijest nedvojbeno je ogrezla o točku prijeloma epoha [1] pri čemu se kao paradigma iskristalizirala antropocentrička sebičnost te posvemašnji gubitak odgovornosti [2] spram planeta i okoliša, dok antroposna vrsta sve intenzivnije alijenira te disjuncira od onog kauzalno-prirodnog [3], stvarajući umjetni kulturološki svijet kojemu je onaj prirodni neprijatelj kojeg valja savladati [4] te destruirati kako bi se kalibrirao po mjeri čovjekovih potreba i komfora. Moralni nihilizam raznih segmenata i disciplina egzaktnih znanosti bez sumnje doprinosi navedenom scenariju, prevođen i provođen utjecajem enormnih financijskih sredstava koji dirigiraju znanstvene smjerove, a koje nihiliziraju moralnu dimenziju djelovanja, uz analogni nestanak odgovornosti što se očituje sve većim onečišćenjem okoliša i moralnog nihilizma. U ovom će se radu nastojati istražiti veza psihičkog stanja ljudi i destrukcije okoliša, te nastojati propitati može li orijentativna disciplina integrativna bioetika ponuditi odgovore na navedena pitanja, odnosno pružiti metodološke alate za integraciju raslojenih i fragmentiranih karakteristika koje doprinose destrukciji planeta i okoliša, te pritom bivati svjetionik usred oluje moralne relativnosti, te spriječiti apokaliptični brodolom kojemu čovječanstvo sve više stremi. U ovom članku će se konstelacija evolutivne organizmičnosti svekolikog života semantički obujmuti termininom „svejednota“ [5], te će uz dotičnu analogijski promatrati i psiha pojedinca, odnosno balans pojedine psihe u odnosu na harmoniju cjelokupne organizmičnosti Svejednote, a u kontekstu zaštite okoliša kao direktnog pragmatičnog ispoljka navedene konstelacije. Zadatak koji će predstavljati predmetnu vodilju ovog spisa jest propitivanje imaju li čistoća okoliša i zdravlje pojedine psihe kauzalne veze, odnosno nadopunjuju li se uzajamno pod nišom odnošenja, dakle djelovanja bivstvujućih?
Nakon sažetog uvoda u problematiku definiranja fenomena psihe i njegova dovođenja u vezu s fenomenom života i popratnog balansa u odnosu na moralitet, psihu će se nastojati prikazati kao dijalektiku, dakle suodnošajni koloplet uma i tijela, pri čemu će naglasak biti na Kantovoj liniji moralne dužnosti kao vrhunca umnosti. Kao pragmatični pokušaj rezoniranja i elaboriranja zadanih rasprava koristit će se metodologija i predmetni senzibilitet integrativne bioetike.

2. EKSPERIMENTALNI DIO

S obzirom na kompleksnost izazova definiranja psihe [6], fokusirat ćemo se na eksperimentalni modus definiranja psihe kao dijalektike [7] uma i tijela. Pritom se um uzima kao svojevrsna potencija kretanja, dakle potencijalna preteča fizičkog kretanja koje biva aktualizirano fizičkim tijelom i njegovim suživotom sa i djelovanjem na ostala tijela u fizičkom prostoru, a što neminovno pobuđuje etičke konotacije.

Definiranje psihe itekako otežava njezino percipiranje kao duše u klerikalnom smislu, stoga se valja držati fenomenoloških motiva koji su bliski znanstvenom opserviranju i elaboriranju, prije svega kao prostorno-penetrirajuća životna energija konveksnog i konkavnog karaktera. Jung u *Dinamici nesvjesnog* o psihi iznosi:

»Ako se postavimo na tlo običnog opažanja i uzdržimo od isuviše širokih filozofskih razmatranja, onda ćemo učiniti najbolje moguće ako psihički proces jednostavno shvatimo kao životno zbivanje. Na taj način uski pojam psihičke energije proširujemo do daljeg pojma životne energije, koji takozvanu psihičku energiju supsumira kao specifikaciju. Time stječemo prednost na taj način, što smo u stanju da kvantitativne dosege pratimo i zvan uskih opsega psihičkog, sve do bioloških funkcija uopće, čime se udovoljava neosporno postojećoj i već od davnina diskutiranoj nedjeljivosti duše i tijela.« [8].

Promatramo li ljudsku psihu kao umnu životnu energiju, što ona jamačno na fizikalnoj razini i jeste, ta energija se neminovno prostire energetskim poljem objektiviteta planeta Zemlje, ispreplićući se i nameću kozmološkom kauzalitetu. Dotična energija nosi potenciju kreiranja ili destruiranja, te je u općenitom suvremenom globalnom modusu evidentno da aktualizacija zadane energičnosti preteže na stranu destrukcije, a u vidu onečišćenja okoliša i potpunog odsutstva odgovornosti spram destruiranja, pri čemu odnošajna paradigma poprima obličje prirodnosti onečišćavanja, odnosno nuspojavne nužnosti tehnomanskog društva. Naime, čovječanstvo mahom ne biva uznemireno poradi općeg enormnog onečišćenja (dakako da postoje vrijedne inicijative i pokreti, no statistički gledano – većina nezainteresirano okreče glavu) uzimajući dotično stanje normalnim, prirodnim i povijesnim, a navedenom definitivno doprinosi i tehnomanija kao obilježje suvremene epohe [9], a uz sva čuda smjerova i potencija koju tehnološko usavršavanje nosi u odnosu na komfor antroposa, tehnoznanstvena sfera još uvijek nije uspjela, analogno razvoju tehnike, razvijati i „tehniku morala“, te s toga ne čudi enormni raskorak između razvoja tehnike i morala, čak štoviše – razvoj se odvija dijametralno suprotno i u agonalnom odnosu [10]. Oswald Spengler iznosi:
»Zajedno s racionalizmom 'vjera u tehniku' gotovo postaje materijalističkom religijom: tehnika je vječna i neprolazna kao Bog Otac; ona spašava čovječanstvo kao Sin; ona nas prosvjetljuje kao Duh Sveti, a njen obožavatelj je malograđanin 'novog doba' od Lamettriea do Lenjina.« [11].

Moralni balans u problematskom diskursu ovog članka stavlja se u analogijski odnos s psihičkim stanjem bivstvujućih, a kao prilog navedenom dala bi se iskoristiti misao da je svaki psihički čin ujedno i etički čin samim time što je djelovanje, a što automatski zaposjeda bioetičko polje analize. Pritom činom uzimamo i samo mišljenje bivstvujućih, a što znači da se psiha aktivira u kretanju, u probijanju prostornosti koja izvire iz sebstva bivstvujućih, ispunjavajući energetski prostor svekolike jave. Postavlja se zahtjev za promišljajnim i praktičkim integritetom bivstvujućih u odnosu na život okoliša, dakle prirode od koje se uporno kao vrsta alijeniramo.

Valja se zapitati može li tehnika usmjeriti psihu bivstvujućih u putanju morala, ili pak ljudskost robotizira u kalupe U.I. modula i algoritama? Nipošto ne bi bilo problematično kad bi se umjetna inteligencija mogla etički izbaždariti, no činjenica je da njezin razvoj biva diktiran stjecanjem kapitala, a nipošto unapređivanje morala, te stoga moralitet umjetne inteligencije povlači mnoga pitanja.

Kao reakcija na aktualno otuđenje znanstvenog ophođenja nastala je orijentacijska disciplina integrativna bioetika, obilježena predmetnim senzibilitetom zaštite sviju oblika i modusa života, te metodološkim postulatima pluriperspektivnosti, integrativnosti, interdisciplinarnosti i transdisciplinarnosti [12], a znanstvena energija i potencija koju navedena disciplina neminovno nosi, itekako može ukazati na smjerove i nadići problematiku odnosa pojedine psihe i destrukcije okoliša konkretnim rješenjima. Pritom bioetičku edukaciju uzimamo za temelj očuvanja mentalnog i moralnog zdravlja koje se proteže na odnos čovjeka i okoliša, a s naglaskom na svijesti o jedinstvu života kao početnoj telosnoj točki navedene edukacije, a u odnosu na odgovornost spram života nameće se moment pluriperspektivnosti kao potencija za zahvaćanje svekolikog kozmološkog diverziteta.

Vezano uz moralitet tehnoznanstvene sfere, neminovno je ponoviti i naglasiti da tehnika diktira napredak znanosti, a Hrvoje Jurić sjajno primjećuje:

»U svakom slučaju, na temelju Jonasova "izbora iz povijesti moderne znanosti i tehnike" može se zaključiti kako se njihova *differentia specifica* u odnosu na one pred-moderne sastoji prvenstveno u tome što je, kao prvo, u konstruiranju tehničkih naprava udio znanosti (znanstvenih istraživanja, rješenja, planiranja i zahtjeva) sve veći, a kao drugo, to što – i *usprkos* prethodno izrečenom, ali *upravo zbog toga* – tehnika diktira razvoj znanosti, znanstvenih spoznaja, a konačno i samoga znanstvenog *znanja*.« [2].

3. REZULTATI I DISKUSIJA

Zapitajmo se je li tehnološki okoliš pandan prirodnom te može li kategorički uopće predstavljati surogata? Najbolji primjer za istraživanje zadane teze očituje se pri dominaciji simulakruma [13], dakle virtualnog realiteta koji je zamijenio „stvarni", a koji probija iz medijskih kanala. Pritom se kroz zanemarivanje i destrukciju sunositosti sa stvarnim ontičkim principom svejednotnosti iz vida posve gubi odgovornosna orijentacija te mogućnost prijanjanja uz modus zaštite okoliša, tuđih psiha i cjelokupne evolucijske vrtnje Svejednote, a upravo je odgovornost jedan od temeljnih pojmova integrativne bioetike.

Dualiziranje od prirode povlači pregršt aporičnih konzekvenci na psihu pojedinca, a što se kauzalno proteže na cjelokupnu kulturno-političku bilancu. Pod utjecajem sebičnosti i narcisarije pojedine psihe često se zaboravlja da je i antropos – svojevrsni vrhunac evolucije – još uvijek dio biotičke zajednice svejednote, dakle vezan je sponom života i organizmički sjedinjen s objektivitetom od kojeg se sve više udaljava, a što valja promatrati kao uzrok mnogih psihičkih poteškoća, te istraživanja usmjeriti u navedenom smjeru. Hrvoje Jurić iznosi:

»… upravo ono čime je čovjek podređen čitavoj prirodi, njegovo jedinstveno obilježje- duh-ne rezultira više u jednom višem poretku njegova bitka u totalitetu bitka, nego suprotno tomu obilježava nepremostivi jaz koji ga dijeli od ostatka zbiljnosti. Čovjek je tako otuđen od zajedništva bitka u cjelini, njegova ga svijest čini strancem u svijetu i svaki istinski akt refleksije posvjedočuje upravo ovu stranost.« [2].

Usred tehnomanijskog doba, čija je kritika iskazivana kroz rad, evidentno i sama psiha biva tehnicizirana, odnosno parametrizirana kroz algoritme trgovanja i kupovanja, pri čemu se bitkovna vrijednost pretvara u robu, a empatijski aktivizam izaziva sprdnju i djeluje kao evo suvišna evolucijska disleksija. Reflektiranje psihičke konkave čije kretanje biva usmjereno na unutrašnjost, dakle spram narcističkog etosa, očituje se destrukcijom okoliteta i objektiviteta, a teza koja se nudi jest da navedeno čahurenje i zatvaranje dovodi do nihilizacije svijesti, odnosno halucinatorne izbojbine kao paradigme općeg misaonog odnošenja spram realiteta svejednote, dakle harmonične organizmičnosti života po sebi. Sličnu halucinatoriju

primjećujemo i pri etosu koji destrukciju okoliša uzima normalnom stavkom, a što je, tvrdim, posljedica simulakrizacije i tehnizacije psihe. Dakle, upućujemo na povezanost odsutstva empatije i psihičkog disbalansa, a što potvrđuje sve veći panel psihijatrijske dijagnostike [14] i shizofrenizacije bivstvujućih, te sve veća konzumacija psihofarmaka kao potvrda tehnizacije psihe i tretmana nad njom.

Harmonija svejednote u odnosu na antropose očituje se na tri temeljne razine: mikrorazinu pojedinca, mezorazinu političke zajednice i makrorazinu cjelokupne kozmičke zajednice. Antroposi nažalost mahom spoznajno ostaju na prvoj razini, zanemarajući dobrobit ostalih članova društvene, ali i prirodne zajednice, te nužno valja ponoviti krucijalnu tezu o bioetičkom edukacijskom senzibiliranju čovječanstva u smjeru svijesti i povezanosti sponom života.

Tehnika psihičke energetike može se preslikati na globalni kozmološki plan i to bi valjala biti misao vodilja pri argumentiranju o neophodnosti promišljanja nerazdvojnosti čovjeka i okoliša, a psihička prostornost prelazi, transegenerira u psihički okoliš, dakle energetski koloplet cjelokupne evolutivne kretnje. Iako stremi bogovstvu, dakako da je čovjek još uvijek životinja i utoliko povezan s prirodnošću, te svako dualiziranje u odnosu na prirodnost otvara prostor psihičkog i moralnog rascjepa, čemu svakodnevno i sve intenzivnije svjedočimo kroz aktualnu epohu. Lijek napaćene psihe, pa analogno i napaćene biotičke zajednice nužno bi se trebalo potražiti pri integrativnom odnošenju uz bioetički senzibilitet [15] obilježen sviješću i odgovornošću koja budi optimizam i pruža orijentaciju. Pritom je očito da je ljudska psiha fenomenološki most između subjektiviteta i objektiviteta, te se uvodi teza da upravo pri zacjeljivanju ljudske psihe valja promatrati početnu točku za zacjeljivanje onečišćenog planeta. Problem se očituje pri isključivo tehnološkom psihfarmakološkom onošenju psihijatrije, koje dobrim dijelom pateće osobe još dalje udaljava od spoznajnnog jedinstva sa svejednotom. Harmonija pojedine psihe nesumnjivo je u analogiji s harmonijom okoliša, te bi navedeno valjalo predstavljati jedan od stupova bioetičke edukacije i pragmatične koristi na svekoliki život, koju navedena potencijalno nosi.

4. ZAKLJUČAK

Dolazimo do zaključka da pod opasnošću financijski i tehnomanski nahođene antropocentričke paradigme bivstvujućih svi i svo bivamo ugroženi, otprilike kao globalnim zagrijavanjem, ali ipak, nezavidnu situaciju opasnosti kojom smo izloženi bolje je nazvati globalnim zaleđivanjem mozga (a s obzirom na to da se predviđaju i brutalne suše, možda i isušivanjem mozga).

Planet Zemlja prepun je raznovrsnosti i agonalnih sukoba koje sačinjavaju biće bivstvujućih, a koje valja promatrati pluriperspektivno, te dotičnu pluriperspektivnost oslikavati na društvenu, nadalje znanstvenu zajednicu, a na način kako sugerira disciplina integrativna bioetika. Naš napaćeni planet prepun je biljaka blagotvornog i ljekovitog djelovanja spram raznih psihičkih smetnji, te se pitam zašto ne krenuti putem znanstvenog razvoja i otkrivanja prirodnih supstancija kojima nas nagrađuje ovaj naš napaćeni planet, a koje posjeduju ljekovita svojstva za „duševne bolesti“ i poremećaje (koje bi nas i pragmatičnom modusu povezivale sa prirodnošću), nasuprot razvoju kemikalija, čiji tehnološki procesi usput neizostavno onečišćuju okoliš? Zašto barem ne pokušati? Odgovor je jasan: tehnomanskoj industriji nije bitno zdravlje i dobrobit ljudi, bitna im je zarada, a s tim neminovno dolazi obveza za thanatosom duha bivstvujućih. Lišavajući psihičke patnike mogućnosti kritičkog razmišljanja, otpora, nezadovoljstva, patnje i sreće, kočeći potenciju napretka, neminovno i neupitno ih pretvarajući u nebivstvujuća – u „zombije“. Međutim,

naglašavam da psihički pateća bivstvujuća ne trebaju isključivo smirenje i pasivu, nego poticaj za borbu usmjerenu k autonomnom odabiru sebe-bitka, dok ih opcija „zibanja psihe u kolijevki tableta“ – psihofarmaka koji oslabljuju srž i degradiraju duh – vode mahom u neslobodu, unatoč privremenom zatomljivanju simptoma psihičke patnje (a što je u teškim slučajevima psihoza ili suicidalnih depresija često puta nužnost i potreba, ali navedena graničnost se zamaguljuje te konzumiranje psihofarmaka postaje opća paradigma, dok patniku ne ostaje sloboda odabira). Nadalje, zaključujem da se ključni historijski problem vezan uz pojam psihe nalazi pri činjenici da je ona u odnosu na pojam uma fenomenološki vazda bivala isuviše udaljena. Isuviše mnogo bijaše distingvirana kroz razne mitove, umu nepristupačne romantičarske i religijske transcendencije vezane uz apsolut sreće i problematiku besmrtnosti, a tvrdim da nužno mora biti promatrana filozofskim znanstvenim očima usmjerenima na tjelesnu prostornost kozmosa. Psiha je poveznica s potencijalnim bogom, psiha je poveznica između uma i tijela, ali apriorni pojam koji obilježava svaku našu pojedinačnu psiho-tjelesnu kretnju jest um, a poznato je kako upravo znanost filozofije pri umu nalazi svoj najvrjedniji predmet izučavanja. S druge pak strane, filozofska pitanja i problematika patnje psihe (samim tim i patnje uma) nikako ne mogu adekvatno izaći na kraj bez etičke refleksije i moralne – ponajprije integrativno-bioetičke – prakse očuvanja i unapređenja života na Zemlji i održavanja harmonije svejednote, vođene ključnim riječima „treba da“ (*Sollen*) [16], koje prekoračuju ono postojeće, unapređuju ga i proizvode vođene svjetlošću bioetičkog „logosnog deona“, te održavaju ljudsko djelovanje u balansu s onim prirodno-kauzalnim.

Što je manje psihičkog prostora, to je manje svijesti i subitkovine s okolišem, što je manje psihičkog kretanje i spoznajnog sljubljivanja sa svejednotom, to je manje onečišćenog zraka, šuma i tla. Ljudska kultura smatra da krčenjem šuma bivamo povezaniji, da je prostor čišći, no događa se upravo suprotno – vidimo sve manje, gužva je sve veća, a udaljenost u odnosu na prirodnost sve intenzivnija. No integrativno-bioetičko odnošenje itekako može pomoći pri snalaženju i orijentiranju kroz tu nesnosnu gužvu i aporetiku, a prije svega ukazati na nužnost integracije s „majkom Zemljom“ koja nam i nudi fizikalnu mogućnost bivstvovanja, stoga ne valja očajavati zapadati u srdžbe i strahove, nego odlučno krenuti u borbu za zaštitu okoliša i psihičkog prostora. Za to je prije svega potrebna spoznaja, svijest i odgovornost spram života, a što u predmetnom i metodološkom panelu nosi upravoorijentacijska disciplina integrativna bioetika.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

EFFECTS OF COFFEE WASTE ADDITION TO BRICK CLAY "ČAVKA"

Marina Jovanović*, Adnan Mujkanović*, Erna Tutić**

* University of Zenica, Faculty of Metallurgy and Technology, Zenica, Bosnia and Herzegovina
** University of Zenica, Polytechnic Faculty, Zenica, Bosnia and Herzegovina

corresponding author: Marina Jovanović, e-mail: marina.jovanovic@mtf.unze.ba

Original scientific paper

ABSTRACT

In this paper, the influence of the addition of coffee waste, as household waste material, to the properties of brick clay "Čavka" near Busovača was studied. Coffee waste was added to clay in amounts of 5 wt.% and 10 wt.%. The effect of coffee waste addition on the standard consistency, plasticity, Atterberg plastic and liquid limits, then on drying and firing behaviour, and ultimately on the characteristics of the samples fired at 1173 K: water absorption rate, apparent density, apparent porosity, water absorption, flexural and compressive strength and thermal conductivity was investigated. Tests have shown that coffee waste increases the standard consistency, plasticity, Atterberg plastic and liquid limits, weight loss during drying and firing, water absorption rate, water absorption and apparent porosity. The addition of the coffee waste reduces the linear shrinkage at drying and firing, apparent density, compression and flexural strength and thermal conductivity. Tests have shown that the coffee waste, although waste material, can be successfully used as an addition to the examined clay and to produce lighter products with better isolation characteristics and less drying sensitivity, while other properties remain within the required limits for brick industry.

Keywords: *brick clay, coffee waste, thermal conductivity, waste utilization*

1. INTRODUCTION

With modern way of life and population increasement, bigger quantities of the waste appear. The waste becomes problem due to bigger environmental pollution and there is a need for recycling or finding the new ways to use it in the industry. The biggest possibility for using the waste can be found in the sector of construction which generally demands huge quantities of raw materials. Bricks are widely used as building components composed of inorganic non-metallic materials. Raw materials in the brick industry are clay and clayey materials. Part of raw material can be replaced by waste material which would lead to savings

natural raw materials and solving problems connected to disposal of certain types of the waste.

Due to environmental regulations, the demand for bricks with high insulation capacity is increasing, since decreasing the thermal conductivity is a decisive factor in limiting energy consumption. One way to increase the insulation capacity of the bricks is to generate porosity [1]. The high porosity is a characteristic sought-after today in order to save energy. One of the most conventional ways to increase porosity and reduce thermal conductivity in ceramic materials is to modify their microstructure by incorporating lightening, pore-forming, organic combustible additives into the clay matrix. During firing, the combustible material burns out, and leaves a large fraction of pores within the fired body. The presence of pores in the materials helps to reduce the thermal conductivity and increases therefore its isolation and produced bricks are lighter than traditional [2]. The thermal conductivity not only depends on their total porosity, but also on their pore size and shape, chemical and mineralogical composition [3]. The porous character of light bricks will increase the quality of structures in terms of heat and noise isolation, thereby reducing heating costs in turn affecting environment positively [4].

Since the organic waste is energetically enriched, organic waste is easily consumed during the firing and with their combustion, they contribute to increasement of the temperature in the furnace. This allows economic use of the energy needed for firing. This allows economic use of the energy needed for firing [2] and shortens the firing time [5].
Coffee waste is the type of organic waste, currently not recycled or used in farming compost production. Coffee is consumed by around 40 % of the world's population and for many people, especially in Western countries, the coffee drinking is a part of their lifestyle and an everyday habit [6]. The rate of generation of coffee grounds was estimated at an average rate of 3 t of waste per million euros of product sales [7].

Properties of bricks are affected as a result of physical, chemical and mineralogical alteration. In this paper the effect of coffee waste addition on the clay "Čavka" was investigated.

2. EXPERIMENTAL

2.1. Materials

The raw materials used in this investigation were clay "Čavka" and coffee waste from the household. Deposit of the clay "Čavka" is situated in the Central Bosnia and Herzegovina near Busovača. About 100 kg of the clay, which has undergone all stages of preparation, was sampled at the Factory "Termo ziegel Nigma Busovača". The clay was crushed in Laboratory, sieved through the sieve 1 mm and dried at 373 ± 5 K. Coffee waste was also dried at 373 ± 5 K.

2.2. Methods of characterization

Standard methods (JUS B.B8.070, JUS B.H8.346, JUS B.H8.320) and Atomic Absorption Spectroscopy (Perkin Elmer 3100) were used for determination of the chemical composition of the clay and coffee waste. DTA and TG analyses were carried out to investigate the clay, coffee waste and mixtures behaviour during the thermal treatment.

It was done on STA 409 CD in nitrogen atmosphere up to 1473 K with heating rate 20 K/min.

2.3. Samples preparation

Three types of mixtures were prepared:

- clay without additives,
- mixture of clay and 5 wt.% of coffee waste,
- mixture of clay and 10 wt.% of coffee waste.

The effect of the coffee waste addition on the standard consistency, plasticity and Atterberg plastic and liquid limits was investigated. Standard consistency was determined using Vicat apparatus (figure 1 left). The clay was crushed well, as to passes through the sieve 425 μm, and then by adding different amounts of water, the pastes of different consistencies was tested to determine the penetration depth of the Vicat needle. For some clay paste it is said to have a standard consistency if Vicat needle penetrates 5 minutes trough a paste of 4 cm height [8].



Figure 1. Vicat (left), Pfeffercorn (middle) and Atterberg (right) apparatus

Plasticity was determined by the Pfefferkorn device shown in figure 1 middle. Cylinders were made in metal mould (Ø = 30 mm, h = 40 mm) with different amounts of water and impacted on a Pfefferkorn device, where the heights after impaction was read off. The diagram of the dependence of the Pfefferkorn height and relative humidity of the clay pastes was drawn. The coefficient of plasticity is the relative humidity for the height of 12.1 mm read from the diagram. The following types of clay are distinguished by coefficient of plasticity:

13.8 - 16.7 → poorly plastic,
16.7 - 20.0 → moderately plastic,
20.0 – 23.1 → good plastic and
23.1 - 28.6 → highly plastic [9].

Standard consistency was determined by the equation (1) and relative humidity by the equation (2).

$$\text{Standard consistency} = \frac{m_1 - m_2}{m_2} \times 100 \ (\%) \quad (1)$$

$$\text{Relative humidity} = \frac{m_1 - m_2}{m_1} \times 100 \ (\%) \quad (2)$$

where is:

m_1 - mass of wet clay (g),
m_2 - dry clay mass (g).

The Atterberg plastic limit (PL) is defined as minimum moisture content (equation 1) at which the clay paste can be rolled into the cylinder of thickness 3.2 mm and length 70 mm on the flat non-porous surface. Cylinder was made from plastic paste, after which it was being reformed until the gapes show up due to evaporation of water.

For Atterberg liquid limit (LL) determination Fall Cone Method was used. Metallic cone (80 g of mass and an apex angle of 30°) is placed to be touching the clay paste in the mould (ϕ 55 mm, depth 44 mm). It was set to fall freely and to penetrate through the paste for 5 s. The depth of the penetration was measured for pastes with different water content. Water content (equation 1) for penetration depth of 20 mm is considered as the liquid limit.

The plasticity index (I_P) is the measure of the plasticity, i.e. water quantity needed for the paste to change from semisolid to liquid. This index represents the difference between the liquid limit and plastic limit [10]:

$$I_p = \text{PL} - \text{LL} \ (\%) \quad (3)$$

For testing drying and firing behaviour and the properties of fired samples, handmade tiles, prisms and plates were prepared by using appropriate mould (figure 2). The dimensions of the tiles were 80x40x14 mm. Diagonals were drawn on the prepared tiles and using a metal device (figure 2 left), a circle was drawn with a center at the intersection of the diagonals. The cross-section of the circle with the diagonals gave the benchmark points which were used to determine drying and firing shrinkage.



Figure 2. Moulds for the tiles (left), prisms (middle) and plates (right)

The prisms were of a dimension of 160x40x40 mm and were used for the testing of compressive and flexural strength at the compression and flexural testing machine.

Plates sizes of 300x300x30 mm were used for determination thermal conductivity on LAMBDAMETAR, STIROLAB LM305 according to BAS EN 12667:2002. Since we were not able to make completely flat plates, the obtained results for thermal conductivity are not real values but serve only for mutual comparison.

The samples were air-dried for 3 days, then one day at 303 K and one day at 373 K in a drying oven. After drying, the samples were fired according to the regime shown in table 1. The tiles were used to test the loss of mass and shrinkage during drying and firing and the water absorption rate, water absorption, apparent porosity and apparent density.

Table 1. Firing regime

Step	Temperature (K)	Time (min)
1	683	600
2	823	350
3	1038	100
4	1123	50
5	1173	50
6	1173	120

The equations for loss of mass and shrinkage determinations are:

$$\text{Loss of mass} = \frac{G_0 - G_1}{G_0} \times 100 \ (\%) \tag{4}$$

$$\text{Shrinkage} = \frac{S_0 - S_1}{S_0} \times 100 \ (\%) \tag{5}$$

where is:

G_0 – mass of tile before thermal treatment (g),
G_1 - mass of tile after thermal treatment (g),
S_0 – distance between benchmark points before thermal treatment (mm),
S_1 - distance between benchmark points after thermal treatment (mm).

After weighing the tile was placed in water so that bed face was 5 mm below water level. After one minute the tile was withdrawn, dried with a damp cloth and weighed. Water absorption rate was calculated in kg/m^2 from the weight increase and the bed face area [11].

To saturate tiles with water they were first 24 hours placed in water to the half of their height and the second 24 hours fully immersed. The next equations were used to determine water absorption (WA), apparent porosity (P_a) and apparent density (γ):

$$\text{WA} = \frac{m_3 - m_1}{m_1} \times 100 \ (\%) \tag{6}$$

$$P_a = \frac{m_3 - m_1}{m_3 - m_2} \times 100 \ (\%) \tag{7}$$

$$\gamma = \frac{m_1}{m_3 - m_2} \times \rho_w \ (\text{g/cm}^3) \tag{8}$$

where is:

m_1 – mass of dry tile (g),
m_2 – mass of saturated tile in water – hydrostatic weighing (g),
m_3 – mass of saturated tile on air (g),
ρ_w – water density (g/cm^3).

3. RESULTS AND DISCCUSION

The chemical compositions of clay and coffee waste are shown in table 2.

Table 2. Chemical composition of clay and coffee waste

Component	Chemical composition (%)	
	Clay	Coffee waste
SiO_2	54.1	0.08
Al_2O_3	19.1	< 0.01
Fe_2O_3	10.2	0.01
TiO_2	1.5	0.25
CaO	0.36	0.78
MgO	2.82	0.17
K_2O	3.51	0.47
Na_2O	1.15	0.01
MnO	0.14	< 0.01
P_2O_5	0.183	0.206
LOI	6.57	98.7
C	-	52.8
H	-	8.54
N	-	2.52

The chemical composition of the examined clay shows that clay is typical brick clay with slightly increased Fe_2O_3 content and a small CaO content. The chemical composition of the coffee waste indicates that it is an organic material that by heating mostly passes into gaseous products.

The measurement results shown in the figure 3 purple lines indicate that the decomposition of coffee waste occurs at low temperatures, mostly below 873 K. At the temperature below 378 K dehydration is occurred and an increase in temperature causes the main pyrolysis to decompose mostly into volatile products in the range of 473 - 653 K. Above 653 K coffee waste enters the third stage, termed as the carbonization process of residues [11]. A slight endothermic change between 773 and 873 K is observed on the DTA curve for clay (figure 3, green line), which corresponds to the dehydroxylation of clay minerals illite [8, 12] and kaolinite. At this temperature interval, the transition from low-temperature quartz to high-temperature modification occurs.

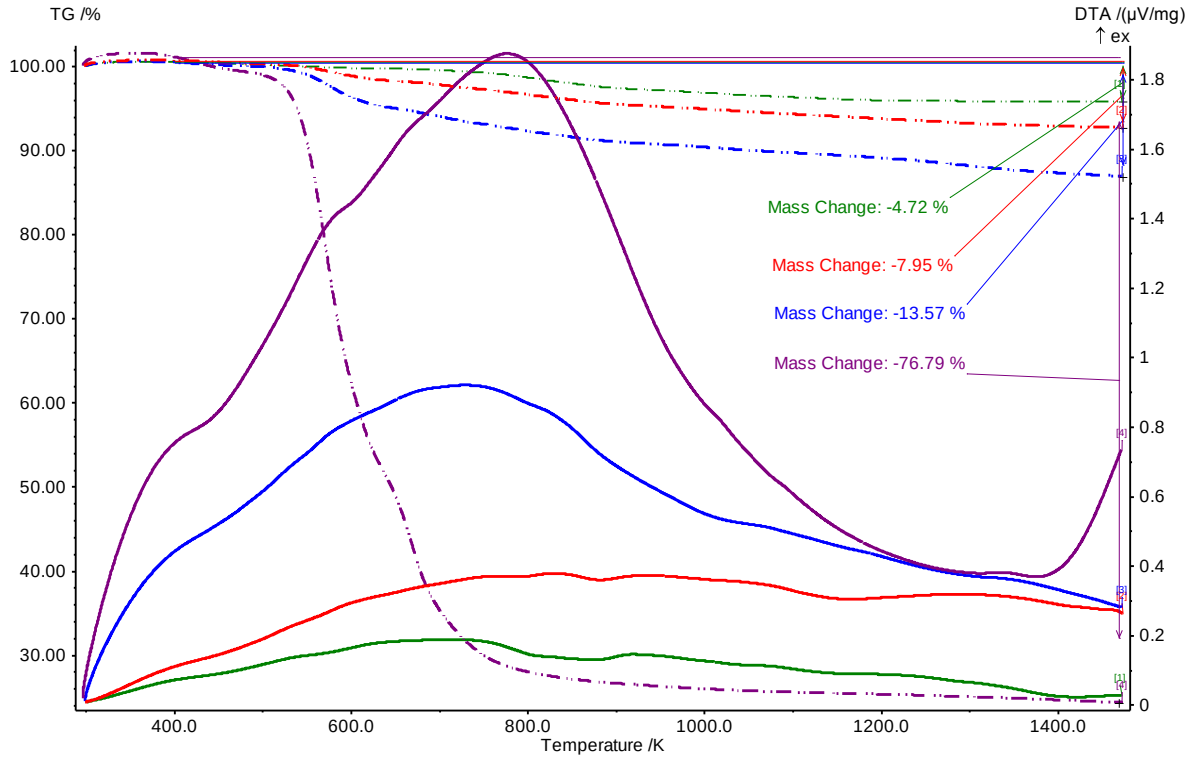


Figure 3. DTA/TG curves for clay (green), coffee waste (purple), clay with 5 wt.% coffee waste (red) and clay with 10 wt.% coffee waste (blue)

The results for the standard consistency, Pffefercorn plasticity and Atterberg limits are given in the table 3.

Table 3. Standard consistency, plasticity and Atterberg limits

Coffee waste content (%)	Standard consistency (%)	Pffefercorn plasicity	LL (%)	PL (%)	l_P (%)
0	25.7	25.51	32.45	20.3	12.13
5	28.8	27.55	36.09	22.8	13.29
10	32.4	30.32	39.73	25.9	13.83

Standard consistency, Pffefercon plasticity and Atterberg limits increase with increasing of the coffee waste content. This means that the addition of the coffee waste requires a larger amount of water to obtain the desired clay workability. The results of loss of mass and shrinkage are presented in the table 4.

Table 4. Loss of mass and shrinkage

Coffee waste content (%)	Loss of mass (%)		Shrinkage (%)	
	Drying	Firing	Drying	Firing
0	20.60	6.33	4.73	1.62
5	22.82	10.86	4.46	0.9
10	24.26	14.57	3.72	0.54

With increasing of coffee waste content loss of mass increase which is expected, since the coffee waste burns and evaporates, and the greater is the amount of water added to the mixes, so it also evaporates when drying. An interesting phenomenon is the decrease in shrinkage by increasing the percentage of coffee waste. This is very favourable effect as it reduces clay sensitivity on drying process and possibility of cracking. On this way it is possible to reduce drying time and save energy.

Apparent porosity and water absorption increase with increasing of coffee waste content (table 5). By coffee waste combustion pores are formed that leads to decreasing of apparent density. Specimens with lower apparent density are lighter that can be consider as positive effect for the transport aspect, handling and installation of bricks.

Due to porosity increasing, flexural and compressive strength decrease (table 5), although compressive strength is still acceptable according the standard. Compressive strength for brick is from 2 to 20 MPa and flexural strength is not standardized [9].

Addition of coffee waste to the clay has positive effect on isolation properties. Thermal conductivity decreases with increasing of coffee waste content (table 5). That can be explained by increasing of porosity with increasing coffee waste content.

Table 5. Properties of fired samples

Coffee waste content (%)	Apparent porosity (%)	Water absorption (%)	Apparent density (g/cm^3)	Water absorption rate (kg/m^2)	Thermal conductivity (W/mK)	Flexural strength (MPa)	Compressive strength (MPa)
0	27.22	15.64	1.74	1.88	0.262	4.20	21.10
5	34.91	23.49	1.49	2.8	0.192	2.69	12.80
10	40.13	31.20	1.28	4.52	0.174	2.20	5.47

4. CONCLUSION

Coffee waste can be used in brick clay production in 10 wt.% due to positive effect on final product and conclusions are as follows:

- addition of coffee waste increases plasticity of the clay,
- addition of coffee waste has positive effect on sensibility of clay during drying and enables decreasing of drying time,
- considering that coffee waste combusts during process that leads to the increasing of porosity and decreasing of apparent density,
- with increasing of porosity, compressive strength decreases but it is still in acceptable values,
- higher porosity leads to the lighter bricks which can be more easily transported,
- thermal conductivity decreases with increasing of coffee waste content.

Tests have shown that the coffee waste, although waste material, can be successfully used as an addition to the examined clay and to produce lighter products with better isolation characteristics and less drying sensitivity, while other properties remain within the required limits for brick industry. On this way, energy can be saved in the process of drying products, in their transportation and in heating of objects made of these light bricks. It is possible to get better product and dispose waste in the same time.

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Acknowledgements

We express our gratitude to the Federal Ministry of Education and Science of Federation Bosnia and Herzegovina for financial support for this research.

OSNOVE CJELOVITA PRISTUPA OKOLIŠU: RACIONALNOST I SENZIBILITET, ODGOVORNOST I SKRB

FOUNDATIONS OF A HOLISTIC APPROACH TO ENVIRONMENT: RATIONALITY AND SENSIBILITY, RESPONSIBILITY AND CARE

Hrvoje Jurić*

* Sveučilište u Zagrebu, Filozofski fakultet, Zagreb, Hrvatska

autor za korespondenciju: Hrvoje Jurić, e-mail: hjuric@ffzg.hr

Prethodno priopćenje

SAŽETAK

Polazeći od pretpostavke da je cjeloviti pristup okolišu preduvjet ne samo primjerenog sagledavanja okoliša, odnosno znanja o okolišu, nego i zaštite i opstanka ne-ljudske prirode, čovječanstva i Planeta, u ovom radu razmatramo filozofijske i (bio)etičke osnove cjelovita pristupa okolišu, koje nalazimo u uvažavanju dviju dimenzija ljudskoga bića, kojima se filozofija odvajkada bavila (racionalnost i senzbilitet), te u dvama konceptima na kojima se baziraju mnoge suvremene (bio)etičke teorije (odgovornost i skrb). Naravno, time se ne iscrpljuje interdisciplinarna rasprava o cjelovitu pristupu okolišu, ali se naglašavaju mogući doprinosi filozofije i (bio)etike toj raspravi.

***Ključne riječi**: okoliš, filozofija, bioetika, odgovornost, skrb*

ABSTRACT

Starting from the assumption that a holistic approach to environment is a postulate of not only appropriate consideration of the environment, i.e. knowledge on environment, but also protection and survival of non-human nature, humankind and the Planet, in this paper we examine philosophical and (bio)ethical foundations of a holistic approach to environment, which can be found in recognizing two dimensions of human being, which have been considered by philosophy since its beginnings (rationality and sensibility), as well as in two concepts which are the basis of many contemporary (bio)ethical theories (responsibility and care). Certainly it does not exhaust the interdisciplinary discussion on holistic approach to

environment, but it emphasize possible contributions of philosophy and (bio)ethics to this discussion.

***Keywords**: environment, philosophy, bioethics, responsibility, care*

1. O CJELOVITOSTI

Polazeći od pretpostavke da je cjeloviti pristup okolišu preduvjet ne samo primjerenog sagledavanja okoliša, odnosno znanja o okolišu, nego i zaštite i opstanka ne-ljudske prirode, čovječanstva i Planeta, u ovom ćemo se radu posvetiti nekim konceptima za koje smatramo da trebaju biti osnova cjelovita pristupa okolišu, a koje pronalazimo u filozofiji i (bio)etici.

No najprije valja reći što, u našoj perspektivi, znači 'cjelovitost'. Pojam cjelovitosti, u kontekstu teorijskih, praktičkih i poietičkih rasprava o okolišu, treba biti shvaćen dvojako.

Kao prvo, 'cjelovitost' se treba ticati općeg pogleda na prirodu, odnosno slike svijeta u kojoj se na prirodu gleda kao cjelinu koja uključuje i ljudska živa bića i ne-ljudska živa bića i uvjete njihova života, a koja uzima u obzir kako neizmjernu diferenciranost i raznolikost tako i jedinstvo svega što jest. Priroda, u tom smislu, uključuje i čovjeka (kao prirodno, kulturno i socijalno biće) i ne-ljudsko, a u pogledu čovjeka uključuje i prirodnu i kulturnu, i materijalnu i duhovnu dimenziju njegove egzistencije, kao i međusobna preplitanja tih dimenzija.

Kao drugo, 'cjelovitost' se treba ticati pristupa prethodno navedenoj raznolikosti, a to znači da se cjelovit pristup okolišu ne može postići ni jednim posebnim znanstvenim pristupom, pa ni isključivo znanstvenim pristupom, nego je nužan interdisciplinarni i pluriperspektivni pristup koji uključuje kako sve znanstvene tako i ne-znanstvene (tj. kulturne) perspektive [1] koje u raspravi o okolišu mogu otkriti i razjasniti relevantne dimenzije problematike. Znanje je, kao i istina, uvijek neka cjelina, a da bi se „otkrilo“ ili „konstruiralo“ cjelinu treba otvoriti put za sve moguće prinose tom procesu. Primjerice, položaj čovjeka (u smislu ljudske vrste ili roda) u prirodi ne može se shvatiti reducirajući čovjeka samo na jednu dimenziju njegova opstanka: uz sociosferu i tehnosferu, uvijek valja uzeti u obzir i biosferu i ekosferu, kao i točke susreta (stapanja ili napetosti) navedenih sfera. Postavimo li to kao cilj razumijevanja čovjekova položaja u prirodi i zapitamo li se koje nam znanosti mogu pomoći u odgovaranju na pitanja koja se u tom sklopu pojavljuju, nužno ćemo doći do odgovora da su nam u tom pothvatu nužne spoznaje i prirodnih i tehničkih i humanističkih i društvenih i biotehničkih i biomedicinskih znanosti, kao i da nam neki ne-znanstveni pristupi (poput religioznog i umjetničkog) također mogu raskriti neke aspekte tih pitanja.

2. O CJELOVITU PRISTUPU OKOLIŠU

U uvodniku prvoga broja časopisa *The Holistic Approach to Environment* urednik Damir Hršak kaže:

„Cjeloviti pristup okolišu ne postavlja samo pitanje kako postići neki cilj nego i *zašto* je to nužno te doprinosi li to dobrohotnome suživotu svih bića. Dobrohotnost uključuje miroljubivost, savjesnost, skrb i odgovornost sada i u budućnosti.“ [2].

To je ekstenzivnije razrađeno i šire kontekstualizirano u članku „Uvod u holistički environmentalizam“ istoga autora u časopisu *Jahr* [3], gdje se ponovno ističe koncept dobrohotnosti (u razlici spram nižerangirane dobronamjernosti), kao i koncepti odgovornosti i skrbi, a također se naglašavaju i one dimenzije (cjelovita) pristupa okolišu u kojima se apelira na promišljanje (teoriju) i djelovanje (praksu) te na ljudski razum i (su)osjećajnost.

Iz toga, među ostalim, možemo izvesti zaključak da čovjek kao cjelina stupa u odnose s okolišem kao cjelinom. Naime, čovjek sa svojim umom, emocijama i nagonima stupa u odnose s društvom, kulturom, ne-ljudskim bićima, ne-ljudskom prirodom i kozmosom, pa i transcendencijom, a ti odnosi nisu (ili barem ne bi smjeli biti) nereflektirani, nego vođeni određenim moralnim i etičkim principima, normama i kriterijima koji omogućuju balansiranje svih navedenih elemenata.

Ukratko, cjeloviti pristup okolišu podrazumijeva onaj temeljni stav, onaj način mišljenja i ono djelovanje koji počivaju, s jedne strane, na odgovornosti i skrbi, a s druge strane, na racionalnosti i senzibilitetu, jer te dvije ljudske dimenzije suoblikuju ono što nazivamo odgovornošću i skrbi.

3. O ODGOVORNOSTI

Sve navedene dimenzije – dimenzije racionalnosti i senzibiliteta, kao i dimenzije uma, emocija i nagona – igraju važnu ulogu u odgovornosti i upravo u tome sastoji se relevantnost i snaga koncepta odgovornosti na kojemu se baziraju mnoge (bio)etičke teorije današnjice [4].

Jedna od najutjecajnijih suvremenih etika odgovornosti, ona Hansa Jonasa, prezentirana u njegovu djelu *Princip odgovornost* [5], može se uzeti kao potporni stup cjelovita pristupa okolišu, ako on treba uzeti pojam odgovornosti kao ključni etički pojam u prethodno naznačenu smislu, jer Jonas nudi jedan novi tip odgovornosti, koji se od nas zahtijeva u dobu ekološke krize kao krize znanstveno-tehničke civilizacije, a koji bi trebao obuhvatiti ono sadašnje i ono buduće, ono ljudsko i ono ne-ljudsko, istraživano i moralnim obzirom obuhvaćeno na različitim razinama, u različitim aspektima.

Ako današnji čovjek djeluje drugačije negoli je to bio slučaj u dosadašnjoj povijesti čovječanstva, onda mora biti i drugačije odgovoran. Srž Jonasova shvaćanja principa odgovornosti jest u tome da je današnji čovjek odgovoran šire i dublje negoli je to ikada bio slučaj: odgovoran je ne samo za bližnje i suvremenike, niti samo za ljudsku zajednicu ovdje i sada, nego je odgovoran i za ne-ljudska živa bića, te za uvjete opstanka jednih i drugih, dakle, za život i prirodu u cjelini. Tako se antropo-lokalna odgovornost tradicionalne etike proširuje na bio-globalnu odgovornost, zahtijevajući otklon kako od „etika istovremenosti“, tako i od „antropocentričkih etika“. Jonas smatra da novi tip odgovornosti, koju ovdje nazivamo globalno-ekološkom odgovornošću, nije nešto što nam je posve nepoznato i što bismo tek trebali izumiti. Mi nju već imamo u zametnom obliku, kao egzistencijalnu ili antropološku karakteristiku, i to u – roditeljskoj odgovornosti, odgovornosti roditelja za dijete. Naime, lako se može se iznijeti racionalne argumente u prilog spomenutih zahtjeva i svatko ih može shvatiti. Ali kako motivirati ljude da djeluju, primjerice, u korist budućih, još nepostojećih ljudi, što zahtijeva odricanja „aktualnih“ za dobro „potencijalnih“, ili u korist ne-ljudskih živih bića, u slučaju kojih je empatijska distanca kudikamo veća, odnosno spoznajno nepremostiva, a moralno teško premostiva? Kako pobuditi i razviti osjećaj za one koji još ne postoje, ali će jednom postojati kao mi, ili za one koji jesu živa bića (te su nam, u tom aspektu, nalik), ali nisu i nikad neće biti kao mi? U svome članku „Tehnika, sloboda i odgovornost“ Jonas na to odgovara ovako:

„[…] imamo ideju odgovornosti i ponosni smo što smo sposobni za to, a duboko u sebi imamo i osjećaj odgovornosti, koji se od pamtivijeka objavljuje u odnosu roditelja i djeteta. On nadilazi svaku neposrednost i širi se u nedoglednu budućnost. Ovaj osjećaj, kad se proširi u ideju, može stvoriti most od etike bližnjega do onoga što nam je daleko i što je tek u našoj predodžbi, do onoga što nam još ne govori svojim glasom, ali znamo da je prepušteno samovolji naše moći. Odgovornost kaže da je to njoj povjereno.“ [6].

U knjizi *Princip odgovornost* Jonas navodi tri idealno-tipične karakteristike roditeljske odgovornosti. To su: *totalnost, kontinuitet* i usmjerenost na *budućnost* [5]. *Totalnost* se izražava u tome što se roditeljska odgovornost ne odnosi na egzistenciju djeteta u ovom ili onom pogledu, nego na „dijete kao cjelina i u svim njegovim mogućnostima, ne samo u onim neposrednim potrebama“. Roditeljska odgovornost ima u vidu „puki bitak kao takav, a onda najbolji bitak ovoga bića“, pa je prema tome usmjerena i na održanje života i na ukupni razvoj djeteta. Dakle, roditelji bi, u idealnom slučaju, trebali brinuti i o fizičkom, i o psihičkom, i o mentalnom, i o emocionalnom razvoju djeteta, a roditelje bi trebale oponašati i institucije koje se djelomično ili u iznimnim situacijama brinu o djeci (vrtići, škole, bolnice). Ovo nas upućuje na drugu značajku roditeljske odgovornosti, a to je – *kontinuitet*. Kao što odgajateljica u vrtiću, učitelj u školi ili zdravstvena djelatnica u bolnici ne mogu prekinuti svoju brigu oko djeteta sve dok im je ono povjereno (primjerice, od ponedjeljka do petka između 8 i 16 sati), tako se roditeljska briga ne može prekinuti *nikada*. I kada dijete spava, ili je u vrtiću i školi, ili je kod bake i djeda – roditeljska se odgovornost ne prekida, ni na svjesnoj razini, ni u emocionalnom smislu. Ali kontinuitet se ne odnosi samo na protok sati, dana, tjedana, mjeseci i godina, nego znači i to da roditeljska odgovornost uvijek mora imati u vidu prošlost, sadašnjost i budućnost, odnosno čitavu povijest predmeta odgovornosti, tj. djeteta. Tako dolazimo i do treće karakteristike roditeljske odgovornosti, o kojoj je već bilo riječi na neki način, jer ona se odnosi na – *budućnost*. Odgovornost roditelja je odgovornost za jedan život, jednu cjelokupnu egzistenciju, izvan njezine neposredne sadašnjosti, s onu stranu precizne izračunljivosti. Usmjerenost na budućnost znači da je u skrb o onome što je danas uvijek već uključeno obaziranje na ono sutra, iako se sutrašnjica, dogledna i nedogledna budućnost zapravo ne mogu predviđati. No, ono što nam se na dnevnoj razini nadaje iz naše vremenitosti – pa u tom smislu ne bi predstavljalo nikakvu novinu ni u etičkoj raspravi ni općenito – kod Jonasa, kako i on sam kaže, „dobija jednu posve drugu dimenziju i drugi kvalitet u vezi s 'totalnom odgovornošću' kakvu ovdje razmatramo“. Onako kako roditelj preuzima i nosi odgovornost za dijete, čovječanstvo bi (naravno, u drugim razmjerima) trebalo preuzeti odgovornost za život i uvjete života na Zemlji. Ali ne samo čovječanstvo kao globalna moralna i politička zajednica nego i svaki čovjek-pojedinac na onim razinama i u onoj mjeri u kojoj njegovo djelovanje utječe na druge ljude, druga živa bića i životni okoliš.

4. O SKRBI

Odgovornost je, slijedimo li Hansa Jonasa, prihvaćanje izvršenja skrbi (ili brige) nad onim što nam je povjereno, a što je (u manjoj ili većoj mjeri, isključivo ili jednim dijelom) u našem djelokrugu. Skrb (ili briga) je, također, kao i odgovornost, koncept koji ovisi jednako i o racionalnosti i o senzibilitetu; uključuje i primjenu principa i normi putem naše razumske refleksije i ono što (neposredno ili reflektirano) osjećamo i možemo osjetiti vezano uz predmet naše odgovornosti. Ovdje ćemo ukazati na dva, naizgled posve različita, pojma skrbi, tj. na dvije, naizgled posve različite, etike skrbi, a to su: feministička etika skrbi i kršćansko-teološka etika skrbi Leonarda Boffa.

Feministička etika općenito napada tradicionalno filozofijsko i etičko stajalište da je ljudski subjekt (jastvo) sve razvijeniji što se više emancipira, odijeli od drugih subjekata, ljudi. Nasuprot tome, feministički je stav da je subjekt, osoba bolja što je više povezana s drugima. Dakle, ovdje se preferira „biće zajednice“ pred tradicionalnim „autonomnim čovjekom“. A uzor za izgradnju jedne nove etičke paradigme, jedne nove etike jest – žena.

U tom smislu, Carol Gilligan [7] kritizira frojdovsku teoriju koja je, u osnovi, tvrdila da su žene manjkavi (nedovršeni) muškarci i da u tom smislu nikad ne mogu postati potpune osobe, pa ni potpuni i ravnopravni moralni subjekti. Žene kroz čitavu povijest žive pod dominacijom muškaraca, ali su u toj „zavjetrini“ (baveći se djecom, obitelji, domaćinstvom) razvile poseban svijet, sa svojim jezikom, svojim vrijednostima, vrlinama, itd. Gilligan kaže da postoji: „muški“ jezik pravednosti i prava (koji počiva na onom racionalnom, odjeljujućem i isključujućem), te „ženski“ jezik brige i odgovornosti (koji počiva na onom osjećajnom, spajajućem i uključujućem). Za razliku od muškaraca, žene mogu ovladati s oba jezika (iako preferiraju, naglašavaju i prakticiraju više ovaj drugi), dok muškarcima ide teže ovladavanje „ženskim jezikom“. Nel Noddings [8] također razvija etiku koja uvažava vrline i vrijednosti tradicionalno povezane sa ženama. Prema njenu mišljenju, u etici se radi o pojedinačnim odnosima između dviju strana: one koja skrbi i one za koju se skrbi.

„Prava se skrb ne sastoji u deklariranju nečije univerzalne ljubavi prema čovječanstvu, niti se sastoji u slanju pomoći žrtvama rata, gladi ili prirodnih katastrofa. Prava skrb zahtijeva konkretne odnose s određenim pojedincima i ne može se svesti na općenitu skrb za sve.“ [8].

Sara Ruddick [9] naglašava da se skrbnički odnos ne tiče jednako informiranih i jednako moćnih osoba, nego uvijek postoji između nejednakih osoba koje su međuovisne, te u tom smislu, kao i Jonas, Ruddick uzima kao primjer roditeljstvo, tj. odnos majke i djeteta.

U svakom slučaju, sve feminističke teoretičarke naglašavaju da je pojam skrbi usko povezan s pojmom odgovornosti, što zahtijeva balansiranje onog emotivnog i onog racionalnog, ali vraćaju u igru u etiku emotivnu, senzibilnu stranu ljudskoga bića te naglašavaju individualni odnos u moralu i etici, za razliku od naglašavanja onog univerzalnog, apsolutnog i formalnog. Time se, naravno, ne obesnažuje važnost etičkoga univerzaliziranja, jer smatramo da se ono što se u feminističkoj etici skrbi čini kao „partikulariziranje“ jest samo strateško-taktičko „partikuliziranje“ čiji je cilj kritika onih univerzalizama koji su implicitno isključivali drugo i drugačije.

No etika skrbi, na koju smo se fokusirali, nije isključivo „feministički proizvod“, nego postoje i drugi i drugačiji etički koncepti koji se baziraju na pojmu skrbi. Ovdje se uzima kao primjer teologa Leonarda Boffa, odnosno njegovu knjigu *Esencijalna briga: Etika ljudske naravi* [10]. Boff smatra da je „znak našeg vremena“ – nebriga, odsustvo brige ili skrbi. A živimo, kako on kaže, u vremenu „materijalističkog realizma“, u kojem (materijalno) imamo sve, ali za to plaćamo cijenu: gubitak nekih (za istinski human život) bitnih, esencijalnih, suštinskih stvari.

Nasuprot nebrizi, bešćutnosti i bezobzirnosti, Boff ističe – brigu ili skrb, i to kao fundamentalni način ljudskoga bivanja, kao ljudsku bit:

„Briga je, zapravo, istinska podrška kreativnosti, slobode i inteligencije. Briga je fundamentalni ethos ljudskoga bića. To znači da u brizi nalazimo principe, vrijednosti i stavove koji usmjeravaju život u dobro življenje i djelovanja u pravična djelovanja. [...] Ja njegujem skromno uvjerenje da briga, s obzirom na to da je bitna (esencijalna), ne može biti ni potisnuta ni odbačena. [...] Pitanje brige služi kao kritika agonije u kojoj se nalazi naša civilizacija, ali služi i kao inspirativan princip za novu paradigmu zajedničkog života. [...] Briga je suprotnost odbijanju i nebrizi. Brinuti za koga je više od pukoga čina; radije bih rekao da je to – stav. Stoga briga obuhvaća više od trenutka svjesnosti, žara i posvećenosti. Ona predstavlja stav djelovanja, obzirnosti, odgovornosti i afektivne povezanosti s drugima.

Stav je kao fontana; on služi kao izvor za djelovanja koja izražavaju stav koji se nalazi u pozadini.“ [10].

5. ZAKLJUČAK

Esencijalna skrb, koju naglašava Boff, ali i (skrbnička) odgovornost, kako je formulirana i kod Jonasa i kod feminističkih teoretičarki, itekako je plodno tlo za razvijanje jedne nove etike koja bi mogla i trebala biti osnovica *cjelovita pristupa okolišu*, odnosno – kako kaže Damir Hršak [3] – *holističkog environmentalizma*. Koncept *integrativne bioetike* [11] u suglasju je s time, pa ga završno navodimo kao putokaz za daljnja promišljanja onih pitanja koja se ispostavljaju kao polazište velikog, ali nezavršenog i možda nedovršivog projekta koji stoji kao zadaća pred čovječanstvom.

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JAVNE PORUKE O ODVAJANJU OTPADA I PROMJENA NAVIKA

SEPARATE WASTE COLLECTION PUBLIC MASSAGES AND HABBIT CHANGE

Sanja Kalambura*, Nikolina Kadoić*, Dejan Kalambura**

* Veleučilište Velika Gorica, Velika Gorica, Hrvatska
** BBS Projekt, Zagreb, Hrvatska

autor za korespondenciju: Sanja Kalambura, e-mail: sanja.kalambura@vvg.hr

Izvorni znanstveni rad

SAŽETAK

Javne poruke u području gospodarenja otpadom predstavlja vrlo važan segment izgradnje sustava. Otpad je jedan od najvećih problema zaštite okoliša, koji ima izravan utjecaj na ljude, ljudsko zdravlje i sve što nas okružuje. Nastaje u sve većim količinama, kao rezultat našeg načina života. Veliki utjecaj na ekološku svijest građana stvaraju mediji. Mediji služe građanima kao izvor informacija o cjelovitom sustavu gospodarenja otpadom, a uloga im je ujedno i edukativna. Za potrebe rada, obavljeno je istraživanje o načinu kako je poruka djelovala na grupu ispitanika kroz promidžbeni video Fonda za zaštitu okoliša i energetsku učinkovitost, pod nazivom „Naviku usvojimo, otpad odvojimo". Anketom je provedeno istraživanje o segmentima reklamne kampanje i postignutim rezultatima na 147 ispitanika. Temeljem dobivenih rezultata evidentiran je na 88 % ispitanika pozitivan dojam. Opisana je kao informativna, edukativna i simpatična. No ipak 12 % ispitanika smatra da je prebrza, prekratka ili nerazumljiva, te nisu previše impresionirani. 59 % ispitanika ju je vidjelo prvi puta iako se ovakva reklama u medijima pojavljivala prije emitiranja više mjeseci. 40 % ispitanika je smatra informativnom dok se 56 % izjašnjava djelomično a 3 % ispitanika je ne smatra informativnom. U radu će biti prikazano detaljno istraživanje te opći dojam i potreba za javno odašiljanje poruka u medije u svezi problematike otpada.

***Ključne riječi**: javne poruke, otpad, zaštita okoliša, ekološka svijest, mediji*

ABSTRACT

Public massages in waste management sector are important part of the whole waste management system. Waste is one of the biggest environmental problems that has a direct impact on people, human health and everything that surrounds us. Waste increasing in

quantities and it is directly result of our lifestyle. The media has a great impact on the environmental awareness of citizens. The media is to citizens a source of information so the rule of them is also educative. For the purpose of work, a survey was conducted on how the message was affecting a group of respondents through the promotional video of the Environmental Protection and Energy Efficiency Fund, entitled "Adopt habit, separate waste". Survey conducted on 147 respondents. Based on the results obtained, 88 % of respondents noted a positive impression. It is described as informative, educative and sympathetic. However, 12 % of respondents think it is too fast, too short, or incomprehensible, and they are not too impressed. 59 % of the respondents saw it for the first time, even though such ads appeared in the media before broadcasting for several months. 40 % of the respondents are considered informative while 56 % of them are partially informed and 3 % of respondents are not considered informative. The paper will present detailed research and general impression and the need for public broadcasting of media messages related to waste issues.

Keywords: *public messages, waste, environmental protection, ecological awareness, media*

1. UVOD

Otpad koji proizvodimo sastavni je dio našeg života te na našu veliku žalost nastaje svakodnevno. Prema statistici, svaki građanin Hrvatske, u 12 mjeseci proizvede gotovo 400 kilograma otpada [1]. U Svijetu je evidentan rast količina otpada, razlozi su različiti. No ne treba zaboraviti činjenicu da se društvo u globalu značajno brojčano povećalo te je nekako način života i društvo kojeg pokreće maksimalna proizvodnja i potrošnja, stvorilo sve veće količine otpada ali i nove teme te odnose u 21. stoljeću. Problem je što su teme o zbrinjavanju otpada, kao i svim drugim problemima zaštite okoliša, vrlo malo zastupljene u medijima. Pravilno gospodarenje otpadom sastoji se od nekoliko segmenata:

- odgoj, obrazovanje, edukacija (prevencija),
- izbjegavanje nastajanja i smanjivanja štetnosti,
- ponovna upotreba otpada,
- recikliranje i oporaba otpada,
- odlaganje inertnog otpada.

Prevencija nastajanja otpada je najvažniji segment u konceptu gospodarenja otpadom [2]. Edukaciju je potrebno provoditi već od vrtićkog uzrasta i dalje kroz školstvo, kako bi im od najranije dobi pobudili svijest da shvate važnost pravilnog gospodarenja otpadom. Izbjegavanje nastajanja je najpovoljnija metoda rješavanja problema otpada. Potrebno je što je više moguće smanjiti količinu nastalog otpada [3, 4]. Stanovnici moraju znati da su oni ti koji odlučuju koliko otpada će proizvesti, odnosno neće proizvesti. Prilikom kupovine trebali bi birati proizvode koji se mogu ponovo upotrijebiti, tj. reciklirati, koji su sastavljeni od reciklirajućih materijala s naznakom da je proizvođač istih odgovoran za svoj proizvod. Također je potrebno smanjiti, odnosno odreći se proizvoda napravljenih ili zapakiranih u toksične materijale. Prvenstveno smanjivanje i izbjegavanje treba krenuti od proizvođača, prilikom proizvodnje materijalnih tvari, dobara i energije putem čistije proizvodnje, burze otpada, proizvodnjom potaknutom korištenjem sekundarnih sirovina i proizvodnjom proizvoda s manjim potencijalom otpada. Ponovna upotreba označava bilo koji postupak kojim će se otpad ponovo koristiti za istu svrhu za koju je i originalno bio napravljen. Ponovna uporaba se uglavnom odnosi na povratnu ambalažu. Recikliranje je pojam koji

označava izdvajanje materijala iz otpada i njegovo ponovno korištenje odnosno izradu novih proizvoda iz iskorištenih materijala [5]. Uključuje sakupljanje otpada i najvažnije od svega odvajanje prema vrstama otpadaka, jer se većina stvari (proizvodi/sirovine) može ponovno iskoristiti uz uvjet da su odvojeno sakupljeni. Pod oporabom se podrazumijeva svaki oblik ponovne obrade otpada čime se postiže njegovo korištenje u materijalne ili energetske svrhe. Glavni cilj je da otpad zamjeni druge materijale koji bi se inače upotrijebili za određenu svrhu, čime se postižu značajne uštede. Oporaba obuhvaća: sve vrste recikliranja, obradu zemljišta koje je korisno za poljoprivredu, korištenje otpada kao goriva, ponovna prerada iskoristive nafte, regeneracija kiselina i lužina. Posljednje mjesto zauzima zbrinjavanje, odnosno odlaganje otpada. Najniže je rangirano, jer je najmanje poželjna opcija. Mora se provoditi na način koji je prihvatljiv za okoliš.

Od 24. srpnja 2014. godine svi građani Republike Hrvatske imaju zakonsku obavezu sortiranja otpada [5]. No jesmo li dovoljno educirani, a samim tim i svjesni načina na koji se treba odvajati otpad?

Veliku ulogu u educiranju imaju upravo institucije koje svojom infrastrukturom i medijskim kampanjama mogu prodrijeti gotovo u svako kućanstvo. Fond za zaštitu okoliša i energetsku učinkovitost je do sada izdao niz edukativnih brošura iz područja energetske učinkovitosti i gospodarenja otpadom. Jedna od njih je nazvana „Naviku usvojimo, otpad odvojimo“ [6 - 8]. Uz brošuru, napravljeno je i nekoliko edukativnih videa u trajanju od 30 sekundi u kojima na jednostavan i brz način saznajemo zašto je važno uključiti se u sustav gospodarenja otpadom, te koje dobrobiti to donosi društvu i okolišu.

No koja je uloga upravo javnih poruka? Javne poruke su poruke upućene široj javnosti, odnosno svim članovima društva. Prenose se putem medija. Mediji su glavno sredstvo javne komunikacije i djeluju kao posrednici u prenošenju informacija i komunikacije upućenih građanima. Dijele se na: tiskane medije (knjige, novine, časopisi, brošure, letci...),radio, televiziju i internet [9].

Vrlo često nazivaju sedmom silom zbog svoje društvene snage. Izuzetno su moćni i mogu utjecati na formiranje javnog mišljenja i stavova ljudi, te njihovo ponašanje u društvu. Razvitkom tehnologije, mediji su se proširili, pa možemo reći da povezuju svijet. Sukladno tome omogućeno je brže širenje informacija i lakši pristup željenim informacijama.

Mediji imaju veliki utjecaj na društvo, pa tako i na pojedinca. Utjecaj medija se zasniva na izboru teme (sadržaj), na isticanju nekih sadržaja i načinu prikaza sadržaja (kontekst). Samim izborom sadržaja određuju o čemu će ljudi misliti [9, 10] Sadržaj koji iznose i način na koji je on prezentiran uvelike utječe na naše stavove i raspoloženje pa su danas zapravo glavno sredstvo usmjeravanja i oblikovanja stavova građana. Mediji su postali društvena stvarnost, više nisu samo prikupljači, prenositelji i širitelji informacija, nego oblikuju javno mišljenje. Ovdje se nameće pitanje novinarske etike. Svi etički kodeksi kao temelj novinarstva ističu služenje istini, no nažalost u današnje vrijeme, masovni mediji su puni izmišljenih/neprovjerenih informacija i senzacionalizma, a u vrijeme „3S“ formule (seks, sport i skandali) istina je u drugom planu. Ipak, istina je prvo načelo novinarskog poziva, stoga je još davne 1947. godine Komisija za slobodu medija u izvješću *Sloboda i odgovornost medija,* formirala okvir društvene odgovornosti medija u pet zahtjeva koji tvore funkcije medija [9 - 11]:

1. Mediji bi trebali dati istiniti, sveobuhvatan i inteligentan prikaz dnevnih događaja u kontekstu koji daje smisao,
2. Mediji bi trebali služiti kao forum za razmjenu primjedbu razmjeni i kritika,
3. Trebali bi biti način isticanja mišljenja i stavova različitih društvenih grupa,
4. Mediji bi trebali predstavljati i razjašnjavati vrijednosti društva,

5. Građani bi trebali imati pristup dnevnim obavijestima, odnosno mediji bi trebali biti način dopiranja do svakoga člana društva putem aktualnih obavijesti, misli i osjećaja.

Zbog svog velikog utjecaja, mediji imaju važnu ulogu u podizanju svijesti građana o ekologiji, da na pravilan način i s razumijevanjem ukažu na probleme zaštite okoliša, ujedno i na probleme gospodarenja otpadom. Gospodarenje otpadom je, nažalost, vrlo malo zastupljena tema u medijima. Kaže se da čega nema u medijima, to ni ne postoji [12, 13]. Zbog nedostatka informacija, građani nisu ni svjesni koliko je pravilno gospodarenje otpadom bitno i kako svaki pojedinac malim promjenama (poput odvajanja otpada, umjesto bacanja u kantu za smeće) uvelike pridonosi dobrobiti svih građana.

Stječe se dojam da se u medijima o gospodarenju otpadom najviše govorilo i pisalo prije nego li je i kada je postalo zakonski obavezno. Građani su dobivali informacije kako postupati s otpadom i kako ga na pravilan način odvajati. Na kućne adrese dolazili su letci i brošure o vrstama spremnika i popisom vrsta otpada koji idu uz odgovarajući spremnik. Radionice koje se održavaju u današnje vrijeme, kao i organizirano skupljanje građana koji promoviraju pravilno postupanje s otpadom, dobivaju vrlo malo mjesta u medijima i ne dopiru do šire javnosti. Informativne emisije na televiziji i radiju su ograničene vremenskim rokom i u maloj minutaži moraju obraditi što više informacija, što u slučaju odvajanja otpada nije dovoljno, a nekima niti dovoljno zanimljivo. Slično je i s novinama. Novinari imaju veliki izbor neiskorištenih tema i mogu građanima pružiti korisne informacije, te ih motivirati da se brinu o okolišu i otpadu, no to nažalost nije tako u praksi [14 - 16]. „Zelene“ teme nisu dovoljno bombastične da bi prodavale novine, pa im medijski prostor zauzima druga boja, odnosno „žutilo“. Velik broj informacija pronalazi se na internetu te se upravo internet portali smatraju najvećim medijima današnjice. Preko interneta se gleda televizija, filmovi, sluša radio, čitaju novine. No problem edukacije građana putem interneta je taj što se ključni sadržaj neće pojaviti sam, za razliku od radija i televizije. Prilikom gledanja televizije gledatelj sam bira program, ali uloga mu je pasivna, jer gleda sadržaje koje mu izvor prosljeđuje. Traženjem po internetu osobe imaju aktivnu ulogu i sami biraju informacije koje žele.

2. EKSPERIMENTALNI DIO

Za potrebe rada, ispitanicima je prezentiran edukativni video Fonda za zaštitu okoliša i energetsku učinkovitost pod nazivom „Naviku usvojimo, otpad odvojimo“. Putem anketnog upitnika ocjenjivalo se kakav dojam je video ostavio na ispitanike te koliko je sadržaj bio edukativan. U istraživanju je sudjelovalo 147 ispitanika, a anketni upitnik se sastojao od 11 pitanja: 5 otvorenog tipa, 7 pitanja s višestrukom mogućnošću izbora i 2 pitanja koja su kombinacija prethodnih.

3. REZULTATI I RASPRAVA

Cilj istraživanja bio je analizirati utjecaj medija na ispitanike kroz jednostavnu i kratku video poruku te mogućnosti usvajanja navike o odvajanju otpada. Rezultati istraživanja ukazuju na to kako i koliko je medijska poruka utjecala na ispitanike i je li ih potaknula na odvajanje otpada.

Prvo pitanje je bilo opisno. Ispitanicima je postavljeno pitanje kakav dojam je na njih ostavila reklama „Naviku usvojimo i otpad odvojimo“. Za 88 % ispitanika, reklama je bila pozitivna. Opisuju je kao informativnu, edukativnu i simpatičnu dok 12 % ispitanika smatra da je prebrza, prekratka ili nerazumljiva, te nisu previše impresionirani.

Najčešći odgovori ispitanika bili su:

- zanimljiva,
- edukativna,
- kratka, jasna, podiže razinu svijesti,
- odlična, potaknula me na razmišljanje da i ja odvajam otpad,
- ostavlja dobar dojam, jer potiče ljude na očuvanje okoliša i recikliranje otpada,
- prekratka je i glasovno pre ubrzana,
- ne stigne se sve procesuirati,
- vrlo kratka i stoga nejasna.

Iz navedenog odabira najčešćih odgovora ispitanika vidljivo je kako je reklama ostavila različit dojam te se upravo ta različitost povezuje s percepcijom poruka i prilagodljivosti medijske poruke svim ciljanim skupinama. Kako je važno imati na umu da određivanje ciljane skupine ima presudnu važnost za uspješnost prihvaćanja neke poruke postavlja se pitanje koliko je stvarno ovakva poruka primjerena javnoj televiziji i medijima. Ohrabruje činjenica da je opetovano prikazivanje reklame polučilo ipak veći postotak onih koji su razumjeli poruku nakon 2 - 4 gledanja.

Drugo pitanje se odnosilo na to jesu li već prije vidjeli ovu poruku. Poruku je 59 % ispitanika vidjelo prvi put, 40 % ispitanika je čulo za nju ili ju je primijetilo na televiziji, dok 1 % nije dao odgovor na pitanje.

Koliko je reklama za bila informativna odgovorili su gotovo svi ispitanici: u cijelosti je bila informativna za 40 % ispitanika, djelomično je informativna za 56% ispitanika, dok za njih 3% nije nimalo informativna, 1 % nije dao odgovor.

Uslijedilo je pitanje na koje su ispitanici trebali odgovoriti što su zapamtili iz poruke. Odgovor na ovo pitanje nisu dala 3 ispitanika, a od preostala 144 ispitanika njih 10 % smatra kako su zapamtili cijelu reklamu, dok 1 % tvrdi da nisu zapamtili ništa. Preostalih 89 % ispitanika pojedinačno je nabrojalo što su sve zapamtili, a neki od najčešćih odgovora su:

- u posljednjih 10 godina bačeno korisnih sirovina u vrijednosti od 5 milijardi kuna,
- recikliranje,
- energetska oporaba,
- otvaranje novih radnih mjesta,
- karta zelene hrvatske,
- očuvanje okoliša,
- koliko škola se je moglo izgraditi,
- slogan „naviku usvojimo, otpad odvojimo“,
- hrvatska puna šuma.

Kod ovakvog otvorenog tipa pitanja, a koje se odnosi na direktno memorijsko percipiranje poruke, iz velikog broja odgovora ističe se povezivanje problematike otpada s novcem, odnosno nekim novčano brojčanim pokazateljima. To ukazuje na činjenicu da kod ispitanika takav oblik poruke doprinosi stvaranju jasnije slike kada se predoči u vrijednosti koje su ispitanicima bliže u svakodnevnim životu. Analizirajući ostatak najčešćih odgovora stječe se dojam kako je vizualni identitet poput zelene karte ili hrvatske pune šuma također presudan u stvaranju bolje percepcije.

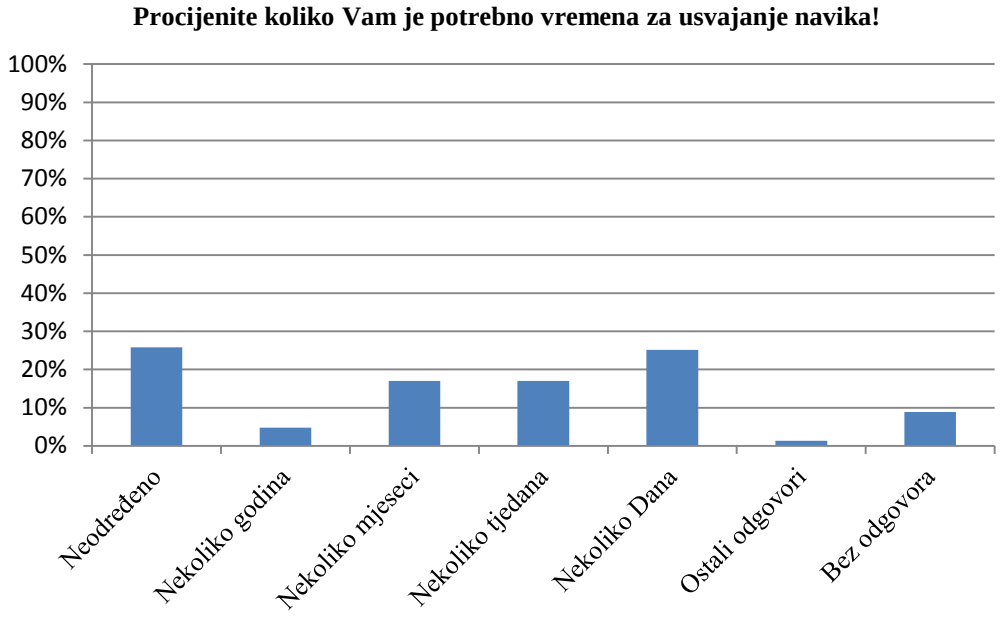
Nadalje se istraživala druga strana percepcije poruke, a to je odbojnost prema sadržaju ili poruci općenito. Kod 127 ispitanika poruka nije stvorila odbojnost, a kod 20 ispitanika je stvorila. Od svih navedenih odgovora 32 % ispitanika je obrazložilo svoj odgovor. Budući da 86 % ispitanika tvrdi kako im ništa u reklami nije stvorilo odbojnost, može se zaključiti da je to razlog zbog kojeg nisu smatrali kako je potrebno dodatno objašnjenje. Kao najčešći razlog zašto se stvorila odbojnost navodi se brzina kojom se daju informacije, odbojnost prema otpadu i odlagalištima te stvarnoj situaciji vezano za otpad. Analizom dobivenih odgovora zaključuje se kako je dio odgovora usmjeren na prenošenje poruke dok jedan dio stvara odbojnost kroz sam sadržaj poruke i opću sliku o otpadu u RH.

Iduće pitanje odnosilo se na to je li nešto iz poruke kod ispitanika stvorilo izrazitu naklonost uz navođenje i specificiranje odgovora. Potvrdno je odgovorilo 76 ispitanika, 1 nije odgovorio, a kod njih 70 nije izazvalo naklonost. Obrazloženje na odgovor je dalo 50 % ispitanika. Naklonost kod ispitanika najčešće je stvorilo: briga za okoliš i prirodu, otvaranje novih radnih mjesta, preispituje ljudsku svijest i potiče na razmišljanje, potiče na recikliranje i savjesno postupanje s otpadom.

U sljedećem pitanju odgovor je trebao biti vezan uz to koliko je reklama bila edukativna. Za 39 % ispitanika poruka je u cijelosti edukativna, za 53 % ispitanika djelomično je edukativna, a za 8 % ih nije nimalo edukativna. Na žalost nitko od ispitanika nije obrazložio navedene odgovore.

U sljedećem dijelu istraživanja ispitanici su povezivali opću percepciju mijenjanja navika kroz sljedeće tvrdnje: težak proces preobrazbe, potrebna je volja za usvajanje navike, kad je jaka volja, sve se može; uvođenje nečeg novog u život i kad to počnemo raditi svakodnevno, dugotrajan proces, treba prilagodbe; ponavljanje istog prijeđe u naviku, usvajanje navika je proces mijenjanja loših navika ka boljima, u smislu odvajanja otpada; ovisi o „težini“ navike, što je teža duže je usvajam; jednostavan, uz pravu motivaciju.

Nadalje, ispitanici su trebali procijeniti koliko im je vremena potrebno za usvajanje navika. Pitanje je bilo otvorenog tipa, a podaci su grupirani u tablici prema najčešćim odgovorima (slika 1).



Slika 1. Vrijeme potrebno za usvajanje navika

Percepcija poveznice vremena i usvajanja navika značajno se razlikovala kod ispitanika, tako 17 % smatra kako je potrebno od 1 do 11 mjeseci kako bi se navika promijenila, 17 % procjenjuje kako im je za usvajanje nove navike potrebno nekoliko tjedana (vremenski period od 1 - 4 tjedna), a 25 % iskazuje da se radi o danima (vremenski period 1 - 7 dana), 1 % smatra kako je potrebno između 5 - 10 ponavljanja da se usvoji navika, dok 26% anketiranih nije moglo procijeniti koliko bi im vremena trebalo. Odgovor od nekoliko godina da bi usvojili naviku smatra 5% ispitanika. Neki smatraju da je potrebna 1 godina, dok neki misle da nije dovoljno ni više od 10 godina.

Prema znanstvenim istraživanjima, potreban je 21 dan uzastopnog ponavljanja, kako bi nešto prešlo u naviku te se prema navedenim odgovorima može zaključiti kako je ovakav oblik poruke potrebno opetovano prikazivati u terminima kada je gledanost najveća a i koristiti različite alate informiranja. Poticaj je najvažniji čimbenik u stjecanju novih, tj. promjeni starih navika. Nakon toga dolazi ponavljanje, kako bi određena radnja postala rutina, a za kraj slijedi nagrada. Nagrada u slučaju ispitanika je znanje da su učinili nešto korisno, kako za sebe i druge ljude, tako i za prirodu.

Na pitanje o tome misle li ispitanici da je usvajanje novih navika jednostavno, 26 % ih je odgovorilo da je jednostavno, dok 74 % ih smatra upravo suprotno. S izjavom da je usvajanje novih navika isto što i stvaranje novih navika slaže se 60 % ispitanika, dok 40 % smatra da nije tako.

Na posljednjem pitanju, ispitanici su dali odgovor o tome misle li da je poruka prilagođena svim uzrastima. Od ukupnog proja ispitanih 50 % ih smatra da je poruka prilagođena svima, a 39 % da nije, neodlučnih je 6 %, a 5 % nije dalo odgovor. Obrazloženja na navedeno pitanje su različita, od toga da je prebrza i neshvatljiva - ponajviše djeci, do toga da je vedra, puna ilustracija i da je baš zbog toga djeci primamljiva. Neki od odgovora koje su navodili ispitanici koji tvrde da nije prilagođena svima su: nije za djecu i starije, nije dovoljno jasna mlađoj i starijoj populaciji i manje obrazovanom stanovništvu, prebrza je s previše informacija, koriste se stručni izrazi pa je mlađima i starijima neshvatljiva, prebrzo traje da bi se u potpunosti sve podrobnije shvatilo i dr.

Na pitanje o tome hoće li odvajati otpad nakon što su vidjeli poruku, 73 % ispitanika je odgovorilo potvrdno. Njih 24 % ne želi odvajati otpad nakon što su vidjeli reklamu, dok 1% ispitanika tvrdi da se nada da hoće, dok 1 % ispitanika nije dalo nikakav odgovor.

4. ZAKLJUČAK

Temeljem rezultata dobivenih anketnim istraživanjem, vidljivo je se da je poruka ispitanike navela na razmišljanje o postupanju s otpadom. Mnogi su tek sada shvatili kolika je novčana vrijednost iskoristivih sirovina koje su završile na odlagalištu otpada i koliko toga se moglo i još uvijek može napraviti i izgraditi, ako se pravilno postupa s otpadom i odvaja ga. Većina ispitanika smatra da usprkos tome što je kratka, poruka je vrlo poučna i informativna. Neki od anketiranih smatraju kako poruka nije za sve uzraste, ponajviše za djecu, jer ne mogu shvatiti stručne termine, koji se emitiraju u videu. Analizom danih odgovora, može se zaključiti da ispitanici nisu bili dovoljno informirani o odvajanju otpada, odnosno nisu bili svjesni posljedica koje nastaju ne odvajanjem otpada. Velika većina anketiranih smatrala je kako su informirani o toj temi, no svejedno nisu odvajali otpad. Mediji na sličan način mogu pomoći, ponajviše da pokrenu inicijativu kod građana, budući da je ne informiranost jedan od značajnijih problema zbog kojeg sustav upravljanja otpadom ne funkcionira u potpunosti. Mediji bi trebali teme vezane uz cjeloviti sustav gospodarenja otpadom prenijeti stanovništvu, koje treba provoditi konkretna rješenja za smanjenje otpada i pravilno postupanje s otpadom,

što opet treba biti popraćeno medijskim sadržajem. Povezanost medija s ljudima, proporcionalna je onoj povezanosti ljudi s otpadom. Tehnologija i mediji se šire, dolaze do gotovo svakog kutka svijeta i imaju pristup gotovo svakom pojedincu. S druge strane, zbog velike potrošnje materijala sve su i veće količine otpada i problema vezanih uz njegovo zbrinjavanje.

Poseban naglasak treba biti usmjeren na prevenciju nastajanja otpada, ponovnu upotrebu, odvojeno prikupljanje otpada i recikliranje. Kako bi se informiranje putem medija poboljšalo potrebno je emitirati puno više emisija koje se bave tom tematikom, te pomoću promidžbenih poruka, kao što je „Naviku usvojimo i otpad odvojimo“. Promidžbene poruke ili oglase potrebno je prilagoditi različitim formatima medija: oglasi za tisak, radijski oglasi, TV oglasi, internetski oglasi. Uz internet oglase poželjno je napraviti internet stranicu, gdje bi bile dostupne sve opće informacije o pojedinim vrstama otpada i njihovu odvajanju, te fotografije i videozapisi kojima bi se promovirala praksa odvajanja otpada i educiralo građane na koje načine mogu iskoristiti otpad, uz primjere, kako iz starog napraviti novo, kako sami kompostirati. Također, na internet stranicama, trebalo bi programirati chat profile, gdje bi građani mogli postavljati pitanja ili izmjenjivati iskustva. Informiranju pridonosi i izrada jumbo plakata, te promotivnih letaka, koji trebaju biti dovoljno jasni, slikoviti i zanimljivi kako bi što bolje ispunili svoju funkciju.

Informiranje je potrebno provoditi kontinuirano, jer ako promidžba stane i neko vrijeme nije dostupna, past će u zaborav i sve će se vratiti kako je bilo i prije oglašavanja, što znači da neće imati veliki učinak. Budući da informiranje treba biti sveprisutno, potrebno je paziti na sadržaj, koji mora biti zanimljiv, mijenjati se i iznova zainteresirati građane, jer u suprotnom može doći do zasićenja i stvaranja suprotnog učinka od očekivanog.

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METODA KOMPOSTIRANJA I POTENCIJALNI RIZICI U OKOLIŠU

COMPOSTING METHOD AND POTENTIAL RISKS IN ENVIRONMENT

Sanja Kalambura*, Tomislav Pavlečić*, Nives Jovičić*

* Veleučilište Velika Gorica, Velika Gorica, Hrvatska

autor za korespondenciju: Sanja Kalambura, e-mail: sanja.kalambura@vvg.hr

Pregledni rad

SAŽETAK

Pod pojmom gospodarenja otpadom podrazumijeva se ekonomski i po okoliš razumno upravljanje cjelokupnim životnim vijekom otpada, od njegova nastanka, skupljanja, prijevoza, iskorištavanja, obrađivanja i odlaganja. Gospodarenje otpadom je skup aktivnosti, odluka i mjera usmjerenih na sprječavanje nastanka otpada, smanjivanje količine nastalog otpada, smanjivanje štetnog utjecaja otpada na okoliš, kontrolu toku otpada od nastanka do oporabe ili zbrinjavanja. Jedna od važnih karika je i kompostiranje otpada. Kompostiranje predstavlja prirodni postupak koji se redovito događa u prirodi čime se omogućuje cirkulacija materijala u prirodi, odnosno zahvaljujući biorazgradnji organske materije u prirodi nema otpada. Prepoznajući ovaj prirodni postupak za razgradnju biorazgradivog otpada, čovjek pokušava primijeniti i ubrzati ovaj postupak u kontroliranim uvjetima. No i metoda kompostiranja može utjecati na okoliš, a koji se očituje u onečišćenju vode, tla, zraka, lošoj kvaliteti komposta, plijesnima i buci. Međutim, suvremene tehnologije i znanje omogućuju izvođenje kompostiranja u maksimalno sigurnim uvjetima za okoliš i ljudsko zdravlje, no implementacija takvih procesa u Hrvatskoj još uvijek nije pravilo, već iznimka. Rad donosi elemente utjecaja na okoliš procesa kompostiranja.

***Ključne riječi**: gospodarenje otpadom, kompostiranje, okoliš, procjena rizika, zaštita okoliša*

ABSTRACT

The concept of waste management implies economic and environmental management of the entire life span of waste since its inception, collection, transport, exploitation, processing and disposal. Waste management is a set of activities, decisions and measures aimed at preventing waste generation, reducing the amount of waste generated, reducing the

harmful impact of waste on the environment, controlling the waste stream from its onset to recovery or disposal. One of the important links is composting method. Composting is a natural procedure that is regularly carried out in nature and this process allows the circulation of materials in nature, i.e. due to the biodegradation of organic matter in nature there is no waste. Recognizing this natural process for the degradation of biodegradable waste, man is trying to apply and accelerate this process under controlled conditions. When composting, there is a walking effect on the environment, which is reflected in the pollution of water, soil, air, poor quality of compost, mold and noise. However, modern technologies and knowledge enable composting in the safest environment for human health. However, the implementation of such processes in Croatia is still not a rule, but an exception. The paper presents elements of environmental impact of the composting process.

Keywords: *waste management, composting, environment, harmful impact, environmental protection*

1. UVOD

Gospodarenje otpadom počiva na hijerarhiji mjera kojima se prvo nastoji maksimalno smanjiti količina stvaranog otpada i njegov štetan utjecaj na okoliš, potom se nastoji maksimalno upotrijebiti/reciklirati otpad koji je ipak nastao, a tek se na kraju ono što se nikako nije moglo ni spriječiti, ni upotrijebiti, obrađuje/odlaže na okolišno najmanje štetan način. Promatrano organizacijski i tehnološki, odložiti/spaliti otpad puno je jednostavnije nego uspostaviti kulturu i sustav okolišno prihvatljivije proizvodnje i proizvoda, te odvojenog prikupljanja otpada. Ekološki ispravan pristup uključuje proizvođača otpada na sudjelovanje u njegovu zbrinjavanju, dakle uključuje kreatora problema u njegovo rješavanje.

S porastom stanovnika na globalnom nivou te poboljšanjem standarda, rastu i količine otpada. Velik udio u cjelokupnom komunalnom otpadu je upravo bio komponenta otpada koja može biti između 40 i 60 % ukupne količine. Bio komponenta se može obrađivati na razne načine no jedna od najstarijih metoda je aerobna razgradnja ili kompostiranje. Kompostiranje predstavlja zapravo prirodni oblik recikliranja koji se kontinuirano odvija u prirodi. Razgradnja se prirodno javlja svuda gdje rastu biljke, odnosno kada biljke umiru one se razgrađuju od strane insekata i mikroorganizama iz tala. Takav prirodan postupak razgradnje može se poboljšati i unaprijediti ukoliko se stvore optimalni uvjeti za razgradnju. U procesu kompostiranja za uspješnu biorazgradnju pomoću mikroorganizama i beskralježnjaka potrebno je osigurati vodu, kisik i hranjiva. U svemu tome je važno znati da biorazgradivi otpad predstavlja visoko iskoristivi dio komunalnog otpada, a njegovo recikliranje najvažnija je karika svake dobre strategije gospodarenja otpadom, gdje se organski ostatci odvajaju od ostalog otpada na mjestu nastanka. Izdvajanje organskog otpada iz smeća značajno povećava postotak otpada koji ne završava na odlagalištu, što je i implementirano u EU-direktivama.

Međutim, loša mehanizacija kao i loša provedba postupka kompostiranja mogu dovesti do brojnih štetnih djelovanja kompostišta na okoliš. Također, štetni utjecaji mogu biti posljedica i plijesni nastale u kompostu. Iz navedenog razloga, proces kompostiranja zahtjeva stroge uvjete provedbe i laboratorijske analize dobivenih proizvoda.

Cilj rada je analizirati proces kompostiranja te njegovu ulogu u gospodarenju otpadom kao i moguće štetne utjecaje na okoliš. Na temelju postavljenog cilja, definirani su slijedeći zadaci:

- pojmovno određenje biorazgradivog otpada,

- pregled hrvatskih i europskih iskustava u pogledu kompostiranja,
- rizici koji se pojavljuju prilikom kompostiranja,
- uloga kompostiranja u cjelovitom sustavu gospodarenja otpadom.

2. POJMOVNO ODREĐENJE BIORAZGRADIVOG OTPADA I BIOMASE

Biorazgradivi komunalni otpad obuhvaća biološki razgradive vrste otpada podrijetlom iz kućanstva i otpad koji je po prirodi i sastavu sličan otpadu iz kućanstva, primjerice otpadni papir, biorazgradivi tekstil, zeleni otpad od održavanja javnih površina i sl., osim proizvodnog otpada i otpada iz poljoprivrede i šumarstva. Biootpad je biološki razgradivi otpad iz vrtova i parkova, hrana i kuhinjski otpad iz kućanstava, restorana, ugostiteljskih i maloprodajnih objekata i slični otpad iz proizvodnje prehrambenih proizvoda [1]. Ne treba zaboraviti i biomasu koja je najsloženiji oblik obnovljivih izvora energije te obuhvaća široku sirovinsku osnovu[2]. Biomasa je obnovljivi izvor energije koji je sačuvan u prirodi te se obnavlja ili u cijelosti ili djelomično. Ona je biorazgradivi dio proizvoda, ostataka i otpadaka od poljoprivrede (uključujući i biljne i životinjske tvari), šumarstva, drvne industrije, kao i biorazgradivi dijelovi komunalnog i industrijskog otpada čije je energetsko korištenje dopušteno [3]. Sa stajališta sirovine obuhvaća šumsku i poljoprivrednu biomasu, biomasu nastalu prilikom proizvodnih procesa različitih industrija ili otpad u smislu komunalnog otpada, otpad koji nastaje pri pročišćavanju voda i kanalizacijskog mulja.

3. PROCES KOMPOSTIRANJA

Cilj kompostiranja je da se sav sirovi organski materijal koji podliježe raspadanju i koji se nalazi u kompostnoj hrpi, prevede tj. pretvori u stabilnije humusne spojeve, te da se izbjegnu neugodni mirisi, uništi sjeme korova i patogeni organizmi.

Temelj dobrog kompostiranja je miješanje: suhih i vlažnijih dijelova biootpad, većih i sitnijih dijelova biootpada, svježih i starijih dijelova biootpada te kuhinjskog i vrtnog biootpada.

Kompostiranje je kontrolirani proces biorazgradnje organskog otpada u stabilni produkt pomoću mikroorganizama, pri čemu se razvija CO_2 , voda i toplina. Proces je kontroliran jer se mikroorganizmima stvaraju povoljni uvjeti u svrhu ubrzanja prirodne razgradnje organske tvari [4].

Proces kompostiranja moguće je se kemijski opisati sljedećom kemijskom reakcijom, uz pretpostavku da je biorazgradiva tvar glukoza:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + kompost + (-\Delta H_r)energija$$

Glukoza je samo jedna od organskih tvari koje mikroorganizmi tijekom kompostiranja razgrađuju. U tablici 1 navedeni su podaci za neke materijale za koje već postoji praksa kompostiranja.

Tablica 1. Vrste materijala za kompostiranje i njihov C:N omjer (omjer ugljika i dušika) i vlažnost [4]

Materijal	C:N	Vlažnost, %
Novinski papir	398 - 852	3 - 8
Piljevina	200 - 750	19 - 65
Slama	48 - 150	4 - 27
Voće	20 - 49	62 - 88
Povrće	11 - 13	-
Trava	54	38
Mulj (obrada otp. voda)	5 - 16	72 - 84

Na proces kompostiranja utječu brojni čimbenici od kojih su najvažniji temperatura, sadržaj vlage supstrata, omjer C:N, protok zraka (aeracija), veličina čestica i vrsta organizama [5].

Nastaje kompost koji je zreli proizvod kompostiranja, kontroliranog procesa bio-oksidacije krutog heterogenog organskog supstrata koji uključuje i termofilnu fazu. Pored navedene definicije, postoji čitav niz definicija samog procesa i produkata kompostiranja. Vukadinović i Lončarić navode da su komposti organska gnojiva dobivena kompostiranjem različitih organskih, prvenstveno biljnih ostataka izmiješanih s tvarima mineralnog podrijetla kao što su vapno, pepeo, mineralna gnojiva (organomineralni komposti) i druge tvari [6]. Autori "*Support document for compost quality criteria*" iznose različite definicije komposta:

- "homogena rastresita mješavina djelomično razgrađene organske tvari sa ili bez tla." [6],
- "kruti otpad podvrgnut biološkoj razgradnji organske tvari, dezinficiran kompostiranjem ili sličnom tehnologijom, stabiliziran do stupnja koji je potencijalno koristan za rast biljaka, koristi se kao poboljšivač tla, kao umjetni površinski sloj tla, kao supstrat za uzgoj presadnica ili u slične svrhe." [6],
- "sva organska tvar (biljna ili životinjska), sa ili bez dodataka (organski ili anorganski), podvrgnuta povećanoj temperaturi (40°C) u smislu aerobne aktivnosti mikroorganizama i određenom stupnju stabilizacije (humifikacije) organske tvari." [6],
- "organski kondicioner dobiven fermentacijom mješavine koja početno uglavnom sadrži različite biljne ostatke, eventualno i organsku tvar životinjskog porijekla, te ima ograničen sadržaj mineralne tvari." [5],
- "organski kondicioner (poboljšivač) tla dobiven dekompozicijom mješavine koja se sastoji uglavnom od različitih biljnih ostataka, eventualno i organske tvari životinjskog porijekla, te ima ograničen sadržaj mineralne tvari." [7].

Kompostni materijal razgrađuju mikroorganizmi sve dok temperatura ne dosegne približno 40 °C. Tada razgradnju nastavljaju termofilni mikroorganizmi sve dotle dok temperatura ne dostigne svoj maksimum od 60 °C. U toj fazi razgradnju preuzimaju aktinomiceti. Djelovanjem navedenih skupina mikroorganizama razgrade se: voskovi, bjelančevine i hemiceluloza. Nešto se manje razgrade celuloza i lignin. Kada se temperatura počinje snižavati, razgradnju celuloze nastavljaju termofilne gljive te se na taj način temperatura ponovno povisi do 60 °C [3].

4. KOMPOSTIRANJE U PRIRODI I KONTROLIRANIM UVJETIMA

Proces kompostiranja provode mješovite kulture mikroorganizama koje u osnovi sadrže bakterije, kvasce, gljivice i aktinomicete. Svaka od vrsta ima veći ili manji afinitet prema razgradnji određene vrste otpada. Bakterije razgrađuju lako topive komponente, a kvasci, gljivice i aktinomicete celulozu i hemicelulozu. Mikrobiološka aktivnost izravno je povezana sa temperaturom kompostne mase. Veća mikrobiološka aktivnost, znači i bržu razgradnju organske tvari odnosno povećanu temperaturu (otpuštanje topline iz reakcijske smjese – kompostne mase). Sniženje temperature kompostne mase, signalizira uglavnom nedostatak kisika. Regulacija temperature kompostne mase vrši se najčešće regulacijom dotoka kisika. Ako koncentracija kisika padne ispod 10 % u kompostnoj masi, dolazi do stvaranja anaerobnih uvjeta u kompostnoj masi i pojave smrada (ponajviše zbog stvaranja H_2S).

Proces kompostiranja odvija se u tri faze:

1. Termofilna faza (T = 40 – 70 °C) - to je faza visoke temperature. U njoj se pomoću termofilnih mikroorganizama razgrađuju proteini, masti, celuloza te se uništavaju patogeni organizmi (higijenizacija).
2. Mezofilna faza (T = 25 – 40 °C) – to je faza umjetne temperature prilikom koje se uz pomoć mezofilnih mikroorganizama ubrzano razgrađuju topivi i lako razgradivi organski spojevi (šećer i aminokiseline).
3. Faza rashlađivanja i zrenja (T = 20 – 25 °C) – u toj se fazi temperatura ponovno snižava te se time prouzrokuje rast i razmnožavanje mezofilnih organizama. Oni razgrađuju ostale organske spojeve [8].

Kompost se u osnovi proizvodi na dva načina: nereaktorskim i reaktorskim postupcima. Nereaktorski postupci dijele se na statičke i dinamičke. Statički postupci podrazumijevaju aeraciju materijala za kompostiranje bez miješanja tj. prevrtanja. Aeracija se može provoditi prirodno ili prisilno upuhivanjem zraka u materijal za kompostiranje [9]. Dinamički postupci podrazumijevaju aeraciju uz stalno prevrtanje odnosno miješanje mase koja se kompostira. Reaktorski postupci se dijele prema tehnološkoj izvedbi na vertikalne, horizontalne i nagnute. Vertikalni reaktori pune se odozgo, a zrak se upuhuje kroz dno reaktora. Horizontalni reaktori sastoje se od sustava ćelija u kojima je masa za kompostiranje statična, a zrak se upuhuje odozdo ili se odsisava sa dna ćelije. Nagnuti reaktori uglavnom su rotacioni bubnjevi kod kojih se masa za kompostiranje kreće zbog rotacije reaktora [10].

5. KOMPOSTIRANJE U REPUBLICI HRVATSKOJ

Prema Strategiji gospodarenja otpadom u Republici Hrvatskoj [11], gospodarenje otpadom treba planirati i provoditi na način da se osigura:

- postupno organiziranje središta gospodarenja otpadom s postrojenjima za obradu, odlagalištima i drugim sadržajima: uz Zagreb, 20 županijskih i 4 regionalna središta, uz postupnu sanaciju i zatvaranje većine postojećih odlagališta,
- zabranu odlaganja otpada na otocima i gradnju pretovarnih stanica s odvojenim skupljanjem, reciklažom i baliranjem ostatnog otpada i prijevoz u centre na kopnu,
- posebnu zaštitu podzemnih voda na krškom području od eventualnog prodora procjednih voda iz odlagališta i drugih građevina,
- sprječavanje ispuštanja otpada u more, jezera, rijeke i potoke,

- centar za gospodarenje opasnim otpadom s mrežom sabirališta,
- kontrolirane prioritetne tokove otpada,
- visok stupanj sudjelovanja domaće industrije, opreme i usluga u projektima gospodarenja otpadom kao doprinos smanjivanju nezaposlenosti i deficita vanjsko-trgovinske bilance,
- angažman stranih partnera i kapitala na temelju nezavisnih studija opravdanosti i potporu zajedničkim ulaganjima na osnovi javnog i privatnog partnerstva na bazi IPPC - BAT (BEST AVAILABLE TECHNIQUES) tehnologije,
- jačanje postojeće organizacije gospodarenja otpadom i osnivanje međuresorne koordinacije za gospodarenje otpadom, što bi osiguralo suradnju relevantnih ministarstava za pojedine tokove otpada,
- edukaciju javnosti, stručnjaka i upravnih struktura: programi i aktivnosti za podizanje razine znanja trebaju imati razvojni, istraživački i djelatni pristup.

U Hrvatskoj postoji nekoliko kompostana što ukazuje na još uvijek nedovoljno riješen problem saniranja biootpada. Većina hrvatskih županija biootpad odlaže na odlagališta komunalnog otpada i na taj način „uništava“ mogućnost obrade i ponovnog korištenja biootpada..

Svaka kompostana specifična je zbog svog procesa kompostiranja, dovoza odvojeno sakupljenog otpada te postupanje s kompostom kao nusproizvodom. Sve kompostane obrađuju kuhinjski otpad, vrtni i zeleni otpad, ostali biorazgradivi otpad, a neke kompostane i saturacijski mulj koji se doveze na kompostište. Vrste kompostana, kao i budući planovi svake kompostane prikazuju se u tablici 2.

Danas postoji više razloga za provedbu zbrinjavanja organskog otpada kompostiranjem. Temeljni razlog je činjenica da je kompostiranje dobar način za zbrinjavanje organskog otpada. Smanjuje se volumen za odlaganje te se dobiva hranjivima bogato gnojivo koje se može plasirati na tržište. Osviještenost o potrebi zaštite okoliša u Hrvatskoj još uvijek nije na dovoljnoj razini što se uočava i u trendovima zbrinjavanja otpada. Nekolicina gradova ima riješeno odvojeno sakupljanje otpada u domaćinstvima, reciklažna dvorišta i odlagališta otpada koja zadovoljavaju europske i svjetske standarde. Navedena činjenica ukazuje na to da je potrebna reforma društva vezano uz postupanje s otpadom na svim razinama te edukacija stanovništva o štetnim posljedicama neadekvatnog zbrinjavanja otpada.

Učinkovito korištenje resursa, tj. održivog razvoja gospodarstva i društva mjera je politike zaštite okoliša koja je izazov na europskoj i hrvatskoj razini. Prema podacima Hrvatske agencije za okoliš i prirodu, unatoč aktivnostima provedenim na ovom području, još uvijek nije u potpunosti postignuto održivo gospodarenje otpadom u Hrvatskoj [1].

Ukupna količina proizvedenog komunalnog otpada u 2015. godini iznosila je 1.653.918 tona, odnosno 386 kilograma po stanovniku. U razdoblju od 2010. do 2015. godine zabilježen je porast udjela komunalnog otpada izravnog upućenog na oporabu. Za 2010. taj je udio iznosio 4 % dok je u 2015. iznosio 18 %. Uz 18 % oporabljeno (pri čemu se samo 2 % odnosi na kompostiranje i anaerobnu digestiju) i 80 % odloženog otpada u 2015. godini, preostalih 2 % čine količine privremeno uskladištenog komunalnog otpada i procijenjene količine za neobuhvaćeni dio stanovništva. Kompostiranjem je u 2015. godini obrađeno tek 27.432 tone.

Procijenjene količine proizvedenog biootpada iz komunalnog otpada se od 2012. godine ne mijenjaju te u prosjeku iznose oko 530.000 tona. Udio biootpada u miješanom komunalnom otpadu iznosi 37 %. Na odlagališta otpada u Republici Hrvatskoj godišnje se odloži gotovo 500.000 tona biootpada. Prosječno se odvojeno sakupi oko 11 % ukupno proizvedenog biootpada, a od toga se tek polovica proslijedi na oporabu (kompostiranje, anaerobna digestija) [1].

Tablica 2. Usporedbe tehnologija kompostiranja u kompostanama RH

KOMPOSTANA	Vrsta kompostane i trajanje procesa kompostiranja	Površina za kompostiranje	Korištenje dobivenog komposta	PLANOVI
Prelog	Kompostana pod nadstrešnicom. Trajanje procesa 3 mjeseca i dulje.	Asfaltirana – vodonepropusna podloga punjena gelom s pojačanim padom.	Pakiranje komposta u vreće, te prodaja istog.	Nabava sijačice za kompost, te nabava ostale potrebne opreme.
Imbriovec	Otvoreni tip kompostane. Trajanje procesa do 4 mjeseca.	Vodonepropusna armiranobetonska podloga s blagim nagibom.	Korištenje na okolnim poljoprivrednim površinama.	Povećanje kapaciteta biootpada.
Herešin – Koprivnica	Otvoreni tip kompostane. Trajanje procesa do 12 mjeseci.	Asfaltirana – vodonepropusna podloga s blagim nagibom.	Korištenje za održavanje gradskih zelenih površina. Dio odlazi u prodaju.	Povećanje udjela odvojeno sakupljenog otpada. Podjela posuda i kompostera.
Jankomir, Markuševac, Prudinec	Kompostane Jankomir i Markuševac: otvoreni tip. Trajanje procesa 8 – 10 mjeseci. Kompostana Prudinec: kontejnerski (zatvoreni) tip kompostane. Trajanje procesa 6 – 8 mjeseci.	Vodonepropusna asfaltno – betonska podloga s blagim nagibom.	Prodaja komposta, a kompost dobiven u kompostani Prudinec koristi se na lokalnom nasipnom terenu za kultiviranje tla.	Povećanje količina biootpada, podjela kompostera. Modernizacija postrojenja kompostana.
Kloštar Ivanić	Kompostana u kutiji/tunelu (zatvoreni tip). Trajanje procesa do mjesec dana.	Betonska podloga.	Prodaja i dijeljenje komposta kroz razne akcije.	Izgradnja sortirnice odvojeno prikupljenog otpada.
Ponikve – otok Krk	Otvoreni tip kompostane. Trajanje procesa 3 mjeseca i dulje.	Betonska podloga s blagim padom.	Pakiranje i prodaja komposta.	Unaprjeđenje sustava odvojenog prikupljanja otpada.
Perušić	Otvoreni tip kompostane. Trajanje procesa do godine dana.	Asfaltirana podloga s obodnim kanalima.	Korištenje komposta u hortikulturi i poljoprivredi.	Povećanje broja spremnika i posuda za biootpad.

Odvojeno sakupljanje biootpada u 2015. godini provodilo se u 96 jedinica lokalne samouprave.

U samo 17 % jedinica lokalne samouprave provodi se odvojeno sakupljanje biootpada. Najviše se radi o biorazgradivom otpadu iz vrtova i parkova s javnih površina, a količine odvojeno sakupljenog biootpada iz kućanstava su zanemarive. Najzastupljeniji način gospodarenja ovom vrstom otpada još uvijek je odlaganje [1].

6. POTENCIJALNI RIZICI KOMPOSTANA U OKOLIŠU

Tijekom procesa kompostiranja kao posljedica vlaženja otpada mogu nastajati otpadne vode, odnosno tijekom padalina će se oborinske vode procjeđivati kroz biorazgradivi otpad zbog čega mogu biti onečišćene, uglavnom, organskim onečišćujućim tvarima. Moguće negativne posljedice za okoliš su i mikotoksini te neugodni mirisi na području kompostiranja. Dodatne emisije koje se pojavljuju su buka od transportnih sredstava te stroja za prevrtanje, vlaženje i aeriranje kompostnih hrpa. Da bi se smanjili rizici vezani uz onečišćenje i štetno djelovanje na okoliš, kompostiranje mora biti provođeno u kontroliranim uvjetima te se moraju provoditi mjere vezane uz smanjivanje ili otklanjanje štetnih utjecaja kompostiranja na okoliš.

Podzemne i površinske vode u kontaktu s otpadnim se onečišćuju ovisno o svojstvima biootpada otpada i količini vode koja se procjeđuje kroz tijelo kompostne hrpe. Ovo zagađenje smatra se ekološkom nesrećom i ova pojava je moguća u redovnom radu kompostišta. Procjedne vode nastaju prolaskom kroz kompostnu hrpu te se tako onečiste različitim organskim i anorganskim tvarima, a te vode se sakupljaju u sabirni bazen i lagunu i ne odlaze s lokacije odlagališta [12].

Na zatvorenom obodu kompostišta nastaju slijevne vode. Slijevne vode sakupljaju se u betonski kanal oko kompostišta čime se čiste oborinske vode. Također se trebaju napraviti trokutasti rigoli po površini zatvorenih dijelova kompostišta kako bi se smanjila količina nastale procjedne vode u kompostani [12].

U koliko kompostana radi na ispravan način, onečišćenje podzemnih voda je minimalno. Ukoliko dođe do kontakta podzemne vode s procjednom, sadržaj organskog ugljika u podzemnoj vodi uzrokuje povišenu BPK5 u podzemnoj vodi što povećava mogućnost reprodukcije patogenih mikroorganizama [13].

Danas se sve više govori o problemu prisutnosti mikotoksina u hrani za ljude i životinje. Mikotoksini su toksični sekundarni metaboliti većeg broja saprofitskih pljesni koji u organizam životinja ili ljudi dolaze preko kontaminirane hrane, a u hranu mogu doći preko komposta ako je kompost previše zasićen mikotoksinima. Do danas je otkriveno više od 300 različitih vrsta mikotoksina koji su u većoj ili manjoj mjeri štetni za zdravlje ljudi i životinja. Najpoznatiji su aflatoksini, ohratoksini, zearalenon i trihoteceni. Optimalni uvjeti za razvoj pljesni ovise o vrsti, ali općenito gledano zahtijevaju visoku temperaturu i vlažnost supstrata. Većina pljesni su mezofilni organizmi koji rastu na umjereno visokim temperaturama u opsegu od 10 – 40 ^{0}C, pri čemu je optimalna temperatura između 25 – 35 ^{0}C. Samo mali broj pljesni ubraja se u termofilne organizme koji rastu na visokim temperaturama u opsegu od 20 – 50 ^{0}C (max 58 ^{0}C) i imaju veliki značaj u procesima kompostiranja. Osim termofilnih, na visokim temperaturama se razvijaju i termotolerantne pljesni koje za razliku od termofilnih mogu rasti i na temperaturama ispod 20 ^{0}C. Povećanje temperature i potencijalnog rizika od infestacije plijesnima može biti izazvano i tehnološkim procesima zaštite komposta u skladištima. Sušenje na visokim temperaturama izaziva oštećenje ovojnice, a to predstavlja kritičnu točku za infekciju u višem stupnju. Osim toga u mjesecima s visokom temperaturom, a posebno kod direktne izloženosti sunčevim zrakama, dolazi do zagrijavanja skladišta, a toplina se prenosi na sam kompost. Povećanje temperature izaziva isparavanje vode koja se

kondenzira na hladnijim mjestima stvarajući rizične vruće točke za naseljavanje pljesni, a kao posljedica povećanja vlažnosti.

U praksi najviše primjenjivan način ublažavanja i eliminiranja štetnog djelovanja mikotoksina je korištenje adsorenata koji imaju sposobnost fizičkog vezivanja za određene supstance te time sprječavaju njihovu resorpciju. Najčešće se primjenjuju neorganski adsorbenti [14].

Otpad organskog porijekla, u kompostištu, podliježe, brže ili sporije, različitim mikrobiološkim procesima razgradnje pri čemu se stvaraju razne vrste plinova, ovisno o kemijskom sastavu i svojstvima biorazgradljivih materijala. U kompostanama se javlja prašina i raznošenje laganog otpada uslijed vjetrova. Na ovom području prevladavaju jugozapadni i sjeverozapadni vjetrovi koji navedene vrste otpada mogu raznositi u okoliš. Otvorena ploha otpada mora se na kraju radnog dana prekriti internim materijalom. Nakon smirivanja vjetrova sav razneseni otpad mora se pokupiti sa drveća i ograde.

Neugodni mirisi u kompostanama nastaju kao rezultat anaerobne razgradnje organskih dijelova otpada. Sulfati prelaze u sulfide koji u kombinaciji s vodikom formiraju sumporvodik. Za suzbijanjeneugodnih mirisa obavezno se moraju otvorene plohe otpada prekrivati internim materijalom koji služi kao filtar [12].

U kompostanama se stvara buka koju treba razmatrati sa dva gledišta: buku koju proizvodi oprema u kompostanama i buku koju proizvode transportna sredstva (smećari, kamioni) prilikom kretanja i istovara otpada.

Uslijed rada mehanizacije na radnom polju očekuje se buka od oko 80 dBA. Taj intenzitet buke procjenjuje se na udaljenosti oko 3 m od izvora. Buku, također, stvaraju transportna sredstva. Ocjenjuje se da buka pojedinačno ne prelazi 75 – 80 dBA.

7. MJERE ZAŠTITE ZA PROIZVODNJU KOMPOSTANA

Za prikupljanje slijevnih oborinskih voda trebaju biti izgrađeni vodonepropusni betonski obodni kanali oko cijelog odlagališta otpada, a ne samo oko kompostane. Nakon kontrole sastava i utvrđivanja zadovoljavajućih parametara moguće je ispuštanje istih u obodni kanal.

Anaerobnom razgradnjom otpada u tijelu kompostišta mogu nastati i plinoviti produkti poput CH_4 i CO_2. Od 1 kg krutih otpada nastaje 0,45 m^3 plinova dok se stvarno može očekivati vrijednost od 0,03 do 0,18 m^3/kg. Količinski produkcija metala u direktnoj je vezi s intenzitetom razgradnje otpada te nakon brzog postizanja maksimuma produkcija metana pada. Mjesta odzračnika dolaze na cca 40 m, a na vrh odzračnika postavlja se biofiltar (kompost debljine 2 m).

Širenje neugodnih mirisa najčešće se javlja kod neorganiziranog ili loše provedenog kompostiranja. Razgradnjom organske materije, a kao produkt fermentacije, stvaraju se neugodni mirisi koji se mogu širiti i na velike udaljenosti, stvarajući poteškoće lokalnom stanovništvu. Ovu pojavu moguće je izbjeći dobrim organiziranjem kompostiranja, tj. prekrivanjem otpadaka na kraju radnog dana. U sušnom periodu u kompostanama se javlja prašina. Njezina pojava sprečava se prskanjem radnih površina i privremenih putova vodom.
Tlo se štiti tako da se dno kompostišta izvodi kao vodonepropusno (posteljica „sendvič-sloj“ – prirodni prašinasti materijali slabe vodopropusnosti debljine 0,5 do 1 m + bentonitni tepih koji zamjenjuje glinu debljine 1 m i k = 10 - 9 m/s + HDPE folija + geotekstil + drenažni sloj 30 – 50 cm). Također, na kraju svakog radnog dana vrši se prekrivanje otpada slojem internog materijala [15].

Uobičajene mjere za zaštitu od požara koje se provode u kompostanama su:

- svakodnevno prekrivanje otpada slojem internog materijala ili LDPE vatrootpornom folijom pa su tako dijelovi otpada međusobno razdvojeni,
- kontrolirano evakuiranje nastalih plinova da ne dođe do sakupljanja metana unutar tijela kompostišta, a s time i do mogućnosti eksplozije,
- kontroliranje otpada koji dolazi u kompostanu kako se ne bi odlagale lako zapaljive i eksplozivne tvari,
- kontroliranje otpada da se ne bi odlagao zapaljeni ili tinjajući otpad,
- kontroliranje ulaza u kompostanu kako treće osobe ne bi mogle namjerno izazvati požar,
- postavljanje odgovarajućeg broja protupožarnih aparata,
- telefonska veza s profesionalnom vatrogasnom jedinicom,
- osposobljenost zaposlenika za zaštitu od požara,
- izrađenost servisne ceste oko kompostane.

Pojavu štetočina u kompostani (štakori, insekti i ptice) izbjegava se pravilnom tehnologijom odlaganja otpada, tj. prekrivanjem otpada te držanjem radne površine otvorenih otpadaka što manjom. Osim toga, potrebno je provoditi dezinsekcijau i deratizaciju. Problemi se mogu pojaviti kod istresanja otpada na radno polje. Jedna od metoda za sprečavanje ove pojave je postavljanje prenosivih žičanih ograda oko radnog polja, a u smjeru vjetra. Rad strojeva u kompostani izaziva buku. Zbog toga kompostanu treba locirati dovoljno daleko od naselja.

Nedostatci primjene komposta vezani su za kontaminaciju tla biljnim patogenima, teškim metalima te sjemenom korova što se može izbjeći pažljivim odabirom sirovina i pravilnim postupkom kompostiranja. U biološko-dinamičkoj poljoprivredi primjenjuje se kompost obogaćen kompostnim pripravcima i barelski kompost. Neodgovarajuće pripremljen kompost može u tlu povećati sadržaj biljnih patogena, sjemenki korova ili otrovnih organskih ili anorganskih onečišćenja u tlu. S druge strane, dobro pripremljen kompost može povećati razinu organske tvari u tlu te stimulirati porast uzgajanih biljaka, ali u isto vrijeme i zaštiti uzgajane biljke od bolesti [16].

U kompostnu hrpu, također, se ne smije odlagati meso, riba, mlijeko i mliječni proizvodi, cigarete te kuhani ostaci hrane. Sav taj otpad mogao bi privući životinje koje bi kopale po tome i tim kopanjem oslobađale neugodne mirise. U otpad koji se kompostira ne smiju se odlagati štetne i otrovne tvari jer one uništavaju mikro i makroorganizme i samim svojim djelovanjem zagađuju kompost.

8. ZAKLJUČAK

Gospodarenje otpadom u svakoj razvijenoj državi usmjereno je na preventivno djelovanje, a ono uključuje planiranje nastanka, izbjegavanje nastanka otpada, minimiziranje nastalog otpada, oporabom otpada te odlaganjem samo otpada koji se ne može iskoristiti. Konačno odlaganje najmanje je prihvatljivo opcija u gospodarenju otpadom. Uspješno gospodarenje rezultat je aktivnog uključivanja različitih dionika: proizvođača otpada, onih koji otpadom gospodare (prikupljaju, prevoze, obrađuju i sl.), javnosti, ekoloških udruga, nadležnih tijela – inspekcija zaštite okoliša i predstavnika vlasti. Postupak kompostiranja omogućava ponovno korištenje kvalitetnih sastojaka iz biootpada i predstavlja jedan od prioriteta u postupanju s biootpadom u razvijenim zemljama. Osnovni cilj kompostiranja

biootpada je razgradnja organskog dijela otpada podložnog procesima truljenja u stabilno stanje, čime dolazi i do dezinfekcije patogenima inficiranog organskog otpada, te proizvodnja sastojaka koji se mogu koristiti kao poboljšivač tla ili u neke druge korisne svrhe. Razgradnja se može odvijati posvuda u prirodi, ali i u vrtnim kompostanama i u velikim kompostanama komunalnih poduzeća.

No, u Republici Hrvatskoj postoji i problem nedovoljne implementacije suvremenih tehnologija u proces kompostiranja, a loša provedba procesa kompostiranja može dovesti do iznimno štetnih posljedica ovog procesa na okoliš i ljudsko zdravlje. Kompostiranje, ako se ne provodi u kontroliranim uvjetima i pod strogim nadzorom, može dovesti do zagađenja vode, tla, zraka te indirektno ljudskog zdravlja. Nadalje, mehanizacija u kompostanama može stvarati veliku buku što se, također, smatra nuspojavom ovog procesa. Stoga je važno kompostane graditi na primjerenim lokacijama, ali i u skladu s najnovijim rješenjima vezanim uz kompostiranje.

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EDUKACIJA O OTPADU KAO MOTIVACIJSKI POKRETAČ SUSTAVA GOSPODARENJA OTPADOM

EDUCATION FOR WASTE AND MOTIVATION IN WASTE MANAGEMENT SECTOR

Sanja Kalambura*

* Veleučilište Velika Gorica, Velika Gorica, Hrvatska

autor za korespondenciju: Sanja Kalambura, e-mail: sanja.kalambura@vvg.hr

Pregledni rad

SAŽETAK

Znanje je nužan uvjet za provedbu mjera sprječavanja nastanka otpada, no ipak je motivacija ona koja na kraju definira uspješnost provedbe mjera sprječavanja nastanka otpada. U osnovi motivacija može biti *pozitivna* (na primjer isticanje pozitivnih iskustva ali i *negativna* (primjerice upoznavanje javnosti s dokazanim primjerima neodrživog postupanja s otpadom). Motivacija za sprječavanje nastanka otpada u proizvodnji se donekle razlikuje od mjera sprječavanja otpada u potrošnji. U svakoj suvremenoj tvrtki odgovorno se provode mjere sprječavanja nastanka i naročito mjere kružnog gospodarenja otpadom. Motivacija pučanstva je vrlo složena i uključuje niz vrlo različitih mjera. U tim okvirima i cijena vezana za otpad kod društveno odgovorne promidžbe važan je faktor. Uspješna motivacija uvijek je kombinacija pozitivne (metoda mrkve) i negativne (metoda biča) metode. Provedena su brojna istraživanja koja pokazuju da se nikada samo kaznama ne može spriječiti smanjenje otpada. S druge strane učinkovito smanjenje nastajanja komunalnog otpada se ne postiže samo primjerice uvođenjem naplate prema obujmu ili količini otpada. Rad donosi pregled različitih motivacijskih metoda s ciljem stvaranja društveno odgovornog društva i zaštite okoliša u cjelini.

Ključne riječi: *otpad, motivacija, edukacija, utjecaj na društvo, okoliš u cjelini*

ABSTRACT

Knowledge is a necessary precondition for the implementation of waste prevention measures, but it is motivation that ultimately defines the success of waste prevention measures. Motivation can be positive (for example, highlighting positive but negative

experiences (for example, getting to know the public with proven examples of unsustainable waste management). In each modern company, measures are being implemented to prevent the emergence and, in particular, the measures of circular waste management. The motivation of the population is very complex and involves a number of very different measures. In these frameworks and the price of waste related to socially responsible advertising is an important factor Successful motivation is always a combination of positive (carrot method) and negative (briquette method), numerous studies have shown that only penalties cannot be prevented from reducing waste, on the other hand, effective reduction of municipal waste generation is not achieved, for example, by introducing collection by volume or amount of waste. The paper provides an overview of various motivational methods with the aim of creating a socially responsible society and protecting the environment as a whole.

Keywords: *waste, motivation, education, impact on society, the environment*

1. UVOD

Zahvaljujući industrijskoj revoluciji naš život je naizgled postao puno jednostavniji, a različite potrepštine dostupnije. Kako je potražnja rasla tako se i industrija razvijala, ručni rad je zamijenjen automatiziranim radom, stvorena je brža proizvodnja, pojedini predmeti su značajno pojeftinili, a kvaliteta postaje imperativ [1]. U 20. stoljeću negdje oko pedesetih godina bilo je svega 1,65 milijardi ljudi na Zemlji. Činjenica je da nas je danas više od 7,2 milijarde na istom prostor naše planete. To ukazuje na činjenicu da se prirodni resursi neminovno troše ali i da svojim djelovanjem svatko od nas ostavlja pečat na zemlji kroz svoje dnevne aktivnosti [2]. Kada se govori o okolišu, društvo trenutno iscrpljuje resurse više nego se Zemlja obnavlja, što zahtijeva zapravo u naravi za naše potrebe 1,5 planetu Zemlju. Otpad je također dio naše svakodnevnice. Oko metoda zbrinjavanja otpada raspravlja se u najvišim akademskim krugovima te se razvoj tehnologija učinkovitog zbrinjavanja otpada postavlja kao imperativ. Iako se u zadnje vrijeme stopa recikliranja konstantno povećava diljem Svijeta, većina materijala i proizvoda se i dalje odbacuje umjesto da se ponovno koriste ili recikliraju, što ostavlja prostora za značajna poboljšanja i prilike. Recikliranje predstavlja postupak sakupljanja odbačenih materijala i proizvoda, razvrstavanje te pretvaranje u nove materijale za izradu novih proizvoda ili proizvoda iste namjene. Recikliranjem već upotrijebljenih materijala sprječava se korištenje novih sirovina tamo gdje to nije neophodno, već se kao sirovine iskorištavaju rabljeni materijali koji se svrstavaju u otpad i koji su ekološko opterećenje za okoliš. U procesu recikliranja dolazi i do smanjenja potrošnje energije i emisija stakleničkih plinova u usporedbi s proizvodnjom uz upotrebu novih sirovina. Sami izraz „reciklirati“ dolazi od engleske izvedenice riječi *recycle* što u slobodnom prijevodu znači „ponovno kruženje“.

No ipak bez obzira na činjenice o dobrobitima reciklaže suočeni smo s nedostatkom hrabrih odluka, visokom cijenom energije, vode i drugih prirodnih resursa koji bi pomogli da filozofija održivog razvoja kao osnovni dio ekonomskih i okolišnih politika razvijenih zemalja kao i zemalja u razvoju stvarno zaživi [3].

Izbjegavanje nastajanja otpada, prevencija i sprječavanje otpada u direktnoj su korelaciji s njegovim smanjenje te predstavljaju početak vrlo važnog procesa kojim se mogu riješiti određeni problem vezani uz otpad [4]. Uglavnom se mjere koje vode ka rješavanju ovakvih problema vežu uz procese proizvodnje ili uz mjesto gdje otpad nastaje unutar proizvodnog procesa. Ponovnom upotrebom, recirkulacijom otpada u proizvodne procese značajno se utječe na njegovo smanjenje bez da uopće zapravo otpad i nastaje. Tu uvelike

pomaže stjecanja statusa nusproizvoda. No, ne treba gledati na ovu problematiku na način da se ulazi u ideološke zamke te da izbjegavanje otpada i njegovo smanjivanje postaje glavna okosnica cjelovitog sustava. Otpad je oduvijek nastajao i problemi oko njegovog zbrinjavanja ostaju i ostat će izazovom i u budućnosti.

Razlozi tome su mnogobrojni: prenamjena proizvodnje, zamjena toksičnih elemenata manje toksičnim ili ne toksičnim, novi dizajn proizvoda koji je pogodan za recikliranje i sl. Dakle prevencija je usko vezana uz proizvod koji kupujemo i koji se nalazi na tržištu, no ekonomske prilike tjeraju nas u isto vrijeme na postupanje koje nije u skladu s navedenim te je teško očekivati značajan napredak u ovo području [5]. U isto vrijeme to nam ne daje pravo da ne upozoravamo na karakteristike proizvoda koji su na tržištu te koji mogu biti ili jesu izrađeni od potpuno ne reciklirajućih materijala. Pri tome je važna činjenica da proizvođači trebaju biti odgovorni za proizvode koje stavljaju na tržište, dok potrošači temeljem vlastitog izbora mogu utjecati na ovaj vrlo važan korak u cjelovitom sustavu.

Važna karika između proizvodnje i potrošnje je uloga vladajućih koji kroz zadatak informatora stanovništva preuzima značajnu ulogu u informiranju o svim mogućnostima koje su dostupne, vodeći računa da pristup bude jasan i prvenstveno informativan. Ujedno im je zadatak poticati proizvođače ne promjenu temeljem zakonskih i ekonomskih mjera, posebno nakon što temeljitom analizom detektiraju i prepoznaju proizvođače koji nisu u skladu s postavkama reciklaže. Društvo u cjelini plaća cijenu za smanjenje poremećaja u okolišu, no ta cijena treba biti tolika da ne zaustavi gospodarski rast, ali niti preniska jer bi ekološki disbalansi mogli postati kočnicom gospodarskog rasta. Jasno usmjeravanje financijskih sredstava Fonda za zaštitu okoliša i energetsku učinkovitost treba biti u smjeru gdje postaju najučinkovitija, što zapravo u naravi znači reviziju svih kriterija dodjeljivanja sredstava. Je li ispravno ulaganje u primarno odvajanje otpada, iako je ono početak cijelog sustava, kad znamo da se otpad odvojen na takav način kasnije zbrinjava odlaganjem? Okoliš i rješenja koja su usko vezana uz prevenciju otpada vrlo su složeni, povezani s različitim ekonomsko-tržišnim faktorima te uvjetovani raznim eksternim utjecajima. Stoga je prvi i najvažniji korak u planiranju ove točke sustava realno sagledavanje svih parametara koji utječu na ovaj kompleksan problem.

2. KOMUNIKACIJA S JAVNOŠĆU I EDUKACIJA

Osim dugoročnih ciljeva i jasne vizije, uspostavljanje cjelovitog sustava gospodarenja otpadom zahtjeva temeljitu i kvalitetnu komunikaciji svih sudionika izgradnje sustava gospodarenja otpadom - nadležna tijela, lokalna samouprava, struka, građani i nevladine udruge, što do sada nije bila praksa. Kako bismo postigli kvalitetnu i učinkovitu komunikaciju potrebno je osvijestiti vlastitu ulogu i odgovornost za gospodarenje otpadom [6]. Time je moguće prevladati trenutno dominantni pristup prebacivanja krivnje na druge sudionike u sustavu.

Način na koji se sadašnji okvir sudjelovanja javnosti predstavlja je zastario i dovodi do 'zamora sudjelovanja'. Posebno se to ističe kroz dominanti pristup donošenju odluka 'odluči-objavi-obrani', a da se pri tome susrećemo s površno organiziranim konzultacijama s građanima, najčešće organiziranim u cilju zadovoljenja formalnih zahtjeva [7]. Ovakav pristup, iako na prvi pogled ubrzava postupke, u praksi ih usporava, a ponekad i onemogućuje provođenje različitih projekata gospodarenja otpadom.

Za cjelovit pristup komunikaciji s javnošću potrebno je imati jasna i ciljana istraživanja stavova javnosti kako bi se utvrdilo početno stanje, odnosno razina informiranosti i razumijevanja pojedinih područja gospodarenja otpadom, kao i Plan komunikacije s

javnošću, s analizom okruženja, ciljeva, poruka prilagođenih za svaku skupinu javnosti, spleta komunikacijskih aktivnosti i metoda evaluacije očekivanih rezultata i ishoda. U evaluaciji rezultata je važno razlikovati rezultate od ishoda, jer su pojedini informativni materijali samo sredstvo za postizanje očekivanih ishoda: bolja informiranost, usvajanje novih navika, promjene u ponašanju itd. Preporučuje se provođenje istraživanja kojima će se mjeriti rezultati aktivnosti informiranja i edukacije te tako stvoriti povratna veza. Ulaganje u značajne napore u postizanju zajedničkog razumijevanja svih sudionika gospodarenja otpadom europskog i nacionalnog okvira gospodarenja otpadom vodi ka uspješnom sustavu. Različiti sudionici često različito razumiju i tumače temeljne dokumente gospodarenja otpadom što često dovodi do sukoba i konfliktnih situacija [8]. Posebno je to slučaj s hijerarhijom otpada i razumijevanja ciljeva gospodarenja otpadom. Praksu informiranja i educiranja građana potrebno je intenzivirati i unaprijediti i to na svim razinama. Težište informiranja i edukacije važno je usmjeravati na nove medije (društvene mreže) i direktne oblike komunikacije s različitim skupinama javnosti te ujedno dobro proučiti djelotvornost svakog pojedinog kanala i oblika komunikacije u odnosu na zacrtane ciljeve, a posebno ciljeve izdvajanja određenih vrsta komunalnog otpada.

Posebno je važna činjenica nedostatka odgoja i obrazovanja za okoliš koji je bio jedan od najvažnijih obrazovnih koncepata devedesetih godina prošlog stoljeća [9]. Uspostavljen je se s ciljem razvijanja svijesti i razumijevanja problema okoliša, što vodi k odgovornim pojedinačnim i skupnim akcijama, no nije zaživio u cijelosti u RH. Jedan od zaključka prvog Hrvatskog sabora o odgoju i obrazovanju za okoliš, održanom još 1996. godine bio je da obrazovanje za okoliš treba ući u minimum svih predškolskih programa te u programe svih osnovnih i srednjih škola, stoga je potrebno ugraditi odgoj i obrazovanje za okoliš u nastavne predmete svih onih predmeta čiji su sadržaji logički vezani uz to područje (kao npr. priroda, biologija, zemljopis, kemija, sociologija). S obzirom da je sudjelovanje građana u zbrinjavanju otpada vrlo važno, potrebno je provesti edukaciju stanovništva i podići razinu svijesti o potrebi adekvatnog zbrinjavanja otpada kako bi se postigli ciljevi Strategije gospodarenja otpadom.

Da bi stanovnici bili motivirani za izbjegavanje otpada, kao prvi i osnovni element cjelovitog sustava gospodarenja otpadom, moraju za početak biti educirani i upoznati s karakteristikama otpada, te posljedicama neadekvatnog zbrinjavanja. Efikasna edukacija trebala bi uputiti potrošače kako da reduciraju količine otpada koje proizvode. Između eko-edukacije i eko-kulture postoji uzajamni odnos s uzročno-posljedičnim vezama. Ekološkom edukacijom omogućiti će se stjecanje ekoloških znanja i vještina s ciljem povećanja razine svijesti svakog pojedinca za učinkovito sudjelovanje u provođenju sustava gospodarenja otpadom.

Ekološka edukacija u području zaštite okoliša i gospodarenja otpadom treba biti shvaćena kao grana obrazovanja koja može stimulirati nove naraštaje da steknu nove navike u skladu s principima održivog razvoja. Vrlo je bitno da se svijest o očuvanju okoliša zbrinjavanjem otpada izgrađuje od najmlađih, jer se time može utjecati i na ponašanje odraslih. Uzevši u obzir važnost učenja kod djece u periodu prije škole izuzetno je važno da edukacija kroz igru bude bio programa predškolskih ustanova budući je poznata činjenica da navike stvorene u djetinjstvu ostaju za čitav život stoga je važno već u najranijoj dobi djeteta stvoriti navike kako bi odvojeno prikupljanje otpada postao ustaljen obrazac ponašanja [10]. Nužno je povezati odgoj i obrazovanje u području gospodarenja otpadom budući odgoj u užem značenju obuhvaća "emocionalnu i voljnu sferu čovjekova bića", odnosno "izgrađivanje i oblikovanje ličnosti i karaktera", a obrazovanje je usmjereno na intelektualnu sferu ljudske osobnosti. Edukacija i obrazovanje predstavljaju vrlo važan segment cjelovitog sustava gospodarenja otpadom.

Učinkovito gospodarenje otpadom složen je proces, a izazovu će se lakše odgovoriti ako svi budu osposobljeni i potaknuti na sudjelovanje u provođenju cjelovitog sustava gospodarenja otpadom. Kurikulum odgoja i obrazovanja za okoliš pa tako i u području gospodarenja otpadom mora obuhvatiti znanja, vještine, stavove i vrijednosti. Također naglasak treba biti na pedagoško-didaktičkim metodama i otvorenim oblicima poučavanja okrenutim prema studentu/učeniku te razvoju kritičkog mišljenja pri čemu se ne prenosi samo znanje, već je važan segment motiviranje i aktiviranje studenata/učenika na odgovorniji, svjesniji odnos prema okolišu.

3. MJERE PREVENCIJE OTPADA

U dosadašnjoj praksi je dokazano, da porastom standarda života odnosno BDP-a najčešće se povećava i količina otpada. Veći BDP omogućuje veću potrošnju, a povećana potrošnja kao konačni rezultat ima nastajanje većih količina otpada. Svijet je u globalu primjenjivao linearne modele zbrinjavanja otpada dok se tek zadnjih 30 godina počinje razmatrati i uporabna vrijednost otpada. Započinje se najprije s reciklažom papira pa zatim stakla i na kraju polimera koji čine gotovo ugrozu 21. stoljeća. Važno je naglasiti da je smanjivanje otpada uz porast BDP moguće prvenstveno uz provedbu mjera sprječavanja otpada. Time se smanjuje odlaganje otpada te potiče rast i razvoj te gradnja postrojenja za oporabu i obradu otpada. Zakonom o održivom gospodarenju otpadom propisano je:

„Sprječavanje nastanka otpada su mjere poduzete prije nego što nego li je tvar, materijal ili proizvod postao otpad, a kojima se smanjuju:

a) količina otpada (ponovnom uporabom i/ili produženjem životnog vijeka proizvoda),
b) štetan učinak otpada na okoliš i zdravlje ljudi,
c) sadržaj štetnih tvari u materijalima i proizvodima!“

U praksi se mjere sprječavanja nastanka otpada naziva i prevencija, te se razvrstavaju na nekoliko načina:

- *mjere izbjegavanja otpada (**A**void)* - imaju najveći učinak u odgovornom postupanju s otpadom. U javnosti se te mjere često nazivaju mjere „nula otpada“ (Zero waste). Mjere izbjegavanja se neodgovorno idealiziraju, a na taj se način obezvrjeđuje problematika gospodarenja otpadom. Naime ako je moguće otpad izbjeći, zašto se treba opterećivati vrlo složenim mjerama postupanja otpadom,
- *mjere smanjivanja otpada (**R**educe)* su naročito važne, a mogu se primijeniti u svim područjima ljudske aktivnosti (npr. umjesto nepovratne koristi se trajna vrećica ili košara za kupovinu i sl.),
- *mjere ponovne uporabe bez obrade (**R**euse)* sve se češće koriste u domeni kružnog gospodarenja otpadom. (npr. dulja upotreba knjiga kod istog i/ili drugog posjednika i sl.),
- *mjere ponovne uporabe otpada uz obradu, za istu namjenu (**R**ecovery)* potiču na povratak u vremena kada su više i duže korišteni pojedini predmeti i uređaji (npr. korištena odjeća se krojački proširi ili skrati i zatim ponovo koristi),
- *mjere ponovne uporabe uz obradu, ali za drugu namjenu (**R**ecycling)* je nešto manje učinkovita mjera. Primjerice recikliranjem otpadnih autoguma proizvodi se

regranulat, koji se koristi za proizvodnju drugih tvorevina, kao primjerice izrada gumenih tepiha i slično.

4. KVANTITATIVNE I KVALITATIVNE MJERE ZA SMANJENJE OTPADA

Mjere za smanjenje količine otpada ili kvantitativne mjere najčešće su u središtu javnosti te se dijele na:

- izravne kvantitativne mjere sprječavanja (npr. *Low Waste Technologies* – tehnologije manje otpada; razdioba i prijevoz otpada uz manje otpada; vrtno – kućno kompostiranje itd.),
- neizravne kvantitativne mjere sprječavanja (npr. odvojeno sakupljanje iskoristivog otpada: stakla, papira, metala, biootpada itd.).

Mjere za smanjenje štetnosti otpada odnosno kvalitativne mjere od velike su važnosti i dijele se na:

- izravne kvalitativne mjere što bi značilo zamijeniti proizvode koji opterećuje okoliš s proizvodima koji manje opterećuju okoliš (npr. koristiti boje i lakove koji se razrjeđuju vodom umjesto kemikalijama, koristiti isključivo toplomjere i termometre bez žive, i sl.),
- neizravne kvalitativne mjere (npr. nakon upotrebe proizvode koji sadrže štetne tvari (lijekovi, baterije i sl.) i vratiti na mjesto kupnje ili odvojeno odložiti u reciklažno dvorište).

Prilikom definiranja mjera važno je naglasiti da je neizostavan dio cijelog ovog procesa održiva proizvodnja i potrošnja. Nastajanje otpada može se i prevenirati samo treba prilagoditi proizvodni proces te svaku stvar promatrati unutar životnog vijeka nekog proizvoda [11].

5. ZAKLJUČAK

Na kraju svega nameće se zaključak kako je edukacija neizostavna mjera i pokretač svih aktivnosti unutar cjelovitog sustava gospodarenja otpadom. Različita istraživanja dovela su do sličnih razmišljanja, no postavlja se pitanje zašto još uvijek imamo problem kada je u pitanju prihvaćanje rješenja koja se odnose na učinkovito zbrinjavanje otpada. Uspješna motivacija uvijek je kombinacija pozitivne metode (mrkva) i negativne (bič) metode. Stoga je poruka da se učinkovito smanjenje nastajanja komunalnog otpada ne postiže samo primjerice uvođenjem naplate prema obujmu ili količini otpada ili uvođenjem kazni.

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IMPLEMENTATION OF THE ENERGY MANAGEMENT INFORMATION SYSTEM IN BOSNIA AND HERZEGOVINA

Danijela Kardaš*, Amila Ajdinović, Elvis Hadžikadić****

* University of Banja Luka, Faculty of Mechanical Engineering, Banja Luka, Bosnia and Herzegovina
** United Nations Development Programme, Sarajevo, Bosnia and Herzegovina

corresponding author: Danijela Kardaš, e-mail: danijela.kardas@mf.unibl.org

Professional paper

ABSTRACT

Since 2013, United Nations Development Programme in Bosnia and Herzegovina is implementing the Green Economic Development Project financed by the Government of Sweden, the Environmental Fund of the Federation of Bosnia and Herzegovina and the Environmental Protection and Energy Efficiency Fund of Republic of Srpska, in cooperation with the partners at the state, entity, cantonal and local level. The Project is implementing in the field of energy efficiency and contributes to the market development and economic progress, as well as environmental protection. One of the project components is the institutionalization of energy management and introduction of the Energy Management Information System in public buildings. This project activity contributes and is in accordance with the guidelines of the European Union and the Energy Community Treaty, and the obligation of Bosnia and Herzegovina to report energy consumption and savings. Project results and implementation of this project component will be presented in this paper.

***Keywords**: energy efficiency, energy management, public buildings, environmental protection*

1. INTRODUCTION

In most of Bosnia and Herzegovina's (BiH) buildings, both residential and non-residential, thermal comfort cannot be achieved because the heat losses are very high. There is existing high energy conservation potential within both mentioned sectors, as building stock is characterized by poor heat-insulated characteristics. In order to meet this energy intensive consumption demand, a significant amount of budget funds must be allocated for energy expenditures of public buildings (educational, health, cultural, municipal and entity/state institutions etc.). Given the state of these facts, energy efficiency is ideal opportunity for the restoration of buildings and general improvement of the economic development in BiH. Energy efficiency is widely viewed as one of the most effective ways to achieve multiple

economic, social and environmental benefits and is at a core of making significant progress towards Sustainable Development Goals (SDGs) [1]. Measures of energy efficiency in principle aim to reduce energy consumption, costs, and greenhouse gas emissions. However, co-benefits arising from the implementation of energy efficiency measures are numerous, and sometimes perhaps even more important than their primary objective. The purpose of every load monitoring is mostly to facilitate the conservation of the energy by taking energy efficiency measures like using less energy consumption devices, appropriate timing of the appliance usage and eliminating energy unwanted activities [2]. Home energy monitoring and automation can motivate the consumers to use the energy more efficiently and wisely by having the overview of their appliances consumptions [3, 4]. There are identical and commercial settings, where load management is of vital importance consumed significant percentage of the total energy generated. This percentage depends on the level of industrialization of a country, hence the focus on energy monitoring and management is equally important [5]. Energy use in buildings currently account for about 32 % of the global total final energy consumption in the world. In terms of primary energy consumption, buildings represent around 40 % in most IEA (International Energy Agency) countries and 65 % of the total electric consumption. Buildings are also responsible for 36 % of the EU CO_2 emissions [6]. On the other hand, accordingly to its obligations under the Energy Community, and its ambitious for EU integration, BiH must have functional transposition of the energy efficiency acquis in BiH. International assistance is viewed as moderately effective in increasing the level of energy efficiency investments in most of the countries of South-East Europe, as well as in BiH. Since 2013, United Nations Development Programme in Bosnia and Herzegovina (UNDP) is implementing the Green Economic Development (GED) project which primarily goal is to contribute to the creation of a favourable environment for investing in energy efficiency measures.

2. LEGAL FRAMEWORK IN ENERGY SECTOR IN BOSNIA AND HERZEGOVINA

Constitution of BiH defines that entities have jurisdiction in establishment and implementation of policy in the field of energy. It also defines that the institutions of BiH are responsible for the implementation of international commitments undertaken by BiH. BiH is a member of the following international agreements that directly regulate activities in the field of energy efficiency and climate change:

- Energy Charter Treaty,
- The Energy Community Treaty,
- United Nations Framework Convention on Climate Change.

On its way to European Union (EU) approach BiH has to transpose EU Directives into its legislation in the field of energy. In order to legally regulate the energy efficiency and meet the obligations under the Treaty establishing the Energy Community of South East Europe, and promote and implement the energy efficiency improvement measures in final consumption, Republic of Srpska has adopted the Law on Energy Efficiency in 2013 and Federation of Bosnia and Herzegovina in 2017. These lows define obligations and rules regarding energy management [7, 8] and some of them are: a) appointment of a person responsible for energy management, b) provision of conditions for the energy consumption metering, c) periodic analysis (monthly, seasonal, and at least once a year) of energy

consumption, f) keeping a database on energy consumption, and g) annual submission of data to the Fund for the purpose of keeping a database on energy efficiency. This legal framework set a ground for system establishment for energy management in Bosnia and Herzegovina.

3. GREEN ECONOMIC DEVELOPMENT PROJECT IN BOSNIA AND HERZEGOVINA

The aim of the UNDP's Green Economic Development (GED) Project is to:

1. develop capacity and skills of Environmental Funds (systematic approach to decision making processes of energy efficiency investments),
2. develop and adopt sustainable financial mechanisms within Environmental Protection Funds for energy efficiency project financing (performance based granting, revolving mechanisms, soft-loans, etc.),
3. institutionalize energy monitoring and reporting mechanisms / energy management,
4. achieve budget cost savings through implementation of energy efficiency projects in public sector buildings and reinvest savings into energy efficiency or other infrastructure projects,
5. generate employment of domestic workforce,
6. increase public awareness and understanding of energy efficiency benefits,
7. contribute to BiH's EU accession (EPBD and EED directives).

In accordance with the goal, the Programme consists of five interlinked and supplementing project components (figure 1):

1. capacity building (development and capacity building of Environmental Funds and energy professionals),
2. institutionalization of energy management (institutionalisation of energy, costs and emission management and monitoring in public sector buildings of BiH),
3. legislative framework/financial mechanisms (development and adoption of sustainable financial mechanisms within Environmental Protection Funds),
4. infrastructure measures (implementation of energy efficiency measures in public buildings),
5. public awareness/marketing campaign (increasing public awareness on energy efficiency).

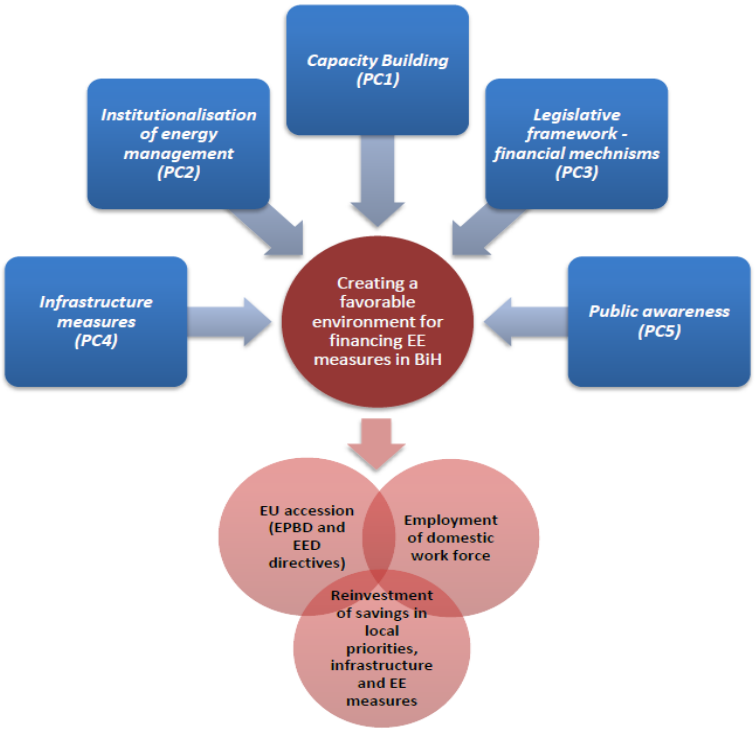


Figure 1. Green Economic Project Components [9]

3.1. Institualisation of Energy Management in Bosnia and Herzegovina

Energy management includes strategic planning and sustainable management of energy resources. In BiH is lack of statistical data, as well as un-adjustable energy related indicators and parameters required for systematic energy management decision making and reporting. Improvement of the current countrywide organizational set-up and implementation arrangements in the area of energy monitoring database management and reporting is one of the key energy related challenges. Large number of institutions collects data on various environment indicators, energy consumption and energy emission indicators from public buildings. These data are not recorded, monitored or analysed in an organizational, structured way, and quality assurance is questionable too. In order to help to overcome these challenges, to provide authorizes with a reliable monitoring tool through which they can base their future energy efficiency and renewable energy investment decision on, and to contribute to BiH's reporting obligations to multilateral agreements, UNDP in BiH is guiding its efforts to develop structured and unified energy and CO_2 emission monitoring and reporting system in both entities in BiH. This is possible through implementation Energy Management Information System (EMIS), which shall provide authorities the operational component for energy and emission indicator (consumption, costs, etc.), target setting and achieving, management and reporting monitoring tool. Moreover, it will enable state, entity and cantonal line institutions to develop their baseline building stock and statistical database of public buildings under their jurisdiction. By using a software which enables a continuous monitoring of energy consumption and costs (monitor parameters before/after energy efficiency measures implementation) additional energy savings can be achieved (for example, it has been proved in public sector buildings in Croatia that just using EMIS brings energy consumption down up to 20 %, since the awareness of users is improved, and they know that every usage is monitored) [9].UNDP staff provide training for end-users on EMIS, energy efficiency /

energy management in public buildings identified in public sector buildings end-users. UNDP organize training facilities throughout BiH and provide technical support and assistance to trained persons throughout project implementation.

3.2. Energy Management Information System

Energy Management Information System (EMIS) is web based application for tracking, analysing and evaluating energy and water consumption in public sector buildings (figure 2).

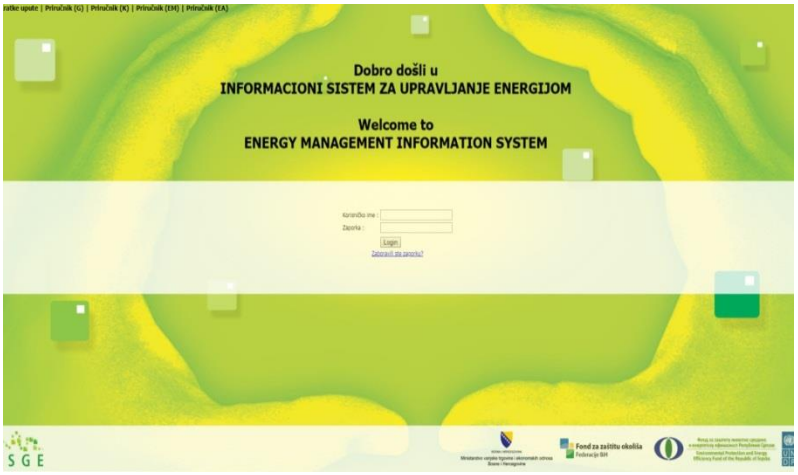


Figure 2. EMIS access web platform

Energy management includes strategic planning and sustainable management of energy resources therefore, application as such represents necessary tool for energy management. In Croatia, 9000 public sector buildings are currently monitored via EMIS for Law on energy efficiency purposes [9]. EMIS is also establishing in Serbia as a tool for energy management in public buildings [10]. In BiH system can be accessed on the website www.isge.ba. Bosnia and Herzegovina has two entities, Republic of Srpska (RS) and Federation of Bosnia and Herzegovina (FBIH) and District Brčko. FBIH has 10 Cantons and each Canton has its own government and adopts its own laws (harmonized with the FBiH legislation). Republic of Srpska has a centralized government. Duo to that, implementation of EMIS system is divided on two parts (for each entity) and has two types of structure. Figures 3 and 4 show EMIS implementation structure for RS and FBIH.

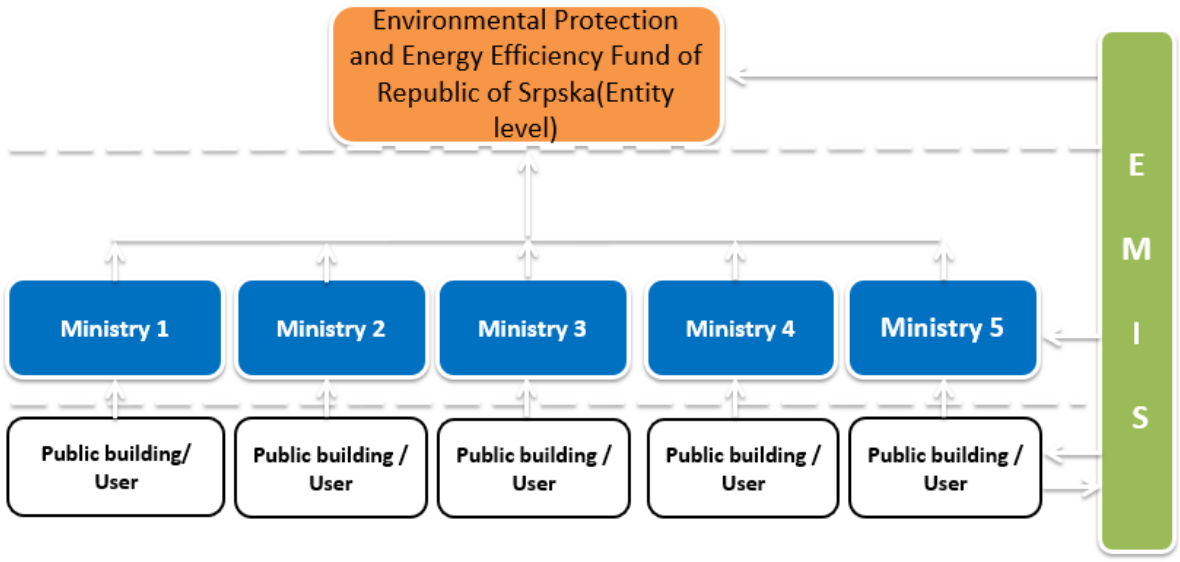


Figure 3. EMIS structure in Republic of Srpska

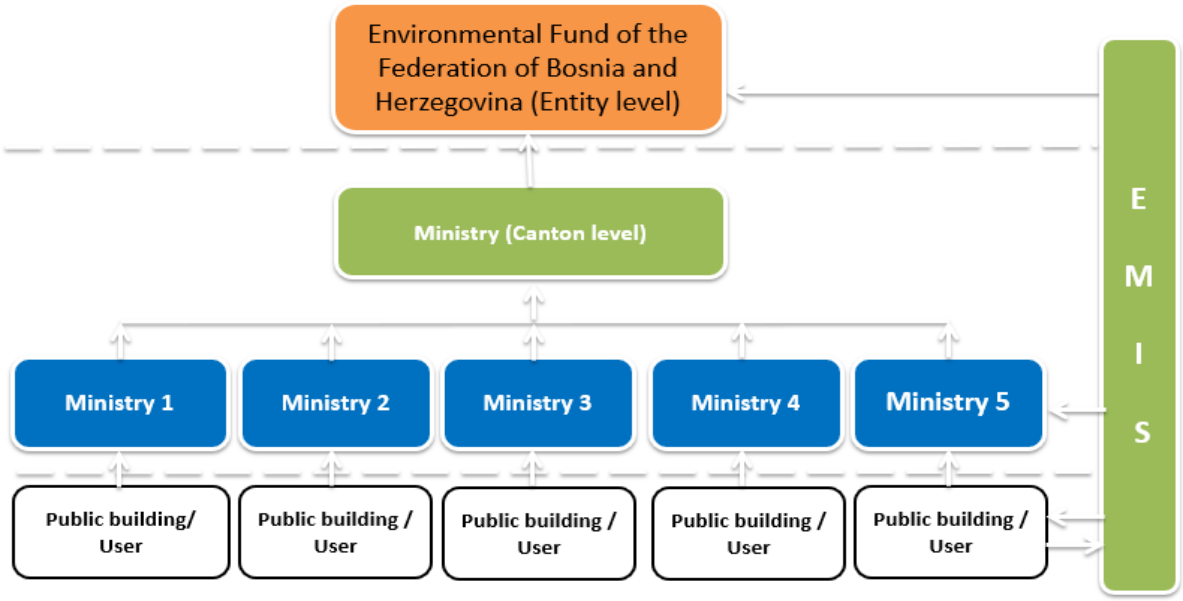


Figure 4. EMIS structure in Federation of Bosnia and Herzegovina

Public buildings are entered into EMIS system and every building has unique and invariable ID. To every public building is joined user account. Each user gets unique username and password to access EMIS. The system is designed in such a way that it can support an unlimited number of roles, with these five pre-defined: the system administrator (SA), an energy administrator (EA), energy manager (EM), user (U) and guest (G). For buildings owned by the public sector; municipalities, cantons and entities (administrative buildings, hospitals, schools, etc), the person responsible for managing energy, input relevant information about buildings that are under their jurisdiction. In compliance with the level of responsibility, each user is assigned certain rights in the software. The EMIS users first enter static information about building, which include construction and energy properties of the building. Monthly consumption data is entered based on the utility bills that are delivered.

This data is either entered manually, by reading it from the meters/energy bills or automatically by installing automatic remote metering systems, which can provide hourly consumption data directly to EMIS. Data entered into system is used for calculating, analysing and control and enables a better understanding of where, when and how we consume energy and water in buildings. It also allows comparison of spending between the selected buildings as well as the identification of unwanted and excessive spending. A software tool is also used as a central database of public buildings, as well as for analytical interpretation of entered data. EMIS greatly eases the process of systematic energy management in public sector buildings, in a way which allows easier access to information on consumption and energy costs. It provides a simple graphical representation or tabular presentation of the data collected as a result of predefined analysis (figure 5).

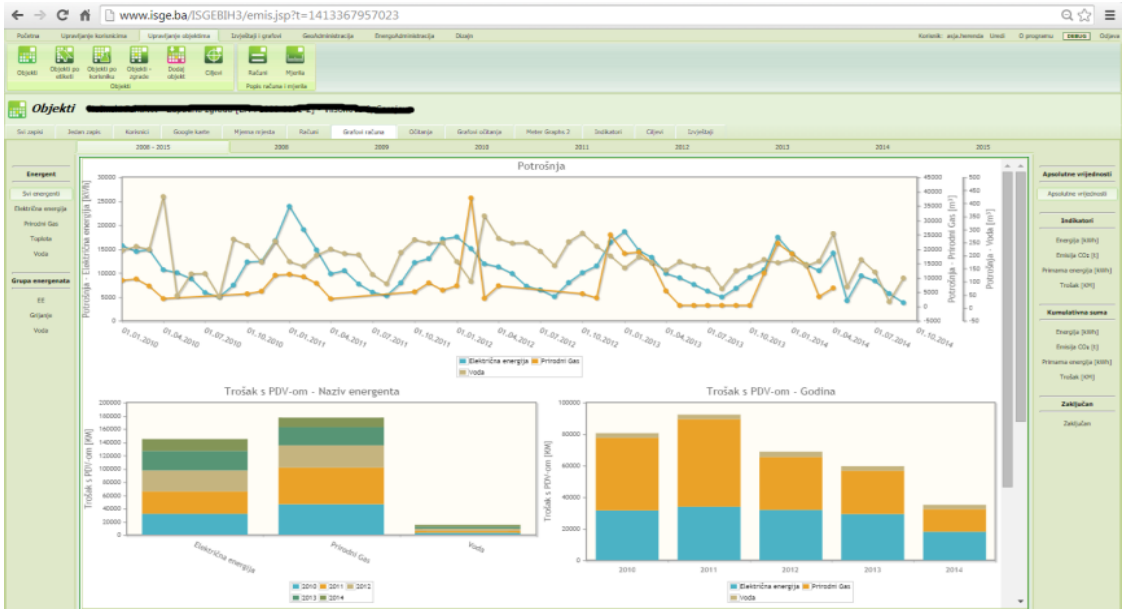


Figure 5. Example of graphical interpratation of monthly consumption and cost based on enetered data for one building (object)

Continuous monitoring of expenditure through EMIS provides a transparent view and control of energy consumption, energy savings, emission and emission reduction in public sector buildings. Mail functionalities are:

1. collect and enter basic information about the buildings and the control of energy and water consumption on a monthly, weekly and daily basis,
2. easy access to information on energy use, consumption patterns and places of consumption,
3. calculations and analysis of consumption for the purpose of identifying unwanted and excessive consumption of energy and water, as well as identifying opportunities to increase energy and financial savings,
4. verification of realized energy and water savings (kWh, €, t CO_2 and any other standardized indicator),
5. calculation of various consumption indicators,
6. different options for different levels of users,
7. advanced database filtering,
8. easy export of data info PDF or excel formats,
9. filtering based on building type.

3.3. Implementation of Energy Management Information System

As it's mentioned above, EMIS is implemented in Bosnia and Hercegovina under the project Green Economic Development. At this point more than 4000 public building were entered into EMIS system and 1827 representatives of these institutions have been trained how to use the system. At this point, 257 137 bills for energy and water consumption were entered into system. EMIS data base is growing every day because users are entering monthly bills on daily basis for their buildings. Idea is to enter all public buildings in Bosnia and Herzegovina into EMIS system under GED implementation into the future. Figures 6, 7 and 8 include example for energy consumption and cost analyse in EMIS for one object (building). On this object energy efficiency measures were implemented. Object is primary school and under the GED project whole building was reconstructed and heating system was replaced with new one (from fuel oil to pellet). Based on entered data for last years, figures 6, 7 and 8 show cost and energy savings as well emission reduction of CO_2.

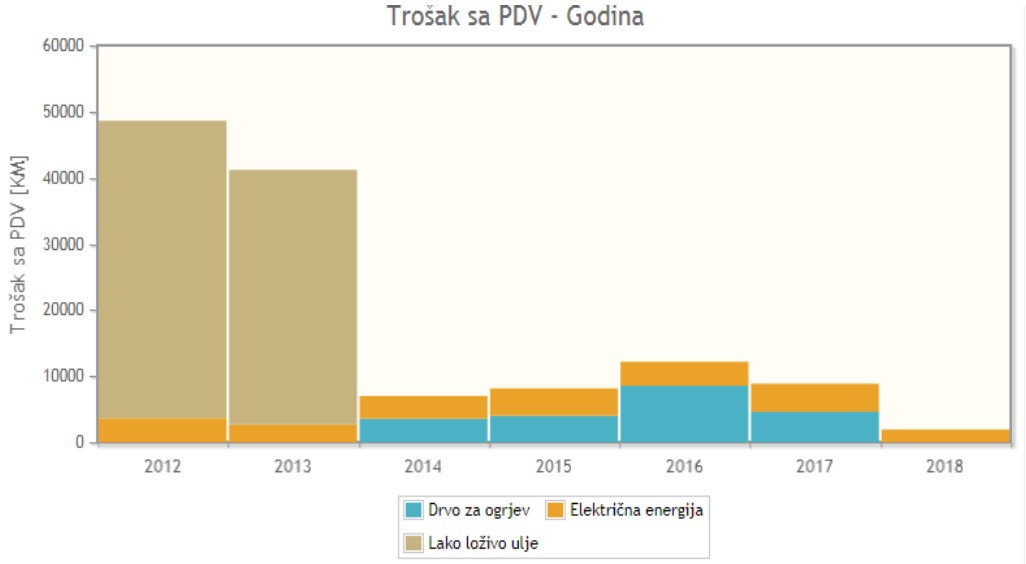


Figure 6. Cost for reconstructed object through years

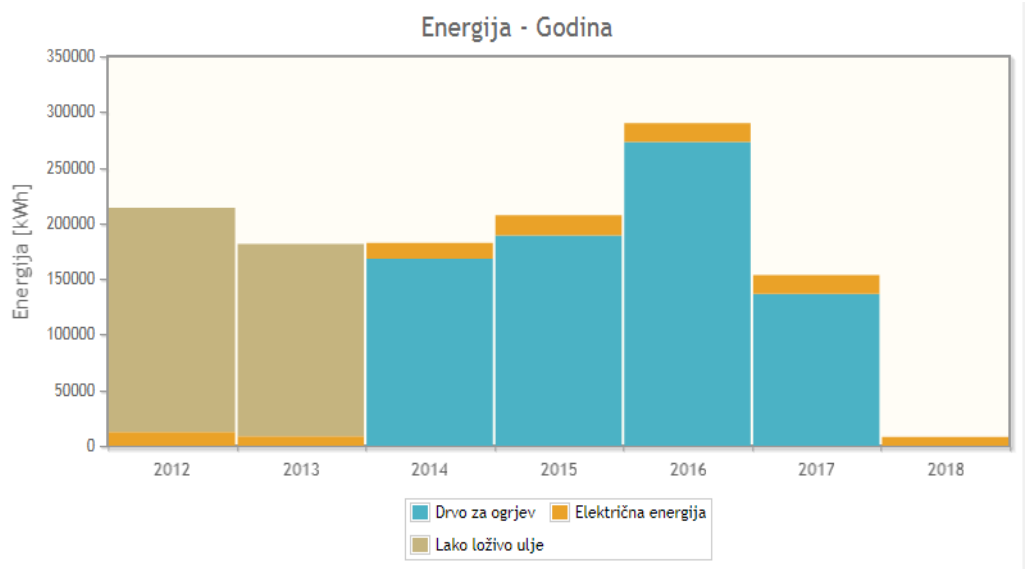


Figure 7. Energy consumption for reconstructed object through years

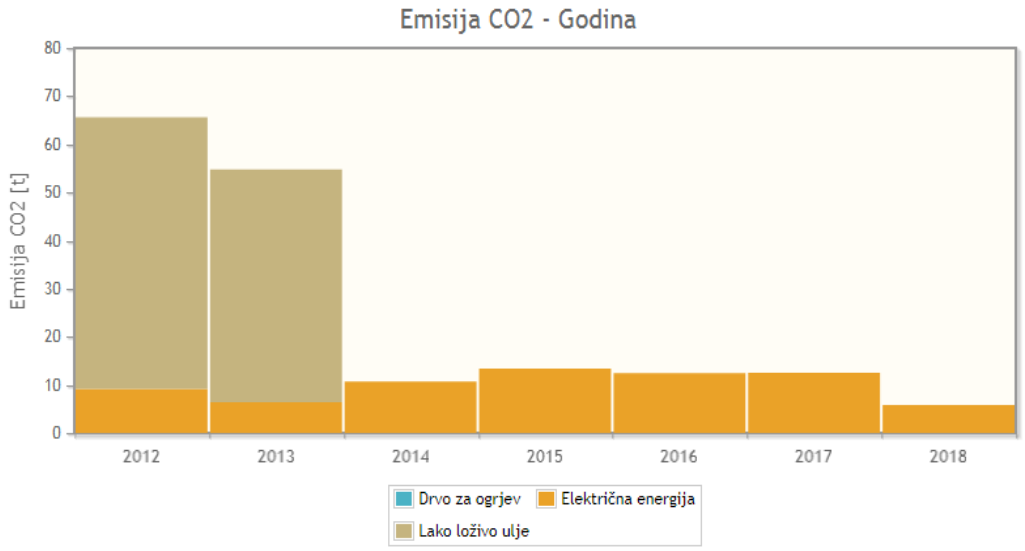


Figure 8. CO_2 emission for reconstructed object through years

As figures 9, 10 and 11 show energy consumption, costs and CO_2 emission for five public buildings (two primary schools and three health care buildings) which have been reconstructed udder GED project. As it can be seen, coal was the most used energy source for heating for analysed buildings. What also can be seen is that through the years consumption of coal is decreasing and pellet is increasing. This is duo to that under reconstruction was implemented energy efficiency measures and they switched their heating systems from coal to pellet. Bosnia Herzegovina generally has developed pellet market last few years. Pellet is one of the most popular and affordable renewable energy source in our region. Figure 9 shows decreasing in CO_2 emissions through years. This is direct consequence of switching from coal to pellet for heating systems. Through investments in energy efficiency measures and renewable energy, the project contribute to the reduction of health hazards and negative effects on the economy from high levels of air pollution generated by fuels such as coal, charcoal, fuel oil, etc. Among environment protection and impact on climate change, all implemented projects provide better conditions for its beneficiaries.

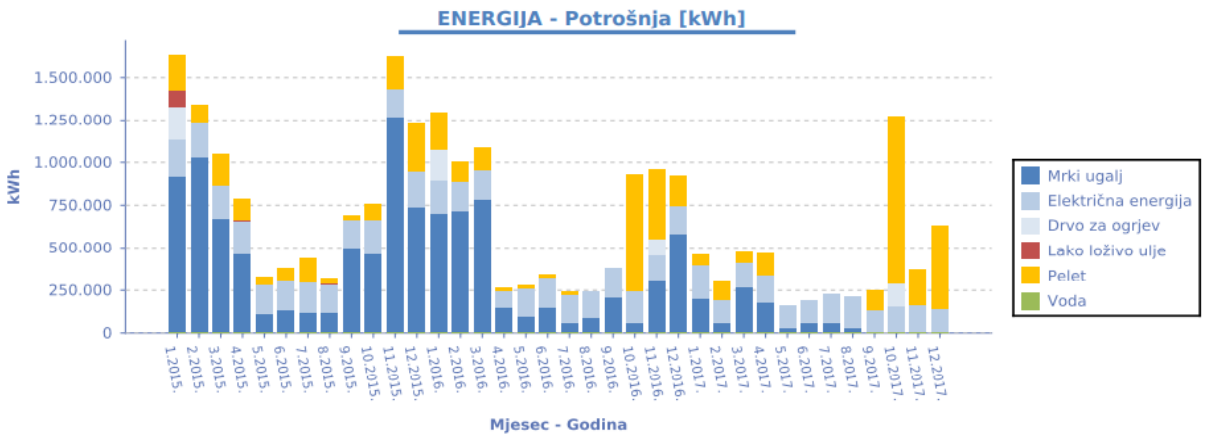


Figure 9. Summary energy consumption for five reconstructed objects

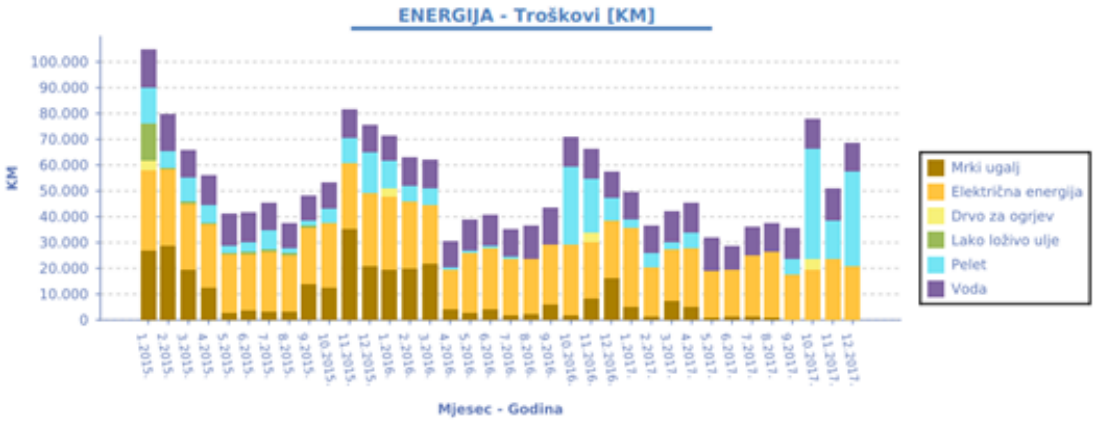


Figure 10. Summary costs per fuel for five reconstructed objects

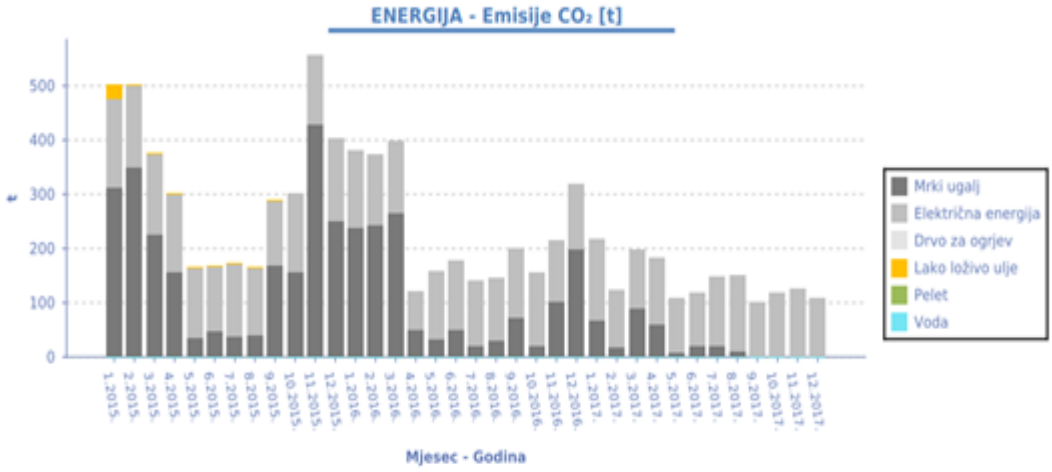


Figure 11. Summary CO_2 emissions per fuel for five reconstructed objects

4. CONCLUSION

It is expected that up to the end of the GED project all public facilities in BIH to be entered in the EMIS database. It would be database for public building stock and also a tool for monitoring energy and water consumption. As mentioned above Low of energy efficiency set rules and obligations for energy management and EMIS can be a tool for its implementation. As data entered into EMIS system are real consumption and costs for public buildings, are not predicted or in some way calculated, these data are also an excellent basis for planning energy efficiency measures in public sector. On the other hand, case studies showed that if the objects has a system of energy consumption monitoring that increase the awareness of employees and leads to 5 % in energy savings without any investment. Also, through project implementation, many representatives from public institutions have been trained to use EMIS system and that leads also to increasing the awareness about energy consumption and energy efficiency. As already noted, BiH and has commitments to the Energy Community regarding monitoring and reporting of energy consumption at the state level and EMIS is a database which can be used for this purpose. A systematic energy

management and information system together is good basis for the establishment of a sustainable energy management, both at the state level and at the level of individual facilities.

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Acknowledgments

This paper was prepared based on project results of Green Economic Development Project implemented in Bosnia and Herzegovina by UNDP. The content of this publication, as well as the findings presented there, are the sole responsibility of the authors and in no way reflects the views of United Nations Development Program (UNDP).

SMANJENJE ONEČIŠĆENJA OKOLIŠA PRIMJENOM BIOGORIVA U BRODSKIM MOTORIMA S UNUTRAŠNJIM IZGARANJEM

THE REDUCTION OF ENVIRONMENT POLLUTION BY USING BIOFUEL IN MARINE INTERNAL COMBUSTION ENGINES

Igor Kegalj*, Luka Traven, Iva Šebelja*****

* Pomorska škola Bakar, Bakar, Hrvatska
** Medicinski Fakultet u Rijeci, Rijeka, Hrvatska
*** SAIPEM S.p.A., Rijeka, Hrvatska

autor za korespondenciju: Igor Kegalj, e-mail: igor.kegalj@skole.hr

Pregledni rad

SAŽETAK

U nesigurnoj energetskoj situaciji u kojoj se nalazi Europa, upotreba obnovljivih izvora energije sve više dolazi u središte energetske politike svih država EU. Smanjenjem ovisnosti o fosilnim gorivima povećava se s jedne strane sigurnost energetske opskrbe, a s druge strane poboljšava se energetska učinkovitost tj. efikasnost i racionalno korištenje energije. Upotreba biogoriva u motorima s unutrašnjim izgaranjem, pa tako i na brodskim pogonskim motorima ima poseban ekološki značaj koji se manifestira smanjenjem negativnih učinaka na okoliš. Cilj ovoga rada je sljedeći: (1) identificirati postojeće pokazatelje utjecaja biogoriva u motorima s unutrašnjim izgaranjem na okoliš, (2) pronalaženje optimalnih ekonomskih, tehničkih i ekoloških opravdanosti korištenja biodizela kao pogonskog goriva brodova.

Uporaba biogoriva u pomorskom prometu, doprinosi smanjenju ovisnosti pomorskog sektora o fosilnim gorivima, smanjenju udjela emisije stakleničkih plinova iz pomorskog prometa te doprinosi podupiranju održivog razvoja.

Ključne riječi: *biogoriva, pomorski promet, brodski motori s unutrašnjim izgaranjem, okoliš, održivi razvoj*

ABSTRACT

In the uncertain energy situation of today in Europe, the use of renewable energy sources is increasingly becoming the focus of energy policy of all EU countries. The reduction of our dependence on fossil fuels increases the certainty of energy supply, on the

one hand, and improves energy efficiency, i.e. the efficiency and rational use of energy, on the other hand. The use of biofuels in internal combustion engines, including ship engines, has a particular environmental significance manifested in the reduction of negative environmental impact. The goal of the paper is the following: (1) identify the existing indicators of biofuel environmental impact in internal combustion engines, (2) find optimal economic, technical and environmental justifications for using biodiesel as ship fuel.

The use of biofuel in maritime transport reduces the dependence on fossil fuels in maritime sector and greenhouse gas emission share from maritime transport, thus supporting sustainable development.

Keywords: *biofuel, maritime transport, marine internal combustion engines, environment, sustainable development*

1. UVOD

Strategija održivog razvoja EU (engl. Sustainable Development Strategy) predlaže okvire strateške politike kojima se definiraju načini pristupanja razvojnim trendovima, sukladno načelima održivog razvoja. To je posebno važno s obzirom da je trenutni globalni pristup te politička moć zemalja koja proizlazi iz činjenice da posjeduju naftu u odnosu na one koje ju nemaju postaje neodrživ. Ograničene količine fosilnih goriva i sve naglašeniji štetan utjecaj na okoliš nametnuli su potrebu sustavnog istraživanja primjene obnovljivih izvora energije. U nesigurnoj energetskoj situaciji u kojoj se nalazi Europa, korištenje obnovljivih izvora energije dolazi u središte energetske politike, kako razvijenih, tako i zemalja u razvoju, pa tako i Republike Hrvatske.

Obnovljivi izvori energije pomažu u povećanju industrijske konkurentnosti čime se otvaraju nove šanse poduzetništvu i gospodarstvu, i imaju pozitivan utjecaj na regionalni razvoj i zapošljavanje. Alternativna goriva iz obnovljivih izvora energije mogu se koristiti za grijanje i hlađenje, proizvodnju električne energije i kao biogoriva za potrebe prometa. Korištenje biogoriva u prometu doprinosi povećanju sigurnosti opskrbe i smanjenju ovisnosti prometnog sektora o nafti, smanjenju udjela emisije stakleničkih plinova iz prometa te podupiranju održivog razvoja ruralnih područja. Upotreba biogoriva za promet (biodizel i bioetanol) ima više prednosti, a najvažnije su mogućnost korištenja postojeće infrastrukture (opskrbne mreže i motora), smanjenje emisija ispušnih plinova, njihova mogućnost brze razgradnje, neotrovnost te smanjenje ekoloških rizika u prometu i skladištenju.

2. GORIVA U POMORSKOM PROMETU

Ukupna potrošnja goriva svjetske flote iznosila je oko 369 milijuna tona[1]. Prema jednoj od nekoliko procjena broja brodova svjetske flote koja se danas sastoji od nešto više od 102 200 brodova veličine najmanje 100 GT i većih [1], i prosječne potrošnje goriva po brodu u 2011. godini potrošnja goriva je iznosila približno 376 milijuna tona pa je analogno prosječna emisija CO_2 s brodova bila oko 1190 milijuna tona, što je povećanje u odnosu na 2007. godinu za oko 12 %, tj. godišnje povećanje emisija CO_2 s brodova je oko 3 %. Tako se u Second IMO GHG Study 2009 [2], navodi procijenjena donja i gornja granica potrošnje

[1] IMO/Group of Experts (2007).

ukupne količine goriva svjetske pomorske flote s obzirom na različite ulazne podatke, te u konačnici daju procjenu srednje vrijednosti potrošnje koja je dobivena konsenzusom unutar IMO Expert Grupe. Također dana je procjena potrošnje po vrsti goriva i vrsti stroja. Međunarodna energetska agencija IEA (International Energy Agency), je na zahtjev lidera zemalja G-20 provela analizu koja je pokazala da bi se ukidanjem subvencija za fosilna goriva koje su u 2010. godini iznosile 409 milijardi dolara, značajno doprinijelo energetskoj sigurnosti, očuvanju okoliša, te smanjenju emisija CO_2 i ostalih emisija [3]. Prema istraživanju IEA potražnja za primarnom energijom je u proteklih 27 godina rasla 2% godišnje, a prema predviđanjima IEA-e po sva tri scenarija (New Policies Scenario, Current Policies Scenario, 450 Scenario) potražnja za fosilnim gorivima do 2035. godine rasti će od 19 % do 38 %, odnosno 0,7 % do 1,4 % godišnje. S obzirom na očekivanu i predviđenu potražnju za fosilnim gorivima IEA predviđa u svom scenariju „New Policies, World Energy Outlook (WEO 2010)“ da će emisije CO_2 od izgaranja goriva nastaviti s trendom rasta, iako smanjenom brzinom, i dostići razinu od 35,4 Gt CO_2 do 2035. Ovo predstavlja poboljšanje u odnosu na „Current Policies Scenario WEO-a“ te je u skladu s najgorim predviđanjem od strane Međuvladine skupine o klimatskim promjenama (IPCC) u njihovom izvješću „Fourth Assessment Report (2007)“, kojim oni predviđaju povećanje svjetske temperature od 2,4 °C do 6,4 °C do 2100. godine [4].

3. ONEČIŠĆENJE OKOLINE UPOTREBOM GORIVA U POMORSKOM PROMETU

Iako se pomorski promet, u usporedbi s ostalim načinima prijevoza, relativno blagonaklono odnosi prema okolišu, ipak svi ti brodovi na neki način uzrokuju onečišćenje okoliša budući da koriste pogonsko gorivo lošije kvalitete od pogonskog goriva drugih prijevoznih sredstava. Ta loša kvaliteta goriva sadrži visoku količinu sumpora, a izgaranjem nastaju ispušni plinovi sadržaja veće količine antropogenih sastojaka nego kod skupljeg kvalitetnijeg goriva (slika 1). Izgaranjem goriva u motorima s unutrašnjim izgaranjem s brodova svjetske pomorske flote u atmosferu se ispuštaju antropogeni plinovi, čija se količina ispusta izražava u milijunima tona: NO_x (25 mil.t), SO_x (15 mil.t), CO (2,5 mil.t), PM (1,8 mil.t), NMVOC (3,1 mil.t), CH_4 (0,24 mil.t), N_2O (0,03 mil.t), HFC (0,0005 mil.t) [2]. Emisije s brodova kategoriziraju se kao emisije ispušnih plinova, emisije brodskog tereta, emisije radnih tvari i ostale emisije. Emisije sumporovih oksida SO_x s brodova u pomorskom transportu predstavljaju oko 60 % od ukupnih SO_x emisija svjetskog prometa. Emisije NO_x s brodova u pomorskom transportu predstavljaju oko 40 % od ukupnog svjetskog transporta roba, te 15 % svih svjetskih antropogenih NO_x emisija. Ukupne emisije CO_2 u svjetskom transportu iznose oko 23 – 25 % svih emisija CO_2. U cjelokupnom svjetskom transportu roba pomorski promet učestvuje u stvaranju oko15% CO_2 emisija, što na globalnoj razini znači 3,3 – 5 % svih CO_2 emisija. Evidentno je da emisije ispušnih plinova s brodova nisu zanemarive, naprotiv zbog povećanja godišnjeg broja brodova koji prevoze najrazličitije terete i putnike oceanima i svjetskim morima, ta se količina ispuštenih plinova izgaranja povećava, a time i njihov štetni učinak. Upravo je to jedan od značajnijih razloga što su pomorska privreda i pomorski promet u stalnom procesu svekolikih promjena na globalnoj razini.



Slika 1. Emisije ispušnih plinova iz brodskog motora [2]

Emisije s brodova su trenutno odgovorne za 10 do 20 % onečišćenja sumporom u obalnim područjima, ali se očekuje porast do više od 30 % do 2020. godine na većini područja Europe te do 50 % u obalnim područjima [5]. Procjenjuje se da će broj smrtnosti u Europi, uzrokovana onečišćenjem emisijama s brodova u međunarodnom prometu rasti pa se procjenjuje da će 2020. godine broj umrlih porasti na približno 53 000 [6].

4. UČINAK BIOGORIVA NA OČUVANJE OKOLIŠA

Biogoriva su ekološki prihvatljivija od fosilnih, ali im je proizvodnja još uvijek skuplja. Biogoriva definiramo kao tekućine ili plinove koji mogu biti proizvedeni direktno iz biljaka ili indirektno iz industrijskog, komercijalnog, domaćeg i poljoprivrednog otpada. S obzirom na sirovinsku bazu iz koje se proizvode dijele se na biogoriva prve i druge generacije, te biogoriva treće generacije (iz algi). Prva generacija biogoriva se dobiva iz šećera, škroba, celuloze, biljnih ulja ili životinjskih masti, dok se za proizvodnju druge generacije biogoriva koristi poljoprivredni i šumski otpad. Sam pojam biogoriva odnosi se na sva ukapljena ili plinovita goriva koja se proizvode od biljaka i njihovih nusproizvoda, a danas se smatraju važnim sredstvom smanjenja štetnih plinova koji se ispuštaju u atmosferu te alternativom neobnovljivim fosilnim gorivima. Dvije su osnovne prednosti biogoriva pred fosilnim gorivima: količina biogoriva koja se može proizvesti nije ograničena, za razliku od fosilnih goriva koja će se prije ili poslije iscrpiti, te činjenica da je ukupni ugljikov trag biogoriva gotovo jednak nuli zbog zatvorenog ugljikova kruga. Zatvoreni ugljikov ciklus znači da biljke koje se koriste za proizvodnju biogoriva iz atmosfere uzimaju ugljikov dioksid i vraćaju kisik u postupku fotosinteze, a kasnijim izgaranjem biogoriva iz atmosfere se uzima kisik i ispušta se ugljikov dioksid. Time se ne povećava ukupna količina ugljikova dioksida u atmosferi, za razliku od otvorenog ugljikova ciklusa fosilnih goriva u kojemu se ugljikov dioksid samo ispušta u atmosferu, a nikad se iz nje ne uzima [7]. Za proizvodnju biodizelskoga goriva najvažniji su uljana repica, suncokret, soja, palma, otpadno jestivo ulje i goveđi loj [8]. Dakle, značajna svojstava biodizela u odnosu na dizelsko gorivo nalaze se u činjenici da mu je emisija štetnih plinova upola manja te da gotovo nema sumpora, fosfora, olova a količina lebdećih čestica u ispušnim plinovima ja također za upola manja od mineralnog dizela.

5. MOGUĆNOST PRIMJENE BIODIZELA KAO POGONSKOG GORIVA BRODSKIH MOTORA

Sve više propisa za sigurnost plovidbe i zaštitu okoliša koji reguliraju međunarodnu plovidbu morem unificiraju se i donose konvencijama, protokolima, direktivama i međunarodnim pravilima. Dizelsko gorivo koje služi za pogon brodskih strojeva sadrži i do

nekoliko tisuća puta više sumpora u usporedbi s dizelskim gorivom kojim se koriste automobili. Međunarodne zakonske odredbe koje se odnose na smanjenje emisija SO_2 i NOx s brodova su donesene i njihovo je provođenje započelo, tako se umjesto dopuštene granice sumpora od 4,50 % u pogonskom gorivu brodova na globalnoj razini i od 1,50% u SECA područjima, definirane Annexom VI Marpola iz 2005. godine, Pravilom 14 i Pravilom 4 te Annexom VI Marpol Konvencije od 01.01.2012. na globalnoj razini granica dopuštenog sumpora u pogonskom gorivu (bunkeru) svih brodova smanjuje na maksimalno 3,50 %, a u SECA područjima na 1,00%. Unatoč potencijalu IMO pravila za smanjenje emisija smatra se da samo ta pravila neće biti dostatna za apsolutno smanjenje ukupnih emisija s brodova. Također predviđa se da će rast svjetske trgovine premašiti postignuto smanjenje emisija CO_2 po bilo kojem scenariju. Naprotiv, procjenjuje se da će do 2050. godine emisije s brodova u pomorskom prometu doseći razinu od 15 % ukupnih svjetskih emisija nastalih transportom (BAU *businus as usualy scenario*). Jedan od načina smanjivanja potrošnje goriva jest smanjenje brzine brodova, čime bi se istovremeno smanjili i troškovi i emisije onečišćivača, posebno glavnog stakleničkog plina CO_2 [9]. Drugi značajni pristup rješavanja takvog problema je iznalaženje mogućnosti primjene biodizela kao pogonskog goriva brodova. Posebno je važno istraživanje i ispitivanje primjene alternativnih goriva u pomorskom prometu, a biodizel zbog svojih dobrih karakteristika i posebnosti postaje fokusom raznih studija i istraživanja koja imaju za cilj pronalaženje optimalnih ekonomskih, tehničkih i ekoloških opravdanosti korištenja biodizela kao pogonskog goriva brodova.

6. TEHNIČKI ASPEKTI PRIMJENE BIODIZELA KAO POGONSKOG GORIVA NA BRODOVIMA

Studije o primjeni biogoriva (biodizela) na brodovima provodile su različite države s ciljem da se pokuša smanjiti onečišćenje okoline, ponajviše emisijama ispušnih plinova koji imaju značajan utjecaj na zdravlje ljudi u naseljenim područjima, te svih živih organizama. Biogoriva se naime u pomorskom prometu koriste u vrlo ograničenim količinama, a provedene studije su pokazale kratkoročne i dugoročne učinke uporabe biogoriva na brodskim strojevima [10]. Veći broj studija izvodljivosti primjene biodizela na brodovima proveden je na području Velikih Jezera, kao npr. Great Lakes Biodiesel Market Development Program, Great Lakes Environmental Research Laboratory (GLERL), Great Lakes Maritime Research Institute, Washington State Ferries, Annis Water Research Institute, RCCL, BioMer Project, Aquabus Vancouver. Tim navedenim projektima obuhvaćeni su veliki putnički i cruiser brodovi, trajekti i manji brodovi koji su namijenjeni za istraživanje ili rekreaciju. U tim su se projektima istraživala tehnička i ekonomska učinkovitost primjene biodizela proizvedenog iz soje i iz otpadnih ulja. Studije su pokazale određene poteškoće u primjeni biodizela na brodovima. Jedan od problema očitovao se u čestom začepljenju filtara, koje se može umanjiti upotrebom biljnog ulja pomiješanog s biodizelom. Još jedan nedostatak biodizela je njegovo svojstvo otapala, zbog kojega nagriza brtve. Veliki je problem i distribucija tj. opskrbna mreža biodizelom je nedostatna. Tome je vjerojatno uzrok još uvijek visoka cijena biodizela. Svim se studijama zaključilo kako je biodizel manje štetan po okoliš jer su njegovim izgaranjem manje količine čađe i SO_x u ispušnim plinovima. Zaključak više studija je da je biodizel zbog svojih karakteristika, povoljnog utjecaja na okoliš i ekonomske održivosti gorivo koje bi u budućnosti moglo zamijeniti fosilna goriva, ali za sada je njegova primjena ograničena na manjim brodicama [10].

Studije provedene u europskim državama (Velika britanija, Norveška, Danska) pokazale su primjenjivost biodizela na manjim motorima trajekata bez potrebne prilagodbe

motora i na motorima brodica za rekreaciju. Tim studijama zaključeno je da značajnu prepreku u široj uporabi biodizela predstavlja nedostatna proizvodnja uljene repice s jedne strane, te cijena biodizela s druge strane. U posljednjih dvadesetak godina, najveći proizvođači dizelskih dvotaktnih sporokretnih i četverotaktnih srednjekretnih motora istražuju mogućnost primjene i ekonomsku opravdanost biogoriva kao pogonskog goriva za te motore u zamjenu za fosilna goriva. U pomorskom sektoru manje se istražuje primjena biogoriva zbog ekonomskih aspekata fosilnih goriva tj. brodskih goriva na svjetskom pomorskom tržištu, odnosno njihove relativno manje cijene u odnosu na biogoriva. Ta relativno velika razlika u cijeni biogoriva u odnosu na fosilna goriva koja se primjenjuju na brodskim pogonima glavna je prepreka istraživanju primjene biogoriva na brodskim motorima. MAN B&W vršio je testiranja na stacionarnim motorima snage 2,6 – 8,7 MW. Istraživanja su pokazala da su biogoriva primjenjiva na tim motorima, ali se treba pažljivo kontrolirati njihova temperatura kako bi se održala točna razina viskoznosti. Kada se primjenjuju biogoriva u dvotaktnim sporokretnim dizelskim motorima na brodovima potrebno je prilagoditi sustav goriva motora vršeći preinake na cjevovodima, skladišnim tankovima, pripremi goriva, pumpama, brtvama i dr. Troškovi navedenih preinaka motora daleko su manji u odnosu na razlike u cijeni goriva, a oni iznose svega nekoliko postotaka cijene motora.

Wartsila je devedesetih godina vršila istraživanja o kompatibilnosti biogoriva s njihovim motorima, te je ulje uljane repice identificirano kao najkompatibilnije biogorivo koje se u Wartsilinim motorima može koristiti uz minimalne preinake. Rezultati testova primjene biogoriva su dobri, a vremenski interval između generalnog pregleda ostaje isti kao i kod motora na teško gorivo [11]. Svi najznačajniji proizvođači motora istražujući mogućnost primjene biodizela kao pogonskog goriva koje će zamijeniti fosilna pogonska goriva identificirali su slične probleme, koji se uglavnom odnose na kavitacije visokotlačnih pumpi goriva, korozivno djelovanje biodizela na dijelove motora, te začepljenja filtara i cjevovoda goriva.

7. ZAKLJUČAK

Povećanje udjela stakleničkih plinova na globalnoj razini posljedica su utjecaja konvencionalnih fosilnih goriva. Kako je potrošnja energije u pomorskom prometu sve veća potrebno je razvijati nove i alternativne izvore energije i goriva, koji će zadovoljiti potrebe pomorskog prometa i potrebe ostalih sektora.

Alternativna goriva kao obnovljivi izvori su sposobni odgovoriti na ograničenje trenutno postojećih izvora energije i njihove povećane potrošnje te mogu doprinijeti daljnjoj modernizaciji energetskog sektora i sveukupnoj strategiji održivog razvoja. Nadalje, obnovljivi izvori doprinose industrijskoj konkurentnosti i imaju pozitivan utjecaj na regionalni razvoj i zapošljavanje.

Biodizel je prvo, i za sada jedino, alternativno gorivo koje je prošlo kompletnu evaluaciju emisije ispušnih plinova i potencijalnih zdravstvenih rizika po programu propisanom od agencije EPA (*Environmental Protection Agency*). Ova ispitivanja su pokazala da dizelski motori s pogonom na biodizel imaju značajno manju emisiju dima i čestica. Smanjenje emisije u prosjeku iznosi oko 40 %. Niža emisija dima i čestica postiže se i pri primjeni mješavine konvencionalnog dizelskog goriva i ME-a. Slični rezultati se dobijaju i u pogledu redukcije emisije CO (smanjenje oko 40 %) i ugljikovodika (smanjenje oko 65 %). S obzirom na vrlo nizak sadržaj sumpora u biodizelu, moguće je efikasno primjenjivati naknadni tretman ispušnih plinova u tzv. de-NOx katalizatorima. Na taj se način efikasno

smanjuju emisije NO_x. Značajno je istaći i da je emisija policikličnih aromatičnih ugljikovodika (PAH - Polycyclic Aromatic Hydrocarbons), izrazito kancerogenih frakcija čestične emisije, niža za oko 80 %.

Povećanje energetske učinkovitosti u sektoru prijevoza, pa tako posebno i u pomorskom prometu jedan je od glavnih ciljeva Strategije održivog razvitka. Određivanje budućih energetskih potreba i uporaba energenata važan je segment u planiranju energetskih sustava koji se planiraju za razdoblje od 20 do 40 godina. Planira se smanjenje emisija stakleničkih plinova za 20 % do 2020. godine, povećanje udjela obnovljivih izvora energije na 20 % te 20 %-tno povećanje energetske efikasnosti. Ostvarenjem tih ciljeva moguće je postići pretpostavke za potpunu dekarbonizaciju predviđenu za 2050.-tu godinu.

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CJELOVIT PRISTUP OKOLIŠU I GMO – SLUČAJ ZLATNA RIŽA

HOLISTIC APPROACH TO THE ENVIRONMENT AND GMOs – THE CASE OF GOLDEN RICE

Ivica Kelam*, Darija Rupčić Kelam**

* Sveučilište Josipa Jurja Strossmayera u Osijeku, Centar za integrativnu bioetiku, Osijek, Hrvatska
** Sveučilište Josipa Jurja Strossmayera u Osijeku, Filozofski fakultet, Osijek, Hrvatska

autor za korespondenciju: Ivica Kelam, e-mail: kelamivica@gmail.com

Prethodno priopćenje

SAŽETAK

Cilj je rada na primjeru zlatne riže, ukazati na temeljne razlike između pristaša i protivnika tehnologije genetičkog modificiranja. Pristaše zlatnu rižu predstavljaju kao ogledni primjer blagodati tehnologije genetičkog modificiranja te istovremeno optužuju protivnike za odgađanje komercijalne sjetve. Protivnici od samih početaka ukazuju na problem zlatne riže kao parcijalnog instant rješenja nedostatka vitamina A, pri čemu se zanemaruje kompleksnost problema nedostatka vitamina A u prehrani stanovnika nerazvijenih zemalja svijeta. Danas, 18 godina nakon predstavljanja zlatne riže u medijima, ova tehnologija još uvijek nije spremna za komercijalnu upotrebu, ne zbog protivljenja Greenpeace-a i ostalih protivnika, već zbog elementarne činjenice da unošenje genetički modificiranih svojstava u živi okoliš predstavlja izazov na koji znanost još uvijek ne može adekvatno odgovoriti. U radu ćemo na primjeru zlatne riže ukazati na važnost cjelovitog pristupa okolišu, u čemu nam integrativna bioetika daje važan uvid u kompleksnost i nepredvidljivost uvođenja novih biotehnoloških izuma u okoliš.

***Ključne riječi*:** *biotehnološka industrija, zlatna riža, Greenpeace, nedostataka vitamina A, integrativna bioetika*

ABSTRACT

The aim of this paper is to point out the fundamental differences between supporters and opponents of genetic modification technology by using a brief analysis of the development and controversy that surrounds the genetically modified golden rice. Supporters present golden rice as a typical example of the benefits of genetic modification technology and, at the same time, accuse opponents for delaying commercial planting. Opponents from

the very beginning point to the problem of golden rice as partial quick fix of vitamin A deficiency, whereby the complexity of the problem of vitamin A deficiency in the diet of the population of underdeveloped countries is being ignored. Today, 18 years after the presentation of golden rice in the media, this technology is still not ready for commercial use, not because of opposition by Greenpeace and other opponents, but because of the elementary fact that introducing genetically modified plants into a living environment is a challenge that science cannot yet adequately respond. In this paper on the golden rice example, we will point out the importance of holistic approach to environment where integrative bioethics gives us an insight into the complexity and unpredictability of introducing new biotechnological inventions into the environment.

Keywords: *biotech industry, golden rice, Greenpeace, vitamin A deficiency, integrative bioethics*

1. UVOD

Za razvoj i uspješnu implementaciju genetički modificiranih usjeva, jedan je od ključnih elemenata podrška javnosti. Budući da od samih početaka kontinuirano postoji otpor javnosti prema sjetvi genetički modificiranih usjeva, zlatna je riža osim svojih zdravstvenih svojstava, predstavljena i kao ogledni primjer dobrobiti i korisnosti tehnologije genetičkog modificiranja. Nevladine udruge na čelu s Greenpeaceom tvrde da zlatna riža nije rješenje problema nedostatka vitamina A, već sredstvo nametanja neželjene tehnologije sumnjičavoj javnosti. Saga oko zlatne riže traje već 18 godina, te se u tom razdoblju razmjenjuju teške optužbe od želje za korporativnom dominacijom do optužbi za holokaust. U radu ćemo kroz kratku analizu povijesti razvoja i kontroverzi oko zlatne riže poseban naglasak staviti na nedostatak istraživanja utjecaja zlatne riže na okoliš i društvo iz kojih je vidljivo da ova tehnologija unatoč svojoj plemenitoj namjeri ostaje samo neostvareni san svojih tvoraca.

2. ZLATNA RIŽA – PREGLED POVIJESNOG RAZVOJA

Ingo Potrykus, profesor sa švicarskog saveznog instituta za tehnologiju, pojavio se na naslovnici Time Magazina a ispod njega je bio naslov „Ova riža mogla bi spasiti milijun djece godišnje“ [1]. U članku se opisuje Potrykusovo stvaranje genetički modificirane riže obogaćena karotenom koja bi prema njegovim tvrdnjama mogla spasiti djecu u nerazvijenim zemljama svijeta od sljepoće i smrti. Projekt zlatna riža započet je još 1980-ih godina. Dvanaest godina kasnije u kolovozu 2012., nevladina udruga Greenpeace alarmirala je javnost zbog studije objavljene u znanstvenom časopisu u kojoj se opisuje pokus s hranjenjem genetički modificiranom rižom 24 kineske djece u dobi od 6 do 8 godina [2]. Greenpeace je tvrdio da navedena studija, koju je podržalo Ministarstvo poljoprivrede Sjedinjenih Američkih Država, nije mogla biti provedena bez kršenja postulata znanstvene i medicinske etike. Predstavnik Greenpeace za istočnu Aziju u reagiranju na ovu vijest, izjavio je: „Nevjerojatno je uznemirujuće pomisliti da je američko istraživačko tijelo koristilo kinesku djecu kao zamorce za genetički modificiranu hranu, unatoč jasnoj direktivi protiv ovog eksperimenta koje su izdale kineske vlasti 2008 godine“ [2]. Kontroverzna studija na koju se referira Greenpeace je studija koja je procjenjivala učinkovitost bio konverzije β-karotena u vitamin A kod djece hranjene zlatnom rižom [3]. Istraživanje, objavljeno u American Journal

of Clinical Nutrition u 2012., zaključilo je da je β-karoten u zlatnoj riži jednako učinkovit kao čisti β-karoten u ulju i bolji od onog u špinatu u zadovoljavanju potreba djece za vitaminom A [3]. Promotori zlatne riže iskoristili su ovu studiju u medijske svrhe, neprestano ističući opravdanost što brže kultivacije zlatne riže na polja. No, nakon tri godine neočekivano je 29. srpnja 2015. izdavač povukao članak pri čemu je naveo etičke razloge za to [4]. Prvo, autori nisu pružili dovoljno dokaza da je studiju odobrio lokalni odbor za etiku u Kini na način koji je u potpunosti u skladu s smjernicama Nacionalnog instituta za zdravstvo. Drugo, nisu mogli dokazati punu suglasnost roditelja djece uključenih u studiju putem dokumentarnih dokaza, budući da roditelji nisu uopće bili upoznati s činjenicom da će se njihova djeca hraniti znatnom rižom. Nakon povlačenja studije, u lipnju 2016. skupina od 107 nobelovaca u otvorenom pismu javnosti optužuje protivnike GMO-a, u prvom redu Greenpeace za smrt milijuna djece i odraslih u siromašnim zemljama diljem svijeta [5]. Peticija je izazvala veliku pozornost u javnosti, budući da su promotori biotehnologije iskoristili ovo otvoreno pismo da još jednom pokušaju javnosti nametnuti nužnost što hitnije implementacije genetički modificiranih usjeva, o čemu je jedan od autora rada Ivica Kelam javno progovorio u dnevnim novinama *Glas Slavonije* pri čemu je istaknuo slijedeće: „Posebno iritira emotivna obojenost pisma, koja prelazi u otvorenu ucjenu pri čemu se legitimno protivljenje Greenpeacea "zlatnoj riži" naziva "zločinom protiv čovječnosti". To potvrđuje sumnje da je ideja ove peticije potekla iz biotehnološke industrije, koja jedina ima koristi od GMO-a. Nije Greeenpeace odgovoran za propast "zlatne riže", o kojoj se govori u pismu, nego ta genetički modificirana riža ni nakon više od 20 godina istraživanja nije spremna za komercijalnu sjetvu. Stoga je iluzorno optuživati Greenpeace i kritičare GMO-a za njezinu propast (…) GM usjevi sredstvo su moći kojim međunarodne korporacije žele, na štetu zdravlja ljudi, životinja i okoliša, ostvariti što veći profit i moć. Poražavajuća je činjenica da se 107 nobelovaca dalo svjesno ili nesvjesno izmanipulirati i dovesti u situaciju da promiču korporativne interese a na štetu općeg dobra [6]."

Da bi se razumjela važnost problema koji je proizašao izumom zlatne riže i kontroverza koja se razvila, treba prvo sagledati neke činjenice. Više od pola svjetske populacije jede rižu na dnevnoj osnovi budući da im je riža temelj svakodnevne prehrane. Riža je slab izvor mnogih esencijalnih mikro-elemenata i vitamina. U jugoistočnoj Aziji 70 % djece mlađe od 5 godina pati od nedostatka vitamina A, koji dovodi do povećane osjetljivosti na razna oboljenja i do problema s vidom, koja u težim slučajevima vodi prema sljepoći. Prema predviđanjima UNICEF-a povećanje unosa vitamina A kroz prehranu moglo bi spriječiti prijevremenu smrt između 1 i 2 milijuna djece u dobi od 1 do 4 godine [7]. Pobornici tvrde da nema alternative zlatnoj riži u borbi protiv nedostatka vitamina A, te optužuju vladine agencije i kritičare za ugrožavanje života milijuna djece. U optužbama se posebno ističe neukusni apel Adriana Dubocka koji je izračunao kako 50 000 djece oslijepi svaki mjesec zbog kašnjenja s dovođenjem zlatne riže na tržište [8]. Drugi navode kako su vladine agencije i nevladine udruge sudionici holokausta usmjerenog protiv siromašne djece globalnoga Juga [9]. Nadalje, kako bi se ubrzalo dovođenje zlatne riže na tržište i smanjili troškovi razvoja, pobornici zahtijevaju opće smanjenje standarda za procjenu rizika kod genetički modificiranih biljki [10].

Pobornici genetičkog modificiranja krivce za početak komercijalne sjetve zlatne riže pronalaze u prekomjernoj regulaciji i konstantnoj kampanji anti-GMO aktivista i organizacija poput već spomenutnog Greenpeacea. Tako je primjerice Bjørn Lomborg, autor knjige *The Skeptical Environmentalists* napisao članak u veljači 2013. godine, u kojem navodi bez ikakvih dokaza da se komercijalna sjetva zlatne riže odgađa već 12 godina zbog „neumoljivog suprotstavljanja GM hrani" od strane „bogatih, dobronamjernih stanovnika globalnog Zapada", dok je za to vrijeme „oko 8 milijuna djeca u svijetu umrlo zbog nedostatka vitamina A" [11]. Lomborg poseže za emotivnom ucjenom, budući da pomoću preuveličavanja broja

umrle djece zbog nedostatka vitamina A, želi izvršiti pritisak na javnost i regulatorne službe s ciljem nekontroliranog uvođenja genetički modificiranih usjeva na polja, pri čemu zaboravlja elementarnu biološku činjenicu na koju upozorava članak objavljen u *Science* 2008., u kojem se ističe kako je pred komercijalnom sjetvom zlatne riže „dug put“, u procesu križanja zlatne riže s sortama riže Indica koja je najpopularnija među poljoprivrednicima i potrošačima širom Azije [12]. S druge strane kritičari zlatne riže poput nutricionistkinje Marion Nestle navode slijedeće:„Iako još nije komercijalno dostupna, danas se zlatnom rižom pobornici biotehnološke industrije naveliko koriste u uvjeravanju javnosti, kako dobrobit genetski manipulirane hrane nadmašuje svaku opasnost za zdravlje, okoliš ili društvo. Ona u javnosti treba ojačati uvjerenje, prema kojem je biotehnologija ključ za rješenje svih problema povezanih s prehranom rastućeg stanovništva planete. No, imajući na umu osnovna načela prehrane, vjerojatnost da riža s povećanim sadržajem beta karotena može riješiti nedostatak vitamina A i time nastale zdravstvene probleme siromašnog stanovništva juga, naprosto ne postoji. Biološka dostupnost beta karotena iznimno je niska samo 10 % ili manje. Da bi postao aktivan, beta karoten (provitamin A) mora se uz pomoć enzima u crijevnoj sluznici ili jetri podijeliti na dvije molekule vitamina A, beta karoten isto kao i vitamin A topiv je u mastima. Dakle, za usvajanje, probavu i prijenos beta karotena neophodan je funkcionalni probavni sustav, te odgovarajuća količina masti, bjelančevina i energije u hrani. Mnoga djeca sa simptomima nedostatka vitamina A pate i od općenite pothranjenosti, kao i od crijevnih zaraza koje onemogućavaju usvajanje beta karotena. Puno djelotvornije, cilj se može postići kombinacijom više mjera: dopunom i pojačanjem hranidbenih sastojaka, općenito poboljšanjem hranidbenih navika, te što je posebice važno poboljšanjem društveno-ekonomskog položaja stanovništva. Iz tih razloga dobrobit koju najavljuje biotehnologija ostaje samo teoretska mogućnost“ [13]. Vandana Shiva tvrdi da zlatna riža nije rješenje za problem nedostatka vitamina A, budući da prva generacija zlatne riže proizvodi u sebi premalo vitamina A. Preporučena dnevna doza vitamina A za odraslog čovjeka iznosi 750 mikrograma, a da bi je dobio, odrastao čovjek bi trebao prema izračunu Vandane Shive dnevno pojesti 2,272 kilograma suhe riže na dan, koja nakon kuhanja nabubri na nekoliko kilograma. Prema njenim riječima nije rješenje genetički modificirati rižu, već treba omogućiti ljudima raznoliku prehranu, budući da mnoge biljke koje rastu u tim dijelovima svijeta imaju puno veći postotak vitamina A u sebi. Žene u Bengalu koriste više od 200 vrsta različitih biljaka u svojoj prehrani. Više od 3 milijuna ljudi u Bangladešu zahvaljujući uzgoju povrća u svome vrtu bogatog vitaminom A riješilo se opasnosti od sljepoće i bolesti [14]. Peter Rosset tvrdi da zlatna riža ne rješava problem nedostatka vitamina A: „Nedostatak vitamina A nije dobro opisati kao problem, već radije kao simptom. (…) Ljudi ne doživljavaju nedostatak vitamina A zbog toga što riža sadrži premalo vitamina A ili beta karotena, već zbog toga što je njihova prehrana reducirana samo na rižu i gotovo ništa drugo“ [15]. Spomenimo kako se prevalencija nedostatka vitamina A u nerazvijenim zemljama značajno smanjila tijekom vremena. Godine 1991. 39 % djece u dobi od 6 - 59 mjeseci bolovalo je od nedostatka vitamina A u tim zemljama, da bi on pao na 29 % u 2013. U istočnoj i jugoistočnoj Aziji i Oceanije, primjetan je još drastičniji pad od 42 % do 6 %, a u Latinskoj Americi i Karibima s 21 % na 11 %. Međutim, u Južnoj Aziji i Subsaharskoj Africi, ona je i dalje ostala visoka, te se malo toga promijenilo u ovim regijama tijekom protekla dva desetljeća. Tako je primjerice, u 2013. prevalencija nedostatka vitamina A bila je 44 % u Južnoj Aziji i 48 % u Subsaharskoj Africi. Također, važno je napomenuti da se više od 95 % smrti povezanih s nedostatkom vitamina A dogodilo u ove dvije regije [16]. S druge strane promotori zlatne riže opovrgavaju navode Vandane Shive, te ističu da nove generacije zlatne riže sadrži u sebi puno veću koncentraciju beta karotena, te bi prema izračunima, već svakodnevna konzumacija jedne zdjelice zlatne riže po osobi značajno doprinijela smanjenju nedostatka vitamina A [17].

3. ZLATNA RIŽA I OKOLIŠ

Unatoč povećanoj koncentraciji beta karotena u novim generacijama zlatne riže, treba istaknuti da nakon više od 25 godina istraživanja i milijuna dolara utrošenih u razvoj, zlatna riža nije još spremna za komercijalnu sjetvu, unatoč višegodišnjim pokusnim sjetvama provođenim od strane međunarodnog instituta za istraživanje riže s Filipina. Štoviše, pokusne sjetve na Filipinima pokazale su da zlatna riža ima manji prinos u odnosu na konvencionalne sorte [18]. Nadalje, indijski su istraživači u studiji objavljenoj 2017. otkrili da geni zlatne riže imaju neželjene učinke. Kada su unijeli gene zlatne riže u njihovu visoko rodnu i agronomski superiornu sortu indijske riže, ona je postala blijeda i zakržljala, cvjetanje je odgođeno a korijenje je abnormalno poraslo. Prinosi su bili tako smanjeni da nije bila prikladna za uzgoj [19]. Poseban problem predstavlja mogući negativni utjecaj na okoliš kroz međusobnu oplodnju s divljom rižom. Studije potvrđuju da hibridi nastali međusobnom oplodnjom iskazuje neočekivane biološke karakteristike, poput boljih značajki u vegetativnom i reproduktivnom stadiju, duže stabljike, više izdanaka vlati i klasića po biljki [20]. Ovi učinci mogu prouzročiti nekontrolirano širenje ovih hibridnih biljaka u okolišu. Poboljšana sposobnost biljaka bila je neočekivana istraživačima, koji ove promjene ne mogu objasniti specifičnim promjenama unesenim u biljke uz pomoć genetičkog inženjeringa. To znači da imamo vrlo ograničenu sposobnost predviđanja potencijala proliferacije i bioloških značajki transgenske riže i njenih križanaca. Drugi problem je da u slučajevima prelaska na lokalne sorte riže mogu doći do značajnih fluktuacija u sadržaju vitamina A riže. Genetska konstrukcija nije uvijek pouzdano prenesena iz jedne biljke riže do sljedeće generacije biljaka [21]. Stručnjaci ističu da kod međusobnog križanja biljaka dolazi do toga da veći broj gena mijenja aktivnost, dok do toga ne dolazi kod transgeneze (vidi npr. [22, 23]). Promjene u aktivnostima gena zapravo su vrlo česte u postupcima oplemenjivanja biljaka. Biljke također prirodno reagiraju na uvjete okoliša prilagođavajući svoju aktivnost gena. Reprodukcija i rast mogu također uzrokovati aktivnost koja dovodi do istovremene promjene mnogih gena. No treba naglasiti da je broj promijenjenih gena od male važnosti, budući da su pojedini segmenti DNK u cijelosti pod kontrolom složenih mehanizama prirodne regulacije gena, odnosno fleksibilnog sustava koji reagira na promjene u uvjetima na način da sinhronizira aktivnost gena. U genetičkom modificiranju biljaka, ne koriste se prirodni mehanizmi regulacije gena, štoviše, oni se namjerno zaobilaze. Kod genetički modificirane biljke djelovanje umetnutih gena regulirano je promotorima koji nisu podložni općem reguliranju gena u biljkama i koji reguliraju ekspresiju umetnutih gena. To je razlog zašto biljke ne mogu kontrolirati novi metabolički put. Neke biljke reagiraju na uvođenje stranih gena isključivanjem ili deaktiviranjem novo umetnutih gena, ovaj fenomen naziva se utišavanje gena. Ovo je prirodni zaštitni mehanizam koji se nalazi u biljkama, te služi kao obrana od kontaminacija virusnom DNK [24]. Da bi se spriječila inaktivacija umetnutog genetički modificiranog genetskog konstrukta i osigurala njegova biološka ekspresija, upotrebljavaju se promotori koji prisilno aktiviraju genetički modificirane umetnute gene. Najkraće rečeno, znanstvenici pokušavaju koristiti genetičko inženjerstvo za reprogramiranje biljaka. Nasuprot tome, konvencionalno oplemenjivanje biljaka koristi prirodni genetski potencijal u biljkama i njihov sustav regulacije gena. Ova je razlika iznimno bitna i za pojašnjenje zdravstvenih rizika i procjenu posljedica ulaska transgena u ekološke sustave i genski bazen divljih i kultiviranih biljaka. Sve promjene u ekspresiji izvornih gena u biljci uzrokovane umetanjem dodatnih umetnutih gena trebaju se uvijek pažljivo ispitati, jer to može biti pokazatelj poremećaja u normalnom sustavu regulacije gena. Budući da umetanje genetički modificiranih gena u biljke ni na koji način nije precizan proces, može se očekivati da će se genetički modificirani gene implementirati na neželjeni položaj te dovesti do pleiotropnog učinka (kada gen utječe na nekoliko svojstava istovremeno). Genetska intervencija kao posljedica umetanja genetički

modificiranog gena u biljku može rezultirati čitavim nizom bioloških učinaka koji su relevantni za procjenu rizika. Moguće reakcije uključuju opće slabljenje biljaka popu primjerice povećane osjetljivosti na bolesti, niži prinosi, smanjena tolerancija biljke na stres kao što su klimatski uvjeti, ali i poboljšane sposobnosti biljke kroz primjerice povećanu proizvodnju peludi i sjemenki ili proizvodnju neželjenih, antinutritivnih, imunogenih ili otrovnih komponenti. Na primjer kod zlatne riže, postoji nenamjerna promjena u sastavu karotenoida u stabljici riže [25]. Novo umetnuti geni aktivni su u cijeloj biljci, ne samo u zrnu, pa tako i oni djeluju zajedno s komponentama u zelenim dijelovima biljke. Za sada nije jasno kakav to ima učinak na biljku zlatne riže u cjelini. Postoji vjerojatnost da će određeni okolišni uvjeti izazvati neželjene reakcije u genetički modificiranim biljkama ili može biti potrebno nekoliko generacija biljaka da dođe do takve reakcije. Zanimljivo je kako sustavna istraživanja međudjelovanja genetički modificiranih biljaka i njihovog okoliša trenutno nisu potrebna u okviru procesa odobravanja EU. No treba istaknuti da postoji sve veći broj znanstvenih istraživanja koji se bave neželjenim svojstvima u genetički modificiranim biljkama, kao npr. kod petunije [26], pamuka i kukuruza [27], krumpira [28], pšenice [29] i soje [30]. Navedena istraživanja zorno pokazuju koliko su nužna ovakva istraživanja za procjenu utjecaja na okoliš genetički modificiranih biljaka. Gore spomenuta studija genetički modificirane pšenice pokazala je da, za razliku od biljaka iz staklenika koje ne pokazuju neočekivane reakcije, biljke pšenice koje su izrasle na pokusnom polju imale su znatno niži prinos i pokazale su veće stope zaraze s izuzetno toksičnim gljivicama ergot. Ovo pokazuje koliko su relevantna ova pitanja za procjenu rizika [31]. Stoga Zeller i sur. u svom radu zahtijevaju provođenje studija o ekološkom ponašanju genetički modificiranih biljaka. Nadalje [32] u svom radu preporučuju uvođenje testova otpornosti na stres. Ovo se odnosi na sustavne studije reakcije genetički modificiranih biljaka na okolišne čimbenike u kontroliranim uvjetima. Kada je u pitanju puštanje genetički modificirane zlatne riže u okoliš, tada treba imati na umu da u regijama gdje se planira sjetva zlatne riže raste korov riža (vrsta divlje riže koje se klasificira i tretira kao korov) s kojom se zlatna riža može lako međusobno križati preko peludi i na taj način prenijeti umetnute modificirane gene u korov rižu. Vrste divlje riže vrlo su česte u mnogim poljoprivrednim regijama [33] [34]. Genetski prijelaz između kultivirane riže u poljima i divljih sorti koje rastu u okruženju često se događa [34]. U takvim okolnostima teško se može spriječiti nekontrolirano širenje u okoliš genotipa čija je prirodna regulacija gena modificirana tehničkom primjenom. Postoji mogućnost da se genetički modificirani geni mogu širiti i akumulirati u korov riži [34]. Studije rađene u Kini pokazuju da hibridi nastali uslijed križanja između kultivirane genetički modificirane riže i njenih divljih srodnika mogu pokazati neočekivane biološke značajke. Na primjer, koncentracija Bt toksina otrovnih za insekte povećana je u nekim biljkama koje su bile križanac između biljaka genetički modificirane riže i divlje sorte [35]. Nadalje, hibridne biljke bile su poboljšane sposobnosti u usporedbi s ne-transgeničnim roditeljskim biljkama [36]. Ti učinci mogu uzrokovati širenje rasprostranjenosti biljaka. Poboljšana sposobnost hibridnih biljaka bila je neočekivana, te ih znanstvenici ne mogu objasniti specifičnih promjena koje su uvedene kao posljedica genetičkog modificiranja u biljku. Ovo znači da su znanstvenici ograničeni u sposobnosti predviđanja potencijala za nekontrolirano širenje i bioloških značajki genetički modificirane riže i njenih križanaca. U svakom slučaju, izgleda malo vjerojatno da se strani genetički modificirani geni, jednom kada se prošire među divljom populacijom, mogu ograničiti odnosno vratiti natrag u laboratorij (vidi [37]). Najnovija istraživanja pokazuju da će buduće klimatske promjene uzrokovati da će genetički modificirani geni još brže i lakše prelaziti u populaciju korov riže [38]. Treba naglasiti da ova spomenuta karakteristika riže, koja može dugo ostati neaktivna da širi sjeme izvan polja i u okoliš, predstavlja opasnost za ekosustav i može uzrokovati ozbiljne poteškoće u uzgoju riže općenito. Genetska razmjena nije jednosmjerna ulica, ona se odvija u oba smjera. Razmjena

gena između kultivirane riže s polja i okolnih sorti divlje riže može se razviti u redovni ciklus. Polen divljih rižinih sorti može također odvesti genetički modificirane gene natrag u polja - čak i na polja gdje se uzgaja konvencionalna riža. Na taj način kultiviranje zlatne riže potencijalno prijeti izazivanjem nepredvidljivog i izuzetno problematičnog scenarija na način da: 1. Dođe do ukrštavanja genetički modificiranih sorti rižinih kultura i njihovih divljih srodnika, koje mogu ispoljiti iznenađujuće biološke osobine pomoću kojih se mogu brzo proširiti u okoliš, s nepredvidivim ekološkim posljedicama. 2. Jednom kada se genetički modificirani strani geni uspiju pomiješati s populacijom divlje riže, nije više moguće kontrolirati, ograničiti ili preokrenuti njihovo širenje. 3. Osim toga, treba biti svjestan da kako se genetički modificirani strani geni šire u populaciji divlje riže, neizbježna je kontaminacija konvencionalnih usjeva riže, a što to znači za sigurnost opskrbe hrane ne treba naglašavati. Možemo zaključiti da u slučaju buduće komercijalne sjetve zlatne riže nužno je pridržavati smjernica istaknutih u radu Bauer-Panskusa i suradnika koji ističu slijedeće: Mogućnost otklanjanja genetski modificiranih biljaka treba biti preduvjet za njihovu uporabu. Ne može se znanstveno predvidjeti s odgovarajućim stupnjem sigurnosti srednjoročni i dugoročni učinak njihovog puštanja na evolucijske procese, biološku raznolikost i ljudsko zdravlje. Puštanje genetički modificiranih usjeva u okoliš može se prihvatiti samo ako se može kontrolirati dužina trajanja i mjesto puštanja (vidi [39]. Ukoliko bi se držali ovih smjernica u prosudbi komercijalne sjetve genetički modificirane riže ne bi trebali strahovati od mogućih štetnih posljedica, budući da bi sjetva definitivno bila zabranjena.

4. ZAKLJUČAK

Slučaj zlatne riže već 18 godina izaziva veće ili manje zanimanje javnosti, zbog silnih kontroverzi koje izaziva. Nakon silnih obećanja o spašavanju milijuna djece od sljepoće i smrti, ništa od navedenog nije ostvareno. Promotori zlatne riže za to optužuju protivnike biotehnologije na čelu s Greenpeaceom, te uporno ističu da su kritičari zlatne riže i prestroga regulatorna pravila glavni krivci za kašnjenje u komercijalnoj sjetvi zlatne riže. Kao što je vidljivo u radu, istina je puno jednostavnija. Zlatna riža jednostavno zbog svoje kompleksnosti i mnoštva problema od smanjenog prinosa, do pojave odumiranja biljaka na poljima, nije još uvijek u komercijalnoj sjetvi, te je vrlo upitno kada i da li će uopće biti spremna za komercijalnu sjetvu. Neuspjeh uspješne kultivacije zlatne riže, još jednom potvrđuje koliko je teško neko svojstvo koje je u laboratoriju genetički modificirano i implementirano u biljku kasnije teško uspješno prenijeti u okoliš i stvarni svijet. Saga oko zlatne riže potvrđuje sumnje kritičara o mnoštvu nepoznanica koje okružuju ovu tehnologiju, te je jedino razumno u razvoju i eventualnoj sjetvi zlatne riže strogo se pridržavati načela opreza, budući da kao što pokazuju istraživanja može doći do nepovratne štete za okoliš, te svakako imati u vidu holistički pristup koji sagledava sve interakcije koje se događaju unutar okoliša u kojem bi se trebala uzgajati zlatna riža.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

ASSESSMENT OF THE IMPACT OF GLOBAL CLIMATE CHANGE ON THE SURFACE RUNOFF OF THE UPSTREAM OF THE CHIRCHIK RIVER

Kodirov Sobirjon M.*

* Tashkent institute of Irrigation and Agricultural Mechanization Engineers, Tashkent, Uzbekistan

corresponding author: Kodirov Sobirjon M., e-mail: smqodirov@gmail.com

Preliminary note

ABSTRACT

The Charvak Reservoir is the largest reservoir in the territory of the Republic of Uzbekistan. It is surrounded by The Tien Shan Mountains. The Chirchik River begins from the dam of the reservoir (mean annual flow rate 208 m^3/s) and it is one of the biggest right tributaries of The Syr Darya River. The Chatkal River (long term flow rate 108 m^3/s) is the biggest tributary of The Chirchik River. On the basis of long-term data from 8 hydrological and meteorological stations, intra annual surface runoff distribution was evaluated. Main hydrologic features of The Chatkal River, detection and removing of linear trends, test for homogeneity, longterm fluctuations of the time series, calculation of annual stream flow under different frequency distributions were estimated The data set of statistical characteristics and their standard errors are estimated, for average flow rates the error does not exceed 10%, for the coefficient of variation; the error does not exceed 15%. To describe frequency distribution The Gumbel Distribution was applied.

Keywords*: the Chatkal River; the Charvak Reservoir; hydrology; intra-annual runoff distribution; average flow rate*

1. INTRODUCTION

1.1. General information about focusing area

The article deals with features of the hydrological regime of the Chatkal River which is located in the territory of Uzbekistan and Kyrgyzstan. Chatkal – is a mountain river and it begins from a nameless moraine lake in the territory of Kyrgyzstan [1]. It flows mainly to the west along the westernmost part of The Tien Shan Mountains. Near to the Burchmulla village (Tashkent region, Uzbekistan), it flows into The Charvak reservoir. Length of the river is 217 km (until 1965 223 km) and catchment area is 6580 km^2 (7110 km^2 until 1965) [1]. The

study of the hydrological regime of the Chatkal River is necessary for effective regulation of water resources. *The objective* of the research is to study the hydrological regime of the Chatkal River and to evaluate the main characteristics of the intra-annual distribution of river surface runoff.

As observation data, we used a series of meteorological and hydrological characteristics for 8 stations and we set up hydrological series of the average monthly, daily annual water discharge data set. *All meteorological stations of the study* area considered being high mountain stations in terms of altitude and all rivers surrounding The Charvak Reservoir format Charvak reservoir catchment area. The nearest meteorological station to the Charvak reservoir is Chimgan and it is located on 1265 m above the sea level, the farthest station Oigaing, on the other hand, located on 2175 m above the sea level.

Hydrologic and meteorological stations opened the last century. After filling the Charvak reservoir The Chatkal River – hydrologic station at Charvak village closed. At present, the nearest hydrological station to The Charvak Reservoir is located upstream of the mouth of The Khudoydodsay River [2].

2. EXPERIMENTAL

2.1. Initial data

The paper, we used the average monthly and average annual water discharge data from 4 hydrological stations of the focusing area. Location of the hydrologic stations is given in table 1. The data of annual flow rates received from the department of water cadaster and meteorological measurements, Centre of Hydrometeorological Service at Ministry of Emergency Situations of The Republic of Uzbekistan and hydrologic yearbooks of the library of Russian State Hydrometeorological University.

Table 1. Hydrological stations of the Chatkal River

№	River – station	*F*, km	The period of observation	observations, year
1	Chatkal River – at Khudoydodsay station	6580	1965 - 2014	50
2	Chatkal River – at Nayzatukay station	5520	1933 - 1963	26
3	Chatkal River – at Ters station	4090	1933 - 1975	39
4	Chatkal River – at Charvak village station	7110	1932 - 1963	35

2.2. Extension of the records and observations

The manner in which the various models available for filling in missing data and extension of records of the annual stream flow, corresponding to the availability and the length of data are based on the following methods commonly used methods: 1) for a long period of observations, the calculation is carried out directly from the observation data; the time period from this dataset is used in computations if its duration is 50 - 60 years and more; 2) if observation is short it should be filled relatively to a longer period of observation by

applying the method of hydrological analogy (river analog); 3) in the case of a series of observations very short or no data at all, annual runoff is determined by generalizations of the results of studied river or the water balance equations are used [3].

For design at a site where data are available the method of *hydrological analogy* was applied. A hydrological station, where it is necessary to fill the gaps of records of The Chatkal River, the parameters of the linear regression equation for the connection of average annual discharge is calculated. Average-flows gauged in the Khudoydodsay station are related to contemporaneous data for the Charvak village station, enabling average-flow characteristics for the Charvak village station to be transferred through the relation to the Khudoydodsay station. Figure 1 shows average flow rate relationship between two hydrologic stations. Statistically, correlation coefficient should be at least 0.7. In our case it was 0.95.

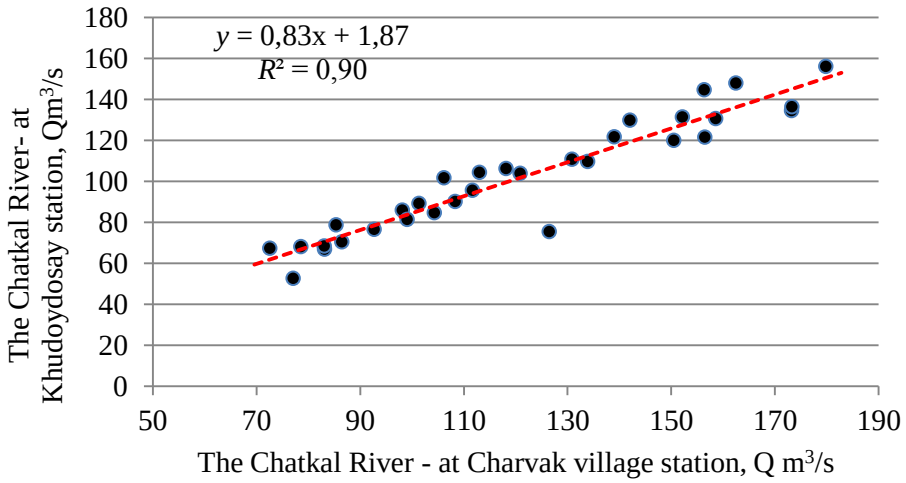


Figure 1. Average-flow correlations between two The Chatkal River streams, Khudoydodsay station and Charvak village station, 1933 - 1966

For practical estimation the correlation coefficient (R) ought to be at least 0.7 and in case table 2 this parameter is 0.95., that means we have excellent relationship.

Table 2. The parameters of the average-flow correlations plot of the annual discharge values between two stations of The Chatkal River – at Khudoydodsay station and The Chatkal River – at Charvak village station

Characteristics	Value
estimated river (Y)	Chatkal River – at Khudoydodsay station
analog-river (X)	Chatkal River – at Charvak village station
Observations (n)	32
The correlation coefficient (R)	0.95
Standard error of R (σ_R)	0.04
R/σ_R	23.3
the coefficient of regression (a)	0.83
Standard error a (σ_a)	0.05
a/σ_a	16.65
Independent member (b)	1.87
Regression Equation	$Y = 0.83 \cdot x + 1.87$

Also for better result it is necessary to use at least six years of simultaneous observations and in our example it was 32 years.

3. RESULTS AND DISCUSSION

3.1. Extension of data set

The initial dataset for The Chatkal River – at Khudoydodsay station was from 1965 to 2014 (figure 2). After recovery is was extended to 32 years and became 1933 - 2014.

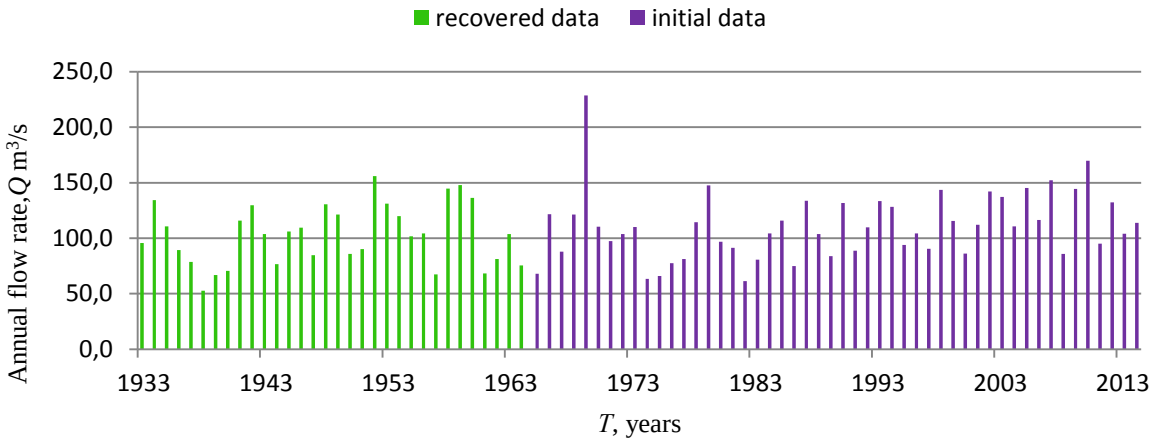


Figure 2. Histogram of annual stream flow for the Chatkal River – at Khudoydodsay station, initial with the recovered data set

3.2. Results of the estimation of main hydrological characteristics

Table 3 gives results for all analysed hydrological stations of The Chatkal River modulus of flow (amount of water that is originating from unit area per second in litres) varies within 15-17 l/s·km^2, the coefficient of variation - C_v varies between the of 0.21 - 0.27. At the same time, the statistical error of the average annual water flow is 8 – 9 % and the error of C_v does not exceed 15 %.

Table 3. Outcomes of the estimations of the main hydrological characteristics

Hydrological Station	Catchment area, km^2	Q_m, m^3/s	Q_m, l/s·km^2	C_v	C_s	C_s/C_v	Relative error, %		
							Q_m	C_v	C_s
The Chatkal River-Nayzatukay	**5520** (1932-1964)	82.8	15.0	0.21	0.22	1.03	4.2	14.2	108
The Chatkal River-Ters	**4090** (1915-1962, 4290)	64.0	15.6	0.23	0.26	1.12	4	12	61
The Chatkal River-Khudoydodsay	**6580** (1965-2015)	108	16.4	0.27	0.87	3.21	8.7	8.1	32
The Chatkal River-village Charvak	**7110** (1933-1967)	121	17.0	0.25	0.22	0.85	4	12	85
Average value	–	–	16	0.24	0.39	1.53	5.15	11.5	71.5

3.3. The probabilistic methods of calculation of the average annual stream flow

This section provides computations of several families of distributions which are widely used in hydrology. Based on recovered data set of The Chatkal River at Khudoydodsay Station, mean annual stream flow is estimated and exceedance probability distribution plotted for the following families of distributions: Normal, Lognormal, Gumbel and Kritskiy-Menkel [4]. For a calculated return period annual flow rate is given in figure 3.

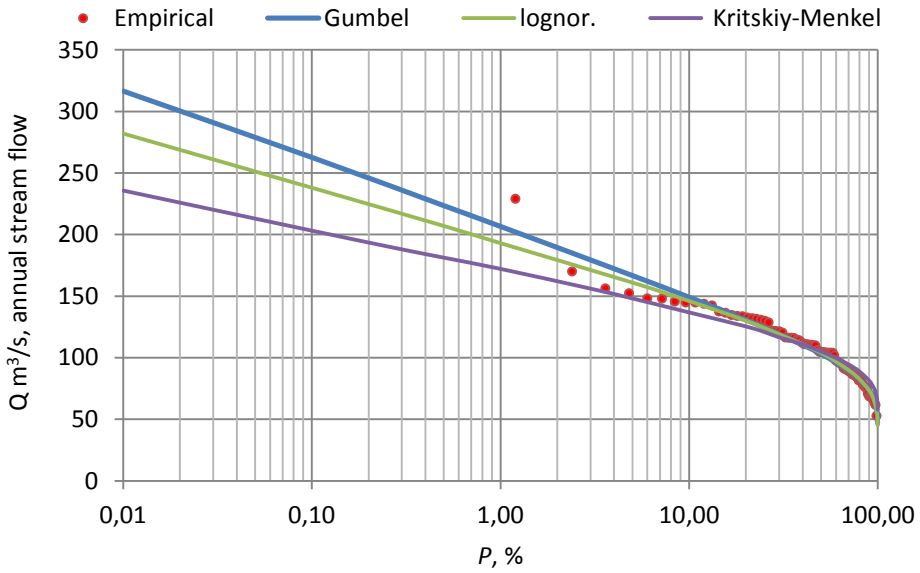


Figure 3. Comparative illustration of the average annual water flow of the exceedance probability distributions Normal, Lognormal, Gumbel and Kritskiy-Menkel

As an example, it was the Gumbel (Generalized Extreme Value Distribution Type-I) was chosen. In the empirical distribution plot, one observation year is strongly deviates from the others. This is the average annual water discharge for 1969, which was extremely high due to heavy snowfall and relatively long winter. The Gumbel distribution best fits because it lays more close among others to this point, hence it illustrates fits the maximum average annual flow rate.

4. CONCLUSION

As a result of the work done, the following conclusions can be drawn:

- filling in missing observations and extension of records were fulfilled,
- for all data set, statistical characteristics and their errors are estimated, for average flow rates the error does not exceed 10 %, for the coefficient of variation, the error does not exceed 15 %,
- the empirical and Gumbel security curves were plotted. As an analytic Gumbel curve was chosen for analysis,
- the impact of Global Climate Change to Tien-Shan mountains is obvious, but this impact still keeps the figures within statistically allowed interval or statistically insignificant.

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ANALIZA TRANSPORTA ODABRANIH FARMACEUTIKA U PODZEMNIM VODAMA

ANALYSIS OF SELECTED PHARMACEUTIALS TRANSPORT IN GROUNDWATER

Srđan Kovačević*, Nevena Živančev*, Milan Dotlić, Milenko Pušić**, David Mitrinović**, Milan Dimkić*/****

* Univerzitet u Novom Sadu, Fakultet tehničkih nauka, Novi Sad, Srbija
** Institut za vodoprivredu "Jaroslav Černi", Beograd, Srbija

autor za korespondenciju: Srđan Kovačević, e-mail: srdjankovacevic@uns.ac.rs.

Izvorni znanstveni rad

SAŽETAK

U radu su prikazani rezultati primene modela i analiza transporta odabranih farmaceutika u podzemnim vodama. Model transporta farmaceutika u podzemnim vodama je definisan na osnovu dostupnih podataka, kao i na osnovu prethodno dobijenih eksperimentalnih rezultata. Hidrodinamički model podzemnih voda je prethodno definisan, dok su linearni koeficijenti sorbiranja za farmaceutike karbamazepin, trimetoprim, diklefenak i metabolit metamizola N-acetil-4-amino-antipirin dobijeni na osnovu rezultata kalibracije modela transporta. Dobijeni rezultati za linearne koeficijente sorbiranja ispitivanih farmaceutika su upoređeni sa literaturnim podacima. Najveći kapacitet za sorbiranje ima trimetoprim sa linearnim koeficijentom sorbiranja *Kd* = 0,64 mL/g, dok nešto manji potencijal sorbiranja imaju: karbamazepin *Kd* = 0,135 mL/g, N-acetil-4-amino-antipirin *Kd* = 0,09 mL/g i diklofenak, *Kd* = 0,075 mL/g. Rezultati pokazuju da su podaci koji su dobijeni na osnovu modela primjenljivi za procenu ponašanja ispitivanih farmaceutika prilikom transporta u aluvijalnim podzemnim vodama.

***Ključne riječi**: model, transport,farmaceutici, sorbiranje, podzemne vode*

ABSTRACT

The paper presents the results of the transport model application for analysis of selected pharmaceutics transport in groundwater. The transport model was defined on the basis of the available data and previously obtained experimental data. Hydrodynamic model of groundwater was defined, and linear coefficients of sorption for carbamazepine,

trimethoprim, diclofenac, and metamizole metabolite N-acetyl-4-amino-antipyrene were obtained based on the calibration of the transport model. The derived results for linear coefficients of sorption were compared with the literature data. The highest sorption capacity was for trimethoprim with a linear sorption coefficient *Kd* = 0.64 mL/g, while other investigated pharmaceutical have lower sorption potential: carbamazepine *Kd* = 0.135 mL/g, N-acetyl-4-amino-antipyrin *Kd* = 0.09 mL/g and diclofenac *Kd* = 0.075 mL/g. The results show that the data obtained from the transport model are applicable for assessing the behaviour of selected pharmaceuticals in alluvial groundwater.

***Keywords**: model, transport, pharmaceuticals, sorption, groundwater.*

1. UVOD

Termin emergentne organske supstance (*EOS*) se odnosi ne samo na supstance koje su nedavno sintetisane već i na supstance koje se otkrivaju u životnoj sredini, a koje se već koriste duži vremenski period i mogu imati potencijalno negativne efekte na životnu sredinu [1]. Farmaceutici predstavljaju grupu *EOS* koje su prisutne u životnoj sredini i pojavljuju se konstantno u veoma niskim koncentracijama. Sa razvojem novih analitičkih metoda detekcije farmaceutika, sve veći broj farmaceutika može da se detektuje u matriksima životne sredine, a posebno u akvatičnoj sredini.

Poređenjem eksperimentalnih i literaturnih podataka o stepenu sorbiranja odabranih farmaceutika dobijaju su ulazni podaci za 3D model transporta farmaceutika koji se koriste za definisanje stepena uklanjanja farmaceutika tokom prolaska kroz aluvijalni akvifer. Detaljnije su analizirana četiri farmaceutika koji pripadaju različitim klasama: trimethoprim - antibiotik, karbamazepin - antiepileptici i psihijatrijski farmaceutici, diklofenak i metabolit metamizola N-acetil-4-amino-antipirin (*4-AAA*) - analgetici i antiinflamatorni farmaceutici.

U slučaju intergranularnih akvifera, simulacije i predviđanje toka podzemnih voda, kao i transporta supstance u podzemnoj vodi zahteva veoma dobro poznavanje prirode kao i prostorne raspodele akvifera. U većini slučajeva, navedeni podaci nisu dostupni ili je veoma zahtevno prikupljanje podataka, stoga je neophodno sprovođenje terenskih eksperimenata. Na osnovu raspoloživih podataka i hidrodinamičkog modela podzemnih voda, korišćen je model transporta farmaceutika u podzemnim vodama na osnovu čega su određeni linearni koeficijenti sorbiranja. Osnovni cilj rada je da se primenom modela transporta farmaceutika u podzemnim vodama odrede linearni koeficijenti sorbiranja i uporede sa podacima koji su određeni eksperimentalno, kao i sa literaturnim podacima.

2. EKSPERIMENTALNI DEO

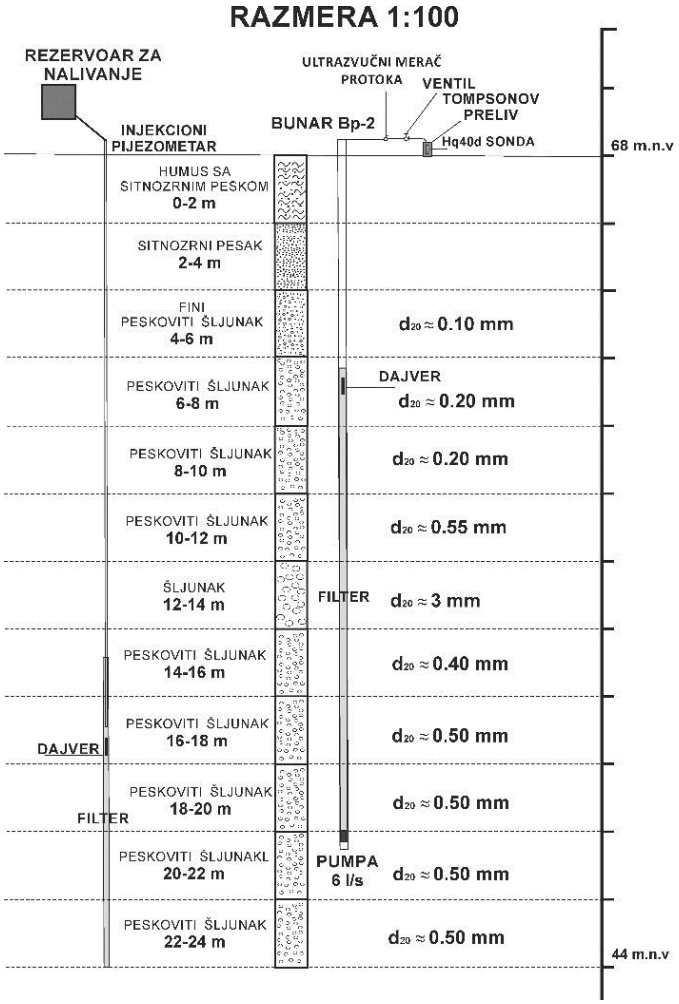
2.1. Opis lokacije i hidrogeoloških uslovi

Ispitivani bunar Bp-2 je lociran na prostoru drenažnog sistema Kovin - Dubovac (slika 1). Sedimenti najporoznijeg dela akvifera odakle se crpi obalski filtrat pripadaju starijem Kvartaru. Gornji delovi akvifera pripadaju kasnom Holocenu i delom gornjem Pleistocenu sastoje se od naslaga peska i šljunka, kao i naslaga alevrita u gornjem delu aluvijalne ravni. Debljina vodonosnog sloja je u proseku od 15 do 20 m. Povlata se sastoji od naslaga peska, šljunka alevrita, kao i prašine i gline. Prosečna debljina povlate je oko 7.5 m.



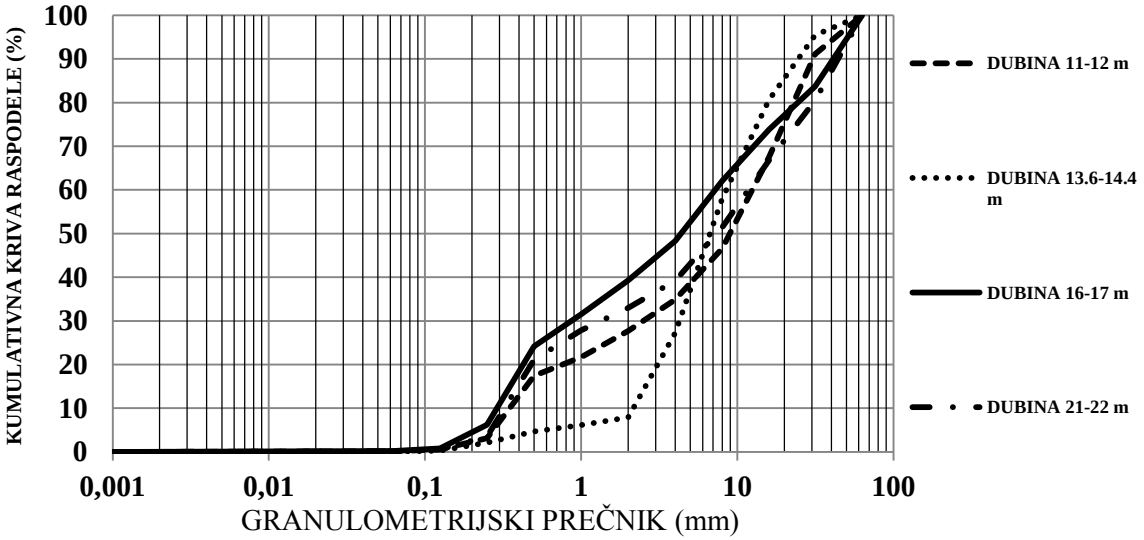
Slika 1. Mapa Republike Srbije i lokacija sprovođenja terenskog traserskog eksperimenta na drenažnom sistemu Kovin - Dubovac [2]

Podaci o granulometrijskom sastavu bušotine koja je izrađena u svrhu istraživanja, kao i podaci o filtracionim karakteristikama su detaljno opisani u radu [2]. Na slici 2 šematski je prikazana postavka traserskog eksperimenta i geološki presek.



Slika 2. Šematski prikaz postavke traserskog eksperimenta i geološki presek (m.n.v. – metara nadmorske visine , d_{20} – 20 % prečnik krive granulometrijskog sastava (mm) [2]

Ukratko, istražna bušotina je izrađena konvencijalnom metodom korišćenjem sržne bušilice i bućke. Tokom bušenja, uzorci vode su prikupljani svaka tri metra i na kraju je napravljen kompozitni uzorak radi daljeg ispitivanja. Kriva granulometrijskog sastava je određena prosejavanjem materijala korišćenjem seta sita prema standardu SRPS L.J9.010. Na osnovu prikupljenih podataka, određeni su teoretski koeficijenti filtracije korišćenjem empirijske formule USBR [3], gde je za materijal akvifera efektivni prečnik zrna $d_{ef} = d_{20}$. Slika 3 prikazuje kumulativnu krivu raspodele granulometrijskog prečnika uzoraka sedimenta sa različite dubine.



Slika 3. Kumulativna kriva raspodele granulometrijskog prečnika uzoraka sedimenta sa različite dubine

2.2. Analitičke metode

Analitički standardi visoke čistoće (95 %) dobijeni su od farmaceutskih kompanija (Hemofarm, član STADA grupe, R. Srbija, Zorka Pharm, Vršac, R. Srbija). Metabolit metamizola *4-AAA* je nabavljen od "Sigma Aldrich". Svi korišćeni rastvarači namenjeni za HPLC su dobijeni od FLUKA (Buchs, Švajcarka) ili Sigma Aldrich (St. Louis, MO). Destilovana voda je dobijena propuštanjem vode iz vodovoda kroz aparat za dejonizaciju "Gen Pure" (TKA, Niederelbert, Nemačka). Rastvori pojedinačnih analitičkih standarda su pripremljeni u metanolu koncentracije 100 mg/l i skladišteni u zamrzivaču.

Radni standardi su pripremani jednom nedeljno u različitim koncentracijama, mešanjem odgovarajućih količina standardnog rastvora i metanola. Svi rastvori su čuvani na temperaturi od - 4°C.

Uzorci vode su pripremljeni metodom ekstrakcije na čvrstoj fazi ("solid phase extraction" - SPE). Pripremljeni ekstrakti su analizirani korišćenjem analitičke metode tečne hromatografije tandem masene spektrometrije (LC-MS/MS). Detaljne informacije u vezi sa korišćenom analitičkom procedurom, instrumentalnim parametrima, vremenima odziva, kalibracionim krivama, kao i preciznost metode, limiti detekcije i kvantifikacije metode su detaljno opisani u prethodno objavljenim radovima. [4, 5].

2.3. Terenske eksperimentalne postavke

Parametri koji su praćeni tokom trajanja terenskog eskeprimenta, kao i eksperimentalni uslovi su detaljnije opisani u radu [2]. Ukratko, tokom celokupnog terenskog eksperimenta praćeni su svi eksperimentalni uslovi. Pre početka terenskog eksperimenta praćeno je početno stanje i utvrđeni su početni uslovi. Traserski eksperiment je sproveden pod veštački izazvanim gradijentom, korišćenjem pumpe u bunaru sa konstantnim protokom 6 L/s. Eksperimentalni parametri su praćeni kontinualno, a uključivali su praćenje nivoa podzemnih voda (ručno merenje nivoa i merenje automatskim meračima nivoa podzemnih voda – „diver“), protoka na pumpi bunara (ultrazvučni merač protoka, propelerni merač protoka, volumetrijska metoda), kao i parametara kvaliteta podzemne vode pomoću multi parametarske sonde HQ40d: električna provodljivosti (χ), *pH*, rastvoreni kiseonik (O_2), kao oskido/redukcioni potencijal (*Eh*). Analize ukupnog organskog ugljenika („total organic carbon“ TOC) su sprovedene u laboratorijskim uslovima, na uređaju „Shimadzu Total Organic Carbon Analyzer (TOC-5050a)“, primenom standardne metode SMEWW 21st, „Standard Methods for The Examination of Water and Wastewater 21st Edition“ 2005 APHA, AWWA, WEF. Titracija uzoraka podzemne vode na izlivu bunara, koja je sprovedena kako bi se utvrdila zavisnost elektorprovodljivosti i koncentracije jona hlora (Cl^-), realizovana je na licu mesta tokom trajanja eksperimenta korišćenjem „Eppendorf top buret M“ uređaja.

2.4. Model podzemnih voda

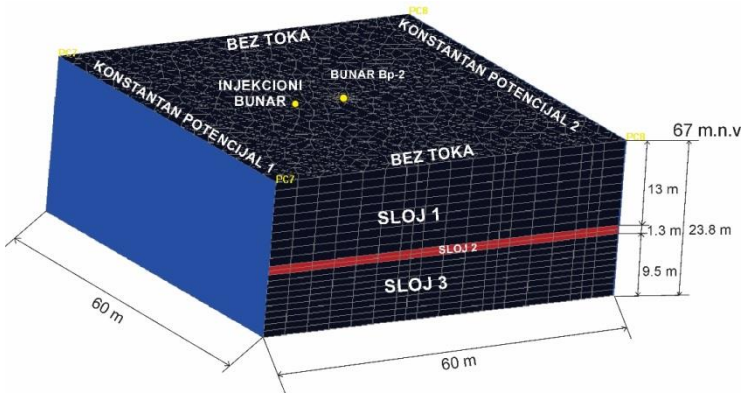
Podaci koji su dobijeni za lokaciju bunara Bp-2 su organizovani i obrađeni kako bi se dobile neophodne podloge za postavku pojednostavljenog hidrodinamičkog modela podzemnih voda. Efektivna poroznost je proračunata na osnovu krive granulometrijskog sastava, kao i na osnovu rezultata kalibracije modela transporta trasera. Na osnovu krive granulometrijskog sastava, dobijene su polazne vrednosti filtracionih parametara za formiranje i kalibraciju hidrodinamičkog modela. Kalibracija modela transporta trasera je sprovedena na osnovu merenih vrednosti koncentracije trasera Cl^- tokom trajanja eksperimenta, dok je model transporta farmaceutika u podzemnim vodama, formiran na osnovu rezultata analize prisutnosti farmaceutika u podzemnim vodama tokom trajanja eksperimenta.

Obrada podataka i postavke mikromodela lokacije su realizovani pomoću softverskog paketa WODA („Well Outline and Desgn Aid“) koji rešava jednačine podzemnog strujanja u anizotropnoj diskontinualnoj sredini primenom metoda konačnih zapremina razvijen u Institutu za vodoprivredu „Jaroslav Černi“ [6, 7]. „Lizza“ predstavlja grafički i korisnički interfejs pomoću koga se definiše model podzemnih voda za koje se sprovodi proračun. Solver WODA radi na nestrukturnim mrežama koristeći metod konačnih zapremina. Metod konačnih zapremina je najmlađi a pojavio se sedamdesetih godina dvadesetog veka. Opis metoda konačnih zapremina, teorijske osnove, diskretizacija, nelinearnost, balans i rešavanje nelinearnih jednačina su detaljno opisani u radovima [6, 7].

3. REZULTATI I DISKUSIJA

3.1. Opis modela

U hidrodinamičkom kontekstu aluvijalni akvifer na lokaciji drenažnog sistema Kovin-Dubovac u blizini reke Dunav je tipični troslojni sistem: povlata, vodonosni sloj i podina. Na prostoru celokupnog drenažnog sistema vodonosni sloj je relativno homogenih karakteristika, ali se na mikrolokaciji sprovođenja eksperimenta (bunar Bp-2) izdvaja jedan propusljiviji sloj na dubini između 12 - 14 metara od površine terena sa efektivnim prečnikom zrna d_{20}=3 mm i koeficijentom filtracije 4x10^{-2} m/s, dok su ostali delovi vodonosnog sloja relativno homogeni sa koeficijentom filtracije od 4-7x10^{-4} m/s (slika 2). U skladu sa postavkom problema i raspoloživim podacima, primenjena je jednostavnija hidrogeološka šema sa tri sloja. Domen numeričkog modela dimenzija 60x60x23,8 m (slika 4) je definisan sa tri sloja, diskretizacija mreže je sprovedena zadavnjem maksimalne površine elementa 5 m^2, dok je je maksimalni ugao elementa mreže 30°. Elevacija donje granice domena modela je zadata sa 43,2 m, dok je gornja elevacija domena modela zadata sa 67 m nadmorske visine. Definisano je uniformno polje toka sa gradijentom 0.5 ‰, zadavanjem graničnog uslova konstantnog potencijala sa dve strane modela, kao i sa graničnim uslovom bez toka za suprotne vertikalne strane modela, tokom celokupnog toka simulacije. Bunar sa pumpom Bp-2 je zadat u centru modela (X = 30 m i Y = 30 m) dok je nalivni pijezometar zadat kao nalivani bunar koje se nalazi na udaljenosti 8,2 m od bunara Bp-2 (X = 21,8 m i Y = 30 m), u skladu sa realnim postavkama traserskog eksperimenta. Protok u nalivanom bunaru je podešen na 0,046 L/s za vremenski interval 40 min, što odgovara vremenu nalivanja prilikom sprovođenja eksperimenta, dok je protok u bunaru sa pumpom Bp-2 zadat sa 6 L/s, za celokupan vremenski interval simulacije. Filtarska kolona u bunaru Bp-2 ima sledeće dimenzije, dno filtera se nalazi na koti 47,6 m, dok je vrh filtera na koti 62 m iznad nivoa mora. Prečnik bunara je 0,26 m. Kota dna filtarske kolone u nalivnom bunaru je 43,2 m dok je vrh filtarske kolone na koti 55,5 m iznad nivoa mora. Geometrija slojeva je definisana na sledeći način: prvi sloj ima kotu vrha 67 m i kotu dna sloja 54 m, drugi, najpropustljiviji sloj ima kotu vrha 54 m, dok je kota dna sloja 52,7 m i treći sloj ima kotu vrha sloja 52,7 m i kotu dna sloja 43,2 m iznad nivoa mora.



Slika 4. Šematski prikaz domena modela (m.n.v - metara nadmorske visine)

Kalibracija mikromodela bunara Bp-2 je sprovedena na osnovu rezultata koji su dobijeni tokom terenskog eksperimenta [2]. Na osnovu rezultata kalibracije definisana je geometrija modela, prikazana na slici 4, a određeni su i koeficijenti filtracije za sva tri sloja. Za sloj 1 i za sloj 3, horizontalni koeficijent filtracije je Kx,y = 5x10^{-4} m/s, dok je vertikalni koeficijent filtracije Kz = 3,5x10^{-4} m/s, teorijska efektivna poroznost je n_{ef} = 0,15. Za sloj 2 koji je dominantno propustljiv, vertikalni i horizontalni koeficijent filtracije su isti Kx,y,z =

5,8 x 10^{-3} m/s, dok je teorijska efektivna poroznost n_{ef} = 0,2. Koeficijent specifične izdašnosti svih slojeva je $\varepsilon = 7x10^{-5}$ l/m.

3.2. Određivanje linearnih koeficijenata sorbiranja

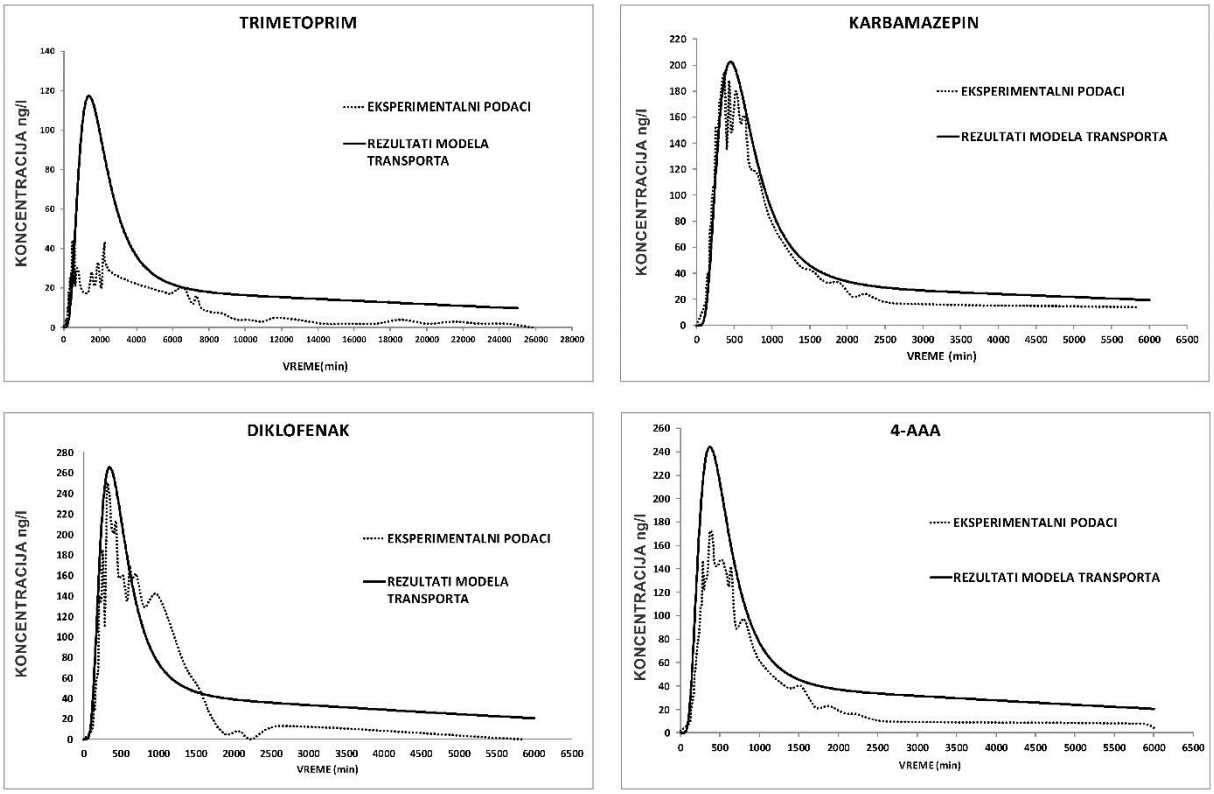
Programski paket WODA je korišćen kako bi se odredili linearni koeficijenti sorbiranja. Sorpcija u solveru WODA se zadaje preko parametra b - koeficijent distribucije voda/sediment, čija je zavisnost u odnosu na linearni koeficijent sorbiranja *Kd* predstavljena sledećom jednačinom:

$$b = \frac{1 - n_{ef}}{\rho_b Kd} \tag{1}$$

gde je:
b - koeficijent distribucije voda/sediment (-); n_{ef} - efektivna poroznost (-); ρ_b - specifična gustina (kg/m^3); *Kd* – linearni koeficijent sorpcije (m^3/kg).

Inicijalne koncentracije odabranih farmaceutika su zadate u skladu sa eksperimentalnim podacima za traserski test i nalivanje farmaceutika [2]: trimethoprim 2.5 mg/L, karbamazepim 1 mg/L, dikolofenak 1 mg/L i 4-AAA 1 mg/L.

Kalibracijom vrednosti b, dobijeni su rezultati za linearni koeficijent sorbiranja *Kd* na osnovu podataka koji su dobijeni na osnovu traserskog eksperimenta i eksperimenta injektiranja odabranih farmacutika [2]. Rezultati kalibracije modela transporta su prikazani na slici 5.



Slika 5. Rezultati kalibracije modela transporta ispitivanih farmaceutika u odnosu na merene vrednosti koncentracije na izlivu bunara Bp-2

Rezultati ukazuju da trimetoprim ima najveći sorpcioni potencijal *Kd* = 0,64 mL/g, zatim sledi karbamazepin *Kd* = 0,135 mL/g, dok *4-AAA*, *Kd* = 0,09 mL/g i diklofenak *Kd* = 0,075 mL/g imaju najmanji potencijal za sorbiranje. Na osnovu rezultata koji su dobijeni u drugoj studiji [8] na osnovu laboratorijskog eksperimenta određivanja linearnog koeficijenta sorbiranja *Kd* za uzorak sedimenta na lokaciji bunara Bp-2, najveći sorpcioni potencijal ima diklofenak, zatim karbamazepin, potom trimetoprim i na kraju najmanju sorpcioni kapacitet ima metabolit metamizola *4-AAA*. Kvalitativni odnos između linearnih koeficijenata sorpcije je sličan, dok su vrednosti koje su dobijene na osnovu modela transporta farmaceutika u podzemnim vodama nekoliko puta manje od laboratorijski dobijenih podataka.

Uzorak sedimenta je analiziran i utvrđen je sadržaj frakcije ukupnog organskog ugljenika $f_{OC} \approx 0{,}229$ %. Sadržaj organske materije u uzorku sedimenta je relativno mali. Dominantna frakcija sedimenta je prečnika manjeg od 1 mm i sadrži: glinu (0 %), prašinu (0,42 %), pesak (38,33 %) i šljunak (60,53 %). Procenat organske materije je određen analizom uzorka sedimenta sa dubine od 10 - 14 m uzimanjem uzorka sedimenta na svaki metar i mešanjem u jedan reprezentativan uzorak.

Na osnovu rezultata, trimetoprim ima najveću vrednost linearnog koeficijenta sorbiranja *Kd* (0,64 mL/g). Na osnovu literaturnih podataka za studiju koja je sprovedena sa 13 različitih tipova sedimenta [9], sprovedena u različitim eksperimentalnim uslovima (laboratorijski eksperiment), trimetoprim ima veću vrednost *Kd* (3,5 mL/g), za sediment koji ima veći procenat frakcija organske materije u sedimentu akvifera f_{OC} = 0,36 %.

U okviru istraživanja [8], koje je sprovedeno u prethodno pomenutim uslovima za uzorak sedimenta sa lokacije terenskog eksperimenta sprovedenog u okviru istraživanja, dobijen je linearni koeficijent sorbiranja *Kd* = 12,18 mL/g, za uzorak sedimenta sa istom frakcijom organske materije f_{OC} = 0,229 %.

Na osnovu eksperimentalno dobijenih podataka karbamazepin ima relativno malu vrednost linearnog koeficijenta sorbiranja *Kd* = 0,135 mL/g. U laboratorijskom eksperimentu [10], linearni koeficijent sorbiranja je sličan *Kd* = 0,13 mL/g, dok je manji sadržaj organske frakcije sedimenta f_{OC} = 0,002 %.

U drugoj studiji [11], laboratorijskog određivanja linearnih koeficijenata sorbiranja karbamazepina, gde je procenat frakcije organske materije nešto veći f_{OC} = 0,41 %, i linearni koeficijent sorbiranja karbamazepina je veći *Kd* = 1,45 mL/g. U laboratorijskom eksperimentu sa sedimentom u kolonama [12], sa manjim procentom organske frakcije f_{OC} = 0,0013 %, linearni koeficijent sorbiranja karbamazepina je veći *Kd* = 1,43 mL/g. U studiji [8], koja je sprovedena na uzorku sedimenta sa lokacije terenskog traserskog eksperimenta, linearni koeficijent sorbiranja za karbamazepin je znatno veći *Kd* = 16,35 mL/g, iako je procenat frakcije organske materije u sedimentu isti kao i za istraživanje sprovedeno u laboratorijskim eksperimentalnim uslovima f_{OC} = 0,229 [8].

Na osnovu rezultata kalibracije modela transporta diklofenak ima linearni koeficijent sorbiranja *Kd* = 0,075 mL/g. U laboratorijskim eksperimentu [9] u kome sediment ima manji procenat frakcije organske materije f_{OC} = 0,002 %, vrednost linearnog koeficijenta sorbiranja diklofenaka je nekoliko puta veća *Kd* = 1,87 mL/g.

U drugom laboratorijskom eksperimentu [13], sa većim procentom frakcije organske materije f_{OC} = 0,5 %, vrednost linearnog koeficijenta sorbiranja diklofenaka je takođe veća *Kd* = 0,55 mL/g. U eksperimentu sa kolonama [12] sa znatno manjim procentom organske frakcije f_{OC} = 0,002 %, linearni koeficijent sorbiranja je takođe veći *Kd* = 0,57 mL/g, dok je u laboratorijskom eksperimentu [8] linearni koeficijent sorbiranja diklofenaka znatno veći *Kd* = 33 mL/g, iako je procenat frakcije organske materije isti kao i u terenskom eksperimentu u okviru istraživanja.

Metabolit metamizola 4-AAA ima linearni koeficijent sorbiranja *Kd* = 0,09 mL/g. Za sada nema podataka za linearne koeficijente sorbiranja u literaturi. Samo u jednoj studiji [14],

metabolit metamizola 4-AAA se nije soribirao na sedimentu sa sličnim procentom frakcije organske materije f_{OC} = 0,2 %.

Uzimajući u obzir da je uzorak sedimenta prečnika manjeg od 1 mm, na osnovu kumulativne krive raspodele granulometrijskog prečnika uzoraka sedimenta (slika 3), može se pretpostaviti da je procenat organske materije znatno manji (okvirno 10 puta) od $f_{OC} \approx$ 0,229 %, jer manje od 10 % krive raspodele granulometrijskog prečnika obuhvata zrna prečnika manjeg od 1 mm. Granulometrijski sastav uzorka sedimenta koji je analiziran nije u potpunosti reprezent realnog sastava sedimenta u prirodi, zbog efekta razmere i nehomogenosti akvifera.

4. ZAKLJUČAK

Većina literaturnih podataka se odnosi na laboratorijske eksperimente i eksperimente u kolonama za uzorke sedimenta različitog sastava, tako da se u praksi navedeni podaci moraju pažljivo razmotriti i ne mogu se podjednako komparirati. Terenski eksperimentalni uslovi se znatno razlikuju od laboratorijskih uslova, uz efekat razmere koja značajno utiče na konačan rezultat. Pored efekata razmere, preferentni tokovi podzemne vode utiču na brzinu kretanja podzemne vode u prirodnim uslovima i značajno utiču na konačan rezultat terenskog eksperimenta. Uzorak sedimenta analiziran u laboratorijskim uslovima ima prečnik manji od 1mm, dok uzorak sedimenta sa lokacije terenskog eksperimenta ima prečnik zrna krive granulometrijskog sastava od 0,1 mm do 70 mm, što značajno utiče na efekat sorbiranja u laboratorijskim uslovima i ne može biti reprezent realnih uslova na terenu. Navedena činjenica se ogleda u evidentnoj razlici u dobijenim linearnim koeficijentima sorbiranja na osnovu modela transporta farmaceutika u podzemnim vodama na osnovu terenskog eksperimenta i rezultata dobijenih laboratorijskim eksperimentom određivanja izotermi sorpcije za uzorak sedimenta sa lokacije terenskog eksperimenta. Linearni koeficijenti sorbiranja dobijeni laboratorijskim eksperimentom su od 8 (4-AAA) do 200 (diklofenak) puta veći od linearnih koeficijenata sorbiranja dobijenih na osnovu modela transporta na osnovu sprovedenog terenskog eksperimenta. Navedena činjenica ukazuje da su za sitnozrne uzorke sedimenta akvifera dominantni različiti mehanizmi sorbiranja u odnosu na krupnozrni sediment akvifera u prirodi (podzemna voda prolazi kroz najkrupniji materijal akvifera), kao i da je sorbiranje znatno izraženije na sitnijem materijalu akvifera. Procenat organske materije f_{OC} za uzorak sedimenta analiziran u laboratorijskim uslovima je nekoliko puta veći od f_{OC} u prirodnim uslovima na terenu, tako da je kod laboratorijskih eksperimenata izraženije sorbiranje na organskoj materiji, što utiče na konačan rezultat.

Rezultati jasno ukazuju da podaci dobijeni na osnovu laboratorijskih eksperimenata moraju biti uzeti u obzir sa određenom rezervom, zbog efekata razmere eksperimenta, reprezentativnosti uzorka (granulometrijskog sastava uzorka sedimenta), preferentnih tokova podzemne vode i laboratorijskih uslova. Usled navedenih razlika može doći do velikih odstupanja u dobijenim *Kd* vrednostima, a samim tim i grešaka tokom proračuna budućih modela transporta supstance u podzemnoj vodi. Takođe, fizička sorpcija na neorganskoj materiji akvifera, hemisorpcija i jonska imena imaju značajnu ulogu u ukupnom sorpcionom potencijalu ispitivanih farmaceutika aluvijalnih akvifera pošto je procenat frakcije organske materije u ispitivanom uzorku zanemarljiv.

Prema rezultatima istraživanja, farmaceutici koji se najbrže transportuju u podzemnim vodama su diklofenak i 4-AAA, dok je trimetoprim imao najmanju brzinu transporta u podzemnim vodama. Dobijeni linearni koeficijenti sorbiranja *Kd* za ispitivane farmaceutike su znatno manji od vrednosti zabeleženih u literaturi, sem za 4-AAA, gde je *Kd* proračunat po

prvi put na osnovu modela transporta podzemnih voda i rezultata trenskih eksperimenata (opita).

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Zahvala

Rezultati koji su objavljeni na osnovu istraživanja su realizovani u okviru projekta Ministarstva Prosvete Nauke i Tehnološkog Razvoja Republike Srbije (TR37104) pod nazivom „Metodologija za procenu, projektovanje i održavanje aluvijalnih izvorišta podzemne vode u zavisnosti od stanja aerobnosti“.

ZNANJE KAO INTEGRALNI FENOMEN

KNOWLEDGE AS AN INTEGRAL PHENOMENON

Tomislav Krznar*

* Sveučilište u Zagrebu, Učiteljski fakultet, Zagreb, Hrvatska

autor za korespondenciju: Tomislav Krznar, e-mail: tomislav.krznar@ufzg.hr

Prethodno priopćenje

SAŽETAK

U ovom radu nastojimo promotriti, koji je utjecaj čovjeka na okoliš, konkretno, kakve su po okoliš implikacije znanstvenog načina mišljenja. Nastojimo nadalje promotri fenomen znanja, posebice znanstvenog znanja, te kako ovaj fenomen razumijevamo u kontekstu zapadnjačkog načina mišljenja. U ovoj stvari poseban naglasak dajemo na etičke opservacije vezano uz primjenu znanja. Želimo razabrati zašto je uopće potrebno govoriti o cjelovitosti, i kako bi to doprinijelo oblikovanju kritičke diskusije o problemima znanja. Ukratko, znanje se ne može percipirati kao vrijednosno neutralni fenomen. Znanstveno znanje nije jedini oblik znanja i ono mora, posebice zbog svojih učinaka čija se štetnost vidi i u fenomenu uništenja okoliša, imati ograničenja u vrijednosnoj procjeni primjene. Nastojimo stoga na platformi bioetike, ocrtati problem orijentacijskog znanja, i te razložiti način kako ove pozicije korespondiraju s razumijevanjem života u misli suvremenog čovjeka.

***Ključne riječi**: znanje, vrijednosti, orijentacija, život kao cjelina, bioetika.*

ABSTRACT

In this paper, we try to examine what is the impact of human on the environment, specifically, what are the environmental implications of the scientific way of thinking. We look at the phenomenon of knowledge, especially scientific knowledge, and in the how we understand this phenomenon in the context of Western way of thinking. In this matter we give a special emphasis on ethical observations regarding the application of knowledge. We want to find out why it is necessary to speak about holism, and how it will contribute to shaping a critical discussion of problems of knowledge. In short, knowledge cannot be perceived as a value-neutral phenomenon. Scientific knowledge is not the sole form of knowledge, and it must have limitations in the value assessment of its application, especially because of its effects. This can be seen especially in the phenomenon of environmental degradation. We

therefore strive for the bioethics platform, to outline the problem of orientation knowledge, and to elaborate how these positions correspond to the understanding of life in the thought of modern man.

***Keywords**: knowledge, values, orientation, life as a whole, bioethics.*

1. UVOD

„Tko danas ima društvenu moć?“, pitao je španjolski filozof Ortega y Gasset (1883-1955), i dodao:

> „Tko u epohi nameće strukturu svojeg duha? Nedvojbeno, građanstvo. Koga unutar toga građanstva smatramo superiornom skupinom, današnjom aristokracijom? Nedvojbeno, stručnjaka: inženjera, liječnika, bankara, profesora itd. Tko u toj skupini stručnjaka na najvišoj razini i najjasnije predstavlja tu skupinu? Nedvojbeno, znanstvenik. Kad bi neko izvanzemaljsko biće posjetilo Europu s namjerom da je ocijeni, pa bije pitalo na temelju koje vrste ljudi želi biti ocjenjivana, Europa bi nedvojbeno, mirna i sigurna u povoljnu ocjenu, izabrala svoje znanstvenike. Zvjezdano biće, naravno, ne bi pitalo za pojedince, nego bi potražilo pravilo, generički tip 'znanstvenika', vrh europskoga čovječanstva. Dakle: današnji je znanstvenik prototip čovjeka-mase. I to nije slučajno, ne zbog osobnih nedostataka svakog znanstvenika, nego i zato što ga sama znanost – korijen civilizacije – automatski pretvara u čovjeka-masu; odnosno pretvara ga u primitivca, suvremenog barbara“ [1].

Pred nama su riječi Ortege y Gasseta jednog od najznačajnijih mislilaca dvadesetog stoljeća. Ove riječi možemo pročitati u njegovu, možda najznačajnijem djelu, *Pobuna masa*, objavljenom 1930. u Madridu, a koje je doživjelo planetarnu recepciju [2]. Vrijeme u kojem su nastale ove misli bilo je uistinu burno, a buran je i cijeli Ortegin opus, osobito kada je riječ o kritici znanosti i njezine uloge u životu suvremenog čovjeka, a to je problem koji je Ortega često tematizirao. Ovdje možemo zastati i uočiti ključno određenje Ortegine misli koje i mi preuzimamo u razlaganju problematike ovog rada.

Termin „kritika“, učeći i od Ortege, koristimo u kantovskom značenju riječi, dakle govorimo o uočavanju biti fenomena koji promišljamo, i o uočavanju granica tog fenomena. Ortega je uočio da je znanost esencija zapadnjačkog misaonog kozmosa, ona je „ono nešto“ što naš život, kako ga mi zapadnjaci poimamo čini mogućim, i to ne samo u banalnom značenju proizvodnje artefakata koji olakšavaju život (poput komunikacijske tehnologije, transportnih sredstava i sl.) ili život uopće čine mogućim (poput lijekova, medicinskih usluga, proizvodnje hrane, osiguravanja pitke vode, topline i sl.), nego više u pogledu načina mišljenja koji je dominantno prisutan u socijalnom, kulturnom i kognitivnom određenju neke skupine ljudi. Ukoliko želimo ići Orteginim tragom, recimo da je ta skupina ljudi Europa i oni dijelovi svijeta koje je europski čovjek „osvojio“, a način mišljenja je numerički, kvantitativni, računski i više od svega okrenut učinku. No, i ovaj način mišljenja, bez obzira na dobra koja proizvodi, ima svoje granice, koje kad pređe, kako kazuje Ortega upada u barbarstvo, Ovaj termin „barbarstvo“ u ortegijanskoj vizuri možemo razumjeti kao rigidni partikalarizam, kao nesposobnost dohvaćanja cjeline, i kao radikalno nastojanje oko nijekanja mogućnosti drugačijih pogleda na svijet. Naime, znanost je – kako je ona shvaćena u konturama zapadnjačkog načina mišljenja – jedini ispravni mehanizam korespondencije s istinom, znanost je mogućnost verificiranja sadržaja koji dobivaju u socijalnom i kulturnom pogledu obvezujući značaj. No, nije sve „dohvatljivo“ znanošću, tim više što – kako je promislio Ortega – znanost „posao“ kojim se bave znanstvenici, koji u svojim nastojanjima, bilo zbog osobnih nedostataka, bilo zbog zanesenosti svojim istraživanjima mogu iz vidokruga izgubiti cjelinu života kojim se bave i pomisliti da je njihovo djelovanje nadređeno

životu. To je situacija koju Ortega naziva barbarstvom, a mi bismo je nazvali bolnom potrebom za promišljanjem fenomena integralnosti. Ovu poziciju je potrebno sagledati razlaganjem njenih socijalnih, etičkih, ekonomskih i kulturnih aspekata.

U tom pogledu nastojimo, što se tiče ovog rada promotriti, prvo, koji je utjecaj čovjeka na okoliš, konkretno, kakve su po okoliš implikacije gore prikazanog znanstvenog načina mišljenja. Drugo, u ovom radu nastojimo promotri fenomen znanja kako ovaj fenomen razumijevamo u kontekstu zapadnjačkog načina mišljenja. U ovoj stvari poseban naglasak dajemo na etičke opservacije vezano uz primjenu znanja. Treće, moramo razabrati zašto je uopće potrebno govoriti o cjelovitosti, ili bolje može li nam „govorenje“ o cjelovitosti, na način kritičke diskusije o problemima znanja, donijeti nešto novo u našem poznavanju problema znanja i kako ove pozicije korespondiraju s razumijevanjem života u misli suvremenog čovjeka.

2. ČOVJEK I/ILI OKOLIŠ

Nema dvojbe da je čovjek biće koje gradi svoj svijet na sasvim poseban način, sasvim drugačije od svih drugih „svjesnih“ oblika života. Dakako, ovo treba nadopuniti jasnim kazivanjem da je temeljni supstrat ljudskog bića „isto ono životno“ što možemo naći i u beskraju drugih oblika života. Ono što čovjeka, kao ljudsko biće, kao misaoni i senzibilni entitet, razlikuje od drugih oblika života jest to da proizvodi kulturne obrasce u kojima živi, kojima nastoji sebi objasniti svoje postojanje, i putem kojih komunicira s drugim ljudskim bićima, i s drugim oblicima postojanja. Kulturni konstrukti o kojima govorimo su filozofija, religija, umjetnost, mit, znanost, ekonomija i drugi. Možda možemo reći da je i okoliš kulturni konstrukt, ukoliko pristajemo na tezu da je okoliš „prerađena“ priroda ili pojedini dijelovi preuzeti iz strukture cjeline života „oblikovani“ u čovjeku služeće modele. Mogli bismo reći da je čovjek – u različitim oblicima geografske i historiografske zatečenosti – spoj „prirodnosti“ vlastitog bića i okoliša koji je svojim proizvodnim nastojanjima oblikovao. Vrijedi ovdje napomenuti da termine „okoliš“ i „priroda“ ne koristimo kao jednoznačne, kao što i vrijedi napomenuti da radije umjesto termina „priroda“ radije koristimo termin „cjelina života“. Nema dvojbe, da sam termin okoliš upućuje na antropocentrično razumijevanje čovjekova odnosa prema cjelini života.

Upravo u ovoj točki – onoj ocrtanoj antropocentrizmom – dolazimo do prvog značajnog problema ovog rada. Upravo je problem antropocentrizma kao vrijednosnog određenja odnosa, i istovremeno, kao operativnog mehanizma ljudskog djelovanja glavni pokretač uništenja cjeline života. Možemo reći da termin antropocentrizam razumijevamo u vrijednosnom, konkretno etičkom, pogledu na način čovjekove ekskluzivizacije, izdizanja iz cjeline života. Sukladno ovom tumačenju, život je imao smisla ako služi čovjeku, čovjek je mjera svih oblika postojanja i cjelokupno se postojanje mjeri ljudskim vrijednostima, ljudskom iskustvu i ljudskim doživljajima [3]. U operativnom pogledu, konkretno s socio-kulturnog gledišta, antropocentrizam omogućuje beskonačnu potrošnju prirodnih resursa, izgradnju proizvodnih kapaciteta koji daleko nadmašuju potrebe čovječanstva u cjelini, oblikovanje mehanizama proizvodnje koji ne mare za potrošnju energije, emisiju štetnih tvari ili uništenja staništa, ili pak cijelih područja zemlje. Ovim dvama određenjima mogli bismo dodati treće, ono političko, ono u kojemu je supremacija ljudskih bića nad životom dobila dimenziju moći ljudskih bića nad drugim ljudskim bićima. Ovi nas uvidi upućuju na promatranje fenomena iskorištavanja ljudskog rada, stvaranja nesigurne pravne regulative u području radnog prava ili, s druge strane, (premda u biti paralelno i usmjereno), stvaranja konstrukcija hiperpotrošačkog društva.

Sve ovo nam, u raspravi o problematici zaštite okoliša, posebno u problematici cjelovitog pristupa, nužno nameće dva problema ili bolje pitanja. Prvo, zašto uopće govoriti o okolišu, konkretno koji su razlozi da govorimo o okolišu i što tim „govorenjem“ želimo postići? I drugo, koje je „posljednje“ obilježje same mogućnosti govora o okolišu, ili sasvim konkretno, što taj govor čini mogućim? Odgovori na ta pitanja zapravo su jednostavni, iako istovremeno zastrašujuće obvezujući. Odgovor na prvo pitanje je sljedeći: o okolišu govorimo zbog same činjenice uništenja života, koju čovjek „čini“ mehanizmima svoje tehnološke moći. Ovdje je potrebno zastati i ocrtati odnos znanosti i tehnologije. U novovjekovnim konstrukcijama znanost je bila zamišljena kao mehanizam otkrivana skrivenih zakutaka zbilja, i kao mehanizam objašnjavanja svijeta. S vremenom, povećanjem spoznaja, povećanjem učinkovitih modela istraživanja pojava, stvaranjem sve snažnijih učinaka istraživanja raste i svijest o moći znanosti, a ta se moć koncentrira u tehnologiji, u artefaktima koji su proizvod znanosti, znanstvenog rada i znanstvenog načina mišljenja. S rastom kvalitete i učinkovitosti tehnoloških artefakata, raste i moć tehnologije. Znanost tako postaje pogled na svijet, više nego istraživanje nepoznatog, a tehnologija, konkretno tehnološki artefakti, oruđa onih koji dijele taj pogled na svijet. Razumije se da svi resursi dolaze iz prirode, i svi se potrošeni artefakti vraćaju u prirodu. Zastrašujući opseg ovih događanja upućuje nas na potrebu propitivanja razloga njihova nastanka, i ne samo to, na potrebu uklanjanja onih postupaka koji postaju prijetnja čovjeku [4].

Upravo je spomenuti termin tehnološke moći točka u kojoj se sabiru svi ranije spomenuti problemi. Naime, sasvim pojednostavljeno, čovjek putem kultura proizvodi artefakte koji trebaju riješiti neke konkretne probleme života, primjerice hladnoću ili bolesti, povećati sigurnost života ljudi, ili u krajnjoj konsekvenci povećati komociju života. S vremenom, sve je veći broj tih artefakata, istovremeno sve je i veća komocija života. Razumije se, za artefakte su potrebni resursi, potrebna je energija za njihovo održavanje, a potrebna su i odlagališta sve ono što je upotrijebljeno i nepotrebno. Sve ovo čini pritisak na okoliš, posebno na neke njegove prirodne dijelove, ovaj pritisak očituje se i kao prijetnja čovjeku i njegovom postojanju kao zasebnog entiteta. U ovoj se točki počinjemo pitati o uništenju okoliša koje uzrokuje povećana potrošnja prirodnih resursa, nezaustavljivo emitiranje štetnih tvari različitih oblika i na različite načine u biosferu, uništenje biljnih i životinjskih vrsta, čak i uništenja habitata u cjelini [5]. Sve ovo nam je dovoljno da se upitamo zašto, i to u obliku drugog ranije izrečenog pitanja.

3. ZNANJE – OPERATIVNO I/ILI VRIJEDNOSNO ODREĐENJE

U ovome se krije i odgovor na drugo pitanje. Prisjetimo se, koje je „posljednje“ obilježje same mogućnosti govora o okolišu, ili sasvim konkretno, što taj govor čini mogućim? Treba dakako razabrati negativni impuls ove mogućnosti. Imajući pred očima ranije rečeno, pokušajmo sagledati problem iz drugog kuta. Naime, u pozadini svakog djelovanja je određeno „shvaćanje situacije“ u kojoj netko djeluje, kada koristimo termin „shvaćanje situacije“ mi referiramo na koncept znanja, konkretno poznavanje činjenica i procesa, te ujedno poznavanje mehanizama djelovanja koji proizvode učinke. U suprotnom djelujemo bez svijesti o vlastitim postupcima. Kako smo rekli, govoreći o znanosti, govorimo o kulturnom konstruktu koji je obilježen posebnim načinom mišljenja, onim koji polaže povjerenje u racionalnost, logičko konstruiranje iskaza, eksperimentalno provjeravanje pretpostavki, i više od svega, onim koji je usmjeren na učinak [6].

Sada se moramo poduhvatiti najtežeg zadatka našeg promišljanja u ovom radu. Trebamo postaviti pitanje o odnosu znanja i znanosti, ili bolje o karakteru znanstvenog

znanja. Prije daljnjih razlaganja dobro je konsultirati definicije samog termina. Tako, prema G. Petroviću, znanje je

> "(...) rezultat spoznaje, objektivno zasnovana uvjerenost u istinitost nekog suda ili sudova, također sud ili skup sudova u čiju je istinitost netko s pravom uvjeren" [7].

Drugi autor, Z. Čuljak naglašava:

> "(...) znanje je opravdano istinito vjerovanje ili istinito vjerovanje za koje subjekt ima dostatno opravdanje u obliku dokazne građe ili epistemičkih razloga, tj. razloga koji upućuju na njegovu istinitost ili je u nekom stupnju jamče" [8].

Ovdje trebamo, na temelju rečenog, istaknuti dvije stvari. Prva je ta da znanje ima neke veze s istinom, da je zabilješka istine ili model njena prijenosa. Druga je ta, je „nositelj" znanja neki subjekt, individuum, dakle pojedinac, ili bolje osoba. Nema dvojbe, znanje je ono provjerljivo, racionalno, priopčivo, i istovremeno, ono što je nesavršeno, podložno kritici i podložno neprestanim rekonstrukcijama. Ovdje se moramo osvrnuti na dvije stvari, prva je da se „znanje događa" uvijek u nekom kulturnom horizontu, i druga je da je „nositelj znanja" uvijek pojedinac. Oba ova određenja dodatno naglašavaju nesavršenost znanja kao temeljno obilježje. Ovdje je potrebno vratiti se u raniji tok našeg promišljanja, u dio o znanosti kao kulturnom konstruktu, načinu mišljenja koji je vlastiti „zapadnjačkom čovjeku", i ponajprije, o tehnološkoj moći koja je postala svrha znanstvenog znanja. Konkretno, znanje, kako ono „postoji" u zapadnjačkom misaonom kozmosu, lišeno je vrijednosne odrednice, i stoga „ono", u operativnom pogledu, „proizvodi" (iako ne proizvodi samo to kako smo već rekli) uništenje života. Ovu situaciju je koristeći termin opasnog znanja opisao američki onkolog i bioetičar V. R. Potter na sljedeći način:

> „Kako je znanost postajala sve složenijom i kako se količina relevantnog znanja započela udvostručivati u sve kraćim vremenskim razmacima, to su se znanstvenici započeli usavršavati. Kako su znanstvenici postajali sve više upoznati na sve manje toga, znanstvenik pojedinac sve manje se oslanjao na vlastitu sposobnost organizacije svog specijaliziranog znanja u većem kontekstu znanosti i društva. Više nije mogao posvetiti svoje vrijeme kozmičkim pitanjima ili brinuti se o krajnjoj istini" [9].

Mogli bismo dodati da znanstvenici sve više znaju o sve manje toga, i sve su manje upućeni u ono što drugi znaju. Možda zato Potter i dodaje:

> "(…) kada govorimo o opasnom znanju moramo odmah potvrditi da znanje samo po sebi ne može biti bitno dobro ili loše. Ono što je potaklo vjerovanje u koncept opasnog znanja je znanje koje predstavlja moć, a kada je znanje jednom dostupno, iskoristit će se kao moć kad god je to moguće. Jednom stečeno znanje nikada se ne može ostaviti u knjižnici da skuplja prašinu ili zaključati u trezor. Nitko ne brine o znanju koje se ne koristi. Njegove primjene su te koje ga čine opasnim i korisnim" [9].

Kao i Ortega y Gasset i Potter naglašava ključni moment znanja, njegovu moć i tu vidi opasnost, stoga dodaje:

> „(…) opasno znanje definirano je kao znanje koje se nakupilo brže nego ga je mudrost mogla svladati. Današnje metode za svladavanje rascjepa između znanstvenog znanja i političkih smjernica nisu adekvatne" [9].

Vrijedi nam se zapitati kako to da je u zapadnjačkim misaonim konstrukcijama znanje postalo moć, i to upravo kao moć nad životom. Možda je razlog izravna usmjerenost da dobrobit ljudi, na izgradnju struktura sigurnosti i komocije. Sve vidljiviji učinci ovakvog postupanja prema životu doveli su do potrebe za promišljanjem korijena ovih postupaka, i do

potrebe osmišljanja novih putova kojima bi se kretalo čovječanstvo. Razvidno je da su oblici znanja, kako je ono oblikovano u znanstvenim konstrukcijama, posebno u segmentu upućenosti na učinak nedostatni. Riječ je o partikularnim i jednodimenzionalnim izvedbama kojima nedostaje cjelina: cjelina ljudskog bića i cjelina života.

4. ZAŠTO UOPĆE GOVORITI O CJELOVITOSTI

Dospjeli smo do sljedeće pozicije: znanje, pa time i znanstveno znanje, moramo razumjeti kao vrijednosni a ne „čisto“ operativni koncept. Ukoliko je znanje „ono“ što je stvoreno“ u horizontu neke kulture, kako smo zapazili, te istovremeno ono što je bitno vezano za neki subjekt, nije moguće umaći zaključku da je znanje „nešto“ što nužno nosi vrijednosno obilježje. Naša zapažanja o znanstvenom znanju ukazuju da, ako je suditi po učincima, no ne nosi vrijednosno obilježje. Stoga, ako nastojimo oko razumijevanja problema holističkog pristupa okolišu, posebno s gledišta uzroka koji su doveli do uništenja okoliša, pa stoga i do potrebe promjene gledanja na ulogu čovjeka u životu, potrebno je nastojati oko oblikovanja znanja kao integralnog, a ne primarno operativnog fenomena te, temeljem rečenog, oko izgradnje novog pogleda na svijet, nazovimo ga bioetikom, u kojemu je u temelje upisana obazrivost kao bitno određenje.

Istovremeno, obazrivost je upisana i u određenje „integralnog“ jer samo razumijevanje integralnog počiva na de-izolaciji mislitelja / djelovatelja, konkretno, čovjeka čije djelovanje nije više usmjereno na sebe sama, i na vlastitu komociju, što je ishodište procesa uništenja života. Kada je u pitanju okoliš, vraćamo sa na početak, na fenomen uništenja života, naše temeljno pitanje je sljedeće: koji bi koncept znanja odgovarao očuvanju života a ne njegovom uništenju? Međutim, još je jedno pitanje prije toga, u kojem horizontu bi se ono oblikovalo? Pokušajmo riječima H. Jurića oblikovati odgovor na drugo pitanje, riječ je o bioetici, i to shvaćenoj na sljedeći način:

> “(…) otvoreno područje susreta i dijaloga različitih znanosti i djelatnosti, te različitih pristupa i pogleda na svijet, koji se okupljaju radi artikuliranja, diskutiranja i rješavanja etičkih pitanja vezanih za život, za život u cjelini i u svakom od dijelova te cjeline, za život u svim njegovim oblicima, stupnjevima, fazama i pojavnostima“ [10].

Kako vidimo riječ je o potrebi izgradnje novog sustava znanja, no istovremeno i novog pogleda na svijet. Potrebno je učiniti korak od razumijevanja života kao resursa, kojemu je čovjek superioran, do razumijevanja života kao beskrajno složene i neizmjerno značajne pojave, kojoj je čovjek samo dio. U tom novom horizontu ljudskog postojanja potrebno je i izgraditi novi koncept znanja, i ovdje se vraćamo na malo prije postavljeno pitanje, a odgovor ćemo dati riječima I. Cifrića koji kazuje da je suvremenom čovjeku potrebno orijentacijsko znanje, dakle ono znanje, „koje će omogućiti kriterije raspolaganja znanstvenim znanjem, poglavito u segmentu odnosa prema životu.“ No istovremeno, važno je naglasiti, orijentacijsko znanje vodi računa o posljedicama primjene znanja [11].

Tome je tako jer je život cjelina, i niti jedan drugi pristup životu osim cjelovitog nije opravdan. Cjelina, geometrijski gledano, ima bezbroj središnjih točaka i niti jedna ne može postojati izolirano, posebno zato što se cjelina vidi u snazi odnosa među dijelovima. Razumije se, nisi svi dijelovi jednako složeni, niti možda jednako značajni za postojanje cjelina, no, stupanj važnosti upućuje na odgovornost, a ne na pravo na dominaciju. Upravo ovo posljednje, temeljno je određenje bilo kojeg holističkog razumijevanja sustava života.

5. ZAKLJUČAK

Temeljni problem koji smo postavili u ovom radu odnosi se na karakter tipa znanja koji dominantan u našem vremenu. Pri tom pod „našem vremenu“ razumijevamo zapadnjačke misaone strukture, i vrijeme znanstveno-tehnološke civilizacije. U tom pogledu nastojali smo, što se tiče ovog rada promotriti, prvo, koji je utjecaj čovjeka na okoliš, konkretno, kakve su po okoliš implikacije gore prikazanog znanstvenog načina mišljenja. Konstatirali smo da znanje usmjereno na učinak proizvodi uništenje okoliša, budući da je izgrađeno u antropocentričnom modelu i da nema vrijednosnih ograničenja. Drugo, u smo ovom radu nastojimo promotri fenomen znanja kako ovaj fenomen razumijevamo u kontekstu zapadnjačkog načina mišljenja. U ovoj smo poziciji nastojali ocrtati kulturna određenja vlastita zapadnjačkim društvima i razloge zašto ona „proizvode“ upravo taj oblik znanja. U toj stvari naznačili smo da je način mišljenja okrenut učinku, a djeluje u modelima racionalnosti, mjerivosti i izračunljivosti. U ovoj stvari poseban naglasak dajemo na etičke opservacije vezano uz primjenu znanja, u toj stvari spomenuli smo problem orijentacijskog znanja i horizont bioetike u kojemu se ovaj tip znanja izgrađuje. Treće, nastojali smo razabrati zašto je uopće potrebno govoriti o cjelovitosti. Ili bolje može li nam „govorenje“ o cjelovitosti, na način kritičke diskusije o problemima znanja, donijeti nešto novo u našem poznavanju problema znanja i kako ove pozicije korespondiraju s razumijevanjem života u misli suvremenog čovjeka [12].

Nema dvojbe da je hiperacionalistički konstrukt koji znanje poima kao korist ljudi, pokazao ne samo svoje nedostatnosti, nego i proizveo brojne nezaobilazne mehanizme uništenja života. Postavljamo stoga pitanje, kako je suvremenom čovjeku moguće živjeti, a da pri tom ne uništi život u cjelini. Potrazi za odgovorom na ovo pitanje posvećeno je i ovo izlaganje.

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Zahvala

Ovaj rad dio je rezultata istraživanja provedenih u okviru potpore istraživanja „Uloga filozofije u oblikovanju refleksivnih potencijala – primjer odgojiteljske profesije“, koja se (2018/19.) provodi na Učiteljskom fakultetu Sveučilišta u Zagrebu, voditelj: izv. prof. dr. sc. Tomislav Krznar, potporu financira Sveučilište u Zagrebu.

PILOT PROJEKT SAKUPLJANJA OTPADNOG JESTIVOG ULJA IZ KUĆANSTAVA

PILOT PROJECT OF COLLECTING USED COOKING OIL FROM HOUSEHOLDS

Vesna Kučan Polak*, Slavica Rukavina*, Mato Burić*, Tea Tonković Pleša*

* INA d.d., Zagreb, Hrvatska

autor za korespondenciju: Vesna Kučan Polak, e-mail: vesna.kucan-polak@ina.hr

Stručni članak

SAŽETAK

Kao društveno odgovorna kompanija usmjerena ka održivom razvoju INA je od listopada 2017. godine na odabranim maloprodajnim mjestima pokrenula pilot projekt: nova „zelena" usluga – prikupljanje otpadnog jestivog ulja.

Cilj ovog pilot projekta je ispitati mogućnosti prikupljanja otpadnog jestivog ulja iz hrvatskih domaćinstava na prodajnim mjestima INA-e. Prikupljene količine otpadnog jestivog ulja mogle bi se iskoristiti u proizvodnji naprednog biogoriva čiji je energetski doprinos dvostruko veći u ispunjenju ciljeva korištenja biogoriva u prijevozu budući da je proizveden iz otpada, a ne iz sirovina koje se koriste u ljudskoj ili životinjskoj prehrani.

U Hrvatskoj kućanstva godišnje stvore značajnu količinu otpadnog jestivog ulja koje ukoliko završi u okolišu kao otpad u značajnoj ga mjeri zagađuje. S druge strane, otpadno jestivo ulje korisna je sirovina te se obrađeno može koristiti za proizvodnju gore spomenutih naprednih biogoriva, ali i drugih proizvoda (deterdženata, sintetskih guma i sl.). Ovim projektom INA ide u korak i sa svjetskim industrijskim trendovima koji sve više koriste obnovljive izvore energije ili recikliranjem koriste energiju iz otpada.

***Ključne riječi**: otpadno jestivo ulje, biogorivo iz otpada, otpad*

ABSTRACT

As a socially responsible company focused on sustainable development, in October 2017 INA offered to customers a new "green" service - collecting of used cooking oil at selected retail locations.

The aim of this pilot project is to examine the possibilities of collecting used cooking oil from households in Croatia at the INA retail locations. Collected amounts of used cooking

oil could be used in the production of advanced biofuels, whose energy contribution is double counted in fulfilling the targets of using biofuels in transport, since it is produced from waste, not from raw materials for human or animal food.

In Croatia, households generate a significant amount of used cooking oil. If it ends in the environment as waste, it pollutes it significantly. On the other hand, used cooking oil is a useful raw material. It could be used to produce already mentioned advanced biofuels and other products (synthetic rubber, detergents etc.).This INA project is in line with world-wide industrial trends that are increasing using renewable energy sources or using recycled energy from waste.

***Keywords**: used cooking oil, waste based biofuel, waste*

1. UVOD

Ograničeni prirodni resursi i negativni utjecaji na okoliš uzrokovani njihovom potrošnjom zahtijevaju iznalaženje novih modela za njihovo održivo korištenje. Strategija razvoja EU do 2020. kao jedan od osnovna tri prioriteta predlaže održiv rast, tj. promicanje ekonomije koja učinkovitije iskorištava resurse, koja je zelenija i konkurentnija, a središnji aspekt ove strategije je prelazak s postojećeg linearnog na kružno gospodarstvo. Ovakav ekonomski model osigurava održivo gospodarenje resursima i produžavanje životnog vijeka materijala i proizvoda, a čime se ujedno smanjuje nastajanje otpada na najmanju moguću mjeru.

Sustavno upravljanje zaštitom okoliša sastavni je dio Inine poslovne politike, a posebna pozornost posvećena je sigurnim i zdravim radnim uvjetima te brizi za okoliš uz primjenu načela predostrožnosti i racionalnog gospodarenja resursima. U cilju provedbe navedene politike posebna pažnja posvećuje se očuvanju prirodnih resursa, povećanju korištenja obnovljivih izvora energije, racionalnom korištenju energetskih resursa, promicanju i razvoju pro aktivne kulture na zaštiti okoliša te poboljšanje učinkovitosti u zaštiti okoliša.

Otpadno jestivo ulje (OJU) značajno onečišćuje vodne tokove, a već i male količine u vodi rezultiraju povećanim troškovima separacije i smanjenom učinkovitošću pročišćavanja. Biljna ulja pa tako i otpadna jestiva ulja vrijedna su sirovina za proizvodnju biogoriva. Biodizel [1] je metilni ester masnih kiselina (FAME) koji se proizvodi od biljnog ili životinjskog ulja, koji ima svojstva dizela i proizvodi se transesterifikacijom. Biogorivo se može proizvesti i obradom ulja vodikom, samostalnim procesom ili u procesima sa postojećim naftnim tokovima pri čemu nastaje tzv. hidrogenirano biljno ulje. Hidrogenirano biljno ulje je po svom sastavu ugljikovodik, uglavnom smjesa n- i izo-parafina i kao takvo se može koristiti za namješavanje u dizelsko gorivo kako bi mu se poboljšala svojstva i smanjile emisije onečišćujućih tvari u zrak [2].

Nacionalni Akcijski plan poticanja proizvodnje i korištenja biogoriva u prijevozu za razdoblje 2011 - 2020 u Hrvatskoj izrađen 2010., propisuje cilj od 10 % biogoriva u transportu do 2020. godine [3]. Tijekom 2014. i 2015. godine dolazi do izmjena kriterija u korištenju biogoriva (tzv. ILUC (Indirect land use change) direktive [4], na način da se ograničava korištenje biogoriva dobivenih iz sirovina pogodnih za ljudsku i životinjsku prehranu. Članak 2. direktive i aneks IX dopunjen je i listom sirovina (otpad, ostatci, ne-jestivi materijal i lignocelulozne tvari) te biogoriva proizvedena iz navedenih sirovina imaju dvostruki energetski doprinos u ispunjavanju cilja. To je ujedno i glavni motiv za istraživanje ovakvih tipova sirovina, njihovog potencijala i mogućnosti prikupljanja u Hrvatskoj a u svrhu proizvodnje tekućih biogoriva.

2. EKSPERIMENTALNI DIO

2.1. Otpadno jestivo ulje

Pravilnik o gospodarenju otpadnim uljima [5] 124/06, 121/08, 31/09, 156/09, 91/11, 45/12, 86/13, definira način gospodarenja otpadnim uljima te druga pitanja u svezi gospodarenja otpadnim uljima.

»Otpadno jestivo ulje (OJU)« je svako ulje koje nastaje obavljanjem ugostiteljske i turističke djelatnosti, industriji, obrtu, zdravstvenoj djelatnosti, javnoj upravi i drugim sličnim djelatnostima u kojima se priprema više od 20 obroka dnevno. Otpadno jestivo ulje u katalogu otpada ima ključni broj 20 01 25 i predstavlja neopasni otpad.

Iz gore navedenog vidljivo je da zakonsku obavezu sakupljanja otpadnog jestivog ulja ima tzv. HORECA kanal (hoteli, restorani, catering) dok se odvajanje i prikupljanje otpadnog jestivog ulja iz kućanstava oslanja isključivo na svijest i stav pojedinca.

Ovaj rad stavlja u fokus isključivo prikupljanje OJU iz domaćinstava budući da u Hrvatskoj ne postoje učinkovita sustavna rješenja u prikupljanju ove vrste otpada kao što je to slučaj s npr. papirom ili plastikom.

2.1.1. Procjena potencijala količina OJU iz kućanstava

Budući da se Hrvatska priključila EU 2013-te godine, studije koje su se bavile ovom problematikom na razini EU nisu uključivale područje Hrvatske, stoga su prve procjene o statusu i potencijalu OJU iz kućanstava na području Hrvatske dobivene vlastitom analizom dostupnih literaturnih podataka u 2014.-toj godini.

Analiza potencijala otpadnog jestivog ulja izrađena je na temelju procjene godišnje količine rafiniranog jestivog ulja za kuhanje na hrvatskom tržište, a koja iznosi oko 50.000 t/godišnje.

Temeljem odnosa korištenja jestivog ulja u HORECA kanalu i kućanstvima u omjeru od 50:50 dolazimo do količine od cca 25.000 t jestivog ulja godišnje koje se konzumira u kućanstvima. Ako konzervativnim pristupom pretpostavimo da nakon korištenja ostane samo 50 % otpadnog jestivog ulja, jer se dio apsorbira u hranu, dolazimo do količine od cca 13.000 t godišnje kao minimalnog tehničkog potencijala OJU na godišnjoj razini u Hrvatskoj.

Noviji podaci i najbolja EU praksa [6] pokazuje danas da se može postići efikasnost skupljanja od 64 %, a što bi u slučaju Hrvatske značilo cca 16.000 t. Dakle, može se zaključiti da se potencijalna količina OJU koja nastane u kućanstvima u Hrvatskoj procjenjuje u rasponu od 13.000 - 16.000 t /godišnje.

Nadalje, studije na primjerima EU [7] procjenjuju da se po glavi stanovnika u EU i temeljem prehrambenih navika, u prosjeku može prikupiti 8 L po stanovniku što bi u slučaju Hrvatske značilo da je ukupan potencijal oko 30.000 t/godišnje te ako od te količine 50 % pripada potrošnji u kućanstvima dolazi se do brojke od 15.000 t/godišnje, a što potvrđuju već ranije izrađene procjene.

2.1.2. Količine prikupljenog OJU

Bio otpad je kuhinjski otpad (ostaci od pripreme hrane) i vrtni ili zeleni otpad. Čini gotovo trećinu kućnog otpada te zauzima značajno mjesto u programima odvojenog sakupljanja bio otpada europskih institucija na način da se odlaganje otpada od hrane na razini EU smanji za 50 %.

Odvojeno sakupljanje pojedinih vrsta komunalnog otpada (prvenstveno papir, staklo, plastika, metal) provodi se sakupljanjem s kućnog praga putem spremnika na javnim površinama, zelenih otoka, reciklažnih dvorišta. Odvojeno sakupljanje korisnih vrsta otpada iz komunalnog otpada organizirano od strane jedinice lokalne samouprave i provodilo se tijekom 2015. godine u oko 400 općina i gradova u Hrvatskoj. Iako se broj izgrađenih reciklažnih dvorišta povećao sa 17 u 2010. godini na 84 u 2016. godini, te je do 2016. godine nabavljeno i 46 mobilnih jedinica, ukupne količine sakupljene putem reciklažnih dvorišta se nisu značajno povećale [8]. Konkretno za slučaj prikupljanja otpadnog jestivog ulja iz kućanstva, prema informacijama od strane ZG Čistoće (2017 god.) do sada, u reciklažnim dvorištima grada Zagreba količina prikupljenih otpadnih jestivih ulja iznosi 0, tj. nije prikupljena niti jedna litra.

Baza ROO (Registar Onečišćivača Otpada) je skup podataka o izvorima, vrsti, količini, načinu i mjestu ispuštanja, prijenosa i odlaganja onečišćujućih tvari i otpada u okoliš iz pojedinačnih izvora), sastavni je dio informacijskog sustava zaštite okoliša Republike Hrvatske koji obuhvaća i dionike izvan sustava FZOE (Fond za zaštitu okoliša i energetsku učinkovitost).

Količine sakupljenog OJU iz tzv. HORECA kanala u Hrvatskoj prikazane su u tablici 1.

Tablica 1. Količine otpadnih jestivih ulja sakupljene od početka provedbe pravilnika koji uređuju gospodarenje posebnim kategorijama otpada (FZOEU i HAOP, 2016.) [8]

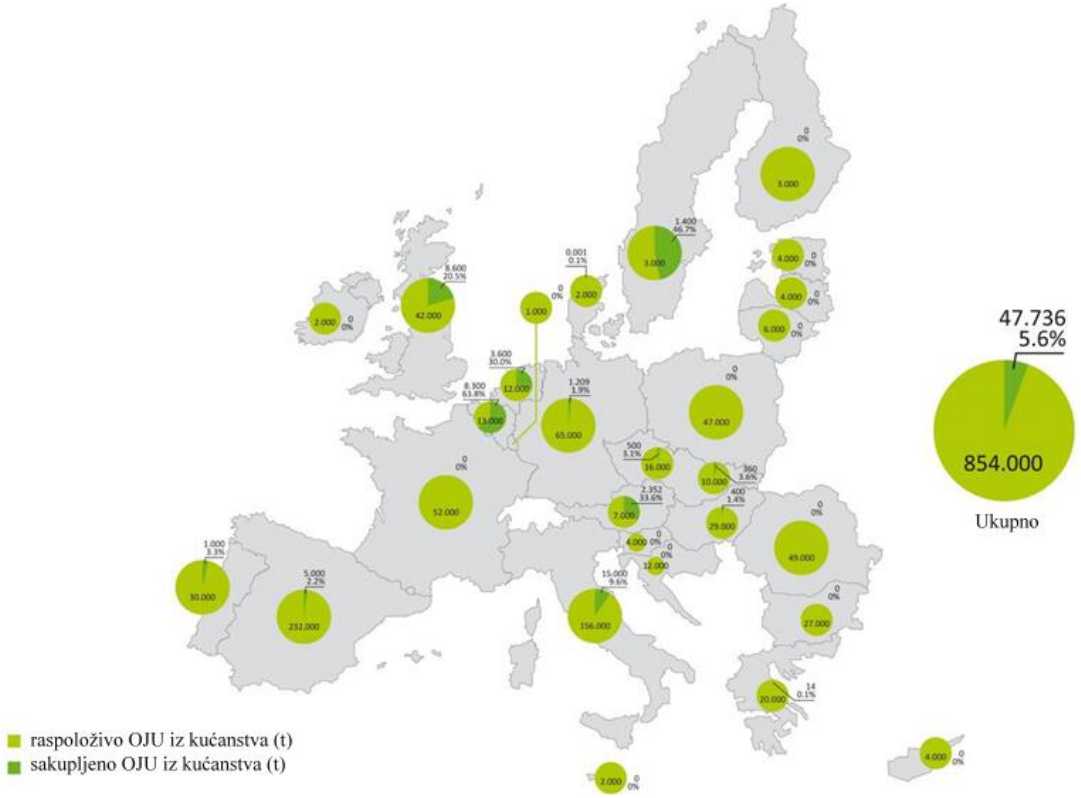
Posebna kategorija otpada	Sakupljeno									
	2006	2007.	2008.	2009.	2010.	2011.	2012.	2013.	2014.	2015.
Otpadna ulja -jestiva (t)	-	1.132	1.606	2.145	1.260	1.196	911	718	721	759

Do 2009. godine se količine sakupljenog otpada sustavno povećavaju, a nakon 2009. godine se bilježi stagnacija ili pad u sakupljenim količinama, što je najvjerojatnije uvjetovano smanjenom količinom proizvoda koji se stavljaju na tržište uslijed gospodarske krize. U 2015. godini sakupljene količine većine posebnih kategorija otpadom rastu.

Prema podacima FZOEU-a u 2015. godini ukupno je sakupljeno 759 t otpadnih jestivih ulja unutar sustava FZOEU-a i oporabljeno je 761 t.

Međutim podaci HAOP-a generirani iz podataka prijavljenih u bazu ROO koji obuhvaćaju dionike izvan sustava FZOEU-a pokazuju da je u 2015. godini sakupljeno 4.163 tona otpadnih jestivih ulja od čega je 1.400 t oporabljeno u RH, a 2.500 t izvezeno na oporabu u druge zemlje.

Procjenjuje se da se u EU trenutno prikupi manje od 50.000 tona OJU iz kućanstava, dok se istovremeno ukupan potencijal procjenjuje na razinu od 800.000 – 900.000 t godišnje [9] To znači da se trenutno iskorištava samo 5 %, a navedena je i procjena za Hrvatsku od 12.000 t godišnje. Situacija u zemljama EU prikazana je na slici 1:



Slika 1. Sakupljanje OJU u EU; sakupljene količine i potencijal [9]

2.1.3. Primjeri iz prakse: načini prikupljanja OJU iz kućanstava u EU

Najučinkovitiji način organiziranja prikupljanja OJU iz kućanstava je putem lokacija prikupljanja koje se nalaze diljem zemlje. Građani mogu donijeti svoje OJU u boci ili posebno dizajniranom spremniku, kantici, na sabirne lokacije koje su u blizini naselja, na ulicama, parkiralištima, supermarketima, školama itd. Pokazalo se da lokacija prikupljanja OJU, a ne njihov broj najviše utječe na količine ulja prikupljene u gradu ili regiji.

Također, uspješnost prikupljanja OJU iz kućanstava određena je i dobro osmišljenom informativnom i promotivnom kampanjom. Ljudi moraju biti dobro informirani o nužnosti i mogućnosti recikliranja OJU-a, te moraju razumjeti zašto bi to trebali učiniti i kakve će koristi biti, inače vjerojatno neće započeti sakupljanje kod kuće. Također je vrlo važno uključiti djecu.

Načini promocije ovise o pojedinoj regiji i prehrambenim navikama stanovništva. U nekim državama članicama svijest ljudi i odnos prema odvajanju otpada je na visokoj razini, dok kod nekih je potrebno razviti istu, odnosno organizirati razne događaje, natjecanja s nagradama, TV spotovima itd. kako bi se postigli slični rezultati.

Postoje tri mogućnosti načina prikupljanja:

1. Decentralizirano sakupljanje ("od vrata do vrata"): OJU se prikuplja izravno od pojedinih kućanstava, često od strane tvrtki za gospodarenje otpadom koje već djeluju u regiji i skupljanjem drugih vrsta otpada,
2. Centralizirano sakupljanje: točke prikupljanja smještene su po gradovima i gradovima u školama, trgovačkim centrima, parkiralištima, ulicama itd. na dva različita načina:

a) OJU se izlijeva izravno iz malog spremnika ili boce u predviđene spremnike na sabirnim mjestima ili centrima za recikliranje otpada,
b) OJU se sakuplja u bocama ili malim kanticama koje se mogu upotrijebiti više puta. Pune boce/kantice se ostavljaju i razmjenjuju za čiste,
3. Kombinirano sakupljanje: koriste se obje navedene metode: sabirne točke po gradovima i "od vrata do vrata".

Najbolji primjeri iz prakse prikazani su u tablici 2.

Tablica 2. Primjeri prikupljanja OJU iz nekih zemlja EU [6]

Država	Br. stanov., * mil	Broj lokacija	Sakupljena količina, god, t	Sakupljeno kg / glavi stanovnika,	Sakupljeno po lokaciji sakupljanja, t	Procjena potencijala kg/po glavi stanovnika	Sakupljeno % od potencijala
Belgija	11,3	700	8.300	0,73	11,9	1,16	64
Austrija	2,4	-	2.400	1	-	0,8	34
Nizozemska	16,9	2000	3.600	0,21	1,8	0,7	30

* na području pokrivenom sakupljanjem

2.2. INA pilot projekt prikupljanja OJU iz kućanstva

Otpadno jestivo ulje može se iskoristiti u proizvodnji naprednog biogoriva čiji je energetski doprinos dvostruko veći u ispunjenju ciljeva korištenja biogoriva u prijevozu budući da je proizveden iz otpada, a ne iz sirovina koje se koriste u ljudskoj ili životinjskoj prehrani.

Cilj INA pilot projekta je ispitati mogućnosti prikupljanja korištenog ulja za kuhanje iz domaćinstava u Hrvatskoj na prodajnim mjestima INA-e i proizvodnja biogoriva. Proizvodnja biogoriva razmatra se u Rafineriji nafte Rijeka u postojećim rafinerijskim tokovima procesom hidrogenacije ili u suradnji sa proizvođačima biodizela koji koriste otpadno jestivo ulje.

Pilot projekt pokrenut je 16. listopada 2017. na 30 odabranih INA maloprodajnih lokacija središnje Hrvatske.

Da bi olakšali odvajanje i sakupljanje OJU, nabavljen je tzv. eko lijevak koji olakšava prikupljanje OJU i besplatno se dijeli kupcima i građanima na određenim maloprodajnim mjestima. Eko lijevak je prikazan na slici 2.



Slika 2. Eko lijevak

Sam način sakupljanja vrši se na način da kupci prilikom posjeta maloprodajnom mjestu (MPM) donesu bocu s uljem i odlože kod INA djelatnika koji je prazni u za to

posebno predviđenu bačvicu, a plastičnu ambalažu odlaže u za to postavljen spremnik, kako je prikazano na slici 3.



Slika 3. Način skladištenja OJU na MPM INA-e

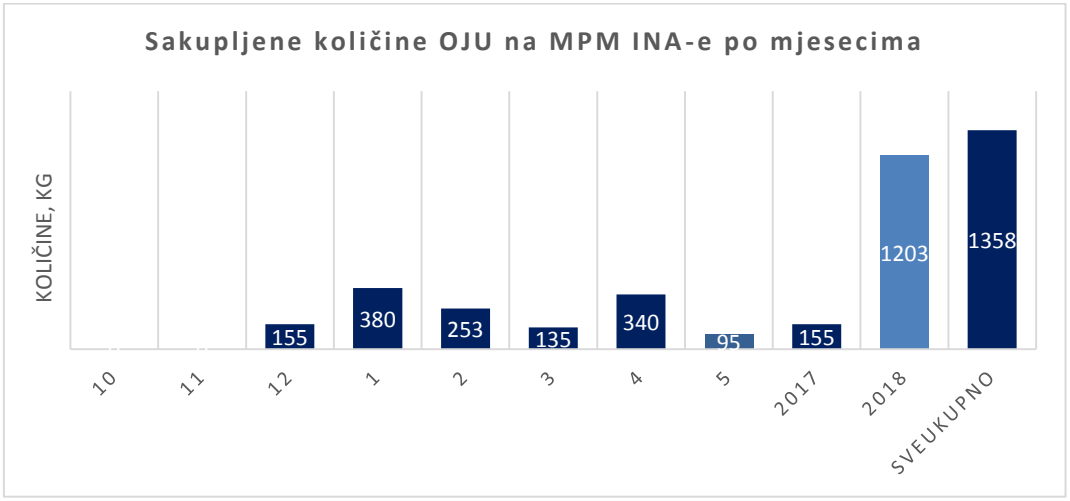
U realizaciju pilot projekta INA je ušla u suradnji s tvrtkom Agroproteinka d.o.o. koja je preuzela ulogu ovlaštenog sakupljača i prijevoznika otpada i koja brine o odvozu i zamjeni punih bačvica.

U pilot fazi projekta koja traje godinu dana odabrano je 30 lokacija u maloprodajnoj mreži regije Zagreb koja obuhvaća 9 županija.

3. REZULTATI I DISKUSIJA

Dva mjeseca nakon početka pilot projekta krenuo je odvoz prvih prikupljenih količina otpadnog jestivog ulja. Početak projekta bio je popraćen brojnim objavama u medijima i društvenim mrežama a TV reklama koja se emitirala vrlo kratko vrijeme (2 tjedna) zauzima 12. mjesto zamijećenosti Ininih reklama. Također, sama kampanja je ušla i u finale nagrade Grand PRix Hrvatske udruge za odnose s javnošću.

Tijek i količine prikupljanja OJU po mjesecima prikazane su na slici 4.

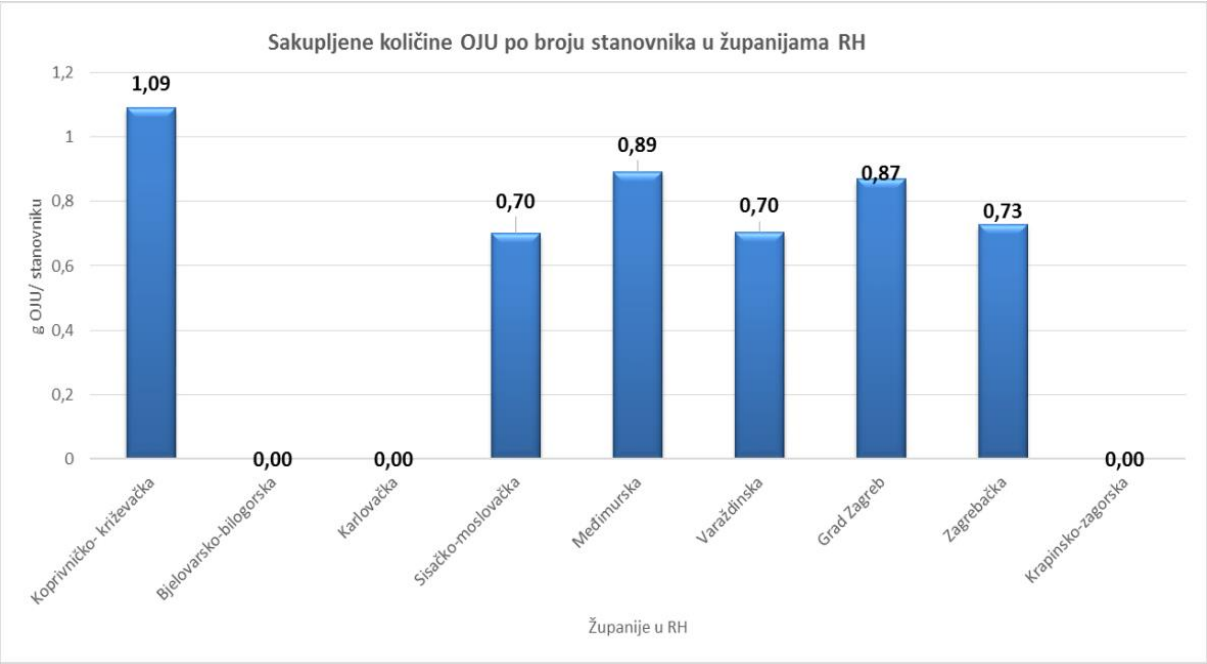


Slika 4. Sakupljene količine na MPM INA-e po mjesecima

U prikupljanju količina prednjače lokacije iz urbanih sredina, npr. Zagreb Maksimir i Trešnjevka, a slijede Varaždin, Koprivnica, Zaprešić i Čakovec. Od 30 lokacija, njih nekoliko nije pokazalo značajne rezultate u sakupljanju. Razloga za lošiji odaziv ima nekoliko:

- starija populacija,
- navike stanovništva,
- alternativno korištenje OJU za kompost ili životinjsku hranu,
- neadekvatna lokacija za sakupljanje,
- slaba informiranost o projektu.

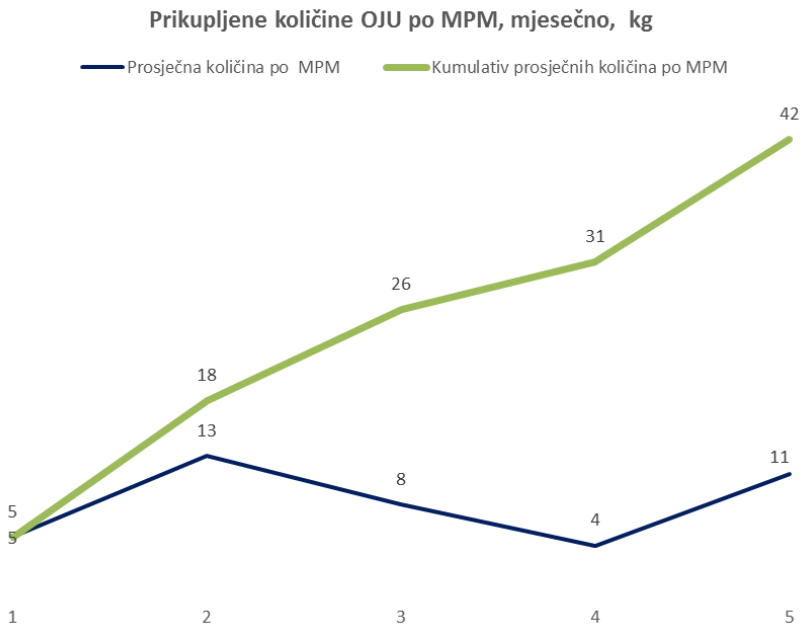
Pogleda li se odnos stanovnika i prikupljenih količina po županijama što prikazuje slika 5, zamjećuje se da je predvodnik u skupljanju Koprivničko-Križevačka županija, slijedi Međimurska, zatim grad Zagreb te Zagrebačka županija.



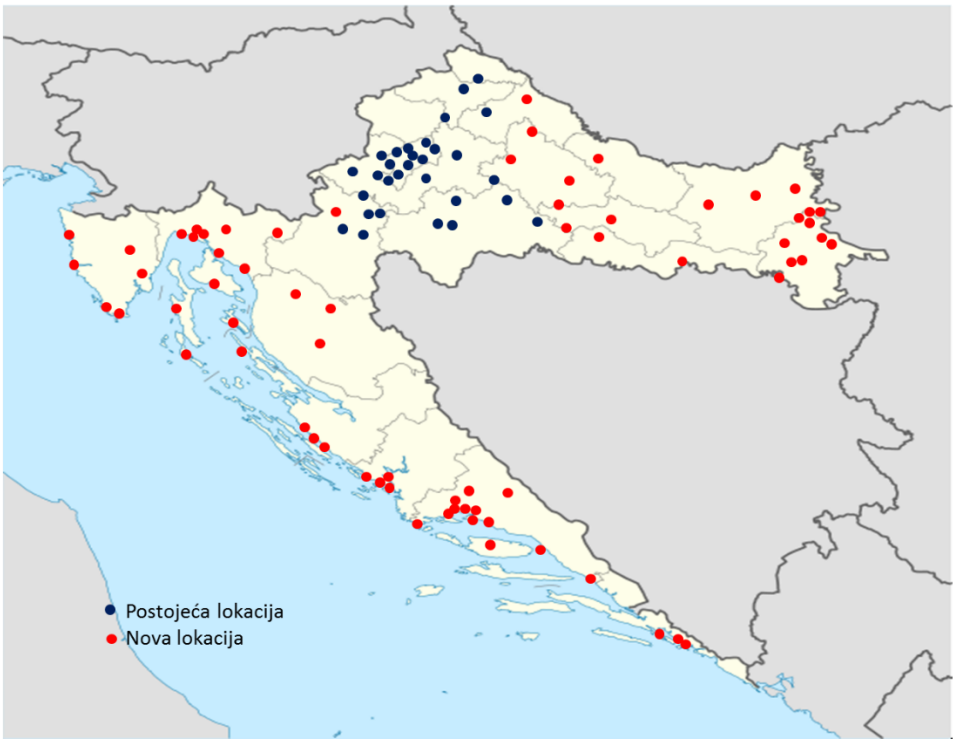
Slika 5. Odnos sakupljenih količina OJU i broja stanovnika po županijama

Ako količine prikupljenog otpada podijelimo s brojem lokacija u prosjeku i ukupno gledajući, rast prikupljanja po lokaciji je intenzivan u vrlo kratkom razdoblju. Konkretno, u 5 mjeseci se povećao 8 puta, što prikazuje slika 6.

Temeljem vrlo dobrog odziva građana planira se proširenje projekta na cijelu Hrvatsku što je prikazano na slici 7.



Slika 6. Prosječno prikupljene količine OJU po MPM INA-e



Slika 7. Plan proširenja lokacija za prikupljanje OJU u RH

Plan je proširi projekt na sve županije u RH i utrostručiti broj lokacija. Također, posebna pozornost planira se posvetiti informiranju javnosti, posebice mladih o važnosti prikupljanja i načinu korištenja OJU. Istovremeno, raditi će se na testiranju prikupljenog OJU, analizirajući kvalitetu i mogućnosti prerade procesom hidroobrade u Rafineriji nafte Rijeka.

4. ZAKLJUČAK

Temeljem dosadašnjih rezultata pilot projekta možemo zaključiti:

- po prvi puta u Hrvatskoj prikupila se količinu OJU koja je do sada vjerojatno i uglavnom završavala u odvodu,
- obzirom na mali broj lokacija i kratku medijsku kampanju odziv građana je vrlo pozitivan,
- u prikupljenim količinama prednjače urbane sredine,
- lokacije koje su lošije reagirale trebaju se dodatnim prikladnim aktivnostima potaknuti na prikupljanje,
- potrebno je pojačati svijest i razloge prikupljanja te načine korištenja što je u našem slučaju proizvodnja biogoriva.

INA u Hrvatskoj ima 392 benzinske postaje i zastupljena je i u udaljenim i slabo povezanim lokacijama (npr. otoci). Uvođenjem ove usluge na našim maloprodajnim mjestima možemo povećati broj lokacija prikupljanja u Hrvatskoj ove vrste otpada, a bez dodatnih investicija za jedinice lokalne zajednice. Prema dosadašnjim rezultatima, a i proširenjem projekta, smatramo da možemo pokazati ekonomski primjer kružnog gospodarstva, učinkovito upravljati resursima na način da se smanji otpad, a istovremeno ga iskoristiti kao sirovinu za nove vrste biogoriva. Ovim projektom INA ide u korak i sa svjetskim industrijskim trendovima koji sve više koriste obnovljive izvore energije ili recikliranjem koriste energiju iz otpada.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

COMPOSTING OF AGROINDUSTRIAL WASTE AND BIOWASTE IN A CLOSED REACTOR

Dajana Kučić Grgić*, Monika Šabić*, Tomislav Domanovac, Vesna Ocelić Bulatović*, Marija Vuković Domanovac***

* University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia
** IPZ Uniprojekt TERRA d.o.o., Zagreb, Croatia

corresponding author: Dajana Kučić Grgić, e-mail: dkucic@fkit.hr

Original scientific paper

ABSTRACT

Tobacco waste, olive mill waste, grape waste and biowaste can be treated by composting process in which biodegradable matter is decomposed in to stabile product (compost) with release of heat, gases (CO_2, NH_3, H_2S, CH_4) and water.

In this work composting process of tobacco waste (TW-P1), mixture of tobacco and grape waste (TGW-P2), mixture of tobacco and olive mill waste (TOW-P3), mixture of tobacco, grape and olive mill waste (TGOW-P4), mixture of tobacco and biowaste (TBW-P5) and biowaste (BW-P6) in thermally insulated reactor with working volume of 10 dm^3, airflow of 0.8 dm^3 min^{-1} and initial moisture of 60 % was conducted.

During the 21 days of composting process conversions of 47 % (P1), 56 % (P2), 50 % (P3), 52 % (P4), 65 % (P5) and 71 % (P6) were reached. The highest production of CO_2 and NH_3 was detected in experiments P6, and P1, respectively.

Keywords: *composting, agroindustrial waste, biowaste, adiabatic reactor*

1. INTRODUCTION

The tobacco, olive oil and wine industry, which are classified as agroindustries, generates large quantities of processing waste. Environmentally friendly disposal of these waste materials is a significant challenge to these industries. Biowaste is a very unstable, quickly biodegrading waste fraction. Its treatment is challenging in terms of avoiding odour and pathogen nuisance. Currently, these wastes (agroindustrial waste and biowaste) in Croatia are disposed predominantly through landfilling. This management practice is under environmental and regulatory scrutiny due to the limited amount of land available for disposal and to increase environmental concerns (groundwater contamination, odour problems). Composting is a suitable way for recycling such type of waste because it helps to solve the

problem of their disposal, reduce emissions of greenhouse gas, and also result in a useful soil improving agent - compost [1, 2]. Composting process is a biological treatment in which aerobic mesophilic and thermophilic microorganisms transform the biodegradable organic matter into CO_2, NH_3, H_2O and compost [3]. The exothermic process produces energy in the form of heat, which results in an increase of the temperature in the mass. A spontaneous process, therefore, passes through a thermophilic phase, which is preceded and followed by two mesophilic phases. The process starts with the oxidation of easily degradable organic matter (decomposition) and the second phase (stabilization) includes not only mineralization of slowly degradable molecules, but also includes more complex processes such as the humification of ligno-cellulosic compounds [4]. Composting process is affected by some environmental conditions like temperature, moisture content, pH value, aeration and substrate characteristic C/N ratio, particle size, nutrients contents and free air space [5]. According to literature [5 - 8] the optimum C/N ratio, moisture content, pH value and particle size for composting process is between 25/1 to 35/1, 50 to 65 %, 5.5 to 8.0 and 1 to 5 cm, respectively. Furthermore, according to Haug [8] oxygen concentration should not be lower than 5 to 7 % and proper aeration of the composting material will only be possible if porosity and free air space (FAS) are around 30 % in composting piles. These factors can be adjusted by mixing different raw waste i.e. co-composting. Tobacco waste (TW), olive waste (OW) and grape waste (GW) used in this work are from the same part of Croatia, Istria, and mixing them in one substrate makes it possible to obtain an optimal initial conditions needed for composting process [3, 9 - 11]. These wastes can't be composted by themselves because TW has low C/N ratio and optimal pH value, GW and OW have high C/N ratio and low pH value [9 - 11]. The biowaste (BW) (vegetable waste, fruit waste, green waste) also can't be composted alone because the fraction of biowaste has low C/N ratio and high content of moisture (> 80 %) [12]. Composting of nitrogen-rich wastes can be associated with substantial gaseous nitrogen losses. Biowaste can be mixed with agroindustrial waste or with some bulking agent that provides the optimum FAS and regulates the water contents of waste to be composted. Bulking agents are commonly fibrous with carboneus material with low moisture contents and high C/N ratio [13].

In this work six experiments (P1-P6) of composting process with six different mixed substrates, TW (P1), TGW (P2), TOW (P3), TGOW (P4), TBW (P5), BW (P6) were conducted. The aim of this work was to determine how different substrate compositions influence composting process, i.e. temperature, biodegradation rate and CO_2 and NH_3 emission.

2. EXPERIMENTAL

2.1. Substrate characterization

In this work six different substrates were used, tobacco waste (TW), mixture of tobacco and grape waste (TGW), mixture of tobacco and olive waste (TOW), mixture of tobacco, grape and olive waste (TGOW), mixture of tobacco and biowaste (TBW) and biowaste (BW). Tobacco waste was generated during tobacco production in tobacco factory TDR, Rovinj, Croatia. The TW product was composed of very fine powdery residues, leaf stalks and wet leaf parts with average moisture content of about 75 %. TW was dried at room temperature until the moisture content was 10 % and then was stored in cartons. Grape waste was generated in the wine production on Plešivica hill in western part of Croatia. In order to avoid any kind of degradation, fresh grape waste was kept in a freezer at -18 ºC until it was

used for the experiments. Olive waste was generated during the extraction of olive oil using three-phase centrifugation process in olive factory Agrolaguna d.o.o, Poreč, Istria, Croatia.

The olive waste contained the olive husk and olive pomace and it was collected in autumn and also was kept in a freezer at -18 ºC until it was used for the experiments. Biowaste (vegetables, fruit and green waste) was collected at Dolac Market: Fresh Goodies, Zagreb, Croatia.

2.2. Composting experiments

The composting experiments, P1 (TW), P2 (TGW), P3 (TOW), P4 (TGOW), P5 (TBW) and P6 (BW), were conducted in a closed thermally insulated column reactor with effective volume of 10 dm^3, figure 1. The reactor was operated at an airflow rate of 0.6 dm^3 min^{-1} kg_{VM}^{-1} and the temperature was monitored by thermocouples connected to the data logger during the 21 days of composting period. The moisture content of the substrate (TW and TGW) was set to about 60 % by adding the water (P1 - P5) and different masses of wet substrates were put into reactor from the top, table 1. In experiment P6 the water was not added because of high initial moisture of vegetables and fruits (> 90 %) and bulking agents were added to adjust moisture, C/N ratio and to provide optimum FAS. To ensure permanent air humidity at the reactor's inlet, the air was saturated with moisture prior to entering the reactor by passing through a Drechsel bottle. After leaving the reactor, the hot spent air was allowed to cool naturally and the condensate was collected in the graduated cylinder.

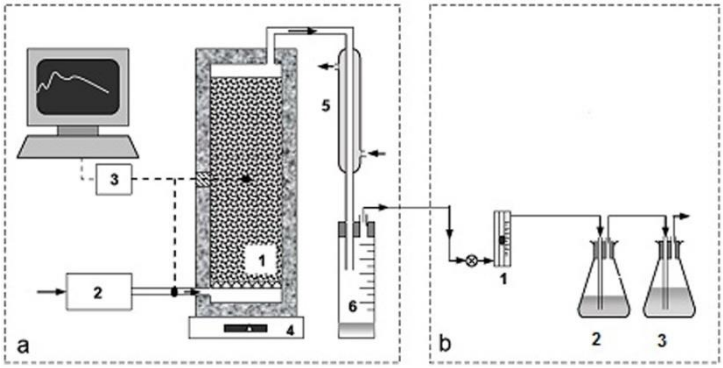


Figure 1. Schematic diagram of composting process (a) - 1 - composting reactor, 2 - compressor and airflow regulation, 3 - temperature data acquisition, 4 - scale, 5 - condenser, 6 - graduated cylinder; and gas absorption and analysis (b) - 1 - flowmeter, 2 - H_3BO_3, 4 %, 3 -NaOH, 1 mol dm^{-3}

Table 1. The initial working conditions of composting processes for experiments P1-P6

	P1 (TW)	P2 (TGW)	P3 (TOW)	P4 (TGOW)	P5 (TBW)	P6 (BW)
V (reactor) / dm^3	10					
q_z / dm^3 min^{-1}	0.84					
$m_{(wet\ substrate)}$ / kg	4.5				4	2.5
w (DM) /%	40					
w (VM) /%	78	87	85	82	85	87
C/N ratio /-	21/1	25/1	27/1	25/1	23/1	34/1
pH - value / -	6.50	5.31	6.45	6.23	5.13	6.26

2.3. Analytical methods

Composting samples, taken periodically from reactor, were tested for pH value, moisture, volatile solid contents and carbon and nitrogen (C/N) ratio. The dry matter (DM) and volatile matter (VM) in the composting mass were determined gravimetrically [14], pH value was measured with pH meter and the total nitrogen content using Kjeldahl method. The exhaust gases, ammonium and carbon dioxide, were absorbed into 4 % boric acid and in 1 mol dm^{-3} sodium hydroxide, respectively, and were determined titrimetrically.

3. RESULTS AND DISCUSSION

From table 1 it can be seen that the initial mass of wet substrates in experiments P1-P4 was the same, but in P5 and P6 was different because of voluminous of the substrate. In experiment P6 the mass of added biowaste was the smallest because it contained leaves, tree branches, peel of onions which are very voluminous. The content of volatile matter in experiment P1 was lower than in other experiments because it contained only tobacco waste which has lower percentage of organic matter then experiments P2, P3 and P4 where grape waste was added, which has high content of volatile matter, 93 % [3, 15]. The initial C/N ratio was the highest in experiment P6 because of bulking agent and the lowest in experiment P1 [3, 10]. The initial pH value in all experiments was between 5 - 6.

Temperature is one of the most important parameters for maintaining the efficiency of composting process. Biological activity is an indicator of biodegradation of organic matter because aerobic microorganisms produce heat in composting mass [16]. This exothermic process produces a relatively large quantity of energy. Only 40 to 50 % of this energy can be utilized by microorganisms to synthesise ATP; the remaining energy is lost as heat in the mass [4, 8]. The temperature undergoes considerable changes due to a calorific effect, resulting from oxidative cleavage of covalent bonds in the substances during composting. Figure 2 shows the temperature changes and evolved CO_2 in exhaust gas during 21 days of composting process for experiments P1 to P6. It can be seen that in all experiments temperature increased to about 55 °C and lasted about five days. In experiments P1 and P2 the temperature at the beginning increased and then after few days decreased and again increased because some microorganisms were activated later. The thermophilic phase in experiments P2 and P3 lasted longer than in experiment P1 probably because of presence of grape and olive waste which contains sugars which are easily biodegraded. In experiment P4 the thermophilic phase was achieved at day seven, but in other experiments during 48 hours. The reason can be presence of olive waste. Olive waste which was used in experiment P4 was a fresh waste, picked from the plant for production of olive oil, and olive waste used in experiment P3 was from the same plant but it was stored in a freezer and some of chemical characteristics were changed. The olive waste contains considerable amount of phenols which is toxic to most microorganisms and longer period of adaptation to this substrate (P4) was needed [17]. The temperature curve for experiments P5 and P6 are almost the same, except that in P6 where temperature increased faster than in P5, probably because of presence of tobacco waste in P5. Thermophilic phase lasted two days longer in experiment P5 than in experiment P6. This was probably due to the combination of organic compounds found in these wastes, in which organic matter is mainly composed of easily degradable and energetic compounds such as protein and fats, and large amount of organic nitrogen (tobacco waste) are available [18]. The curve of CO_2 in all experiments had the same trend as the curve of temperature. The most

CO_2 was detected in thermophilic phase during the intense biodegradation of organic fraction of the substrate.

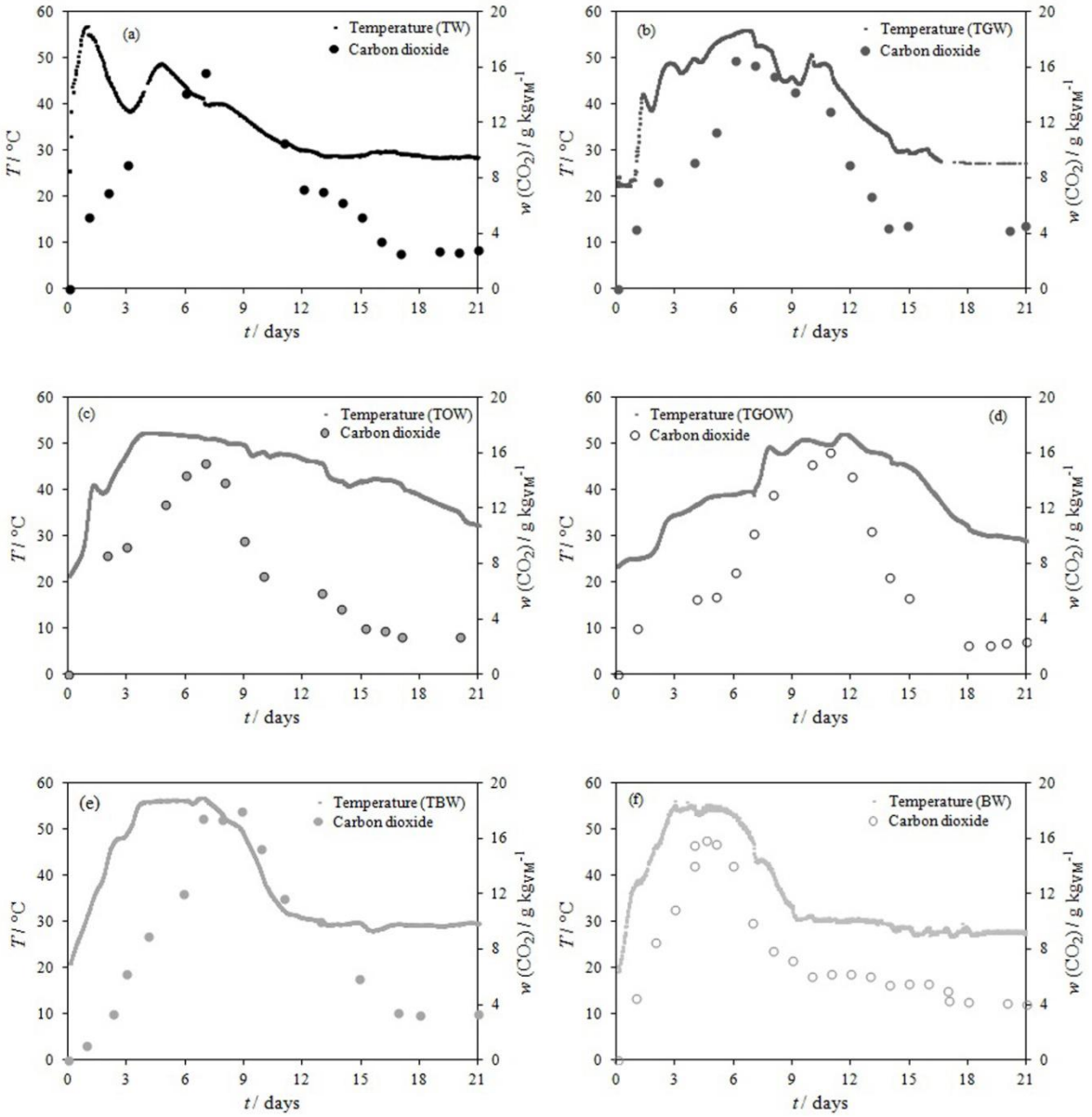


Figure 2. Temperature changes and evolved CO_2 in exhaust air during 21 days of composting process in experiments P1 (a), P2 (b), P3 (c), P4 (d), P5 (e) and P6 (f)

From table 2 and figure 3 it can be seen that the highest production of CO_2 was detected in experiment P6, 186.48 g kg_{VM}^{-1}, where obtained conversion was X = 71 %. Obtained results show that the most intense biodegradation was in experiments P6 and P5. Conversion was in all experiments, except in experiment P1 above 50 %. In experiment P1 it was 47 % because the initial volatile matter of tobacco waste (P1) was lower than in other experiments.

Table 2. Results of composting experiments P1 to P6

	P1 (TW)	P2 (TGW)	P3 (TOW)	P4 (TGOW)	P5 (TBW)	P6 (BW)
w (H_2O) /%	64	71	67	70	73	73
w (VM) /%	52	77	73	79	78	70
C/N ratio /-	9/1	12/1	14/1	17/1	13/1	10/1
pH value / -	9.3	8.7	8.29	8.74	8.81	8.83
w (CO_2) / g kg_{VM0}	101.23	141.42	115.27	121.76	137.84	186.48
w (NH_3) / mg kg_{VM0}	436.49	71.00	2.11	88.79	249.94	147.35
X / %	47	56	50	52	65	71

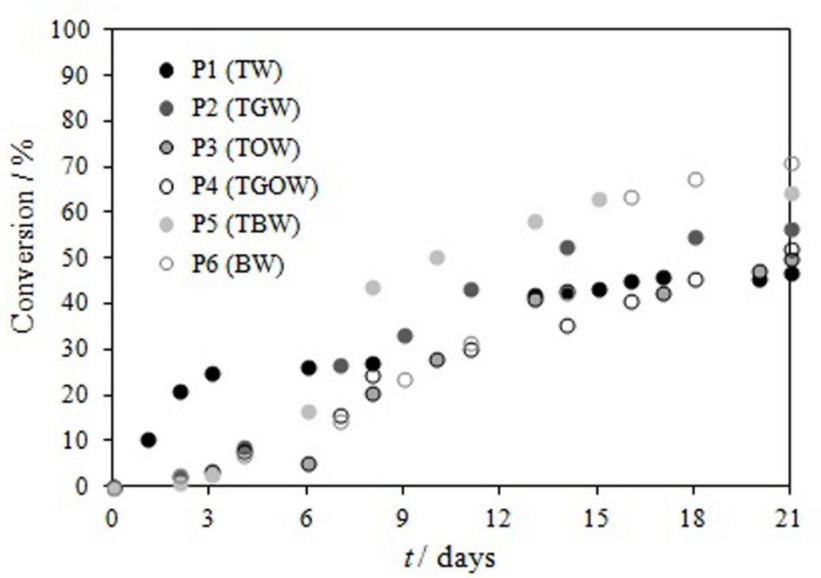


Figure 3. Changes in volatile solid mass in substrate expressed as conversion during 21 days of composting process in experiments P1 to P6

Figure 4 shows change of pH value in the substrates and evolved ammonia in exhaust gases during 21 days of the composting processes in experiments P1 to P6. It can be seen that the pH value in experiments P2 and P4 at the beginning of process dropped into the acidic range (pH was 4 to 5) because of the production of organic acid from grape waste [10]. In all experiments pH value after seven days increased to pH value 8 to 9 due to the decomposition of organic nitrogen that liberates ammonium [15]. Ammonium was detected in all experiments as temperature of substrate decreased and pH value increased. It is well known that NH_3 emissions are highly dependent on the pH value of the composting substrate and that NH_3 evolves when the pH value of the composting mass exceeds approximately 8 [18]. The highest production of ammonia was in experiment P1, 436.49 mg kg_{VM}^{-1}, where tobacco waste was composted, which contains high concentration of nitrogen, and has a low C/N ratio. High concentration of ammonia was detected in experiment P5 (mixture of tobacco waste and biowaste). The production of ammonia during composting of biowaste mainly depends on C/N ratio of substrates which are an integral part of biowaste. During 21 days of composting the C/N ratio and volatile matter decreased in all experiments (table 1 and table 2).

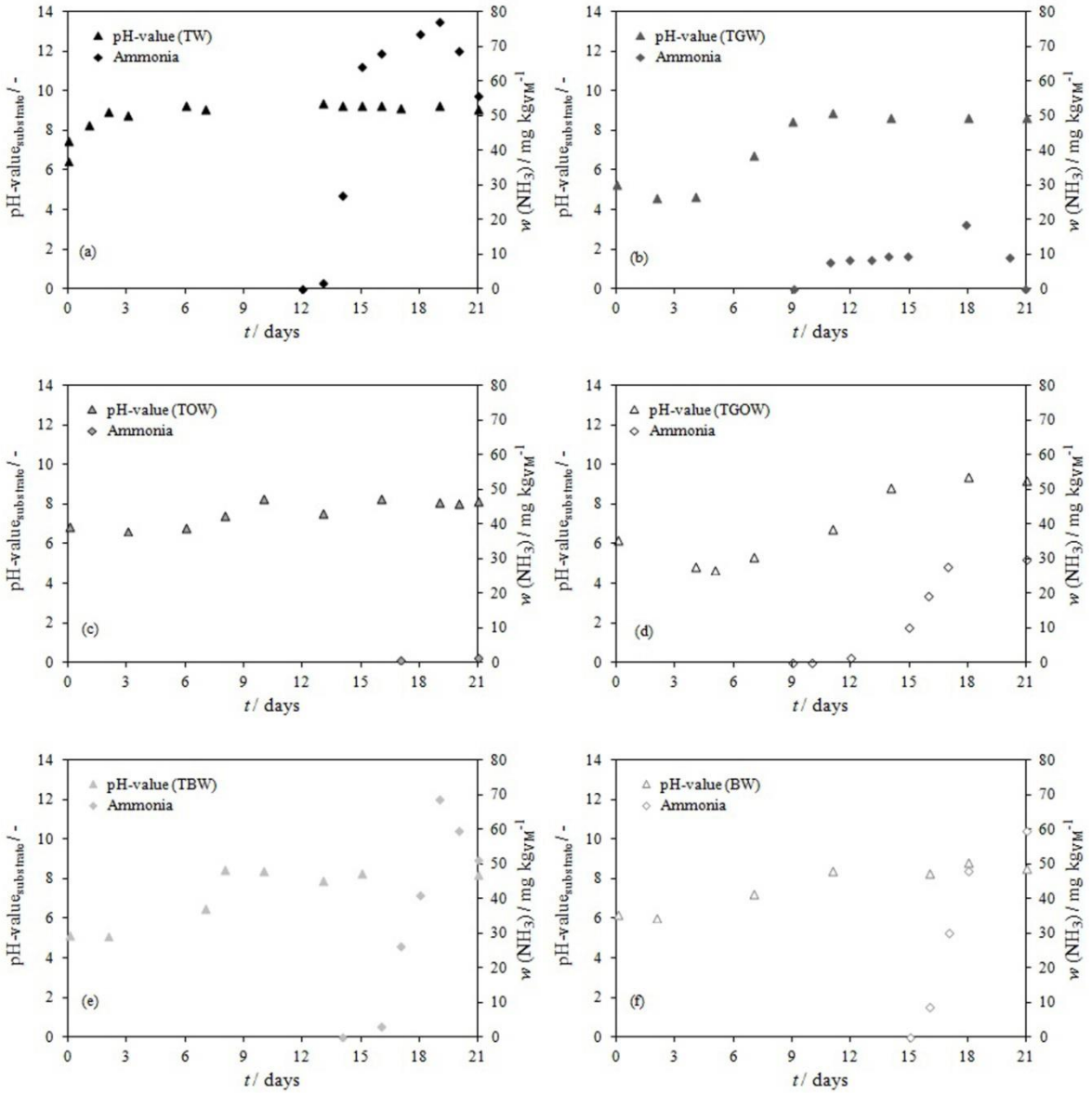


Figure 4. pH value changes in substrate and evolution of NH_3 in exhaust air during 21 days of composting process in experiments P1 (a), P2 (b), P3 (c), P4 (d), P5 (e) and P6 (f)

4. CONCLUSION

In this study different substrates, tobacco waste (P1), mixture of tobacco and grape waste (P2), mixture of tobacco and olive waste (P3), mixture of tobacco, grape and olive waste (P4), mixture of tobacco and biowaste (P5) and biowaste (P6), were composted during 21 days. The following results were recorded:

- in all experiments temperature has reached thermophilic phase (55 °C) which lasted seven to ten days,
- the most CO_2 was produced (186.48 g $kg_{VM}^{-}1$) in experiment P6 due to the highest amount of biodegradation of organic matter (71 %),
- the most NH_3 was evolved (436.49 mg kg_{VM}^{-1}) in experiment P1 because of composting of tobacco waste which contains high concentration of nitrogen and low C/N ratio,

- obtained conversion in experiments P1, P2, P3, P4, P5, P6 was 47 %, 56 %, 50 %, 52 %, 65 % and 71 %, respectively.

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ALTERNATIVE FUELS – NEW CHALLENGES FOR PETROLEUM LABORATORY

Lucija Kurte*, Dijana Blažek*, Lucija Konjević*

* INA d.d., Centralni ispitni laboratorij, Zagreb, Hrvatska

corresponding author: Lucija Kurte, e-mail: lucija.kurte@ina.hr

Professional paper

ABSTRACT

Crude oil refining industry and petroleum laboratories are being more focused on the topics concerning biofuels and alternative fuels due to regulatory, and in general, society pressures. Considering basic equipment and its main purpose, petroleum laboratory faces various challenges while testing these samples. However, by modifying existing methods and by developing new methods based on many years of experience and expertise, along with modern multipurpose instruments and techniques, physical and chemical properties of biomass and alternative fuels can be determined. In this work, the carried out testing quality and applicability of certain types of alternative second generation biofuels will be shown. In addition, test results of biomass for the production of bioethanol, waste animal fats, waste edible oils, and pyrolysis oil, will be shown as well.

***Keywords**: alternative fuels, biofuels, biomass, petroleum laboratory*

1. INTRODUCTION

Increasing population and urbanization combined with depleting fossil fuel reserves have resulted in the need for the development of an alternative transport fuel source [1]. Biofuels as one of alternative source offer benefits on environmental impact in comparison to fossil fuels. As Croatia became a full member of the EU, it is important to mention that there are certain directives that define the objectives that members must meet. For example, EU 2020 climate & energy package sets high goals in the form of a formula of 20-20-20 to be achieved by 2020. That formula applies to the reduction of greenhouse gas emissions, increasing the share of energy from renewable sources and increase energy efficiency by 20 %. Also, Directive 2009/28/EC prescribes a plan to increase up to 10% renewable fuels in transport. In 2014, the European Council agreed the 2030 framework for climate and energy. The new 2030 climate & energy framework sets out the European Union target of at least 27

% for the share of renewable energy, increasing energy efficiency up to 27 % and reduction of greenhouse gas emissions by 40 % [2].

Considering all above mentioned, it is necessary to turn to the research and production of suitable alternative fuels that will facilitate and accomplish all mentioned requirements. In this paper analysis of alternative biofuels, its physical and chemical characteristic and development of new analytical methods and modification of existing are shown.

1.1. Classification of biofuels

Although there are several different classifications of biofuels, one of the most commonly used is classification into three generations, depending on the source of biomass, costs of production and CO_2 emissions.

First (1^{st}) generation i.e. conventional biofuels are produced by the fermentation of edible sugars and starch sourced from crops grown primarily for the production of food. Unfortunately, issues arise in the production of 1^{st} generation biofuels as the growth of crops for energy, as opposed to food, results in reduced food production and, consequently, increased food prices [3].

Second (2^{nd}) generation biofuels offers a potential solution as it utilizes non-edible lignocellulosic biomass found in abundance in readily available agricultural wastes such as corn stover, sugarcane bagasse, straw, and woodchips. [3] Food crops can act as second generation biofuels if they have already fulfilled their food purpose, for example, waste edible oil [4].

In general, third (3^{rd}) generation term is applied to any biofuel derived from algae. These biofuels are given their own separate class because of their unique production mechanism and their potential to mitigate most of the problems of 1^{st} and 2^{nd} generation biofuels. [4] Algae biofuels are carbon neutral renewable fuels that can be produced without compromising the supply of food and freshwater and the need to prevent further deforestation. To produce biomass for this kind of biofuels, algae are grown using carbon dioxide and industrial wastes, which reduces the cost of culture medium nutrients and alleviates the environmental problems caused by these effluents [5].

2. EXPERIMENTAL

In Central Testing Laboratory (CTL) 1^{st} and 2^{nd} generation of biofuels were analysed. In order to characterize biofuels and biofuel feedstocks CTL experts perform physical and chemical analysis, and determination of composition with advanced analytical techniques. Analyses of different conventional and advanced biofuels preformed in CTL from 2015 to April 2018 are shown in figure 1.

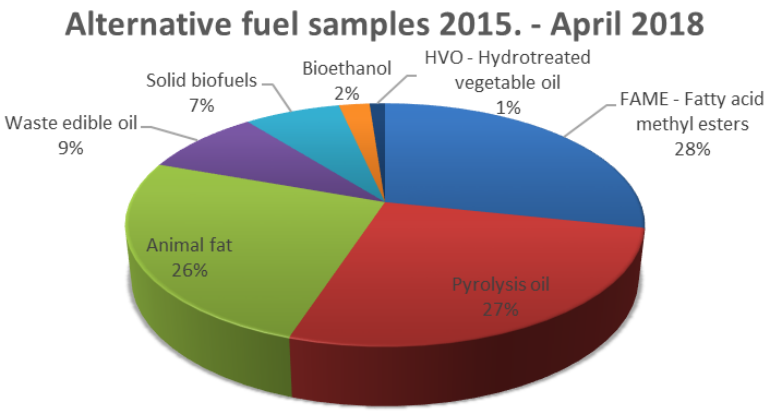


Figure 1. Alternative fuels analysis performed in CTL

2.1. Lignocellulosic biomass

Different types of biomass were analysed but most attention was given to *Miscanthus x giganteus* as high quality lignocellulose biomass for the production of bioethanol.

Miscanthus is a perennial energy crops not used for human consumption and can be grown on soils of lower quality, which in the Republic of Croatia has over 600,000 ha [6]. Rapid growth, high lignocellulose yield, suitability for wide range of soil types, low input requirements for production, low moisture content, low content of ash, potassium, chlorine, nitrogen and sulphur make *Miscanthus* a favourite choice as a biofuel [7]. Depending on the intended conversion process, *Miscanthus* could be used as an input for bioethanol production or it is burned to produce heat and steam for power turbines.

In order to determine physical and chemical characteristic of *Miscanthus*, it was necessary to carry out some pre-treatment processes such as milling, extraction for gravimetric determination of cellulose and lignin content and microwave digestion as pre-treatment process for determination of content of minor and major elements. In figure 2 mechanical shredded samples of *Miscanthus* are shown.



Figure 2. Mechanically torn samples of *Miscanthus*

Milling of biomass samples as pre-treatment process for another analysis was completely new procedure in CTL. Some existing methods needed modification, for example the change of temperature conditions for ash content determination or change mass of sample for elemental determination of biomass sample.

2.2. Waste edible oils and animal fats as feedstocks for biofuels production

Waste edible oil (WEO) is the waste product of cooking or frying foods. The disposal of WEO is difficult and thus the use of WEO as a biofuel would both alleviate the problem of disposal in addition to providing a renewable source of biodiesel. Physical and chemical properties of waste edible oil change during the frying process – resulting with an increased in free fatty acids content – up to 15 % in comparison with the 0.5 % content of refined virgin vegetable oil; a change in oil colour to dark brown or red; an increase in viscosity and specific heat; and in increased tendency to form foam [8].

Generally three broad categories of waste animal fats are described — tallow and related raw fats from processing industries, yellow grease from waste cooking oil used to cook, for example, chicken, and brown grease that is obtained from traps used to prevent waste fats and oils being released into the environment. Physically, animal fats are solid or semi solids at room temperature. A significant percentage of waste animal fat can be converted to biodiesel using similar techniques to those used for plant oils, the main process being transesterification. The triglycerides in animal fats are saturated, compared to unsaturated plant triglycerides, and this has some implications when used as biodiesel. In particular the cloud point, the temperature at which the oils solidify, is higher for animal fats [8].

2.3. Bio-pyrolysis oil

Non-food cellulosic material is used for production of bio-pyrolysis oil. It is a dark liquid, with an appearance similar to espresso coffee and a smoky odour (figure 3). It is a water-soluble, oxygenated fuel consisting of "depolymerized" components of wood or other biomass. It is consisting of primarily carbon, hydrogen and oxygen. The pyrolysis oil contains a very low ash amount. The density of the liquid is higher than 1000 kg/m^3, which is denser than fuel oil and it has lower value of higher heating value compared to fossil fuel.



Figure 3. Bio-pyrolysis oil

Pyrolysis oil has a low pH value of around 3 and it has a tendency to degrade by aging. Due to large amount of oxygenated components present, the oil has a polar nature and

does not mix readily with hydrocarbons [9]. It can be used in district heat production for hot water or steam at industrial sites, and in Co-processing [10].

2.4. Pyrolysis oil from waste tires

Pyrolysis oil is a renewable fuel obtained from plastic, waste and rubber tier by pyrolysis process. It is a complex series of chemical and thermal reactions to decompose or depolymerize organic material under oxygen-free conditions. It is a mixture of C5 to C20 with a characteristic odour due to high aromatics substance, thick liquid and dark colour [11].

Pyrolysis oil from waste tires is a potential component for blending in crude oil. The EU Directive 2015/1513 from September 9, 2015, in Annex IX has recognized pyrolysis oil produced from waste tires and plastics, non-biological origin, as such component whose contribution is considered twice as valuable as its original energy content.

It can be used as a cutter for blending fuel oil and marine fuel, as component for blending the motor fuel, and in the co-processing.

3. RESULTS AND DISCUSSION

3.1. Lignocellulosic biomass

Lignocellulosic biomass samples were the most challenging due its aggregate state and homogeneity of samples. Completely new methods which were developed for characterization of biomass samples include determination of water soluble content of Cl^-, Na^+, K^+ by Inductively Coupled Plasma (ICP) Spectrometry, determination of moisture content, determination of cellulose and lignin content. Also advanced analytical techniques such as Nuclear Magnetic Resonance (NMR) and Infrared (IR) spectroscopy were, and are being used as proven and powerful tools for analysis of structure of lignin, cellulose and hemicellulose. In table 1 results of physical and chemical properties determined in CTL are shown.

Table 1. Results of physical and chemical properties of *Miscanthus x giganteus*

Property	Result
Extractive matter, (%)	1.90
Cellulose content, (%)	68.51
Lignin content, (%)	27.34
Cl^-, (mg/kg)	674
Na^+, (mg/kg)	2
K^+, (mg/kg)	5287
Ash content, (%)	2.0
Heat of combustion, (MJ/kg)	15.33
Water content, (m/m %)	0.5
Carbon, (m/m %)	46.6
Hydrogen, (m/m %)	5.83
Nitrogen (m/m %)	0.18

Results in table 1 show high concentration of cellulose which suggests the possibility of better utilization of biomass for the production of bioethanol. High concentration of potassium points out possibility of formation of deposits with silicates which could result with biofuel usage problems. Presence of chlorine in metal pipes can cause corrosion. The concentration of sodium is low and cannot affect the level of deposits [12, 13]. Macro elements in solid biocomponents for biofuels production are more represented in the ashes of the combustion of fuel, than in the fuel. By specifying these elements we can predict solubility and the possibility of the formation of deposits of ash. Determination of physical and chemical properties is necessary for completed characterization of biomass samples and prediction of behaviour of final products.

3.2. Waste edible oils and animal fats as feedstocks for biofuels production

Waste edible oils (WEO) and animal fats were analysed to determine the most important properties, such as density, kinematic viscosity, sulphur and metal content, CHN analysis, composition (NMR, Comprehensive Two-dimensional Gas Chromatography, GC x GC), distillation parameters, total acid number, water content, cold temperature properties and total contamination.

Distillation parameters were determined by simulated distillation, method ASTM D 2882 extended obtained by GC gas chromatographic technique (figure 4). Some of the analysed properties show higher values then common petroleum samples (table 2), and it was possible to determine most of those properties with existing methods and instruments.

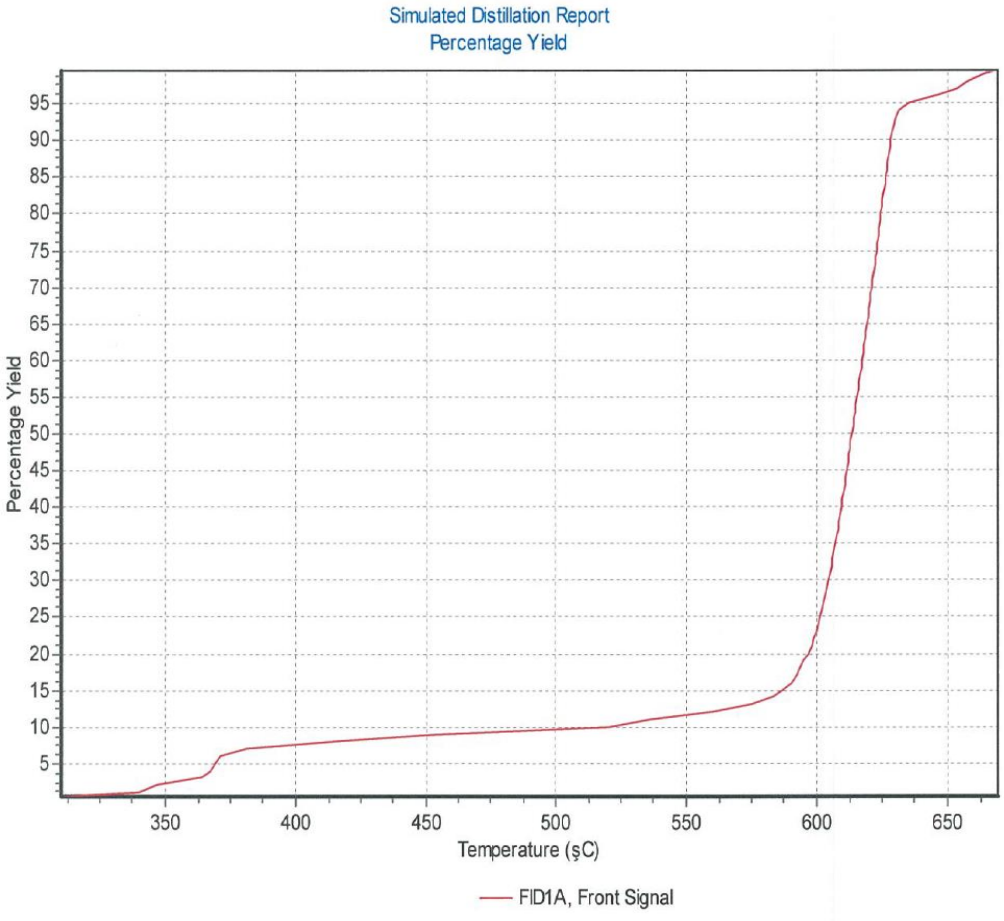


Figure 4. Example of simulation distillation results obtained by GC analyser

Table 2. Comparison WEO (waste edible oil), animal fats, FAME (fatty acid methyl esters) and diesel fuel properties

Property	FAME	Diesel fuel	Animal fat	Waste edible oil
Density at 15 °C, (kg/m^3)	882.7	830	917.1	922.9
TAN (total acid number), (mg KOH/g)	0.288	0.023	16.93	5.02
Kinematic viscosity at 40 °C, (mm^2/s)	4.513	3.046	56.34	43.27
Sulphur content, (mg/kg)	< 3	7.12	58	/

Because of the nature of a sample, during determination of a total contamination some of the difficulties occurred. An attempt was to determine total contamination according to the test method HRN EN 12662. A sample was weighed and filtered under vacuum through a pre – weighed filter [14], but the filter plugged immediately and sample could not pass through it. These difficulties were solved by developing new method for sizing and counting particles by automatic particle counter by ASTM D 7619 method.

3.3. Bio-pyrolysis oil

Analysed properties and methods of bio-pyrolysis oil and typical properties range are shown in table 3. Heat of combustion, water content, viscosity, density, sulphur content and ash content, pH, flash point and pour point and CHN content are required properties according method ASTM D 7544 for pyrolysis liquid biofuel [15].

Table 3. Analysed properties of bio-pyrolysis oil

Properties	Method	Typical range values from the literature [16]
Heat of combustion, (MJ/kg)	ASTM D240	13 - 18
Water content, (% m/m)	HRN ISO 3733	20 - 30
Kinematic viscosity at 40 °C, (mm^2/s)	ASTM D7042	15 - 40
Density at 15 °C, (kg/m^3)	HRN EN ISO 12185	1,110.0 – 1,300.0
Sulphur content, (% m/m)	ASTM D2622	< 0.05
Ash content, (% m/m)	HRN EN ISO 6245	< 0.3
Flash point, (°C)	HRN EN ISO 2719	40 - 110
Carbon, (% m/m)	ASTM D5291	50 - 60
Nitrogen, (% m/m)	ASTM D5291	< 0.5
Hydrogen, (% m/m)	ASTM D5291	7 - 8
Oxygen, (% m/m)	ASTM D5291	35 - 40

Some of existing test methods need to be modified and some new ones need to be developed, because of the nature of samples.

Problem occurred with determination of density at 15 °C due to very high results as well as with method for determination of water content by Karl Fisher titration. The instruments has an option to measure the water content up to 5 % and pyrolysis oil can have water content up to 30 %. Furthermore, classical ICP method for determination of metal

content was not suitable. For that purpose, new sample preparation method which includes wet ashing with fuming sulphuric acid, was developed.

3.4. Pyrolysis oil from waste tires

The properties of pyrolysis oil from waste tires analysed in CTL are presented in table 4. High sulphur content, total acid number (TAN), nitrogen and chlorine content are some of undesirable properties of these samples.

Table 4. Analysed properties and methods of pyrolysis oil

Property	Method	Range of results
Density at 15 °C, (kg/m^3)	HRN EN ISO 12185	886.3 – 1,066.8
Kinematic viscosity at 50 °C, (mm^2/s)	ASTM D7042	1.573 – 5.473
Flash point, (°C)	HRN EN ISO 2719	51.5 – 61.0
Pour point	ASTM D5950	< -54 - -9
Total acid number, mg (KOH/g)	ASTM D 664	4.20 – 6.25
Aromatics, (% m/m)	In-house method	25.5 – 46.0
Olefins, (% m/m)		15.6 – 23.4
Benzene content, (% v/v)	HRN EN 283	< 0.13 – 0.85
Chlorine oxides, (% m/m)	In-house method	0.115
Bromine oxides, (% m/m)		0.113 – 0.17
Silicon oxides, (% m/m)		0.011 – 0.020
Iron oxides, (% m/m)		0.017 – 0.162
Chrome oxides, (% m/m)		0.003 – 0.034
Sulphur content, (% m/m)	ASTM D2622	0.06 – 0.870
Ash content, (% m/m)	ASTM D5291	<0.001 – 0.012
Carbon residue, (% m/m)	HRN EN ISO 10370	< 0.01 – 0.26
Water and total contamination content, (% v/v)	HRN EN ISO 3734	0.2
Water content, (mg/kg)	ASTM D 6304	600 - 800
Chlorine content, (mg/kg)	In-house method	16.8 – 135.5
Carbon, (% m/m)	ASTM D5291	81 - 87
Hydrogen, (% m/m)		11
Nitrogen, (% m/m)		0.54 – 0.75
Asphaltene content, (% m/m)	ASTM D6560	0.5 – 0.7

Distillation process of pyrolysis oil was performed according to ASTM D86, and fractions below and above 180 °C were collected. It is necessary to distillate pyrolysis oil before use due to removing the volatile component that contains high amount of benzene content. The properties of fraction above 180 °C were analysed and compared with diesel fuel sample (table 5). Results of analysis conducted on pyrolysis fraction above 180 °C show higher values for total acid number, density, sulphur content and final boiling point compared to commercial diesel fuel which indicate that usage of pyrolysis could affect final quality of diesel fuel.

Table 5. Properties comparison between pyrolysis fraction and diesel fuel

Property	Fraction above 180 °C	Diesel Fuel
TAN (total acid number), (mg KOH/g)	6.25	0.023
Density at 15 °C, (kg/m^3)	924.5	830
Flash point, (°C)	66.0	60
Pour point, (°C)	-18	-9
Sulphur, (mg/kg)	8630	7.12
Distillation; 10 % v/v, (°C)	176.00	208.6
Distillation; 50 % v/v, (°C)	294.00	278.6
Distillation; 95 % v/v, (°C)	430.00	352.7

Moreover, the possibility of co-processing with crude oil was examined - two concentrations of pyrolysis oil and crude oil were blended. The distillation of different blends was performed on two distillation unit, TBP according to ASTM D2892 and Postill according to ASTM D5236 method. Physical and chemical characterization of fractions were executed in order to prepare crude oil assay, also the results were compared with results of crude oil fractions (figure 5.).



Figure 5. Crude oil fractions

Blending 1 % and 2.5 % of pyro oil in the crude oil doesn't significantly change the distillation curve (figure 6) as well as sulphur content. On the other hand, total acid number increases with increasing the content of pyrolysis oil in blend (figure 7). The largest increase in total acid number is observable in heavy naphtha, kerosene and heavy gas oil. Also, total acid number measured after 3 and 6 months in some samples increased, however, differences in the results are within the reproducibility of the method ASTM D664.

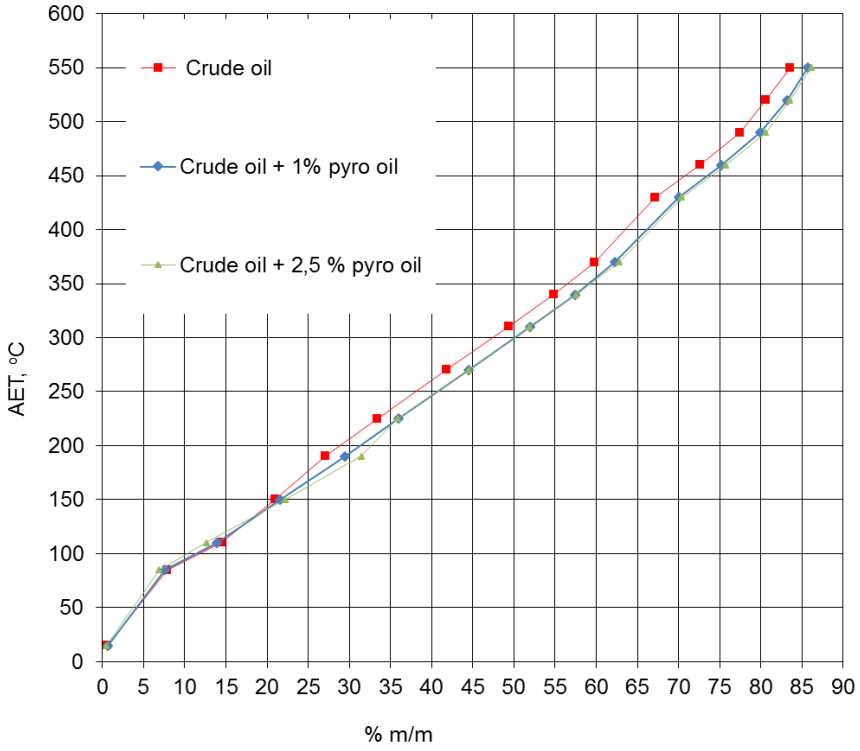
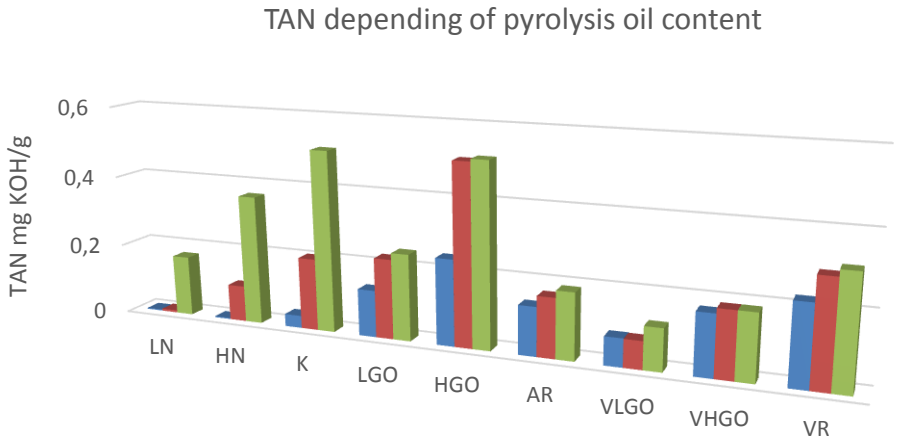


Figure 6. Distillation curve of different blend crude oil and pyrolysis oil



	LN	HN	K	LGO	HGO	AR	VLGO	VHGO	VR
Crude oil	0,003	0,003	0,035	0,132	0,242	0,137	0,079	0,171	0,224
Crude oil + 1 % pyro	0,006	0,102	0,203	0,224	0,507	0,167	0,078	0,185	0,293
Crude oil + 2,5 % pyro	0,17	0,364	0,509	0,243	0,514	0,187	0,118	0,185	0,311

Figure 7. Total acid number depending of pyrolysis oil content in crude oil fractions; light naphtha (LN), heavy naphtha (HN), kerosene (K), light gas oil (LGO), heavy gas oil(HGO), atmospheric residue (AR), vacuum light gas oil (VLGO), vacuum heavy gas oil (VHGO), vacuum residue (VR)

4. CONCLUSION

In the last decade, many studies related to the production of solid and liquid fuels from biomass, as a possible replacement for gasoline and diesel fuels, as well as for the production of electricity and heat through cogeneration are conducted. The development of new alternative fuels that do not depend on fossil fuels is a major challenge facing society today. Different type of biomass source results with different final products so beside production of alternative fuels it is necessary to conduct continuous research of biofuel feedstock and final product properties. All mentioned have an effect on work of petroleum laboratory, which must familiarize with new requirements. Alternative samples were challenge for analysis in CTL, because they have different properties than common petroleum fuel samples. Considering nature of those samples, modified manipulation and sample preparation was needed. Higher values of main properties outcomes with modification of existing methods and development of new methods.

Continuous improvement of existing methods by exploring literature and introducing new methods in order to find new solutions to resolve all mentioned problems is required. Also, participation in interlaboratory comparison program would be a good confirmation for accuracy and reliability of achieved results.

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BRIGA ZA OKOLIŠ I ZDRAVLJE U BIOETIČKOM KONTEKSTU

CARE FOR ENVIRONMENT AND HEALTH IN BIOETHICAL CONTEXT

Jelena Loborec*, Saša Zavrtnik*, Damir Žubčić, Marija Sivonjić***

* Sveučilište u Zagrebu, Geotehnički fakultet, Varaždin, Hrvatska
** Sveučilište u Zagrebu, Veterinarski fakultet, Zagreb, Hrvatska

autor za korespondenciju: Jelena Loborec, e-mail: jloborec@gfv.hr

Stručni članak

SAŽETAK

Zdravlje predstavlja osnovno svojstvo i preduvjet živoga bića da normalno funkcionira, da je u ravnoteži svojih fizioloških potreba ili, ako se gleda isključivo zdravlje ljudi, da vodi socijalno produktivan život. Okoliš kao cjelina svega što nas okružuje predstavlja također bitan i neodvojiv segment života. Zajedničkim pogledom na ta dva pojma u istom kontekstu nameće se zaključak da se zdravlje prostire na različita područja ljudske egzistencije te neminovno uključuje i druga živa bića s kojima čovjek koegzistira, materiju te nematerijalna dobra. Integrativna bioetika nudi područje međudjelovanja različitih znanosti i struka te susreta raznoraznih pogleda na svijet i život u cjelini. U ovom kontekstu sagledava se briga o zdravlju ljudi i životinja kao nešto povezano i podložno sve izraženijem antropogenom utjecaju na sve segmente biosfere i na sve oblike života u njoj. Ovakav sveobuhvatni pristup može svaki pojedinac razvijati počevši od sebe i takvo djelovanje može početi na lokalnoj razini integrirajući znanja različitih područja spomenute problematike na zajedničko mjesto njihova dodira.

***Ključne riječi**: okoliš, zdravlje, bioetika*

ABSTRACT

Health is the basic feature and basis of a living being to function normally, in the balance of its physiological needs or, if it is viewed exclusively on human health, to lead a socially productive life. Environment as a union of everything that surrounds us is also an important and unseparated segment of life. Mutual view on those two terms in the same context gives the conclusion that health spans on different areas of human life and activities including all other living beings with whom men coexists, mater and unmaterial goods. Integrative bioethics offers the place for interaction of different sciences and professions as

well as place for meeting of different worldviews and life as a whole. In such context care for human and animal health is seen as something connected and subdued to increasingly prominated anthropogenic impact on every segment of biosphere and on all life forms. Every individual can develop that kind of comprehensive approach and such actions can start on local level by integrating the ideas of different areas from mentioned problematics on one common ground.

***Keywords**: environment, health, bioethics*

1. UVOD

Zdravlje je prema Svjetskoj zdravstvenoj organizaciji definirano kao stanje potpunog fizičkog, psihičkog i socijalnog blagostanja, a ne samo odsustvo bolesti i iznemoglosti [1]. S druge pak strane, Zakon o zaštiti okoliša definira okoliš kao zajednicu čovjeka i svega što mu omogućuje postojanje te daljnji razvoj: zrak, voda, tlo, zemljina kamena kora, energija te materijalna dobra i kulturna baština kao i svi drugi organizmi u svoj svojoj raznolikosti i međudjelovanju [2]. Iz ovih definicija proizlazi vidljiva uzročno posljedična povezanost, međuovisnost i slobodno možemo reći uvjetovanost zdravlja ljudi, naravno i drugih oblika života, s obzirom na stanje „zdravlja“ okoliša.

U vrijeme kada saznanja toliko rastu da se svakim danom vidi koliko utjecaja, i to većinom negativnoga, čovječanstvo ima na svijet oko sebe, ističe se potreba povezivanja i uvažavanja drugih struka, umrežavanja primjerice tehničke, biomedicinske, prirodne i humanističke znanosti sa svrhom razvoja sintetiziranog pristupa problematici zdravlja čovjeka i okoliša. Odavno je prošlo vrijeme kada smo mogli zatvarati oči pred posljedicama svojih (ne)djela u prirodi. Više je nego očito kako ono što se naziva rješenjima u našoj svakodnevici s druge strane samo otvara nove probleme.

Stoga je cilj ovog rada da se prikaže međuovisnost zdravlja čovjeka, zdravlja okoliša i svega živoga u njemu te odgovornost pojedinca za stanje okoliša koje trenutno vlada. Jedan od ciljeva je također naglasiti koliko je danas možda više nego ikad prije prijeko potrebno stvarati veze među znanstvenim i stručnim kao i „laičkim“ krugovima u svrhu što bržeg iznalaženja rješenja za određenu problematiku i kako bi ono bilo što sveobuhvatnije.

2. OKOLIŠ I ZDRAVLJE

Poznata i raširena narodna izreka i/ili mudrost kaže: „U zdravom tijelu zdrav duh.“ Da li je tome uistinu tako, moglo bi se raspravljati jer da li ono što nazivamo zdravim i tjelesnim stvarno jest preduvjet onome što smatramo duhovnim i duševnim nije tako lako odrediti. No, iskustvo pokazuje da ukoliko nam je tijelo zdravo, tada postoji velika vjerojatnost da će i naše psihičko i emocionalno stanje biti povoljnije. Međutim, ovdje se treba zapitati ima li zdravog tijela bez zdravog okoliša? Mnogi su filozofi, mislioci i znanstvenici uočili da je u svijetu, na ovom našem plavom planetu, sve povezano u vidu akcije i reakcije. Na neki način ova plava kugla je zatvoreni sustav što nam ne daje previše manevarskog prostora za nerazumno i neodgovorno ponašanje.

Po pitanju odgovornost postoji vrlo zanimljiva tvrdnja koju iznosi Cifrić u svom radu kada govori da je odgovornost za moralno ili ne moralno ponašanje prema drugim živim bićima i prirodi ustvari pitanje kulture, te da neodgovorno ponašanje prema životu čovjeka u

društvu, zasigurno znači i neodgovoran odnos čovjeka (društva) prema ostalim živim bićima u prirodi [3]. Zato se problematika okoliša često sagledava u kontekstu moralne krize društva u cjelini. I tome zaista jest tako.

2.1. Problematika okolišnih čimbenika

Jedno od temeljnih ljudskih prava zajamčeno Ustavom RH je pravo na zdrav život i čisti okoliš. Između ostalog u Ustavu stoji da država osigurava uvjete za zdrav život te da je dužnost svakog pojedinca da posebnu brigu vodi o zdravlju ljudi te očuvanju okoliša i prirode [4]. Sve to zvuči jako lijepo i pravedno i trebalo bi vjerovati da je to doista tako, no, nažalost, svakodnevni primjeri svjedoče suprotno. Pojedinac ne polaže veliku važnost u svoje postupke jer polazi od pretpostavke da je nebitan za situaciju u globalnom mjerilu, no najčešće je to potpuno netočno. Upravo u edukaciji pojedinaca od najranije dobi leži ključ uspjeha jer se samo razvojem osobne svijesti o problematici odgovornog ponašanja spram okoliša i zdravlja može utjecati na krajnje promjene globalno. Važno je također razlučiti na koje stvari je moguće utjecati, a na koje ne. Postoje različiti segmenti djelovanja koji izravno utječu na zdravlje i opće stanje čovjeka, na neke od njih se može utjecati, a drugi pak su izvan osobnog utjecaja. Neki od čimbenika na koje se ne može utjecati su najčešće obilježja dobivena rođenjem: dob, spol, genetska obilježja, predispozicija za određene bolesti i sl. Zatim postoje i čimbenici na koje se može utjecati jer se odnose na životni stil, a u njih se ubrajaju prehrambene navike, tjelesna aktivnost, sklonost konzumaciji alkohola, cigareta ili opojnih droga. Međutim postoje i čimbenici koji mogu izravno utjecati na zdravlje ljudi, ali nisu izravno pod kontrolom pojedinca već ovise o različitim socijalnim, ekonomskim, gospodarskim i društvenim uvjetima. U tu skupinu spadaju okolišni čimbenici kao što su voda, zrak, hrana, uvjeti stanovanja, izloženosti različitim biološkim, kemijskim i fizikalnim agensima uslijed prirodnih događanja ili ljudskog djelovanja [5]. Upravo u tom aspektu otvara se veliki prostor gdje svaki čovjek svojim odlukama i postupcima ima priliku postupiti odgovorno ili neodgovorno i izravno utjecati na stanje okoliša, svoje zdravlje kao i zdravlje drugih oko sebe. Odgovornost bi ovdje trebala biti svjesnost pozitivne odluke, ne samo zato jer zakon tako nalaže ili će u protivnom uslijediti novčana kazna, već iz razumijevanja odnosa.

2.2. Zdravlje kao najveće bogatstvo

Često se može čuti da kad čovjek ima zdravlje ima sve i da će sve ostalo u život biti lakše ako je osoba zdrava. U svakodnevnom životu opterećenim često puta doslovnom borbom za puku egzistenciju to i jest tako. U tom slučaju ako nisi zdrav, ne možeš normalno funkcionirati, raditi pa ni stvoriti temelje za ono osnovno. Prema tome, pojedinac ne može normalno stvarati njemu svojstvenu vrijednost niti pridonositi društvu. A onda ako on nije zdrav, možda i društvo nije u potpunosti zdravo pošto jedna njegova stanica nije zdrava. Znači u interesu društva je da su sve njegove sastavnice zdrave.

2.3. Industrija kućnih ljubimaca

Da se čitava priča ne razvije samo u smjeru onečišćenja okoliša, postoje i drugi primjeri gdje je zorno vidljiva povezanost ljudi, ljudskog zdravlja i drugih živih bića. Danas smo svjedoci kako je u posljednjih pola stoljeća došlo do novog pristupa domaćim

životinjama, odnosno kućnim ljubimcima. Domaće životinje koje su stoljećima doslovno i opravdano smatrane blagom, u posljednje vrijeme su „pretvorene“ u objekte proizvodnje, doslovno su industrijalizirane. Primjera radi tu je pas, koji je nekad primarno bio čuvar, a sada ga vidimo kao ljubimca kojeg se na neki način industrijalizira. Općenito ona uključuje troškove hrane, smještaja, zatim njege i higijene kućnih ljubimaca, ali i preventive i liječenja, odnosno brige za njihovo zdravlje. Prolaze vremena kada su hrana, voda i kućica bile dovoljne prosječnom vlasniku životinja, odnosno ljubimca.

Da nije sve samo materijalna korist, dobro je navesti istraživanja koja ukazuju da u prosjeku 86 % vlasnika pasa i 85 % vlasnika mačaka te 54 % onih koji nemaju nikakve kućne ljubimce smatraju kako životinje djeci pomažu u razvoju. Visok postotak ove četveronošce doživljava i kao članove obitelji, oko 80 % vlasnika kućnih ljubimaca i 51 % ne-vlasnika. Još je više onih koji misle kako pomažu u relaksaciji, 90 % vlasnika i 66 % ne-vlasnika, dok ih 70 %, odnosno 51 % smatra da su životinje i izvrsna terapija pri ozdravljenju. Možemo se zapitati da li su danas životinje, konkretnije kućni ljubimci, neovisno o trošku njihove egzistencije, važna odražavajuća komponenta „prirode u stanu“, ili možda „komunikacijski medijator“ ili pak “aditiv ljudskog zdravlja”? Iskustvo i praksa govore da kroz taj odnos možemo doći do suosjećajnosti naspam drugih ljudi, pa i boljeg razumijevanja onih društveno slabijih, ali i do odgovornijeg i zdravijeg ponašanja i načina života [6, 7].

3. BIOETIČKI KONTEKST ZA ZDRAVLJE

Teško je bioetiku današnjice prikazati jednom ili jednoobraznom definiciju. Prvi razlog je taj što je ona započela u praksi pa se tek kasnije pretočila u teoriju. Drugi je zasigurno taj što je zaživjela u biomedicinskim krugovima koji su se kroz desetljeća širili, kao u koncentričnim kružnicama, s vremenom obuhvaćajući sve više i više raznorodnih područja. O tome lijepo govori sljedeće shvaćanje bioetike: „Bioetika (…) se razumijeva kao interdisciplinarno zasnovana znanost o preživljavanju, koja prvenstveno želi izgraditi mostove između duhovnih i prirodnih znanosti. Usmjerena protiv puko instrumentalnog odnosa prema prirodi, bioetika se bavi gospodarskim, društvenim, političkim, kao i kulturnim pretpostavkama ljudskoga odnosa prema prirodi. Proširena u područje biomedicinske etike, ona razmatra ćudoredna pitanja rađanja, života i smrti, osobito s obzirom na noviji razvoj i mogućnosti biologijsko-medicinskoga istraživanja i terapije. Ona istražuje, među ostalim, moralnu problematiku pobačaja, sterilizacije i kontrole rađanja, (genske) manipulacije, eutanazije i eksperimenata na ljudima (…), kao i zaštitu životinja.” [8]. Iz ovoga slijedi kako bioetika pokriva sve što se tiče živoga i života. Jurić je to sažeto i konkretno iznio: „Bioetika je otvoreno područje susreta i dijaloga različitih znanosti i djelatnosti, te različitih pristupa i pogleda na svijet, koji se okupljaju radi artikuliranja, diskutiranja i rješavanja etičkih pitanja vezanih za život, za život u cjelini i u svakom od dijelova te cjeline, za život u svim njegovim oblicima, stupnjevima, fazama i pojavnostima.” [9].

Bioetika pruža jednu dosad neviđenu mogućnost pluriperspektivnog pristupa. Ona kroz svoju interdisciplinarnost daje podstrek suradnji različitih disciplina unutar nekog područja, kroz svoju multidisciplinarnost omogućuje povezivanje različitih područja, svojom transdisciplinarnost pruža mogućnost nadilaženja međusobnih sputavajućih i ograničavajućih razlika. Uza sve to teži ostvarivanju zajedničkog temelja raznolikim gledištima u svrhu umrežavanja i suradnje. Stoga je izuzetno pogodna za tako kompleksnu i široku tematiku poput zdravlja koje uključuje biomedicinu, znanosti o okolišu, prirodoslovlje, tehničke znanosti, društvene znanosti i mnoge druge.

4. ZAKLJUČAK

Čovjek samim svojim postojanjem mijenja prirodu i okoliš i to najčešće u negativnom smislu. Ipak, postoje načini da se taj utjecaj smanji jer postoji izrazita potrebu za promjenom odnosa čovjeka i okoliša iz onoga „znanje kao moć ovladavanja prirodom“ u „znanje kao odgovornost očuvanja prirode“ [10]. Upravo za tu promjenu odnosa pogodna je primjena osnovnih koncepata integrativne bioetike i održivog razvoja.

Slijedeći misao da je: „Pružanje orijentacije za odgovaranje na neke od ključnih problema čovječanstva i Planete bio bi stoga prvi i najvažniji cilj integrativne bioetike.”[9]. evidentno je kako se široki pojam zdravlja čovjeka, drugih živih bića i okoliša lijepo uklapa u ovakav koncept bioetike. Ona nam pruža jednu široku i združenu platformu za iznalaženje najboljih modusa glede zadržavanja zdravlja kao i ozdravljenja.

Jedan od načina kako djelovati i ostvariti spomenuto zasigurno jest raditi na obrazovanju i odgoju različitih struktura stanovništva. Odluke i aktivnosti svakog pojedinog inženjera, liječnika, biologa, pravnika ili bilo koje druge struke imaju dalekosežan utjecaj na cjelokupno ljudsko društvo kao i na svijet u kojem živimo. Zbog toga je važno da svaki pojedinac, bio on stručna osoba, aktivist, volonter ili jednostavno dobronamjernik, svoje odluke i postupke temelji na pravilima struke, ali i pravednosti, nepristranosti i poštenju. Dobro je da uvijek bude usmjeren prema općoj zaštiti života, zdravlja, da doprinosi napretku, sigurnosti i svekolikoj dobrobiti. U svemu tome neosporno je da mora biti suosjećajan spram bližnjih kao i drugih oblika života [11].

Bioetički koncepti mogli bi pridonijeti i obogatiti formalno obrazovanje kao primjerice kod struka poput inženjera okoliša, eko inženjera, medicinara i srodnih. Integrativna komponenta trebala bi se očitovati u bioetičkom odnosu čovjeka koji rješavanjem određene problematike nastoji služiti zajednici. Čineći tako u svakom trenutku i svugdje svjestan je odgovornosti očuvanja zdravlja i dobrobiti živog svijeta u svom okolišu i prirodi [7].

Povjereno nam je zdravlje ili bolest budućnosti. Odgovorni smo za to da li ćemo za sobom u ruke svojoj djeci ostaviti mogućnost da budu zdrava ili već unaprijed predispoziciju da obole jer smo mi bili neodgovorni prema okolišu u kojem živimo, djelujemo, stvaramo.

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PREGLED MOGUĆNOSTI PRIMJENE ALGI ZA OBRADU OTPADNIH VODA I PROIZVODNJU BIOGORIVA

AN OVERVIEW OF ALGAE UTILIZATION FOR WASTE WATER TREATMENT AND BIOFULE PRODUCTION

Lana Magić*, Jelena Parlov-Vuković*, Lucija Konjević*, Andrea Budiša**

* INA d.d., Centralni ispitni laboratorij, Zagreb, Hrvatska
** IRB, Centar za istraživanje mora, Rovinj, Hrvatska

autor za korespondenciju: Lana Magić, e-mail: lana.magic@ina.hr

Pregledni rad

SAŽETAK

Alge sve više dobivaju na značaju kao izvor biomase koja se može iskoristiti za proizvodnju biogoriva treće generacije. Biomasa je obnovljivi izvor energije te predstavlja alternativu fosilnim gorivima [1]. Proizvodnja biomase iz algi zahtjeva prostor, sunčevu svijetlost, vodu, CO_2 i hranjive tvari [2]. Zbog povoljnog utjecaja na okoliš postoji veliki interes da se postrojenja za uzgoj algi iskoriste za pročišćavanje otpadnih voda iz industrijskih postrojenja kao što su rafinerije nafti i elektrane na ugljen ili povežu s uređajima za pročišćavanje komunalnih otpadnih voda. Mnoge vrste mikroalgi uspješno rastu u otpadnim vodama zahvaljujući sposobnosti korištenja organskog ugljika te anorganskog dušika i fosfora. Alge će iskoristiti hranjive tvari zajedno s CO_2 i pomoću procesa fotosinteze proizvesti će biomasu te tako dolazi do procesa ko-generacije. Nastalu biomasu potrebno je izdvojiti iz hranjive podloge. Izdvojena biomasa može se na nekoliko načina prevesti u biogorivo. Ostatci biomase mikroalgi mogu se također koristiti kao stočna hrana, sirovina za anaerobnu razgradnju te kao organsko gnojivo [1]. U odnosu na fosilna goriva, upotrebom biogoriva proizvedenih iz biomase manja je emisija stakleničkih plinova. Količina CO_2 prilikom izgaranja u atmosferu smatra se zanemarivom s obzirom na činjenicu da alge tijekom rasta apsorbiraju približno istu količinu CO_2.

***Ključne riječi**: alge, mikroalge, biomasa, biogoriva, otpadne vode*

ABSTRACT

Algae are gaining ever so more on their importance as the source of biomass which can be used for the production of third generation biofuels. Biomass is a renewable energy source and an alternative to fossil fuels. Production of algal biomass requires space, sunlight, water, CO_2 and nutrients [1]. Due to a positive impact on the environment, there is a great interest in using plant algal cultivation systems for treatment of wastewater from industrial units, such as oil refineries, and coal-fired power plants or to connect them to wastewater treatment plants. Many microalgae species are able to grow efficiently in wastewaters due to their capability to use abundant organic carbon and inorganic nitrogen and phosphorus. Algae take up nutrients along with CO_2 and produce biomass through the process of photosynthesis and this leads to co-generation processing. Formed biomass must be separated from the culture medium. Separated biomass can then be transformed to biofuel by several pathways. Microalgal biomass residues can also be used as animal feed, feedstock for anaerobic digestion and as organic fertilizer [2]. Compared to fossil fuels, usage of biofuels produced from biomass reduces greenhouse gases emission. The amount of CO_2 formed during the combustion and released to the atmosphere is considered negligible due to a fact that during the growth, algal absorb approximately the same amount of CO_2.

***Keywords**: algae, microalgae, biomass, biofuels, wastewaters*

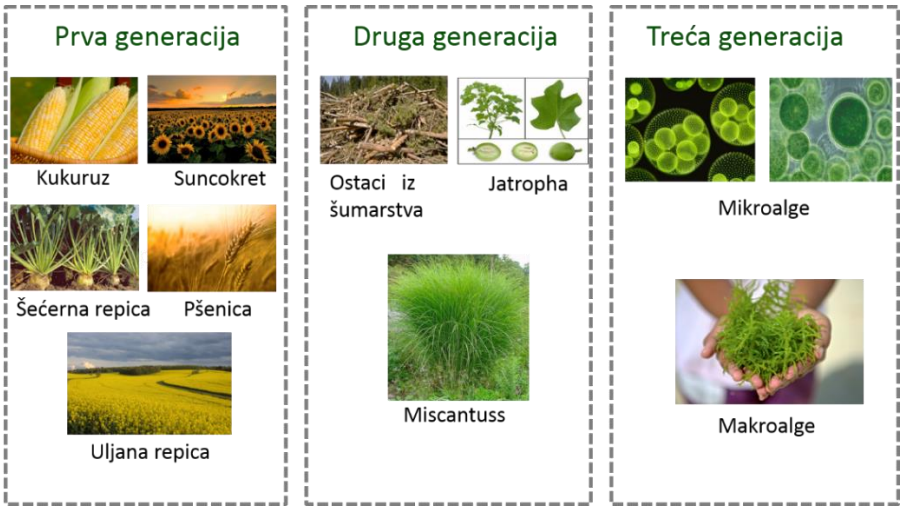
1. UVOD

Posljednjih godina biogoriva sve više dobivaju na značaju zbog ograničene raspoloživosti rezervi sirove nafte, ubrzanog razvoja automobilske industrije i ukupnog transportnog sektora što rezultira povećanjem emisija ispušnih plinova u okoliš. Nastali plinovi smanjuju kvalitetu zraka i negativno utječu na ljudsko zdravlje. Veliki problem predstavlja i činjenica da se neka industrijska biogoriva natječu s poljoprivrednim kulturama namijenjenim proizvodnji hrane čime povisuju cijenu hrane, što posebno utječe na stanovništvo zemalja u razvoju [3]. Također postoji i dodatni pritisak na vodene tokove jer se voda koristi za natapanje poljoprivrednih kultura i za daljnju proizvodnju biogoriva u rafinerijama [3]. U Europskoj uniji (EU) doneseno je više direktiva u području energetike i zaštite okoliša. Ovdje je važno spomenuti Direktivu poticanju upotrebe energije iz obnovljivih izvora 2009/28/EZ gdje je propisano postizanje udjela energije dobivenog iz obnovljivih izvora u gorivu za transport od 10 % do 2020. Također do kraja 2020, EU definira ciljeve koji uključuju smanjenje emisije stakleničkih plinova od 20 %, povećanje udjela energije iz obnovljivih izvora te povećanje energetske učinkovitosti za 20 % (slika 1).



Slika 1. Strateški ciljevi EU do 2020. godine

Ovisno o vrsti korištene biomase razlikujemo biogoriva prve, druge i treće generacije. Prva generacija biogoriva, bioetanol i bio-butanol, proizvodi se fermentacijom iz škroba iz kukuruza, pšenice, raži ili krumpira odnosno šećera iz šećerne trske ili repe, dok se biodizel proizvodi transesterifikacijom biljnih ulja i životinjskih masti [4]. Za proizvodnju druge generacije koristi se lignocelulozni dio biomase koji potječe od biorazgradivih dijelova otpada i biljaka. Trećom generacijom se smatraju biogoriva podrijetlom iz mikro i makro algi gdje se biokemijskom i termokemijskom pretvorbom mogu dobiti različite vrste biogoriva (slika 2). Istraživanja pokazuju da su mikroalge idealni izvor sirovina za proizvodnju biogoriva treće generacije zbog izuzetno brzog rasta, fiksacije CO_2 i proizvodnje lipida [5].

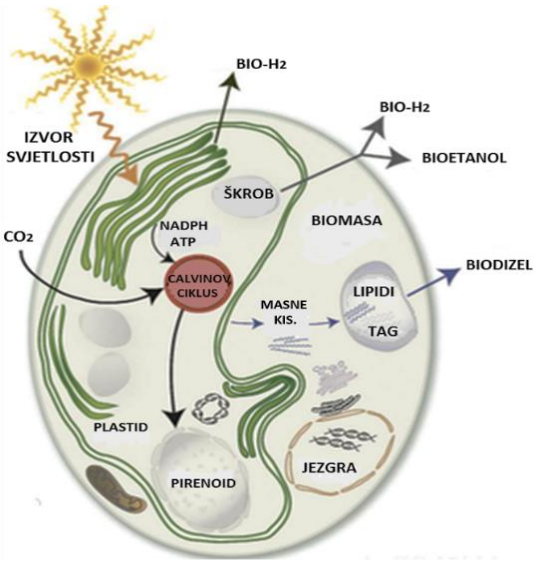


Slika 2. Klasifikacija biogoriva prema sirovini

2. PREGLEDNI DIO

2.1. Mikroalge

Mikroalge prema staničnoj građi mogu biti prokariotski i eukariotski fotosintetski jednostanični i višestanični mikroorganizmi [6]. Mikroalge su stanične "tvorevine" koje uz pomoć sunca pretvaraju ugljikov dioksid u potencijalna biogoriva, hranu, stočnu hranu i bioaktivne tvari (slika 3) [7]. Smatra se da postoji preko 50 000 različitih vrsta mikroalgi. Glavni predstavnici prokariotskih mikroalgi su cijanobakterije (Cyanophyceae), a eukariotskih mikroalgi su zelene mikroalge (Chlorophyta), dijatomeje (Bacyllariophita) i zlatne alge (Chrysophyceae) [8]. Mikroalge rastu mnogo brže nego usjevi hrane, i mogu proizvesti stotine puta više ulja po jedinici površine. Budući da žetveni period algi traje između 1 i 10 dana, njihovo uzgajanje omogućuje puno više žetvi u odnosu na kopnene vrste, koje se najčešće beru jednom godišnje [9]. Neke vrste mikroalgi posjeduju svojstvo prilagodbe promjenama u okolini mijenjajući vlastiti kemijski sastav kao odgovor na biološku varijabilnost. To svojstvo omogućuje akumulaciju željenih produkata u mikroalgama manipulacijom određenih čimbenika rasta.



Slika 3. Metaboličke reakcije mikroalge [10]

2.2. Kultivacija mikroalgi

Pri uzgoju mikroalgi potrebno je obratiti pozornost na nekoliko važnih parametara. Oblikovanje metaboličke reakcije algi ovisi o okolišnim, kemijskim i hidrodinamičkim uvjetima. Da bi se osigurao optimalan prinos i sastav biomase potrebno je definirati salinitet, temperaturu i svjetlost, omjere potrebnih hranjivih tvari kao što su dušik, fosfor i ugljikov dioksid te protok, količinu, prijenos i miješanje korištene vode. Dizajn i optimizacija adekvatnih bioreaktora u kojima će se uzgajati mikroalge predstavlja glavni korak u strategiji kultivacije. Sustavi za uzgoj moraju zadovoljavati nekoliko kriterija: visoku produktivnost, prihvatljivu cijenu i pouzdanost. Razlikujemo nekoliko sustava za kultivaciju algi, a osnovna podjela odnosi se na otvorene i zatvorene sustave (slika 4). Otvoreni sustavi mogu biti prirodni vodeni tokovi, jezera i lagune, te umjetno iskopani kanali i bazeni [11]. Takvi sustavi osjetljivi su na vremenske uvjete. Ne dopuštaju kontrolu temperature vode, isparavanja i osvjetljenja. Osim toga u sustavima otvorenog tipa postoji mogućnost kontaminacije ili invazije neke druge neželjene vrste mikroorganizama. Zatvoreni sustavi nazivaju se još i fotobioreaktorima. Razlikuju se po konstrukciji prilagođenoj fiziološkim specifičnostima mikroalgi i potrebama za njihov optimalan rast. Prednost je u tome što omogućuju potpunu kontrolu svih uvjeta rasta što u konačnici donosi i veći prinos biomase. Ovakvi sustavi vrlo se lako mogu povezati s postrojenjima koja služe kao izvor CO_2 i s otpadnim vodama koje predstavljaju dobar izvor hranjivih tvari.



Slika 4. Različiti sustavi za kultivaciju algi

2.3. Integracija uzgoja mikroalgi

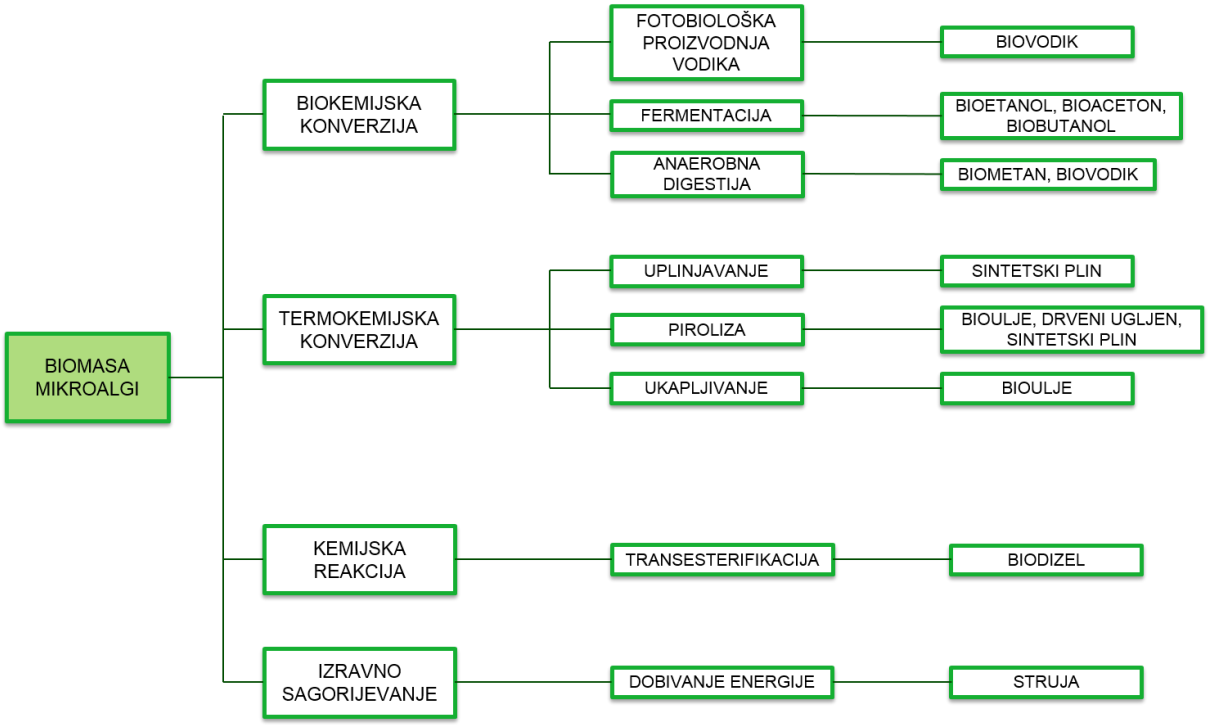
Industrijske i komunalne otpadne vode predstavljaju dobar izvor jeftinih hranjivih sastojaka te se mogu koristiti za pripravu hranjivih podloga i uzgoj mikroalgi. Prije uzgoja otpadne vode je potrebno prilagoditi potrebama mikroalgi te pripremiti hranjivu podlogu s dovoljnim količinama izvora biogenih elemenata [1]. Upotrebom otpadnih voda za pripremu hranjivih podloga moguće je reducirati udjele kemijskih elemenata dušika i fosfora do 55 %,te ostvariti značajne ekonomske uštede [12]. Velika prednost bioremedijacije otpadnih voda je u tome što se nakon kultivacije u okoliš mogu ispustiti vode s dovoljno niskim udjelima dušika i fosfora čime se sprečava nastanak eutrofikacije prirodnih prijemnika.

2.4. Mogući postupci izdvajanja biomase iz medija

Nakon kultivacije potrebno je izdvojiti nastalu biomasu. Kako bi se uklonile velike količine vode i obradili veliki volumeni biomase mikroalgi potrebno je provesti nekoliko koraka koji uključuju izdvajanje mikroalgi iz hranjive podloge, sušenje stanica mikroalgi i obradu da se dobije željeni produkt [13]. Glavne tehnološke operacije izdvajanja biomase algi iz hranjive podloge su centrifugiranje, flokulacija, filtracija, prešanje, sedimentacija i flotacija [14]. Veća količina biomase mikroalgi može se izdvojiti iz hranjive podloge procesom centrifugiranja. Nedostaci navedenog postupka su visoki utrošak energije i oštećenje stanica mikroagli tijekom centrifugiranja [1]. Da bi se izbjegli navedeni nedostaci potrebno je prilagoditi izbor i redoslijed operacija. Flokulacija se može provoditi dodatkom anorganskih flokulanata (soli aluminija i željeza) pri čemu dolazi do adsorpcije aluminijevih ili željeznih iona na površini negativno nabijenih stanica, te stvaranja nakupina stanica i taloženja [15]. Nedostaci navedenog postupka su stvaranje velike količine mulja te osjetljivost flokulacije na primjene pH vrijednosti. Sedimentacija mikroalgi iz hranjive podloge najčešće je korištena metoda kod izdvajanja biomase mikroalgi nakon uzgoja u otpadnim vodama, a brzina sedimentacije ovisi o specifičnoj težini mikroalgi. Korištenje procesa filtracije za izdvajanje biomase mikroalgi je učinkovito samo ako se koriste filtri odgovarajuće konstrukcije i pora [1].

2.5. Proizvodnja biogoriva – konverzija biomase

Izdvojenu biomasu potrebno je prevesti u biogorivo. Biokemijska konverzija podrazumijeva upotrebu bakterija, mikroorganizama i enzima pomoću kojih se biomasa razgrađuje do tekućih i plinovitih biogoriva. Najčešće upotrebljavane biokemijske konverzije su fermentacija i anerobna digestija pomoću kojih se dobivaju bio-etanol, bio-aceton, bio-butanol te bio-metan i bio-vodik. Termokemijska konverzija odnosi se na termičku razgradnju organske tvari sadržane u biomasi. Tu spadaju procesi uplinjavanja, pirolize i ukapljivanja pomoću kojih se mogu dobiti sintetski plin, bioulje i drveni ugljen. Kod ove vrste konverzije postoji potencijal za integraciju s postojećim postrojenjima prerade nafte. Kemijskom reakcijom transesterifikacije moguće je dobiti biodizel, a izravnim sagorijevanjem biomasa se može iskoristiti kao energija, npr. za proizvodnju struje (slika 5).



Slika 5. Konverzijski procesi za proizvodnju biogoriva iz biomase mikroalgi [16]

3. ZAKLJUČAK

U ovome preglednom radu opisane su mogućnosti primjene mikroalgi u proizvodnji biogoriva uz istovremenu integraciju s uređajima za pročišćavanje otpadnih voda. Proizvodnja i upotreba biogoriva obveza je koju su nametnule klimatske promjene, ali i smanjenje mogućnosti iskorištenja izvora fosilnih goriva. Značajna prednost mikroalgi u odnosu na druge sirovine je u tome što predstavljaju izvor ugljik neutralnog goriva. Ukupni ugljikov trag biogoriva iz mikroagli gotovo je jednak nuli zbog zatvorenog ugljikova kruga. Zatvoreni ugljikov ciklus znači da biljke koje se koriste za proizvodnju biogoriva iz atmosfere uzimaju ugljikov dikosid i vraćaju kisik u postupku fotosinteze, a kasnijim izgaranjem biogoriva iz atmosfere se koristi kisik i ispušta se ugljikov dioksid [3]. Na ovaj način ukupna količina ugljikova dioksida u atmosferi se ne povećava.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

RECOMMENDATIONS FOR IMPROVEMENT OF CRITICAL AND RARE EARTH METALS RECOVERY FROM PRINTED CIRCUIT BOARDS IN PRE-TREATMENT PROCESSES

Tijana Marinković*, Bojan Batinić*, Miodrag Živančev*, Maja Brborić*, Senka Bubulj*

* University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia

corresponding author: Tijana Marinković, e-mail: tijanamarinkovic@uns.ac.rs

Review paper

ABSTRACT

Electrical and electronic waste is a fast-growing waste stream, which from the aspect of 'urban mining' concept presents a significant secondary resource of valuable metals. Currently, the extraction of metals from ores is energy intensive and involves environmental risks due to the toxic chemicals involved. Through the currently applied recycling processes of complex e-waste stream, critical and rare earth metals are lost completely. The aim of this paper is to indicate the shortcomings of recycling processes and to present the possibilities for their improvement. The main focus is on the printed circuit boards which are due to high content of valuable materials, recognized as a very important e-waste stream for processing. The paper gives an overview of the most relevant PCB's components in terms of critical and rare earth metals concentrations and recommendations on how to achieve the highest degree of separation of valuable materials using a semi-automated system.

***Keywords**: electrical and electronic waste, printed circuit board, critical metals, rare earth metals, pre-treatment*

1. INTRODUCTION

Increasing of world global population and enhancement average living standards as well as technological innovation increases demands for mineral raw materials which are necessary for the production of goods that would satisfy the growing human needs. One of these products is electrical and electronic devices whose production requires the use of raw materials in large quantities. According to [1] in the eighties, 12 elements were used in the manufacture of computer chips, in the nineties 16 elements were used, and in 2006, as many as 60 elements were used in the manufacture of high-speed, high-capacity integrated circuits

[1]**.** The massive use of electrical and electronic products, but also the shorter lifespan, results in the generation of 20 - 50 million tons of waste electrical and electronic equipment (WEEE) every year [2]. Nearly 45 million tons of e-waste is generated globally per year [3], and The UN Environment Programme estimates that amounts are rising three times faster than other forms of municipal waste [2]**.**

Waste electrical and electronic equipment contains valuables (e.g. non-precious metals: iron, steel, copper, aluminum, etc.; precious metals: Au, Ag, Pd, Pt, etc.; critical metals: Y, Nd, Eu, etc.; plastics) and hazardous substances (e.g. lead-containing glass, Hg, Cd, batteries, flame retardants, chlorofluorocarbons and other coolants with hazardous potential and environmental impact) [4, 5]. A number of legislative documents refer to the restriction of hazardous substances in electrical and electronic equipment (EEE), such as Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE), RoHS Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment, and Directive 2005/32/EC of the European Parliament and of the Council of 6 July 2005 establishing a framework for the setting of ecodesign requirements for energy-using products have been drafted and implemented in the EU [6]. The strategic target of these legislations is implementation of an extended producer's responsibility covering the whole life cycle of EEE and obliging producers to decrease the content of hazardous materials, and in the first place to increase the recycling of EEE products [7].

The main challenge for national and regional economies with limited production is to provide access to stable supplies of many raw materials. EU economy relies on imports of many minerals and metals needed by industry, including many critical raw materials. China is the largest global supplier of critical raw materials (70 %), as well as major consumer of several critical raw materials. Russia and South Africa are also important global suppliers of platinum group metals (PMGs), USA for beryllium and helium and Brazil for niobium. European Raw Materials Initiative, launched by European Commission (EC) in 2008, is an integrated strategy that establishes targeted measures to secure and improve access to raw materials for the EU. One of the priority actions of the Initiative was to establish a list of critical non-energy raw materials at EU level. The first list was established in 2011 and it is updated every three years [8].

As the critical raw materials (CRMs) are both of high economic importance for the EU and vulnerable to supply disruption [9], to determine the criticality serves two parameters and those are Supply Risk (SR) and Economic Importance (EI) [8]. Supply Risk means that the supply is associated to a high risk of not being adequate to meet EU industry demand. High economic importance means that the raw material is of fundamental importance to industry sectors that create added value and jobs, which could be lost in case of inadequate supply and if adequate substitutes cannot be found [9].

Raw materials which have strategic importance for EU manufacturing industry, high economic importance and high supply risk, were identified as critical raw materials at EU level [10]. According to the European Commission Report for 2017, a list of 27 raw materials was submitted, of that 15 rare earth elements (REEs) are split into two sub-categories: 'heavy' rare earth elements (HREEs), consisting of ten individual materials and 'light' rare earth elements (LREEs), comprising five individual materials. The five platinum group metals (PGMs), excluding Os are grouped under one group [8]. According to [8] the Import reliance rate takes into account net imports of specific CRM in EU divided by EU net imports plus EU domestic production. This relationship shows that the dependence of EU imports on 11 materials of 27 is equal to 100 %. These materials are marked with red on the figure 1.

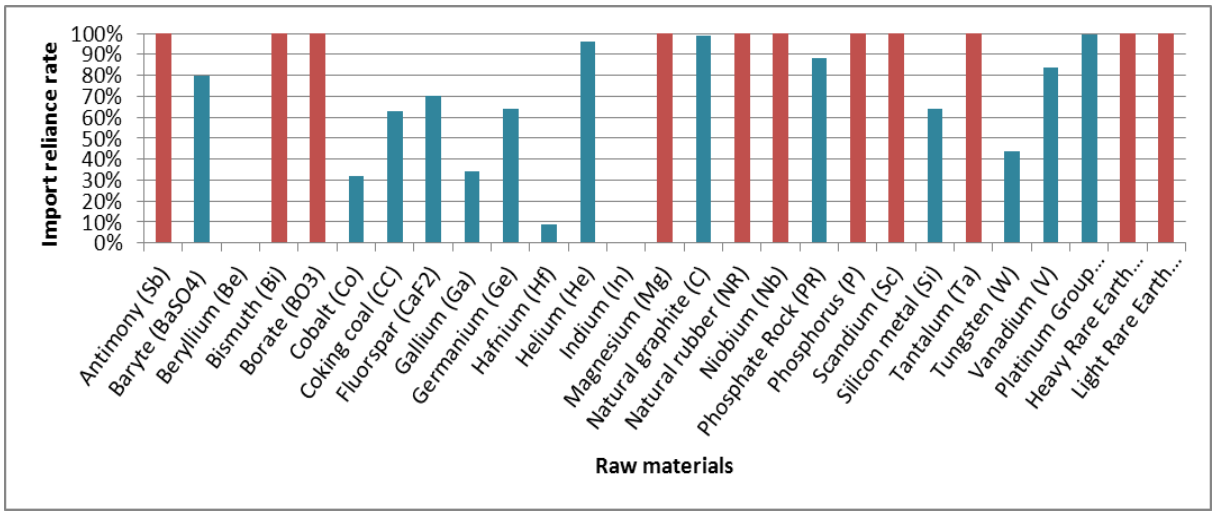


Figure 1. Reliance on import for selected CRMs on EU level [8]

Mining, extraction and production of raw materials have direct pollution impacts on environment, responsibility for around 5 % of global carbon dioxide emissions, direct social impacts on isolated mining communities, and responsible for 7 – 10 % of global energy consumption [11]. Urban mining seems to be the ideal solution for several reasons: WEEE contains relatively high concentrations of critical metals (CMs), extraction and processing of anthropogenic stocks is necessary, and the generation of an economic benefit is essential [11].

2. QUANTITIES OF CMs AND REE IN PRINTED CIRCUIT BOARDS

Since the printed circuit boards (PCBs) are a key part of almost all electrical and electronic devices that are used every day throughout the world, their production will be constantly increasing. According to [2], the global PCBs production in 2008 increased by 8.7 %, while the percentage of production for south east Asia increased by 10.8 % and in China by 14.4 %. It's also important that China produces half of PCBs for the world market [12]. Due to the reduction in the lifespan of EEE products, the amount of PCBs in the total amount of waste is increased, and it's estimated that PCBs make about 3 % of the total waste [13].

Elemental composition of PCBs varies depending on type of device, year of manufacture, and other factors [14]. The material present in PCBs can be categorized in three groups: ~23 % plastics [15] (with contents of flame retardants and paper), ~ 28 % metals [15] (base metals such as Cu, Fe, Al and Sn; precious metals such as Au, Ag, and Pd; REEs and PGMs) and other is ceramics. PCB also contains hazardous metals such as Cr, Pb, Be, Hg, Cd, Zn, Ni [12].

Electronic components are mounted on PCBs using various types of connections: socket pedestal, through-hole device (THD), surface mounted device (SMD), screw joint, and rivet [16]. Through-hole technology requires holding the circuit board to place the components that cross through all layers. In contrast, SMDs are soldered on the circuit board or assembled with a small amount of adhesive on the underside, without the necessity of holding the circuit board [17]. Tantalum is used in tantalum high-performance capacitors, elements such as Ga, In, Ti, Si, Ge, As, Sb, Se, and Te can be found in chips and other units. Solder joints contains Au, Pd, Pb and Cd whereas bridges and slots on boards are made of ceramics including, BeO and glasses. Semiconductors contain Ga, Si, Se, Ge, and other elements in smaller quantities [16]. The PMGs are present in joints relays, switches or in

sensors [18]. Integrated circuits and semiconductors consist of small amounts of Ga, In, Ti, Ge, As, Se and Te. Ni is used in its pure form and increasingly used in contacts as additive. According to [19] key parts of PCBs to be included in the recycling process are: Transistors (Al, SiO_2, As, Ni, Sn and Ge), IC chips/microchip (SiO_2, Cu, Ag, Au, Pd, Ga, In and Pd), Tantalum capacitors, Aluminum electrolytic capacitor (Al and one of NbO_2, TaO_2, VO_2 or a combination thereof), Ceramic capacitors (ZrO, Cu, Ni, $BaTiO_3$, Ag-Pd alloy), Chip resistors, Thermisters, Connectors (Cu, Au, Ag, SiO_2, Ni, Al). Table 1 lists the quantities of critical metals that can be found in PCBs.

Table 1. Material composition of PCBs from different electronic device, expressed as milligram per kilogram (redrawn from [20]).

PCB type	Critical metals [mg/kg]								
	Ba	Be	Bi	Cd	Cr	Co	Ga	Sb	Ta
DVD player	4300	-	85	2	320	110	9	1200	77
Gas discharge lamps	-	-	-	-	10	-	-	-	-
Mobile phone	19000	11	220	2	105	140	70	880	1300
PC	3480	8	83	3	400	85	19	1625	1422
Power tools	-	-	-	-	210	-	-	-	-
Printer	3000	-	9	-	32	220	3	530	-
TV (CRT,PDP, LCD)	2825	-	127	6	52	18	-	2200	50
Casette recorder	1300	-	230	7	140	28	11	2150	16
Camera	16667	10	157	1	1933	107	22	1967	5300
Portable CD/MD player	13800	60	880	-	2385	115	-	1300	5135
Game console	5100	-	260	1	800	100	16	2900	83

Although there are numerous initiatives to encourage recycling of e-waste, only 9 % of the collected e-waste is recycled [7]. The end-of-life recycling rates which represent the recovery rates over all stages of the recycling process (collection, preparation, refining) from the post-consumer sector are currently less than one percent to zero for all REE and also for gallium and indium [21]. Tantalum is also one of the large group of metals which still exhibit end-of-life recycling rates of < 1 %. The rare earth metals are not absorbed with high yields in a copper phase but end up diluted in the form of their oxides in slags and have therefore not been available for recycling [22, 23] in conventional recycling processes. Similar in the standard pyro-metallurgical processes tantalum is converted to the resulting slags as tantalum oxide, due to its base character. Consequently recycling tantalum from the capacitors in PCBs would require a mechanical separation of these capacitors from the PCBs [7]. In addition to the above factors that influence the low rate of CMs allocation, the most important factor is the inadequate treatment of e-waste, i.e. lack of pre-treatment.

3. THE CURRENT SYSTEM OF RECYCLING OF PCB

The recycling process is based on the sorting of waste and the separation of components that can be manually dismantling such as PCB, cathode ray tubes, processors, hard drives, and similar. On the other hand, mechanical process that involves size reduction (primary grinding of equipment on the "shredder" and additional grinding by mills). In the

subsequent sorting process the particles are separated based on properties such as density, magnetic, or conductivity [24]. Magnetic separator are separating ferrous metals (Fe, steel, Ni, etc.), while Eddy-current and corona electrostatic separators are separating non-ferrous fractions (Cu, Al, plastic, glass, etc.) [25]. Under advanced treatment / refining is meant hydro-metallurgical, pyro-metallurgical or bio-metallurgical processes of separating valuable metals.

Losses of critical metals are almost 100 % because recycling processes focus on the separation of basic and precious metals. As a prerequisite for the recovery of these materials, recycling processes must be adapted to provide CM-rich output stream [7]. Currently the greatest need for the technical optimization of recycling is to improve manual disassembly during the pre-treatment stage [26]. It has been shown that shredding entire components in classical recycling processes leads to the loss of critical metals, which cannot be compensated by the downstream sorting and refining processes. To improve the recovery of valuable metals, it is essential to manually remove the PCBs and feed these components separately to recycling facilities [10].

4. ADVANCED DISASSEMBLY SYSTEM

The goal of the dismantling process is to isolate reusable and environmental hazardous components so that the rest of the PCB can be sent to mechanical processing and further processes. The disassembly process may be manual, automatic or semiautomatic [12]. At present, manual disassembly process is most common, but it is not an economically viable option [16].

Semi-automatic dismounting systems require manual disassembly of the PCB from the rest of the device, then PCBs assemblies are fixed on frames and fed into a dismantling cell [27]. Recognition system with an image-processing, called “Vision System”, identifies significant components on the PCBs assemblies [16]. Components can be mapped comparing the shape, labels, size, type, position, etc. [27, 28] i.e. the dimension and location of the component [28], with a database containing information from manufacturers and information from the reuse market [27]. Modern identification systems use one, two or three–dimensional (3-D) picture, radiograph, and infrared pictures like optical measures for recognition [16]. The following steps, such as the de-soldering system, and a robotic system are focused on extracting rich CMs components. The de-soldering system is usually a combination of heating over the melting point of the solder and applying such external forces as impact, shearing and vibration [27]. There are numerous research and projects on the development of economically viable and efficient semi-automatic and automatic PCB disassembly systems. From the example of good practice presented in this paper, it can be concluded that each step of the process can be realized in different ways. The efficiency of the automated system of recycling PCB is 65 %, while for the conventional recycling ratio is 25 % [27].

4.1. The first example of a semi-automated process

Semi-automated cell, that can be seen in figure 2, consists of a vision system that classifies components using high-quality image detecting system, a transport system and de-soldering- robot-system. The de-soldering system removes surface mounted device (SMD), while the robot removes through-hole device (THD), and other complex connections, and also after disassembly collects them and sends to the next phase [16].

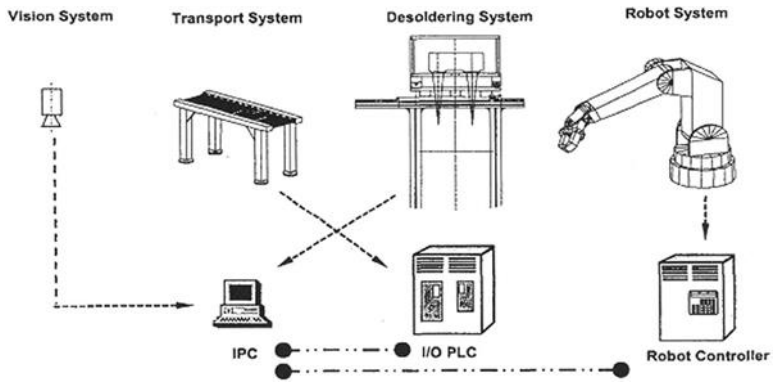


Figure 2. Example of a semi-automated process with de-soldering- robot-system [29]

4.2. The second example of a semi-automated process

Legarth et al. gave an example in which 3D images are used to identify and collect information to compare with the database [30]. Picture processing algorithms provide coordinates and rotation angles to determine which components are important and how to extract them. For de-soldering surface-mounted device components, small force, hot air and vacuum gripper are used. While hot liquid and a parallel-jaw gripper [27] are used for disassembling the through-hole device components.

4.3. The third example of a semi-automated process

Another example is flexible dismantling cell that is equipped by vision system, de-soldering system with laser and infrared heating removal station, robot removal station, and stock for de-soldered components [19]. After a manual dismantling from the rest of the device PCB maximum size of 300 x 220 mm is secured to the holder and enters the disassembly cell (figure 3). Recognition system with high quality image processing comparing the shape and labels of the parts with a database containing information from manufacturers and information from the re-use market. Beside this the system has to determine the position, size, and the centre of area of the considered component and provide this data as input for the next stations. This information is needed for the next phase so that the vision system can reach the position with 0.1 mm accuracy in order to recognize the characters on the part by means of Optical Character Recognition (OCR). Components that contain CMs are separated by laser or infrared heating. Additionally the infrared heating appliance unsoldering technology is used to extract components which are not suitable or valuable enough for the laser unsoldering station. In the next process step, this component is removed using special robotic grippers [19].

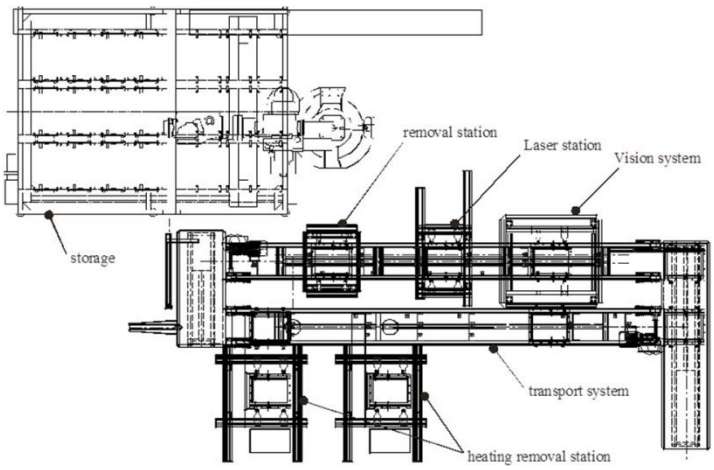


Figure 3. Components of the intelligent flexible Disassembly Cell [19]

In short, the recycling system of PCBs with the aim of separating critical metals consists of the following steps:

- manual dismantling: separating PCB from the rest of the device,
- transport system: PCB attached to the holder,
- visual system: the image processing and database,
- separating components rich CMs: dismantling using hot air, vacuum gripper, hot liquid and a parallel-jaw gripper, lasers, or infrared heating,
- shredding and additionally grinded mill,
- separation: magnetic separation, eddy current, corona separation,
- metallurgical processes: hydro-metallurgical, pyro-metallurgical, bio-metallurgical.

5. RECOMMENDATIONS FOR IMPROVEMENT OF CMs RECOVERY FROM THE PCB

In order to be able to talk about raising the CMs recycling rate, it is necessary to revise the regulations that govern this area. Today's practice is that recycling rates are targeted at the entire product, and it is primarily necessary to define for this group of materials. Also, the collection rates and the gray market need to be regulated so that PCBs processing plants achieve continuity in operation, since they need large quantities of these products. In order to achieve easier manual disassembly of products and release components rich of critical metals, it is necessary to improve product design.

The main driving force for recycling CMs is an economic aspect, so it is necessary to develop processes that are cost-effective, as well as more investments and further research in this area. Developing pre-treatment is not possible without relevant information on CMs content in precisely defined PCB components. From the examples of good practice it can be seen that each of them requires a knowledge base on the content and types of PCBs that can be found on the market.

The optimization of the recycling process, which involves separating the PCB from the rest of the device, automatic recognition, sorting as well as de-soldering components with high concentration of CMs. provide more efficiently recover CMs from heterogeneous WEEE flows [26, 31].

6. CONCLUSION

There is a lack of adequate legislation that would harmonize requirements for collection rates and recycling rates with the aim of allocating critical metals, as well as requirements for improving design of products that would facilitate easier de-assembly of components resulting in a low separation rate of critical metals. The most important factor is the inadequate treatment of WEEE, which refers to the lack of pre-treatment. In the conventional processes of shredding the whole component the critical metals, which are in very low concentrations in the order of ppm, are mixed with the rest of the material flow. In this way it is not possible to extract valuable metals from the mixed flow by further processes such as separation and metallurgical processes. In order to ensure the output flow of materials suitable for further processes, it is necessary to improve the pre-treatment system. In addition, it is necessary to develop processes that would be economically viable so that they can be applied in industrial plants around the world. The application of manual dismantling of PCBs from the rest of the device and the automatic process of recognizing valuable components, as well as the disassembly of the recognized components make the semi-automatic system the most optimal option for extraction CMs.

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Acknowledgements

This research was supported by Ministry of Education, Science and Technological Development, Republic of Serbia (TR31025).

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

RAČUNALNO MODELIRANJE PROCESA SELEKTIVNE KATALITIČKE REDUKCIJE ZA SMANJENJE EMISIJA NO_X

COMPUTATIONAL MODELLING OF SELECTIVE CATALYTIC REDUCTION PROCESS FOR NO_X EMISSION REDUCTION

Matija Martinjak*, Jakov Baleta, Milan Vujanović***, Xuebin Wang****, Min Zeng******

* HEP Proizvodnja d.o.o., TE-TO Sisak, Sisak, Hrvatska
** Sveučilište u Zagrebu, Metalurški fakultet, Sisak, Hrvatska
*** Sveučilište u Zagrebu, Fakultet strojarstva i brodogradnje, Zagreb, Hrvatska
**** Xi'an Jiaotong University, Laboratory of Thermo-Fluid Science and Engineering, Xi'an, Shaanxi, Kina

autor za korespondenciju: Matija Martinjak, e-mail matija.martinjak@gmail.com

Izvorni znanstveni rad

SAŽETAK

Podizanje svijesti o očuvanju okoliša ima za posljedicu prilagodbu postojeće tehnologije aktualnim okolišnim zahtjevima. Posebni naglasak stavljen je na onečišćujuće emisije dimnih plinova, poglavito NO_x-a. Zbog sve strože ekološke legislative, primarne mjere kontrole ispušnih plinova u velikom broju slučajeva više nisu dovoljne. Rješenje za daljnje smanjenje koncentracija NO_x-a je u naknadnoj obradi ispušnih plinova. Najperspektivnija tehnologija u tom području je selektivna katalitička redukcija (eng. *Selective Catalytic Reduction* - SCR), koja ima široku primjenu, kako u transportu, tako i u industriji. Zbog kompleksnosti reakcija i prostorne raspodjele plinova unutar katalizatora, veliki resursi ulažu se u razvoj matematičkih modela pomoću kojih bi se dovoljno dobro opisao proces selektivne katalitičke redukcije. Ideja ovog rada je prezentirati mogućnosti numeričkih modela integriranih unutar komercijalnog koda za računalnu dinamiku fluida AVL Fire za opis SCR procesa na bazi usporedbe rezultata dobivenih simulacijama s eksperimentalnim podacima cijevnog reaktora.

***Ključne riječi**: selektivna katalitička redukcija, računalna dinamika fluida, obrada dimnih plinova*

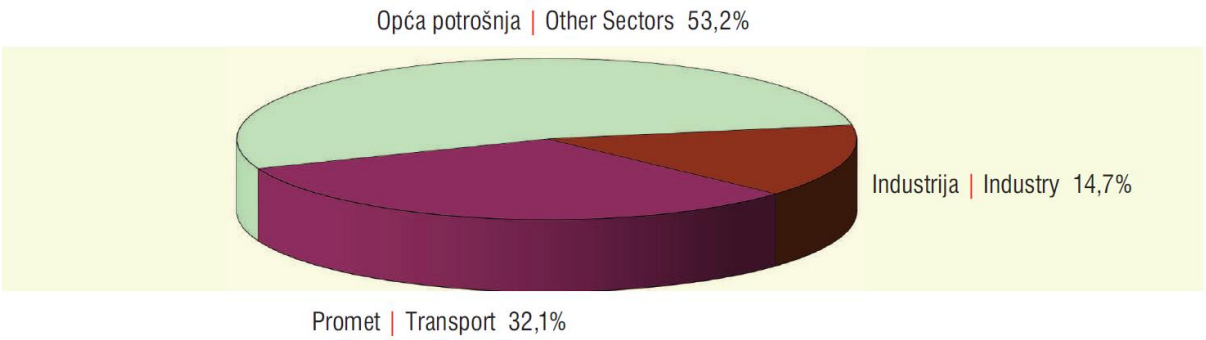
ABSTRACT

Awareness regarding environmental protection has resulted in the adaptation of existing technology to the current environmental demands. Special emphasis is being put on the emission of various gases, most notably NO_X. Due to sterner ecological legislature primary measures of emission control have been found insufficient in many cases. The solution for further decrease of NO_X is to employ exhaust gas after treatment. The most perspective technology in that area is Selective Catalytic Reduction (SCR), especially given its frequent and wide usage in the industry and transport. Vast effort has been made recently to describe the SCR process due to the complexities of reactions involved and spatial distribution of gases in catalysts. The general idea of this work is to demonstrate the possibilities of numerical models integrated within the commercial code for computational fluid dynamics AVL Fire for SCR process description on the basis of comparison of simulation results with experimental data of pipe reactor.

***Keywords**: selective catalytic reduction, computational fluid dynamics, flue gas after treatment*

1. UVOD

Razvoj energetike kroz povijest može se povezati s razvojem civilizacije, a pri tome je moguće promatrati razne aspekte napredovanja čovječanstva. Ukoliko se prati razvoj energetike, može se zaključiti da potreba za energijom neprestano raste te da se takav trend očekuje i u narednim godinama [1]. Povećanje potrošnje energije iz fosilnih goriva kroz povijest može se povezati s onečišćenjem okoliša. Usku poveznicu onečišćenja okoliša i potrošnje energije iz fosilnih goriva danas je moguće pratiti i analizirati [2]. Sektori u kojima je najizraženiji konzum energije su: industrija, promet, zgradarstvo i poljoprivreda [3]. Sektor industrije i prometa karakterizira značajna upotreba fosilnih goriva, a samim time i značajna proizvodnja ispušnih plinova. U Republici Hrvatskoj 2015. godine gotovo polovica od ukupne potrošene energije otpadala je na transport i industriju, što je prikazano na slici 1. Obzirom da promet i industrija imaju velik udio u potrošnji energije, kako u Hrvatskoj tako i u svijetu, potrebno je poduzeti mjere kojima bi se proizvodnja onečišćujućih tvari svela na minimum. Brojna istraživanja provedena su sa ciljem smanjenja polutanata u industriji i prometu [4].



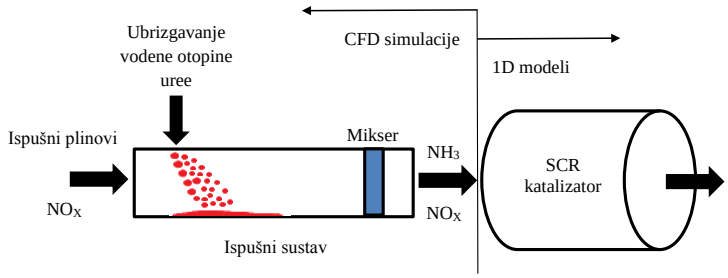
Slika 1. Udjeli sektora u neposrednoj potrošnji energije u RH za 2015 godinu [5]

Prilikom izgaranja fosilnih goriva nastaju produkti izgaranja, a njihovi značajniji predstavnici su: CO_2, CO, NO_X i SO_X. Niz zakona i legislativa [6] govori o regulaciji ispušnih plinova, gdje su, ovisno o sektoru i namjeni, koncentracije ispušnih plinova ograničene na određene vrijednosti. Dušikovi oksidi (NO_X) kao jedni od značajnijih posebno su interesantni za promatranje i analizu obzirom da imaju izrazito štetan utjecaj na okoliš koji se očituje kroz stvaranje fotokemijskog smoga, zakiseljavanje, globalno zagrijavanje (razaranje stratosferskog ozona) i eutrofikaciju tla i vode. Generalno se može reći da su temperatura izgaranja, sastav goriva, pretičak zraka, konstrukcija gorionika i komore za izgaranje faktori koji utječu na produkciju NO_X-a. Mehanizmi nastajanje NO_X-a mogu se podijeliti [7]:

1. Termalni NO_X
2. NO_X podrijetlom iz goriva
3. Promptni NO_X

Termalni NO_X javlja se pri visokim temperaturama izgaranja (iznad 1500 °C). NO_X podrijetlom iz goriva nastaje oksidacijom dušika vezanog uz gorivo. Obzirom da su kruta goriva bogata dušikom, ovaj mehanizam nastajanja karakterističan je za biomasu i ugljen. Promptni NO_x nastaje u bogatim smjesama goriva reakcijom radikala iz goriva s atmosferskim dušikom. Generalno gledajući metode prevencije nastajanja NO_X-a možemo podijeliti na primarne i sekundarne [8]. Primarne metode prevencije nastajanja NO_X-a imaju zadatak reducirati NO_X pri samom procesu izgaranja, u komori za izgaranje. Jedna od najraširenije primarne metode prevencije nastajanja NO_X-a nastoji regulirati ulazni zrak u komori za izgaranje, stvarajući pri tome zone bogate gorivom i zone siromašne gorivom. Djelovanje ove primarne metode očituje se u smanjenju termalnog NO_X-a i NO_X-a podrijetlom iz goriva. Za sektor prometa specifična je recirkulacija dimnih plinova koja kao primarna metoda prevencije nastajanja NO_X-a nastoji smanjiti udio termalnog NO_X-a, kroz smanjenje temperature izgaranja i suviška zraka. Kada primarne mjere nisu u mogućnosti reducirati koncentraciju NO_X-a koriste se sekundarne metode prevencije. Sekundarne mjere podrazumijevaju naknadnu obradu dimnih plinova, gdje se selektivna katalitička redukcija pokazala kao jednom od najperspektivnijih tehnologija na tom polju [9].

Selektivna katalitička redukcija (SCR) je katalitički proces koji se uspješno primjenjuje u industriji već dugi niz godina [10]. Upotreba SCR-a u transportu izražena je posljednjih godina kod Diesel motora uslijed sve strožih ekoloških normi [11]. Danas je SCR jednako važna tehnologija, kako na stacionarnim postrojenjima u industriji, tako i u prometu. Kod stacionarnih postrojenja kao reducens koristi se čisti amonijak, dok se u prometu uglavnom koristi urea, odnosno vodena otopina uree. Obzirom da je čisti amonijak toksičan, kao takav je problematičan za sigurnu pohranu i upotrebu. Urea je znatno sigurnija za korištenje i pohranu, ali ju je prije ulaska u katalitičku reakciju potrebno termički konvertirati u amonijak. Vodena otopina uree (trgovački naziv AdBlue) koja se koristi kod motora s unutrašnjim izgaranjem je mješavina od 32.5 % uree visoke čistoće i 67.5 % demineralizirane vode. Sama potrošnja otopine iznosi oko 3 - 5 % potrošnje Diesel goriva. AdBlue otopina je neotrovna ali je korozivna, pa svi dijelovi sustava za korištenje i skladištenje otopine moraju biti izrađeni od polimera i nehrđajućih čelika. Sama efikasnost SCR sustava u kopnenom prometu je iznimno velika (do 90 % smanjenje NO_X-a) [11]. Jednostavni prikaz SCR sustava dan je na slici 2.



Slika 2. Prikaz SCR sustava [12]

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Razna eksperimentalna mjerenja imaju za cilj na što efikasniji način smanjiti emisije ispušnih plinova [13], a poglavito NO_X-a. Cijena i brzina provedenih eksperimenata postaju sve važniji, kako u znanstvenom, tako i u inženjerskom svijetu. Računalna dinamika fluida (RDF), odnosno računalne simulacije, nametnule su se kao novi trend kao bi mogle upotpuniti i u nekim dijelovima zamijeniti eksperimentalna mjerenja [14]. Cilj ovog rada je prezentirati mogućnosti numeričkih modela za opis SCR procesa na bazi usporedbe rezultata dobivenih simulacijama s eksperimentalnim podacima cijevnog reaktora. Nakon uvodnog razmatranja u kratkim crtama predstavljen je matematički model provedene računalne simulacije. Zatim su prezentiranje eksperimentalne odnosno simulacijske postavke u kojima je ujedno objašnjen i odabir mreže promatrane geometrije. Rezultati su predstavljeni u karakterističnim trenucima za karakteristične vrijednosti, u cilju kasnije usporedbe s mjerenjima eksperimenta. Zaključak je izveden sukladno usporedbi simulacije i eksperimenta te su predstavljene preporuke za daljnji rad.

2. MATEMATIČKI MODEL

Svaku računalnu simulaciju možemo opisati određenim matematičkim modelom koji u sebi sadrži niz pretpostavki koje nastoje aproksimirati fenomene dokazane eksperimentima. Najčešće se matematički zakoni fizikalnih fenomena prezentiraju u obliku parcijalnih diferencijalnih jednadžbi koje se zbog svoje složenosti obično rješavaju na računalu numeričkim putem.

Osnovne jednadžbe dinamike fluida koje vrijede za svaku materiju su: zakon o očuvanju mase, zakon o očuvanju količine gibanja i zakon o očuvanju energije. Zajedničku formu svih predstavljenih jednadžbi predstavlja standardna transportna jednadžba, koja je ujedno jedna od temeljnih izraza za determiniranje transportnih procesa. Standardna transportna jednadžba glasi:

$$\frac{\partial(\rho\phi)}{\partial t}+\frac{\partial(\rho v_i\phi)}{\partial x_i}-\frac{\partial}{\partial x_i}\left(\gamma_\phi\frac{\partial\phi}{\partial x_i}\right)=S_\phi(\phi), \tag{1}$$

pri čemu ϕ predstavlja masenu gustoću promatranog fizikalnog svojstva, ρ gustoću kontinuuma, t vrijeme, x_i prostorne koordinate, v_i komponente brzine gibanja u smjeru prostornih koordinata, γ_Φ koeficijent difuzije, a S_Φ pripadajući izvorski član. Članovi standardne transportne jednadžbe redom se nazivaju nestacionarni, konvekcijski, difuzijski i izvorski član. Nestacionarni član označava lokalnu promjenu fizikalnog svojstva, konvekcijski član označava prijenos uslijed strujanja fluida, a difuzijski član označava difuzijski transport uslijed gradijenta fizikalne veličine. Konačno, izvorski član označava

volumensku gustoću nastajanja ili nestajanja fizikalnog svojstva ϕ. Za matematičko determiniranje procesa važna je metoda kontrolnih volumena koja predstavlja jednu od najčešće korištenih metoda za diskretizaciju jednadžbi mehanike fluida. Diskretizacijom standardne transportne jednadžbe dolazi do pretvaranja sustava integralno-diferencijalnih jednadžbi u odgovarajući sustav algebarskih jednadžbi. U prvom koraku diskretizacije, na svaki kontrolni volumen geometrijske mreže primjenjuje se integralni oblik opće transportne jednadžbe, a nakon toga se primjenom neke od shema diferencije modeliraju konvekcijsko-difuzijski protoci fizikalne veličine kroz stranice kontrolnih volumena. Ovim postupkom sustav diferencijalnih jednadžbi matematičkih modela postaje sustav algebarskih jednadžbi, pojedini nelinearni članovi sustava se linearizirаju, a rješenje se dobiva iterativnim postupkom.

Diskretizacija jednadžbe (1) primjenom metode kontrolnih volumena formulirana je integracijom po kontrolnom volumenu V_P i vremenu, i može se zapisati:

$$\int_{t}^{t+\Delta t}\left[\int_{V_P}\frac{\partial\rho\phi}{\partial t}\,dV+\int_{V_P}\frac{\partial}{\partial x_i}\cdot\left(\rho v_i\phi\right)dV\right]dt=\int_{t}^{t+\Delta t}\left[\int_{V_P}\frac{\partial}{\partial x_i}\left(\gamma_\phi\frac{\partial}{\partial x_i}\phi\right)dV+\int_{V_P}S_\phi(\phi)\,dV\right]dt \qquad (2)$$

Fenomen višefaznog strujanja prisutan je kod simulacija spreja. Takav fenomen traži numeričko rješavanje jednadžbi očuvanja za plinsku i kapljevitu fazu istovremeno. S obzirom na kapljevitu fazu, većina kalkulacija za sprej u inženjerskoj domeni zasnivaju se na statističkoj metodi koja se naziva DDM (eng. *Discrete Droplet Method*). DDM funkcionira na način da rješava diferencijalne jednadžbe za trajektoriju, količinu gibanja i transfer mase pojedine grupe identičnih neovisnih kapljica podjednake veličine i fizikalnih svojstava koje nazivamo parcelom (eng. *parcel*). Stoga jedan član grupe predstavlja ponašanje cijele parcele. Parcele se uvode u domenu toka s početnim uvjetima pozicije, veličine, brzine, temperature i broja kapljica u parceli. Programski paket Fire podržava unos kapljica u obliku spreja kroz zone ulaza. Izmjena količine gibanja za kapljicu/plin, turbulentno raspršivanje, isparavanje kapljice, sekundarni raspad, sudaranje kapljica i interakcija između kapljice/zida su obuhvaćeni velikim brojem modela koji omogućavaju korištenje sprej modula za realne slučajeve. Masa isparenih kapljica predstavlja izvor za transportne jednadžbe plinske faze. Parcele se prate Lagrangeovim pristupom kroz računalnu mrežu koja se također koristi i za rješavanje plinske faze. Potpuna dvosmjerna sprega (eng. *coupling*) između plinske i kapljevite faze se pri tome uzima u obzir. U slučajevima zanemarivog utjecaja raspršene (disperzirane) faze na kontinuiranu, tok plinske faze može se simulirati unaprijed, a simulacija kapljica se može izvršiti poslije. Jednadžba količine gibanja nam govori da je promjena količine gibanja kapljice spreja jednaka sumi svih sila koje djeluju na kapljicu.

$$m_d\frac{du_{id}}{dt}=F_{idr}+F_{ig}+F_{ip}+F_{ib}, \qquad (3)$$

gdje je F_{idr} sila otpora (eng. *Drag*), F_{ig} je sila koja uključuje efekte gravitacije i uzgona, F_{ip} sila tlaka, F_{ib} sumira sve ostale vanjske sile kao što su tzv. virtualne sile mase, magnetske ili elektrostatičke sile i sl. Integriranjem gornje jednadžbe moguće je dobiti brzinu kapljice koja je ulazni parametar za sljedeću jednadžbu:

$$\frac{dx_{id}}{dt}=u_{id}\,, \qquad (4)$$

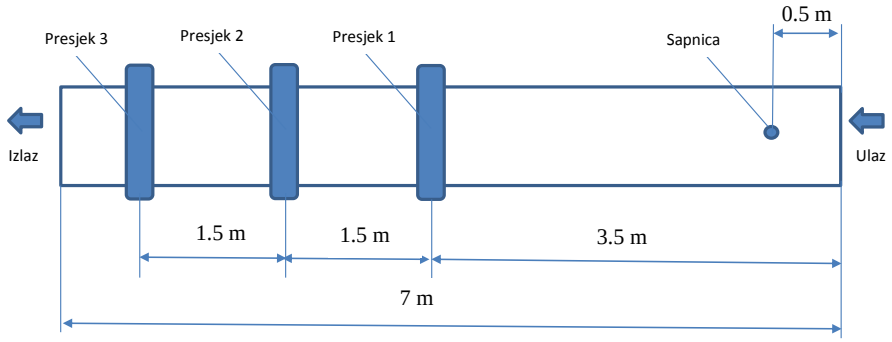
Integriranjem ove jednadžbe dobiva se trajektorija kapljice spreja u računalnoj domeni.

3. OPIS EKSPERIMENTA

Akademski članak „*Numerical prediction on the characteristic spray induced mixing and thermal decomposition of urea solution in SCR system*“ [15] iz kojega su preuzete eksperimentalne postavke, poslužio je kao temelj daljnja razmatranja u ovome radu. Geometrija promatrane cilindrične cijevi zadana je u tablici 1, odnosno prikazana je slikom 3.

Tablica 1. Parametri geometrije cijevi

Naziv	Duljina (m)
Ukupna duljina cijevi	7 m
Promjer cijevi	0,3 m
Udaljenost sapnice od početka cijevi	0,5 m
Udaljenost presjeka 1 početka cijevi	3,5 m
Udaljenost presjeka 2 početka cijevi	5 m
Udaljenost presjeka 2 početka cijevi	6,5 m
Kut ubrizgavanja spreja	70˚



Slika 3. Geometrija cijevi s karakterističnim detaljima [12]

Eksperiment započinje izgaranjem LNGa (eng. *Liquefied natural gas*) u generatoru dimnih plinova. Pri tome se stvaraju vrući dimni plinovi temperature 1200 °C koji se miješaju s hladnim zrakom da bi se dobila temperatura i protok koji odgovaraju realnim sustavima (motorima s unutarnjim izgaranjem) čiji su parametri prikazani tablicom 2. Sastav dimnih plinova je sljedeći: N_2 = 0,81436 [mol/mol], O_2 = 0,1567 [mol/mol], H_2O = 0,01234 [mol/mol], CO_2 = 0,0166 [mol/mol].

Tablica 2. Parametri izgaranja plinova iz ložišta

Temperatura ispušnih plinova [°C]	300	350	400
Volumni protok, [m^3/min]	0,616	0,567	0,524
Prosječna brzina, [m/s]	6,55 9,04	6,39 9,08 10,77	6,03 8,33 10,84
Gustoća ispušnih plinova, [kg/m^3]	27,78 38,35	27,08 38,49 45,69	25,55 35,33 45,97
NH_3 koncentracija kod 100% pretvorbe [ppm]	454,7 329,5	507,2 356,9 300,6	580,7 420,0 322,8

Tijekom provođenja eksperimenta vodena otopina uree ubrizgava se protokom od 0.018 dm^3/min. Ako se pretpostavi potpuna pretvorba otopina uree u amonijak dobiti će se protok od 6 dm^3/min amonijaka. Razdioba veličine čestice spreja, aproksimirana je Rosin-Ramlerovom distribucijom sa koeficijentima prikazanim u tablici 3,

Tablica 3. Eksperimentalni podaci ubrizgavanja otopine uree

F	X	Q	U_d [m/s]
Slučaj 1	62,3	2,5357	6,7
Slučaj 2	45,6	2,7491	9,5
Slučaj 3	44	3,2657	10,6

4. POSTAVKE NUMERIČKE SIMULACIJE I STUDIJA UTJECAJA MREŽE

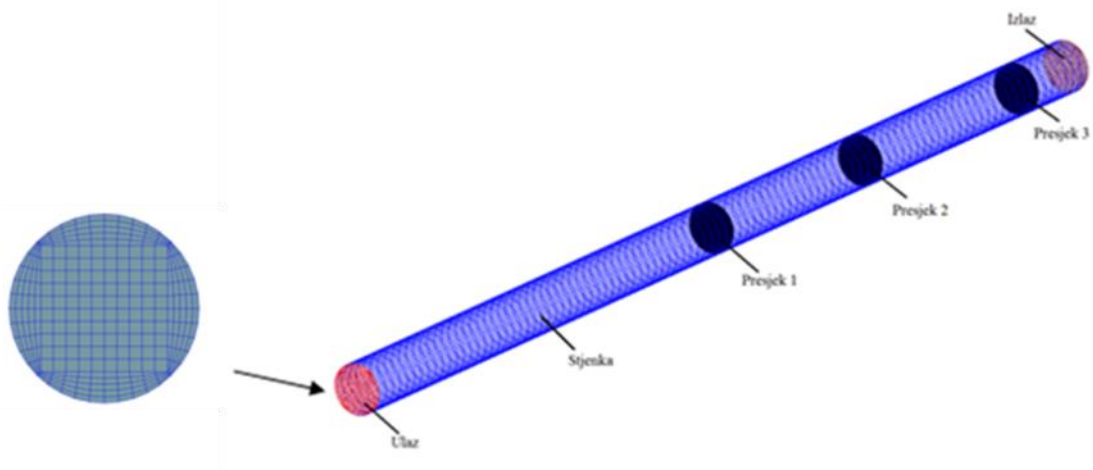
Primjenom komercijalnog programskog paketa AVL-Fire sukladno eksperimentalnim postavkama generirana je mreža kontrolnih volumena. Geometrija promatrane cijevi je preuzeta iz eksperimenta. Tako je sapnica postavljena na 0,5 metara (u z-smjeru koordinatnog sustava) od ulaznog presjeka, a kut ubrizgavanja kapljevine kroz sapnicu iznosi 70 °. Više detalja o samoj sapnici može se pronaći u [15]. Postavke vremenskog koraka postavljene su tako da se veličinom vremenskog koraka obuhvate tranzijentne pojave, što je jedan od preduvjeta za stabilnu kalkulaciju. Vrijednosti ulaznih rubnih uvjeta brzina i temperatura su odabrani sukladno eksperimentu, odnosno sličnosti temperaturama u realnim sustavima. Veličina karakteristične duljine turbulencije iznosi 10 % promjera cijevi, što je opravdana pretpostavka za razvijeno turbulentno strujanje. Sastav dimnih plinova postavljen je sukladno eksperimentalnim mjerenjima pri čemu je pretpostavljeno potpuno izgaranje. Obzirom na kratko vrijeme retencije dimnih plinova (< 1sec) opravdano je pretpostaviti adijabatski rubni uvjet. Izlazni rubni uvjet predstavljen je statičkim tlakom od 1 bar. Realni početni uvjeti rezultirat će bržom konvergencijom simulacije. Također je primijenjena implicitna diskretizacija vremenske domene prvoga reda, pri čemu je korišten SIMPLE algoritam za spregu polja brzine i tlaka, dok je za model turbulencije odabran K-ε model model turbulencije. Postavke numeričke simulacije dane su tablicom 4.

Tablica 4. Postavke numeričke simulacije

Vremenski korak [sec]	10^{-04}	
Rubni uvjeti	Temperature [°C]	300 - 450
	Brzina [m/s]	6,03 – 10,99
	Turbulentna kinetička energija [m^2/s^2]	0,001
	Karakteristična duljina turbulencije [m]	0,03

Za jednadžbe turbulencije, energetsku jednadžbu i skalarnu jednadžbu odabrana je uzvodna shema diferencije. Za jednadžbu kontinuiteta je odabrana shema centralnih razlika. Za jednadžbu količine gibanja odabrana je kombinirana shema između uzvodne i sheme centralnih razlika s faktorom miješanja 0,5. Kao kriterij konvergencije postavljeno je da reziduali moraju pasti četiri reda veličine.

Uzimajući u obzir nestabilnost rješavača komercijalnog programskog paketa AVL-Fire za cilindričan raspored kontrolnih volumena na ulaznoj površini (sklonost divergiranju), za daljnja razmatranja uzet je predefinirani tip mreže na ulaznoj površini Cilinder Hexahedron prikazan na slici 4. Zahtjevi za kvalitetu mreže postavljaju se u odnosu na točnost i potrebu za računalnim resursima. Sukladno postavljenim zahtjevima za kvalitetu mreže validirali su se sljedeći parametri: turbulentna brzina, srednja brzina, polje turbulentne kinetičke energije i polje disipacije kinetičke energije. Tri mreže sa različitim brojem ćelija odnosno kontrolnih volumena uzete su u razmatranje, gdje je konfiguracija mreže prikazana u tablici 5.

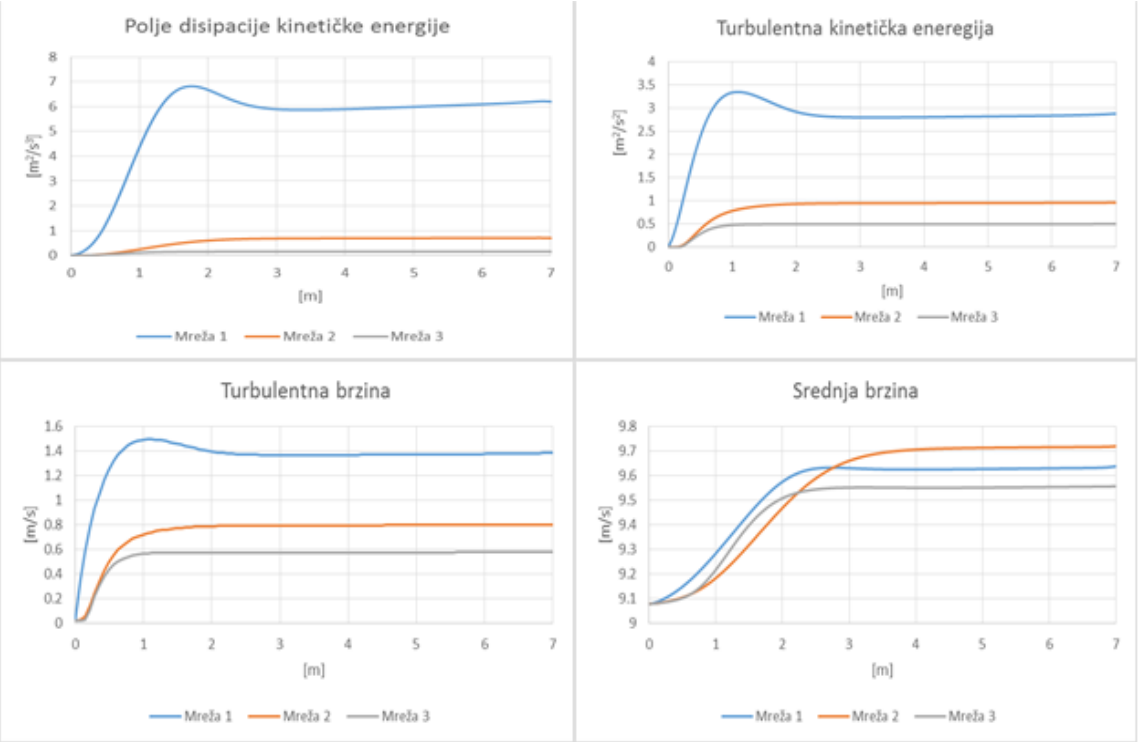


Slika 4. Prikaz Cilinder Hexahedron mreže na ulazu cijevi [14]

Tablica 5. Prikaz razmatranih mreža na ulazu u cijev

	Broj ćelija unutar kvadratnog dijela mreže	Broj ćelija unutar prstena, a izvan kvadratnog dijela mreže	Broj ćelija po duljini	Broj kontrolnih volumena
Mreža 1	10	10	100	30000
Mreža 2	14	6	100	36400
Mreža 3	14	6	200	72800

Validacijom parametara sukladno postavljenim zahtjevima za kvalitetu (na slici 5) vidljivo je da „Mreža 3“ daje najbolje vrijednosti. Po kvaliteti je slijedi „Mreža 2“, dok najmanju kvalitetu daje „Mreža 1“. Obzirom da „Mreža 3“ zahtjeva znatno više računalnih resursa nego „Mreža 2“, daljnja promatranja će se vršiti na „Mreži 2“ čije su vrijednosti (zahtjevi za kvalitetu) dovoljno bliske vrijednostima gušće „Mreže 3“.

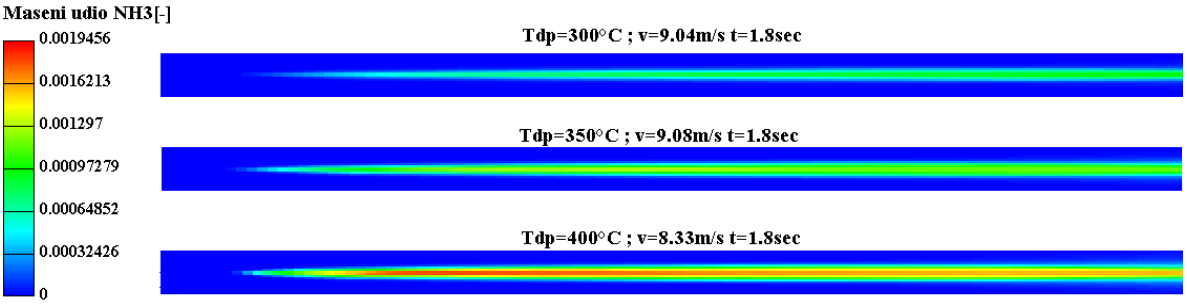


Slika 5. Prikaz rezultata validacije mreže promatrane geometrije [12]

5. REZULTATI I DISKUSIJA

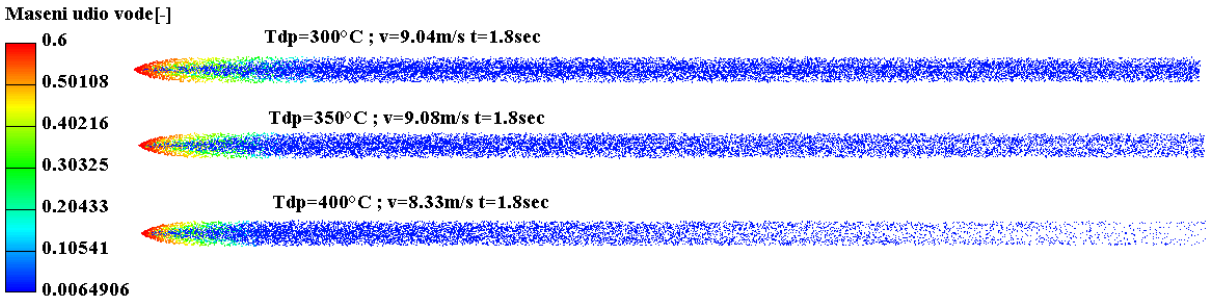
Pregled rezultata je prikazan za različite temperature i brzine ispušnih plinova sukladno eksperimentu. Pri tome će se rezultati simulacije usporediti s rezultatima provedenog eksperimenta.

Za prikaz rezultata pri različitim temperaturama uzet je jedan karakterističan vremenski trenutak od 1,8 s. U tom vremenskome trenutku profil je zauzeo cijelu duljinu cijevi, te su koncentracije masenih udjela poprimile karakteristične vrijednosti. Prvo je promatran maseni udio NH_3 pri unaprijed određenim brzinama, odnosno temperaturama. Iz slike 6. je vidljivo da je maseni udio NH_3 najveći pri najvećoj temperaturi, odnosno vidljiv je porast koncentracije s temperaturom. Ova pojava može se objasniti činjenicom da se kemijske reakcije brže odvijaju pri višim temperaturama procesa koji imaju jednaku brzinu i protok. Brže kemijske reakcije doprinose bržem isparavanju vodene otopine uree, odnosno termalnoj dekompoziciji vodene otopine uree i hidrolizi izocijanske kiseline, što ima za posljedicu (ubrzano) stvaranje amonijaka i izocijanske kiseline. Lagani pad koncentracije NH_3 koji se može zamijetiti u dugoj polovici cijevi (kod sve tri simulacije) je relativan. Ovdje se radi o prividnom padu NH_3 uslijed povećanja koncentracije CO_2. Molarna masa CO_2 (44) je veća nego molarna masa NH_3 (17,031), a obzirom da je na slici prikazan maseni udjel NH_3 simulacija će prikazati relativni pad masene koncentracije, dok će apsolutna koncentracija ostati jednaka.



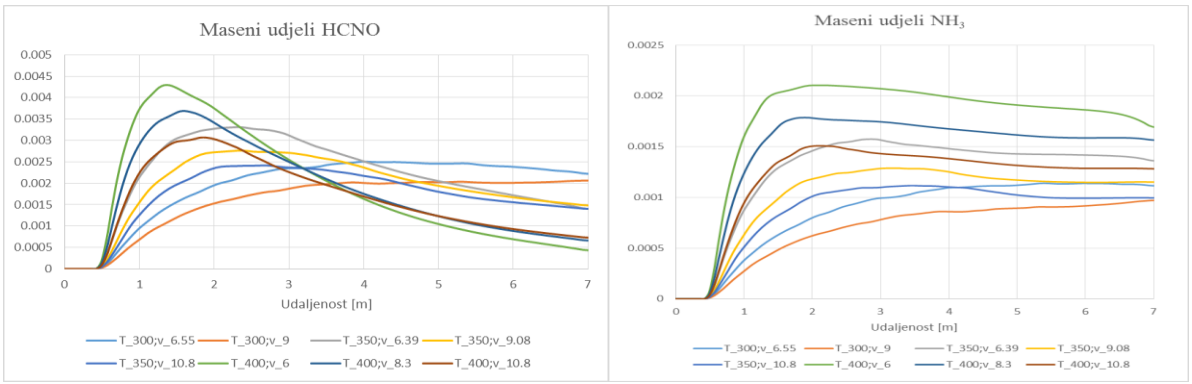
Slika 6. Prikaz masenog udjela NH_3[14]

Slika 7. prikazuje da je najveća koncentracija H_2O u kapljicama spreja blizu sapnice. Udaljavanjem od sapnice doći će do pada koncentracije isparavanjem. Pad koncentracije s udaljavanjem od sapnice izraženiji je na višim temperaturama gdje dolazi do bržeg isparavanja kapljica.



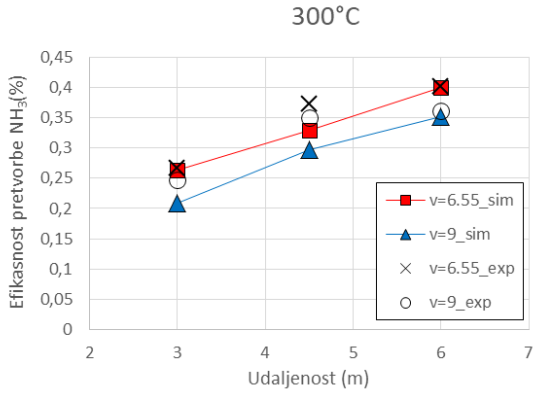
Slika 7. Prikaz masenog udjela vode u spreju[12]

Ukoliko prikažemo konverziju svih osam slučaja u jednom karakterističnom trenutku, moguće je izvesti određene zaključke o kvaliteti pojedine konverzije. Kvalitetna konverzija sa stajališta izocijanske kiseline podrazumijeva stvaranje izocijanske kiseline na početku cijevi, te trošenje kiseline na kraju cijevi. Ova tvrdnja odnosi se na proces termolize (stvaranje izocijanske kiseline) na početku cijevi, te daljnje hidrolize (trošenja izocijanske kiseline i stvaranja amonijaka). Uspješnost ovih procesa diktira ukupnu uspješnost sustava. Iz slike 8 može se zaključiti da najbolju konverziju daje temperatura od 400 °C, te da sličan trend prate i ostale simulacije (temperature). Pri konverziji NH_3 treba uzeti u obzir da se NH_3 proizvodi termolizom i hidrolizom, stoga će kvalitetnija konverzija biti ona koja daje veću vrijednost NH_3. Ukoliko se promotri konverzija NH_3, (slika 8) vidljivo je da će najkvalitetniju konverziju imati simulacija s temperaturom od 400 °C. Ovdje je također moguće zapaziti i sličnost trendova kod svih simulacija, kao što je to slučaj kod izocijanske kiseline. Na temelju provedenih simulacija može se zaključiti da kvalitetnu konverziju sa stajališta izocijanske kiseline i amonijaka daju više temperature i manje brzine, odnosno veći unos topline u sustav s duljim vremenom retencije reaktanata u cijevi.

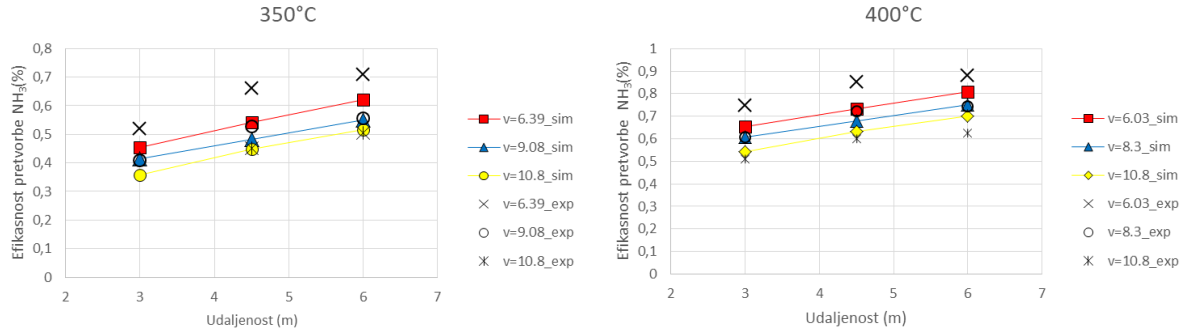


Slika 8. Prikaz masenog udjela HCNO i NH_3 za sve simulacije [12]

Slike 9 i 10 prikazuju usporedbu rezultata dobivenih eksperimentom i simulacijom, odnosno efikasnost pretvorbe NH_3. Generalno se može reći da su preklapanja simulacije i eksperimenta zadovoljavajuća. Odstupanja koja postoje su minimalna i za većinu slučajeva kreću se u granicama 1 -2 %. Najveća odstupanja prisutna su pri malim brzinama i iznose do 21 %, dok veće brzine pokazuju dobro preklapanje.



Slika 9. Usporedba rezultata simulacije i rezultata dobivenih eksperimentalnim mjerenjem pri temperaturi ispušnih plinova od 300 °C [12]



Slika 10. Usporedba rezultata simulacije i rezultata dobivenih eksperimentalnim mjerenjem pri temperaturi ispušnih plinova od 350 °C (lijevo) i 400°C (desno) [12]

6. ZAKLJUČAK

Sagledavši sve rezultate može se vidjeti blisko podudaranje vrijednosti simulacije i eksperimenta. Generalni zaključak koji se može izvesti je da primjena računalne dinamike fluida u velikoj mjeri može konkurirati eksperimentalnim mjerenjima. Osim što financijski iziskuje znatno manje sredstava vremenski je također efikasnija. Ovakvi računalni modeli danas se koriste u realnom inženjerskom svijetu, i daju konkretne rezultate. Do sada su postupci ispitivanja u pogonskim uvjetima bili dugotrajni, skupi te se riskiralo oštećenje samih strojeva i uređaja. Danas je to sve pojednostavljeno, te se na temelju simulacija mogu izvesti određeni zaključci i smanjiti vrijeme djelovanja. Usprkos jednostavnoj geometriji korištenoj u ovom radu, simulacija se nameće kao dobra alternativa eksperimentalnim mjerenjima. Korištenjem složenije geometrije realnog sustava ispušnih plinova (npr. u industriji) postoji prostor za daljnje istraživanje.

Svaki napredak na polju računalne dinamike fluida povezan je s napretkom očuvanja okoliša. Korištenje računalnih simulacija pozitivno djeluje na okoliš jer štedi resurse potrebne za provođenje eksperimenata, izradu prototipova i sl. Ukoliko je predmet promatranja računalne simulacije bio određen utjecaj na okoliš, korist je višestruka jer ne samo da se uštedila energija potrebna za eksperiment, nego se uštedilo vrijeme potrebno za provođenje eksperimenta. Također postoji mogućnost višestrukog sagledavanja raznih slučajeva i stvaranja novih korisnih i perspektivnih ideja. Zaključno se može reći kako računalna dinamika fluida ima svijetlu budućnost za razmatranje mnogih pojava, te da će se njenim unaprjeđenjem unaprijediti konačni proizvodi i smanjiti štetan utjecaj na okoliš.

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MOGUĆNOSTI ISKORIŠTAVANJA I UPOTREBE SIRUTKE

POSSIBILITIES IN WHEY UTILIZATION AND DISPOSAL

Bojan Matijević*

* Veleučilište u Karlovcu, Karlovac, Hrvatska

autor za korespondenciju: Bojan Matijević, e-mail. bojan.matijevic@vuka.hr

Pregledni rad

SAŽETAK

Sirutka je sporedni proizvod koji nastaje iz mlijeka tijekom proizvodnje sira i/ili kazeina. Ukupna svjetska proizvodnja sirutke u svijetu u 2016. godini iznosila je oko 190 milijuna tona s tendencijom rasta. Sirutka se tradicionalno smatrala nepoželjnim sporednim proizvodom, koji se najprije bacao, a tek kasnije koristio kao stočna hrana ili prerađivao u različite proizvode. Bez obzira na veliki potencijal, još uvijek se svega 70 % sirutke koristi u prehrambenoj i fermentativnoj industriji, dok se ostatak ispušta u vodene tokove bez prethodne obrade. To predstavlja ozbiljan gubitak sirovine i uzrokuje znatne ekološke probleme, s obzirom na visoke KPK (kemijska potrošnja kisika) i BPK (biološka potrošnje kisika) vrijednosti sirutke. Ovaj rad prikazuje sastav i potencijalnu primjenu sirutke kao hrane za ljude i životinje te napredniju primjenu kao što je upotreba proteina sirutke kao promotora zdravlja i proizvodnju čitavog niza korisnih tvari.

***Ključne riječi**: sirutka, sastav sirutke, proizvodi od sirutke*

ABSTRACT

Whey is a by - product from milk in cheese and / or casein production. World whey production in 2016 was about 190 million tons with a growth trend. Traditionally whey considered as undesirable product, which first thrown, and later used as forage or processed into different products. Regardless of the great potential, only 70 % of whey still used in the food and fermentation industry, while the rest released into sewerage system without processing. This represents a serious loss of raw material and causes significant environmental problems, because of high values COD (chemical oxygen demand) and BOD (biological oxygen demand) of whey. This paper present the composition and potential use of

whey as food for humans and animals and a more advanced application such as the use of whey proteins as a health promoter and the production of a whole range of useful substances.

***Keywords**: whey, whey composition, whey products*

1. UVOD

Sirutka je sporedni proizvod koji nastaje u tehnološkom procesu proizvodnje sira (oko 96 %) ili kazeina (oko 4 %). To je žuto-zelenkasta tekućina koja se izdvaja iz gruša nakon koagulacije kazeina iz mlijeka djelovanjem kiseline (kisela sirutka) ili djelovanjem enzima (slatka sirutka). Prema prosječnom kemijskom sastavu sirutka sadrži oko 93% vode, a u nju prelazi oko 50 % suhe tvari mlijeka. Najveći dio sirutke čini laktoza, dok je manje od 1% proteina sirutke [1]. Proteini sirutke nisu osjetljivi na djelovanje kiseline i enzima pa tijekom koagulacije mlijeka ostaju nepromijenjeni i u cijelosti prelaze u sirutku [2]. Sirutka se može dobiti od različitih vrsta mlijeka. Najveća količina sirutke potječe od kravljeg mlijeka, a u nekim dijelovima svijeta potječe i od ovčjeg, kozjeg, pa čak i devinog mlijeka [3].

U današnje vrijeme sirutka je glavna sekundarna sirovina suvremene industrije sira. Ukupna proizvodnja sirutke u svijetu u 2016. godini iznosila je oko 190 milijuna tona s tendencijom rasta od 1 do 2 % godišnje [4]. Vodeći proizvođači i prerađivači sirutke su Europa i Sjedinjene Američke Države te čine oko 70% ukupne svjetske proizvodnje [5]. Oni godišnje proizvedu oko 7,7 milijuna tona sirutke u prahu i proteina sirutke.

Bez obzira na veliki potencijal, od ukupne količine proizvedene sirutke 70 % se prerađuje u različite prehrambene proizvode ili koristi u fermentativnoj industriji, dok se ostalih 30% koristi kao hrana za svinje, rasprostranjuje kao gnojivo na poljoprivredno zemljište ili ispušta u vodene tokove bez prethodne obrade. Nesavjesno zbrinjavanje sirutke predstavlja ozbiljan gubitak sirovine i uzrokuje znatne ekološke probleme jer ima kemijsku potrošnju kisika (KPK) > 60.000 ppm i biokemijsku potrošnju kisika (BPK) > 35.000 ppm, od čega oko 90 % otpada na laktozu [3, 6]. Tona sirutke ispuštene u sustav za obradu otpadne vode izazove opterećenje ekvivalentno onom koje uzrokuje 470 ljudi. Ako se uzme u obzir da sirana može ispustiti dnevno od nekoliko pa do 150 m^3 onda se vidi da to odgovara količini otpada koju stvore ljudi jednog po veličini srednjeg grada [7].

Prema istom autoru za biološku oksidaciju jednog m^3 sirutke ispuštene u rijeku treba 4,500 m^3 nezagađene, aerirane vode. Također treba imati u vidu da kisela sirutka korodira metale (metalni tankovi, cjevovodi, oprema) što predstavlja dodatni problem.

Iz navedenog je jasno da je upotreba sirutke kao sirovine imperativ ne samo sa stanovišta njenog iskorištenja nego i sa stanovišta smanjenja troškova za njenu obradu kao otpadnog materijala i zaštite čovjekove okoline.

S obzirom na vrijedne sastojke koje sirutka sadrži, ali i štetne posljedice koje može imati za okoliš, znanstvenici proučavaju različite alternativne mogućnosti ekonomski isplative prerade sirutke u vrijedne sirovine ili proizvode. Sirutka se danas uglavnom prerađuje u koncentrate proteina sirutke ili izolate proteina sirutke, sirutku u prahu, stočnu hranu, laktozu i albuminski sir. Zbog velikog udjela vode prerada sirutke u različite napitke nameće se kao najprihvatljivija alternativa. Tako je do danas razvijena čitava paleta sirutkinih napitaka, bilo da su proizvedeni od slatke ili kisele sirutke, od deproteinizirane sirutke, zatim od svježe sirutke razrijeđene vodom, fermentirane sirutke, pa sve do napitaka u prahu uz dodatak raznih aroma [8]. Sirutka je i dobra podloga za rast mnogih vrsta mikroorganizama te može biti sirovina i za pripravu probiotičkih fermentiranih napitaka koji su hranjivo vrjedniji od običnih

sokova [9]. Osim toga sirutka može služiti i kao supstrat za proizvodnju mliječne kiseline i bioetanola.

2. KEMIJSKI SASTAV SIRUTKE

U suvremenoj tehnologiji prerade mlijeka postoji puno vrsta sireva, a samim time i puno izvora različitih vrsta sirutke. Zbog navedenoga, količina i kakvoća sirutke mogu biti vrlo promjenjivi [2], a sirutka se može razlikovati po kemijskim, fizikalnim i mikrobiološkim karakteristikama. Obično se dobiva od 60 do 90 % sirutke u odnosu na količinu mlijeka prerađenog u sir, a može biti: sirutka od tvrdih, polutvrdih i mekih sireva, sirutka od svježih sireva; sirutka od zrnatog svježeg sira; sirutka od kiselog kazeina ili slatkog kazeina, deproteinizirana sirutka i druge.

Uobičajeno je sirutku prema kiselosti svrstati u tri skupine [2]: slatka sirutka: pH-vrijednost od 5,8 do 6,6 i titracijska kiselost od 4,5 do 8 °SH; srednje kisela sirutka: pH-vrijednost od 5,0 do 5,8 i titracijska kiselost od 8 do 16 °SH te kisela sirutka: pH-vrijednost manja od 5,0 i titracijska kiselost veća od 16 °SH.

Kemijski sastav sirutke može znatno varirati (tablica 1), a na njega utječe čitav niz različitih čimbenika kao što su: vrsta mlijeka, vrsta proteinskog proizvoda, tehnološki proces i godišnje doba. Kemijski sastav mlijeka najznačajnije utječe na sadržaj pojedinih sastojaka sirutke. U sirutku obično prelazi oko 50 % suhe tvari mlijeka u kojoj je najzastupljenija laktoza, nakon koje slijede proteini, mineralne tvari i mliječna mast [5]. Sadržaj suhe tvari sirutke najčešće varira od 5,5 do 7,5 %, a u prosjeku se kreće oko 6,4 %. Kod prerade mlijeka u sireve pojedini sastojci prelaze u sirutku u različitim količinama. Od ugljikohidrata u sirutku prelazi najviše laktoze, preko 90 %, te nešto glukoze i galaktoze, oligosaharida te aminošećera, a zatim mineralnih tvari preko 80 % i vitamini topljivi u vodi preko 60 %. Preko 20 % dušičnih tvari mlijeka prijeđe u sirutku, a ispod 10 % masti i vitamina topljivih u mastima [10]. Velika razlika postoji između sirutke dobivene od različitih vrsta mlijeka. U odnosu na sirutku od kravljeg mlijeka, ovčja sirutka se odlikuje većim udjelom suhe tvari (8,38 %), lipida (0,65 %) i dušičnih tvari (ukupni dušik 2,933 g/L), a sadrži manje laktoze u suhoj tvari (60,23 %). U usporedbi sa sirutkom kravljeg mlijeka, sirutka kozjeg mlijeka ima manje suhe tvari (6,29 %) i lipida (0,63 %) [10].

Tablica 1. Prosječan sastav (g/L) slatke i kisele sirutke [11]

Sastojak	Slatka sirutka	Kisela sirutka
Ukupna suha tvar	63,0 - 70,0	63,0 - 70,0
Laktoza	46,0 - 52,0	44,0 - 46,0
Proteini	6,0 - 10,0	6,0 - 8,0
Kalcij	0,4 - 0,6	1,2 - 1,6
Fosfati	1,0 - 3,0	2,0 - 4,5
Laktati	2,0	6,4
Kloridi	1,1	1,1

Kazeinska kisela sirutka je slična sirutki od kiselih svježih sireva. U odnosu na slatku sirutku, ona sadržava manje proteinskog dušika, ali zato sadrži više mineralnih tvari, Ca i P [10].

3. PROIZVODI OD SIRUTKE

3.1. Sirutka u prahu

Tekuća sirutka se lako kvari i potrebno ju je što prije preraditi. Sušenje je proces koji se najčešće primjenjuje u obradi sirutke i to 70 % prerađene sirutke se prevede u sirutku u prahu. Osim toga sušenje je i dio tehnološkog procesa dobivanja koncentrata proteina sirutke (KPS) i izolata proteina sirutke (IPS) [5].

Sušenjem sirutke ne nastaju sekundarni proizvodi koje je potrebno naknadno obraditi, a sirutka u prahu se može čuvati i više od 18 mjeseci, što čini osnovnu prednost ovog procesa. Međutim, sušenje ima i neke nedostatke: visoka financijska ulaganja u opremu, visok utrošak energije tijekom procesa proizvodnje i niska tržišna vrijednost sirutke u prahu [12].

Proizvodnja sirutke u prahu uključuje obiranje masti, toplinsku obradu (pasterizacija), ugušćivanje sirutke, kristalizaciju laktoze i sušenje. Ugušćivanjem se sirutka koncentrira od 40 do 70 % suhe tvari čime se štedi energija u samom procesu sušenja. Kristalizaciju laktoze nije potrebno provesti prije sušenja, ali ako nije provedena sirutka u prahu će sadržavati laktozu u amorfnom obliku. Amorfna laktoza je higroskopna i na sebe veže vlagu iz atmosfere te postaje ljepljiva, što dovodi do aglomeracije čestica praha. Sirutka u prahu bez prethodne kristalizacije laktoze jedino je prihvatljiva kao stočna hrana. Kristalizacijom se laktoza prevodi u α- mono-hidrat koji nije higroskopan i ne uzrokuje aglomeraciju čestica praha tijekom skladištenja. Iako nije moguće postići 100 % kristalizaciju laktoze, primarni cilj je transformirati što je moguće više laktoze u α-mono-hidratirani oblik (90 – 95 %). Sušenje sirutke moguće je provesti na valjcima ili raspršivanjem. Sušenje na valjcima je jeftiniji proces, ali se rjeđe koristi zbog loše kvalitete sirutke u prahu (proizvod postaje tamne boje zbog Maillardovih reakcije između proteina i laktoze što uzrokuje slabu topljivost praha). Raspršivanje je prihvatljiva metoda sušenja jer se dobije sirutka u prahu koja sadrži 95% suhe tvari, ima dobru topljivost i željena senzorska svojstva [12].

Sirutka u prahu najviše se koristi u ishrani stoke i/ili u proizvodnji stočne hrane jer je jeftin izvor visoko kvalitetnih proteina i ugljikohidrata. Visoka prehrambena vrijednost sirutku u prahu čini vrijednom sirovinom i u prehrambenoj industriji za različite proizvode, te je svoju primjenu našla u proizvodnji konditorskih proizvoda, pekarstvu, mliječnim proizvodima, dječjoj hrani, mesnim proizvodima i proizvodnji bezalkoholnih pića, juha, umaka, preljeva i krema. Sirutka u prahu utječe na različita svojstva prehrambenih proizvoda, kao što su: (a) poboljšanje senzorskih svojstava, (b) poboljšanje fizičkih svojstava, poput sposobnosti stvaranja pjene, stabilnosti voća i regulacija kiselosti, i (c) upotrebljava se kao adsorbens i kao nosač masti i ulja. Visok udio mineralnih tvari čini sirutku u prahu nepoželjnom sirovinom zbog izraženog slanog okusa. Stoga, prije sušenja je potrebno provesti demineralizaciju sirutke (ionska izmjena, elektrodijaliza ili nanofiltracija) [5].

3.2. Sirevi od sirutke

Proizvodnja sira iz sirutke (albuminskog sira) stara je koliko i proizvodnja sira iz mlijeka. To je tradicionalan način kojim su u domaćinstvima nastojali iskoristiti sirutku, a uz modifikaciju tradicionalnog postupka i primjenu tehnologije ova vrsta sira proizvodi se u industriji. Postupak uključuje taloženje proteina albumina i globulina, koji nisu koagulirali tijekom sirenja mlijeka, a nalaze se u sirutki i koaguliraju pod utjecajem topline. “Skuta“ je naziv za sir dobiven iz sirutke od ovčjeg mlijeka, koji se uglavnom proizvodio u domaćinstvu. U različitim se zemljama sir od sirutke razlikuje po sastavu, okusu, konzistenciji, a ta svojstva ovise o načinu proizvodnje i dodacima koji se stavljaju u sirutku prilikom proizvodnje. Tako

se u Italiji tradicionalni sir od sirutke naziva "Ricotta", u Njemačkoj "Ziger", u Skandinavskim zemljama "Mysost", "Primost" i "Gjetost" [2].

Tradicionalna proizvodnja se razlikuje od područja do područja, ali se najčešće sirutka ugušćuje kuhanjem ili se obogaćuje mlijekom (obranim ili punomasnim), te se može dobiti sir mazive do čvrste konzistencije. Sirutka se kuha uz miješanje, prilikom čega nastaje pjena, koja se odvaja i baca. Stvara se gruš, koji se odvaja cijeđenjem. Cijeđenje može trajati po nekoliko sati, jer je sirutka tekuća sirovina koja prvenstveno sadrži najviše vode. Nakon cijeđenja sir se lagano preša. Od obrane sirutke dobiva se albuminski sir slatkastog okusa, nježne konzistencije i bijele do sivkaste boje. Sirevi od sirutke mogu biti odlična osnova u pripremi krema za kolače. Sir se može soliti uz dodatak vrhnja ili sušiti te tako čuvati duži period [5].

Slično tradicionalnoj je i industrijska proizvodnja sira "Ricotta". Ovčja sirutka se zagrijava do 85 °C, zakiseljava dodatkom octene ili limunske kiseline, te se nakon koagulacije prebacuje u kalupe u kojima se cijedi. Nakon cijeđenja, koje traje od 4 do 6 sati, sir se pakira. Danas se "Ricotta" proizvodi i od mješavine sirutke i mlijeka ili od samog mlijeka. Neki se sirevi poput "Mysosta" i "Gjetosta" dobivaju postupkom ugušćivanja sirutke klasičnom evaporacijom do 60 % suhe tvari. Nastaje masa smećkaste boje (zbog karamelizacije laktoze), koja se prebacuje u vakumski uparivač i još jednom ugušćuje do 80 do 85 % suhe tvari. Postupak traje sve dok se ne dobije sir željene smeđe boje i arome. Nakon toga masa se mijesi dok ne postigne teksturu sličnu maslacu. Nakon toga se stavlja u kalupe i pakira, te se može čuvati više od 6 mjeseci na temperaturi od 5 °C [2].

Znanstvenici sve veću pažnju posvećuju razvoju novih postupaka prerade sirutke u albuminski sir. Tako se od usitnjenih čestica koncentrata proteina sirutke mogu proizvoditi zamjene za mliječnu mast, koje se koriste za proizvodnju niskokalorične hrane kao što su kremasti ("light") sirevi.

3.3. Napici na bazi sirutke

Zbog velikog udjela vode (oko 94 %) prerada slatke ili kisele sirutke u različite napitke nameće se kao najprihvatljivije rješenje. Istovremeno, to je najjednostavniji postupak prerade s raznim mogućnostima pojedinih faza prerade. Prerada sirutke u napitke počela je još 70-ih godinama prošlog stoljeća, a jedan od najstarijih sirutkinih napitaka je švicarska *Rivella*. Do danas je razvijena čitava paleta sirutkinih napitaka, bilo da su proizvedeni od nativne slatke ili kisele sirutke, od deproteinizirane sirutke, zatim od svježe sirutke razrijeđene vodom, fermentirane sirutke, pa sve do napitaka u prahu uz dodatak raznih aroma. Također postoje i alkoholni napitci, poput sirutkinog piva ili vina te napitci malog sadržaja alkohola (manje od 1,5 %) [8, 13].

Pri proizvodnji napitaka od tekuće sirutke javljaju se određene poteškoće. Visok udio vode te kemijski sastav čine tekuću sirutku pogodnim supstratom za rast i razmnožavanje mikroorganizama, zbog čega je nužna toplinska obrada. S druge strane, proteini sirutke su termolabilni i počinju se denaturirati već pri temperaturi od 60 ºC [2] pa se tako pri uobičajenoj toplinskoj obradi (72 ºC/15 - 20 s) dio prisutnih proteina taloži. Kako bi se to izbjeglo nastoji se visoku toplinsku obradu zamijeniti membranskim procesima kao što je mikrofiltracija ili primjenom ultrazvuka. Ultrazvuk djeluje na proteine sirutke tako da im može povećati topljivost [14] te bi se na taj način mogla smanjiti količina taloga nastalog tijekom čuvanja napitaka. Osim toga, zakiseljavanjem sirutke na pH < 3,9 proteini sirutke postaju termostabilni te tako ne koaguliraju čak ni provedbom UHT sterilizacije [11, 15].

Mineralne tvari u sirutki daju nepoželjan slano-trpki okus koji je posebno izražen kod kisele sirutke u kojoj je zbog povišenog udjela mliječne kiseline prisutna veća količina

otopljenih mineralnih tvari što u proizvodnji sirutkinih napitaka može uzrokovati grudičavost i prekomjernu kiselost konačnog proizvoda te nastanak veće količine taloga pri toplinskoj obradi [16].

Unatoč svim tim poteškoćama, prerada izvorne tekuće sirutke pokazala se najekonomičnijim tehnološkim rješenjem. Stoga se odavno radi na razvoju napitaka uz dodatak voćnih koncentrata, kako bi se dobio proizvod prihvatljivih senzorskih svojstava, pritom ponajprije misleći na okus [17]. Dodaci koji se najviše koriste su citrusi i tropsko voće, poput manga, banane ili papaje, jer je dokazano kako upravo te arome najbolje uspijevaju prikriti nepoželjan miris sirutke po kuhanom mlijeku te kiselo-slani okus.

Kao jedna od boljih opcija za dobivanje proizvoda poželjnih senzorskih karakteristika pokazala se proizvodnja fermentiranih napitaka na bazi sirutke. Pri tom se za fermentaciju sirutke koriste uglavnom starter kulture bakterija mliječne kiseline i probiotički sojevi, dok se u slučaju alkoholnih fermentacija najčešće primjenjuju vrste kvasaca *Kluyveromyces.* Tako je omogućena proizvodnja fermentiranih napitaka od tekuće sirutke poželjnih nutritivnih i senzorskih svojstava, a bez primjene kompliciranih i skupih tehnologija poput ultrafiltracije i uparavanja koje se primjenjuju u slučaju korištenja koncentrata i izolata proteina sirutke ili pak sirutke u prahu.

Skupini bezalkoholnih napitaka od sirutke pripadaju još i dijetetski napitci, napitci s hidroliziranom laktozom, napitci slični mlijeku i napitci u prahu. Zahvaljujući svom sastavu, i s njime povezanim svojstvima, sirutka je veoma pogodna sirovina za proizvodnju dijetetskih napitaka na jednostavan način koji uključuje dodatak nekog sladila (najčešće saharina i ciklamata), dodatak voćne baze jabuke ili nekog tropskog voća te dodatak stabilizatora. Ovi napitci imaju vrlo nisku energetsku vrijednost koja se kreće oko 104 do 113 kJ/100 mL, te su stoga pogodni za široku skupinu potrošača [8, 15].

3.4. Proteini sirutke

3.4.1. Koncentrat proteina sirutke (KPS)

Koncentrat proteina sirutke (KPS) je prah dobiven sušenjem retentata ili koncentrata, koji se dobiva ultrafiltracijom sirutke. Koncentrat proteina sirutke koji sadrži do 60 % proteina sirutke u suhoj tvari dobiva se isključivo ultrafiltracijom, dok je veći udio proteina u suhoj tvari KPS-a moguće ostvariti procesom dijafiltracije. Proteini se mogu koncentrirati do 80 % udjela u suhoj tvari [16].

Ekonomski promatrano, dalje koncentriranje može se opravdati jedino u slučaju kada se ovaj proizvod ugrađuje u finalni proizvod visoke tržišne vrijednosti, kao što su dijetalni proizvodi, farmaceutski ili specijalni kozmetički proizvodi.

Prva generacija koncentrata proteina sirutke u prahu sadržavala je 30 – 40 % proteina te značajne količine laktoze, masti i denaturiranih proteina. Nazvana je „koncentratom“ (WPC, „Whey Protein Concentrate“). Tako proizvedene proteine sirutke prvotno su izdvajali raznim postupcima taloženja (najčešće pomoću karboksimetilceluloze), pri čemu je dobiven denaturirani sirutkin protein visoke nutritivne vrijednosti ali smanjenih funkcionalnih osobina, što je često bila i posljedica termičkog tretmana koji se primjenjuje pri njihovu izdvajanju. S razvojem tehnike membranske separacije, omogućena je proizvodnja nedenaturiranih koncentrata proteina sirutke koji se mogu frakcionirati na različite proteinske komponente važne za proizvodnju dječje hrane [12].

Ultrafiltracija sirutke je jedna od najperspektivnijih tehnologija koja se koristi za koncentriranje i izdvajanje nativnih proteina sirutke. Tehnološki proces dobivanja koncentrata sirutkinih proteina korištenjem ultrafiltracije, vrlo je jednostavan. Započinje centrifugalnim

separatorom pomoću kojeg se vrši separiranje masti i čestica sira. Nakon separiranja vrši se pasterizacija, hlađenje i održavanje na određenoj temperaturi, a zatim slijedi ultrafiltracija ili dijafiltracija te sušenje. Tako proizvedeni koncentrati proteina sirutke sadrže 70 – 80 % (pa čak i nešto više) proteina u suhoj tvari uz reduciranu količinu laktoze i masti.

Pretpostavlja se da je KPS (kao gotov pripravak) inferioran prema izolatima proteina sirutke (IPS), no to baš i nije tako. Iako KPS sadrži manje proteina u omjeru „gram za gram" negoli izolat, koncentrat visoke kvalitete sadrži raznovrsne interesantne sastojke koje rijetko možemo pronaći u izolatima (zbog različitih procesnih rješenja) [18].

3.4.2. Izolat proteina sirutke (IPS)

Izolat proteina sirutke (IPS) najčešće se dobiva primjenom postupka ionske izmjene pri čemu u ovakvom tipu proizvoda zaostane više od 90 % proteina u suhoj tvari. Upravo je koncentracija proteina u suhoj tvari postala osnova prema kojoj razlikujemo koncentrate od izolata, premda je, tehnički gledano, pojam «izolat» dugo vremena bio vezan isključivo uz način dobivanja ionskom izmjenom. IPS sadrži minimalne količine laktoze i gotovo ništa masti. Prednost dobrog IPS-a je upravo u tome što sadrži više proteina, a manje laktoze, masti i pepela po gramu nego KPS [12]. Neposredno prije procesiranja ionskom izmjenom potrebno je podesiti pH vrijednosti sirutke zbog postizanja željenog naboja proteinske molekule. Sirutka zatim prolazi kroz ionski izmjenjivač koji adsorbira proteinske molekule dok se deproteinizirana sirutka ispire iz reaktora, a potom se podešava pH-vrijednost kako bi se postigla desorpcija proteina koji se tada koncentriraju ultrafiltracijom te naknadno suše raspršivanjem. Ovdje je potrebno naglasiti da je tijekom procesiranja proteina sirutke potrebno posebnu pažnju pokloniti sprječavanju uklanjanja biološki aktivnih sastojaka sirutke. Zadržavanje prirodnog, nedenaturiranog stanja proteina od iznimne je važnosti za njegovu antikancerogenu i imuno-stimulativnu aktivnost. Protein mora biti procesuiran na niskoj temperaturi, s niskim udjelom djelovanja kiselina kako ga se ne bi obezvrijedilo. Zbog tih razloga u proizvodnji izolata proteina sirutke često se koristi mikrofiltracija, tzv. Flow micro filtration (FMF) – protočna mikro-filtracija. Pri mikrofiltracijskom postupku koriste se niske temperature koje osiguravaju visok udio proteina (oko 90 %) uz zadržavanje važnih subproteinskih frakcija, mali udio masti i laktoze, gotovo bez denaturiranih proteina [18]. FMF je postupak filtriranja sirutke kroz keramičke membrane (filtere) bez upotrebe kemijskih reagenasa poput klorovodične kiseline ili natrijevog hidroksida koji se često koriste za podešavanje pH vrijednosti sirutke. Nakon provedenog postupka mikrofiltracije, proteini se najčešće suše raspršivanjem. Izolati proteina sirutke upotrebljavaju se u namirnicama gdje odlučujuću ulogu imaju čvrstoća gela, viskoznost, vezanje vode i topljivost, pri čemu izolati proteina sirutke mogu značajno poboljšati okus i teksturu gotovog proizvoda. Ovakvi proteini najčešće se dodaju zamrznutim desertima, pićima, sladoledima te sportskim suplementima [2, 18].

3.5. Laktoza

Laktoza je glavni sastojak sirutke i čini oko 70 % ukupne suhe tvari, pa se sirutka smatra dobrom sirovinom za njezino dobivanje. Obično se laktoza dobiva iz deproteinizirane sirutke primjenom različitih postupaka kao što je koncentracija sirutke uparavanjem, kristalizacija laktoze iz koncentrirane sirutke i odvajanje dobivenih kristala pomoću centrifuga ili dekantera [19]. Na taj način se dobiva sirova ili rafinirana laktoza. Tehnološke

operacije i oprema koja se koristi za dobivanje laktoze vrlo su slični onima koji se koriste za proizvodnju saharoze iz šećerne trske.

Uparavanjem sirutke dobije se koncentrirana i prezasićena topla sirutka, koja se podvrgava kristalizaciji [20]. Kristalizacija laktoze je vrlo složen proces, a podrazumijeva difuziju molekula laktoze na površinu kristala. Formiranje kristala laktoze praćeno je otpuštanjem energije kristalizacije u otopinu, a odvija se spontano ili zbog prezasićenja sirutke ili zbog dodavanja centara kristalizacije u svrhu nastanka kristala, pri čemu se zadnji način češće primjenjuje. Cilj procesa kristalizacije je dobivanje velikog broja kristala slične veličine (prosječni promjer od 0,2 mm), što olakšava dobro razdvajanje. Centri kristalizacije se dodaju prije ulaza ili izravno u spremnike za kristalizaciju. Na taj način spriječena je kristalizacija laktoze tijekom uparavanja. Učinkovitost kristalizacije ovisi o nekoliko čimbenika kao što je raspoloživi prostor kristalizacije, čistoća i viskoznost sirutke, stupanj zasićenja, temperaturu procesa i intenzitet mehaničkog tretmana, kao i njihova međusobna interakcija, koja utječu i na kinetiku reakcije [5].

Nerafinirani kristali laktoze (poznata kao α-laktoza monohidrat) odvajaju se bilo kontinuiranim centrifugama ili dekanterima. U oba slučaja koriste se dva paralelna uređaja. Kada se primjenjuju centrifuge izdvajanje kristala je kontinuirano, ali u slučaju primjene dekantera kristali se isperu svježom čistom vodom, te se odvajanje i ispiranje provode u isto vrijeme. Voda za ispiranje sadrži određenu količinu otopljene laktoze, ali u usporedbi s ugušćenom sirutkom iz koje se dobivaju kristali laktoze, ima veći stupanj čistoće. Stoga se voda za ispiranje vraća natrag u proces kristalizacije. Koncentrat laktoze može se ponovno obraditi (ukupna suha tvar 38 - 48 g/100 g od čega je 30 g/100 g laktoza), ali se prvo mora razrijediti dodavanjem sirutke ili vode dok se sadržaj suhe tvari ne smanji do 15 g/100 g. Nerafinirana laktoza proizvedena na ovaj način sadrži 10 - 14 g/100 g vode i oko 99 % laktoze u ukupnoj suhoj tvari.

Ukoliko se laktoza ne pročišćava, podvrgava se sušenju u vibracionoj sušari na 70 °C sve dok ne dostigne sadržaj vode od oko 0,1 do 0,5 g/100 g, a tako dobiveni prah naziva se „sirova“ laktoza. Sušenje ne bi trebalo biti prekratko, inače se na površini kristala α-hidrata formira tanki sloj amorfne laktoze. Ova pojava može uzrokovati aglomeraciju kristala laktoze tijekom skladištenja proizvoda. Ostale tehnološke operacije, kao što su mljevenje, prosijavanje i/ili pakiranje, vrlo su slični onima za proizvodnju obranog mlijeka u prahu. Rafinirana laktoza koja je namijenjena farmaceutskoj industriji (sadržaj laktoze 99,6 g/100 g i bez proteina), dobiva se na sličan način kao i nerafinirana laktoza. Faze proizvodnje su jednake do odvajanja i ispiranja kristala laktoze. Ove operacije slijedi rafiniranje, što podrazumijeva da se laktoza otopi, obrada je na višim temperaturama, uključujući dodavanje različitih kemikalija, filtriranje, uparavanje, kristalizacija i izdvajanje kristala. Nakon toga, faze procesa su jednake kao u slučaju nerafinirane laktoze. Tijekom procesa prerade dodaje se 1 % aktivnog ugljena kako bi se izbjegla pojava nepoželjne boje i uklonile druge nečistoće. Osim toga dodaje se i kiselina (npr. HCl) radi korekcije kiselosti, otapanja mineralnih tvari ili denaturacije proteina (ako proteini nisu prethodno uklonjeni), te kako bi se povećala učinkovitost aktivnog ugljena. Za pročišćavanje se dodaju sredstva za bolju učinkovitost filtracije (npr. 0,1 % Kieselguhr) ili sredstva za izbjeljivanje (oko 0,22 % Na-bisulfita). Budući da se sadržaj spremnika za preradu zagrijava, potrebna je neutralizacija dodavanjem alkalnog agensa do postizanja pH od 5,4 do 5,8. Nakon toga sadržaj se podvrgava intenzivnom vrenju kroz nekoliko minuta pri čemu prisutni proteini flokuliraju, dok se ugljik i netopljive soli ne istalože. Nastali sedimenti se odvajaju filtracijom, a proizvod je dobivena bistra otopina laktoze. Otopina laktoze zatim se podvrgava sušenju do postizanja koncentracije od 65 - 70 g/100 g ukupne suhe tvari [5].

Prehrambena i rafinirana laktoze svoju primjenu nalaze u farmaceutskoj i prehrambenoj industriji. Primjene u prehrambenoj industriji uključuju proizvodnju dojenačkih

formula (budući da majčino mlijeko sadrži više laktoze nego kravlje) ili dječje hrane, kao i za proizvodnju modificiranih i rekonstituiranih mliječnih proizvoda. Osim toga, laktoza poboljšava konzistenciju i trajnost konditorskih proizvoda; poboljšava okus, izgled i pecivost tijesta. Nadalje, laktoza se također može upotrijebiti kao nosač hlapljivih spojeva arome, za adsorpciju neželjenih aroma ili kao sredstvo za zaslađivanje hrane kako bi se poboljšala aroma proizvoda. Laktoza se također uobičajeno koristi za proizvodnju pudinga, umaka, salata, itd. Glavne prednosti primjene laktoze u prehrambenoj industriji su relativno mala slatkoća, sposobnost poboljšanja karakterističnog okusa proizvoda i stabilizaciju proteina, kao i sposobnost izazivanja promjena boja gdje je to prikladno (npr. pekarskih i konditorskih proizvoda) zbog Maillardovih reakcija.

3.6. Dobivanje mliječne kiseline

Mliječna kiselina i njezini derivati imaju široku primjenu u prehrambenoj, kozmetičkoj, farmaceutskoj, kožnoj, tekstilnoj i kemijskoj industriji. U novije vrijeme mliječna kiselina se koristi i kao sirovina u proizvodnji biorazgradive plastike. Osim toga ona se koristi i kao zamjena za limunsku ili vinsku kiselinu, u proizvodnji bezalkoholnih pića, bombona, lijekova i sl. Godišnje se proizvede oko 80.000 tona mliječne kiseline i to fermentacijom uz bakterije mliječne kiseline i/ili sintetski hidrolizom laktonitrila. S obzirom na sadržaj laktoze u suhoj tvari, uz vitamine, mineralne tvari i proteine, te relativno nisku tržišnu cijenu, razvijeni su brojni biotehnološki procesi u kojima sirutka (ultrafiltrat sirutke) ima industrijsku važnost kao supstrat od kojeg se dobiva mliječna kiselina [21].

Fermentacija sirutke provodi se s različitim vrstama bakterija mliječne kiseline (BMK) koje se međusobno razlikuju po načinu razgradnje laktoze što rezultira proizvodnjom različite količine i izomera mliječne kiseline (tablica 2). Visoka stopa pretvorbe laktoze u mliječnu kiselinu ostvaruje *Lb. helveticus* jer može proizvesti gotovo dva puta veću količinu mliječne kiseline u usporedbi s drugim sojevima BMK. Proces fermentacije može se pospješiti obogaćivanjem sirutke ekstraktom kvasca ili hidrolizatom proteina kvasca (peptoni) [21]. Osim upotrebe BMK, mliječnu kiselinu proizvodi i kvasac *Kluyveromyces marxianus* var. *marxianus*. Znanstvena istraživanja ukazuju na učinkovitiju proizvodnju mliječne kiseline kada se koriste kombinirane kulture BMK u usporedbi s mono-kulturama zbog sinergističkih učinaka koji postoje među tim organizmima [21]. Najbolje iskorištenje sirutke za proizvodnju mliječne kiseline (19,8 g/L) postignuto je korištenjem kombinirane mikrobne kulture *Kluyveromyces marxianus* var. marxianus u kombinaciji s homofermentativnim LAB sojevima (*Lb. delbrueckii* subsp. *bulgaricus* i *Lb helveticus*). Primjena imobiliziranih sustava mikrobnih stanica značajno povećava proizvodnju mliječne kiseline u industrijskoj proizvodnji. Tehnologija imobilizacije omogućuje reutilizaciju korištenih stanica, kontinuirani rad i veće gustoće stanica u bioreaktoru, kao i bolje pročišćavanje krajnjeg proizvoda [21, 22].

Tablica 2. Bakterije mliječne kiseline koje se koriste za fermentaciju sirutke [2]

Rod	Vrsta fermentacije	Glavni produkt	Izomer laktata
Streptococcus / Lactococcus(2)+/-	homo	laktat	L
Pediococcus	homo	laktat	L, DL
Lactobacillus			
a) samo homo	homo	laktat	L, D ili DL
b) fakultativno hetero	homo	laktat	L, D ili DL
	hetero(1)	laktat : acetat	L, D ili DL
c) samo hetero	hetero	laktat : acetat : CO_2	L, D ili DL
Leuconostoc(2)	hetero	laktat : acetat : CO_2	D
Bifidobacterium(2)	hetero	laktat : acetat	L

(1) kod fermentacije pentoza
a) *Lactobacillus delbrueckii* ssp. *lactis* (2)
Lactobacillus delbrueckii ssp. *bulgaricus*
Lactobacillus acidophilus (2)
Lactobacillus helveticus (2)

(2) bakterije koje metaboliziraju i galaktozu (Gal+)
b) *Lactobacillus casei* ssp. *casei*
Lactobacillus plantarum
c) *Lactobacillus brevis*
Lactobacillus fermentum (2)
Lactobacillus kefir

3.7. Proizvodnja bioetanola

Laktoza kao glavni sastojak sirutke može služiti kvascima za proizvodnju laktoze. Naime, za proizvodnju KPS-a iz sirutke koristi se mambranska tehnologija, a nusproizvod je permeat koji sadrži laktozu i odličan je supstrat za proizvodnju bioetanola. Permeat je jeftin i dostupan u velikim količinama i može biti dobra zamjena za sirovine kao što je šećerna trska ili šećerna repa, različite poljoprivredne kulture ili celulozni resursi (drveni hidrolizati, poljoprivredni nusproizvodi) iz kojih se do sada dobivao bioetanol [5, 23].

Fermentacija sirutke može se provesti s različitim vrstama kvasaca, a obično se koriste isti oni kvasci koji se koriste za fermentaciju hrane, *Saccharomyces cerevisiae*, *Candida pseudotropicalis* i *Kluyveromyces fragilis*. Kvasci *C. pseudotropicalis* i *Kluyveromyces* mogu izravno metabolizirati laktozu, dok *Saccharomyces cerevisiae* ne može metabolizirati laktozu te je potrebno prije fermentacije provesti njezinu hidrolizu. Međutim, taj proces je otežan visokim koncentracijama ekstracelularne glukoze, što uzrokuje katabolitnu represiju korištenja galaktoze [15, 23].

Vrste kvasaca iz roda *Kluyveromyces* pokazuju dobru učinkovitost u proizvodnji bioetanola. Permeat sirutke koji je sadržavao različite koncentracije laktoze, fermentiran je sa kvascem Kluyveromyces fragilis. Za proizvodnju bioetanola najprikladniji je bio permeat koji je sadržavao 200 g/L laktoze i inokuliran je s 1 g/kg inokuluma, a fermentacija je provedena pri 35 °C/44 h. U takvim uvjetima dobiveno je najbolje iskorištenje procesa i količina bioetanola od 80,95 g/kg [24]. Upravo za komercijalnu proizvodnju bioetanola iz sirutke, koja sve više raste, koriste se kvasci iz roda *Kluyveromyces* i to u Irskoj, Danskoj, Novom Zelandu i Sjedinjenim Američkim Državama [5].

4. ZAKLJUČAK

Značaj sirutke kao sirovine sve više raste, od nusproizvoda postala je vrijedna sirovina. Tome su pridonijeli strogi zakonski propisi koji reguliraju njezino odlaganje u okoliš, ali i razvoj tehnologije koja omogućava dobivanje različitih sastojaka za prehrambenu industriju i biotehnološke procese. Tako od sirutke danas možemo dobiti sirutku u prahu, koncentrat i izolat proteina, laktozu, različite napitke s dodanom vrijednošću, a unaprijeđena je i tradicionalna proizvodnja albuminskog sira. Bez obzira na veliki potencijal još uvijek postoji velika količina sirutke koju treba obraditi, a to se može postići njenim korištenjem kao sirovine u proizvodnji bioetanola, posebno ako se ova tehnologija unaprijedi i smanje troškovi proizvodnje.

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„ZERO WASTE“ – KONCEPT UPRAVLJANJA OTPADOM

„ZERO WASTE“- CONCEPT IN WASTE MANAGEMENT

Nedžad Mekić*, Amra Serdarević**

* Ministarstvo privrede Kantona Sarajevo, Sarajevo, BiH
** Univerzitet u Sarajevu, Građevinski fakultet, Sarajevo, BiH

autor za korespondenciju: Nedžad Mekić, e-mail: nedzadmekic@gmail.com

Pregledni rad

SAŽETAK

„Zero Waste“ je filozofija upravljanja otpadom koja podstiče redizajn resursa u toku životnog vijeka tako da se svi proizvodi, u različitim fazama, mogu ponovo iskoristiti. Cilj ovakvog pristupa je da se otpad ne treba odlagati na deponije ili spaljivati, odnosno da su svi odbačeni materijali dizajnirani tako da postanu resursi za druge namjene. Ovakav koncept podrazumijeva cjeloviti sistemski pristup koji ima za cilj masovnu promjenu načina protoka materijala kroz društvo. Sprječavanje zagađenja je ugrađeno u propise o recikliranju, planove upravljanja čvrstim otpadom, programe konzervacije resursa te zakonsku regulativu vezanu za industriju u pogledu dizajna proizvoda i ambalaže, proizvodnih procesa i odabira materijala. Razmatrajući koncepte upravljanja otpadom, sa mogućnošću smanjenja količina i potpunog iskorištenja otpada, regija Istočna Bosna, sa Goraždem kao regionalnim centrom, opredijelila se dugoročno za koncept „*Zero Waste*“. U međuvremenu realiziraju se projekti na uspostavljanju Regionalnog centra za upravljanje otpadom Goražde što je i prikazano u ovom radu.

Ključne riječi: *otpad, „Zero Waste“, prevencija, reciklaža, kružna ekonomija*

ABSTRACT

"Zero Waste" is a waste management philosophy that encourages redesign of resources over a lifetime so that all products can be reused at different stages. The aim of this approach is to avoid disposal of waste on landfills or burning, meaning that all discarded materials have been designed to become resources for other purposes. This concept implies a complete systemic approach that aims to massively change the way materials flow through society. Pollution prevention is embedded in recycling regulations, solid waste management plans, resource conservation programs, and industry-related legislation related to the design of

products and packaging, production processes and material selection. Considering the concepts of waste management, with the possibility of reducing waste and full waste utilization, East Bosnia region, with Goražde as a regional center, opted for the concept of *"Zero Waste"* as long term strategy. In meantime the projects on the establishing Regional Center for Waste Management Goražde are being realized, which are presented in this paper.

Keywords: *waste, "Zero Waste", prevention, recycling, circular economy*

1. UVOD

Otpad je produkt čovjekovih i prirodnih aktivnosti, koji zbog svojih svojstava i količina ima uticaj na zdravstveni, ekonomski, socijalni i okolišni aspekt društva. Današnji stupanj razvoja društvene zajednice, s tendencijom povećanja broja stanovnika, raznovrsnosti proizvodnih procesa i potrebe savremene civilizacije, utiče na povećanje produkcije otpada. Međutim, čovjek svojim djelovanjem, pojedinačno ili u zajednici, ponaša se tako da stvara procese kojima uništava kružni sistem i uspostavljenu prirodnu ravnotežu, direktno ugrožavajući sistem koji ga održava. Strateško planiranje upravljanja otpadom ovisi o stupnju razvoja države i mogućnostima da se doneseni zakonski akti uspješno provedu u realnim uvjetima. U Bosni i Hercegovini strateškim planovima se uvode obaveze smanjenja nastajanja otpada, recikliranje otpada kao i drugi postupci i metode koje su usklađene sa hijerarhijom upravljanja otpadom. Unatoč donesenim planovima, sama implementacija ide dosta sporo, pa se još uvijek najveći dio količina otpada odlaže na uređene, ali i na neuređene deponije. Urađeni su brojni planovi zatvaranja lokalnih deponija, prelazeći na koncept regionalnih centara za upravljanje otpadom, ali generalno bi se moglo reći da je implementacija planova i dalji koraci još uvijek vrlo spori i sa dosta promjena i problema u provedbi.

Međutim, postoje i svijetli primjeri, općine pa i regije koje prepoznaju upravljanje otpadom kao mogućnost za razvojne planove i dobit za društvenu zajednicu kroz ekonomski, socijalni i ekološki aspekt.

Tako su se neke općine odlučile za potpunu promjenu u pristupu „otpadu“ ili sirovinama koje koristimo da bi u konačnici odbacili „otpad“ koji nas zatrpava i guši. Umjesto toga, može li se razmišljati o smanjenju produkcije otpada svaki dan? Može li se smanjiti odbacivanje i uvesti višekratno korištenje ambalaže, proizvoda i sl.? Može li se razmišljati o proizvodnji proizvoda razmatrajući opcije zamjene prirodnih resursa recikliranim? Na ova i na mnoga druga pitanja se može pozitivno odgovoriti i takav koncept se već primjenjuje u svijetu kao *„Zero Waste“*.

„Zero Waste“ je filozofija upravljanja otpadom koja podstiče redizajn resursa u toku životnog vijeka tako da se svi proizvodi, u različitim fazama, mogu ponovo iskoristiti. Cilj ovakvog pristupa je da se otpad ne treba odlagati na deponije ili spaljivati, odnosno da su svi odbačeni materijali dizajnirani tako da postanu resursi za druge namjene. Ovakav koncept podrazumijeva cjeloviti sistemski pristup koji ima za cilj masovnu promjenu načina protoka materijala kroz društvo. Sprječavanje zagađenja je ugrađeno u propise o recikliranju, planove upravljanja čvrstim otpadom, programe konzervacije resursa te zakonsku regulativu vezanu za industriju u pogledu dizajna proizvoda i ambalaže, proizvodnih procesa i odabira materijala.
Implementacija ovog konecpta nije jednostavna niti laka i zahtijeva dobro koordiniran i uvezan zajednički plan nadležnih institucija, privrede, fizičkih lica, edukativnih akcija ali i akcija nadležnih inspekcija i drugih subjekata zaduženih za provedbu planova za minimizaciju stvaranja otpada i njegovo adekvatno iskorištenje.

Koncept *„Zero Waste“,* kako je već rečeno, nije jednostavan za uvesti i vrlo često se planovi prilagođavanja provode postepeno, po utvrđenim koracima. Analizom stanja privrede i planova razvoja lokalne zajednice predlažu se i iznalaze najbolja tehničko-tehnološka rješenja za zamjenu prirodnih resursa, redizajn proizvoda, usavršavanja tehnoloških linija, pakiranja i transporta. Uporedo se razmatraju strateške odrednice u pogledu recikliranja i konačnog zbrinjavanja otpada te se razmatraju opcije kojima se isti koristi kao resurs.

Na području općine Goražde usvojen je Plan upravljanja otpadom 2013.- 2018. godina. U Bosansko – Podrinjskom kantonu (BPK) planirana je, po Strategiji, međuentitetska regionalna deponija. Međutim, još uvijek su u fazi pripremni radovi, iako je davno završena tehnička dokumentacija za otvaranje regionalnog centra za upravljanje otpadom. Pitanje upravljanja otpadom u BPK se paralelno rješava i na druge načine, pa se na području općine Goražde zatvaraju postojeće i divlje deponije i pokušavaju se uvesti aktivnosti u skladu sa osnovnim načelima upravljanja otpadom, a to je minimizacija, selekcija i recikliranje otpada. Uporedo sa navedenim aktivnostima, u ovoj općini postoje planovi sa tendencijom da se postepeno uvodi koncept *„Zero Waste“* zajedno sa privrednim razvojem općine, kroz planove i dugoročna opredjeljenja.

2. PREGED STANJA U UPRAVLJANJU OTPADOM U BOSNI I HERCEGOVINI

Bosna i Hercegovina ima izgrađen zakonodavni i institucionalni okvir, usklađen sa regulativom EU, koji je dobra osnova za realizaciju i unaprjeđenje sistema upravljanja otpadom. Međutim, i pored tako postavljenog zakonskog okvira, evidentno je da stanje u domenu upravljanja otpadom nije na zavidnom nivou te je njegovo unaprjeđenje u narednom periodu neophodno.

Generalno, Strategijom upravljanja otpadom u BiH odlučeno je da se uspostave regionalni centri za upravljanje otpadom, sa regionalnim sanitarnim deponijama i pratećim objektima za recikliranje i iskorištenje otpada (kompostane, proizvodnja RDF/SRF-a, i dr.).

Na kantonalnim, odnosno općinskim nivoima je ostavljena obaveza da se donose planovi upravljanja otpadom koji uključuju sve aktivnosti i mjere u skladu sa hirerahijom upravljanja otpadom. Uspostavljanje regionalnih centara ne realizira se predviđenom dinamikom, uglavnom zbog administrativnih razloga, iznalaženja lokacija i rješavanja organizacionih i ekonomskih obaveza između općina. Iz tog razloga još uvijek su prisutne lokalne, općinske deponije koje baš i ne zadovoljavaju sve okolišne uvjete odlaganja otpada. Prikupljanje otpada i dopremanje do deponija je uglavnom organizirano, sa različitim stepenom obuhvata stanovništva, ali se generalno može ocijeniti kao dobro. Međutim, projekti smanjenja produkcije otpada, dalji postupak ponovne upotrebe, reciklaže i energetskog iskorištenja otpada su na vrlo niskom nivou [1]. Tako se npr. u „Planu upravljanja otpadom Kantona Sarajevo za period 2015.- 2020. godina“, navodi da iako je pravni okvir za upravljanje otpadom u značajnoj mjeri razvijen na području Federacije BiH i Kantona Sarajevo, glavni nedostatak je činjenica da se mjere predviđene strateškim dokumentima ne provode [2]. Zbog niskog stepena iskorištenosti ekonomski iskoristivih komponenti iz otpada, upravitelji otpadom i lokalne zajednice gube ogromna finansijska sredstva koja bi mogla poslužiti za unaprijeđenje tehnoloških procesa obrade i iskorištenja otpada.

Količine i vrste otpada koje se proizvedu u BiH zavise od specifičnosti regije, stepena urbanizacije, razvijenosti privrede i različite su po regijama, a produkcija otpada se kreće u opsegu od 0,8 - 1,5 kg/st/dan u Kantonu Sarajevo [2], do 0,55 kg/st/dan [3], u gradu Goraždu. Primjer procjene količina reciklabilnih materijala u komunalnom otpadu u Kantonu Sarajevo i procenat iskorištenja je prikazan u tabeli 1.

Tabela 1. Količine pojedinih vrsta otpada u Kantonu Sarajevo

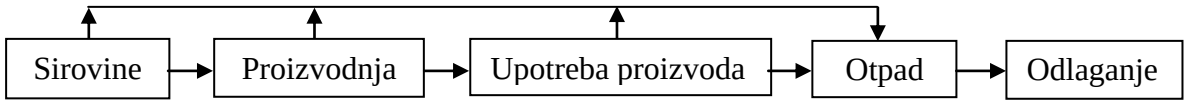
Vrsta otpada	Procijenjena količina (t/god)	Procenat u komunalnom otpadu	Iskorištenost otpada t/god
Staklo	5042	2,5 %	240 (4,8 %)
Plastika	28.236	14 %	500 (1,8 %)
Papir i karton	201.684	17 %	10.000 (29 %)

Može se zaključiti da je trenutni način upravljanja otpadom u BiH, baziran na odlaganju na sanitarne deponije, s malim procentom iskorištenja sirovina iz otpada, ali s tendencijom da se ubrza realizacija donesenih strateških planova i planova upravljanja otpadom.

3. „ZERO WASTE“- KONCEPT UPRAVLJANJA OTPADOM

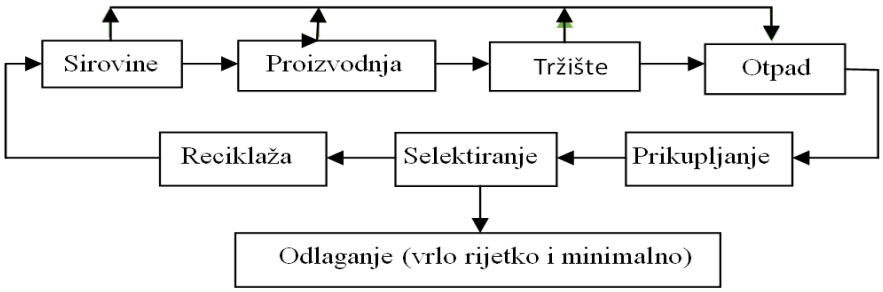
Koncept *"Zero Waste"* je koncept upravljanja otpadom koji podstiče redizajn resursa u toku životnog vijeka tako da se svi proizvodi, u različitim fazama, mogu ponovo iskoristiti. Cilj ovakvog pristupa je da se otpad ne treba odlagati na deponije ili spaljivati, odnosno da su svi odbačeni materijali dizajnirani tako da postanu resursi za druge namjene. Ovakav koncept podrazumijeva cjeloviti sistemski pristup koji ima za cilj masovnu promjenu načina protoka materijala kroz društvo. Ovaj koncept karakteriše maksimalnu angažovanost svih subjekata društva. Realizacija koncepta *"Zero Waste"* podrazumijeva čist i zdrav okoliš u kojem se stvara ambijent za zdravo življenje, produktivno, razvijeno, uređeno i konkurentno društvo, organsku poljoprivredu, upotrebu bioplina za toplotnu i električnu energiju, reciklirane sirovine za industriju, zaštitu i očuvanje prirodnih resursa od prekomjerne eksploatacije. Neophodno je paralelno sa uvođenjem koncepta *"Zero Waste"* započeti aktivnosti prelaska sa „*linearnog*“ na „*kružni*“ model ekonomije.

Koncept linearne ekonomije bazira se na načelu: *„uzmi, izradi, koristi, baci“*, a ovaj model ekonomije utemeljen je na pretpostavci neograničenosti i lakoj dostupnosti resursa i predstavlja model rasta s velikim količinama neiskorištenog otpada. Takav koncept u vremenu savremenih tehnologija i visokih standarda zaštite životne sredine je neodrživ pa je neophodno preći na koncept „*kružne“* ekonomije u kojem se iskorištava otpad i štiti okoliš. Na slici 1 prikazan je koncept linearne ekonomije.



Slika 1. Koncept linearne ekonomije u domenu upravljanja otpadom

Koncept kružne ekonomije zasniva se na kružnom kretanju u kojem se nastali otpad prikuplja, ponovo koristi, reciklira i energetski iskorištava u cilju maksimalne iskorištenosti i smanjenja negativnih uticaja na okoliš i zdravlje ljudi, a odlaže se samo onaj dio otpada koji se ne može iskoristiti. Koncept kružne ekonomije je prikazan shematski na slici 2.



Slika 2. Koncept kružne ekonomije

3.1. Počeci razvoja koncepta „*Zero Waste*“ u BiH

Koncept kružne ekonomije i *„Zero Waste“* predstavljaju novinu i još uvijek dosta nerealne i vrlo zahtjevne projekte za njihovu implementaciju u BiH. Međutim, razvojem planova upravljanja otpadom po kantonima, odnosno općinama, pojavili su se dugoročno postavljeni ciljevi za ekološke sredine i primjenu dugoročnih razvojnih planova ka uspostavljanju *„Zero Waste“* koncepta. Regija Istočna Bosna sa gradom Goraždem kao regionalnim centrom, još je od 2005. godine krenula u opsežne planove u oblasti upravljanja otpadom.

Postoje problemi kojima se moralo pristupiti urgentno (interventni planovi na sanacijama divljih deponija, unaprjeđenje sistema prikupljanja i dr.), zatim realizacija srednjoročnih planova koji su u skladu sa Strategijom upravljanja čvrstim otpadom u BiH [4], te razvoj dugoročnih planova na iskorištenju otpada, očuvanju resursa i okoliša. Analizirajuću pozitivna iskustva koje je koncept *„Zero Waste“* donio lokalnim zajednicama i gradovima u svijetu koji su se opredijelili za ovakav način zaštite okoliša i resursa, postavljeni su dugoročno vrlo visoki zahtjevi u pogledu upravljanja otpadom. Međutim, kako bi se uopće moglo razmišljati o uvođenju koncepta *"Zero Waste"* u općini Goražde, pa čak i u dalekoj budućnosti, neophodno je realizirati niz aktivnosti koje su međusobno zavisne i povezane, a odnose se na edukaciju stanovništva i privrednih subjekata u pogledu redizajniranja proizvoda i unaprjeđenja tehnoloških linija, na smanjenje produkcije otpada, na uspostavu učinkovite kaznene politike kroz zakonsku regulativu, uvođenje destimulativnih cijena za odlaganje otpada na deponije, te prenošenje vizije s definiranjem benifita koje daje ovaj koncept uz promoviranje lokalne zajednice kao ekološke sredine.

Za tako opsežne planove treba vrijeme za implementaciju, obezbjeđenje sredstava i dostignut zavidan nivo u upravljanju otpadom. Za sada, realni uvjeti u općini Goražde, odnosno cijeloj regiji Bosansko-podrinjskog kantona Goražde (BPK Goražde) za koncept „*Zero Waste“* su još uvijek daleko, međutim urađeno je dosta toga na unaprjeđenju kontroliranog prikupljanja, minimizaciji produkcije, edukaciji stanovništva, te je urađena tehnička dokumantacija za zatvaranje divljih deponija i otvaranje Regionalnog centra za upravljanje otpadom BPK Goražde.

3.2. Uspostavljanje RCUO Goražde

Nadležne institucije BPK i komunalna preduzeća čine ogromne napore na promidžbi aktivnosti u upravljanju otpadom povezujući sektor privrede i razvojne planove Kanotna kao i na edukaciji i razvoju lokalne zajednice. Pokušava se dugoročno razmišljati o minimizaciji produkcije otpada što je i postavljeno kao strateško opredjeljenje i dugoročni plan.

Općina Goražde je još u 2015. godini, putem Općinskog vijeća, donijela odluku da se realizira „*Projekat izgradnje regionalne sanitarne deponije "Trešnjica" sa Regionalnim centrom za upravljanje otpadom-RCUO"*, sa maksimalnim iskorištenjem otpada u krugu RCUO. Donošenju ove odluke prethodilo je usvajanje „Plana upravljanja otpadom Bosansko-podrinjskog kantona Goražde za period 2013. - 2018. godina", kojim se planira smanjenje produkcije otpada i umanjenje rizika otpada na okoliš. Plan je usvojen u 2014. godini i to je provedbeni planski dokument kojim se u navedenom periodu definiraju uslovi za upravljanje otpadom na području cijelog kantona. Prema planu prosječna produkcija komunalnog otpada iznosi 0,55 kg/st/dan, a teži se smanjiti produkcija otpada na nivou razvijenih zemalja EU-e, te postepeno uvođenje i poticanje razvoja koncepta *„Zero Waste"*. Pokrivenost prikupljanja otpada na području općine Goražde iznosi 74 %, a cilj je dostići 100 % pokrivenosti.

U cilju strateškog definiranja upravljanja otpadom naknadno su izrađena i usvojena dva strateška dokumenta i to: „Strategija razvoja BPK Goražde za period 2016. - 2020. godine" [5] i „Kantonalni akcioni plan za zaštitu okoliša Bosansko-podrinjskog kantona za period 2016. - 2022.godina" [6]. Usvajanjem ova dva strateška dokumenta potvrđeni su strateški pravci integralnog upravljanja otpadom i uklapanje planova upravljanja otpadom u planove zaštite okoliša i razvoja regije. Kako je već navedeno, prostornim planom i tehničkom dokumentacijom planirana je izgradnja Regionalnog centra za upravljanje otpadom (RCUO) u čijem je sastavu sanitarna deponija „*Trešnjica*". Sadržaj regionalnog centra je prikazan na slici 3. RCUO je rješenje za konačno zbrinjavanje i iskorištenje otpada za domaćinstva i privredne subjekte sa područja općina: Foča, Foča/Ustikolina, Goražde, Pale/Prača, Novo Goražde, Čajniče, Rogatica, Višegrad i Rudo, u skladu s Strategijom upravljanja čvrstim otpadom u BiH. U prelaznom periodu bi se zatvorila općinska odlagališta otpada. Pregled broja stanovnika i produkcije otpada za navedenu regiju je prikazan u tabeli 2.

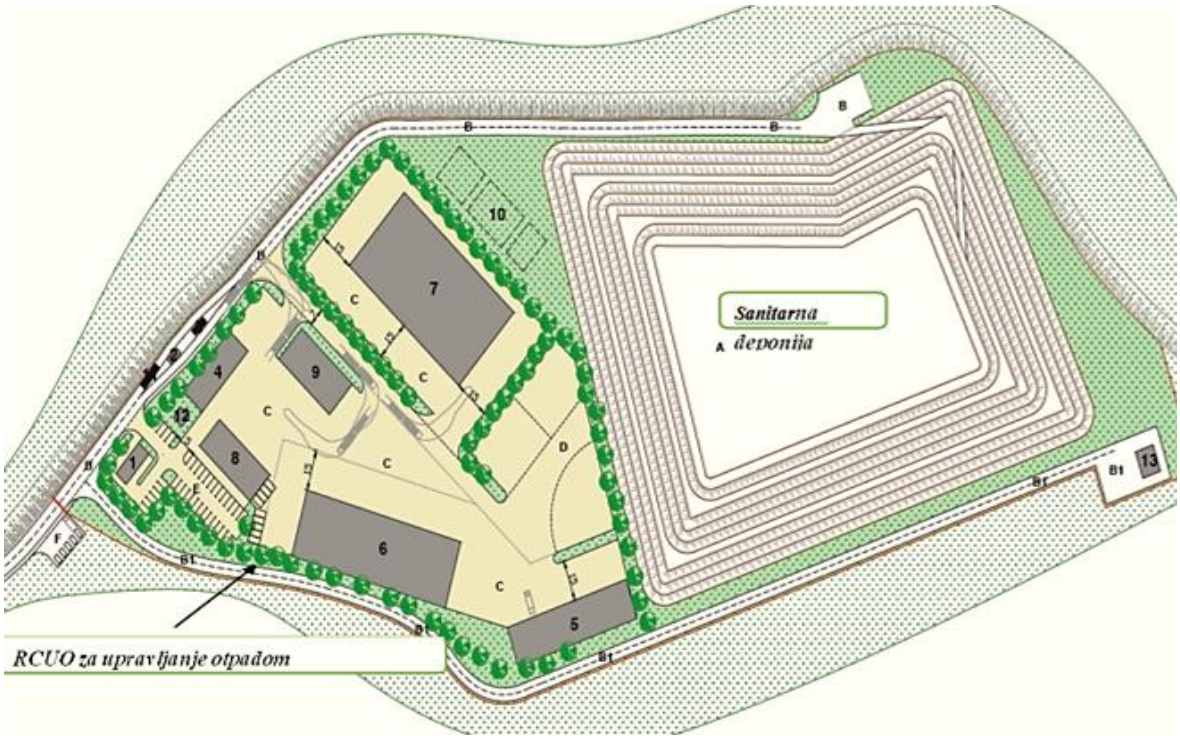
Tabela 2. Ukupne količine i vrste otpada po općinama BPK Goražde

Općina	Broj stanovnika	Dnevna količina (kg/st/dan)	Ukupna količina (kg/st/dan)	Vrsta otpada	Procenat %
Foča	25489	0,8	20391	Organski otpad	15,0
Foča – Ustikolina	2800	0,8	2240	Plastika	10,0
Goražde	32000	0,8	5600	Staklo	7,0
Pale-Prača	1 000	0,8	800	Papir i karton	33,0
N. Goražde	4 000	0,8	3200	Biomasa	5,0
Čajniče	5 311	0,8	4248	Metal	9,0
Rogatica	14850	0,8	11880	Koža i guma	7,0
Višegrad	13500	0,8	10800	Tekstilni otpad	9,0
Rudo	10000	0,8	8000	Ostalo	2,0
Ukupno:	**108.950**	**0,8**	**87 160**	Opasni otpad	3,0

RCUO Goražde se sastoji od sljedećih objekata/cjelina, naznačenih na slici 3:

- Upravna zgrada (1) sa portirnicom (2) i kolskom vagom na ulazu (3),
- Radionica (4) i nadstrešnica za dovezeni otpad (5),
- Objekat za mehaničku obradu otpada, sortiranje – Sortirnica (6),
- Objekat za obradu biološkog otpada – Digestori (7),
- Nadstrešnica za balirani otpad po frakcijama (8),
- Objekat za tehnološki proces rasplinjavanja (gasifikacija) (9),

- Objekat za tretman otpadnih procjednih voda (10),
- Rezervoar čiste vode (11),
- Sanitarna deponija (A).



Slika 3. Situacioni prikaz RCUO Goražde sa sanitarnom deponijom "Trešnjica"

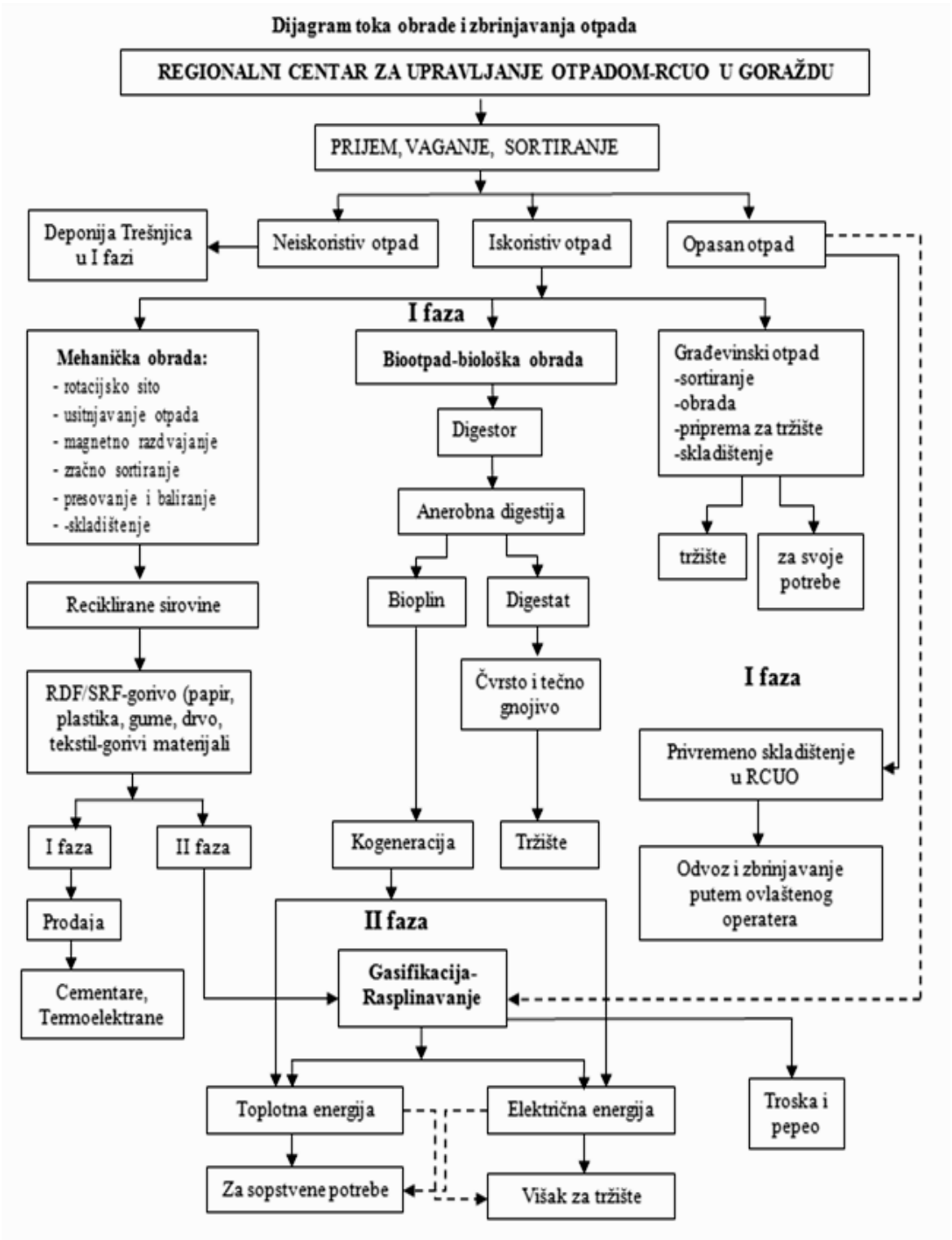
Uspostavom RCUO Goražde planirano je maksimalno iskorištenje otpada kao sirovine i otvaranje manjih i srednjih preduzeća koja bi dobivenu sirovinu pretvarali u novi proizvod. Obradom otpada i primjenom tehnoloških procesa i tehnologija u RCUO planirano je da bi se proizvode sljedeći proizvodi:

- *Sirovine*: papir, plastika, metali, RDF/SRF, staklo,
- *Organska gnojiva*: čvrsta i tečna dobijena anaerobnom digestijom u digestoru,
- *Električna i toplotna energija*: nastala od biogasa proizvedenog tokom procesa anaerobne digestije i procesa rasplinjavanja,
- *Reciklirani građevinski pijesak i šljunak*: proizveden drobljenjem i sedimentacijom građevinskog otpada.

Opravdanost izgradnje RCUO, određena je usporedbom finansijskih ulaganja za izgradnju centra i nabavku tehnološke opreme u odnosu na ostvarenu dobit iz prodaje korisnih odvojenih materijala i finalnih proizvoda iz otpada u odnosu na period povrata investicionih ulaganja. RCUO je koncipiran tako da može finansirati sve troškove poslovanja i imati dobit u svim godinama poslovanja pa je kao takav samoodrživ i ekonomski prihvatljiv.

3.3. Opis tehnoloških procesa obrade otpada u RCUO Goražde

Na osnovu urađenih studija i tehničke dokumentacije predložen je tehnološki proces obrade otpada u RCUO Goražde, a prikazan je na slici 4. Izgradnja i razvoj RCUO Goražde je planiran u 2 faze, u zavisnosti od razvoja koncepta upravljanja otpadom u cijeloj regiji.



Slika 4.Tehnološka shema obrade otpada u RCUO Goražde

Prema planovima, I faza bi obuhvatala prikupljanje i obradu otpada u sklopu RCUO, sa promoviranjem primarne reciklaže. U ovoj fazi, u RCUO Goražde otpad bi se razvrstavao i sortirao u različite frakcije, iskoristivi dio bi se vraćao u sirovine, a biootpad bi se koristio za proizvodnju komposta i bioplina (anaerobna digestija).

U II fazi, dugoročni planovi, uvođenjem koncepta *„Zero Waste"* smanjivala bi se produkcija otpada, a deponija bi se zatvorila. Za slučaj da količine otpada budu pristizale na RCUO Goražde, tehnološkim projektom je razmatrana opravdanost termičke obrade otpada (gasifikacija).

U toku je implementacija I faze, a provode se i aktivnosti na poboljšanju prikupljanja, selektiranja otpada i edukacije stanovništva.

4. ZAKLJUČAK

Klasično odlaganje otpada na sanitarne deponije je opće prihvaćen pristup zbrinjavanju otpada, međutim nosi sa sobom niz nedostataka koji se ogledaju u brzom smanjenju zapremine prostora deponije, nedostataku materijala za prekrivku slojeva, štetnim emisijama koje značajno utiču na okoliš, obezbjeđenje velikih prostornih obuhvata, veliki troškovi održavanja, neiskorištenost ekonomski vrijednih resursa iz otpada, nezadovoljstvo stanovništva koje živi u blizini deponije, te trend i implementacija zakonodavstva kojim se uvodi zatvaranje deponija. Koncept upravljanja otpadom u smislu samo istresanja se u skladu sa hijerarhijom upravljanja otpadom u EU odavno napustio, a pomalo se napušta i u regiji. Pokreću se novi koncepti koji imaju za cilj minimalno odlaganje otpada na deponije, visoku iskorištenost sirovina iz otpada i bolju zaštitu okoliša. Razvijene zemlje, ali uređene manje lokalne zajednice se opredjeljuju čak i za još veći i zahtjevniji koncept *„Zero Waste"*. O takvim planovima se razmišlja i u nekim općinama i regijama u BiH, iako, nažalost se mora realno sagledati stanje koje je daleko od tih standarda. Međutim, promoviranje zaštite resursa u svim privrednim granama i zakonska regulativa razvija i uvodi pojmove i razvojne planove usko vezane za iskorištenje sirovina koje nastaju na različite načine, a u skladu sa konceptom kružne ekonomije.

Za BiH aktivnosti na smanjenju otpada i uvođenju koncepta *„Zero Waste"* ne postoje ili su to „snovi" manjih lokalnih zajednica, međutim realno stanje je bolje u odnosu na prethodne godine. Uvode se načela hijerarhije upravljanja otpadom, sa smanjenjem produkcije, razdvajanjem otpada na mjestu nastajanja i recikliranjem otpada te se realiziraju projekti uspostavljanja regionalnih centara za upravljanje i iskorištenje otpada, u skladu sa Strategijom upravljanja čvrstim otpadom u BiH. Primjer aktivnosti koje se odvijaju u BiH, te uvjeti za primjenu „*Zero Waste*" koncepta su prikazani na primjeru BPK Goražde. Uspostava RCUO Goražde bi trebala doprinjeti boljem konceptu upravljanja otpadom u regiji i iskorištenju otpada kao resursa, a u planu su otvaranja i pogona za iskorištenje sirovina i proizvodnju novih proizvoda na osnovu sirovina iz otpada. Općina Goražde zajedno sa drugim općinama BPK Goražde, teži da izgradnjom planiranog Regionalnog centra za upravljanje otpadom postigne postavljene ciljeve na zaštiti okoliša, zaštiti resursa uz postizanje ekonomske opravdanosti investicije i uspostavljanje samoodrživosti Centra.

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PESTICIDE RESIDUES ON FOOD OF PLANT ORIGIN IN CROATIA

Aleksandar Mešić*, Boris Duralija*, Aleš Vokurka*, Tihomir Miličević*, Ivana Pajač Živković*

* University of Zagreb, Faculty of Agriculture, Zagreb, Croatia

corresponding author: Aleksandar Mešić, e-mail: amesic@agr.hr

Professional paper

ABSTRACT

Pesticides (biological, biotechnical and/or chemical) are regularly used in plant production. Considering their toxic and/or repellent effect on plant pests and weeds, they present a health risk on food consumers. Maximum residue level – MRL (mg active ingredient/kg of food) is the maximum content of the residues of certain pesticides in or on treated plants and plant products which must be determined when these products are put into circulation on the market. National monitoring programs for pesticide residues are the food safety indicators in the EU member states. European Food Safety Authority (EFSA) collects and interprets the results of monitoring programs from different member states. Results from Croatian national monitoring program show lower share of samples that had measurable residues above the analytical reporting level but below or at the MRLs, than average results that EU member states reported to EFSA. Those results could be the consequence of two scenarios:

a) analysed food is safer for consumer than EU average, or

b) results from Croatian national monitoring program are misleading if they are not sufficiently detailed.

Anyhow, Croatian residues monitoring program should be enhanced by analysing all the active substances that are currently available on Croatian market.

***Keywords**: food safety, pesticide residues, monitoring, MRL, health safety*

1. INTRODUCTION

One of the most common methods of protecting plants and plant products from the effects of harmful organisms is the use of active substances in pesticides - plant protection products. However, a possible consequence of their use may be the presence of residues in the treated products, in animals feeding on those products and in honey produced by bees exposed to those substances [1]. Contamination hazards in the agricultural food chain can stem from a

range of sources, including residues of agrochemicals (plant protection products, fertilizers etc.) and natural toxins. Aside from important public health considerations, the economic impact of food contamination can be significant and might adversely affect international trade [2]. Food contaminants are substances that may be present in certain foodstuffs due to environmental contamination, cultivation practices or production processes. If present above certain levels, these substances can pose a threat to human health. European Union rules ensure that food placed on the market is safe to eat and does not contain contaminants at levels which could threaten human health [3]. Maximum residue level (MRL) is the maximum content of the residues of certain pesticides in or on treated plants and plant products which must be determined when these products are put into circulation on the market [4]. As a general rule, the application for authorization of a pesticide and the corresponding maximum residue level must be submitted at the same time. Food and/or feed cannot be placed on the market without a fixed maximum level. All active substance/product combinations without an existing authorization of pesticide and without fixed MRLs, are generally controlled with a value of 0.01 mg/kg [1].

2. THE AIM, MATERIALS AND METHODS

The aim of this research was to summarize results of Croatian national program for the pesticide monitoring and to compare it with the results of the European Union countries. Materials for this research are official reports of Croatian Ministry of Agriculture, regulations and directives of the European Union and documents of European Food Safety Authority (EFSA). Deductive and inductive method and analysis were used to accomplish this research and paper.

3. RESULTS AND DISCUSSION

According to the EU legislation, EU Member States and two EFTA countries (Iceland and Norway) have to carry out national control programs on pesticide residues in food commodities and to report the results to the European Commission and EFSA. General legal provisions for food inspections and monitoring were established by Regulation (EC) No. 882/2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare [5].

3.1. Croatian national pesticides residues monitoring program

The National program for the monitoring of pesticide residues in and on plant originating products was established pursuant to the Act on Plant Protection products which is aligned with the provisions of Directive 91/414/EEC, which is amended with Regulation (EC) No. 396/2005. The program is prepared and coordinated by the Ministry of Agriculture. Sanitary inspectorate of the Ministry of Health collected food samples from the market and the Croatian Public Health Institute analysed those samples for the presence of pesticide residues. The objective of the monitoring program is to determine the quantity of pesticide residues in food and to verify compliance with stipulated MRLs. Every year, Ministry of Agriculture revises and expands the Program and Instructions with new insight and

amendments to the EU legislation [6]. Summarized results of food samples analysis for presence of pesticide residues achieved by implementation of the Croatian national program for the pesticides residues monitoring in the period 2007 - 2014 are presented in table 1.

Table 1. Active compounds and number of samples in which MRLs were exceeded, reported in Croatian monitoring program [5 - 13]

	2007	2008	2009	2010	2011	2012	2013	2014
Number of product types	9	14	14	15	15	15	14	15
No. of analysed active substances	77	87	87	88	107	110	114	114
Number of analysed samples	112	246	292	409	416	417	335	378
Samples without residues	70 %	73 %	70.9 %	86 %	71.9 %	72 %	76.4 %	82 %
Samples with residues below MRL	23 %	23 %	27.1 %	13 %	28.1 %	27 %	33.6 %	18 %
Samples with residues above MRL	7 %	4 %	2 %	1 %	0.2 %	0.2 %	0 %	0 %
Annual budget, EUR (approximately)	26,000	67,000	94,000	134,000	134,000	134,000	106,000	134,000

3.2. EFSA collected results of pesticides residues monitoring

The percentage compliance might be used as a statistical parameter for comparison with the results of previous years and to indicate possible emerging trends, which require further investigation. Over the years, the percentage of samples with residues above the MRLs increased from 3.0 % in 1996 to 5.5 % in 2002/2003. Since 2003, there has been a decrease, with 3.99 % of samples non-compliant in 2007. The annual comparability of the data is problematic though. This is because the number of countries reporting data has increased from 16 in 1996 to 29 in 2007 and because the national programs differ not only from each other but also over time. In 2007, in total 74,305 samples of approximately 350 different food commodities were analysed for pesticide residues under the national and the EU coordinated programs. In 2007, the analytical methods used by the reporting countries for pesticide residue analysis allowed detection of total 870 different pesticides (including metabolites) in food samples. Compared with 2006, the total number of pesticides sought has increased by 13%. On average, reporting countries tested for 218 different pesticides. In 2007, 96.01 % of the samples analysed in the framework of the national and the coordinated monitoring programs were compliant with the legal MRLs, while in 3.99 % of the samples the legal limits were exceeded for one or more pesticide [5].

2008 was an important year for the harmonization of the Maximum Residue Levels (MRLs) for pesticides at European level. Whereas before 1 September 2008 a mixed system with harmonized Community MRLs for ca. 250 active substances and national MRLs for the remaining substances was in place, after this date harmonized MRLs became applicable for all active substances used in plant protection products that have the potential to enter the food chain. Because of these substantial changes in the European MRL legislation, the results of

previous monitoring reports published by EFSA and the European Commission are not directly comparable with the results reported in this report. The comparability of the data among reporting countries and over time is hampered not only by the important change in the legal situation but also by other factors, such as the change in the number of the reporting countries over time, the difference in the design of the national monitoring plans and the data validation and recoding. A total number of 11,610 samples of nine different commodities were analysed for 78 pesticides (including the relevant metabolites, as specified in the legal residue definition). 2.2 % of the samples exceeded the MRL, while the percentage of samples with measurable residues above the quantification level, but at or below the MRL, was 35.7 %. In 62.1 % of the samples no residues were detected. The overall MRL exceedance rate was comparable with the previous year rate (2.3 %). It is noted that the percentage of samples without measurable residues increased from 52.7 % in 2007 to 62.1 % in 2008 [14].

The analysis of the results of the 2009 EU-coordinated program has shown that 1.2 % of the 10,553samples exceeded the MRL, while 37.4 % of samples had measurable residues above the analytical reporting level but below or at the MRL. 61.4 % of the samples were free of measurable pesticide residues [15].

The analysis of the results of the 2010 EU-coordinated program shows that 197 (1.6%) of the 12,168 samples exceeded the MRL, while 5,802 (47.7 %) of the samples had measurable residues above the reporting level but below or at the MRL. 6,169 of the samples (50.7 %) were free from measurable pesticide residues. According to the results of the last four EU-coordinated programs (2007 to 2010), the percentage of samples exceeding the MRLs was rather stable, with only small variations; the % of samples exceeding the legal limits in this reference period ranged from 1.2 % to 2.3 % [16].

The analysis of the results of the 2011 EU-coordinated program, which requested the control of12 different food products, shown that 1.9 % of the samples numerically exceeded the MRL (245 out of the 12,676 samples); of those, 1.1 % was also found to be non-compliant with the legal limits when the measurement uncertainty was taken into account. 44.7 % of the samples (5,660 samples) contained measurable residues within the legally permitted levels. In 53.4 % of the samples (6,771 samples), no quantifiable residues were found (residues below the limit of quantification). Out of the 179 pesticides covered by the EU-coordinated program, 40 pesticides were not detected in any of the samples analysed [17].

The analysis of the results of the 2012 EU-coordinated program, which requested the control of 12 different food products for 205 different pesticides, has shown that 0.9 % of the samples numerically exceeded the Maximum Residue Levels (MRLs) (92 out of the 10,235 samples); approximately half of them 0.5 % of the samples) were found to be non-compliant with the legal limits when the measurement uncertainty was taken into account. Measurable residues within the legally permitted levels were found in 39 % of the samples (3,992 samples). In 59.9 % of the samples (6,771 samples), no residues were detected (residues below the limit of quantification) [18].

In 2013, the reporting countries analysed 80,967 samples for a total of 685 different pesticides. On average, samples were analysed for 200 pesticides. Overall, 97.4 % of the samples analysed fell within the legal limits; 54.6 % of the samples tested were free of detectable residues while 42.8 % of the samples analysed contained measurable residues not exceeding the permitted residue concentrations. 2.6 % of all the samples exceeded the MRL (2,116 samples); 1.5 % of the samples clearly exceeded the legal limits, taking into account the measurement uncertainty [19].

In 2014, the reporting countries analysed in total 82,649 samples for a total of 778 different pesticides. On average, samples were analysed for 212 pesticides. The majority of samples (57,399 samples, 69.4 %) originated from EU and EEA countries; 21,219 samples (25.7 %) concerned products imported from third countries. For 4,031 samples (4.9 %), the

origin of the products was not reported. Overall, 97.1 % of the samples analysed under the national control programs fell within the legal limits; 53.6 % of the samples tested were free of quantifiable residues (residues below or at the limit of quantification, LOQ) while 43.4 % of the samples analysed contained measurable residues not exceeding the permitted residue concentrations. A total of 2.9% of the samples exceeded the maximum residue levels (MRLs) permitted in the EU legislation (2,421 samples); taking into account the measurement uncertainty, 1.6 % of the samples (1,341 samples) clearly exceeded the legal limits (non-compliance) triggering legal or administrative actions by competent authorities. The results of 2014 are comparable with the previous year (2013: 97.4 % of samples within legal limits; 54.6 % free of quantifiable residues) [20].

3.3. Discussion

A comparative analysis of the results of the monitoring of residuals in the Croatian national monitoring program and of the one reported by the EFSA is presented in tables 2 and 3.

Table 2. Percentage of samples without traceable residues in Croatia and in EFSA collected results

	2007	2008	2009	2010	2011	2012	2013	2014
Croatia	70 %[6]	73 %[7]	70.9 %[8]	86 %[9]	71.9 %[10]	72 %[11]	76.4 %[12]	82 %[13]
EFSA	52.7 %[5]	62.1 %[14]	61.4 %[15]	50.7 %[16]	53.4 % [17]	59.9 %[18]	54.6 %[19]	53.6 % [20]

Results presented in table 2 show that there is a significant difference in samples without traceable residues between results of Croatian national monitoring program and the one published by EFSA.

Table 3. Percentage of samples exceeding MRLs in Croatia and in EFSA collected results

	2007	2008	2009	2010	2011	2012	2013	2014
Croatia	7 %[6]	4 %[7]	2 %[8]	1 %[9]	0.2 %[10]	0.2 %[11]	0 %[12]	0 %[13]
EFSA	3.99 %[5]	2.2 %[14]	1.2 %[15]	1.6 %[16]	1.1 % [17]	0.9 %[18]	1.5 %[19]	1.6 %[20]

Because of these substantial changes in the European MRL legislation, the results before 2008 monitoring reports published by EFSA and the European Commission are not directly comparable [5].

Results for period 2010 - 2014 presented in tables 2 and 3 show that smaller number of samples collected in Croatia contains pesticide residues compared with results presented by EFSA. Those results could be consequence of two scenarios:

a) analysed food is safer for consumer than EU average or
b) results from Croatian national monitoring program are misleading.

From this point of view, it is not possible to give a realistic estimate of those two scenarios. The second scenario is corroborated by the results presented in table 4.

Table 4. Comparative analysis of the number of active substances involved in monitoring and the number of active substances (a.i.s) with an authorization for use in Croatia

	2008	2009	2010	2011	2012	2013	2014
Number of a.i.s authorized in Croatia	263[21]	245[22]	220[23]	220[24]	219[25]	2019[26]	222[27]
Number of a.i.s analysed within program (including their isomers and metabolites)	87[7]	87[8]	88[9]	107[10]	110[11]	110[12]	114[13]

It should be emphasizing that majority of active ingredients analysed within the National monitoring programs in Croatia are banned to use for many years (e. g. DDT, aldrin, atrazine, lindane) [6 - 12]. Simultaneously, that analysis does not include new active substances that are currently in use.

4. CONCLUSION

National programs for pesticide monitoring provide valuable information on food safety on the markets of different EU member states. Reports from 2010 - 2014 indicate that food safety in Croatia is above EU average, regarding the levels of pesticide residues. Croatian national residues monitoring program should be enhanced by analysing all the active substances that are currently available on Croatian market.

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TEHNOLOGIJE OBRADE OTPADA U RH - ZAŠTO SMO ZA ILI PROTIV?

WASTE TREATMENT TECHNOLOGIES IN THE REPUBLIC OF CROATIA: WHY ARE WE FOR OR AGAINST?

Zlatko Milanović

autor za korespondenciju: Zlatko Milanović, e-mail: zlatko.milanovic1@gmail.com

Pregledni rad

SAŽETAK

Republika Hrvatska unutar EU najviše komunalnog otpada odlaže, a najmanje oporabljuje. Međutim, već krajem prošlog stoljeća u Hrvatskoj su stručnjaci promovirali Cjeloviti sustav gospodarenja otpadom. U razvitku tog Cjelovitog sustava gospodarenja otpadom, sustavno se zanemaruje potreba oporabe i adekvatne obrade otpada. Stalno se donose novi propisi, koji se zatim ne provode. Neki stručnjaci i nastavno zelene udruge već više od trideset godina izrazito se protive projektima spaljivanja i suspaljivanja, a „šutke prihvaćaju" neuređeno i neusklađeno odlaganje. Svjesno ili nesvjesno u aktualnom Planu gospodarenja otpadom RH utvrđeni su ciljevi za odvojeno sakupljanje reciklabilnih frakcija komunalnog otpada, a zanemaruje se provedba cjelovitog gospodarenja otpadom. Nedostatak znanja i komunikacija u Hrvatskoj temeljni je problem ne provedbe odgovornog postupanja s otpadom.

Ključne riječi: *otpad, gospodarenje otpadom , tehnologije obrade otpada*

ABSTRACT

The Republic of Croatia belongs to the EU countries which landfill highest percentage of communal waste and recover a smallest portion of valuable components. However, already at the end of the last century, experts in Croatia have promoted the Integrated Waste Management System. In the development of that system, systematically was neglected the need for recovery and proper waste treatment. New regulations are constantly being passed, which are then not being implemented. For some thirty years, certain experts and green nongovernment organizations have been strongly opposing waste incineration and co-incineration projects, and silently accept unreasonable and non-sanitary landfilling. Consciously or unconsciously, in the current Waste Management Plan of the Republic of

Croatia, the goals for separate collection of recyclable municipal waste fractions have been established but the implementation of integrated waste management is neglected. Lack of knowledge and communication in Croatia is a fundamental problem of non-compliance with responsible waste management.

***Key words**: waste, waste management, waste treatment technologies*

1. UVOD [1 - 3]

Kad se razmatra problem otpada gotovo isključivo se podrazumijeva materijalni otpad koji proizvode ljudi. Problem antropogenog materijalnog otpada izravno je povezan s razvojem ljudskog društva. U prirodi također nastaje materijalni otpad (potresi, šumsku požari, poplave itd.), ali priroda ga uvijek sama manje - više postupno uspješno rješava. Gospodarenje otpadom je u osnovi postupanje s potrošačkim i proizvodnim ostacima. Od pamti vijeka ljudi se susreću s ostacima odnosno smećem. Sve do osamnaestog stoljeća, ljudi su smeće redovito zbrinjavali odvozom čim dalje od mjesta boravka. U osamnaestom stoljeću evidentirane su ozbiljne ugroze zdravlja ljudi, koje su između ostalog bile posljedica neodgovornog postupanja s otpadom. Industrijska proizvodnja postupno je povećava potrošnju robe i time količinu otpada, a na kraju i količinu odloženog otpada. Industrijsko sortiranje, recikliranje i spaljivanje otpada je počelo krajem devetnaestog stoljeća. Početkom dvadesetog stoljeća u Rijeci je izgrađena prva hrvatska spalionica.

Tijekom prvog i drugog svjetskog rata problem otpada razumljivo je bio zanemaren. Nakon drugog svjetskog, rata u blizini gradova koji su bili jako bombardirani, izrasla su brda ispunjena građevnim otpadom. Međutim tada u uništenoj Njemačkoj upravo recikliranje otpadnih metala je doprinijelo razvitku njemačke industrije. Pokazalo se da gospodarenje otpadom može biti inicijator razvoja eko gospodarstva. To i pokazuje i ne tako davni primjer iz Hrvatske. Konkretno na prostoru bivše tvornice OKI Zagreb, iznikla je kao ptica feniks iz pepela, tvrtka za recikliranje proizvodnog i komunalnog otpada (*e kolektor).*

U Hrvatskoj je duga tradicija odvojenog sakupljanja i recikliranja (primarna reciklaža) odvojeno prikupljenih otpadnih metala i otpadnog papira. Međutim nakon drugog svjetskog rata širom svijeta i dalje najveće se količine otpada i dalje odlažu na smetlišta odnosno neslužbena neuređena odlagališta. Sve brže raste proizvodnja i po količini i vrsti proizvoda. Započinje industrijska proizvodnja plastike i sve složenijih vrsta ambalaže. Broj smetlišta (neuređenih odlagališta) se drastično povećava, te u većim europskim zemljama radilo je i nekoliko stotina tisuća smetlišta. U Hrvatskoj je evidentirano više od 3.000 smetlišta, koja izravno ugrožavaju okoliš i zdravlje ljudi. Sve veći je broj „divljih“ deponija (u Zagrebu i nekoliko stotina), koja se redovno čiste a na poglavito sličnim mjestima redovno nastaju. Odlagališta ne mogu bita divlja, već su divlji ljudi koji ih stvaraju. „Divlja“ smetlišta nastaju u šumama, ali i pod morem i jezerima.

Brojna službena smetlišta u okolici počela su ugrožavati širenje naselja, te je oko šezdesetih godina prošlog stoljeća i u Zagrebu zatvoreno niz legalnih manjih smetlište i otvoreno središnje službeno smetlište uz naselje Jakuševec. U to vrijeme sve brže rastu i količine otpada, povećavaju se smetlišta, ali dolazi do ozbiljnih ugroza zdravlja ljudi. Tako je i smetlište Jakuševec zauzelo površinu od gotovo 100 hektara, ali su i onečišćeni svi kućni bunar pitke vode u naselju Jakuševec. To idilično turopoljsko naselje na toj lokaciji je opstajalo stotinama godinama, a smećem je ugroženo već nakon dvadesetak godina od početka dovoza komunalnog ali i proizvodnog i opasnog otpada.

U razvijenim zemljama, o velikim opasnostima odlaganja otpada počelo se promišljati krajem šezdesetih godina prošlog stoljeća odnosno upravo kada je započelo odlaganje na smetlištu Jakuševec. Već tada se uvidjelo, da je otpad najlakše odvesti od mjesta boravka, ali i da je:

„Otpad je najveći problem zaštiti okoliša“.

Znanstvenici su također istovremeno ukazivali i da je otpad izvor brojnih vrijednosti (sirovina, energije). Primjerice već 1995. godine u Njemačkoj je tiskana Enciklopedija kružnog gospodarstva (slika1).



Slika 1. Enciklopedija kružnog gospodarstva

Začuđuje da u današnje doba neki otkrivaju kružno gospodarstvo. Isto tako recikliranje određuje materijalnu oporabu otpada odnosno sirovinsko iskorištavanje otpada. Recikliranje je povezano s kružnim gospodarenja, a zaboravlja se da riječ recikliranje sastavljeno od grčkih riječi *Re + Cycle = ponovno kruženje.*

Najučinkovitiji način recikliranja biootpada je kućno kompostiranje, koje ljudi prakticiraju već tisućama godinama. Problem je samo, što u agresiji potrošačkog društva, suvremeni urbanizirani čovjek je *zaboravio kompostirati.* Problem je i što se sve veći broj frakcija komunalnog ne može kompostirati odnosno biološki obraditi. Proizlazi da je kreacija novih tvorevina iskonski problem tehnologija gospodarenja otpadom. Otpad je produkt života ljudi, te s promjenama društva dolazi do promjena količine i vrste otpadnih tvari.

Primjerice u RH posljednjih godina je došlo do **plastifikacije** komunalnog otpada. Tako u Planu gospodarenja otpadom RH 2007. – 2015. je utvrđen sljedeći morfološki sastav komunalnog otpada:

Plan gospodarenja otpadom RH 2007.-2015. (% mase)

- Kuhinjski i ostali biootpad 42,10 %
- Papir i karton 20,00 %
- Koža i kosti 3,10 %
- Drvo 1,30 %
- Tekstil 8,00 %

- Staklo 6,80 %
- Metali 4,10 %
- Inertni otpad 1,90 %
- **Plastika 12,00 %**
- Guma 0,70 %
- Posebni otpad 0,30 %

Međutim ni deset godina kasnije Agencija za zaštitu okoliša (AZO) objavljuje sljedeći sastav miješanog komunalnog otpada (MKO):

Procjena sastava MKO (AZO 2015.)

- Kuhinjski otpad 30,7 %
- Vrtni otpad 5,7 %
- Papir/karton 23,2 %
- **Plastika 22,9 %**
- Drvo 1,0 %
- Tekstil/odjeća 3,7 %
- Staklo 3,7 %
- Metal 2,1 %
- Guma 0,2 %
- Koža/kosti 0,5 %
- Sitnica (nesortirano) 6,3 %

Iako su stručnjaci odavno upozoravali na problem otpadne plastike, tek sada kada „*čovjek uronjen u plastiku sve više plastike jede i pije*“ u javnosti sazrijeva svijest o problemima s otpadnom plastikom. Europska komisija je također upozorila da dolazi do „nezaustavljivog“ akumuliranja otpadne plastike u okolišu. Plastika je izvrstan materijal, a središnji problem je ljudsko ponašanje s plastičnim proizvodima.

Problem nije samo promjena udjela plastike, već i stalne promjene sastava proizvodnog i komunalnog otpada. Proizvodni otpad prvenstveno ovisi od tehnologije proizvodnje proizvoda, te se načelno promjene mogu predvidjeti. S druge strane komunalni otpad ovisi naročito od bruto društvenog proizvoda, načina života i tržišnoj ponudi tvorevina. Stalno se mijenja komunalni otpad, te je izuzetno opasno temeljiti tehnologije obrade na postojećim analizama sastava komunalnog otpada. Poteškoće u radu postrojenja za obradu, a nastavno i sudski procesi, su bili posljedica promjene sastava komunalnog otpada. Za RH u primorskim JLS golemi problem višestruko je povećanje količine otpada tijekom turističke sezone.

Otpadna plastika izvrsno pokazuje neodgovornog (neekološkog) promišljanja suvremenih ljudi. Plastika ima brojne prednosti, gotovo kao nijedan drugi materijal. Najveći nedostatak (a to je ujedno i prednost) plastike je vrlo spora biološka razgradivost. Ljudi koriste brojne prednosti, između ostalog i nisku proizvodnu cijenu plastike. Pri tome svjesno ili nesvjesno se zanemaruje da u prodajnoj cijeni plastičnih tvorevina nisu sadržani troškovi održivog gospodarenja otpadnom plastikom.

Do sada se u RH zanemarivala mogućnost oporabe smeća. Međutim u MKO - miješanom komunalnom otpadu se nalaze vrlo velike količine iskoristivih otpadnih tvari. To nije problem samo naše zemlje, pa je Komitet europskog parlamenta za okoliš u amandmanima na prijedlog izmjene okvirne direktive o otpadu naveo i sljedeće*:„Unatoč odvojenom sakupljanju, mnoge reciklabilne komponente još uvijek završavaju u miješanom otpadu. S visokokvalitetnim sortiranjem, osobito optičkim tehnikama, znatna količina materijala može se izdvojiti iz preostalog otpada i naknadno reciklirati i preraditi u sekundarne sirovine. Zemlje članice trebale bi stoga poduzeti mjere kako bi se osiguralo da i otpad koji se ne sakuplja odvojeno ipak razvrstava“.*

2. CJELOVITI SUSTAV GOSPODARENJA OTPADOM [4 - 6]

Različiti pojmovi korišteni su za rješenje problema otpada: odstranjivanje, neutralizacija, zbrinjavanje, gospodarenje itd. Samo Cjeloviti sustav gospodarenja otpadom (CSGO) jamči odgovorno i održivo postupanje s otpadom. Pojednostavljeno to znači da o otpadu treba promišljati prije nego što je otpad nastao. U RH, već osamdesetih godina prošlog stoljeća, se počeo promišljati o CSGO, i to čak prije nego u mnogim razvijenih zemalja (npr. simpoziji Sardinija i Beč CSGO u naslovi koristili iza Zagreba). U to su vrijeme u Zagrebu postavljeni prvi spremnici za odvojeno sakupljanje (OS) komunalnog otpada sustavom donošenja, a već 1995. godine u Zagrebu je započelo u tri različita naselja OS biootpada sustavom „*od vrata do vrata.*

Potrebno je naročito naglasiti da odvojeno sakupljanje nije CSGO. Zeleni aktivisti često, u dobroj namjeri ali i u neznanju, OS izjednačuju s početkom recikliranja otpada. Ponekad se zanemaruje i činjenica da je naročito važno osigurati OS opasnog i problematičnog otpada.

U RH vrlo su pozitivna iskustva u OS i recikliranju posebnih kategorija otpada (PKO). Do sada u RH već su ostvareni za neke vrste PKO zavidni rezultati (npr. gospodarenje otpadnim autogumama, EE otpadom, otpadnim uljima, dijelom otpadne ambalaže itd.). To je i najbolji način provedbe načela „sljedivosti“ gospodarenja otpadom. To je najbolji pokazatelj da apsolutno treba inzistirati na CSGO. Kod OS posebnih kategorija otpadom cjelovitim pristupom se osigurava financijska podrška cijelom sustavu od osmišljavanja, projektiranja, proizvodnje i potrošnje do gospodarenja otpadom. U RH postojeće sustave gospodarenja PKO samo treba dograditi proširenjem i većem ulogom tržišnih kriterija.

Neprijeporno OS je tek jedna od karika CSGO, koju na svakoj razini treba prihvatiti, ali tek uz Analizu životnog ciklusa (AŽC). Cjelovito i odgovorno nije odvojeno sakupljeni otpada na odlagalištu pomiješati s ostalim vrstama otpada (npr. odvojeno prikupljeni glomazni (krupni) otpada). OS jamči kvalitetnu provedbu svih tehnologija oporabe i obrade otpada, ali uvijek samo u okvirima CSGO. Također OS nije početak CSGO! Početak je i to na svim razinama, EDUKACIJA, slijedi osmišljavanja novih tvorevina i proizvoda itd.

Svjetska iskustva treba stalno pratiti i iz njih uvijek učiti. Nikada ih ne treba prihvatiti bez kritičke analize. Niz je loših primjera iz razvijenih zemalja (npr. gradnja kompostana za MKO; ili Beč 1986. godine gradnja velikog postrojenja (600 milijuna ATS) za strojno recikliranje MKO). Treba znati i zašto je, u samo godinu dana, EU administracija počela umjesto „nula otpada“ počela promovirati „kružno gospodarstvo“. Jednako je EU promijenila i ciljeve gospodarenja otpadom do 2030. godine:

	Barroso (2014.)	Juncker (2015.)
Stupanj reciklaže KO	70 %	65 %
Odlaganje KO	5 %	10 %
Stupanj recikliranja otp. amb.	80 %	75 %
Smanjenje morskog otpada	30 %	> 25 %

Da li je do promjene došlo slučajno odnosno bez cjelovitog pristupa?

Njemački časopis Recycling, krajem 2017. godine, ukazuje da su najveći problemi gospodarenja otpadom u RH:

- obrada biootpada,
- građevni otpad,

- otpadni mulj,
- opasni otpad.

Ujedno to je i pokazatelj da te vrste otpada treba OS i zatim istim odvojeno pristupati. Nema jedne tehnologije koja na jedinstveni način. Rješenje je uvijek CSGO. Svakako osobiti problem u RH je i *morski otpad,* a za tu vrstu otpada treba ne samo uvažiti EU propise nego i međunarodne konvencije koje je Hrvatska usvojila!

3. IZBJEGAVANJE I SMANJIVANJE (PONOVNA UPORABA) OTPADA [7]

Izbjegavanje i smanjivanje otpada (prevencija) su hijerarhijski prioritetne mjere. Ostaje otvoreno pitanje, može li se izbjeći stvaranje otpada? Teoretski sve je moguće, ali praktično (koncept „*zero waste*“) nijedna zemlja u svijetu nije postigla izbjegla stvaranje otpada. Vrtno odnosno kućno kompostiranje je školski primjer izbjegavanja otpada, ali cjelovita AŽC pokazuje da ni to ipak nije koncept bez proizvodnje otpada.

Knjiga o izbjegavanju i smanjivanju otpada u RH je objavljena početkom novog milenija. Bila je izvrsno prihvaćena i doživjela je čak četiri izdanja. Objavljeni sadržaj je aktualan i u današnje vrijeme (2018.). Ljudi u tranzicijskoj zemlji, kao što je RH, pritisnuti svakodnevni promocijama potrošačkog društva zanemaruju na prevenciju otpada. U Zagrebu stotine „jumbo“ plakata potiče potrošnju, a samo jedan jedini poziva na prevenciju otpada (slika 2) Nažalost i taj plakat je početkom 2018. „nestao“.



Slika 2. Jumbo plakat koji poziva na prevenciju otpada

Jedini plakat koji je više od dvadeset godina promovirao mjere izbjegavanja i smanjivanja otpada, nestao je (bez javne pozornosti) u svibnju 2018. godine (privremeno ili stalno?)

Izbjegavanje i smanjivanje otpada započinje u glavama ljudi, a promišljanja ljudi je najteže promijeniti. To je moguće isključivo dobro osmišljenim stalnim učenjem. Edukacija je stalan proces u kojem se poimaju osnove održivosti i to je osobiti način otpora potrošačkom društvu.

Nema jasnih kriterija mjerenja učinaka edukacije. Sasvim sigurno mjere prevencije su najsloženije i najdugotrajnije mjere gospodarenja otpadom. Začuđujuće je kako su tri bivša ministra ukinula neke od u RH propisanih mjera suvremenog gospodarenja otpadom (OS

ambalaže, obrazovanje za gospodarenje otpadom) i/ili podržali neuređeno odlaganje otpada. Nije bitno koji su bili razlozi, već je ključno da su to učinili iz razloga nedovoljnog znanja.

Izbjegavanje i smanjivanje otpada su prioritet prioriteta, ali zašto je onda praksa poglavito u javnim tvrtkama drugačiji:

- anketom među stručnjacima iz značajnim komunalnim tvrtki, na jednom skupu Tehnix održanom u 2016., pokazalo se da godišnje planirana financijska sredstva za mjere izbjegavanja i smanjivanja su i manje od *1 posto* ukupnih sredstava. Pored toga, kada tijekom godine dolazi do rebalansa, prvo se umanjuju planirana sredstva za mjere prevencije,
- plan gospodarenja otpadom RH, donesen u siječnju 2017. godine za provedbu mjera edukacije predvidio je samo *1,8 %*. S druge strane za najviše planiranih financijskih sredstava predviđeno je za postupanje s otpadom koji je već nastao i to davno prije (sanaciju starih opterećenja otpadom). Da li se na taj način potiče neprovedba propisa na lokalnoj razini,
- u časopisu *Građevinaru* (11/2017.) objavljen je članak „Financijska i socioekonomska analiza projekta gospodarenja otpadom“, koji pokazuje da su operativni troškovi izbjegavanja i smanjivanja otpada oko *3,4 %*,
- zanimljivo je podsjetiti kako je početkom 2018. godine na TV programu objavljen dobrih set emisija o izbjegavanju i smanjivanju otpada, ali na kraju obvezno u emisiji je poruka *financirano sredstvima EU!*

U travnju 2018. u Zagrebu se pojavio „jumbo“ plakat, koji promovira smanjenje ambalaže i/ili jeftiniju potrošnju, ali i taj je plakat nakon oko mjesec dana nestao (slika 3).



Slika 3. Jumbo plakat, koji promovira smanjenje ambalaže i/ili jeftiniju potrošnju

Načelno se procjenjuje učinke mjera izbjegavanja i prevencije na smanjivanje za oko 5 posto mase otpada. U radnom materijalu „Brošura IZBJEGAVANJE NASTAJANJA OTPADA“ nešto je detaljnija analiza mogućnosti smanjivanja otpada temeljem visine društvenog bruto proizvoda. Već otvaranje diskusije o mogućnostima smanjivanja otpada je izvrsni početak učinkovite edukacije.

4. RECIKLIRANJE OTPADA [8 - 14]

Recikliranje je materijalna oporaba otpada. To je treća prioritetna mjera CSGO. Sustavi OS komunalnog otpada (slika 4) su u nadležnosti JLS. U legislativi RH nije jednoznačno određenje mjera recikliranja. Međutim EU legislativa kao i ZOGO (2013.) utvrđuju ciljeve *recikliranja* koje treba dugoročno ostvariti. Nažalost Plan usvojen 2017. godine određuje dugoročne ciljeve *odvojenog sakupljanja (OS).* Plan je na taj način nepotrebno otvorio nedoumice. Svima je dobro znano da OS nije recikliranje. Kada određena JLS odvojen prikupi propisane frakcije komunalnog otpada što s njima? Ako odvojeno prikupljene vrste KO JLS ne može tržišno plasirati i time reciklirati, što s njima? Ako se prema Planu odvojene frakcije odlože (što nije dopušteno), stvara se dodatna ekološka ugroza i financijski nepotreban trošak. Apsurdno JLS mogu odvojeno prikupiti propisane frakcije KO, te kad ih ne mogu tržišno plasirati dostaviti ih onome tko je predlagatelj Plana?



Slika 4. Odvojeno prikupljanje sustavom „od vrata do vrata“, Velika Gorica 1996

Komunalne tvrtke u RH vrlo uredno prikupljaju KO (> 99 % mase) i održavaju primjernu čistoću gotovo svih urbanih prostora. Upravo grad Zagreb je nedavno primio priznanje za čistoću javnih površina. U posljednje vrijeme, nakon donošenja Uredbe o gospodarenju komunalnim otpadom, dolazi do poteškoća i to osobito na lokacijama za OS. Uzroci tih problema su različiti i treba vjerovati da su privremeni.

U javnim istupima predlagatelji Plana ističu da komunalne tvrtke trebaju za tržište pripremiti samo „grubo“ sortirane frakcije komunalnog otpada. Pri tome pojam grubo je tehnička nejasan. Često se i zanemaruje da recikliranje prvenstveno (isključivo) ovisi od privatnog gospodarstva. RH je mala zemlja velikih prometnih udaljenosti što malim komunalnim tvrtkama (poglavito na otocima) otežava recikliranje.

Recikliranje nije samo OS, a svakako nije nabava kanti različitih boja i kamiona za pražnjenje tih kanti. Sposobnost recikliranje svakako nije da se sredstvima Fonda financira

nabava kanti različitih boja i kamiona za odvojeno prikupljanje. Recikliranje nije uvođenje naknade za kućni otpad prema količini ili prema broju pražnjenja kanti. Recikliranje nije samo povremeno izdavanje promotivnih letaka i brošura. Recikliranje nije samo promovirati OS komunalnog otpada, a zanemariti OS proizvodnog otpada. Recikliranje nije samo promovirati OS komunalnog iskoristivog (reciklabilnog) otpada, a zanemariti OS problematičnog otpada. Recikliranje nije zanemariti potrebu stalne komunikaciju između onih koji proizvode otpad i onih koji gospodare otpadom.

Recikliranje se uspješno provodi samo u okvirima CSGO. To između ostalog zahtijeva zajedništvo svih čimbenika i to naročito na lokalnoj sredini. U sve većem broju JLS postižu se izvrsni ciljevi OS i osobito ciljevi recikliranja KO. S druge strane u RH veliki je broj JLS koje jako zaostaju u ispunjavanju propisanih ciljeva recikliranja KO i za to gotov (još) ne snose posljedice. Gospodarstvo RH uglavnom odgovorno gospodari PO, uz izuzetak postupanja s građevnim otpadom.

Apsolutni prioritet recikliranja iskoristivog otpada u RH je OS otpadnog papira koji (ovisno od čistoće i vrste) dostiže visoku otkupnu cijenu (više ili manje od 0,50 kn/kg). Godišnje tržišni potencijal otpadnog papira u KO je oko 200 milijuna kuna. Pored toga, što je još možda i važnije, otpadni papir i karton su biorazgradivi otpad i snažno opterećuju odlagališta otpada. Trenutno (2018.) u Zagrebu otpadni papir je čak u malootkupu, a to znači da za odvojeno prikupljeni papir građani mogu odmah dobiti novac.

Za recikliranje otpada također je ključna uloga edukacije. U RH edukacija je često zanemarena karika CSGO i to na većini razina. U 2018. godini provedeno je kratko istraživanje gospodarenja otpadom na tri susjedna zagrebačka fakulteta koja se nalaze na udaljenosti manjoj od kilometar. Pokazalo da su goleme razlike. Na svim fakultetima ipak se počeo razvijati sustav OS i recikliranja otpadnog papira (slika 5). Nepoznato je, a to je primjer nedovoljne edukacije na najvišoj razini obrazovanja, da fakultetu koji je postigao najbolje rezultate, uspio količinu otpada smanjila čak tri puta! Međutim na tom fakultetu da bi se smanjila naknada trebalo je s komunalnom tvrtkom ugovoriti plaćanje prema količini, a ne prema površini.



Slika 5. Primjerno gospodarenje otpadom na FSB Zagreb (travanj 2018.)

Važno je postupno prijeći na naplatu kućnog otpada po količini ili broju pražnjenja posude. Na taj se način kućanstva motiviraju za OS, ali naročito treba upozoriti da to treba provoditi vrlo oprezno. Iskustva pokazuju da naplata po količini (obujmu) tek u kombinaciju sa stalnom edukacijom jamči dobre rezultate OS komunalnog otpada. Može se dogoditi, da kada se takav sustav uvede da građani „kućni otpad nose na posao“. Analize u nekim komunalnim tvrtkama neprijeporno su pokazale, da kada se strogo provodi po količini ili

obujmu građani kućni otpad spaljuju u kućnim pećima. To je izuzetno velika ugroza okoliša i naročito zdravlja ljudi.

5. MEHANIČKA OBRADA I MBO POSTROJENJA [9, 12]

Mehanička obrada je najčešći način postupanja s otpadom. Već tijekom sakupljanja otpada započinje mehanička obrada. Također tijekom završne faze zbrinjavanja odnosno odlaganja otpada provodi se mehanička obrada. Poznato je da mehanička obrada otpada sadržana je prije i nakon biološke, termičke i toplinske obrade/oporabe otpada. Osobito važna prednost mehaničke obrade je prilagodljivosti lokalnim uvjetima (provedba „načela blizine"). Nastavno strojevi poglavito postrojenja mehaničke obrade su modularna te se u svakom trenutku mogu prilagoditi promjenama količine pa i promjena ulaznih osobina otpada. Postrojenja za mehaničku obradu se vrlo brzo izgrade, a isto tako premjeste na drugu lokaciju. Sastoje se od strojeva koji su dobro provjereni u praksi. Automatska postrojenja postižu izvanrednu veliku čistoću izlaznog proizvoda, rade s vrlo velikom brzinom sortiranja i omogućavaju robotizaciju procesa obrade otpada.

„Mehanička obrada čvrstog otpada skup je postupaka ili procesa kojima se otpad podvrgava jednoj ili više mehaničkih operacija sa ciljem razdvajanja i pripreme frakcija za neki od procesa ponovne uporabe ili recikliranje kroz materijalnu i/ili energijsku oporabu." [12]

Širom RH se koristi tehnike mehaničke obrade, ali se može se ustvrditi da su ipak još zanemarene mogućnosti mehaničke obrade. Strojeve i postrojenja za mehaničku obradu proizvode i ugledne hrvatske tvrtke. Mehanička obrada je idealan postupak upravo za čitavo područje RH. Velika osobitost postupaka mehaničke obrade je što se može vrlo jednostavno koristit i kod malih i kod velikih količina otpada. To omogućava prihvatljivost i za male lokalne sredine, kao što su primjerice i hrvatski otoci. Dokazano da jedno malo postrojenje za sortiranje hrvatskog proizvođača može se vrlo uspješno jedan dan koristiti za sortiranje odvojenog sakupljanja papira, drugog dana za sortiranje odvojeno sakupljanje odvojeno sakupljanje otpadne plastike itd. Za veća naselja optimalna su automatska, strojna i elektronska, postrojenja za mehaničku obradu.

Primjer krupnog (glomaznog) otpada najbolje pokazuje velike mogućnosti tehnike mehaničke obrade u rješavanja problema kućnog otpada. U RH krupni otpad se redovito odvojeno prikuplja a zatim, još uvijek u mnogim JLS, se na odlagalištu pomiješa s MKO i time obezvrijedi uz snažno opterećenje okoliša. Vrlo je jednostavno glomazni otpad mehanički obraditi i zatim gotovo u potpunosti reciklirati i/ili energijski oporabiti.

Propisima je određena besplatno odvojeno prikupljanje biootpada, otpadnog papira, otpadne plastike itd. Proizlazi da će dugoročno u MKO zaostajati i manje od polovice ukupne količine ukupnog kućnog otpada. Inače glomazni otpad čini 5 do 10 % mase ukupne količine komunalnog otpada (ne samo kućnog otpada). Međutim kad se dosljedno provede odvojeno prikupljanje kućnog otpada u zaostalom MKO glomazni otpad će imati udio i veći od 50 % mase. Vrlo je jednostavno utvrditi količinu glomaznog otpada koju proizvodi pojedino kućanstvo, i to bez uvođenje složenih računalni programa za nadzor količine kućnog otpada. Osim toga ti računalni programi za nadzor količine u pravilu ne nadziru koliko glomaznog otpada proizvodi pojedino kućanstvo. Nažalost nedavno (2017.) usvojeni propis u RH, određuje da komunalna tvrtka paušalno naplaćuje svim korisnicima jednako bez obzira koliko proizvode krupnog otpada.

Osnovni postupci mehaničke obrade su:

- zbijanje,
- rezanje,
- drobljenje,
- mljevenje,
- miješanje,
- sortiranje.

Naročito važna zadaća mehaničke obrade je očistiti pojedinu frakciju za prihvatljivost na tržištu sekundarnih sirovina. Mehanička obrada osigurava razlikovanje odvojeno sakupljenog otpada od sekundarne sirovine. To je posebno osjetljiva točka gospodarenja komunalnim otpadom, koja povezuje javno i privatno gospodarstvo. Privatno gospodarstvo najčešće provodi materijalnu i energijsku oporabu otpada (slika 6). S druge strane u RH, najvećim dijelom, javne tvrtke u vlasništvu JLS prikupljaju komunalni otpad. Upravo mehanička obrada određuje na kojoj razini će otpad javna tvrtka predati privatnom gospodarstvu.



Slika 6. Balirana otpadna miješana plastika na hrvatskom uređenom odlagalištu

U diskusijama neki navode da grubo sortiranje treba provoditi u javnoj tvrtki, a fino sortiranje u privatnoj tvrtki. Kod toga pojmovi grubo i fino nisu jasni. Načelno što je manje nečistoća cijena sekundarne sirovine je viša. Međutim to također nije dovoljno precizno. Naime neke odvojeno sakupljene frakcije (npr. miješanu otpadnu plastiku) tržište ne prihvaća odnosno ne može se dobiti prihod veća treba za preuzimanje dodatno platiti. Iskustva pokazuju, da i nakon dugog godina, u odvojenom sakupljenim frakcijama komunalnog otpada može bit od 10 pa i više od 30 % mase.

Problem je i kod pripreme komunalnog otpada za energijsku oporabu. Primjerice gorivo iz otpada (GIO) treba iz komunalnog otpada mehaničkom obradom pripremiti točno prema zahtjevu korisnika GIO (pojam SRF). Svaki korisnik GIO (cementna peć, energana i sl.) ima vlastiti tehničke uvjete, te ako nije provedena kvalitetna tehnička priprema, proizvedeni GIO se neće moći prihvatiti u postrojenju za energijsku oporabu.

Uvodno je već navedeno da i EU ukazuje da u MKO otpadu zaostaje brojne prirodne vrijednosti. Za sada u RH nema sortirnice MKO, a tek su izgrađena dva prva ŽCGO-a koja postupkom mehaničke obrade iz MKO izdvajaju energijski vrijednu frakcije te do 5 % mase reciklabilnog otpada. U svakom slučaju mehanička obrada može i treba u RH biti kvalitetnije iskorištena u vrednovanju MKO.

5.1. MBO postrojenja

Prema Planu za gospodarenje KO poglavito MKO treba izgraditi dvadesetak CGO i ŽCGO s MBO postrojenjima. Grad Zagreb je odustao od spalionice, te također planira gradnju MBO postrojenja. Dva ŽCGO (Marišćina, Kaštijun) su izgrađena ali nailaze na probleme (cijena obrade, energijska oporaba, bioreaktorsko odlagalište). Izgrađeno je i jedno MBO postrojenje u privatnom vlasništvu, koje prima MKO uz cijeno 900 kn/t. Ta je cijena realna (?), ali za sada (05.2018.) je bitno viša od MBO u izgrađenim ŽCGO-ima.

Mehaničko biološka obrada (MBO) prvenstveno je novija tehnologija razvijena sa ciljem da se tehnikom suspaljivanja iskoriste (kao GIO) energetski vrijedne frakcije otpada (nerecaklibilne vrste papirnatih, plastičnih i tkanih tvari i sl.). Na određeni način MBO postrojenja su konkurencija spalionicama. MBO postrojenja su jednostavnija i jeftinija alternativa za gospodarenje MKO. Mehaničkom obradom iz MKO se proizvodi GIO. Najčešće suspaljivanje GIO se provodi u malo modificiranim: cementnim pećima, toplanama, termoelektranama, industrijskim energanama, ciglanama isl. Takva i slična postrojenja nisu pogodna za spaljivanje KO naročito MKO. Upravo mehanička obrada jamči proizvodnju točno specificiranu kakvoću goriva iz otpada, kako se ne bi ugrozila osnovna proizvodnja.

„Suspaljivanje otpad je postupak oporabe, odnosno zbrinjavanja otpada čija je prvenstvena svrha proizvodnja energije ili materijalni produkata (proizvoda) i u kojim se otpad koristi kao redovno i dopunsko gorivo ili u kojem se otpad termički obrađuje radi zbrinjavanja. To uključuje oksidacijsko spaljivanje otpada, kao druge termičke procese, poput pirolize, rasplinjavanja ili plazma procese, sve dok se rezultirajući produkti tih obrada nakon toga spaljuju.“(Zakon o održivom gospodarenju otpadom).

Mehanička obrada također početno omogućava naročito tehnikama usitnjavanja, prosijavanja i sortiranja iz MKO izdvojiti dvije frakcije:

- sitniju – težu i vlažniju frakciju (energetski manje vrijednu),
- krupniju – lakšu i suhu frakciju (energetski vrlo vrijednu).

Teža frakcija biološki se obrađuje, a lakša frakcija nizom mehaničkih operacija se pripreme za prijam u postrojenju za suspaljivanje. Postoje cementne peći odnosno cementare koje su opremljene tako da mogu u tehnološkom procesu čak 100 % koristiti GIO. U susjednoj Austriji cementna industrija 70 % energije osigurava korištenjem GIO.

S druge strane u RH, iako je cementna industrija spremna, zbog protesta zelene javnosti neke tvornice cementa jednostavno odustaju od korištenja GIO. Vrlo je zanimljivo da zeleni aktivisti koji su spriječili oporabu GIO u tvornici cementa godinama toleriraju i još će tolerirati neuređeno i neusklađeno odlaganje komunalnog otpada. Ipak jedna tvornica cementa u RH energijski oporabljuje odvojene frakcija otpada i to uvijek uz primjernu tehnologiju (NRT). Ta tvornica već godinama postiže izvrsne rezultate u održivom kružnom gospodarenju otpadom.

Tvornice cementa su u RH izvrsno geografski raspoređene i mogle bi izvrsno pomoći u o razvitku CSGO. Problem je što hrvatske cementare, kada bi sve mogle htjele prihvatiti GIO, nemaju ni približno dovoljan kapacitet. Naime ako se izgrade svi CGO-i i ŽCGO-i

proizvele bi se količine GIO drastično veća od kapaciteta cementara. Realno je problem i što su cementare privatno gospodarstvo, a većina MBO postrojenja trebala bi po Planu biti javno vlasništvo. Otvara se realna mogućnost korištenja GIO u termoelektrani – toplani Zagreb ili gradnja energane na GIO i otpadni mulj u Zagrebu (javno ili javno privatno vlasništvo).

Drugi veliki problem MBO postrojenja u dva izgrađena ŽCGO je planirani postupak biološke obrade. Tehnike mehaničke i biološke obrade se godinama provjerene, ali mogu biti krivo akceptirane. U ŽCGO je planirano da se izdvojena teža frakcija postupkom biološke obrade osuši, te zatim do 5 godina odlagati u bioreaktorsko odlagalište. Nakon pet godina odnosno nakon što se napuni kazeta i izvede gornji brtveni sloj kazete, projektirano je ovlaživanje odloženog otpada. Unošenje vlage u kazeti se potiče biološka razgradnja i proizvodnja odlagališnog plina, koji se zatim rabi za proizvodnju energije.

Neki hrvatski stručnjaci su od početka ukazivali na probleme tako osmišljenih bioreaktorskih odlagališta. Međutim gradnju dva ŽCGO-a podržala je i stručno i financijski EU. U međuvremenu EU, i naročito njen konzultant, naknadno odustaju od tehnologije bioreaktorskog odlagališta. To je za RH najbolji primjer da ne treba, bez kritičke analize prihvaćati strana stručna mišljenja. Na stručnim skupovima u RH uporno godinama se predlaže, za sve velike projekte (CGO, spalionica, odlagališta) revizija neovisnih uglednih hrvatskih stručnjaka. To treba poimati kao iskonsku podršku investitoru odnosno županijama i JLS.

Izuzetno je važno ukazati da postoje i druge tehnologije MBO otpada. U Austriji nedaleko Graza (Frohnleiten) radi postrojenje s također aerobnom biološkom obradom, ali ne za početno sušenje, već za ubrzanje razvitka aerobnih mikroorganizama. U Ljubljani je izgrađeno veliko postrojenje RECRO koje se temelji na anaerobno biološkom procesu i bioplinskoj tenlogiji. Zaključiti se može da edukacija, kako stručnjaka tako i javnosti, za RH je bila, ostaje i biti će središnji problem razvitka i MBO tehnologije.

6. BIOLOŠKA OBRADA

U RH je daleko premalo postrojenja za biološku obradu, a osobito je premalo kompostana za zeleni otpad. Kompostane nisu tehnički složena postrojenja, te nema razloga da se u RH ne inzistira na gradnji kućnih, vrtnih, kvartovskih i središnjih kompostana. Ljudi su oduvijek kompostirali vlastiti biorazgardivi otpad. Suvremeni, posebice urbanizirani, čovjek zaboravio je kompostirati. U komunalnom otpadu najveći je udio biorazgradivih frakcija (oko 70 % mase). Biorazgardive frakcije u tijelu odlagališta uzrokuju brojne nepoznate biokemijske reakcije. Zbog toga EU i hrvatska legislativa izričito propisuju odvojeno sakupljanje biootpada. Odvojeno sakupljeni biootpad treba obvezno biološki oporabiti i/ili obraditi. Međutim u nedostatku postrojenja za biološku obradu velika je opasnost da će se uz dodatne troškove i ugroze okoliša odvojeno sakupljeni biootpad negdje odložiti (baciti). Vrijedno je naglasiti da opremu za kompostiranje proizvode i hrvatske tvrtke. Izgradnja kompostana, osobito malih je brza i jednostavna, a može se i treba prilagoditi lokalnim uvjetima

Prva kompostana u RH (Zagreb Jankomir) je izgrađena krajem prošlog stoljeća. U RH trenutno u pogonu je dvadesetak postrojenja za biološku obradu otpada i to poglavito kompostana. U RH ima kompostana koja rade dobro koja čak i proširuju kapacitet. Nažalost bilo je problema s projektima komopostana. Prvenstveno poradi neugodnih mirisa prva komopstana (Jankomir) je zatvorena. U posljednje vrijeme, iako su kompostane prioritet CSGO, neki projekti za gradnju novih kompostana u RH nisu uspjeli (Prelog, Zagreb Obreščica itd.). Ponekad se zaboravlja da je i prije kod pripreme projekata biološke obrade

bilo protivljenja i zaustavljanja aktivnosti. Glavni razlog tih problema je bio nedostatak edukacije i komunikacije. Za pripremu projekata gospodarenja otpadom uz ekonomske i ekološke čimbenika, vrlo je važan (ako ne i najvažniji) sociološki čimbenik. Bez informiranja i suradnje s javnošću ne može se realizirati ni projekte biološke obrade.

Biološka obrada može se realizirati na svim razinama CSGO:

- vrtno odnosno kućno kompostiranje je mjera prevencije, umjesto odlaganja u kantu biootpad biološki obrađuje i koristi u kućanstvu,
- središnje kompostiranje je mjera recikliranja, biootpad se odvojeno prikuplja i zatim prijevozi do lokacije za aerobnu biološku obradu, a proizvedeni kompost povoljno je rabiti najčešće na i u okolici područja sakupljanja biootpada,
- anaerobna biološka obrada je mjera energijske oporabe, a kada se nastavno izvodi s kompostiranjem digestata tada to je i mjera recikliranja,
- proizvodnja stabilata je mjera tehnika biološke obrade u kojoj se smanjuje biološka razgradivost otpada i time smanjuju rizici njegovog odlaganja odnosno postupanja.

Gotovo se zaboravilo da su prvi vrtni komposteri u RH proizvedeni davne 1996. godine. Neki građani u Zagrebu i danas ih koriste, te vole naglasiti da su bolje kakvoće od onih koje je „ovih dana podijelio Bandić“ (2018.). Edukacijom nužno je motivirati pučanstvo da lokalno (vrtno, kućno) nije moda nego i najveći vlastiti prinos zaštiti okoliša. Kod lokalnog kompostiranja građanin izravno pazi koje tvari odlaže u komposter i time izravno osigurava za vlastitu upotrebu najkvalitetniji kompost. U središnje kompostane ulazi odvojeno sakupljeni biootpad, a teško je očekivati da netko u posudu za biootpad ponekad ne odloži i druge vrste otpada (pa čak i problematičan otpad).

Najveći problem kompostiranja je osigurati kvalitetu odnosno čistoću biootpada. Sasvim sigurno što u biootpadu ima manje nečistoća to će i proizvedeni kompost biti kvalitetniji.

Propisima konačni produkt aerobne biološke obrade je razvrstan u tri osnovna materijala, koji se onda namjenski rabe od ekološke poljoprivrede do usklađenog odlagališta:

- kompost određene kakvoće,
- kompostu sličan materijal,
- stabilat.

Osamdesetih godina prošlog stoljeća bile su zatvorena većina kompostana MKO. Gotovo sve su preuređene na kompostane odvojeno sakupljenog biootpada. Propisi inače zahtijevaju da se kompostira odvojeno sakupljeni biootpad. Aktualna su i promišljanja, da se mehaničkom obradom iz MKO izdvoji biorazgradive frakcije i zatim biološki obrađuju odnosno pripremaju za kasniju biološku obradu.

Kakvoća biootpada ovisi i od proizvodnog procesa (kod proizvodnog biootpada) odnosno od lokacije na kojoj se odvojeno prikuplja biootpada (kod komunalnog biootpada). Također biološki procesi uvijek se trebaju prilagoditi lokalnim uvjetima. Za kompostiranje je tako između ostalog važno i koliko je pučanstvo educirano i motivirano za mjere odvojenog sakupljanja biootpada.

Često se zanemaruje da biološka obrada osigurava energijsku oporabu biootpada. Suvremeni gradovi, polazeći od prioriteta CSGO, upravo na sinergetskim mogućnostima kombinacije biološke i termičke energijske oporabe otpada ostvaruju stanje „nulte emisije CO_2“.

Činjenica je da se komunalni biootpad sastoji iz dvije frakcije:

- zeleni otpad, ostaci povrća te voća i slično, izvrsno se kompostirjaju odnosno aerobno biološki obrađuju,
- ostaci kuhane hrane, ostaci ribe mesa i slično, izvrsno u anaerobno biološki se iskorištavaju za proizvodnju bioplina, koji se zatim na različite načine može energijski oporabiti (slika 7).



Slika 7. Prvo urbano bioplinsko postrojenje osim proizvodnog biootpada može koristiti i komunalni biootpad, a izgrađeno je u blizini Zagreba 2017. (Agroproteinka)

U komunalnom otpadu biorazgardive frakcije su velike vlažnosti, te nisu osobito pogodne za termičku obradu. Odvojenim sakupljanjem biootpada smanjuju se količine otpada pogodnog za termičku obradu i na taj način ujedno se postiže bitno veća učinkovitost postrojenja za termičku obradu. Propisana je obveza odvojenog sakupljanja biootpada iz kućanstva, a tako sakupljeni biootpada se najčešće kompostira. Zato komunalne tvrtke često educiraju kućanstva da u biootpad ne odlažu ostatke mesa, ribe i kuhane hrane. S druge strane u EU nije dopušteno više hraniti domaće životinje napojem. Tako primjerice grad Beč odovojeno prikupljeni biootpad iz kućanstva u središnjim kvartovima odvozi u bioplinsko postrojenje, a odvojeno prikupljeni biootpad iz okolnih kvartova odvozi se u središnje postrojenje za kompostiranje.

U Beču središnja kompostana (Lobau) je na otovrenoj površini, a većina kompostana u Hrvatskoj također nije u zatvorenoj hali. Neke kompostane u RH su samo natkrivene, čime se bitno smanjuje utjecaj vremenskih nepogoda (prevelikih oborina, prevelikog isušivanja). U kompostnoj hrpi treba stalno održavati ispravnu količinu vlage. U svijetu mnoga postrojenja za aerobnu biološku obradu nalaze se zatvorenoj hali. Dva kontejnera za biološku obradu u Zagrebu su izvedena za potpuno automatski rad, a zrak iz tih kontejnera – boksa se izvlači pere i propušta kroz biofiltar.

Bioplinska postrojenja koja koriste biootpad su izvrsna tehnologija materijalne i energijske oporabe biorazgradivih frakcija otpada. U RH izgrađeno je desetak bioplinskih postrojenja za biootpad uključujući i otpadni mulj iz uređaja za pročićivanje otpadnih voda. Također u RH su dva bioplinska postrojenja (Zagreb, Rijeka) koja koriste odlagališni plin. Bioplinska postrojenja su zatvorena i mala je opasnost od širenja neugodnih mirisa. Osobiti problem bioplinskih postrojenja je gospodarenje ostatkom takozvanim digestatom. Ovisno od vrste biootpada izravno ovisi i sastav odnosno kakvoća digestata. Europska komisija skoro donošenje legislative „*DIGESTAT U GNOJ“*.

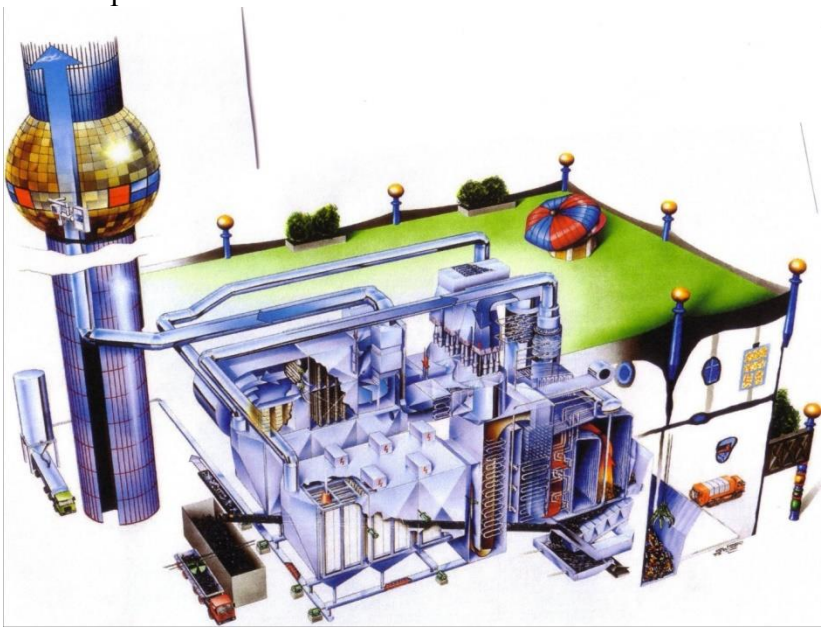
7. TERMIČKA I TOPLINSKA OBRADA [7, 13, 14]

Nužno je razlikovati energijsku oporabu od termičke oporabe otpada. Principijelno energijska oporaba je širi pojam, te uz termičku obradu uključuje i anaerobnu biološku oporabu (bioplin). Razlikovati treba i termičku oporabu od termičke i toplinske obrade.

„Termička obrada otpada (TO) su postupci spaljivanja, suspaljivanja i drugi postupci obrade otpada kojima se promjenom temperature otpada postiže promjena strukture i svojstava otpada.“(Zakon o održivom gospodarenju otpadom).

„Postrojenje za termičku obradu otpada ili „spalionica“ je svaka nepokretna ili pokretna tehnička jedinica u kojoj se spaljuje otpad s iskorištavanjem topline proizvedene izgaranjem. To uključuje oksidacijsko spaljivanje otpada, kao i druge termičke procese, poput pirolize, rasplinjavanja ili plazma procesa, sve dok se rezultirajući produkti tih obrada nakon toga spaljuju.“(Pravilnik o načinima i uvjetima termičke obrade otpada).

Razvijen je vrlo veliki broj postupaka za termičku i toplinsku obradu (slika 8). Najčešće se u javnosti pod pojmom *termička obrada* podrazumijeva spaljivanje miješanog komunalnog otpada, koji se danas poglavito rabi u kogeneracijskom ili trigeneracijskom procesu. Energija koja proizvedena spaljivanjem otpada, i to u ložištu vrlo sličnom onom za loženje ugljenom, se iskorištava za proizvodnju električne i toplinske energije (kogeneracija) i za hlađenje (trigeneracija). Kada se osigura, najmanje 70 % iskorištavanje energije otpada, tada je spaljivanje postupak energijske oporabe, a kada je manje iskorištavanje energije tada je to termička obrada otpada.



Slika 8. Spalionica Spettelau (Beč) estetski oblikovao Hundertwasser (eko aktivan)

Širom svijeta uspješno radi vrlo velik broj suvremenih spalionica, kod kojih središnji dio je postrojenje čišćenje dimnih plinova (75 % investicije). Ostaci spaljivanja komunalnog otpada iznose oko 30 % ulazne mase i tek oko 10 % ulaznog obujma otpada. Od toga je do 5 % masa opasnog otpada, koji se podzemno odlaže uz mogućnost da se u budućnosti reciklira. Neopasni ostaci spaljivanja (šljaka) se reciklira i zatim ili koristi u građevinarstvu ili koriste za prekrivanje i gradnju bočnih stijena odlagališta neopasnog otpada.

U zemljama koje uopće ne odlažu odnosno koje najmanje otpada odlažu (Švicarska, Japan, Njemačka, Švedska) spaljivanje je važan čimbenik CSGO. U pravilu spaljivanje smanjuje odlaganje otpada. To pokazuje i usporedba gospodarenja komunalnim otpadom u

velikim EU mediteranskim zemljama. Najmanje odlaže Francuska (28 %) u kojoj je i najveći udjel spaljivanja (33 %). Najviše odlaže Grčka.

CSGO u mediteranskim zemljama EU

	Odl.	*Spalj.*	*Rec.*	*Komp.*
• *Francuska (534 kg/stanov.))*	*28 %*	*33 %*	*23 %*	*16 %*
• *Italija (529 kg/stanov.))*	*41 %*	*20 %*	*24 %*	*14 %*
• *Španjolska (464 kg/stanov.))*	*63 %*	*10 %*	*17 %*	*10 %*
• *Grčka (503 kg/stanov.)*	*82 %*	*0 %*	*16 %*	*2 %*

Naročito je važna prednost termičke obrade je učinkovito smanjenje pa i otklanjanje opasnih svojstava otpada (npr. zaraznosti, biorazgradivosti). Termičku obradu otpada isključivo treba provoditi prema NRT (engleski BAT), a tada se jamči i učinkovito izdvajanje teških metala te razgradnja dioksina i furana. Vrijedna osobitost termičke obrade, i to u okvirima CSGO, je smanjenje emisije stakleničkih plinova (osobito u odnosu na odlaganje otpada). Europska komisija je 2017. godine naglasila da: „energijska oporaba podupire ciljeve akcijskog plana za kružno gospodarstvo, te je u skladu s EZ-ovom hijerarhijom otpada. Ispituje kako se uloga procesa proizvodnje energije iz otpada može poboljšati da pridonosi ispunjavanju ciljeva utvrđenih u EU energijskoj strategiji i u Pariškom sporazumu.“

Neprijeporno termička obrada ima i nedostataka. Vrlo su visoki investicioni troškovi i vrlo je velika složenost postrojenja za spaljivanje i suspaljivanje. Apsolutno nije opravdano spaljivati reciklabilni otpad. Projekt termičke obrade ne smije biti glavni cilj odgovornog postupanja s otpadom. Uvijek postrojenja za spaljivanje i suspaljivanje treba realizirati isključivo u okviru CSGO. Europska komisija je jasno ukazala da je energijska oporaba i sastavni dio kružnog gospodarenja otpadom.

Energijska oporaba u RH je tabu tema. Stručnjaci koji realno govore energijskoj oporabi se bez argumenata optužuju. Vlada strah od diskusije o spaljivanju (na Konferenciji jedan apsolutni hrvatski ekspert za termičku obradu izjavio „da tek sada (2018.) prvi put slobodno govori“). Zeleni aktivisti ponose se kada „zbog birokratskih grešaka u proceduri“ sruše projekt suspaljivanja, a kada u njihovom gardu dolazi do drame s odlagalištem otpada šute. Vrlo rado ističu primjere OS i recikliranja iz razvijenih zemalja (npr. Švicarske, Njemačke, Austrije itd.), a „zaborave“ ukazati da upravo u tim zemljama je najveći udio spaljivanja i suspaljivanja. Neki kvazi stručnjaci u javnim nastupima čak svjesno ili nesvjesno ističu da je „bolje“ odlaganje nego spaljivanje MKO.

Aktualni Plan neopravdano energijsku oporabu je, i to bez AŽC, odbacio za sljedeće plansko razdoblje (iza 2022.). S druge strane Plan, također bez AŽC, produljuje korištenje neuređenih i neusklađenih odlagališta. Odgovorni za predlaganje Plana bilo je dobro znano da zbog toga prijeti plaćanje penala prema EU. To je u osnovi neodgovorno bježanje od problem („stavljanje glave u pijesak“).

8. ODLAGANJE OTPADA [1]

Dobro je znano da RH među EU zemljama neslavno prednjači u odlaganju otpada. Nekoliko se puta u RH pokušalo propisima ograničiti neuređeno odlaganje neobrađenog komunalnog otpada. Do sada to nije uspjelo, a do sada nijedan čelnik JLS zbog toga nije smijenjen. Neodgovorno „eko znalci“, umjesto da upozoravaju ne neprocjenjivo velike rizike po okoliš i osobito zdravlje ljudi (slika 9), u javnim nastupima ističu probleme plaćanja

penala EU. Početkom 2018. godine u RH je središte pozornosti pribaviti besplatna sredstva za nabavu oprema, a ne kako u okviru CSGO povećati recikliranje i naročito izbjeći odlaganje.



Slika 9. Predizborni plakat u Zagrebu koji je prvi u RH osigurao („sanirao“) odlagalište

Temeljna Europska direktiva o otpadu iz 2008. propisuju prvenstveno smanjivanje odlaganje otpada: *„Prvi cilj je smanjivanje štetnih utjecaja na zdravlje ljudi i djelovanja na okoliš, te smanjenje nastanka otpad. također ciljevi su ponovna uporaba i smanjivanje iskorištavanja primarnih izvora (sirovina i energije“*[13].

Desetak godina kasnije Europska komisija, u Izvješću [14] o provedbi akcijskog plana za *kružno gospodarstvo* (iz 2015.) opetovano ističe prioritet smanjenja odlaganja otpada: *„Paket je uključivao zakonodavne prijedloge o otpadu s dugoročnim ciljevima za smanjenje odlaganja otpada na odlagalištima te povećanje recikliranja i ponovne uporabe.“*

Odlaganje je, naročito kratkoročno gledano, najjeftiniji i najjednostavniji način zbrinjavanja otpada. U praksi bez ikakvog nadzora se odlagalo sve vrste opasnog i neopasnog otpada. Tako su nastala smetlišta, koja sadašnja generacija treba uz deset puta veće troškove i goleme (teško procjenjive) ugroze zdravlja ljudi osigurati i/ili sanirati. Neuređeno odlaganje je:

- **nehumano,**
- gubitak prirodnih vrijednosti (sirovina i energije),
- povezano s nedovoljno poznatim rizicima (teške kovine, organski otrovi, prioni …).

Nažalost dobro je poznato da u RH se najveće količine KO (oko 80 % mase, 2017.) odlažu bez obrade. Pozitivno je što se sve više odlagališta sanira (stvarno samo osigurava) i zatvara. Trenutno (2018.) je aktivno oko 140 odlagališta. Sanira se postupno sve veći broj „crnih točaka“ (opasnim otpadom onečišćene lokacije). Uz prvenstveno podršku Fonda. Grad Zagreb je prvi započeo (1995.) i završio osiguranje smetlišta Jakuševec, te izgradio uređeno odlagalište Prudinec (2003.) bez financijske pomoći Fonda. Gradnja uređenog odlagališta Prudinec je provedeno prema tehnologiji EU, koja je kvalitetnija od tehnologije prema propisima RH (kombinirani sustav brtvljenja). U Zagrebu odlaganje KO se plaća oko 430 kn/t, ali još uvijek OS propisanih vrsta KO (pa čak ni otpadnog papira?) nije u potpunosti razvijeno.

Ulaskom u EU Hrvatska je preuzela vremenski određeno:

- zabrana odlaganja na neuređena odlagališta (ta se obveza od 2004. sustavno produljuje, a aktualni rok je 2019.),
- postupno smanjivanje količine KO koja se odlaže (do sada se ta obveza donekle ispunjavala),
- postupno smanjivanje odlaganja biorazgradivih frakcija KO (tu obvezu ni približne se ne ispunjava).

Za neispunjenje obveza RH prema EU prijeti plaćanje penala. Na upravo (2018.) održanoj Konferenciji predstavnica Svjetske banke Nataša Vetma ukazala je da RH kasni u apsorpciji financijskih EU sredstava. Zbog toga RH ne ostvaruje odgovarajući napredak u provedbi CSGO, što bi moglo dovesti do pokretanja postupka protiv RH. Očekuje se da postupak protiv RH neće završiti prije 2023. godine. Procjenjuje se da mogući iznos penala (kazne), temeljem postupanja EU prema Grčkoj i Italiji dijeli na paušalni iznos od 10.234.080 eura te iznos od 42.024 eura dnevno.

Tu prijetnju mnogi političari, pa i poneki „zeleni“, rabe za međusobno optuživanje i prozivanje. Nažalost se zanemaruje činjenica, da je zbog neuređenog odlaganja otpada, od EU penala daleko važnija ugroza okoliša i zdravlja ljudi u Hrvatsko. Neshvatljivo je kako većina stanovništva nehumano prihvaća proteste stanovništva koje stanuje uz neuređena odlagališta. Kada dolazi čak i do nasilnog zatvaranja, do sada se isplatom „naknade za izgubljenu vrijednost nekretnine“ omogućio nastavak odlaganja.

Stručnjaci izrazito ističu da se štete od odlaganja vrlo teško mogu procijeniti. Propisom EU zahtijeva da se nakon završetka odlaganja, odlagalište nadzire najmanje 30 godina (prije je bilo 20 godina). Stručnjaci ukazuju da su opasnosti na okoliš od odlaganja otpada bitno veći i od sto godina. Tijekom prvih trideset godina bitno se smanjuje proizvodnja odlagališnog plina i osobito količine procjedne vode. Međutim kod osiguranog odlagališta neobrađenog procesa dolazi do mumifikacije otpada, ali ne i do potpuno biološke i kemijske razgradnje. Kada kasnije, u mumificirano odlagalište KO i sličnog PO uđe voda odlagalište se ponovo aktivira.

Bez odlagališta otpada, u ovom času (2018.), hrvatske općine i gradovi ne bi mogli preživjeti. Švicarska je prva zemlja koja je prestala odlagati neobrađeni otpad (2002. godine). To je ostvarila provedbom CSGO i to poglavito sinergetski usklađenom djelovanju mjera materijalne i energijske oporabe. Mnogi ističu, Švicarska je bogata, a RH je siromašna te „mora“ neuređeno i neusklađeno odlagati. Posljednjih godina Švicarska je i dalje sve bogatija, a RH je i dalje siromašna iako zbrinjava milijune tona godišnje na „najjeftiniji“ način. Slično je i unutar RH gdje najbogatije županije najmanje „jeftino“ odlažu i najviše recikliraju, te su sve bogatije. S druge strane područja u RH, koja najviše odlažu a najmanje recikliraju su sve siromašnija. Zanimljivo je da među područja koja najviše odlažu i najmanje recikliraju spadaju i „siromašni“ gradovi Split, Zadar, Dubrovnik?

Stručnjaci posebno ističu da „jeftino“ odlaganje izravno ugrožava provedbu CSGO, te da treba čim prije uvesti naknadu za odlaganje. Može se i treba osmisliti tako da naknada za odlaganje otpada nije novi parafiskalni namet već izravni poticaj razvitku humanog gospodarstva. Određena iskustva neprijeporno pokazuju da upravo ekološko humano gospodarstvo postiže i najbolje izvozne rezultate.

U svakom slučaju za razvitak CSGO treba prvenstveno smanjiti urediti i uskladiti tehnologije odlaganja. Nužno je educirati, prema ciljnim grupama, sve društvene razine. Nedavno i opet jedan političar (u Zagrebu) otkriva tehnologiju „pustopolja“ za probleme lokacija odlagališta i drugih građevina za otpad. Također mnogi odgovorni za gospodarenje otpadom ne znaju razlikovati uređeno od usklađenog odlaganja.

9. ZAKLJUČAK

Nije moguće pregled tehnologija obrade otpada u RH zaključiti, a da se ne istakne:

- postala je tradicija da svaki novi ministar, bez cjelovite analize, predlaže novi Plan gospodarenja otpadom, a poneki su čak promišljali o promjeni strateških prioriteta,
- RH je bila dvije godine bez državnog Plana gospodarenja otpadom, a o krivcima za kašnjenje i posljedicama kašnjenja se uopće ne otvara diskusija,
- osnovni problemi gospodarenja otpadom se jednostavno „stavljaju pod tepih“ (nedovoljan nadzor toka otpada, javno – privatno, kašnjenje građevina za gospodarenje otpadom, neprovedba propisa, donošenje propisa koji kažnjavaju primjerne JLS, ne uvažavaju se lokalne osobitosti itd.),
- potrebno je postaviti pitanje, da li su za dugogodišnje ugroze okoliša i zdravlja ljudi u RH (odlaganjem otpada) odgovorni oni koji kao ekolozi stalno ukazuju na nedostatke termičke obrade i slično?

U RH, bar na riječima, postoji jedinstvo glede provedbe prioritetnih mjera (izbjegavanje, smanjivanje, recikliranje, kompostiranje) i na istima treba inzistirati. Međutim u RH se već trideset godina otvaraju diskusije oko termičke obrade. Na taj način stvara se prostor za kašnjenje u provedbi prioritetnih mjera. Primjerice vrijedno je analizirati zašto jedna bivši ministar ukida obveza edukacije, a u Planu za edukaciju predviđena drastično premala sredstva. Drugi bivši ministar smanjuje OS i recikliranje otpadne ambalaže. Treba i analizirati izravno djelovanje pojedinaca u obezvrjeđivanju projekata kompostana.

Preuveličavanje mogućnosti recikliranja je također zatvaranje oči pred problemima otpada i to ne samo u RH već i u mnogim nerazvijenim zemljama („*recikliranjem će se potpuno riješiti problem otpada i još će se zaraditi“).* Iskustva razvijenih zemalja, gdje se počelo poticati OS komunalnog otpada godinama prije RH, pokazuju da je praktično ostvariva granica oko 70 % ukupne mase komunalnog otpada. Zanemaruje se da u odvojenom sakupljenom komunalnom otpadu udio nečistoća je najmanje 10 %, a nerijetko dostiže i 30 % mase. S druge strane u zaostalom MKO, prema iskustvima iz Njemačke, nalazi se i do 30 % mase reciklabilnih frakcija. Dobro je poznato da se tijekom faza recikliranja neki materijali postupno se onečišćuje i gubi izvorna vrijedna svojstva (npr. otpadni papiri i kartoni), te nije ih moguće bezbroj puta reciklirati.

Nevjerojatno je koliko se u RH zanemaruje mišljenje stručnjaka. Ne postoji primjerice analiza zaključaka stručnih skupova koji se u RH usvoje tijekom kalendarske godine. U želji da se nadležnom ministarstvu pomogne u rješavanju nagomilanih problema otpada, osam stručnjaka je izradilo i osobno predalo ministru (2016.) Stručno mišljenje o gospodarenju otpadom [9]. Do danas nije pridobiven nikakav odgovor ili komentar.

Gospodarenje otpadom je *gospodarenje resursima.* Međutim problem otpada je vrlo kompleksan. Trenutno nije moguće izbjeći proizvodnju otpada, nije moguće ni sve količine otpada odvojeno prikupiti, a isto tako nije moguće sve odvojeno sakupljene količine reciklirati. Redovito se pod otpadom podrazumijeva antropogeni materijalni otpad, a suvremene spoznaje ukazuju da se ne smije zanemariti *nematerijalni otpad.* Ljudi proizvode materijalni otpad, ali proizvode i nematerijalni otpad (internet virusi, destruktivni računalni programi isl.). Temelj proizvodnje antropogenog materijalnog i nematerijalnog otpada je „glava“ ljudi. Edukacija uključujući komunikaciju su jedini način da se postupno promijene promišljanja u pozitivnom smjeru.

Upravo na tim osnovama aktualni dokument EU (2018.) polazi od inzistiranja na *inovacijama i ekološkom design-u* proizvoda odnosno ljudskih tvorevina. Europska komisija je potvrdila potrebu da se proizvod prvenstveno popravi i ponovo koristi (smanjenje otpada)

ili da se reciklira. Kod recikliranja može se iskoristiti cijeli proizvod ili se recikliraju dijelovi proizvoda za isu namjenu ili se recikliraju materijal za druge namjene. Proizvod treba reciklirati prvenstveno za istu namjenu, a tek zatim za drugu namjenu.

Osobito je važno englesku riječ *design* ne poimati samo kao osmišljavanje projekta, već kao cjelovitost stvaranja ljudske svijesti. Primjerice Europska komisija zahtijeva i od europskih organizacija da normizaciju da razviju norme srodnih područja za dulju trajnost, mogućnost ponovne uporabe i recikliranja određenih proizvoda. Sve tri europske organizacije za normizaciju su prihvatile inicijativu Europske komisije. Poticanje ekološki osmišljenih inovacija je i u RH najveća mogućnost razvitka tržišno orijentiranog i izvoznog gospodarstva. To najbolje pokazuju prezentacije hrvatskih tvrtki na nedavno održanom najuglednijem svjetskom sajmu zaštite okoliša IFAT 2018.

Nadzor toka otpada i dalje je golemi problem gospodarenja otpadom u RH. Nepoznati tokovi otpada su razumljivo i izravna posljedica zanemarivanja provedbe hrvatskih propisa. Nelagodno je spoznati da jedan ugledni hrvatski dnevni list u lipnju 2018. godine objavljuje da istražuje nenadzirani tok otpada. Tri godine taj časopis je proučavao krajnje neodgovorno postupanje s otpadom i nazvali ga ekocidom. U isto doba je jedna od nacionalnih TV kuća emitirala emisiju o „divljem" odlagalištu otpada u Zagrebu (odlagalište nije divlje, već su divlji ljudi koji ga stvaraju). Snimljeni su i kamioni koji dovoze nenadzirani otpad, ali … Na taj problem, da i kada se snimi vrijeme i broj registracije kamiona koji je istovario otpad nema poduzimanja kaznenih mjera. Već prije deset godina na taj je problem izričito upozorenu na Simpoziju u Zagrebu. Nakon deset godina u RH nije riješen problem nadziranog toka otpada, ali u razvijenim zemljama taj je problem učinkovito riješen.

Nenadzirani tokove otpada treba prioritetno spriječiti. Kod nenadziranog toka otpada nijedna održiva tehnologija obrada otpada nije prihvatljiva. Polazište ekološkog pristupa uvijek je stalna edukacija i komunikacija. Svi trebaju učiti i to stalno. Samo oni koji znaju kako učiti i od onih koji su siromašni znanjem. Znanje odnosno svekolika edukacija je temelj uspjeha razvitka odgovornog – održivog – kružnog gospodarstva u RH.

P.S.*: Završavam u očekivanja našeg finala citatima iz teksta „Bez plastike i gume ne bismo bili u finalu!", koji je 13. srpnja 2018. objavio Prof. Igor Čatić, naš najugledniji stručnjak za plastiku i gumu:*

„... stručnjaci Zelene akcije uopće nisu upoznati sa stvarnim stanjem i obmanjuju javnost. Ono što oni zagovaraju totalno je suprotno regulativi EU-a!

... Strategija o plastici Europske komisije i Prijedlog o zabrani jednokratnih plastičnih proizvoda uopće ne podržavaju kompostabilne plastične proizvode.

... No zelena akcija propagira kompostabilne vrećice, ambalažu i ostale proizvode koji se mogu kompostirati. Podržavaju EU strategiju za borbu protiv plastike, a ne znaju da najčešće bioplastika uopće nije kompostabilna, kao primjer bio-PE ili bio-PET. Pored toga kompostabilni proizvod ne može se reciklirati.

... Gumena lopta postoji 3.600 godina, te se smatra prvom kreacijom ljudskog bića."

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

SELECTION OF THE MOST RELEVANT AQUATIC POLLUTANTS IN THE CITY OF NOVI SAD AND RISK ASSESSMENT

Dusan Milovanovic*, Jelena Radonic*, Ivana Mihajlovic*, Mirjana Vojinovic Miloradov*, Miodrag Zivancev*, Veselin Bezanovic*, Maja Petrovic*

* University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia

corresponding author: Dusan Milovanovic, e-mail: dusanmilovanovic@uns.ac.rs

Original scientific paper

ABSTRACT

In order to reduce number of pollutants for water monitoring programs and optimize monitoring operating procedures, prioritization approach has been applied. The analytical data collected during the sampling campaigns of wastewater, surface water and raw water used for production of drinking water in the city of Novi Sad were used for these purposes. Priority list of pollutants has been developed based on the eco-toxicity data and respective concentration levels of selected compounds. Compounds with concentration levels exceeding eco-toxicity thresholds were taken into consideration and ranked according to the level of exceedance. For the purpose of risk assessment and risk management the decision-making tree has been developed, together with the standard operating procedures for the most relevant inorganic compounds and groups of organic compounds. As the result of this study, the system for continuous monitoring of inorganic and organic relevant compounds has been installed at the water factory of PUC "Vodovod i Kanalizacija" Novi Sad, which has also adopted developed standard operating procedures.

***Keywords**: prioritization, water pollution, monitoring, standard operating procedure*

1. INTRODUCTION

The status of the environment significantly influences the life quality not only of humans but also of other living organisms from mammals, birds, fish to microorganisms like algae, bacteria or yeasts. The water is considered as one of the most important element in life of all organisms, but at the same time it can be easily contaminated and produce also negative effects. That is the reason why monitoring of quality of water bodies has a great importance.

In European Union, Water Framework Directive (WFD) as the first joint legislation in this field, defines strategies against water pollution with the aim to achieve the good (ecological and chemical) status of all water bodies within the member states and candidate

countries. The first legislation which establishes the maximum allowed limit values (EQS) for 33 priority substances was put into effect in 2008 (Directive on Environmental Quality Standards 2008/105/EC). The both directives were replaced in 2013 by the Directive 2013/39/EU which brings additional 12 new substances, significantly modified EQS for numerous priority pollutants, and added requirements for biota monitoring in case of 8 substances, where EQS values were very low. Moreover, there is a requirement to monitor other, non-priority chemicals, which are discharged in significant quantities (defined by risk ratio) and are considered as part of Ecological status evaluation. "Indicative list of chemicals" was defined in Annex VIII of the WFD and serves as a tool for Member States to identify the potential pollutants of concern as part of Ecological status evaluation.

Serbia defined the water quality monitoring parameters within its own Law on Water (Official Gazette of Republic of Serbia 30/10, 93/2012 and 101/2016). However, in the past, the monitoring was limited to physico-chemical parameters and analysis of inorganic compounds, while organics were completely neglected. After becoming candidate country in 2012, Serbia had the obligation to implement EU legislation in all fields, including water quality monitoring. Part of the legislation has already been harmonized, but it has not been fully implemented mainly due to the equipment limitations and expertise. Currently, monitoring of the quality of surface water in Serbia is conducted by the Serbian Environmental Protection Agency (SEPA). However, regular monitoring of water quality is also performed by Institute of Public Health of Vojvodina and local public utility companies in charge of waterworks and sewerage.

For the purpose of conducting the risk assessment, prioritization procedure for detected compounds should be applied for all water bodies in order to define the specific, most relevant pollutants. The prioritization approaches have evolved in the last 20 years. Since the adoption of the WFD, it has become the obligatory procedure in the EU member states.

City of Novi Sad, as the second largest city in Serbia, with population of over 300.000 people is still without central Wastewater treatment plant. The most of the industry such as meat industries, graphic enterprises, chemical production, and farms also do not have any wastewater treatment systems, as well. Untreated wastewater is directly discharged into the Danube River at several locations, of which two are in the vicinity of the well fields used for abstraction of raw water.

In addition, the municipal solid waste (MSW) landfill with an undeveloped simple drainage system that collects leachate and storm water in the peripheral landfill canals is located in the northern part of the construction area of Novi Sad. These canals are connected to a small stream that flows into the Danube-Tisa-Danube canal, and ultimately, into the river Danube [1].

This environmental study was conducted for several reasons: to identify the most relevant pollutants in Danube surface water that could be hazardous for living organisms in surface water of Novi Sad region, to plan and implement the system for continuous quality of the raw water used for production of drinking water, and to define and implement standard operating procedures in case of emergency situation.

2. EXPERIMENTAL

Based on the location of the entire sewerage network in the City of Novi Sad 9 sampling points have been selected for the campaigns (figure 1). Four sites were located within municipal wastewater collectors (GC1', GC2', RO', RP'), five were in the Danube's riverbed, 100 m downstream of wastewater discharges (RI, GC1", GC2", RO", RP"). Sampling site RI is located upstream of the city of Novi Sad, before all discharge points, and it has been selected in order to assess the eco toxicological status of the river Danube prior to any local urban impact [2].



Figure 1. Sampling locations

All samples were collected in plastic and glass bottles and stored at 4 °C until analysis. A 800 ml aliquot of water sample were spiked with internal standard to achieve final concentration of 1μg/l and extracted with two 50 ml portions of Dichloromethane for 20 minutes. After extraction, both extracts were combined and dried with anhydrous Sodium sulphate. Small aliquots of copper powder were added into obtained extract to remove elementary sulphur. After filtration, the combined extract was evaporated using Kuderna-Danish apparatus to final volume of 1 ml. A 50 μl of extract was injected into Agilent 6890 gas chromatograph with Agilent 5973 mass spectrometric detector. The GC system was equipped with PTV injector that was programmed from 60 ^{0}C to 260 ^{0}C (5 minutes) at a rate of 40 °C/min. Capillary GC analysis was performed on a 30 m x 250 mm I.D., 0.25 mm df DB-XLB and HP-5MS column. Helium was used as carrier gas. The MSD was used in SIM mode for all samples. Each target compound was qualified by two qualifier ions and quantified by one specific or base ion. Water samples (10 ml) were placed in 20 ml gas-tight vials. No special sample preparation was required for analysis [3].

Based on the two target analyses (TA), around 300 compounds from diverse chemical groups have been selected for ecotoxicity assessment. Quantitative Structure-Activity Relationships (QSAR) approach was used to predict toxicity of selected identified organic pollutants based on their chemical structure. As the results of this analysis, lowest values of Predicted no effect concentration (PNEC) were obtained for 350 compounds. These values were obtained in three ways: EU directives, ecotoxicity databases and QSAR approach based on the acute toxicity to the standard test organisms *Daphnia magna, Pimephales promelas* as well as *Selenastrum capricornutum.*

Applied prioritization approach is based on the evaluation of the exceedance of environmental threshold values - PNEC, for all organic compounds monitored in the wastewater, Danube water, and raw water used for production of drinking water [4, 5]. PNEC values represent necessary input data for the prioritization approach. In order to identify the extent of exceedance of ecotoxicity thresholds, PNEC value for each analyte was compared to Maximum concentration (MC), obtained within TA. The MC/PNEC ratio is the indicator for ranking of all compounds of concern according to their relevance and potential negative impact on living organisms in aquatic environment. Only compounds with MC/PNEC ratio above 1 were marked as relevant and presented in this paper.

3. RESULTS AND DISCUSSION

Results of calculated prioritization based on comparison of maximum concentration levels obtained within TA and eco-toxicity thresholds are presented in table 1. Pollutants are ranked according to their relevance and threat to human population and the environment.

MC of 27 organic compounds exceeded the predicted no effect concentrations (PNEC). The highest exceedance (2.100.000 times) was noted for Heptachlor, commonly used insecticide and consequently Heptachlor epoxide (250.000 times), which is degradation product of Heptachlor formed by plants, animals and even humans after exposure to heptachlor [6].

The most hazardous compounds that are considered for continuous monitoring are classified as linear and branched alkanes, which can be explained by proximity of Oil refinery. Other important groups of compounds include hormones, pesticides, industrial chemicals, and PAHs [7].

For detection of relevant organic pollutants semi-automated device has been installed at the drinking water factory of the Public Utility Company Vodovod i Kanalizacija Novi Sad. The monitoring of organic substances was performed by semi-automated system that consists of two separate instruments: device for automated sample treatment and device for automated determination of organic pollutant concentration. The automated sample treatment device is based on membrane solid phase extraction, capable to work with unfiltered water samples containing high amount of particulate matter. The automated system sequentially delivers solvents to precondition the disk containing sorbent material, and then passes the water sample through the disk. After a preset air-dry time, the disk is washed of captured pollutants into a collection vessel using the required amounts of solvents. The delivered equipment reduces the amount of used solvents up to 90 % compared with the conventional liquid-liquid extraction method. The analytical system for determination of organic pollutants contains gas chromatograph connected to mass selective detector.

The group of experts from the relevant institutions in Serbia and Slovakia has developed Standard operating procedures (SOP) document, which was adopted by the management of PUC and will be applied in case of contamination.

Table 1. Results of MC/PNEC ratio

Compound name / NIST library	Lowest PNEC [ng/l]	Max concentration [ng/l]	MC/PNEC
Heptachlor	0.0002	420	2100000.0
Heptachlor epoxide	0.0002	50	250000.0
Benz(a)anthracene	1.8	210	116.7
Fluoranthene	6.3	510	81.0
DDT-4,4'	10	500	50.0
Endosulfan-alpha	5	230	46.0
Chlorpyrifos	1	40	40.0
Dieldrin	10	270	27.0
DDD-4,4'	25	620	24.8
Pyrene	20	490	24.5
Phenanthrene	30	360	12.0
PCB-194	0.2	1.2	6.0
Hexachlorocyclohexane-gamma	5.5	30	5.5
Octylphenol	100	540	5.4
Hexachlorobenzene	10	50	5.0
DDE-4,4'	25	110	4.4
Trichloromethane	2500	9720	3.9
Nonylphenol	300	1150	3.8
4-nonylphenol	300	1140	3.8
1,2-benzenedicarboxylic acid, dibutyl ester	600	2150	3.6
Anthracene	100	280	2.8
Di(2-ethylhexyl)phthalate (DEHP)	1300	2630	2.0
Fluorene	100	140	1.4
Chrysene	100	130	1.3
4-(1,1,3,3-tetramethylbutyl)-phenol	100	110	1.1
Toluene	4300	4410	1.0
Trifluralin	30	30	1.0

Risk management plan for each group of compounds of concern has been developed by the expert team. The Plan explains the procedures that should be put in place to reduce the impact of certain compound and the measures to reduce the concentration level below EQS. Flow chart (figure 2) summarizes the procedure for reaction in case of alarm set off at PUC.

The SOP implies that in case when the exceedance of EQS is detected for certain monitored pollutant following procedure should be applied:

- in case of alarm set off, additional sampling will be conducted at the source, and the backup analysis at the laboratory will be required to confirm the high concentration level of particular pollutant,
- when the alarm sets off, and the additional backup analysis confirms the incident, risk management plan for the pollutant with critical concentration level will be applied.

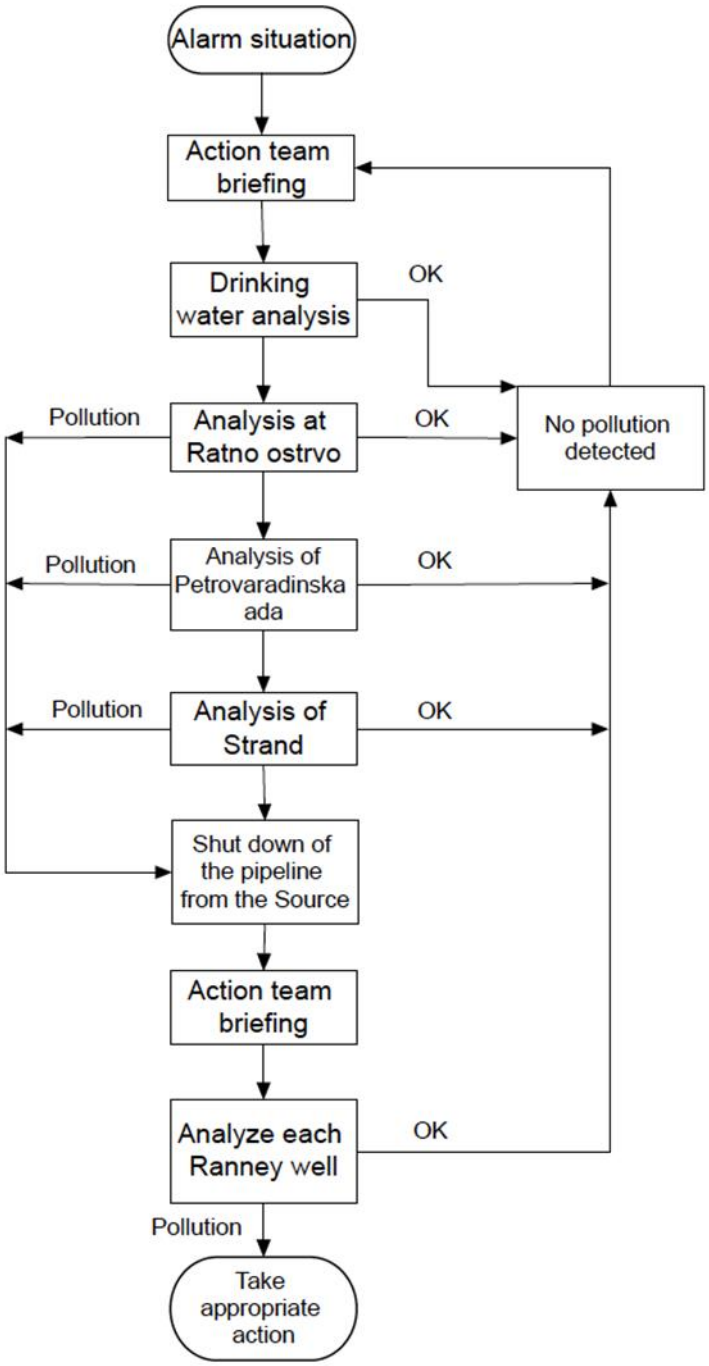


Figure 2. Flow chart of the Decision-making process

4. CONCLUSION

The objectives of this environmental were: identification of the most relevant pollutants in Danube surface water according to the Priority Substances Directive (2013/139/EC), development and implementation of raw water quality monitoring program and development and implementation of standard operating procedures for emergency situation. The most hazardous compounds that were identified as the obligatory ones for

future monitoring programs are straight-chain and branched higher alkanes, mostly originating from oil. Other important groups of detected compounds include hormones, pesticides (Heptachlor epoxide, DDT and DDD), industrial chemicals, PAHs, phenols (nonylphenols) and phthalates. According to the Priority Substances Directive (2013/139/EC) regular reviews of the current list of priority substance and priority hazardous substances are obligatory. Serbia, as a Candidate country, has not yet conducted the prioritization approach on any of the water bodies. In order to continue the work on determination of the most relevant pollutants in water bodies in Serbia it is necessary to apply up-to-date, highly-sophisticated equipment and analytical procedures in order to enable monitoring of the substances which occur in the environment in very low concentration levels.

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Acknowledgements

This environmental study has been financially supported NATO Project DriWAQ-NS ESP.EAP.SFP 984087NATO, Project of the Government of Vojvodina no. 114-451-1821/2016-03 and Ministry of Education, Science and Technological Development, Republic of Serbia (Project III46009 and Project TR34014).

UTICAJ NOVE TEHNOLOGIJE PREČIŠĆAVANJA SIROVOG KOKSNOG PLINA NA ZAGAĐENJE RADNE I ŽIVOTNE SREDINE

THE EFFECTS OF NEW PURIFICATION TECHNOLOGY OF THE CRUDE COKE GAS ON THE WORKING AND LIVING ENVIRONMENT

Sulejman Muhamedagić*, Mirsada Oruč*, Ilhan Bušatlić*

* Metalurško-tehnološki fakultet, Zenica, Bosna i Hercegovina

autor za korespondenciju: Sulejman Muhamedagić,
e-mail: sulejman.muhamedagic@mtf.unze.ba

Pregledni rad

SAŽETAK

Sirovi koksni plin, sadrži (katran, benzol, naftalin, amonijak, sumpor, amonijačnu i fenolnu vodu) i određenu količinu sitnih čestica nekoksovanog uglja i koksa. Iz sirovog koksnog plina se moraju odstraniti nus-proizvodi, koji se dalje prerađuju u hemijskoj industriji, a čisti plin se koristi kao plinsko gorivo. Kod konvencionalnih koksara proces prečišćavanja sirovog koksnog plina obuhvata veliki broj postrojenja i uređaja. Tehnologija konvencionalnog načina prečišćavanja sirovog koksnog plina izrazito zagađuje radnu i životnu sredinu. Svijet kontinuirano radi na poboljšanju postrojenja i tehnologije procesa koksovanja u cilju zaštite okoliša. Za efikasno energetsko korištenje plina iz procesa koksovanja, već su nove tehnologije istražene i testirane. U budućnosti će nove savremene koksare, nus-proizvode u sirovom koksnom plinu određenim metodama spaljivati i prevoditi u plin. Koksni plin, zajedno sa plinom iz plinifikacije katrana (katranski plin), koristiti će kao gorivuu u procesu proizvodnje i prerade čelika. Sve isparljive komponente koje se nalaze u sirovom koksnom plinu spaljuju se u kotlu utilizatoru i proizvodi se para koja se koristi za proizvodnju električne energije. U ovom radu će se usporediti tehnologije prečišćavanja sirovog koksnog plina.

Ključne riječi: *koksni plin, prečišćavanje, nus-proizvodi, okoliš*

ABSTRACT

The crude coke gas contains tar, benzene, naphthalene, ammonia, sulphur, phenolic and ammonia water and certain amount of small particles of coke and crude coal. By-products from the crude coke gas have to be removed and further processed in the chemical industry, while remain pure gas is used as a fuel. The purification process of the crude coke gas, in conventional coke ovens, requires many facilities and appliances. The conventional method of purifying crude coke is extremely polluting the working and living environment. Scientists around the world are continually working on improving all the steps in the technology of coking in order to protect the environment. New technologies for efficient energy consumption of gas from the coking process have already been explored and tested. In the future, by using specific methods, the modern coke ovens will burn their by-products or convert these by-products into gas. The coke gas along with the gas obtained by gasification of the tar is used as fuel in the process of steel production and processing. All volatile components contained in raw coke gas are burned in the boiler installation and the generated steam is used in the electrical energy production. In this paper, the technologies of purification of raw coke gas will be compared.

Keywords: *coke gas, purification, by-products, environment*

1. UVOD

Prva visoka peć u Bosni i Hercegovini izgrađena je 1891. godine u Varešu, kad počinje i eksploatacija željezne rude. U periodu 1892. -1893. godine u Zenici su izgrađena prva postrojenja za proizvodnju i preradu čelika. Godine 1954. puštena je u rad I visoka peći i prva koksna baterija. U periodu 1955-1958. godine izgrađene su visoka peć, II i III i koksne baterije II, III i IV. U 1979. godini izgrađena je visoka peć IV, zapremine 2002 m^3, kapaciteta 1 250 000 t /godinu. U 1982-oj godini puštena je u rad koksna baterija V, sa 65 kosnih peći, kapaciteta 720 000 t koksa /godinu [1].

Osnovna djelatnost koksara kao dio integralne željezari je da proizvede koks za potrebe visoke peći i isporuči prečišćeni koksni plin za potrebe ostalih potrošača. Koksna baterija se sastoji od više koksnih peći**,** koje rade u istom tehnološkom režimu. Koks se proizvodi u koksnim pećima suhom destilacijom (koksovanjem) kamenih ugljeva, koji imaju koksujuću sposobnost, bez prisustva zraka na temperaturama 950 do 1000 ^{0}C. Danas veći udio svjetske proizvodnje metalurškog koksa se proizvodi u konvencionalnim koksnim baterijama tipa vertikalnih peći. U procesu koksovanja nastaje koks i plinoviti nus-proizvod (sirovi koksni plin). U cilju iskorištenja koksnog plina u procesu proizvodnje gvožđa i čelika potrebno je izvršiti njegovo hlađenje i čišćenje. Proizvodnja koksnog plina je oko 400 Nm^3/t koksa, toplotne moći oko 18,0 MJ/m^3. Sastav sirovog koksnog plina zavisi od vrste koksujućih ugljeva (sadržaja isparljivih komponenti) i procesa koksovanja. Sirovi koksni plin pored osnovnih komponenata H_2, CH_4, CO i CO_2 sadrži u manjoj količini: katranske pare, benzolske ugljikovodike, amonijak, naftalin, sumporna jedinjenja, cijanidna jedinjenja i dr. Na koksari u Zenici iz koksnog plina se izdvaja: katran, amonijak, naftalin, proizvodi amonijum sulfata, a prečišćavaju se amonijačne i fenolne otpadne vode [2].

U 2008. godini puštena su u rad rekonstruisana i modernizovana postrojenja gdje je uvedena nova tehnologija biološkog tretiranja otpadne vode. Otpadne vode koksare biološki se obrađuju uz primjenu nitrifikacije, denitrifikacije i mikro-organizama. Nakon prečišćavanja

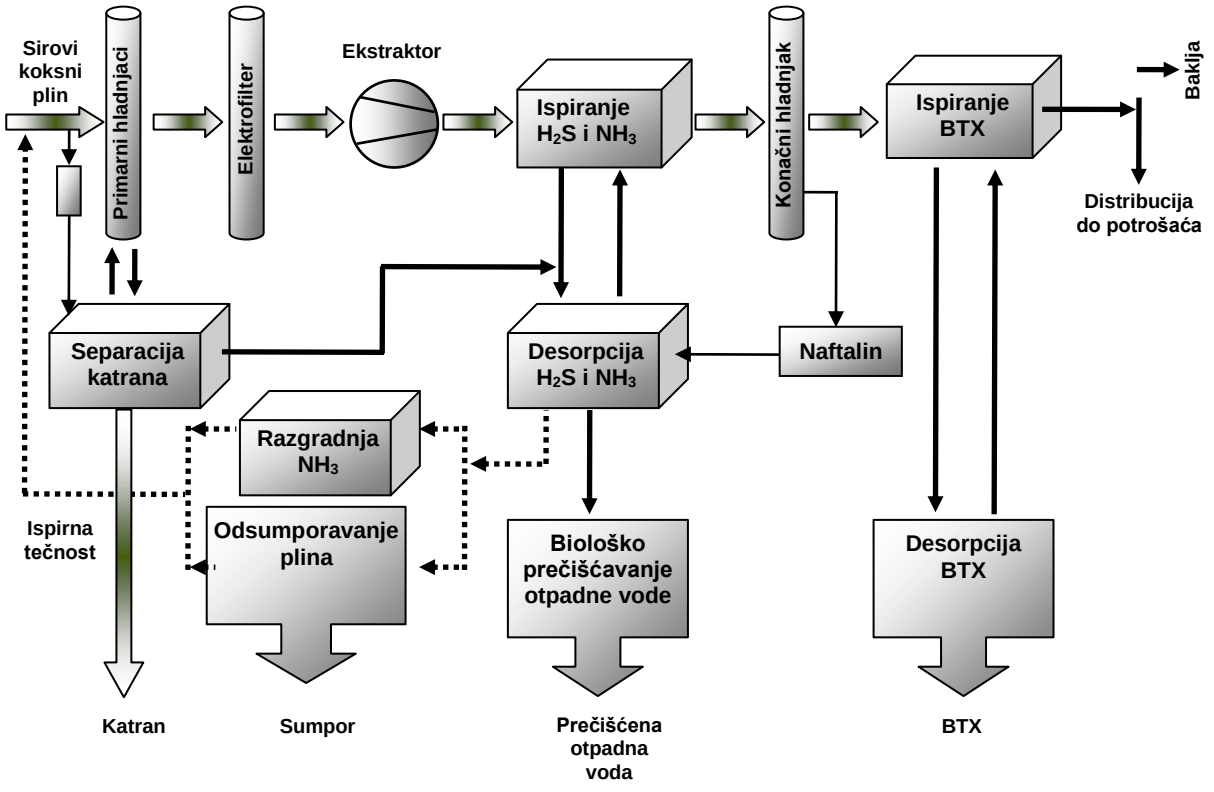
otpadna voda se ispušta u rijeku Bosnu. Koksara u Zenici nema postrojenja za odsumporavanje plina i izdvajanje: Benzena, Toluena, Ksilena (BTX).

Posljednjih 20 godina u svijetu se kontinuirano radi na poboljšanju postrojenja i tehnologija za proizvodnju koksa i prečišćavanja sirovog koksnog plina u cilju zaštite radne i životne sredine. Za efikasno energetsko korištenje plina iz procesa koksovanja, već su istražene i testirane nove tehnologije obrade i korištenja koksnog plina.

2. PREČIŠĆAVANJE SIROVOG KOKSNOG PLINA NA KONVENCIONALNIM KOKSARAMA

2.1. Hlađenje sirovog koksnog plina

Sirovi koksni plin nastaje u procesu koksovanja. Iz koksnih peći sirovi koksni plin sa temperaturom 700 do 850 ^{o}C odlazi u sabirni plinovod u kojem se hladi pomoću amonijačne vode do 80 - 85°C. Na slici 1 data je blok šema prečišćavanja sirovog koksnog plina na novo izgrađenim konvencionalnim koksarama [3].



Slika 1. Blok šema prečišćavanja sirovog koksnog plina [3]

Hlađenjem sirovog koksnog plina u sabirnom plinovodu pored kondenzacije katrana i vodene pare u vodi, dolazi do rastvaranja NH_3, CO_2, H_2S, HCN, HCl, SO_2, SO_3 i niza drugih spojeva. Ovaj plin dalje odlazi u plinski separator u kojem se odvaja tečna faza (amonijačna voda, katran i sitne čestice nekoksovanog uglja i koksa). Iz plinskog seperatora plinovita faza odlazi u primarne hladnjake sa horizontalnim cijevima za hlađenje vodom do 30 - 35 °C. U hladnjacima iz sirovog koksnog plina izdvaja se kondenzat plina (lagani katran, naftalin, amonijačna voda). Koksni plin poslije hladnjaka prolazi kroz elektrofiltere radi

elektrostatičkog čišćenja od čestica katrana, koje se nalaze u maglovitom stanju. Plin dalje odlazi u ekstraktor, gdje se vrši odsisavanje i transport plina na ispiranje H_2S i NH_3. Nakon desorpcije H_2S i NH_3 plin ulazi u konačni hladnjak. Dalje hlađenje plina vrši se u konačnom hladnjaku svježom tehničkom vodom temperature 20 – 25 °C. Pri hlađenju ispire se naftalin. Radi potpunijeg izdvajanja amonijaka temperatura koksnog plina poslije konačnog hladnjaka treba da bude maksimalno 30 °C. Ohlađeni i prečišćeni plin od naftalina poslije konačnog hladnjaka odlazi u naftalinske ispirače (skrubere). U skrubere sa dna ulazi plin a sa vrha se dozira voda koja iz plina vrši apsorpciju amonijaka. Po završetku ispiranja amonijaka plin se koristi kao gorivo u pogonima željezare. U toku prečišćavanja sirovog koksnog plina nastaju amonijačne i fenolne otpadne vode koje se biološki prečišćavaju uz primjenu nitrifikacije, denitrifikacije i mikro-organizama [2].

Koksare koje su izgrađene u posljednjih 20 godina, imaju nova postrojenja za izdvajanje: Benzena, Toluena, Ksilena (BTX), desorpciju BTX-a i odsuporavanje prečišćenog plina.

2.2. Seperacija katrana i amonijačne vode

U seperatoru se izdvajaju sitne čestice uglja, koksa i kondenzat katrana iz sirovog koksnog plina i odlaze do dekantera, također kondenzat katrana iz primarnih hladnjaka dolazi u dekantere. U dekanterima se procesom sedimentacije odvoji voda od katrana, a čvrste čestice se talože. Mehanički očišćena amonijačna voda otiče iz dekantera do tanka za amonijačnu vodu koja se pumpama u zatvorenom ciklusu doprema do sabirnog plinovoda za hlađenje sirovog koksnog plina. U toku prečišćavanja sirovog koksnog plina izdvaja se oko 39,00 kg katrana/t koksa. Odvajanje katrana od amonijačne vode vrši se u sistemu mehaniziranih dekantera.

2.3. Primarni hladnjak

Plin sa temperaturu 82 – 85 ^{0}C, s podpritiskom 0,5 – 1,0 kPa i visokim sadržajem vodene pare prolazi kroz primarne hladnjake sa horizontalnim cijevima. Ova smjesa se hladi (rashladnom) vodom iz zatvorenog ciklusa. Primarni hladnjak ima zadatak da ohladi koksni plin i izvrši izdvajanje kondenzata katrana sa naftalinom i amonijačnom vodom. U tabeli 1 dat je prosječan hemijski sastav sirovog koksnog plina pri ulazu u primarni hladnjak [4].

Tabela1. Hemijski sastav sirovog koksnog plina na ulazu u primarni hladnjak [4]

H_2O para	H_2	CH_4	N_2	CO	CO_2	C_nC_m	H_2S	Amonijak	Naftalin	Benzol	Katran
%	%	%	%	%	%	%	g/m^3	g/m^3	g/m^3	g/m^3	g/m^3
43	29	13	5	3	2	1	14	max. 8,5	max. 10	max.30	max.40

U toku cirkulacije kondenzata i amonijačne vode na primarnim hladnjacima dolazi do ispiranja naftalina i do intenzivne absorbcije NH_3 i kiselih sastojaka iz plina: CO_2, H_2S i HCN. Za obezbjeđenje kvalitetnog hlađenja plina bitna je optimalna temperatura i potrebna količina rashladne vode. U ovim hladnjacima se veći dio vodenih para kondenzira i izvrši se kontinuirano izdvajanje kondenzata katrana sa naftalinom i amonijačnom vodom. U tabeli 2 dati su osnovni parametri za sirovu amonijačnu vodu pri kondenzaciji u primarnom hladnjaku [4].

Tabela 2. Osnovni parametri sirove amonijačne vode [4]

NH_3-voda	Ukupni NH_3	Vezani NH_3	Fenol	Katran	SO_4	Cl	pH	Viskoznost na 40 ^{0}C
m^3/h	g/l	g/l	g/l	mg/l	mg/l max.	mg/l max		Pa.s
20	4-6	1,2-1,6	1,1-2,4	200-1000	250	1500	8,5-9	$0,7x10^{-3}$

U tabeli 3 dati su osnovni parametri kondenzata katrana iz primarnih hladnjaka [4].

Tabela 3. Osnovni parametri kondenzata katrana iz primarnih hladnjaka [4]

Kondenzat katrana iz		Ukupni NH_3	Vezani NH_3	Katran	Čvrste čestice	Gustoća	pH	Viskoz-nost na 25 ^{0}C
hladnjaka	plina							
m^3/h	m^3/h	g/l	g/l	%	%	kg/dm^3		Pa.s
136	27	5-8	1,2-1,6	5	2	1,01-1,03	8,5-9	1,35

Plin sa visokim sadržajem vodene pare se ohladi u primarnim hladnjacima na temperaturu 25 - 28 ^{0}C i izlazi s podpritiskom 1,5 – 2,5 kPa prema ostalim postrojenjima za prečišćavanje.

2.4. Elektrofilteri i extraktor

Ohlađeni koksni plin temperature 30 – 35 °C odlazi iz donjih dijelova primarnih hladnjaka sa manjom količinom kapi katranovog kondenzata i katrana i prolazi kroz elektrofiltere. U elektrofilterima se vrši čišćenja plina od čestica katrana, koje se nalaze u maglovitom stanju.
Plin dalje odlazi u ekstraktore, gdje se vrši odsisavanje i transport koksnog plina, zatim kroz konačni hladnjak i amonijačno odjeljenje do potrošača koksnog plina. Estraktor isisava sirovi koksni plin od sabirnog plinovoda koksnih baterija kroz seperator, primarne hladnjake i elektrofilter, a zatim ga tlači kroz ostala postrojenja nus-produkata do potrošača. Ekstraktori predstavljaju centralna postrojenja, jer povezuju rad baterije (odvođenje plina, hidraulični režim vuče) sa radom svih odjeljenja nus-produkata i dalje sa svim potrošačima koksnog plina [2].

2.5. Izdvajanje amonijaka

Odvajanje katrana od sirove amonijačne vode vrši se filtracijom, pomoću pješčanih filtera. Isparen NH_3 vodom se hladi u izmjenjivačima toplote i pločastim hladnjacima. Ukupni sadržaj amonijaka (slobodni i čvrsto vezani amonijak) u amonijačnoj vodi potrebno je razgraditi, tj. smanjiti na vrijednost manje od 200 mg/l. Ohlađena isparena amonijačna voda (tabela 4) odlazi na biološko prečišćavanje otpadnih voda [4].

Tabela 4. Parametri za isparenu amonijačnu vodu [4]

NH_3-voda	Temp. iz		Ukupni NH_3	Cijanidi	Fenol max.	Katran max.	Cl	S	SO_4	pH
	1*	2**								
m^3/h	^0C	^0C	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
24	100	30	200	20	2000	50	1500	5	250	9-9,5

* izlaz iz destilacione kolone; ** izlaz iz hladnjaka

2.6. Proizvodnja amonijum sulfata

Koksni plin nakon prolaza kroz ekstraktor hladi se u konačnom hladnjaku s horizontalnim cijevima. Hlađenje koksnog plina vrši se svježom tehničkom vodom temperature 20 – 25 °C, u količini od 100 m^3/h. Pri hlađenju ispire se i naftalin. Kondenzat plina koji je zasićen naftalinom iz konačnog hladnjaka neprekidno se odvodi u rezervoar (saturator) u tvornicu za proizvodnju amonijum sulfata. Ovdje se vrši razdvajanje amonijaka iz plina prolaskom kroz otopinu sumporne kiseline. Prolaskom kroz otopinu sumporne kiseline amonijak prelazi u amonijum sulfat oko 12,00 kg/t koksa, koji kristalizira na dnu saturatora. Suspenzija kristala u vlastitom rastvoru se ispumpava iz saturatora ejektorom i odvodi na centrifugiranje. Koksni plin nakon odstranjivanja kapi vlastitog rastvora u seperatoru odlazi plinovodom do konačnog hlađenja [2].

2.7. Konačno hlađenje koksnog plina i izdvajanje naftalina

Koksni plin poslije ekstraktora dovodi se u konačni hladnjak s horizontalnim cijevima iz postrojenja za proizvodnju amonijum sulfata. Hlađenje koksnog plina vrši se svježom tehničkom vodom temperature 20 25 °C, u količini od 100 m^3/h. Na vrhu konačnog hladnjaka se doprema pumpama smjesa plinskog kondenzata i djelimično zasićenog ulja i to je prvi stepen ispiranja naftalina. Za efikasno izdvajanje naftalina iz plina potrebno je obezbjediti dovoljnu količinu i temperaturu industrijske vode kao i potrebnu emulziju ulja. Veća kontaktna površina plina i ispirnog ulja omogućuje veći stepen izdvajanja naftalina. Ohlađeni i prečišćeni koksni plin od naftalina poslije konačnog hladnjaka odlazi u naftalinski ispirač u tri uzastopno spojena amonijačna skrubera (ispirača). U ovim ispiračima se vrši drugi stepen odvajanja naftalina.

Nakon izdvajanja naftalina kemijska analiza očišćenog koksnog plina data je u tabeli 5 [5].

Na koksari u Zenici nema postrojenja za odsumporavanje koksnog plina. Kod novo izgrađenih koksnih baterija očišćeni koksni plin od naftalina odlazi u postrojenja za odsumporavanje.

Tabela 5. Hemijska analiza očišćenog koksnog plina [5]

Komponente	Sadržaj, %
H_2	55,83 - 59,69
CH_4	24,28 - 26,94
N_2	4,52 - 9,94
CO	3,34 - 3.78
Etilen	2,01 - 2,31
CO_2	1,58 - 2,02
Etan	0,68 - 0,82
O_2	0,38 - 0,87
H_2S	0,38 - 0,59
Benzol	0,01 - 0,19
Propilen	0,12 - 0,17
Propan	0,06 - 0,12
Acitilen	0,04 - 0,10
Cijanovodik	0,0008 – 0,12
Amonijak, g/Nm^3	max. 5,0
Naftalin, g/Nm^3	max. 0,3
Katran, g/Nm^3	max. 6,0

2.8. Izdvajanje benzola

Benzol se sastoji iz lako isparljivih ugljikovodika, uglavnom benzen, toluen, xylen, (BTX). Benzol se izdvaja iz koksnog plina prvenstveno radi toga što je koristan nus-proizvod za dalju preradu u hemijskoj industriji. Na koksari u Zenica se ne izdvaja benzol.

2.9. Biološko prečišćvanje otpadnih voda

Do 2008. godine tehnološki proces prečišćavanja amonijačni i fenolni voda je bio bez nitrifikacije i denitrifikacije a baziran na spoljašnjem gajenju bakterija, naročito za uklanjanje sulfocianida [6]. Rad svih postrojenja i proces prečišćavanja otpadnih voda se vodio ručno. U 2008. godini puštena su u rad rekonstruisana i modernizovana postrojenja za novi proces biološkog tretiranja koksne otpadne vode. Novi proces biološkog tretiranja projektovan je i izveden tako da koristi posljednja naučna i tehnološka znanja na polju biološkog tretiranja (obrade) koksne otpadne vode uz primjenu nitrifikacije, denitrifikacije i micro-organizama. [7]. Prečišćena voda iz bazena za prerađenu otpadnu vodu pumpama se kontinuirano doprema na pješčani filter i poslije filtriranja odlazi u rijeku Bosnu. U tabeli 6 dati su projektovani, očekivani, ulazni i izlazni parametri kvaliteta vode sa postrojenja za biološko prečišćavanje otpadnih voda [6].

Tabela 6. Parametri ulazne i izlazne vode [6]

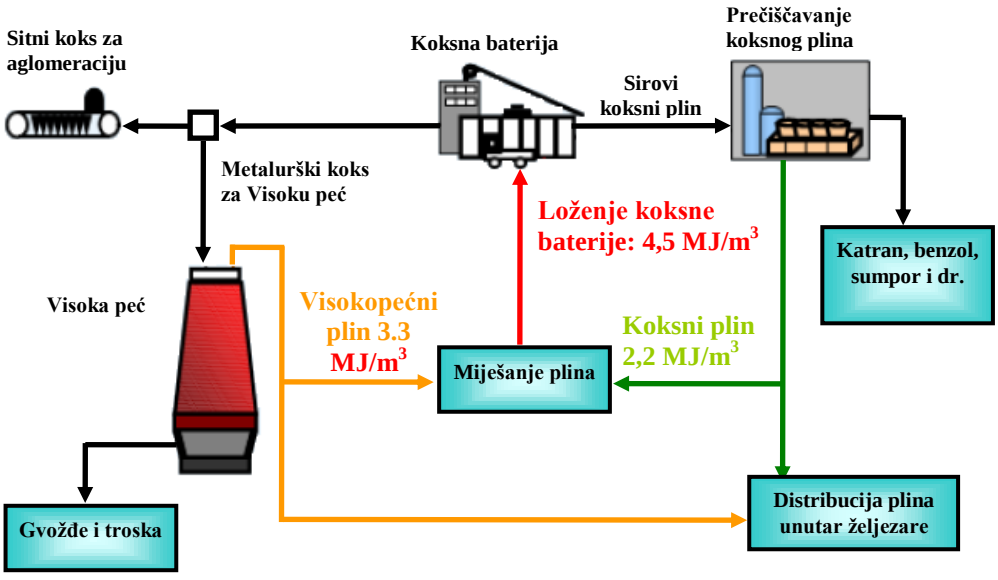
Komponente	Projektovani	Očekivani	Ulaz	Izlaz	Efikasnost
COD, mg/l	5000	500	3769-4400	60-114	97,77
Fenoli, mg/l	1300	0,1	1080-1475	0,038-0,062	99,99
Cijanidi, mg/l	15	0,01	12,8-18,6	0,001-0,003	99,98
Nitrati, mg/l	30	10	51-134	6-10	90,71
Amonijak, mg/l	200	10	146-200	5-9	94,35

2.10. Baklja koksnog plinovoda

Baklja koksnog plinovoda namijenjena je za rasterećenje plinovoda koksnog plina. U slučaju kada se trenutno pojavi višak koksnog plina zbog poremećaja bilansa potrošnje dolazi do povećanja pritiska u plinovodu. U takvim situacijama baklja se automatski otvara višak koksnog plina se spaljuje. Kad se uspostavi novi bilans potrošnje baklja za zatvara i prestaje sagorijevanja viška plina.

2.11. Korištenje koksnog plina

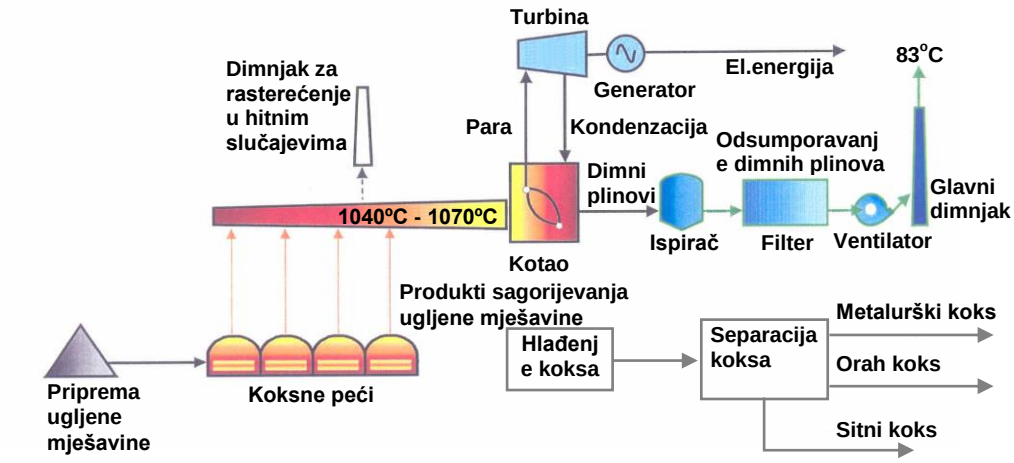
Očišćen koksni plina se koristi kao energent za grijanje koksnih peći i u ostalim pogonima u integralnoj proizvodnji gvožđa i čelika. Na slici 2 data je blok šema potrošnje očišćenog koksnog plina u željezari [3].



Slika 2. Tipični tok korištenja koksnog plina u integralnoj željezari [3]

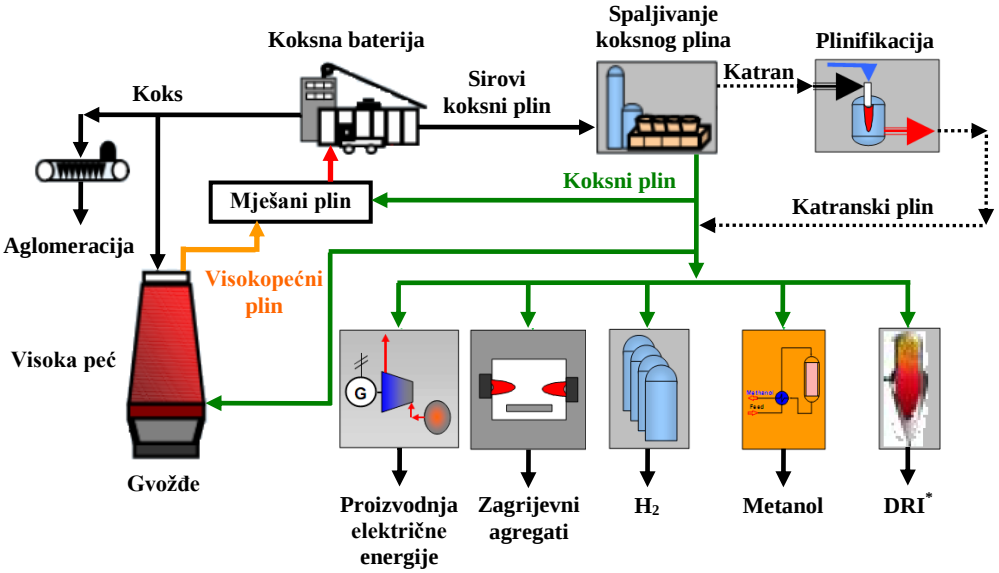
3. PREČIŠĆAVANJE SIROVOG KOKSNOG PLINA NA NOVO IZGRAĐENIM KOKSARAMA

Prečišćavanje koksnog plina i dalja prerada nus-proizvoda su izraziti zagađivači radne i životne sredine. U svijetu se kontinuirano radi na poboljšanju postrojenja i procesnih tehnologija koksovanja u cilju zaštite okoliša. Za efikasno energetsko korištenje plina iz procesa koksovanja, već su istražene i testirane nove tehnologije. Na slici 3 dat je šematski prikaz postrojenja za proizvodnju električne energije, gdje se sve isparljive komponente iz koksne mješavine spaljuju u kotlu utilizatoru i proizvodi para koja se koristi za proizvodnju električne energije [8].



Slika 3. Šema postrojenja za proizvodnju električne energije [8]

U budućnosti nove savremene koksare će imati dva proizvoda, koks i plin. Na slici 4 data je šema potrošnje koksnog plina kod nove tehnologije prečišćavanja koksnog plina [8].



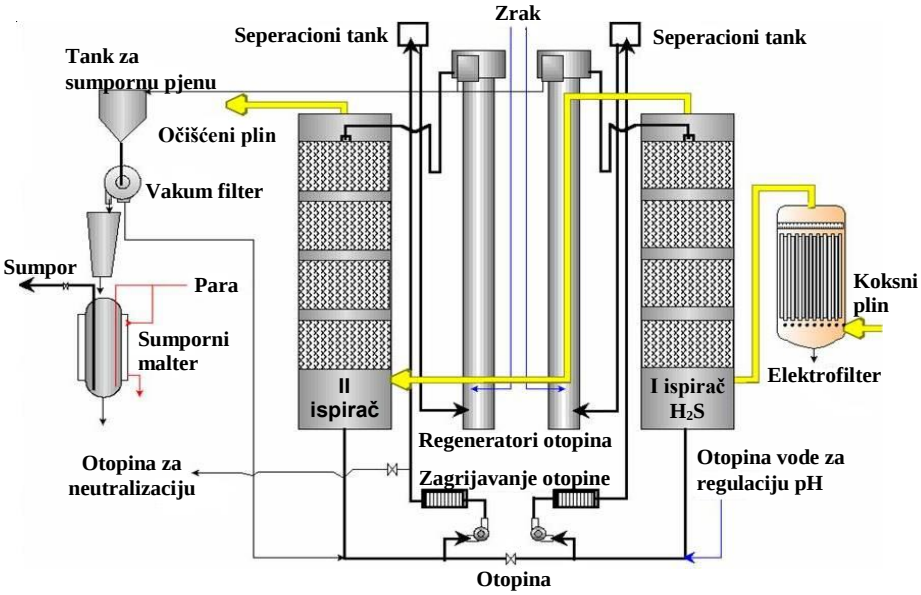
* postrojenje za proizvodnju direktno reduciranog gvožđa [8]

Slika 4. Šema nove tehnologije obrade i korištenja koksnog plina

Nus-proizvodi se određenim postupcima spaljuju i prevode u plin. Koksni plin se zajedno sa plinom iz plinifikacije katrana (katranski plin) koristi za loženje koksne peći, proizvodnju električne energije, za loženje zagrijevnih peći, u hemijskoj industriji i u procesu proizvodnje direktno reduciranog gvožđa (DIR) i dr. Kalorična moć plina je oko 23,2 MJ/Nm^3 [8].

3.1. Odsumporavanje koksnog plina

Koksare koje su građene u posljednjih 20 imaju postrojenja za odsumporavanje koksnog plina. Postoji više tehnologija koje se koriste za odsumporavanje koksnog plina. Na slici 5 data je tehnološka šema jednog postrojena za odsumporavanja koksnog plina. Ova tehnologija odsumporavanja koksnog plina se koristi u mnogim novoizgrađenim koksarama [9].



Slika 5. Šema odsumporavanja koksnog plina [9]

4. ZAKLJUČAK

- na starim koksnim baterijama, kod prečišćavanja sirovog koksnog plin izdvajaju se nus-proizvodi: katran, amonijak, amonijum sulfat, naftalin i benzol kao poluproizvodi za preradu u hemijskoj industriji,
- kod hlađenja i čišćenja sirovog koksnog plina nastaju amonijačne i fenolne otpadne vode,
- za prečišćavanje sirovog koksnog plina i prečišćavanje amonijačne i fenolne otpadne vode potrebna su zahtjevna postrojenja sa specifičnim tehnologijama i korištenje velikog broja hemijskih jedinjenja,
- postrojenja za prečišćavanja sirovog koksnog plina, amonijačne i fenolne otpadne vode su veliki zagađivači radne i životne sredine,
- investicioni i troškovi održavanja postrojenja za izdvajanje nus-proizvoda kod prečišćavanja sirovog koksnog plina su visoki, što utiče na povećanje cijene proizvedenog koksa,

- savremene koksare imaju dva proizvoda, koks i plin,
- sirovi koksni plin se određenim postupcima spaljuje i prevode u plin, koji se može koristiti kao energent u procesu proizvodnje i prerade čelika u kemijskoj industriji ili za proizvodnju električne energije,
- nova tehnologija obrade sirovog koksnog plina, manje zagađuje radnu i životnu sredinu i
- ovakva tehnologija obrade sirovog koksnog plina ima niže investicione i troškove održavanja, što utiče na smanjene cijene proizvedenog koksa.

5. LITERATURA

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POVEĆANJE EFIKASNOSTI PRIMJENE KALCIJEVOG LETEĆEG PEPELA U CEMENTNIM KOMPOZITIMA PUTEM MEHANIČKE PRIPREME

ENHANCING THE EFFECT OF CALCAREOUS FLY-ASH IN CEMENT COMPOSITES THROUGH MECHANICAL PREPARATION

Adnan Mujkanović*, Marina Jovanović*, Amel Zahirović**

* Metalurško-tehnološki fakultet, Zenica, BiH
** Institut Kemal Kapetanović, Zenica, BiH

autor za korespondenciju: Adnan Mujkanović, e-mail: adnan.mujkanovic@mtf.unze.ba

Izvorni znanstveni rad

SAŽETAK

Leteći pepeo je nusproizvod koji nastaje sagorijevanjem ugljena. Koristi se kao dodatak cementima i cementnim kompozitima, te poboljšava obradivost, povećava kasne čvrstoće i trajnost cementnih kompozita. U ovom radu istraživan je utjecaj mehaničke prerade kalcijevog letećeg pepela na svojstva cementnih kompozita. Pripremljena je referentna mješavina bez letećeg pepela, te mješavine u kojima je izvršena zamjena 30 mas. % cementa s netretiranim letećim pepelom, s prosijanim pepelom, te sa samljevenim pepelom. Ispitana je standardna konzistencija, vrijeme vezivanja, postojanost volumena, tlačna i savojna čvrstoća, te je zaključeno da mehanička priprema ima veliki utjecaj na svojstva cementnih kompozita.

***Ključne riječi**: nus-proizvodi, leteći pepeo, prosijavanje, mljevenje, mehanička prerada, zamjena za cement*

ABSTRACT

Fly ash is a byproduct of coal combustion. It is widely used as a supplementary cementitious material that improves late-age strength, workability and durability of concrete. This paper investigates the effect of mechanical processing of calcareous fly ash, used as partial substitute for cement, on the performance of cement composites. Reference mixture without fly ash and mixtures with 30 wt. % of fly ash as a cement replacement were investigated. Mixtures with fly ash were prepared with raw fly ash, sieved fly ash and grinded fly ash. Setting time, standard consistency, soundness, flexural and compressive strength of

mixtures were tested, and it was concluded that mechanical preparation of fly ash has excessive influence on its effectiveness as supplementary cementitious material.

***Keywords**: by-product, fly ash, sieving, grinding, mechanical processing, cement replacement*

1. UVOD

Leteći pepeo je nusproizvod sagorijevanja ugljena u termoelektranama koji se pomoću elektrostatskih filtarskih uređaja izdvaja iz otpadnih plinova. Ovaj materijal je potrebno zbrinuti i prema njemu postupati kao prema građevinskom otpadu, izuzev u slučajevima kada spada u klasu opasnih otpada. Zbog svojih specifičnih fizikalno kemijskih svojstava koristi se kao djelomična zamjena za cement, čime se poboljšavaju svojstva svježeg i očvrsnulog cementnog kompozita, ali i smanjuje potrošnja prirodnih resursa, fosilnih goriva, te emisija štetnih plinova (CO_2, NO_x, SO_x...). Naime, leteći pepeo pripada grupi tzv. pucolanskih materijala, a to su materijali koji ne posjeduju vezivna svojstva, ali zbog toga što su bogati amorfnim SiO_2 imaju sposobnost da kroz reakciju s hidratacijski nastalim portlanditom ($Ca(OH)_2$) doprinose prirastu čvrstoće cementnih kompozita. Utjecaj letećeg pepela u cementnom kompozitu u najvećoj mjeri ovisi o njegovom kemijskom sastavu, odnosno o udjelu amorfne faze i finoći čestica [1].

Leteći pepeo se koristi na dva osnovna načina: kao mineralni dodatak cementu i kao mineralni dodatak betonu, a njegova upotreba je regulirana odgovarajućim standardima. U standardu BAS EN 197-1:2013 definirani su kriteriji za upotrebu kalcijevog i silicijevog letećeg pepela u proizvodnji portland cemenata s dodacima (CEM II), pucolanskih cemenata (CEM IV) i miješanih portland cemenata (CEM V) [2]. Standard BAS EN:450-1:2012 propisuje kriterije koje leteći pepeo mora zadovoljiti da bi se mogao koristiti kao mineralni dodatak za proizvodnju betona [3]. Kalcijev leteći pepeli ne zadovoljavaju kriterij maksimalnog dozvoljenog sadržaja reaktivnog CaO (max. 10 %) i to je razlog da je njihova direktna primjena kao dodatka betonu svedena na minimum [4].

Kalcijevi leteći pepeli nastaju sagorijevanjem lignita i većeg broja mrkih ugljena i stoga se ogromne količine ovog pepela svakodnevno proizvode u termoelektranama širom svijeta. Posljedica toga je povećavanje pritiska na tijela zadužena za standardizaciju da donesu odgovarajuće smjernice i propise kojima bi se omogućila racionalna upotreba ove vrste letećeg pepela kao mineralnog dodatka za beton [5].

To je razlog i zašto se vrše intenzivna istraživanja različitih aspekata utjecaja kalcijevog letećeg pepela na svojstva cementnih kompozita. Jedno od najznačajnijih svojstva letećeg pepela, neovisno o njegovom podrijetlu i vrsti, je reaktivnost koja pokazuje u kojoj mjeri ovaj dodatak posjeduje pucolanska svojstva. Do sada su razvijene različite fizikalne i kemijske metode povećanja reaktivnosti letećeg pepela. Kemijske metode aktivacije zasnivaju se na modifikaciji površine pomoću kemijskih reagensa, dok u mehaničke metode spadaju mljevenje i klasifikacija (prosijavanje ili zračna separacija). U ovom radu predstavljeni su rezultati ispitivanja utjecaja mehaničke prerade kalcijevog letećeg pepela na najvažnija fizikalno kemijska svojstva cementnih kompozita.

2. EKSPERIMENTALNI DIO

U okviru eksperimentalnog programa ispitana su najvažnija fizička i kemijska svojstva letećeg pepela iz Termolektrane Kakanj u skladu sa zahtjevima standarda BS EN 450-1:2012. Potom je pripremljena potrebna količina mljevenog letećeg pepela pomoću laboratorijskog kugličnog mlina, te potrebna količina fine frakcije letećeg pepela (< 75 μm) mokrim prosijavanjem. Pomoću laserskog analizatora veličine čestica Malvern Mastersizer 2000 određena je raspodjela veličine čestica netretiranog, mljevenog i prosijanog letećeg pepela. Blaineovom metodom, prema standardu BAS EN 196-6:2011, određena je specifična površina uzoraka letećeg pepela [6]. Mikroskopska analiza karakteristika čestica letećeg pepela izvršena je pomoću pretražnog elektronskog mikroskopa Mira Tescan FESEM (20 keV).

Nakon toga pristupilo se ispitivanju utjecaja načina pripreme letećeg pepela na svojstva paste i maltera u kojima je izvršena djelomična zamjena cementa s letećim pepelom. Kao osnovno vezivo korišten je cement CEM I 52,5 N iz Tvornice cementa Kakanj, čija je Blain-ova specifična površina 3850 cm^2/g. Pripremljeni su referentni uzorci cementne paste (U1) i uzorci u kojima je 30 mas. % cementa zamijenjeno s netretiranim letećim pepelom (U2), s prosijanim pepelom (U3), te s mljevenim pepelom (U4). Na uzorcima cementne paste provedena su sljedeća ispitivanja: početak i kraj vremena vezivanja, standardna konzistencija i postojanost zapremine u skladu sa standardom BAS EN 196-3 + A1:2009 [7].

Pored toga, u cilju utvrđivanja sadržaja portlandita ($Ca(OH)_2$), izvršena je termička analiza (DTA/TG) osušenih usitnjenih uzorka cementnih pasta starosti 7 i 28 dana pomoću uređaja Netzsch STA 409. Ispitivanje je provedeno u atmosferi dušika do 600 °C, uz brzinu zagrijavanja od 10 °C/min. Portlandit je jedan od produkata hidratacije silikatnih minerala cementa. Zbog činjenice da smanjuje otpornost na koroziju uslijed karbonizacije, a pri tome ne doprinosi čvrstoći, predstavlja nepoželjan sastojak hidratizirane cementne paste. Uvođenjem pucolanskih dodataka u sastav cementnih kompozita, portlandit reagira sa amorfnim SiO_2 i prelazi u C-S-H fazu koja predstavlja glavni faktor u procesu očvršćivanja. Na temelju promjene mase pri zagrijavanju očvrsnule paste moguće je odrediti sadržaj hidratacijski nastalog portlandita-$Ca(OH)_2$ (gubitak mase u temperaturnom području od 450 - 530 °C). Na uzorcima maltera ispitana je čvrstoća na pritisak i savijanje nakon 2, 7 i 28 dana u skladu sa standardom BAS EN 196 – 1: 2016 [8].

3. REZULTATI I DISKUSIJA

3.1. Leteći pepeo

Za pripremu uzoraka korišten je leteći pepeo iz Termoelektrane Kakanj, čija su najvažnija svojstva, usporedo sa zahtjevima standarda EN 450-1:2012, predstavljena u tablici 1.

Tablica 1. Fizikalno kemijska svojstva letećeg pepela Termoelektrane Kakanj

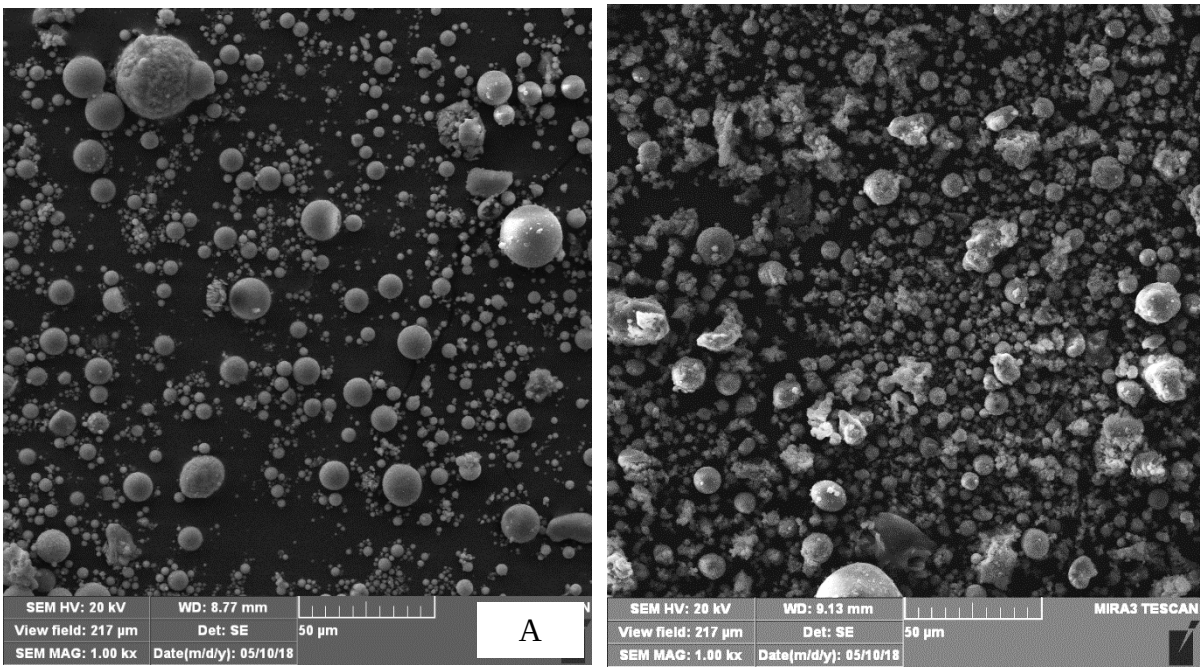
Svojstvo	Vrijednost	Zahtjev standarda BAS EN 450-1:2012
Gubitak žarenjem, mas. %	4,2	Kategorija A: ≤ 5,0 Kategorija B: ≤ 7,0 Kategorija C: ≤ 9,0
Kloridi, mas.%	0,003	≤ 0,10
SO_3, mas.%	1,4	≤ 3,0
Slobodni CaO, mas.%	2,2	≤ 2,5
Reaktivni CaO, mas.%	15,2	≤ 10,0
Reaktivni SiO_2, mas.%	4,06	≥ 25,0
SiO_2+Al_2O_3+Fe_2O_3, mas.%	70,1	≥ 70,0
Alkalije, mas.%	1,8	≤ 5,0
MgO, mas.%	3,6	≤ 4,0
Fosfati, mas.%	-	≤ 5,0
Indeks aktivnosti, %	80 95	28 dana: ≥ 75 90 dana: ≥ 85
Gustoća, g/cm^3	2,57	-
Postojanost zapremine (Le Chatelierova metoda), mm	1,5	-

Na osnovu rezultata prikazanih u tablici 1 može se zaključiti da leteći pepeo iz Termoelektrane Kakanj zbog visokog sadržaja reaktivnog CaO ne zadovoljava zahtjeve standarda BAS EN 450-1:2012. To znači da su za direktnu primjenu ovog pepela kao mineralnog dodatka betonu u skladu sa standardom EN 206:2014 potrebna dodatna ispitivanja, prije svega utjecaja na trajnost i korozijsku otpornost betona [9]. U tablici 2 predstavljeni su rezultati ispitivanja granulometrijskog sastava i specifične površine letećeg pepela.

Tablica 2. Granulometrijski sastav i specifična površina netretiranog, mljevenog i prosijanog letećeg pepela

Vrsta pepela	Ostatak na situ otvora mm (mas. %)							Spec. površina (cm^2/g)
	0	0,063	0,075	0,090	0,125	0,250	0,500	
Netretirani leteći pepeo	66,1	7,4	10,1	7,2	6,4	2,8	0	2490
Mljeveni leteći pepeo	82,5	6,6	5,4	2,8	2,1	0,6	0	3850
Prosijani leteći pepeo	89,8	7,9	0,9	0,8	0,6	0	0	4770

Leteći pepeo je samljeven u laboratorijskom kugličnom mlinu na Blaineovu specifičnu površinu 3850 cm^2/g. Pri mljevenju nije vršena separacija čestica, tako da je nakon mljevenja preostao značajan udio krupnijih čestica, što se može uočiti na SEM mikrografima uzoraka netretiranog i mljevenog letećeg pepela (slika 1).



Slika 1. SEM snimci uzoraka netretiranog (A) i mljevenog letećeg pepela (B) (povećanje 1000×)

3.2. Cementna pasta

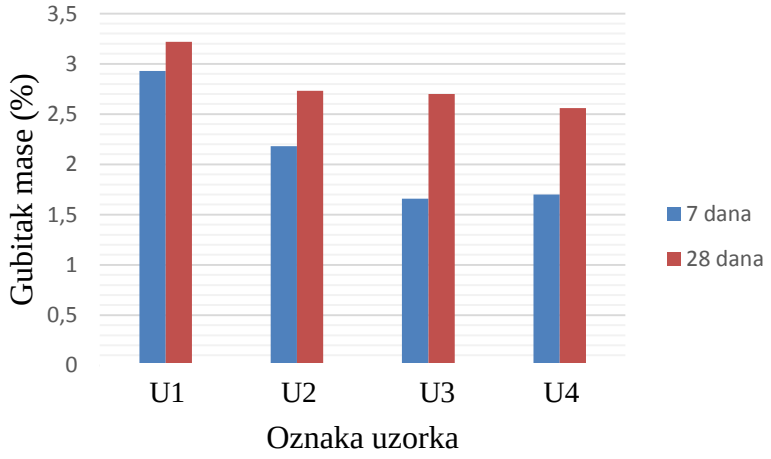
U cilju ispitivanja utjecaja pripreme letećeg pepela na svojstva cementnih kompozita, provedena su osnovna ispitivanja na cementnoj pasti: vrijeme vezivanja, standardna konzistencija i stalnost zapremine, a rezultati su predstavljeni u tablici 3.

Tablica 3. Rezultati ispitivanja svojstava cementne paste

Oznaka uzorka	Vrijeme vezivanja (min)		Standardna konzistencija (%)	Postojanost zapremine po Le Chatelieru (mm)
	Početak	Kraj		
U1	120	180	24,5	0,5
U2	180	240	22,5	1,5
U3	150	210	25,0	1,0
U4	160	210	26,5	1,0

Prema očekivanju svi uzorci s letećim pepelom imaju duže vrijeme vezivanja od referentnog uzorka, što se objašnjava njihovim manjim sadržajem hidrauličnog veziva. Najizraženije produženje vremena vezivanja zabilježeno je kod netretiranog letećeg pepela. Standardna konzistencija, koja predstavlja potrebnu količinu vode za postizanje zadate obradivosti, najmanja je kod uzorka sa netretiranim pepelom, a najveća kod uzorka sa prosijanim pepelom. Potreba za vodom je u direktnoj vezi sa finoćom čestica. Čisti cement ima veću specifičnu površinu od netretiranog pepela i stoga se zamjenom cementa takvim pepelom smanjuje standardna konzistencija. Pored toga čestice letećeg pepela su sferičnog oblika i glatke površine (slika 1) za razliku od čestica cementa, te je potrebna manja količina vode da bi se čestice obavile vodom i postale pokretljive, a time i pasta postala fluidna. S

druge strane prosijani leteći pepeo ima najveću specifičnu površinu (4770 g/cm^2) te je unatoč sferičnosti i glatkoj površini čestica potrebna veća količina vode za postizanje zadate obradivosti nego u slučaju paste sa čistim cementom. Što se tiče postojanosti zapremine, uočeno izvjesno povećanje zapremine kod uzoraka sa letećim pepelom u odnosu na referentne uzorke. Međutim, razmak kazaljki Le Chatelierovog prstena je kod svih uzoraka daleko ispod maksimalne dozvoljene vrijednosti (10 mm). Gubici mase ispitivanih uzoraka u temperaturnom intervalu 450 - 530 °C, očitani sa TG krive, predstavljeni su u dijagramu na slici 2.



Slika 2. Gubitak mase u intervalu 450 - 530 °C

S obzirom da se kod pasti sa letećim pepelom u periodu od 7 do 28 dana sadržaj portlandita značajno povećava može se zaključiti da se pucolanska reakcija još uvijek ne odvija. Naime, u pucolanskoj reakciji hidratacijom nastali portlandit reagira sa amorfnim SiO_2 iz letećeg pepela, što rezultira smanjenjem njegovog sadržaja u očvrsnuloj pasti. Činjenica je da su najveći gubici mase zabilježeni kod referentnog uzorka (U1), ali to je isključivo posljedica veće količine silikatnih minerala čijom se hidratacijom formira portlandit. Od uzoraka koji sadrže leteći pepeo najveći sadržaj portlandita zabilježen je u slučaju kada je korišten netretirani leteći pepeo.

3.3. Cementni mortovi

Pri pripravi uzoraka cementnog morta kao agregat korišten je standardni pijesak. Omjer agregat : cement iznosio je 1:3, a vodocementni faktor 0,50. Pored kombinacija cement – leteći pepeo korištenih za pripremu pasti, pripravljeni su i uzorci cementnog morta u kojima je zamjena cementa letećim pepelom izvršena u omjeru cement : leteći pepeo = 1:1,3 po masi. U ovim uzorcima (U5) izvršena je korekcija granulometrijskog sastava agregata na način da je dio frakcije 75 - 150 µm standardnog kvarcnog pijeska isključen iz mješavine za pripremu uzoraka. Naime, ispitivanjem granulometrijskog sastava letećeg pepela utvrđeno je da je sadržaj frakcije +75 µm cca. 25 - 30 %. Krupne čestice letećeg pepela zbog manje specifične površine imaju slabiju reaktivnost i manje doprinose razvoju čvrstoće cementnih kompozita. Zato je u uzorcima oznake U5 samo frakcija letećeg pepela < 75 µm u proračunu sastava tretirana kao dio vezivne komponente, te je bilo potrebno u mješavinu unijeti veću masu letećeg pepela od izdvojene mase cementa. Krupna frakcija letećeg pepela (> 75 µm) tretirana je kao dio agregata i zato je izvršena korekcija granulometrijskog sastava agregata na način da je dio frakcije 75 - 150 µm standardnog pijeska isključen iz mješavine za pripremu

uzoraka. Značaj ovakvog pristupa projektiranju sastava je u tome da se na ovaj način ukloni bilo kakva mehanička priprema letećeg pepela, čime se smanjuju troškovi i pojednostavljuje proces proizvodnje. Rezultati ispitivanja tlačne i savojne čvrstoće prikazani su u tablici 4. Zabilježen je pad čvrstoće uzoraka sa dodatkom letećeg pepela u odnosu na referentne uzorke (U1) u svim ispitivanim periodima. Međutim, mljevenjem (U3) i prosijavanjem pepela (U4), kao i zamjenom cementa većom količinom letećeg pepela (U5) smanjuje se pad čvrstoće u odnosu na uzorke sa netretiranim letećim pepelom (U2).

Tablica 4. Rezultati ispitivanja čvrstoće cementnih mortova

Oznaka uzorka	Tlačna čvrstoća (MPa)			Savojna čvrstoća nakon 28 dana (MPa)
	2 dana	7 dana	28 dana	
U1	25,6	40,4	54,9	8,4
U2	16,2	25,1	39,9	7,5
U3	19,3	28,9	43,3	8,0
U4	18,6	28,7	46,2	8,0
U5	18,0	28,6	45,5	8,1

4. ZAKLJUČAK

Na osnovu rezultata ispitivanja kemijskih i fizičkih svojstava može se zaključiti da leteći pepeo Termoelektrane Kakanj zadovoljava sve kriterije standarda „Leteći pepeo za beton“ EN 450-1:2012, izuzev sadržaja reaktivnog CaO. Čestice letećeg pepela su pretežno sferičnog oblika i glatke površine. Ispitivanjem uzorka paste utvrđeno je da djelomična zamjena cementa letećim pepelom dovodi do izraženih promjena u trajanju vezivanja i potrebi za vodom, dok se stalnost zapremine bitno ne mijenja. Dodatak netretiranog pepela smanjuje potrebu za vodom, ali i najviše usporava proces vezivanja. S druge strane, mljeveni i prosijani pepela imaju nešto manji utjecaj na vrijeme vezivanja, ali dovode do povećanja standardne konzistencije. Rezultati termičke analize upućuju na zaključak da način pripreme letećeg pepela nema bitnog utjecaja na odvijanje pucolanske reakcije u prvih 28 dana, dok su potrebna dodatna ispitivanja kako bi se utvrdio utjecaj i uloga pepela u kasnijim periodima.
Generalno, zamjena dijela cementa letećim pepelom rezultira smanjenjem tlačne i savojne čvrstoće u svim ispitivanim periodima. Najveće smanjenje čvrstoće pretrpjeli su uzorci sa netretiranim pepelom. Kao najvažniji zaključak istraživanja može se istaći činjenica da u pogledu razvoja čvrstoće u prvih 28 dana dodavanje letećeg pepela u suvišku u odnosu na cement ima gotovo isti utjecaj kao mehanička priprema letećeg pepela. Potrebno je provesti dodatna istraživanja kako bi se utvrdilo kakav utjecaj i ulogu ima leteći pepela u kasnijim periodima hidratacije, kada se odvija intenzivnija pucolanska reakcija. Na ovaj način otvara se prostor za ekonomičniju upotrebu letećeg pepela kao dodatka betonu, jer se uklanjaju troškovi pripreme letećeg pepela.

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CJELOVITI PRISTUP ZBRINJAVANJU POLJOPRIVREDNE BIOMASE I PEPELA POLJOPRIVREDNE BIOMASE ISTOČNOG DIJELA REPUBLIKE HRVATSKE

INTEGRATED APPROACH TO THE DISPOSAL OF AGRICULTURAL BIOMASS AND BIOMASS ASHES IN THE EASTERN PART OF THE REPUBLIC OF CROATIA

Ivanka Netinger Grubeša*, Ivana Barišić*, Marija Trkmić, Tajana Radić*****

* Građevinski fakultet Osijek, Osijek, Hrvatska
** Centralni kemijsko-tehnološki laboratorij (CKTL) – HEP Proizvodnja d.o.o., Zagreb, Hrvatska
*** Hrvatska poljoprivredna komora, Zagreb, Hrvatska

autor za korespondenciju: Ivanka Netinger Grubeša, e-mail: nivanka@gfos.hr

Izvorni znanstveni rad

SAŽETAK

U radu se procjenjuju količine poljoprivredne biomase na području istočnog dijela Republike Hrvatske raspoložive za uporabu u industriji kao zamjena za uobičajeno korištene energente. Prikazane su kalorijske moći pšenice, ječma, soje i ljuski sjemenki suncokreta te uspoređene sa kalorijskim moćima uobičajeno korištenih energenata. Korištenjem spomenutih biomasa u industriji nastaju velike količine pepela koje predstavljaju ekološki problem. U radu su prikazani preliminarni rezultati ispitivanja primjene pepela biomase u građevinarstvu; u području visokogradnje i niskogradnje. Sukladno rezultatima istraživanja, poljoprivredna biomasa ravnopravan je energent drvnoj sječki a pepeo poljoprivredne biomase ima potencijala za uporabu u građevnim proizvodima.

***Ključne riječi**: poljoprivredna biomasa, kalorijska vrijednost, pepeli poljoprivredne biomase, građevni proizvodi*

ABSTRACT

The paper estimates the quantities of agricultural biomass in the eastern part of the Republic of Croatia available for use in industry as a substitute for commonly used fuels. The calorific values of wheat, barley, soy and sunflower seed shells are given and compared to the calorific values of conventional sources of energy. Use of agricultural biomass in industry

produces large quantities of ashes which represent an ecological problem. The paper presents preliminary results of the application of biomass ashes in civil engineering area; in structural concrete and road construction. According to the research results, agricultural biomass as energy source is similar to wood chips and the ash of agricultural biomass has potential to be used in civil engineering products.

***Keywords**: agricultural biomass, calorific value, agricultural biomass ashes, civil engineering products*

1. UVOD

Direktiva 2009/28/EZ Europskoga parlamenta i Vijeća od 23. travnja 2009. o poticanju uporabe energije iz obnovljivih izvora [1] postavila je kao obvezatni cilj 20 %-tni udio energije iz obnovljivih izvora u potrošnji energije cjelokupne Zajednice do 2020. Pod pojmom energije iz obnovljivih izvora energije se ovdje podrazumijeva energija iz obnovljivih nefosilnih izvora, tj. vjetroenergija, solarna energija, aerotermalna energija, geotermalna energija, hidrotermalna energija te energija oceana, hidroenergija, energija biomase, plin dobiven od otpada, plin dobiven iz uređaja za obradu otpadnih voda i bioplin. Biomasa se ovdje odnosi na svaki organski materijal koji potječe od trenutno živih ili donedavno živućih biljaka ili životinja [2]. Prema [3], biomasa se može podijeliti na:

- poljoprivrednu biomasu: zrna hrane, otpaci u preradi šećerne trske, stabljike kukuruza, slama, ljuske sjemenki, ljuske orašastog voća, gnoj stoke, peradi i svinja,
- šumsku biomasu: drveće, drvni otpad, drvo ili kora te piljevina,
- gradska biomasa: kanalizacijski mulj, gorivo dobiveno iz otpada, otpaci hrane, otpadni papir,
- energetske usjeve: topole, vrbe, proso, lucerna, kukuruz, soja i druga biljna ulja,
- biološka biomasa: životinjski otpad.

Uporabom biomase kao energenta u industriji tj. spaljivanjem biomase nastaje anorganski ostatak zvan pepeo biomase čija mogućnost primjene su područje interesa brojnih istraživača. Najviše istraživača [4 - 9] proučava mogućnost djelomične zamjene cementa sa ovim pepelima. U radu [4] proučavana je mogućnost zamjene cementa sa 10 %, 20 % i 30 % pepela rižinih ljuskica, stabljike šećerne trske i pšenice te je zaključeno da udio do 10 % ovog pepela u betonu neće umanjiti njegovu tlačnu čvrstoću. Trajnosna svojstva betona sa 2 % i 5 % cementa zamijenjenog s pepelima stabljike kukuruza, slame pšenice i stabljike suncokreta istraživana su u [5] te je zaključeno da sve ove vrste pepela poboljšavaju otpornost betona na cikluse smrzavanja-odmrzavanja kao i otpornost na habanje. Pozitivan učinak pepela pšenične slame na otpornost betona na cikluse smrzavanja-odmrzavanja potvrđen je i u [6]. Zamjenom 15% cementa sa mješavinom pepela pšenične slame i rižinih ljuskica povećava se tlačna i vlačna čvrstoća betona što se objašnjava sinergijskim učinkom između ova dva pepela zbog udruženog djelovanja pucolanske reakcije i filer efekta [7]. Dodatak ovih pepela povećava vrijeme vezanja cementne paste [8] a istraživači u radu [9] upozoravaju na velik sadržaj alkalija u ovakvim pepelima.

Pored istraživanja mogućnosti primjene pepela poljoprivredne biomase u konstruktivnom betonu i mortu, sve više se istražuje njihova primjena i u cestogradnji obzirom na velike količine prirodnih materijala koje se tradicionalno koriste. Tako su istraživanja prikazana u [10] pokazala kako je 6 – 8 % cementa i 10 – 15 % pepela rižinih

ljuskica, optimalni dodatak rezidualnom tlu u smislu poboljšanja svojstava plastičnosti, zbijenosti, čvrstoće, ali i sa ekonomskog aspekta. U radu [11] prikazana je stabilizacija aluvijalnog tla pepelima rižinih ljuskica i ostacima šećerne trske koja je rezultirala smanjenjem indeksa plastičnosti sa porastom udjela pepela od 2,5 % na 12,5 % dok se optimalnim udjelom pepela pokazalo 7,5 %. Miješanje glinovitog tla sa pepelom ljuskica, slame i ostataka u obradi riže rezultira i većom optimalnom vlažnošću s porastom udjela pepela [12]. Dodatak od 20 – 25 % pepela rezultirao je i povećanjem vrijednosti Kalifornijskog indeksa nosivosti (CBR-a) glinovitog tla. Stabilizacija glinovitog tla mješavinom pepela ljuskica riže i ostataka u obradi šećerne trske u kombinaciji s vapnom kao aktivatorom rezultirali su povećanjem tlačne čvrstoće, što je opisano u radu [13]. Slični rezultati su prikazani i u radu [14], dodatak pepela iz otpada šećerne trske ekspanzivnom tlu rezultirao je povećanjem vrijednosti CBR-a, tlačne čvrstoće i maksimalne suhe prostorne mase, ali i smanjenjem linearnog bubrenja [15]. Pepeo slame šećerne trske također može biti učinkovit stabilizator pri poboljšanju geomehaničkih karakteristika lateritnog tla [16]. Pozitivan utjecaj na geomehanička svojstva tla ima i kombinacija pepela slame pšenice i šećerne trske [17]. Ložišni pepeo iz ostataka prerade maslina također može biti korišten kao materijal ispune pri izradi nasipa cesta [18], dok se leteći pepeo pokazao manje efektivnim dodatkom u slučaju stabilizacije lapornog tla te bi njegova efikasnost mogla biti ovisna o tipu tla koje se tretira [19]. Ipak, karakteristike pepela ovise o karakteristikama biomase, tehnologije spaljivanja i dijelu peći gdje se pepeli sakupljaju [20] te svaki pepeo zasebno treba istražiti.

U ovom radu se istražuje potencijal poljoprivredne biomase na području istočnog dijela Republike Hrvatske koja zaostaje na poljima nakon žetve kao zamjene za uobičajeno korištene energente u industriji. S ciljem nulte tolerancije prema otpadu, pepelima koji nastaju spaljivanjem biomase u industriji pokušava se pronaći dodana vrijednost istraživanjem njihove mogućnosti primjene u građevnim proizvodima.

2. RASPOLOŽIVE KOLIČINE BIOMASE U ISTOČNOM DIJELU REPUBLIKE HRVATSKE

Tablica 1 prikazuje ukupne količine najvažnijih ratarskih kultura u Republici Hrvatskoj čiji žetveni ostaci se mogu koristiti kao zamjena za energent u industriji. Podaci za petogodišnje razdoblje preuzeti su iz dokumenata naziva Biljna proizvodnja u 2012 - 2016 koji se svake godine objavljuju na stranici Državnog zavoda za statistiku Republike Hrvatske [21] te uprosječeno prikazani tablicom 1. Obzirom da je istočni dio Hrvatske najizraženije ratarsko područje u Republici Hrvatskoj, smatra se da većina od ovdje iskazanih ukupnih količina pripada upravo tom području. Količina biomase preostale nakon žetve ovih kultura jednaka je ili čak i veća od količine požnjevenih usjeva [22].

Poljoprivredna struka podržava zaoravanje žetvenih ostataka usjeva te smatra da se time poboljšava struktura tla [23]. Međutim, uslijed povećanih troškova za gorivo i mehanizaciju pri zaoravanju žetvenih ostataka te nedovoljne edukacije individualnih proizvođača, neki su poljoprivrednici pribjegavali rješavanju problema biomase njezinim spaljivanjem što ne samo da donosi štetu u poljoprivredi kroz gubitak organske tvari u tlu i uništavanje živih organizama već i zagađivanju okoliša. Iako je ovo u Republici Hrvatskoj u današnje vrijeme zabranjeno kroz [24], još uvijek imamo priliku vidjeti da se na poljima žetveni ostaci (slama, a naročito kukuruzovina) spaljuju. Razloge za takvo ponašanje treba prije svega tražiti u tehničkim problemima koji se javljaju kod zaoravanja te usitnjavanja i pripreme tla za narednu kulturu, naročito kada se radi o velikim količinama žetvenih ostataka

i zaostaloj masi [25]. U takvim slučajevima bi idealno bilo preusmjeriti suvišnu biomasu u lokalnu industriju koja bi je koristila kao zamjenu za gorivo.

Tablica 1. Prosječne količine ratarskih usjeva u Republici Hrvatskoj za period 2012. – 2016.

Ratarska kultura	Požnjevena količina (u tonama)
Pšenica	873 251,4
Kukuruz	1 816 510
Ječam	213 865
Raž	3 236,6
Zob	72 686,4
Pšenoraž	59 903
Ostale žitarice	4 638
Soja	155 992,8
Suncokret	104 945
Uljana repica	63 046,8
Ostale uljarice	2 318
Ukupno	3 370 393

3. POTENCIJAL POLJOPRIVREDNE BIOMASE KAO ENERGENTA U INDUSTRIJI

U ovom dijelu rada je provedena karakterizacija poljoprivredne biomase sa područja istočnog dijela Republike Hrvatske. Analizirani su: slama ječma, pšenice i soje te ljuske sjemenki suncokreta (slika 1).



a) b) c)

Slika 1. Izgled biomasa: a) ljuske sjemenki suncokreta, b) slame ječma i pšenice, c) slama soje

Uzorci poljoprivredne biomase i uzoraka pepela su dostavljeni u Centralni kemijsko-tehnološki laboratorij (CKTL) HEP-Proizvodnje d.o.o. te je provedena njihova analiza prema ispitnim metodama navedenim u tablici 2. Uzorci biomase se prvo suše te im se određuje ukupna vlaga, zatim se usitnjavaju u mlinu ne veličinu čestica manjim od 1 mm, nakon čega im se određuje sadržaj pepela, sumpora i klora te ogrjevna vrijednost. Određivanje sadržaja pepela provodi se gravimetrijski, žarenjem u peći, te na osnovu tog rezultata moguće je

procijeniti količine pepela koje će nastati izgaranjem biomase u energetskim postrojenjima. Sumpor i klor u biomasi se nalaze u vrlo niskim koncentracijama, međutim tijekom izgaranja goriva mogu uzrokovati koroziju na izmjenjivačkim površinama te je njihovo određivanje bitno. Ogrjevna vrijednost predstavlja količinu toplinske energije koja se može dobiti izgaranjem biomase u energetskom postrojenju. Na ogrjevnu vrijednost najviše utječu kemijski sastav i vlažnost biomase. Ogrjevna vrijednost određuje se mjerenjem u kalorimetru. Razlikuju se gornja i donja ogrjevna vrijednost. Gornja ogrjevna vrijednost predstavlja onu količinu topline koja nastaje potpunim izgaranjem jedinične količine goriva, pri čemu se dimni plinovi ohlade na 25 °C, a vlaga iz dimnih plinova izluči kao kondenzat. Donja ogrjevna vrijednost predstavlja onu količinu topline koja nastaje potpunim izgaranjem jedinične količine goriva, pri čemu se dimni plinovi ohlade na 25° C, a vlaga u dimnim plinovima ostaje u parnom stanju i toplina kondenzacije ostaje neiskorištena [26].

Tablica 2. Pregled metoda ispitivanja uzoraka poljoprivredne biomase

Parametar	Jedinica	Metoda	Instrument
Sadržaj ukupne vlage	mas.%	HRN EN ISO 18134-1:2015 [27]	Sušionik Heratherm OMH 750
Sadržaj pepela	mas.%	HRN EN ISO 18122:2015 [28]	Mufolna peć Nabertherm B180
Sadržaj sumpora	mas.%	HRN EN ISO 16994:2015 [29]	CHNS -TrueSpec-LECO
Sadržaj klora	mas.%	HRN EN ISO 16994:2015 [29]	EDXRF NEX CG- Rigaku
Ogrjevna vrijednost	MJ/kg	HRN EN ISO 18125:2017 [30]	Kalorimetar C2000-IKA

Na slikama 2 a), b) i c) su prikazane fotografije nekih od instrumenata korištenih u analizama poljoprivredne biomase a kasnije i sastava njihovih pepela.



a) b) c)

Slika 2. Uređaji u CKLT-u: a) određivanje vlage sušionikom Heratherm OMH 750, b) EDXRF spektrometar NEX CG Rigaku za određivanje sadržaja klora i sastava pepela, c) hidraulička preša za pripremu uzoraka pepela

U tablici 3 su prikazani rezultati analiza poljoprivredne biomase. Rezultati ukupne vlage su izraženi na dostavnom stanju, dok su rezultati sadržaja pepela, sumpora i klora izraženi na suho stanje, odnosno uzorak bez vlage. Gornja i donja ogrjevna vrijednost izraženi su i na suhom i dostavnom stanju.

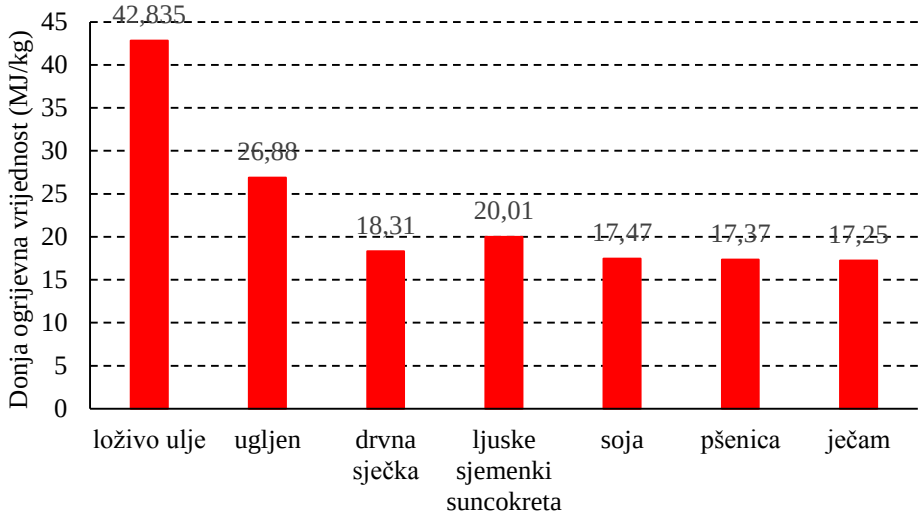
Iz rezultata je vidljivo da ječam ima najmanji (7,7 mas.%), a soja najveći udio vlage (11,5 mas.%). Sadržaji pepela su podjednaki u svim uzorcima, s time da je najmanji kod suncokreta (4,0 mas.%), a najveći u ječmu (6,5 mas.%). Sadržaj sumpora je najmanji u soji

(0,053 mas.%), a najveći u suncokretu (0,109 mas.%), dok je sadržaj klora znatno manji u soji (0,072 mas.%), a najveći u žitu (0,145 mas.%). Uspoređujući ogrjevne vrijednosti najveću donju ogrjevnu vrijednost ima suncokret (17,50 MJ/kg). Prema dobivenim rezultatima se može zaključiti da je suncokret najpogodniji za spaljivanje kao biogorivo zbog najviše ogrjevne vrijednosti i najmanjeg sadržaja pepela.

Tablica 3. Rezultati ispitivanja poljoprivredne biomase

Parametar	Jedinica	Osnova	Ječam	Pšenica	Soja	Ljuske sjemenki suncokreta
Sadržaj ukupne vlage	mas.%	dostavno	7,7	8,0	11,5	11,2
Sadržaj pepela	mas.%	suh	6,5	5,5	4,2	4,0
Sadržaj sumpora	mas.%	suh	0,072	0,062	0,053	0,109
Sadržaj klora	mas.%	suh	0,134	0,145	0,072	0,117
Ogrjevna vrijednost, gornja	MJ/kg	suh	18,45	18,59	18,71	21,36
		dostavno	17,03	17,10	16,56	18,97
Ogrjevna vrijednost, donja	MJ/kg	suh	17,25	17,37	17,47	20,01
		dostavno	15,74	15,78	15,18	17,50

Na slici 3 je prikazan odnos dobivenih donjih ogrjevnih vrijednosti poljoprivredne biomase u odnosu na izmjerene ogrjevnih vrijednosti drvne sječke, te fosilnih goriva loživog ulja i ugljena. Prikazane vrijednosti su eksperimentalno izmjerene vrijednosti u laboratoriju.



Slika 3. Usporedni prikaz donjih ogrjevnih vrijednosti pojedinih vrsta goriva

Iz slike 3 je vidljivo da fosilna goriva imaju znatno veću ogrjevnu vrijednost, međutim biogoriva zbog svoje obnovljivosti i niza prednosti s aspekta okoliša imaju sve veću upotrebu. Također, iz grafa je vidljivo da ljuske sjemenki suncokreta imaju višu ogrjevnu vrijednost od drvne sječke, dok ostala poljoprivredna biomasa ima nešto nižu ogrjevnu vrijednost u odnosu na drvnu sječku ($\Delta \approx 0{,}8$ MJ/kg).

4. PRELIMINARNI REZULTATI ISTRAŽIVANJA PRIMJENE PEPELA POLJOPRIVREDNE BIOMASE U GRAĐEVNIM PROIZVODIMA

Tvornica ulja Čepin koristi ljuske sjemenki suncokreta kao gorivo u svojem postrojenju. Pri tome se generiraju dvije vrste pepela: leteći pepeo i pepeo sa ekonomajzera u omjeru 50:50. Količina pepela koja godišnje nastaje procjenjuje se na 84 tone. Leteći pepeo i pepeo sa ekonomajzera ljuski sjemenki suncokreta uzorkovani su u ovom pogonu. U peći Tvornice ulja Čepin pokušana je zamjena ljuski sjemenki suncokreta sa slamom ječma i pšenice kao energentom. Gorenjem slama svake kulture nastala su po tri pepela: leteći pepeo, pepeo sa ekonomajzera i ložišni pepeo. Sojin pepeo je preuzet iz kućanstva koje slamu soje koristi kao ogrjev. Uzorci pepela dostavljeni u CKLT prosijani su na veličinu čestica manju od 50 μm te tabletirani na hidrauličkoj preši. Tako pripremljene tablete pepela analizirane su na EDXRF spektrometru NEX CG-Rigaku. Kemijski sastav pepela, određen prema ISO/TS 16996:2015 [31], prikazan je tablicom 4.

Tablica 4. Sastav uzoraka pepela

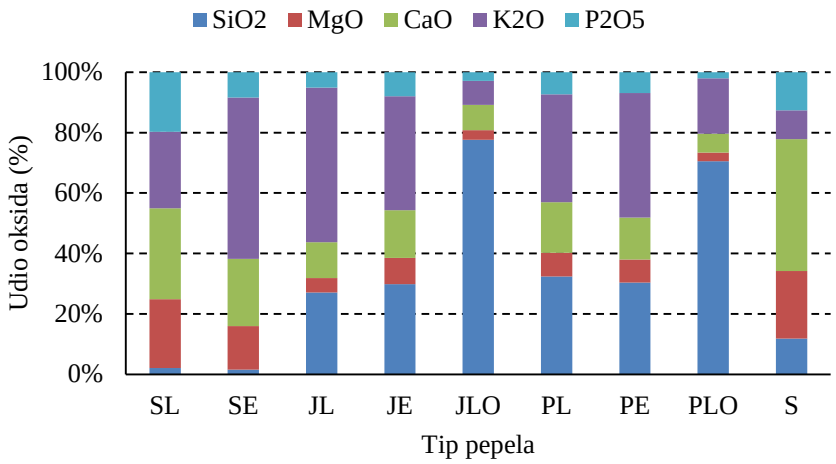
Oksidi (mas.%)	SL	SE	JL	JE	JLO	PL	PE	PLO	S
P_2O_5	18,71	6,83	4,40	7,12	2,69	6,70	6,12	1,90	11,80
Na_2O	<0,10	0,25	0,26	0,26	0,54	0,21	0,35	0,21	<0,10
K_2O	24,13	43,58	44,16	33,86	7,48	32,46	36,48	17,70	8,98
CaO	28,68	18,19	10,20	14,15	7,86	15,26	12,34	6,09	41,02
MgO	21,68	11,75	4,15	7,80	2,93	7,19	6,71	2,78	21,09
Al_2O_3	0,52	0,52	0,68	0,99	3,01	0,86	1,03	1,24	2,50
TiO_2	0,01	0,01	0,03	0,07	0,35	0,05	0,08	0,34	0,22
Fe_2O_3	0,31	0,19	0,38	0,92	1,43	0,63	0,99	0,54	1,71
SiO_2	1,96	1,24	23,38	26,78	72,86	29,49	26,89	68,05	11,07
MnO	0,08	0,04	0,03	0,05	0,04	0,05	0,05	0,06	0,05
SO_3	3,91	17,39	12,34	8,02	0,83	7,11	8,96	1,10	1,56

Oznake uzoraka u tablici: *SL* - leteći pepeo suncokreta, *SE* - pepeo suncokreta sa ekonomajzera, *JL* - leteći pepeo ječma, *JE* - pepeo ječma sa ekonomajzera, *JLO* - pepeo ječma sa ložišta, *PL* - leteći pepeo pšenice, *PE* - pepeo pšenice sa ekonomajzera, *PLO* - pepeo pšenice sa ložišta, *S* - pepeo soje sa ložišta.

Iz tablice 4 je vidljivo da postoji razlika u sastavu pepela i to najviše u sadržaju SiO_2 (1,24 - 68,05 mas. %), K_2O (7,48 - 44,16 mas.%), CaO (6,09 - 41,02 mas.%), MgO (2,78 - 21,68 mas.%) i P_2O_5 (1,90 - 18,71 mas.%). Grafički prikaz odnosa udjela tih oksida u uzorcima pepela je prikazan na slici 4.

Praćenje sastava pepela ima važnu ulogu u razmatranju izgaranja biomase, pa tako kalcijevi i magnezijevi oksidi povećavaju temperaturu tališta pepela dok ih kalijev oksid smanjuje jer silicij s kalijem tvori niskotaljive silikate u letećem pepelu. S obzirom na relativno velike količine kalija, pepeo poljoprivredne biomase se sinterira i tali na znatno nižim temperaturama u usporedbi s pepelom drvnih goriva. Kalij i natrij u kombinaciji s klorom i sumporom igraju glavnu ulogu u korozijskim mehanizmima. Ovi elementi djelomično isparavaju za vrijeme izgaranja i tvore alkalne kloride koji se kondenziraju na

izmjenjivačkim površinama i reagiraju s dimnim plinovima formirajući sulfate i oslobađajući klor [26].



Slika 4. Prikaz udjela pojedinih oksida u sastavu različitih vrsta pepela

Kod svih navedenih pepela ispitane su gustoće sukladno normi HRN EN 1097-7:2008 [32]. U cilju ocjene kvalitete pepela, gustoća je određena i za cement CEM I 42,5 R. Rezultati ispitivanja gustoće su prikazani tablicom 5.

Tablica 5. Svojstva pepela

Svojstvo/Oznaka uzorka	R	SL	SE	JL	JE	JLO	PL	PE	PLO	S
Gustoća (kg/m3)	2,983	2,401	2,400	2,400	2,399	2,397	2,400	2,399	2,398	2,400

4.1. Istraživanje primjene pepela ljuske sjemenke suncokreta u konstruktivnom betonu

Pri izradi betonskih mješavina korišten je dolomitni agregat, frakcije 0 - 4 mm, 4 - 8 mm i 8 - 16 mm, gustoće 2,75 kg/dm3. U svim mješavinama korišten je cement CEM I 42.5 R, gustoće 3,0 kg/dm^3. Količina veziva u svim mješavinama bila je 400 kg/1 m^3 betonske mješavine. Sve mješavine projektirane su s istim vodovezivnim omjerom, v/c = 0,5. Sastav betonskih mješavina prikazan je tablicom 6. Svojstva svježeg betona prikazana su tablicom 7.

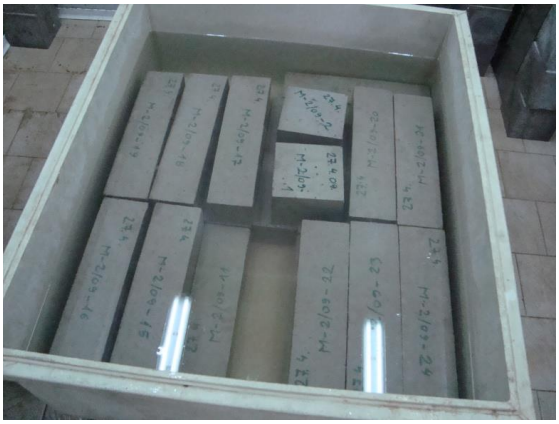
Tablica 6. Sastav mješavina betona [33]

Komponente	M0		M5		M7.5		M10	
Voda/vezivo (v/v)	0,5		0,5		0,5		0,5	
Cement [kg]	400		380		370		360	
Pepeo ljuske sjemenki suncokreta [kg]	-		20		30		40	
Voda [kg]	200		200		200		200	
Agregat [kg]	1764		1764		1764		1764	
Dolomit 0–4 mm [%–kg]	42	741	42	741	42	741	42	741
Dolomit 4–8 mm [%–kg]	19	335	19	335	19	335	19	335
Dolomit 8–16 mm [%–kg]	39	688	39	688	39	688	39	688

Table 7. Svojstva svježeg betona [33]

Svojstva	M0	M5	M7.5	M10
Gustoća (kg/m^3)	2433	2370	2356	2343
Sadržaj zraka (%)	2,5	3,0	2,7	3,2
Konzistencija slijeganjem (mm)	210	30	25	10

Konzistencija slijeganjem se značajno smanjuje s povećanjem udjela pepela u ukupnom udjelu mase (tablica 7). Uzrok ovom se nalazi u manjoj gustoći pepela u odnosu na cement što znači da ista masa pepela daje veći volumen nego to daje masa cementa. U nastavku, veći volumen pepela uz uvijek istu količinu vode rezultira manjim slijeganjem svježe betonske mješavine. Za potrebe ispitivanja tlačne čvrstoće od svake su mješavine izrađene 3 kocke brida 15 cm te za ispitivanje vlačne čvrstoće savijanjem 3 prizme dimenzija 10/10/40 cm. Nakon jednog dana starosti, uzorci betona su izvađeni iz kalupa te potopljeni pod vodu gdje su ostavljeni do 28. dana starosti (slika 5). Po 28. danu starosti, na uzorcima su ispitana sljedeća svojstva očvrslog betona: tlačna čvrstoća sukladno normi HRN EN 12390-3:2009 [34] i vlačna čvrstoća savijanjem sukladno normi HRN EN 12390-5:2002 [35]. Rezultati ispitivanja prikazani su tablicom 8.



Slika 5. Njega uzoraka pod vodom

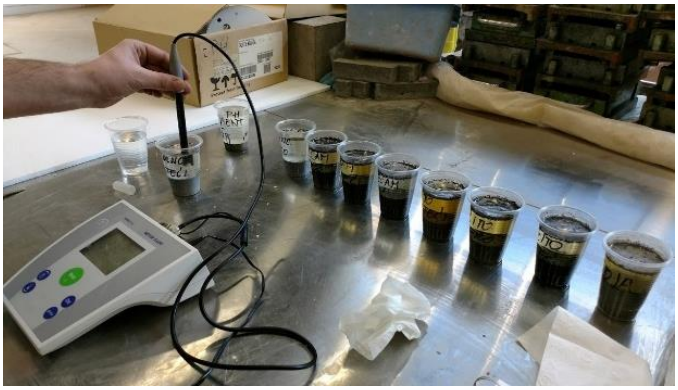
Tablica 8. Rezultati ispitivanja očvrslog betona [33]

Svojstva	M0	M5	M7.5	M10
Tlačna čvrstoća [MPa]	40,80	39,70	37,80	33,70
Vlačna čvrstoća [MPa]	5,00	5,60	4,08	5,06

Rezultati ispitivanja prikazuju da je moguća zamjena cementa u betonu sa pepelom ljuske sjemenke suncokreta. Kao optimalni udio zamjene cementa sa pepelom ljuske sjemenke suncokreta preporučuje se 5 % obzirom da se sa povećanjem udjela pepela iznad 5 % u ukupnoj količini veziva u betonu dolazi do opadanja mehaničkih svojstava betona. Kako je cement ujedno i najskuplja komponenta u betonu, zamjenom cementa sa pepelom došlo bi do smanjenja ukupne cijene betona. U nastavku, u laboratoriju Građevinskog fakulteta Osijek se istražuje mogućnost uporabe pepela ljuski sjemenki suncokreta kao i ostalih gore navedenih pepela kao punila u betonu.

4.2. Istraživanje primjene pepela ljuske sjemenke suncokreta u cestogradnji

Istraživanja provedena u ovom dijelu rada obuhvaćaju karakterizaciju različitih vrsta biopepela kao zamjene određenog udjela veziva (vapna) pri stabilizaciji tla za potrebe izrade posteljice, temeljnog tla ili nasipa u cestogradnji. Kao osnovni material korištena je glina niske plastičnosi CL prema USCS (Unified Soil Classification System) klasifikaciji. Obzirom na raspoložive količine, odabrani su leteći pepeli ječma, suncokreta i pšenice, pepeli ječma i pšenice uzeti sa ložišta i prosijani, pepeo suncokreta sa ekonomajzera te pepeo soje. Optimalni udio veziva (vapna) određen je prema normi ASTM D 6276:2006 [36] mjerenjem pH vrijednosti mješavine tla i vapna tj. kombinacije vapna i biopepela (slika 6).



Slika 6. Mjerenje pH vrijednosti za određivanje optimalnog sadržaja veziva

Usvojen je optimalni udio veziva od 7 % suhe mase gline te je za leteće pepele usvojena zamjena od 20 % mase vapna dok je za ostale pepele usvojena zamjena od 30 % od mase vapna u mješavini. Na tako definiranim mješavinama, provedena su ispitivanja prema normi EN 13286-2:2003 [37] za određivanje najveće suhe prostorne mase i optimalne vlažnosti (Proctorov pokus) te tlačne čvrstoće određene prema normi EN 12386-41:2010 [38]. Uzorci različitih sadržaja vlažnosti su prikazani slikom 7.



Slika 7. Uzorci tla sa različitim sadržajem vlažnosti

Prvi, preliminarni rezultati govore da dodatak biopepela rezultira povećanjem optimalne vlažnosti i smanjenjem najveće suhe prostorne mase. Utjecaj zamjene dijela veziva sa biopepelima analizirano je kroz rezultate tlačnih čvrstoća nakon 28 dana njege. Ispitivanje tlačne čvrstoće i tipičan izgled sloma uzorka prikazani su slikom 8.



Slika 8. Tipični izgled sloma uzorka tla prilikom ispitivanja tlačne čvrstoće

Sve ispitane mješavine pokazale su tlačne čvrstoće veće od 0,5 MPa što zadovoljava uvjete postavljene za primjenu vapnom vezanog/tretiranog materijala u temeljnom tlu, nasipima i posteljici, prema Hrvatskim i Srpskim smjernicama – OUT [39, 40]. Ako se kao referentna mješavina uzme tlo stabilizirano sa 7 % vapna, tada samo mješavine sa letećim pepelom suncokreta i pepelom pšenice sa ložišta pokazuju pad tlačne čvrstoće, ali i dalje zadovoljavajući minimalnu vrijednost od 0,5 MPa. Ostali pepeli pokazuju poboljšanje 28 dnevne tlačne čvrstoće. Nastavak istraživanja usmjeren je na analiziranje utjecaja biopepela na vrijednosti Kalifornijskog indeksa nosivosti (CBR indeksa) i linerarno bubrenje, kao još jedne od osnovnih svojstava materijala namijenjenog za temeljno tlo, nasipe i posteljicu, a također i utjecaj na druga geotehnička svojstva tla (granice konzistencije, gustoću, granulometriju).

5. ZAKLJUČAK

Raspoložive količine poljoprivredne biomase u Hrvatskoj za petogodišnje razdoblje kreću se prosječno oko 3 370 393 tona. Prema Strategiji energetskog razvoja Republike Hrvatske (2009) nije moguće iskoristiti svu raspoloživu sirovinu. Od ukupne biomase koja nastaje na polju, 40 % se mora vratiti u tlo zaoravanjem, 30 % se koristi u ishrani životinja ili na farmama, a preostalih 30 % se iskorištava u proizvodnji biogoriva. Preusmjeravanje suvišne poljoprivredne biomase u lokalnu industriju donijelo bi korist i poljoprivrednicima koji je posjeduju a i industriji koja bi je koristila. Naime, suvišna biomasa trenutno ostaje zarobljena na poljima ili je pak poljoprivrednici spaljuju onečišćujući tako okoliš. Prodajom biomase industriji poljoprivrednici bi ostvarili financijsku korist. S druge strane, poljoprivredna biomasa je otpadni proizvod te se očekuje da bi se prodavala za manju cijenu od uobičajeno korištenih energenata što bi donijelo određene uštede industriji koja je koristi kao energent. Sagorijevanjem poljoprivredne biomase u industriji generiraju se velike količine pepela koja će biti potrebno zbrinuti. Preliminarna istraživanja pokazuju potencijal ovog pepela za primjenu u građevinskim proizvodima ali i nužnost proučavanja svakog od pepela biomase zasebno, bez poopćavanja.

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Zahvala

Autori zahvaljuju na financijskoj potpori za ovo istraživanje pruženoj kroz projekt Eco build – Poljoprivredni otpad – izazovi i poslovne mogućnosti u sklopu natječaja Interreg IPA programa prekogranične suradnje Hrvatske-Srbije za period 2014-2020.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

APPLICATION OF NANOPOWDER MIXTURE FOR PHOTOCATALYTIC DECOMPOSITION OF IBUPROFEN IN AQUEOUS SOLUTIONS

Mladenka Novaković*, Veselin Bežanović*, Maja Petrović*, Goran Štrbac, Dragana Štrbac*, Ivana Mihajlović***

* University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia
** University of Novi Sad, Faculty of Sciences, Novi Sad, Serbia

corresponding author: Mladenka Novaković, e-mail: mladenkanovakovic@uns.ac.rs

Original scientific paper

ABSTRACT

Contaminants of emerging concern, such as hazardous pharmaceuticals, have not been regulated by national law and discharge limits for these compounds have not been defined, yet. In addition, available wastewater treatment technologies are not effective in removal of organic micropollutants. Due to the growing importance of low concentrated pharmaceutical pollution, the photocatalytic decomposition of ibuprofen by applying combination of metal oxides (ZnO/SnO_2) has been investigated. Ibuprofen, as non-steroidal anti-inflammatory drug, has strong impact on the environment, even in small concentrations. In this study, the Langmuir-Hinshelwood (L-H) model was used to follow photocatalytic kinetics. The correlation coefficient ($R^2 = 0.99$) showed a good agreement with pseudo-first kinetic model. After 60 minutes of artificial UV exposure, almost 90 % of ibuprofen was degraded. Even though there is a lack of knowledge concerning the complete decomposition of low concentrated pollutants, the obtained results showed that applied nanopowder mixture has good performance in degradation of ibuprofen.

***Keywords**: nanomaterials, pharmaceuticals, photocatalysis, wastewater*

1. INTRODUCTION

In recent decades, a wide range of contaminants of emerging concern (CEC) was detected in water matrices. Pharmaceutical active compounds are defined as emerging micropollutants due to their adverse effects on biodiversity and potential negative effects on human beings. A wide range of pharmaceutical residues are detected in ngL^{-1} – mgL^{-1} levels in a water environment [1]. Pharmaceutical microcontaminants are biological active in trace concentrations and they may pose significant adverse effects on water systems and aquatic

organisms. Even their half-lives are short, their continuous input into aquatic matrices, defines them as pseudo-persistent compounds. The active pharmaceutical ingredients are mostly non-volatile and charged molecules, which removal in conventional wastewater treatment plants varies from incomplete to moderate. For the most of organic pollutants defined as emerging substances, there are no legally regulated systems and discharge limits are not yet defined. The European Commission formed the First Watch List (Directive 2013/39/EU) which included three compounds, the prescription drug diclofenac, 17-Beta-estradiol (E2), and 17-Alpha-ethinylestradiol (EE2). Lately, the list was updated with new chemicals which include chemicals such as macrolide antibiotics (erythromycin, clarithromycin and azithromycin) [2].

Non-steroidal anti-inflammatory drugs (NSAIDs) are widely consumed medication all over the world. Ibuprofen, the 2-[3-2(methyl propyl) phenyl] propionic acid is one of the most used NSAIDs [3]. Ibuprofen is used for pain relief because of its analgesic, antipyretic and anti-inflammatory properties. The concentration of ibuprofen in surface waters is estimated between 2 ng L^{-1} and 8.77 μg L^{-1} [4]. This compound occurs in unchanged or metabolized form which is through excretion introduced in water streams. Although it is present in low concentrations, it represents danger for aquatic life [5]. Ibuprofen acts like persistent micropollutant because of its inability to be completely eliminated by conventional biological treatment. Traditional wastewater treatment plants are based on using biological treatment with activated sludge to degrade organic substances, but most of them are recalcitrant compounds and cannot be significantly removed by this process. Figure 1 represents a structural formula of ibuprofen.

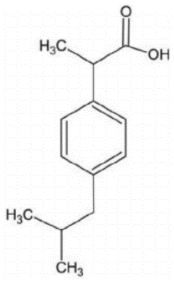


Figure 1. Structural formula of ibuprofen [6]

Implementation of new wastewater treatments should be explored. In recent scientific research, advanced oxidation processes such as ozonation, Fenton, photo-Fenton oxidation and heterogeneous photocatalysis have shown a great potential as future methods in wastewater treatment plants. The basic of AOPs is in formation of free radicals, mainly hydroxyl radicals (•OH) which have high reduction potential (E^0 = 2.80 V/SHE). The main advantage of free radicals is their non-selective nature and ability to transform the most resistant organic molecules into less toxic compounds or in mineralization products, CO_2 and H_2O [7]. One of the most investigated AOPs is heterogeneous photocatalysis with semiconductor [8]. The photocatalytic reaction is based on a photoexcited electron from the valence band (VB) of semiconductor to the empty conduction band (CB) as adsorbed photon energy which is equals or exceeds the band gap thus creating an electron–hole pair and this lead in formation of hydroxyl radicals.

The most studied photocatalyst is titanium dioxide because of its unique properties such as oxidizing ability, excellent chemical stability, long durability and water insolubility. It has drawbacks such as poorly developed porosity and difficulty of separating nanoparticles which reduces the potential application [9]. Because of its disadvantages, modification of TiO_2 or applications of alternative nanomaterials is necessary in order to overcome limitations [10]. Besides of TiO_2, other semiconductor materials such as ZnO, WO_3, CdS, ZnS, $SrTiO_3$

and SnO_2 have also been utilized [11]. Some studies are focused on studying photocatalytic properties of mixed oxide nanopowders, which with high photostability and photoactivity can be used as the advanced photocatalysts in destruction of a wide range of organic pollutants [12].

In this study, the possibility of implementation of new, unexplored nanopowder mixture in photocatalytic decomposition of ibuprofen was investigated. For this propose, new developed nanomixture, zinc-tin oxide (ZnO/SnO_2), was used in order to analyse its photocatalytic ability.

2. EXPERIMENTAL

2.1. Chemicals

The analytical standard of ibuprofen was purchased from Sigma-Aldrich. All reagents (Acetonitrile, purity 99.9 % for HPLC and acetic acid) used in the experiment, were HPLC grade. The tested concentration of pharmaceutical was 5 mgL^{-1}. The stock solution was prepared in 50 mL of acetonitrile (initial concentration of 200 mgL^{-1}). Nanopowder mixture was prepared by a solid-state method, where starting precursors (purity 99.9 % and particle size $\leq$ 1 mm) were ground in an agate mortar, annealed at 700 ˚C in air for 2 h and ground again [13]. Preparation of nanomaterials was carried out at Department of Physics, Faculty of Sciences, University of Novi Sad.

2.2. Experimental procedure

The experimental part of study was carried out in Laboratory for monitoring of landfill, wastewater and air, at Faculty of Technical Sciences, University of Novi Sad. Batch experiment was performed in 100 mL of aqueous solutions. The photocatalytic setup consists of 100 mL aqueous solution spiked with 5 mgL^{-1} of ibuprofen. Nanopowder mixture, zinc– tin oxide (ZnO/SnO_2) was added, 40 mg in model solutions. The system was left in dark for 60 minutes in order to achieve adsorption-desorption equilibrium. After dark experiment, photocatalytic decomposition of ibuprofen was performed by applying artificial UV light. The magnetic stirrer was used in order to provide good mixing and achieve uniformity of catalysts.

The changes in ibuprofen concentrations were followed in time intervals (5 - 60 minutes). During continuous stirring, the aliquots of 10 mL were taken in every interval and then filtrated through filter papers and 0.45 μm Syringe filters.

2.3. Analytical determination of ibuprofen

Detection and quantification of ibuprofen was achieved using HPLC system with diode array detector. Isocratic elution of ibuprofen was performed using reversed phase column, Eclipse XDB-C18 (150 x 4.6, particle size 5μm). Mobile phases consist of binary mixture: acetonitrile (A) and 0.1 % acetic acid in ultrapure water (B). Injection volume of sample was 10 μL and detection of ibuprofen was carried out at absorbance of 220 nm at room temperature. The flow rate was set at 0.8 $mLmin^{-1}$.

3. RESULTS AND DISCUSSION

In order to investigate photocatalytic kinetics, Langmuir-Hinshelwood (L-H) model was used. It is widely used for analysis of photocatalytic kinetic degradation of organic pollutants in aqueous matrix. Linear form of pseudo-first order kinetics is described by next equation:

$$\ln\left(\frac{C_t}{C_0}\right) = -kKt = -k_{app}t \quad (1)$$

where k_{app} is apparent rate constant (min^{-1}), c_0 - initial concentration of ibuprofen (mgL^{-1}), c_t - concentration of ibuprofen after photocatalysis at time t (mgL^{-1}) and t - irradiation time (min).

Figure 2 shows changes in ibuprofen concentration. By increasing the time of irradiation, concentration of target pollutant linearly decreased.

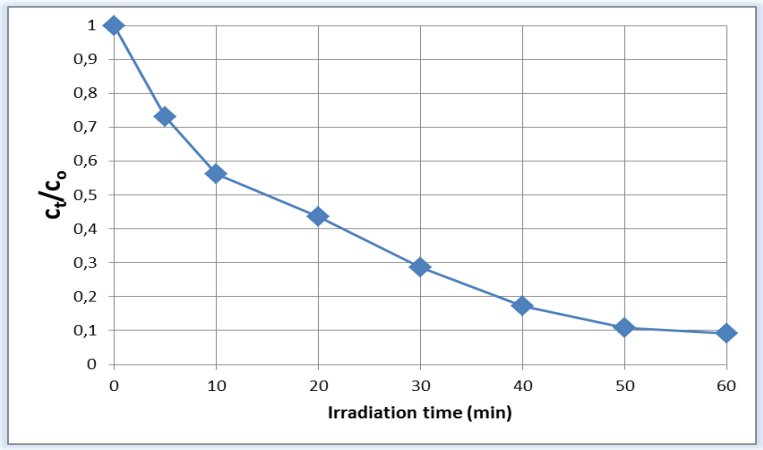


Figure 2. Photocatalytic decomposition of ibuprofen by ZnO/SnO_2

Figure 3 represents the curve of ln c_0/c_t vs t, exhibiting linear trend and demonstrating that degradation of analysed pollutant was fitted to pseudo first order kinetic model. The regression analysis of the presented linear curve enables the calculation of the values of pseudo-first order constant.

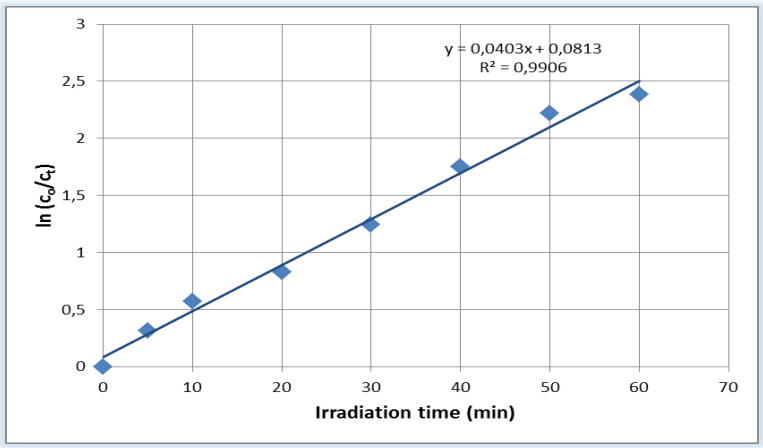


Figure 3. Pseudo first order kinetics for photocatalytic degradation of ibuprofen with ZnO/SnO_2

The value of pseudo-first rate constant for photocatalytic degradation of ibuprofen with ZnO/SnO_2 is 0.0403 min^{-1}. Similar results are reported in other scientific papers [14 - 17]. In paper [18] decomposition of ibuprofen by TiO_2 was followed by pseudo-first order model (pseudo first order constant was 0,054 min^{-1}). The photocatalytic activity of nanopowder mixture ZnO/SnO_2 in the decomposition of the selected pharmaceutical has not been yet reported by other authors.

Table 1 shows that after one hour of UV exposure, 90.81 % of ibuprofen decomposition was achieved by using ZnO/SnO_2. By-products of parent compound were formed slowly while time of UV exposure increased. The obtained results demonstrate that nanomaterial mixture is adequate material for decomposition of organic micropollutants in water samples.

Table 1. Removal efficiency of ibuprofen with ZnO/SnO_2

Irradiation time (min)	Removal efficiency (%)
0	0.00
5	27.01
10	43.68
20	56.33
30	71.30
40	82.69
50	89.17
60	90.81

4. CONCLUSION

In this study, the possibility of ibuprofen degradation by appling nanoparticle mixtures was investigated. Non-steroidal antiinflammatory drug- ibuprofen was chosen as target pollutant because it represents one of the widely used pharmaceutical. The unexplored, nanopowder mixture of zinc-tin oxide was used. Kinetic study was evaluated in order to follow decomposition of ibuprofen in time interval of 5 to 60 minutes. After one hour of UV exposure, degradation efficiency of ibuprofen by application of ZnO/SnO_2 was 90.81 %. As irradiation time increased, the concentration of ibuprofen decreased. This mean, that photocatalytic intermediates are slowly formed by the time. The pseudo-first order reaction explained the pharmacetical decomposition (high correlation coefficient – 0.99).

The obtained results have proved that use of new nanopowder material for destruction of organic micropollutants is efficient. The next step of photocatalytic process is its optimization which includes influence of parameters such as: concentration of catalyst, time of irradiation, initial concentration of investigated pollutant, reuse of nanocatalyst, effect of pH value, water composition and identification of by-products. The application of nanopowder mixture has shown great potential as alternative photocatalyst for traditional titanium oxide. Photocatalytic process can be defined as promising post-treatment in real wastewater systems for reduction of pharmaceutical residues in different water streams.

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Acknowledgements

The presented research is partly financed within a project of the Government of Vojvodina "Synthesis and application of new nanostructured materials for the degradation of organic pollutants from municipal landfill leachate in Vojvodina", 142-451-2387/2018-01/02 and Ministry of Education, Science and Technological Development, Republic of Serbia (Project III46009).

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Croatia, Sisak, September 13th-14th, 2018

ENERGY RECOVERY POTENTIAL OF *ACACIA MANGIUM* LEAVES THROUGH SEVERE TORREFACTION

Bemgba Bevan Nyakuma*

* Universiti Teknologi Malaysia, Institute of Future Energy, Centre for Hydrogen Energy, Skudai, Johor Bahru, Malaysia
* Universiti Teknologi Malaysia, Faculty of Chemical & Energy Engineering, Department of Chemical Engineering, Skudai, Johor Bahru, Malaysia.

corresponding author: Bemgba Bevan Nyakuma, e-mail: bnbevan2@live.utm.my

Original scientific paper

ABSTRACT

Acacia mangium is a flowering tree cultivated and distributed across Malaysia for its wood-based products and forestry programmes. Due to its fast growth rates, the tree generates large quantities of leaves which present challenges for forest management establishments. However, its high rate of leaf litter can provide an abundant and accessible supply of lignocellulosic biomass for bioenergy recovery. Therefore, this study examined the energy recovery potential of *Acacia mangium* leaves (AML) under severe torrefaction conditions from 300 - 400 °C for 30 minutes through thermogravimetric analysis. The results revealed that temperature significantly influenced torrefaction, resulting in significant increase in mass loss (M_L, %) and decrease in mass yield (M_Y, %). However, the higher heating value showed an increasing trend with increasing severity of torrefaction. On average, the M_Y, M_L and HHV were; 40.5 %, 59.8 %, and 25.4 MJ/kg, respectively. In general, the results revealed AML is a potentially good feedstock suitable for energy recovery by direct or co-firing technologies.

Keywords: *energy recovery, Acacia mangium, leaf litter, torrefaction, Malaysia*

1. INTRODUCTION

Acacia mangium is a fast-growing tree species native to Australia, Indonesia, and Papua New Guinea [1]. Although it is now widely distributed in Malaysia, where it is cultivated for as plantation species for its wood-based products and various forestry programmes [2]. Due to its fast growth and high seed rates, *A. mangium* is considered one of the most promising forest plantation in the country [3]. However, its high rate of leaf litter, deposition and accumulation on forest floors is a growing concern for forest management authorities due to its propensity for harbouring pests and diseases. Furthermore, the

accumulation of leaves on forest floors is cited as the precursor to forest fires which destroys trees, animal species and peat carbon sinks [4].

In spite of this, *A. mangium* leaves (AML) contain high lignocellulose content [5, 6], which makes it is a potential feedstock for energy recovery through various biomass conversion technologies such as combustion, gasification or pyrolysis. However, the outlined technologies are prone to problems such as low carbon conversion efficiencies, low gas yield, and tar formation. Additionally, problems of agglomeration, gas pollutant and particulate matter emissions pose technical challenges [7 - 11].

Furthermore, bioenergy recovery is hampered by its inherent physicochemical fuel properties. These typically include high moisture content, ash and alkali composition along with low energy density and calorific value [12 - 14]. However, the pre-treatment and thermal upgrading of biomass by drying, mechanical fractionation, pelletization and torrefaction can potentially address these challenges. Furthermore, this can improve its potential for energy recovery and efficient conversion [15 - 17]. Torrefaction is the thermal pre-treatment process for upgrading biomass properties under mild (200 °C to 300 °C) or severe (300 °C to 400 °C) temperature conditions [17]. The process of torrefaction converts biomass feedstocks into bioenergy products with high calorific value, grindability, and hydrophobicity. Torrefaction typically occurs in fixed bed, fluidised or transported reactors under oxidative or non-oxidative conditions [18, 19]. Other studies have examined torrefaction through thermogravimetric analysis (TGA) [20 - 23]. The results revealed significant improvements in the physicochemical and thermal fuel properties of various feedstocks including woody biomasses [24], sewage sludge [25], and oil palm wastes [26]. However, to the best of the author's knowledge, there have been no studies on the torrefaction of *Acacia mangium* leaves (AML) under severe conditions.

Therefore, this study seeks to examine the energy recovery potential of AML under severe torrefaction conditions. The torrefaction of AML will be examined through thermogravimetric analysis (TGA) from 300 °C to 400 °C (50 °C steps) under nitrogen gas for 30 minutes. Lastly, the mass yields (M_Y, %) and higher heating value (HHV, MJ/kg), will be calculated to examine energy recovery potential of AML through torrefaction.

2. EXPERIMENTAL

The torrefaction of *Acacia mangium* leaves (AML) was performed through isothermal and non-isothermal thermogravimetric analysis on the Shimadzu TG analyser (Model: TG-50, Japan). For each run, approximately 10 mg of pulverised AML (sieved to 250 μm) was heated in an alumina crucible at 25 °C/min under non-isothermal conditions from 300 °C to 400 °C (at 50 °C steps). The process was performed to examine the torrefaction of the feedstock under severe temperature conditions. At the selected torrefaction temperature, the heating program was switched to isothermal conditions to ensure torrefaction of AML for holding (residence) time of 30 minutes. During the tests, the system was purged with ultra-pure nitrogen gas (N_2, 99.99%) to flush the evolved gases and maintain non-oxidative conditions for torrefaction. At the end of the program, the raw TG data files were retrieved and analysed to deduce the weight loss (TG, %) and derivative weight loss (DTG, %/min) which were plotted against time (minutes) to examine the torrefaction for AML under severe conditions. Next, the thermal degradation behaviour (TDB) and torrefaction performance parameters (TPP) for the AML torrefaction process were examined accordingly. The TPPs examined in this study were; mass yield (M_Y, %) and higher heating value (HHV, MJ/kg). The HHV was calculated from non-dimensional calorific value relation proposed by Chen *et al.*, [27]. Based

on the TDB and TPP, the energy recovery potential of *Acacia mangium* leaves (AML) under severe torrefaction conditions are presented in section 3.

3. RESULTS AND DISCUSSION

3.1. Thermal Degradation Behaviour

Figures 1 - 3 present the weight loss (TG, %), derivative weight loss (DTG, and temperature profiles for the torrefaction for AML at 300 °C, 350 °C, and 400 °C for 30 minutes.

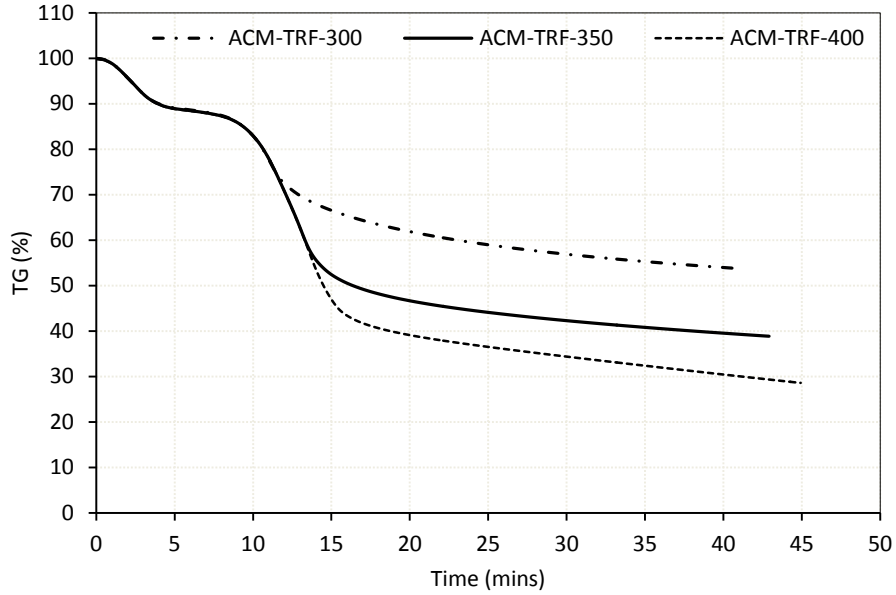


Figure 1. TG plots for AML Torrefaction

As observed, the torrefaction for AML resulted in a progressive mass loss (M_L, %) of the sample. This is evident in the similar shaped downward sloping TG plots observed in Figure 1. Furthermore, the M_L of AML increased as torrefaction temperature was varied from 300 °C to 400 °C during TGA. This indicates temperature significantly influenced the process of AML torrefaction under the conditions examined in this study. Similarly, the DTG plots experienced thermal modifications during the TG torrefaction process.

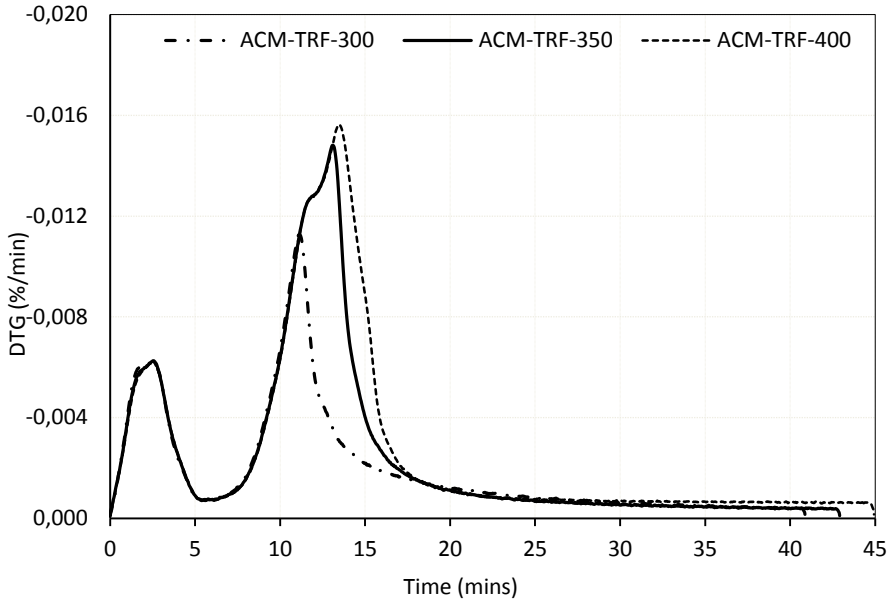


Figure 2. DTG plots for AML Torrefaction

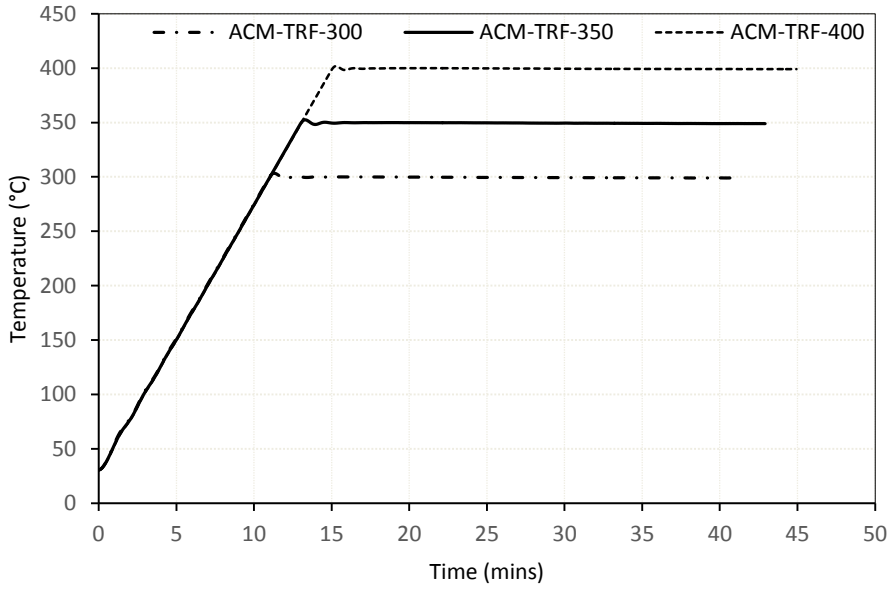


Figure 3. Temperature profiles for AML Torrefaction

As observed in figure 2, the process resulted in two sets of endothermic peaks for each torrefaction temperature. The peaks were occurred in the ranges; 0 – 6 minutes and 6 – 18 minutes whereas a long tailing occurred from 18 minutes till the end of the process. On completion, the residual mass (R_M, %) and mass loss (M_L, %) were deduced to estimate the torrefaction parameters; mass yield (M_Y, %) and higher heating value (HHV, MJ/kg) as presented in section 3.2.

3.2. Torrefaction Performance Analyses

The mass yield (M_Y, %) and higher heating value (HHV, MJ/kg) were calculated from the residual mass (R_M, %) and mass loss (M_L, %) of the weight loss (TG) and derivative weight loss (DTG) data. The M_Y and HHV for AML torrefaction are presented in table 1.

Table 1. Parameters for Torrefaction of AML

Torrefaction Temperature (°C)	Mass Loss (M_L, %)	Residual mass (R_M or M_Y,%)	Higher Heating Value (HHV, MJ/kg)
300	46.19	53.81	24.16
350	61.07	38.93	25.55
400	71.23	28.77	26.50

As observed, the M_L increased from ~ 46 % to 71 % whereas the R_M decreased from ~ 54 % to 29 % during the torrefaction. The observed trends can be ascribed to the loss of moisture, volatile matter, and lignocellulosic biomass components in AML. Since the RM is the solid mass remaining after the processes, it is termed the mass yield (M_Y, %) of the process. Consequently, it can be observed that the M_Y decreased by 12.5 % on average during the TG torrefaction of AML under the conditions examined in this study.

However, the HHV increased from ~ 24.2 MJ/kg to 26.5 MJ/kg after torrefaction. This demonstrates that torrefaction can thermally upgrade the biomass energy content to the threshold typically reported for coal in the literature [28 - 30]. Also, the results indicate a marked improvement of about 14.4 % to 25.5 % in the HHV of raw AML of 21.12 MJ/kg reported in the literature [4]. The HHV results reveal a high potential for energy recovery in future power generation.

4. CONCLUSION

The study examined the energy recovery potential of *Acacia mangium* leaves (AML) under severe torrefaction conditions from 300 °C to 400 °C for 30 minutes through under isothermal and non-isothermal thermogravimetric analysis (TGA). The results showed that temperature significantly influences the process resulting in a mass loss (M_L, %) and the formation of biochar denoted by the residual or mass yield (M_Y, %). The higher heating value of the biochar was significantly high and comparable to coal reported in the literature. On average, the values for mass yield (M_Y, %), mass loss (M_L, %) and higher heating value (HHV) were; 40.5 %, 59.8 %, and 25.4 MJ/kg, respectively. Overall, the results indicate that AML is a potentially good feedstock for energy recovery through direct or co-firing technologies for biomass conversion.

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Acknowledgements

The author wishes to acknowledge the support of Dr Tuan Amran Tuan Abdullah for the technical assistance during the TGA experiments at the Laboratory of Hydrogen Energy, Universiti Teknologi Malaysia, UTM Skudai campus. Many thanks also accrue to Dr Olagoke Oladokun for the useful discussions during the manuscript drafting process.

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Croatia, Sisak, September 13th-14th, 2018

VALORISATION OF *ACACIA MANGIUM* LEAVES INTO BIO-COAL BY MILD TORREFACTION

Bemgba Bevan Nyakuma*

* Universiti Teknologi Malaysia, Institute of Future Energy, Centre for Hydrogen Energy, Skudai, Johor Bahru, Malaysia
* Universiti Teknologi Malaysia, Faculty of Chemical & Energy Engineering, Department of Chemical Engineering, Skudai, Johor Bahru, Malaysia.

corresponding author: Bemgba Bevan Nyakuma, e-mail: bnbevan2@live.utm.my

Original scientific paper

ABSTRACT

Acacia mangium is an evergreen tree species extensively cultivated in Malaysia for wood-based products and afforestation programmes. However, its high leaf litter accumulation generates large quantities of aboveground biomass which can be exploited for clean energy. Therefore, this study examined the torrefaction of *Acacia mangium* leaves (AML) into bio-coal through thermogravimetric analysis. The results revealed that temperature significantly influenced the mass loss (M_L, %) and mass yields (M_Y, %) during torrefaction. Therefore, the M_L increased from 14.6 % to 46.1 % whereas M_Y decreased from 85.4 % to 53.9 % with increasing torrefaction temperatures from 200 °C to 300 °C after the 30-minute process. Furthermore, the heating value increased from 21.2 MJ/kg to 24.2 MJ/kg indicating the AML was thermally upgraded to coal like fuel properties. This was attributed to drying, devolatilization, and depolymerisation of lignocellulose components. Lastly, the results showed torrefaction is a potentially practical route for the valorisation of AML into high heating value solid biofuel for future bioenergy recovery and power generation.

Keywords*: energy recovery, Acacia mangium, leaf litter, torrefaction, Malaysia*

1. INTRODUCTION

Acacia mangium is an evergreen flowering tree species native to Australia, Indonesia, and Papua New Guinea [1]. Due to its fast growth and high seed rates along with its tolerance for various climes [2], *A. mangium* is now widely distributed across the globe [3]. It is also considered one of the most promising forest plantation species worldwide [4]. In Malaysia, *A. mangium* is extensively cultivated as a plantation species for various afforestation, forest regeneration, and wood-based products [1, 4]. However, *A. mangium* has a high rate of leaf

litter accumulation which results in the deposition of large quantities of aboveground biomass on forest floors [2]. Over the years, this has further resulted in significant challenges for management authorities due to the proliferation of pests and diseases in plantations [5]. Also, the role of decomposing forest leaf biomass on the emission of greenhouse gases such as methane remains an environmental challenge [6, 7]. Therefore, sustainable solutions are urgently required to address the large quantities of accumulated leaf litter generated in *A. mangium* plantations in Malaysia.

One potential solution is to generate clean, renewable and sustainable energy from *A. mangium* leaves (AML). The biological origins of AML suggest it contains high *holocellulose* and lignin which make it a potential biomass feedstock for energy recovery. Therefore, AML can be valorised into high value solid, liquid or gaseous biofuels through biomass conversion technologies such as torrefaction [8]. The process of torrefaction ensures the efficient pre-treatment and thermal upgrading of biomass into high calorific value fuel for clean energy applications [9 - 11]. Also, torrefaction generates solid biofuels with low moisture, high grindability, and hydrophobicity which can be directly converted into clean energy or co-fired for power generation [12, 13].

Therefore, this study proposes to examine the valorisation of AML into bio-coal under mild torrefaction temperatures. Furthermore, the study will examine the energy recovery potential of AML through the torrefaction parameters; mass yield (M_Y, %) and higher heating value (HHV, MJ/kg) from 200 °C to 300 °C for 30 minutes through thermogravimetric analysis (TGA).

2. EXPERIMENTAL

The valorisation of *Acacia mangium* leaves (AML) was examined by thermogravimetric analysis (TGA Model: Shimadzu TG-50, Japan) from 200 °C to 300 °C (at 50 °C steps) under nitrogen (N_2) gas for 30 minutes. The process was aimed at performing torrefaction under isothermal and non-isothermal conditions through TGA.

For each test, approximately 10 mg of pulverised AML (sieved to 250 μm) was placed in an alumina crucible and heated at 200 °C, 250 °C, to 300 °C based the dynamic (non-isothermal) heating rate of 20 °C/min. At the selected torrefaction temperature, the program was switched to isothermal conditions to perform AML torrefaction for 30 minutes. During the torrefaction tests, the TGA was flushed with ultra-pure nitrogen gas (N_2, 99.99 %) to maintain the inert atmosphere and purge the system of evolved gases. On completion, the TGA data was retrieved in its raw (.tad) file format and analysed to deduce the weight loss (TG, %) and derivative weight loss (DTG, %/min).

Next, the TG-DTG data was plotted against time (in minutes) to examine the valorisation of AML under mild torrefaction conditions. Subsequently, the degradation behaviour and torrefaction performance of AML during TGA was examined. The parameters examined in this study were; mass yield (M_Y, %) and higher heating value (HHV, MJ/kg). The HHV was calculated from the relation for non-dimensional calorific values proposed by Chen *et al.*, [14]. Based on the results, the valorisation and energy recovery potential of *Acacia mangium* leaves (AML) under mild torrefaction conditions were examined, as presented in section 3.

3. RESULTS AND DISCUSSION

3.1. Thermal Characteristics

The weight loss (TG, %), derivative weight loss (DTG, and temperature profiles for the torrefaction for AML at 200 °C, 250 °C to 300 °C for 30 minutes holding time are presented in figures 1 - 3.

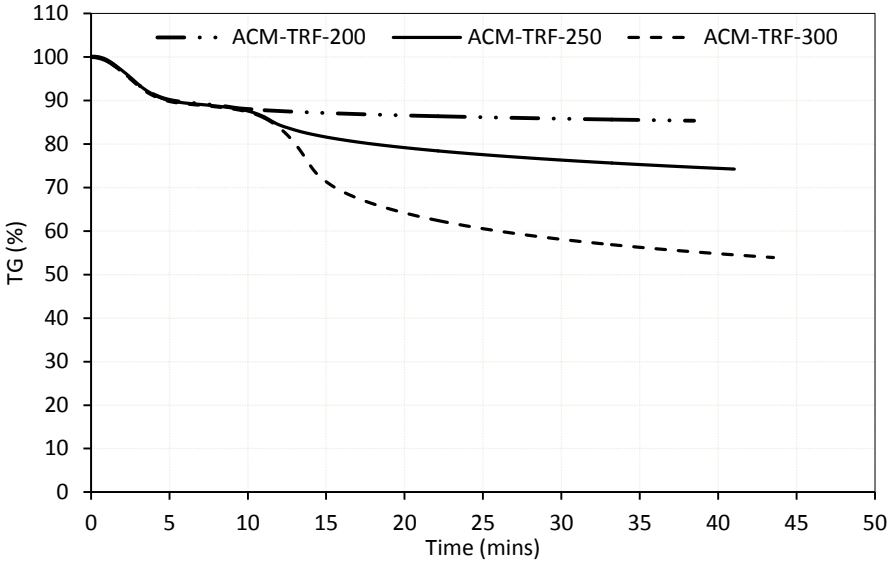


Figure 1. TG Plots for Mild Torrefaction of AML

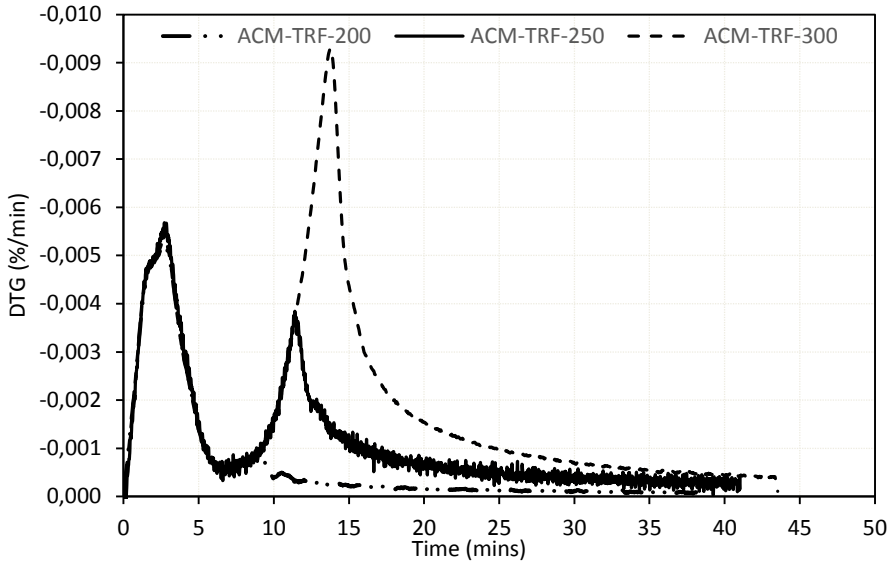


Figure 2. DTG Plots for Mild Torrefaction of AML

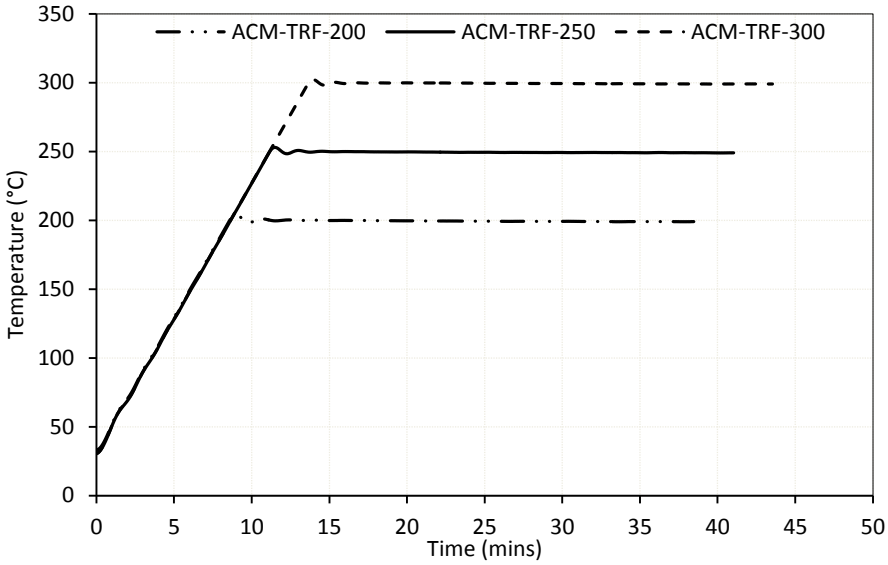


Figure 3. Temperature Profiles for Mild Torrefaction of AML

As observed in figures 1 and 2, the TG torrefaction of AML from 200 °C to 300 °C for 30 minutes resulted in a progressive mass loss (M_L, %). The M_L is apparent in the downward sloping TG curves observed at each selected AML torrefaction temperature. Furthermore, it can be observed that the M_L increased with increase in torrefaction temperature with the lowest and highest values observed at 200 °C and 300 °C, respectively. Overall, the result showed that temperature significantly influenced M_L during the torrefaction process.

Likewise, the effect of temperature was evident in the DTG peaks, as presented in figure 2. As observed, the shape, size, and symmetry of the peaks for each torrefaction temperature were enlarged at higher temperatures of torrefaction. Furthermore, the results showed that TG torrefaction process resulted in two sets of endothermic peaks below 100 °C or 7 minutes and within the range of torrefaction temperatures. These observations indicate the observed peaks are due to the loss of moisture and degradation of lignocellulosic biomass components. At the end of the process, the leftover mass after TG torrefaction was computed as the residual or mass yield (M_Y, %) during torrefaction along with the mass lost (M_L, %). The M_Y and M_L were subsequently employed to examine the performance of the process, as presented in section 3.2.

3.2. Torrefaction Performance Analyses

Table 1 presents the mass yield (M_Y, %) and higher heating value (HHV, MJ/kg) for the torrefaction of AML under the conditions examined in this study. The parameters were calculated from the residual mass (R_M, %) and mass loss (M_L, %).

Table 1. Parameters for Mild Torrefaction of AML

Torrefaction Temperature (°C)	Mass loss (M_L, %)	Residual mass (R_M or M_Y %)	HHV (MJ/kg)
200	14.63	85.37	21.22
250	25.85	74.15	22.26
300	46.09	53.91	24.15

The M_L increased from ~ 14.6 % to 46.1 % or an average of 28.9 % whereas the R_M or M_Y decreased from ~ 85.4 % to 53.9 % or 71.1 % on average during the torrefaction of AML from 200 °C to 300 °C for 30 minutes. The observed trends can be attributed to the loss of moisture, volatile matter and lignocellulosic biomass components due to the processes of drying, devolatilization and thermal depolymerisation of AML during torrefaction. However, the HHV of the resulting biochar increased from ~ 21.2 MJ/kg to 24.2 MJ/kg or on average 22.6 MJ/kg after torrefaction. The finding represents improvement of 0.8 % to 14.4 % in the HHV of raw AML of 21.12 MJ/kg reported in the literature [15]. Furthermore, the results indicate that the process improved the HHV of AML by upgrading its calorific value to the range of values typically reported for coals in the literature [16 - 19]. Furthermore, the results demonstrate that AML possesses a high energy recovery potential that can be adapted for future biomass power generation.

4. CONCLUSION

This paper examined the potential for the valorisation of *Acacia mangium* leaves (AML) into bio-coal under mild torrefaction conditions from 200 °C – 300 °C for 30 minutes through thermogravimetric analysis (TGA). The results showed that the temperature variations significantly influenced the mass loss (M_L, %) and mass yields (M_Y, %) during the torrefaction of AML. As a result, decreasing M_L and increasing M_Y trends were observed in the TG and DTG plots. The trends were attributed to drying, devolatilization, and depolymerisation of the lignocelluloses during the TGA torrefaction processes. Despite the trends, the higher heating value (HHV, MJ/kg) of the resulting chars showed values indicating the calorific content of AML was thermally upgraded to coal like fuel properties. Lastly, the results showed torrefaction is a potentially viable route for the valorisation of AML.

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Acknowledgements

The author wishes to acknowledge the technical support of Dr Tuan Amran Tuan Abdullah during the TGA experiments at the Laboratory of Hydrogen Energy, Universiti Teknologi Malaysia, UTM Skudai campus. Many thanks also accrue to Dr Olagoke Oladokun for the useful discussions during the manuscript drafting process.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

CHEMICAL QUALITY OF AQUATIC ENVIRONMENT IN THE PROTECTED NATURAL AREA IN SERBIA

Boris Obrovski*, Ivana Mihajlović*, MirjanaVojinović Miloradov*, Maja Petrović*, Maja Sremački*, Miodrag Brkić, Jelena Radić****

* University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering, Novi Sad, Serbia
** University of Novi Sad, Faculty of Technical Sciences, Department of Power, Electronic and Telecommunication Engineerin, Novi Sad, Serbia

corresponding author: Boris Obrovski, e-mail: borisobrovski@uns.ac.rs

Preliminary note

ABSTRACT

There is a certainty and request for reliable technologies and techniques for surveillance and investigative monitoring of the physico-chemical parameters of aquatic systems. Ecogoals of Interreg-IPA CBC, Croatia-Serbia is the implementation of innovative and challenging wireless and sensor methods for research, control and holistic monitoring of water environment. Sensor methods will be support by standard laboratory analysis which would be the aid to determine the level of contamination in the examined protected natural area Lake Zobnatica. The paper presents the first preliminary results of analytical laboratory analyses of water lake samples of Lake Zobnatica in Vojvodina. Monitoring of surface water in Lake Zobnatica, since it is used as touristic center, is needful to control the quality of surface water using for various human recreational activities. Nine chemical parameters were screened and compared with the values according to Serbian low and bylows. The data of the preliminary analysis on surface lake water pollution will be the platform for make decisions of the future research and experimental activities.

Keywords: *chemical parameters, surface water, protected natural area*

1. INTRODUCTION

Three types, the surveillance, operational and investigative monitoring programs of the ground and surface water quality is extremely important from the aspect of environmental protection owing to increasing contamination of water bodies caused by anthropogenic activities [1]**.** Water pollution from agricultural sources is a common problem of the Pannonia r**e**gion. The poor water quality is not only causing the loss of biodiversity in wetlands, but

often makes the surface waters inappropriate for irrigation. Predicted climate changes, in North Serbia and eastern part of Croatia, raise the needs for the extension of irrigation capacities and for the improvement of landscape resilience by habitat revitalization and establishment of green infrastructure. Filter/buffer function of the bank vegetation have no wider recognition, data from the region are scarce and gained by indirect methods. The frequent summer droughts considerably increase the costs of the afforestation and hedge planting. Hence, there is a need to find the optimal vegetation structure, adapted for local climatic conditions and effective in pollution reduction.

Impaired and degraded ecosystems have reduced tolerance and adaptability to environmental condition variations. The optimal revitalisation of ecosystem require high inter and transdisciplinary, cross-border activities. The IPA project *Active SEnsor monitoring Network and environmental evaluation for protection and wiSe use of WETLANDS and other surface waters - SeNs Wetlands* addresses one of the major cross-border challenges of the Pannonia Region and the bordering agricultural landscapes characterized by the high percent of arable land and increased pressures on the natural systems.

One of the main ecogoals of IPA Project is the implementation of continuous environmental research of the quality and the status of aquatic environment and the establishment of adequate green infrastructure, for the purpose of improvement of ecosystem services. Wireless and sensor methods which are supported by laboratory analytical analyses in ecomonitoring present new and challenging measures of ecological status for improvement of environmental protection. Fiber optic color sensor (FOS) was proved to be applicable for monitoring of orthophosphate, nitrite, sulfate, chlorine and hexavalent chromium in surface water in laboratory controlled conditions [1]. FOS has also been developed for measuring of temperature and potassium ions [2] multiparametar device for measurement of ammonia, nitrite and chromium [3] and probe for measurement of organic pollutants [4].

This paper presents the preliminary analysis of main physico-chemical parameters in Nature Park in Serbia in order to develop and implement active continuous sensor monitoring system in Serbia and also in Croatia, which will provide measurement of water quality parameters and enable the collection and evaluation of cross-border data on water pollution.

2. EXPERIMENTAL

IPA Project sites are within hydrological systems of water courses recognized as ecological corridors. The wetland in Croatia has a direct influence on the quality of the Natura 2000 site, the site in Serbia is proposed for the Nature Park. This paper is focused on sampling site in Serbia.

Samples of surface water for laboratory analysis were collected from five sampling sites Zobnatica lake (figure 1). Zobnatica lake was formed in 1976 in the valley of the river Krivaja with an area of 226 ha and a length of about 5 km. The primary task of the reservoir is irrigation of agricultural land, but in recent years the lake has become a tourist center, especially in the summer period.

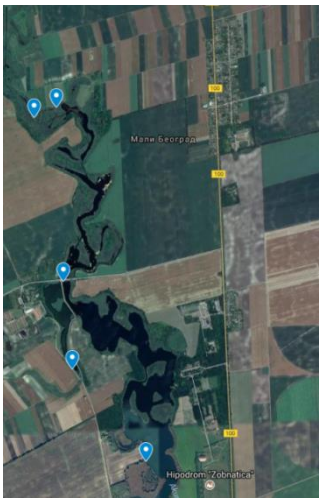


Figure 1. Five sampling sites, Zobnatica lake, Nature park in Serbia

Samples are poured into 1 L bottles, stored in hand refrigerator at 4 ^{0}C, and transported to the laboratory. Analyses were carried out in accredited Laboratory for monitoring of landfills, wastewater and air, Department of Environmental Engineering and Occupational Safety and Health in Novi Sad.

Concentrations of orthophosphate in samples were analysed according to the Standard Methods of Environment Protection Agency (EPA 365.3) Hexavalent chromium, sulfate, total chlorine, nitrite, nitrate, ammonia, chloride and fluoride were analysed according to the HACH Methods (HACH 8023 for hexavalent chromium, HACH 8021 for sulfate, HACH 8167 for total chlorine, HACH 8507 for nitrite, HACH 8192 for nitrate, HACH 8155 for ammonia, HACH 8113 for chloride and HACH 8029 for fluoride). The concentrations of all parameters were measured with UV-VIS spectrophotometer (DR 5000, HACH, Germany).

3. RESULTS AND DISCUSSION

Identification and monitoring of concentration levels for specific and key pollutants in surface water, in order to reduce the risk of negative effects, has great significance for the overall improvement of the status of the environment and creating a platform for the development of quality monitoring program. Monitoring of water bodies in Nature Park, especially if it is used as tourist center, is necessary due to use of surface water in various human activities. It is important to ensure hygienic water that does not have a negative impact on human health.

An analysis of selected physicochemical parameters was performed in laboratory conditions (table 1). Laboratory analyses will be followed by development of continuous sensors monitoring in future sampling campaigns.

Table 1. Analysis of surface water samples from five sample points in Zobnatica lake

Chemical parameters (mg/L)	Sampling site 1	Sampling site 2	Sampling site 3	Sampling site 4	Sampling site 5
Ortophosphate	**0.637**	**0.103**	**0.252**	0.017	**0.150**
Nitrate	0.010	0.014	0.014	0.017	0.008
Nitrite	0.03	0.02	0.03	0.03	0.02
Total Chlorine	0.04	0.05	0.02	0.08	0.06
Sulfate	91	85	97	69	88
Chromium (VI)	0.035	0.025	0.023	0.026	0.022
Chloride	38.8	35.8	37.2	**203.5**	53.3
Fluoride	< 0.02	< 0.02	0.66	0.69	< 0.02
Ammonia	0.13	0.10	0.04	0.06	0.08

The concentrations of the analysed samples are compared with the Regulation on limit values of pollutants into surface and groundwater and sediments and deadlines for accomplishing these goals (Official Gazette of the Republic of Serbia 50/2012). Concentrations of orthophosphate in samples of surface water from Zobnatica lake were higher (except sampling site 4) than limit value for II class of the ecological status of surface waters. Concentration of chloride was higher than limit value corresponding to good ecological status of lake water (class II) at sampling site 4. Around the Lake there is mostly agricultural land which rinsing out generates wastewater with increased concentrations of orthophosphate and chloride. Waste water which enters the lake leads to contamination. The main sources of orthophosphate and chloride on agricultural land are fertilizers loaded with nutrients and pesticides.

The continuous investigative monitoring by sensors and analyses of pollutants in first horizon of groundwater will provide information on bank vegetation effectiveness in retaining the pollutants from the arable lands, providing vital data. Analyses of physicochemical parameters performed by analytical methods were conducted in order to select key physicochemical parameters which will be analysed by in-situ fiber optical system (FOS). The obtained results can improve existing laboratory practice and could be applied on the other geolocations. It will indicate the possibilities of integrated and sustain planning in order to strengthen the ecological functions of the bank vegetation, with a special focus on pollution control, habitat quality and landscape connectivity.

Investigative monitoring by sensors located in measurement wells will produce data about the quantity and seasonal dynamics of the most important pollutants responsible for the eutrophication. Analyses will be useful for the management of protected wetlands and ecological corridors, and for the surface waters quality improvement. The inter(trans)disciplinary approach to problems will enable harmonization of agriculture and nature protection sectors. It will provide data and practices for the neglected field of the agro-biodiversity conservation, improving the Agro-Environmental Programmes.

4. CONCLUSION

The new gained data on the state of the aquatic environment resulting from analysis of physicochemical parameters in surface water by analytical methods will generate a new insight into ecostatus of water body, aquifers and wells. The significance of this type of the

results is important and equally worthy for mutually impact on cross-border area. Sampling sites are very similar for whole cross-border area Serbia-Croatia, due to the geological and hydrological origin, similar climatic and geochemical characteristics, which will enable the two parties jointly changing of behaviour. This will help to increase knowledge, experiences and awareness of water pollution and influence on improved management and new concept of protection environment and biodiversity. The development of all three types of monitoring system will have scientific contribution and influence on the upgraded research and extension in wireless sensor network area.

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Acknowledgments

“The research leading to these results has received funding from the Interreg IPA Cross-border Cooperation Programme Croatia-Serbia 2014-2020 under the project "Active SEnsor monitoring Network and environmental evaluation for protection and wiSe use of WETLANDS and other surface waters - SeNs Wetlands ", grant agreement n [2017HR-RS135].”

EKOLOŠKI PRIHVATLJIVI BIOKOMPOZITI

ENVIRONMENTAL FRIENDLY BIOCOMPOSITES

Vesna Ocelić Bulatović*, Lucija Mandić*, Anamarija Turković*, Dajana Kučić*, Emi Govorčin Bajsić*

* Sveučilište u Zagrebu, Fakultet kemijskog inženjerstva i tehnologije, Zagreb, Hrvatska

autor za korespondenciju: Vesna Ocelić Bulatović, e-mail: vocelic@fkit.hr

Izvorni znanstveni rad

SAŽETAK

Više od 40 % sintetskih polimera koji se koriste za proizvodnju plastičnih ambalažnih materijala (ambalaže) dobiveni su iz naftnih derivata. Nedostatak plastične ambalaže je što nije biorazgradljiva i ne može se u potpunosti reciklirati te predstavlja ozbiljan ekološki i ekonomski problem uslijed povećanja količine plastičnog otpada.

U cilju dobivanja biokompozita ovo istraživanje usmjereno je na modifikaciju polietilena niske gustoće (PE-LD) s prirodnom lignocelulozom (rižinim ljuskama (RLJ). Istražen je utjecaj RLJ kao i čestica mikro TiO_2 kao potencijalnog antibakterijskog sredstva na toplinska svojstva, apsorpciju vode i propusnost vodene pare biokompozita PE-LD/RLJ. Apsorpcija vode i propusnost vodene pare ovise o udjelu RLJ u filmovima i dodatku TiO_2. Ispitan je antibakterijski učinak biokompozitnih filmova na gram-negativnu (*Escherichia coli*), gram-pozitivnu bakteriju (*Bacillus subtilis*) i plijesan (*Aspergillus niger*) određivanjem inhibicijskih zona oko pojedinih filmova. Biokompoziti ne pokazuju antibakterijsku aktivnost u prisutnosti TiO_2.

Ključne riječi: *biokompoziti, rižine ljuske, PE-LD, TiO_2, antibakterijsko djelovanje*

ABSTRACT

More than 40 % of the synthetic polymers are used as a packaging material produced by petroleum-based plastics. However, most of these plastic packaging materials are nonbiodegradable and totally recyclable and cause serious economic and environmental problems related to the increasing volume of the plastic waste.

In this study, low density polyethylene (PE-LD) was melt-blended with natural lignocellulose, rice husk (RH) to form biocomposites. The effects of RH and micro particles of TiO_2 as a possible antibacterial agent on the thermal properties, water resistance and water

vapor permeability of the PE-LD/RH biocomposites were investigated. Water resistant and water vapor permeability strongly depending on the RH content and incorporation of TiO_2 in biocomposite films. Antibacterial activities of the biocomposite films against gram-negative (*Escherichia coli*), gram-positive bacteria (*Bacillus subtilis*) and fungi (*Aspergillus niger*) were determined by measuring the inhibition zone around each film. However, the biocomposite films did not show any antibacterial activities in the presence of TiO_2

Keywords: *biocomposites, rice husk, PE-LD, TiO_2, antibacterial activity*

1. UVOD

Plastični ambalažni materijali zauzimaju značajno mjesto u svakidašnjem životu za pakiranje prehrambenih i drugih proizvoda. Međutim problem vezan za plastičnu ambalažu je što se ona nakon korištenja nekontrolirano odlaže ili se baca u okoliš. Također, većina ambalaže koristi se jednokratno, što ima za posljedicu svakodnevno nastajanje velike količine plastičnog ambalažnog otpada. Problem nakupljanja ambalažnog otpada potiče nas na razvoj svijesti o zbrinjavanju i recikliranju istog. Svijest o ograničenoj količini fosilnih sirovina i sve većoj potrebi za zaštitom okoliša i zdravlja ljudi, značajno doprinosi povećanju interesa za iskorištavanje potencijala obnovljivih izvora. Stoga se sve veći naglasak stavlja na razvoj biorazgradljivih polimernih materijala kao i sami proces biorazgradnje, te modifikaciju strukture i time svojstava široko uporabljivih polimernih materijala koji nalaze svakodnevnu primjenu kao plastični ambalažni materijali za pakiranje. Osnovna uloga ambalažnog materijala je zaštita upakiranog proizvoda od različitih vanjskih čimbenika, a nakon zadovoljavanja te uloge, ambalažni materijal postaje otpad te je važno poticanje proizvođača na primjenu ekološki prihvatljivih ambalažnih materijala. Kako polimerni materijali ne bi zauvijek ostali obilježeni kao najveći onečišćivači našeg planeta, a ne kao revolucionarni materijali koji su pridonijeli industrijskom i društvenom napretku nužno je ne odlagati i nagomilavati ambalažni otpad u okoliš [1]. Da bi se smanjila primjena sintetskih polimernih materijala, a s druge strane zadržala kvaliteta i niska cijena ambalaže, biokompozitni polimerni materijali predstavljaju dobro rješenje. Biokompozitni materijali mogu se proizvesti od prirodnih vlakana i nerazgradivih polimera dobivenih iz naftnih derivata, sintetskih vlakana i biopolimera ili prirodnih vlakana i biopolimera [2, 3]. Proizvode se s ciljem poboljšanja postojećih, primjenskih, svojstava, dobivanjem novih svojstava, te postizanjem ciljane promjene svojstava s izrazitim naglaskom na biorazgradnju. Jedan od prvih sintetskih polimera te ujedno i jedan od najpoznatijih polimera današnjice, koji svoju najveću primjenu nalazi kao ambalažni materijal je polietilen niske gustoće, PE-LD. Spada u skupinu termoplasta te ima jako važnu ulogu u industriji polimernih materijala. Najvažniji parametri koji izravno utječu na svojstva polietilena su njegov stupanj kristalnosti, prosječna molekulska masa kao i raspodjela molekulske mase [4, 5]. Povećanjem udjela kristalne faze, odnosno stupnja kristalnosti, povećava mu se gustoća, temperatura taljenja te mu se istodobno poboljšavaju mehanička svojstva kao što su tvrdoća, vlačna čvrstoća, prekidno istezanje, otpor prema puzanju, krutost, i smanjuje se propusnost vodene pare i plinova [4, 5]. Riža (*Oryza sativa L.*) je jedan od najvećih usjeva na svijetu i prehrambenih proizvoda [6]. Pokriva oko 1 % površine zemlje [6]. Rižine ljuske (RLJ) su jeftin nusprodukt prerade riže koji se odvaja od rižinog zrna tijekom postupka mljevenja riže, te nagomilava kao poljoprivredni otpad. Zbog izuzetne dostupnosti RLJ, niske gustoće, niske vodljivosti topline, velike otpornosti na djelovanje štetnih mikroorganizama te dobrih antikorozivnih svojstava RLJ pokazuju veliki potencijal za njeno iskorištenje [6 - 8]. U svom preglednom radu Arjmandi i

suradnici [9] ističu prednosti rižinih ljuski, kao poljoprivrednog otpada, u pripremi biokompozitnih polimernih materijala. Neke od prednosti su niska molekulska masa, niska cijena i ono najvažnije ekološki su prihvatljive za okoliš. Zanimljivo je navesti istraživanje Chuayjuljita i suradnika [10] koji su izolirali siliku iz rižinih ljuski i ustanovili da za razliku od komercijalne silike, silika iz rižinih ljuski ima finije čestice te biokompoziti imaju manju poroznost zbog manje specifične površine čestica silike i njihove manje gustoće uslijed čega dolazi do poboljšanja toplinskih i mehaničkih svojstava. Ayswarya i suradnici [11] su istraživali utjecaj pepela riže na svojstva polietilena visoke gustoće, PE-HD i dobili su znatno povećanje toplinske stabilnosti PE-HD-a dodatkom pepela riže. Rahman i suradnici [12] istraživali su utjecaj veličine čestica rižinih ljuski na svojstva PE-HD i zaključili što je veličina čestica RLJ veća manja je mogućnost aglomeracije i bolja dispergiranost RLJ u biokompozitu.

Cilj ovog rada je pripremiti biokompozitne materijale na osnovi najzastupljenijeg ambalažnog materijala, polietilena niske gustoće. U matricu PE-LD umješano je 10 – 50 mas. % rižinih ljuski (prirodne lignoceluloze) koje nastaju kao nusprodukt/otpad prilikom proizvodnje riže. Ispitan je utjecaj dodatka 2 mas.% mikropunila TiO_2 kao potencijalnog antibakterijskog sredstva na PE-LD/RLJ biokompozite. Priprema biokompozita provedena je u laboratorijskoj Brabender gnjetilici, te su ispitni uzorci dobiveni prešanjem na hidrauličkoj preši. Karakterizacija PE-LD/RLJ biokompozita provedena je u cilju određivanja njihovih toplinskih svojstava tehnikom termogravimetrijske analize (TGA). Istražen je utjecaj RLJ kao i čestica mikro TiO_2 na toplinska svojstva i propusnost vodene pare biokompozita PE-LD/RLJ. Ispitan je antibakterijski učinak mikropunila TiO_2 PE-LD/RLJ biokompozitnih filmova na gram-negativnu (*Escherichia coli*), gram-pozitivnu bakteriju (*Bacillus subtilis*) i plijesan (*Aspergillus niger*) određivanjem inhibicijskih zona oko pojedinih filmova biokompozita.

2. EKSPERIMENTALNI DIO

2.1. Materijali

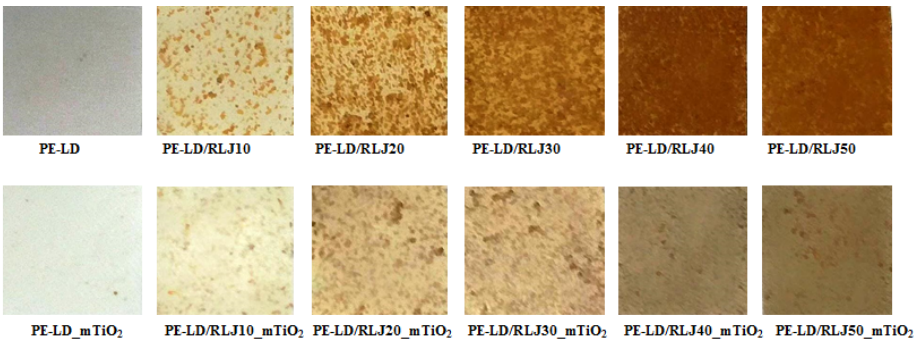
Pripremljeni su biokompoziti na osnovi polietilena niske gustoće (PE-LD) DOW ^{MT} PE-LD 150E, proizvođač Dow Europe, MFR = 0,25g/10 min pri 190 °C (ISO 1133), gustoće 0,921 g/cm^3 (ASTM D 792). Kao punilo korištene su rižine ljuske (raspodjela veličina čestica 180 – 710 μm) porijeklom iz Kočana, Makedonija, tip riže SANT ANDREA, Italija. Kao punilo korišten je mikro titanijev dioksid, mTiO_2 (veličina čestica ~0.6 μm) gustoće 3,9 g/cm^3 tvrtke Aldrich Chemistry.

2.2. Priprava PE-LD/RLJ i PE-LD/RLJ_mTiO_2 biokompozita

Prije umješavanja rižinih ljuski u PE-LD, rižine ljuske su usitnjene u mikseru IKA-WERKE M20 i sušene 24 h u sušioniku na 90 ^oC da bi se uklonila eventualno prisutna vlaga. PE-LD/RLJ i PE-LD/RLJ_mTiO_2 biokompoziti su pripravljeni umješavanjem čistog PE-LD s rižinim ljuskama u omjeru od 10, 20, 30, 40 i 50 mas.% rižinih ljuski bez i s dodatkom 2 mas.% TiO_2. Umješavanje je provedeno u laboratorijskoj Brabender gnjetilici pri temperaturi od 170°C u vremenu od 5 min. Nadalje, filmovi PE-LD/RLJ i PE-LD/RLJ_mTiO_2 biokompozita pripremljeni su prešanjem pomoću hidrauličke preše Fontune, Holland (SRB

140, EC 320x320NB) pri temperaturi od 140 °C u vremenu od 5 min, između dviju teflonskih ploča

Na slici 1 su prikazani pripremljeni filmovi PE-LD/RLJ biokompozita i njihove oznake bez i s dodatkom $mTiO_2$, (PE-LD/RLJ_$mTiO_2$). Broj u oznaci uzorka od 10 - 50 odgovara udjelu dodanih RLJ.



Slika 1. Prikaz pripremljenih biokompozitnih filmova

2.3. Određivanje propusnosti vodene pare

Propusnost vodene pare određivana je pomoću aparata po Herfeldu prema normi DIN 53333 [13]. Herfeldov aparat sastoji se od staklene posudice na koju se stavlja metalni poklopac. Na poklopcu je kružni otvor promjera 36 mm. U staklenu se posudu ulije 50 mL vode, a otvor na poklopcu se prekrije kružno izrezanim filmom uzorka promjera 55 mm. Herfeldov aparat se postavlja u eksikator u kojemu se nalazi 97 %-tna sumporna kiselina. Masa Herfeldovog aparata s epruvetom i vodom određuje se na početku ispitivanja, i nakon određenih vremenskih intervala od 24 h i 48 h. Propusnost vodene pare (PVP) računa se prema izrazu [13]:

$$PVP(g/m^2 dan) = \left[m_0 - (m_1 + m_2)/2\right]/A \quad (1)$$

gdje je m_0 masa aparata s vodom i epruvetom na početku mjerenja, m_1 masa aparata s vodom i epruvetom nakon 24 h, m_2 masa aparata s vodom i epruvetom nakon 48 h, $A = r^2\pi$ površina filma ispitivanog uzorka, r polumjer filma ispitivanog uzorka.

2.4. Termogravimetrijska analiza

Toplinska stabilnost filmova PE-LD/RLJ i PE-LD/RLJ_$mTiO_2$ biokompozita različitog udjela RLJ bez i s dodatkom TiO_2 određena je termogravimetrijskom analizom na uređaju TGA analizator Q500 tvrtke TA Instruments. Ispitivanje je provedeno u temperaturnom intervalu od 25 °C do 700 °C, brzinom zagrijavanja od 10 °C/min u inertnoj atmosferi dušika. Masa ispitivanih uzoraka iznosila je 10 mg.

2.5. Antimikrobno testiranje

Uzorci PE-LD_$mTiO_2$ te PE-LD/RLJ_$mTiO_2$ izrezani su u obliku malih kvadratića dimenzija 1x1 cm. Na navedenim uzorcima napravljen je test osjetljivosti na bakterije

Bacillus subtilis te *Escherichia coli* i plijesan *Aspergillus niger* prema Normi ISO EN 846:1997. U radu je korišten hranjivi agar za uzgoj bakterija i sladni agar za uzgoj plijesni. U sladni agar dodan je 1 cm^3 antibiotika u cilju sprječavanja rasta bakterija.

Priprema suspenzije *Bacillus subtilis* i *Aspergillus niger* te određivanje ukupnog broja stanica mikroorganizma

U dvije epruvete sa 10 mL sterilne vode mikrobiološkom ušicom prenesene su izrasle kulture *Bacillus subtilis* te *Escherichia coli* koje su dan prije precijepljene na kosu hranjivu podlogu. Iz dobro homogenizirane suspenzije napravljena su razrjeđenja te se 1 mL razrjeđenja 10^{-6} zalilo s hranjivim agarom i nakon 24 sati se odredio ukupan broj stanica u mL. U 10 mL sterilne vode mikrobiološkom kukicom prenijela se izrasla kultura *Aspergillus niger* (spore). Ukupan broj stanica u mL odredio se brojanjem spora u Thominoj komorici (1) te neizravnim određivanjem - 1 mL razrjeđenja 10^{-6} zalilo se sa sladnim agarom i nakon 72 sata odredio se ukupan broj stanica u mL (2).

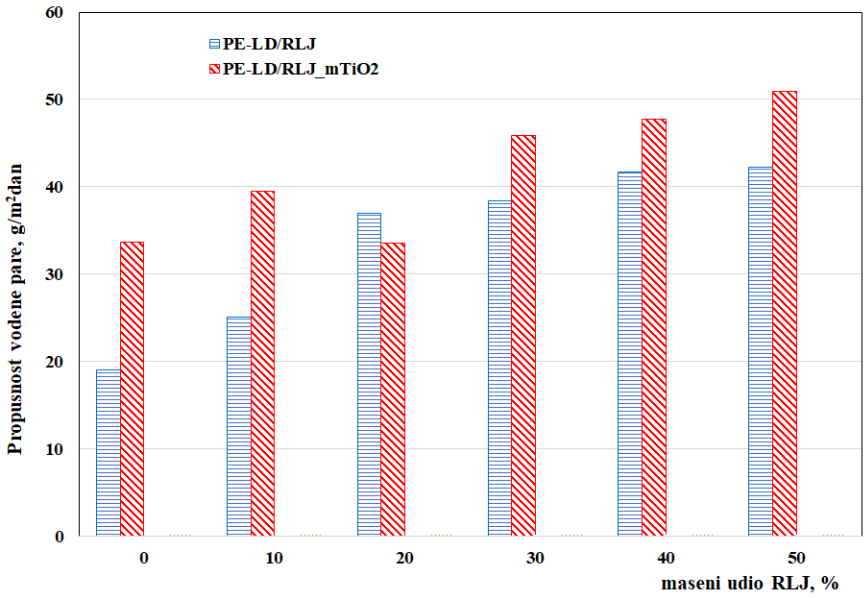
Određivanje prijenosa antimikrobnih sastojaka

Određivanje antimikrobnih sastojaka provodilo se na dva načina (sterilni uvjeti rada): U 5 Petrijevih zdjelica u kojima je bio izliven hranjivi agar dodalo se 0,1 mL suspenzije *Bacillus subtilis* odnosno *Esherichia coli* (10^5 st/mL) i štapićem po Drigalskom homogenizirala se suspenzija te se na četiri mjesta dodao uzorak (u svaku Petrijevu zdjelicu četiri uzorka). Petrijeve zdjelice stavljene su na inkubaciju na 37 °C 24 - 48 sati. Isti postupak napravljen je za *Aspergillus niger*, samo što je hranjiva podloga bila sladni agar, a broj spora 10^6 st/mL. Petrijeve zdjelice stavljene su na inkubaciju na 28 °C 3 - 5 dana.

3. REZULTATI I DISKUSIJA

3.1. Rezultati propusnosti vodene pare

Nedostatak polimernih ambalažnih materijala je njihova propusnost na plinove i vodenu paru što ima značajan utjecaj na trajnost upakiranog proizvoda. Vodena para može prodirati kroz polimerni ambalažni materijal do upakiranog sadržaja što ima negativan učinak na njegovu kvalitetu. Uslijed prisutnosti vodene pare u namirnicama može doći do razvoja mikroorganizama, gljivica te promjene izgleda pakiranog proizvoda. Zbog toga propusnost vodene pare predstavlja bitan parametar kod pakiranja hrane u polimerne ambalažne materijale. Mjerenja propusnosti vodene pare (PVP) provedena su za sve pripremljene PE-LD/RLJ i PE-LD/RLJ_mTiO_2 biokompozite. Vremenski period propuštanja vodene pare bio je 24 i 48 h, nakon čega su ispitivani uzorci vagani. Rezultati propusnosti vodene pare PE-LD/RLJ i PE-LD/RLJ_mTiO_2 biokompozita prikazani su na slici 2.

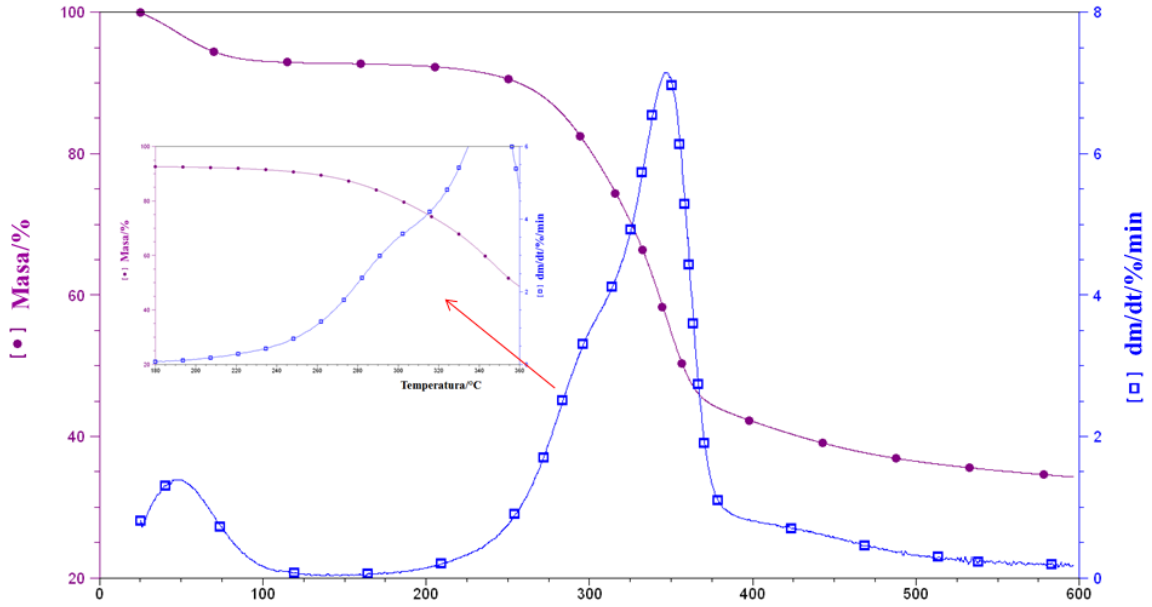


Slika 2. Propusnost vodene pare PE-LD/RLJ i PE-LD/RLJ_mTiO$_2$ biokompozita

Polietilen niske gustoće se odlikuje nižom vrijednosti propusnosti vodene pare, na što su ukazali i rezultati dobiveni u ovom istraživanju, PVP za PE-LD iznosi 19,08 g m^{-2} dan^{-1}. Očekivano je kako će dodatak i povećanje udjela RLJ u PE-LD/RLJ biokompozite utjecati na veću propusnost vodene pare polietilena. Dobiveni rezultati vrijednosti PVP rastu dodatkom i povećanjem sadržaja RLJ u PE-LD/RLJ biokompozitima. Povećanjem udjela RLJ, raste udio hidrofilnog materijala (RLJ), a smanjuje se udio hidrofobnog materijala (PE-LD). Do ovakvog ponašanja dolazi zbog slobodnih O-H skupina koje se nalaze u RLJ i na taj način doprinose hidrofilnom karakteru RLJ uslijed kojeg dolazi do vezanja molekula vode na RLJ preko vodikovih veza, a kao posljedica dolazi do porasta PVP. Pri manjem udjelu dodanih RLJ pretpostavlja se dobra dispergiranost RLJ unutar PE-LD matrice, što utječe na dulji difuzijski put kojim molekule vode penetriraju unutar strukture biokompozita i bivaju apsorbirane RLJ, što utječe na manju propusnost vodene pare u usporedbi s većim sadržajem RLJ u PE-LD/RLJ biokompozitima. Kod većeg udjela RLJ veća je mogućnost koalescencije RLJ kao potencijalnih mjesta za apsorpciju vode. Zbog hidrofilnog karaktera mikropunila TiO$_2$, dodatak mTiO$_2$ utjecao je na porast PVP-a kod PE-LD/RLJ_mTiO$_2$ biokompozite.

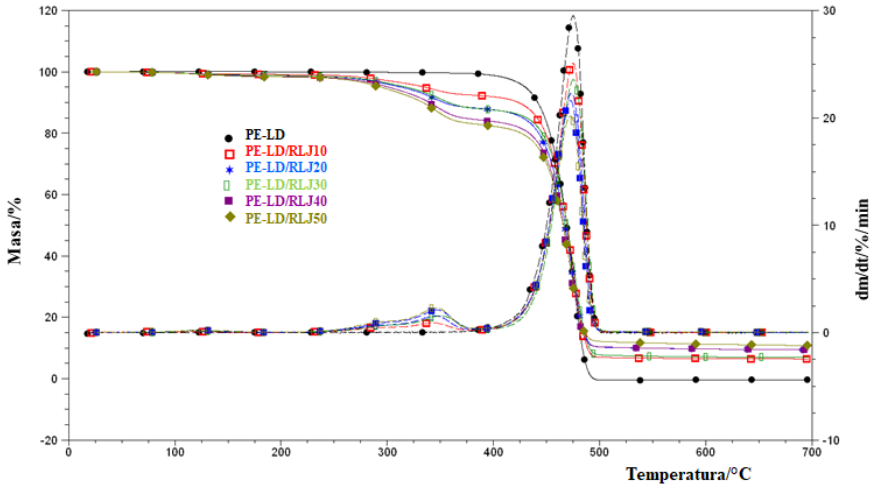
3.2. Rezultati termogravimetrijske analize

U cilju određivanja utjecaja rižinih ljuski i mikropunila TiO$_2$ na toplinsku stabilnost čistog PE-LD-a provedena su termogravimetrijska mjerenja u atmosferi dušika. Toplinska stabilnost vrlo je važna za biokompozitne materijale ojačane prirodnim vlaknima jer kod takvih materijala dolazi do razgradnje na nižim temperaturama što utječe na smanjenje maksimalne temperature njihove pripreme i prerade. Provedena je i TGA analiza rižinih ljuski, te su TG (Masa/%; ljubičasta krivulja) i DTG (dm/dt/%/min; plava krivulja) krivulja rižini ljuski prikazane na slici 3.

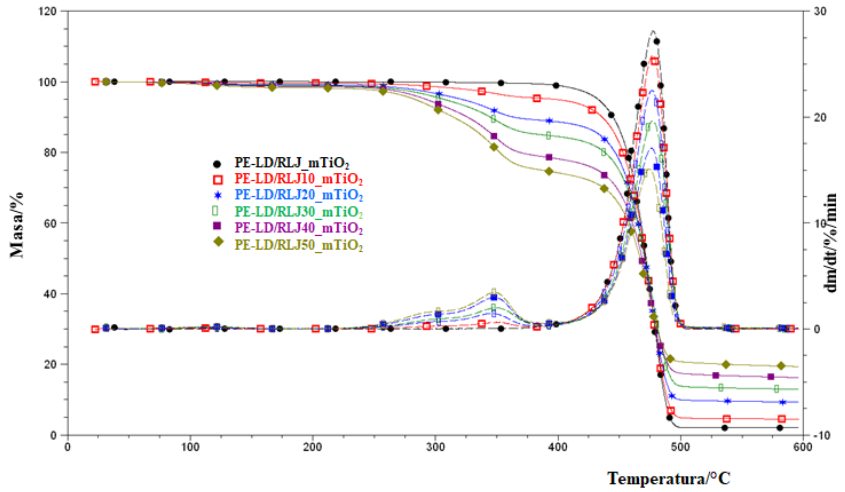


Slika 3. TG (Masa/%) i DTG (dm/dt/%/min) krivulja rižinih ljuski

Na DTG krivulji toplinske razgradnje RLJ javljaju se dva stupnja razgradnje, prvi stupanj razgradnje u području od sobne temperature do 100 ^{o}C vezan je za fizičku apsorpciju vode u rižinim ljuskama kao i/ili površinsko/vanjsko vezanje vode zbog površinske napetosti [14]. Udio vezane vode (vlage) u RLJ iznosi 6,27 %. Nakon isparavanja/gubitka vode dolazi do razgradnje, značajnog gubitka mase, u području temperatura s početkom pri 200 °C do 400 °C s temperaturom maksimalne brzine razgradnje pri 370 ^{o}C. Nadalje, iznad 400 °C proces razgradnje se usporava, no i dalje je vidljiv gubitak mase te se kraj razgradnje postiže pri 600 °C. K. G. Mansaray i A. E Ghaly [15] u svom istraživanju navode da se lignocelulozni materijali sastoje od tri glavne komponente, hemiceluloze, celuloze i lignina, čija se toplinska razgradnja odvija u području od 150 – 500 °C. Navode razgradnju hemiceluloze u području između 150 – 350 °C, dekompoziciju celuloze u području od 275 – 350 °C te postupnu razgradnja lignina između 250 – 500 °C. U korelaciji s navedenim istraživanjem te iz slike 3. TG i DTG krivulje RLJ glavni stupanj toplinske razgradnje RLJ pripisuje se razgradnji celuloze u udjelu od 56,39 %. Na glavnom piku razgradnje RLJ uočava se rame u temperaturnom području od 260 - 310 °C što je vezano za razgradnju hemiceluloze s udjelom od 19,44 % (slika 3). Odnosno, toplinska razgradnja rižinih ljuskica započinje razgradnjom hemiceluloze, zatim slijedi početak razgradnje celuloze, završnom fazom razgradnje celuloze započinje razgradnja lignina. Ostatak na 700 ^{o}C odnosi se na udio pepela odnosno silike u iznosu od 34,44 %. Na krivulji toplinske razgradnje čistog PE-LD-a javlja se jedan stupanj razgradnje u relativno uskom temperaturnom području (slika 4). Početak razgradnje PE-LD-a je pri 429 ^{o}C s temperaturom maksimalne brzine razgradnje na 477 ^{o}C i krajem razgradnje na 489 ^{o}C. Mehanizam toplinske razgradnje PE-LD spada u radikalski mehanizam razgradnje kod kojega u reakciji inicijacije dolazi do nasumičnog cijepanja lanca te toplinska razgradnja i dekompozicija nastaju na bočnim skupinama polimernog lanca PE-LD-a [16]. Dolazi do nastajanja slobodnih radikala i prijelaza vodika iz polimernog lanca što dovodi do smanjenja molekulske mase i konačno do formiranja hlapljivih produkata. Razgradnja polietilena vodi do stvaranja parafina i olefina, bez ostatka razgradnje [16]. Na slikama 4 i 5 prikazane su TG i DTG krivulje čistog PE-LD, PE-LD/RLJ biokompozita bez i uz dodatak mTiO_2. U tablice 1 i 2 sumirani su rezultati TG analize za sve ispitivane biokompozite.



Slika 4. TG (Masa/%) i DTG (dm/dt/%/min) krivulje čistog PE-LD i PE-LD/RLJ biokompozita



Slika 5. TG (Masa/%) i DTG (dm/dt/%/min) krivulje čistog PE-LD i PE-LD/RLJ biokompozita s dodatkom $mTiO_2$

Tablica 1.Rezultati termogravimetrijske analize PE-LD/RLJ biokompozita

Uzorak	$T_{5\%}$/ °C	T^1_{max}/ °C	Δm_1 / %	T^2_{max}/ °C	Δm_2/ %	T^3_{max}/ °C	Δm_3/ %	ΔT/ °C	T_{kraj}/ °C	*Ostatak na 700°C/ %*
PE-LD	430	/	/	/	/	477	100,00	59	489	0,00
PE-LD/RLJ10	336	/	/	343	6,74	474	85,71	154	490	6,43
PE-LD/RLJ20	313	114	0,98	345	10,51	473	78,49	172	485	9,39
PE-LD/RLJ30	313	117	1,12	350	11,02	475	80,62	170	487	6,92
PE-LD/RLJ40	301	117	1,39	347	14,07	472	74,73	183	484	9,38
PE-LD/RLJ50	294	116,62	1,50	345,70	15,60	472	71,37	190,22	485	10,80

$T_{5\%}$ je evaluiran kao temperatura pri 5 mas.% gubitka mase

Tablica 2. Rezultati termogravimetrijske analize PE-LD/RLJ biokompozita s dodatkom $mTiO_2$

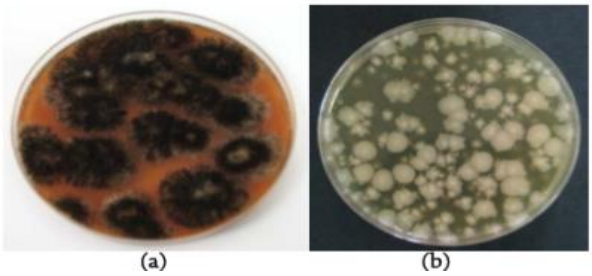
Uzorak	$T_{5\%}$/ °C	T^1_{max}/ °C	Δm_1/ %	T^2_{max}/ °C	Δm_2/ %	T^3_{max}/ °C	Δm_3/ %	ΔT/ °C	T_{kraj}/ °C	*Ostatak na 700°C/ %*
PE-LD_$mTiO_2$	433	/	/	/	/	477	98,26	56	489	2,05
PE-LD/RLJ10_$mTiO_2$	322	/	/	349	4,02	477	90,85	171	489	4,50
PE-LD/RLJ20_$mTiO_2$	318	112	0,660	345	9,96	476	79,63	167	489	9,29
PE-LD/RLJ30_$mTiO_2$	307	116	1,024	349	14,01	477	71,74	183	490	12,95
PE-LD/RLJ40_$mTiO_2$	292	114	1,215	348	19,96	476	62,16	196	488	16,26
PE-LD/RLJ50_$mTiO_2$	283	116	1,557	348	23,45	474	55,23	204	487	19,38

Na osnovi rezultata termogravimetrijske analize (slika 4, tablica 1) dodatkom i porastom udjela RLJ temperatura početka razgradnje pomiče se na niže temperature što ukazuje na smanjenje toplinske stabilnosti PE-LD-a dodatkom RLJ. Iz TGA rezultata u tablici 1. vidljiv je udio vezane vode (Δm_1) koja isparava na temperaturama od oko 100 °C, no udio vezane vode u PE-LD/RLJ biokompozitima je niži u usporedbi s % -tkom udjela vezane vode u RLJ. Udio vode u biokompozitu raste što je veći udio rižinih ljuski u PE-LD/RLJ i PE-LD/RLJ_$mTiO_2$ biokompozitima. Obzirom na hidrofilni karakter RLJ, i prema prethodnim rezultatima propusnosti vodene pare, za očekivati je, da što je veći udio RLJ u biokompozitu bit će i veći udio vezane vode. Toplinska razgradnja PE-LD/RLJ biokompozita odvija se u dva stupnja, prvi stupanj vezan je za razgradnju RLJ dok drugi stupanj odgovara razgradnji PE-LD-a. Iz tablice 1. vidljivo je da se udio gubitka mase (Δm_1) koji je vezan za razgradnju RLJ povećava s povećanjem udjela RLJ u PE-LD/RLJ biokompozitima. Ostatak na 700 °C kod čistog PE-LD iznosi 0,00 %, što ukazuje na potpunu razgradnju PE-LD-a, dok ostatak kod PE-LD/RLJ biokompozita raste povećanjem udjela RLJ (tablica 1.). Ovaj ostatak vezan je za siliku (ukupni udio silike u RLJ iznosi 34,44 %). Na slici 5 prikazane su TG i DTG krivulje PE-LD/RLJ_$mTiO_2$ biokompozita. Početak razgradnje PE-LD_$mTiO_2$ ($T_{5\%}$= 433 ^oC) je na višim temperaturama u odnosu na čisti PE-LD-a ($T_{5\%}$= 430 ^oC). Na osnovi dobivenih rezultata temperature početka razgradnje (tablica 2) može se zaključiti da se toplinska stabilnost PE-LD-a povećala dodatkom $mTiO_2$ te da se razgradnja odvija u kraćem temperaturnom intervalu. Može se pretpostaviti da dodatkom TiO_2 u PE-LD dolazi do smještanja čestica punila u kristalnu fazu PE-LD i porasta stupnja kristalnosti uslijed nukleacijskog učinka TiO_2 što rezultira povećanjem toplinske stabilnosti. Ostatak mase na 700 °C od 2,05 % PE-LD_$mTiO_2$ vezan je za ostatak mikropunila, koji je upravo u tom postotku dodan u PE-LD/RLJ_$mTiO_2$ biokompozite. Dodatkom $mTiO_2$ u PE-LD/RLJ biokompozite temperatura razgradnje se pomiče na niže temperature u odnosno na PE-LD/RLJ biokompozite što ukazuje na smanjenje toplinske stabilnosti. Ovo ponašanje može se dovesti u vezu s lošom raspodjelom i mogućnosti aglomeracijom čestica punila unutar polimerne matrice. Vidljiv je porast ostatka na 700 ^oC u odnosu na biokompozite bez dodatka $mTiO_2$, ovaj ostatak vezan je za $mTiO_2$.

3.3. Rezultati antimikrobnog testiranja

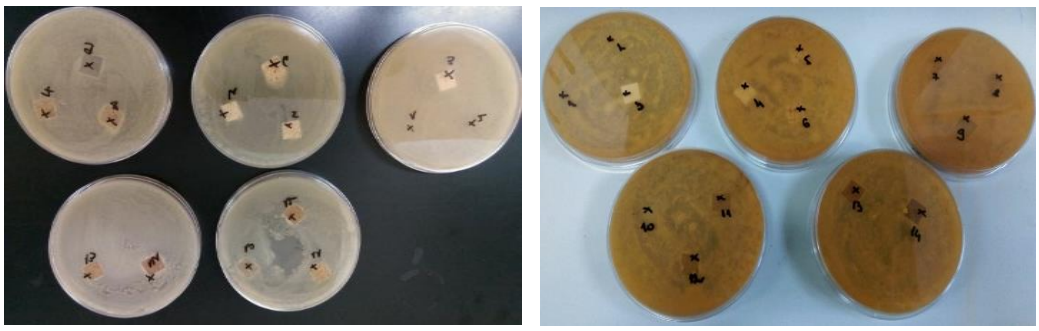
Na pripremljenim filmovima PE-LD_$mTiO_2$, te PE-LD/RLJ_$mTiO_2$ biokompozita s različitim udjelom RLJ proveden je test osjetljivosti na bakterije *Bacillus subtilis* i

Escherichia coli (slika 6) te plijesan *Aspergillus niger* prema Normi ISO EN 846:1997, kako bi se ispitao antimikrobni učinak $mTiO_2$ [17]



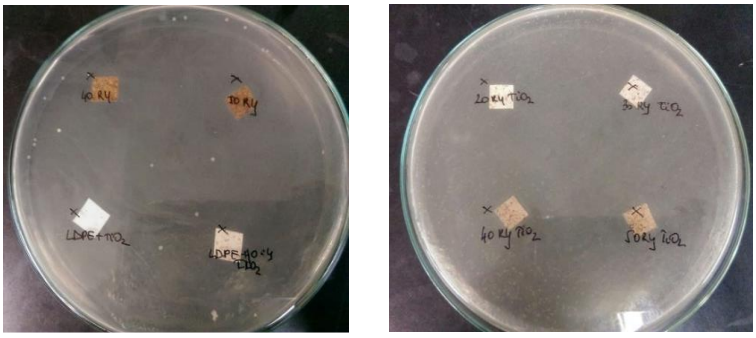
Slika 6. Fotografska slika rasta plijesni Aspergillus niger (a) i bakterije Bacillus subtilis (b)

Prilikom određivanja antimikrobnih svojstava uzoraka na bakterije *Bacillus subtilis* te *Escherichia coli* uočava se (slike 7 i 8) da zone oko uzorka nisu nastale ni u jednom slučaju iz čega zaključujemo da uzorci nemaju inhibicijski učinak na ispitivane mikroorganizme. Prilikom određivanja antimikrobnih svojstava uzoraka na *Aspergillus niger* također se može se vidjeti (slika 7 (b)) da zone oko uzorka nisu nastale ni u jednom slučaju iz čega se može zaključiti da uzorci ne djeluju inhibicijski na ispitivanu plijesan. Na temelju ovih rezultata može se zaključiti da mikropunilo TiO_2 u udjelu od 2 mas.% nije pokazao antimikrobni učinak. Dobiveni rezultati ukazuju da bi se udio $mTiO_2$ u ispitivanim biokompozitima trebao povećati ili umješati nanopunilo TiO_2 zbog veće površine čestica punila [18, 19]. Nadalje, u istraživanje antimikrobnog učinka, svakako treba uključiti i ispitivanje na bakteriju *Staphylococcus aureus* koja je dio čovjekove flore [18, 19].



a) b)

Slika 7. Ispitivanje PE-LD/RLJ_$mTiO_2$ biokompozita na bakteriju Bacillus subtilis (a) i plijesan Aspergillus niger (b)



Slika 8. Ispitivanje PE-LD/RLJ_$mTiO_2$ biokompozita na bakteriju Escherichia coli

4. ZAKLJUČAK

Dobiveni rezultati ukazuju na porast PVP-a dodatkom i povećanjem udjela RLJ u PE-LD/RLJ biokompozitima. Kod toplinske razgradnje RLJ najprije dolazi do isparavanja vezane vode, zatim razgradnje hemiceluloze i početka razgradnje celuloze, nadalje slijedi završna faza razgradnje celuloze i početak razgradnje lignina. Ostatak na 700 ^{o}C odnosi se na udio pepela odnosno silike u iznosu od 34,44 %. Toplinska razgradnja čistog PE-LD-a odvija se u jednom stupnju razgradnje u relativno uskom temperaturnom području. Dodatkom i porastom udjela RLJ temperatura razgradnje se pomiče na niže temperature što ukazuje na smanjenje toplinske stabilnosti PE-LD-a. Dodatkom $mTiO_2$ u biokompozitne sustave PE-LD/RLJ toplinska stabilnost se pomiče prema nižim temperaturama u odnosu na PE-LD i na sustave PE-LD/RLJ. Prilikom određivanja antimikrobnih svojstava uzoraka PE-LD/RLJ_$mTiO_2$ biokompozita na gram-negativnu *Bacillus subtilis*, gram pozitivnu bakteriju *Escherichia coli* te plijesan *Aspergillus niger* zone oko uzorka nisu nastale ni u jednom slučaju iz čega se može zaključiti da uzorci nemaju inhibicijski učinak na ispitivane mikroorganizme. Može se zaključiti da $mTiO_2$ u udjelu od 2 mas.% nije pokazao antimikrobni učinak.

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Croatia, Sisak, September 13th-14th, 2018

INDUSTRIAL ACTIVITY AND SOIL CONTAMINATION IN ELBASAN, ALBANIA

Marilda Osmani*, Aida Bani, Belinda Hoxha*, Armela Mazreku***

* "Aleksandër Xhuvani" University, Faculty of Natural Sciences, Elbasan, Albania
** Agricultural University of Tirana, Faculty of Agriculture and Environment, Tirana, Albania

corresponding author: Marilda Osmani, e-mail: marilda.osmani@uniel.edu.al

Original scientific paper

ABSTRACT

The development of heavy industry contributes on the negative environmental impact. This industry is responsible for the soil contamination. The objective of our study is to determine the level of Ni, Zn, Mn and Cd, in the soils near (1) The Oxygen Plant, (2) Kurum International Sh. A, (3) The Ferro-chrome Plant and (4) The Cement Plant.

The laboratory tests showed that the heavy metal concentrations are: in the first plant (1) Ni was 153 mg kg^{-1}, Zn 76 mg kg^{-1}, Cu 35 mg $kg^{-1}$and Cd 12 mg kg^{-1}; (2) Ni 480 mg kg^{-1}, Zn 280 mg kg^{-1}, Cu 40 mg $kg^{-1}$and Cd 15 mg kg^{-1}; (3) Ni 345 mg kg^{-1}, Zn 102 mg kg^{-1}, Cu 31 mg $kg^{-1}$and Cd 4 mg $kg^{-1}$and (4) Ni 310 mg kg^{-1}, Zn 103mg kg^{-1}, Cu 30 mg $kg^{-1}$and Cd 5 mg kg^{-1}.

The data presented in this study indicate that the soils around each plant are contaminated with heavy metals because of the industrial activities carried out in the past and which continues nowadays as well.

***Keywords**: contaminated soil, heavy metals, impact, heavy industry*

1. INTRODUCTION

Soil contamination, also known as soil pollution is caused by the presence of manmade chemicals in the natural soil environment, mainly the heavy metals. Heavy metals are natural constituents of the earth crust. They primarily result from the weathering of parent materials and from human activities, which including mining, smelting, application of sludge, discharge of wastewaters, production of different oils, foundries, smelters and diffuse sources such as piping, constituents of products, combustion of by products, etc. [1]. The heavy metals are part of the soil, but their high levels are toxic. Soils are critical environment where rock, air and water interface. Consequently, they are subjected to a number of pollutants due to different anthropogenic activities (industrial, agricultural, transport etc.) [2]. The chemical

composition of soil, particularly its metal content is environmentally important, because toxic metals concentration can reduce soil fertility, can increase input to food chain, which leads to accumulate toxic metals in food stuffs, and ultimately can endanger human health [3].

Soil contaminated with heavy metals has become a worldwide problem and pose a serious threat to the environment [4]. In Europe, the most frequent contaminants of soil are heavy metals and mineral oil, and approximately three million sites are estimated to have been potentially affected by activities that can contaminate soil [5]. Albania is part of Europe which is known as a high-pollution and high-risk zone and require immediate rehabilitation [6] interventions. Elbasan is one of the largest cities in Albania, which had the biggest Metallurgical Complex in the country from 1970 - 1990, about 550 hectares [7]. Since 1991, four major heavy industries operate in the city, which are Kurum International Sh. A., which is specialized in the production of iron-steel, the Ferro-chrome production Plant, the Oxygen plant and the Cement plant. The development of these industries contributes on the prosperity of a city, but at the same time, they are the main source of the soil and groundwater contamination with heavy metals [8 - 11].

In recent years, the industrial area is transform into a residential center, because of the population growth and emigration from the village to the city. In addition to the industrial activities that are being carried out, agriculture and livestock farming have been developed here, too. Residents of the Elbasan Municipality mostly complain of respiratory problems, which occur particularly among children and youth. Moreover, the long term pollution also leads to a diversity of cardiac and lung diseases.

The main aim of this work was is to determine the level of heavy metals Ni, Zn, Cu and Cd, in the soil around this plant, which have different industrial activity. Based on the results, through the Geo-accumulation Index (Igeo) and soil quality guidelines, is establish which industry causes more environmental pollution and if the soil around these industries are contaminated with the heavy metals.

2. EXPERIMENTAL

2.1. The study area

The study area is the industrial complex, which is 5 km from the city of Elbasan and covers approximately 300 ha. In the past, the Elbasan smelters have consistently processed 35 000 t ferrochrome and the majority of the 1.0 Mt of iron-nickel ores mined from the Librazhd-Pogradec district [8, 12]. The cement plant is closer the city than the other factories, which are near each other. The sampling locations were collected in 0-30 horizon, from the fields near (1) The Oxygen Plant, (2) Kurum International Sh. A., (3) The Ferro-chrome Plant and (4) The Cement Plant, as presented in figure 1.

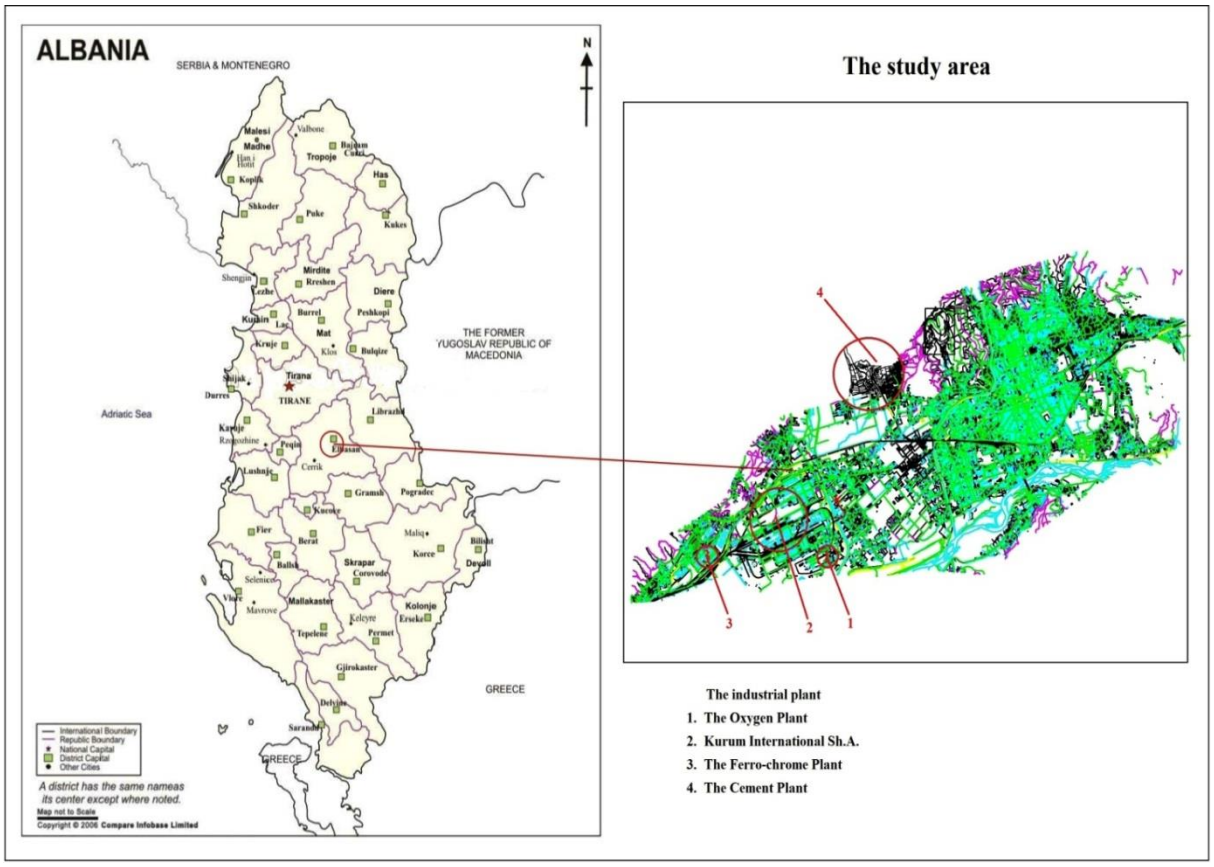


Figure 1. Map of Albania and the study area

2.2. Sampling

12 samples (3 for each field) were collected from each site, 30 cm in deep, during September. Sub samples of each soil were air dried and ground to pass through a 2-mm stainless-steel sieve. A 0.3 g soil sample was digested by adding 8 ml HNO_3 69 % and 2 ml H_2O_2. Solution were filtered and adjusted to 50 ml with distilled water. Heavy metals are determined spectrochemically using Atomic absorption spectrophotometer. The solution obtained after mineralization is filtered and added to 25 ml of 0.1 M HNO_3. All chemical used in assessing these parameters were of AR grade1.

3. RESULTS AND DISCUSSION

3.1. pH and heavy metals in soil

Soil pH (acidity) is an important factor, which controls the behavior of metals and many other soil processes. Heavy metal cations (positively charged metal atoms) are most mobile in acid soils. This means that metal contaminants are more available for uptake by plants or to move into the water supply. Making soil less acidic is one way to reduce the bioavailability of metals [13]. In this study, the pH was alkaline with average of approximately 8.5, so there was no need for intervention.

Based on the results obtained (figure 2) it can be said that the concentration of Ni is higher (480 mg kg^{-1}) in Kurum International Sh.A. and lower (153 mg kg^{-1}) in The Oxygen Plant. The concentration of Zn is higher (280 mg kg^{-1}) in Kurum International Sh. A. and lower (76 mg kg^{-1}) in Oxygen Plant. The concentration of Cu is higher (35 mg kg^{-1}) in Kurum International Sh. A. and lower (30 mg kg^{-1}) in The Cement Plant. The concentration of Cd is higher (15 mg kg^{-1}) in Kurum International Sh. A. and lower (4 mg kg^{-1}) in The Ferro-chrome Plant.

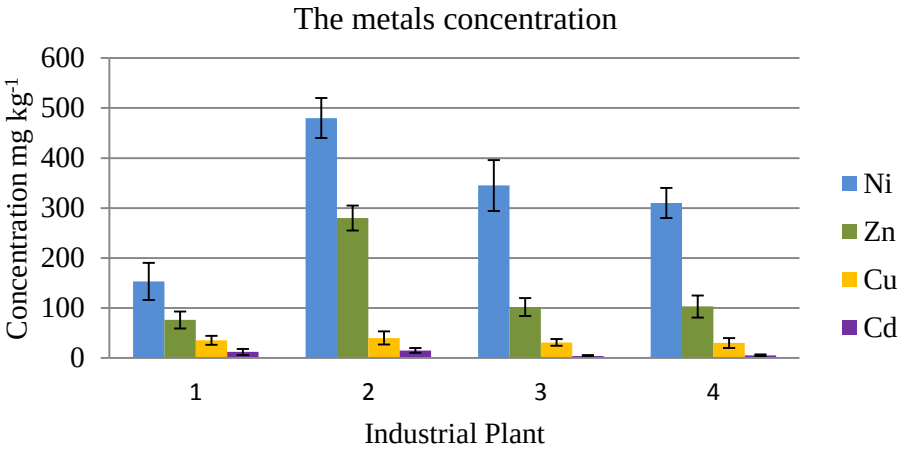


Figure 2. The concentrations of the heavy metals in industrial plant

Nickel content in all samples was greater than the permissible limits according the Directive 86/278/EEC, which is 75 mg kg^{-1} [14]. The permissible limit for zinc according the Directive 86/278/EEC is 300 mg kg^{-1}. According to 86/278/EEC, the limit for copper in soil is 140 mg kg^{-1} and the limit for cadmium is 3 mg kg^{-1}. The concentration of Zn and Cu, in the study is below of the 86/278/EEC limits, while the Cd concentration is over the limit.

The soils in study area are contaminated with heavy metal, Ni and Cd, as a result of industrial activity carried out in the past and the present.

3.2. ANOVA (One-Way) Analysis

The ANOVA test confirms that the Cu has no significant difference, since the exact significance level (0.57835) provided in SPSS output, is greater than alpha (0.05) and for Ni, Zn and Cd the difference are significant ($p < 0.05$) (Tables 1 - 4).

The data show that different types of industrial activities are source of Ni, Zn and Cd in soil contamination.

Table 1. The ANOVA results for Ni

Source of Variation	SS	df	MS	F	p-level	F crit
Between Groups	162234.92	3	54078.31	32.018	0.00008	4.066181
Within Groups	13512	8	1689			
Total	175746.92	11				

Table 2. The ANOVA results for Zn

Source of Variation	SS	df	MS	F	p-level	F crit
Between Groups	79320.92	3	26440.31	61.03	0.00001	4.066181
Within Groups	3466	8	433.25			
Total	82786.92	11				

Table 3. The ANOVA results for Cu

Source of Variation	SS	df	MS	F	p-level	F crit
Between Groups	211	3	70.33	0.699	0.57835	4.066181
Within Groups	804.67	8	100.58			
Total	1015.67	11				

Table 4. The ANOVA results for Cd

Source of Variation	SS	df	MS	F	p-level	F crit
Between Groups	258	3	86	5.034	0.03007	4.066181
Within Groups	136.67	8	17.08			
Total	394.67	11				

3.3. Geo-Accumulation Index (Igeo)

The Geo-accumulation Index (Igeo) is one of the numerous methods for assessing soil contamination. It is defined as follows:

$$Igeo = \log 2 [C_S / 1.5 * C_G] \quad (1)$$

where C_S is the measured concentration of the heavy metal in the soil samples; and C_G is the average geochemical background values of metal in continental crust [15]; the factor 1.5 is used to compensate for possible variations of the reference data due to lithogenic effects. Based on the Igeo value, the degree of heavy metal contamination is classified as follows (table 5) [16].

The Igeo values in the studied area (table 6) range 3.95 to 4.45 for Ni, 3.86 to 4.42 for Zn, 3 to 3.112 for Cu, and -0.31 to 0.26 for Cd.

The average values of Igeo of Ni (4.24) and Zn (4.06), in the present investigation are found in class 6 ($4 \leq Igeo < 5$), indicating that they are strongly to very strongly polluted with respect to these elements in Metallurgical complex in Elbasan. The average value of Cu (3.05) is in class 5 ($3 \leq Igeo < 4$), strongly polluted and for Cd (-0.03) is in class 1 ($Igeo < 0$) unpolluted.

The highest average geo-accumulation index values for Ni (4.24), Zn (4.06) and Cu (3.05) indicate anthropogenic impact, mainly industrial activity, waste generated and not recycled etc.

Table 5. Classification of heavy metal contamination based on the Igeo value

Class	The Igeo value	Classification
1	Igeo < 0	Unpolluted
2	0 ≤ Igeo < 1	Unpolluted to moderately polluted
3	1 ≤ Igeo < 2	Moderately polluted
4	2 ≤ Igeo < 3	Moderately to strongly polluted
5	3 ≤ Igeo < 4	Strongly polluted
6	4 ≤ Igeo < 5	Strongly to very strongly polluted
7	Igeo ≥ 5	Very strongly polluted

Table 6. Geo-accumulation Index (Igeo) for each plant

The Industrial Plant	Ni	Zn	Cu	Cd
The Oxygen plant	3.95	3.86	3.07	0.15
Kurum International Sh.A.	4.45	4.42	3.12	0.26
The Ferrochrome Production plant	4.31	3.98	3.01	- 0.31
The Cement plant	4.26	3.99	3	- 0.21

4. CONCLUSION

The data presented in this study indicate that the soils around the industrial complex of Elbasan are contaminated with Ni, Zn, Cu and Cd. The statistical data of heavy metals shows that Ni, Zn and Cu are higher than average values of the upper continental crust. The fluctuation of heavy metals concentrations in the soils suggests that anthropogenic inputs (industrial activities) and geochemical processes influence their concentration. The heavy metal contaminations are assessed with Igeo and soil quality guidelines. The results indicate that Igeo of metals in soil is dominated by Ni, Zn and Cu, and according the soil quality guidelines Ni and Cd are above the recommended limits. The concentration of metals is higher in Kurum International Sh. A.

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„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

POVEZIVANJE ZELENIH SUSTAVA GRADA ZAGREBA SA ZAŠTIĆENIM PODRUČJEM PARKA PRIRODE MEDVEDNICA

CONNECTING THE GREEN INFRASTUCTURE SYSTEM OF THE ZAGREB CITY WITH PROTECTED AREAS OF NATURE PARK MEDVEDNICA

Petra Pereković*, Kaya Perčič*, Dora Tomić Reljić*

* Sveučilište u Zagrebu, Agronomski fakultet, Zagreb, Hrvatska

autor za korespondenciju: Petra Pereković, e-mail: pperekovic@agr.hr

Stručni rad

SAŽETAK

U ovome radu su preispitane mogućnosti i potencijali povezivanja zelenih sustava grada sa zaštićenim područjem parka prirode Medvednica kao dijela zelene infrastrukture Grada Zagreba. Kontaktno područje parka prirode Medvednica sa sjevernim rubom grada Zagreba izloženo je znatnim pritiscima širenja izgradnje i prateće infrastrukture. Prisutna je sve veća fragmentacija zelenih površina i gubljenje nekadašnjih zelenih koridora između obronka Medvednice i ostatka grada. U radu su analizirani i preispitani potencijalni koridori zelene infrastrukture u južnoj podsljemenskoj zoni iskoristivi za povezivanje zelenih površina grada i Parka prirode Medvednica. Time su determinirani preostali zeleni koridori kao potencijalne prostorno ekološke spone između grada i okolne „prirode" sa svim njihovim dobrobitima za opću kvalitetu života u gradu.

Ključne riječi: *zeleni sustav, zelena infrastruktura, Medvednica, park prirode*

ABSTRACT

This paper examines the possibilities and potentials for connecting the green system of the city with protected areas of Nature Park Medvednica, as a fragment of the green infrastructure of Zagreb. A contact area of Nature Park Medvednica and north edge of the city of Zagreb is exposed to imposing pressures of expansion of construction and infrastructure. Increased fragmentation of green areas is present as well as wasting the former green corridors between Medvednica slopes and the urban area. This paper also analyses and examines potential corridors of green infrastructure in the area under the southern slopes of

Medvednica which can be used for connection of green areas of the city and Nature Park Medvednica. In such way, determined are the rest of the green corridors as potential spatial ecological link between city and surrounding nature with all their benefits for general life quality in the city.

Keywords: *green system, green infrastructure, Medvednica, nature park*

1. UVOD

Ekspanzijom gradova, odnos naseljenog mjesta (izgrađenih površina) i prirodnog okruženja (zelenih površina), postalo je kompleksno pitanje. Ono je uvjetovalo razvijanje preciznijih pokazatelja kvalitativnih i kvantitativnih obilježja gradskih otvorenih prostora te korištenje metoda koje poboljšavaju planerske mehanizme. Osnovni pristupi koji su danas primjenjivani u tu svrhu su „zeleni sustav“ i „zelena infrastruktura“ gradova.

Zelena infrastruktura je strateški planirana mreža prirodnih i poluprirodnih područja koja uključuje sve ekološke značajke nekog područja a zasnovana je i upravljana na način da pruža široki spektar dobrobiti ekosustavu . Uključuje „zelene“ i „plave“ prostore (vodene ekosustave) i druge fizičke značajke u kopnenim, obalnim i morskim područjima bilo da se radilo o ruralnim ili urbanim okruženjima. Ova mreža „zelenih“ i „plavih“ gradskih i izvangradskih prostora donosi prirodne, gospodarske i društvene koristi, doprinosi zdravlju građana, rekreacijskim mogućnostima i općoj kvaliteti života, podupire „zeleno“ gospodarstvo, povećava biološku raznolikost i opće stanje okoliša. Osim toga, planiranje zelene infrastrukture smanjuje ovisnost o „sivoj“ infrastrukturi koja je često skuplja za izgradnju i održavanje. Ovakvu definiciju i osvrt na zelenu infrastrukture daje Europska komisija koja za jedan od ciljeva postavlja osigurati da zaštita, obnova, stvaranje i unapređenje zelene infrastrukture postane sastavni dio prostornog planiranja i teritorijalnog razvoja u slučajevima kada ona predstavlja bolju alternativu standardnim „sivim“ infrastrukturnim sustavima [1].

Iako je zelena infrastruktura noviji i kompleksniji pojam, i pojam zelenog sustava podrazumijeva uspostavu zelenih mreža koje doprinose općim ekološkim, socijalnim, ekonomskim i drugim vrijednostima te općem poboljšanju kvalitete života u gradovima (npr. povećanje rekreacijskih prostora, zdravstvene dobrobiti, ublažavanje posljedica urbanih toplinskih otoka, poboljšanje kvalitete zraka, zaštita prirodnih kvaliteta, povećanje staništa za životinjski svijet). Pritom se „sustav gradskog zelenila“ odnosi se na sve otvorene (neizgrađene) površine u gradu kao i veze s krajobrazom u neposrednoj okolici grada. Čine ga različiti tipovi otvorenih prostora koji mogu biti različitih osnovnih namjena (npr. parkovi, sportsko rekreacijski centri, zaštitno zelenilo, gradske šume, zaštićeni dijelovi prirode), nositi različita obilježja (npr. prirodni, poluprirodni ili oblikovani artificijelni prostori, prostori s većim ili manjim udjelom „zelenila“) te mogu imati različiti doprinos zelenom sustavu grada [2].

U svrhu njegove analize, otvorene prostore prema distribuciji i obilježju povezanosti dijelimo na one koji su jasno čitljivi i izraženi u strukturi grada, nose obilježja koherentnosti, čitljivosti, kontinuiteta i prostranosti (npr. veliki parkovi, prostorne šume, riječni koridori) te čine koherentne i povezane cjeline (područja i koridori). Uz njih, razlikujemo i pojedinačne („točkaste“), izolirane površine ili poteze čija su obilježja disperznost, mala površina i visoki stupanj fragmentacije (npr. blokovsko zelenilo, drvoredi , zeleni otoci). Obično ih u gradskoj strukturi uočavamo kao izdvojene međusobno nepovezane ili indirektno povezane površine. Pri tome, kontinuirani prostrani zeleni potezi i koridori smatraju se osnovicom zelenog

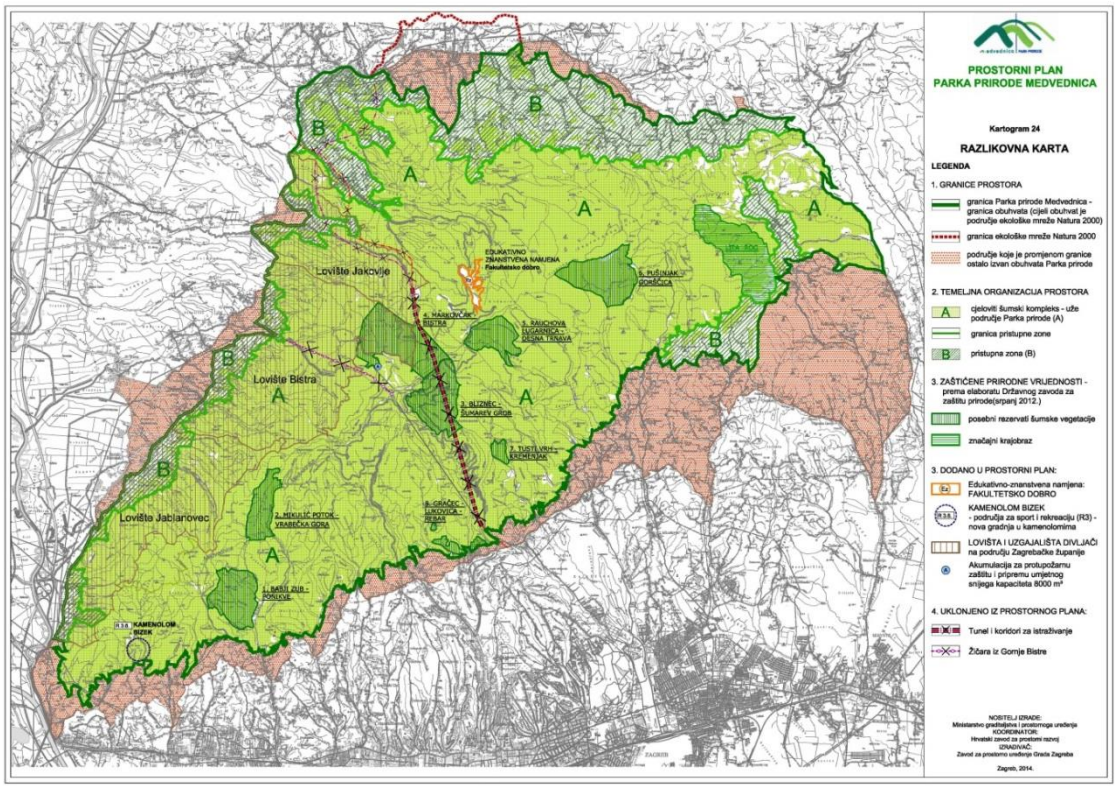
sustava dok fragmentirane, točkaste površine također imaju određeni doprinos ukupnom zelenom sustavu grada no je ograničen (lokalan) i često manje značajan za ukupni ekološki i rekreacijski doprinos gradu. Prema genezi, dijelovi zelenog sustava mogu biti oni koje je čovjek svojim djelovanjem *osmislio* (planirani zeleni potezi „zacrtani“ u prostornim planovima – npr. zagrebačka „Zelena potkova“ i „Plava potkova“), ili oni koje je čovjek *zaštitio i očuvao* u manje-više izvornom obliku (reliktni ili autohtoni krajobrazi). U gradu Zagrebu to je primjerice očuvan i djelomično zaštićen krajobraz Medvednice (park prirode i drugi šumski obronci Medvednice usječeni u strukturu izgrađenih dijelova grada) te u tom smislu možemo shvaćati i koridor rijeke Save (iako je uvelike izmijenjen regulacijom, Sava je ostala dio povijesne memorije grada). Iako neke takve dijelove zelenog sustava smatramo prvorazrednim kulturnim i/ili prirodnim nasljeđem grada, u nekom dužem vremenskom slijedu, njihovo je često obilježje smanjivanje površinom, fragmentacija ili neki drugi oblik promjene ili degradacije. Kako se često radi o dugotrajnim i postupnim promjenama, generiranim nizom manjih zahvata, takve promjene ili degradacije često nisu očigledne i nagle. Stoga u nekom trenutku u vremenu djeluju bezopasne i minorne, no dugoročno, mogu biti uzrok trajnih negativnih posljedica vidljivih tek nakon više desetljeća generiranih promjena.

Jedan od najočitijih primjera takvih procesa je zagrebačka gora - Medvednica, čiji su šumski obronci izvan granice parka prirode Medvednica već desetljećima sustavno ugrožavani pod pritiscima širenja izgrađenog zemljišta, uglavnom stambene izgradnje i prateće infrastrukture. Šumske i prirodne krajobrazne cjeline medvedničkog područja se smanjuju, prekidaju se veze između parka prirode i ogranaka Medvednice izvan zaštićenog područja te bivaju ugrožene i degradirane neke od najvrednijih vizura grada. U tom smislu, najugroženije je prigorsko područje Medvednice smješteno između centralnog gusto izgrađenog dijela grada (podgorja) i gorskog dijela odnosno parka prirode Medvednica (slika 1).



Slika 1. Širenje izgradnje na Medvedničkom području i postepeno stvaranje izgrađenog „obruča“ na rubovima parka prirode Medvednica. Izgradnja na višim nadmorskim visinama i vizualno izloženim predjelima, narušava panoramske vizure na Medvednicu iz mnogih pješačkih smjerova i čvorišta nizinskog djela Zagreba (vizura od Grmoščice -„Milerova brega“ prema Sljemenu, avionski prelet 2016. god.)

To područje čine krajnji južni izdanci Medvednice, nižih nadmorskih visina, čije su nekadašnje autohtone šume povijesnim razvojem grada postepeno krčile, najprije pretvarajući se u oranice, livade, vinograde i voćnjake a danas čine urbanizirane obronke Medvednice sve izraženijih artificijelnih obilježja. Zbog istih pritisaka, smanjena je i granica samog parka prirode Medvednica (slika 2), posljednji puta 2009. god., sa 22.826 na 17.938 ha, ponajprije zato što je dio zagrebačke strane parka postao urbana zona [3].



Slika 2. Smanjivanje granice parka prirode Medvednica (označeno narančasto). Izvor: Prostorni plana područja posebnih obilježja Parka prirode „Medvednica“, 2014., knjiga 3, prilog 24 – razlikovna karta, http://www.mgipu.hr/default.aspx?id=8504)

2. MATERIJALI I METODE

U ovome radu izvršeno je preklapanje i analiza GUP-a Grada Zagreba iz 1970.god. (prva projekcija) i trenutno važećeg GUP-a te je na temelju toga izvršena procjena promjena općih obilježja zelenog sustava grada na južnim obroncima Medvednice. Daljnja analiza obuhvatila je bilježenje i izdvajanje preostalih čitljivih zelenih koridora između Parka prirode Medvednica i rijeke Save. Područje rada obuhvaćeno analizom proteže se Podsusedskog mosta do Sesveta u smjeru istok - zapad te područje između parka prirode Medvednica i rijeke Save u smjeru sjever - jug budući da je u tom području najizraženija ugroženost zelenog sustava grada Zagreba.

U inventarizacijskom postupku i kartografskoj obradi korištena je GIS baza podataka informacijskog sustava zaštite prirode (http://www.bioportal.hr/gis/) koja uključuje: Ekološku mrežu Natura 2000, zaštićena područja, staništa i biotope te digitalnu bazu podataka CORINE Land Cover Hrvatska. Prema unaprijed pripremljenoj bazi podataka u QuantumGIS (QGIS)

programu proveli su se dijelovi analitičkog istraživanja. Dobiveni kartografski prikazi obrađivani su u programima QGIS- u i AutoCAD-u te su grafički prikazani i opisani. U završnoj fazi analiza, kartografski podaci su interpretirani u prijedlog razvoja zelene infrastrukture na temelju kojeg se opisuju rezultati istraživanja. U svrhu izrade rada obavljen je avionski prelet cijelog perimetra Medvednice.

3. REZULTATI I DISKUSIJA

Zeleni sustav Zagreba i njegovu prvorazrednu vrijednost oduvijek je činila njegova prirodna osnovica – Medvednica, koja se uzdiže iznad savske ravnice, te rijeka Sava zajedno sa svojim obalnim područjem. Tu okosnicu zelenog sustava prepoznaje već i prijedlog Direktivne regulacijske osnove Zagreba (1949. - 1953.god.) koja predlaže splet zelenih i rekreacijskih površina koji su trebali predstavljati zelenu osovinu "Sljeme-Sava" spojenu zelenim prodorima – zelenim kracima koji se spuštaju sa Sljemena i obronaka Medvednice na široko područje Save [4]. Takve veze prepoznaje i Urbanistički program grada Zagreba iz 1961.god. koji predviđa povećanje svih kategorija zelenih površina u centralnom dijelu grada koji bi se trebali vezati na poljoprivredne površine nizinskog područja uz Savu ili na šumske površine koje silaze s brdskog područja Medvednice i poput klinova zadiru u tkivo grada [5].

Analiza prve projekcije Generalnog urbanistički plan Grada Zagreba (1970.god.) već u tom periodu prikazuje znatnu fragmentaciju zelenih površina (šuma) prigorskog područja Medvednice nastalu izgradnjom. Ipak, plan sadržava i očuvane zelene koridore odnosno izravne koherentne zelene veze između rijeke Save i Medvednice. Njih možemo podijeliti u dvije kategorije - manje zelene poveznice (poteze) Medvednice koje se prežimlju s centralnim izgrađenim dijelom grada te veće zelene koridore koji se spuštaju od vršnih dijelova Medvednice, prolaze kroz centralne dijelove grada i protežu sve do rijeke Save. Ti koridori čine kontinuirane koherentne zelene koridore izrazio naglašene u strukturi grada (slika 3).



Slika 3. Zelene površine grada Zagreba prema prvoj projekciji Generalnog urbanističkog plana iz 1970.g. (Urbanistički Zavod grada Zagreba). U zelene površine uključeni su: gradske šume i parkovi te sportsko rekreacijske površine

Dva najveća takva koridora su: Podsused - Graberje - Grmoščica - Vrbani III - Jarun na zapadnom dijelu grada te Bliznec - Jazbina - Dotršćina - Maksimir - industrijska zona Peščenica - Žitnjak - Savica, na istočnim dijelu grada. Preostali manji zeleni koridori su značajno fragmentirani ali ipak čine cjelovite međusobno povezane poteze ili „mreže“ koji su direktno ili indirektno povezani sa šumskim krajobrazima gorskog djela Medvednice. Takvi potezi karakteristika su cjelokupnog podsljemenskog područja od istočnih sve do zapadnih dijelova grada uključujući i centralne dijelove Zagreba.

Iako iz današnje perspektive sustavi tada uspostavljenih zelenih veza djeluju brojni, u odnosu na današnje stanje, stručnjaci već tada upozoravaju na neprikladno širenje gradskog izgrađenog tkiva na medvedničkom području koje ugrožava temeljne prirodne, rekreacijske, vizualne i identitetske osnove i vrijednosti grada Zagreba (tablica 1).

Tablica 1. Pregled vrijednosti, pritisaka i ugroza Medvednice prema autorima do 1980. god.

Godina i autor	Osvrt na vrijednosti, pritiske i ugroze Medvednice
1965. Mirjana Popović	Medvednica pored biološkog i ekološkog utjecaja obogaćuje grad svojom plastikom (razigrana konfiguracija južnih obronaka u koju se na centralnim brežuljcima južnih obronaka utkalo gradsko tkivo)... međutim na južnim obroncima Medvednice niču zgrade i jača tendencija naglog rasta naselja te se tako narušava visoka estetska vrijednost tog kraja... nastavili li se to i dalje, gradska panorama će se utopiti u manje i veće skupine kućeraka i enormno velikih prigorskih sela. [5]
1970. Zdenko Kolacio	Sitna izgradnja pokrila je vrijedne terene, a naročito padine Medvednice... mislilo se da će detaljni urbanistički planovi sve nedaće korigirati no i pored planova i raznih administrativnih mjera, navala na lijepe pejsaže grada ne prestaje. [6]
1970. Josip Uhlik	U gradskom krajoliku posebno mjesto pripada Medvednici i savskom priobalju ... Medvednica se u budućnosti treba do maksimuma vrednovati kao najdragocjeniji biološki element sredine i područje velikih mogućnosti za rekreaciju ... pogledi iz južnog Zagreba prema sjeveru već danas predstavljaju vrijednost koju bi trebalo maksimalno sačuvati. [7]
1970. Mirjana Popović	… mnoge su pribrežene doline u gradu ponovo izgrađene ... današnja disperzija i stupanj izgrađenosti prigorskog područja onemogućava kontinuirano fizičko povezivanje gorskog i nizinskog područja s visokom vegetacijom ... neophodno je povezivanje šumskog kompleksa Medvednice i objedinjavanje disperznih zelenih površina u gradu u fizičkom smislu. [8]
1978. Šime Ricov	Medvednica, kao najmarkantniji faktor stabilizacije užeg dijela Zagrebačke regije, treba da dobije status biološko-ekološke cjeline prvog reda ... grad Zagreb trpi zbog izrazitog nedostatka sistematiziranog sustava gradskih zelenih površina, pri čemu neadekvatan značaj i nedefiniranost funkcije kontaktne zone grada i Medvednice potencira nedaće na štetu grada i zdravlja njegovih stanovnika. [9]
1978. Hasan Drljević	... generalni urbanistički plan (1971) predvidio je prodore zelenila i u smjeru sjever-jug, tako da bi se zelenilo Medvednice povezalo sa slobodnim zelenim prostorom Save ... razvoj grada i realizacija GUP-a, o tim mogućnostima ipak ne vodi dovoljno računa, pa se u praksi ovakve veze prekidaju ... [10]
1978. Antoaneta Pasinović	… i taj grad u naručju planine i zagrljaju rijeke nikako da uspostavi zdrav i ozbiljan odnos prema temeljnim topološkim karakteristikama grada … Medvednica danomice na očigled sviju nas propada – gubi svoje prirodne značajke ... sustavna nemilosrdna eksploatacija i bezobzirna ophodnja ne samo sa šumskim fundusom, nego njezinim cjelokupnim i kompleksnim značenjem za Zagreb, degradira prostorno-pejzažne, ekološke, zdravstvene, rekreacijske i prirodno znanstvene vrijednosti te lijepe planine ... ako se ne odredi status Medvednice kao cjeline u odnosu na cjelokupni prostor grada Zagreba i zagrebačke regije, postojat će i dalje opasnost njene daljnje degradacije … planiranje se može izvrgnuti i u svoju suprotnost: u daljnje legaliziranje „eksploatacijskog“ odnosa prema prostoru, koji bi prvenstveno trebalo zaštiti od nekontroliranog apetita…prvobitna namjena treba biti rekreacija uz pažljivo rekonstruiranje devastiranih objekata i obnavljanje desetkovanog šumskog fonda ... minimalna ugroza postojećeg zelenog fonda, prirodno-pejzažnih i izletničko-rekreacijsko-sportskih kvaliteta toliko nam dragocjene Zagrebačke gore. [11]

O neprikladnosti takvog načina razvoja i izgradnje gradske sredine govore stručnjaci i nakon osamdesetih godina 20.st., ali i danas (tablica 2).

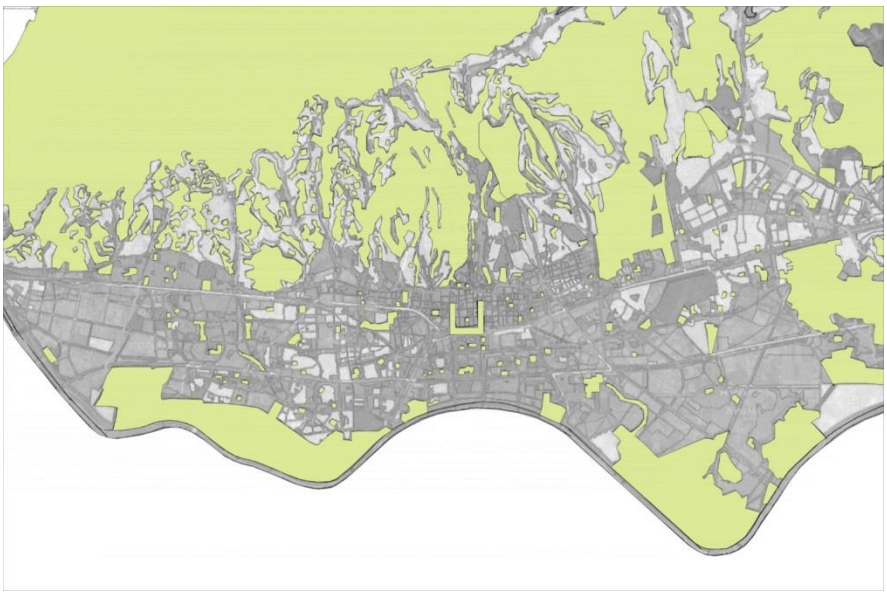
Tablica 2. Pregled vrijednosti, pritisaka i ugroza Medvednice prema autorima nakon 1980.god.

Godina i autor	Osvrt na vrijednosti, pritiske i ugroze Medvednice:
1989. Radovan Ivančević	Samo ako očuvamo zelenilo što neposredno nastavlja prirodnu šumu Sljemena, sačuvali smo povijesnu i suvremenu vrijednost Starog Zagreba. Povijesnu, jer su srednjovjekovni i barokni gradovi bili upravo to: male oaze arhitekture u kontinuiranom moru slobodne prirode i kultiviranog zelenila: suvremenu, jer su sljemenske šume i podsljemensko zelenilo i danas „pluća grada“ i osiguravaju protok svježeg i čistog zraka u Donji grad i Novi Zagreb, a uz to su idealna rekreativna zona za čitav suvremeni Zagreb. [12]
1989. Sonja Jurković	Medvednica je vizualno najsnažnija slika grada. To je platno – paravan na kome se oslikava obris i gabarit grada. Ona je neizbrisiva memorijska slika Zagreba. Ekološki je prisutnost tog biološkog uporišta i rezervata od neprocjenjiva značenja … razvoj je nagrizao prirodno tkivo, uspinjao se na obronke, zadirao duboko u šumske masive. [13]
2013. Krajobrazna studija zagrebačke županije	Studija kao pritiske i negativna obilježja na rubnim dijelovima Medvednice izdvaja: smanjenje kompaktnosti i homogenosti šumskog područja zbog širenja stambenih područja i rubnih naselja; gradnja u izvan građevnim područjima naselja (kuće za odmor, spremišta voća, zgrade turističke namjene, gradnja uz potoke, gradnja telekomunikacijskih antena i sl.); lociranje novih građevina neintegriranih dimenzija i arhitektonskih oblika na pozicije velike vizualne izloženosti posebno na vrhovima brežuljaka; trend nove gradnje koja ne poštuje naslijeđene uzorke i mjerilo prostora i dr. [14]
2013. Ana Mrđa, Bojana Bojanić Obad Ščitaroci	Pejsažni potezi sjevera Zagreba, kao daljnji ogranci šume na Medvednici, međusobno su povezani s ostacima prigorskih šuma koje sežu u sam centar grada. Ti pejsažni potezi, tijekom stoljeća, služe i u doživljajno-estetskom i u biološko-ekološkom smislu kao oslonac i okosnica razvoja identiteta grada Zagreba. [15]
2013. Miklec i sur.	Zagrebačka gora ugrožena je nemilosrdnim širenjem i zadiranjem u prirodne prostore ... neregulirana izgradnja, gotovo nametničkoga karaktera, postupno je izjedala izdanke šume koji su se pružali prema gradu, ali i kroz grad, odsijecajući ih tako od homogene cjeline … do današnjeg vremena izgradnja i urbanizacija je uvelike prodrla u južne obronke gore a Medvednica nije pošteđena ni sa sjeverne strane: niz turističkih i vikend naselja što se pojavljuju kao trend, stvorili su, zajedno s glavnim gradom na južnoj strani, prsten koji se polako steže ne ostavljajući joj mogućnost da slobodno egzistira unutar svojih granica. … u ovom trenutku je Medvednica implodirala, sakupila svoje vrijednosti u relativno ograničen prostor što ne bi smio biti slučaj, ali je realnost i posljedica nekontrolirane urbanizacije grada … prilagodbom prostora može se stvoriti održiva cjelina gdje se zadržava ideja „zelenih prstiju“ Zagreba. [16]

Na to ukazuje i preliminarna analiza zelenog sustava trenutno važećeg Generalnog urbanističkog plana grada Zagreba (slika 4). U njemu je vidljivo, u odnosu na projekciju plana iz 1970.god., smanjenje udjela zelenih površina u podsljemenskoj zoni, potpuno gubljenje značajnih zelenih koridora između Medvednice i rijeke Save te izrazito velika fragmentacija nekada postojećih manjih poteza i koridora južnih obronaka Medvednice. Osobito je primjetan gubitak širokih zelenih spona od Medvednice i rijeke Save na zapadnom dijelu grada (Podsused - Graberje - Grmoščica - Vrbani III - Jarun) te na istočnim dijelu grada (Bliznec - Jazbina - Dotršćina - Maksimir - industrijska zona Peščenica - Žitnjak - Savica).

Primjetno je i generiranje kontinuiranog stambenog „obruča“ oko južne granice parka prirode Medvednica. Taj obruč prekinuo je nekoliko značajnih koridora ali i mnoge manje nekadašnje zelene poteze prema južnim dijelovima grada koji su danas kao fragmentirane „zakrpe“ ostale egzistirati između okolne stambene izgradnje i prateće joj infrastrukture. Osim visokog udjela fragmentiranih zelenih površina (šumskih ili drugih namjena) koje više nisu povezane s parkom prirode, vidljivo je smanjivanje njihove veličine kao i gubitak obilježja međusobnog povezivanja („zelene mreže“) što zapravo znači porast broja usitnjenih, nekoherentnih i „točkastih“ dijelova zelenog sustava. Unutar toga izrazito je naglašena

fragmentacija potencijalnih rekreacijsko-sportskih, pješačkih i biciklističkih zelenih spona odnosno onih koji spadaju u javne otvorene prostore grada.



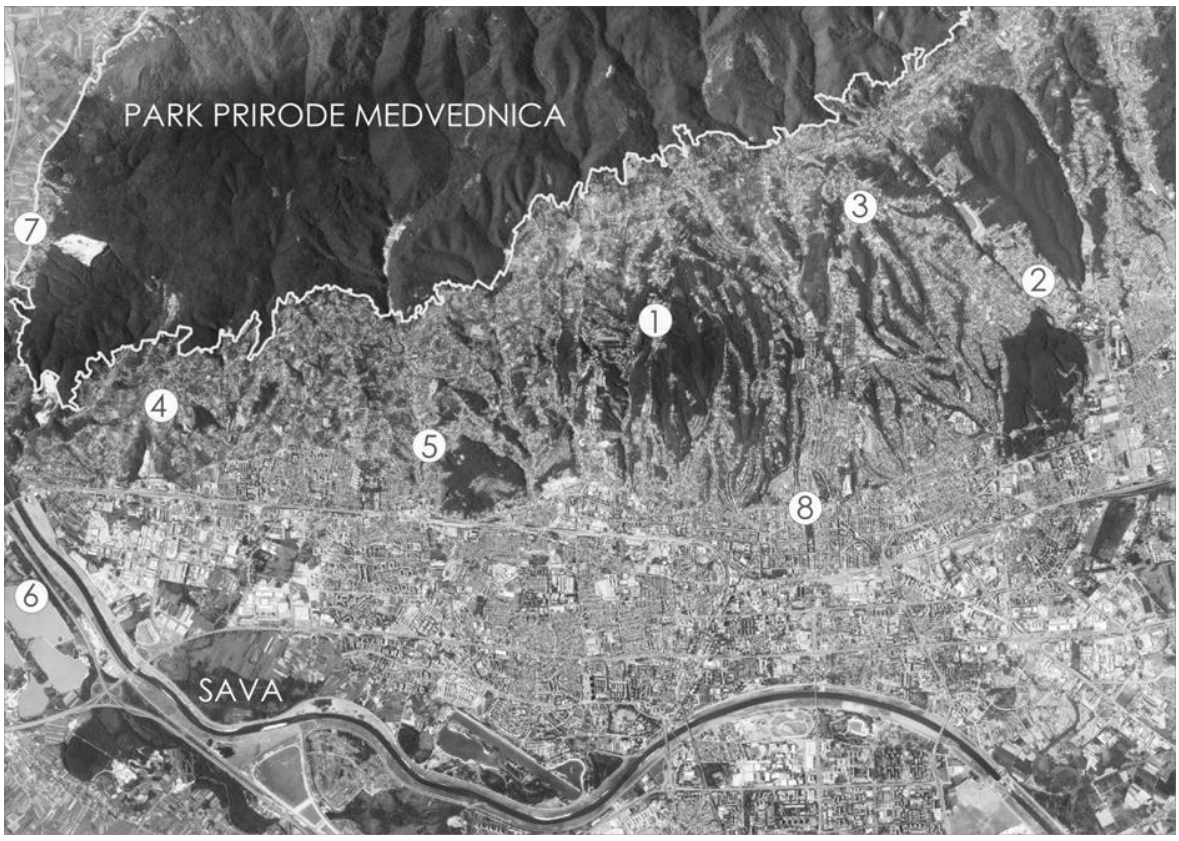
Slika 4. Zelene površina grada Zagreba prema važećem Generalnom urbanističkom planu Zagreba (izvedena karta prema GUP-u grada Zagreba, 9/2016., https://geoportal.zagreb.hr/Karta). U zelene površine uključene su: javne zelene površine – parkovi, park šume, zaštitne i tematske zelene površine

Analizom trenutno važećeg GUP-a, kao preostali i glavni potencijalni zeleni koridori u strukturi grada (slika 5) izdvajaju se: zeleni mreža (koridori) Prekrižje – Kraljevac – Pantovčak – Jelenovac - Cmrok - Zelengaj - Tuškanac - Iličke padine (1); zeleni koridor Dotršćina - Maksimir (2); zeleni potezi Remete (3); Podsused - Kostanjek (4); Grmoščica (5) te zapadna poveznica - "obruč" (potencijalna velikopotezna veza Medvednica - Rakitje - Golf klub - Arena koja povezuje zelene površine obje obale rijeke Save te krajnje zapadne ogranke Medvednice). To su ujedno koridori za koje je od neophodne važnosti uspostaviti i/ili očuvati koherentne veze s parkom prirode Medvednica budući da rijetki od njih prema danas važećem GUP-u imaju direktnu povezanost sa parkom prirode.

Osim njih postoji i veći broj manjih poteza ili fragmenata šumskih i drugih zelenih površina na samoj granici parka prirode Medvednica za koje je neophodno izvršiti detaljne analize na razini gradskih četvrti, pravilno ih valorizirati te na temelju takve analize uključiti ih u procese prostorno planskih odluka.

U tom smislu izrađena je preliminarna detaljna analiza za zelenu mrežu Prekrižje - Kraljevac - Pantovčak - Jelenovac - Cmrok - Zelengaj - Tuškanac - Iličke padine (na slici 5 označena brojem 1). Tu mrežu čine cjeloviti potezi pješačkih zelenih podsustava između važnijih čvorišta grada i planinarskih staza parka prirode Medvednica : POTEZ A (Trg bana Josipa Jelačića - Strossmayerovo šetalište - park šuma Tuškanac i Dubravkin put - Cmrok - Gornje Prekrižje - gradska šuma Kraljevec - gradska šuma Prekrižje - Ulica Šestinski vijenac - planinarski put 12 Šestine-PD Risnjak; POTEZ B (sličan prijašnjoj ruti, no s početkom na Britanskom trgu - zelena aleja - Zelengaj – gradska šuma Tuškanac - Dubravkin put - Cmrok - gradska šuma Kraljevec i Prekrižje - planinarska staza 12 Šestine - PD Risnjak); POTEZ C (Ilica - Ulica Šestinski dol - gradska šuma Šestinski dol - gradska šuma Vrhovec - Jelinovac - gradska šuma Zamorski breg - šumske sastojine u predjelima/ulicama Šestinski vrh i Dedići - planinarska staza 12 Šestine - PD Risnjak). Dijelovi ovih sustava (Trg bana Jelačića -

Strossmajerovo šetalište - Rokov perivoj - gradska šumaTuškanac - Ilirski trg - Krešićeve poljane - Dubravkin put - Cmok - Josipovac - Zelengaj - Britanski trg) drugi autori prepoznaju kao turistički potencijal te kao šumske prostore važnih obilježja za odmor i relaksaciju, aktivnu rekreaciju i kulturnu edukaciju [15].



Slika 5. Smanjenje i visoka fragmentacija šumski krajobraza podsljemenske zone te stvaranje izgrađenog „obruča“ uz granicu parka prirode Medvednica. Vidljivi su i gušće premreženi šumski koridori u središnjem i istočnom dijelu grada te izrazita fragmentacija i gubitak takvih mreža u zapadnom dijelu grada.
Legenda: 1) Prekrižje-Kraljevac-Pantovčak-Jelenovac-Cmrok-Zelengaj-Tuškanac-Iličke padine; 2) Dotršćina-Maksimir; 3) Remete; 4) Podsused-Kostanjek; 5) Grmoščica; 6) Zapadna poveznica - “obruč“; 7) Granica Parka prirode Medvednica; 8)Trg bana Josipa Jelačića

Ovako provedeni tip analiza možemo smatrati tek kao preliminarni i inicijalni analitički postupak budući da bi za sustavnu analizu bilo potrebno izvršiti detaljniju višekriterijsku analizu pojedinih obilježja i međuodnosa dijelova sustava. Primjerice, determinacija dijelova sustava koji imaju ekološke značajke sadrže vlastite analitičke kriterije i podrazumijevaju sve privatne ili javne tipove zelenih površina (neovisne o vlasništvu) koji u većoj ili manjoj mjeri doprinose ekološkoj bilanci grada. S druge strane, zeleni sustavi koje doprinose rekreacijskom potencijalu grada, moraju nositi predznak „javne“ površine i spadati u „javno dobro“ te uvjetuju drugačije kriterije analize. Detaljna analiza treba uključivati i razmatranje otvorenih zelenih površina koji se nalaze i unutar drugih prioritetnih namjena (mješovita i stambena namjena) budući da su i one sastavni dio zelenog sustava grada. Pravilno tretiranje krajobraza Medvednice podrazumijeva i vrednovanje njegovih vizualnih značajki budući da su vizure na šumske krajobraze Medvednice također ugrožene gradnjom a njihovim nestajanjem izgubiti će se i jedna od najvažnijih panoramskih slika grada.

4. ZAKLJUČAK

Intenzivna gradnja južnih medvedničkih obronaka, značajno je smanjila površinu nezaštićenih brežuljkasto brdskih, šumskih krajobraza Medvednice. U kontaktnoj zoni parka prirode i nezaštićenog djela Medvednice prisutan je dugogodišnji trend fragmentacije i smanjivanja izvornih šumskih krajobraza te gubljenje zelenih koridora između Medvednice, centralnog dijela grada i savskog priobalja. Takvom izgradnjom, ponajprije u višim brežuljkasto brdskim predjelima, ugrožene su i panoramske, najvrjednije vizure Grada Zagreba. Na temelju provedenih preliminarnih analiza zelenog sustava tog područja možemo zaključiti:

- planovi starijih generacija zastupaju rahlu dispoziciju i disperziju izgrađenog naseljenog tkiva na obroncima Medvednice koja omogućava kontinuiranu povezanosti zelenih poteza („zelenih prstiju“) koji su se između tih disperznih naseljenih dijelova spuštaju od vršnih dijelova Medvednice sve do centra grada ili rijeke Save;
- između 1970. i 2018.god. prostorni razvoj i izgradnja grada Zagreba smanjila je i fragmentirala veliki dio zelenih površina između Medvednice i rijeke Save a u tom smislu osobito je ugroženo prigorje Medvednice, na razdiobi parka prirode Medvednica i podgorja gdje postoji tendencija daljnje izgradnje odnosno razgradnje zelenih koridora kao ekoloških i rekreacijskih spona između parka prirode, središta grada i rijeke Save;
- kao inicijacija daljnjih istraživanja, preliminarnim analizama u ovome je radu identificirano šest preostalih zelenih koridora i cjelina na južnim obroncima Medvednice koje je potrebno detaljno analizirati, valorizirati i sukladno analizama u procese donošenja prostorno planskih odluka; identificirani su i drugi manji koridori koje je također potrebno uvrstiti u analitičko promišljanje o prostornom razvoju grada i zaštiti njegovih najvrednijih krajobraznih obilježja

Zaštita parka prirode Medvednica ne znači zaštitu cjelokupne Medvednice, nego samo jednog njezinog dijela. Stoga izostankom pravilne valorizacije preostalih krajobraznih vrijednosti južnih nezaštićenih obronaka Medvednice izgubiti će se preostale zelene spone između grada i „prirode“ te njihove potencijalne dobrobiti za kvalitetu života u gradu. Potrebno je stoga provesti detaljnu analizu preostalih zelenih koridora i poteza, uspostaviti i očuvati sve njihove vrijedne komponente i obilježja te ih uključiti u prostorno planske odluke.

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EKOLOŠKI I EKONOMSKI PRIHVATLJIVA ZGRADA

ECOLOGICAL AND ECONOMIC ELIGIBLE BUILDING

Pero Petrović*, Milovan Kotur*, Haris Lulic**

* Univerzitet u Banjoj Luci, Mašinski fakultet, Banja Luka, BiH
** Univerzitet u Sarajevu, Mašinski fakultet, Sarajevo, BiH

autor za korespondenciju: Pero Petrović, e-mail: paroterm@gmail.com

Stručni članak

SAŽETAK

U cilju smanjenja količine energije koja se troši za potrebe grijanje u zimskom, odnosno hlađenje u ljetnom periodu, izvodi se toplinska izolacija objekata. Pitanje na koje bi trebalo dati odgovor je „kako raspodijeliti novčana sredstva namijenjena za izolaciju objekta da bi postigli maksimalni ekonomski učinak, odnosno minimum investicionih i eksploatacionih troškova". Debljina izolacije na pojedinim elementima ovojnice grijanog dijela zgrade trebala bi se određivati na osnovu godišnjih toplinskih gubitaka (veći godišnji toplinski gubici – veća debljina izolacije). Sprezanjem sistema grijanja na biomasu objekata sa sistemima za pripremu potrošne tople vode putem sunčevih kolektora, moguće je postići znatno smanjenje potrošnje električne energije, a samim tim smanjiti i naš utjecaj na životnu sredinu.

***Ključne riječi**: grijanje, toplinska izolacija, solarni kolektori, pirolitički kotao*

ABSTRACT

In order to reduce the amount of energy consumed for heating purposes in winter or cooling in the summer period, the thermal insulation of the buildings is performed. The question that needs to be answered is "how to allocate the funds intended for insulating the facility to achieve the maximum economic effect, i.e. the minimum investment and exploitation costs". The thickness of insulation on individual elements of the heated part of the building should be determined on the basis of annual heat losses (higher annual heat losses - bigger insulation thickness). Heating system based on pyrolytic biomass boiler with solar systems for the preparation of domestic hot water, is possible to achieve a significant

reduction in the consumption of electricity and thereby reduce the impact on the environment as well.

***Keywords**: heating, thermal insulation, solar collectors, pyrolytic biomass boilers*

1. UVOD

Napuštajući svoje prirodno stanište (selo) i naseljavajući urbane sredine, čovjek se doveo u poziciju da mu je energija postala skoro podjednako važna zraku, vodi i hrani koji su neophodni za njegovu egzistenciju. Što je urbana sredina veća, to je i naša ovisnost od energije izraženija, a time i čovjekov utjecaj na životnu sredinu [1]. Način na koji te probleme čovjek danas pokušava da riješi, asocira na mačku koja lovi vlastiti rep.

2. VIDOVI ENERGIJE

Dva su vida energije skoro pa neophodna u današnjem vremenu na ovim geografskim područjima, toplinska i električna. Ta dva vida energije nisu, energetskim rječnikom kazano, podjednaka vrijedna. Električna energija je 2 do 3 puta vrednija od toplinske energije. Pri njenom trošenju (u svrhu pretvaranja u toplinsku energiju), isto toliko puta sa CO_2 više opterećujemo životnu sredinu, pod uslovom da je ona proizvedena iz fosilnih goriva. U svijetu se danas preko 70 % električne energije tako proizvodi. Zbog toga je potrebno osmišljavati rješenja za smanjenje potrošnje oba ova vida energija, a pogotovo eliminirati trošenje (pretvaranje) električne energije u toplinsku (za direktno grijanje objekata, zagrijavanje tople potrošne vode, i sl.). U tržišnim (zapadnim) društvima, električna energija je skupa. To su društva u kojima su ti odnosi (cijene električne i toplinske energije) utemeljeni na termodinamičkoj (znanstvenoj) i tržišnoj logici.

Toplinska energija se danas uglavnom dobiva sagorijevanjem fosilnih goriva, a u posljednje vrijeme i transformacijom dozračene energije od Sunca u toplinu, pomoću različitih vrsta solarnih kolektora. Cijena toplinske energije, odnosno opravdanost korištenja njenih izvora, ovisi od raspoloživosti navedenih izvora na mjestu potrošnje i cijene instalirane opreme za njeno dobivanje.

3. IZOLACIJA OBJEKATA

U području kontinentalne klime na kome živimo, temperatura vanjskog zraka (okolice) se tijekom godine uglavnom kreće u intervalu od -20 °C do +40 °C. Objekte u kojima boravi čovjek, neophodno je grijati gotovo polovicu njihovog eksploatacionog vijeka. To je zbog toga što se čovjek osjeća ugodno u uskom temperaturnom području zraka (20 °C - 26 °C). Iz tih razloga smo prinuđeni da u prostorima u kojima čovjek boravi, održavamo temperature zraka u prostoru (zimi 20 °C, a ljeti 26 °C) uglavnom različite od temperature okolice. To se ne može postići bez potrošnje energije. U cilju smanjenja količine energije koja se troši za potrebe grijanja u zimskom, odnosno hlađenje u ljetnom periodu, izvodi se toplinska izolacija objekata. Pitanje na koje bi trebalo dati odgovor je „kako raspodijeliti

novčana sredstva namijenjena za izolaciju objekta da bi postigli maksimalni ekonomski učinak, odnosno minimum investicionih i eksploatacionih troškova“, slika 1.



Slika 1. Optimalna debljina izolacije

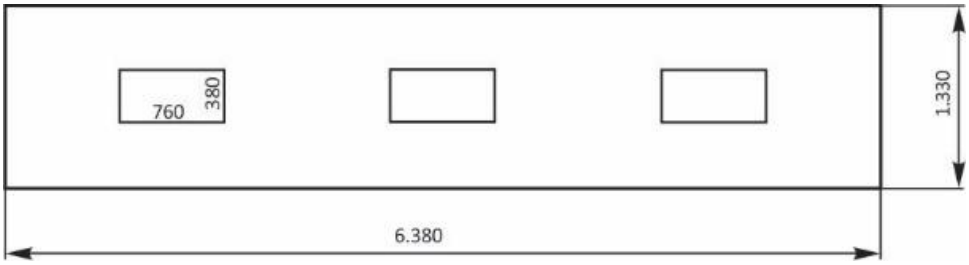
I kao što je obično i u drugim oblastima, tako je i u termotehnici. Znatno je lakše postaviti pitanje nego dati valjan odgovor. Za valjanost (točnost) odgovora presudna su dva podatka: trenutna cijena predviđene toplinske izolacije sa njenom ugradnjom i količina i cijena toplinske energije koja će se izmijeniti kroz nju u budućem eksploatacionom vijeku objekta. Objekti sa svojom okolicom uglavnom, izmjenjuju toplinsku energiju preko svoje ovojnice (omotača). Ovojnica uglavnom razdvaja zrak u prostoru i onaj u okolici. Pošto su oni različitih temperatura, toplina „teče“ sa zraka više na zrak niže temperature (slično toku vode, sa više na nižu nadmorsku visinu).

Da bi količinu izmijenjene topline smanjili, postavljamo joj zapreke, tj. toplinsku izolaciju. Iz navedenog slijedi, da debljina toplinske izolacije prevashodno treba da zavisi od razlike temperatura zraka sa jedne i druge strane vanjskog (unutarnjeg) zida, odnosno temperature zraka u grijanom prostoru i temperature tla. Iz toga proizlazi, da debljina toplinske izolacije na vanjskom i unutrašnjem zidu ili podu, ni u kom slučaju ne treba da je ista. Također ni cijena ugrađene izolacije na navedenim pregradama nije ista.

Debljina izolacije koju treba postaviti na pojedine elemente ovojnice objekta grijanog na temperaturu višu od 12 °C, odnosno višu od 18 °C, definirana je pravilnicima za energetsku certifikaciju zgrada, te je logično pitanje da li su dopuštene vrijednosti za koeficijent prolaza topline (U) omotača objekta, navedene u tim pravilnicima određene tako da zadovoljavaju postavljeni kriterij, tj. da sredstva uložena u izolaciju objekta obezbjeđuju maksimalni ekonomski učinak. Ovo je vrlo važno pitanje i za investitora koji financira izgradnju objekta, jer je on zainteresovan da sa uloženim sredstvima postigne što bolji energetski razred objekta, a samim tim i njegovu tržišnu vrijednost [2].

Da bi provjerili dali se to postiže postojećim pravilnicima o toplinskoj izolaciji objekata koji su u primjeni na ovim prostorima analizirana je primjena navedenih propisa na

stambenoj zgradi sa više etaža i 3 stubišta (šahtnog tipa), slika 2. Zgrada je pravougaonog oblika vanjskih dimenzija 63,8 x 13,3m, a stubišta 7,6 x 3,8m. Zbir obima sva tri stubišta iznosi 44 % obima zgrade.



Slika 2. Osnova analizirane zgrade

Vanjski zidovi izvedeni su od šuplje cigle debljine 20 cm, a unutrašnji zidovi prema negrijanom stubištu od pregrada čiji je koeficijent prolaza topline 2 W/m^{2}K. U analizi je pretpostavljeno da su dozvoljene vrijednosti koeficijenta prolaza topline za vanjski zid 0,4 W/m^{2}K, a za unutrašnji prema stubištu 0,5 W/m^{2}K [3, 4]. Da bi zadovoljili dozvoljene vrijednosti koeficijenata, na vanjski zid bi trebali postaviti 8 cm, a na unutrašnji 6 cm izolacije toplinske vodljivosti, $\lambda = 0{,}04$ W/(mK). S obzirom da u ovoj analizi ne razmatramo utjecaj termičke izolacije poda, krova, vanjske stolarije i orijentacije na energetski razred objekta, već samo vertikalnih zidova, sredstva potrebna za izolaciju prema navedenim debljinama izolacije (8 cm i 6 cm) za analizirani objekt po 1 m njegove visine iznose: za vanjski zid 3.658 EUR, a za stubište 1.505 EUR.

Proračun je rađen pod pretpostavkom da su troškovi nabavke i postavljanja 10 cm izolacije na vanjski zid 25 EUR/m^2, pri čemu je nabavna cijena izolacije 0,7 EUR/(m^{2}cm), a troškovi postavljanja izolacije 18 EUR/m^2. Ako bi sva ta novčana sredstva (5.163 EUR) uložili samo u izolaciju vanjskih zidova zgrade (obujam zgrade je oko 155 m, sl. 2), i to po 1 m njegove visine (s obzirom da izolacija prema stubištu zanemarivo utiče na energetski razred zgrade), troškovi izolacije po m^2 fasade bi iznosili 33,3 EUR/m^2. Troškovi postavljanja (ugradnje) izolacije iznosili bi 2790 EUR (pod pretpostavkom da su troškovi postavljanja izolacije ostali isti). Ostatak novca (2373 EUR) se može utrošiti na nabavku izolacije. Pri tom bi debljina izolacije iznosila 22 cm, a koeficijent prolaza topline vanjskog zida 0,17 W/(m^{2}K). Više je nego očigledno da bi se to odrazilo na energetski razred objekta.

Sa termodinamičkog aspekta, svako direktno zagrijavanje prostora, vode ili bilo čega drugog električnom energijom je neprihvatljivo. Danas, kada se toplinska energija u znatnom periodu godine može povoljno obezbijediti pomoću solarnih kolektora, to bi trebalo iskoristiti za zagrijavanje tople vode ne samo za kupaonice već i za perilice rublja. Od ukupno utrošene energije pri pranju rublja, preko 50 % odlazi za zagrijavanje vode. Za zagrijavanje vode za velike perilice rublja u bolnicama, uglavnom se ne koristi električna, već toplinska energija. Za domaćinstva, na tržištu trenutno nema perilica rublja sa dva priključka (za hladnu i toplu vodu). Sprezanjem sistema za proizvodnju toplinske energije putem kotlova recimo na biomasu i solarnih kolektora uz LED rasvjetu, moguće je potrošnju električne energije u domaćinstvima znatno smanjiti u odnosu na klasična rješenja.

Posebice su za to pogodni pirolitički kotlovi jer je za njih potreban akumulator topline, približno zapremine 50 l/kW snage. Akumulator se može koristiti i za akumulaciju topline sa solarnih kolektora. Sa njim se vrlo efikasno može spregnuti skladištenje toplinske energije dobivene od Sunca i sagorijevanjem goriva. Sa primjenom rješenja za sagorijevanje drvnog otpada dobivenog putem sjeckalica u ovim kotlovima, moguća je proizvodnja toplinske energije po izuzetno konkurentnim cijenama. I kao što u višestambenim zgradama po svakom

stanu mjerimo potrošnju električne energije i hladne vode, tako bi isto mogli mjeriti i potrošnju potrošne tople vode, s tim što bi se ova voda korisnicima isporučivala pri konstantnoj temperaturi.

4. ZAKLJUČAK

Da bi sa sredstvima predviđenim za toplinsku izolaciju objekta postigli ekonomski optimum i što bolji energetski razred objekta, debljina toplinske izolacije na pojedinim elementima ovojnice grijanog dijela zgrade trebala bi se određivati na osnovu godišnjih toplinskih gubitaka (veći godišnji toplinski gubici – veća debljina izolacije). Sprezanjem sistema grijanja na biomasu objekata sa sistemima za pripremu potrošne tople vode putem sunčevih kolektora, moguće je postići znatno smanjenje potrošnje električne energije, a samim tim i našeg utjecaja na životnu sredinu.

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UTICAJ GRADILIŠTA DIJELA AUTOPUTA BANJA LUKA – DOBOJ NA KVALITET ŽIVOTNE SREDINE

THE IMPACT OF THE CONSTRUCTION SITE OF A PART OF THE BANJA LUKA – DOBOJ MOTORWAY ON THE ENVIRONMENTAL QUALITY

Dušica Pešević*, Nebojša Knežević**

* Prirodno-matematički fakultet, Univerzitet u Banjoj Luci, Bosna i Hercegovina
** Institut za građevinarstvo "IG", Banja Luka, Bosna i Hercegovina

autor za korespondenciju: Dušica Pešević, e-mail dusicapesevic@gmail.com

Izvorni znanstveni rad

SAŽETAK

U radu je predstavljen uticaj gradilišta dijela autoputa Banja Luka – Doboj, dionica 1, u naselju Miloševci, na kvalitet životne sredine u skladu sa zahtjevima Ekološke dozvole i odobrenim monitoring planom iz Plana upravljanja životnom sredinom i socijalnim pitanjima u toku izgradnje. Uporednom analizom podataka dobijenih kontinuiranim monitoringom kvaliteta voda, vazduha, zemljišta i nivoa vanjske buke, sa podacima njihovog nultog stanja, odnosno vrijednostima prije početka gradnje, dobija se realna slika o uticaju građevinskih radova na kvalitet životne sredine na predmetnom gradilištu. U slučaju da se pokaže da izvođenje građevinskih radova ima negativan uticaj na kvalitet životne sredine, utvrdiće se uzrok negativnog uticaja i preduzeće se dodatne mjere na sprečavanju, smanjenju ili ublažavanju uticaja.

***Ključne riječi**: uticaj, životna sredina, monitoring, autoput*

ABSTRACT

The paper presents the impact of the construction site of a part of the Banja Luka – Doboj motorway, section 1, in the settlement of Miloševci, on the quality of the environment in accordance with the requirements of the Environmental Permit and the approved monitoring plan from the Construction Environment and Social Management Plan. Comparative analysis of the data acquired by continual monitoring of the quality of water, air, soil, as well as the level of external noise and their zero state, i.e. their values before the

beginning of construction, gives a realistic overview of impacts of the construction site on the quality of the environment on the subject building site. In the case that the execution of civil works proves to have a negative impact on the quality of the environment, the cause of negative impacts shall be determined and additional measures of prevention, reduction or mitigation of impacts shall be taken.

***Keywords**: impact, environment, monitoring, motorway*

1. UVOD

Decenijama unazad je poznato da su fizički, hemijski i biološki uticaji nastali izgradnjom autoputeva dovoljno ozbiljni da opravdavaju primjenu različitih mjera kontrole životne sredine [1]. Procjene uticaja na životnu sredinu (EIA) nisu nove i postoje mnogi primjeri iz cijelog svijeta, ali su ipak malobrojni autori koje se konkretno bave efektima tokom izgradnje autoputa na kvalitet životne sredine [2]. Mnogo su brojniji radovi koji se bave uticajem izgrađenog autoputa na elemente životne sredine [3 - 7]. Kvantitativna procjena uticaja građevinskih aktivnosti na životnu sredinu može pomoći donosiocima odluka da identifikuju glavne faktore uticaja na životnu sredinu i naprave planove za zaštitu životne sredine u ranim fazama izgradnje [8]. Autoput Banja Luka – Doboj, u dužini 71,91 km, predstavlja ključnu regionalnu vezu u Republici Srpskoj, Bosni i Hercegovini. On će povezati autoput Gradiška – Banja Luka (E-661) sa Koridorom Vc. Autoput se proteže od istoka prema zapadu, između Mahovljanske petlje kod Banja Luke i petlje Johovac, nedaleko od Doboja. Pri izvođenju građevinskih radova na razmatranom gradilištu dijela autoputa Banja Luka – Doboj postoji određeni broj aktivnosti, koje mogu prouzrokovati negativne posljedice na kvalitet životne sredine [9]. Predmetna istraživanja uticaja na životnu sredinu vršena su na lokaciji gdje se izvode radovi na izgradnji autoputa Banja Luka – Doboj, Dionica 1: Banja Luka – Prnjavor, u skladu sa zahtjevima Ekološke dozvole i odobrenim monitoring planom iz Plana upravljanja životnom sredinom i socijalnim pitanjima u toku izgradnje - CESMP. Plan upravljanja životnom sredinom je pripremljen na temelju rezultata ekološke procjene uticaja i uključuje mjere kako bi se smanjili mogući negativni uticaji koji će se primijeniti tokom implementacije navedenog projekta. Potencijalni negativni uticaji se mogu svesti u dozvoljene granice primjenom odgovarajućih mjera koje su definisane u ekološkoj dozvoli [10]. Mjere za ublažavanje u fazi izgradnje uglavnom se odnose na implementaciju dobrih građevinskih praksi kako bi se izbjegli negativni uticaji na stabilnost tla, kvalitet voda, vazduha i zemljišta, te na nivo buke. U radu su prikazani i analizirani rezultati monitoringa kvaliteta voda, vazduha i zemljišta, te nivo izmjerene buke, u periodu februar - septembar 2017. godine.

2. ANALIZA KVALITETA VODE NA PREDMETNOM GRADILIŠTU DIJELA AUTOPUTA BANJA LUKA - DOBOJ

Pri izvođenju građevinskih radova na razmatranom gradilištu dijela autoputa Banja Luka – Doboj postoji određeni broj aktivnosti, koje mogu prouzrokovati negativne posljedice na kvalitet voda. U tom pogledu najveću opasnost predstavljaju građevinski radovi (skidanje prirodnog pokrovnog sloja i poremećaje prirodnih pravaca prihranjivanja), zatim građevinske mašine (akcidentno izlijevanje nafte i naftnih derivata) i zasipanje korita vodotoka građevinskim materijalom usljed nepažnje izvođača [9]. Tradicionalni pristupi procjeni

kvaliteta riječne vode se zasniva na poređenju eksperimentalno određene vrednosti parametara sa postojećim lokalnim normativima. Za vjerodostojno određivanje kvaliteta voda na području gradilišta autoputa Banja Luka – Doboj, u naselju Miloševci, izvršeno je mjerenje većeg broja parametara (18) na dvije lokacije, odnosno iz korita rijeka Vrbas i Crkvena. Preko rijeke Vrbas gradi se most dužine 340 metara (slika1). Ovo je najsloženiji objekat na autoputu Banja Luka – Prnjavor i nalazi se na trećem kilometru autoputa. Koordinate uzetog uzorka rijeke Vrbas nizvodno od lokacije gdje je u toku gradnja mosta u sklopu autoputa, uzorak 1: 44°54'40.28"N i 17°21'23.73"E (slika 2). Koordinate uzetog uzorka iz rijeke Crkvene, uzorak 2: 44°54'3.48"N i 17°21'22.56"E. Kompletna ispitivanja uzoraka vode vršena su u skladu sa akreditovanim metodama koje propisuje BAS/EN, u akreditovanoj laboratoriji „Euroinspekt“,d.o.o. Osječani, Doboj, a rezultati sintetizovani i prezentovani u vidu tabela (tabela 1 i 2).



Slika 1. Gradnja mosta preko rijeke Vrbas



Slika 2. Mjesto uzorkovanja iz korita rijeke Vrbas

2.1. Rezultati mjerenja kvaliteta vode

Procjene ekološkog i hemijskog statusa površinskih voda izvršene su u skladu sa Zakonom o vodama (Službeni glasnik RS broj 50/06) [11] i Uredbom o klasifikaciji voda i kategorizaciji vodotoka (Službeni glasnik RS broj 42/01) [12]. Prema normativnim definicijama ekološkog statusa kvaliteta voda i dopuštenim graničnim vrijednostima za pojedine parametre kvaliteta, sve površinske vode obuhvaćene pomenutom Uredbom svrstavaju se u pet klasa, od 1 do 5.

Tabela 1. Rezultati mjerenja, rijeka Vrbas, nizvodno od lokacije gradnje mosta

Parametar, jed. mjere	Ispitna metoda	FEB.	MAR	APR.	MAJ	JUN	JULI	AVG	SEP.
Temper. vode, ºC	BAS DIN 38404-4:2010	4,2	9,0	9,8	12,2	20,0	19,0	20,0	14,0
pH – vrijed.	BAS ISO 10523:2002	7,98	7,96	7,82	8,03	8,03	7,89	7,73	7,97
Uk. suvi ost.,g/m³	BAS EN 872:2006	274	253	268	190	154	260	262	228
Sus.mat., g/m³	BAS DIN 38409-1:2010	14,2*	11,2*	13,4*	3,0*	2,5*	2,0*	2,6*	13,5*
Elektr. Provodlj. μScm^{-1}	BAS EN 27888:2002	402*	361*	364*	359*	396*	416*	423*	453*
BPK5, gO_2/m^3	BAS ISO 5815-2:2004	4,3	3,9*	1,9*	1,3*	1,2*	2,29*	1,3*	1,93*
HPK, gO_2/m^3	BAS ISO 6060:2000	14,9*	12,6*	8,6*	11,0*	8,0*	7,0*	9,0*	8,2*
Gvožđe, mg/m³	BAS ISO 6332:2000	176,0*	154,0*	136,9*	123,0*	115,0*	87,0*	115,0*	80,0*
Mangan, mg/m³	BAS ISO 6333:2003	32,8*	25,3*	<0,01*	14,2*	12,4*	91,0*	<0,01*	<0,01*
Kadijum, mg/m³	BAS ISO 8288:2002	<0,005	<0,005	<0,005	<0,005	<0,05	<0,05	<0,05	<0,05
Hrom	BAS EN 1233:2002	<5,0	<5,0	<5,0	<5,0	<0,05	<0,05	<0,05	<0,05
Bakar, mg/m³	BAS ISO 8288:2002	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0
Nikl, mg/m³	BAS ISO 8288:2002	<0,05*	<0,05	<0,05*	<0,05*	<0,05*	<0,05*	<0,05*	<0,05*
Cink, mg/m³	BAS ISO 8288:2002	<1,0	<1,0	<1,0	<1,0	<0,1	<1,0	<1,0	<1,0
Olovo, mg/m³	BAS ISO 8288:2002	<0,1	<0,1	<0,1	<0,1	<1,0	<0,1	<0,1	<0,1
Masti i ulja, mg/m³	EPA 1664-R-A:1999	<2,7	<2,7	<2,7	<2,7	<2,7	<2,7	<2,7	<2,7
Sulfati, g/m³	ASTM D 516:2007	39,8	34,8	29,3	14,9	20,7	26,9	32,94	31,56
Hloridi, g/m³	JUS ISO 9297:1989	4,3	3,9	2,5	4,7	5,4	6,0	6,2	5,35

* Vrijednosti smanjene u odnosu na nulti monitoring
** Vrijednosti povećane u odnosu na nulti monitoring

Prema ekološkom kvalitetu voda koji se mora održati ili postići uvođenjem preventivnih mjera i najboljih ekonomskih dostupnih tehnologija, površinski tok rijeke Vrbas se svrstava u II kategoriju vodotoka, a rijeka Crkvena pripada I kategoriji kvaliteta voda [12].

Tabela 2. Rezultati mjerenja, Rijeka Crkvena, na mjestu najbližem gradilištu

Parametar, jed. mjere	Ispitna metoda	FEB.	MART	APR.	MAJ	JUN	JULI	AVG.	SEP.
Temper. vode, ºC	BAS DIN 38404-4:2010	2,0	10,0	10,5	16,0	22,5	24,0	22,0	16,0
pH – vrijednost	BAS ISO 10523:2002	7,92	7,90	7,92	7,97	7,65	7,69	7,48	7,57
Uk. suvi ost., g/m³	BAS EN 872:2006	290	285	238,0	264	187	289	218	220
Suspendo v. mat., g/m³	BAS DIN 38409-1:2010	18,7	15,3	15,3	1,0*	1,5*	1,2*	1,8*	9,0*
Elektrolit. Provodlj. μScm^{-1}	BAS EN 27888:2002	398*	377*	379*	393*	418*	474*	512*	452*
BPK5, gO_2/m^3	BAS ISO 5815-2:2004	4,9	4,1	3,9*	1,2*	1,3*	1,5*	1,4*	2,98*
HPK, gO_2/m^3	BAS ISO 6060:2000	17,3	15,2	12,8*	13,0*	14,0*	11,0*	12,0*	13,2*
Gvožđe, mg/m³	BAS ISO 6332:2000	87,0	72,6	81,2	95,7	92,0	96,3	75,0	84,0
Mangan, mg/m³	BAS ISO 6333:2003	38,9*	31,3*	<0,01*	14,3*	15,4*	85,9	95,4	69,0
Kadijum, mg/m³	BAS ISO 8288:2002	<0,005	<0,005	<0,005	<0,005	<0,05	<0,05	<0,05	<0,05
Hrom	BAS EN 1233:2002	<5,0	<5,0	<5,0	<5,0	<0,05	<0,05	<0,05	<0,05
Bakar, mg/m^3	BAS ISO 8288:2002	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0
Nikl, mg/m^3	BAS ISO 8288:2002	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Olovo, mg/m³	BAS ISO 8288:2002	1,1	1,0	1,0	0,8	0,9	0,8	0,9	<1,0
Cink, mg/m³	BAS ISO 8288:2002	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Masti i ulja, mg/m³	EPA 1664-R-A:1999	<2,7	<2,7	<2,7	<2,7	<2,7	<2,7	<2,7	<2,7
Sulfati, g/m³	ASTM D 516:2007	42,8	37,9	34,5	26,0	28,2	21,7	21,9	27,56
Hloridi, g/m³	JUS ISO 9297:1989	10,3	8,6	6,4	6,7	14,0	14,7	12,7	16,72

* Vrijednosti smanjene u odnosu na nulti monitoring
** Vrijednosti povećane u odnosu na nulti monitoring

Dobijeni rezultati kvaliteta vodotoka rijeke Vrbas (tabela 1) pokazuju da se kvalitet vodotoka u odnosu na pojedine parametre kreće od prve do četvrte klase vodotoka. Parametri koji ne ispunjavaju vrijednosti za II kategoriju vodotoka, u koju je svrstana rijeka Vrbas prema Uredbi o klasifikaciji voda i kategorizaciji vodotoka [12] su najčešće sljedeći: BPK_5, HPK i suspendovane čvrste materije. Međutim, u odnosu na nulti monitoring većina parametara zadovoljavaju istu klasu kvaliteta vodotoka. Kod određenih parametara

determinisane su i manje vrijednosti koje predmetni vodotok svrstava u bolju klasu kvaliteta u odnosu na nulti monitoring (tabela 1).

Dobijeni rezultati kvaliteta vodotoka rijeke Crkvena (tabela 2) pokazuju da se kvalitet vodotoka u odnosu na pojedine parametre kreće od prve do pete klase kvaliteta vodotoka. Prema Uredbi o klasifikaciji voda i kategorizaciji vodotoka rijeka Crkvena pripada I kategoriji kvaliteta voda, a parametri čije vrijednosti odstupaju od ove klase su najčešće bili sljedeći: suspendovane čvrste materije, BPK_5, HPK, elektrolitička provodljivost i mangan. Međutim, u odnosu na nulti monitoring većina parametara zadovoljavaju istu klasu kvaliteta vodotoka, a kod određenih parametara determinisane su i manje vrijednosti koje predmetni vodotok svrstava u bolju klasu kvaliteta u odnosu na nulti monitoring (tabela 2).

Analizom dobijenih rezultata može se zaključiti da radovi koji se izvode na izgradnji autoputa ne utiču na kvalitet vode u vodotocima Vrbasa i Crkvene. Na njihov kvalitet dominantan uticaj imaju vremenski uslovi, otpadne sanitarne vode gradova i naselja, koje se ispuštaju bez prethodnog tretmana, otpadne vode industrije, kao i divlje deponije koje su nalaze na obalama posmatranih vodotoka.

Prilikom izvođenja građevinskih radova na izgradnji autoputa, primjenjuju se mjere predviđene Planom upravljanja zaštitom životne sredine, i socijalnim pitanjima u toku izgradnje - CESMP, tačka 2. Predviđene mjere za ublažavanje uticaja na segmente životne sredine i tačka 4. Plan upravljanja otpadnim vodama i čvrstim otpadom.

U daljem redovnom monitoringu pratiće se kvalitet vodotoka Vrbasa i Crkvene, i u slučaju da se pokaže da izvođenje građevinskih radova ima negativan uticaj na kvalitet vodoka ovih rijeka utvrdiće se uzrok negativnog uticaja i preduzeće se dodatne mjere na sprečavanju, smanjenju ili ublažavanju uticaja.

3. ISPITIVANJA KVALITATA ZEMLJIŠTA NA PREDMETNOM GRADILIŠTU

Uzorkovanje zemljišta vršeno je jednom mjesečno u periodu februar – septembar 2017. godine, na lokaciji pored privremenog platoa za smještaj mehanizacije, koja se koristi za izgradnju tog dijela dionice autoputa, u reonu naselja Miloševci, na mjestu gdje je uzorkovano zemljište prilikom vršenja nultog monitoringa.

Analiza kompozitnog uzorka zemljišta obuhvatala je sljedeće parametre: ukupni Cd, Ni, Pb, Cr.

Uzorak zemljišta je uzorkovan u skladu sa metodologijom proisanom od strane Poljoprivrednog instituta Republike Srpske, na način:

- prosječan uzorak je uzet sa površine kruga prečnika 3 m,
- centar kruga je geopozicioniran,
- uzorak zemljišta je uzet iz sloja zemljišta dubine od 0 do 10 cm,
- prosječan uzorak zemjišta se sastoji od 5 pojedinačnih uzoraka uzetih sa sledećeh mjesta:
- jedan iz centra kruga,
- četiri sa mjesta gdje kružnica presijeca pravac istok, zapad, sjever, jug.
- pojedinačni uzorci su dobro izmješani i odvojeno je 1 kg koji je dostavljen na analizu u institut,
- uzorak je upakovan i označen tako da je zaštićen od svih vidova kontaminacije.

3.1. Rezultati analiza uzoraka zemljišta

Rezultati ukupnog sadržaja teških metala i potencijalno toksičnih elemenata tumače se na osnovu Pravilnika o dozvoljenim količinama opasnih i štetnih materija u poljoprivrednom zemljištu i vodi za navodnjavanje i metodama za njihovo ispitivanje („Službeni glasnik Republike Srpske“ broj 56/16) [13]. Na osnovu pedeološke karte Republike Srpske, predmetno zemljište pripada tipu zemljišta fluvisol ili aluvijalno zemljište. S obzirom da se maksimalno dozvoljene količine (MDK) teških metala i potencijalno toksičnih elemenata (tabela 3) određuju u zavisnosti od teksture zemljišta, izvršena je mehanička analiza zemljišta na osnovu koje je predmetno zemljište okarakterisano kao praškasto-ilovasto-zemljište.

Na osnovu dobijenih rezultata mehaničke analize zemljišta i dobijenih rezultata hemijskih analiza uzoraka zemljišta (tabela 4) možemo zaključiti da količine ispitivanih štetnih materija teških metala u ukupnom obliku, u uzorkovanom zemljištu, ne prelaze maksimalno dozvoljene koncentracije utvrđene Pravilnikom [13] izuzev ukupnog sadržaja nikla izmjerenog u mjesecu septembru koji prelazi MDK za praškasto ilovasto zemljište, ali ne prelazi vrijednost izmjerenu za nulti monitoring.

Tabela 3.Maksimalno dozvoljene količine (MDK) sadržaja teških metala i potencijalno toksičnih elemenata u poljoprivrednom zemljištu [13]

Teški metali i potencijalno toksični elementi (ukupni oblik)	Maksimalno dozvoljene količine (MDK) u zavisnosti od teksture zemljišta (mg/kg)		
	Pjeskovito zemljište	**Praškasto – ilovasto zemljište***	Glinovito zemljište
Olovo (Pb)	50	100	150
Kadmijum (Cd)	0,5	1	2
Hrom (Cr)	40	80	120
Nikl (Ni)	30	50	75

*Na osnovu dobijenih rezultata mehaničke analize zemljišta od 13.10.2016. godine (br. DO-IGBL- IN- EK-4044/16)

Tabela 4. Rezultati hemijskih analiza uzoraka zemljišta (mg/kg)

	FEB.	MART	APR.	MAJ	JUN	JULI	AVG.	SEP.
Olovo (Pb)	22,9	23,4	15,9	20,7	20,1	19,4	19,4	13,8
Kadmijum (Cd)	0,06	<0,1	<0,1	0,04	< 0,01	< 0,05	0,25	0,08
Hrom (Cr)	40,8	72,5	57,1	61,3	77,5	76,9	43,85	68,8
Nikl (Ni)	39,8	47,5	38,4	45,2	46,3	48,3	45,47	82,9

Registrovane koncetracije teških metala u predmetnom uzorku zemljišta ne potiču od antropogenog uticaja već su geološkog porijekla. Za slučaj prekoračenja pravilnikom propisanih vrijednosti postupiće se u skladu sa tačkom 3.2.5. Mjere za zaštitu flore i faune u fazi izgradnje i tačkom 3.2.10. Mjere koje se preduzimaju u incidentnim situacijama, po zahtjevima iz ekološke dozvole.

4. ANALIZA KVALITETA VAZDUHA NA PREDMETNOM GRADILIŠTU

U svrhu ocjenjivanja kvaliteta vazduha na lokaciji naselja Miloševci, naselja u kojem je započeta izgradnja autoputa Banja Luka – Doboj (dionica Banja Luka – Prnjavor, naselje Miloševci), pomoću pokretne stanice opremljene analizatorima za mjerenje imisionih koncetracija zagađujućih materija izvršeno je mjerenje kvaliteta vazduha. Izabrano mjerno mjesto se nalazi na otvorenom prostoru, uz granicu prema stambenim objektima naselja Miloševci, udaljeno od trase autoputa oko 70 m. Na poziciji u pravcu ka najbližim susjednim objektima izvršeno je mjerenje kvaliteta imisionih koncentracija osnovnih polutanata u vazduhu. Koordinate mjernog mjesta broj u naselju Miloševci su 44°54'3.58" N i 17°21'14.13" E.

Mjerenje kvaliteta vazduha na navedenoj lokaciji odobuhvatilo je imisione koncetracije SO_2, CO, NO, NO_2, NOx, ULČ (ukupne lebdeće čestice), istovremeno sa mjerenjem mikrometeoroloških parametara: brzina i smjer vjetra, temperatura i relativna vlažnost vazduha.

Odredbama definisanim u članu 21. Zakona o zaštiti vazduha (Sl. Glasnik RS, br. 124/11) utvrđene su 3 kategorije kvaliteta vazduha prema nivou zagađenosti, polazeći od propisanih graničnih i tolerantnih vrijednosti definisanih Uredbom o vrijednostima kvaliteta vazduha [14] i na osnovu rezultata mjerenja. Ako za neku zagađujuću materiju nije propisana granica tolerancije, njena granična vrijednost uzima se kao tolerantna vrijednost. Granične i tolerantne vrijednosti i granice tolerancije za sumpor dioksid, azot dioksid, suspendovane čestice (PM_{10}) i ugljen monoksid date su u tabeli 5, a ciljna vrijednost za prizemni ozon u tabeli 6.

Tabela 5. Granične, tolerantne vrijednosti i granice tolerancije za zaštitu zdravlja ljudi [14]

Period uzorkovanja	Granična vrijednost	Granica tolerancije	Tolerantna vrijednost
Sumpordioksid			
Jedan sat	350 μg/m^3	150 μg/m^3	500 μg/m^3
Jedan dan	125 μg/m^3	-	125 μg/m^3
Kalendarska godina	50 μg/m^3	-	50 μg/m^3
Azotdioksid			
Jedan sat	150 μg/m^3	75 μg/m^3	225 μg/m^3
Jedan dan	85 μg/m^3	40 μg/m^3	125 μg/m^3
Kalendarska godina	40 μg/m^3	20 μg/m^3	60 μg/m^3
Suspendovane čestice PM_{10}			
Jedan dan	50 μg/m^3	25 μg/m^3	75 μg/m^3
Kalendarska godina	40 μg/m^3	8 μg/m^3	48 μg/m^3
Ugljenmonoksid			
Maksimalna dnevna osmočasovna vrijednost	10 mg/m^3 (10000 μg/m³)	6 mg/m^3 (6000 μg/m³)	16 mg/m^3 (16000 μg/m³)
Jedan dan	5 mg/m^3 (5000 μg/m³)	5 mg/m^3 (5000 μg/m³)	10 mg/m^3 (10000 μg/m³)
Kalendarska godina	3 mg/m^3 (3000 μg/m³)	-	3 mg/m^3 (3000 μg/m³)

Tabela 6. Ciljna vrijednost za prizemni ozon [14]

Ciljna vrijednost za prizemni ozon		
Cilj	Period računanja prosječne vrijednosti	Ciljna vrijednost
Zaštita zdravlja ljudi	Maksimalna dnevna osmočasovna srednja vrijednost	120 μg/m^3

U zoni i aglomeracijema u kojima je nivo predmetnih zagađujućih materija, ispod graničnih vrijednosti utvrđenih gore datim tabelama, potrebno je da se koncentracije zagađujućih materija zadrže na nivou ispod graničnih vrijednosti.

4.1. Rezultati mjerenja kvalitata vazduha

Rezultati mjerenja kvaliteta vazduha na predmetnoj lokaciji za period februar – septembar 2017. godine su prikazani u tabeli 7.

Tabela 7. Rezultati mjerenja kvaliteta vazduha

Polutant	Period Uzorkovanja	FEB.	MART	APR.	MAJ	JUN	JULI	AVG.	SEP.
$PM_{10,}$ μg/m^3	24h	29,62	34,69	24,45	24,47	28,99	32,20	24,06	29,54
CO, mg/m^3	24h	2,02	0,72	0,26	0,65	0,24	0,24	0,30	0,33
	8h	1,66	0,60	0,21	0,59	0,22	0,22	0,28	0,35
$SO_{2,}$ μg/m^3	24h	28,87	29,41	23,75	21,15	13,02	13,15	11,37	12,21
	1h	45,04	39,79	29,83	27,11	14,52	20,17	13,61	15,18
$NO_{2,}$ μg/m^3	24h	30,70	31,78	24,86	26,47	21,51	19,91	19,25	20,48
	1h	48,00	37,30	31,02	21,80	23,11	22,72	22,79	21,99
$O_{3,}$ μg/m^3	8/24h	45,63	41,12	44,35	52,71	51,02	58,18	54,44	47,98

Prosječna dnevna koncentracija ukupnih lebdećih čestica na mjernoj lokaciji u toku mjernog perioda februar – septembar je iznosila 28,5 μg/m^3 (tabela 7). Najviša izmjerena vrijednost u avgustu od 34,69 μg/m^3 je znatno niža od granične vrijednosti propisane Uredbom [14]. Prosječna usrednjena vrijednost registrovanih koncentracija CO za 24-h mjerni period registrovanih od februara do septembra iznosila je 0,59 mg/m^3 (tabela 7), pri čemu najviša vrijednost izmjerena u februaru 2017. godine je daleko ispod graničnih vrijednosti propisanih Uredbom (tabela 5). Prosječna dnevna koncentracija NO_2 u vazduhu na mjernoj lokaciji u periodu februar – septembar je iznosila 24,37 μg/m^3. Najviša vrijednost, od 31,78 ug/m^3, zabilježena u mjesecu martu, je znatno niža od graničnih vrijednosti propisanih Uredbom (tabela 5). Prosječna vrijednost dnevnih koncentracija SO_2 u vazduhu, u razmatranom periodu, na odabranoj mjernoj poziciji je imala vrijednost od 19,12 μg/m^3, dok je najviša vrijednost od 29,41 μg/m^3 takođe ispod dozvoljenih graničnih vrijednosti propisanih Uredbom [14]. Najviše prosječne dnevne koncentracije ozona u vazduhu, izmjerene u julu 2017. godine (58,18 μg/m^3), ne prelaze ciljane vrijednosti od 120 μg/m^3 (tabela 6).

Na osnovu analize rezultata mjerenja kvaliteta vazduha možemo zaključiti da izmjerene vrijednosti polutanata u vazduhu ne prekoračuju granične vrijednosti propisane Uredbom o vrijednostima kvaliteta vazduha (Službeni Glasnik Republike Srpske broj: 124/12) [14]. Za slučaj prekoračenja mjerenih parametara postupiće se u skladu sa tačkom 3.2.1. Mjere sprečavanja emisija u vazduh, za vrijeme izgradnje, prema zahtjevima iz ekološke dozvole.

5. MJERENJE VANJSKE BUKE NA PREDMETNOM GRADILIŠTU

Mjerenje stanja vanjske buke na lokaciji gdje se izvode radovi na izgradnji autoputa Banja Luka – Doboj, Dionica 1: Banja Luka – Prnjavor, u skladu je sa zahtjevima Ekološke dozvole i odobrenim monitoring planom iz Plana upravljanja životnom sredinom i socijalnim pitanjima u toku izgradnje - CESMP. Izabrano mjerno mjesto se nalazi na otvorenom prostoru uz granicu eksproprijacije u naselju Miloševci, kod najbližih stambenih objekata. Koordinate mjernog mjesta su 44°54'0.60"N; 17°21'12.22"E.

U realnim uslovima čest je slučaj da je nivo zvuka (buke) promjenjiv sa vremenom (buka u industriji, komunalna buka, saobraćajna buka). Da bi se procjenjivaala štetnost takvog zvuka na čovjeka ili komparirala izmjerena vrijednost nivoa sa dozvoljenom, uveden je ekvivalentni nivo zvuka (buke) L_{eq} [dB(A)] koji predstavlja konstantni nivo zvučnog pritiska u mjernom intervalu i odgovara po štetnom dejstvu posmatranom, vremenski promjenljivom nivou u istom intervalu. Izražavanjem buke u vremenski nestacionarnom zvučnom polju pomoću „ekvivalentnog“ nivoa uspostevljena je veza sa vremenom kao parametrom koji u procjeni štetnog dejstva buke nedvosmisleno izražava dužinu ekspozicije i frekvencijom korišćenjem A-težinske krive pri određivanju ekvivalentnog nivoa:

$$L_{eq} = 10\log\tfrac{1}{T}\int_0^T\left[\frac{p(t)}{p_0}\right]^2 dt$$

gdje je T vremenski interval mjerenja.

U cilju unapređenja kvalitetnih vrijednosti analize strukture zvučnog polja vremenski promjenljive buke u amplitudnom domenu, statističkom obradom nivojskog spektra mogu se izračunati i procentualni nivoi L_n koji predstavljaju nivo koji je premašen u n% ukupnog mjernog vremena. Osnovna svrha mjerenja buke u životnoj sredini jeste određivanje mjerodavnog nivoa ukupne buke na definisanim mjernim mjestima za referentne vremenske intervale utvrđene propisima i standardima. Za mjerenje buke korišten je integrisani mjerač zvuka (bukomjer) „EXTECH“ 407780 mjernog opsega 30-130 dB, korištenjem filtra (A) odnosno sistem za mjerenje i akvizaciju podataka koji omogućava automatski vremenski zapis ekvivalentnog nivoa buke L_{eq} korištenjem (A) frekvencijske krive. Bukomjer zadovalja zahtjeve standarda IEC 651, IEC 804 Type 1. i ANSI S1.4 Type 2.

Dinamička karakteristika instrumenta je „fast“, „slow“, „impulse“. Standardni bukomjer (sonometar) kao mjerač nivoa inteziteta zvuka ili zvučnog pritiska sastoji se od:

- mikrofona,
- pojačivača,
- standardnog filtra,
- detektora za pojačivanje,
- pokrivača nivoa jačine koju mjerimo.

Osnovni dio mjerača zvučnog pritiska je mikrofon. Zadatak mikrofona je da promjeni zvučni pritisak p=f (t), pretvori u odgovarajuću promjenu električnog napona u=(t). Ako je promjena zvučnog pritiska harmonička funkcija (sinusoidna) onda je i dobiveni napon na izlazu iz mikrofona sinusoidan (harmoničan). Promjanjivi napon se pojačava u predpojačivaču, a dalje preko filtera i elektronskog pojačivača, mjerni signal dovodi u indikator gdje se očitava nivo akustične veličine koja se mjeri.

Bukomjer je izgrađen na osnovu jednačine:

$$L = 20 \log P/ P_0 = 10 \log I/I_0 \, [dB]$$

Izmjereni nivoi vanjske buke na posmatranoj lokaciji normirani su u skladu sa nivoima buke propisanim Pravilnikom o dozvoljenim granicama intenziteta zvuka i šuma ("Službeni list SRBiH" broj: 46/89) [15]. Neposredno prije mjerenja buke, bukomjer je kalibrisan odgovarajućim etaloniranim kalibratorom zvuka EXTECH 407776 radi provjere čitavog mjernog sistema.

5.1. Rezultati mjerenja intenziteta buke

Prema Pravilniku o dozvoljenim granicama intenziteta zvuka i šuma ("Službeni list SRBiH" broj: 46/89) [15], mjerenje buke na otvorenom prostoru vrši se na propisanoj udaljenosti od prepreka koje reflektuju buku (najmanje 3 m od objekta), te odgovarajućoj visini od nivoa terena (1,2 – 2,0 m). Mjerenje nivoa buke na otvorenom prostoru izvršeno je po suvom vremenu bez padavina i vjetra brzine 1,2 m/s.

Rezultati mjerenja 15-minutnih ekvivalentnih nivoa buke (Leq) na navedenim mjernim mjestima prikazani su u tabeli 8.

Tabela 8. Rezultati mjerenja vanjske buke duž budućeg gradilišta autoputa Banja Luka – Doboj, Dionica 1 (mjerni interval 15 min.)

Akustično područje (zona) IV; Trgovačko, poslovno, stambeno i stambeno uz saobraćajne koridore, sladišta bez teškog transporta								
Mjerna veličina	FEB.	MART	APR.	MAJ	JUN	JULI	AVG.	Najviši dozvoljeni nivo dB (A)
$L_{eq,}$ [dB(A)]	57,2	57,9	58,9	58,8	57,9	56,2	56,9	60
$L_{1,}$ [dB(A)]	67,1	68,8	69,6	67,9	66,7	67,3	68,0	75

L_{eq} - ekvivalentni nivo buke
L_1 - nivo zvučnog pritiska premašen u 1% mjernog intervala

Vrijednosti izmjerenog petnaestominutnog ekvivalentnog nivoa vanjske buke na mjernim mjestima koja se nalaze na otvorenom prostoru uz granicu eksproprijacije prema stambenim objektima, prilikom izvođenja radova na izgradnji autoputa Banja Luka – Doboj, Dionica 1, ne prekoračuje najviši dozvoljeni nivo vanjske buke za akustičnu zonu IV, definisanu Pravilnikom o dozvoljenim granicama intenziteta zvuka i šuma ("Službeni list SRBiH" broj: 46/89). Za slučaj prekoračenja dozvoljenih vrijednosti postupiće se u skladu sa tačkom 3.2.1. Mjere za zaštitu od buke, za vrijeme izgradnje, prema zahtjevima iz ekološke dozvole.

6. ZAKLJUČAK

Uticaji izgradnje dijela autoputa Banjaluka – Doboj, dionica 1, na kvalitet vode, vazduha, zemljišta i nivo vanjske buke su prikazani kontinuiranim monitoringom tokom 8 mjeseci. U okviru Studije uticaja na životnu sredinu navedeni su zahtjevi za praćenje faze

izgradnje i operativne faze Projekta. Analizom dobijenih rezultata i poređenjem sa „nultim monitoringom“, odnosno vrijednostima parametara prije početka gradnje, može se zaključiti da radovi koji se izvode na izgradnji dijela predmetnog autoputa nemaju negativan uticaj na kvalitet vode u vodotocima Vrbasa i Crkvene. U uzorkovanom zemljištu, količine ispitivanih štetnih materija teških metala u ukupnom obliku ne prelaze maksimalno dozvoljene koncentracije utvrđene Pravilnikom, izuzev ukupnog sadržaja nikla, čije koncentracije ne prelaze vrijednost izmjerenu za nulti monitoring. Na osnovu analize rezultata mjerenja kvaliteta vazduha možemo zaključiti da izmjerene vrijednosti polutanata u vazduhu ne prekoračuju granične vrijednosti propisane Uredbom o vrijednostima kvaliteta vazduha. Vrijednosti izmjerenog ekvivalentnog nivoa vanjske buke na mjernim mjestima ne prekoračuje najviši dozvoljeni nivo vanjske buke definisane Pravilnikom. Mjere za ublažavanje u fazi izgradnje uglavnom se odnose na implementaciju dobrih građevinskih praksi kako bi se izbjegli negativni uticaji na stabilnost tla, kvalitet voda, vazduha i zemljišta, te na nivo buke.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

ROMANIA AND THE IMPACT OF THE EUROPEAN ENVIRONMENTAL FUNDS ON THE COUNTRY'S ECONOMY

Ana Monica Pop*

* Babeş-Bolyai University, Faculty of European Studies, Cluj Napoca, Romania

corresponding author: Ana Monica Pop, e-mail: monica.pop@ubbcluj.ro

Review paper

ABSTRACT

The present article will analyse how the problematic perspective provided by contracting and implementing projects through the European environmental funds has influenced the socio-economic development of Romania. Thus, through an interdisciplinary analysis of maximum actuality, we will discuss how our country has responded to the European Union's requirements regarding the environmental principles, priorities and objectives. Since 2000, the Romanian environmental policy has adapted to the standards and strategy issued by the European Commission within Agenda 2000, through the implementation of the Phare Programme, the ISPA Programme, the LIFE Programme, and the 7th Environmental Action Programme. Also, the adoption of the new environmental policies has led to the establishment of new bodies of public administration (the Environmental Fund Administration) that ensure sustainable development by highlighting the EU policies and environmental standards in Romania and the national environmental ones. These institutions will have a distinct importance in the research.

Keywords: *European funds, environmental programmes, sustainable development*

1. INTRODUCTORY ASPECTS ON THE RELEVANCE OF THE RESEARCH

This study addresses a highly debated issue in the context of many scientific circumstances that analyse the interrelationship between environmental, economic and human society issues. Even more, some specialists are talking about optimizing the triad between the economic, ecologic and social balance.

The present research is of utmost importance given the specialized papers, the doctoral theses, the articles and the specialized studies elaborated on this subject. Also, according to specialists in the field, "the impact of European Funds on economic growth or development became a research topic in the last years with interesting and conclusive results". In one of the articles consulted for the present study, C Păun briefly centralizes the approaches of Rodriguez-Pose A. and Fratesi U. which "used panel regression to test the impact of European

funds on economic development and found an insignificant impact in infrastructure and business support, a short term positive effect in case of agriculture and a medium term positive impact for education and human resource development sector", along with those of Puigcerve-Penalver M.C.; Varga J.; Vel J. I.; Jora, O.D.; V.M. Topan and R. Muşetescu [1] to which we add the contributions signed by Tătulescu A. and Patrui A. regarding the "Structural Funds and Economic Crises: Romania's Absorption Paradox" published in Procedia Economic and Finance from 2014, and also the article "Structural Funds as the Solution to the Present Crisis: Romania- a case study", published in the Review of Social and Economic Issues, no. 1 from 2015 etc.

We can observe that from the relevant economic literature, the impact of European Funds on the economic development of European Union member states is considered to be often reduced, even negative.

At European Union level, there is considerable concern for major environmental problems that are systemic and need to be integrated into a common policy. Environmental protection is a central element of the economic and social policy of each state because we ourselves are a component not only of the society, but also of nature. According to specialists, the prospects for Europe's environment are mixed, but they emphasize the opportunities to make the environment more adaptable to future risks and changes. Among these, we can mention the huge information resources on innovative technologies, resource accounting methods and a renewed commitment to the precautionary and preventive principles, the compensation for damage to the source and the "polluter pays" principle [2].

We mention that Romania's participation in the Convention for Combating Desertification represents a first important step for the progress of the Romanian economy, the conservation of environmental resources in our country and the adoption of the European model. Desertification can lead to a decrease in food production, soil infertility and a reduction in the natural resistance of land and its carbon storage capacity, after Phil Wynn Owen declaration, Member of the Court in charge of this audit, and also in areas adjacent to the Black Sea from Romania, which is also a part to many others global Conventions and trades in the environmental protection.

2. THE IMPLEMENTATION OF EUROPEAN FUNDS IN ROMANIA BEFORE AND AFTER ACCESSION

At the level of all the member states, the European Union has established a common regional policy focusing on cohesion, competitiveness and cooperation in Europe. To achieve this goal and reduce the existing disparities, important amounts have been allocated through several structural instruments – the European Regional Development Fund, the European Social Fund, the Cohesion Fund and the European Fisheries Fund, meant to contribute to the development of European countries, to improve the infrastructure, to improve human resources, innovation and to protect the environment. In another train of thoughts, almost all European countries linked their economic growth to European Union funding absorption capacity. The impact of these funds on economic growth is inconclusive: countries with higher absorption rate have lower economic growth than countries with lower absorption, with very few exceptions. Countries that relied in their economic development on such funds (Spain, Italy, Portugal, Greece or Ireland) are faced now with long recession and obvious recovery problems [3].

The European pre-accession programmes of Romania in the European Union structures have supported investments in the field of environmental protection through the

following structures: Assistance for economic restructuring in the countries of Central and Eastern Europe - PHARE, Instrument for Structural Policies for pre-Accession -ISPA, Infrastructure Development Programme in Small and Medium-sized Towns- SAMTID, Special Accession Programme for Agriculture and Rural Development - SAPARD, Financial and Operational Performance Improvement Programme - FOPIP. Among these programmes, PHARE was the first pre-accession instrument with non-reimbursable funding, which was set up in 1989 and played a leading role in supporting the countries of Central and Eastern Europe that were to adhere to the European integration process. From 1991 to 2004, the European Union has allocated the amount of € 1.7 billion for non-reimbursable financial assistance, and since 2000, the absorption rate has increased. The allocated funds concerned areas such as environmental protection, agriculture, economic cohesion, etc. [4].

After joining the European Union structures, Romania has adopted since 2008 the National Strategy for Sustainable Development in order to align our country with the requirements of sustainable development of the European Union. The National Strategy has established strategic objectives in the short, medium and long term:

- **Horizon 2013** - organic incorporation of the principles and practices of sustainable development within the assembly of public programmes and policies of Romania as a EU member state,
- **Horizon 2020** - reaching the actual medium level of the EU countries according to the main indicators of sustainable development,
- **Horizon 2030** - significant approach of Romania towards the medium level from that year of the EU member states from the perspective of sustainable development indicators.

The strategy application would provide the conditions that GDP per capita, expressed in standard purchasing power, to exceed in 2013, half of the European Union average at that moment, to approach 80 % of the European Union average in 2020 and to rise slightly above the European average in 2030 [5].

For the period 2007 - 2013, Romania has allocated € 19.057 billion for the implementation of seven Operational Programmes, centralized in table no. 1.

Among them, The Sectoral Operational Programme Environment is the document that establishes the strategy for the allocation of European Funds for the environmental sector in Romania for the period 2007 - 2013. **The general objective of the SOP ENV is to improve the living standards of the population and the environmental standards in order to comply with the acquis communautaire and to reduce the difference regarding the environmental infrastructure that exists between Romania and the European Union both in terms of quantity and quality**. The implementation of the programme will result in more efficient and performing public services related to water supply, sewage and heating, taking into account the principle of sustainable development and the "polluter pays" principle. According to the information found on the official site of the Ministry of Environment, the SOP ENV includes five priority axes corresponding to each environmental sector funded by the programme and a Priority axis of Technical Assistance to support the Managing Authority and the intermediate bodies, responsible for the management of the programme.

2.1. Data regarding the absorption degree of European funds at country level

The absorption level of structural funds can be determined by the degree of achieving the financial plan of the operating programme calculated by reporting the public expenditures declared to the European Commission at a given moment to the total funding approved by the operational programme (community funds and national contribution). The data for the absorption rate were provided by KPMG annual reports for Central and Eastern Europe, EUROSTAT data and some data provided by the Ministry of European Funds.

According to the information found on the website of the Ministry of European Funds at the 31st of March 2017, the absorption of European funds centralized on operational programmes for the period 2007 - 2013 is presented in table 1.

Table 1. The absorption degree for the 2007 - 2013 operational programmes at 31st of March 2017 (mil. euro) [6]

2007-2013 Operational Programmes	Allocation 2007 -2013 - EUR -	Advance received from the EC for the period 2007-2013 - EUR -	Eligible expenditures requested to the EC within the allocation limit of the OP (current absorption rate)		EC reimbursements (effective absorption rate)		Amounts received from the EC (with pre-financing)	
			Value	%	Value	%	Value	%
	1	2	5	6=(5/1) *100	7	8(7/1) *100	9	10=9/1*100
SOP Increasing economic competitiveness	2.536.646.054	229.879.990	2.536.646.054	100.00	2.179.933.761	85.94	2.409.813.751	95.00%
OP Technical Assistance	170.237.790	15.321.401	170.237.790	100.00	146.404.499	86.00	161.725.900	95.00%
SOP Environment	4.412.470.138	520.775.940	3.727.595.995	84.48	3.463.047.369	78.48	3.983.823.309	90.29%
Regional OP	3.966.021.762	335.341.959	3.704.771.672	93.41	3.372.867.345	85.04	3.708.209.303	93.50%
SOP Development of human resources	3.200.038.455	451.898.849	2.906.089.651	90.81	2.347.832.808	73.37	2.799.731.658	87.49%
SOP Transport	4.288.134.778	525.615.535	3.476.561.531	81.07	3.200.095.644	74.63	3.725.711.179	86.88%
OP Development of Administrative Capacity	208.002.622	27.040.341	208.002.622	100.00	170.562.150	82,00	197.602.491	95.00%
TOTAL	18.781.551.599	2.105.874.015	16.729.905.315	89.08	14.880.743.577	79.23	16.986.617.591	90.44%

The detailed analyses for each programme and funding axis reveal some significant aspects and differences. Thus, the highest value of the current absorption rate of the European funds is registered for the Operational Programme Increasing Economic Competitiveness, the Operational Programme Technical Assistance, and the Operational Programme Development of Administrative Capacity, which are leading the ranking of the European programmes for Romania.

On the other hand, the Sectoral Operational Programme Environment has a current absorption rate of 84.48 % and the lowest value is registered for the Operational Programme Transport (54.51 %) [7]. The structure for the resources allocated to the mentioned programmes reveals the following details: SOP ENV approx. 23 %, SOP Transport approx.

23 %, OP Regional approx. 20 %, SOP DHR approx. 18 %, OP DAC 1 % and OP TA 0.9 %. [8].

From the table 2 regarding the financial situation of allocation and expenditures, one can notice that at the end of 2015, the expenditures declared to the European Commission, through public contribution, amounted to € 2.911.502.939,95, representing an absorption rate of 55.09 % compared to the total financial allocation (community funding and national contribution) of € 5.191.141.331,00. At the same time, the highest level of absorption was registered for axis no. 4 (66.21 %) and the lowest level for axis no. 1A (5.92 %), both financed by the European Regional Development Fund.

Table 2. Financial allocation and expenditures declared to the EC for SOP environment (mil. euro) [6]

Priority Axis	Financial allocation	Declared expenditures	Achievement
1. Extension and modernization of water and wastewater systems	3.140.423.956.00	1.886.917,926.42	59.91 %
1 A Support for the development of infrastructure projects in the water/ wastewater sector related to the next programming period	122.728.555.00	7.266.782.67	5.92 %
2 Development of the integrated waste management systems and rehabilitation of historically contaminated sites	878.476.962.00	494.789.805.08	56.32 %
3. Reduce pollution and mitigate the effects of climate change by restructuring and rehabilitating urban heating systems to achieve energy efficiency targets in the localities most affected by pollution	388.640.131.00	212.898.212.38	54.78 %
4. Implementation of appropriate management systems for nature protection	191.098.548.00	126.534.647.75	66.21 %
5. Implementation of adequate infrastructure to prevent natural hazards in areas most at risk	315.839.375.00	162.563.539.31	51.47 %
6. Technical assistance	144.933.804.00	20.532.026.34	14.17 %
Total	5.191.141.331.00	2.911.502.939.95	55.09 %

The Priority Axes SOP Environment, centralized in table 2, focused on the environmental sectors:

- water and wastewater- expansion and modernization of water and sewage supply systems; construction and modernization of water and sewage treatment plants,
- waste and historically polluted sites- construction of ecological storage tanks; construction of sorting, composting, and transfer stations; closure of non-compliant municipal landfills; acquisition of containers for selective collection, and means of waste transportation etc.,
- nature protection- management and conservation of protected natural areas; elaboration of scientific studies, management plans and conservation measures of natural areas; mapping of protected areas etc.,
- floods and coastal areas- construction of dams and other types of infrastructure to prevent floods or reduce their effects; develop maps with flood risk areas etc.,
- technical assistance- strengthen the management, monitoring, control and evaluation systems of the SOP ENV implementation; ensure the visibility of the European financial assistance granted through the SOP ENV.

The population that will benefit from the effects of the SOP ENV is estimated at 10 million people, so 70 % of the Romanian population will be connected to the water and sewage systems at regional level; the selective collection of recyclable waste will be widely applied and there will be ecological storage tanks in 30 counties; the pollution caused by centralized district heating systems will be significantly reduced; 240 protected natural areas will have management plans and 60% of the protected areas will benefit from conservation measures; the flood risk will be eliminated for 1.5 million localities prone to flooding (Ministry of Environment, 2009) [9].

According to KPMG's report for the period 2007 - 2015 on the European Union funds allocated to central and eastern European member countries, at the end of December 2015, Romania's effective absorption rate reached 59 %, with interim payments from the European Commission reaching € 11.2 billion out of a total amount of € 19,1 billion available to the country. The comparative analysis between our country and the other member states highlights the fact that Romania is positioned in one of the last places in the European Union in terms of Structural and Cohesion Fund (SCF) absorption [10]. The same view is shared in the economic forecast report for 2017, within which is stated that currently the absorption rate for Romania is not mediocre if a comparative investigation is to be made on the evolution of the absorption in the last years. However, unfortunately, the reported situation is not favourable to our country because we are situated below Bulgaria's absorption rate, a member state that also joined the European Union structures in 2007 and with which we are constantly compared to for the last two places in the ranking, and at a distance of 5 points from Poland, a country of Central and Eastern Europe, which has been repeatedly noted for the outstanding results achieved in managing the European funds [11].

The low absorption rate of accessing and contracting European funds is argued in the same report as due to "difficulties in absorbing SCF caused to the persistent flaws in the management and control systems which led to frequent suspension or interruption of some Operational Programmes. Romania's low uptake of European Union funds is also apparent according to an inconsistent application of the procurement rules which has triggered substantial financial corrections applied to the beneficiaries. Lack of optimized coordination among various institutions involved in SCF management and implementation has also contributed to low absorption of EU funds [12].

3. THE REGIONAL ECONOMIC DEVELOPMENT OF ROMANIA

According to the data provided by Eurostat, the GDP per capita in 2007 was 43 % of the European Union average, but at the end of 2015, the GDP per capita was 57 % of the European Union average, thus achieving the strategic goal set during the accession period to the European structures [13].

At national level, as can be seen from the table 3, there are 4 NUTS 1 regions, 8 NUTS 2 regions and 42 NUTS 3 regions. At regional level, there are some differences in economic development, with an accelerated development in Bucharest and the Ilfov area, which have a diversified infrastructure and the most highly skilled demographic potential. By contrast, the regions in the East and South show some discrepancies due to a state management inherited from the time of industrialization. This highlights the fact that the new type of regionalism still has inefficient leadership policies [2].

Table 3 classification nuts in romania [14]

NUTS 1	Macro region 1	Macro region 2	Macro region 3	Macro region 4
NUTS 2	North-West/Center	North-East/South-East	South-Muntenia/Bucureşti-Ilfov	South-West/West
NUTS 3	Bihor, Bistriţa-Năsăud, Cluj, Maramureş, Satu Mare, Sălaj/Alba, Braşov, Covasna, Harghita, Mureş, Sibiu	Bacău, Botoşani, Iaşi, Neamţ, Suceava, Vaslui/Brăila, Buzău, Constanţa, Galaţi, Tulcea, Vrancea	Argeş, Călăraşi, Dâmboviţa, Giurgiu, Ialomiţa, Prahova, Teleorman/Bucureşti. Ilfov	Dolj, Gorj, Mehedinţi, Olt, Vâlcea/Arad, Caraş-Severin, Hunedoara, Timiş

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In the absence of implementation reports from the operational programmes for 2015, we present in the table 4 below, the total number of output and result indicators, implicitly the number of non-achieved indicators compared to the initial plan for this period.

Table 4. Results of indicators in according to the annual implementation report [13]

P0	Total number of physical (output or result) indicators included in the Annual Implementation Report (AIR) 2014	Number of indicators (output or result) in the Annual Implementation Report (AIR) that are identified as non-achieved against the targets set for 2015
SOPIEC	12	5
SOPT	20	15
SOP ENV	22	18
ROP	22	11
OPACD	Data not available	Data not available
SOPHRD	46	26

The analysis of the development indicators (employment rate, electricity consumption, GDP per capita) at country level highlights a particular situation due to a different regional economic development that was also influenced by the absorption of European funds. As a region, Bucharest-Ilfov has the largest contribution to the national GDP, amounting to RON 185,83 billion (27.88 % of the total), equivalent to over two regions and 25 % of Romania's GDP both in 2013 and 2014.

The analysis of the absorption of European funds can be done by taking into account the data transmitted in the Single Information Management System (SIMS) by the 7 managing authorities within the ministries that manage these structural and cohesion instruments. Thus, a ranking of the development regions can be created according to the number of contracted projects. According to the ranking of the regions based on the number of contracted projects, it is noticed that the Bucharest-Ilfov region is on the first place in the ranking.

4. CONCLUSION

The economic developments of the last decades have ignored nature's requirements, leading to a real ecological crisis, a crisis of the natural ecosystems, which is why it is necessary to adopt measures for the rapid restructuring of the economy, and to solve the entire crisis system.

Thus, at the level of each Member State of the European Union, important actions were carried out through these structural instruments in order to optimize the relationship between the economy and the natural environment or even to restructure the economy without destroying the natural systems that support it.

Without claiming to be exhaustive of all environmental programmes and measures, we emphasize that by signing and adopting these projects, our country is oriented towards an environmental management integrated to the European model of eco-economy.

The obstacles encountered can be overcome by a joint effort of all the institutions engaged in the implementation of these environmental programmes aimed at reducing the gaps between the EU Member States and dealing with the serious threats to the environment due to negative phenomena. This is the reason why the Member States and also those wishing to join this European body must not accept the existence of a degraded natural environment but it is imperative to optimize the eco-business, eco-development and sustainability relationship.

Even if the economic activities have a negative impact on the environment, the institutions involved in the smooth running of these environmental programmes make real efforts to meet the standards imposed by the European Union and to support the strengthening of the economic, social and territorial cohesion, taking into account the national, regional and local characteristics of the country.

In conclusion, we believe that these environmental programmes have laid the foundations for an environmental infrastructure that is in line with the European standards required to ensure adequate quality support to everything that involves life and the human being.

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EKOLOŠKE SMJERNICE U TEHNOLOGIJI PRANJA TEKSTILIJA

ENVIRONMENTAL GUIDELINES IN WASHING OF TEXTILES

Tanja Pušić*

* Sveučilište u Zagrebu, Tekstilno-tehnološki fakultet, Zagreb, Hrvatska

autor za korespondenciju: Tanja Pušić, e-mail: tpusic@ttf.hr

Pregledni rad

SAŽETAK

Čimbenici u pranju opisani su Sinner-ovim krugom koji uključuje kemiju, mehaniku, temperaturu i vrijeme. Suvremeni procesi pranja se temelje na tehnološkim zahtjevima i ekološkim smjernicama održivog razvoja: kako smanjiti potrošnju energije? upotrijebiti manje štetnih kemikalija? uz istovremeno postizanje povoljnih učinaka i uklanjanje svih patogenih mikroorganizama. Ovaj koncept se u posljednje vrijeme ostvaruje kroz niskotemperaturne procese pranja (LTW), koji iziskuju visokoučinkovite deterdžente, obogaćene sadržajem tenzida, aktivatora bijeljenja i enzimatskih kompleksa. Uz ekonomsko-ekološke benefite ovih procesa je neophodno pratiti kvalitetu tekstilija i njihov životni ciklus.

***Ključne riječi**: tekstil, pranje, deterdžent, ekologija*

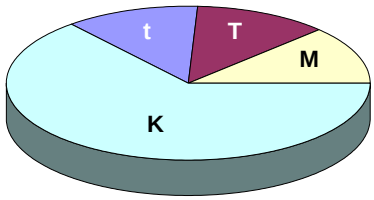
ABSTRACT

Theoretical and practical presentation of washing processes includes mechanical agitation, chemistry, temperature and time as parameters of Sinner cycle. Modern washing processes are based on technological requirements and environmental guidelines for sustainable development: how to reduce energy consumption? to use less harmful chemicals? while at the same time achieve favourable effects and remove all pathogenic microorganisms. This concept has recently been realized through low-temperature washing processes (LTWs), which require high-performance detergents, enriched with surfactants, bleach activators and enzyme complexes. Along with the economic and environmental benefits of these processes it is necessary to monitor the quality of textiles and their lifetime.

***Keywords**: textiles, washing, detergent, environmental issues*

1. UVOD

Proces pranja se teorijski razmatra i praktično predstavlja Sinner-ovim krugom (slika 1) koji je 1959. g. postavio organski kemičar dr. Herbert Sinner. Proces je određen kroz djelovanje četiri čimbenika: kemija, mehanika, vrijeme i temperatura, koje povezuje voda kao medij u kojem se proces provodi [1]. Teorijski gledano njihov udio je podjednak, a u realnim sustavima promjenjiv. Ukoliko se jedan čimbenik mijenja, on mora biti kompenziran s jednim ili više čimbenika s ciljem postizanja povoljnih učinaka.



Slika 1. Sinner-ov krug pranja (t -vrijeme, T - temperatura, M - mehanika, K - kemija)

Udio čimbenika Sinner-ovog kruga u suvremenim uvjetima pranja se mijenja u skladu s tehnološkim zahtjevima i smjernicama održivog razvoja kroz:

- uštedu energije,
- uštedu vode,
- uštedu kemikalija,
- produljen životni ciklus tekstilija,
- smanjen stupanj opterećenja otpadnih voda.

2. SMJERNICE ODRŽIVOG RAZVOJA

Proces pranja na visokim temperaturama odlikuju visoke entalpije, dobar učinak i visok stupanj dezinfekcije (termička dezinfekcija). Činjenice da se više od 80 % potrošnje energije u praonicama Europe i Sjeverne Amerike troši na zagrijavanje vode, visoka cijena energije kao i potreba smanjenja emisije CO_2 su uvjetovali potrebu racionalizacije procesa pranja [2]. Mjera održivosti je pranje na nižim temperaturama (LTW), gdje je termički utjecaj u Sinner-ovom krugu neophodno kompenzirati primjenom visokoučinkovitih deterdženata i mehaničkim djelovanjem. Sinergija svih čimbenika u LTW procesima treba osigurati zadovoljavajući stupanj čistoće, dezinfekciju opranog rublja i mali stupanj opterećenja okoliša. Korporativne kampanje populariziraju niske temperature pranja, pa je strateški tvrtka Novozymes objavila LCA (*Life Cycle Assessment*) studiju u kojoj je analiziran ekološki utjecaj strojnog pranja rublja na 40 °C i 30 °C. U pranju na 40 °C i 30 °C je korišten europski standardni deterdžent koji sadrži enzim proteazu, dok je pranje na 30 °C provedeno istim deterdžentom uz dodatak enzima dizajniranih za hladno pranje (proteaze, amilaze, lipaze). Danska studija je pokazala da sniženje temperature pranja s 40 na 30 °C može doprinijeti 30 % uštedi energije po ciklusu pranja u kućanstvu [2]. Dodatan benefit enzima se može sagledati kroz manju emisiju CO_2 za oko 100 g po ciklusu pranja.

Istraživanje u kojem je provedena usporedba pranja na temperaturama 40 °C i 15/20 °C je potvrdilo da se pranjem u hladnom (*cold wash*) uštedi oko 60 % električne energije u usporedbi s pranjem na 40 °C [3]. Enzimi - bioinovatori zamjenjuju agresivne kemikalije u pranju, a biorazgradivost ih čini ekološki prihvatljivima za pranje na nižim temperaturama. Kako bi enzimi bili primjenjivi kao komponente deterdženata, moraju zadovoljiti sljedeće zahtjeve:

- stabilnost u pH području 7 - 11,
- stabilnost u temperaturnom području 20 - 50 °C i više,
- stabilnost na odležavanje,
- odgovarajuću selektivnost prema raznim mrljama,
- kompatibilnost s drugim komponentama u deterdžentima poput tenzida, bildera i aktivatora bijeljenja i to u uvjetima primjene i odležavanja.

Strategija održivog razvoja koja uključuje ekološke zahtjeve, procjenu i analizu rizika utjecala je na unapređenje postojećih i razvoj novih tehnoloških postupaka i procesa. U skladu s tim i proizvodnja deterdženata značajno se mijenjala proteklih dvadesetak godina. A.I.S.E. (*Association Internationale de la Savonnerie, de la Detergence et des Produits d'Entrtien* - Međunarodno udruženje proizvođača sapuna, deterdženata i sredstava za čišćenje) sastavljeno od nacionalnih udruženja iz cijele Europe, 2007. g. je pokrenulo ekološku inicijativu koja je između ostalog rezultirala koncentriranim (više tenzida) i kompaktnim (veća nasipna masa) deterdžentima za pranje, koje je nemoguće proizvesti samo raspršivanjem [4]. Time je ujedno postignuto smanjenje udjela kemikalija, ambalažnog materijala i energije. A.I.S.E. povezuje proizvođače i potrošače koji se putem brojnih inicijativa informiraju o promjenama formulacija deterdženata koje direktno utječu na njihovu uporabu. Proizvođač informira korisnika o sastavu, načinu primjene kroz doziranje ovisno o stupnju zaprljanja i tvrdoći vode, upozorava ih o mogućim štetnim utjecajima i slikovno ističe specifičnosti proizvoda, npr. članstvo u A.I.S.E. Prema Pravilniku o deterdžentima *(NN 001/2011)* propisani su uvjeti koje moraju ispunjavati deterdženti i površinski aktivne tvari prilikom stavljanja na tržište, opći uvjeti proizvodnje i stavljanja na tržište deterdženata i površinski aktivnih tvari za deterdžente te prava, dužnosti i ovlasti nadležnih tijela u vezi s deterdžentima i površinski aktivnim tvarima proizvedenim u Republici Hrvatskoj ili uvezenim i stavljenim na tržište Republike Hrvatske [5].

Udio mehanike kao čimbenika u Sinner-ovom krugu je značajan s obzirom na činjenicu da dobro koncipirani strojevi mogu značajno doprinijeti racionalizaciji i kvaliteti procesa. Strojevi za pranje mogu biti kućanski i industrijski (diskontinuirani i kontinuirani). Potreba smanjene potrošnje vode u pranju je uvjetovala na manje omjere kupelji, koji su u kontinuiranim strojevima za pranje smanjeni na 1:2 (1:3), u diskontinuiranim 1:4 (1:5), a u kućanskim perilicama 1:5 (1:7).

Racionalizacija procesa, ekološka usklađenost i unapređenje kvalitete procesa pranja u industrijskim praonicama se provodi kroz implementaciju KET (*key enabling technologies*) tehnologija, čija primjena u odnosu na klasične tehnologije omogućava višestruke benefite, tablica 1.

Tablica 1. Tehnološka unaprijeđenja u industrijskim praonicama - KET tehnologije [6]

Tehnološka unaprijeđenja
niži omjeri kupelji
povrat vode
dezinfekcija vode
superkritično uplinjavanje
niskotemperaturni procesi
visokoučinkovita sredstva
redukcija kemikalija
ekološki prihvatljiva sredstva
dezinfekcija rublja
direktno zagrijavanje plinom
elektrokemijsko bijeljenje
smanjenje utroška energije
tehnika sušenja rublja
ultrazvučno pranje

Ovako postavljen koncept i organizacija praonice se veže uz pojmove *Green Laundry, Smart Laundry*, pri čemu je potrebno naglasiti da to uključuje obveznu digitalizaciju procesa i potpunu kontrolu svih segmenata praonice rublja.

Kvaliteta vode u industrijskim praonicama, koja svakim danom postaje ekološki i ekonomski značajnija prema sustavu kontrole kvalitete RAL-GZ 992 je definirana parametrima, tablica 2.

Tablica 2. Parametri kvalitete tehnološki priređene vode za pranje [7]

tvrdoća (mg/l)	0 - 100
pH	6,0 - 7,5
Fe (mg/l)	≤ 0,1
Mn (mg/l)	≤ 0,03
Cu (mg/l)	≤ 0,05
T (°C)	15 ± 5

Na primjeru praonice rublja koja pere 20 t/dan, smanjenje potrošnje vode u iznosu 2 l/kg koja se ostvaruje kroz povrat (*re-use*) kroz 250 radnih dana /godinu donosi uštedu oko 60.000 EUR godišnje.

Jedan od potencijalnih rizika niskotemperaturnih procesa pranja, smanjene potrošnje vode, te sastava deterdženata koji ne sadrže bjelila je nastanak biofilma u strojevima, koji je naročito izražen u kućanskim perilicama. Pojava biofilma vuče probleme koji se očituju kroz neugodan miris, požućenje i križnu kontaminaciju rublja.

3. KVALITETA OPRANIH TEKSTILIJA PO INOVATIVNOM KONCEPTU

Izazovi u suvremenoj tehnologiji pranja, osim potrebe za smanjenjem potrošnje energije i vode, iziskuju produljenje životnog ciklusa tekstila. Zastupljenost udjela pojedinih čimbenika Sinner-ovog kruga sa svim pod elementima reflektira se na kvalitetu opranog

rublja, koja se može sagledavati na temelju različitih kriterija i sustava. Sveobuhvatan sustav kontrole može ukazati na prednosti i eventualne nedostatke novo koncipiranih postupaka u usporedbi s klasičnim postupcima pranja, koje karakterizira visoka entalpija. Naravno, razina kvalitete mora biti u korelaciji sa zahtjevima proizvodnje i troškova. Kvaliteta opranog rublja se vrednuje na temelju: čistoće (primarni učinak), stupnja bjeline, čvrstoće, sadržaja depozita (sekundarni učinak) i higijene (dezinfekcijski učinak).

Primarni učinak - uklanjanje mrlja ili zaprljanja (S), se vrednuje nakon provedenog ciklusa pranja, mjerenjem remisije svjetla sa standardno zaprljane tkanine prije i poslije pranja. Učinak se vrednuje na temelju razlike tristimulus vrijednosti ΔY (razlike Y vrijednosti prije i poslije pranja) ili ΔR_{460} (razlika u remisiji pri valnoj duljini 460 nm, R460, prije i nakon pranja). Ukoliko se u postupku pranja ne uklanjaju mrlje, postoji opasnost da se poveća omjer odnosno količina rublja koju je potrebno ponovno oprati (*re-wash*). Ovaj omjer je karakterističan za svaku industrijsku praonicu rublja, a povećanje omjera može biti pokazatelj loše optimiranih uvjeta u pranju, ukoliko se ne može objasniti drugim parametrima (viša stopa proizvodnje, novi zahtjevi naručitelja).

Primaran učinak u pranju se ocjenjuje na temelju uklanjanja specifičnih zaprljanja (tablica 3) [8, 9].

Tablica 3. Princip utvrđivanja uklanjanja specifičnih zaprljanja

Kriterij	Test tkanine* (Monitori)	Mjerenje
Primarni učinak, S (%) (*S-Stain removal*)	Različite vrste standardno zaprljanih tkanina. Sirovinski sastav ovih tkanina bi trebao odgovarati vrsti rublja koja se ispituje (pamuk, mješavine pamuka i poliestera). Dodatno, ovisi i o zahtjevima kupca i razini kvalitete.	Spektralne karakteristike, npr. remisija R) ili tristimulusna vrijednost Y. Mjerenje se provodi prije i nakon pranja uz izvor svjetla bez UV komponente.

**može se nabaviti od nekoliko dobavljača u Europi*

Kriteriji kontrole kvalitete višestruko opranih tkanina, opis i poteškoće su prikazane u tablici 4.

Inovativni tenzidi, napredni enzimatski sustavi, visokoučinkovita bjelila i dobra sinergija čimbenika Sinner-ovog kruga doprinose kvaliteti opranih tekstilija. Održivost tekstila u pranju na nižim temperaturama se očituje kroz:

- povišen stupanj bjeline,
- smanjenje posivljenja tekstilija,
- smanjen stupanj obezbojavanja obojenih tekstilija.

Tablica 4. Sekundarni učinci, kriteriji

Kriterij	Opis i poteškoće
stupanj bjeline (s/bez UV stimulacije) W_B, W_{GG} (Berger, Ganz Griesser)	**Bjelina** je važan kriterij kvalitete bijelih materijala. Ovisi o sastavu deterdženta, prisutnosti optičkih bjelila i izvoru svjetla. **Posivljenje** može ukazati na redepoziciju obojenih pigmenata i anorganskih soli iz vode. Postoji opasnost da se prljavštine tijekom višestrukih ciklusa vežu na materijal i prouzroče posivljenje. Posivljenje je teško ukloniti, posebno ukoliko su čestice prljavština jako sitne. **Požućenje** je uvjetovano križnom kontaminacijom iona metala u tragovima, prisutnošću bjelila na bazi klora, nepotpunim ispiranjem, taloženjem organskih tvari, npr. sapuna.
prekidna sila, Fp (N)	Tekstil je izložen brojnim fizikalno-kemijskim utjecajima, pri čemu su ključni: sastav kupelji, temperatura, vrijeme i mehanika. Analizom prekidne sile se može ocijeniti utjecaj navedenih čimbenika na mehanička svojstva. Mjeri se prekidna sila uzoraka u mokrom stanju prema [10] i jer je poznato da je prekidna sila pamučne tkanine u mokrom 20 % veća od prekidne sile u suhom prije intenzivnog pranja [11].
talozi/depoziti anorganski, P (%) organski	Odnose se na kvalitetu vode, učinak ispiranja i redepoziciju u pranju. Sadržaj taloga (anorganski i organski) je nakon višestrukih pranja potrebno kontrolirati. Ujedno se na bazi sadržaja pepela (P) kontrolira tvrdoća vode. Količina organske tvari na materijalu ukazuje na prisutnost i količinu tenzida na opranom materijalu, tablica 5. Ta količina na materijalu se kontrolira po protokolu. Oprano rublje koje sadrži anorganske i organske taloge ima sivi ton, neugodan miris, krut opip i potencijal iritacije kože u nošenju [12].
kemijsko oštećenje, s	Kemijsko oštećenje je uvjetovano agresivnim kemikalijama, uglavnom sredstvima za bijeljenje koji izazivaju oštećenje pamučne celuloze i smanjuju stupanj polimerizacije. Ovaj rizik se povećava ukoliko su prisutni ioni teških metala, koji već u tragovima kataliziraju raspad sredstava za bijeljenje, čime povećavaju mogućnost oštećenja u tragovima.

Niže temperature pranja doprinose očuvanju stupnja bjeline, poglavito kroz zadržavanje optičkih bjelila. Visoke temperature pranja skidaju više optičkog bjelila s tekstila.

Na povišenim temperaturama se povećava tendencija posivljenja sintetskih materijala, poglavito tekstilija od PES vlakana [13].

Kontrola ispiranja i neutralizacije je važan kriterij u kontroli kvalitete procesa pranja, pri čemu je važno odrediti pH vrijednost opranog rublja. Ukoliko je rublje nedovoljno isprano i neutralizirano, može doći do iritacija tijekom nošenja. Organske kiseline, octena, mravlja i limunska [14 - 16], najčešće se koriste u posljednjem postupku ispiranja s ciljem podešavanja pH vrijednosti rublja. Preporuka prema sustavu RAL-GZ 992 je da pH opranog rublja treba biti u granicama od 6,5 do 8,3 [9,17]. Nakon višestrukih ciklusa pranja i ispiranja je potrebno provesti analizu prisutnih organskih taloga (tenzidi), čije su granične vrijednosti dane u tablici 5.

Tablica 5. Granične vrijednosti tenzida na tekstilu nakon višestrukih ciklusa pranja i ispiranja [18]

Tenzidi	Koncentracija, μg/g
Anionski	< 200
Neionski	< 200

Sušenje i glačanje kao završne faze obrade opranih tekstilnih proizvoda dodatno utječu na njihov životni ciklus, tablice 6 i 7 [18 - 20].

Tablica 6. Utjecaj pranja i sušenja na parametre kvalitete tekstila [19, 20]

Parametar	50 ciklusa pranja	50 ciklusa pranja i sušenja
Pad čvrstoće (%)	11,5	14,6
Stupanj oštećenja	0,1	0,3
Anorganske inkrustacije (%)	0,1	0,1

Tablica 7. Utjecaj pranja i glačanja na parametre kvalitete tekstila [21]

Parametar	50 ciklusa pranja	50 ciklusa pranja i glačanja		
Tlak pare (bar)	-	4	9	12
Pad čvrstoće (%)	4,7	12,3	19,0	23,8
Stupanj oštećenja	< 0,1	0,1	0,3	0,5

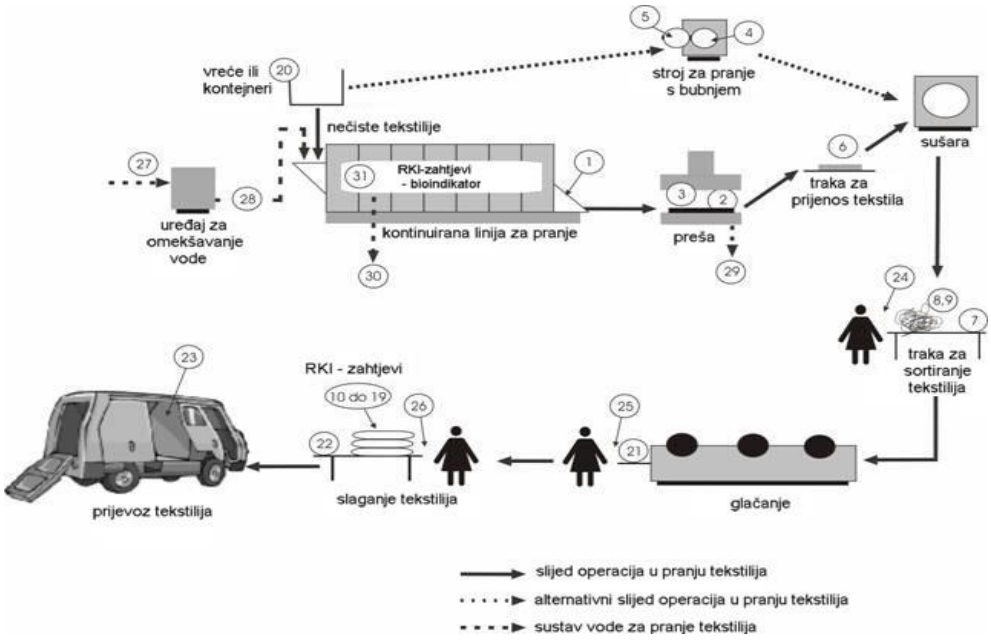
Uvjeti glačanja u profesionalnim uvjetima utječu na promjene svojstava, tablica 7, pri čemu je vidljivo da povećanje tlaka pare utječe na svojstva celuloznih tekstilija, koje se očituje kroz pad čvrstoće i povećan stupanj oštećenja.

Optimalne temperature glačanja doprinose:

- manjim gubicima energije,
- višem stupnju bjeline,
- manjem stupnju sublimacije bojila,
- manjem stupnju oštećenja celuloze,
- produljenju trajnosti vodilica,
- manjem riziku od požara.

Higijenski uvjeti su također važan kriterij posebno za praonice koje peru bolničko rublje i rublje za potrebe prehrambene industrije [9]. Higijenski zahtjevi su vezani uz odredbe RAL-GZ 992/2 i RAL-GZ 992/3 koji dodatno moraju biti zadovoljeni uz navedene kriterije za odredbu RAL-GZ 992/1. Ovaj dio odredbe uključuje dezinfekciju svih radnih prostora, upotrijebljenih strojeva, naprava, vozila, djelatnika, uredbu za rukovanje nečistim bolničkim rubljem te posebne postupke pranja bolničkog rublja. Kontrola stupnja higijene u praonici rublja se provodi na temelju kritičnih kontrolnih točaka (CCP - *Critical Control Points*), slika 2. CCP - je segment gdje se provodi kontrola u svrhu utvrđivanja, smanjivanja ili eliminiranja rizika biokontaminacije. Prema slici 2, CCP uključuju:

- bioindikatore,
- uzorkovanje površina pomoću RODAC pločica,
- tehničku opremu,
- police za slaganje,
- kolica,
- ruke djelatnika,
- mikrobiološku analizu uzoraka vode.



- otisci tehničke opreme (1 - 7)
- otisci vlažnih tekstilija (8 - 9)
- otisci izglačanih i složenih tekstilija (10 - 19)
- otisci skladišnih polica (20 - 23)
- otisci ruku djelatnika (24 - 26)
- analiza uzoraka vode (27 - 29)
- analiza uzoraka vode (30)
- rast bioindikatora nakon pranja tekstilija (31)

Slika 2. Kritične kontrolne točke prema sustavu RAL-GZ 992 [7]

Uzorkovanje površina provodi se pomoću RODAC-agar pločica na 10 nasumce odabranih izglačanih i složenih bolničkih tekstilija, pri čemu: 9 od 10 uzoraka ne smije

sadržavati više od 20 cfu/dm^2, tablica 8. Na njima se ne smije naći nijedan patogeni mikroorganizam. U skladu s preporukama Robert Koch Institute (RKI) za određivanje stupnja dezinfekcije se koriste bioindikatori: *Enterococcus faecium*, ATCC 6057 i *Staphylococcus aureus*, ATCC 6538 (CCP-30 na slici 2). DGHM – Njemačko udruženje za higijenu i mikrobiologiju, po novoj nomenklaturi VAH – Udruženje za primjenjenu higijenu kontrolu provodi putem većeg broja standardnih bioindikatora: *Staphylococcus aureus* ATCC 6538, *Enterococcus faecium* ATCC 6057, *Pseudomonas aeruginosa* ATCC 15442, *Mycobacterium terrae* ATCC 15755 i *Candida albicans* ATCC 10231.

Tablica 8. RAL GZ-992/2 – Granične vrijednosti kontrole higijene [18]

Granične vrijednosti	
• Otisci izglačanih i složenih tekstilija	• 9 od 10 uzoraka ne smije sadržati više od 20 cfu/dm^2
• Bioindikatori	• Moraju biti uništeni
Preporučene vrijednosti	
Vlažne tekstilije	< 30 cfu/dm^2
Voda za pranje	< 100 cfu/ml
Voda nakon mekšanja	< 100 cfu/ml
Voda za pretpranje	< 1000 cfu/ml
Voda nakon ispiranja	< 100 cfu/ml
Orjentacijske vrijednosti	
Tehnička oprema	< 100 cfu/dm^2
Skladištenje/Transport	< 100 cfu/dm^2
Higijena ruku	< 100 cfu/dm^2

4. ZAKLJUČAK

Globalno gledajući, suvremeni uvjeti pranja se usklađuju sa smjernicama održivog razvoja: smanjenje potrošnje energije u procesu, smanjenje gubitka energije, upotrebu manje štetnih kemikalija, primjenu učinkovitih i biorazgradivih deterdženata, smanjenje omjera kupelji, smanjenje opterećenja otpadnih voda, produljenje životnog ciklusa tekstilnih proizvoda i smanjenje udjela otpadnog tekstila. Potencijal mjera iziskuje njihovu popularizaciju i angažiranost dionika:

- EU politike – potrebno je revidirati EU *Ecodesign Regulation* s ciljem preporuke pranja slabo i normalno zaprljanog rublja na niskim temperaturama pranja, koje će osigurati dobre učinke procesa,
- proizvođači strojeva za pranje, deterdženata i trgovci kroz aktivnu i kontinuiranu promidžbu pranja na niskim temperaturama za blago i normalno zaprljano rublje, pri čemu je potrebno optimirati čimbenike Sinner-ovog kruga, posebice formulacije deterdženata aktivne na tim temperaturama,
- ekološke organizacije, društva potrošača, energetske agencije kroz aktivno i kontinuirano informiranje o benefitima pranja na niskim temperaturama,
- akademska zajednica, istraživačke institucije, laboratoriji kroz objave studija o nisko temperaturnom pranju.

5. LITERATURA

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Zahvala

Autor se zahvaljuje Hrvatskoj zakladi za znanost na financiranju projekta 9967 Advanced textile materials by targeted surface modification, ADVANCETEX, za kojeg je ovaj rad tematski vezan.

POVIJESNI I TEHNOLOŠKI RAZVOJ LOKACIJE TE-TO SISAK U SVRHU CJELOVITOG PRISTUPA OKOLIŠU

POWER PLANT SISAK HYSTORICAL AND TECHNOLOGICAL DEVELOPMENT WITH HOLISTIC ENVIRONMENT IMPACT GOALS

Ivana Roksa*, Matija Horžić*

* HEP-Proizvodnja d.o.o., Pogon TE-TO Sisak, Sisak, Hrvatska

autor za korespondenciju: Ivana Roksa, e-mail: ivana.roksa@hep.hr

Stručni članak

SAŽETAK

Svrha rada je prikazati tehnološki i povijesni razvoj postrojenja termoelektrane u Sisku, uz osobiti naglasak na prestanak korištenja teškog loživog ulja kao primarnog goriva i ulaganja u moderne tehnologije i obnovljive izvore energije koji osiguravaju budućnost lokacije kao proizvođača električne i toplinske energije.

Izgradnjom kombi-kogeneracijskog Bloka C u TE-TO Sisak smanjen je utjecaj na okoliš sa lokacije budući je isti zamjena za stare kondenzacijske Blokove A i B. Uz visok stupanj iskorištenja goriva (kombi postrojenje) i povećanu učinkovitost (kogeneracija), smanjile su se i emisije u zrak, jer kao gorivo isključivo koristi prirodni plin te je smanjena potrošnja voda i nastanak otpadnih voda.

U radu je uspoređen utjecaj na okoliš starih Blokova A i B i novog kombi-kogeneracijskog Bloka C s naglaskom na emisije onečišćujućih tvari u zrak te je prikazana analiza utjecaja Bloka C na kvalitetu zraka u Sisku.

***Ključne riječi**: termoelektrana, obnovljivi izvori energije, Blok C, utjecaj na okoliš, emisije u zrak*

ABSTRACT

It is paper intention to evaluate technological and historical development of thermal power plant in Sisak, with specific accent to abandoning of old-fashioned technology solutions and usage of heavy fuel oil as primary energy source, and also the results achieved during investment period which included modern technologies and renewable energy sources which will benefit in continuation in electrical and thermal energy production.

The new combined-cogeneration Unit C in thermal power plant has reduced the environmental impact from the site as it is the substitute for old Units A and B. With high fuel efficiency (combined plant) and increased efficiency (cogeneration), air emissions have also decreased as natural gas is exclusively used as fuel. Water consumption is also reduced as well as wastewater generation.

The paper compares the environmental impact of old Units A and B and the new combined-cogeneration Unit C with an emphasis on emissions of pollutants into the air and analyses the impact of Unit C on air quality in Sisak.

***Keywords**: thermal power plant, renewable energy sources, Unit C, environmental impact, air emissions*

1. UVOD

Odluka o lociranje termoelektrane u Sisku 70-tih godina prošlog stoljeća bila je posljedica jake potrebe za energetskim izvorom u privrednom i industrijskom centru Hrvatske što je Sisak tada nedvojbeno i bio. Glavni razlozi takvoj odluci su blizina Rafinerije nafte (glavni dobavljač goriva), te dovoljne količine rashladne vode iz rijeke Save. Izgradnja prvog bloka, snage 210 MW, počela je 8. srpnja 1967. godine, a isti je uključen u elektroenergetski sustav 3. listopada 1970. godine. Drugi blok, istovjetne snage 210 MW, građen je u vremenu od 5. siječnja 1974. godine do 2. srpnja 1976. godine, kada je pušten u pogon.

U planu je razvoj lokacije predviđao izgradnju i trećeg istovjetnog bloka, ali je nakon naftne krize 80-tih ta ideja konačno i napuštena. Razvoj lokacije pošao je nakon toga u drugom smjeru i počelo je ozbiljno razmatranje izgradnje novog kombi-kogeneracijskog postrojenja na plin.

1.1. Blok C

Nakon domovinskog rata u elektroenergetskom sustavu RH pojavljuje se stalan trend povećanja potrošnje električne energije, uz nedostatak novih proizvodnih kapaciteta. Postojeći blokovi rade s lošom iskoristivosti i koriste loživo ulje kao pogonsko gorivo kojega je sve teže nabaviti na tržištu i ima vrlo visoku cijenu. Postojeća lokacija ima potencijal za izgradnju još jednog bloka istovjetne snage zbog postojanja postrojenja koja će u mnogome umanjiti cijenu izgradnje novoga objekta (rashladna voda, demi voda, rasklopište i sl.). Osim opreme postoji energetska tradicija koja se očituje u postojanju raspoloživih i stručnih kadrova. U periodu od 1996. do 2004. godine prikupljene su informativne ponude s izmijenjenim zahtjevom za izgradnju postrojenja snage 250 MWel i 50 MWt. Nakon obrade ponuda, javlja se nova mogućnost prebijanja klirinškog duga s Rusijom putem isporuke energetske opreme.

Tijekom 2004. i 2005. godine HEP-ov tim za izgradnju Bloka C u Sisku, uz pomoć konzultantske kuće iz Finske vodi opsežne pregovore i pripreme koje dovode do konačne Ruske ponude u srpnju 2005. godine koja uključuje sve vitalne dijelove novog energetskog postrojenja u Sisku. Osim pregovaračkih aktivnosti započeli su i prvi radovi koji su nužni za ostvarenje projekta: izgradnja plinovoda, modernizacija dijela parovoda za grijanje gradskih naselja, projektiranje modernizacije crpne stanice rashladne vode, rekonstrukcija upravne zgrade, projektiranje modernizacije kemijske pripreme vode i sl.

Ruski partner TECHNOPROMEXPORT (TPE) u okviru međudržavnog ugovora o rješenju klirinškog duga RF prema RH, isporučuje tzv. „energetski otok" te ima ugovornu obvezu izraditi kompletan bazni i detaljni projekt, na osnovu kojega domaća projektantska kuća izrađuje podloge za dobivanje potrebnih dozvola za građenje.

Kombi-kogeneracijska elektrana s jednom plinskom turbinom, kotlom na ispušne plinove i jednom parnom turbinom ukupnog instaliranog kapaciteta od 230 MWe i 50 MWt gradi se u slijedećim fazama:

1. Glavni pogonski objekt (GPO),
2. Rasklopno postrojenje 220 kV s energetskim transformatorima,
3. Postrojenje za pripremu plina i diesel agregat,
4. Prometnice i infrastruktura.

U sam proces izvedbe projekta uključen je veći broj domaćih i stranih izvoditelja radova. Konačno, postrojenje Blok C prvi je puta pušteno u pogon u drugoj polovici 2015. godine, te je trenutno u pokusnom radu do izdavanja uporabne dozvole.

1.2. BE-TO Sisak

HEP je početkom listopada 2014. godine objavio međunarodno nadmetanje za nabavu usluga isporuke i izgradnje za projekt BE-TO Sisak te je ugovor potpisao u travnju 2015. godine s konzorcijem koji je sastavljen od tvrtki Đuro Đaković Holding i HoSt B.V. iz Nizozemske. Vrijednost ugovora za BE-TO Sisak je 18,95 mil. EUR.

Izgradnja postrojenja je započela u siječnju 2016. godine, a dovršetak probnog pogona i komercijalna proizvodnja krajem 2017. godine. Proizvedena električna energija se isporučuje u elektroenergetski sustav u svojstvu povlaštenog proizvođača električne energije iz obnovljivih izvora energije dok se toplinska energija isporučuje za centralizirani toplinski sustav odnosno u obliku pare industrijskim potrošačima u okruženju. U okviru investicije u Sisku je izgrađen i magistralni vrelovod koji povezuje toplinsku stanicu u sklopu BE-TO postrojenja s toplinskim stanicama u naseljima Caprag i Brzaj.

Bioelektrana-toplana BE-TO Sisak smještena je pored postojeće Energane koja je u vlasništvu HEP-a. Postrojenje je spojeno na postojeće sustave TE-TO Sisak i osigurava stabilnu isporuku toplinske energije za CTS grada Siska uz zamjenu zastarjelog parnog sustava novim vrelovodnim koji s obzirom na veličinu nove toplinske stanice može biti temelj za daljnju ekspanziju CTS-a u Sisku.

2. ANALIZA RADA PROIZVODNIH POSTROJENJA TE-TO SISAK

2.1. Proizvodna postrojenja u TE-TO Sisak

Proizvodne jedinice na lokaciji TE-TO Sisak su: Blokovi A i B, Blok C, pomoćna kotlovnica (pomoćni kotlovi PK1 i PK2) i parni kotao PK3 (u izgradnji). Nova proizvodna jedinica na udaljenoj lokaciji u poslovnoj zoni je BE-TO Sisak.

Blokovi A i B su kondenzacijski blokovi, svaki instalirane električne snage 210 MW. Oba bloka su gotovo potpuno istovjetne osnovne opreme, istovjetnog tehnološkog procesa, a svaki od blokova sastoji se od dva parna kotla učina 2 x 330 t/h, ložena loživim uljem i/ili prirodnim plinom, jedne trokućišne kondenzacijske parne turbine te generatora. Proizvedena

električna energija odvodi se s lokacije preko rasklopnih postrojenja i dalekovoda na naponskoj razini 110 kV i 220 kV. Zbog dotrajalosti, isti su stavljeni van funkcije, odnosno donesena je odluka o njihovoj potpunoj konzervaciji i najvjerojatnije slijedi proces dekomisije. Loživo ulje je potpuno uklonjeno s lokacije, a spremnici loživog ulja (R-1, R-2 i R-4) su prazni i fizički odvojeni od postrojenja.

Kombi-kogeneracijska elektrana Blok C (KKE Sisak 235 MWel/50 MWt) namijenjena je proizvodnji električne i toplinske energije. Postrojenje čine: glavni pogonski objekt (GPO), rasklopište 220 kV s transformatorima, postrojenje za pripremu plina i diesel agregat, prometnice i infrastruktura. Proizvodni dio Bloka C sastoji se od plinske turbine s generatorom, kotla na ispušne plinove te parne turbine s generatorom. Kombinirani proces je sastavljen od plinsko-turbinskog i parno-turbinskog dijela i procesa u kogeneraciji (proizvodnja električne i toplinske energije).

Pomoćna kotlovnica se sastoji od dva parna kotla kapaciteta 2 x 28 t/h koji služe za proizvodnju pregrijane vodene pare koja se koristi prilikom pokretanja jednog od Blokova A i B ili kao tehnološka para za potrebe pogona i HEP-Toplinarstva d.o.o., Pogon Sisak. Kotlovi kao gorivo koriste prirodni plin.

Trenutno je u izgradnji mali parni kotao kapaciteta 12,5 t/h pare (nazivnog opterećenja 14,29 t/h) zbog minimalne potrebe CTS-a za tehnološkom parom (grijanjem) u ljetnim mjesecima. Kao pogonsko gorivo prvenstveno će koristiti prirodni plin, a plinsko ulje je pričuvno gorivo.

BE-TO Sisak je obnovljivi izvor energije u sklopu kojeg se nalazi nova toplinska stanica koja je ujedno i ishodište vrelovodnog sustava grada Siska. Postrojenje je bazirano na kotlu koji kao gorivo koristi drvnu sječku, te turbinskom postrojenju s mogućnošću proizvodnje 3 MWe i 10,5 MWt. Ovo postrojenje osigurava potrebe za toplinskom energijom tijekom prijelaznog i ljetnog razdoblja.

Osnovni podaci proizvodnih jedinica TE-TO Sisak navedeni su u tablici 1.

Tablica 1. Osnovni podaci proizvodnih jedinica TE-TO Sisak

Proizvodne jedinice TE-TO Sisak	Gorivo	Nazivno opterećenje	Toplinska snaga goriva	Godina puštanja u pogon
Blok A	PP	210 MWe	2 x 274 MW_{tg}	1970.
Blok B	PP	210 MWe	2 x 274 MW_{tg}	1976.
PK1	PP	28 t/h	23 MW_{tg}	1989.
PK2	PP	28 t/h	23 MW_{tg}	1989.
Blok C	PP	235 MWe / 50 MWt	465,7 MW_{tg}	2015.
BE-TO (Blok D)	Drvna sječka	3 MWe / 10,5 MWt	17,4 MW_{tg}	2017.
PK3	PP / ELLU	14,29 t/h	10,86 / 10,84 MW_{tg}	2018.

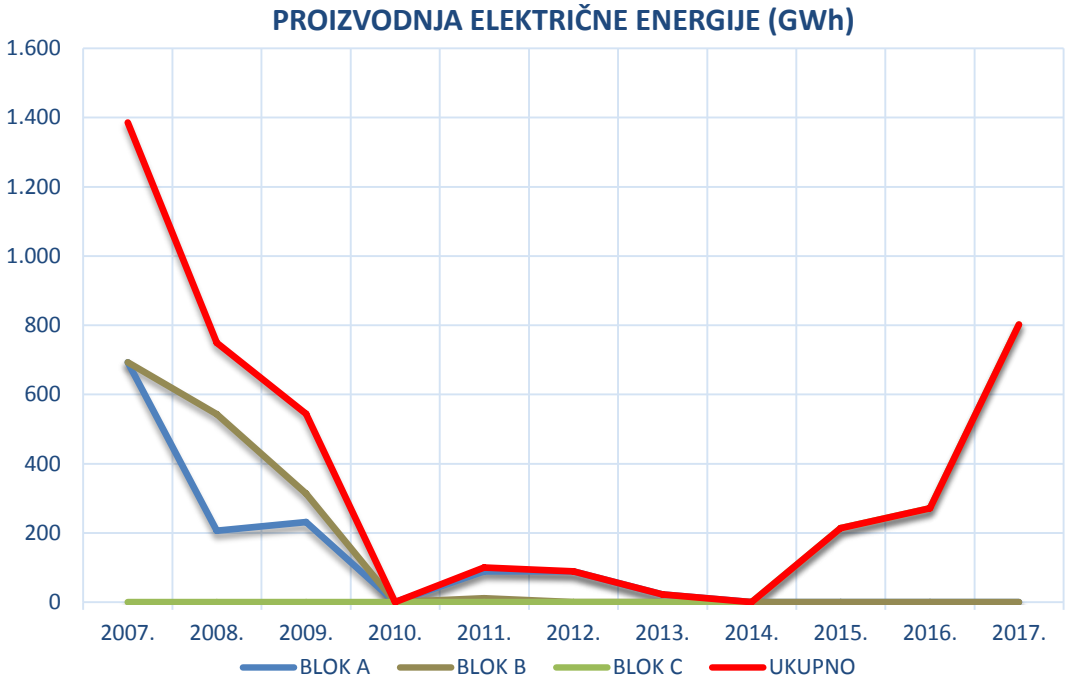
2.2. Analiza rada postrojenja

Dugi niz godina Blokovi A i B bili su uzdanice elektroenergetskog sustava u Republici Hrvatskoj, a ujedno i elektrana najveće instalirane električne snage. Proizvodni rezultati bili su vrlo visoki tijekom domovinskog rata kada nije bilo isporuke električne energije iz NE-Krško. U svom dugogodišnjem radnom vijeku ovi su blokovi proizveli više od 35 TWh električne energije, a za navedenu je proizvodnju utrošeno preko 7.000.000 tona loživog ulja i 1.700.000.000 m^3 zemnog plina. Blok A odradio je gotovo 200.000 radnih sati, a Blok B oko 180.000 sati.

Iz tablice 2 i slike 1 vidljivo je da je angažman Blokova A i B bitno smanjen od 2007. do 2013. godine. Blok A nije bio u pogonu od kolovoza 2013. godine, a Blok B od lipnja 2011. godine. Razlog tome su povoljne hidrološke prilike za rad hidroelektrana, starost postrojenja, samim time i niža učinkovitost proizvodnje električne energije te puštanje u rad kombi-kogeneracijskog Bloka C.

Tablica 2. Podaci o radu, proizvodnji i potrošnji goriva TE-TO Sisak [1]

TE-TO Sisak			godina										
			2007.	2008.	2009.	2010.	2011.	2012.	2013.	2014.	2015.	2016.	2017.
Blok A	potrošnja goriva	LU / t	43.147	44.688	24.270	0	18.928	19.429	6.529	0	0	0	0
		PP / m^3 x 10^3	114.604	13.449	47.728	0	8.289	5.914	1.111	0	0	0	0
	el. energ. prag	MWh	513.133	206.653	231.072	0	88.538	89.113	23.635	0	0	0	0
	rad	h	4.773	1.966	1.951	0	881	876	248	0	0	0	0
Blok B	potrošnja goriva	LU / t	84.249	44.872	31.342	0	2.194	0	0	0	0	0	0
		PP / m^3 x 10^3	133.180	122.888	66.215	0	1.648	0	0	0	0	0	0
	el. energ. prag	MWh	692.713	543.066	313.314	0	11.255	0	0	0	0	0	0
	rad	h	5.948	4.414	2.800	0	135	0	0	0	0	0	0
Blok C	potrošnja goriva	PP / m^3 x 10^3	0	0	0	0	0	0	0	0	50.108	63.763	175.147
	el. energ. prag	MWh	0	0	0	0	0	0	0	0	214.531	277.711	809.389
	rad	h	0	0	0	0	0	0	0	0	1.411	1.931	4.374



Slika 1. Proizvodnja električne energije u TE-TO Sisak

3. UTJECAJ NA OKOLIŠ TE-TO SISAK

S gledišta utjecaja TE-TO Sisak na okoliš, svakako najznačajnije je pitanje emisija onečišćujućih tvari u zrak. Izgaranjem goriva nastaju emisije onečišćujućih tvari u zrak koje ovise o vrsti i kvaliteti goriva (prirodnog plina, loživog ulja). Osim o gorivu, emisije ovise i o opterećenju i režimu rada pojedinih proizvodnih jedinica (kotlova, plinske turbine). Mjere za smanjenje emisija onečišćujućih tvari u zrak odnose se na vrstu i kvalitetu goriva, konstrukcijska rješenja (primarne mjere) i tehnologije za pročišćavanje dimnih plinova (sekundarne mjere). Sukladno Uredbi o graničnim vrijednostima onečišćujućih tvari u zrak iz nepokretnih izvora, NN 87/17 (Uredba o GVE) na kotlovima Blokova A i B i plinskoj turbini Bloka C kontinuirano ili povremeno mjere se slijedeće onečišćujuće tvari:

- ugljikov monoksid (CO),
- oksidi dušika izraženi kao dušikov dioksid (NO_2),
- krute čestice,
- oksidi sumpora izraženi kao SO_2.

Otpadne vode koje nastaju u TE-TO Sisak obrađuju se na uređajima u Postrojenju za obradu otpadnih voda i muljeva. Instalirani uređaji za obradu otpadnih voda su: separatori za obradu zauljenih voda, reaktor za obradu agresivnih otpadnih voda, neutralizacijski bazeni za podešavanje pH vrijednosti kiselih odnosno lužnatih voda, retencijski bazeni te filtar preša kojom se smanjuje volumen otpada. Nakon obrade otpadne vode se internim kanalizacijskim sustavom ispuštaju u rijeku Savu u skladu s Rješenjem o objedinjenim uvjetima zaštite okoliša (Rješenjem o okolišnoj dozvoli). Prije ispusta otpadnih voda u recipijent rijeku Savu, na mjernom oknu II, kontrolira se kvaliteta otpadnih voda od strane ovlaštenog laboratorija.

Tijekom redovitog rada i poslova održavanja pogona TE-TO Sisak nastaju različite vrste opasnog i neopasnog otpada. Otpad se sakuplja odvojeno u predviđene spremnike / skladište otpada koji se nalaze na lokaciji Pogona te predaje ovlaštenim sakupljačima otpada u skladu s važećim zakonskim propisima iz područja gospodarenja otpadom.

TE-TO Sisak od 2007. godine ima uveden i certificiran sustav upravljanja kvalitetom i okolišem sukladno međunarodnim normama ISO 9001 i ISO 14001 za proizvodnju električne i toplinske energije iz tekućih i plinskih goriva, a trenutno se uvodi sustav upravljanja energijom prema ISO 50001.

3.1. Emisije u zrak iz Blokova A i B

Sukladno Uredbi o GVE kotlovi Blokova A i B su veliki uređaji za loženje (svaki 274 MW_{tg}) koji kao gorivo mogu koristiti loživo ulje i/ili prirodni plin. Dimni plinovi nastali izgaranjem goriva ispuštaju se kroz 140 m (Blok A) i 200 m (Blok B) visoke dimnjake. Kod izgaranja prirodnog plina emisije SO_2 su male, dok kod izgaranja loživog ulja emisije SO_2 ovise o kvaliteti goriva. Emisije krutih čestica nastaju izgaranjem tekućeg goriva i ovise o kvaliteti istog. Nastajanje emisija NOx pri primjeni konvencionalnih goriva ovisi o temperaturi plamena tijekom izgaranja, pretičku zraka za izgaranje i količini dušika u gorivu.

Na kotlovima Blokova A i B (2001. godine na Bloku B te 2003. na Bloku A) izvršena je rekonstrukcija sustava izgaranja ugradnjom "lowNOx" plamenika (gorača) i modernizacijom sustava vođenja. Ugrađeni "lowNOx" plamenici s parnim raspršivanjem stare su generacije, što je bilo primjereno tadašnjem stanju. Izvršenom rekonstrukcijom sustava izgaranja poboljšano je sagorijevanje i ostvarena je manja potrošnja goriva uz smanjenje emisija, a omogućeno je i istovremeno korištenje loživog ulja i prirodnog plina. Smanjena je emisija NOx pri korištenju prirodnog plina te emisije CO i krutih čestica pri izgaranju loživog ulja. Ugrađeni "lowNOx" plamenici su zadovoljili garantne uvjete u odnosu na kvalitetu korištenog loživog ulja [2].

Sustav za kontinuirano mjerenje emisija onečišćujućih tvari u zrak (CEM sustav) na kotlovima Blokova A i B ugrađen je 2001. godine (za svaki kotao posebno). Isti je moderniziran početkom 2008. godine ugradnjom novog softvera za praćenje emisije dimnih plinova kako bi se uskladio s novim propisima. Sustav mjeri četiri komponente istovremeno (CO, NO, SO_2, volumni udio kisika (O_2)) putem analizatora te krute čestice. Povremena mjerenja emisija u zrak većinom su se provodila pri korištenju loživog ulja ili mješovitog goriva, jer su kotlovi Blokova A i B rijetko radili isključivo na prirodni plin. Sukladno Uredbi o GVE emisije se izražavaju masenom koncentracijom onečišćujućih tvari pri temperaturi od 273,15 K, tlaku od 101,3 kPa te pri standardnom sadržaju O_2 od 3 %. U tablici 3 i tablici 4 prikazani su rezultati povremenih mjerenja emisija u zrak od strane ovlaštene tvrtke [3, 4].

Tablica 3. Pregled rezultata povremenih mjerenja kotlova Bloka A

Izvor emisije	Onečišćujuće tvari	Mjerna jedinica	Podaci o emisijama					
			god. / gorivo					
			2007./LU	2007./LU	2011./LU	2012./ LU	2012./LU	2013./LU
Kotao A1 Bloka A	CO	mg/m^3	10	8	5	4	3	6
	NO_x	mg/m^3	562	588	510	587	605	590
	krute čestice	mg/m^3	68	79	40	58	46	73
	SO_2	mg/m^3	2.937	2.959	3.276	2.784	2.694	2.892
Kotao A2 Bloka A	CO	mg/m^3	11	10	5	8	7	5
	NO_x	mg/m^3	541	534	531	551	584	627
	krute čestice	mg/m^3	85	62	44	49	58	62
	SO_2	mg/m^3	2.948	2.914	3.232	2.955	3.007	2.805

Tablica 4. Pregled rezultata povremenih mjerenja kotlova Bloka B

Izvor emisije	Onečišćujuće tvari	Mjerna jedinica	Podaci o emisijama				
			god. / gorivo				
			2007./LU	2007./LU	2009./LU	2009./LU	2011./PP/LU
Kotao B1 Bloka B	CO	mg/m^3	9	9	10	8	5
	NO_x	mg/m^3	579	567	651	665	438
	krute čestice	mg/m^3	76	39	55	-	46
	SO_2	mg/m^3	2.908	2.976	3.395	3.517	2.490
Kotao B2 Bloka B	CO	mg/m^3	10	10	11	7	3
	NO_x	mg/m^3	539	498	665	726	357
	krute čestice	mg/m^3	63	33	-	30	-
	SO_2	mg/m^3	2.937	2.950	3.605	3.701	1.907

3.2. Emisije u zrak iz Bloka C

Otpadni plinovi koji nastaju radom postrojenja KKE Sisak 235 MWe/50 MWt - Blok C ispuštaju se putem dimnjaka visine 65 m. Plinska turbina Bloka C (PTA Bloka C) isključivo koristi prirodni plin koji je u pogledu utjecaja na okoliš najpovoljnije fosilno gorivo, a najznačajnija emisija dimnih plinova u atmosferu proizlazi od dušikovih oksida (NOx). U cilju snižavanja emisije dušikovih oksida na postrojenju plinske turbine Bloka C primjenjuju se primarne mjere za redukciju emisije NO_X spojeva, koje se sastoje od tzv. suhih komora izgaranja ("drylowNOx", DLN) [5].

Prema Uredbi o GVE, emisije CO, NOx, volumni udio kisika, emitirani maseni protok i temperatura u otpadnim plinovima iz plinskih turbina ukupne ulazne toplinske snage veće od 100 MW koje kao gorivo koriste prirodni plin, utvrđuje se kontinuiranim mjerenjem. Mjerenje emisije SO_2 i krutih čestica provodi se povremeno (svakih šest mjeseci). Emisije za plinske turbine se izražavaju masenom koncentracijom onečišćujućih tvari pri temperaturi od 273,15 K, tlaku od 101,3 kPa te pri standardnom sadržaju O_2 od 15 %. U tablici 5 prikazani su rezultati povremenih mjerenja emisija u zrak iz PTA Bloka C od strane ovlaštene tvrtke. [6, 7]

Tablica 5. Pregled rezultata povremenih mjerenja plinske turbine Bloka C

Izvor emisije	Onečišćujuće tvari	Mjerna jedinica	Podaci o emisijama			
			Povremena mjerenja (2015. – 2017.)			
Plinska turbina Bloka C	CO	mg/m^3	6,87	11,3*	3,3	2,4
	NO_x	mg/m^3	43,1	34,8*	37,2	37,6
	krute čestice	mg/m^3	0,13	-	0,10	0,21
	SO_2	mg/m^3	3,87	-	1,04	1,63

** opterećenje PTA manje od 70 %*

3.3. Analiza utjecaja Bloka C na kvalitetu zraka

U lipnju 2017. godine izrađena je Analiza utjecaja Bloka C na kvalitetu zraka Grada Siska. Korišteni su podaci iz godine prije početka rada Bloka C (2014. godina), godine u kojoj je Blok C počeo s radom (2015. godina) i prve cijele godine u kojoj je Blok C radio (2016. godina). U analizi se uspoređuju koncentracije (mjerni podaci) onečišćujućih tvari u zraku sa mjernih postaja na području grada Siska (Sisak-1, Sisak-2 i Sisak-3) s proizvedenom energijom u vrijeme rada Bloka C. Prikazane su i obrađene vrijednosti koncentracija NO_2, CO, SO_2 i krutih čestica (PM10) te ruže onečišćenja za obrađene onečišćujuće tvari s mjernih postaja Sisak-1 i Sisak-3 s kojih su bili dostupni meteorološki podaci. Kategorizacija kvalitete zraka u Gradu Sisku oko mjernih postaja Sisak-1, Sisak-2 i Sisak-3 za promatrano razdoblje je prikazana u tablici 6 [8].

Tablica 6. Kategorizacija kvalitete zraka u Gradu Sisku u 2014., 2015. i 2016. godini

Mjerna postaja	Onečišćujuća tvar	Kategorija kvalitete zraka		
		2014.	2015.	2016.
Sisak - 1	CO	I kategorija	I kategorija	I kategorija*
	NO_2	I kategorija	I kategorija	-
	krute čestice (PM10)	II kategorija	II kategorija	II kategorija
	SO_2	I kategorija	I kategorija	I kategorija*
Sisak - 2	CO	I kategorija	-	I kategorija
	NO_2	I kategorija*	I kategorija	I kategorija
	krute čestice (PM10)	II kategorija	II kategorija	II kategorija
	SO_2	-	I kategorija*	I kategorija
Sisak - 3	CO	I kategorija	I kategorija	I kategorija
	NO_2	I kategorija	I kategorija	I kategorija
	krute čestice (PM10)	II kategorija	II kategorija	II kategorija
	SO_2	I kategorija	I kategorija	I kategorija

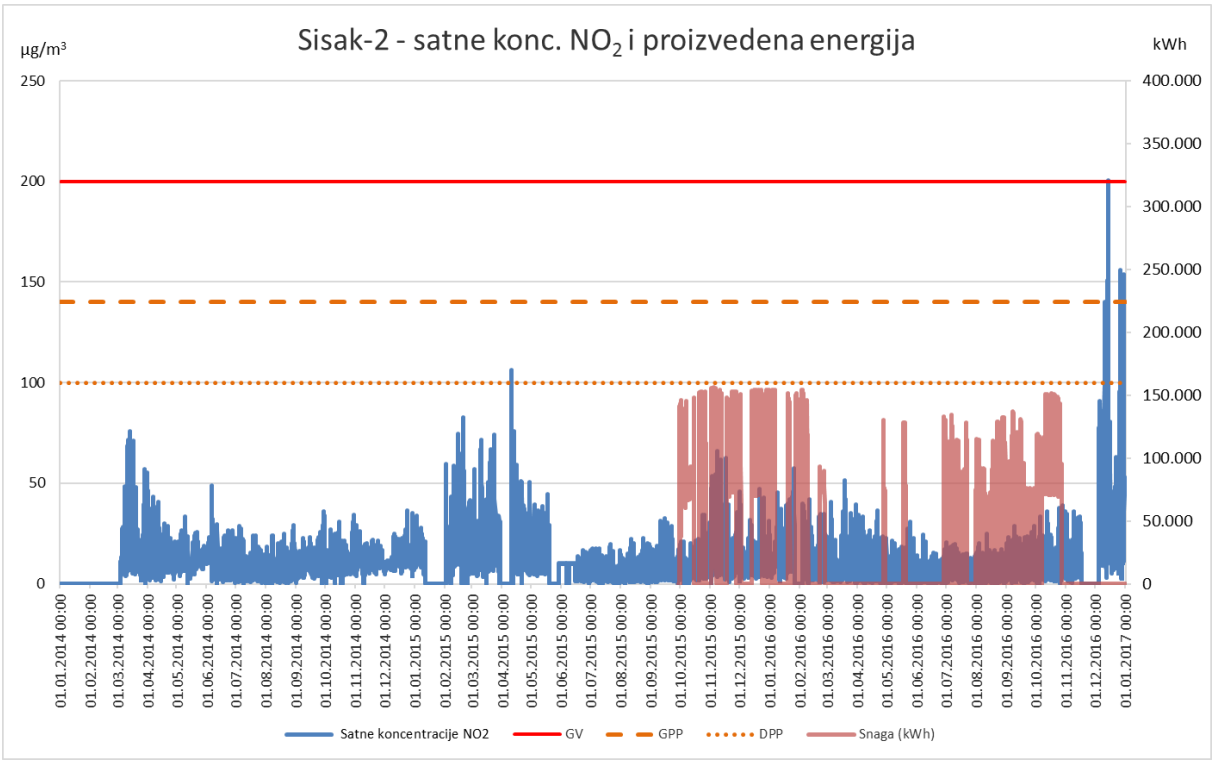
** Uvjetna kategorizacija – obuhvat podataka bio je manji od 90 % i veći od 75 %*
- kategorizacija nije izvršena zbog nedostatnog obuhvata podataka

Iz rezultata analize može se zaključiti da su koncentracije NO_2, CO i SO_2 znatno niže od graničnih vrijednosti, nema onečišćenja zraka s navedenim onečišćujućim tvarima, a zrak je prve kategorije na svim promatranim postajama u cijelom promatranom razdoblju. Koncentracije krutih čestica PM10 povišene su na svim mjernim postajama na području

Grada Siska u cijelom promatranom razdoblju, ali se znatno ne razlikuju od koncentracija na mjernim postajama u drugim gradovima kontinentalne Hrvatske.

Važno je naglasiti da Blok C kao pogonsko gorivo koristi isključivo prirodni plin. Emisija čestica iz plinske turbine je mala, reda veličine koncentraciji čestica u okolišnom zraku, jer se zrak za izgaranje filtrira prije ulaska u kompresor plinske turbine, a izgaranje prirodnog plina ne generira krute čestice te Blok C ne može utjecati na kvalitetu zraka s obzirom na krute čestice. Također ne može utjecati ni na kvalitetu zraka s obzirom na SO_2, budući da je emisija SO_2 proporcionalna sadržaju sumpora u gorivu, a prirodni plin sadrži neznatnu količinu sumpora što rezultira pojavom zanemarivih količina SO_2 pri izgaranju.

U pogledu utjecaja na kvalitetu zraka NOx su glavne plinovite onečišćujuće tvari kada je riječ o uporabi prirodnog plina kao goriva. Satne koncentracije NO_2 u razdoblju od 1.1.2014. do 31.12.2016. prekoračile su satnu graničnu vrijednost (GV) jedan put na mjernoj postaji Sisak-2 (u vrijeme kada Blok C nije radio), a na mjernim postajama Sisak-1 i Sisak-3 nisu prekoračile GV niti jedan put. Srednje godišnje vrijednosti u istom periodu bile su znatno niže od propisane godišnje granične vrijednosti od 40 $\mu g/m^3$ i kretale su se u rasponu od 9,29 do 16,78 $\mu g/m^3$. Također je iz slike 2 vidljivo da koncentracije NO_2 nisu povišene u periodu kada je Blok C u radu nego su na približno istoj razini kao i u vrijeme kada Blok C ne radi [8].



Slika 2. Satne koncentracije NO_2 na mjernoj postaji Sisak-2 u periodu od 1.1.2014. do 31.12.2016. i proizvedena energija u Bloku C od početka rada do 31.12.2016. [8]

4. SMANJENJE UTJECAJA NA OKOLIŠ SA LOKACIJE TE-TO SISAK

Kombi-kogeneracijski Blok C ima sljedeće prednosti:

- veća iskoristivost toplinske energije goriva, posebno u kogeneracijskom režimu,
- manje emisije onečišćujućih plinova u zrak po proizvedenoj energiji,
- manju potrošnju vode,
- usklađenost s najboljim raspoloživim tehnikama (NRT-om) te zahtijevanim graničnih vrijednosti emisija iz Direktive o industrijskim emisijama,
- vrlo visoka raspoloživost i pouzdanost,
- bolja kontrola procesa zbog visokog stupnja automatizacije,
- vrijeme upuštanja u pogon je znatno kraće u usporedbi s klasičnom elektranom.

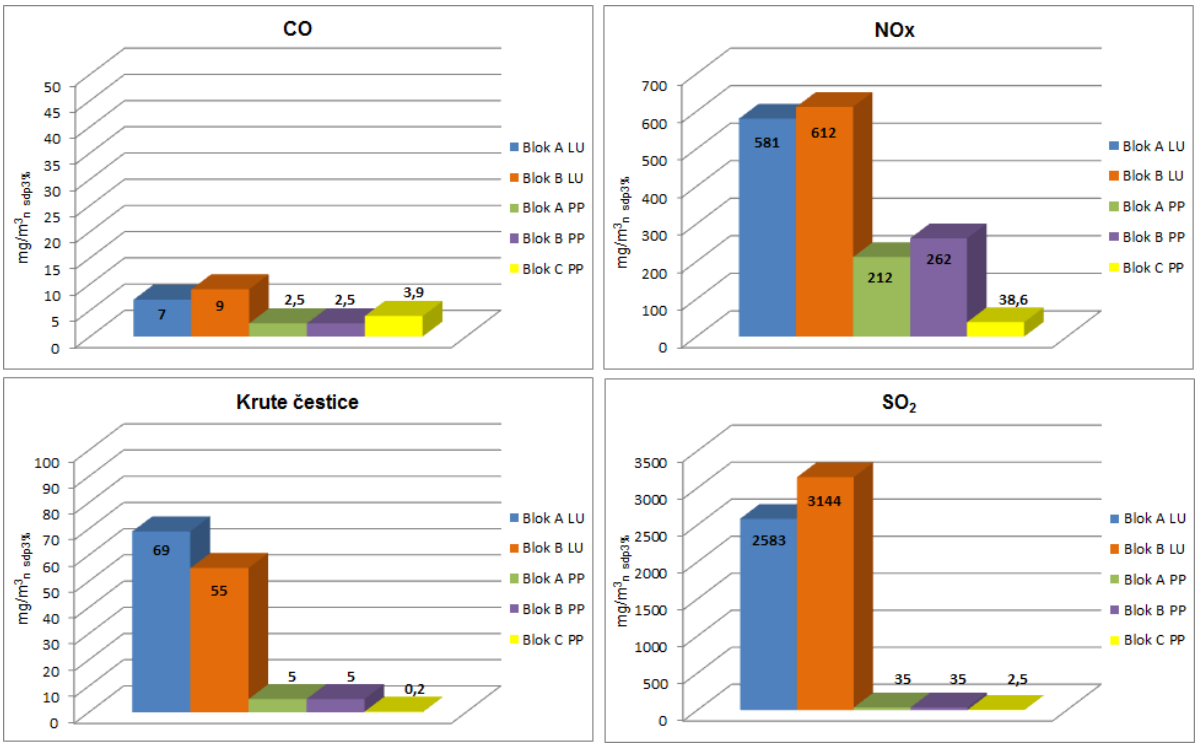
Rad kombi-kogeneracijskog Bloka C neusporedivo je efikasniji u odnosu na stara postrojenja. Efikasnost u kondenzacijskom režimu je za Blok C oko 52 %, dok je kod Blokova A i B ista iznosila oko 34%. To znači da je za proizvodnju istih količina električne i toplinske energije potreban znatno manji unos energije goriva, što ima direktan utjecaj na financijski, ali i okolišni aspekt rada pogona.

Za procjenu raspona emisija u zrak (tablica 7) korišteni su podaci emisijskih koncentracija onečišćujućih tvari u zrak iz sustava za kontinuirano mjerenje emisija Blokova A, B i C (za razdoblje od 2007. do 2017. godine), te rezultati prvih, povremenih i kontrolnih mjerenja emisija onečišćujućih tvari u zrak.

Tablica 7. Raspon emisija u zrak iz Blokova A, B i C u TE-TO Sisak

Izvor emisije	Onečišćujuće tvari	Mjerna jedinica	Podaci o emisijama	
			Gorivo: loživo ulje	Gorivo: prirodni plin
Dimnjak Bloka A Kotao A1 (274MW_{tg}) Kotao A2 (274 MW_{tg})	CO	mg/m^3	3 - 11	0 - 5
	NO_x	mg/m^3	410 - 751	160 - 264
	krute čestice	mg/m^3	26 - 112	< 5
	SO_2	mg/m^3	1.890 - 3.276	< 35
Dimnjak Bloka B Kotao B1 (274MW_{tg}) Kotao B2 (274 MW_{tg})	CO	mg/m^3	7 - 11	0 - 5
	NO_x	mg/m^3	498 - 726	192 - 332
	krute čestice	mg/m^3	30 - 79	< 5
	SO_2	mg/m^3	2.587 - 3.701	< 35
Dimnjak Bloka C Plinska turbina (465,7 MW_{tg})	CO	mg/m^3	-	1,00 - 6,87
	NO_x	mg/m^3	-	34,0 - 43,1
	krute čestice	mg/m^3	-	0,10 - 0,21
	SO_2	mg/m^3	-	1,04 - 3,87

Iz rezultata mjerenja emisija onečišćujućih tvari u zrak vidljivo je da su emisije iz Bloka C puno manje od emisija iz Blokova A i B zbog korištenja prirodnog plina čijim sagorijevanjem nastaju znatno manje emisije onečišćujućih tvari u zrak nego korištenjem tekućih goriva. Emisije CO, SO_2 i čestica su neznatne, a emisije NOx ograničavaju se primjenom "drylowNOx" (DLN) komora izgaranja (slika 3). Znači, radom Bloka C smanjile su se emisije svih onečišćujućih tvari po jedinici proizvedene električne i toplinske energije u odnosu na proizvodnju iz starih Blokova A i B.



Slika 3. Usporedba emisija onečišćujućih tvari u zrak iz Blokova A i B i Bloka C

Uz smanjenje emisija onečišćujućih tvari u zrak smanjila se potrošnja rashladne vode po jedinici proizvedene energije (budući da je snaga parne turbine Bloka C oko 78 MWe (1/3 snage) dok preostalih oko 157 MWe (2/3 snage) daje plinska turbina) te nastaje i manja količina otpadnih voda. Također, izgradnjom novog Pogona za kemijsku pripremu vode u sklopu Bloka C ostvareno je optimalno korištenje kemikalija pri obradi vode automatizacijom procesa, ostvarena je ušteda vode, te je smanjena količina otpadnih voda povratom dijela otpadne vode u proces predobrade. Količina otpadnih voda je smanjena i prestankom korištenja loživog ulja (nema zauljenih otpadnih voda s pretakališta i mazutnog gospodarstva).

5. ZAKLJUČAK

Puštanjem u rad Bloka C koji ima visok stupanj iskorištenja goriva (kombi postrojenje) i povećanu učinkovitost (kogeneracija) i obzirom na donesenu Odluku HEP-a o potpunoj konzervaciji Blokova A i B malo je izgledno da će Blokovi A i B više raditi.

Prestankom rada Blokova A i B i prestankom korištenja loživog ulja na lokaciji smanjene su emisije svih onečišćujućih tvari u zrak te je smanjen ukupan nepovoljan utjecaj na okoliš s lokacije TE-TO Sisak.

Iz rezultata Analize utjecaja Bloka C na kvalitetu zraka Grada Siska vidljivo je da Blok C ne utječe na narušavanje kvalitete zraka s obzirom na NO_2, CO, SO_2 i čestice.

6. LITERATURA

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[2] Zahtjev za utvrđivanje objedinjenih uvjeta zaštite okoliša za postojeće postrojenje TE Sisak, Zagreb, svibanj 2013., APO d.o.o., Ekonerg d.o.o.

[3] Izvještaji povremenih mjerenja emisija u zrak iz kotlova Bloka A, Ekonerg d.o.o., 2007., 2011., 2012., 2013.

[4] Izvještaji povremenih mjerenja emisija u zrak iz kotlova Bloka B, Ekonerg d.o.o., 2007., 2009., 2011.

[5] Kogeneracijska kombi elektrana Sisak 250 MWe/50MWt – blok C; Glavni projekt; Tehničko tehnološko rješenje zaštite okoliša; Z3-E92.01.30-S01.0 - Elektroprojekt d.d. Zagreb, 2009.

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ODRŽIVI RAZVOJ I OKOLIŠ

SUSTAINABLE DEVELOPMENT AND ENVIRONMENT

Željko Rozić*

* Sveučilište u Mostaru, Građevinski fakultet, BiH

autor za korespondenciju: Željko Rozić, e-mail: zeljko.rozic@gf.sum.ba

Pregledni rad

SAŽETAK

Okoliš je sve ono što nas okružuje (Sve ono što nisam ja, A. Einstein) i zbroj svih uvjeta i utjecaja (fizički i biološki čimbenici) koji djeluju na planetu Zemlji. Ljudi doživljavaju okoliš kroz različite aspekte (krajobraz, prirodni resursi, nestajanje šuma, industrijsko onečišćenje) i koriste ga za mnogo različitih namjena (rekreacija, izvor resursa, odlaganje otpada). Okoliš zbog prevelikog utjecaja ljudi gubi sposobnost ispravno obavljati sve te potrebne i željene funkcije, kako za život čovjeka kao pojedinca, tako i za cjelokupno čovječanstvo kao vrstu. Zaštita okoliša i održivi razvoj dva su pojma koja se u svojoj biti tako jako preklapaju i nadopunjuju da se jednostavno mogu objediniti u pojam - okolišno-održivi razvoj. S druge strane ne treba zaboraviti ljudsku kreativnost i sposobnost prilagodbe. Vjerujemo također kako čovječanstvo može imati i gospodarski rast i planet Zemlju na kojemu se stanje okoliša neće dalje pogoršavati no što je to danas slučaj. Okolišno-održivi razvoj je jedina prihvatljiva opcija za čovječanstvo i ona će se sigurno i ostvariti.

***Ključne riječi**: okoliš, održivi razvoj, upravljanje okolišem i okolišno inženjerstvo*

ABSTRACT

The environment is all that surrounds us (All that I'm not, A. Einstein) and the sum of all conditions and influences (physical and biological factors) that work on planet Earth. People experience the environment through different aspects (landscape, natural resources, forest noise, and industrial pollution) and use it for many different uses (recreation, resource, waste disposal). The environment because of the overwhelming influence of people loses the ability to properly perform all the necessary and desired functions, both for the life of man as an individual and for the whole of humanity as a species. Environmental protection and sustainable development are two concepts that overwhelmingly overlap and supplement that they can simply be integrated into the notion - environmentally-sustainable development. On

the other hand, one should not forget human creativity and ability to adapt. We also believe that humanity can also have economic growth and a planet Earth in which the state of the environment will not deteriorate further than it is today. Environmentally-sustainable development is the only acceptable option for mankind and it will certainly be achieved.

***Keywords**: environment, sustainable development, environmental management and environmental engineering*

1. UVOD

Pojavom industrijskog razdoblja, stanje u okolišu poprima neodržive značajke. Sveukupna ljudska aktivnost (industrija, graditeljstvo, promet, intenzivna poljoprivreda, eksploatacija rudnoga blaga,…) remeti prirodnu ravnotežu i uništava pojedine ekosustave, pa štete izazvane u biosferi prijete zaustavljanjem održivog razvoja.

Veoma bitni problemi u okolišu nastali pod utjecajem čovjeka su:

1. Onečišćenje tla, podzemnih voda, površinskih voda, mora i zraka,
2. Uništavanje šuma, povećanje pustinjskih predjela, erozija tla,
3. Promjena klime (učinak staklenika),
4. Smanjivanje ozonskog sloja u atmosferi,
5. Smanjenje biološke raznolikosti zbog izumiranja vrsta.

Sva živa bića pokušavaju sve raspoložive rezerve energije iskoristiti kako bi se razmnožavali i širili, što se može opisati kao - *normalno prirodno stanje*. Kolonija bakterija na hranjivoj podlozi razmnožava se neprestano sve dok ne iskoriste svu raspoloživu hranu i tek nakon toga dolazi do izumiranja te kolonije.

Svako živo biće mijenja svoj okoliš, a neka to čine u osobito značajnoj mjeri. Uzmimo primjer jedne livade koja je ostavljena bez ikakvog utjecaja čovjeka. Ona će spontano prerasti u šumu jer će se na njoj naseliti biljke, rasti i razvijati se. Koralji stvaraju minijaturne kućice veličine nekoliko milimetara, ali se svojim međusobnim vezivanjem adiraju u kilometrima dugačke koraljne sprudove. Dabar gradi brane koje sasvim promijene okolni krajobraz.

Općenito gledano, sve biljke i životinje koriste samo ono što već postoji u prirodi. I priroda funkcionira na taj način da niti jedna vrsta na dugo razdoblje previše ne dominira. Ona to čini nestašicom hrane, pojavom prirodnih neprijatelja i uzročnika bolesti, a na kraju i različitim vrstama katastrofa. Ovo možemo potkrijepiti primjerom udara meteora na Zemlju ili erupcijom jednoga supervulkana. Takvi događaji su se u prošlosti događali i veoma značajno utjecali na život na Zemlji. Sličan slučajni utjecaj može se sasvim realno očekivati i u skoroj ili daljoj budućnosti [1].

2. ŠTETNI UTJECAJI NA TLO, VODU I ZRAK

U nastavku ovog poglavlja su ukratko prikazani dominantni štetni utjecaji čovjeka na sve sastavnice okoliša. To se odnosi na štetne utjecaje na tlo, na vodu i na zrak.

2.1. Štetni utjecaji na tlo i posljedice – veliki primjeri iz cijelog svijeta

Pedosfera je nastala kao rezultat djelovanja atmosfere, hidrosfere i biosfere na površini litosfere. Pedosfera je životni prostor za biljke, životinje i ljude.

Planetarna degradacija pedosfere (slika 1) obuhvaća oko 2 milijarde hektara: Azija 39 %, Afrika 25 %, Južna Amerika 12 %, Europa 11 %, Sjeverna Amerika 8 %, Australija i Oceanija 5 % . Sve to čini oko15 % kopna koje pokazuje znakove degradacije. Glavni uzroci su: krčenje šuma, pretjerana ispaša, loše ratarstvo. Globalno gledajući, oko 300 milijuna hektara tla je jako degradirano. Godišnje se gubi 5 - 6 milijuna hektara tla u poljoprivredi zbog jake degradacije [2].

Izumi i otkrića donijeli su niz promjena u organizaciji društva i poljoprivredi. Uvodi se mehanizacija u obradu tla i ono se obogaćuje mineralnim gnojivom. Proizvodnost u industriji prestigla je proizvodnost u poljoprivredi, a porast brojnosti stanovništva doveo je do napuštanja sela i odlaska u gradove. Sve je to prouzročilo promjene u kulturnom krajoliku te se prirodni kulturni krajolik pretvorio u umjetni kulturni krajolik. Razvila se visokoracionalna radno-ekstenzivna poljoprivreda. Uvođenjem mineralnih gnojiva u razdoblju od 1880.-1980., učetverostručio se prosječni prinos ozime pšenice, raži i krumpira. Istodobno, udjel poljoprivrednog stanovništva u Europi pao je, s udjela od oko 40 %, na manje od 5 % [3].

Prve moderne tehnologije razvijene u cilju zaštite okoliša nastaju u drugoj polovici 19. stoljeća kao prisilni odgovor na razne epidemije (epidemiju kolere). Osobito u području pročišćavanja otpadnih voda i odlaganja otpada, razvijaju se tehnike s ciljem ograničenja onečišćenja voda i tla. Na temelju ekonomskih zakonitosti i eksponencijalnog rasta ogromnih količina raznovrsnog proizvodnog otpada, dolazi do neprekidnog poboljšavanja proizvodnih procesa u smjeru rasta produktivnosti i boljeg iskorištavanja prirodnih resursa. Kao upečatljivi primjeri mogu se uzeti podaci iz tablice 1.

Tablica 1. Potrošnja ugljena za dobivanje željeza (prilagođeno Henseling, 1992) [4]

Godina	Potrošnja ugljena za dobivanje jedne tone sirovog željeza, (kg)
1830.	5.000
1840.	2.500
1900.	1.000
1988.	500 (koks)

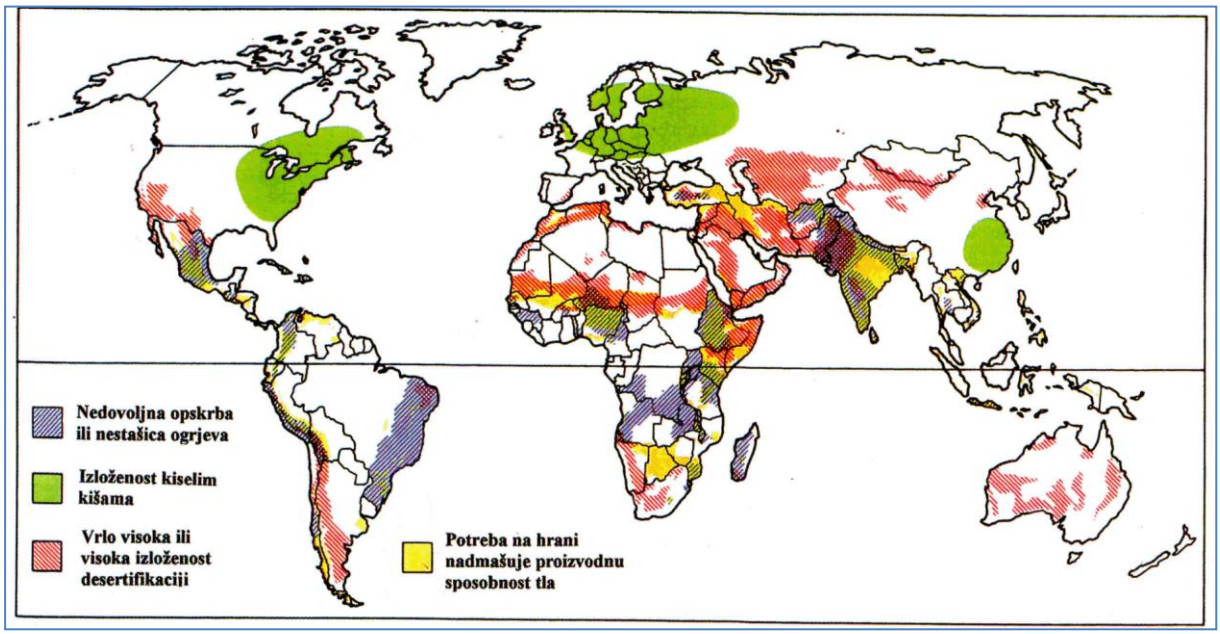
Kao što se iz tablice 1 jasno vidi, potrošnja ugljena potrebnog za dobivanje jedne tone sirovog željeza, smanjila se 10 puta u razdoblju od oko 160 godina! Nažalost, ukupno onečišćenje okoliša je, s vremenom, povećavano jer je, povećanom proizvodnjom, kompenzirano opisano povećanje produktivnosti.

Znači, ipak dolazi do povećanja onečišćenja u apsolutnim brojkama, bez obzira na ogroman porast produktivnosti, odnosno kvalitetnijeg korištenja prirodnih resursa (u ovome prikazanom primjeru ugljena).

Onečišćenje iz poljoprivredne i industrijske djelatnosti prelazilo je povremeno i mjestimično kritične vrijednosti za bilje, životinje i ljude. Opterećenje okoliša raslo je usporedo s porastom broja stanovnika i intenziteta ljudske djelatnosti.

Uvođenje mehanizacije u poljoprivrednu proizvodnju donijelo je i nove utjecaje na tlo. Vožnja strojevima zbija tlo do dubine od 60 cm. Zbijanjem se smanjuje poroznost tla, homogenizira se gornji sloj i razbija struktura tla, čime se smanjuje stabilnost i prozračivanje. U prirodnom tlu se u gornjih 10 cm tla, nalazi 70 - 90 % organske tvari, u preoranom tlu u

tom sloju preostaje < 20 % , a u dubini 15 – 25 cm, nalazi se 60 % ukupne organske tvari u tlu [5].



Slika 1. Degradacija tla na svijetu kao posljedica ljudskih djelatnosti; područja gdje nastaju pustinje i polupustinje, područja u kojima se prekomjerno iskorištava ogrjevno drvo, područja gdje se tla zakiseljuju zbog zagađenja zraka i područja u kojima se prekomjerno iskorištavaju tla poljodjelstvom [6]

U suvremenoj poljoprivrednoj proizvodnji u tlo se unose gnojiva, kao i sredstva za zaštitu bilja. Mineralnim gnojivima unose se u tlo soli kalija, nitrati i fosfati. To dugoročno ne smanjuje plodnost tla, ali uklanja stvaratelje humusa koji su osnova za postojanje edafona. Biljke iskoriste manje od pola upotrijebljene količine mineralnih gnojiva, pa se ostatak s procjednom vodom ispire u podzemnu vodu. Naročito intenzivno ispiru se nitrati koji se slabo ili nikako ne vežu za čestice tla.

Neka fosfatna gnojiva sadržavaju i znatne količine kadmija (2-3 grama Cd na 70 kg/ha). Organska gnojiva poput stajskog gnoja i gnojnice, također ne djeluju uvijek povoljno. Gnoj svinja često sadrži veće količine bakra, a goveđe gnojivo djeluje na gujavice otrovno. Stajsko gnojivo može pogodovati i razvoju gljivičnih bolesti biljaka [5].

2.2. Štetni utjecaji na vodu i posljedice

Radi ilustracije prikazano je samo par primjera najznačajnijih nesreća u kojima je došlo do izlijevanja većih količina nafte u more (slike 2 i 3).



Slika 2. (11. travanj 1991.): Tanker *Haven* koji je plovio pod zastavom Cipra, eksplodirao je ispred obale sjeverne Italije. Dva dana kasnije, brod natovaren s 144.000 tona nafte potonuo je ispred luke Genove. Poginulo je šest ljudi, najmanje 50.000 tona nafte dospijeva u more [7]



Slika 3. (21. travanj 2010.): Potonuće naftne platforme Deepwater Horizon u Meksičkom zaljevu, spada u jednu od najtežih katastrofa izazvanih izlijevanjem nafte u povijesti. Procjene se kreću oko 670.000 tona istekle nafte [7]

2.3. Katastrofe čiji je uzrok čovjek, s najvećim djelovanjem na zagađenje zraka

Katastrofe uzrokovane djelatnošću čovjeka, a koje izazivaju katastrofalno zagađenje zraka, možemo podijeliti na dvije velike skupine katastrofa i to one prouzročene:

1. Kemijskim čimbenicima,
2. Radioaktivnim tvarima.

Kemijske tvari pri proizvodnji, skladištenju i transportu mogu izazvati niz neželjenih događaja koji mogu kulminirati katastrofom. Kemijske tvari mogu se širiti zrakom, hranom, vodom – inhalacijom, ingestijom ili preko kože. Nekontrolirano oslobađanje opasnih kemijskih tvari, može ugroziti zdravlje i život velikog broja ljudi, životinja i biljaka, okoliš (zrak, voda, tlo).

Elementi koji određuju težinu kemijske katastrofe su:

1. Opseg kontaminiranog područja,
2. Veličina izloženosti populacije,
3. Količina kemijske tvari,
4. Toksičnost kemijske tvari,
5. Meteorološki uvjeti:
   - vjetrovi
   - atmosferski tlak
   - vlažnost zraka.

Razmjeri učinaka nesreće u najvećoj mjeri ovise o neposrednom odgovoru na neželjeni događaj na samome mjestu događaja.

Najčešći uzroci kemijskih katastrofa:

1. Nepridržavanje propisanih procedura,
2. Propusti u planiranju (izbor lokacije),
3. Nezadovoljavajuća procedura testiranja opreme,
4. Nepostojanje potpune analize procesa/nerazumijevanje procesa,
5. Sukob između proizvodnje i sigurnosti,
6. Neodgovarajuća inspekcija/nepridržavanje preporuka,
7. Loš sustav upozoravanja.

U 80-100% poznatih i analiziranih slučaja nesreće uzrok je bio ljudska pogreška!!!

2.4. Nuklearne katastrofe

Od svih ekoloških katastrofa koji su rezultat ljudskih aktivnosti, nuklearne katastrofe su one s najvećim štetnim potencijalom. Radijacija oslobođena pri takvim nesrećama predstavlja značajne akutne i kronične rizike neposrednom okolišu, a kronične rizike širem zemljopisnom području. Radioaktivno onečišćenje koje se obično dugo zadržava u zraku, s obzirom na vrijeme poluraspada, uzrokuje kontaminaciju koja će trajati stotinama godina. Među radioaktivnim elementima značajni su stroncij-90 i cezij-137, s obzirom na dugotrajno vrijeme poluraspada i jod-131, kratkog vremena poluraspada od osam dana, ali njegova prisutnost uzrokuje rak štitnjače. Najpoznatije nesreće ovog tipa dogodile su se u Černobilu, 1986. i Fukushimi, 2011. godine.

Jasno je da se svi prethodno navedeni utjecaji na okoliš adiraju i u svojoj sinergiji stvaraju dodatne promjene u okolišu koje je vrlo teško unaprijed procijeniti.

Ugrožene su sve sastavnice okoliša: tlo, voda i zrak.

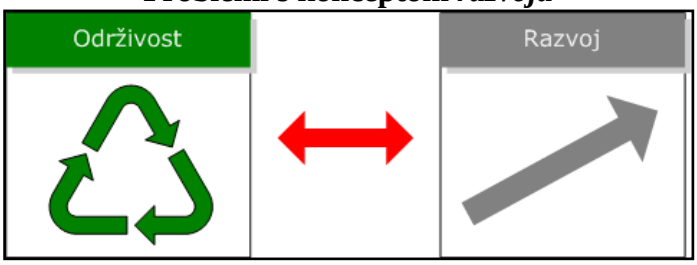
3. OKOLIŠNO-ODRŽIVI RAZVOJ

3.1. Neke definicije održivog razvoja

- *Održivi razvoj je takav razvoj koji zadovoljava potrebe današnjice bez ugrožavanja sposobnosti budućih naraštaja u zadovoljavanju njihovih potreba.*
- *Održivi razvoj je proces promjena u kojemu su iskorištavanje resursa, smjer ulaganja, orijentacija tehničkog razvoja i institucionalne promjene, u međusobnom skladu i omogućavaju ispunjavanje potreba i očekivanja sadašnjih i budućih naraštaja.*
  Brundtland, Svjetska komisija o okolišu i razvoju 1987., Izvještaj *Naša zajednička budućnost*
- *Razvoj u okvirima prihvatnog kapaciteta ekosustava Zemlje.*
  IUCN - Međunarodna unija za očuvanje prirode
- *Poboljšanje kvalitete života, ali u okvirima prihvatnog kapaciteta ekosustava.*
  Claude Martin, WWF
  Održavanje ravnoteže između ljudske potrebe za poboljšanjem kvalitete življenja i blagostanja s jedne strane te očuvanja prirodnih izvora i ekosustava, o kojima ovise budući naraštaji. The Global Development Research Center

Održivost da - održivi razvoj ne, tako glasi kritika upućena stalnoj kombinaciji dva koncepta - **održivosti** i **razvoja.** Razlog kritike su predrasude prema konceptu razvoja. Želja da se razvoj kombinira s održivošću, predstavlja paradoks. Dok održivost pripada ekološkom svjetonazoru, pojam razvoja potječe iz već davno prevladanog mehaničkog svjetonazora (slika 4).

Problemi s konceptom *razvoja*



Slika 4. Kolizija pojmova *održivost* i *razvoj* [8]

No, ipak, kako kaže Wolfgang Sachs, znanstvenik i istraživač Instituta za pitanja klime, okoliša i energije iz Wuppertala, *spajanjem pojmova 'održiv' i 'razvoj', prešlo se na teren jezične ambivalentnosti. Novi koncept je suptilno pomaknuo geometrijsko mjesto održivosti iz prirode u razvoj, dok se ranije pojam „održivo“ vezao samo za alternativne izvore energije, sada se taj pojam veže za razvoj. Ovakvim pomicanjem promijenilo se i shvaćanje, značenje održivosti se pomaknulo od zaštite prirode na zaštitu razvoja. S obzirom na činjenicu da je razvoj koncepcijski postao samo prazna ljuštura, ono što je trebalo označavati održivost tog razvoja bilo je nejasno i kontroverzno. Zbog toga su tijekom posljednjih godina politički akteri svake vrste, uključujući i zagovornike ekonomskog porasta, bili u stanju svoje namjere ogrnuti plaštom na kojem se nalazi pojam „održivi razvoj“. Pojam je postao samoreferentan, što najbolje pokazuje jedna definicija Svjetske banke: „Što je održivo? Održivi razvoj je razvoj koji ostaje.“* [8, 9].

3.2. Održivi razvoj – isti uvjeti života za sadašnje i buduće naraštaje

Prije četrdesetak godina počelo se uviđati kako je nemoguće imati zdravo društvo i kvalitetno gospodarstvo u svijetu u kojemu postoji toliko siromaštva i uništavanja okoliša. Gospodarski razvoj se ne može zaustaviti, no valja mu promijeniti smjer, kako bi postao manje poguban po okoliš i društveni razvoj. Pretvaranje tih spoznaja u djelo i prijelaz na održive oblike razvoja i načina života, izazov je današnjem dobu.

Koncept održivog razvoja podrazumijeva proces prema postizanju ravnoteže između gospodarskih, socijalnih i ekoloških zahtjeva kako bi se osiguralo *zadovoljavanje potreba sadašnjeg naraštaja bez ugrožavanja mogućnosti budućih naraštaja zadovoljiti svoje potrebe*. Od 1987. godine, kada je, na ovaj način, definiran u Izvještaju Svjetske komisije za okoliš i razvoj, kojom je predsjedavala Gro Harlem Brundtland, pa do današnjeg dana, održivi razvoj je postao jedan od ključnih elemenata u formuliranju i provođenju razvojnih politika u svijetu. Operacionalizacija koncepta i njegova primjena u praksi rezultat su, kako teorijskih, tako i političkih težnji usmjerenih ka osiguravanju dugoročnog razvoja ljudskog društva i očuvanju okoliša. U tom procesu, ključni događaji i pokretačka snaga bili su svjetski skupovi na vrhu u Riju i Johanesburgu te usvajanje Milenijske deklaracije UN-a, u rujnu 2000. Od razine UN-a (i Komisije UN-a za održivi razvoj) i brojnih multilateralnih i međunarodnih institucija i organizacija, preko vlada pojedinih zemalja i EU-a, pa sve do civilnog sektora i lokalne samouprave, provođenje koncepta održivog razvoja je pitanje na kome rade milijuni ljudi diljem svijeta [1].

3.3. Ciljevi održivog razvoja

Održivi razvoj je okvir za oblikovanje politika i strategija kontinuiranog gospodarskog i socijalnog napretka, bez štete za okoliš i prirodne izvore bitne za ljudske djelatnosti u budućnosti. On se oslanja na ambicioznu ideju prema kojoj razvoj ne smije ugrožavati budućnost dolazećih naraštaja trošenjem neobnovljivih izvora i dugoročnim devastiranjem i zagađivanjem okoliša.

Osnovni je cilj osigurati održivo korištenje prirodnih izvora na nacionalnoj i međunarodnoj razini.

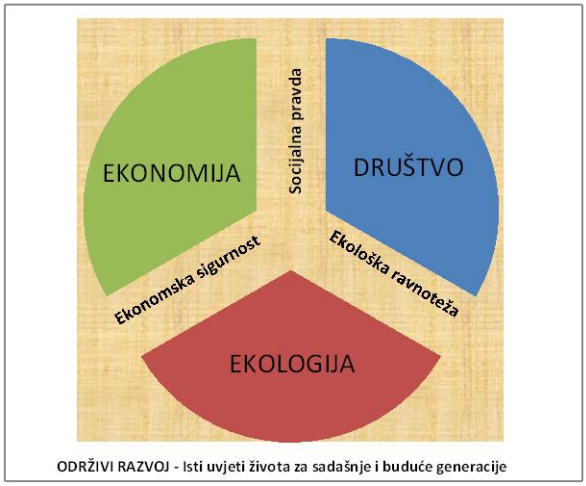
S tako postavljenim ciljem, zaštita okoliša postaje znatno šira od tradicionalnog gledanja, prema kojem se dominantno bavila zaštitom ljudskog zdravlja i očuvanjem cjelovitosti ekoloških sustava. U konceptu održivog razvoja danas nalaze ishodište svi moderni gospodarski1 i društveni trendovi jer su štete okolišu štete sveukupnom društvu, i obrnuto, djelovanje u zaštiti okoliša donosi korist u obliku gospodarskog rasta, zapošljavanja i konkurentnosti.

Globalno gospodarstvo mora odgovarati ljudskim potrebama i opravdanim htijenjima, ali razvoj treba smjestiti u ekološke granice planeta. Ekologija, društvo i ekonomija su tri osnove na kojima se temelji razmišljanje o održivom razvoju.

Bitno je naglasiti potrebu da se **ekonomski ciljevi** (produktivnost, konkurentnost, gospodarski rast), optimiziraju uz uvažavanje **okolišnih ciljeva** (integritet ekosustava, globalna pitanja, biološka raznolikost) i **socijalnih zahtjeva** (humanizacija rada, motiviranost, zajedničko upravljanje, socijalna pokretljivost, društvena skrb, kulturni identitet) koji su u stalnoj interakciji.

Ukratko se to može ovako predstaviti (slika 5):

1. Socijalni ciljevi: pravednost, smanjenje siromaštva,
2. Ekonomski ciljevi: rast i uspjeh,
3. Okolišni ciljevi: upravljanje prirodnim dobrima.

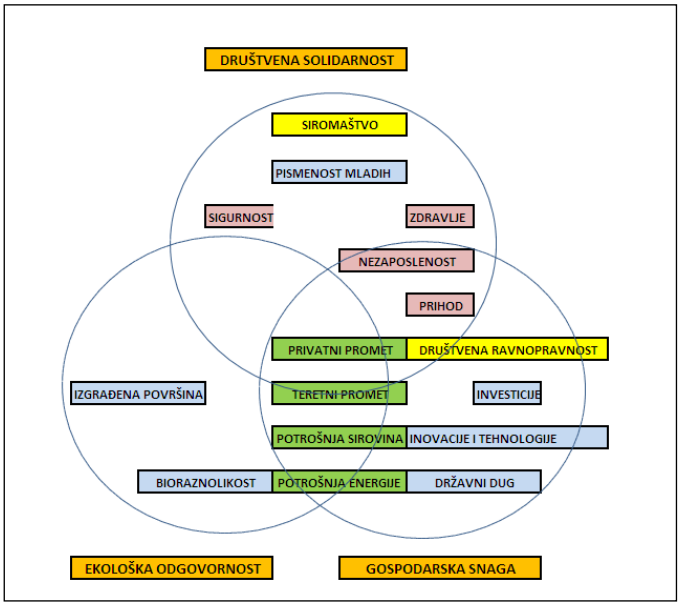


Slika 5. Održivi razvoj – isti uvjeti za sadašnje i buduće naraštaje [10]

3.4. Ključni pokazatelji održivog razvoja

Do sada je poznato jako mnogo podjela i ocjena o važnosti pojedinih vrsta pokazatelja održivog razvoja po kojima bi ovaj razvoj bio mjerljiv u pojedinim društvima, a i globalno usporediv. Ovdje dajemo prikaz pokazatelja koje švicarski znanstvenici smatraju ključnim pokazateljima održivog razvoja (slika 6). Smatraju najvažnijima sljedeće vrste pokazatelja [10]:

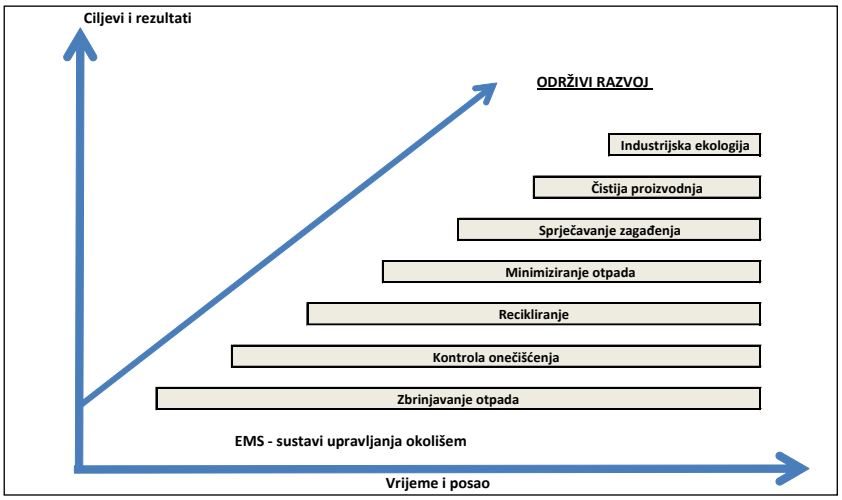
1. Siromaštvo i društvena ravnopravnost,
2. Sigurnost, zdravlje, nezaposlenost, prihod,
3. Pismenost mladih, investicije, inovacije i tehnologije, državni dug, izgrađena površina, bioraznolikost,
4. Privatni promet, teretni promet, potrošnja sirovina, potrošnja energije.



Slika 6. Pregled ključnih pokazatelja održivog razvoja poredanih prema tri ključna cilja: društvenoj solidarnosti, ekološkoj odgovornosti i gospodarskoj (ekonomskoj) snazi [10]

3.5. Stube uspjeha održivog razvoja - sustavi upravljanja okolišem

Održivi razvoj je put ili cilj koji se ostvaruje sustavima upravljanja okolišem (EMS - *Environmental Management System*). EMS se postiže kontrolom aspekata okoliša koji uzrokuju ili mogu uzrokovati štetne utjecaje po okoliš, a uključuje sedam koraka na *stubama* održivog razvoja (slika 7).



Slika 7. Sedam koraka na *stubama* održivog razvoja [11]

4. OKOLIŠNA KUZNETSOVA KRIVULJA I ODRŽIVI RAZVOJ

Zar nisu siromaštvo i glad najveći onečišćivači okoliša? Mi, ni u kojem slučaju, ne želimo i dalje negativno utjecati na okoliš, ali ni u jednom trenutku ne smijemo zaboraviti strašno siromaštvo i bijedu kojim je pogođen veliki broj ljudi. Stanje okoliša se ne može poboljšati ukoliko je alternativa još veće siromaštvo i bijeda. [12].
Indira Ghandi

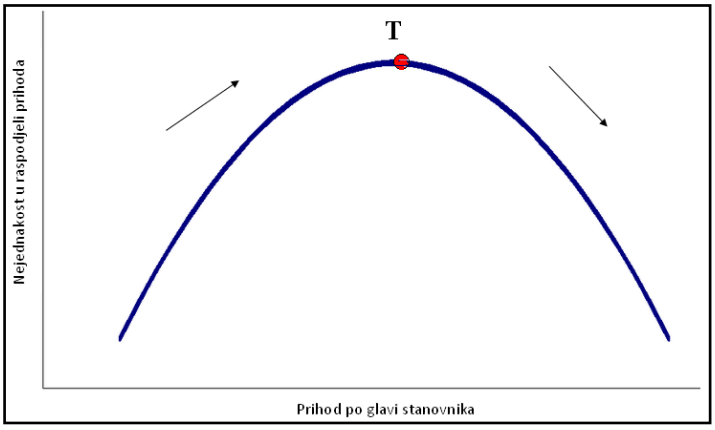
4.1. Osnovna Kuznetsova krivulja

Bez obzira na mnoge nedostatke, ipak se bruto društveni proizvod (BDP, GDP), zbroj svih proizvedenih dobara i usluga u jednom društvu, pokazao kao veličina na koju se možemo osloniti pri raznim prognozama i izračunima. Ne treba smetnuti s uma ni općepoznatu činjenicu kako skoro sva migratorna kretanja idu iz pravca zemalja s manjim BDP-om, prema onima u kojima je BDP veći.

Očekivani ljudski vijek, stupanj pismenosti, kao i unutarnja sigurnost jedne države – sve se to može dovesti u izravnu korelaciju s BDP-om. Što je BDP veći, veći su i svi ovi nabrojani čimbenici. Dobitnik Nobelaove nagrade za ekonomiju Simon Smith Kuznets je, sredinom dvadesetoga stoljeća, istraživao kako BDP djeluje na ukupnu raspodjelu prihoda jednog društva [13].

Kuznetsova krivulja je, u biti, grafičko predstavljanje empirijskog odnosa između gospodarskog rasta i nejednakosti između raspodjele prihoda (slika 8). Svojim oblikom ova krivulja upućuje na to kako gospodarska nejednakost za vrijeme rasta i razvoja jedne zemlje prvo raste do određene razine, a kasnije opada, odnosno dolazi do smanjenja te nejednakosti.

Objašnjenje toga procesa koje je u svome radu ponudio Kuznets [14], temelji se na procesu razvoja društva. Općenito gledajući, svako ljudsko društvo, svaka društvena zajednica koju tvore ljudi, razvija se u fazama - od izrazito poljoprivredne pa do industrijske faze. Na početku ovoga ciklusa razvoja skoro svi uposleni rade u poljoprivredi i za svoj rad su otprilike isto plaćeni. Znači, globalno gledajući, društvena raspodjela dohotka je otprilike jednaka u cijelom društvu.



Slika 8. Kuznetsova krivulja [13]

Kada društvo lagano počinje ići u smjeru industrijalizacije, onda dolazi do fenomena da radnici u velikom broju napuštaju poljoprivredu i odlaze u gradove u kojima se razvija industrija. U gradovima dobivaju različite plaće ovisno o tomu gdje rade, za koga rade, koliko su spretni u radu. To sasvim poremeti globalne odnose plaća u društvu, pa one više nisu niti približno jednake. Prolaskom vremena, sve više ljudi radi u tvornicama pa se tako plaće stabiliziraju ili čak i počinju padati. Istodobno, nedostaje radne snage u poljoprivredi pa u tome sektoru dolazi do blagog rasta prihoda uposlenika. Tako se, u konačnici, plaće ponovno izjednačavaju u okviru cijeloga društva.

Gledajući taj proces u vremenu, on se može grafički predstaviti kao okrenuto slovo *U*. Općenito govoreći, postoji jedna prijelomna točka ***T*** do koje raste nejednakost u raspodjeli prihoda društva, a nakon nje dolazi do izjednačavanja prihoda u cijelome društvu (državi).

4.2. Okolišna Kuznetsova krivulja – EKC

Naslanjajući se na ovu Kuznetsovu teoriju, na području okolišne ekonomije razvija se hipoteza ***o povezanosti prihoda po glavi stanovnika jedne zemlje i stupnja onečišćenja okoliša u toj zemlji*** (EKC – *Environmental Kuznets Curve).*

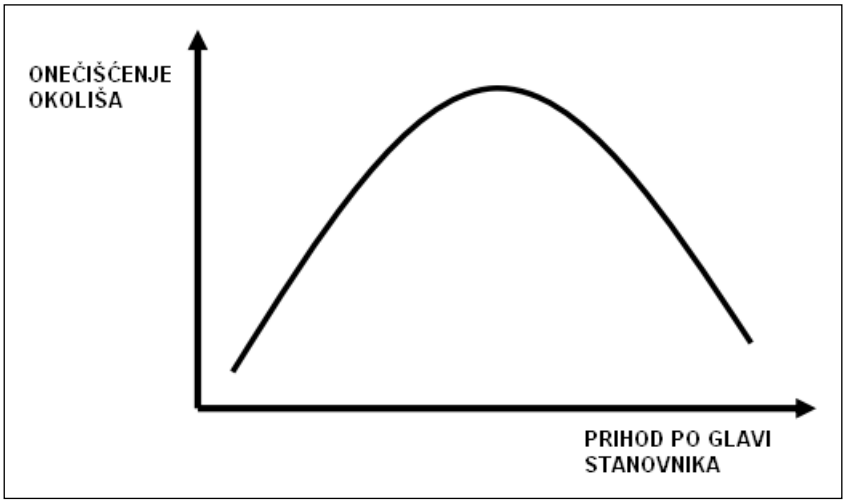
Ova teorija kaže kako emisije raznih tvari štetnih po okoliš u rastućoj ekonomiji, prvo rastu do jedne granice i tada, s nastavkom rasta prihoda po glavi stanovnika, emisije počinju opadati. Slično kao i klasična Kuznetsova krivulja, i ova krivulja ima oblik okrenutog slova *U*.

Kao moguća logična pojašnjenja koja ovu teoriju praktično objašnjavaju navode se ova razmišljanja:

1. Povećani prihod mijenja ljudske prioritete od čisto materijalnih prema neekonomskim dobrima kao što je čistiji okoliš,

2. Razvoj jedne zemlje teče iz jedne relativno čiste ruralne ekonomije, u jedno jako onečišćeno industrijsko društvo, kako bi nakon toga tekao razvoj ka čistijem društvu gdje dominiraju prihodi od uslužnih djelatnosti,
3. Utjecaj, odnosno djelovanje međunarodne robne razmjene, na primjer - premještanje prljavih tehnologija i industrija u manje razvijene zemlje,
4. Stvaranje novih tržišta za prirodne resurse u visokorazvijenim zemljama i time opadanje cijena prirodnih resursa,
5. Efektivno reguliranje koje je povezano s gospodarskim rastom,
6. Nova razmišljanja prema sveobuhvatnom gledanju na probleme cijeloga društva: povećani prihodi država daju prostor za povećanje raspoloživih sredstava koja se mogu iskoristiti za zaštitu okoliša, stvaraju se institucije koje brinu o okolišu, koje podižu svijest javnosti o potrebi zaštite okoliša, a zahtijevaju i tehnologije koje se više brinu o okolišu.

Ovu vezu između okolišnih pokazatelja i gospodarskog razvoja, prvi su put definirali Gorssman i Krüger (1991.), koji su radili *Studiju o utjecaju na okoliš projekta NAFTA-u* [15]. EKC koncept je popularizirana 1992. izvještajem Svjetske banke, a temeljen je na radovima Shafika i Bandyopadhyaya [16].



Slika 9. Okolišna Kuznetsova krivulja [17]

Panayotou je 1993. taj koncept prvi put nazvao EKC – *Okolišna Kuznetsova krivulja* (slika 9). Nakon toga, ovim su se fenomenom bavile mnoge studije koje su uspoređivale različite okolišne pokazatelje s gospodarskim rastom pojedinih zemalja i njihovim odnosom prema okolišu [18 - 23].

4.3. Učinci proizvodnje i EKC

Različiti ekonomski čimbenici govore u prilog postojanja jedne EKC; spomenut ćemo samo neke. Svaki vid proizvodnje utječe na kvalitetu okoliša preko tri učinka:

1. Učinak mjerila,
2. Učinak tehnologije,
3. Učinak kompozicije.

1. ***Učinak mjerila*** opisuje odnos izlazne količine proizvoda u odnosu na iskorištene ulazne prirodne resurse. Izlazna količina može proporcionalno više, jednako ili slabije rasti, ukoliko se količina ulaznih resursa poveća za unaprijed određeni čimbenik. Govori se o stalnom učinku mjerila kada se, pri povećanju ulaznih resursa za određeni čimbenik, izlazna količina proizvoda uveća za isti čimbenik. Na temelju toga bi, uslijed stalnog učinka mjerila, stupanj onečišćenja okoliša rastao istom brzinom kojom raste gospodarstvo.
2. ***Učinak tehnologije*** govori da troškovi za istraživanje i razvoj rastu, ukoliko rastu opći prihodi. Jedno bogato gospodarstvo koje daje više novca za istraživanje i tehnološki razvoj, ide naprijed. Tehnološki razvoj rezultira zamjenom prljavih čistijim tehnologijama i većom učinkovitošću same proizvodnje. To na kraju znači da je, za istu količinu izlaza gotovih proizvoda, potrebno upotrijebiti manje ulaznih resursa.
3. ***Učinak kompozicije*** opisuje vezu između gospodarskog rasta i promjene strukture gospodarstva za vrijeme samoga procesa razvoja. S većim gospodarskim rastom, mijenja se i struktura gospodarstva: od pretežno industrijskog ka gospodarstvu kojim dominiraju uslužne djelatnosti.

Učinak tehnologije i učinak kompozicije zato imaju pozitivan utjecaj na kvalitetu okoliša, dok učinak mjerila ima negativan utjecaj na kvalitetu okoliša.

Naravno, osim nabrojanih, i drugi čimbenici upućuju na postojanje nekoga oblika EKC-a.

Prema EKC teoriji, porastom prihoda (odnosno industrijalizacijom) jedne zemlje, na početku raste i onečišćenost okoliša. Stanovništvo to prihvaća jer mu raste standard, pa ga okolišni problemi pretjerano ne plaše. U jednom određenom trenutku, populacija je već zadovoljila svoje minimalne potrebe pa se javljaju i okolišni zahtjevi. Utemeljena na neovisnim izračunima, točka preokreta dostigne se kada prihod po glavi stanovnika dostigne razinu od oko 8.000 dolara [18].

Ukoliko potražimo podatke o stanju u Bosni i Hercegovini, tu, nažalost, situacija nije pretjerano povoljna. *Izvještaj o razvoju BiH - 2012.*, koji je izdala Direkcija za ekonomsko planiranje 2013., iznosi sljedeće podatke:

Nominalni GDP, prema podacima Centralne banke BiH za 2012. godinu, iznosi 17.010,00 milijuna, a GDP „per capita" je ***4.430,00 dolara*** *i nešto je niži nego u 2011. godini.*

Znači, naš BDP je skoro dvostruko manji nego što bi trebao biti, kako bi se ozbiljno krenulo prema kvalitetnoj zaštiti okoliša!

Prema statističkim podacima, Bosnu i Hercegovinu na prethodnom dijagramu možemo svrstati u područje *2* EKC krivulje.

To je podatak koji bi trebao biti na umu svim strukturama vlasti koje odlučuju o suodnosu gospodarskog rasta i kvalitete okoliša u Bosni i Hercegovini!

5. ZAKLJUČAK

Pojedini zapadni okolišni aktivisti brzi gospodarski razvoj zemalja u razvoju gledaju kritično. Razlog tomu je da s njima rastu brda smeća, ubrzano se troše neobnovljivi izvori sirovina i povećavaju emisije štetnih tvari. Iz toga izvlače zaključak kako se ne smije uzeti model Zapada kao primjer, jer će u tom slučaju doći do uništenja Zemlje.

Nerazumno je želju za rastom nerazvijenih zemalja pokušati zaustaviti, a i štetno je po okoliš!

Globalni programi zaštite okoliša i klime mogu funkcionirati samo u slučaju ako su, barem donekle, ispunjene osnovne ljudske potrebe stanovništva u cijelom svijetu. Onaj tko se bori za preživljavanje, ima drugačije brige nego što je briga o očuvanju flore i faune, ugroženih vrsta, endema…

Potrebna je minimalna razina materijalnog blagostanja kako bi se tek onda jedno društvo počelo zanimati za zaštitu okoliša.

Znanstvena istraživanja su pokazala da, u nerazvijenim i zemljama u razvoju, opterećenje okoliša na početku raste, dok BDP ne dosegne granicu od nekih 8.000 dolara (EKC krivulja). Nakon toga budi se svijest o štetnosti uništavanja okoliša. Ljudi su zadovoljili svoje fiziološke potrebe: hrana, odjeća i stan, i nakon toga u stanju su imati pozitivan odnos prema zaštiti okoliša.

U Kini danas BDP (preračunat prema kupovnoj moći), iznosi oko 8.400 dolara po glavi stanovnika i ovaj proces se može jako dobro pratiti. Čak i vlada promiče ideju zaštite okoliša. Zrak u Pekingu i Šangaju postaje sve čišći. Na jedan jako opipljiv način ljudi su se pokrenuli i pokušavaju dio nestale prirode vratiti u gradove. Otoci između ulica puni su cvijeća i niskog grmlja. Uz autoceste stavljaju se velike saksije cvijeća.

FAO izvještava sljedeće o stanju šuma:

Pratimo stanje i možemo reći kako se stanje šuma poboljšava u zemljama u razvoju koje imaju industrijski rast i to izravno proporcionalno njihovom rastu (Eduardo Rojas-Briales). *To je već viđeno stanje u Europi 19. stoljeća i, evo, ponavlja se i u Aziji. Iako stanovništvo raste, u Aziji raste i ukupna pošumljena površina. Godišnje sama Kina pošumljava milijune hektara* [24].

Kritičari rasta upozoravaju da, iako strojevi postaju štedljiviji i troše manje energije, to ne znači kako se, u apsolutnom broju, manje koriste nafta, plin i ugljen kao energetski izvori. To je nepobitna istina. Čak i kada bi proveli misaoni pokus u kojem bi Kina *odjednom* sve svoje tvornice i energane modernizirala, ipak bi, i u tom slučaju, rasli i potrošnja energije i emitiranje količine CO_2 u Kini.

Industrija u zemljama u razvoju raste tako brzo da je količinski učinak veći od modernizacije, odnosno povećanja energetske učinkovitosti. Taj paradoks se može uočiti i kod visokorazvijenih zemalja na primjeru automobila. Motori postaju sve moderniji, imaju manju potrošnju goriva, a dostižu istu snagu. Ali globalna potrošnja benzina ne opada, jer auti, prema željama korisnika, postaju sve veći, brži i udobniji. Dinamični razvoj, osobito u Kini i Indiji, opterećivat će klimu sve dok se ne dođe do točke kada bude moguće odvojiti emisiju CO_2 od gospodarskog rasta.

To je, nažalost, tako, ali istini se mora pogledati u oči: alternativa (održivom) rastu ne postoji!

Niti jedna zemlja na svijetu se neće pomiriti sa zaostajanjem. Ljudi imaju želje za boljim i to je duboko u ljudskoj prirodi.

Razvijene zemlje moraju sve činiti kako bi podržali nerazvijene na njihovu razvojnom putu. Ne radi se ovdje o nekakvim *Caritas donacijama* za gladne, nego ta pomoć mora biti iskazana izravnim investicijama, zajedničkim radom na tehnološkom razvoju, kao i uklanjaju carinskih i sličnih gospodarskih barijera [1].

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FINANSIJSKI MEHANIZMI PRIMJENJIVI ZA PROJEKTE ENERGETSKE EFIKASNOSTI I OBNOVLJVIH IZVORA ENERGIJE ZA EKONOMIJE U TRANZICIJI

FINANCIAL MECHANISMS APPLICABLE TO PROJECTS OF ENERGY EFFICIENCY AND RENEWABLE ENERGY SOURCES FOR ECONOMIES IN TRANSITION

Faruk Serdarević*, Adnan Gušić*

* Konsultant za energetiku, Sarajevo, Bosna i Hercegovina

autor za korespondenciju: Faruk Serdarević, email: faruk.serdarevic@gmail.com

Pregledni rad

SAŽETAK

Suočeni sa stalnim pritiskom za smanjenjem emisija stakleničkih plinova i potrošnje energije, suvremena društva prepoznaju energetsku efikasnost i proizvodnju energije iz obnovljivih izvora kao ključne aktivnosti u pokušaju da se smanje utjecaji na klimatske promjene i zaštite prirodna i kulturna nasljedstva.

Međutim, sa ulagačevog gledišta, investiranje u zelenu ekonomiju kao što su energetska efikasnost i projekti proizvodnje energije iz obnovljivih izvora se rijetko mogu ekonomski opravdati. Stoga takvi projekti još uvijek trebaju potporu od strane vlada i drugih relevantnih aktera.

Angažman odgovarajućih finansijskih mehanizama kao potpore je kritični segment postizanja obaveznih relevantih ciljeva i njihova primjena uveliko ovisi o makroekonomskoj situaciji u svakoj zemlji pojedinačno. Izazovi su posebno veliki za zemlje zapadnog Balkana koje imaju dodatna ograničenja kao što je veliki javni dug.

Ovaj rad identificira finansijske mehanizme koji se mogu primjeniti u ograničenim ekonomijama u cilju omogućavanja daljnje promocije čiste energije.

Ključne riječi: *zelena ekonomija, investicije, finansijski mehanizmi, obnovljiva energija, energetska efikasnost*

ABSTRACT

Encountered with constant pressure to reduce greenhouse gas emissions and energy consumption, the modern societies recognise energy efficiency and energy generation from renewable energy sources as the key activities in attempt to mitigate effects to the climate changes and protection of natural and cultural heritage.

However, from the investor's point of view, the investments in green economy, such as energy efficiency and renewable energy projects, is usually financially hard to economically justify. Thus such projects still need support from governments and other relevant stakeholders.

Employment of adequate financing mechanisms is a critical segment of achieving relevant mandatory targets and its application depends vastly on macroeconomic situation in each country. The challenges are greater for Western Balkan countries which have additional limitations such as very high public debt.

This paper identifies the financing mechanisms which can be introduced in constrained economies in order to facilitate further promotion of clean energy.

Keywords: *green economy, investments, financial mechanisms, renewable energy, energy efficiency*

1. UVOD - ZNAČAJ UVOĐENJA MEHANIZAMA POTICAJA ZELENE EKONOMIJE ZA GRAĐEVINSKI SEKTOR

Pojam "zelena ekonomija" ("green economy") se prema izvoru Ujedinjenih nacija [1] prvi put spominje 1989. godine u izvještaju sačinjenom za britansku Vladu od strane vodećih ekonomista iz oblasti okoliša. Sam izvještaj je predstavljao praktične mjere politike za "ozeljavanje" savremenih ekonomija i usmjeravanje prema održivom razvoju. Pojam je tek 2008. godine ponovo došao u fokus interesovanja i to u kontekstu rasprava o politikama odgovora na učestale globalne krize.

Zelena ekonomija se može posmatrati kao alternativna opcija razvoja i rasta ekonomije dominantom modelu privrednog rasta usmjerenog primarno na povećanje BDP-a. Ova opcija promiče održivu i rastuću ekonomsku, ekološku i društvenu dobrobit, a rezultat ovog pristupa je sveukupna društvena dobrobit i veća jednakost uz značajno smanjenje rizika po okoliš i ekološku oskudicu [2].

Tranzicija ekonomije u zelenu ekonomiju je dugoročan proces prihvatanja i sprovođenja novih doktrina. Evropska unija je preuzela vodeću svjetsku ulogu kod implementacije zelene ekonomije kroz uvođenje strategija utemeljenih na ekonomiji niske razine ugljika, koje se ispoljavaju kroz programe i projekte rasta ili povećanja produktivnosti na samoodrživ način. Projekti energetske efikasnosti (EE projekti) i proizvodnje električne energije iz obnovljivih izvora energije (OIE projekti) prednjače u nastojanju da se smanji potrošnja resursa i emisije stakleničkih plinova, odnosno da se ublaže negativni učinci na klimatske promjene. I dok se povećanjem energetske efikasnosti smanjuje potrošnja energije i čuvaju resursi, obnovljivi izvori energije igraju značajnu ulogu u smanjenju emisija ugljičnog dioksida i predstavljaju značajan aspekt klimatske i energetske politike.

Osim utjecaja korištenja fosilnih goriva na okoliš, kombiniranjem sprovedbe mjera energetske efikasnosti (EE mjera) i povećanja proizvodnje energije iz OIE dugoročno se doprinosi diversifikaciji proizvodnje energije i sigurnosti opskrbe, smanjenju ovisnosti o

uvozu energenata, povećanju konkurentnosti, otvaranju novih radnih mjesta i razvoju poduzetništva, poticanju razvoja novih tehnologija i domaće privrede u cjelini, gdje posebno mjesto zauzima građevinski sektor.

Građevinarstvo se smatra jednim od ključnih djelatnosti u nastojanju modernog društva da odgovori na klimatske promjene, kroz smanjenje potrošnje energije u zgradarstvu, reduciranje energetskog intenziteta privrede te izgradnju elektrana za proizvodnju električne energije iz OIE. Stoga je sasvim jasno da projekti implementacije energetske efikasnosti i proizvodnje električne energije iz OIE daju podstrek građevinskom sektoru koji pronalazi nove poslovne mogućnosti u rekonstrukciji obiteljskih kuća, zgrada zajedničkog stanovanja, objekata u vlasništvu javnog sektora, a također i izgradnji novih elektrana za proizvodnju električne energije iz OIE.

Iako su benefiti EE projekata i proizvodnje električne energije iz OIE očigledni za društvo u cjelini, kao i za građevinski sektor, sa investitorovog gledišta ovakve investicije mogu predstavljati finansijsko opterećenje sa neprihvatljivim periodom povrata uloženih sredstava, posmatrajući iz ugla bankabilnosti samog projekta. Stoga se građevinski sektor još uvijek ne može prepustiti samoreguliranju mehanizmima slobodnog tržišta, odnosno to treba izvšiti na postepen način i pomoću nekih od mehanizama koji su detaljno objašnjeni dalje u tekstu ovog rada. Sa druge strane, civilizirane države su se obvezale dostići postavljene strateške ciljeve u smislu ušteda energije i povećanju potrošnje energije dobivene iz OIE.

Da bi se postavljeni ciljevi dostigli, potrebna je regulacija tržišta od strane države. Regulacija podrazumijeva uspostavljanje pravnog i institucionalnog okvira za potrebu pružanja podrške ovom sektoru, uz donošenje propisa, nadzor nad njihovom primjenom i sankcioniranje onih koji djeluju protivno propisima. Ključni dio podrške predstavljaju mehanizmi za sprovedbu EE mjera i proizvodnje električne energije iz OIE kojima se prevazilazi jaz između potrebe za dostizanjem postavljenih ciljeva i očekivanja investitora.

Primjena spomenutih mehanizama je ključna za ostvarenje zadatih ciljeva. U praksi su prepoznate brojne opcije, ali primjena pojedinih opcija ovisi uveliko o makroekonomskoj situaciji svake države. Izazovi su dodatno veći za zemlje Zapadnog Balkana gdje dodatna povećanja javnog duga te dodatno opterećivanje krajnjih korisnika nisu opcije koje bi se trebale razmatrati. Do sada su već definirane četiri grupe mehanizama koje bi mogle odgovarati situaciji zemalja Zapadnog Balkana. Iako je fokus stavljen na finansiranje EE projekata, sličan pristup, uz male izmjene, se može primjeniti i kod finansiranja projekata proizvodnje električne energije iz OIE.

Bosna i Hercegovina (BiH) sa svim svojim specifičnostima - izuzetno složenom strukturom države sastavljene od Federacije BiH, Republike Srpske i Brčko Distrikta, predstavlja poseban izazov koji zahtjeva pažljivo razmatranje primjenjivih mehanizama. Neki od identificiranih mehanizama su jednostavno neprimjenjivi ili je njihova implemenacija preuranjena u Bosni i Hercegovini. Ovaj rad identificira moguće mehanizme za sprovedbu EE mjera i proizvodnje električne energije iz OIE sa posebnim osvrtom na prilike u Bosni i Hercegovini.

2. MEHANIZMI ZA SPROVEDBU MJERA ENERGETSKE EFIKASNOSTI I PROIZVODNJE ELEKTRIČNE ENERGIJE IZ OIE

Do sada sprovedena istraživanja ukazuju na četiri grupe mehanizama koji su na raspolaganju državama Zapadnog Balkana u svrhu pružanja podrške projektima energetske efikasnosti [3], slika 1:

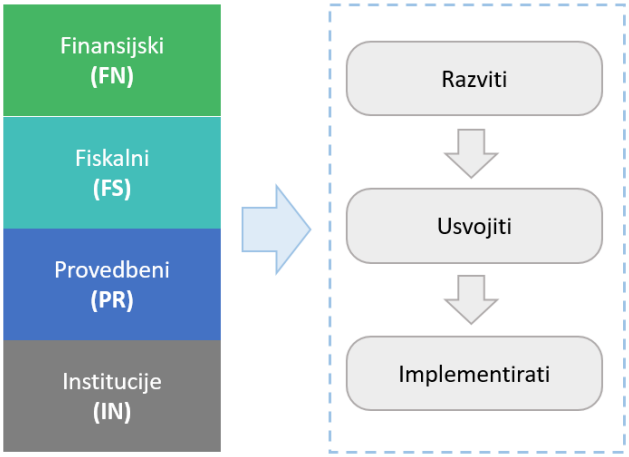
- **Mehanizmi finansiranja** (FN)- mehanizmi koji obuhvataju aktivnosti finansiranja EE mjera putem zajmova / kredita ili višegodišnjeg finansiranja iz proračuna,
- **Fiskalni mehanizmi** (FS) - aktivnosti vezane za sprovođenje EE mjera koje se finansiraju ili potiču poreznom politikom,
- **Provedbeni mehanizmi** (PR) - aktivnosti vezane za energetsku učinkovitost potaknute dostupnom tehničkom pomoći ili nametanjem određenih pravnih obaveza,
- **Institucije** (IN) - skupina aktivnosti uspostavljenih ili sprovedenih od strane javnih institucija.



Slika 1. Pregled preporučenih mehanizama za implementaciju nacionalnih akcijskih planova za zemlje Jugoistočne Evrope

Analizom gore navedenih mehanizama, većinu istih je moguće grupisati prema prirodi toka novca, odnosno prema tome da li se radi o mehanizmu za absorbciju sredstava koje zatim treba dalje alocirati na EE mjere ili je riječ o mehanizmu pomoću kojeg se vrši alokacija sredstava za EE mjere. Dakle, "prihodovni" mehanizmi, u smislu da omogućavaju sakupljanje sredstava u svrhu daljnje alokacije na projekte/mjere povećanja energetske efikasnosti, te "distributivni" mehanizmi, koji upravo služe za realizaciju projekata/mjera povećanja energetske efikasnosti.

Za sve analizirane mehanizme je potrebno uložiti koordinirani napor da se razviju, usvoje i u konačnici implementiraju na nivou koji odgovara razvoju relevantnih tržišta (slika 2).



Slika 2. Proces uspostavljanja mehanizama za implementaciju akcijskih planova

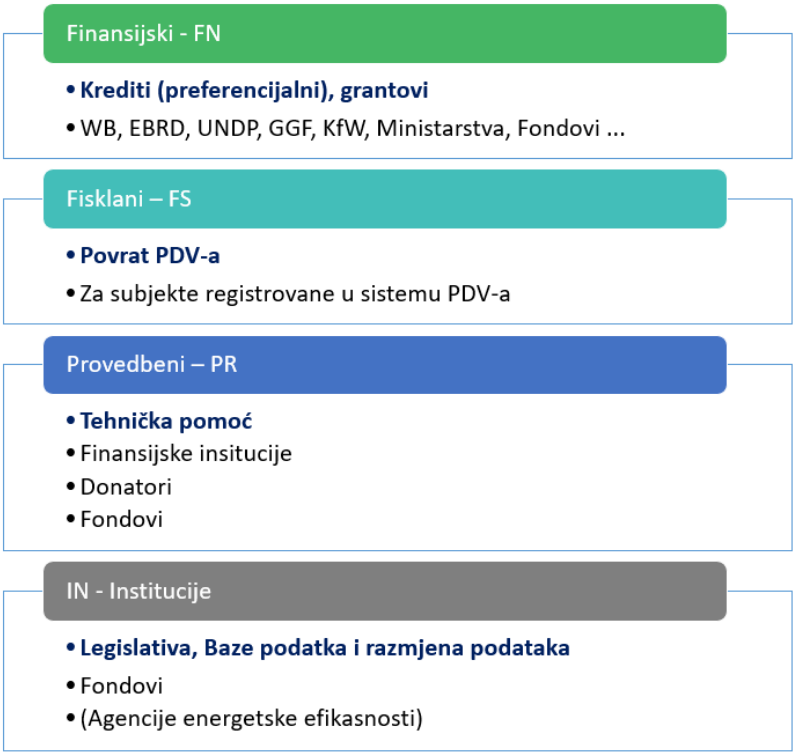
Kada se radi o obnovljivim izvorima energije značajna prepreka široj uporabi je njihova nekonkurentna odnosno previsoka cijena u usporedbi sa cijenom električne energije proizvedene iz konvencionalnih elektrana. Iako većina tehnologija proizvodnje električne enrgije iz OIE nemaju velike operativne troškove, investicioni troškovi su po jedinici proizvodnje mnogo veći u odnosu na konvencionalne elektrane, pa je period otplate takvih elektrana sa tržišnim cijenama energije dobivene iz fosilnih goriva neprihvatljivo veliki za investitore. Mehanizmi koji trenutno postoje kao poticajni sistemi za OIE u Evropskoj uniji uključuju [4]:

- Sistem garantovanih cijena (eng. *feed-in tariff*) je osnovni način poticaja gdje država proizvođačima nudi ugovor o otkupu električne energije (eng. *PPA - power purchase agreement*) sa unaprijed dogovorenom i garantovanom otkupnom cijenom za vrijeme trajanja ugovora koja osigurava proizvođaču povrat investicije do isteka ugovora. Osim garantovane otkupne cijene za proizvedenu električnu energiju, proizvođaču se garantuje prioritetan i cjelokupan otkup proizvedene električne energije iz OIE tokom trajanja ugovora,
- Sistem premija na tržišnu cijenu predstavlja sistem kojim se sektor OIE približava zahtjevima tržišta električne energije. Proizvođači u ovom sistemu prodaju proizvedenu električnu energiju na tržištu, po tržišnim cijenama, te dobivaju podsticaj u vidu premije za prodanu energiju. Premija može biti fiksna ili varijabilna,
- Sistem obvezujućih kvota (zeleni certifikat) se temelji na trgovini zelenim certifikatima koji se dodjeljuju proizvođačima za svaki MWh električne energije proizvedene iz OIE, gdje se učešće energije iz obnovljivih izvora u ukupnoj potrošnji može osigurati kupovinom zelenih certifikata na slobodnom tržištu,
- Sistem natječaja obezbjeđuje da se investitori nadmeću međusobno za raspoloživu kvotu kroz aukcije, gdje u načelu oni s najboljom ponudom pobjeđuju i grade elektrane. Ovaj sistem potiče veću konkurenciju među investitorima i ima učinak smanjenja troškova sistema poticaja,
- Subvencije investicija i razne fiskalne mjere se obično smatraju komplementarnim mehanizmima. Subvencije mogu biti oblik finansijske stimulacije izgradnje elektrana na OIE, dok su fiskalne mjere prisutne u raznim oblicima, kao na primjer, umanjeni porezi na električnu energiju dobivenu iz OIE, sniženi izdaci na emisije i slično.

3. POSTOJEĆI MEHANIZMI U BOSNI I HERCEGOVINI

Bosna i Hercegovina je potpisivanjem i ratifikacijom Ugovora o formiranju Energetske zajednice Jugoistočne Evrope 2005.godine preuzela obavezu transpozicije odredbi relevantnih direktiva Evropske Unije u domaće zakonodavstvo.

Međutim, zbog kompleksnosti državnog ustroja BiH i nepostojanja sveobuhvatnog i harmoniziranog sistematskog pristupa implementacije mehanizama, teško je identificirati svaki trenutno aktivni mehanizam u Federaciji BiH i Republici Srpskoj. U isto vrijeme, podijeljenost djelovanja državnih organa na sektor energetske efikasnosti i proizvodnje električne energije iz OIE otežava sprovedbu mehanizama i projekata iz ovih oblasti. Stoga je za sve analizirane mehanizme potrebno uložiti koordinirani napor da se razviju, usvoje i u konačnici, implementiraju na razini koja odgovara razvoju relevantnih tržišta u BiH (slika 3).



Slika 3. Postojeći mehanizmi za implementaciju Nacionalnog akcijskog plana energetske efikasnosti BiH – oktobar 2017

3.1. Mehanizmi za poticaj Akcijskog plana energetske efikasnosti

Među najvažnijim direktivama koje se odnose na energetsku efikasnost izdvajaju se Direktiva 2012/27/EU o energetskoj efikasnosti [5], Direktiva 2010/31/EU o energetskim karakteristikama zgrada [6] i Direktiva 2010/30/EU o označavanju proizvoda koji troše energiju i standardne informacije o proizvodu [7].

3.2. Mehanizmi finansiranja

U ovoj skupini mehanizama su klasični i najčešće korišteni mehanizmi za implementaciju Akcijskog Plana (AP) energetske efikasnosti. Obzirom na raznolikost

aktivnosti koje potpadaju pod ovu kategoriju, praksa u zemljama Evropske unije je da se mehanizmi klasificiraju u jednu od podgrupa. U Bosni i Hercegovini je identificirano postojanje tri mehanizma finansiranja:

3.2.1. Preferencijalni krediti (često sa periodom odgođenog plaćanja)

Pod ovim mehanizmom se podrazumijeva finansiranje sredstvima državnih institucija putem zajmova i kredita uz povoljnije uvjete nego li tržište nudi (niža kamatna stopa, povoljan grace period i odgovarajući period otplate).

Krediti ove vrste, koji su, između ostalog, namijenjeni za poboljšanje energetske efikasnosti, mogu se naći u BiH. Namjenski uspostavljen revolving fond za energetsku efikasnost je do 2018. godine uspostavljen samo u Federaciji FBiH, ali u oba entiteta postoje i razvojne banke koje nude preferencijalne dugoročne kredite sa povoljnijim kamatnim stopama i srednjeročnim otplatnim planom do 10 godina (uz odoboravanje grace perioda). Sredstva razvojnih banaka za sada nisu eksplicitno namijenjena za finansiranje projekata energetske efikasnosti.

Praksa ukazuje da je za potencijalne investitore teško doći do preferencijalnih kredita za EE projekte jer su limitirana sredstva, koja su ujedno predviđena za široku lepezu projekata iz raznih sektora, nedovoljna za sve potencijalne projekte. Osim toga, postojeći programi ne omogućavaju pristup sredstvima za sve kategorije potencijalnih investitora.

3.2.2. Kreditne linije za mala i srednja poduzeća i kućanstva

U Bosni i Hercegovini egzistira u svakom momentu nekoliko kreditnih linija za finansiranje implementacije EE mjera čiji su izvor međunarodne finansijske institucije. Ponuda finansiranja EE projekata za krajnje korisnike, koja se obično nudi preko lokalne banke ili mikro fonda, je nešto povoljnija od standardnih komercijalnih kredita. Određene banke omogućavaju i druge pogodnosti koje korisnik ne bi imao uz korištenje standardnog komercijalnog kredita (na primjer, uvjetni otpis dijela kredita, besplatna priprema dokumentacije i slično). Međutim, prednost namjenskih kreditnih linija je što finansijske institucije kroz namjensku liniju olakšavaju investitorima kroz standardizaciju procedure apliciranja za sredstvima, te stručniji obradu zahtjeva i lakše identifikovanje dobrih od loših projekata energetske efikasnosti.

Iako trenutno na tržištu ima dovoljno sredstava za finansiranje EE projekata, sam mehanizam nema snažan učinak na poticanje ponajprije zbog prevelike zaduženosti potencijalnih korisnika ovih sredstava, ali i onih koje banke nisu spremne finansirati jer nemaju stalan posao uz odgovarajuću razinu zvaničnih primanja. Sa druge strane, bez obzira na sve pogodnosti koje se nude kroz ove kreditne linije, koje su uvjetima prilagođenije EE projektima nego standardni komercijalni krediti, uvjeti su i dalje nedovoljno primamljivi za veliki broj potencijalnih investitora, a najviše zbog još uvijek niske cijene većine energenata na domaćem tržištu koja ne podstiče štednju energije.

3.2.3. Subvencije (iz vlastitih sredstava) i potpore (iz eksternih sredstava)

Sredstva za subvencioniranje projekata energetske efikasnosti se obezbjeđuju kako iz vlastitih tako i iz eksternih sredstava. Uspostavljanjem mehanizma subvencija i potpore nepovratnih sredstava od strane resora/Vlade moguće je iste strateški usmjeriti, te kriterije

podobnosti prilagoditi na određenu korisničku grupu kredita odnosno podsektora akcijskog plana (AP).

Fondovi za zaštitu okoliša iz godine u godinu osiguravaju sve više nepovratnih sredstava za subvencije i grantove za projekte i iz domena energetske efikasnosti. Međutim, obzirom na veliki broj finansiranih projekata iz oblasti zaštite okoliša, sredstva za energetsku efikasnost su i dalje ograničena.

3.3. Fiskalni mehanizmi

Za sprovedbu AP-a prepoznata su dva mehanizma iz ove podgrupe. Oba mehanizma su djelimično zastupljena u BiH, ali ne u istinskom obliku da bi značajno doprinjela sprovedbi EE mjera.

3.3.1. Porez na ugljik, energetske ili okolišne takse

Naknade za okoliš se plaćaju na entiteskim razinama i za prikupljanje naknada su zaduženi fondovi (Fond za zaštitu okoliša FBiH i Fond za zaštitu životne sredine i energetsku efikasnost RS). Dio prikupljenih sredstava se usmjerava na EE programe i projekte. Međutim, ne postoji harmonizacija između fondova u smislu visine i vrste naknada koje se trenutno prikupljaju.

3.3.2. Povrat poreza (PDV, poticaj za ulaganje)

Bosna i Hercegovina je jedna od zemalja sa nižim stopama poreza na dobit i PDV-a. Niski porezi te sistem sa jedinstvenom stopom PDV-a za sve proizvode i usluge ne daju velike mogućnosti da se značajnije primjene fiskalni mehanizmi za sprovođenje AP-a, ali bi porezne olakšice mogle biti komplementarne postojećim mehanizmima.

3.4. Provedbeni mehanizmi

U Bosni i Hercegovini se primjenjuju dva mehanizama iz ove skupine, tehnička pomoć za identificiranje projekata i pripremu kredita ili javnih nabavki i fondovi energetske efikasnosti (uključujući revolving fondove), a aktivno se radi na uspostavljanju ESCO tržišta, sa ugovoranjem i finansiranjem treće strane i pravne obaveze za javne komunalne kompanije (sa certifikatima za trgovanje).

3.4.1. Tehnička pomoć za identificiranje projekata i pripremu kredita ili javnih nabavki

Tehnička pomoć osigurava jačanje stručnih, ljudskih i tehničkih kapaciteta institucija u BiH, kao i upoznavanje, stvaranje, razumijevanja i jačanje kapaciteta krajnjih korisnika za absorbciju mehanizama za implementaciju AP-a u BiH i implementaciju aktivnosti povećanja EE. Tehnička pomoć se obično ostvaruje kroz alokaciju grant sredstava. Donatori koji duže vrijeme značajnije djeluju u ovoj oblasti u BiH su GIZ (Njemačko društvo za saradnju), USAID (Agencija Sjedinjenih Američkih Država za međunarodni razvoj), UNDP (Razvojni

program Ujedinjenih nacija), EU (Evropska unija), SIDA (Švedska agencija za međunarodni razvoj i saradnju) kao i neki drugi sa relativno manjim dopinosom u ovoj oblasti.

3.4.2. Fondovi energetske efikasnosti (uključujući revolving fondove)

Fond za zaštitu okoliša FBiH je 2016. godine uspostavio revolving fond te objavio javni poziv za dodjelu povratnih sredstava namjenjenih isključivo za energetsku efikasnost koji su namjenjeni i javnim institucijama i komercijalnim korisnicima. Fond za zaštitu životne sredine i energetske efikasnosti Republike Srpske je također započeo potrebne aktivnosti da uspostavi sličan revolving fond za korisnike na teritoriji Republike Srpske.

Osim namjesnkih fondova za finansiranje projekata energetske efikasnosti koji postoje ili se namjeravaju uspostaviti, na teritoriji Federacije BiH je pokrenut trajni revolving fond za industriju. Iako sredstva nisu isključivo namijenjena za podizanje energetske efikasnosti za pravna lica iz industrijskog sektora, sredstva se mogu koristiti i u tu svrhu. U Republici Srpskoj djeluju već pomenuti fondovi kojima upravlja Investicijsko-razvojna banka Republike Srpske.

Sredstva iz fondova se mogu dobiti po povoljnijim uvjetima u odnosu na uvjete koje nude komercijalne banke na tržištu. Međutim, iako revolving fondovi za dodjelu povoljnih kredita djeluju u BiH, iskustva institucija zaduženih za njihovim upravljanjem tek počinju da se stiču, a i novčana sredstva u revolving fondovima su i dalje limitirana.

3.5. Institucije

3.5.1. Agencije energetske efikasnosti

U Bosni i Hercegovini još uvijek nisu uspostavljene agencije na entitetskim nivoima koje bi bile zadužene za aktivnosti vezane za energetsku efikasnost. Kako je energetska efikasnost u nadležnosti entiteta, vlade oba entiteta su uspostavile već pomenute okolišne fondove koji obnašaju aktivnosti za koje bi inače agencija za energetsku efikasnost bila zadužena.

3.5.2. Poticajne mjere za proizvodnju električne energije iz OIE

Najvažnija direktiva Evropske unije koja se odnosi na potrošnju energije iz obnovljivih izvora energije, je Direktiva 2009/28/EC o promicanju uporabe energije iz OIE [8], kojom se određuje da svaka država članica donese nacionalni plan za obnovljivu energiju kojim će definirati učešće OIE u ukupnoj potrošnji energije na nacionalnoj razini.

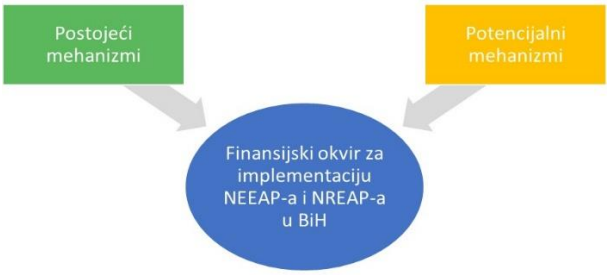
U Bosni i Hercegovini, odnosno njenim enitetima, trenutno se primjenjuje sistem garantovanih cijena i otkupa u Federaciji BiH dok se u Republici Srpskoj primijenio sistem premija i sistem garantovanih cijena i otkupa. Ukupna količina električne energije iz OIE koja će se poticati, a posredno i broj proizvođača, se utvrđuje enitetskim Akcionim planovima.

Trenutno uspostavljeni mehanizmi su imali pozitivan utjecaj na ispunjenje zadatih ciljeva, međutim, činjenica je da se sredstva za poticajne mjere za proizvodnju električne energije iz OIE obezbjeđuju naknadama koje plaćaju krajnji korisnici, te je stoga potrebno razmotriti i druge mehanizme kojim će se omogućiti rasterećivanje krajnjih potrošača. Također, obzirom na veliko interesiranje investitora koje se odražava dugim listama čekanja

za ulazak u poticajni sistem, potrebno je uravnotežiti odnos ponude subvencija i potražnje za investiranjem u OIE projekte, a time bi se smanjio trošak za krajnje potrošače električne energije kroz racionaliziranje poticajnih mjera.

4. POTENCIJALNI SREDNJOROČNI MEHANIZMI I OPRAVDANOST NJIHOVOG UVOĐENJA U BOSNI I HERCEGOVINI

Ukupni finansijski okvir za implementaciju akcijskih planova u BiH je neophodno formirati iz postojećih mehanizama koji već doprinose ovim ciljevima, ali i potencijalnim mehanizmima koje tek treba uspostaviti i omogućiti njihovu operativnost, a sa ciljem: i) stvaranja većeg obima aktivnosti realizacije mjera povećanja energetske efikasnosti i realizacije projekata OIE u BiH, ii) obuhvatanja sva četiri sektora koja su definisana unutar AP dokumenata mehanizmima za njihovu implementaciju te iii) ispunjavanja ciljeva iz nacionalnih AP-a i obaveze BiH u procesu pristupanja EU za oblasti energetske efikasnosti (NEEAP) i obnovljivih izvora energije (NREAP), slika 4.



Slika 4. Struktura finansijskog okvira za implementaciju NEEAP-a i NREAP-a u BiH

Uzimajući u obzir sve društvene, političke i ekonomske utjecaje u Bosni i Hercegovini, mehanizmi koji imaju opravdanost za uvođenje ili osnaživanje u srednjoročnom periodu su:

Preferencijalni krediti

Potrebno je uvesti uz ovaj mehanizam ciljanu alokaciju sredstava na sektor industrije i sektor kućanstva iz AP-a. Ovaj mehanizam je usko vezan za mehanizam uspostavljanja kreditnih linija za energetsku efikasnost za mala i srednja poduzeća i kućanstva od strane resora/Vlade FBiH i RS gdje je moguće takva sredstva strateški usmjeriti, te finansijske modalitete prilagoditi na određenu korisničku grupu kredita odnosno podsektora AP-a.

Mehanizam pokriva najveću grupu korisnika mehanizma poreza na ugljik, energetske i okolišne takse. Naknade koje se plaćaju kroz ovaj "prihodovni" mehanizam bi se ciljano alocirale kroz ovaj mehanizam na grupu mala i srednja poduzeća i kućanstva.

Višegodišnji proračun (javno finansiranje)

Mehanizam omogućava korisnicima (institucijama) javnog proračuna da realiziraju mjere povećanja energetske efikasnosti sa kraćim periodom povrata investicije bez većih kapitalnih ulaganja i napora nabavke i održavanja. Stoga, višegodišnji proračun predstavlja

osnovu uspostave mehanizma ESCO tržišta, te je i interes korisnika (institucija) javnog proračuna prisutan.

Kreditne linije za mala i srednja poduzeća i kućanstva

Mehanizam omogućava povoljne finansijske modalitete za kreditno zaduživanje u svrhu realizacije ciljeva AP-a unutar određenog sektora ili podsektora, uz niže kamatne stope od komercijalnih i povoljan *grejs* period prilagođen prirodi projekta i povrata ulaganja. Obzirom da interes kreditora postoji, a i Bosna i Hercegovina ima iskustva i izgrađene kapacitete za predmetni mehanizam, osnaživanje ovog mehanizma ne predstavlja problem, ali većom ponudom kreditnih linija ne garantuje se i veći broj projekata iz ove oblasti te ovaj mehanizam treba promatrati u kombinaciji sa drugim predloženim mehanizmima.

Subvencije (iz vlastitih sredstava) i potpore (iz eksternih sredstava)

Mehanizam omogućava ciljanu alokaciju sredstava na komercijalni sektor iz AP-a, te sektor industrije i sektor transporta. Uspostavljanjem mehanizma subvencija i potpore od strane resora/Vlade FBiH i RS moguće je iste strateški usmjeriti, te kriterije podobnosti prilagoditi na određenu korisničku grupu.

Bosna i Hercegovina, kroz postojeći rad razvojnih banaka i fondova entiteta, već ima iskustva i dio izgrađenih kapaciteta za predmetni mehanizam te je operativnost subvencija i potpora lako provodljiva, ali potrebno je obratiti posebnu pažnju na obezbjeđivanje transparentnosti kod primjene ovog mehanizma.

Porezi na ugljik, energetske ili okolišne takse

Mehanizam koji već postoji u BiH, međutim nedovoljno razvijen, omogućava prikupljanje znatnog dijela sredstava za uspostavljanje šireg finansijskog okvira za provedbu AP-a u BiH. Legislativa "zagađivač plaća" koja regulira predmetnu oblast već postoji. Potencijal mehanizma se ogleda u primjeni na strateški prikupljena sredstva po sektorima AP-a, te stoga mehanizam predstavlja izvanrednu osnovu za implementaciju AP-a u BiH.

Porezne olakšice (PDV, poticaj za ulaganje)

Poreznim olakšicama je moguće obuhvatiti sva četiri sektora sadržana u AP. Mehanizmom se motiviraju vlasnici objekata da koriste materijale i tehnologije koje doprinose povećanju energetske efikasnosti, te se daje se temelj za uvođenje kriterija energetske efikasnosti u sistem javne nabavke BiH.

Tehnička pomoć za identificiranje projekata i pripremu kredita ili javnih nabavki

I ovim mehanizmom je moguće obuhvatiti sve sektore sadržane u AP-u. Moguće je u fazi pregovora i/ili pripreme projektnih prijedloga sa donatorima, finansijskim institucijama i drugim agencijama i institucijama ciljano alocirati tehničku pomoć na određeni sektor ili podsektor AP-a. Ovim mehanizmom se omogućava jačanje stručnih, ljudskih i tehničkih kapaciteta institucija u BiH, te upoznavanje, stvaranje razumijevanja i jačanje kapaciteta krajnjih korisnika (implementatora projekata energetske efikasnosti).

ESCO tržište

ESCO tržište nedvojbeno doprinosi realizaciji većeg broja EE projekata ponajprije u sektoru javnog zgradarstva. Prednost ovog mehnaizma je što uključuje znanja iz privatnog sektora u domenu planiranja, implementacije i upravljanja EE projektima (bolja efikasnost i djelotvornost). Odluka nabavke usluge utemljena je na efikasnosti - odabir najoptimalnijeg troškovno-efikasnog tehničkog riješenja. Dodatna prednost ovog mehanizma se ogleda u finansiranju EE projekata iz privatnog sektora te izbjegavanje stvaranja javnog duga (proračunski neutralan pristup za javni sektor).

Pravne obaveze za javne komunalne kompanije (sa certifikatima trgovine)

Mehanizam omogućava prikupljanje znatnog dijela sredstava za uspostavljanje šireg finansijskog okvira za implementaicju AP-a u BiH. Određene aktivnosti dijela mehanizma koji se odnosi na električnu energiju su već u toku, međutim, neophodno je, a u cilju osiguranja prihodovne strane finansijskog okvira implementacije AP-a u BiH, isti proširiti i na sektor distribucije toplotne energije/sisteme daljinskog grijanja. Ovaj mehanizam zahtjeva postojanje finansijskih institucija koje bi mogle usmjeravati prikupljena sredstva kroz predmetni mehanizam ka krajnjim korisnicima – entitetski fondovi za zaštitu okoliša i razvojne banke.

Fondovi energetske efikasnosti (uključujući revolving fondove)

Mehanizam omogućava ciljanu alokaciju sredstava na sektore industrija, komercijalni sektor i usluge, te sektor kućanstva iz AP-a. Mehanizam već postoji na djelu BiH, ali ga je potrebno proširiti i osnažiti na području cijele države. Fondovima se obezbjeđuju povoljne kamatne stope za realizaciju mjera povećanja energetske efikasnosti.

5. ZAKLJUČAK

Obzirom na kompleksnost državnog ustroja Bosne i Hercegovine neophodno je koordinirano krenuti sa uvođenjem primjenjivih mehanizama, vodeći računa o uzajamnoj povezanosti većine od njih, odnosno činjenici da bilo koji primijenjeni mehanizam sam za sebe ne može dati optimalan rezultat.

Puni učinak se može ostvariti samo u sistemskoj primjeni svih analiziranih mehanizama na svim administrativnim razinama. Da bi se to postiglo, potrebo je obezbijediti jasnu opredijeljenost za uvođenje mehanizama za implementaciju AP-a u BiH svih ključnih sudionika i osigurati potpuno razumijevanje mehanizama i već spomenute njihove povezanosti.

Jedan od načina osiguranja sredstava za EE projekte je svakako uspostavljanje programa sa značajnijim sredstvima za ciljano investiranje istih. Navedene institucije mogu uz tehničku pomoć eksperata iz sektora energetske efikasnosti i OIE ponuditi kvalitetan i atraktivan proizvod na tržištu koji bi se mogao strateški usmjeriti i prilagoditi na određenu korisničku grupu kredita odnosno podsektora iz AP-a.

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1st INTERNATIONAL CONFERENCE
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Croatia, Sisak, September 13th-14th, 2018

INTEGRATED LANDSCAPE CONSIDERATIONS FOR RURAL DEVELOPMENT: AGRICULTURE, LIVELIHOODS, AND ECOSYSTEM SERVICES: AN ASSESSMENT OF PLANNING EXPERIENCES FROM SELECTED MUNICIPALITIES IN ALBANIA

Laura Shumka*

* Albanian University, Tirana, Albania

corresponding author: Laura Shumka, e-mail: shumkalaura@gmail.com

Preliminary note

ABSTRACT

In the current development trends and transitional circumstances there are clear evidences of an increased contestation among agricultural production, biodiversity and ecosystem service conservation from one side, and economic development in rural landscapes in Albania and other countries of the wider region. So far there are poor initiatives and approaches to integrate landscape management, while new interest of scientists, policymakers, and local stakeholders are at an initial stage of recognizing the need to increase the multi-functionality of agricultural landscapes for food production, livelihood improvement, and ecosystem conservation.

Following the new legal requirements and territorial organizations (entire country organized in 63 municipalities) we investigated participants and managers in integrated landscape initiatives in six selected municipalities following the motivations and objectives, stakeholders and participants, activities and investments, outcomes, and major successes and shortcomings. The approach was following the components of landscape multi-functionality: agricultural production, ecosystem conservation, human livelihoods, and institutional planning and coordination. In our survey we were focused on following key questions with respect to considerations in different planning processes and plans produced in six different municipalities in Albania: (i) where and in what contexts are landscape consideration and initiatives taking place? (ii) What are the bases for considering these initiatives, and what challenges and problems do they addressed? (iii) Who is designing and implementing these initiatives, and how are stakeholders involved? (iv) What investments, activities, and governance structures are included in the initiatives? (v) What positive outcomes have practitioners and stakeholders in considered regions? (vi) What were key successes and failures associated with these initiatives? (vii) Which aspects of initiatives' design, structure, and stakeholder participation most strongly predict levels and types of reported outcomes?

Keywords: *landscape planning, landscape ecology, landscape architecture, Albania, rural areas*

1. INTRODUCTION

Following the complex development and increased human interaction, during the last decades it has been broadly accepted that in the different scale of spatial planning and considerations of ecosystems and habitats are playing a crucial role in the overall biodiversity conservation [1]. This leads conservation measures and actions to be closely connected with territorial planning, while success of species, habitats and ecosystems conservation are relaying on good practices of spatial configurations. Figure 1 shows administrative division map and map of the protected areas in Albania.

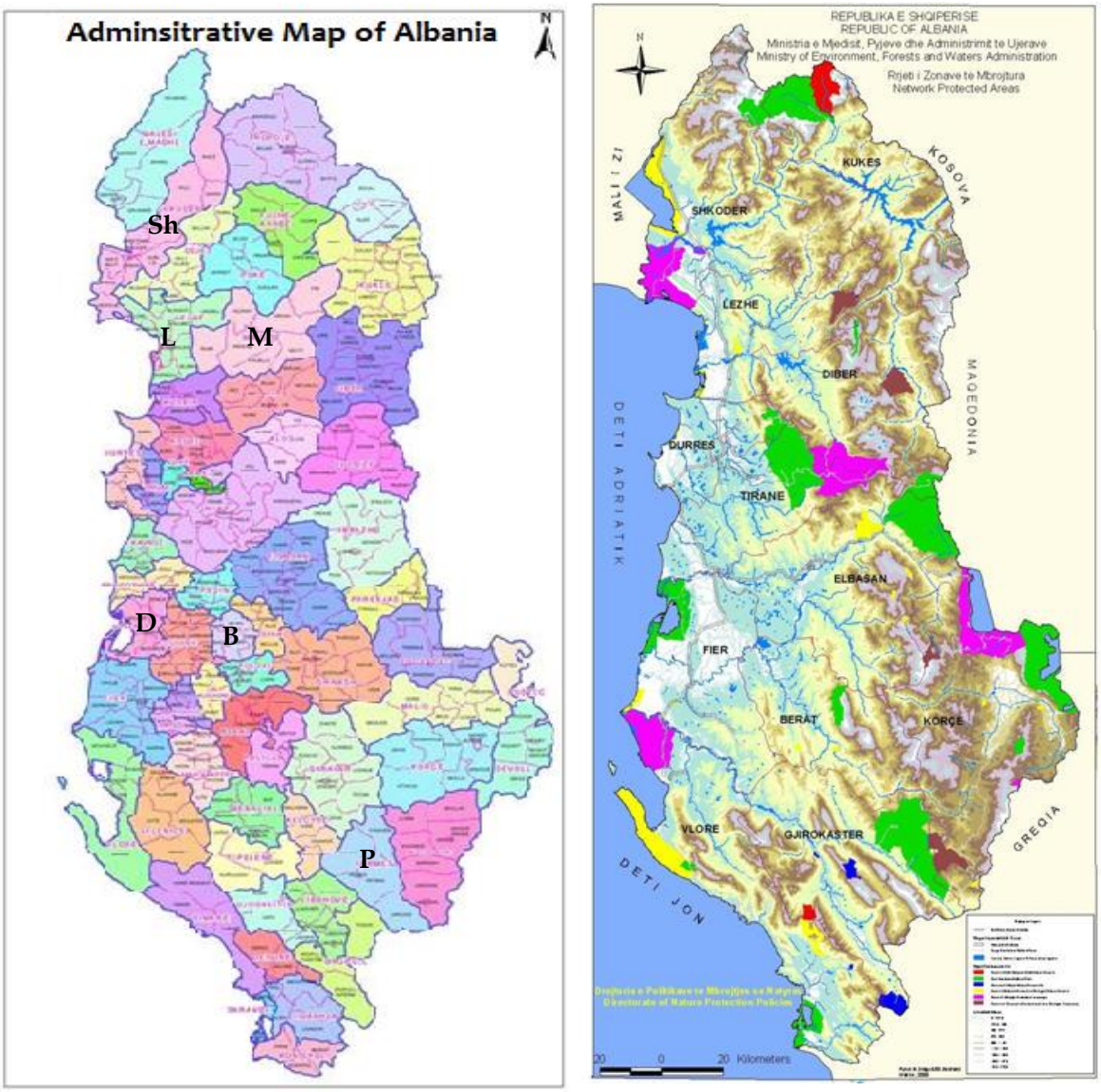


Figure 1. Administrative division map and map of the protected areas in Albania (Sh - Shkodra, L - Lezha, M - Mati, B - Belshi, D - Divjaka and P - Permet) [2, 3]

Connectivity has been long been recognized as a fundamental factor determining species distributions [4 - 10]. Consequently, connectivity measures are widely used in spatial ecology, although different ecological disciplines may use these measures in slightly different contexts [4].

In analysis and consideration of certain area, the better a patch is connected to neighbouring patches, the lower the extinction risk of its species population. Due to political and economic reasons in Albanian before '90, the interventions to different types of ecosystems including forest and pastures, lead to serious fragmentations. In different studies [8, 11, 12], it has been clearly assessed that in heavily fragmented landscapes, species are likely to survive only within networks of patches that are sufficiently connected by dispersing individuals.

The structural connectivity can be measured by analysing landscape structure, irrespective of a species' movement behaviour in the landscape, while functional connectivity explicitly takes this movement behaviour into account [9, 10, 12 - 14].

Why Include Landscape considerations and attributes in Watershed Planning? It is important to include landscape in general and specific planning plans due to the leading role they play in ecosystem function and areas dynamics. Landscapes are a combination of different elements and have an influence on watershed hydrology and water quality as well as contribute to healthy watersheds by influencing important ecological processes. Further on wetlands as a crucial element recycle nutrients, filter certain pollutants, play a role in climatic processes by absorbing and storing elements such as carbon and sulphur, recharge groundwater, and provide energy production and habitat for fish and wildlife. Wetlands also provide goods and services that have economic value. Some examples of the goods wetlands provide include habitat conducive to food production, building products, and fresh water. Some examples of the services wetlands provide include the reduction of peak flows and flood damage, water storage, protection of erodible shorelines, water filtration and particulate removal, and recreational opportunities and amenities. Finally, societies value wetlands for their historic and cultural/religious significance.

Following the Law no. 107/2015 on "Planning and Territorial Development" [15], planning and development of the territory is based on several principles as: i) development must be sustainable and guarantee generation's needs for social equity, economic development and environmental protection; i) the development of the territory is a matter of national importance; it must be fair and the value created should be acquired and absorbed by the society that creates it; iii) planning should harmonize public, private, national and local interests; iv) development should be guided by planning, which is mandatory for all planning authorities under this law; v) planning should take into account the characteristics of the context of the developing territory; vi) harmonization with the European Union's approach in the field of territorial planning and development, as well as environmental criteria, conservation of biodiversity and protected areas, etc.

On the other hand the general local plan has own objectives for: i) balancing national and local needs and interests for developments in the territory; ii) creation of conditions for sustainable development in the territory and according to the principles of the legal framework; iii) direction of development of residential systems and other building systems; iv) regulation of land uses, intensity and extent of construction in the natural, agricultural and urban systems of the territory; v) planning of programs and measures to ensure urban regeneration, environmental protection and sustainable development of natural resources, cultivable land, landscapes and green spaces; vi) regulation of location and programs for public infrastructure and public servitudes, following respective law; vii) regulation of conservation, advancement of the nature protection in accordance with the requirements of the national legislation. The general local plan is implemented through sectoral plans, detailed local plans and development permits [15].

There are in total 800 protected areas (including monuments of nature), which account for over 477.566 hectares, or 16.61 % of the territory of the country. The size of protected areas has been considerably increasing since the Strategy and Action Plan on Biodiversity

[16]. Since 2005, the number of protected areas has more than doubled, out of 5 % to over 16 %. The map and key data for protected areas are part of Annex 8 and 9. The current network of Protected areas includes 119.401 ha coastal areas and 13.261 ha marine areas.

The first marine protected area in Albania was declared in April 2010, the National Marine Park, Karaburun-Sazan. In the Ramsar Sites (wetlands of international importance, as part of important water habitats for water birds include: the wetland of Karavasta; wetland of Butrint; Shkodra lake and wetland complex of Buna river and lakes of the area of Prespa as the 4th Ramsar site in Albania through DCM no. 489, of 13.06.2013. Attachment 10 describes the location of Ramsar sites in the map of Albania. Albania currently has 4 wetlands of international importance, of a surface of 98.181 hectares.

2. EXPERIMENTAL

The approach was following the components of landscape multi-functionality: agricultural production, ecosystem conservation, human livelihoods, and institutional planning and coordination. In our survey we were focused on following key questions with respect to considerations in different planning processes and plans produced in six different municipalities in Albania: (i) Where and in what contexts are landscape consideration and initiatives taking place? (ii) What are the bases for considering these initiatives, and what challenges and problems do they addressed? (iii) Who is designing and implementing these initiatives, and how are stakeholders involved? (iv) What investments, activities, and governance structures are included in the initiatives? (v) What positive outcomes have practitioners and stakeholders in considered regions? (vi) What were key successes and failures associated with these initiatives? (vii) Which aspects of initiatives' design, structure, and stakeholder participation most strongly predict levels and types of reported outcomes? This method is a modified [17] approach.

The survey questionnaire included a combination of closed and open-ended questions oriented around our seven research questions to solicit information on the initiatives' location and context, motivations and impetus, participants and stakeholders, investments and governance structures, outcomes, and most and least successful aspects. The questions related to investments and outcomes were designed to gather information on four key activity domains: agriculture, conservation, livelihoods, and institutional planning and coordination.

3. RESULTS AND DISCUSSION

This study provides the first broad characterization of integrated landscape management in the six selected municipalities covering different regions in Albania and that is based on analyses of general local plans following expert's judgment with contexts of conservation, agriculture, livelihood and climate change (table 1, figure 2).

Table 1. Total scoring results for different motivation categories in six selected municipalities in Albania

Motivations	Shkodra	Lezha	Belshi	Divjaka	Permet	Mat
Water protection	55	20	30	30	35	20
Soil protection	10	15	25	25	20	20
Biodiversity conservation	35	25	20	40	30	25
Halt degradation of natural resources	35	15	30	30	30	30
Enhance food security	30	20	15	20	40	15
Reduce negative impacts of agriculture	15	15	30	15	15	10
Increase locals prosperity	35	30	40	40	45	25
Adaptations to climate changes	15	10	10	15	10	10
Improve the health conditions	35	35	35	30	50	35
Reduce conflicts	10	10	20	10	10	10
Improve livestock production	25	29	10	10	35	30

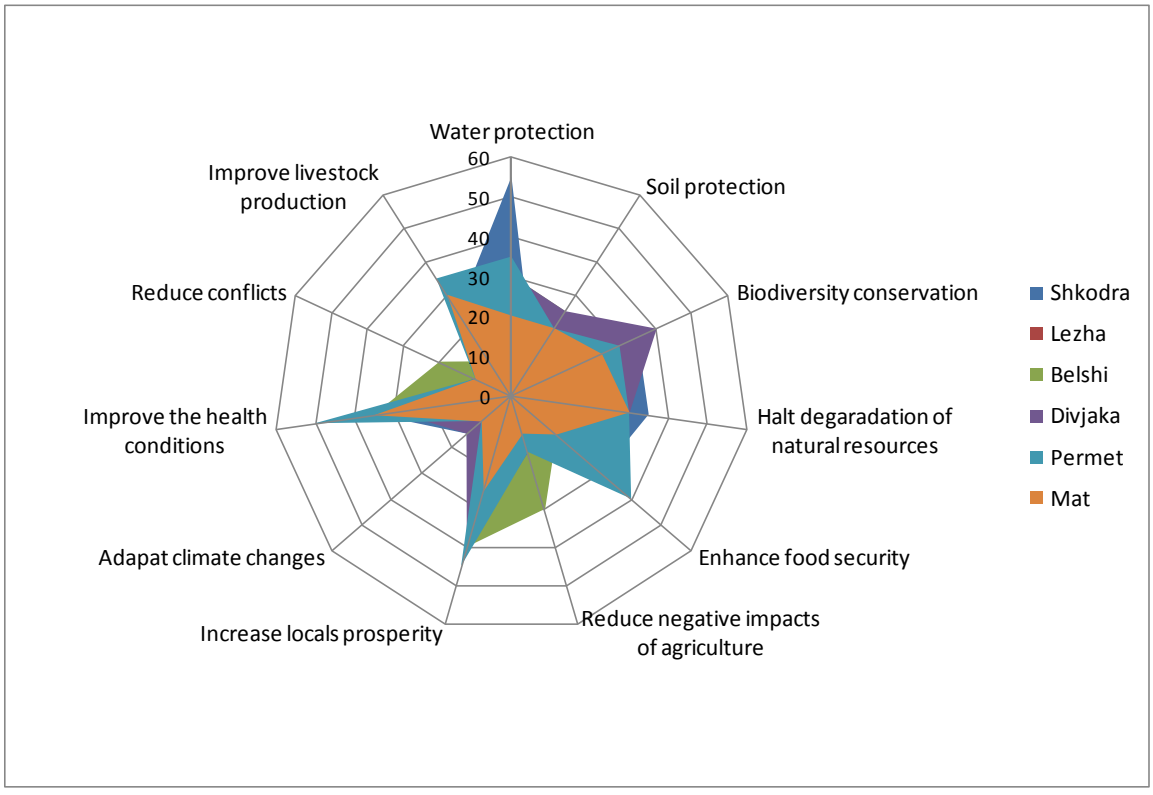


Figure 2. Scoring results for different motivation categories in six selected municipalities in Albania

The basis of the expert judgment approach is a scoring system from 1 as a minimum to 100 as the maximum points. This approach as such is informative for understanding the current state of this field, the challenges and potential benefits of applying such an approach, and the needs for additional analytical research. The size and diversity of the survey sample suggests that integrated landscape management is being poorly applied across the country to address a variety of challenges grouped in four categories: conservation, agriculture, livelihood and climate change.

Following figure 1, all considered municipalities has included in their territories different protected areas category as national park (Category II of IUCN) or landscape protected area (Category IV of IUCN). Beside this as it can be seen from the data presented in table 1 and figures 2 and 3, the general local plans are lacking the requirements for balancing the different motivation categories.

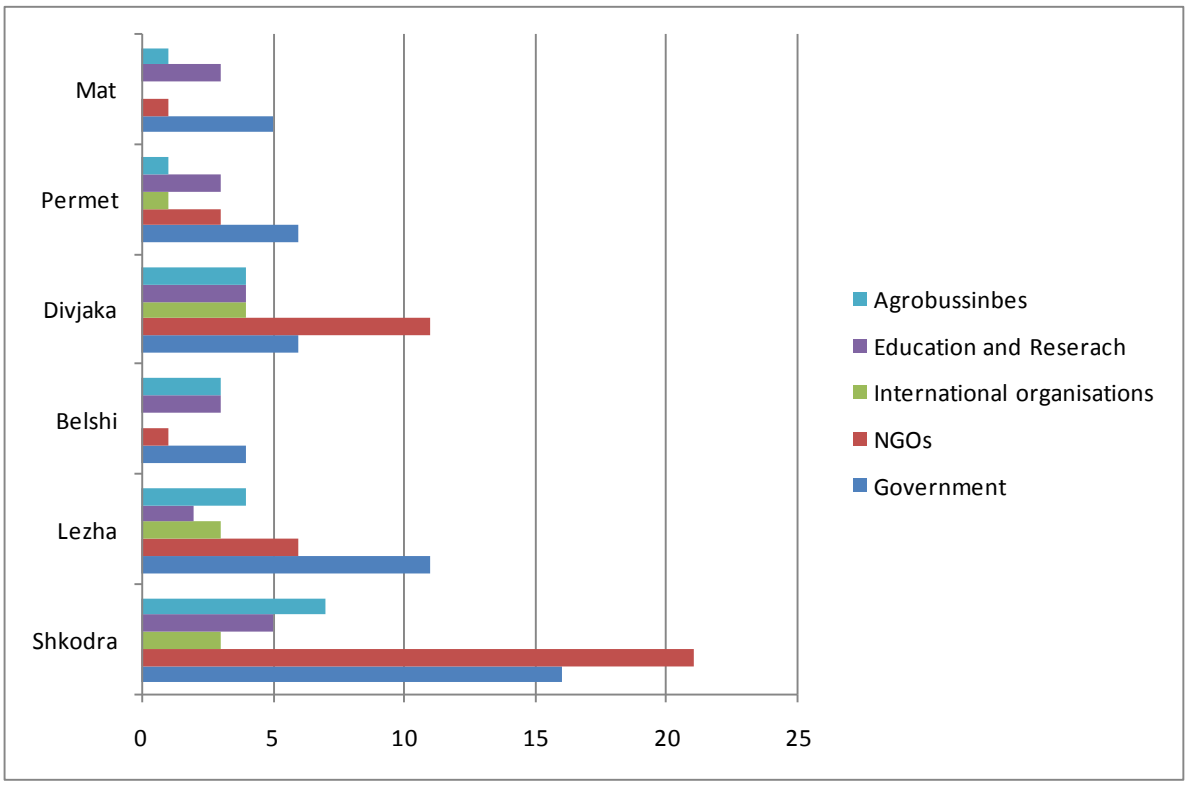


Figure 3. Recorded number of initiatives that included at least one stakeholder group from each of the stated categories within different municipalities

The efforts of integrated landscape management into planning process within different regions in Albania have a history of a couple decades before ’90, being mostly considered within protected area system, while due to ‘lack of planning’ and chaotic developments in the last three decades was facing serious lacking. As integrated landscape management can take many forms in the interest of clearly bounding the purpose of this survey [17], we focus our assessment on integrated landscape initiatives, being defined as projects, programs, platforms, initiatives, or cluster of activities [17], that: explicitly seek to simultaneously improve food production, biodiversity or ecosystem conservation, and rural livelihoods; work at a landscape scale and included participatory planning, policy, management, or support activities; (3) involve inter-sectoral coordination or alignment of activities, policies, or investments at the level of ministries, local government entities, farmer and community organizations, NGOs, donors, and/or the private sector; and how they are highly participatory, supporting adaptive, collaborative management within a social learning framework [10, 17, 18]. Following the use of such parameters we see that in number initiatives is higher in Shkodra municipality (Government 16, and NGOs 22), while the lower number of initiatives are recorded in municipality of Mat (figure 3). Limited efforts like mitigations and adaptations towards climatic changes, were evidenced through all general local plans for territories in all municipalities (with a maximum score of 10 out of 100), while in some of them as Lezha, Shkodra and Divjaka are facing serious threats with particular focus at the coastal areas.

As presented above, this study provides a ground and expert characterization of the practice of integrated landscape management in six selected municipalities following prepared general local plans for territorial planning, but it was not applied to independently evaluate or attribute the impacts of individual plan in quantitative terms. To that fact there are needed further surveys for understanding of landscape approaches and their relative current effectiveness in entire planning process.

4. CONCLUSION

Following our survey it can be concluded that there is a need of an integrated approach for understanding the landscape approaches and their relative current effectiveness in entire planning process. Further on it is important to include landscape in general and specific planning plans due to the leading role they play in ecosystem function and areas dynamics. The particular components as wetlands has to be clearly integrated since they are a crucial element that recycle nutrients, filter certain pollutants, play a role in climatic processes by absorbing and storing elements such as carbon and sulphur, recharge groundwater, and provide energy production and habitat for fish and wildlife.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

DIVERSITY OF ZOOPLANKTON AND ITS DISTRIBUTION IN KARAVASTA LAGOON (CENTRAL ALBANIAN ADRIATIC)

Spase Shumka*, Enkeleda Nikleka*

* Agricultural University of Tirana, Faculty of Biotechnology and Food, Tirana, Albania

corresponding author: Spase Shumka, e-mail: sprespa@gmail.com

Original scientific paper

ABSTRACT

Zooplankton sampling was carried out in July 2015 in the 6 different locations. The samples were collected using a vertically towed conical net (40 cm diameter, 1 m length, 50 µm mesh-size) equipped with a closing mechanism. The hauls were conducted in one interval form the bottom to the surface approximately 0 - 2 m. All sampling was carried out during daylight hours. Filtered water volume was estimated using a Hydro-Bios flow meter attached to the mouth of the net. Sample fixation took place immediately after collection in a 4 % borax-buffered formaldehyde solution. Identification and enumeration of zooplanktonic taxa was performed at the laboratory under an inverted microscope under up to 400x magnification. Rotifers appear to be the most common group within entire lagoon. Different situation is been registered with Copepods-Calanoida, Copepods-Cyclopida and Copepods-Harpacticoida groups that were mostly abundant in the outer part of the lagoon, while the inner part is been less populated.

Increased total number of rotifers in the inner part of the lagoon might be explained with larger values of Nitrates (0.018 mg/l) and Ch-a (2.94 mg/l) in compared with respectively 0.011 mg/l nitrates and 0.617 mg/l Ch-a in the outer part of the lagoon directly connected with marine water. Considering that this is the first report on the zooplankton of this area, and no previous comparable data, this survey is important for the investigation of the different factors affecting the zooplankton community, and could constitute a basis for developing a monitoring process for the biotic elements of the Karavasta lagoon ecosystem.

***Keywords*:** *lagoons, Coastal Adriatic, water quality, indicators, degradation*

1. INTRODUCTION

Albania is located along the eastern seaboard of the Adriatic and the Ionian Seas, bounded by Montenegro and Kosovo to the North and Northeast, Macedonia to the East and Greece to the South. There are significant water resources in the form of large lakes, flooded

valleys, agricultural and drinking water reservoirs, irrigation canals, coastal lagoons and of course the Adriatic and Ionian Seas. Albania has a coastline of about 450 km and territorial waters 12 miles wide; moreover, there are several coastal lagoons with a total surface area of 10,000 ha, three lakes with a total surface of 300 km^2 and around 700 reservoirs with a total surface of 12,000 ha [1 - 4]. The fishery sector in Albania has regional importance though on national scale it is not as critical as agriculture. This sector is providing revenues to government from license fees and other taxes. At the same time, it is receiving no government subsidies and pays the same tax on fuel, the major expenditure like the other sectors of Albanian economy.

The potential sustainable catch from these waters has been assessed at between 14,000 and 17,000 t of fish and shellfish annually (about 8000 - 9000 t of marine fish; 3000 t harvested from lagoons, inland waters and aquaculture; and 3000 t of bivalve molluscs. The contribution from the marine, freshwater and mollusc sectors (the published statistics do not seem too precise during the nineties) has remained roughly constant with an average percentage contribution 57 - 0 %, 20 – 23 % and 17 – 23 % for the years 1984 to 1993. In the forty-five years to 1991, Albania was governed as a largely closed command-led economy. Under this structure the fishery resources of the country were closely managed for productivity using systems of communal management and exploitation. Marine harvests exceeded 8,000 t per year, much of it in the form of small pelagics, whilst freshwater harvests were in excess of 2,000 t per year, with the bulk in the form of Chinese carps. In addition, mussel cultivation in Butrinti lagoon in the south of the country yielded production of several thousand tons a year [1, 5].

Situated at the Myzeqeja costal larger plain of Albania, the Karavasta complex represents the largest wetland site of Albania. The overall wetland complex, composed of lagoons (Karavasta,Godulla, Spiaxho; ca. 5000 ha), sand dunes and a river mouth, has a surface of 10000 ha. It is situated between the Shkumbini River and Terbufi Canal in the north, and the Canal of Myzeqeja and Semani River in the south. The Karavasta lagoon is the largest surface (4100 ha) of this wetland complex; it is 15.4 km long and 4.1 km wide. The maximum depth is 1.3 m with an average depth of 0.7 m. The lagoon is divided from the sea by Divjaka pine forest and Godulla lagoon. Agricultural land borders the lagoon. The coastal morphology of Karavasta lagoon was highly dynamic during the last 135 years because of the changes which occurred to the Shkumbini and Semani river deltas [6 - 8]. Karavasta is connected to the sea via three channels [9]. The northern inlet, at present, is completely blocked and disconnected from the sea. The central and southern inlets communicate with the Godulla lagoon, which is connected to the sea by two other shallow channels. The creation of the drainage canals of Terbufi and Myzeqe in the 1980s, together with associated irrigation and drainage schemes, has isolated Karavasta from a significant part of its former drainage basin area. Early in its formation, which goes back to about 1860, the Karavasta lagoon covered double the area it now occupies. The entire system is under various human impacts. According to [10], even if the Divjaka urban area is not drained to the lagoon, part of its polluting load discharging from Terbufi Canal may reach the lagoon because its plume is directed mainly southward and close to the coast during spring and summer. Sediment analysis from core samples [1] showed that organic matter made up between 7 % and 18 % of the dry weight of the sediment and was most prevalent in the sediment of the east and the centre of the lagoon. The rapid current developments with beach installments, housing, numerous bars, hotels and restaurants is a pressure of concern that along with increased number of summer tourists (number during weekends of August rises up to 9000 visitors per day) appeals for preventive measures and integrated management of entire complex.

Zooplankton organisms represents a very important element in the food webs of lagoon environments not only as consumers of primary production [11, 12], but also as food

items for juvenile fish species of high commercial value [13]. In transitional water bodies zooplankton components are characterized by seasonal outbursts of rotifers, small-sized calanoid copepods and meroplanktonic larvae populations, mainly during the summer-autumn period [14].

2. EXPERIMENTAL

Zooplankton sampling was carried out in July 2015 in the 6 different locations (figure 1). The samples were collected using a vertically towed conical net (40 cm diameter, 1 m length, 50 μm mesh-size) equipped with a closing mechanism. The hauls were conducted in one interval form the bottom to the surface approximately 0 - 2 m. All sampling was carried out during daylight hours. Filtered water volume was estimated using a Hydro-Bios flow meter attached to the mouth of the net. Sample fixation took place immediately after collection in a 4 % borax-buffered formaldehyde solution.

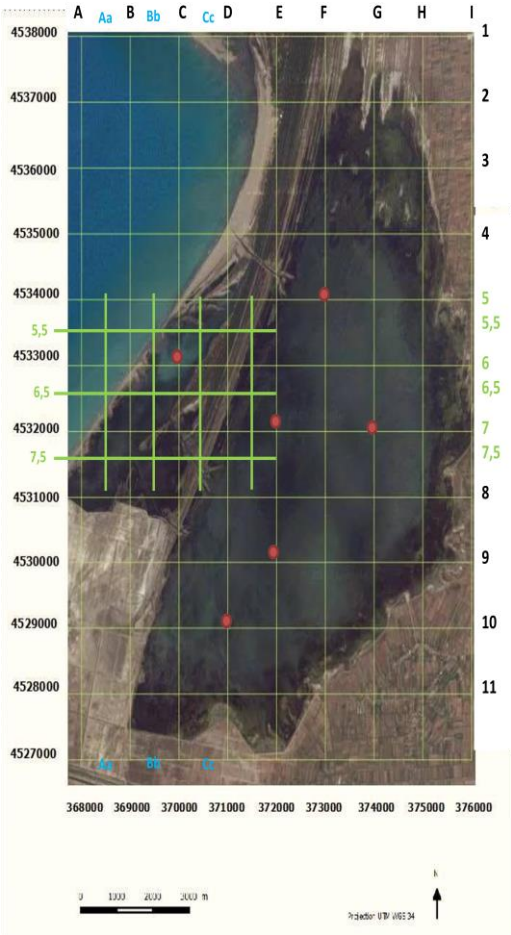


Figure 1. Sampling sites for zooplankton

Identification and enumeration of zooplankton taxa was performed at the laboratory under a inverted microscope under up to 400x magnification. Species identification was based on the keys of [15] for copepods, [16] for rotifers and [17] and [18] for tintinnids. Zooplankton abundance was calculated in terms of density (ind l^{-1}) from aliquots taken with a

Folsom splitter. Aliquot size ranged from 1/1 (whole sample) to 1/64, depending on the density of zooplankton organisms in the sample. In addition, for the estimation of the density of the smaller groups, the whole sample (total volume of 100 ml) was investigated under the microscope in modified Sedwick- Rafter cells. Copepod exuvia and dead copepod carcasses (e.g. copepods in advanced decayed condition) were identified and counted for each sub-sample, but they were not included in zooplankton abundance.

3. RESULTS AND DISCUSSION

This study provides preliminary information on the particular biotic characteristics of Karavasta lagoon through a one-month investigation, not being surveyed at all during the previous time, although the results from the previous mostly hydrological investigation revealed concerns of the hydromorphological structure, as well as the abiotic elements and the trophic condition of the area [1, 8, 19]. In the table 1 are presented the identified species covering main zooplankton groups including Rotifers, Copepoda, Cladocera, Protozoa and Polychaete larvae, while in the table 2 are presented the absolute number of different zooplankton taxa (ind.l^{-1}) .

Table 1. List of the zooplankton taxa recorded in Karavasta Lagoon

ROTIFERS
Bdelloida
Brachionus calyciflorus (Pallas, 1766)
Conochilus unicornis (Rousselet, 1892)
Filinia longiseta (Ehrenberg, 1834)
Gastropus stylifer (Imhof, 1891)
Kellicottia longispina (Kellicott, 1879)
Keratella quadrata (Müller, 1786)
Lecane sp.
Ploesoma hudsoni (Imhof, 1891)
Synchaeta sp.
COPEPODA
Calanoida
Calanipeda aquaedulcis (Kritchagin, 1873)
Paracartia latisetosa (Kritchagin, 1873)
Harpacticoida
Euterpina acutifrons (Dana, 1847)
Harpacticus gracilis (Claus, 1863)
Microsetella sp.
Cyclopoida
Oithona nana (Giesbrecht, 1893)
Nauplii
CLADOCERA
Podon sp. (Lilljeborg, 1853)
PROTOZOA
Tintinnids
Favella ehrenbergii (Claparéde & Laachmann, 1858)
POLYCHAETE LARVAE

Table 2. Absolute number of different zooplankton taxa (ind.l^{-1})

Taxa	Sampling stations					
	F5	G7	E7	E9	D10	C6
Protoza-Tinntinids	3	4	3	3	4	2
Rotifers	18	21	23	20	19	11
Copepods-Calanoida	4	4	5	4	6	20
Copepod-nauplii	22	23	12	17	21	33
Copepods-Harpacticoida	2	1	2	1	1	4
Copeods-Cyclopida	3	4	4	2	2	8
Cladocerans	0	0	3	3	4	12
Polychaeta larvae	0	3	0	1	1	0

Rotifers appears to be the most common group within entire lagoon, where the larger number is registered in E7 and E9 that is the central part of the lagoon, while the lower number in C6, the outer part directly connected with sea. Different situation is been registered with Copepods- Calanoida, Copepods-Cyclopida and Copepods-Harpacticoida, groups that were mostly abundant in C6 the outer part of the lagoon, while the inner part is been less populated (figure 2).

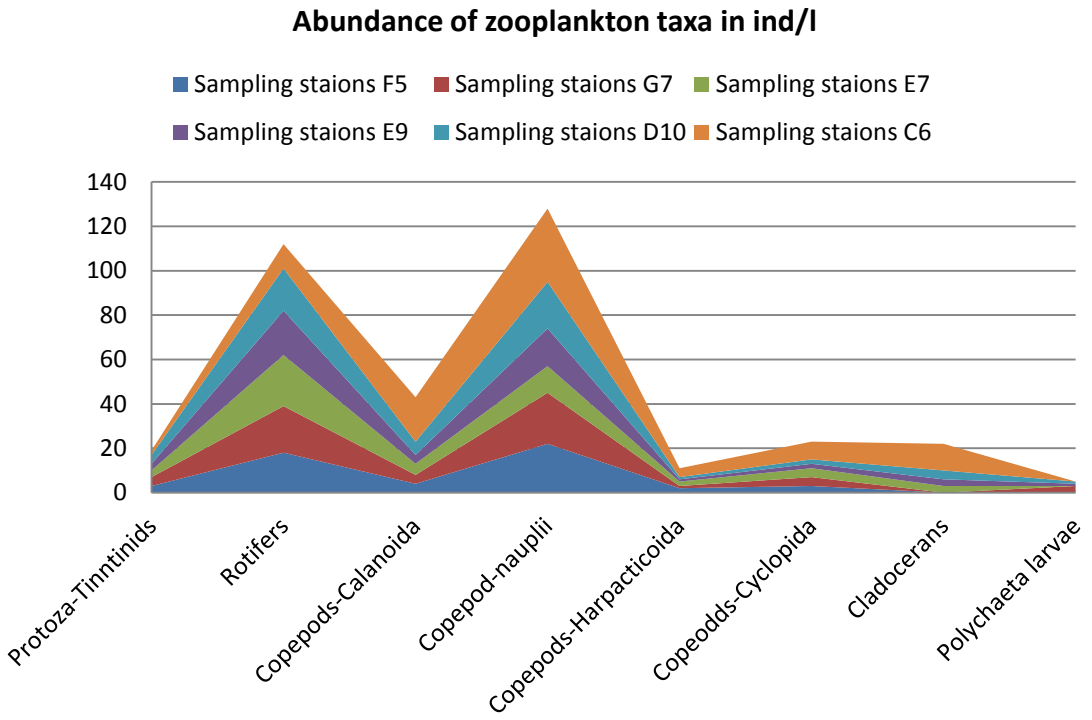


Figure 2. Abundance of zooplankton taxa in ind.l^{-1}

Increased total number of rotifers in the inner part of the lagoon might be explained with larger values of Nitrates (0.018 mg/l) and Ch-a (2.94 mg/l) in E7 compared with respectivelly 0.011 mg/l nitrates and 0.617 mg/l Ch-a in C6, the outer part of the lagoon directly connected with marine water.

Based on other studies it seems that salinity is one of the most important parameters in environments with strong zonation patterns [20], or in cases where man-made changes have altered the freshwater inputs in the ecosystem [21, 22]. In this study, is difficult to do interpretation due the occasional sampling and that's way for further discussions there is a need for seasonal sampling and survey in order to discover any significant influence to zooplankton assemblages.

Considering that this is the first report on the zooplankton of this area, and no previous comparable data, this survey is important for the investigation of the different factors affecting the zooplanktonic community, and could constitute a basis for developing a monitoring process for the biotic elements of the Karavasta lagoon ecosystem.

In general the transitional waters and coastal lagoons possess important natural and economic values for the national economy and the whole Mediterranean region. Advanced data on of zooplankton would serve as good source of information on their productivity and stress conditions including eutrophication process. Further surveys and information covering interrelationship among different lagoon components could help in preventing the risks of further deterioration. Considering an integrated monitoring system that will cover zooplankton as well would help authorities and other interested agencies to understand the ecosystem functioning, proper management and conservation.

4. CONCLUSION

This survey is an important step towards investigation of the different factors affecting the zooplankton community, and could serve as a basis for developing an integrated monitoring system for the lagoon ecosystem. Further data on of zooplankton would serve as good source of information on coastal and transitional ecosystems productivity and an effective determination of measures for halting further eutrophication process.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

THE USAGE OF ALGINATE BEADS FOR PHOSPHATE REMOVAL FROM WATER

Marjana Simonič*

* University of Maribor, Faculty of chemistry and chemical engineering, Maribor, Slovenia

corresponding author: Marjana Simonič, e-mail: addrmarjana.simonic@um.si

Original scientific paper

ABSTRACT

The purpose of this research was to remove phosphate ions from water with adsorption on synthesised beads and comparison between PVA- alginate beads and those with maghemite nanoparticles (PVA-M-beads). By changing different parameters such as time of adsorption, quantity of beads and quantity of maghemite nanoparticle, the efficiency of phosphate removal with both PVA- alginate beads types was studied.

The results of phosphate removal from water using beads have good adsorption activity with the PVA- alginate beads as well as with the maghemite PVA- alginate beads. The removal efficiency of phosphate removal achieved with PVA beads was 97.9 % and PVA-maghemite-beads 98.5 %, respectively. Acceptable decrease after 300 minutes at 98 % of removal with PVA-maghemite-beads was achieved. Concentration decreased below drinking water limit value of 0.1 mg/L PO_4^{3-}.

***Keywords**: maghemite beads, phosphate removal, desorption*

1. INTRODUCTION

Large amounts of phosphate in water could lead to environmental pollution, known as eutrophication. Among the available techniques adsorption is believed to be preferable approach due to many advantages, such as easy operation, high cost effectiveness, high efficiency, etc. [1].

Different natural immobilisation media, such as alginates, chitosan, and cellulose derivatives have been used for algal cell immobilisation, nevertheless alginate is still one of the more frequently used carriers [2]. The immobilization of algae is simple and cost effective.

PVA hydrogel beads prepared by chemical cross-linking in the saturated boric acid solution are low cost, mechanical stable and non-toxic adsorbent [3]. Sodium alginate could be added to provide spherical skeleton for PVA hydrogel. Beads showed good adsorption

properties for phosphate [3]. This way PVA-maghemite-alginate beads were formed. PVA-M-beads were used for efficient removal of iodine from water. [4]

The idea of present study was to enhance adsorption activity of PVA alginate beads towards phosphate. Beads were modified by maghemite. The aim of the research was to study the removal of phosphate from water using PVA-alginate beads. The efficiency was then compared with that of PVA-maghemite-alginate beads. The influence of adsorption time and concentration of maghemite. Desorption was studied. PVA-M-beads were chosen instead of calcium alginate beads due to maghemite leakage [5].

2. EXPERIMENTAL

2.1. Preparation of maghemite nanostructures

Nanoparticles were prepared in the form of nanosheets by a topotactic transformation of a γ-FeO(OH). $FeCl_2 \cdot 4H_2O$ (2 mmol) was dissolved in 100 mL of milli-Q water, which had previously been de-oxygenated. The solution was stirred under a flow of Ar (300 mL/min) for a period of 30 min, after which 2 mL of pyridine was added. The solution was exposed for 1 h in an argon flow. After that, oxygen gas was vigorously bubbled through the reaction mixture with a flow of 300 mL/min for 15 min, followed by 3 h with an oxygen flow of 50 mL/min. The solution immediately turned orange as the pyridine complex oxidized to γ-FeO(OH). The solid product was centrifuged and washed several times with distilled water. The dehydroxilation of the γ-FeO(OH) was performed in a furnace at 280 °C for 1 h in air.

2.2. Preparation of PVA beads

12 g of PVA were dissolved in100 mL of Millipore water at 120º C for 3 h. 1 g of alginate was dissolved in 20 mL water. Both solutions were mixed together.

For preparation of PVA alginate beads with maghemite 0.1 g of maghemite was added into the solution. The solution was stabilised in the solution containing 2 % $CaCl_2$ and 6 % boric acid for 24 h. Then the beads were rinsed and kept in Millipore water for further experiments. In figure 1 PVA- alginate beads are shown at the beginning (a) and after washing with $CaCl_2$ and boric acid. (b).

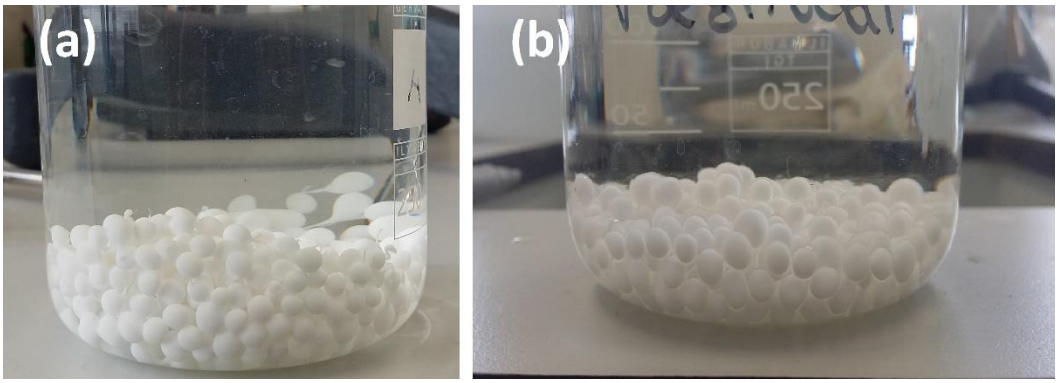


Figure 1. PVA-alginate beads (a) and after washing (b)

Figure 2 shows the PVA- alginate beads with maghemite (a) and after washing with $CaCl_2$ and boric acid (b).

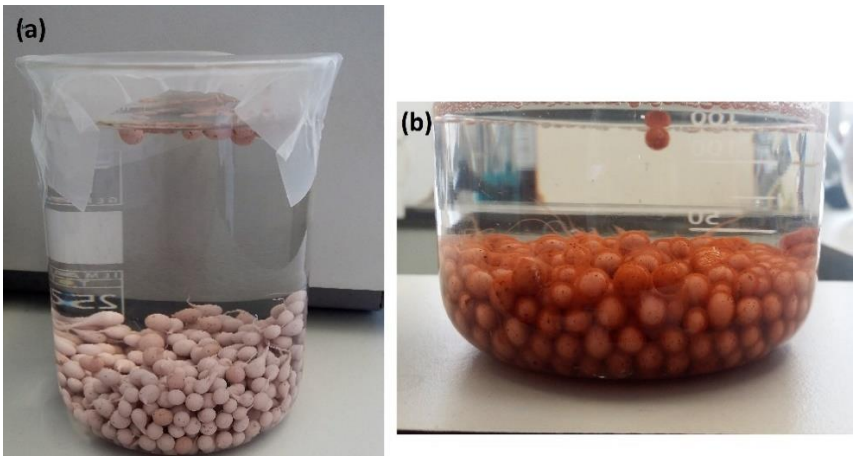


Figure 2. PVA-alginate beads with maghemite (a) and after washing (b)

2.3. Adsorption of phosphate

The phosphate removal rates were then determined by mixing 50 g of each PVA-beads with reaction vessels containing 50 ml of phosphate solution containing 1.375 mg PO_4^{3-}. The concentration was set to the highest concentration of P measured in Slovene ground water [6]. Phosphate solutions were prepared by diluting stock solution with concentration 1 g/L PO_4^{3-} ions. The normal range for pH in ground water systems is 6.5 to 7.5 [6], therefore the adsorption was studied at pH 7. The solution pH condition was adjusted to 7.0 with 0.1 M of HCl and NaOH using a portable pH-meter (WTW Multi 3410, Germany); the reaction vessels were then homogeneously shaken in an orbit shaking incubator at 250 rpm with controlled temperature at 20 °C for 48 h. The samples were immediately filtered using a filter with an opening of 0.45 μm; the phosphate concentrations in the filtrates were then analysed using an Agilent Spectrophotometer. Removal efficiency of phosphate removal (η) is calculated following equation (1):

$$\eta = (c_i - c_f)/c_f \cdot 100 \quad (1)$$

where

c_i is initial concentration and c_f is final phosphate concentration.

After checking the initial and final phosphate concentrations, experimental results have been analysed using three adsorption isotherm Freundlich model, which is expressed as follows:

$$q_e = K \cdot c_e^{1/n} \quad (2)$$

where

q_e is the adsorbed amount of phosphate per unit weight of adsorbent (mg g^{-1}) at an equilibrium concentration of adsorbate in bulk solution (C_e, mg L^{-1}). K is Freundlich constant and n is the heterogeneity factor.

2.4. Desorption of phosphate from beads

The reusability was assessed by consecutive cycles of adsorption/desorption. The same beads were used every cycle. After adsorption process 15 g of maghemite PVA beads were shaken for 60 mins in 200 mL 0.1 M HCl. After desorption supernatant was analysed for the desorbed phosphate ions. The desorbed beads were then recycled for adsorption of phosphate several times. The regenerative efficiency of the PVA-M-beads was determined.

3. RESULTS AND DISCUSSION

PVA-M-beads contained 0.1 g maghemite /100 g PVA- alginate. BET, pore radius and pore volume were determined at 9.38 m^2/g, 1.4 mm and $7.42 \cdot 10^{-2}$ cm^3/g, respectively. The removal efficiency of phosphate removal achieved with PVA beads was 97.9 % and PVA-M-beads 98.5 %, respectively. Acceptable decrease after 300 minutes at 98.0 % of removal with PVA-M-beads was achieved as seen from figure 3. Comparing with PVA-beads it is a great improvement. Only 80 % of phosphate was removed after 300 minutes.

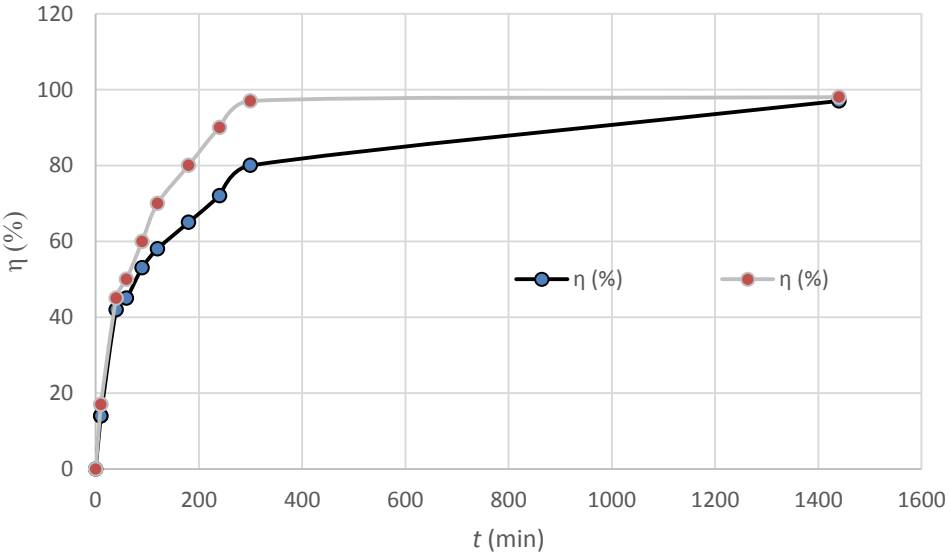


Figure 3. Efficiency of phosphate removal with alginate beads

In the next step the concentration of maghemite was increased by using increased volume of the same beads. The results are seen from figure 4.

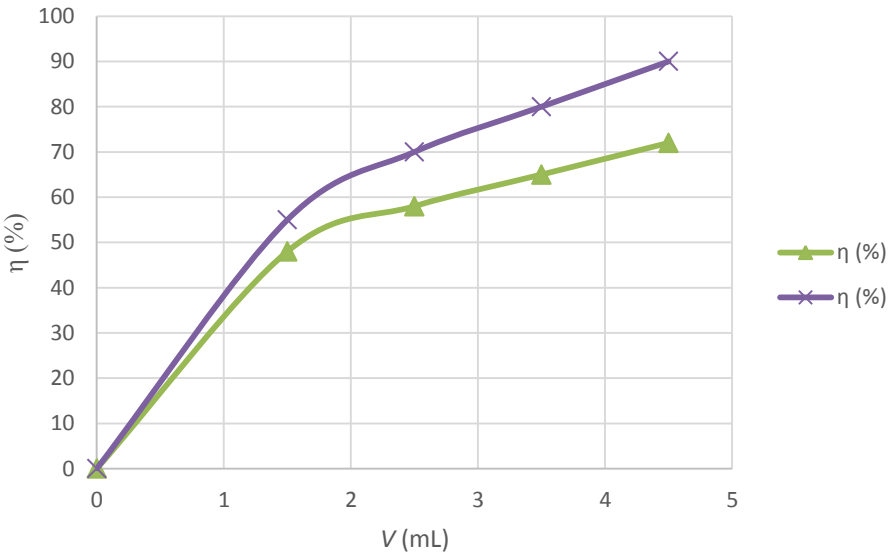


Figure 4. Efficiency of phosphate removal in dependence of alginate beads volume

If the volume of PVA- beds was doubled, the efficiency was increased by 15 %. The results achieved with PVA-M-beads were even better, while by doubling the volume of beads the efficiency of phosphate removal increase was determined by 21 %.

The relationship between adsorption capacity and aqueous equilibrium concentration is called the equilibrium isotherm and it is very important in describing the mechanisms of an adsorbent for adsorbing a target pollutant. PVA-M-beads showed better adsorption potential, therefore, adsorption isotherm with PVA-M-beads was performed. From figure 5 it is seen that Freundlich isotherm fits well the experimental data and the value R^2 was determined above 0.99.

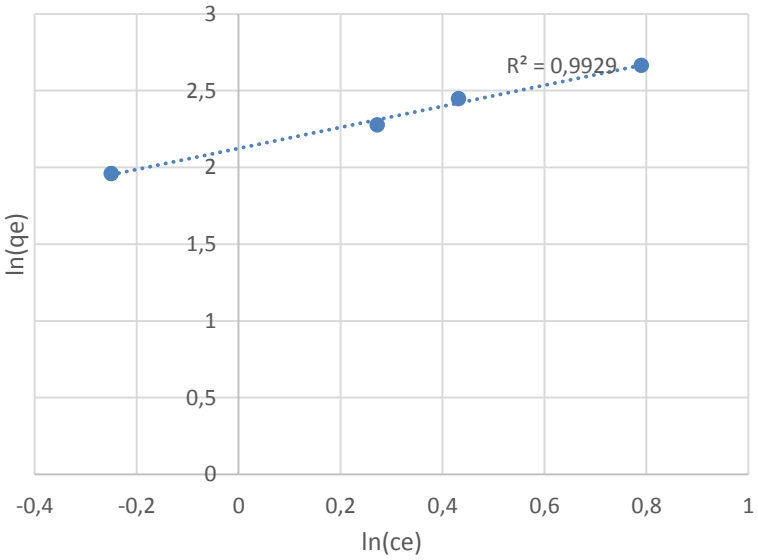


Figure 5. Freundlich adsorption isotherm

3.1. Desorption process of phosphate

In order to evaluate the reusability of the PVA beads, the consecutive adsorption–desorption process for five times by using the same PVA beads were carried out. The results for PVA and PVA-M-beads are shown in table 1. It can be seen that the phosphate adsorption capacity after onetime adsorption–desorption process using PVA-beads drastically decreased by about 10 %. The phosphate adsorption capacities of the PVA-M-beads from the first cycle to the fifth cycle were 5.5 (mg/g P), 5.0 (mg/g P), 5.0 (mg/g P), 5.0 (mg/g P) and 4.5 (mg/g P), respectively. From table 1, it is seen that PVA-beads could be successfully desorbed up to 3 times, while PVA-M-beads could be desorbed up to 5 times. Desorption still remains 82 %. In case of PVA beads it drops more rapidly.

Table 1. Removal efficiency after desorption (%)

	PVA	PVA-M
Desorption 1st cycle	90	99
Desorption 2nd cycle	81	90
Desorption 3rd cycle	79	90
Desorption 4th cycle	71	90
Desorption 5th cycle	56	82

The results are in accordance with another study [3] as they determined the adsorption after 5th cycle around 30 % decrease of adsorption activity. Using PVA-M-beads the decrease in desorption was not so high till 5th cycle.

4. CONCLUSION

PVA- alginate beads and those with maghemite nanoparticles (PVA-M-beads) were applied to determine their characteristics and estimate phosphate adsorption properties including equilibrium isotherms. The concentration of maghemite nanoparticles in PVA-M-beads was determined at 0.1 g/100 g PVA- alginate. It allowed the removal of 2.75 mg of phosphate ions from water while in PVA-beads it was 21 % lower. At twice higher concentrations of maghemite in PVA-M-beads the adsorption increased to 5.5 mg P/g maghemite while in PVA-beads it remains 20 % lower. The obtained phosphate adsorption results indicated that a Freundlich model fits the experimental data suitably well. The phosphate adsorption capacity of 27.5 mg/g P suggests that PVA-M-beads could be used as an adsorbent for phosphate adsorption from aqueous solutions.

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Acknowledgements

The author acknowledges the program Process System Engineering and Sustainable Development, ID P2-0032, was financially supported by the Slovenian Research Agency.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

THE EFFECT OF WASTE DENTAL METALLIC MATERIALS ON ENVIRONMENT

Ljerka Slokar*, Andreja Carek**

* University of Zagreb, Faculty of Metallurgy, Sisak, Croatia
** University of Zagreb, School of Dental Medicine, Zagreb, Croatia

corresponding author: Ljerka Slokar, e-mail: slokar@simet.hr

Review paper

ABSTRACT

Dental medicine is a profession dedicated to promoting and enhancing oral health and well-being and therefore plays a significant role in human health. Dental practices produce many types of dental wastes, such as: heavy metals and biomedical waste, which could cause harm to the environment if it is disposed improperly. Among them, mercury, silver and lead are the most harmful for humans and the environment as well. In order to reduce the impact on the environment dentists should take all possible activities to completely avoid the production of any waste or at least try to reduce the amount of waste to a minimum. In that context, eco-friendly dentistry as a new approach to dental practice is developed. It is based on use of non-toxic products, waste reduction, energy conservation and pollution prevention. Finally, education regarding the proper management and disposal of waste from dental offices needs more attention.

***Keywords**: dental medicine, human health, environment, metallic materials, dental waste*

1. INTRODUCTION

Dental medicine as a branch of medicine plays a significant role in human health. It is a profession dedicated to promoting and enhancing oral health and well-being. For that purpose, dentists use a variety of materials and equipment which present potential challenges to the environment. These materials include heavy metals and biomedical waste. Environment contamination with these materials is a worldwide concern [1 - 3].

Dental practices produce many types of dental wastes which could cause harm to the environment if it is disposed improperly. Therefore, an effective management is required to minimize their environmental effect [4].

Dental waste is classified as medical waste, which is divided into two major groups: common waste and special waste. Since the first one is similar, in terms of quality, to

municipal waste it should be treated in accordance with the law regarding to municipal solid waste. Special waste include: infectious, chemical and radioactive waste. Each of them requires a certain management method. In order to prevent a spreading of the materials containing the dangerous and pathogenic agent that can cause a health and environmental risks, these two types of waste should not be mixed with the municipal waste. Namely, the most important work in the field of dental waste management is to prevent the mixing of all the components, because the components of dental wastes have different characteristics. Therefore, the management method should be performed on the basis of these characteristics. [5]

The waste products generated by dental laboratories impact on the environment as well on human health due to the components of used dental materials. Namely, chemical hazards in denture production include dental alloys (e.g. Vitallium, Wironit, Vicomp), ceramics, investment materials, dental plasters, acrylics (e.g. methyl methacrylate, MMA, ethylene glycol dimethacrylate, EGDMA), polymers, etc.. Metallic alloys used for the crowns, bridges, and dental prostheses production contain 35 - 65 % of cobalt, 20 - 30 % of chromium, 0 - 30 % of nickel balanced by molybdenum, silica, beryllium, boron, tantalum, cadmium. Chromium can cause liver and kidney damage and respiratory disorders as well, while cadmium can cause lung cancer and is also linked to kidney disorder. Nowadays, gold-palladium-based alloys are rarely used. Dental alloys contain silver. It is a heavy metal which could enter in water system due to inadequate disposal of wastes from dental laboratory. Biomedical waste (sharps, disposables, soiled waste) generated during the diagnosis, treatment or immunization is potentially hazardous for human health [6 - 8].

Mercury

Due to its physical and mechanical properties, durability, relatively low cost and ease of use, dental amalgam is one of the most commonly used materials in restorative dentistry for more than a hundred years. It is an alloy made of typically 50 % mercury combined with a powder of silver, copper, tin and sometimes zinc, indium or palladium [9 - 12].

A various waste products could be generated during the placement and removal of dental amalgam restorations. Such as: dental amalgam scrap, i.e. the amalgam particles that have not come into contact with the patient or amalgam waste, i.e. the particles that have come into contact with patient secretions, amalgam sludge, i.e. the fine particles present in dental office wastewater, commonly trapped in chair-side traps and vacuum filters and elemental mercury vapour can be released as well [2].

Since the mercury is its major component, dental amalgam waste has potential harmful effects on humans (toxicity, allergenicity) and environment (bioaccumulative element) which strongly depends on its chemical form. The metallic form, which is only used in dentistry, is mainly absorbed through skin in the human body after which is converted into mercury ions which can be a toxic. In the environment, organic and inorganic mercury compounds are present as well. Hence, mercury can reach the environment through wastewater, vapours or scrap amalgam and accordingly it can be accumulated in aquatic and terrestrial food chains [9 - 12].

Amalgam in dental wastewater originates from waste amalgam fillings. Namely, during the filling tooth cavity dentists always overfill it in order to carve the filling into satisfactory shape. Removed excess of dental amalgam is rinsed into a chair-side drain as well as removed restorations. Discharged mercury in dental wastewater can be present in many forms, such as: elemental, ionic and organic mercury which could be under certain conditions in water converted by microorganisms to highly toxic form of methylmercury. Since fish

cannot eliminate it from their tissue, methylmercury can bioaccumulate up the food chain. Therefore, if fish with high concentrations of methylmercury is consumed regularly, it can be harmful for humans and wildlife [9 - 13].

Despite the fact that dentists produce small amounts of environmentally unfriendly waste, it accumulates and presents a danger to the environment. Because of aforesaid, in recent, a concern about water contamination by heavy metals particularly by mercury from dental amalgam waste was raised [7].

Silver

Another heavy metal that can enter water system in the case of improperly disposed dental waste is silver. It is component of dental amalgam, but also in the form of thiosulfate in radiographic fixer solutions presents negatively affect the environment. Further, not all forms of silver are equally toxic, e.g. free silver ions are more toxic than silver thiosulfate. Fixer used for x-rays development in dental offices is a hazardous material that should not be rinsed down in the drain. Since spent fixer solution could contain up to 4000 mg of silver per liter, a silver recovery unit should be used to recapture the silver from the fixer. However, it should be on mind that many cleaners for x-ray developer systems contain another toxic substance, chromium [1, 4, 7].

When dental radiographic film is processed liquid waste such as: developer, fixer and wash water is generated. This waste is stored in sealed plastic containers. Because of the presence of lead shields, packages of dental radiographic films can have adverse impact on the environment [14].

Lead

The lead shields inside of each x-ray packet are a byproduct of traditional radiography. Although it is a relatively small, a significant amount of waste could be produced. Like mercury and silver, lead persists in the environment. Lead is nonessential element that when is accumulated in the organism it is considered as a toxic for humans and animals. Namely, toxic effects caused by lead can affect almost all organs and systems in the body, particularly blood and nerve system. Since it does not degrade, lead can methylate and contaminate the soil and groundwater during decades. Therefore, lead containing waste should never be disposed of in the regular garbage but should be recycled or treated as a hazardous waste [6, 14].

Other dental metallic waste

Dental activities generate the sharp metallic waste as well. It includes: needles, scalpels, drills, blades, orthodontic wires. For usual patient treatment dentists use sharps, lancets, needles. If these are improperly handled and disposed after use, there is a potential risk for human health as well as for the environment. Hence, in order to prevent the spread of disease, sharps and other potentially infectious waste should not be mixed with the garbage [14, 15].

Dentists should take all possible activities to completely avoid the production of any waste. Avoidance could be achieved by adhering the certain measures, such as: appropriate training programs for staff, monitoring the amounts of all waste sent for treatment and

disposal etc. If that is not possible, it should be tried to reduce the amount of waste to a minimum [16].

Traditional dentistry generates waste materials that harm the environment. A new approach that combines dental practices and environmental protection is Eco-Dentistry or Green Dentistry. Eco‑dentistry association defines green dentistry as "a high‑tech approach that reduces the environmental impact of dental practices and encompasses a service model for dentistry that supports and maintains wellness". It is based on use of non-toxic products, waste reduction, energy conservation and pollution prevention. Furthermore, green dentistry uses a sustainable approach to encourage dentists to implement new strategies to reduce consumed energy and generated waste [2, 17 - 19].

Dental medicine has advanced in terms of materials and techniques as well in order to provide the best to the patient. But, in this context, the environment should be conserved [19]. The green dentistry concept involves high-tech dentistry, reduction of dental waste and pollution, savings of water, energy and money. Namely, by the reduction of waste, overhead costs are reduced and impact on landfills is minimized. The major way for reducing the waste is to extend the life of things that are used. Therefore, the four "R" were introduced: Rethink, Reduce, Reuse and Recycle [17, 19].

Rethink: Environmentalism and sustainability are both considered states of the mind. [16] Implementing small, affordable changes can make a significant impact on long term environmental sustainability. Thinking about practices and protocols and discussing them with dental team may reveal ways to reduce, reuse, and recycle [19].

Reduce: Dentists can reduce materials and water consumption by recycling the bottles, cans, batteries and paper; switching to stainless steel impression trays, using the glasses and mugs instead of disposable cups, using the steam sterilization eliminate the use of chemicals etc. [17].

Reuse: By reusing items instead of throwing them away, resources and energy necessary to manufacture new products are saved. This ensures to prolong the use of items. In that context, dentists should use a reusable face shield, wear cloth lab coats instead of paper ones, provide glass or ceramic rinse cups etc. [19].

Recycle: Recycling is a viable way to reduce overall contamination of the environment. Hence, in dental office should be participate in an instruments recycling program that turns them into industrial metal, use sharp disposal service that recycles them into building materials etc. [19].

In dental offices energy could be conserved by using the solar energy and fluorescent lamps, water heaters and eco-friendly dental technologies, such as CAD/CAM systems and various digital programs [17].

2. CONCLUSION

Dental practitioners should promote not only the human health but the environment as well. Namely, dental activities produce waste that can be harmful for humans and the environment. Therefore the importance of the proper waste disposal should be emphasized. Dentists have to provide the professional training courses for their employees with purpose of obtaining the knowledge about the reduction ways of the environmental impact produced by wastes from dental offices. A proactive approach is a legal obligation to ensure dental services for humans benefit with minimum impact on the environment. It is a moral and ethical obligation as well. Reduction of waste and change of consumption patterns are realistic and could be achieved [2, 14, 17].

Green dentistry is a high-tech approach that reduces the environmental impact of dental practice and therefore it is an environmentally friendly way of practicing dentistry. By combining the health of humans with the health of the environment, ecofriendly dentistry provides an opportunity to reduce further degradation of our planet [18 - 20].

Hence, education regarding the proper management and disposal of waste from dental offices needs attention. In that, academic institution could play a significant role [11].

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

ENVIRONMENTAL IMPACT ASSESSMENT OF LEACHATE FROM BIOWASTE

Monika Šabić*, Dajana Kučić Grgić*, Marija Vuković Domanovac*

* University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia

corresponding author: Monika Šabić, e-mail: msabic@fkit.hr

Original scientific paper

ABSTRACT

Growing affluent lifestyles in many countries around the world in the past few decades have been accompanied by rapid increase in municipal solid waste production. The key environmental problem is the leachate generation which can be significant threat to surface water and groundwater. The leachate has very high concentrations of organic and inorganic pollution substances. This study investigated the physico-chemical and biological characterization of leachate from biowaste. The experiments were conducted in batch conditions with initial concentration of leachate 12206 mg O_2 dm^{-3}. Microscopic analysis indicated the development of biomass during the experiments. The efficiency of the biodegradation process was 88.9 %.

***Keywords**: leachate, biowaste, biodegradation*

1. INTRODUCTION

Due to urbanization, rapid industrialization and population growth, the trend of generation in municipal solid waste per person have significantly increased on global scale [1]. Primary disposal approach worldwide for this type of waste is landfilling [2]. Many developed countries have legal obligation to reduce the quantity of municipal waste sent to landfill, with particular emphasis on biodegradable waste. One of the main reasons for reduction of biodegradable waste in landfill is the leachate generation which represents significant pollution problems if it is not adequately controlled [3]. Biodegradable municipal waste mainly comprises of biowaste which includes kitchen, garden or green waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants [4]. Composition of the leachate depends on the constituents of the wastes, the microbiota type, climatic conditions and the age of the landfill [5]. It is characterized by high organic load expressed as chemical oxygen demand (COD) value, toxicity, unfavourable odour and yellowish to dark brown colour [6].

Biological treatment is relatively simple, reliable, cost-effective and environmentally friendly method which can be used for treating wastewater with high organic loads [7]. Most commonly used biological treatment for wastewater is aerobic process with activated sludge, where microorganisms appear in flocs, mainly composed of bacteria [8]. Because of its origin, biowaste leachate is potential source of microorganisms. Thus, biological treatment with autochthonous microorganisms can be applied for the leachate contaminants degradation.

The aim of this research was to study physico-chemical characterization of leachate from biowaste and to investigate its biodegradation potential by indigenous microorganisms which are naturally present in the leachate.

2. EXPERIMENTAL

In this study biowaste was used for leachate preparation, which consisted of 9 different biodegradable wastes commonly found in households (banana peel, apple peel, tomato, white bread, cabbage, carrot peel, potato peel, wheat straw, onion skin). The biowaste was mixed in mass ratios optimal for composting process. Initial values of C/N ratio, pH value and moisture content of biowaste mixture were 34/1, 5.93 and 57 %, respectively. According to European standard: EN 12457-4:2002 [9], the leachate from biowaste mixture was prepared by adding biowaste into distilled water in ratio 1/10 and mixing it at 100 rpm for 24 hours.

Biodegradation experiments were conducted in batch conditions, using 500 cm^3 of biowaste leachate in 1 dm^3 conical flasks. Experiments were carried out on a rotary shaker at 160 min^{-1} for 10 days, at room temperature (23 ± 1°C), to assess the biodegradation process by the leachate's indigenous microorganisms. Initial concentration of organic matter of leachate was 12206 mg O_2 dm^{-3} expressed as chemical oxygen demand (COD). During the experiment COD, pH value, conductivity, concentration of dissolved oxygen and biomass were monitored.

Physico-chemical characterization of biowaste leachate was carried out at the beginning and at the end of biodegradation experiment. The pH value, conductivity and concentration of dissolved oxygen were measured by WTW Multi 340i set. COD was determined spectrophotometrically (Hach model DR/2400), while mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were determined gravimetrically using Standard methods [10]. MLSS is an indirect measure of sludge concentration which is commonly used to characterize the biological mass in the activated sludge. MLVSS is a measure of the amount of volatile suspended solids found in a sample of MLSS. Variations in the concentration of MLVSS indicate a change in the amount of biomass share [7]. Biochemical oxygen demand (BOD) was determined by Winkler method and toxicity using bioluminescent bacteria *Vibrio fischeri* [11]. Bioluminescence inhibition assay has been widely used in determining toxicity of leachates [12]. Toxicity is expressed as the effective concentration of compound that affects 50 % of bioluminescence inhibition (EC_{50}). When the sample is constituted by a mixture of compounds or contains unknown compounds, the result is expressed as percentage of sample that affects EC_{50} [13].

In order to monitor changes in biomass development, microscopic analysis was performed using optical microscope (Olympus BX50) equipped with system for taking photographs (Olympus DP10 camera). Samples were microscopically examined under 100× and 400× total magnification.

3. RESULTS AND DISCUSSION

A biodegradation experiment was conducted for 10 days, in order to study the biodegradation potential of leachate from biowaste. At the beginning of the experiment BOD_5/COD was 0.65, which means that leachate is biodegradable and biological treatment can be applied.

Between 2nd and 3rd day of the experiment a major change in pH value occurred (figure 1). In only 24 hours, the pH value increased from 5.1 to 7.2, shifting from acidic to neutral pH range. pH value is very important factor for the growth of certain microorganisms. Optimum pH for bacterial growth is neutral pH area, while fungi prefer acidic environments [14]. Biological treatment of wastewater generally occurs at neutral pH, which was maintained till 6th day, while at the end of biodegradation experiment pH value increased till 8.8. Due to the decomposition of organic nitrogen in biodegradation process ammonium is released. Hence, the concentration of NH_4^+ is increased and pH value increases to alkaline range [15].

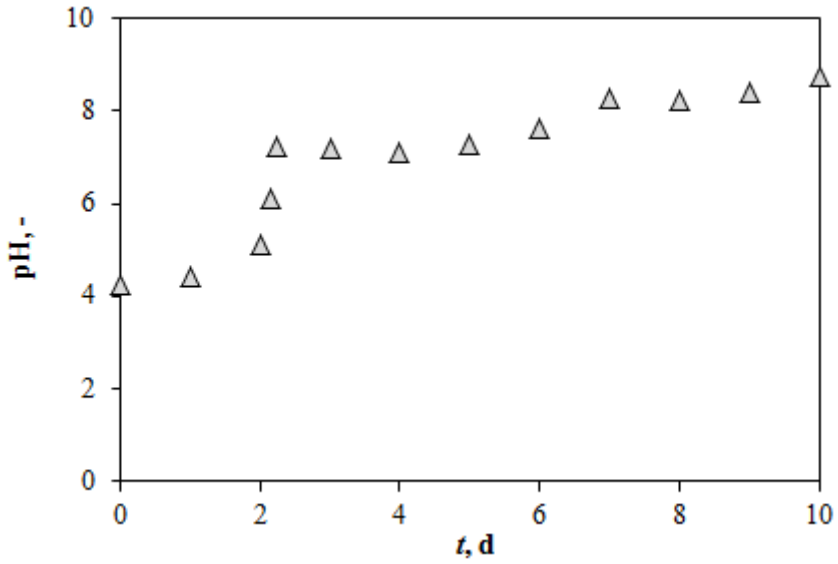


Figure 1. Changes in pH value of biowaste leachate during 10 days in biodegradation process

Figure 2 shows changes that occurred in COD of biowaste leachate during biodegradation process. In the first 3 days of experiment, COD decreased for 35.3 %. The COD value continued to decrease, where in the 6th day obtained concentration of organic matter was 4162 mg O_2 dm^{-3}. The highest biodegradation efficiency was 88.9 %, obtained in 8th day of experiment. From the 8th day till the end of the biodegradation study COD value maintained constant.

Physico-chemical characteristics of leachate from biowaste at the beginning and after the biodegradation experiment are summarized in Table 1. Biodegradable organic matter, in terms of BOD_5/COD ratio, indicated high biodegradability of leachate from biowaste. As a result of biodegradation process, biomass developed and biodegradability decreased, which is shown by final ratio of BOD_5/COD.

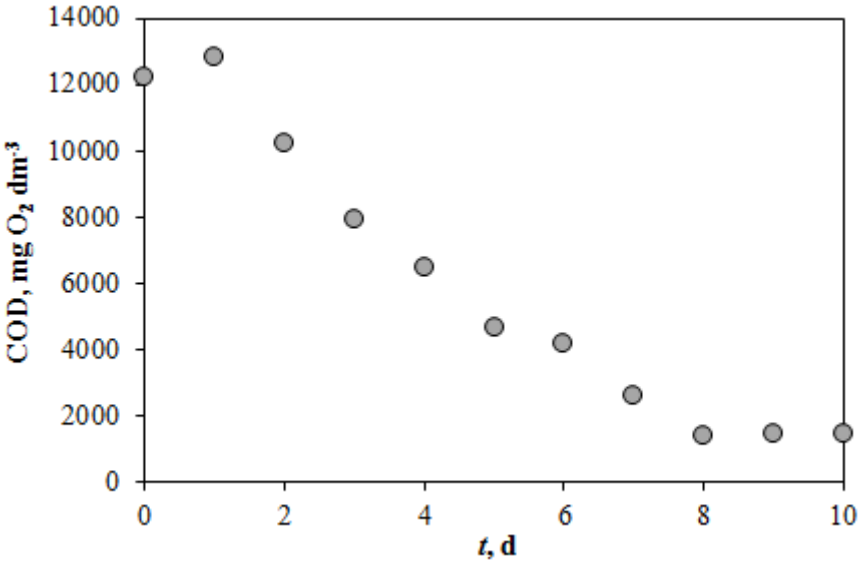


Figure 2. Changes in COD from biowaste leachate during 10 days in biodegradation process

The biodegradation process of leachate from biowaste was induced through stirring conditions, which led to biostimulation of present microorganisms from leachate with dissolved oxygen. At the beginning of the experiment, the concentration of dissolved oxygen was low due to the intensive biodegradation process. At the end of the experiments the concentration of dissolved oxygen increased as the COD concentration decreased (figure 2), which means that the biodegradation process of leachate from biowaste was coming to its end.

Homogenizing and stirring leachate can promote microbial growth and enhance microbial degradation activity on pollutants [16]. During the biodegradation experiment, MLSS gradually increased, indicating the development of activated sludge (table 1). Average obtained value for MLVSS/MLSS ratio was 0.81±0.15, meaning that the amount of viable biomass was maintained through the experiment. With value 4.50±0.13 mS cm^{-1}, conductivity showed no significant changes during the biodegradation process.

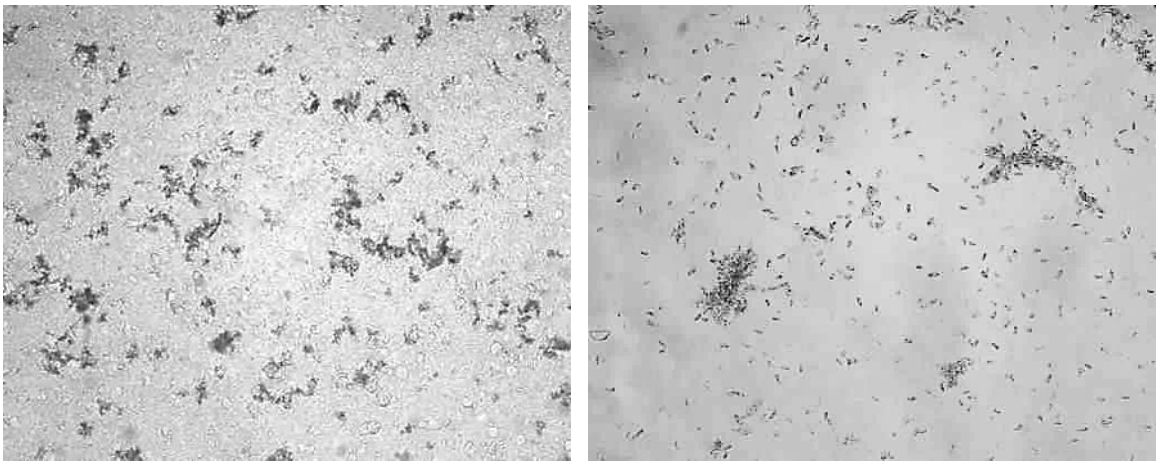
Table 1. Physico-chemical characteristics of leachate from biowaste at the beginning and at the end of biodegradation experiment

Parameters	Initial values	Final values
BOD_5/COD	0.65	0.13
O_2, mg dm^{-3}	2.52	6.61
MLSS, g dm^{-3}	2.17	3.80
EC_{50}, %	6.45	25.33
Odour	unpleasant, acidic	pleasant
Colour	yellowish	orange, slightly brown

In conducted experiment, leachate from biowaste was considered severely toxic [12]. Despite its toxicity, biodegradation treatment was successfully used. Major changes in colour and odour appeared at the end of biodegradation process. Unpleasant, slightly acidic odour, agrees with low pH value at the beginning of the experiment (figure 1). As the process was near end, the odour became more pleasant, because of the removal of organic matter, which

also increased pH value. Due to development of activated sludge and degradation of organic matter the colour of leachate became darker.

Microscopic analysis was conducted in order to give insight in the course of the biodegradation process. The results of microscopic examination are shown in Figure 3. A great number of small sludge flocs, irregularly shaped, with open floc structure which is specific for young sludge [17] can be seen in figure 3a. Transparent and loose flocs indicate development of new biomass during the biodegradation process [7]. In the biodegradation process, as a result of degradation of organic matter, microbial growth appears. Figure 3b shows relatively compact and better shaped flocs, which contributed to the removal efficiency of COD value in the leachate. Over the course of the biodegradation process, some type of protozoa appeared. The presence of higher indicators of sludge quality, such as protozoa, can provide evaluation of biodegradation ability and condition of activated sludge.



a) b)

Figure 3. Microscopic photographs of developed activated sludge flocs in biodegradation process of leachate from biowaste, magnification 100× (a) 3rd day (b) 8th day

4. CONCLUSION

Leachate from biowaste is characterized by high concentration of organic matter, acidic pH value and toxicity so treatment of this kind of wastewater is needed. For organic matter removal from biowaste leachate, biodegradation process can be successfully applied. Aerobic conditions led to the removal of organic matter in leachate by its indigenous microorganisms. Microscopic analysis indicated that biological treatment was feasible due to development of activated sludge flocs and appearance of higher indicators of sludge quality.

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1st INTERNATIONAL CONFERENCE
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Croatia, Sisak, September 13th-14th, 2018

ZOOPLANKTON TRAITS IN THE WATER QUALITY ASSESSMENT AND RESTORATION OF SHALLOW LAKES

Maria Špoljar*, Tvrtko Dražina*, Natalia Kuczyńska-Kippen, Chen Zhang***, Ivančica Ternjej*, Goran Kovačević*, Jasna Lajtner*, Jelena Fressl******

* University of Zagreb, Faculty of Science, Division of Zoology, Zagreb, Croatia
** Adam Mickiewicz University, Faculty of Biology, Department of Water Protection, Poznań, Poland
*** Tianjin University, State Key Laboratory of Hydraulic Engineering Simulation and Safety, Tianjin, China
**** Dvokut-Ecro, Ltd., Zagreb, Croatia

corresponding author: Maria Špoljar, e-mail: maria.spoljar@biol.pmf.hr

Original scientific paper

ABSTRACT

Microscopic invertebrates, including main groups of zooplankton: Rotifera, Cladocera and Copepoda, are sentinel organisms for environmental deterioration and play an important role in the food web connectance of shallow waterbodies. Preservation of these ecosystems is important due to many socio-ecological reasons, i.e. increasing of landscape and biocoenotic heterogeneity. In this study we assessed (i) interplay of environmental factors and zooplankton assemblage in shallow lakes under different climate conditions: temperate, in the north (Poland) and south (Croatia) Europe, and Mediterranean (Adriatic Sea, Croatia), and (ii) zooplankton role in the lake restoration mediated by macrophytes. Results extracted rotifers as most abundant group of zooplankton, and demonstrated an increase of zooplankton diversity with habitat complexity, i.e. macrophyte coverage. Submerged macrophytes were of high importance in the lake restoration, mitigating the lake eutrophication. Zooplankton patterns show a quick response on alteration of environmental conditions and could be applied as an indicator of accelerated climate changes.

Keywords: *temperate vs. Mediterranean climate, biodiversity, macrophyte coverage*

1. INTRODUCTION

Shallow lakes (3 m of relative depth or less) are under great negative impact, primary due to anthropogenic pressure and climate change. These waterbodies are important from several aspects. Apart from ecological significance (biodiversity, microclimate, fish

spawning, birds nesting), shallow lakes provide various ecosystem services, manifested through sport, recreation and tourism [1].

Freshwater zooplankton (Rotifera, Cladocera and Copepoda) is excellent indicator of ecological conditions fom several reasons. These organisms have short life cycles and respond particularly quickly to environmental changes. Also, they have pivotal position in the food web, in transfer of matter and energy between autotrophs and higher consumer, and are crucial for freshwater ecosystems functioning. Thus, zooplankton is regulated by "bottom-up" (nutrients) and the "top-down" (fish, i.e. predators) mechanism [2].

Structure, abundance and biomass of mentioned zooplankton groups in shallow lakes are also influenced by presence or absence of macrophytes. The architectural complexity, size and density of macrophytes modify different physico-chemical conditions and influence biotic interactions, e.g. predation and zooplankton migration [3 - 5]. Therefore, numerous ecological regulators directly affect zooplankton composition.

Recently, in the climate changing environment, many studies indicate significant differences in the trophic structure between cold and warm shallow lakes [6]. Thus, our objective was to determine: (i) interplay of environmental factors and zooplankton assemblage in shallow lakes under different climate conditions: temperate, in north (Poland) and south (Croatia) Europe, and Mediterranean (Adriatic Sea, Croatia), and (ii) zooplankton role in the lake restoration mediated by macrophytes.

2. FIELD AND LABORATORY DESIGN

Samples were collected in two countries, Poland and Croatia, representing two different climatic conditions, temperate and Mediterranean. We selected sampling sites in three regions, as follow: (i) four ponds in NW Poland, close to city of Poznan, as reference for temperate north climate (TN), (ii) five ponds in NW Croatia, close to city of Zagreb, as reference for temperate south climate (TS), and (iii) five ponds on Dugi otok Island (middle Adriatic Sea) in Mediterranean climate (A). All four water bodies in TN are located in the Wielkopolska region, the central-western part of Poland. They represent typical post-glacial ponds, which are called kettle holes. Moreover, all of them are permanent ponds with well-developed macrophyte cover. They are situated within an agricultural landscape, surrounded by fields, pastures and meadows. Ponds in TS are situated in the river valley, and represent mostly oxbow lakes. Adriatic ponds are semi-permanent, situated in karst and they are all fishless.

Zooplankton samples were collected in triplicates with plankton net (26-μm) after filtering 3 × 10 L of the water and were fixed with 4 % formalin. Rotifers, copepods and cladocerans were determined to the genus or species level using determination keys [7 - 9]. Sampling methods and analyses of environmental parameters were described in our previous articles [10, 11]. Prior to statistical analysis, all abiotic and biotic data were logarithmically transformed [*log* (x+1)]. None of the environmental and biocoenotic data showed a normal distribution, based on the Shapiro-Wilk's test, even after transformation, and we applied nonparametric analyses (Spearman coefficient of correlations Kruskal-Wallis test; software package Statistica 12). We used the package Primer v6 software for the further analyses: Shannon diversity index (H'), dissimilarity of zooplankton assemblage checked by SIMPER analysis, NMDS, multivariate analysis of similarities (ANOSIM) was used to identify significance of the regional and habitat heterogeneity differences in zooplankton assemblage. ANOSIM generates a value of R ranging between −1 and +1; a value of zero indicates no difference among a set of data.

3. RESULTS AND DISCUSSION

Zooplankton assemblages in ponds, i.e. shallow waterbodies/lakes, were studied across different latitudes and climates in Europe (table 1, figure 1).

Table 1. Environmental parameters and abundance of main zooplankton groups in studied ponds ± SD

Variable	Temperate North (TN)			Temperate South (TN)			Adriatic (A)		
	Mean		SD	Mean		SD	Mean		SD
Depth (m)	1.3	±	0.6	3.3	±	0.8	1.4	±	1.1
Transparency (m)	0.9	±	0.5	0.9	±	0.4	0.9	±	0.9
Temperature (°C)	21.5	±	5.0	18.9	±	2.6	21.8	±	4.5
Dissolved oxygen (mg O_2 L^{-1})	8.5	±	1.7	6.7	±	1.9	12.6	±	6.7
pH	7.9	±	1.0	7.7	±	0.4	9.5	±	1.1
Conductivity (µS cm^{-1})	748.8	±	437.6	401.0	±	161.3	719.5	±	1046.1
Macrophyte coverage (%)	38.8	±	28.4	2.6	±	2.5	58.0	±	53.1
TN (mg L^{-1})	1.318	±	0.756	1.422	±	0.247	2.567	±	1.448
TP (mg L^{-1})	0.823	±	0.864	0.377	±	0.055	0.312	±	0.419
Chl a (µg L^{-1})	21.103	±	22.424	13.879	±	9.473	2.742	±	2.515
Rotifera abundance (ind. L^{-1})	4782	±	6917	2098	±	2331	1309	±	1269
Cladocera abundance (ind. L^{-1})	410	±	276	127	±	129	40	±	35
Copepoda abundance (ind. L^{-1})	16	±	11	166	±	121	1027	±	1528

The obtained results suggested a decrease of zooplankton species richness from north to the south: 57 ± 12 species in TN, 18 ± 11 species in TS and 14 ± 7 species in A. This decreasing pattern was especially well pronounced for Cladocera species richness (17 TN, 12 TS and 8 A). This resulted in significant differences of Shannon diversity among zooplankton in ponds across studied regions and climates (Kruskal-Wallis test, $H_{2,14} = 8.3$, $p = 0.02$).

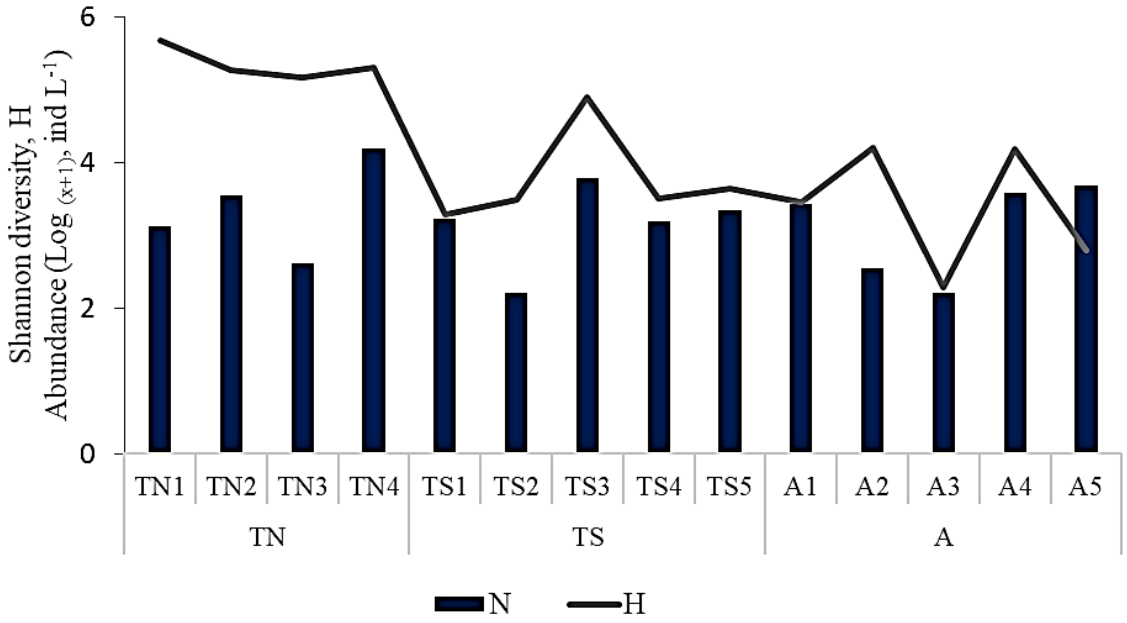


Figure 1. Oscillations of zooplankton abundance and diversity among studied ponds

Macrophyte stands significantly enhanced zooplankton biodiversity ($r = 0.62$, $p < 0.05$). Regardless of the region zooplankton diversity was moderately, but significantly separated according to the macrophyte coverage (ANOSIM, $r = 0.3$, $p = 0.05$; figure 2). In the Adriatic ponds salinity caused scarcity in the species richness ($r = -0.526$, $p < 0.05$).

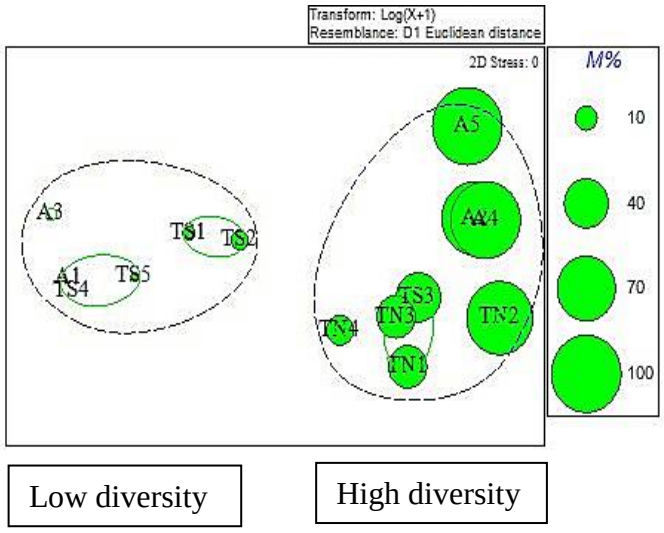


Figure 2. NMDS plot separated ponds of higher (right) and lower (left) diversity related to macrophyte coverage (M%)

Rotifers dominated in zooplankton abundance, as well as in diversity across studied regions, from northern to the southern Europe (table 1). Not only zooplankton diversity but also abundance showed a decreasing trend along with latitudinal increase (Kruskal-Wallis test, $H_{2,14} = 8.3$, $p = 0.02$). Dissimilarities in zooplankton assemblage for all pairs of ponds among three regions amounted from 83 % up to 90 % (SIMPER).

Zooplankton differences along increased latitude, north to south, showed several patterns: macrophyte stands were responsible for increased zooplankton diversity,

detritivorous rotifers were dominating group in the abundance of zooplankton and had the highest diversity, cladocerans diversity and abundance decreased, while copepods abundance increased. This is in accordance with other latitudinal and climate focused research [4, 12]. Macrophyte stands are known for creating habitats rich in various food resources and are places characterised by a high degree of habitat heterogeneity. They constitute reliable shelters to many zooplankton organisms against predators, both invertebrate and planktivorous fish [11]. Thus macrophyte covered littoral zone enhances zooplankton, and overall invertebrate diversity [5]. In the regions exposed to salinization, increased salinity may negatively affect species diversity, particularly that of rotifers [12].

4. CONCLUSION

Zooplankton study across anthropogenic impacted or man-made ponds along latitudes and climates indicates a general trend of deteriorated water quality in terms of biocoenotic and environmental conditions. The re-establishment of aquatic vegetation would be a recommended restoration method in the view of sustaining water quality, biodiversity and ecosystem equilibrium. We suggest further thorough assessment of environmental conditions and protection for the maintenance of these important and valuable ecosystems, especially on islands which have had a strong and sustainable tradition of human-pond relationships through the centuries.

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UČINKOVITOST ADSORPCIJE BAKAR (II) IONA NA OTPADNOJ ČELIČNOJ SAČMI

EFFICIENCY OF ADSORPTION OF COPPER (II) IONS ON WASTE STEEL SHOT

Anita Štrkalj*, Zoran Glavaš*, Ivana Gavranović*

* Sveučilište u Zagrebu, Metalurški fakultet, Sisak, Hrvatska

autor za korespondenciju: Anita Štrkalj, e-mail: strkalj@simet.hr

Izvorni znanstveni rad

SAŽETAK

Čelična sačma koristi se u ljevaonicama za čišćenje površine odljevaka prije nanošenja odgovarajuće zaštite ili prije stavljanja na tržište. Postupak čišćenja odvija se na taj način da čestice sačme velikom brzinom udaraju u površinu odljevka. Prilikom tog postupka dio kuglica sačme biva oštećen i postaje otpad. U ovom radu istraživana je mogućnost uporabe otpadne čelične sačme kao adsorbensa za uklanjanje Cu(II) iona iz vodene otopine. Nakon adsorpcijskog procesa određivana je efikasnost adsorpcije ovisno o početnim koncentracijama otopine Cu(II) iona. Rezultati su pokazali da ova vrsta otpada ima vrlo veliku efikasnost uklanjanja (adsorpcije) Cu(II) ion, čak i preko 80 % što upućuje na zaključak da bi se ova vrsta otpada mogla koristiti kao adsorbens. Na ovaj način bi se omogućilo korištenje, a samim time i smanjivanje ove vrste otpada.

***Ključne riječi**: otpadna čelična sačma, Cu(II) ioni, efikasnost adsorpcije*

ABSTRACT

Steel shot is used in foundries for cleaning surfaces of castings before applying adequate protection or before placing on the market. During cleaning steel shot particles hit the surface of the casting at high speed. In this process one part of the steel shot is damaged and becomes waste. This article investigated the possibility of using waste steel shot as adsorbent for removal of Cu(II) ions from aqueous solutions. After the adsorption process, the adsorption efficiency was determined depending on the initial concentrations of the Cu(II) ion solution. The results show that this type of waste has a very high efficiency of removal

(adsorption) of Cu(II) ion, more than 80 %. This suggests that this type of waste could be used as adsorbents. In this way, it would be possible to use and thus reduce this type of waste.

***Keywords**: waste steel shot, Cu(II) ions, adsorption efficiency*

1. UVOD

Otpadna voda opterećena teškim metalima predstavlja ozbiljan problem. Teški metali su u vrlo niskim koncentracijama neophodni za normalno funkcioniranje, rast i razvoj organizama. Međutim ukoliko su iz vode, zraka, tla hrane ili nekog drugog izvora ušli u ljudski organizam u povišenim koncentracijama mogu stvoriti velike zdravstvene probleme, pa čak i smrt [1].

Povećane količine bakra u ljudskom organizmu (toksična doza iznosi 100 mg/kg) [1] izaziva brojne posljedice, kao što su povraćanje, pospanost, povišeni krvni tlak, oštećenje bubrega, jetre i mozga. U krajnjim slučajevima može doći do kome, ali i smrti. Štetnost bakra naglašava i činjenica da se bakar ne razgrađuje u prirodi, već se akumulira u biljkama i životinjama. Osim toga, najčešće se veže za vodu ili čestice tla [2]. Zbog svega navedenog vrlo je važno koncentraciju bakra držati u granicama koje su regulirane zakonskim direktivama.

U cilju rješavanja problema zagađenja vode danas se koristi vrlo širok spektar metoda kojima se onečišćujuće tvari uklanjaju iz zagađene vode. Svaka od metoda ima i prednosti i nedostatke. Teži se tome da se potencijalni nedostatci uklone, ali i da se metode što više modificiraju i moderniziraju. Jedna od takvih metoda je i adsorpcija. Ova metoda se vrlo često koristi zbog jednostavnosti primjene [3]. Mnoga istraživanja [4 - 6] pokazala su da je aktivni ugljik najbolji adsorbens. Međutim, njegova cijena je dosta visoka. Stoga se nastoji zamijeniti nekim drugim jeftinijim, ali učinkovitim adsorbensima. Do sada su se kao dobri potencijalni adsorbensi pokazali različiti otpadni materijali koji su nusprodukti ili otpadni produkti različitih grana industrije [7, 8].

Pojedine vrste otpada iz metalurške industrije pokazale su se kao dobri adsorbensi [9]. Njihova upotreba jako je značajna s obzirom na veliku količinu otpada koji nastaje u metalurškoj industriji kao rezultat vrlo velike proizvodnje. Metalurški otpad uglavnom se odlaže na odlagalištima koja zbog velike količine otpada znatno opterećuju okoliš. Cilj upotrebom metalurškog otpada kao adsorbensa je smanjenje količine otpada na odlagalištima, ali i smanjenje teških metala i/ili nekih drugih opasnih tvari (boja, fenola i sl.) u otpadnim vodama.

U ovom radu istraživana je mogućnost primjene otpada nakon sačmarenja odljevaka kao potencijalnog ekonomski prihvatljivog adsorbensa za uklanjanje Cu(II) iona iz vodene otopine.

2. EKSPERIMENTALNI DIO

Otpadna čelična sačma predstavlja otpad koji je nastao u ljevaonici tijekom čišćenja odljevaka. Postupak čišćenja provodi se na način da čestice sačme velikom brzinom udaraju u površinu odljevaka i na taj način mehanički uklanjanju čestice kalupne mješavine i odgora. Prilikom toga dio se čestica sačme oštećuje. Budući da za adekvatan postupak čišćenja

odljevaka sačma treba imati odgovarajuća svojstva (tablica 1), oštećene čestice nije moguće ponovo koristiti te zajedno s česticama odgora i otpadne kalupne mješavine postaju otpad.

Tablica 1. Svojstva čelične sačme [10]

Svojstva	Okrugla sačma	Lomljena sačma
Boja	Crna	Crna
Tvrdoća	43-48 HRc	Min 60 HRc
Težina	Od 7,5kg/dm^3	Od 7,5kg/dm^3
Opterećenje po 1 kg	420-448 HV	480-550 HV

Na otpadnom materijalu koji je osim čestica sačme sadržavao i vrlo mali udio čestica kalupne mješavine i odgora koji su otpali s odljevka u postupku sačmarenja (slika 1) provedeni su adsorpcijski eksperimenti kako bi se utvrdila mogućnost korištenja ove vrste metalurškog otpada kao potencijalnog adsorbensa. Nakon uzorkovanja u ljevaonici uzorci su homogenizirani miješanjem i četvrtanjem. Na ovaj način je i masa uzoraka smanjena na masu potrebnu za provođenje eksperimenta.



Slika 1. Otpadna čelična sačma

Dio uzorka (čelične sačme) otopljen je u uređaju za mikrovalnu digestiju i korišten je za ispitivanje kemijskog sastava, a dio uzorka korišten je za provođenje statičkog, tzv. *batch* adsorpcijskog eksperimenta. Kemijski sastav uzorka određen je atomskom adsorpcijskom spektrometrijom i prikazan je u tablici 2.

Tablica 2. Kemijski sastav čelične sačme

Komponente sačme	Fe	C	Mn	Si	S	P
Maseni udio (%)	98,05	0,85	0,60	0,40	0,05	0,05

Kao adsorbat korištena je otopina Cu(II) iona. Iz standardne otopine Cu(II) iona koncentracije 1000 mg/l priređene su radne otopine koncentracija 10, 30, 50 i 70 mg/l. Vagnuto je po 1 g otpada nakon sačmarenja i stavljeno u kontakt sa po 50 ml radnih otopina Cu(II) iona. Ispitivanja su provedena pri temperaturi od 22 °C i pH 5,69.

Nakon 30 minuta (ravnotežno vrijeme koje je određeno u prethodnim mjerenjima) provedeno je filtriranje preko filtar papira plava vrpca te je u filtratima atomskom apsorpcijskom spektrometrijom određena koncentracija iona bakra nakon adsorpcije.

Iz podataka za početnu koncentraciju Cu(II) iona, koncentracije Cu(II) iona nakon adsorpcije (u filtratu), mase adsorbensa i volumena adsorbata izračunat je kapacitet (q_e) i efikasnost adsorpcije (E), te koeficijent distribucije (K_D) prema jednadžbama (1) - (3):

$$q_e = \frac{c_0 - c_e}{m} \cdot V \quad (1)$$

$$E = \frac{c_0 - c_e}{c_0} \cdot 100 \quad (2)$$

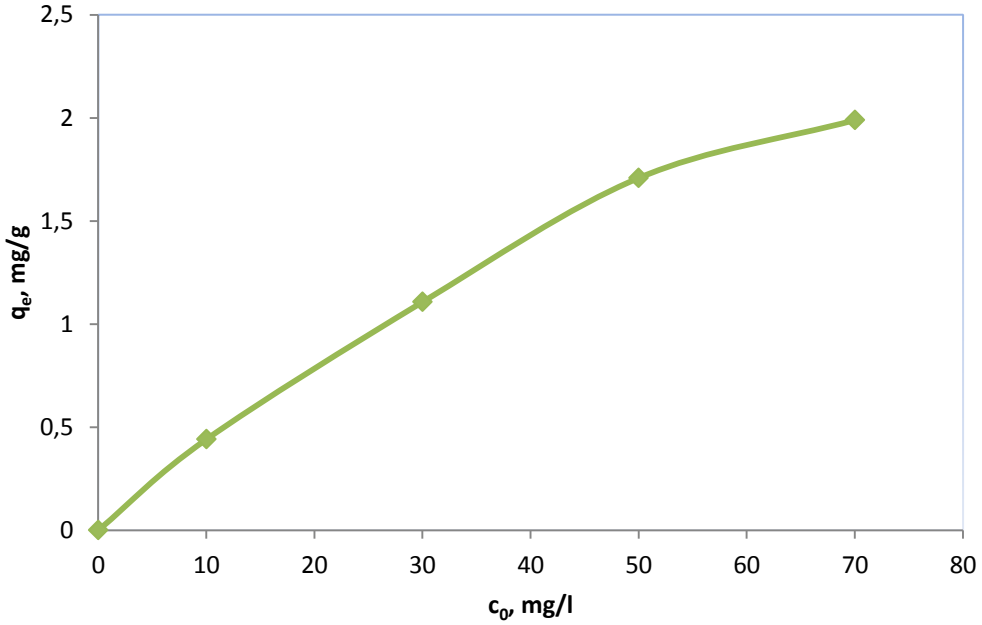
$$K_D = \frac{c_0 - c_e}{c_e} \cdot \frac{V}{m} \quad (3)$$

gdje je:

c_0 - početna masena koncentracija Cu(II) iona u otopini, mg/l,
c_e - ravnotežna masena koncentracija Cu(II) iona u otopini, mg/l,
m - masa otpada nakon sačmarenja, g,
V - volumen otopine Cu(II) iona, l.

3. REZULTATI I DISKUSIJA

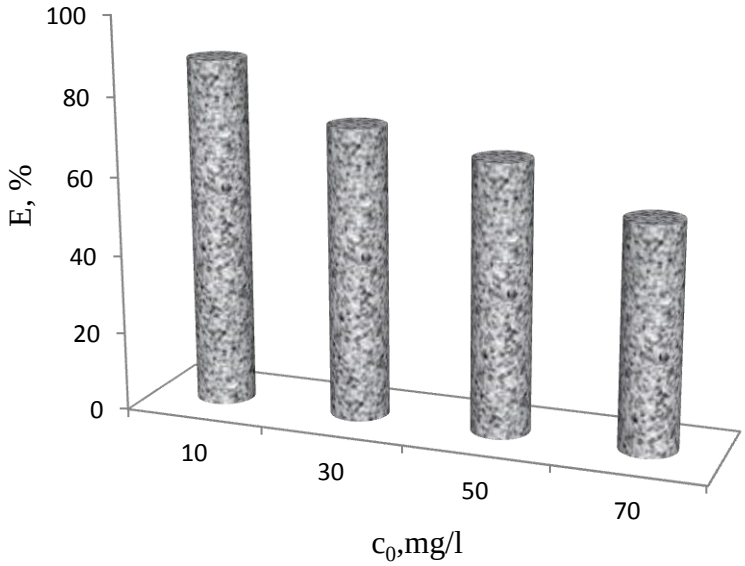
Na slici 2 prikazana je ovisnost kapaciteta adsorpcije o početnoj koncentraciji.



Slika 2. Ovisnost kapaciteta adsorpcije o početnoj koncentraciji Cu(II) iona

Iz slike 2 vidljivo je da kapacitet adsorpcije raste s porastom početne koncentracije Cu(II) iona u otopini. Pri početnoj koncentraciji Cu(II) iona u otopini od 70 mg/l kapacitet adsorpcije je najveći i iznosi 1,99 mg/l. Usporedbom s rezultatima drugih istraživača [11 - 14], kapaciteti adsorpcije Cu(II) iona na različitim adsorbensima iznose i znatno više, ali i manje od navedenog što ovisi o vrsti i svojstvima adsorbensa. Da bi neka tvar bila dobar adsorbens neophodno je da površina potencijalnog adsorbensa ima što više slobodnih mjesta na koje se mogu vezati ioni koje je potrebno adsorbirati. Sve dok je broj slobodnih mjesta dovoljan ioni iz otopine se nesmetano vežu na površinu adsorbensa [15]. Ova pojava se može registrirati preko porasta kapaciteta adsorpcije. Budući da kapacitet adsorpcije Cu(II) iona na otpadu nakon sačmarenja raste s porastom koncentracije može se pretpostaviti da navedenom adsorbensu nisu popunjena sva slobodna mjesta te se proces adsorpcije može nesmetano odvijati.

Na slici 3 prikazan je dijagram ovisnosti efikasnosti adsorpcije otpada nakon sačmarenja o početnoj koncentraciji Cu(II)iona.



Slika 3. Ovisnosti efikasnosti adsorpcije otpada nakon sačmarenja o početnoj koncentraciji Cu(II)iona

Poznato je da je adsorpcija proces na koji utječe veliki broj čimbenika, poput veličine, promjera i ionske jakosti iona adsorbata, volumena i koncentracije adsorbata, specifične površine adsorbensa, veličine čestica itd. [16]. Iz slike 3 vidljivo je da efikasnost adsorpcije otpada nakon sačmarenja opada s porastom početne koncentracije Cu(II) iona. Unatoč tome što kapacitet adsorpcije raste porastom koncentracije, očito niže koncentracije Cu(II) iona povoljnije djeluju na sam adsorpcijski proces te je uslijed toga i efikasnost veća. Ukupno gledajući, efikasnost adsorpcije Cu(II) iona na otpadu nakon sačmarenja je relativno visoka i iznosi od 56,82 - 88,17 %. U tablici 3 dan je literaturni pregled nekih otpadnih materijala koji su korišteni kao adsorbensi.

Usporedbom navedenih podataka i vrijednosti za efikasnost adsorpcije dobivene prilikom ovog istraživanja može se zaključiti da otpad nakon sačmarenja ima relativno dobru efikasnost adsorpcije, te bi se mogao koristiti kao potencijalni adsorbens za uklanjanje Cu(II) iona iz vodenih otopina.

Budući da je aktivni ugljik poznat kao najbolji komercijalni adsorbens u tablici je prikazan i literaturni podatak [17] za efikasnost adsorpcije Cu(II) iona početne koncentracije 50 mg/l na navedenom adsorbensu. Vidljivo je da je efikasnost adsorpcije Cu(II) iona na otpadu nakon sačmarenja (68,33 %) vrlo slična efikasnosti adsorpcije Cu(II) iona na aktivnom ugljiku što je još jedna potvrda da se ispitivani otpad može koristiti kao potencijalni jeftini adsorbens.

Tablica 3. Pregled nekih otpadnih materijala koji su korišteni kao potencijalni jeftini adsorbensi [18 - 26]

Adsorbens	Adsorbat	Efikasnost adsorpcije *E*, %
Aktivni ugljik	Cu(II), (c_0= 50 mg/l) Octena kiselina Cd(II) Hg(II)	71,58 68,13 70 100
Dijatomejska zemlja	pesticidi	55
Biomasa plijesni	boja (metilensko modrilo)	85
Ljuskice riže	Pb(II)	43,59
Pepeo (leteći)	Pb(II) Zn(II)	90 70
Ljuske kikirikija	Cd(II)	10
Kora babane	Mn(II)	28

4. ZAKLJUČAK

Na osnovi provedenih ispitivanja zaključeno je sljedeće:

- otpad nakon sačmarenja moguće je koristiti kao potencijalni jeftini adsorbens za uklanjanje Cu(II) iona iz otpadnih voda,
- kapacitet adsorpcije Cu(II) iona na otpadu od sačmarenja ovisi o početnoj koncentraciji Cu(II) iona u otopini, te raste s porastom početne koncentracije,
- efikasnost adsorpcijskog procesa bolja je pri nižim koncentracijama Cu(II) iona,
- efikasnost adsorpcije Cu(II) iona na otpadu nakon sačmarenja iznosi od 56,82 - 88,17 % što ukazuje na dobra adsorpcijska svojstva navedenog adsorbensa.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

CONCEPTUALIZATION OF THE ARCHITECTURAL DECISION ANALYSIS MODEL – ADAM

Miljan Šunjević*, Sonja Dmitrašinović*, Vladimir Rajs*, Maja Sremački*, Boris Obrovski*, Maja Petrović*, Branislava Savić, Darko Reba*, Mirjana Vojinović Miloradov***

* University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia
** University of Belgrade, Vinča Institute of Nuclear Sciences, Belgrade, Serbia

corresponding author: Miljan Šunjević, e-mail: msunjevic@uns.ac.rs

Preliminary note

ABSTRACT

Despite of several responsive and holistic approaches which are applied, severe pollution is being generated during construction processes, urbanisation, industrialisation and anthropogenic activities. Managing activities aimed to facilitate achievement of sustainable development goals are the basic components of every viable environmental protection platform. To accomplish proclaimed goals of sustainable development, such as a healthier and safer environment, it would be necessary to apply an integral approach as the one here described and entitled the conceptualization of the Architectural Decision Analysis Model with abbreviation ADAM. Recognizing the significance of a holistic approach and importance of related decisions that are being taken regularly, the paper presents an architectural decision analysis model that deals with the consequences of environmental impacts. Decision are being ranked by multi criteria analyses, and evaluated according to the highest impact on the environment they cause. After identification and ranking the most problematic areas, a new, integral and more environmental friendly approach could be taken.

Primary goal of this study is to describe basics of an innovative holistic approach to the decision making process in architectural design, aimed to make environment healthier and safer for all.

***Keywords**: architectural design, decision making, environmental protection, conceptualization.*

1. INTRODUCTION

Construction, urbanisation, industrialisation and anthropogenic activities generate severe pollution as an unavoidable by-product. A proper management and mitigation of the pollution must be primary goal for any responsive and holistic integral approach to environmental protection. It is necessary to understand environmental hazards, and to move from traditional environmental protection models towards new, sustainable and advanced solutions.

Pollution generally occurs in many different waste forms (solid, liquid or gas), and arises from man-made systems. It is being generated during the manufacture of materials and products, during management and use of materials on site, and during other construction processes and related activities. The design and construction phases of every project comprise specifics of materials, as well as use of different equipment, processes and techniques. Almost all processes extensively disturb the environment, whether performed on green field, or previously developed sites. Construction processes and activities posse a high environmental risk by inputting pollutants into the environment, which can adversely affect workers on site, the neighbourhood and quality of soil, water and air. Construction and demolition waste contribute up to about 33 % of the total waste from all the streams, about half of which is demolition waste [1]. Each year in Europe, construction and demolition of structures generate in excess of 450 million tonnes of waste [2].

Construction industry uses a notable amount of natural resources. Materials originate from numerous sources and suppliers, and minimisation of waste is a particular problem. The most of construction sites deal with well known, commonly used materials, but the possibilities to recycle them are limited, and depend on numerous constrains and specific site features. Although built environment has rather long exploitation period, eventual demolition or redevelopment can produce significant amount of waste for disposal, unless the material is re-used.

The main resources used for construction are stone, wood and primary aggregates (sand and gravel). Extraction of these primary resources implies major environmental impact and can result in harming habitats and ecosystems, landscape damage, potential subsidence problems and release of methane. In construction processes, noise and dust along with heavy transport through populated areas is also another segment of generated pollution. The same issues arise in the disposal or processing/recycling of construction waste.

Anthropogenic activities related to the construction, have a major impact on the environment because of huge consumption of energy, both directly and indirectly (due to the energy embodied in the materials used in the process) [3]. In Scotland, the materials used for the structure of buildings represent more than 50 % of the embodied energy in the building [4]. The large amounts of materials needed for construction, consume a great deal of energy for transport. Building construction industry consumes 40 % of the materials entering the global economy and generates 40 – 50 % of the global output of greenhouse gases and the toxic compounds of acid rain (SO_2/SO_3, NO_2, H_2S and others) [5]. For example in the United Kingdom, construction industry consumes about 4.5 % of the national total energy consumption and as a consequence of this energy consumption, construction industry generates over 40 million tons of carbon dioxide (CO_2) which contributes to global warming from the greenhouse [2]. Acid gases and nitrogen dioxide (NO_2) are also produced, contributing to acid rain and photochemical smog production [1]. In the entire life cycle of elements of built environment, large quantities of different type of construction waste are produced. Inadequate design, inappropriate material, size and capacities, engineering changes, over-ordering, etc. are the sources of severe pollution that building activities produces.

With an aim to reduce and to minimize severe pollution, the preliminary concept of the Architectural Decision Analysis Model (ADAM) was created. The main goal of ADAM is to analyse activities and processes during building design and to aid decision making policy phases.

2. MODEL

Above all researches and monitoring aimed at environmental and human hazard assessment, requires the reliable methods to evaluate influence and effects of construction processes. Architectural Decision Analysis Model is based on the decision making theories in undefined complex systems (engineering, ecology, environmental sciences...). Risk assessments are in correlation with decision making, and are exposed to significant inter and intra influences. Through multi criteria analyse, decision are being ranked and evaluated by their highest effect on the environment. After ranking the most problematic areas, a new, integral and more environmental friendly approach is advised.

Data optimisation is one of the main problems that occur. Functions of aggregation and consolidation have the main role in data optimisation for decision making. Aggregation of the data input is the key in multi criteria decision making, engineering design and expert systems. The selection of proper aggregation function depends on character of each specific application, and requires interdisciplinary approach [6].

Decision making procedure and possibilities for improvement must be properly assessed and set. The results obtained by applying of ADAM are determined by K_A coefficient and value of K_A is set as ranking value starting at 0 with no harm for the environment. As K_A grows above 1, the hazard impact follows but is still under the legislation limits. K_A values of 1 and above represent serious hazard impact on the environment. Decision ranked by ADAM with K_A value of 1 and above requires alteration and it is advised to use more environmental friendly approach.

$$K_A = \frac{FD}{L} * K_e * K_C * K_S \quad (1)$$

K_A - ADAM coefficient
FD - Foreseen Decision
L - Legislation limitation
K_e - Economical coefficient
K_C - Correlation coefficient
K_S - Site specific risk assessment coefficient

From the equation (1) it can be seen that ADAM coefficient is principally dependant on relation between foreseen decision and legislation limitations. Other influencing factors are economical coefficient and correlation coefficient. Beside K_C and K_e, coefficients, an off-site specific risk is also one of the key impacting factors.

3. DISCUSSION

According to equation (1) and understanding K_A dependence on relation between foreseen decision and legislation limitations, economical, correlation and site specific risk

assessment coefficient, ADAM is conceptually based on the environmental risk assessment and its sustainability. With K_e economical efficiency of selected decision is tested and its economical sustainability (one of key sustainability factors) is ranked. K_C main purpose is to check correlations between selected architectural design decision and other decision that are part of same project. Correlation coefficient can be considered as one of main advantages of ADAM, thus giving ADAM ability not only to analyse each process and action individually, but also to analyse their relations and cumulative effect. Site specific risk assessment provides this model the broadness during the environmental impact assessment process. K_S estimates potential risks of specific location and shows advantages and limitations. The sum of all relevant factors of the ADAM, produces decision validity based on multiple dependant factors and gives recommendations about next step in decision making. In table 1 possible K_A values with their impact are presented.

Table 1. K_A value decision ranking.

K_A value	Effect on the environment	Decision validity
$K_A \cong 0$	No hazard effect on environment	The decision is valid
$0 < K_A < 1$	No significant hazard effect on environment	The decision is valid
$K_A \approx 1$	Significant hazard effect on environment	The decision is valid, but should be taken into consideration for revision
$K_A \geq 1$	Very significant hazard effect on environment	The decision is not valid and need to be revised

Advantages of ADAM are numerous, but like every model, it possesses some limitations. Main limitation is that although ADAM analyses relations between architectural design decisions, process as whole cannot be observed.

Being aware of limitation that basic ADAM model possess, currently advanced model ADAM+ is being researched and developed.

4. CONCLUSION

In order to facilitate achievement of sustainable and integral development goals, and to create a healthier and safer environment, Architectural Decision Analysis Model-ADAM was created as a basic concept of environmental protection platform. Understanding the significance of holistic approach and decisions that has to be made, the ADAM presents architectural decision analysis constructed with the aim of assessing negative consequences of environmental impacts. ADAM validation of the decisions foreseen by project designer detects flaws in a project that might affect the environment and helps designers to remove or to reduce them. Although ADAM possesses some limitations, it still can be considered as very confident model for a relevant decision analyses.

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Acknowledgements

This research is supported by the Ministry of Education and Science of the Republic of Serbia within the projects “Development of methods, sensors and systems for monitoring of water, air and soil quality” (Project No. *III 43008*) and “New technologies for monitoring and protection of environment from hazard chemical compounds and radial loads” (Project No. *III 43009*).

VPLYV VYBRANÝCH ABIOTICKÝCH ENVIRONMENTÁLNYCH STRESOROV NA OBSAH A FLUORESCENCIU CHLOROFYLU *GLYCINE MAX* (L.) MERRILL

THE INFLUENCE OF SELECTED ABIOTIC ENVIRONMENTAL STRESSORS ON THE CHLOROPHYLL CONTENT AND FLUORESCENCE *GLYCINE MAX* (L.) MERRILL

Ján Tomaškin*, Judita Tomaškinová*

* Matej Bel University, Faculty of Natural Sciences, Banská Bystrica, Slovakia

corresponding author: Judita Tomaškinová, tomaskinova@gmail.com

Original scientific paper

ABSTRAKT

V príspevku uvádzame výsledky vplyvu abiotických chemických stresorov v pôdnom prostredí (zasolenie, acidifikácia, anorganické prvky z priemyslu – odpadové červené kaly s obsahom Al) na obsah a fluorescenciu chlorofylu *Glycine max* (L.) Merrill, cv. Viola. V regulovaných podmienkach nádobového pokusu sme počas vegetačnej sezóny r. 2016 aplikovali stupňované dávky uvedených stresorov a hodnotili sme ich vplyv na efektívny a maximálny kvantový výťažok PSII (yield Y(II), resp. Fv/Fm test). Uvedené testy sa používajú na detekciu stresu rastlín, Y(II) nadobúdal hodnoty v intervale 0,769 – 0,789. Medzi hodnotenými stresormi a kontrolným variantom sme nezaznamenali signifikantné rozdiely. Test Fv/Fm nadobúdal hodnoty 0,799 – 0,839, detekoval stresovú reakciu rastlín predovšetkým na vyššie dávky odpadového červeného kalu. Hodnotený druh je na mierne zvýšený obsah solí (NaCl) a acidifikáciu pôdy (pH 6 resp. pH 5) tolerantný. Uvedenú skutočnosť dokumentuje aj obsah chlorofylu. Na kontrolnom variante a variantoch s menším obsahom solí sme zaznamenali najväčší (signifikantne preukazný) obsah chlorofylu 23,900, resp. 24,367 – 25,933 CCI oproti variantom s vyššou aciditou pôdneho prostredia (pH 4) a odpadovým červeným kalom (16,267, resp. 13,900 CCI).

Kľúčové slová: *acidifikácia pôdy, Glycine max, chemický stresor, fluorescencia chlorofylu, odpadové červené kaly, zasolenie pôdy*

ABSTRACT

In the paper we present the results of the influence of abiotic chemical stressors in the soil environment (salinization, acidification, inorganic elements from industry - red mud with Al content) on the content and fluorescence of chlorophyll *Glycine max* (L.) Merrill, cv. Viola. Under controlled conditions of pot experiment during growing season 2016, we applied graduated doses of these stressors and evaluated their effect on the effective and maximum quantum yield PSII (yield Y (II) or Fv/Fm test). These tests are used to detect plant stress, Y (II) obtained values in the range of 0.769 – 0.789. There were no significant differences between rated stressors and control variant. The Fv/Fm assay ranged from 0.799 to 0.839, detecting the stress response of the plants primarily on higher doses of red mud. The species under consideration is slightly elevated salt content (NaCl) and soil acidification (pH 6 or pH 5) tolerant. This fact is also documented by chlorophyll content. In control variant and variants with lower salt content we recorded the largest (significantly provable) content of chlorophyll 23.900, resp. 24.367 – 25.933 CCI vs. variants with higher acidity of the soil environment (pH 4) and red mud (16.267 and 13.900 CCI respectively).

***Keywords**: acidification of soil, Glycine max, chemical stressor, chlorophyll fluorescence, red mud, salinization of soil*

1. ÚVOD

Jedným z aktuálnych environmentálnych problémov súčasnosti je aj degradácia a kontaminácia pôdy. V príspevku hodnotíme vplyv chemickej degradácie pôdy, konkrétne zasolenie, acidifikáciu a priemyselné znečistenie anorganickými prvkami (odpadové červené kaly s obsahom hliníka) na asimilačné pletivá vegetácie. Vplyv uvedených faktorov sme hodnotili v regulovaných podmienkach nádobového pokusu, kde ako modelový rastlinný taxón sme vybrali kultúrnu plodinu *Glycine max* (L.) Merrill, cv. Viola. Sója svojim zložením a možnosťami využitia zaujíma osobitné postavenie v ľudskej výžive a je dôležitou surovinou krmivárskeho priemyslu. Sója má zo všetkých pestovaných strukovín najvyšší obsah bielkovín v semene (35 – 45 %), ktoré sa vyznačujú i výbornou skladbou esenciálnych amínokyselín. Semeno obsahuje i 18 – 22 % oleja výbornej kvality, 1,8 – 3,2 % lecitínu, 22 – 26 % glycidov, 4 – 6 % minerálnych látok s prevahou K a P, ale s deficitom Ca a široké spektrum vitamínov, predovšetkým skupiny B. Vo svetovom meradle zaberá najväčšie pestovateľské plochy zo všetkých strukovín a radí sa medzi tzv. strategické plodiny [1].

Uvedené formy degradácie pôdy predstavujú abiotické chemické stresory, ktoré majú často negatívny dopad na zdravotný stav vegetácie a v konečnom dôsledku môže dôjsť až k odumieraniu jedincov prípadne celej populácie. Napríklad rastliny vystavené prebytku kovov môžu podstúpiť zmeny v širokom spektre fyziologických vlastností [2]. Vplyv stresorov na rastliny je možné charakterizovať ako stresovú reakciu (stres), ktorá sa prejavuje anatomicko-morfologickými a funkčnými zmenami [3]. Prvým prejavom stresu rastlín resp. ich listov je poškodenie asimilačného aparátu, predovšetkým fotosystému II (PSII) [4]. Meranie fluorescencie chlorofylu poskytuje informáciu o rozsahu, v akom je PSII schopný absorbovať a využívať fotosynteticky účinnú radiáciu. Parametre fluorescencie chlorofylu a jeho obsahu v listoch môžu byť použité ako indikátory stresu vyvolané abiotickými chemickými stresormi [5, 6]. Potvrdzujú to aj niektoré práce [7 - 10], kde sa vplyvom abiotických faktorov prostredia zaznamenali zmeny obsahu chlorofylu v listoch rastlín.

Cieľom práce bolo posúdiť vplyv vybraných abiotických chemických stresorov na obsah a parametre fluorescencie chlorofylu a celkovú vitalitu *Glycine max* (L.) Merrill, cv. Viola.

2. MATERIÁL A METÓDY

Počas vegetačnej sezóny r. 2016 sme v nádobovom pokuse hodnotili vplyv simulovanej salinity, acidifikácie a priemyselného znečistenia anorganickými prvkami z odpadového kalu, ktorý vzniká pri spracovaní bauxitu a výrobe oxidu hlinitého resp. hliníka v Žiari nad Hronom (stredné Slovensko) na obsah a fluorescenciu chlorofylu sóje *Glycine max* (L.) Merrill, cv. Viola. Každý hodnotený stresor bol pripravený v troch stupňovaných dávkach. Salinitu pôdneho prostredia sme simulovali prípravou slaných roztokov rozpustením 20, 30 a 60 g chloridu sodného v objeme dvoch litrov vody, acidifikáciu prípravou kyslých roztokov (na báze kyseliny dusičnej) s pH 6, 5 a 4 v objeme dvoch litrov vody. Odpadové kaly sme získali z blízkeho okolia závodu Slovalco, a.s., Žiar nad Hronom a v dávkach 200, 400 a 600 g sme ich zmiešali s príslušným množstvom záhradníckeho substrátu (výrobca: AGRO CS a.s. ČR). V tabuľke 1 uvádzame varianty pokusu, vrátane kontroly, ktorú tvoril čistý záhradnícky substrát.

Tabuľka 1. Varianty pokusu

Variant	Abiotický chemický stresor	Dávka chemického stresora	Množstvo záhradníckeho substrátu (v litroch)
A1	salinita	20 g NaCl / 2 l vody = 10 ‰	4
A2		30 g NaCl / 2 l vody = 15 ‰	4
A3		60 g NaCl / 2 l vody = 30 ‰	4
B1	acidita	pH 6	4
B2		pH 5	4
B3		pH 4	4
C1	odpadové kaly	200 g	3,8
C2		400 g	3,6
C3		600 g	3,4
kontrola	-	-	4

Odpadové červené kaly majú chemické zloženie: 45 % Fe_2O_3, 15 % Al_2O_3, 13 % SiO_2, 7,5 % Na_2O, 6 % TiO_2, 2 % CaO [11].

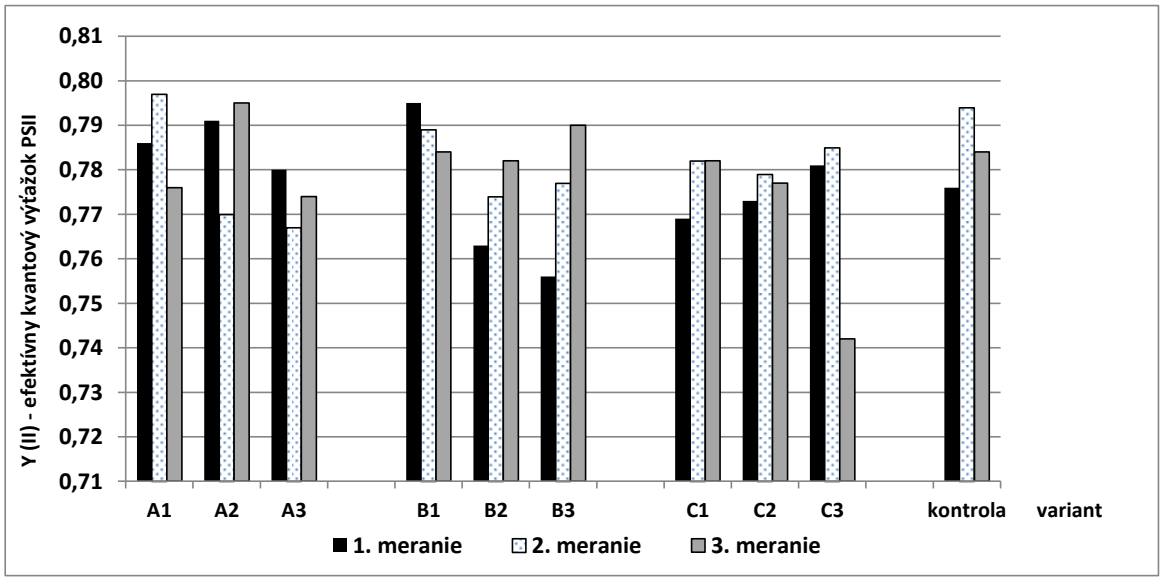
Vplyv uvedených abiotických environmentálnych stresorov na obsah a fluorescenciu chlorofylu sme hodnotili na fotosynteticky dospelých listoch rastlín sóje *Glycine max* (L.) Merrill, cv. Viola. Rastlinný materiál sme predpestovali zo semien, ktoré sme získali od výrobcu certifikovaných osív a sadív poľných plodín na Slovensku**,** spoločnosti OSIVO a. s. Zvolen. Semená boli vysiate do záhradníckeho substrátu v termíne 25. apríla 2016, do hĺbky pôdy 40 mm. Vypestované dospelé jedince sóje sme dňa 4. júla 2016 v počte po 2 ks presadili do veľkoobjemových črepníkov s príslušnými objemami pôdnych substrátov (Tabuľka 1). Na variantoch A1 – A3 a B1 – B3 sme v termíne od 10. júla do 7. augusta v týždňových intervaloch aplikovali zálievku pripravenými roztokmi stresorov v objeme 0,5 l na variant. Rastliny var. C1 – C3 boli zasadené do pôdy kontaminovanej odpadovými kalmi, kontrolné rastliny do 4 l čistého záhradníckeho substrátu. Počas vegetačnej sezóny sme uskutočnili 3 merania obsahu a fluorescencie chlorofylu v termínoch 25. júla, 1. a 8. augusta 2016.

Fluorescenciu chlorofylu fotosyntetického aparátu sme hodnotili testami Yield Y(II) a Fv/Fm prístrojom OS5p chlorophyll fluorometer (Opti-Sciences, Inc., USA). Uvedené testy sú štandardné záťažové testy, ktoré sa používajú na identifikáciu a kvantifikáciu hladiny stresu v rastlinách. Výsledkom meraní je efektívny kvantový výťažok PSII - Y(II) - meraný za denného svetla a maximálny kvantový výťažok PSII - Fv/Fm - meraný po 30 min. zatienenia listov. Fv/Fm nadobúda pre väčšinu rastlinných druhov hodnoty 0,79 – 0,84, znížené hodnoty indikujú stres rastlín [4]. Obsah chlorofylu listov v hodnotách CCI (chlorophyll content index) sme zaznamenali chlorofylmetrom CCM-200 plus (Opti-Sciences, Inc., USA). Vyššie hodnoty CCI indikujú vyššiu koncentráciu chlorofylu. Uvedené merania sme uskutočnili v doobedňajších hodinách (10.00 – 11.00 hod.) v dvoch opakovaniach (v príspevku uvádzame priemerné výsledky).

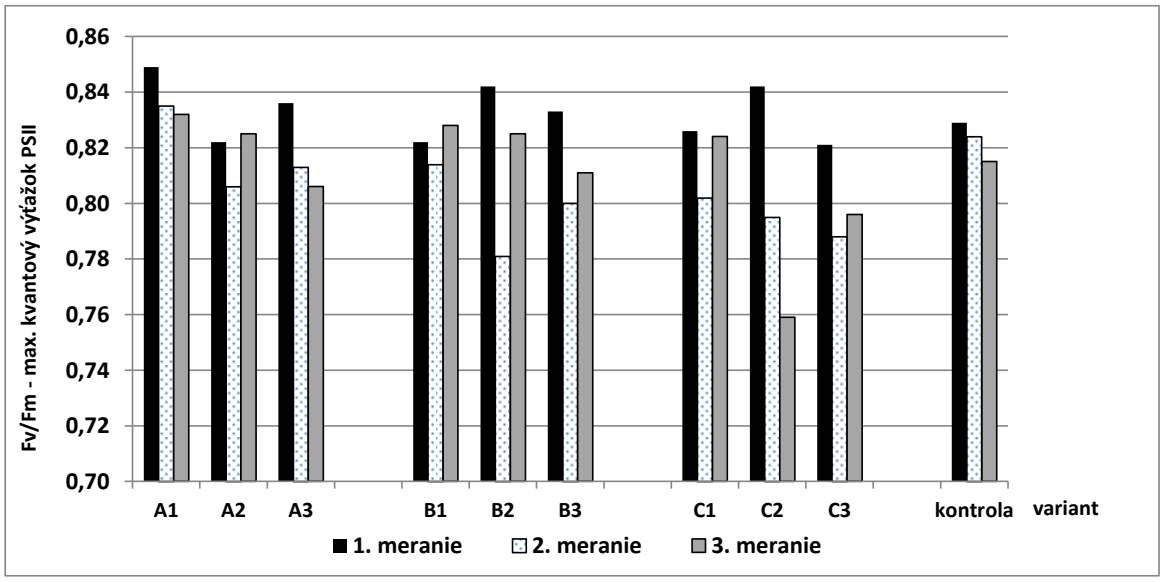
Výsledky obsahu a fluorescencie chlorofylu sme vyhodnotili štatistickým programom Statgraphic verzia 5.0 metódou dvojfaktorovej analýzy variancie (test LSD $\alpha_{0,05}$).

3. VÝSLEDKY A DISKUSIA

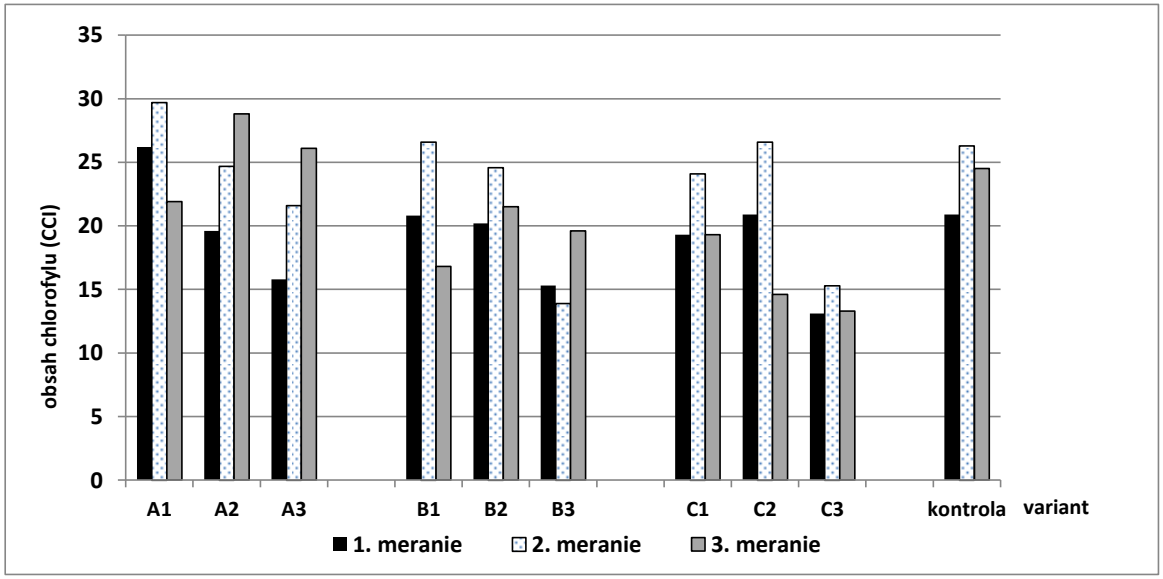
Namerané hodnoty kvantových výťažkov FSII asimilačného aparátu listov sóje hodnotených variantov chemických stresorov a kontroly počas vegetačnej sezóny 2016 dokumentujú obrázky 1 – 2, obsah chlorofylu obrázok 3.



Obrázky 1. Efektívny kvantový výťažok PSII (Yield test) *Glycine max* (L.) Merrill, cv. Viola



Obrázky 2. Maximálny kvantový výťažok PSII (Fv/Fm test) *Glycine max* (L.) Merrill, cv. Viola



Obrázky 3. Obsah chlorofylu (CCI) *Glycine max* (L.) Merrill, cv. Viola

Priemerné hodnoty kvantových výťažkov PSII, obsah chlorofylu a štatistické hodnotenie výsledkov uvádzame v tabuľke 2. Posúdili sme vplyv variantov abiotických chemických stresorov a kontroly a taktiež zmeny v troch termínoch merania na hodnotené parametre.

Tabuľka 2. Vplyv abiotických environmentálnych stresorov
na kvantové výťažky PSII a obsah chlorofylu *Glycine max* (L.) Merrill, cv. Viola

Faktor vplyvu		Kvantové výťažky PSII		0bsah chlorofylu
		Y(II)	Fv/Fm	(CCI)
variant	A1	0,786 a	0,839 b	25,933 c
	A2	0,785 a	0,818 ab	24,367 c
	A3	0,774 a	0,818 ab	21,167 bc
	B1	0,789 a	0,821 ab	21,400 bc
	B2	0,773 a	0,816 ab	22,100 bc
	B3	0,774 a	0,815 ab	16,267 ab
	C1	0,778 a	0,817 ab	20,900 bc
	C2	0,776 a	0,799 a	20,700 bc
	C3	0,769 a	0,802 a	13,900 a
	kontrola	0,785 a	0,823 ab	23,900 c
LSD $\alpha_{0,05}$		0,02148	0,02628	6,00255
meranie	1	0,777 a	0,832 b	19,210 a
	2	0,781 a	0,806 a	23,340 b
	3	0,779 a	0,812 a	20,640 ab
LSD $\alpha_{0,05}$		0,01176	0,01439	3,28773

Štatistická metóda: ANOVA - LSD test ($\alpha = 0,05$), rozdielne písmená a, b, c poukazujú na signifikantné rozdiely pri $p < 0,05$; medzi zhodnými písmenami nie sú významné rozdiely.

Efektívny kvantový výťažok PSII Y(II) asimilačných pletív listov sóje nadobúda hodnoty v intervale od 0,769 (variant C3) do 0,789 (variant B1). V uvedenom rozpätí sa nepotvrdili žiadne signifikantné rozdiely, môžeme teda konštatovať, že nebol potvrdený vplyv abiotického stresora na premenlivosť hodnoteného znaku. Preukazné rozdiely neboli zaznamenané ani v jednotlivých termínoch merania.

Citlivejšie na abiotické stresory reagoval maximálny kvantový výťažok PSII Fv/Fm. Počas merania sme najnižšie hodnoty 0,799 zaznamenali na variante C2, resp. 0,802 na variante C3, najväčšiu hodnotu na variante A1 (0,839). Maximálny kvantový výťažok PSII Fv/Fm asimilačného aparátu listov sóje na variante C2 a C3 je na 95 % hladine LSD testu signifikantne nižší ako na variante A1. Medzi všetkými ostatnými hodnotenými variantmi vrátane kontroly sa výraznejšie rozdiely nepotvrdili. Test Fv/Fm detekoval stresovú reakciu rastlín predovšetkým na vyššie dávky odpadového červeného kalu (varianty C2, C3). Naopak, pri hodnotení vplyvu ďalších dvoch environmentálnych stresorov konštatujeme, že na zvýšený obsah solí NaCl (varianty A1 – A3) a acidifikáciu pôdy (pH 6 resp. pH 5) bol hodnotený druh tolerantný, jeho kvantové výťažky PSII nevykazujú deštrukciu. Uvedenú skutočnosť dokumentuje aj obsah chlorofylu. Na kontrolnom variante a variantoch s menším obsahom solí (A2, A1) sme zaznamenali najväčší (signifikantne preukazný) obsah chlorofylu 23,900, resp. 24,367 – 25,933 CCI oproti variantom s vyššou aciditou pôdneho prostredia (variant B3 s pH 4) a odpadovým červeným kalom (variant C3), kde obsah chlorofylu dosahoval výrazne menšie hodnoty 16,267, resp. 13,900 CCI.

Javor et al. [1] uvádza, že sója ľahko prijíma ťažké kovy z ovzdušia a pôdy, preto pre potravinárske a krmné využitie ju nie je vhodné pestovať v okolí chemických závodov a elektrární. Uvedené riziko sme zaznamenali aj v našom nádobovom vegetačnom experimente prostredníctvom stresovej reakcie rastlín na aplikáciu anorganických prvkov z priemyslu (odpadové červené kaly s obsahom hliníka). Toleranciu *Glycine max* (L.) Merrill k salinite

pôdneho prostredia uvádzajú viacerí autori, druh zaradujú do skupiny poľnohospodárskych plodín stredne tolerujúcich zvýšený obsah solí [12, 13]. Uvádza sa, že pre pestovanie sóje sú vhodné pôdy so slabo kyslou až neutrálnou pôdnou reakciou (pH 6,5 – 7, minimálne však 6). Vysoká hodnota pH je nevyhnutná i pre hrčkotvorné baktérie, ktoré neprežívajú v kyslých pôdach a na mierne kyslých pôdach je ich činnosť redukovaná [1]. Uvedená skutočnosť v experimente síce nebola sledovaná, ale rastliny sóje určitú úroveň acidifikácie pôdneho prostredia tolerovali, nezaznamenali sme stresovú reakciu ich asimilačných pletív.

4. ZÁVER

Hodnotili sme vplyv stupňovaných dávok abiotických environmentálnych stresorov v pôdnom prostredí (zasolenie, acidifikáciu, anorganické prvky z priemyslu – odpadové červené kaly s obsahom hliníka) na obsah a fluorescenciu chlorofylu (kvantové výťažky PSII) *Glycine max* (L.) Merrill, cv. Viola.

Na základe dosiahnutých výsledkov konštatujeme, že hodnotený druh reagoval najcitlivejšie na vyššie dávky odpadového červeného kalu (varianty C2, C3). Uvedenú skutočnosť dokumentujú najnižšie zaznamenané hodnoty Fv/Fm testu (nižšie hodnoty detekujú stresovú reakciu asimilačných pletív rastlín) na variantoch C2 (0,799) resp. C3 (0,802) a tiež najmenší obsah chlorofylu rastlín variantu C3 (13,900 CCI).

Glycine max (L.) Merrill, cv. Viola naopak dobre toleruje vplyv ďalších hodnotených abiotických chemických stresorov. Druh je tolerantný k zvýšenému obsahu solí (NaCl) a acidifikácii pôdneho prostredia (pH 6 resp. pH 5), k poškodeniu fotosyntetického aparátu rastlín nedošlo. Na kontrolnom variante a variantoch s menším obsahom solí (A2, A1) sme zaznamenali najväčší obsah chlorofylu 23,900, resp. 24,367 – 25,933 CCI.

Môžeme predpokladať, že porasty *Glycine max* (L.) Merrill, cv. Viola je možné pestovať aj v mierne zasolenom alebo kyslom pôdnom prostredí.

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Poďakovanie

Uvedená práca vznikla s využitím prístrojového vybavenia získaného v rámci projektu OP Výskum a vývoj – ITMS 26210120024 „Obnova a budovanie infraštruktúry pre ekologický a environmentálny výskum na UMB“.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

THE IMPACT OF SALT STRESS ON SOIL RESPIRATION IN MISCANTHUS X GIGANTEUS HYBRID

Judita Tomaškinová*, Ján Tomaškin*

* Matej Bel University, Faculty of Natural Sciences, Banská Bystrica, Slovakia

corresponding author: Judita Tomaškinová, e-mail: tomaskinova@gmail.com

Original scientific paper

ABSTRACT

Increasing soil salinity is serious land degradation issues and is critical in environmental management, as the areal extents of salinity are predicted to increase. This study was conducted to determine the impact of salt stress simulation induced by the NaCl solution (0 – deionized water; 100, 200, 300 mmol/L) on soil respiration (Rs) of a hybrid *Miscanthus x giganteus* during 2016 and 2017. Results showed that Rs is significantly decreased with increasing NaCl concentrations and may be related to the disruption of biotic processes in the soil environment. The lowest Rs of 0.7509 μmol CO_2 . s^{-1} . m^{-2} was recorded under the concentration of 300 mmol/L NaCl variant, a higher under the concentrations of 200 and 100 mmol/L NaCl, and the highest Rs of 1.5715 μmol CO_2 . s^{-1} . m^{-2} was recorded in the control variant. The obtained results therefore prove a decresed tolerance of *Miscanthus x giganteus* to salt stress.

Keywords*: soil respiration, salinity, abiotic environmental stress, chemical stressor, Miscanthus x giganteus*

1. INTRODUCTION

Abiotic stresses in the environment, such as drought, high salinity, heat stress and deprivation of nutrients, reducing the photosynthetic capacity of the plant and causes the excessive stress [1 - 4], which may manifest itself anatomic and functional alterations [5], lead to anomalies in plant growth and biomass productivity. The plant biomass is the primary product of photosynthesis, the process requiring CO_2, H_2O, biogenic elements and sunlight. At present, the plant biomass productivity is severely affected by adverse environmental stresses resulting from salinity. The most endangered are plants with a long-term growth period, such as perennial crops and trees, where long-term stress can damage the plant. On the contrary, under the influence of long-term exposure to stressors large number of plant species

has developed complex mechanisms to adjust the growth and adapt to different environmental conditions [1 - 4].

Increasing soil salinity is serious land degradation issue worldwide and an understanding of the effect of salinity on soil carbon fluxes is critical in the context of the environmental management [6], as the areal extents of salinity are predicted to increase due to human activities such as land clearing and the use of low-quality water for irrigation [7, 8]. Salinity negatively influences not only plant growth but is also considered as a stress for the soil microorganisms and also affects biomass and microbial community structure, thereby has a negative impact on important biochemical processes involved in turnover of soil organic matter [7, 9, 10]. Rietz and Hayne [11] found that organic matter decomposition was inhibited by increasing salinity. Salinity effects are due to (i) increased osmotic potential making it more difficult to withdraw water from the soil and (ii) ionic effects. Changes in microbial community composition are due to different tolerance among microbial genotypes to salinity [7, 12 - 14].

A key aim for the 21st century is therefore to grow crops with increased survival capacity and optimal growth under the stress conditions. The goal of this work was to assess the effect of salinity on the soil respiration of *Miscanthus x giganteus* and its potential adaptation, even in the context of utilization for the phytoremediation of areas with high concentration of salinity and acidity.

2. EXPERIMENTAL

The experiment focused on monitoring the impact of salt stress simulation on the soil respiration of a hybrid *Miscanthus x giganteus*. Under controlled conditions of a pot experiment which took place in the greenhouse, we applied graduated doses of three treatments and assessed their impact on Net CO_2 Exchange Rate (NCER) during the aspect of spring, summer and autumn season in 2016 and 2017.

Pre-grown rhizomes of *Miscanthus x giganteus* were obtained from the Genetic Bank of Slovakia (VÚRV, Piešťany – Research Institution of Plant Production, Piešťany). From 20th May 2015, the experimental plants were grown in number of 2 pieces in each large volume pot filled with a 10 L of garden substrate (pH 6.0 – 6.5).

Salt stress simulation was induced by the NaCl solution in concentrations of: 0 (deionized water, control (K); 100, 200 and 300 mmol/L NaCl. Such watering took place from 25th April 2016 to 25th October 2017 in each of the seasons (spring, summer, autum), in the amount of 0.5 L stresors of the prepared solution at weekly intervals on the variant. The measurement of the monitored impact was at the end of the each season and took place during five repetitions of each variant. Continuous measurements of current soil respiration (Rs) of the NCER were performed with LCi-SD soil respirator (ADC BioScientific Ltd., Hoddesdon, UK) consisting of a cylindrical measuring chamber (lower ring with stainless steel cuff and top detachable part with acrylic chamber that connects directly to the LCi arm). The measurement is corrected at atmospheric pressure (750 - 1250 mbar) with a special drain valve that prevents undesired pressure fluctuations inside the chamber during measurement (the absence of any distortion). In order to ensure regular measurement intervals, the time function was used for each measurement at minute intervals. The surface area of the "enclosed soil" in the chamber is nominally 97.5 cm^2 and the soil volume in the chamber is nominally 803 cm^3. In this enclosure, a differential CO_2 flow is measured with a high-precision IRGA analyser located in the arm.

2.1. Data and Statistical analyses

Soil Net CO_2 Exchange Rate (soil respiration (R_s) per unit area μmol CO_2 m^{-2} s^{-1}): symbol: *NCER* [μmol m^{-2} s^{-1}]

$$NCER=u_s(-\Delta c) \quad (1)$$

where is:

u_s - molar flow of air per square meter of soil [mol m^{-2} s^{-1}]
Δc - difference in CO_2 concentration through soil pot, dilution corrected [μmol mol^{-1}]:
$\Delta c = C_{ref} - C'_{an}$

where is:

C_{ref} - CO_2 flowing into leaf chamber [μmol mol^{-1}]
C'_{an} - CO_2 flowing out from leaf chamber [μmol mol^{-1}]

The results were statistically evaluated by multifactor analysis of variance at 95 % and 99 % of the level of LSD test, where three variants of salinity (100, 200 and 300 mmol/L NaCl) and K were evaluated as the influence factor. The second factor of influence was the seasonal measurement aspect and third factor was the experimental year.

3. RESULTS AND DISCUSSION

Average values of soil respiration and statistical assessment of the salinity simulation in 3 variants (100, 200 and 300 mmol/L NaCl) and the control variant during three seasons in 2016 - 2017) are presented in figures 1 and 2 and table 1.

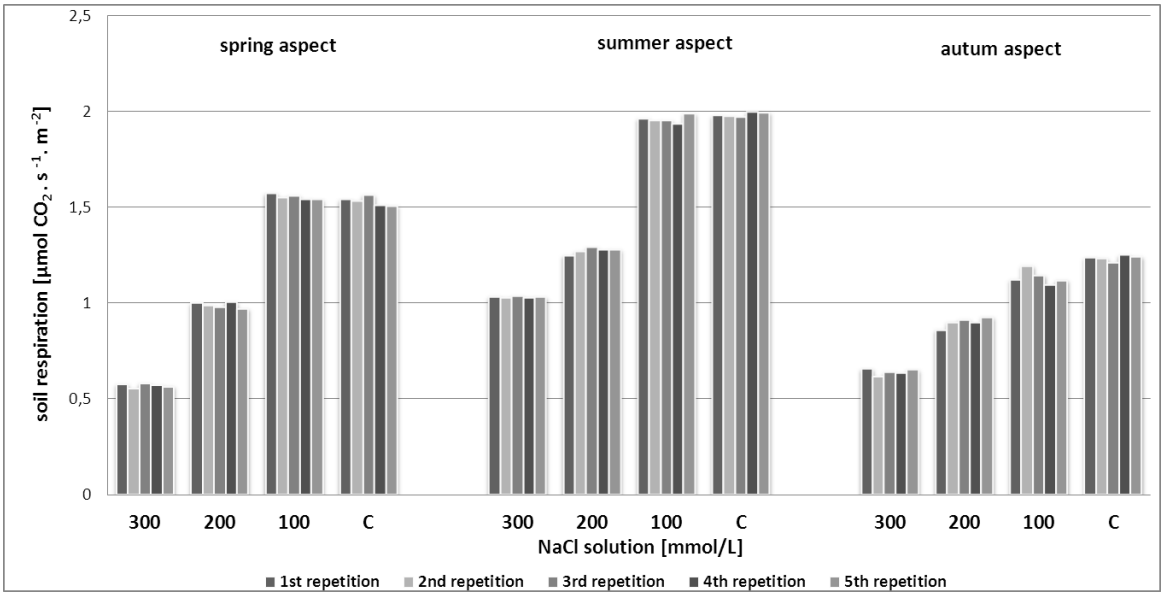


Figure 1. The impact of the salt stress on soil respiration of *Miscanthus x giganteus* in relation to seasonal aspects in year 2016

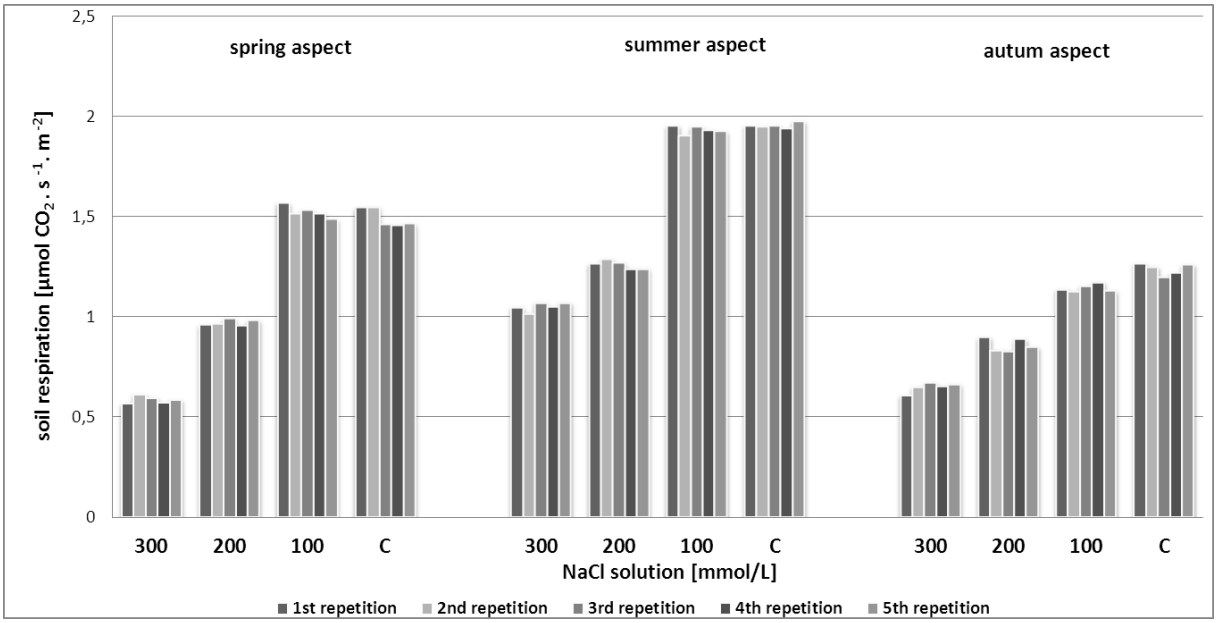


Figure 2. The impact of salt stress on soil respiration of *Miscanthus x giganteus* in relation to seasonal aspect in year 2017

Table 1. The impact of salt stress simulation induced by the NaCl solution on soil respiration of a hybrid *Miscanthus x giganteus*

Factor of the influence		NCER [µmol CO_2 s^{-1} m^{-2}]	Significant differences	
Year	2016	1.2306967	b	a
	2017	1.2208333	a	a
LSD α 0,05			0.00802	
LSD α 0,01				0.01087
NaCl solution	300 mmol/L	0.7509000	a	a
	200 mmol/L	1.0409667	b	b
	100 mmol/L	1.5397267	c	c
	control (C)	1.5714667	d	d
LSD α 0,05			0.01135	
LSD α 0,01				0.01537
Seasonal aspect	Spring	1.1515250	b	b
	Summer	1.5538700	c	c
	Autum	0.9719000	a	a
LSD α 0,05			0.00983	
LSD α 0,01				0.01332
Repetition	1st	1.2265750	a	a
	2nd	1.2259167	a	a
	3rd	1.2286667	a	a
	4th	1.2216667	a	a
	5th	1.2260000	a	a
LSD α 0,05			0.01269	
LSD α 0,01				0.01719

Values within a column marked with different letters a, b, c, d show significant differences at p <0.05 resp. p <0.01; there are no significant differences between the same letters.

The lowest soil respiration of 0.7509 μmol CO_2 . s^{-1} . m^{-2} was recorded under the variant of 300 mmol/L NaCl, higher soil respiration was observed under the variant of 200 mmol/L NaCl, followed by the variant of 100 mmol/L NaCl and the highest soil respiration of 1.5715 μmol CO_2 . s^{-1} . m^{-2} was recorded under the control variant. Among all the evaluated variants, we noted the significant differences in Rs at both standard LSD test levels (LSD α 0.05 and LSD α 0.01). On the basis of the statistical evaluation, the highly demonstrative effect of salinity on the soil respiration was confirmed.

Similarly, soil respiration responded sensitively during the measurement of the seasonal aspects as well. The lowest soil respiration of 0.9719 μmol CO_2 . s^{-1} . m^{-2} was observed in autumn. Significantly higher soil respiration of 1.1515 μmol CO_2 . s^{-1} . m^{-2} was observed in the spring aspect and the highest soil respiration of 1.5539 μmol CO_2 . s^{-1} . m^{-2} was observed in the summer aspect. The aspect of season has a significant impact on the variability of the evaluated parameter. We confirmed this fact at both levels of the LSD test (table 1). We carried out the whole experiment in 5 repetitions, and did not notice the difference between the repetitions, which documents the methodical and experimental correctness of the experiment.

Our study showed that soil respiration decreases with increasing salinity and it is in agreement with previous studies [15 - 22]. *Miscanthus x giganteus* tolerates increased salinity and has not shown a reduction in overall vitality. Tomaskin and Tomaskinova [23] confirmed that the species evaluated tolerates also the effect of abiotic chemical stressors in the form of acidification, and the response to the stress caused is also the resistance of the species to damage of the photosynthetic apparatus. Many authors were focused on the possibilities of *Miscanthus x giganteus* cultivation, even in the slightly contaminated soil environment [23 - 26]. McCalmot, McNamara, Donnison, Farrar, Clifton-Brown [27] suggest to use *Miscanthus* for novel land-use change from agricultural grassland to bioenergy. Large-scale production and utilization of biomass is essential if European targets for decarbonisation of energy supplies to mitigate climate change are to be met [28]. However, producing high-input, high-effort annual food crops for use in energy production is unsustainable in the long term [27, 29 - 31]. Much research effort has been spent for understanding and development of low-input, high-productivity perennial energy grasses to address some of the environmental issues surrounding large-scale bioenergy production [27, 32 - 36]. *Miscanthus x giganteus* is seen as one of the most promising of these second-generation energy crops with much commercial interest as a result [27, 37 - 42]. Much has been learnt in recent times about the potential environmental costs and benefits of a large-scale roll-out of *Miscanthus* production [27, 43 - 45], and it seems clear that, in arable systems particularly, there are significant benefits to be found in utilizing this novel perennial as a long-term break crop in overworked or marginal agricultural soils. What are less clear are the impacts on soil carbon cycling [27].

4. CONCLUSION

The reduction in biotic processes in the soil (root respiration, microbial respiration and respiration of soil insects) is significantly demonstrated with a respond of *Miscanthus x giganteus* plant to the induced environmental stress by simulating salinity in the order of 100, 200 and 300 mmol/L NaCl. An increase in applied salt stress decreases the soil respiration. *Miscanthus x giganteus* tolerates increased salinity and has not shown a reduction in overall vitality.

The results of the research show that *Miscanthus x giganteus* may and should also be used for remediation purposes, for instance in areas affected by increased salinity or to adapt

the use of land to bioenergy generation, thus providing a solution to environmental issues for both phytoremediation and bio-energy uses in the context of the land use planning and management.

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Acknowledgements

This paper was supported by project ITMS 26210120024 "Renewal and development of infrastructure for ecological and environmental research at UMB".

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

ADSORPTION OF REACTIVE BLACK 5 DYES ON ACTIVATED CARBON

Irena Trakoštanec*, Ana Sutlović*, Branka Vojnović*, Mario Cetina*

* University of Zagreb, Faculty of Textile Technology, Zagreb, Croatia

corresponding author: Mario Cetina, e-mail: mario.cetina@ttf.hr

Original scientific paper

ABSTRACT

Textile industry is considered to be one of the major environmental pollutants, primarily due to wastewaters quantity and composition. Therefore, it is important to examine different methods of their treatment. This paper explores a possibility of removing dye Reactive Black 5 by adsorption on activated carbon. For this purpose, the isothermal adsorption of dye Everzol Black B at 45(±1) °C was carried out in time from 30 - 960 minutes, and is compared with results obtained for dye Drimarene Black B. It was found that already after 30 min dye Drimarene Black R-3B was adsorbed by 20 % more compared to dye Everzol Black B. This fact confirmed assumption that dyes of the same chemical constitution, but produced by different manufacturers have a different content of chromophoric component and additional substances, what results in their different behaviour during adsorption. In order to investigate the mechanism of adsorption of Everzol Black B dye on activated carbon a kinetic studies have been also carried out. Experimental data were analysed by a pseudo-first-order and pseudo-second-order kinetic models, as well as intraparticle diffusion model.

***Keywords**: adsorption, reactive dye, wastewaters, activated carbon, adsorption kinetics*

1. INTRODUCTION

Textile finishing industry, as one of the largest water consumption and major environmental pollutant, uses significant quantities of water [1], which is after treatment eliminated as wastewater. The wastewaters have a wide range of pH values, high temperatures ranges, they may be coloured and mainly contain various types of pollutants, most commonly dyes, surfactants, pesticides, oils, fats, solvents, heavy metals, inorganic salts, waste fibres etc. [2]. Special attention is given to dyes and pigments because they are highly visible materials and even the minimum amount released into the environment may cause the appearance of colour in open waters. Coloured water, except aesthetic deficiency, prevents penetration of light into natural water, which negatively affects the entire waters community

and on organisms that depend on water quality. Wastewater stream from the textile dyeing operation contains unutilized dyes (about 8 – 20 % of the total pollution load due to incomplete exhaustion of the dye) and auxiliary chemicals [3]. Besides, some dyes have proven allergenic, toxic and/or carcinogenic properties, which make them dangerous or potentially harmful to environment.

Taking into consideration mentioned above, it is necessary to treat the wastewaters in a way that amounts of harmful substances are reduced to legally limited concentrations. Methods of treatment and disposal of textile industry wastewaters are numerous: coagulation and flocculation, chemical oxidation, biological treatment, membrane separation, reverse osmosis etc. [3 – 5]. One of the most commonly used and effective methods of treatment of coloured water is adsorption, based on the accumulation of the substance from the solution at a solid phase. Adsorption is one of the best treatment methods due to its flexibility, simplicity of design, and sensitivity to toxic pollutants [3, 6]. Activated carbon is the most popular adsorbent because of its adsorption efficiency and great capacity, although some other adsorbents, less expensive and easily available, are also used for wastewater treatment. It is very effective adsorbent for removal of different types of dyes, including reactive dyes [7 – 10].

It is known that adsorption is a time-dependent process, and therefore for removal of dyes from wastewaters it is necessary to know the time of adsorption. Hence, the most important factor in the design of adsorption process is prediction of the rate of adsorption for a given system. This paper aims to present adsorption efficiency of commercial activated carbon for the removal of dye Reactive Black 5 of manufacturer Everlight Chemical Industrial Corp. (Everzol Black B) and compare it with the same dye of another manufacturer, Clariant GmbH (Drimarene Black 3-RB) [11]. It could be assumed that the same dye produced by two manufacturers have a different, unknown content of the chromophoric component and additional substances, and therefore behaviour of these dyes during adsorption could be different. Besides effect of contact time on the adsorption process several kinetic models were applied to correlate the adsorption data and to evaluate the diffusion mechanism of the adsorption process.

2. EXPERIMENTAL

2.1. Materials

Reactive Black 5 dye (Everzol Black B supplied by Everlight Chemical Industrial Corp., C.I. 20505, chemical formula: $C_{26}H_{21}N_5Na_4O_{19}S_6$, M_r = 991.82) was used for adsorption experiment. Powdered activated carbon was purchased from Kemika company, Croatia. Adsorbent was dried in a oven at 105 ^oC for 24 hours and stored in desiccator until it is used.

2.2. Batch mode adsorption studies

Adsorption studies were conducted by contacting 50 ml of dye solution of initial concentration c_0 = 300 mg dm^{-3} with 0.2 g of activated carbon in glass bottles. The experiments were repeated in triplicate. Data in Table 1 and experimental points presented in figures are the average values of three repetitions. Suspensions were shaken at different contact times (30, 60, 120, 180 and 240 minutes and 16 hours until equilibrium is reached)

with impeller speed of 250 rpm at 45(±1) ^{o}C (Heidolph Unimax 1010 with Incubator 1000). After agitation, suspensions were filtered through filter-paper blue ribbon. The residual liquid-phase dye concentration after adsorption was determined spectrophotometrically by monitoring the absorbance using UV–Vis spectrophotometer (Lambda 20, Perkin Elmer) at maximum absorbance wavelength (λ_{max} = 598 nm). The calibration graph of absorbance versus concentration obeyed a linear Beer-Lambert relation.

Amount of adsorbate adsorbed at any time t, q_t (mg g^{-1}), and amount of adsorbate adsorbed at equilibrium, q_e (mg g^{-1}), were calculated by using following equation:

$$q = \frac{V \cdot (c_0 - c_t)}{m} \quad (1)$$

where c_0 (mg dm^{-3}) is the initial dye concentration, c_t (mg dm^{-3}) is dye concentration in the liquid phase after appropriate time of adsorption and when equilibrium is reached (t = 16 hours), V is the volume of liquid phase (dm^3), and m is mass of the adsorbent (g).

Percentage of adsorbed dye (% ads.) is calculated by equation:

$$\%\ ads. = \frac{c_a}{c_0} \times 100 \quad (2)$$

where c_a (mg dm^{-3}) is concentration of adsorbed dye on solid phase ($c_a = c_0 - c_t$).

3. RESULTS AND DISCUSSION

3.1. Effect of contact time on adsorption process

The objective of this work was to assess the effectiveness of activated carbon for the treatment of dye-rich textile wastewaters with special focus on colour pollutants reduction. The initial concentration of dye Everzol Black B was 300 mg dm^{-3}, what is a typical dye concentration in dye-house wastewaters after black hues process of dying. Average values of dye concentration in the liquid phase after appropriate time of adsorption, concentration of adsorbed dye on the solid phase, percentage of adsorbed dye and amount of adsorbate adsorbed at any time t are given in table 1.

Table 1. Average values of dye concentration in the liquid phase after adsorption (c_t), concentration of adsorbed dye on solid phase (c_a), percentage of adsorbed dye (% ads.) and amount of adsorbate adsorbed at any time (q_t) at different adsorption times

t / min	c_t / mg dm^{-3}	c_a / mg dm^{-3}	% ads.	q_t / mg g^{-1}
30	74.0	226.0	75.3	56.5
60	33.0	267.0	89.0	66.8
120	10.5	289.5	96.5	72.4
180	8.2	291.8	97.3	73.0
240	6.7	293.3	97.8	73.3
960	3.0	297.0	99.0	74.3

All data in table 1 show that equilibrium was practically reached quite quickly. Slightly more than 97 % of dye is adsorbed after 3 hours, while for adsorption of 75 % of dye only 30 minutes was needed. This means that activated carbon is proved to be very efficient adsorbent for removal of dye.

The aim of this work was also to compare behaviour during the adsorption of Reactive Black 5 dye produced by two different manufacturers. Thus, adsorption of dye Everzol Black B is compared with adsorption of dye Drimarene Black R-3B (manufacturer Clariant GmbH) under same experimental conditions (initial concentration, time, mass of adsorbent, impeller speed and temperature) [11]. Graphical representation of adsorption of these two dyes is shown in figure 1.

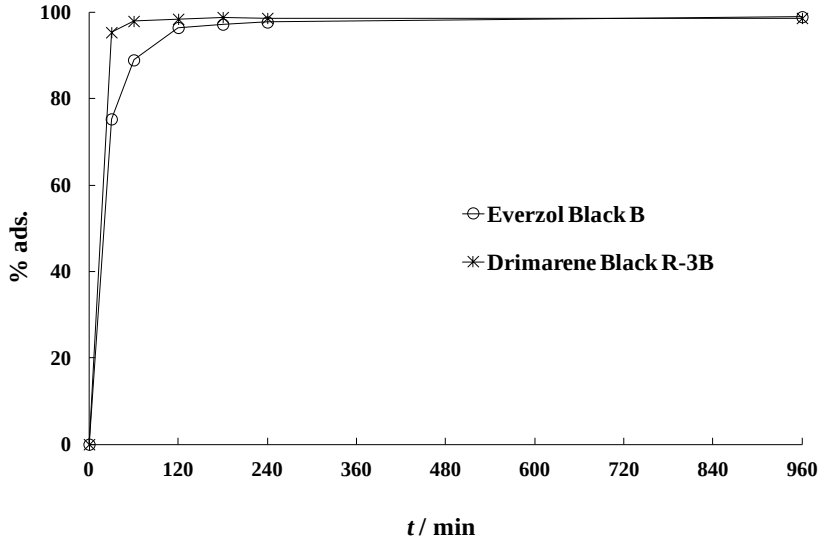


Figure 1. Effect of time on percentage of adsorbed dye Everzol Black B and Drimarene Black R-3B on activated carbon

From figure 1 is obvious that there are large differences in the composition of two Reactive Black 5 dyes of two different manufacturers. The Drimarene Black R-3B dye is adsorbed much faster compared to dye Everzol Black B (table 1). For adsorption of approximately 98 % of dye Everzol Black B 4 hours was needed, whereas for the same percentage of adsorption of dye Drimarene Black R-3B approximately 1 hour was sufficient [11]. Both plots in figure 1 can be approximately divided into three regions. The first region includes very fast initial adsorption, probably governed by rapid external diffusion process and mainly adsorption of dye on the surface of activated carbon. After this step follows second region, milder and gradual increase of adsorbed dye, and third region where it practically reaches the equilibrium state. The reason for the weaker adsorption of Everzol Black B can be in the fact that this dye has more additives which, during adsorption, fill the surface and the pores of activated carbon, and therefore prevents adsorption of dye molecules.

3.2. Kinetics of adsorption

In order to investigate the mechanism of adsorption and potential rate controlling steps a kinetic studies have been performed. Kinetic study is important to an adsorption process because it depicts the uptake rate of adsorbate, and controls the residual time of the whole adsorption process for a given system. The experimental data were analysed by three kinetic

models: a pseudo-first-order and pseudo-second-order kinetic models and an intraparticle diffusion model.

3.2.1. Pseudo-first-order kinetic model

Lagergren [12] proposed a rate equation for the sorption of solute from a liquid solution based on the solid capacity. This the most widely used kinetic model is expressed by following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where k_1 is the rate constant of pseudo-first-order (min^{-1}).

Integrating this equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \tag{4}$$

The kinetic constant k_1 can be determined by plotting $\ln(q_e - q_t)$ against time (t). If the first-order equation is applicable, the plot should give a linear relationship, and allows the calculation of rate constant of pseudo-first-order (k_1) from the slope and amount of adsorbate adsorbed at equilibrium ($q_{e,calc}$) from the intercept.

The kinetic constant k_1 for dye Everzol Black B calculated from the line equation is 0.0138 min^{-1}, and the value of the correlation coefficient is 89.4 %. Despite the relatively high value of this coefficient that can't be neglected, this kinetic model is not suitable for the description of adsorption kinetics. Calculated value of amount of adsorbate adsorbed at equilibrium from the line equation ($q_{e,calc}$) amounts 17.8 mg dm^{-3}, and is not consistent with the experimentally obtained value, Table 1 (t = 16 h; $q_{e,exp}$ = 74.3 mg dm^{-3}).

3.2.2. Pseudo-second-order kinetic model

Ho and McKay [13, 14] developed a second-order equation based on adsorption capacity. This kinetic model is given by following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the rate constant of pseudo-second-order (g mg^{-1} min^{-1}).

Integrating the equation (5) for the same boundary conditions as for the first-order gives equation, which in the linear form is presented as:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \tag{6}$$

If the pseudo-second-order equation is applicable, the plot of t / q_t against time (t) should give a linear relationship, and allows the calculation of amount of adsorbate adsorbed at equilibrium ($q_{e,calc}$) from the slope and afterwards rate constant of pseudo-second-order (k_2) from the intercept.

Graphical representation of this model gives a linear relationship with a very high value of the correlation coefficient of 99.97 %, figure 2. The kinetic constant k_2 calculated from the line equation is 0.001540 g mg^{-1} min^{-1}, while q_e value calculated from the line equation amounts 76.3 mg dm^{-3}, what is approximately equal to the experimentally obtained value of 74.3 mg dm^{-3} (table 1). Therefore, adsorption of Everzol Black B on commercial activated carbon is kinetically controlled assuming a pseudo-second order rather than a pseudo-first-order process. The pseudo-second-order model accounts chemical adsorption as the rate-limiting process.

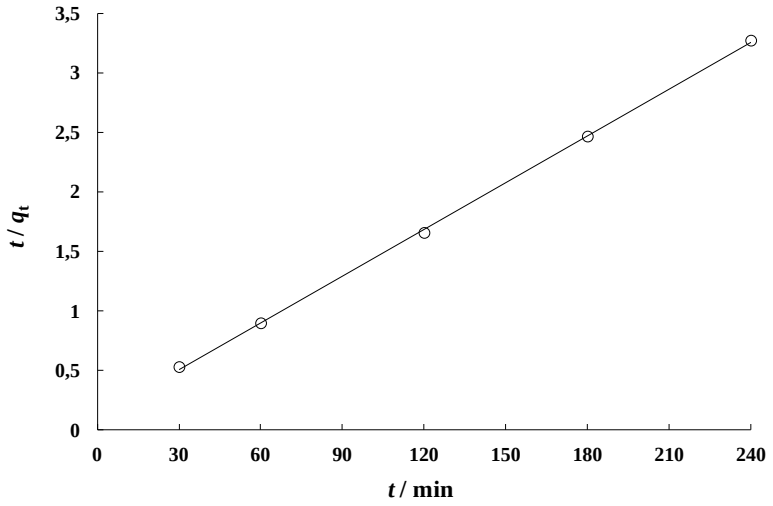


Figure 2. Graphical representation of pseudo-second-order kinetic model for adsorption of dye Everzol Black B on activated carbon

3.2.3. Intraparticle diffusion model

For evaluation of the diffusion mechanism for adsorption of Everzol Black B on activated carbon we also used intraparticle diffusion model. Theoretical treatments of intraparticle diffusion yield complex mathematical relationships, which differ in form as functions of the geometry of the adsorbent particle. The intraparticle diffusion model is based on the following equation [15, 16]:

$$q_t = k_i \cdot t^{0.5} \tag{7}$$

where k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$).

If intraparticle diffusion is rate limiting step of adsorption, *i.e.* intraparticle diffusion controls the rate of adsorption, then plot q_t versus $t^{0.5}$ should be linear and pass through the origin. If plot of q_t versus $t^{0.5}$ presents multi-linearity this indicates that two or more rate controlling steps occur in the adsorption process [15, 17, 18].

Figure 3 shows the root time plot for the adsorption of Everzol Black B dye on activated carbon. It can be seen in the figure that plot is not linear, *i.e.* exhibits multi-linearity. Therefore, it can be concluded that intraparticle diffusion is not the only process which influences on the adsorption rate and that multiple steps took place during the adsorption process. Also, this figure shows that the absorption rate is initially higher and decreases over time, *i.e.* the amount of adsorbed dye or diffusion decreases with time.

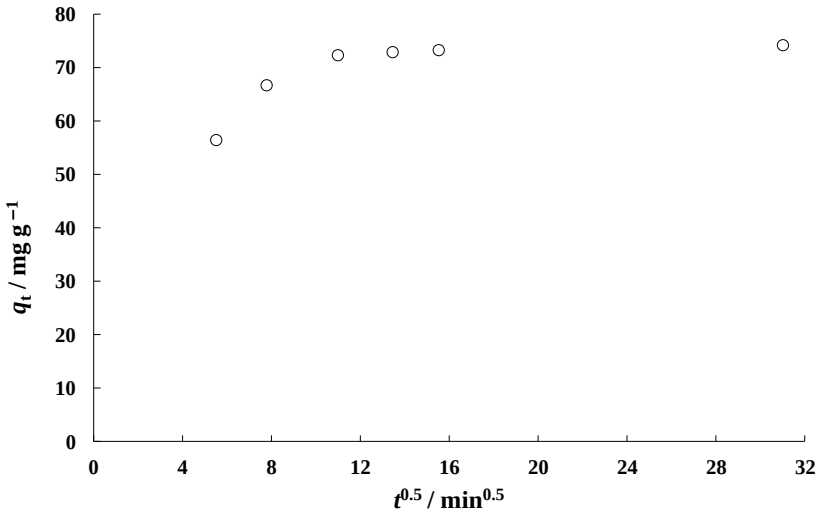


Figure 3. Root time plot for the adsorption of Everzol Black B on activated carbon

3.3. Thermodynamics

Standard Gibbs free energy (ΔG^0, kJ mol^{-1}) values of the adsorption process can be calculated from the equation:

$$\Delta G^0 = -RT\ln(K_c) \tag{8}$$

where R is the universal gas constant, and T is temperature. K_c is equilibrium constant calculated from concentration of dye adsorbed on solid phase at equilibrium, c_s, and concentration of dye after equilibrium is reached in the liquid phase, c_e, [19]:

$$K_c = \frac{c_s}{c_e}. \tag{9}$$

The negative value of ΔG^0 indicates that the adsorption reaction is spontaneous, which means that ΔG^0 value reflects the feasibility of the process. Calculated ΔG^0 value for this adsorption system is −12.2 kJ mol^{-1}, so showing that the adsorption of Everzol Black B dye on activated carbon was a spontaneous process in nature.

4. CONCLUSION

According to the results achieved, adsorption of dye Everzol Black B on activated carbon was fast. As equilibrium was reached quite quickly it was confirmed that activated carbon is very efficient adsorbent for the adsorption of colour pollutants. It was also shown that two Reactive Black 5 dyes, Everzol Black B and Drimarene Black R-3B, have different adsorption behaviour because of their different composition. Another possible reason for this could be that granulations of these two dyes are different, what will be a subject of our future research. Furthermore, results of this research showed that adsorption of Everzol Black B dye on commercial activated carbon is kinetically controlled assuming a pseudo-second order process, and that intraparticle diffusion is not the only process which influences on the

adsorption rate. Finally, calculated ΔG^0 value confirmed that the adsorption of Everzol Black B dye on activated carbon was a spontaneous process.

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PRAĆENJE KVALITETE DRVNE SJEČKE I PEPELA ZA KOGENERACIJSKE ELEKTRANE NA BIOMASU BE-TO OSIJEK I BE-TO SISAK

MONITORING THE QUALITY OF WOOD CHIPS AND ASH FOR BIOMASS FIRED COGENERATION PLANTS BE-TO OSIJEK AND BE-TO SISAK

Marija Trkmić*, Marinela Orlić*

* HEP-Proizvodnja d.o.o., Zagreb, Hrvatska

autor za korespondenciju: Marija Trkmić, e-mail: marija.trkmic@hep.hr

Stručni članak

SAŽETAK

Kontinuirano praćenje kvalitete drvne sječke je najbolji način provjere i potvrđivanja ugovorne kvalitete sječke koja se kao gorivo isporučuje u BE-TO Osijek i BE-TO Sisak. Fizikalno- kemijska svojstva pepela nakon izgaranja važni su pokazatelj rada postrojenja, procesa izgaranja te čistoće, sastava, geografske lokacije i porijekla sječke.

U radu su opisani postupci uzorkovanja i ispitivanja koje provodi Centralni kemijsko-tehnološki laboratorij (CKTL) HEP-Proizvodnje d.o.o. za potrebe kontinuiranog praćenja kvalitete drvne sječke i pepela za bioelektrane BE-TO Osijek i BE-TO Sisak. Svi postupci su standardizirani i većina je akreditirana prema normi *HRN EN ISO/IEC 17025:2007*. Rezultati ispitivanja kvalitete sječke se izražavaju u skladu sa specifikacijom drvne sječke definirane normom *HRN EN ISO 17225-4 Čvrsta biogoriva – Specifikacije goriva i razredi – 4. dio: Klasifikacija drvne sječke*, a rezultati analiza pepela se prate s aspekta praćenja efikasnosti izgaranja postrojenja, daljnjeg iskorištavanja pepela kao daljnje sirovine u industriji i poljoprivredi te odlaganja.

***Ključne riječi**: bioelektrane, biogoriva, pepeo, sječka*

ABSTRACT

Continuous monitoring of the quality of wood chips is the best way to verify and confirm the contractual quality of the wood chips delivered as fuel to BE-TO Osijek and BE-TO Sisak. The physical-chemical properties of ash after combustion are important indicator of

the plant operation, the combustion process but also the purity, composition, geographical location and origin of the wood chips.

The paper describes sampling and testing procedures carried out by the Central Laboratory for Chemical Technology (CKTL) HEP-Proizvodnja d.o.o. for the purpose of continuous monitoring the quality of wood chips and ash from biomass power plants BE-TO Osijek and BE-TO Sisak. All procedures are standardized and most of them are accredited in compliance with *HRN EN ISO / IEC 17025: 2007* standard. The results of conducted tests are expressed according to specification of wood chips defined by the *HRN EN ISO 17225-4 Solid biofuels – Fuel specifications and classes – Part 4: Graded wood chips standard*. The results of the ash analysis are considered from the aspects of combustion efficiency, further possible exploitation as raw material in industry or agriculture and disposal.

Keywords*: biomass plant, biofuels, ash, woodchips*

1. UVOD

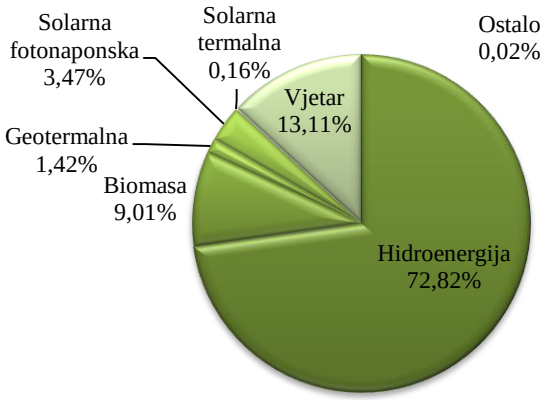
U cilju razumnog, racionalnog i adekvatnog korištenja energije u skladu s današnjim suvremenim i modernim načinom života, potrebno se što više usmjeriti na korištenje višestruko korisnih tehnologija koje bi omogućile maksimalno iskorištenje energije u svim energetskim procesima.

Hrvatska kao potpisnica *Pariškog sporazuma* [1], novog globalnog pravno obvezujućeg sporazuma o klimi, obvezala se smanjiti emisije stakleničkih plinova do 2030. godine, a to doprinosi sve većem porastu korištenja biomase kao jednog od obnovljivih izvora energije, sve u cilju ekonomske i ekološke uštede te smanjenja štetnog utjecaja na okoliš.

Biomasa je prema *Zakonu o obnovljivim izvorima energije i visokoučinkovitoj kogeneraciji* [2] definirana kao biorazgradivi dio proizvoda, otpada i ostataka biološkog podrijetla iz poljoprivrede (uključujući tvari biljnoga i životinjskoga podrijetla), šumarstva i srodnih proizvodnih djelatnosti, uključujući ribarstvo i akvakulturu, kao i biorazgradivi dio industrijskoga i komunalnoga otpada.

Izvori biomase potječu iz raznih sirovina - drvnih goriva, šumskih ostataka, drvenog ugljena, peleta, poljoprivrede, usjeva, komunalnog i industrijskog otpada, bioplina, biogoriva. Općenito, izvori biomase mogu biti svrstani u tri glavne cjeline - šumarstvo, poljoprivreda i otpad. U svijetu, šumarska industrija proizvodi više od 87 % svih sirovina biomase za bioenergiju, poljoprivredni sektor doprinosi 10 % s nusproizvodima životinja i poljoprivrednih proizvoda, dok komunalni kruti otpad i deponijski plin pokrivaju preostalih 3% izvora sirovine biomase [3, 4].

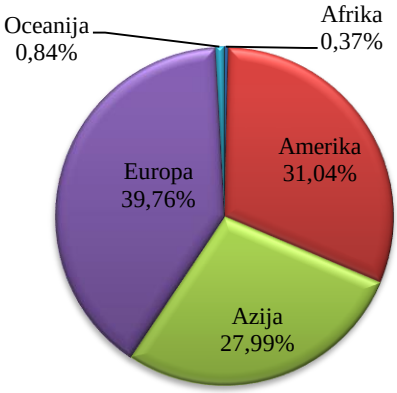
Prema posljednjem izvještaju *World Bioenergy Association* [4] proizvodnjom električne energije od obnovljivih izvora energije još uvijek dominiraju hidroelektrane (slika 1). U 2014. godini proizvodnja u hidroelektranama je iznosila 3 983 TWh električne energije što je gotovo tri četvrtine ukupne proizvodnje iz svih obnovljivih izvora. Međutim, udio hidroelektrana u proizvodnji je pao s 92 % iz 2000. godine na 73 % u 2014. godini, a važan razlog za to je veliki porast solarnih i vjetroenergetskih tehnologija u proizvodnji električne energije. U razdoblju 2000. - 2014. godine bioenergija je u proizvodnji električne energije imala skromni porast od 8,2 % ukupne proizvodnje, što iznosi oko 493 TWh u 2014. godini. To je još uvijek 2,6 puta više dobivene električne energije u odnosu na solarnu energiju.



Slika 1. Proizvodnja električne energije iz obnovljivih izvora energije u 2014. godini [4]

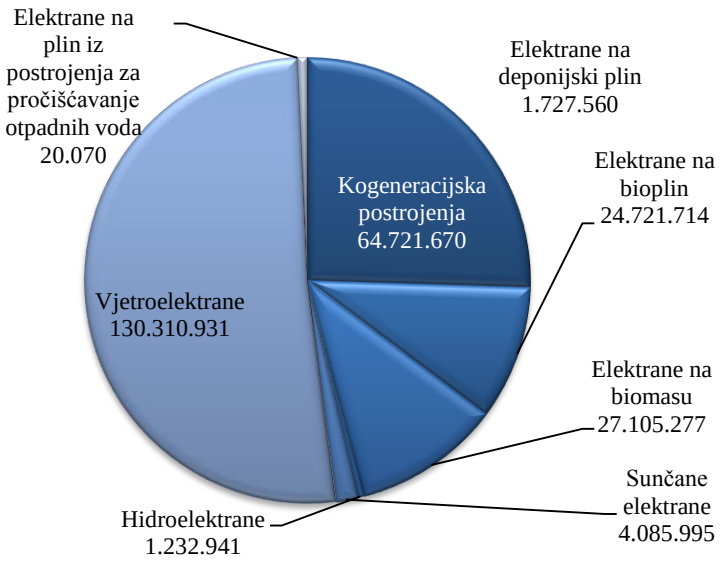
U proizvodnji električne energije iz obnovljivih izvora energije s udjelom od 36,2 % vodi Azija, nakon koje slijede Sjeverna, Srednja i Južna Amerika sa 33,7 %.

S aspekta proizvodnje električne energije iz biomase najveću udio je u Europi, zahvaljujući velikom broju kogeneracijskih postrojenja koja proizvode toplinsku i električnu energiju, kako je prikazano na slici 2 [4].



Slika 2. Udio svjetske proizvodnje električne energije iz biomase u 2014. godini [4]

Prema podacima *Hrvatskog operatora tržišta energije* (HROTE), u izvještaju za siječanj 2018. [5] u Hrvatskoj je trenutno instalirano 17 elektrana na biomasu s instaliranom snagom 35.950 kW te 6 kogeneracijskih postrojenja s instaliranom snagom od 113.293 kW (slika 3).



Slika 3. Proizvodnja povlaštenih proizvođača (kWh); ožujak 2018. [5]

Cilj rada je prikazati postupak kontinuiranog praćenja kvalitete drvne sječke i pepela koji se provodi za potrebe HEP-ovih bioelektrana. Osim samih značajki BE-TO Osijek i BE-TO Sisak u radu će biti detaljno opisani postupci uzorkovanja i laboratorijskih ispitivanja koja se provode u Centralno kemijsko- tehnološkom laboratoriju (CKTL), HEP-Proizvodnje d.o.o. za sada jedinom akreditiranom laboratoriju za uzorkovanje i ispitivanje čvrstih biogoriva u Hrvatskoj.

2. BE-TO SISAK I BE-TO OSIJEK

Izgradnja prvih bioelektrana u Osijeku i Sisku dio je HEP-ove dugoročne strategije dodatnog povećanja udjela obnovljivih izvora energije u postojećem proizvodnom portfelju (tablica 1). BE-TO Sisak, snage 3 MW električnih i 10 MW toplinskih, godišnje će proizvoditi oko 19 300 MWh električne energije i oko 63 900 MWh toplinske energije (slika 4). Vrijednost investicije iznosi 18,95 milijuna eura, a u sklopu investicije se gradi i toplinska stanica te vrelovod do naselja Brzaj i Caprag. BE-TO Osijek, snage 3 MW električnih i 10 MW toplinskih, godišnje će proizvoditi 18 300 MWh električne energije te oko 65 800 MWh toplinske energije za centralizirani toplinski sustav (slika 5). Vrijednost investicije BE-TO Osijek iznosi 16,25 milijuna eura. Obje elektrane će za rad koristiti šumsku biomasu, čiju je nabavu HEP osigurao potpisivanjem dugogodišnjih ugovora o dobavi drvne sječke. Proizvedena električna energija će se isporučivati u elektroenergetski sustav, a izgradnjom novih HEP-ovih bioelektrana-toplana osigurat će se i pouzdani izvori tehnološke pare za industrijske proizvođače u Osijeku, kao i toplinske energije za centralizirane toplinske sustave Osijeka i Siska [6].

Tablica 1. Osnovne značajke BE-TO Sisak i BE-TO Osijek [6]

	BE-TO Osijek	BE-TO Sisak
Neto električna snaga	3 MW	3 MW
Ukupna učinkovitost	73 %	67 %
Toplinska energija	10 MW	10 MW
Proizvodnja električne energije	18.367 MWh/god.	19.375 MWh/god.
Proizvodnja toplinske energije	65.862 MWh/god.	63.908 MWh/god.
Početak izgradnje	kraj 2015.	kraj 2015.
Dovršetak izgradnje i početak pogona	2017.	2017.



Slika 4. Smještaj BE-TO Sisak



Slika 5. Smještaj BE-TO Osijek

3. PRAĆENJE KVALITETE DRVNE SJEČKE I PEPELA

3.1. Ispitivanja drvne sječke

Kvaliteta drvne sječke propisana je normom HRN EN ISO 17225-4:2014*Čvrsta biogoriva – Specifikacije goriva i razredi – 4. dio: Klasifikacija drvne sječke* [7]. Norma propisuje parametre koje je potrebno ispitivati, te razrede u koje se sječka može svrstavati ovisno o rezultatima ispitivanja. Neki od najvažnijih parametara su navedeni u tablici 2.

Tablica 2. Parametri ispitivanja drvne sječke [7]

RAZREDI:		A		B	
ZNAČAJKA KVALITETE Metoda ispitivanja	*JEDINICE*	1	2	1	2
Porijeklo i izvor HRN EN ISO 17225-1	-	1.1.1 Cijelo drveće bez korijenja 1.1.3 Deblovina 1.1.4. Ostaci od sječe 1.2.1 Kemijsko netretirani drvni ostaci	1.1.1 Cijelo drveće bez korijenja 1.1.3 Deblovina 1.1.4. Ostaci od sječe 1.2.1 Kemijski netretirani drvni ostaci	1.1. Drvna, plantažna i ostala djevičanska sječka 1.2.1. Kemijsko netretirani drvni ostaci	1.1. Drvna, plantažna i ostala djevičanska sječka 1.2 Ostaci iz drvne procesne industrije 1.3.1. Kemijski netretirano korišteno drvo
Sadržaj ukupne vlage, *M* HRN EN ISO 18134-1	mas.%	M10≤10 M25≤25	M35≤35	Maksimalna vrijednost treba biti izražena	
Sadržaj pepela, *A* HRN EN ISO 18122	mas.%	A 1.0≤1,0	A 1.5≤1,5	A 3.0≤3,0	
Nasipna gustoća HRN EN ISO 17828	kg/m^3	BD150≥150 BD200≥200 BD250≥250	BD150≥150 BD200≥200 BD250≥250 BD300≥300	Minimalna vrijednost treba biti izražena	
Sadržaj dušika HRN EN ISO 16948	mas.%	NA	NA	N 1.0≤1,0	
Sadržaj sumpora HRN EN ISO 16994	mas.%	NA	NA	S 0.1≤0.1	
Sadržaj klora HRN EN ISO 16994	mas.%	NA	NA	Cl 0.05≤0,05	
Sadržaj arsena HRN EN ISO 16968	mg/kg	NA	NA	≤1	
Sadržaj kadmija HRN EN ISO 16968	mg/kg	NA	NA	≤2,0	
Sadržaj kroma HRN EN ISO 16968	mg/kg	NA	NA	≤10	
Sadržaj bakra HRN EN ISO 16968	mg/kg	NA	NA	≤10	
Sadržaj olova HRN EN ISO 16968	mg/kg	NA	NA	≤10	
Sadržaj žive HRN EN ISO 16968	mg/kg	NA	NA	≤0,1	
Sadržaj nikla HRN EN ISO 16968	mg/kg	NA	NA	≤10	
Sadržaj cinka HRN EN ISO 16968	mg/kg	NA	NA	≤100	
Donja ogrjevna vrijednost HRN EN ISO 18125	MJ/kg	Minimalna vrijednost treba biti izražena		Minimalna vrijednost treba biti izražena	

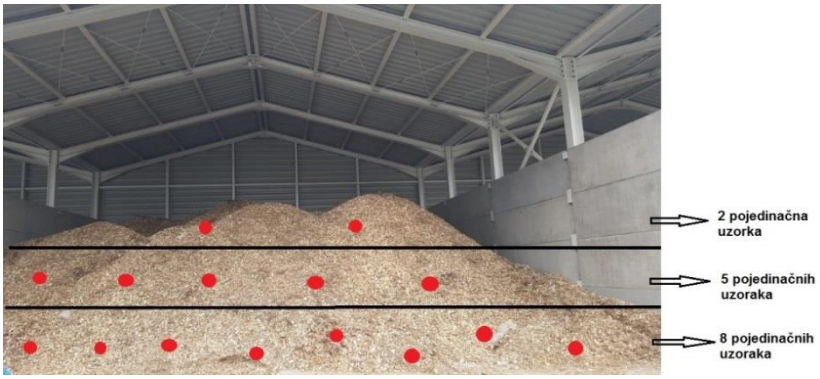
Napomena: NA- nije primjenjivo

Da bi se utvrdilo da li isporučena kvaliteta sječke odgovara ugovorenoj, potrebno je kontinuirano pratiti njenu kvalitetu. Kontrola kvalitete se treba provoditi kroz pravilno uzorkovanje te laboratorijsku analizu u što je moguće kraćem razdoblju.

Centralni kemijsko- tehnološki laboratorij (CKTL) HEP-Proizvodnje d.o.o. je jedini akreditirani laboratorij u Republici Hrvatskoj koji je u mogućnosti provoditi uzorkovanje i

ispitivanje kvalitete drvne sječke u cijelosti. Laboratorij je akreditaciju za ispitivanje čvrstih biogoriva dobio 2013. godine, a za uzorkovanje drvne sječke i pepela 2017. godine.

Uzorkovanje drvne sječke se provodi prema normi HRN EN ISO 18135:2017 *Čvrsta biogoriva – Uzorkovanje* [8]. Sam postupak odvija se ručno, s time da se uzorkovanje može provoditi iz kamiona prilikom istovara sječke ili iz spremnika sječke. Kada se uzorak uzima iz kamiona, obično se uzimaju dva uzorka na početku i kraju istovara sječke, od čega se priprema kompozitni uzorak, čija se količina zatim smanjuje za laboratorijsku analizu. Kada se uzorak uzima iz spremnika sječke, spremnik se vizualno podijeli na tri sloja i iz svakog sloja se uzima nekoliko pojedinačnih uzoraka prema slici 6.



Slika 6. Uzorkovanje drvne sječke iz spremnika

Tako uzeti pojedinačni uzorci se izmiješaju, njihova ukupna količina se smanji četvrtanjem i količina od 5 kilograma se uzima za laboratorijsku analizu. Za svako provedeno uzorkovanje se vode zapisi koji uključuju *Plan uzorkovanja i Zapis o provedenom uzorkovanju*. Uzorak se u laboratorij obično dostavlja u plastičnim kantama ili vrećama. Dostavljenom uzorku je što prije potrebno odrediti ukupnu vlagu, sušenjem na 105 °C, nakon čega se uzorak usitnjava u mlinu na veličinu čestica manju od 1 mm. Tako pripremljen uzorak se naziva analitički uzorak i na njemu se određuju parametri navedeni u tablici 2. Rezultati ispitivanja se preračunavaju sa sadržajem vlage na suhu ili dostavnu osnovu te se tako iskazuju u izvještaju o ispitivanju. U tablici 3 su navedeni osnovni instrumenti za određivanje značajki kvalitete drvne sječke.

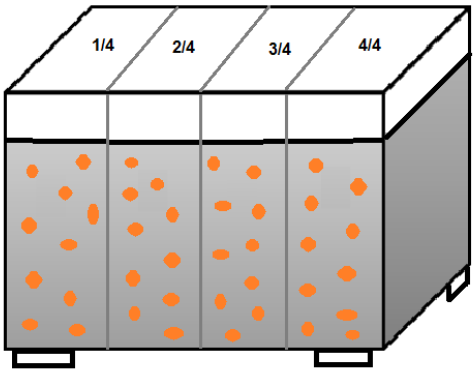
Tablica 3. Pregled ispitnih metoda i instrumenata kojima se provodi analiza sječke u CKTL-u

Parametar	Metoda	Instrument
Sadržaj ukupne vlage	HRN EN ISO 18134-1:2015 [9]	Sušionik Heratherm OMH 750
Sadržaj pepela	HRN EN ISO 18122:2015 [10]	Mufolna peć Nabertherm B180
Sadržaj ugljika, vodika, dušika	HRN EN ISO 16948:2015 [11]	CHNS -TrueSpec-LECO
Sadržaj sumpora	HRN EN ISO 16994:2015 [12]	CHNS -TrueSpec-LECO
Sadržaj klora	HRN EN ISO 16994:2015 [12]	EDXRF NEX CG- Rigaku
Ogrjevna vrijednost	HRN EN ISO 18125:2017 [13]	Kalorimetar C2000-IKA
Sadržaj elemenata u tragovima	HRN EN ISO 16968:2015 [14]	MW Multiwave PRO Anton Paar, ICPE 9000, Shimadzu

Napomena: akreditirana metoda prema HRN EN ISO/IEC 17025

3.2. Ispitivanja pepela

Pepeo je kruti ostatak izgaranja, s time da u bioelektranama pepeo čini smjesu pepela sa dna ložišta (9 5%) i lebdećeg pepela (5 %). Očekivana količina pepela je 1800 t/godišnje za svaku bioelektranu, odnosno 3600 t/godišnje za obje. Dnevna količina je 5 t/danu pepela koja se sprema u odgovarajuće spremnike i odvozi dalje na obradu ili zbrinjavanje. Uzorkovanje pepela se provodi iz spremnika prema normi *HRI CEN/TR 15310-2:2008* [15] na način da se spremnik vizualno podijeli na četiri jednaka djela iz kojih se zatim uzima što više pojedinačnih uzoraka sa što je moguće više različitih mjesta i dubina kontejnera (slike 7 i 8). Svi pojedinačni uzorci se stavljaju u plastičnu kantu te se plastičnom lopaticom homogeniziraju i prenesu u plastični spremnik za transport do laboratorija. Za svako provedeno uzorkovanje vode se zapisi koji uključuju Plan uzorkovanja i Zapisnik o provedenom uzorkovanju.



Slika 7. Spremnik pepela



Slika 8. Postupak uzorkovanja pepela

Dostavljeni uzorak pepela se prvo suši na 105°C, zatim usitnjava u mlinu na veličinu čestica 215, 63 i 50 μm. Priprema uzoraka na različite dimenzije čestica je potrebna zbog

zahtjeva analitičkih metoda koje se provode na uzorcima pepela. Tablica 4 daje pregled ispitivanja koje se rutinski provode u uzorcima pepela.

Tablica 4. Pregled ispitivanja u uzorcima pepela

Parametar	Jedinice	Metoda	Instrument
Suha tvar ▫	mas.%	HRN EN 14346:2007 [16]	Sušionik Heratherm OMH 750
Gubitak žarenjem 950 °C	mas.%	ASTM D 7348-13[17]	Mufolna peć Nabertherm B180
Udio $CaCO_3$	%	HRN ISO 10693:1995 [18]	Scheiblerov kalcimetar
Ukupni ugljik, vodik i dušik	mas %	HRN EN ISO 16948:2005 [11]	CHNS -TrueSpec- LECO
Sadržaj oksida	mas.%	ISO/TS 16996:2015 [19]	EDXRF NEX CG- Rigaku
Sadržaj elemenata u tragovima	mg/kg	HRN EN ISO 16968:2015[14] ISO/TS 16996:2015 [19]	MW Multiwave PRO Anton Paar, ICPE 9000, Shimadzu EDXRF NEX CG- Rigaku
pH vrijednost eluata	-	HRN EN ISO 10523:2012 [20]	pH metar, Lab 845, SI Analytics
Vodljivost	mS/m	HRN EN 27888:2008 [21]	Konduktometar, Lab 945, SI Analytics
Ukupne otopljene krutine (TDS)	mg/kg suhe tvari	HRN EN 15216:2008 [22]	Sušionik Heratherm OMH 750
Sadržaj elemenata u tragovima u eluatu	mg/kg suhe tvari	HRN EN ISO 11885:2010 [23]	MW Multiwave PRO Anton Paar, ICPE 9000, Shimadzu
Određivanje temperatura taljenja pepela	°C	CEN/TS 15370-1:2006 [24]	AF700, LECO

Napomena: ▫ akreditirana metoda prema HRN EN ISO/IEC 17025

Rezultati ispitivanja pepela imaju nekoliko važnih uloga. Osim određivanja parametara koji su direktni pokazatelj efikasnosti izgaranja postrojenja (gubitak žarenjem, sadržaj ugljika u pepelu), određivanje sastava pepela daje važnu informaciju o mogućem korištenju pepela kao sirovine u građevinarstvu i poljoprivredi. Ispitivanje eluata pepela provodi se uslijed zadovoljavanja uvjeta za odlagalištem neopasnog otpada temeljem *Pravilnika o načinima i uvjetima odlaganja otpada, kategorijama i uvjetima rada za odlagališta otpada* (N.N 114/15) [25].

4. ZAKLJUČAK

Kontinuirano praćenje kvalitete drvne sječke je jedini način provjere i potvrđivanja ugovorne kvalitete drvne sječke, što je ujedno i definirano u ugovorima s dobavljačima sječke. Osim sječke, redovito se prate fizikalno-kemijska svojstva pepela kao direktnog pokazatelja efikasnosti izgaranja sječke, sastava pepela zbog ispitivanja mogućnosti njegovog

daljnjeg korištenja te za potrebe odlaganja na odlagalište. Praćenje kvalitete sječke i pepela obuhvaća uzorkovanje, dostavu uzorka i laboratorijsku analizu. Predviđena dinamika ispitivanja je jednom mjesečno za svaku bioelektranu, s time da se po potrebi uzorci uzimaju i analiziraju češće i u većem broju kao što je tijekom garantnih ispitivanja te ispitivanja emisija. Broj i vrsta parametara koji se ispituju su definiranim zakonskim propisima i odgovarajućim normama, međutim ovisno o zahtjevu naručitelja ili svrhe ispitivanja, parametre je potrebno prilagođavati. Primjer za to su različiti setovi parametara koji se analiziraju u pepelu radi njegovog daljnjeg korištenja ovisno o primjeni u građevinarstvu ili u poljoprivredi.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

THE STATE OF WHITE-TAILED EAGLE PAIRS (AVES: *HALIAEETUS ALBICILLA* LINNAEUS 1758) FOR THE DANUBE DELTA BIOSPHERE RESERVE AND ITS SURROUNDINGS

Alexe Vasile[1,2], Doroşencu C. Alexandru[1], Marinov Mihai[1], Kiss J. Botond[1], Attila D. Sándor[3], Ceico Tănase[4], Tudor Marian[1], Nanu Cristina-Nicoleta[1], Ivanov Grişa[5], Enescu Romeo[6], Moise Vasile[6], Murariu Dumitru[7]

[1] Danube Delta National Institute for Research and Development, Tulcea, Romania
[2] Bucharest University, Faculty of Biology, Bucharest, Romania
[3] Babeş-Bolyai University, Department of Taxonomy and Ecology, Cluj-Napoca, Romania
[4] National Environmental Guard, Commissariat of the Danube Delta Biosphere Reserve, Tulcea, Romania
[5] National Forest Directorate - Forest District Rusca, Tulcea, Romania
[6] National Forest Directorate - Forest District Babadag, Babadag, Romania
[7] Romanian Academy's Institute for Biology, Department of Ecology, Taxonomy and Environment Protection, Bucharest, Romania

corresponding author: Alexe Vasile, e-mail: vasile.alexe@ddni.ro

Professional paper

ABSTRACT

This article presents data on the nesting ecology of the White-tailed Eagle (*Haliaeetus albicilla*) collected during 2009 - 2017 in the Danube Delta Biosphere Reserve and its surroundings. A total of 127 different nests were recorded in this period. The preferred tree species for nesting in the area were the White Willow (*Salix alba*) with 64 % of all identified nests, 30 % were in poplars (*Populus* sp.), 3 % in alders (*Alnus* sp.), 2 % oaks (*Quercus* sp.) and 1 % in linden (*Tilia* sp.). Tree nests were located in the tallest and savailable on the site and were placed at heights between 5 and 24 meters, with 62 % being above 13 meters and (38 %) at heights of less than 13 m. For the White-tailed Eagle nest site selection may be a response both to tree availability in the foraging habitat as well as food supply.

Keywords: *Haliaeetus albicilla, nest, White-tailed Eagle, Danube delta biosphere reserve*

1. INTRODUCTION

The Danube Delta Biosphere Reserve (DDBR) due to its geographic location and to the temperate continental climate with Pontic influences in the coastal area hosts a remarkable diversity of flora and fauna. At the same time, the DDBR is traversed by an important migration route. In this area, during the autumn over 90,000 birds of prey, 30,000 pelicans, 240,000 storks and thousands of limicoline and passerine birds from in Northern Europe and West Siberia cross the western Pontic area along their migration route to wintering sites [1].

One of Romania's most impressive diurnal birds of prey in this area is the White-tailed Eagle (*Haliaeetus albicilla* Linnaeus 1758). Of the 8 species belonging to the *Haliaeetus* genus, only *H. albicilla* [2] nests in Europe. This diurnal raptor is the largest sedentary bird nesting in Romania. At the European level, the White-tailed Eagle was a very common species at the beginning of the 20th century [3 - 5].

Anthropogenic factors in effect during the period 1950 - 1960 led to the rapid decrease of the size of the White-tailed Eagle population in Romania, but also in many other European countries. The main causes that led to the decline of the species were: pesticides, poaching and habitat destruction [6 - 12]. The decline of the White-tailed Eagle population in Romania continued until the early 1990s [8, 13 - 18]. In 1990, when the Danube Delta Biosphere Reserve was established, the White-tailed Eagle population was remediated. At the same time, it has been proven that the existence of an ecological surveillance structure can provide reliable information, in particular on nesting, but also on wintering or transit effectives' monitoring. During this period, the number of reproductive White-tailed Eagles was estimated to be between 10 - 20 pairs [19 - 25].

2. EXPERIMENTAL

The monitoring of White-tailed Eagle nests within the DDBR and its surroundings began in 2009, intensifying with 2015. Identification of the White-tailed Eagle nests was carried out in two stages: the first was carried out during the winter period (December - March), when tree are without leaves and the nests are visible and can be observed even from a few kilometres, and the second stage took place during the spring-summer period (April-June), to investigate nesting of the White-tailed Eagles. Among the methods used to identify the White-tailed Eagle nests, the method of transects and fixed point was used, in the following areas: Parcheș, Somova, Nufăru, Victoria, Băltenii de Sus, Enisala, Mândra forest (Agighiol) and Murighiol-Dunavăț [26].

The method for nest searching within the DDBR was particularly complex. Searching for nests involved navigating the territory by boat on the DDBR's canals and lakes. Thus, on a lake or on a backwater, the trees around the lake were scanned using binoculars. When an adult bird was seen on a tree, the observer headed in the bird's direction by boat and started looking for the nest in a 300-meter radius. Usually, the adult bird (generally the male) is standing guard near the nest. This method has produced good results and in this way a significant number of White-tailed Eagle nests were found.

A large part of the nests were located with the help of the ornithologists and the field workers of the Danube Delta National Institute for Research and Development (DDNIRD) and others were reported by the inspectors and the ecological agents (rangers) of the Danube Delta Biosphere Reserve Administration (DDBRA) and the environmental commissioners within the Danube Delta Biosphere Reserve Commissariat, but also with the help of the forestry technicians and foresters who are assigned to the territory of Tulcea County. At the

same time, fishermen and locals from the study area were also involved, following the check of the nests by the author.

Vehicles were used for terrestrial routes and boats with engines ranging from 6 to 20 HP were used for aquatic routes. The identification of birds from a distance was done using optical instruments (binoculars and photo camera).

The GPS (Global Positioning System) was used in order to locate as accurately as possible the White-tailed Eagle nests. These points were taken at the tree, or where this wasn't possible, near it, followed by coordinates' correction using ArcGIS.

3. RESULTS AND DISCUSSION

Investigations on the distribution of White-tailed Eagle pairs and nests within the DDBR and its surroundings were carried out during 2009 - 2017.

The recent distribution of the White-tailed Eagle nests and pairs in Northern Dobruja is limited particularly to the DDBR, with some local presence in the wooded massifs at the limits of the DDBR, the only areas where they can be found. At present, the only areas with White-tailed Eagle nests that are known since 2008 are the Babadag-Enisala and Mândra (Agighiol) forests on the continental side that still have inhabited nests. At the same time, these areas are also known as roosting places for the non-nesting population, or for individuals that are migrating in southern Europe and remain within the DDBR during the cold period, thus passing during their seasonal journeys through the delta territory. The studies conducted during the 8 years of investigation of White-tailed Eagle nests and pairs in the DDBR and its surroundings attest to the existence of 127 occupied, unoccupied and destroyed nests (table 1, figure 1). The number of nests in table 1 columns 3 and 4 is doubled because each year the old nests were counted, but other nests were found next to them. Figure 2 shows the situation of the White-tailed Eagle nests within the DDBR and its surroundings since 2017.

Table 1. The evolution of White-tailed Eagle (*Haliaeetus albicilla*) nesting success between 2009 and 2017 within the DDBR and its surroundings (Romania)

Year	No. of nests visited	No. of occupied nests	No. of alternative nests (feeding, rest, etc.)	No. of nests destroyed	No. of successfully completed nestings
2009	36	21	15	7	11
2010	43	21	22	6	9
2011	55	20	35	2	10
2012	71	25	46	8	13
2013	71	26	45	0	17
2014	71	31	40	5	19
2015	63	29	34	3	23
2016	64	34	30	13	24
2017	62	38	24	16	34

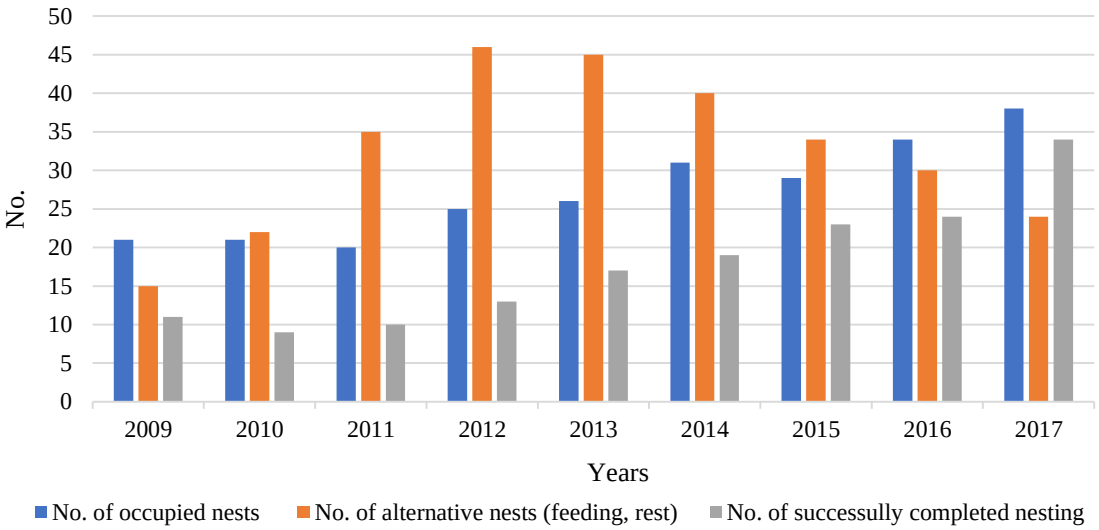


Figure 1. The evolution of White-tailed Eagle (*Haliaeetus albicilla*) nesting success between 2009 and 2017, within the DDBR and its surroundings, in numbers and presented graphically (Romania)

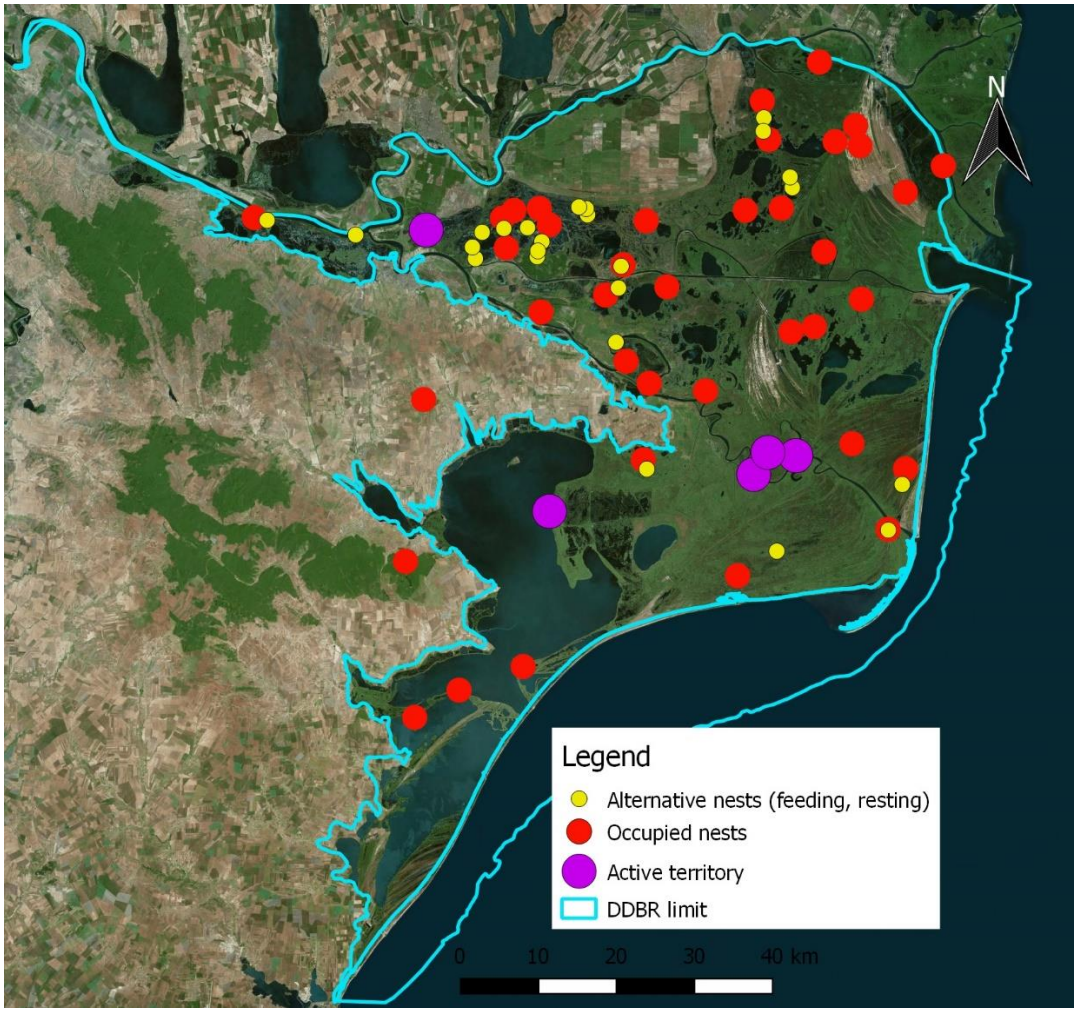


Figure 2. Distribution of White-tailed Eagle nests (*Haliaeetus albicilla*) in 2017 from the DDBR and its surroundings

The only studies related to White-tailed Eagles within the DDBR and its surroundings during the last few years appear in subchapters in doctoral dissertations, some of them being published [27 - 31], but a more comprehensive situation regarding current nesting on the territory of the DDBR of this bird of prey can be found in more recent works [32 - 34]. During 2009 - 2017, there were 74 nests within the DDBR and its surroundings, out of which 61 nests proved the success of the nesting, with a total of 193 chicks, thus the average of the reproduction in all the years of research was calculated at 1.2 chicks/nest. The issue of nesting success will be debated in another article.

The nests in figure 2 have been marked with different colours, depending on the information regarding their usage. In 5 cases we marked the position of some nesting pairs in which the nests were not located, but the adult birds were seen during the breeding period, exhibiting territorial behaviour.

The spatial layout of the nests within the DDBR shows two concentrations, which account for more than half of the identified nests. Both are located on the north side of the Delta with a total of 70 nests, most of them located between the Chilia and Sulina branches. The first important area is located in the fluvial Delta Sontea-Fortuna complex, with a total of 47 nests (occupied, unoccupied, destroyed), marking the most important part of the DDBR for the studied species. The second area is located in the maritime delta, especially on the territory of Letea, the Matita-Merhei Complex and the Ceamurlia Fishery, with a total of 23 nests. We mention that some of the monitored nests are over 9 years old.

From our own data, collected from the field, we can note that in some pairs of White-tailed Eagles, if the nest was destroyed by natural causes, that pair built another nest near the fallen one, either 10 - 20 meters away or not more than 100 - 200 meters away, depending on the old trees available within that habitat. But if the nest was destroyed due to the human factors, that pair would not build another nest near the fallen one.

Out of the total of 127 White-tailed Eagle nests (occupied, unoccupied, destroyed) reviewed within the DDBR and its surroundings during 2009-2017, the height of 117 nests could be estimated. It should be noted that during the study no nests were found at the ground level, all of them being placed on trees at different heights (figure 3).

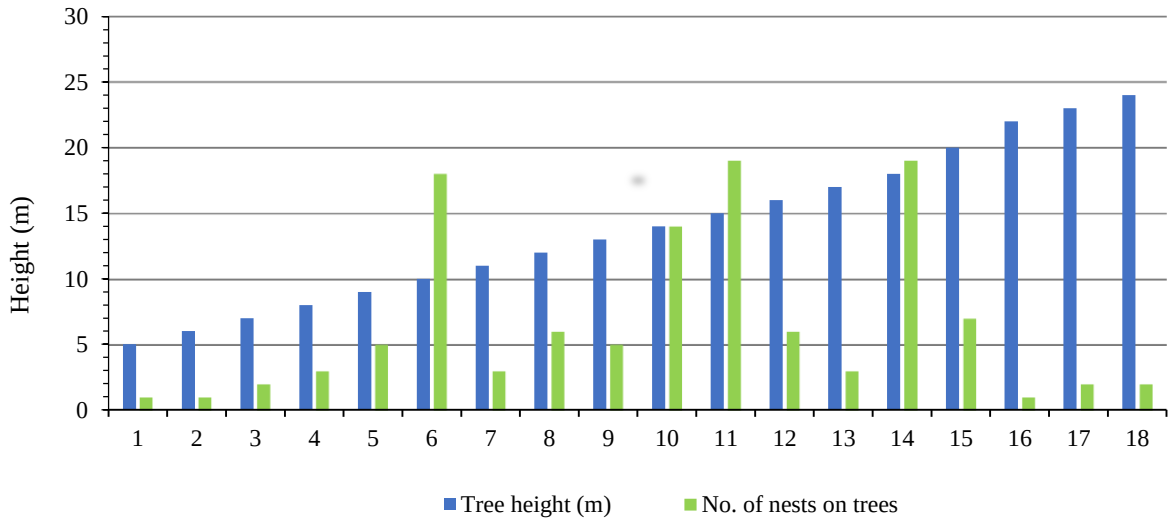


Figure 3. Selection of trees for nest site depending on height, from the DDBR and its surroundings during 2009 - 2017 (n = 117)

As can be seen from figure 3, the nests were located at heights of 5 to 24 m from soil or water, with more than half, 73 nests (62 %) being found at heights greater than 13 m, and

44 nests (38 %) at heights under 13 m. We mention that the trees within the study area are on average lower than in other geographical areas of the country.

A newly built nest on the ground was found in 2010 in the area of the St. George arm by the ranger Acsentiev Nicu (personal communication) from the Danube Delta Integrated Commissariat of Control of the DDBRA.

By the time the article was written, we succeed in measuring 23 trees of the 127 nests that were inventoried in the DDBR and its surroundings, so the average was calculated at 2,86 m.

According to our own investigations, it was found that out of the 127 nests located in the DDBR and its surroundings, 64 % were located on willows, 20% on white poplars, 10 % on hybrid poplars, 3 % on alders, 2 % on oaks and 1 % on lindens (figure 4). This demonstrates that *H. albicilla* selects habitats with old willows for nest construction, so we can mention that we'll take into account the deforestation that will be practiced in the next period, an issue that was observed by other authors [32 - 34].

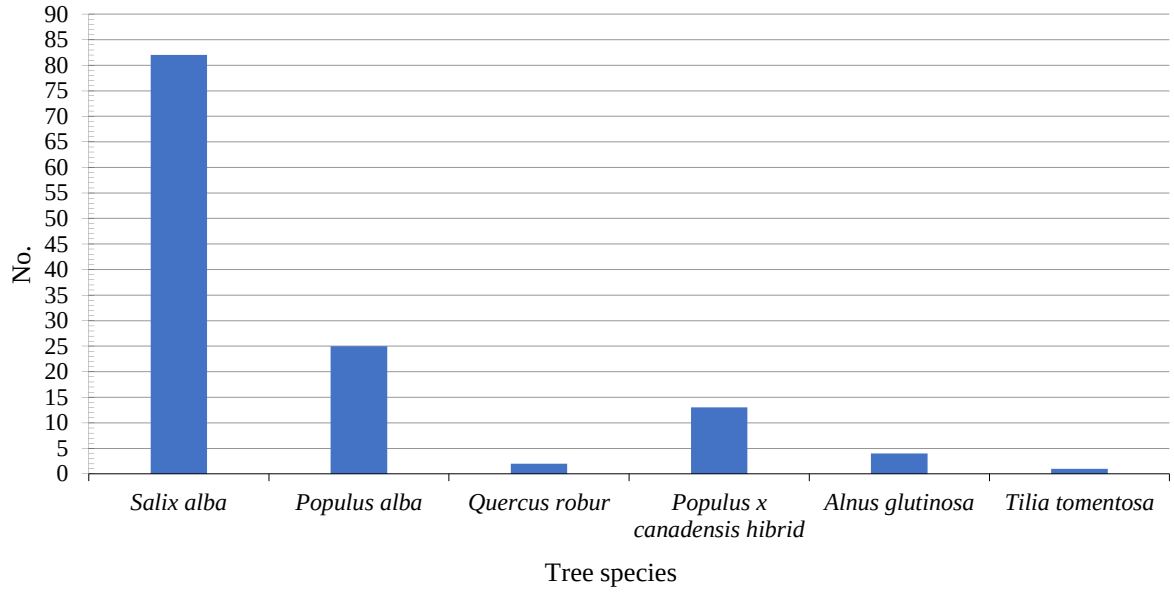


Figure 4. Numerical distribution of tree species used to support nests (*Haliaeetus albicilla*) in the DDBR and surroundings during 2009-2017 (no = 127)

As can be observed, the species of nesting tree seems to be another determining factor for the nest location.

In figure 5 we present the current trend over time of White-tailed Eagle nesting and effective number of chicks in the DDBR and its surroundings, based on data published in specialized literature (1971-1990), unpublished data (1996) and own data (2009 - 2017).

As can be seen from the graph in figure 5, over the years the White-tailed Eagle population has a slightly increasing trend, valid for the last quarter of a century.

Based on observations during 2009 - 2017, the total number of nesting pairs in 2017 within the DDBR was estimated at about 44 - 55.

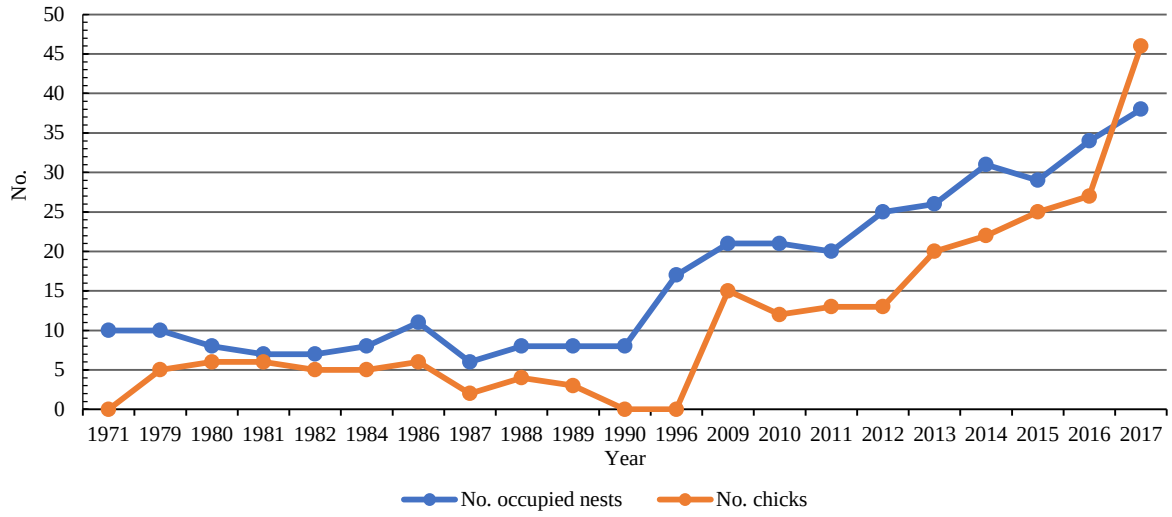


Figure 5. The trend of White-tailed Eagle (*Haliaeetus albicilla*) effectiveness in the DDBR and its surroundings, (according to data found in literature and own data)

4. CONCLUSION

Between 2009 and 2017 in the DDBR and surrounding area there were 127 nests (occupied, unoccupied, destroyed) and another 5 adult pairs were noticed in 2017, but their nests were not found.

Out of a total of 117 nests located between 2009 and 2017, on the territory of DDBR and its surroundings, 73 nests are at heights greater than 13 m and 44 at heights below 13 m.
Of the total of 127 old and newest nests in the studied area, reviewed during the period mentioned above, 64% are located on willows, 20 % on white poplar, 10 % on hybrid poplar, 3 % on alders, 2 % on oak and 1 % on lindens.

Out of the 127 nests found in the study area, only 5 are not located within the Danube Delta, the rest being located in DDBR, and most of these occupied nests are located between the Chilia and Sulina branches.

The total number of nesting pairs in 2017 within DDBR was estimated at about 44 - 55, noting that some nests from the inaccessible areas could not be controlled by the methods we dispose. Thus, we can mention that the White-tailed Eagle population within DDBR is increasing.

The factors that are damaging to the White-tailed Eagle nests within DDBR are those caused by humans (through fishermen's disturbance during the White-tailed Eagle's breeding period, construction of fishermen's huts near the nest, fires caused by locals, photography at nests during hatching) or caused by natural factors (falling of trees or branches that support the nests, strong winds during the year, liquid and solid precipitation).

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Acknowledgments

We would like to thank: The Danube Delta Biosphere Reserve Authority, the National Environmental Guard, the Danube Delta Biosphere Reserve's Commissariat, the nongovernmental organization SOS Danube Delta, and Acsentiev Nicu, Băcescu Gheorghe, Babencu Dan, Bucur Gheorghe, Cîrpăveche Paul, Caracudă Iordan, Gal Anton, Iacovici George, IosifNicolae, Ivanov Sorin, Mihalcea Marian, Stelea Cătălin, Timofei Arsene, Trâteanu Aurel Voicu Mirel, Filipov Cristi, Alexe Mihaela-Gabriela, Dima Luminiţa-Loredana and Albu Alexandru, for the collection and supply of field data.

IZMEĐU TEHNICIZMA I TEHNOFOBIJE

BETWEEN TECHNICISM AND TECHNOPHOBIA

Lino Veljak*

* Sveučilište u Zagrebu, Filozofski fakultet, Zagreb, Hrvatska

autor za korespondenciju: Lino Veljak, e-mail: lveljak@ffzg.hr

Prethodno priopćenje

SAŽETAK

Tehnička primjena rezultata znanstvenih istraživanja na ljudsko ovladavanje prirodom i na rast proizvodnih moći rađa i strahovanjima od budućnosti. Nasuprot tehnicističkom optimizmu javlja se i tehnofobija, koja se očituje i u ideji odbacivanja znanstveno-tehničkog napretka. U radu se pokazuje neprihvatljivost nekritičkog povjerenja u sposobnost tehnike i tehnologije da udružene s mehanizmima slobodnog tržišta otklone bojazni od ugrožavanja prirodne osnove života na našem planetu, jednako kao i neprihvatljivost ideje povratka predmodernim oblicima života. Naznačena je alternativa, koja bi se sastojala u povezivanju interdisciplinarnih i multidisciplinarnih istraživanja globalnih problema s idejom humanog društva oslobođenoga od dominacije logike profita.

Ključne riječi: *znanstveno-tehnički napredak, tehnika, tehnologija, tehnicizam, tehnofobija, okoliš*

ABSTRACT

Use by the technicians of the results of scientific research to master the nature and enhance the production power brings about fears of the future. Contrary to technicistic optimism appears technophobia, bringing the idea of rejecting scientific and technical progress. This paper will show that uncritical confidence in technology and technics, joined with free market mechanisms will cancel the fears of endangering the natural basis of life on our planet in inacceptable, as well as the idea of returning to pre-modern ways of life. An alternative is outlined, which points toward interconnections of multidisciplinary and interdisciplinary research of global problems with the idea of a human society, liberated from the domination of profit-minded logic.

***Keywords**: scientific and technical progress, technics, technology, technicism, technophobia, environment*

1. UVOD

Od početaka industrijalizacije do današnjih dana sve intenzivnijega kvantitativnog i kvalitativnog napretka tehničke primjene rezultata prirodoznanstvenih (ali i drugih znanstvenih, osobito informatičkih) istraživanja u području jačanja proizvodnih snaga i općenito ljudskog ovladavanja prirodom lice zemlje se stubokom promijenilo. Pokazatelji su u tom pogledu jednoznačni i neumoljivi.

S tim – kako se čini nezaustavljivim – procesima povezan je rast bojazni od budućnosti. Središnja dimenzija tih strahovanja odnosi se na pitanje je li čovječanstvo u stanju kontrolirati učinke svojih tehničkih i tehnologijskih moći, čija bi nepromišljena primjena mogla dovesti do razaranja prirodne osnove opstanka života (pa stoga, dakako, i opstanka čovječanstva) na našem planetu. Stoga su aktualne rasprave obilježene antitezom između *tehnicizma* i *katastrofizma* (koji u stanovitim varijantama poprima oblik *tehnofobije*).

2. TEHNICIZAM

Tehnicizam označava stav koji je obilježen vjerovanjem prema kojemu tehnika i tehnologija poboljšavaju ljudsko društvo, a u svojoj ekstremnoj varijanti to vjerovanje dovodi do stava da se znanstveno-tehničkom kontrolom svijeta mogu riješiti svi problemi čovječanstva. Dapače, u nekim varijantama tehnicizma govori se kako takvo rješavanje svih problema označava abdikaciju religije kao izvora vrhovnog moralnog autoriteta, te onda znanosti i tehničko-tehnologijska primjena njezinih otkrića stupaju na mjesto najvišega moralnog autoriteta [1]. Dakako, tehnicizam je, i u svojim umjerenijim a osobito u svojim radikalnim varijantama, obilježen optimizmom, posebice ukoliko je povezan s transhumanizmom zasnovanom na uvjerenju da tehnika i tehnologija mogu, povezujući rezultate znanstvenih istraživanja u prirodnim, biologijskim i informacijskim znanostima dovesti do toga da ljudi nadmaše sve barijere vlastitih biologijom uvjetovanih ograničenosti, uključujući i praktičku besmrtnost [2]. Naći će se i autora [3] koji već predviđaju kako će se tzv. singularnost (obilježena stvaranjem superinteligencije) dogoditi u vrlo skoroj budućnosti, 2045. godine. Tako će nakon fizikalno-kemijske epohe, epohe života, epohe ljudskog mozga, epohe tehnike i epohe umjetne inteligencije nastupiti epoha univerzalne kolonizacije.

Doduše, još je koncem 18. stoljeća francuski teoretičar napretka Condorcet predviđao da će razvitak biologijskih istraživanja i medicine dovesti, pored rješavanja svih drugih problema ljudi kao individua i ljudskoga društva u cjelini, do dosezanja praktičke besmrtnosti [4]. No, danas su takva predviđanja mnogo realnija nego što je to bio slučaj u vremenima kada je ova vrsta neobuzdanog optimizma budila sumnje da je ona utemeljena na pukim tlapnjama.

Skepsa u pogledu transhumanizma ne očituje se danas toliko na planu sumnje u tehničku dosezivost transhumane singularnosti, već se u prvom redu oblikuje posredstvom pitanja što transhumanost znači s obzirom na ljudskost, nije li tu riječ o procesu zastarijevanja i iščezavanja čovjeka, kako je to još u drugoj polovini 20. stoljeća formulirao njemački mislilac GűntherAnders [5]. Donekle slično Andersu, američki komunikolog Neil Postman upozorava na upitne perspektive ljudskoga bića u društvima u kojima dominira ideologija (i

praksa) znanstveno-tehničkog napretka kojom se u *tehnopolisima* marginaliziraju kulturne, vrijednosne i svjetonazorne dimenzije ljudskoga bića [6]. Na tom je tragu također i američki povjesničar znanosti i tehnike David Noble, posebice u svojoj knjizi znakovita naslova *Religija tehnike* [7].

3. EKOLOGIZAM

Ipak, bitna je antiteza tehnicizmu vezana uz pitanje ne vodi li nepromišljeno korištenje tehnike i tehnologije za svrhe ljudskog ovladavanja prirodom (a u konzekvencijama i ovladavanja društvom u smislu, primjerice, njegove racionalizacije) ugrožavanju samih pretpostavki održanja života na našem planetu, dakle ugrožavanju okoliša. Tu se oblikuju razne varijante *environmentalizma* (što je u najmanju ruku nezgrapan izraz, te bi prikadnije bilo koristiti termin *ekologizam,* koji je potisnut, najprije na engleskom govornom području, a potom i drugdje, spomenutim nezgrapnim izrazom). Pod tim pojmom podrazumijeva se politički i etički pokret koji smjera jačanju i zaštiti prirodnog okoliša posredstvom promjena koje bi dovele do uklanjanja po okoliš štetnih ljudskih aktivnosti kao i posredstvom preispitivanja odnosa ljudi i prirode (što bi imalo rezultirati uspostavljanjem holističkog pristupa tom odnosu). Dakako, taj se pokret mora temeljiti na odgovarajućim znanstvenim i teorijskim elaboracijama, koje su po definiciji interdisciplinarnog i, više od toga, integrativnog karaktera, kako to posebice dolazi do izražaja u integrativnoj bioetici [8 – 10].
Kao primjer takvoga interdisciplinarnog pristupa može se navesti djelo američkoga filozofa i ekologa Dalea Jamiesona *Etika i okoliš* [11], koje nudi obuhvatan pregled filozofijskih problema etike okoliša, od normativno-etičkih i onih koji se odnose na etiku vrlina, preko kantovske perspektive i novijih etičkih i bioetičkih pozicija pa do aktualne problematike posljedica onečišćenja atmosfere ugljičnim dioksidom ili pitanja smijemo li klati krave i svinje radi hrane. Moguću optužbu da toj problematici pristupa moralistički (te da bi tu na djelu bio etički redukcionizam) Jamieson unaprijed opovrgava, naglašavajući kako nije njegova namjera da inzistira na tvrdnji prema kojoj su problemi s okolišom isključivo etički problemi (te da oni nemaju ekonomijski i tehnologijski karakter), već samo to da problemi s okolišom posjeduju snažnu etičku dimenziju [11].

Iskušenjima etičkog redukcionizma (koji nužno rezultira nemoćnim moralizmom) izmiču i kvalitetnija razmatranja pitanja ekologijske ravnoteže, već i utoliko što uzimaju u obzir dinamičke i fragilne dimenzije prirodnih populacijskih i ekologijskih sistema, a pri analizi kompleksnih sistema nerijetko koriste i matematičke modele [12, 13]. Naglašavajući nužnost holističkog pristupa problemima okoliša [14], te diskusije oblikuju antitezu svim mogućim vrstama redukcionizma i atomizma, te time i tehnicističkom kvaziracionalizmu kakav je svojstven nekritičkom vjerovanju prema kojemu znanstveno-tehnički napredak jamči rješavanje svih problema, uključujući posebice i onih problema koji su povezani s opasnostima od ugrožavanja prirodnih osnova života ili bar opstanka čovječanstva; ti tipovi nekritičkog vjerovanja postaju osobito problematični kad se oni – kako se to nerijetko događa - integriraju s jednako tako nekritičkim vjerovanjem u automatsko reguliranje nastajućih neravnoteža mehanizmima slobodnih tržišta i profita. Spomenuta integracija zadobiva dodatnu dimenziju dramatičnosti u kontekstu razvijanja modernih informatičkih medija. Kako upozorava kanadski politolog Darin Barney, tehnički razvitak u toj sferi dovodi i do onemogućavanja postavljanja pitanja o tomu u čemu bi se trebao sastojati dobar život, jer je odgovor na to pitanje već dan: dobar život je onaj život koji se sastoji u korištenju sve veće i veće količine sve naprednije tehnologije, a restruktiriranje privrede u duhu apsolutno

slobodnog tržišta ne može više biti predmetom rasprave [15]. Više ne možemo ni pitati kako da živimo naše živote [16].

Opravdava li sve to *katastrofizam,* vjerovanje da u skoroj budućnosti predstoji samoskrivljena propast čovječanstva, te odatle proizlazeću*tehnofobiju* i odbacivanje znanstveno-tehničkog napretka? Pod tehnofobijom se podrazumijeva, dakako, strah od tehnike i tehnologije, a naročito strah od njihova korištenja. Na počecima industrijske revolucije tehnofobija se iskazivala u formi ludističkog pokreta, koji je ponajprije bio motiviran klasnim razlozima [17], a njegov je najznamenitiji glasnogovornik bio lord Byron. Danas se pod „neoludizmom" podrazumijevaju različiti osviješteni oblici otpora uvođenju novih tehnologija i općenito korištenju tehnike (posebno one informatičke), ali, šire, pod tim se terminom ponegdje također razumije i odbijanje konzumerizma [18].

4. ZAKLJUČAK

Ne čini se izglednim da bi odbacivanje tehničko-tehnologijskog napretka moglo rezultirati bilo kakvom perspektivom razrješavanja problema što ih taj napredak donosi. Prije svega bi moralo biti jasno da otpor napretku može zaustaviti sam napredak u onoj mjeri u kojoj su ludisti spriječili industrijalizaciju u Engleskoj, a pod hipotetičnom pretpostavkom da bi povratak u predindustrijsku eru uopće i bio izvediv, nije nimalo jasno koji bi to dobitak predstavljalo za čovječanstvo. Vjerojatno bi negativne posljedice tehničkog napretka u pogledu ugrožavanja okoliša iščezle, ali bi cijena koju bi se za to moralo platiti bila nesrazmjerna u odnosu na učinke povratka u pećinski način života po kvalitetu ljudskog života.

No, smije li se u ime evidentne neprihvatljivosti neoludističkih ideja širom otvoriti put nekritičkom prihvaćanju danas dominantnih modaliteta znanstveno-tehničkoga i tehnologijskog napretka? Čini se da bi tek primjerena sinteza svih triju dimenzija praktičke filozofije (a to znači: etike, ekonomije i politike, s naglaskom na pitanju o smislu i sadržaju valjanog života) s interdisciplinarnim i multidisciplinarnim istraživanjima konkretnih globalnih problema do kojih razvitak tehnike i tehnologije dovodi, istraživanjima koja bi smjerala na pronalaženje racionalnih rješenja tih problema, utemeljenih na zamisli humanog društva (što implicira korjenito preispitivanje opravdanosti tehnicističko-ekonomicističkog prihvaćanja neupitnosti primata logike profita), bila u stanju ponuditi izlaz iz bespuća lažne alternative tehnicizma i tehnofobije.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

ARSEN U POPULACIJI ISTOČNE HRVATSKE

ARSENIC IN POPULATION OF EASTERN CROATIA

Marina Vidosavljević[1], Dinko Puntarić[2], Vlatka Gvozdić[3], Domagoj Vidosavljević[4], Matijana Jergović[5], Miroslav Venus[6], Ada Puntarić[7], Dragana Jurić[8]

[1] Opća županijska bolnica Vinkovci, Vinkovci, Hrvatska
[2] Sveučilište Josip Juraj Strossmayer Osijek, Odjel za kemiju, Osijek, Hrvatska
[3] Hrvatsko katoličko sveučilište, Zagreb, Hrvatska
[4] Medicinski fakultet Osijek, Osijek, Hrvatska
[5] Zavod za javno zdravstvo Dr. Andrija Štampar, Zagreb, Hrvatska
[6] Zavod za javno zdravstvo „Sv. Rok" Županije virovitičko-podravske, Virovitica, Hrvatska
[7] Sveučilište u Zagrebu, Prehrambeno- biotehnološki fakultet, Zagreb, Hrvatska
[8] Zavod za javno zdravstvo Brodsko-posavske županije, Slavonski Brod, Hrvatska

autor za korespondenciju: Marina Vidosavljević, e-mail: vidosavljevic.marina@gmail.com

Izvorni znanstveni rad

SAŽETAK

Problem koncentracije arsena u okolišu Istočne Hrvatske je predmet istraživanja posljednjih 20-ak godina, a zajedničko je zemljama u okruženju (Srbija, Rumunjska).

Cilj istraživanja bio je istražiti dugotrajnu izloženost arsenu analizom sadržaja arsena u kosi.

Uzorci kose kod odraslih ispitanika uzeti su u područjima: Vladislavci, Čepin, Osijek, Dalj, Vukovar, Vinkovci i Slavonski Brod i analizirani pomoću ICP -MS metode.

Ovisno o istraživanom području, prosječne su koncentracije bile u rasponu od 0,018 (Vinkovci) do 32 μg g^{-1} (Vladislavci) pri čemu je u potonjem znatno premašila gornju granicu referentne vrijednosti (0,31 μg g^{-1}). Koncentracije arsena iz Našica, Osijeka, Slavonskog Broda, Vukovara i Vinkovaca bile su unutar ili nešto iznad maksimalno dopuštenog referentnog raspona. Najviše su koncentracije zabilježene kod ispitanika u naseljima Vladislavci (647,60 μg g^{-1}) i Čepin (526,78 μg g^{-1}).

Rezultati dopunjuju zaključak da stanovništvu treba omogućiti pristup pročišćenoj vodi bez arsena ili vodi iz vodonosnih područja sliva rijeke Save.

Ključne riječi: *arsen, kosa, Hrvatska, ICP-MS*

ABSTRACT

Problem of elevated arsenic concentrations in environment of east Croatia has been investigated for the past 20 years in Croatia, and surrounding countries (Serbia, Romania).

Aim of the study was to investigate long term exposure to arsenic by analysing the arsenic content in hair. Arsenite (As III) reacts readily with sulfhydryl group (-SH) in a variety essential enzymes and proteins.

Method: The hair samples were taken in areas of Vladislavci, Čepin, Osijek, Dalj, Vukovar, Vinkovci and Slavonski Brod and analysed using ICP –MS method.

Depending the investigated area, the mean concentrations ranged from 0,018 (Vinkovci) to 32 $\mu g\ g^{-1}$ (Vladislavci) whereby these last value, significantly exceeded the upper range of reference value (0,31 $\mu g\ g^{-1}$) . The arsenic concentrations from Našice, Osijek, Slavonski Brod, Vukovar and Vinkovci area were within or slightly above maximum allowed reference range. Maximum As concentrations in hair samples were detected in the Vladislavci (647,60 $\mu g\ g^{-1}$) and Čepin (526,78 $\mu g\ g^{-1}$) areas.

Results add to the conclusion that population should be enabled an access to arsenic non-contaminated water, either filtered or from areas of Sava basin.

Keywords: *arsenic, hair, Croatia, ICP-MS*

1. UVOD

Prisutnost arsena u vodi za piće jedan je od najvećih javnozdravstvenih problema u svijetu te se arsen smatra najopasnijim geogenim kontaminantom današnjice. Prisutnost arsena u vodopskrbnim sustavima istočne Hrvatske, napose vinkovačke i osječke regije izazivaju interes šire javnosti, a zbog povišenih vrijednosti objavljenih u medijima i zabrinutost kod lokalnog stanovništva.

Povišene koncentracije prirodno prisutnog arsena u vodonosnicima registrirane su diljem svijeta, a područje delti Gangesa, Brahmaputre i Meghne su među najugroženijima [1]. U Europi su podzemne vode onečišćene arsenom pronađene u aluvijalnim vodonosnicima Panonskog bazena: zapadna Mađarska, sjeveroistočna Rumunjska, sjeverna Srbija-Vojvodina; u aluvijalnim naslagama rijeke Aksios i u krškim vodonosnicima u Kalikratiji, sjeverna Grčka; u središnjoj Španjolskoj; u Slovačkoj i u Švicarskoj. U većini slučajeva arsenom onečišćena voda koristi se za javnu vodoospkrbu, ali postoje i iznimke u pojedinim mjestima, poput Zrenjanina u Banatu, gdje su od 2004 godine na snazi mjere zabrane uporabe vodovodne vode , izuzev kao tehničke, zbog povišenih vrijednosti arsena [2]. U središnjoj Bosni i Hercegovini, Srbiji i Makedoniji duboke mineralne vode prirodno sadrže povišene koncentracije arsena, a u Makedoniji je zabilježeno i onečišćenje voda koje su namijenjene javnoj vodoopskrbi [3].

Podzemne vode (ali i površinske) mogu biti onečišćene arsenom zbog prirodne kontaminacije i/ili uslijed ljudskih aktivnosti. Prirodna kontaminacija posljedica je geološkog sastava tla i sedimenata kao i hidrogeoloških karakteristika područja. Onečišćenje okoliša arsenom uslijed ljudskih aktivnosti uključuje taljenje ruda, emisiju plinova nastalih sagorijevanjem fosilnih goriva, razvoj drvne, farmaceutske i industrije stakla, upotrebu pesticida i herbicida na bazi arsena (npr. pesticid - na bazi olova i arsena koji se koristi u vinogradarstvu; herbicid - kompleks bakra, kroma i arsena koji se koristi kao defolijant u industriji pamuka) i odlaganje industrijskog kemijskog otpada. U novije vrijeme arsen se

koristi i kao antibiotik u uzgoju peradi, a preko izmeta i degradacije pomoću nitrata i organskih tvari, također prisutnih u izmetu, dospijeva u okoliš u obliku arsenata i arsenita [4]. Problem prisustva arsena u pitkoj vodi dijela istočne Hrvatske predstavlja značajan javnozdravstveni problem i potencijalni rizik po zdravlje stanovništva.

U istočnoj Hrvatskoj je prisutnost arsena u vodi pitanje hidrogeokemijskog svojstva tla u vodovodima koji pripadaju Dravskom slivu i djelomično Podunavlju. Prema istraživanju M. Ujević, izvori pitke vode iz područja sliva rijeke Save imaju do 10 puta niže vrijednosti arsena [5]. Problem arsena u vodovodima Osijeka i Čepina su ranije objavili Ćavar i sur. i Habuda Stanić i sur; a u ostalim dijelovima Osječko baranjske županije Gvozdić i sur. , Vidosavljević D. i sur. [6 - 9]. Pri tome treba naglasiti da se prema nekim autorima, više vrijednosti arsena u tlu mogu naći i u vrtovima na tim područjima, vjerojatno kao posljedica zalijevanja vodovodnom vodom, te u maslačku i kupusu kao fitoindikatorskim biljkama, a koje ujedno i čine dio hranidbenog lanca [9, 10].

Arsen i njegovi spojevi su otrovni i upotrebljavaju se kao insekticidi, kod izrade pesticida i pigmenta za boje. Toksičan je pri unosu 5 – 50 mg arsena. Smrtonosna doza mu iznosi od 50 do 300 mg a LD_{50} (oralno) iznosi 100 mg. Arsenove soli i plinovi su vrlo otrovni. U malim dozama arsen djeluje kao stimulator metabolizma, ali je karcinogen i vjerojatno teratogen. Količina u čovjeku varira u ovisnosti o ciljnom tkivu; u serumu iznosi 0,5 - 4,2 ng/ml, u urinu 5,3 - 11,7 ng/ml, u kosi 0,067 μg/g, u kostima 0,08 – 1,6 ppm; u jetri 0,023 – 1,61 ppm, a u mišićima 0,009 – 0,65 ppm [4, 11]. Dnevni unos se kreće 0,04 – 1,4 mg, a ukupna masa u prosječnoj osobi iznosi oko 7 mg, iako varira u opsegu 0,5 – 15 mg, ovisno o vrsti prehrane. Neka izvješća također pokazuju relativno visok stupanj apsorpcije nakon udisanja arsena. U vojnoj industriji se koristi u proizvodnji streljiva, pirotehničkih sredstava i kemijskog oružja (defolijant – „Agent Blue“) [4]. Arsen se u okolišu javlja u organskim i anorganskim spojevima, kao trovalentan ili peterovalentan oblik. Određene ribe i rakovi sadrže vrlo visoke razine organskog arsena, a u većini ostalih prehrambenih proizvoda, razina arsena su niske. Organski arsen u plodovima mora, kao i anorganski arsen u vodi, piću i lijekovima se lako apsorbiraju (70 – 90 %) u probavnom traktu.

S izuzetkom nekih vrsta ribe, rakova i algi, većina hrane sadrži nisku razinu arsena, obično ispod 0,25 mg/kg [12]. Stupanj unosa arsena u biljke je povezana s koncentracijom arsena u tlu, kemijskim sastavom tla i vrsti bilja [13]. Koncentracije arsena u morskim organizmima i algama su, općenito, značajno viša od onih u drugim namirnicama. Mnoge vrste riba sadrže između 1 i 10 mg/kg, dok određene vrste riba koje obitavaju na morskome dnu, rakovi i morske alge mogu sadržavati više od 100 mg/kg arsena, a meso, riba i perad čine većinu unosa arsena ingestijom , te su procijenili prosječni dnevni unos arsena iz hrane u SAD-u na 0,01 – 0,02 mg. Dnevni unos ukupnog arsena u Japanu, po nekim autorima iznosi 0,07 do 0,37 mg/po osobi dnevno [4].

Toksičnost arsena:

Procijenjeno je da je akutna smrtonosna doza progutanog anorganskog arsena u ljudi oko 1 - 3 mg/kg/dan, dok se udisanje i kožna ekspozicija ne može povezati s akutnom smrtnošću [14].

Akutni i subakutni toksični učinci arsena uključuju mnoge organske sustave, uključujući gastrointestinalne, kožu, živce, bubrege, jetru, hematološki, kardiovaskularni, respiratorni sustav i vid. Najčešći put unosa je gutanje velike doze arsena što izaziva akutni gastrointestinalni sindrom, koji počinje pojavom metalnog okusa ili okusa češnjaka u ustima sa sa suhoćom, osjećajem prženja usana i disfagijom. Gastrointestinalni sindrom može dovesti do smanjenja volumena krvi i pada krvnog tlaka uz elektrolitski disbalans i šok. U akutnom trovanju arsenom, dominantno zbivanje je oštećenje endotela kapilara što zatim dovodi do

generalizirane vazodilatacije, transudacije plazme i multiorganskog zatajenja. Arsen oštećuje zatim glomerule i tubule, a pojavljuje se i neuropatija zbog degeneracije aksona [14 - 16].

Kronični učinci se najbolje i najčešće vide kao kožne manifestacije-hiperpigmentacije s depigmentacijom i palmoplantarnu hiperkeratozu, kod profesionalno izloženih. Kožni učinci su javljaju nakon gutanja arsenom kontaminirane vode, najviše u dijelovima svijeta sa neadekvatnom vodoopskrbom poput Argentine, Bangladeša, Čile, Kine, Japana, Meksika, Mongolije i Tajvana [15, 17].

Dugotrajno izlaganje niskim dozama progutanog arsena dovodi do različitih gastrointestinalnih poremećaja koji se manifestiraju kroz simptome poput dispepsije, mučnine, proljeva, anoreksije i boli u trbuhu te krvave proljeve.

Periferna polineuropatija je često među posljedicama akutnog oralnog trovanja arsenom. Periferni neuritis, kognitivni poremećaji i poremećaji pamćenja su zabilježeni kod stanovnika Teksasa izloženih arsenu [18].

Kronična izloženost arsenu u lijekovima i vodi za piće izaziva cirozu jetre, portalnu hipertenzija bez ciroze i masnu degeneraciju [14 - 17]. Istovremena prekomjerna uporaba alkohola pospješuje nastanak ciroze tako da je zabilježena povećana smrtnost od ciroze jetre kod radnika u topionicama bakra [19]. Zbog pijenja arsenom zagađene vode u Indiji su zabilježeni slučajevi hepatomegalije među ispitivanim stanovništvom [15, 20].

Dugotrajno izlaganje arsenu djeluje suprimirajuće na hematopoetski sustav. Hematološke promjene uključuju normocitnu anemiju, megaloblastičnu anemiju, agranulocitozu, trombocitopeniju, aplastičnu anemiju i mijelodisplaziju. Kronični respiratorni učinci arsena se javljaju prvenstveno kao posljedica profesionalne izloženosti udisanjem prašine ili dima bogatih arsenom [15, 16], ali mogu nastati i uzimanjem vode za piće kontaminirane arsenom. Respiratorni efekti čine rinitis, faringitis, laringitis, traheobronhitis, kronični kašalj, krepitacije, kratkoća daha i kronična opstruktivna plućna bolest, te rak pluća [17, 20].

Metabolički učinci se najviše očituju u povećanoj prevalenciji šećerne bolesti. Među stanovnicima jugozapadnog Tajvana izloženima arsenu je zabilježen porast broja oboljelih od dijabetesa [21]. Glikolizirani hemoglobin je bio statistički značajno veći među radnicima izloženima arsenu u Danskoj u odnosu na ne izložene [22].

Dugotrajno izlaganje arsenu uzrokuje i zamućenje leće kao oftalmološku posljedicu.

Izloženost arsenu gutanjem ili udisanjem ima i značajne kardiovaskularne učinke koji uključuju elektromiografske abnormalnosti, naročito produljenje QT intervala i poremećaje ST spojnice, kao i bolesti koronarnih i cerebralnih krvnih žila, aterosklerozu karotida, perikarditis, arterijsku hipertenziju i poremećaje mikrocirkulacije [15,17].

Poseban klinički entitet i najdojmljivija posljedica kronične ekspozicije arsenu je „Bolest crnih stopala“ (eng. *„Blackfoot disease“*) Ova bolest obilježena je progresivnim gubitkom cirkulacije u rukama i nogama što dovodi u konačnici do nekroze i gangrene. Radi se o endemskoj bolesti koja se javlja isključivo na području Tajvana, gdje je opća populacija izložena visokim koncentracijama arsena preko vode za piće koje se najčešće kreću od 170 do 800 μg/L ,što odgovara dnevnoj dozi od 0,014 do 0,065 mg/kg.

Osim ove bolesti, na Tajvanu se kao posljedica izloženosti visokim koncentracijama arsena javljaju cerebrovaskularne i hematološke bolesti i ishemijske bolesti srca. Dok se „bolest crnih nogu“ javlja isključivo na Tajvanu, drugi učinci na krvožilni sustav česti su u područjima u kojima je populacija izložena visokim koncentracijama arsena, a uključuju povećanu učestalost Raynaudovog sindroma, cijanozu prstiju ruku i nogu, povišeni krvni tlak, zadebljanje i vaskularnu okluziju krvnih žila. [4]

Kronična ekspozicija arsenu uzrokuje rak mokraćnog mjehura i bubrega , naročito uroepitela [15, 17, 23] Vinari s područja Moselle koji su konzumirali vino zagađeno pesticidima s grožđa imaju povećanu smrtnost od raka mjehura [24]. Ekološke studije su

potvrdile vezu povišenih koncentracija arsena u vodi za piće i smrtnosti od raka mokraćnog mjehura i bubrega u Tajvanu [21, 23]. Ispitanici koji imaju znakove arsenijaze (rak kože ili *„Blackfoot"* bolest) imaju i povećan rizik od raka mokraćnog mjehura kao i radnici u topionicama bakra u SAD-u i Japanu [25].

Angiosarkom jetre i hepatocelularni harcinom kao i maligne neoplazne limfnog i hematopoetskog sustava te raka prostate su povezani s kroničnom ekspozicijom arsena posebice kod profesionalno izloženih radnika u zaštiti bilja i topionicama [15, 17, 25, 26].

2. ISPITANICI I METODE

Ispitanici su bili 391 punoljetne osobe sa ispitivanog područja Osječko-baranjske županije i 24 ispitanika s područja grada Vinkovaca. Obzirom da je istraživanje dio projekta „Istraživanje dugotrajnih posljedica rata na zdravlje populacije" terenski dio istraživanja je proveden sukcesivno, kroz više etapa od 2007. - 2013. godine, u mjestima Dalj, Ćelije, Vladislavci, Čepin, Dopsin, Hrastin, Potnjani, Draž, Osijek i Našice u Osječko-baranjskoj županiji, a uzorci kose su uzeti radi komparacije kod punoljetnih ispitanika s područja grada Vinkovaca , Vukovarsko-srijemska županija .

Prilikom istraživanja poštivana su etička načela u skladu s preporukama Etičkog povjerenstva Medicinskog fakulteta u Osijeku, uz potpisani obrazac informiranog pristanka za svakog od ispitanika.

Uzorak kose kod svih 415 ispitanika je uzet s zatiljka (cca. 1cm širine i 3cm dužine) pomoću škara od nehrđajućeg čelika i pohranjen u polietilenske vrećice. Uzorci kose oprani su u destiliranoj vodi, namočeni sat vremena u aceton, isprani deioniziranom vodom deset puta i sušeni na filter papiru na zraku kroz 24 sata. Na svakih 0,1 g uzorka dodano je 1 ml 65 % HNO_3. Nakon dva sata namakanja uzorak je stavljen u mikrovalnu pećnicu (Ethos D Microwave Labstation, Milestone, Brondby, 1996) zagrijan, ohlađen i razrijeđen do volumena od 12mL i prebačen u kivetu automatskog uzorkivača (AS 93 plus, Perkin Elmer, 2008). Uvjeti rada na pećnici za mikrovalno spaljivanje uzoraka: 5 min 250 W; 5 min 400 W; 5 min 500 W; 10 min ventiliranje.

Nakon toga je uslijedio postupak analize metodom masene spektrometrije induktivno spregnutom plazmom (ICP-MS; ELAN DRC-e, Perkin Elmer, Waltham, MA, USA).

3. REZULTATI I DISKUSIJA

Dobne i spolne značajke te teritorijalna distribucija ispitanika prema naseljima su prikazane u tablicama 1 i 2.

Tablica 1. Opće značajke ispitanika prema spolu i dobi

	Broj ispitanika	Aritmetička sredina ($\mu g\ g^{-1}$)	Minimalna vrijednost ($\mu g\ g^{-1}$)	Maksimalna vrijednost ($\mu g\ g^{-1}$)	Standardna devijacija ($\mu g\ g^{-1}$)
Muškarci	204	47,84	18,00	80,00	15,53
Žene	187	49,27	18,00	87,00	15,30
Ukupno	391	48,52	18,00	87,00	15,42

Tablica 2. Raspodjela ispitanika u odnosu na spol i mjesto stanovanja

	Čepin	Dalj	Našice	Osijek	Vladislavci
Muškarci	40 (19,6 %)	43 (21,1 %)	31 (15,2 %)	52 (25,5 %)	38 (18,6 %)
Žene	12 (6,4 %)	63 (33,7 %)	50 (26,7 %)	12 (6,4 %)	50 (26,7 %)
Ukupno	52 (13,3 %)	106 (27,1 %)	81 (20,7 %)	64 (16,4 %)	88 (22,5 %)

Rezultati analize As koncentracija u uzorcima kose i vode prikazani su u tablicama 3 i 4.

Tablica 3. Izmjerene vrijednosti As u kosi kod ispitanika

As /kosa/ (mg kg^{-1})						
Lokacija	N	Mean	Median	Min.	Max	SD
Vladislavci	88	32,342	0,373	0,062	647,35	95,940
Dalj	106	3,501	0,824	0,011	38,21	6,950
Čepin	52	28,943	0,974	0,022	526,43	105,60
Našice	81	0,091	0,051	0,004	0,701	0,133
Osijek	64	0,623	0,312	0,033	8,503	1,192
Vukovar	56	0,052	0,043	0,002	0,303	0,052
Slavonski Brod	31	0,019	0,015	0,001	0,080	0,017
Vinkovci	24	0,018	0,019	0,002	0,054	0,013

Tablica 4. Rezultati analize uzoraka vode za piće na području Osječko-baranjske županije

Voda	Maksimalna dozvoljena vrijednost za pitku vodu: 10 μg L^{-1}				
Mjesto	N	Mean (μg L^{-1})	Min. (μg L^{-1})	Max (μg L^{-1})	SD (μg L^{-1})
1. Vladislavci	16	16,34	0,33	160,17	62
2. Dalj	19	1,43	0,14	8,85	3,30
3. Čepin	12	184,34	30,6	251,4	91,40
4. Našice	8	0,13	0,04	0,59	0,38
5. Osijek	12	23,60	12,3	37,16	13,30

Kao što je prikazano u tablici 3, srednje vrijednosti razina arsena u uzorcima kose prikupljenih u pet naselja istočne Hrvatske, kretale su se od 0,11 do 35,86 μg g^{-1}. Četiri od pet istraživanih mjesta imale su značenje kao koncentracije koje su bile dvije do više od jedanaest puta veće od dopuštene Direktivom EU (0,034 - 0,319 μg/g). Maksimalne koncentracije muških ispitanika bile su od niskih 0,08 do vrlo visokih vrijednosti od 526,78 μg g^{-1}. Koncentracije arsena u kosi u kontrolnom području (Našice) niže su od 0,319 μg g^{-1}, što se smatra gornjom granicom referentne vrijednosti.

Žene su pokazale sličnu razinu koncentracije, srednju koncentraciju u rasponu od 0,077 do 41,34 μg g^{-1}. Ovisno o istraživanom području, maksimalne koncentracije kretale su se od 0,58 do iznimno visokih 647,32 μg g^{-1}, pri čemu je ova zadnja vrijednost za 2000 puta

prekoračila gornju granicu referentne vrijednosti. Glavne koncentracije arsena iz uzoraka kose s kontrolnog područja (Našice) bile su unutar dozvoljenog referentnog raspona.

Tijekom 2010. godine analizirani su uzorci vode za piće u nekoliko gradova i sela na području istočne Hrvatske. Analize su pokazale da su u nekim uzorcima na području Čepina koncentracije arsena (250 μg L^{-1}, Čepin) 20-tak puta veće od dozvoljene (tablica 4).

Izračun korelacija pokazao je postojanje statistički značajnih i pozitivnih korelacija između uzoraka kose muškaraca i uzoraka vode za piće Osječko-baranjske županije. (r = 0,98, p = 0,003). Slično je utvrđeno i u slučaju uzoraka kose dobivenih od osoba ženskog spola i vode korištene za piće (r = 0,87, p = 0,05).

Vrijednosti As izmjerene u kosi ispitanika s područja Vinkovaca su značajno niže u odnosu na ispitanike s područja Osječko-baranjske županije.

Rezultati analize pokazali su sljedeće vrijednosti maksimalnih koncentracija arsena u: vodoopskrbnom sustavu Osijeka (37,16 μg L^{-1}), Čepina (251,4 μg L^{-1}), Dalja (8,85 μg L^{-1}), Našice (0,59 μg L^{-1}).) i Vladislavaca (160,17 μg L^{-1}). U kontrolnom području Našice gdje je maksimalna izmjerena koncentracija As u vodi bila 0,59 μg L^{-1}, maksimalna koncentracija As u uzorcima kose bila je vrlo malo iznad gornje granice referentnog raspona (0,034 - 0,319 μg g^{-1}). Regionalni vodovod Sikirevci isporučuje vodu niskog sadržaja As 1,96 μg L^{-1} dok su u ostalim naseljima vinkovačkog kraja zabilježene visoke koncentracije arsena (tablica 5).

Tablica 5. Prikaz izmjerenih vrijednosti koncentracija As u pojedinima naseljima Vukovarsko-srijemske županije (Izvor Vinkovački vodovod i kanalizacija)

Koncentracije As u uzorcima vode	MDK=10 μg L^{-1}
Regionalni vodovod	1,96 μg L^{-1}
Komletinci	137 μg L^{-1}
Privlaka	98 μg L^{-1}
Mirkovci	19,6 μg L^{-1}
Vinkovci	*28 μg L^{-1}

MDK-maksimalna dozvoljena koncentracija
* Podatak iz 2002. godine, sada na regionalnom vodocrpilištu Sikirevci

U Čepinu i Vladislavcima (izložena) maksimalna koncentracija vode u vodi premašila je maksimalnu dopuštenu razinu koju je EU odredila (tj. 10 μg L^{-1}). Slijedom toga, u tim područjima maksimalna pronađena koncentracija arsena u kosi bila u rasponu od 396,82 do 526,78 μg g^{-1} (muški) i od 393,14 do 647,35 μg g^{-1} (ženski), prelazeći referentni raspon od 0,034 - 0,319 μg g^{-1} za nekoliko tisuća puta. U područjima s umjereno povišenim koncentracijama arsena u uzorcima vode (Osijek: 37,16 μg L^{-1} i Dalj: 8,85 μg L^{-1}), maksimalne vrijednosti arsena u uzorcima kose kretale su se između vrijednosti kontrolnog i izložbenih područja (vidi tablice 3 i 4), što se također ne smatra normalnoj razini. U slučaju uzoraka kose muških ispitanika rezultati su pokazali značajne i snažne pozitivne korelacije između maksimalnih koncentracija u uzorcima vode i kose (ρ = 0,99 $p < 0,05$). Iako je i za uzorke ženske kose (r = 0,80) utvrđen jak pozitivan odnos između maksimalnih koncentracija u uzorcima vode i kose, na $p < 0,05$ nije pronađena statistički značajna povezanosti između maksimalnih koncentracija arsena u uzorcima vode i kose žena. Koncentracija As u uzorcima kose osoba muškog i ženskog spola OBŽ iznosila je 0,11 μg g^{-1} odnosno 0,07 μg g^{-1}. Kod ispitanika s područja Vinkovaca izmjerene vrijednosti As u kosi su se kretale od 0.002 do 0,054 μg g^{-1} - prosječno 0,018 μg g^{-1}, što se može protumačiti korištenjem vode siromašne arsenom na području VSŽ.

Kosa je značajna kao pokazatelj dugotrajnije ekspozicije pojedinom kontaminantu, u ovom slučaju arsenu iz pitke vode.

Vrijednosti arsena u kosi kod ispitanika iz naselja Čepin su druge najviše među ispitivanim naseljima ali značajno više u odnosu na ostala ispitivana naselja. Arsen je najviši u Vladislavcima i Čepinu, uz povišene vrijednosti u Osijeku, što se može povezati s konzumacijom vode bogate arsenom.

Ćurković je u svom radu pokazao povezanost između arsena i nikla u kosi i podzemnoj vodi za piće naselja Ćelije i Draž [27].

Ministarstvo zdravstva RH je prema svojim ovlastima za dio naselja koje opskrbljuju lokalni vodovodi istočne Hrvatske podiglo dozvoljene vrijednosti arsena u vodi do 50 ug/L do 01.srpnja 2019 ali i zabranilo upotrebu vode za piće za lokalne vodovode naselja Komletinci, Korođ, Markušica i Ostrovo zbog izmjerenih vrijednosti od 100 - 220 ug/L. Navedeno je uzrokovalo izuzetan interes a dijelom i prosvjede mještana u navedenim naseljima.

Zbog svega navedenog , Zavod za javno zdravstvo VSŽ je učinio analizu morbiditeta i mortaliteta stanovnika dijela naselja VSŽ. Po svim navedenim pokazateljima, analizom dijela naselja istočnog dijela bivše Općine Vinkovci (Otok, Komletinci i Privlaka) nije zabilježen statistički značajno veći broj hospitalizacija zbog navedenih skupina bolesti i pojedinih dijagnoza u odnosu na podatke za Republiku Hrvatsku i Vukovarsko-srijemsku županiju. Također, incidencija ukupnog raka, te raka pluća i mokraćnog mjehura ne razlikuje se od incidencije na razini Republike Hrvatske. Smrtnost od kardiovaskularnih bolesti, zloćudnih novotvorina, te raka pluća i mokraćnog mjehura također nije viša od očekivane prema podacima na razini Republike Hrvatske. Dakle, ne postoje podaci koji bi ukazivali na povećani pobol i smrtnost od bolesti koje se povezuju s izloženosti arsenu u naseljima istočnog dijela bivše općine Vinkovci u proteklih 15 godina.

Obzirom na maksimalnu dopuštenu koncentraciju arsena u vodi za ljudsku potrošnju od 10 mikrograma na litru, koja je dogovorena na temelju epidemioloških istraživanja provedenih u populaciji/ama koje su izložene daleko većim koncentracijama arsena od onih koje su zabilježene u Hrvatskoj, stanovništvo je dugotrajno izloženo arsenu u koncentracijama većim od dopuštenih u vodi koju koriste, te je zbog tog u riziku za razvoj neke od opisanih bolesti koje potencijalno arsen može izazvati. Koliki je taj rizik teško je procijeniti jer se za koncentracije ispod 200 mikrograma po litri sasvim sigurno radi o matematičkim interpolacijama rizika koje mogu dati i velike varijacije, a radi se najvjerojatnije o riziku manjem od 1:10 000 za najčešće istraživani karcinom mokraćnog mjehura, što bi konkretno značilo jedan karcinom mokraćnog mjehura uzrokovan arsenom (dakle uz ostale koji nisu uzrokovani arsenom nego drugim čimbenicima) na svakih više od 10 000 izloženih stanovnika; ali se prema literaturi posljedice po zdravlje populacije mogu očekivati tek pri vrijednostima iznad 600 mg/L.

Dakle, treba posebice navesti, da se akutne posljedice trovanja arsenom u populaciji ne mogu očekivati.

Najvažnija mjera koju treba što prije poduzeti je svakako prekinuti izloženost stanovništva, dakle omogućiti stanovništvu opskrbu zdravstveno ispravnom vodom, kao što je to riješeno u mnogim drugim mjestima, alternativnom opskrbom, pročišćavanjem ili priključivanjem na regionalne vodovode.

4. ZAKLJUČAK

U kosi ispitanika iz Osječko baranjske županije su izmjerene prosječne vrijednosti arsena u dijelu naselja veće od referentnih vrijednosti objavljenih u literaturi, što predstavlja posljedicu konzumacije vode za piće iz lokalnih vodovoda koji su bogati arsenom, što je i statistički dokazano. Vrijednosti arsena izmjerene u kosi ispitanika na području Vinkovaca su niže od ostalih izmjerenih vrijednosti u istočnoj Hrvatskoj. Treba naglasiti da sam grad Vinkovci i dio okolnih naselja od 2010. god. prima vodoopskrbu s regionalnog vodocrpilišta Sikirevci, koje ima vodu izuzetne kakvoće i vrlo niskog udjela teških metala.

Po svim navedenim pokazateljima, u naseljima istočnog dijela Vukovarsko-srijemske županije nije zabilježen statistički značajno veći broj hospitalizacija zbog navedenih skupina bolesti i pojedinih dijagnoza u odnosu na podatke za Republiku Hrvatsku i Vukovarsko-srijemsku županiju. Također, incidencija ukupnog raka, te raka pluća i mokraćnog mjehura ne razlikuje se od incidencije na razini Republike Hrvatske. Smrtnost od kardiovaskularnih bolesti, zloćudnih novotvorina, te raka pluća i mokraćnog mjehura također nije viša od očekivane prema podacima na razini Republike Hrvatske. Dakle, ne postoje podaci koji bi ukazivali na povećani pobol i smrtnost od bolesti koje se povezuju s izloženosti arsenu u naseljima VSŽ u proteklih 15 godina.

Obzirom na maksimalnu dopuštenu koncentraciju arsena u vodi za ljudsku potrošnju od 10 mikrograma na litru, koja je dogovorena na temelju epidemioloških istraživanja provedenih u populaciji/ama koje su izložene daleko većim koncentracijama arsena od onih koje su zabilježene u Hrvatskoj, stanovništvo dijela vinkovačkog područja (naselja Otok, Privlaka, Komletinci) je dugotrajno izloženo arsenu u koncentracijama većim od dopuštenih u vodi koju koriste, te je zbog tog u riziku za razvoj neke od opisanih bolesti koje potencijalno arsen može izazvati. Koliki je taj rizik teško je procijeniti jer se za koncentracije ispod 200 mikrograma nisu dokazale uzročno posljedične veze između arsena u vodi i negativnih utjecaja na ljudsko zdravlje, dok su iste zabilježene tek pri vrijednostima arsena iznad 500 ug/L.

Najvažnija mjera koju treba što prije poduzeti je svakako prekinuti izloženost stanovništva, dakle omogućiti stanovništvu opskrbu zdravstveno ispravnom vodom, kao što je to riješeno u mnogim drugim mjestima, alternativnom opskrbom, pročišćavanjem ili priključivanjem na regionalne vodovode. U tom smislu treba promatrati i zabranu uporabe vode za piće u lokalnim vodovodima izdanu od strane Ministarstva zdravstva Republike Hrvatske, te ubrzano priključivanje naselja na regionalno vodocrpilište Sikirevci, koje pripada savskom bazenu.

Treba na kraju naglasiti da su potrebna dodatna opsežna javnozdravstvena istraživanja kako bi se dobiveni podaci u ovom istraživanju stavili u realne okvire i zatvorili jednu znanstveno – istraživačku cjelinu.

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Zahvala

Rad je dio projekta Ministarstva znanosti obrazovanja i sporta Republike Hrvatske: Istraživanje dugotrajnih posljedica ratnih zbivanja na zdravlje stanovništva. Voditelj: prof.dr.sc.Dinko Puntarić, prim.dr.med., Medicinski fakultet, Osijek. (MB: 219-1080315-0288).

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

REUSE OF WASTE SULFUR AS A BINDING AGENT IN CONCRETE

Milica Vlahović*, Sanja Martinović*, Aleksandar Savić, Zoran Stević*** Tatjana Volkov Husović******

* Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia
** University of Belgrade, Faculty of Civil Engineering, Belgrade, Serbia
*** University of Belgrade, Technical Faculty in Bor, Belgrade, Serbia
**** University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

corresponding author: Milica Vlahović,e-mail: mvlahovic@tmf.bg.ac.rs

Original scientific paper

ABSTRACT

Mainly due to the strict global environmental regulations regarding the oil and gas refining processes, which limit the maximum quantity of sulfur in combustibles, the availability of waste sulfur has been considerably growing during the last decades and it is evident that there will be a continuous abundant supply of waste sulfur in the future. Finding new ways for waste sulfur consumption thus becomes very important. In this research, possibility of using waste sulfur as a binding agent in concrete was analyzed and the properties of the obtained sulfur polymer concrete in aggressive environments were examined using destructive and non-destructive testing methods. Compressive strength changes were insignificant. Ultrasonic measurements indicated significant homogeneity changes and slight internal degradation. Based on the obtained results, the material with satisfying quality for possible application in corrosive environment was produced.

***Keywords**: waste sulfur, sulfur polymer concrete, destructive testing methods, non-destructive testing methods*

1. INTRODUCTION

During the last decades, environmental concerns have resulted in severe sulfur emission constraints that requires the active management of industrial sulfur. Therefore, the availability of sulfur has considerably grown worldwide, mostly owing to the oil and gas refining processes. Sources of sulfur are organic sulfur compounds in crude oil and hydrogen sulfide in sour natural gas. Organic sulfur compounds in crude oil are converted to hydrogen sulfide by a hydrogenation process [1]. Hydrogen sulfide from both crude oil and natural gas is converted to elemental sulfur by Claus process, summarized in Eq.(1):

$$3\ H_2S + 3/2\ O_2 \rightarrow 3/X\ S_x + 3\ H_2O + 620\ kJ \quad (1)$$

Claus process is schematically presented in figure 1.

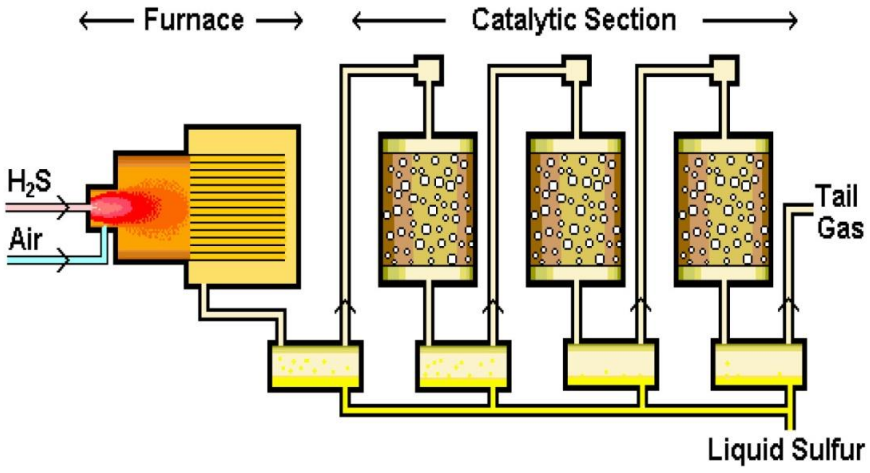


Figure 1. Scheme of Claus process [2]

Produced sulfur can be made into several forms. Piles and blocks of sulfur produced by Claus process are given in figure 2.



Figure 2. Piles [3] and blocks [4] of sulfur produced by Claus process

Waste sulfur from oil processing has been stored leading to more or less controlled disposal, while waste sulfur from ore processing, in the form of gaseous oxides, is usually converted into sulfuric acid and onwards used for artificial fertilizers. Sulfur demand has to increase drastically or thorough disposal practices must develop, otherwise, sulfur by-product will persist as a chemical waste problem. Modern industrial production still needs further development of technologies that would provide incorporating waste sulfur into useful products, thus removing it from the environment. Construction materials should always be considered as potential recipients of large amounts of wide range of waste that can be inertized by incorporating into usable and sustainable construction materials. Therefore, construction materials are preferred acceptors because of huge amounts of secondary sulfur. On the other hand, they have wide practical application [5].

Sulfur can completely substitute Portland cement to form new, stable, hard concrete product. Using sulfur as a binder is based on its physico-chemical characteristics: chemical passivity, hydrophobicity and excellent resistance to aggressive agents (mainly acids and salt solutions, but not bases) [6]. Unlike concrete with Portland cement, concrete made from sulfur needs heating during production, usually by the combustion of fossil fuels. In spite of heating, concrete made with sulfur releases far fewer greenhouse gas emissions compared

with Portland cement concrete. By using sulfur as a binder, the emissions released in the calcination process during clinker production as well as the combustion emissions generated to supply heat to the calcination process are eliminated.

Consuming sulfur for the production of sulfur polymer concretes and mortars is a relatively new technology that has to be proven in practice. Recent experience shows that concrete produced with sulfur binder instead of cement and water has significant chemical and physico-mechanical advantages comparing with Portland cement concrete. Sulfur polymer concrete is environmentally friendly and cost-effective with relatively simple composition and manufacture, and interesting properties. Due to its mechanical strength, fast hardening, quick setting and corrosion resistance, it belongs to high performance materials suitable for numerous applications, especially those in which other materials fail.

Sulfur polymer concrete is a high performance environmentally sustainable and durable thermoplastic composite material made of mineral aggregates and modified sulfur as a replacement for cement and water in conventional Portland cement concrete at temperatures above the hardening point of sulfur (120 °C). Additionally, such material allows using large amounts of sulfur from worldwide oil refineries and metallurgical industry. This relatively new building material can possibly replace conventional Portland cement concrete in many branches of construction [7].

The possibility of using sulfur by-product as a binder for concrete production was investigated in this research. Mechanical strength, internal destruction and homogeneity of the obtained sulfur polymer concrete during acid and salt resistance testing was examined.

2. EXPERIMENTAL

2.1. Technological procedure of sulfur polymer concrete production

The initial materials for the production of sulfur polymer concrete were aggregate, sulfur and modified sulfur and filler.

Sand with maximum grains size of 2 mm, obtained by sieving of locally available classical building mixture of sand and gravel, was used as an aggregate. Classical chemical analysis combined with AAS and AES indicated that the aggregate mainly consisted of oxides of silica (89.98 %), aluminium (3.61 %), calcium (0.84 %), iron (0.62 %), potassium (0.59 %), sodium (0.57 %), and magnesium (0.19 %).

Elemental sulfur, the basic component for a modified sulfur binder, as a granular shape with purity of 99.9 % originates from oil refining process by Claus's procedure in the Oil Refinery Pancevo, Serbia. Dicyclopentadiene (DCPD), cyclic hydrocarbon, was used for sulfur modification. The modification procedure consisted of mixing elemental melted sulfur and DCPD in the temperature range from 120 to 140 ºC and ambient pressure for 30 min, and then rapid cooling and solidification of the obtained sulfur polymer [8].

Fillers used in this production were: talc (technical quality, China), alumina (Almatis, Germany), microsilica (Sika, Switzerland) and fly ash (Power Plant ”Nikola Tesla - A”, Obrenovac, Serbia). Filler plays an important role because with sulfur it forms paste that coats and binds the aggregate particles. Talc, microsilica and fly ash fulfill these requirements and therefore are recommended for the sulfur polymer concrete production [1], while fine fractions of calcined alumina are used as fillers for refractory concretes [9]. Particles size of all used fillers was below 75 μm.

The applied manufacturing technological procedure for sulfur polymer concrete preparation is described in literature [10]. Preheated aggregate and filler (up to 160 ºC) were stirred for about 15 min in a mixer, then melted sulfur and modified sulfur were mixed into homogenized dry mixture of aggregate and filler at sulfur melting temperature, 132 - 141°C. Preheating is desirable to avoid solidification of the molten sulfur by contact with aggregate at a low temperature and to reduce the mixing time. The heated aggregate and filler were then properly mixed with the molten modified sulfur until a homogenous viscous mixture was obtained. After 2 minutes of homogenization and mixing, the sulfur polymer concrete mixture was casted into molds preheated at 120 ºC and vibrated for 10 seconds. Any extra material was removed to get a well-finish at top surface and left inside the molds at room temperature for hardening. Sulfur polymer concrete hardens very rapidly (from 15 minutes to several hours, depending on size and shape of the sample), which allows removal from the mold and curing in a relatively short time. The samples were demolded after 3 h and then kept at room temperature for 24 h. For the purpose of this testing, prism-shaped samples with dimensions (4 x 4 x 16) cm were prepared.

2.2. Characterization of sulfur polymer concrete

Characterization of sulfur polymer concrete was realized before and during acid and salt resistance testing. The prepared prism-shaped samples were immersed in three solutions: 10 % HCl, 20 % H_2SO_4 and 3 % NaCl for 360 days.

The experimental program consisted in performing the following properties measurements on sulfur polymer concrete samples.

- *Compressive strength*

Compressive strength was conducted using the "Amsler" press (Germany) with maximum load of 200 kN, and method for testing the strength of concrete according to the standard [11].

- *Ultrasonic pulse velocity*

The measurement of ultrasonic pulse velocity was realized to monitor the internal material degradation and to discuss its homogeneity. It was performed using the equipment OYO model 5210 (Japan) according to the standard testing procedure (SRPS D. B8. 121.).

3. RESULTS AND DISCUSSION

3.1. Visual inspection

The appearance of sulfur polymer concrete samples after 12 months in acid and salt solutions is presented in figure 3. Obviously, there are no signs of destruction.

It is well known that Portland cement concrete is not resistant to acid and salt influence.

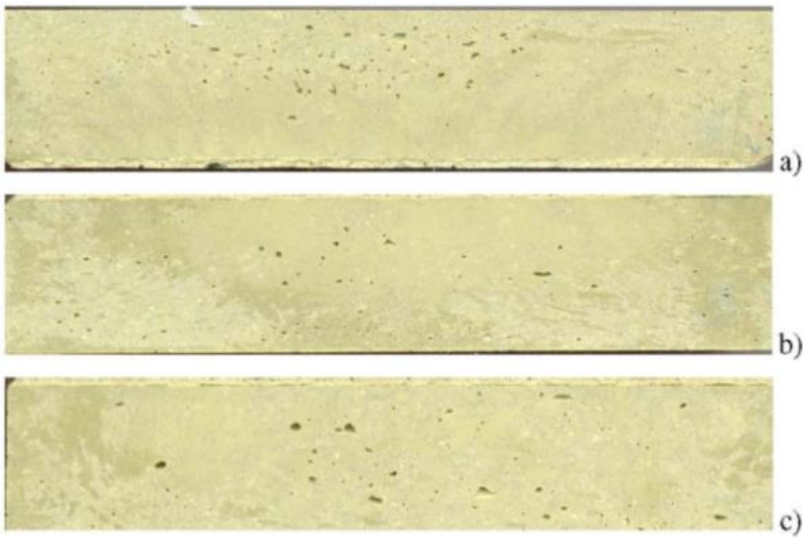


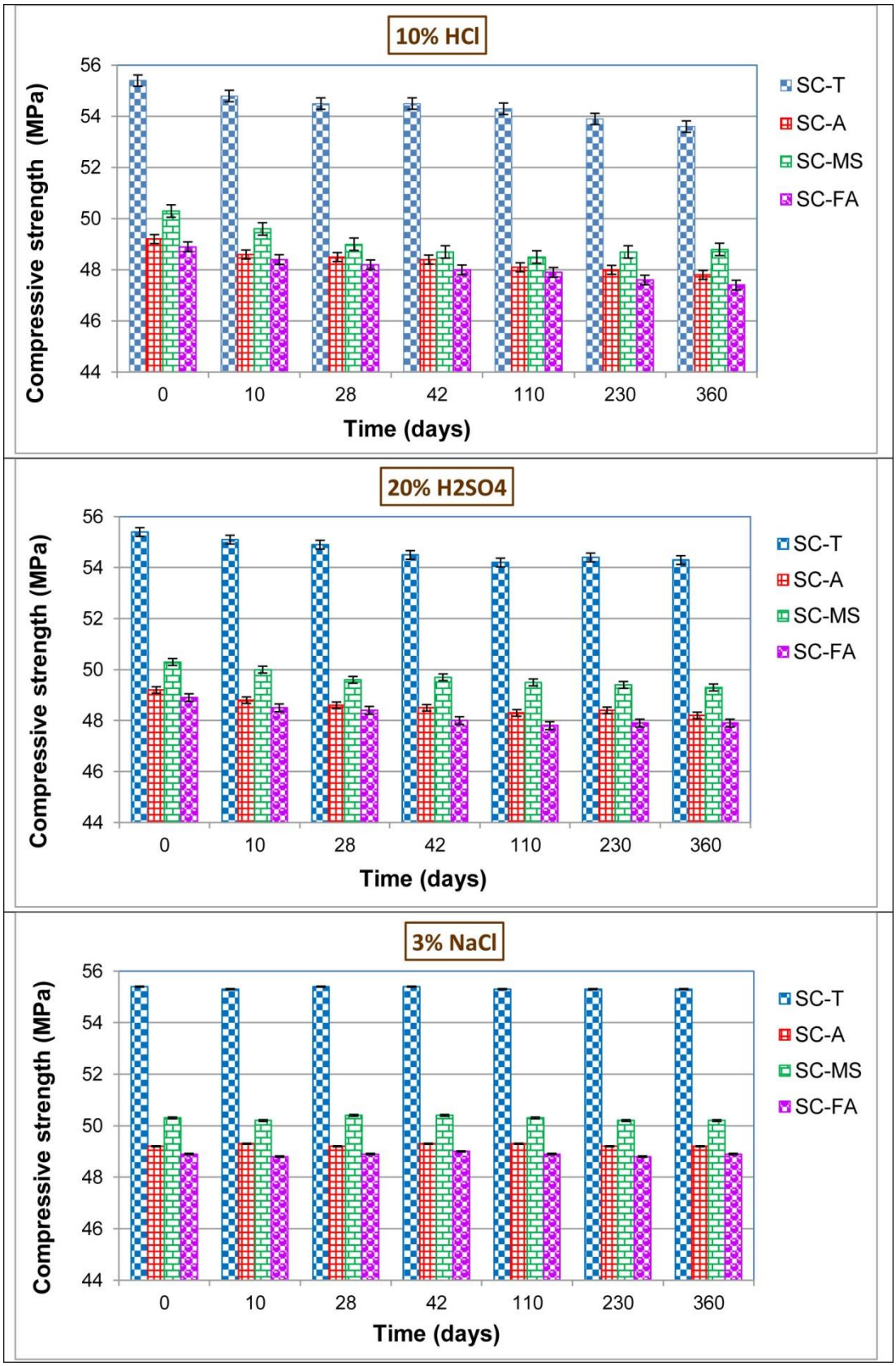
Figure 3. Surfaces of sulfur polymer concrete samples after one year:
a) with talc in 10 % HCl solution, b) with microsilica in 20 % H_2SO_4 solution,
c) with fly ash in 3 % NaCl solution

3.2. Compressive strength

The obtained results, given in figure 4, represent durability of sulfur polymer concrete samples depending on the filler type and solution expressed through compressive strength change as a function of immersion time.

According to these results, behavior of the sulfur polymer concrete samples with different fillers regarding compressive strength changes was quite uniform in three solutions. Generally, all sulfur polymer concrete samples after 360 days lost ~ 3 % of their strength in 10 % HCl, ~ 2 % in 20 % H_2SO_4 and negligibly in 3 % NaCl. It means that the type of filler did not exhibit significant influence on strength degradation [12].

Since mechanical strength is dependent on the defects in concrete microstructure, it can be assumed that the reason for mechanical strength degradation lies in increased porosity of the treated sulfur polymer concrete samples compared with the untreated samples. Porosity is related to the movement of chemical substances into and out of the material and consequently affects durability of concrete, as it is connected to deterioration processes driven by the transport properties of concrete. In sulfur polymer concrete, the majority of the matrix is composed of sulfur coated materials (aggregate and filler) and sulfur accumulated in the voids between particles.



SC-T = sulfur polymer concrete with talc, SC-A = sulfur polymer concrete with alumina, SC-MS = sulfur polymer concrete with microsilica, SC-FA = sulfur polymer concrete with fly ash

Figure 4. Compressive strength of sulfur polymer concrete with different fillers in acid and salt solutions

3.3. Ultrasonic pulse velocity

The measured values of ultrasonic pulse velocities, both longitudinal (V_p) and transversal (V_s), in three directions (x, y, z) during the immersion time suggest that sulfur polymer concrete was very stable regarding internal degradation, as velocity decrease was negligible - less than 5 % at the end, which means that the porosity increase was not significant.

Based on differences between maximum and minimum values of ultrasonic pulse velocities in three directions (ΔV) during the immersion time, homogeneity of sulfur polymer concrete can be discussed. As an example, those differences for sulfur polymer concrete sample with alumina as filler in 10 % HCl are presented in figure 5.

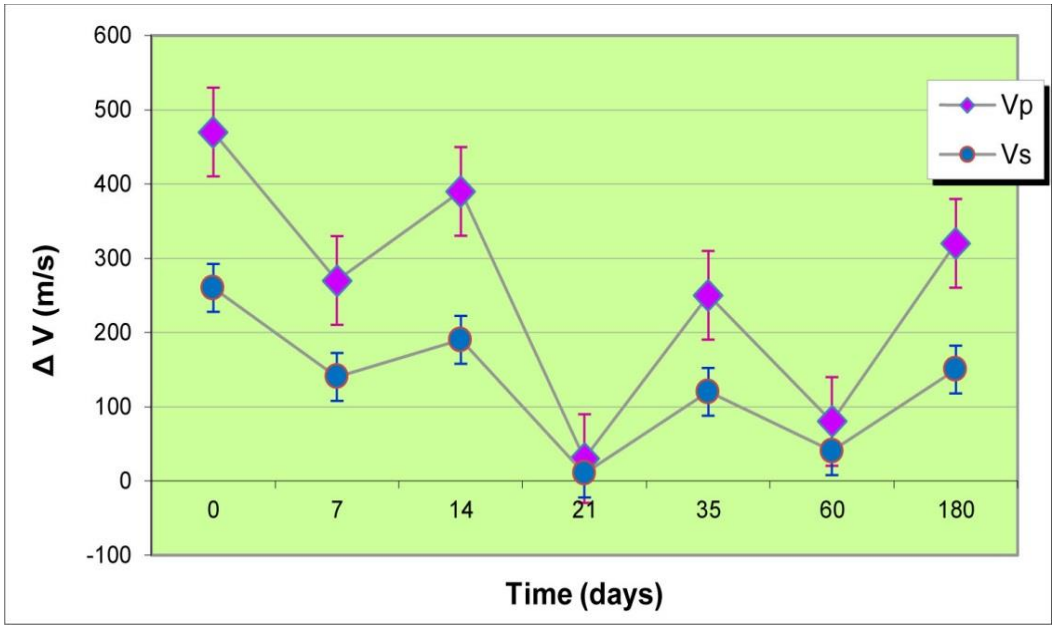


Figure 5. Differences between maximum and minimum values of ultrasonic pulse velocities in three directions for sulfur polymer concrete with alumina during immersion in 10 % HCl

Greater differences between maximum and minimum values of ultrasonic pulse velocities of the samples before the immersion compared to those after 180 days of immersion indicate that the material after acid treatment became more homogeneous. Since those differences for 21 days of immersion are negligible, the material can conditionally be considered as homogenous. For that period compressive strength was the highest (figure 4). All observed homogeneity changes are the result of material structure rearrangement caused by the acid influence.

4. CONCLUSION

In this study the possibility of using waste sulfur from oil refinery as a binding agent for concrete production was successfully proved. Technological procedure for obtaining sulfur polymer concrete was precisely given. Sulfur polymer concrete was produced of the secondary sulfur from oil refining process, sand as an aggregate, and various fillers. Modification of sulfur was performed by cyclic hydrocarbon, dicyclopentadiene. Behavior of produced sulfur polymer concrete during acid and salt resistance testing was investigated. The

compressive strength did not change significantly. Ultrasonic measurements indicated significant homogeneity changes as a result of structure rearrangement provoked by acid influence but internal degradation was insignificant. It can be concluded that by adequate technological procedure and selection of the initial components, sulfur polymer concrete with satisfying mechanical strength and good resistance to acid and salt solutions was obtained. This in turn will make this material a good candidate for its use in construction industry and for other applications where high resistance to corrosive effect of the environment is required.

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Acknowledgements

Authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for the funding provided for this study under the project numbers TR 33007, TR 36017 and III 45012.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

POSSIBLE USE OF GROUND SULFUR AS PETROLEUM INDUSTRY BYPRODUCT IN SELF COMPACTING CONCRETE PRODUCTION

Tatjana Volkov-Husović*, Sanja Martinović*, Milica Vlahović*, Aleksandar Savić, Zoran Stević*****

* University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia
** University of Belgrade, Faculty of Civil Engineering, Belgrade, Serbia
*** University of Belgrade, Technical Faculty of Bor, Belgrade, Serbia

corresponding author: Aleksandar Savić, e-mail: savic.alexandar@gmail.com

Original scientific paper

ABSTRACT

The quantities of component materials used for production of concrete are high on the global scale, therefore alternative materials are experimented on, in order to replace the natural ones. The possibility of using ground waste sulfur from the oil refining (petroleum) industry as a filling component of self-compacting concrete is presented in the paper, based on common concrete laboratory tests. The physical and mechanical properties of self-compacting concrete decrease to some extend due to use of ground sulfur, but this concrete remains useful for some building applications.

***Keywords**: filler, self-compacting concrete, sulfur, fresh and hardened properties*

1. INTRODUCTION

Being a material produced in high quantities, concrete presents "number one" building material in the world. For the production of concrete huge quantities of water, aggregate and cement are used, resulting in a rising environmental concern. Therefore, the principles of sustainable development are being implemented in the building industry, presenting ever new aspects regarding materials and technologies.

One of the revolutionary changes in the field of concrete is Self-Compacting Concrete (SCC) [1]. This type of concrete is defined as a self-placeable concrete, which doesn't require any means of vibration (otherwise a must, for usual concrete types). It flows and fills the formwork by its own weight, under the influence of gravity, wrapping the re-bars, even densely spaced ones, and filling even the narrowest spaces in the formwork.

For production of SCC, in most cases, powder type material is needed, that, besides cement, provides resistance to the internal segregation of concrete. There are two types of such powder type materials, active (such as silica fume, fly ash, slag) and inert (limestone and dolomite powder, ground concrete and such).

This work presents a study of potential use of ground (pulverized) sulfur as filler for the production of SCC. Elemental sulfur is a major byproduct of metallurgy and oil refining industry, and its annual production was in 2015 estimated to 69.5 million tons [2] (figure 1).



Figure 1. Sulfur as a byproduct of petroleum industry

2. MATERIALS

Natural river aggregate originated from the river Danube was separated and washed, and used in production of SCC (figure 2). Self-Compacting Concrete is usually produced with the largest grain size restricted to less than 22.5 mm. Therefore, the fractions used for the synthesis of SCC included three standard fractions: I (0/4), II (4/8) and III (8/16).



Figure 2. River aggregate for production of concrete

Particle size distribution of used aggregate, tested according to the standard procedure [3], is shown in table 1, together with the particle size distribution of the mixture of aggregates used for this study.

Table 1. Particle size distribution shown as percentage passes in different sieves

	Sieve diameter	0.125	0.25	0.5	1	2	4	8	16	31.5	63
Pass (%)	I (0/4)	2.0	10.5	66.6	76.9	87.1	98.9	100	100	100	100
	II (4/8)	0	0	0	3.1	8.0	13.3	99.6	100	100	100
	III (8/16)	0	0	0	0	0	0.2	8.8	96.9	100	100
	Mixture	1	4	33	39	44	57	76	100	100	100

River aggregate can be successfully used for the production of Self-Compacting Concrete, as for the production of all of the commonly used concrete types. Nevertheless, the composition of the mixture of aggregate for the production of SCC can be tricky, in order to avoid segregation and provide proper workability and later strength.

Fines can present a particular problem when it comes to the production of SCC and therefore their content has to be determined for every fraction of aggregate used [4]. Also, the content of fines has to be periodically checked during the production of concrete, in order to notice any possible variation with time. The highest content of fines was recorded for the fine aggregate fraction I (0/4) and it amounted to less than 1.68 %.

Aggregate fractions proportions play an important role in the strength bearing system in the hardened concrete. In this work, mass ratio of fractions II and III was determined through the laboratory test that included the highest value of density for the mixture of these fractions in dry compacted state and was adopted to be 1:1. Content of fraction I in aggregate mixture was determined based on the pilot mixtures and it was 31.8 % of SCC total volume.

Portland cement *CEM I 42.5R, Lafarge, Serbia* was used in laboratory investigations. Density of cement was 890 kg/m^3 in loose, and 1440 kg/m^3 in compacted state, while gravity of cement was 3.04. Specific area of cement, measured by Blaine method, was 4240 cm^2/g. Limestone powder (*Granit Peščar, Ljig*) was used as filler. This material is characterized as carbonate filler with medium grain size of 250 μm. Density of the limestone powder was 780 kg/m^3, and gravity 2.72. Specific surface area of 3800 cm^2/g was measured by Blaine method.

Sulfur was obtained from the oil refining process by Claus`s procedure in the Oil Refinery Pančevo, and its purity was 99.9 %. Gravity of used sulfur was 2.05. Before the use in SCC, sulfur was ground to the size of particles below 0.09 mm with the aid of disintegrating mill (figure 3). The mineral filler obtained in such way had specific surface area measured by Blaine 2600 cm^2/g.

Glenium Sky 690 (*BASF Construction Chemicals, Italy*) was used as superplasticizer. This superplasticizer is a poly-carboxylate based, with gravity of 1.06, pH of 5 - 8, and with low amount of chlorides (chlorite ion content 0.01 %).



Figure 3. Disintegrating mill used for grounding of sulfur

3. MIXTURES AND METHODS

Five series of concrete were made, with 380 kg/m^3 cement and 220 kg/m^3 of filler. Fillers used in this study were limestone powder, and ground sulfur. Ground sulfur replaced the same mass amounts of limestone powder, i.e. in contents of 0 % (SCC1), 2 % (SCC2), 5 % (SCC3), 10 % (SCC4) and 20 % (SCC5). Water to cement ratio was constantly 0.482.

Fresh concrete mixtures were tested according to the standard methods for SCC, including slump-flow time and diameter measurement [5], V-funnel time [6], L-box test [7], and segregation ratio [8]. Entrained air content was measured according to [9], and fresh concrete density according to [10].

Results of investigations on hardened SCC with ground sulfur included compressive [11], flexural [12], and ultrasonic pulse velocity [13] measurements.

4. RESULTS AND DISCUSSION

4.1. Properties of fresh SCC

Based on the slump-flow test, flowability of SCC with added sulfur was higher than in referent SCC1 series, which was made without sulfur. It can be concluded that, with the slump-flow values ranging from 761 mm to 820 mm, all of the SCC series belong to the category of SF3 according to the relevant provisions [14]. Also, when it comes to the time of slump-flow up to the diameter of 500 mm, all series can be categorized as VS2/VF2 with t500 > 2 s and tv > 9 s (except in case of SCC2 and SCC3). Since differences among t500 values of all series are less than 1 s it turned out that content of ground sulfur has no significant influence on this property. According to the L-box test, all concretes achieved class PL2

(H2/H1 > 0.8). Segregation resistance of the SCC mixtures with ground sulfur turned out to decrease when compared to the reference SCC1.

The value of density of SCC decreases with the increase of ground sulfur content. This decline can be explained by lower density of ground sulfur in comparison to the substituted limestone powder. This decline is quite small and reaches 0.9 % for replacement of limestone powder with the ground sulfur up to 20 %.

As for the content of entrained air in these SCC mixtures, there was no significant change with the incorporation of ground sulfur. Entrained air contents ranged between 1.2 % and 1.9 %. Either way, the values of entrained air recorded on these SCC series were lower than expected for SCC generally, 2 % being the usual value of entrained air content for most SCC mixtures.

4.2. Properties of hardened SCC

Compressive strength was tested on three samples (cubes of 10 cm edge length) for each SCC series, at the ages of 3, 7, 14, and 28 days, while the average values are shown in the Figure 4. Results ranged from 54.6 MPa (for SCC5) to 62.2 MPa (for SCC1 as reference). All series achieved 75 – 85 % of final compressive strength (at the 28 days of age) already at the age of 3 days. Velocities of compressive strength increase for all tested SCC were similar, as it can be observed on the same figure (figure 4).

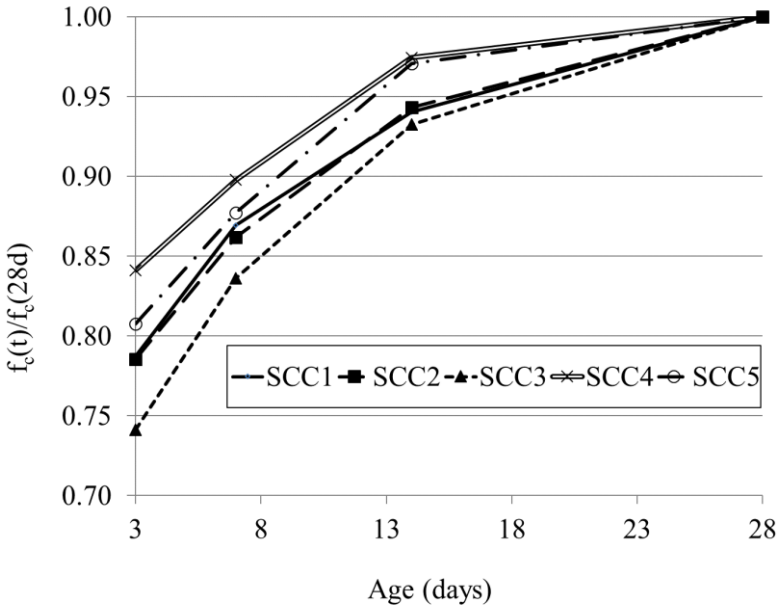


Figure 4. Compressive strength increase for all series

Flexural strength values were in the range of 6.9 (SCC5) to 10.5 MPa (SCC1), see figure 5. Bond strength values were within the limits of 5.8 MPa (SCC1) and 6.3 MPa (SCC4) for the Ø50 dolly, thus these concretes own sufficient bond strength for any structural application.



Figure 5. Flexural strength values

Overall analysis shows that ultrasonic pulse velocity is decreasing with the increase of sulfur content in the SCC while it is increasing with the age, see figure 6.

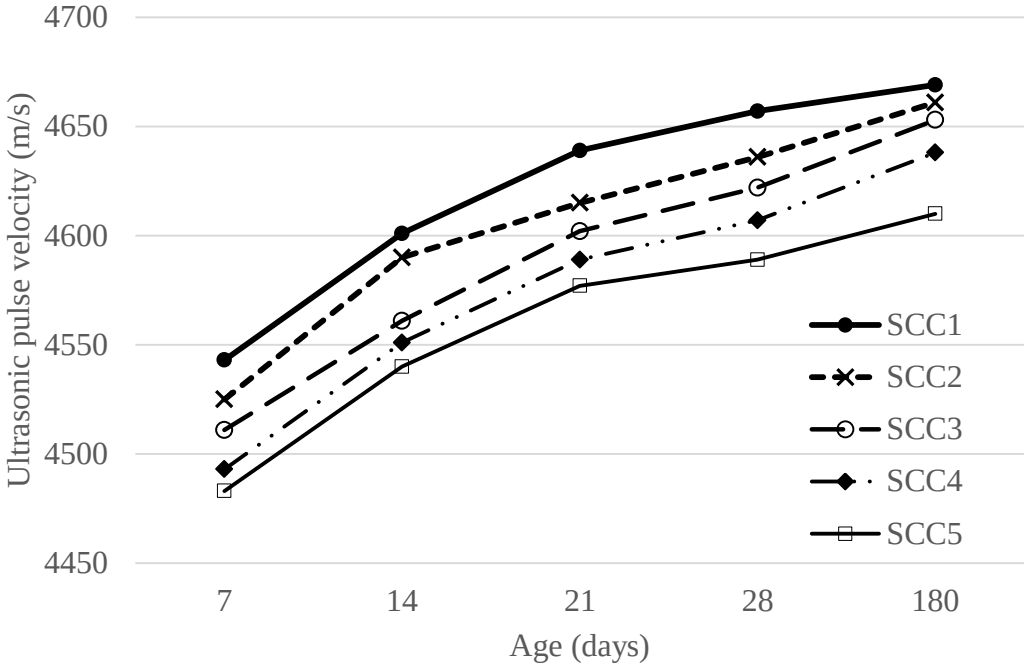


Figure 6. Change of ultrasonic pulse velocity with age

5. CONCLUSION

The results obtained in this study demonstrate the feasibility of ground sulfur use as filler for Self-Compacting Concrete. From the results and discussion, the important conclusions have been summarized as follows:

- that content of ground sulfur had no significant influence on flow ability, passing ability and segregation resistance. Also, there was no significant change in entrained air content,
- the increase in ground sulfur content resulted in a slight decrease of SCC density,
- compressive strength decreased up to 12 % with increase in ground sulfur content up to 20 % of filler. The reason is probably lower mechanical properties of sulfur itself (lower strength and hardness),
- when the curves slopes are analysed, velocities of compressive strength increase for all tested SCC were similar,
- flexural strength decrease was up to 34.3 %, with the highest content of ground sulfur (20 % of the total filer mass),
- ultrasonic pulse velocity through Self-Compacting Concrete with ground sulfur decreased for all ages with sulfur content almost linearly, up to 1.3 %.

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Acknowledgments

Results from this work arising from research funded by the Ministry of Education, Science and Technological Development of Republic of Serbia, within the projects III 45012, TR 33007 and TR36017. This support is gratefully acknowledged.

1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

HOLISTIC DIMENSIONS OF AGROECOLOGY

Ana Vovk Korže*, Danilo Korže**

* University of Maribor, Faculty of Arts, International Centre for ecoremediation, Maribor, Slovenia
** University of Maribor, Faculty of Electrical Engineering and Computer Science, Maribor, Slovenia

corresponding author: Ana Vovk Korže, e-mail: ana.vovk@um.si

Professional paper

ABSTRACT

The term agroecology is used for sustainable practices based on traditional and local farmer's knowledge, consistent with the characteristics of the local environment and conservation of the biodiversity and cultural landscape. In the article will be shown the dimensions of agroecology (as a science: combining ecology and agronomy, the application of ecological science to the study). In agricultural approach the agroecology can be defined as a holistic and transitional process to make the agri-culture more sustainable. As a movement includes two main categories of civil society actors: farmers and NGOs. Agroecology in action shows that it can be used effectively only when networks of farmers, scientists, and other stakeholders learn together. The perspective of agroecology in future is basis for sustainable way of life. For example establishing the ecovillages and ecocities, using green technologies and developing the green working places and long-term life learning for all generations on the field of self-sufficiency.

***Keywords**: agroecology, ecovillage, green technology, self-sufficiency, sustainability*

1. INTRODUCTION

Agroecology is recognized as a path to sustainable agriculture. In adapting to climate changes and in implementing sustainable approaches to the economical use of natural resources, agroecology is gaining an important role as a combination of science, practice and sustainable movements. This leads to the decline of conventional farming, which has a negative impact on water, soil, air and the entire natural system. Agroecology is a multidimensional concept that includes science, social movement and agricultural practices [1]. These dimensions interconnect the knowledge of different technical and social sciences and influences different stakeholders from producers to consumers. The modern trends of teaching agroecology are based on a systemic approach that enables observation and analysis

of complex situations in agriculture and food systems. The research and teaching of agroecology stems from sustainable agriculture, which deals with biodiversity protection, concern for fresh pure water, limited natural resources, the availability of agricultural land, food security, social justice and adapting to climate change, among others, which increasingly and drastically affect the production of the quality food. With innovative pedagogical approaches and alternative research methods, the experts in the field of agriculture and food production systems deal with more extensive systemic issues in order to achieve efficient use of renewable resources, food security in modern society, and the resilience of production systems to adverse conditions [2].

Recent literature has helped define and categorize different understandings and definitions of agroecology. In Euro-educATES (2018) the authors systematically categorize different perspectives of agroecological traditions in various key playing countries. They describe the different traditions of AE through examples from these key countries. The three categories given are AE as a scientific discipline, a movement, and a practice.

2. METHODOLOGY

Practical education in the field of agroecology can be implemented as a practical lecture (in school), or as a practical work experience (among employers). Schools can connect the content of agroecology to all subjects and offer them as additional options of practical education. The modules in the manual can be used separately and independently by the teachers or parts of the modules can be included in the contents of the treated subjects during the lessons. The contents of the modules are designed to promote practical work, so they can be also used to activate education in nature, for field research, and for connecting schools with the environment.

Numerous research and experiences in modern teachings of agroecology have shown that pupils learn most from various practical and research activities, which include case studies and collaboration with different stakeholders in the local environment, e.g. teachers, parents, experts, local farmers, etc. This makes it easier for them to understand the complexity of systems that include the environmental, social and economic dimension. It also gives them a sense of responsibility when executing and completing their projects. Learning agroecology is based on the so-called experiential learning in real-life situations (figure 1), the key approach being " learning by doing " as justified by John Dewey [2]. This approach enables young people to develop critical thinking skills and the ability make independent decisions on finding solutions and taking measures to solve real problems in their everyday life and the local environment. While the teacher takes up the role of a mentor, mediator and observer through the learning process, he also encourages and directs students to find a solution for themselves [3].

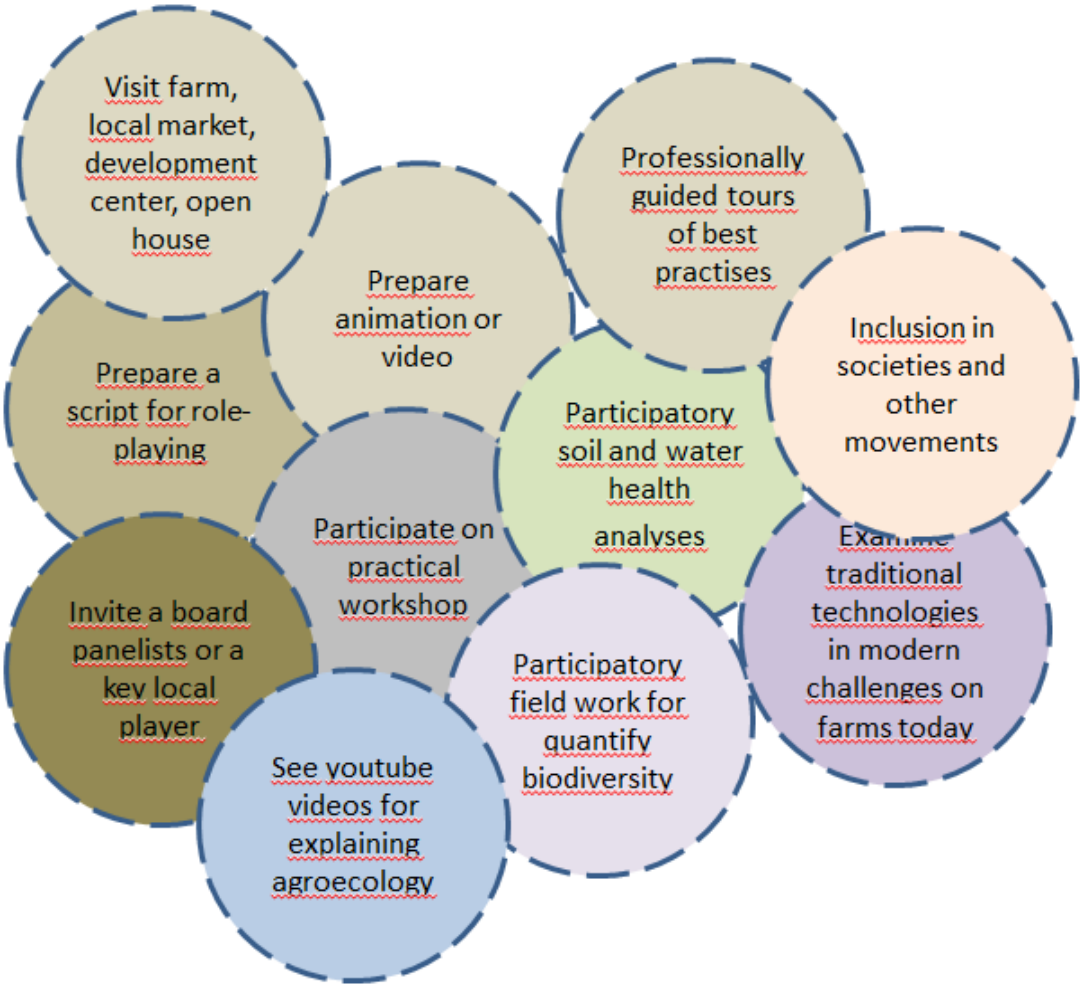


Figure 1. Some possibilities of practical agroecological experiences

3. RESULTS AND DISCUSSION

3.1. Development of agroecology

The systems approach in agriculture is a multi-perspective way of seeing the world, distinct from that employed by single disciplines. Holistic thinking requires a systemic approach to observing and analysing complex situations in agriculture and food systems (figure 2). While research on individual components of a system is often essential, this work is most valuable when conducted with an appreciation for and the whole system in mind. When looking at the likely impacts of a new high-yielding wheat variety, for example, it is important to consider the prices and long-term availability of needed inputs, the impacts on the local and regional environment, and the social consequences of introducing this variety, such as farm size, concentration of markets, and distribution of benefits. These are factors not often considered by the plant breeder who is closely focused on the goal of increasing genetic production potential. Agroecology provides a framework within which to study the multiple consequences of the new technology introduction [2].

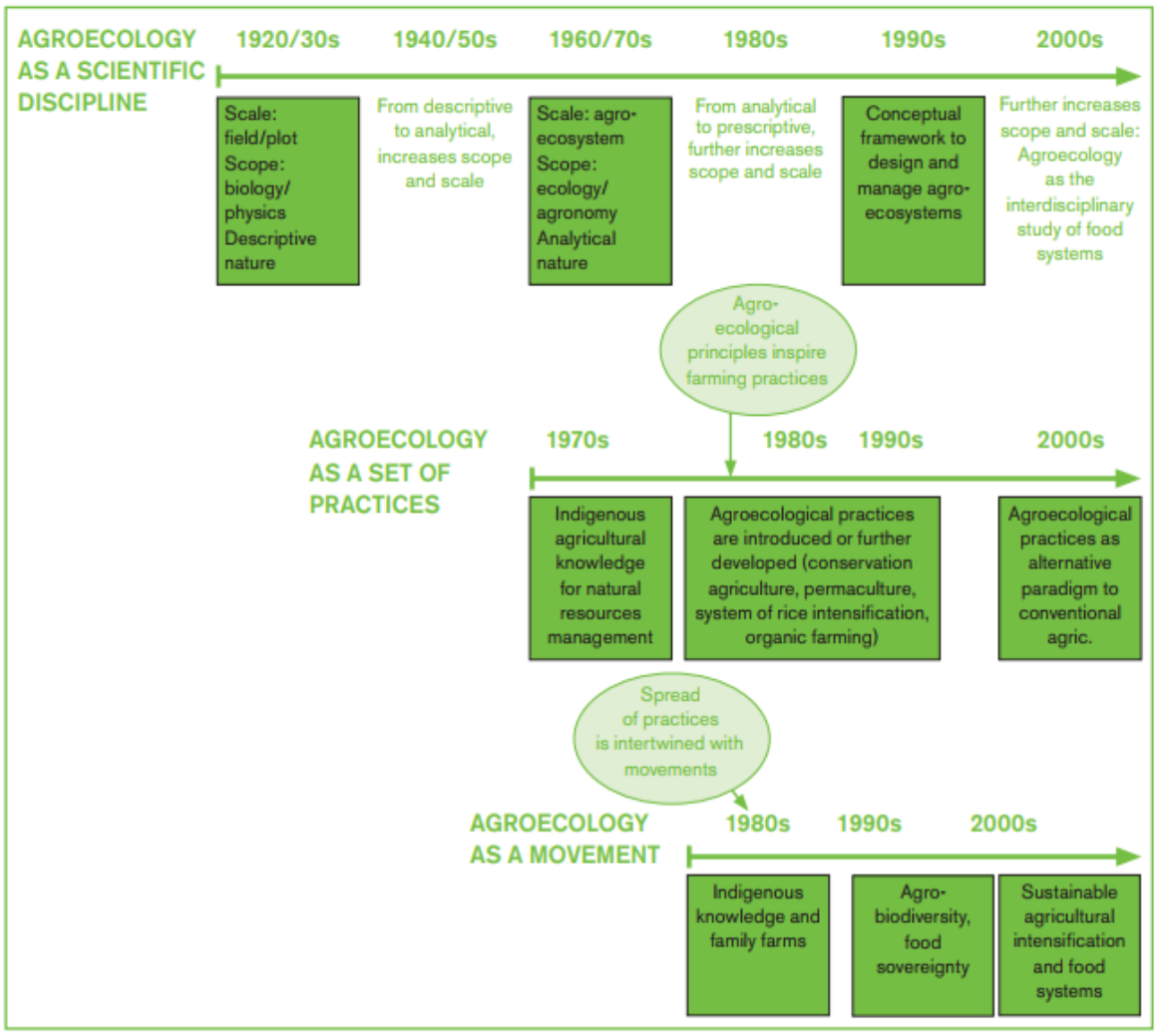


Figure 2. Temporal changes in scale and dimension of the definition of agroecology and in applied researches (Scilici, 2014). Source: http://pubs.iied.org/pdfs/14629IIED.pdf

On the website www.agroecology.org.we can find the interesting representation of agroecology in the world. We find that agroecology today appears in response to emerging conflicts in nature and society, and as a different - alternative way of farming. Agroecological methods should activate traditional practices and link them with innovations, knowledge and new skills as well as people's attitude towards food with emphasis on healthy and locally produced food. The approaches in agroecology are the most developed in France, which is the leading country in planning, education and implementation of such activities in practice. In the French Action Plan, the Ministry of Agriculture noted the importance of agroecology as an all-encompassing process until 2020, when France becomes the leading country in this field and will integrate farmers into the agroecological farming). The implementation of agroecology was based on farmers' education, activation of the research and acquired knowledge transfer into practice. They are developing agroecological subsistence systems, including the public and monitoring the effects of agroecology in practice (monitoring and evaluation). They devote a lot of attention to education, especially in the field of professional qualifications. In Italy, in 2016, agroecological approaches were classified as mandatory in the organic food production and agroecology was enacted by regulations. The main emphasis now is on the awareness that farms must function as holistic ecosystems. As science, agroecology is part of ecology or landscape ecology, which deals with ecological conditions

and processes in agro-ecosystems and with agricultural ecosystems as whole. It does not apply only to agricultural use, meadows and fields for example, but also deals with forests, swamps and processes of degradation, erosion and the outflow of water [4].

The definitions of the term agroecology differ greatly in terms of specificity which defines the term 'ecology'. According to this definition agroecologists can study the state of soil health, water and air quality, meso- and micro-fauna, local plants, toxic substances and other natural contents. A more common definition of the term can be found with authors who see agroecology as a study of interactions between plants, animals, people and the environment in agricultural systems. Therefore, agroecology itself is a multidisciplinary science including factors from agronomy, ecology, sociology and economy. Agroecology is also differently defined depending on the geographical location. This approach is the result of understanding the ecosystems as elaborated by Eugene Odum [5]. His approach is based on the assumption that natural systems with their stability and resistance are the best model for imitation in agricultural ecosystems. Usually the ecosystems of agroecology are not actively involved in social sciences, however, this school is based primarily on the belief that large-scale farming with massive use of chemicals is detrimental to society. The basic approach of agroecology is derived from agronomy including traditional agricultural practice, which is considered as the heritage of the area [4].

The concept of agroecology appears to be replacing the concept of sustainable development, which has not brought about any significant changes in the recent decades. In agroecology the focus is on using sustainable practices for food production (organic farming). Agroecology is therefore the type of farming that supports nature and does not reduce its ecosystemic benefits and services. It includes ecology also in its products and uses a holistic approach from cultivation to processing. It links ecology with culture, economy and society with the aim of creating a healthy society [6]. Such systems are characteristic of agricultural areas in African and Asian countries, where they provide themselves with food and energy completely. The use of agroecology increases the soil fertility; the soil becomes more resistant to drought and climate changes, the communities are more connected and positively affect the entire ecosystem (water is retained by vegetation not using artificial irrigation and pesticides) [4]. Agriculture and food production are the basis of life and have multifaceted effects on society. They have an important influence on prosperity and hunger, on climate changes and the environment. They both involve women workforce and offer a variety of jobs. Agroecological production involves the local environment and seeks solutions on the local level (Euro-educATES intellectual output O1, 2018).

The concept of agroecology may seem complicated, but in reality it is clearly based on skills and knowledge, efficient use of resources to the maximum, problem solving and reducing the costs [6]. This requires constant adaptability and innovations. The transition to green agriculture is beneficial to all and allows local communities to plan and create their own development. The quality of food depends on the way how it is produced and directly affects the health of all living beings.

In order to apply the principles of agroecology it is important to know the holistic sustainable production system based on traditional knowledge and local experiences, which needs to be upgraded with modern ecological, social and agronomic knowledge. The purpose of this approach is also to preserve and improve agricultural production, to ensure a healthy natural and living environment and to provide quality food as well as maintaining self-sufficiency of local communities.

The agroecological system can operate on various levels, either on the field, garden or farm level, local community or in the entire region or state. The essential agroecological strategy of creating a stable system is based on the integration of diversity in the agricultural land and the local landscape. The diversity on the field level or farm level is understood as

species diversity, crop rotation, polyculture instead of monoculture, forestry, a combination of agriculture and livestock farming, the use of green manure plants and drapes. On the landscape level it is the establishment and maintenance of a system of green infrastructures, which is co-shaped by borders, wind-barriers, ponds, grass belts, bypass and water corridors. These stable and varied agroecological systems boost the improvement of soil quality, resistance to disease and higher productivity of crops as well as preserve the nutrients.

With the help of agroecological arrangements on the micro-level, i.e. in the garden, field or the entire farm, we adapt to the natural factors as much as possible and use natural local renewable sources. We use natural resources such as solar energy for heating water and electricity, we collect and reuse water sources such as spring water or rainwater and use the energy of soil to store seeds and crops. This reduces the need for external energy inputs and reduces the operating costs of farming.

We use the excess of biomass for composting purposes and return it to beds after a year. Compost will additionally retain moisture and consequently we will improve the quality of the soil. To cover the field surfaces, use hay or straw mulch, which prevents the growth of weeds, keeps moisture and improves the soil, therefore no earth-working machines are required. As for simple garden arrangements, such as shaft beams and other supporting garden elements, recycled natural materials can be used. We can also include useful organisms in the farming system, which are attracted by properly regulated housing and food sources. With such agroecological approaches we will conclude a series of natural processes in the garden or in the field and strengthen the natural system to remain self-sufficient and resistant to external negative factors such as weather disturbances, pests and diseases. The nature will reward us with the abundance of quality crops that will help us live healthily.

At macro level, agroecology is becoming more and more established as a way of living and functioning of the community, and as responsible management of natural resources. Agroecology is based on scientific and traditional knowledge. It is a science that bridges ecological and socio-economic aspects. It can work at various levels – farm, community, national, regional, etc. Biological processes are enhanced using agroecological principles and these principles can be shared via farmer-to-farmer exchanges. Agroecology needs to be built from the bottom up, especially through social movements in rural areas [7]. Agroecologists often see the addition or the umbrella of agroecology to organic agriculture as a possibility to further guide the current organic system by including additional agroecological principles. Because of agroecology's distance from institutionalisation to the extent of organic with standards, regulation, certification, and political agendas, it is also seen as a possibility to circumvent some of the economic and institutional interests and to replace resulting hindrances with possibilities that come from a less manipulative form of sustainable agriculture [8]. Agroecology is seen by some as a possibility to rescue organic farming from the risks of conventionalization.

Climate change, altered global water, cycle, human migration, population growth, urbanisation, food production and food security, energy and natural resource management are interconnected and intertwined and therefore they cannot be addressed separately. Policies are essential instruments for promoting the sustainability of landscapes, agriculture, cities and rural development.

Cooperation is required at all levels and especially among different sectors in order to ensure that agriculture, forestry and fisheries policies are planned and integrated within national development strategies and complimentary to trade, environment, climate and energy policies, to name but a few policy areas. More importantly, policies must reward sustainability and support continuous improvements.

3.2. Dimension of agroecology

Ecosystemic dimension **-** Although in sustainable concepts the emphasis is on equally balanced development of the environmental, economic and social systems, more attention must be paid to the environment and nature in order to achieve prosperity. Ecosystems with their ecosystemic services are essential to our survival. Therefore, in stressing the importance of the connection of all subsystems in the region or in local communities, the ecosystemic dimension, which provides connections with other systems, should be highlighted as a priority.

Dimension of integrity - The concept of sustainable development combines components, in particular the capital of a certain region (environmental capital, human capital, economic capital) and develops these together, not individually. A prime example of an insufficiently holistic approach is the Natura 2000 project, under which many protected areas are stagnating because no connection was made between natural capital and social, human and economic capital.

Dimension of prosperity - Economic growth focused on the production of material goods should not have such a fatal influence on the processes in society and nature as it had in the past. Research shows that the population living on Earth in 2050 will experience heat waves, droughts, floods and storms. Many of today´s plants and animals will die out because of the construction of new infrastructures and the use of phytopharmaceutical resources in agriculture. Quality of life and economic growth will be reduced because of the loss of biodiversity, which provides a balanced ecosystem.

Dimension of self-sufficient supply and active public involvement - The activation of neglected potential, relations between and motivation of people as well as regulated legislation are all of key importance for initiating self-sufficient supply. Self-sufficient supply, based on respect for the ecosystem, can be used, by cross-sections of subsystems, to develop many new cross-sections, which create a solid network and links between man and nature, activate many different interests. Self-sufficient supply should be the basis for comprehensive regional development [9].

3.3. Innovation in agroecology

Innovation in agroecology seeks to make the best use of biodiversity and other ecological services while contributing to an equitable development of rural areas and establishing trust in the food chain. Farmers, consumers, other actors throughout the food chain and rural communities need to be involved in the whole system and not only be seen as end-users of knowledge.

The development of innovative practices that improve the triple (environmental, economic and social) performance of farms [10] is necessary not to freeze the systems and practices but to resort to agronomic or organizational innovation. This implies the implementation of techniques offering alternatives to those developed during the intensification of agriculture (products plant, chemical fertilizers, grubbing-up of hedges...) and allowing the good functioning of agro-ecosystems. Researchers and farmers are experimenting and imagining new systems based on agricultural innovations such as the use of bio-controls, the search for autonomy.

The innovation needs to be boosted throughout European agriculture and for this reason the European Innovation Partnership for Agricultural Productivity and Sustainability (EIP-AGRI) was established in 2012 [11]. The European Innovation Partnership: opportunities for innovation in organic farming and agroecology help to generate new insights

and co-ownership. It mobilises scientific and practical knowledge to foster innovation improves the speed of uptake of solutions by practitioners and helps to better target the research agenda towards practice needs. It is about bringing expertise from the worlds of farming and science together to learn from each other and develop ideas, knowledge and innovative actions together. It aims to build bridges between science and practice, in particular through practical innovation projects, bottom-up approaches, partnerships and networking activities. It is about growing an innovation culture in European farming that embraces the sector in all its diversity and which is not blind to the prospects that lie in traditional and practical knowledge. Today is self-sufficiency an extremely broad issue and is not only the domain of the agricultural profession (figure 3).



Figure 3. Self-sufficiency on the local level (Vovk Korže, 2016)

A transition towards more sustainable agriculture can only be achieved if the proper policies are put in place. It also requires political interest from the stakeholders and their active engagement in order to implement such policies [12].

4. CONCLUSION

Agroecology is a multidimensional concept that includes science, social movement and agricultural practices. These dimensions interconnect the knowledge of different technical and social sciences and influences different stakeholders from producers to consumers. The modern trends of teaching agroecology are based on a systemic approach that enables observation and analysis of complex situations in agriculture and food systems. The research and teaching of agroecology stems from sustainable agriculture, which deals with biodiversity protection, concern for fresh pure water, limited natural resources, the availability of agricultural land, food security, social justice and adapting to climate change, among others, which increasingly and drastically affect the production of the quality food. With innovative pedagogical approaches and alternative research methods, the experts in the field of agriculture and food production systems deal with more extensive systemic issues in order to

achieve efficient use of renewable resources, food security in modern society, and the resilience of production systems to adverse conditions [13] and [14].

The systems approach in agriculture is a multi-perspective way of seeing the world, distinct from that employed by single disciplines. Holistic thinking requires a systemic approach to observing and analysing complex situations in agriculture and food systems. While research on individual components of a system is often essential, this work is most valuable when conducted with an appreciation for and the whole system in mind. When looking at the likely impacts of a new high-yielding wheat variety, for example, it is important to consider the prices and long-term availability of needed inputs, the impacts on the local and regional environment, and the social consequences of introducing this variety, such as farm size, concentration of markets, and distribution of benefits. These are factors not often considered by the plant breeder who is closely focused on the goal of increasing genetic production potential. Agroecology provides a framework within which to study the multiple consequences of the new technology introduction. Numerous research and experiences in modern teachings of agroecology have shown that pupils learn most from various practical and research activities, which include case studies and collaboration with different stakeholders in the local environment, e.g. teachers, parents, experts, local farmers, etc. This makes it easier for them to understand the complexity of systems that include the environmental, social and economic dimension. It also gives them a sense of responsibility when executing and completing their projects.. This approach enables young people to develop critical thinking skills and the ability make independent decisions on finding solutions and taking measures to solve real problems in their everyday life and the local environment. While the teacher takes up the role of a mentor, mediator and observer through the learning process, he also encourages and directs students to find a solution for themselves.

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BIOTERORIZAM

BIOTERRORISM

Silvija Zeman*, Sven Hižman*

* Međimursko veleučilište u Čakovcu, Čakovec

autor za korespondenciju: Silvija Zeman, e-mail: szeman@mev.hr

Pregledni rad

SAŽETAK

Bioterorizam je aktivnost terorističkih skupina s ciljem rasprostiranja straha, bolesti i smrti na cjelokupno stanovništvo određenog područja koje se tretira biološkim oružjem i izazivanjem panike i straha kod ostatka populacije.

Opće prihvatljiva podjela američkog Centra za kontrolu zaraznih bolesti je podjela u tri glavne skupine, tzv. skupinu A, B i C. Biološka oružja iz kategorije A lako se šire i prenose, uzrokuju visok mortalitet. U biološka oružja B kategorije ubrajaju se agensi koje karakterizira nizak mortalitet, ali teško detektiranje. U oružje skupine C ubraja se i gripa koja se zbog visoke zaraznosti i širenja pojavljuje u vidu epidemije ili čak pandemije.

U slučaju zlouporabe biološkog agensa koji mogu dovesti do epidemije ili do oboljenja od zaraznih bolesti velikog broja osoba, određuju se mjere sprječavanja i suzbijanja širenja zaraznih bolesti. Zaključeno je da je bioterorizam fenomen suvremenog doba koji zbog svoje surovosti predstavlja moćan faktor destabilizacije neke države. Za ovaj rad proučavana je literatura, zakonski akti vezani uz ovaj problem, te primjeri pojave bolesti na temelju kojih možemo doći do određenih zaključaka.

***Ključne riječi**: bioterorizam, biološko oružje, klasifikacija, rizici, agens*

ABSTRACT

Bioterrorism is activity of terrorist groups with the aim of spread of fear, diseases and death on general population of a specific area, which is treated with a biological weapon, and spreading panic and fear with the rest of the population.

Generally accepted division of CDC is classification into three groups, so called A, B and C group. Biological weapons from A category, easily spread and have a high mortality rate. B category of chemical weapon includes agents for which is characteristic low mortality,

but they are also difficult to detect. In class C weapons, we include flu, which because of its high contagion and fast spreading, appears in a case of epidemic or pandemic.

In the case of misuse of biological agents that can lead to epidemic or sickness of infectious diseases of a large number of people, measures to prevent spread infectious diseases, measures of containing and preventing the outbreak of the diseases are taken. It is concluded that bioterrorism is a phenomena of modern age, which because of it cruelness represents a potent factor in destabilization of a nation. For this paper, it was studied literature, legal acts related to this problem, and examples of the onset of illnesses, which can lead to certain conclusions.

***Keywords**: bioterrorism, biological weapons, classification, risks, (chemical) agent*

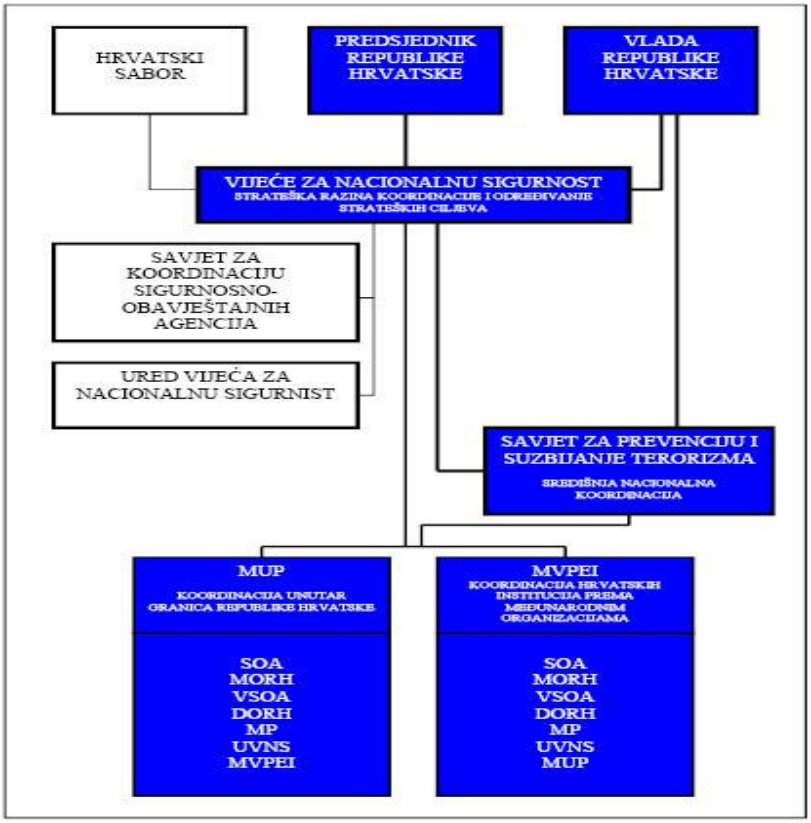
1. UVOD

Moderan bioteroristički čin proizašao iz povijesnog konteksta prerastao je u posebnu „priču“ s ulogom sijanja straha, bolesti i štete. U ratne svrhe biološko oružje može se primijeniti otvoreno ili prikrivenim putem u obliku disperzivnih sustava, raspršivanjem, raketnim zrnima, avio-bombama, disperzijom ili ubacivanjem među ljude, životinje, objekte, hranu i vodu. Najpoznatiji virusi koji se mogu upotrijebiti kao biološko oružje u masovnoj depopulaciji budućnosti biti će, po američkim znanstvenicima, virus (ptičje) gripe (H5)N1, zatim HPV i dr.

Rizici terorističke upotrebe biološkog oružja su rijetko predvidivi, procjenjuju se kao i rizici globalnih nesreća s nesagledivim posljedicama i teškim i dugim oporavkom u fizičkom, psihološkom, političkom i ekonomskom smislu. Zbog sprečavanja i nepredvidivosti širenja zaraze, pravovremenog identificiranja patogena, izrađena je Nacionalna strategija zemlje, ugrađene su mjere prevencije i djelovanja hitnog postupanja na terenu. Zbog osiguranja brzog prepoznavanja biološkog oružja i potrebnih sanitarnih mjera, važno je podizati suradnju između institucija javnog zdravstva, organizacija prve pomoći kao i svih zdravstvenih ustanova, temeljem propisa određenih nacionalnim zakonodavstvom.

2. UPRAVLJANJE DRŽAVNIM SUSTAVOM ZA PREVENCIJU I SUZBIJANJE TERORIZMA

Da bi se sigurno upravljalo državnim sustavom, potrebno je postaviti sustav iz razloga što predstavlja ugrožavanje nacionalne sigurnosti. U svrhu sprječavanja terorizma i ugrožavanja nacionalne sigurnosti ustrojen je hijerarhijski sistem koji se može prikazati shemom na slici 1.



Slika 1. Shema sudionika sustava za prevenciju [1]

U Republici Hrvatskoj na snazi je Zakon o sigurnosno obavještajnom sustavu RH (NN 79/2006) kojim je određeno da je Vijeće za Nacionalnu strategiju najviše tijelo izvršne vlasti zemlje kad je sigurnost u pitanju. Vijeće nacionalne sigurnosti omogućava predsjedniku i vladi RH provođenje nadležnosti koje imaju u izvanrednim situacijama temeljem Ustava. Upravljanje shematski prikazanim sustavom detaljno je obrađeno u dokumentu Akcijski plan za prevenciju i suzbijanje terorizma (NN br. 136/2012). Za određivanje smjernica u protuterorističkom napadu zadužen je Savjet za koordinaciju i Ured vijeća za Nacionalnu strategiju. Važnu ulogu u takvim okolnostima obavlja Ministarstvo unutrašnjih poslova RH koje surađuje s drugim operativnim tijelima i suradnim institucijama kao što su Ministarstvo obrane, Ministarstvo vanjskih poslova i drugim domaćim i međunarodnim institucijama. Državna uprava za zaštitu i spašavanje ima ulogu organizirati terenske operativne snage koje će djelovati na sprječavanje širenja terorizma i sanaciju ugroženog stanovništva, životinja i osiguranja objekata. Ostala državna tijela, zavodi, instituti i agencije, djeluju svaki po svojoj nadležnosti, dinamikom i po sadržaju koje je odredio Akcijski plan i nadležni Savjet i/ili Ured vijeća za Nacionalnu strategiju.

3. POJAM BIOLOŠKOG ORUŽJA I BIOLOŠKOG RATA

Biološko oružje je korišteno s ciljem namjernog izazivanja masovnih infektivnih bolesti ljudi, životinja i korisnog bilja u epidemijskim razmjerima i slabljenja ratnih potencijala protivnika. Međunarodne konvencije koriste dvojne nazive kao “bakteriološko (biološko) oružje” i “bakteriološki (biološki) rat”. Biološki i toksični agensi uključuju sve patogene mikroorganizme kao što su virusi, rikecije, bakterije, gljivice i protozoe, prirodne,

izmijenjene ili sintetizirane (genetičkim inženjerstvom ili drugim biotehnološkim postupcima) i njihove toksine ako su namijenjeni za nemiroljubive svrhe.

Prema definiciji NATO-a biološki i toksični ratni agensi su mikroorganizmi i toksini koji uzrokuju bolest ljudi, životinja i biljaka ili koji uzrokuju razgradnju tvari. Prema Konvenciji o zabrani bakteriološkog (biološkog) i toksičnog oružja iz 1972. godine, biološko i toksično oružje su mikrobiološke i druge tvari koje sadržavaju biološke agense ili toksine bez obzira na njihovo podrijetlo ili metodu proizvodnje, vrstu i količine koje nemaju pravno opravdanje za profilaktičke, zaštitne i druge miroljubive svrhe. Pojam biološko oružje je bolji, ali preširok jer osim mikroorganizama obuhvaća i višestanične organizme. Zato bi najbolji naziv bio mikrobiološko oružje koji se međutim ipak ne koristi.

Kad su patogeni mikroorganizmi proizvedeni u određenim laboratorijima i određenim metodama (selekcije, izmjene i stabilizacije sojeva uzročnika), u određenim količinama i s određenom namjenom [izazivanje epidemija (ljudi), epizootija (životinje), epifitocija (biljke)], označavaju se kao biološki ratni agensi.

Kad su uključeni u sisteme za njihovu primjenu i prenošenje u borbeno stanje, postaju biološka i toksična oružja. Brojne zarazne bolesti i intoksikacije uzrokuju tzv. dvostruko prijeteći agensi (DPA). Ovaj termin se danas često koristi u literaturi i podrazumijeva viruse, bakterije, rikecije, gljivice i protozoe kao i toksine koji nisu samo prirodno opasni za živi organizam već mogu biti namjerno korišteni kao biološko ili toksično oružje uzrokujući bolest i smrt ljudi, životinja i biljaka.

Biološki rat i bioterorizam se zato definira kao namjerno korištenje biološkog oružja tj. bakterija virusa ili toksina izoliranih u namjeri da ubiju ili izazovu bolest kod ljudi, životinja i biljaka [2].

Korištenje štetnih agensa od strane pojedinaca ili grupe, uvijek je motivirano političkim, religijskim, ekološkim i drugim ideološkim razlozima.

U odnosu na kemijske i nuklearne agense, biološko oružje ima visok stupanj djelovanja, slabo uočavanje i lako distribuiranje. Biološki materijal kao što su bakterije i virusi generiraju razne zarazne bolesti. Jedna od opće prihvatljivih podjela biološkog oružja je podjela američkog Centra za kontrolu zaraznih bolesti.

Klasificira ga u tri osnovne kategorije: A, B i C.

3.1. Oružja A kategorije

Bedrenica (antraks)

Najčešći uzročnik je Bacillus anthracis, čiji primarni izvor infekcije su, točnije izlučevine životinja, sirovine životinjskog podrijetla, hrana, voda zagađena sporama Bacillus anthracis te tlo. Bacillus anthracis ulazi u organizam preko povrijeđene kože , kroz dišni takt ili kroz probavni takt. Plućni antraks, koji je puno opasniji od kožnog, nosi simptome prehlade i često završi smrću. Crijevni oblik antraksa nastaje konzumacijom zaražene hrane. Spore bakterije su izuzetno otporne i ostaju u tlu infektivne petnaestak i više godina, a u laboratorijskim uvjetima i pedesetak godina. Zadnji javnosti poznat primjer je korištenje antraksa koji je 2001. godine usmrtilo pet osoba u Sjedinjenim Američkim Državama, a 17 njih je bilo zaraženo.

Prema informacijama Ureda za tehnološke procjene američkog Kongresa, kada bi nad Washingtonom bilo izbačeno stotinu kilograma spora bedrenice, umrlo bi od 13.000 do 3.000.000 ljudi. Najnoviji slučajevi oboljenja ove bolesti kod Amerikanaca i napisi medija oko moguće veze pojave bolesti s terorizmom uzrokovale su neviđenu paniku u SAD-u [2].

Godine 2001. u Hrvatskoj, u vrličkom naselju Podsoju, zaseoku Grabićima, od antraksa je uginulo sedam ovaca. Leševi životinja su spaljeni, a slučajevi zaraze kod ljudi nisu zabilježeni. Uzrok zaraze je, prema Veterinarskoj stanici Split, kontakt životinja sa sporama antraksa koje su preživjele u tlu nakon nepravilnog tretiranja leševa životinja uginulih od ove bolesti početkom osamdesetih godina. U Hrvatskoj, posebno u Posavini. postoje mnoga mjesta gdje su se prije zakopavale uginule životinje, tzv. mrcilišta, a koje su prije 80 ili 100 godina uginule od antraksa.

U Hrvatskoj je na snazi Pravilnik o mjerama za suzbijanje i iskorjenjivanje bedrenice kod životinja, po kojem se vrlo rigorozno preventivno čini sve da se bedrenica kao stočna bolest ne pojavi. Primjerice, područje bedrenice podrazumijeva geografsko područje u kojem je u posljednjih 20 godina ustanovljen barem jedan pozitivni slučaj kod životinja. Preventivno se goveda i ovce u ovakvim područjima cijepe svake godine do 30. travnja i ova bolest tretirana je kao zarazna bolest životinja koja se sprečava, otkriva i suzbija po zakonu. Nespecifična profilaksa podrazumijeva suzbijanje odnosno sprječavanje širenja antraksa neškodljivim uklanjanjem leševa. Također, suzbijanje je izbjegavanje nabave hrane koja potječe iz bedreničnih područja kao i izbjegavanje ispaše životinja u tim područjima. Specifična profilaksa ili imunoprofilaksa podrazumijeva primjenu cjepiva protiv antraksa.

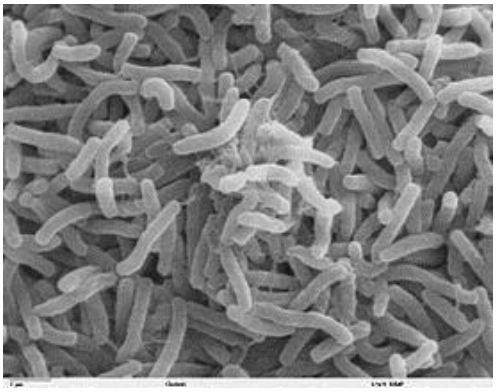
Kuga (crna smrt)

Kuga, kao pandemija harala je cijelim srednjim vijekom. Uzročnik je bacil Yersinia pestis. Nazivala se još i bubonska što potječe od riječi bubon, a odnosi se na njezin najpoznatiji simptom – otečene limfne žlijezde pod pazuhom. Postoje dva oblika iste bolesti: plućna kuga i kužna sepsa. Ako se ne liječi, dvije trećine pacijenata umre u roku 2 - 6 dana od izbijanja simptoma. U 14. stoljeću je izazvala smrt 30 – 60 % stanovnika Europe.

Prvenstveno je bolest divljih glodavaca. Koliko je velik strah od kuge pokazuje činjenica da je cijeli grad stavljen u karantenu kada je Kini 2014. obolio jedan stanovnik zarazivši se. Od 19. stoljeća nema je nigdje osim u Indiji i dijelovima Afrike.

Kolera

Uzročnik je *Vibrio cholerae*, bakterijski štapić, prikazan na slici 2. Čovjek oboli kada je u kontaktu s pitkom i morskom vodom koje su zagađene izlučevinama oboljelih ljudi i životinja ili konzumirajući ribu i druge organizme iz zagađene morske vode. Očituje se visokom temperaturom i proljevima. Zadnji slučaj kolore u Hrvatskoj bio je 1913. godine. U svijetu, najviše oboljelih od kolere bilo je nakon potresa na Haitiju, 2010. godine [3].



Slika 2. Bakterijski štapić *Vibrio cholerae* [4]

Tularemija

Tularemija je akutna, febrilna, granulomatozna zoonoza, primarno bolest glodavaca, koju prenosi bakterija Francisela tularensis. Na čovjeka se prenosi izravnim kontaktom s bolesnom životinjom, posebno divljeg zeca, ugrizom životinje ili insekta, naročito krpelja, konzumacijom zaraženog mesa, vodom ili inhalacijom aerosola s inficirane životinje odnosno prašine. Način prijenosa određuje razvoj kliničkih manifestacija ove zoonoze. Nekada se nazivala vojničkom bolesti. Jedan od simptoma prikazan je na slici 3.



Slika 3. Tularemija, tzv. zečja groznica [5]

3.2. Oružja B kategorije

Q groznica

Q-groznica je uzrokovana bakterijom rikecije, *Coxiella burnetii*. Najčešći prijenosnici bolesti su goveda, ovce i koze. Ostali prirodni prijenosnici bolesti su psi, mačke i ptice. Zaražene životinje ne razviju bolest, ali čuvaju veliki broj organizama u tjelesnim tekućinama i posebno velikom broju u koštanoj srži. Ljudi se zaraze udisanjem kontaminiranog aerosola. Q-groznica u febrilnim stanjima s atipičnom pneumonijom može nalikovati na mikoplazme i legionarsku bolest, upale pluća, psitakozu i hantavirusne infekcije. Više progresivnih slučajeva može sličiti tularemiji ili kugi. Uzročnik je otporan na toplinu i smrzavanje i vrlo je zarazan putem aerosola. Razdoblje inkubacije je 2 - 14 dana, varira ovisno o broju udahnutih organizma. Bolest se prezentira kao ograničenje akutne febrilne bolesti s glavoboljom, umor i mijalgija. Upala pluća, očituje se abnormalnom temperaturom, x-zrake prepoznaju bolest u 50 % bolesnika, a akutni hepatitis razvija u 33 % bolesnika. Kultura bolesti je negativna kao u endokarditisu, hepatitisu, aseptički meningitisu, encefalitisu i osteomijelitisu, ali to su rijetke komplikacije Q groznice.

Escherihia coli

Bakterija *Escherichia coli* stanovnik je ljudskog probavnog sustava, ali također i jedan od najučestalijih uzročnika infekcija**.** Premda najčešće dovodi do infekcija mokraćnog i probavnog sustava, može uzrokovati i upalu žuči, upalu pluća, meningitis kod novorođenčadi, kao i teške oblike sepse. Ovaj mikroorganizam prvi je opisao znanstvenik Theodor Escherich 1885. godine kad ga je izolirao iz stolice novorođenčadi, a kompletni genom je sekvencioniran 1997. godine. Mikrobiološki se radi o gram-negativnoj štapićastoj

bakteriji koja može biti odvojena ili u paru, a kretanje joj omogućuje specifična rotacija trepetiljki.

Ljudski probavni trakt se ovom bakterijom uglavnom kolonizira unutar 40 sati po rođenju vezanjem za sloj sluzi koja oblaže sluznicu crijeva. Unatoč činjenici da se radi o glavnom fakultativno anaerobnom mikroorganizmu u probavnom sustavu, na *E. coli* otpada tek malen dio ukupne bakterijske mikroflore. Ipak, zbog redovite prisutnosti *E. coli* u ljudskim crijevima i stolici, ovaj uzročnik nam često služi kao indikator fekalne kontaminacije, tj. zagađenja hrane i vode [3].

Uslijed specifičnih promjena u genetskom materijalu određeni sojevi *E. coli* mogu postati patogeni te dovesti do vrlo raznolikih bolesti pomoću tzv. čimbenika virulencije s učincima na stanične procese. Najčešće sijelo infekcija bakterijom *E. coli* jest mokraćni sustav. Smatra se da više od 90 % svih nekompliciranih urinarnih infekcija uzrokuje upravo ovaj uzročnik, a u 44 % oboljelih se unutar 12 mjeseci infekcija ponovi.

Do infekcije dovode tzv. uropatogeni sojevi *E. coli* koji imaju sposobnost vezanja za stanice mokraćnog trakta, pokazuju otpornost na imunološku reakciju domaćina, a imaju i druge čimbenike virulencije. Infekcijama donjeg mokraćnog sustava su sklonije žene jer imaju kratku mokraćnu cijev koja se nalazi u blizini završnog dijela debelog crijeva. Infekcije mokraćnog trakta kreću se u rasponu od asimptomatske bakterije koja je karakterizirana prisutnošću bakterija u mokraći bez simptoma, cistitisa gdje je infekcija ograničena na mokraćni mjehur, pa sve do pijelonefirtisa gdje je zahvaćen bubreg. Glavni simptomi i znakovi infekcije su povišena tjelesna temperatura te povišen broj leukocita u krvnoj slici [3]. Cistitis uobičajeno prolazi bez posljedica, dok pijelonefritis može ostaviti trajne posljedice, pa čak i rezultirati smrtnim ishodom. Kompliciranе kliničke slike češće se viđaju u starijih pacijenata sa strukturalnim abnormalnostima mokraćnog sustava ili u kateteriziranih pacijenata.

3.3. Oružja kategorije C

Gripa

Virusi influence jedinstveni su po tome što mogu prouzročiti globalne pandemije i akutne dišne bolesti u svim dobnim skupinama. Takvo širenje virusa influence posljedica je održavanja virusa influence A među životinjama (najčešće ptice, svinje) i povremenoga prenošenja na ljude te česte i nepredvidive antigenske izmjene. Virus influence tipa A uključuje virus ljudske, konjske i svinjske influence te virus kuge u peradi. Tip B inficira samo ljude, a tip C može inficirati i životinje (svinje) [6]. Još je Hipokrat u 5 st. prije Krista opisao gripu riječju „influenca“ - koja potječe iz srednjevjekovne Italije. Ptice se smatraju rezervoarom novih humanih i životinjskih tipova. Kod izbijanja pandemije ljudski soj virusa rekombinira se sa životinjskim sojem. Influenca se uglavnom javlja u obliku pandemija, a prvi je virus influence izoliran 1933. godine. Posebno su osjetljiva djeca i ljudi starije životne dobi. Poznato je da su u vrijeme epidemije najvažniji prijenosnici prvo djeca školske dobi, a u kasnijoj fazi i odrasli. Virus se najbolje održava zimi zbog vlažnosti i niskih temperatura, može preživjeti na glatkim predmetima 24 sata. Prenosi se govorom, kašljanjem, kihanjem (aerosol). Pandemije nastale nakon antigenskih promjena u influenci obično počinju u jednom području i onda se opisanim načinu šire po cijelom svijetu. Inkubacija influence traje od 18 sati do 3 dana, bolest započinje naglo, tresavicom, bolovima u zglobovima i mišićima, dok djeca mogu imati febrilne konvulzije, upalu srednjeg uha. Prisutan je često i produktivan kašalj s bolom u prsima, u ždrijelu zaraženih osoba nalazi se povećan broj bakterija (najčešće stafilokok). U fazi detekcije virusa poznato je da se brzo otkrivanje virusa tipa A i B izvodi

raznim metodama, a najbrža je imunoenzimski postupak. Za liječenje influence tipa A i B propisuju se razni lijekovi za ublažavanje simptoma. Nažalost, danas je poznato i to, da neke vrste influence mogu razviti rezistenciju na lijekove, stoga se preporučuje cijepljenje, pogotovo starijih osoba. Virus influence pogodno je biološko oružje budućnosti kao dodatak klasičnom obliku ratovanja [3].

4. MJERE ZAŠTITE I JAVNO ZDRAVSTVENA PREVENTIVA U RH

Imajući u vidu da su bioterorizam i upotreba biološkog oružja globalna opasnost, međunarodne organizacije poput Crvenog križa, Svjetske zdravstvene organizacije, liječnička i farmaceutska društva i stručnjaci apeliraju da je neophodno da svaka država svojim zakonodavstvom uspostavi kontrolu nad radom mikrobioloških i genetičkih laboratorija dajući posebnu važnost transparentnosti i dostupnosti javnosti kako bi se spriječile eventualne zloupotrebe. Važno je uspostavljanje pravne regulative za sankcioniranje zloupotrebe bioloških agensa kao oružja i međudržavne suradnje po nadležnostima.

Osnovu za izradu zakonske regulative predstavlja Konvencija o zabrani biološkog oružja iz 1975. godine. Ona sadrži obavezu ugradnje međunarodnih standarda u nacionalno kazneno pravo. Republika Hrvatska poduzima sve mjere sigurnosti da bi ostala zemlja sa visokim stupnjem zdravstvene, ekonomske i vojne sigurnosti.

4.1. Javno zdravstvena prevencija u RH

U slučaju zlouporabe biološkog agensa ili elementarnih nesreća poplava, potresa, požara i drugih događaja koji mogu dovesti do epidemije ili do oboljenja od zaraznih bolesti velikog broja osoba, određuju se mjere sprječavanja i suzbijanja zaraznih bolesti. To uključuje mobilizaciju zdravstvenih radnika i drugih osoba, rekviziciju opreme, lijekova, medicinskih proizvoda, prijevoznih sredstava, privremenu upotrebu poslovnih i drugih prostorija za pružanje zdravstvene zaštite, izolaciju i liječenje. Definiraju se posebni zadaci pravnim osobama koje obavljaju zdravstvenu djelatnost i privatnim zdravstvenim radnicima.

U prekograničnom prometu, radi zaštite pučanstva od mogućnosti unošenja zaraznih bolesti, obveza je provesti inspekcijski nadzor nad građanima, njihovim stvarima i sredstvima. Preporučuje se karantena kao mjera suzbijanja zarazne bolesti. Ona se sastoji u ograničenju slobode kretanja i provođenju zdravstvenih pregleda za vrijeme trajanja karantene. Osobe za koje je utvrđeno ili za koje postoji sumnja da su oboljele od kuge ili virusnih hemoralgijskih groznica (ebola), stavljaju se u karantenu. U slučaju sumnje na epidemiju, osobe koje dolaze u Republiku Hrvatsku kao npr. tražitelji azila i slično, stavljaju se u karantenu zbog sprječavanja mogućnosti širenja zaraze. Ministar donosi odluku o osnivanju karantene.

Radi zaštite pučanstva Republike Hrvatske od širenja kolere, kuge, virusnih groznica, žute groznice, gripe i drugih zaraznih bolesti, poduzete su određene mjere međunarodnim ugovorima kojih je RH potpisnica i zakonima RH koji su na snazi.

To su sljedeće mjere:

1. provođenje obvezne protuepidemijske dezinfekcije, dezinsekcije i deratizacije,
2. osnivanje karantene,
3. zabrana putovanja i općenito kretanja u zaraženim ili ugroženim područjima,
4. zabrana prometa pojedinih vrsta robe i proizvoda,
5. obvezno sudjelovanje zdravstvenih djelatnika i ustanova u suzbijanju bolesti,

6. zabrana upotrebe pojedinih objekata, opreme i prijevoznih sredstava i druge potrebne mjere.

Obvezna protuepidemijska dezinfekcija obavlja se prilikom pojave kolere, kuge, sarsa i drugih zaraznih bolesti koje su dovele do epidemioloških indikacija.

Tijekom kliconoštva ili nakon ozdravljenja (dezinfekcija u tijeku) odnosno smrti bolesnika ili kliconoše (završna dezinfekcija) potrebno je provesti dezinfekciju koja obuhvaća:

- lučevine i izlučevine bolesnika i kliconoše,
- osobne i druge predmete iz okoline bolesnika i kliconoše,
- stambene i druge prostorije u kojima boravi ili je boravio bolesnik ili kliconoša te uređaje i sustave koji su put prijenosa i mjesto razmnožavanja uzročnika bolesti,
- prijevozna sredstva kojima je prevezen bolesnik ili kliconoša, odnosno osoba umrla od zarazne bolesti.

Nadležni operativci su dužni osigurati obveznu protuepidemijsku deratizaciju prilikom pojave ili opasnosti od pojave kuge, a prema epidemiološkoj indikaciji u slučaju leptospiroze ili drugih zaraznih bolesti čiji izvor mogu biti štetni glodavci. Obvezna protuepidemijska deratizacija obuhvaća:

- stambene objekte, javne prostorije i objekte naseljenih mjesta,
- pristaništa, pomorske, riječne i zračne luke i željezničke stanice te druge objekte javnog prometa,
- sredstva javnog prometa (autobuse, brodove, kamione, zrakoplove, željezničke vagone i druga sredstva za prijevoz hrane, predmeta koji dolaze u neposredan dodir s hranom i predmete opće upotrebe),
- radne prostorije, skladišta i ostale pomoćne prostorije za proizvodnju i promet hrane, predmeta koji dolaze u neposredan dodir s hranom i predmeta opće upotrebe te za upotrebljavanje drugih djelatnosti koje pogoduju stvaranju uvjeta za život i razmnožavanje štetnih glodavaca,
- teren, okoliš ili područje na kojem žive ili imaju uvjete za razvoj štetnih glodavci koji prenose i šire zarazne bolesti.

Cilj prevencije u borbi protiv biološkog oružja je pravodobno prepoznavanje bolesti i provođenje liječenja kojim se sprječavaju razvoj i smrt oboljelih.

Mjera ranog otkrivanja bolesti još uvijek se smatra jednom od najvažnijih mjera koje pruža suvremena medicina. Najvećim uspjehom preventivne medicine drži se iskorjenjivanje (eradikacija) neke bolesti. Najbolji primjer je iskorjenjivanje velikih boginja (*variola vera*) do kojeg je došlo nakon uspješno provedenog cijepljenja. Tijekom provođenja mjera prevencije, vrši se intervencija (lat. *interventio* = miješanje, posredovanje), koja predstavlja pravodobno pitanje u tijek bolesti, ali to je već prva intervencija u fazi kad je bolest raširena.

5. ZAKLJUČAK

U ovom radu iznesene su osnovne značajke, pojmovi, klasifikacija bioterorizma, njegova povijest i potencijalna uloga koju razvojem moderne genske tehnologije može dosegnuti u budućnosti. To je uloga skrivenog i podlog napadača koja predstavlja prijetnju sigurnosti, širi strah i paniku, nemir kod stanovništva nekog područja ili države.

Kroz povijest je zabilježeno da su veliki gubici zbog zaraznih bolesti koje su harale ratištima, premašivale brojke poginulih i ranjenih u bitkama. To nisu bile bolesti koje su se slučajno pojavile u tim okolnostima. Ubačene su s ciljem da izazovu pomor u neprijateljske redove jer u ratu je cilj pobijediti ne birajući sredstva. Zaraziti stoku, uništiti usjeve, posijati glad i bolest, zarazu koja se prenosi na ljude, izazvati epidemiju, učiniti područje ovisnim i bolesnim, nadjačati u svakom smislu, ostao je cilj bioterorizma nekad i danas.

Već su zasigurno proizvedena i otkrivena sofisticirana biološka oružja kojima se može neopaženo i lako probiti sigurnosni sustav neke zemlje, onesposobiti i zaraziti područje, ljude, stoku, izazvati veliku gospodarsku i političku štetu. Spremnost na brz i djelotvoran odgovor kroz prepoznavanje agensa, agilnost sustava za nadzor javnog zdravlja koji podrazumijeva posebnu spremnost i na lokalnoj i državnoj razini, otvaranje karantene i saniranje posljedica napada, mjere su protiv terorističkih aktivnosti.

Brojnost i raznolikost potencijalnih bioloških agensa ukazuje na potrebu da se zdravstvena infrastruktura opremi tako da brzo riješi krizne situacije nastale napadom biološkim oružjem. Sveobuhvatan pristup u borbi protiv bioterorizma i zloupotrebe biološkog oružja podrazumijeva i zakonodavnu suradnju koja se odnosi na usklađivanje nacionalnog zakonodavstva s međunarodnim aktima. Ipak, najbolja zaštita stanovništva od ovakve vrste napada podrazumijeva preventivu i pravovremeno prepoznavanje ove vrste opasnosti.

U žrtve ubrajamo oboljele i umrle kao i one snage koje su prevenirajući, sanirajući i pružajući pomoć živjele uz teror.

Dosadašnji brojčani pokazatelji o stradalima od bioterorizma šokantni su. Posljedice bioterorizma za cjelokupno čovječanstvo, biljni i životinjski svijet dalekosežne su, vrijedne respekta i održavanja visoke razine preventivnih mjera i zaštite.

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1st INTERNATIONAL CONFERENCE
„The Holistic Approach to Environment"
Croatia, Sisak, September 13th-14th, 2018

POSSIBILITIES FOR IMPLEMENTATION OF CIRCULAR ECONOMY FOR LITHIUM-ION BATTERIES IN SERBIA

Miodrag Zivancev*, Dejan Ubavin*, Tijana Marinkovic*, Veselin Bezanovic*, Dusan Milovanovic*

* University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia

corresponding author: Miodrag Zivancev, e-mail: miodragzivancev@uns.ac.rs

Review paper

ABSTRACT

Lithium-ion batteries are extremely valuable in society today due to the exceptional performances that they provide. With the increased usage of this type of batteries, due to the development of the electric car industry, grows the concern for disposing of waste batteries. Used batteries consist of various metals, among which are some rare metals, such as lithium. The aim of this paper is to apply the strategy of circular economy to lithium-ion batteries and thus eliminate waste by recycling materials within the system, and to reserve natural resources of lithium. The consequence of the applied circular economy could be resource and energy efficiency, but also profitability. This paper will present the development of waste lithium-ion batteries collection system, recycling and production of new batteries as a proposed circular economy model for Serbia.

***Keywords**: circular economy, lithium, batteries, recycling*

1. INTRODUCTION

Lithium-ion batteries (LIBs) have excellent properties such as high battery voltage, long charging-discharging cycles, high energy and power densities, long lifespan and large operating temperature range, so in comparison with other rechargeable batteries they have mentioned advantages [1]. Due to these facts, LIBs have been widely used in energy storage including portable instruments, hybrid electric vehicles (HEVs) and electric vehicles (EVs) since the 1990s. Lifetime of LIBs is in the range of 3 to 5 years (about 1000 charging-discharging cycles), whether they are used or not. This means that these batteries will eventually end up as waste. Typical LIBs are consisted of 5 - 20 % Co, 5 - 10 % Ni, 5 - 7 % Li, 5 - 10 % other metals (Cu, Al, Fe, etc.), 15 % organic chemicals and 7 % plastic, which leads to the value of about 7,000 US dollars for 1 t LIBs spent. With the growth of energy demand for HEVs and EVs the batteries consumption greatly increases and the need for

lithium as a raw material for LIBs enlarges [2, 3]. Today LIBs represent about 37 % of the rechargeable battery world market and their use is constantly expanding at a very fast rate. Market for large LIBs will continue to grow for powering HEVs and EVs and the demand for small rechargeable cells for sectors such as computers, video cameras will continue to grow constantly [2]. From 2011 to 2014 global lithium-ion battery consumption increased by an average of 27 % per year. The result of this increase will be a growth of waste batteries, which must be recycled.

Waste batteries are important secondary source of metals, which can be in very high concentration, in some cases even higher than those found in the ores can. Also recycling of batteries is critical from environmental point of view [4]. Taking into consideration the expected overall world market evolution of the LIBs products and the average life of secondary LIBs, we can conclude how the correct disposal of waste LIBs may become a problem. Based on this, engineers, environmentalist and researches are interested in the recovery of all the valuables contained in the form of pure compounds that can be used for production of new LIBs. This would affect the sustainable management of natural resources, environment and per capita energy consumption, but also lead to the achieving of quantitative recycling of these materials and close the loop for a circular economy [5].

The concept of circular economy represents a system that builds long-term resilience, generates economic and business opportunities and provides environmental and social benefits. Linear economy is recognized as unsustainable, therefore circular economy is developed as an alternative approach, which values raw materials differently [6]. The general aim of the circular economy is to utilize the maximum value of resources and keep the minimum use for as long as possible. In a circular economy, materials and products are designed with waste prevention in mind, and they are re-used, recycled or recovered. Policy and market conditions should be adapted across all sectors, in order for effective functionality of the circular economy. Increasing resource efficiency, reducing cost and environmental effects are goals that demand changing of governments and businesses views.

Multiple research efforts and the identification of best practice examples have shown that a transition towards the circular economy can bring benefits of a more innovative, resilient and productive economy that would last for longer periods.

Model of circular economy is based on three principles: design out waste and pollution, keep products and materials in use and regenerate natural systems. Technical cycles are based on recovering and restoring products, components, and materials through strategies like reuse, repair, remanufacture or recycling [7].

The aim of this paper is to apply the strategy of this model to LIBs and thus eliminate waste by recycling materials within the system and achieve resource and energy efficiency as well as profitability. This will be represented through the developed system of collecting waste LIBs, recycling and production of the new ones.

2. MARKET OF LITHIUM ION BATTERIES

Global consumption of LIBs between the years 2000 and 2004 stood at around 500 – 700 million cells, while the number of mobile telephone users exceeded 7,74 billion in 2017, according to the International Telecommunications Union (ITU) [8]. LIBs pose a very specific threat, because they contain a high percentage of dangerous heavy metals. From the 4000 t of used lithium-ion batteries collected in 2005, 1100 t of heavy metals and more than 200 t of toxic electrolytes were generated [9]. Some of the components of these batteries are difficult to break down and discarding them after their end-of-life into municipal waste

landfill sites may pollute the soil and underground water, while their incineration contaminates the air by releasing toxic gases [10]. Environmental pollution caused by irresponsible disposal of LIBs and conservation of natural resources are main drivers for development of necessary technologies to recover and recycle LIBs [11].

Forecast for lithium consumption, estimates that the battery industry will demand more lithium each year and until the year 2024, this industry will demand the amount of lithium that is currently sufficient for all purposes. Therefore, it is necessary to develop a simple process with mild recycling conditions for the sustainable recovery of valuable metals from spent LIBs.

Considering the current global lithium production with respect to projected demand, environment and regulation, green energy and energy security, cradle-to-cradle technology management and circular economy of critical metal and minimization of waste crime and maximization of the urban mining, recovery and recycling status of lithium should be well understood.

Taking into account the expected overall world market evolution of the LIB products and average life of the secondary LIBs (Maximum life cycle of $LiCoO_2$ cathode material is 1000 cycles [12], we can reasonably conclude that correct disposal of spent LIBs is necessary, if we want to avoid serious environmental problem, and if we want to recover valuable materials. The future supply crisis can only be prevented through 100 % LIB recycling with minimum 90 % lithium recovery [13].

In Serbia there are no data about used LIBs, there are data about overall usage of batteries. According to the Serbian environmental protection agency, the quantity of portable batteries and accumulators placed on the market of the Republic of Serbia is around 575.1 t annual, and for industrial batteries and accumulators is 3434.5 tons. According to the available data, the total quantity put on the market of Republic of Serbia is 13041,4 t/year [14].

According to the reports of operators of the waste re-use facility, 9407 t of this kind of waste was processed in 2016. On the basis of the annual report on cross-border movement of waste, 5249 tons of this type of waste were exported, and 163 tons were imported in the same period [14]. Mentioned data are presented in table 1.

Table 1. The amount of batteries and batteries placed on the market of the Republic of Serbia in period of 2010 – 2015 [14]

Year	Starters	Portable batteries or accumulators (t)	Industrial batteries and accumulators (t)	Total (t)
2010	9415.53	554.99	2202.70	12173.22
2011	9478.03	537.85	4016.52	14032.40
2012	8474.55	512.96	3685.41	12672.92
2013	10398.08	584.77	3825.77	14808.62
2014	8994.85	587.79	3001.18	12583.81
2015	9761.43	581.99	2609.22	12952.64

To establish a waste management system for waste batteries and accumulators the following collection rates are determined:

1) by 31 December 2012 - at least 25 % of the collection rate of batteries and accumulators;

2) by 31 December 2016 - at least 45 % of the rate of accumulation of batteries and accumulators.

$$Collection\ rate\ (SS3) = 3 * S3 / (P1 + P2 + P3)$$

- Sales in Year (P1)
- Sales in Year 2 (P2)
- Sales in Year 3 (P3)
- Collected in Year 3 (S3)

3. COLLECTING OF LITHIUM-ION BATTERIES

The battery types used in the laptops and cellphones are valuable in metal value and thus desired raw material for the recycling operators. Furthermore, consumers are expecting to get benefits when giving away their old gadgets, otherwise they will easily remain in drawers just in case one will use it later on. Thus, consumers must be motivated in order to dispose, in an adequate way, of their gadgets with LIBs and small chargeable LIBs.

Most legislation and policies currently refer to the principle of "Extended Producer Responsibility", which emerged in academic circles in the early 1990s. It is generally seen as a policy principle that requires manufacturers to accept responsibility for all stages in a product's life cycle, including end-of-life management. In addition, "Extended Producer Responsibility" requires producers to organize and/or finance the collection, treatment, and recycling of their products at end-of-life.

In the collection phase, there are two key success factors of waste portable battery collection: to provide nationwide sufficient conveniently-situated waste battery collection points and to shape end-user behavior through consistent awareness measures to dispose of waste batteries correctly.

Retailers have a big influence in the collection phase. The effectiveness of the retailers' take-back obligation is driven by additional parameters such as whether or not organizations provide retailers with collection containers (an important element of awareness creation); whether or not retailers can return batteries to municipal collection points; and the clarity of the retailers' obligation to provide information about the presence of collection points.

In order to ensure the best recovery system possible, the following measures have been planned:

- manufacturers and importers of LIBs are obligated to pay a tax, which could contribute to the creation of a fund for financing the collection of used LIBs, their transport to special warehouses or recycling plants and informing buyers of the consequences of uncontrolled waste disposal and economic benefits of an organized policy of used batteries disposal,
- there should be more collection points and waste LIBs can be returned to retailers that have obligation to accept the used LIBs. Otherwise, these batteries can be brought to municipal collection points (intended for LIB disposal) or to recycling plants,
- in order for the end-users to be motivated and to actively participate in LIB-collection, retailers who sell LIBs for mobile phones, PCs and video cameras should provide consumers who are buying new LIBs with certain discounts.

Another way to motivate buyers is to put special containers/bins in supermarkets, where every day buyers can bring small chargeable LIBs that will be disposed of in an adequate way. The idea is to put an ad with information about negative effects of LIBs and importance of proper management at the entrance of the supermarkets, and so motivate consumers to bring used LIBs.

4. TECHNOLOGIES FOR THE RECYCLING AND RECOVERY OF WASTE LIBs

As it was mentioned before, lithium-ion batteries contain heavy metals, organic-chemical products, and plastics, 5 – 20 % of cobalt, 5 – 10 % of nickel, 5 - 7 % of lithium, 15 % of organic chemical products and 7 % of plastics. This composition may vary slightly depending on the manufacturer. When the waste generated by spent LIBs is properly processed, the heavy metals such as cobalt or lithium can be recovered. The recovery of these metals is also very important and desirable for the conservation and the environment protection [1]. Recycling of electric vehicle batteries could provide 50 % of the lithium requirement for new batteries by 2040 [3].

Existing methods for recycling and regeneration of LIBs are principally consisted of physical and chemical processes.

The physical processes include mechanical separation, thermal treatment, mechanic-chemical processes and dissolution processes. The chemical processes include acid leaching, bioleaching, solvent extraction, chemical precipitation and electrochemical processes.

It should be decided which process is the best and applicable in Smederevo or Bor smelter. Installation of new technology in smelter will enable achieving of rare metals recovery by adaptation of existing plant. Recycling and reuse of lithium and cobalt, which are contained in LIBs, is an important part of circular economy that is subject of this paper.

One of appropriate recycling technology is shown on figure 1.

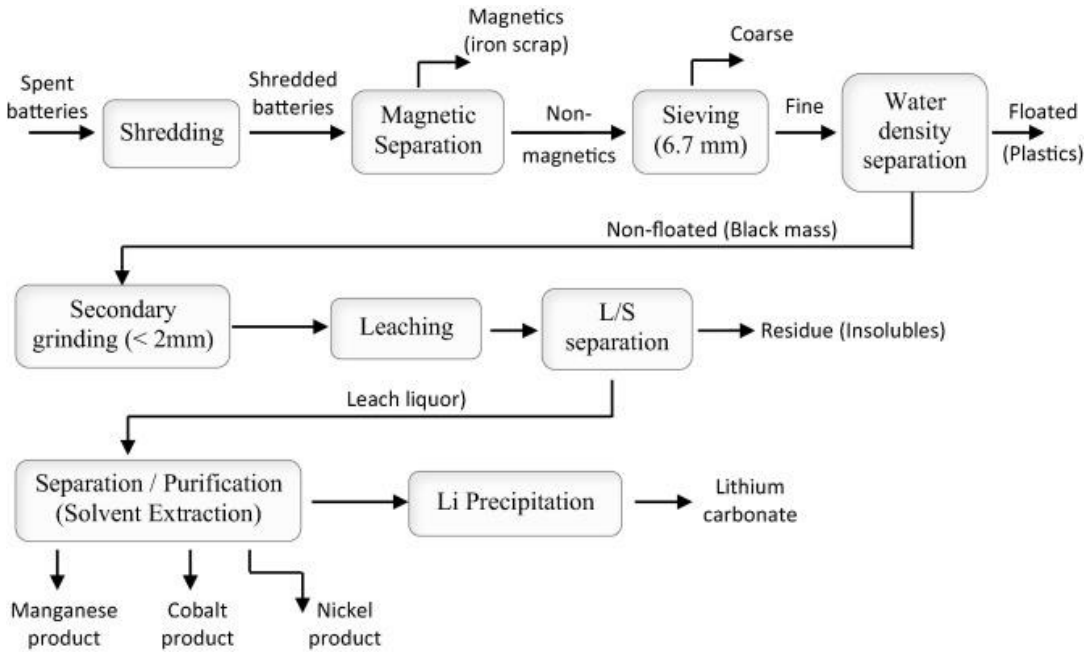


Figure 1. Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite [15]

A hydrometallurgical process has many advantages such as high extraction efficiency, low energy consumption, little hazardous gas emission, and low capital cost [16]. Process has a god potential for industrial realization, so it could be implemented in existing smelter.

5. PRODUCTION OF NEW BATTERIES

Developing of new materials and chemistry for LIBs is necessary in order to achieve better performance. Electrification of the transport demands better batteries with high-energy-density at low price. The main challenges of LIB technology are related to chemistry, material deterioration, lifetime, operating temperatures, energy and power output, and, scaling up, long-term material supply for some, and overall costs [17]. New design of batteries should enable controlled disintegration and separation of critical elements and compounds without compromising the functionality of LIBs.

In Serbia, there are several companies for battery production, "TAB d.o.o.", "Krusik" holding corporation, "Triax power". Production of LIBs is a great opportunity for those companies to become more competitive on the market. Investment in their plants is necessary in order to extend their production program with LIBs for cars and other consumption.

Battery production demands several parts, current collector for cathodes is aluminum foil, copper foil is used as a current collector for anodes, and cell manufacturing. The global market for electrolytes for all applications of LIBs was slightly bigger than 62000 tons in 2015; revenues generated were 900 million US dollars and the compound annual growth rate (CAGR) in 2005 to 2015 amounted to 20 % [18].

There are different types of battery chemistries, which are capable to advance their performance: Lithium metal (Li metal) batteries, Solid State batteries (SSB), Lithium-sulfur (Li-S) batteries, Lithium-air (Li-air) batteries.

Li metal batteries have more than ten times capacity compared to LiC6 anode that is currently in use. SSBs that use solid electrolytes (SEs) (either inorganic or polymer) instead of liquid ones could offer both high energy and high power density. The Li-air battery, which uses oxygen from air, has the highest theoretical specific energy density of any battery technology – 3500 Wh/kg. Estimates of practical energy storage are uncertain, as many factors are unknown, but values in the range 500 to 1000 Wh/kg – sufficient to deliver significantly in excess of a 500 km driving range if deployed in an electric vehicle battery – have been proposed [18]. Li-S batteries based have sulfur-containing cathodes and lithium anodes, have the greatest potential to achieve a high-energy-density system at low cost.

Production of new batteries should be based on new design that provides easy disassembling, and recovery of rare metals, in order to achieve close loop. In addition, new chemistry of battery is necessary for better performances at low cost. Manufacturer requires a sufficient amount of raw material, so if recovered amount is not enough, Serbia also has a geological reserve of lithium in the Jadar Basin of about 227 million tons, so they have security for their investment.

6. CONCLUSION

Lithium-ion batteries show the best performance and in combination with electrification of transportation system demands of lithium rapidly increase. Natural reserves of lithium are limited and attention must be paid to save these reserves but also to satisfy all needs. Therefore, a circular flow for this valuable resource is being considered.

Circular economy requires attention in every step of lithium utilization:

- production of new batteries should provide easy disassembling and material recovery,
- and after use waste LIBs should be adequately collected and sent to recycling process.

All of mentioned steps are an opportunity for new jobs and ideas.

For the sustainable development and conservation of natural resources, it is important to apply a circular economy. Economic gain would not be visible in the near future, but on the other hand, a healthy environment is invaluable. By the application of circular economy, the production of new Li-ion batteries would be a great opportunity to enter into the European market.

Decision makers play a major role for the application of such systems, which in developing countries is more likely to be defined as a linear economy rather than a circular one. The linear economy brings in revenues in a shorter time frame, and most of them choose this model, but maybe they should consider circular model in case of rare metals such as lithium.

Accurate data about lithium usage in Serbia, is one of the first steps for establishing appropriate system for LIBs. Public awareness and determination of decision makers are crucial for further implementation of circular economy of LIBs.

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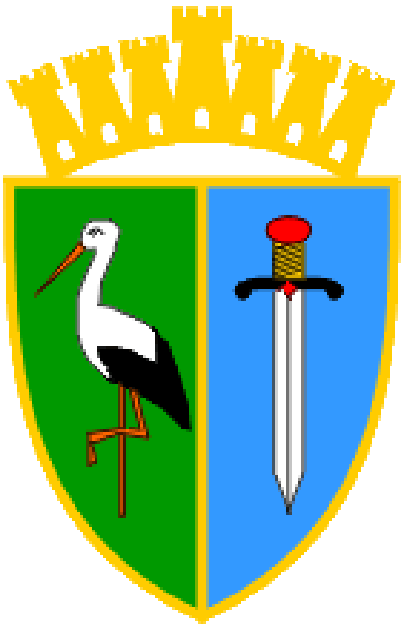
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Acknowledgments

The presented research partly financed by Provincial Secretariat for Higher Education and Scientific Research, Autonomous Province of Vojvodina, within project No. 114-451-2249.

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Kompanija Tehnix vodeća je eko industrija u Republici Hrvatskoj i Europskoj uniji. Razvili smo strojeve, opremu i tehnologije kojima se na najbolji način vrši industrijska reciklaža komunalnog otpada. Primarna reciklaža se potpuno uklapa u sustav industrijske reciklaže kojom se dopremljeni otpad na postrojenje reciklira prema uporabnim vrijednostima te ponovno vraća u industriju. Veliko iskustvo, znanje i razvoj novih tehnologija za zaštitu okoliša omogućili su da na globalnom tržištu ostvarujemo veliki interes za primjenu MBO-Te nove tehnologije kojom se postiže kružno gospodarstvo. o je tehnološka inovacija reciklaže u održivom gospodarenju komunalnim otpadom. Sa našim dostignućem upoznali smo stručnjake iz EU koji novim priopćenjima Europske komisije daju podršku kojom se ostvaruju ciljevi europske politike za kružno gospodarstvo i sa kojima se želi bitno unaprijediti dosadašnji model gospodarenja otpadom u europskim zemljama, podržavajući projekte koji daju najbolje rezultate u postupku reciklaže.

Posebno se napominje da građevine i postrojenja za gospodarenje otpadom trebaju biti u skladu sa zahtjevima najbolje raspoloživih tehnika i tehnologija koje se primjenjuju pri projektiranju, gradnji, održavanju reciklažnih postrojenja. Na razvoju nove tehnologije radili smo više od 15 godina za što smo dobili stotine priznanja i odličja iz cijeloga svijeta. Europska komisija podržava one tehnologije koje daju najbolji stupanj reciklaže, a to je MBO-Te tehnologija industrijske reciklaž otpada razvijena u Tehnix-u.

TEHNOLOŠKE PREDNOSTI IZGRADNJE RECIKLAŽNOG CENTRA ZA OBRADU MIJEŠANOG I PREDSORTIRANOG KOMUNALNOG OTPADA

Na postrojenjima ugrađenim u reciklažni centar vrši se postupak potpune reciklaže. Dopremljeni komunalni otpad se sortira prema uporabnim vrijednostima i potrebi tržišta. MO = mehanička obrada iz koje dobivamo 8 vrsta izdvojenih, baliranih sirovina – plastika, karton, papir, PET, MET, tekstil, staklo, metal.



Sve sirovine su potpuno čiste, baliraju se i plasiraju na globalno tržište za proizvodnju novih proizvoda u industriji. BO = biološka obrada organskog otpada i zelenog otpada. Postupak bioreaktorskog kompostiranja omogućuje ciklus proizvodnje eko komposta u vremenu od samo 2 mjeseca. Kompostiranje se obavlja u potpuno kontroliranim tehnološkim uvjetima bez negativnog utjecaja na okoliš, bez zagađenja vode, zemlje i zraka. Eko kompost se koristi na poljoprivrednim površinama obogaćen mineralima i fosfatom. TO = termička obrada. Ostatak gorivog otpada, koji se zbog veličine materijala i strukture ne može reciklirati, suši se i sredira te automatski balira bez prisutnosti čovjeka. Prosječna energetska vrijednost suhog RDF goriva u balama je 4 MW po toni. Ukupni postotak reciklaže otpada na MBO-Te postrojenju Tehnix je do 100 %. Takvim postupkom postižemo ciljeve održivog razvoja i kružne ekonomije. Gotovo stotine svjetskih i nacionalnih priznanja iz Europe i svijeta potvrđuju prednosti naših tehnoloških dostignuća u recikla ži, a izgrađena postrojenja za reciklažu trajno dobro funkcioniraju. Izgradnja reciklažnih centara traje manje od godinu dana od izdavanja građevinske dozvole. Mala dimenzija projekta omogućuje tehnološku racionalnost i protočnost procesa reciklaže. Na krovištu izgrađenih objekata instaliraju se solarni paneli. Obradom komunalnog otpada postižemo tri sustava opće vrijednosti: Ekonomičnost - sve što ulazi se naplaćuje i sve što izlazi se naplaćuje. Ekologičnost procesa reciklaže omogućuje najveći stupanj reciklaže. Socijalna prednost je u zapošljavanju ljudi na procesu reciklaže, i to one strukture koja na tržištu rada teže dobiva trajni posao. Postrojenja TEHNIX vrlo dobro se prilagođavaju lokalnim uvjetima. Koncipirano je da odgovara malim i srednje velikim sredinama. Može se jednostavno ugraditi u stare hale, te na taj način oplemeniti zapuštene građevine.



U osnovi to je industrijsko postrojenje s malim utroškom energije, koje jamči učinkovito sortiranje uz zapošljavanje lokalnih radnika. Utjecaj na okoliš je izuzetno mali, a radni prostor u hali za ručno sortiranje ventiliran i klimatiziran. U velikim naseljima industrijska TEHNIX postrojenja za sortiranje mogu se realizirati na dvije i više lokacija, čime se smanjuje promet unutar naselja i jamče provedba načela blizine u cjelovitom sustavu gospodarenja otpadom. Mehaničko-biološka reciklaža predsortiranog ili miješanog komunalnog otpada tehnološko je otkriće razvijeno u kompaniji Tehnix. Takva tehnologija je veliki napredak u ekonomičnosti gospodarenja komunalnim otpadom upravo zbog svoje tehnološke fleksibilnosti jer omogućuje one tehnološke inovacije kojima se postiže veliki učinak i niski troškovi u reciklaži dopremljenog komunalnog otpada.

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Quelle: Tehnix

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Agroproteinka je prijatelj i čuvar okoliša i zdravlja ljudi i životinja. Naš okoliš štiti od negativnih utjecaja i čini ga čišćim i zdravijim. Novo vrijeme donosi nove izazove, i nove načine na koje možemo dodatno raditi na očuvanju okoliša, odnosno nove tehnologije u koje Agroproteinka neprestano ulaže. Na nove izazove, Agroproteinka je odgovorila novim bioplinskim postrojenjem koje je završeno s izgradnjom u ožujku 2017. Od tada smo u mogućnosti uz ,životinjske nusproizvode, sakupljati otpad biljnog podrijetla.

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Široka paleta proizvoda koje nudimo, u kombinaciji s našim znanjem i iskustvom stečenim radom u laboratoriju, omogućuje nam da ponudimo najbolje rješenje za sve vaše analize.

Jedno od naših temeljnih načela jest etikom vođeno poslovanje, jer se tako zadovoljavaju ključne vrijednosti: vjerodostojnost, pouzdanost, kompetentnost i čestitost.

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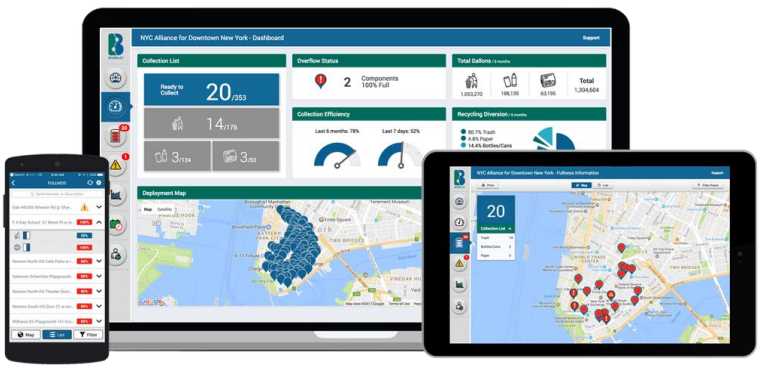
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U Hrvatskoj je najbolji primjer grad Dubrovnik koji je implementacijom Bigbelly rješenja smanjio učestalost pražnjenja kanti za javni otpad za 88%. Smanjili su broj odlazaka na svaku od lokacija gdje su postavili Bigbelly spremnike u godišnjem prosjeku s 35 na 3 puta tjedno. Time su bitno smanjili svoje operativne troškove i povećali stopu prikupljanja reciklabilnog javnog otpada, jer su dodatno postavili Bigbelly spremnike za odvajanje otpada (plastična i metalna ambalaža).

Zahvaljujući posebnom dizajnu Bigbelly spremnika koji čini potpuno zatvoreni sustav, nema vidljivog i razbacanog otpada od strane vjetra i životinja kao niti neugodnih mirisa, a životinje ne mogu ući u spremnike. Samo neki od svijetlih primjera iz svijeta koji koriste Bigbelly rješenje su gradovi New York, Hamburg, Dublin, Stockholm, Pariz te mnogi drugi. Temeljni ciljevi Bigbelly cjelovitog rješenja su povećanje kvalitete života, ušteda novca poreznih obveznika, poboljšanje operativne učinkovitosti i edukacija građana o važnosti održivog gospodarenja otpadom. Saznajte više: bigbellysolar.hr



CLEAN Management je središnji softverski dio Bigbelly rješenja koji omogućava uvid u sve operacije unutar sustava. Nije potrebna IT infrastruktura, jer se softver nalazi u oblaku. Čini ga set alata za uspostavljanje, upravljanje, nadzor i optimizaciju sustava.



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Godinama smo autorizirani distributer najrenomiranijih europskih proizvođača, a uz to surađujemo i s nekoliko specijaliziranih veletrgovaca u Europi.

Na vlastitom skladištu kraj Zagreba kontinuirano držimo više od 3.000 artikala, spremnih za isporuku u Vaš laboratorij unutar 24h.

Naših 20 zaposlenika stoji Vam, sa svojim stručnim znanjem i dugogodišnjim iskustvom, na usluzi savjetom, ljubaznošću, korektnom i brzom uslugom te razumnim cijenama i kvalitetnim proizvodom.

Vrlo rado ćemo Vam pomoći kod:

- Odabira laboratorijskog namještaja,
- Odabira laboratorijskih uređaja i pribora,
- Odabira analitičkih metoda,
- Odabira i traženja specijalnih roba ili proizvođača.

Od ožujka 2005 godine potvrdili smo svoju kvalitetu ISO 9001 certifikatom.

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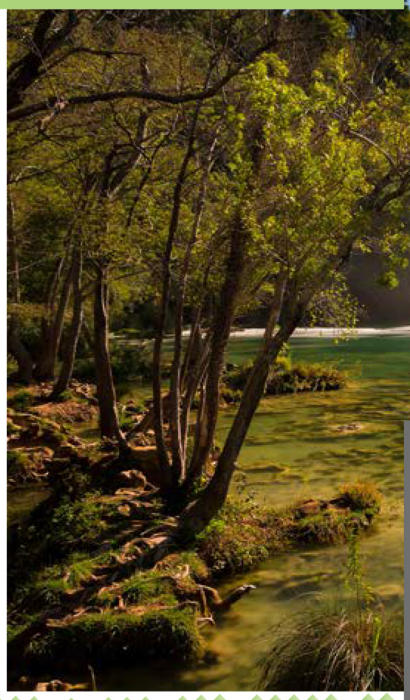
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VITA PROJEKT d.o.o. pruža cjelovitu uslugu u širokoj sferi zaštite okoliša i prirode te krajobrazne arhitekture. Ovlašteni smo od Ministarstva zaštite okoliša i energetike za obavljanje stručnih poslova zaštite okoliša i prirode.



Naša tvrtka zapošljava stručnjake s višegodišnjim iskustvom rada na stručnim poslovima zaštite okoliša, ekološke mreže i krajobrazne arhitekture.
Interdisciplinarnim pristupom i pametnim dizajnom stvaramo i obnavljamo održive ekosustave.
Ocjenjujući prihvatljivost svih vrsta projekata za okoliš, po potrebi ih optimiziramo i time povećavamo njihovu učinkovitost, smanjujemo troškove, ublažavamo okolišne pritiske i pritom štedimo resurse.



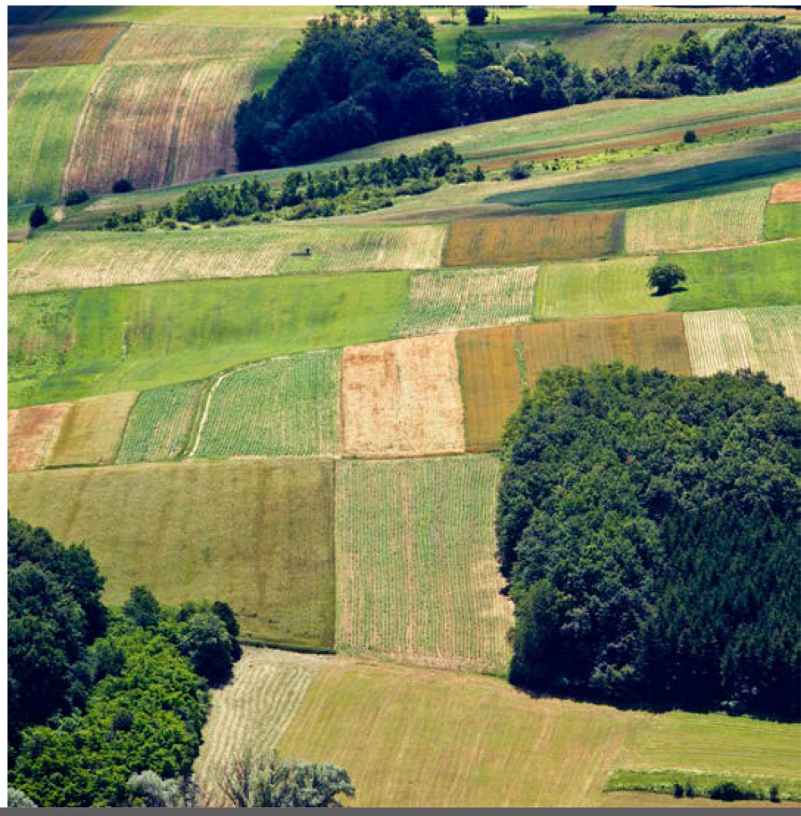
- **STRATEŠKE STUDIJE UTJECAJA STRATEGIJA, PLANOVA ILI PROGRAMA NA OKOLIŠ I EKOLOŠKU MREŽU**
- **ELABORATI ZAŠTITE OKOLIŠA**
- **STUDIJE OCJENE PRIHVATLJIVOSTI ZA EKOLOŠKU MREŽU**
- **STUDIJE RAZVOJA ZELENE INFRASTRUKTURE GRADA**
- **STUDIJE I PROJEKI REVITALIZACIJE DEGRADIRANIH PODRUČJA**
- **BIOLOŠKA, KRAJOBRAZNA I GEOEKOLOŠKA VREDNOVANJA**
- **ANALIZE KLIMATSKIH RIZIKA I PROGRAMA PRILAGODBE KLIMATSKIM PROMJENAMA**
- **PROJEKTI KRAJOBRAZNE ARHITEKTURE – UREĐENJE JAVNIH ZELENIH POVRŠINA**

STRATEŠKE PROCJENE UTJECAJA NA OKOLIŠ
Strateška studija utjecaja na okoliš Strategije razvoja Općine Jelsa 2016.-2020. s glavnom ocjenom prihvatljivosti za ekološku mrežu
Strateška studija utjecaja na okoliš Strategije razvoja Grada Omiša do 2020. s glavnom ocjenom prihvatljivosti za ekološku mrežu
Strateška studija utjecaja na okoliš Županijske razvojne strategije Istarske županije do 2020. godine s glavnom ocjenom prihvatljivosti za ekološku mrežu
...

STUDIJE GLAVNE OCJENE PRIHVATLJIVOSTI ZA EKOLOŠKU MREŽU
Studija glavne ocjene prihvatljivosti zahvata za ekološku mrežu: Održavanje korita potoka Dretulja i Vrnjika
Studija glavne ocjene prihvatljivosti zahvata za ekološku mrežu: Izgradnja nasipa Kupe, obaloutvrde, zaštitnog zida i objekata sustava odvodnje zaobalja unutar trase nasipa, na lijevoj obali Kupe od naselja Selce do Rečice
Studija glavne ocjene prihvatljivosti za ekološku mrežu za zahvat: Vjetroelektrana Mideno brdo
Studija glavne ocjene prihvatljivosti zahvata za ekološku mrežu: Zaštita naselja Gradac i grada Pleternice od velikih voda rijeke Orljave - 2. etapa
Studija glavne ocjene prihvatljivosti zahvata za ekološku mrežu: Održavanje korita rijeke Dretulje
...

KRAJOBRAZNA ARHITEKTURA
Idejno arhitektonsko -urbanističko i krajobrazno rješenje uređenja javnog gradskog parka Z1-14 u Rijeci
Glavni projekt - Obnova i revitalizacija I. i II. Jezera u Parku Maksimir
Idejni i glavni projekt - krajobrazno uređenje okoliša starog grada u Đurđevcu
Elaborat krajobraznog uređenja - Golf igralište Porto Mariccio
Idejni i glavni projekt - krajobrazno uređenje prostora uz šetnicuod plaže Vajavina do plaže Kozica u Vrbniku
Idejni projekt krajobraznog uređenja Park s dječjim igralištem i sportskom rekreacijom na zelenoj površini između Pantovčaka i Zelengaja
Glavno-izvedbeni projekt krajobraznog uređenja javnih zelenih površina naselja Đelekovec - Park "Centar" , Park i dječje igralište "Škola", park i dječje igralište "Eko-zona"
...

VIŠE OD 100 RAZLIČITIH ELABORATA ZAŠTITE OKOLIŠA...



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projektiranje i savjetovanje u zaštiti okoliša

Zavod za ispitivanje kvalitete d.o.o.

Zavod za ispitivanje kvalitete d.o.o. (ZIK) je najstarija i najveća hrvatska tvrtka koja se bavi isključivo poslovima kontrole kvalitete i sigurnosti roba, proizvoda i usluga. ZIK je utemeljen 1957. godine odlukom Skupštine grada Zagreba. Dokument o osnivanju sadrži deset točaka kojima su određeni temeljni zadaci i način rada. U prvoj točki odluke o osnivanju se navodi:

„Osniva se Zavod za ispitivanje kvalitete kao ustanova sa samostalnim financiranjem čiji je zadatak da ispituje kvalitetu robe, daje stručno mišljenje, te ateste o kvaliteti".

Ove odrednice opisuju rad zavoda tijekom više od 60 godina. ZIK je privatna tvrtka u stopostotnomu hrvatskom vlasništvu i certificirana je prema normama: HR EN ISO 9001,HR EN ISO 14001, i akreditirana prema normama HR EN ISO/IEC 17020, HR EN ISO/IEC 17025,HR EN ISO 17065 s misijom neovisne i respektabilne tvrtke, na poslovima unapređivanja kvalitete i sigurnosti.

ZIK ima najširu lepezu ovlaštenja, akreditacija i usluga što omogućuje da na jednom mjestu riješite sve zahtjeve i potrebe.

Ponuda usluga ZIK-a je znatno proširena zato što imamo razvijenu dugogodišnju poslovnu-tehničku suradnju s brojnim kontrolno-ispitnim laboratorijima u EU i izvan nje.





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CVJEĆARNA
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Osnovana 2002. tvrtka sa 60 zaposlenih i 30 dostavnih vozila te kamion-šleper obavlja distribuciju na području cijele Hrvatske, opskrbljujemo škole, državne ustanove, bolnice, banke, osiguravajuće kuće, te veliki broj poduzeća. Sa ukupno preko 10.000 korisnika i više od 12.000 lokacija za dostavu zauzimamo sam vrh na tržištu RH. u segmentu prodaje i distribucije. Provodeći zakonske odredbe o zbrinjavanju otpada te redovnim kontrolama, ispitnim izvještajima i potrebnim certifikatima želimo i doprinosimo zaštiti okoliša u kojem radimo i živimo.



Spremni smo u svakom trenutku odgovoriti na zahtjeve sadašnjih te potencijalnih klijenata i u roku 24 sata dostaviti komplementarnu robu do odredišta ili fco kupca.



VIZIJA I MISIJA

Pružiti kupcu najbolju vrijednost kroz novac i uslugu.

Zadovoljstvo kupnje imperativ je našeg poslovanja.

Biti najbolji, kako u kvaliteti tako i u profesionalnom pristupu u svim segmentima poslovanja.