



PRODUCTION OF CELLULOLYTIC ENZYMES ON AGRICULTURAL WASTE BY DIFFERENT ZYGOMYCETES

¹Miklós TAKÓ, ¹Szabina LUNG, ²Judit KRISCH, ¹Tamás PAPP, ¹Csaba VÁGVÖLGYI

¹Department of Microbiology, Faculty of Sciences and Informatics, University of Szeged, Közép Fásor 52., H-6726 Szeged, HUNGARY

²Department of Food Engineering, Faculty of Engineering, University of Szeged, Mars Tér 7, H-6724 Szeged, HUNGARY

Abstract:

Filamentous fungi are good producers of different extracellular enzymes. Due to this feature, some of them assumed to play an important role in the decomposition of plant and other organic materials. Several members of the class Zygomycetes are involved in different biotechnological applications, in consequence of their efficient extracellular enzyme production. Because of the increasing interest in the microbial biodegradation, isolates of *Mucor corticolus* (syn.: *M. circinelloides* f. *corticolus*) and *Gilbertella persicaria* were screened for their secreted cellobiohydrolase (1,4- β -D-glucan cellobiohydrolase) and beta-glucosidase activities. These enzymes are key-players in the microbiological degradation of cellulose biomass. The aim of the present study was to evaluate the production of these cellulolytic enzymes on a cheap, exploitable agricultural waste. To investigate the production of cellobiohydrolase and beta-glucosidase, solid-state fermentations were performed on chopped corn-stalks and corn leaves as carbon source. Cultures incubated at 25°C for 12 days were repeatedly sampled to monitor changes in the enzyme activities. Results show that isolates of both species showed intensive growth on these substrates, and high activities of the investigated enzymes were observed during the fermentation period. The potential application of these fungi for biodegradation and enzyme production is discussed.

Keywords:

Gilbertella, *Mucor corticolus*, solid-state fermentation (SSF), cellobiohydrolase, beta-glucosidase

1. INTRODUCTION

Corn is a major crop in the eastern European countries and therefore large amount of corn stalk arise as agricultural waste. Bioconversion may convert corn stalk to ethanol, which is a clean burning fuel and chemical feedstock. Utilization of this resource requires hydrolyzes of cellulose to fermentable reducing sugars in the first step. Cellulases, responsible for the hydrolysis of cellulose, are complex mixture of enzyme proteins with different specificities to hydrolyze the β -1,4-glycosidic linkages bonds. Three major enzyme activity classes are found in the cellulose enzyme complex [5]: endoglucanases (EC 3.2.1.4), cellobiohydrolases (1,4- β -D-glucan cellobiohydrolase; EC 3.2.1.91) and beta-glucosidases (β -D-glucoside glucohydrolase; EC 3.2.1.21). Cellobiohydrolase is the major component of the fungal cellulase systems accounting for 40–70% of the total cellulase proteins [4]. Cellobiohydrolases remove monomers and dimers from the end of the glucan chain. Beta-glucosidase hydrolyzes glucose dimers and in some cases cellulose oligosaccharides to glucose [2].

Zygomycetes fungi are widely distributed in soil and plant debris, on dung and other moist organic matter in contact with soil. Some species cause fungal rots, especially in fruits and vegetables, while others are important as spoilage microorganisms of certain foods. Several members of this fungal group are well known from biotechnological applications in consequence of its effective extracellular enzyme production [13-16]., e.g. mainly proteases

and lipases [12, 1]. Solid-state fermentation (SSF) is a process carried out in the absence or near absence of any fluid in the space between particles [9]. In comparison with other processes used for enzyme production, SSF has the advantage that it allows the usage of solid agricultural and agro-industrial residues as a substrate for microbial growth [10, 11]. Such residues have yielded good results in the production of cellulases and xylanases [3, 8]. Currently, the rapidly evolving biotechnological applications require the isolation and characterization of new cellulose-degrading microorganisms. The aim of the present study was to investigate the production of cellulolytic enzymes by *Gilbertella persicaria* and *Mucor corticolus* on corn stalks and corn leaves as sole carbon source.

2. THE STUDY

Strains and culture conditions. In this study, *Gilbertella persicaria* (G1) and *Mucor corticolus* (M21; syn.: *M. circinelloides* f. *corticolus*) strains were used. Isolates were maintained on malt extract agar slants (0.5% malt extract, 0.5% yeast extract, 0.5% glucose, 1% KH₂PO₄, 1.5% agar) at 4 °C. For the solid-state fermentation, Cultivation of fungi was performed in 250 ml Erlenmeyer flasks; the culture medium contained 5 grams of chopped corn stalks and corn leaves moistened with 5 ml distilled water. Autoclaved media were inoculated with 10⁶ spores and incubated at 25 °C for 12 days.

Sample preparation: Fungal cultures were extracted with 50 ml distilled water at 4 °C for 3 h. After filtration, extracts were centrifuged (10.000 x g, 20 min, 4 °C) and the supernatant was assayed for enzymatic activities.

Enzyme assay: Beta-glucosidase and cellobiohydrolase activities were measured using the appropriate *p*-nitrophenyl- β -D-glucopyranoside (pNPG, Sigma) and *p*-nitrophenyl- β -D-cellobioside (pNPC, Sigma) as substrates. Reaction mixture consisted of 0.1 ml of 7 mM substrate, 0.8 ml of sodium acetate buffer (pH 5.0) and 0.1 ml of crude extract. After incubation at 50 °C for 30 min, the reaction was stopped with 2 ml of 0.1 M sodium carbonate. The released *p*-nitrophenol was measured spectrophotometrically (DU[®]-65, BECKMAN) at 405 nm. One unit of enzyme activity was defined as the amount of enzyme that liberated 1 μ mol of *p*-nitrophenol per min under the described assay conditions.

3. ANALYSIS AND DISCUSSION

The fungal isolates used in this study were selected in previous experiments in which wheat bran was used as substrate. The present assay used corn stalks, corn leaves as carbon source, and strains were grown for 12 days at 25 °C: enzyme activities were determined from the crude water extracts obtained every second day. Both isolates showed intensive growth on these substrates, but they revealed high differences in the production of the cellulolytic enzymes. Extracellular beta-glucosidase activities of these fungi were found to be higher than their cellobiohydrolase activities; similar observation was recorded for mixed cultures of *Aspergillus ellipticus* and *A. fumigatus* in solid-state fermentation [6].

Cellulolytic enzyme production of *M. corticolus* are shown in Fig. 1. The highest beta-glucosidase and cellobiohydrolase activities were reached on the twelfth day after the inoculation (10.4 U/ml and 2.5 U/ml, respectively). Amounts of both enzymes were permanently increased during the fermentation period, and remarkable rises in the activities were detected at the tenth and twelfth culturing day. It is worth to mention that beta-glucosidase activity of *M. corticolus* used in the present analysis is comparable to those of a *Trichoderma viride* wild type and a mutant strain reported by a recent study [7]. These isolates produced the enzyme within a range of 4-15 U/ml on wheat bran.

In contrast to *M. corticolus*, *G. persicaria* had the maximum yield of both enzymes on the eighth day of the cultivation (Fig. 2). In this fermentation, the highest value for beta-glucosidase and cellobiohydrolase activity was 3.1 U/ml and 1 U/ml, respectively. Further increase of the incubation period resulted in decreased enzyme production. It is supposed that the lower extracellular enzyme production led to the reduction in the enzyme activities at *G. persicaria*, and longer fermentation period is required to produce higher amounts of cellulolytic enzymes in case of *M. corticolus* on corn-stalks as substrate.

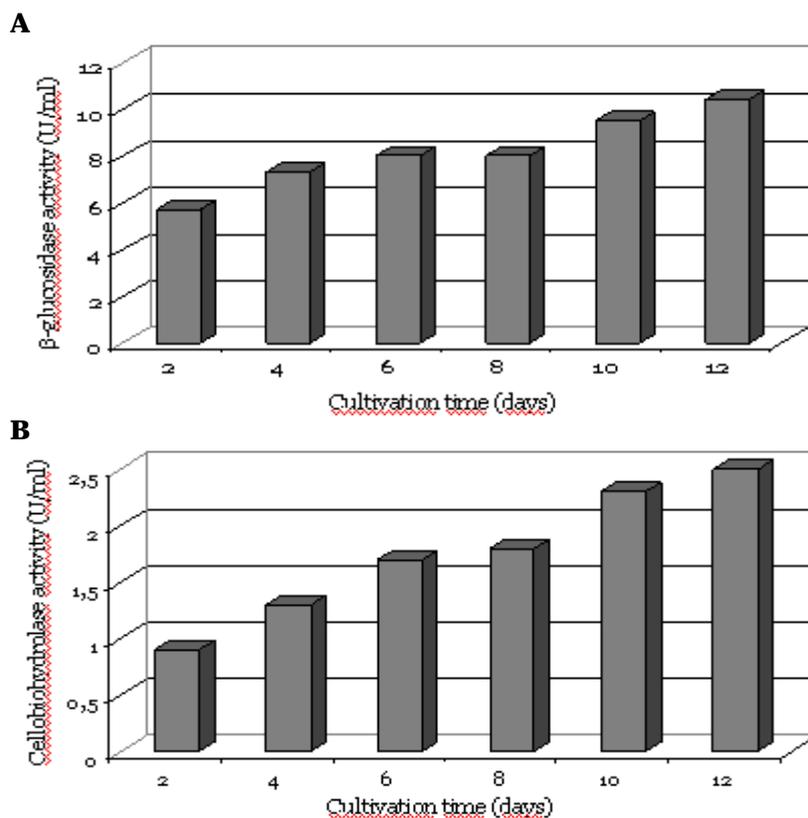


Figure 1. Time course profiles of beta-glucosidase (A) and cellobiohydrolase (B) production by *M. corticolus* by using corn-stalks and corn leaves alone as substrate.

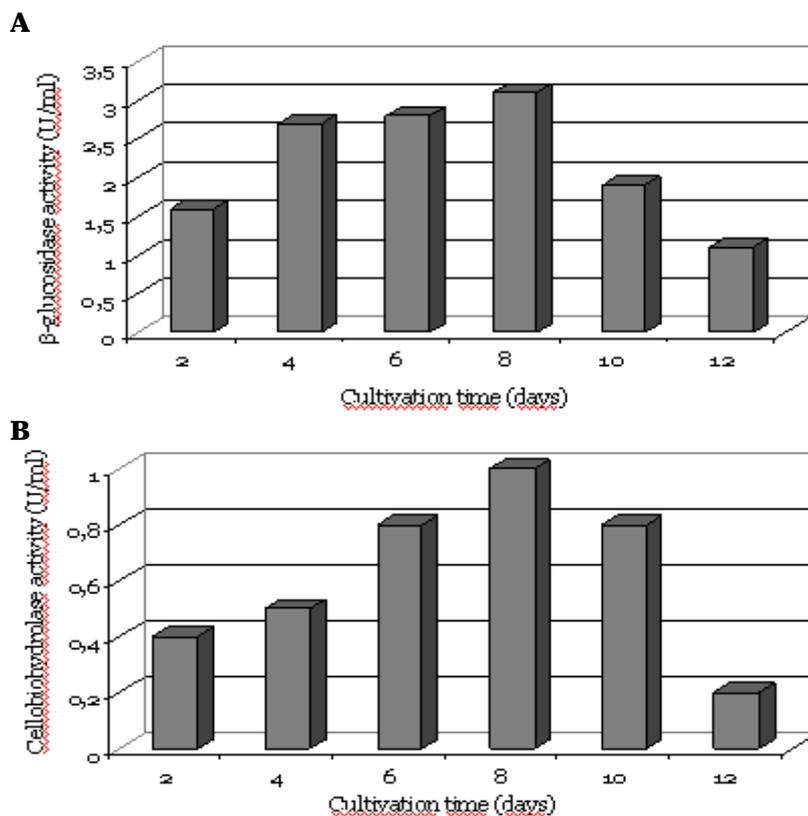


Figure 2. Time course profiles of beta-glucosidase (A) and cellobiohydrolase (B) production by *G. persicaria* by using corn-stalks and corn leaves alone as substrate.

ACKNOWLEDGEMENTS

This research was supported by ETT grants (214/2006; 261/2006) and the J. Bolyai Research Scholarship of the Hungarian Academy of Sciences.

REFERENCES

- [1] Alves MH, Campos-Takaki GM, Porto ALF, Milanez AI: Screening of *Mucor* spp. for the production of amylase, lipase, polygalacturonase and protease. *Braz J Microbiol* 33: 325-330, 2002
- [2] Bhatia Y, Mishra S, Bisaria VS: Microbial β -glucosidases: cloning, properties, and applications. *Crit Rev Biotechnol* 22: 375-407, 2002
- [3] Carmona EC, Fialho MB, Buchgnani EB, Coelho GD, Brocheto-Braga MR, Jorge JA: Production, purification and characterization of a minor form of xylanase from *Aspergillus versicolor*. *Process Biochem* 40: 359-364, 2005
- [4] Esterbauer H, Steined W, Labudova I, Herman A, Hayn M: Production of *Trichoderma* cellulase in laboratory and pilot scale. *Bioresour Technol* 36: 51-65, 1991
- [5] Goyal A, Ghosh B, Eveleig D: Characterization of fungal cellulases. *Bioresour Technol* 36: 37-50, 1991
- [6] Gupte A, Madamwar D: Production of cellulolytic enzymes by coculturing of *Aspergillus ellipticus* and *Aspergillus fumigatus* grown on bagasse under solid state fermentation. *Appl Biochem Biotechnol* 62: 267-274, 1997
- [7] Haq I, Javed MM, Siddiq Z, Saleem T: Triggering of β -glucosidase production in *Trichoderma viride* with nutritional and environmental control. *J Appl Sci Res* 2: 884-889, 2006
- [8] Kalogeris E, Christakopoulos P, Katapodis P, Alexiou A, Vlachou S, Kekos D, Macris BJ: Production and characterization of cellulolytic enzymes from the thermophilic fungus *Thermoascus aurantiacus* under solid state cultivation of agricultural wastes. *Process Biochem* 38: 1099-1104, 2003
- [9] Lonsane BK, Ghildyal NP, Butiatman S, Ramakrishma SV: Engineering aspects of solid state fermentation. *Enzyme Microb Technol* 7: 258-265, 1985
- [10] Panagiotou G, Kekos D, Macris BJ, Christakopoulos P: Production of cellulolytic and xylanolytic enzymes by *Fusarium oxysporum* grown on corn stover in solid state fermentation. *Ind Crop Prod* 18: 37-45, 2003
- [11] Pandey A: Solid-state fermentation. *Biochem Eng J* 13: 81-84, 2003
- [12] Rao MB, Tanksale AM, Ghatge MS, Deshpande VV: Molecular and biotechnological aspects of microbial proteases. *Microbiol Mol Biol Rev* 62: 597-635, 1998
- [13] Takó M, Farkas E, Papp T, Vágvölgyi Cs: Detection of extracellular beta-glucosidase activity in Zygomycetes fungi. *Power of Microbes in Industry and Environment, Zadar, Abstracts* 64, 2007
- [14] Takó M, Linka B, Papp T, Vágvölgyi Cs: Isolation and characterization of a novel β -glucosidase gene from *Rhizomucor miehei*. *Acta Microbiol Immunol Hung* 53: 351-352, 2006
- [15] Takó M, Papp T, Krisch J, Vágvölgyi Cs: Purification and partial characterization of extracellular beta-glucosidase from *Rhizomucor miehei*. *Acta Microbiol Immunol Hung* 55: 251 2008
- [16] Vágvölgyi Cs, Manczinger L, Krisch J, Takó M, Papp T: New microbial enzymes: clues for environment friendly biorefinery technologies. *Cereal Res Com* 35: 1265-1268, 2007



BETA-CAROTENE PRODUCTION BY MUCORALEAN FUNGI

Tamás PAPP¹, Gábor NAGY¹, Árpád CSERNETICS¹,
András SZEKERES², Csaba VÁGVÖLGYI¹

¹University of Szeged, Faculty of Sciences and Informatics,
Department of Microbiology, Szeged, HUNGARY

²FumoPrep Ltd, Mórahalom, HUNGARY

Abstract

Although some fungi belonging to the order Mucorales (Zygomycetes), such as *Phycomyces blakesleeanus*, *Blakeslea trispora* and *Mucor circinelloides*, have been traditionally involved in the study of the fungal carotenoid biosynthesis, the majority of the related species have not been studied from this aspect. As morphological observations indicates that a number of other species also seems to be promising producers, the main objective of the present study was to investigate the beta-carotene production ability of several Mucoralean fungi belonging to the genera *Mucor*, *Backusella* and *Gilbertella*. After cultivation under different conditions, the total carotenoid level and the beta-carotene content in the mycelia were measured by an HPLC method. Pigment production of *Gilbertella persicaria* was worth to mention only if it was cultured as a mixture of isolates with opposite mating types. Some *Mucor* and *Backusella* strains produced beta-carotene in significantly higher amounts than the *M. circinelloides* reference strain or the wild-type *B. trispora*, a model organism of the carotenogenic studies. Effects of the illumination, the carbon source and the growth temperature on the carotene production were examined.

Keywords

pigment production, carotenoid, Zygomycetes, *Mucor*

1. INTRODUCTION

Carotenoids are one of the most important groups of natural pigments. They are used in the food, pharmaceutical and cosmetic industry and as feed colour additives. Carotenoids recently attracted great attention, due to their beneficial effects on human and animal health; for example, their antioxidant property linked with a preventive action on different types of cancer [5] and the enhancement of the immune system [2]. Most of the carotenoid production is performed by chemical synthesis and only a few natural compounds can be obtained from cheap plant sources [1]. Currently there is an increasing interest in sources of carotenoids from microbial origin, especially in cases of the β -carotene and its oxygenated derivatives.

In Zygomycetes fungi β -carotene is the predominant carotenoid species. Traditionally three Zygomycetes, e.g. *Blakeslea trispora*, *Phycomyces blakesleeanus* and *Mucor circinelloides*, have been involved in the study of the carotene biosynthesis.

The aim of the present study was to obtain information on the carotenoid production, especially on the β -carotene content of some Mucoralean fungi in order to determine new producer strains potentially applicable in further analyses and developments.

2. THE STUDY

Strains and growth conditions.

The 21 fungal strains involved in this study are listed in Table 1. Strains were cultured on plates containing malt extract medium (5 % malt extract, 0.5 % yeast extract, 1% D-glucose, 1.5 % agar), grown for 4 days under continuous light.

Carotenoid extraction and analysis.

Carotenoids were extracted from 500 mg mycelial powder with 500 µl acetone and vortexing. This extraction step was repeated until the pellet was found to be devoid of pigments. Extracts were combined and then partitioned with an equal volume of 10% diethyl ether in petroleum ether. To facilitate the separation and to remove dissolved acetone, 1 ml distilled water was added. The petroleum ether fractions were combined and dried under nitrogen gas [6].

For high-performance liquid chromatography (HPLC), samples were analyzed by using a modular Shimadzu low-pressure gradient HPLC system equipped with an UV-Vis detector. The dried samples were dissolved in 100 µl tetrahydrofuran supplemented with butylated hydroxytoluene (100 µg/ml) directly before the analysis and 3 µl was subjected to HPLC analysis on a Phenomenex Prodigy column (4.6 x 250, ODS 3 µm). The separation was performed with a gradient (where min/solvent A%/solvent B% was 0/99/1; 8/60/40; 13/46/54; 15/0/100; 18/0/100; 21/99/1; 25/99/1) using 4% water-96% methanol as solvent A and 4% water-96% methyl-*tert*-butyl ether as solvent B, at a flow rate of 1 ml/min. The detection wavelength was 450 nm. To identify the carotenoids, the following standards were used: astaxanthin, lycopene and β-carotene from Sigma, β-cryptoxanthin, zeaxanthin and canthaxanthin from Carl Roth, and echinenone from DHI Water and Environment.

For spectrophotometry, samples were dissolved in petroleum ether; total carotenoid content was measured at 450 nm.

3. ANALYSIS AND DISCUSSION

For the study, 21 fungal isolates were selected on the basis of morphological observations, e.g. of their colony colour (Table 1). These isolates represent 10 different species belonging to the genera *Mucor*, *Rhizopus*, *Backusella* and *Gilbertella*. Overall carotenoid content of the isolates tested are shown in Fig. 1. The carotene production showed high variability even among the isolates of a same species. The most promising producers were the isolates M19, M59, M76 and MH1 with a carotene production more than 400 µg/g dry mass; *M. circinelloides* (M20) and *B. lamprospora* (B1) also had remarkable production. Maybe the high production of *M. bainieri* strain M76 can be connected with the obligate azigospore forming nature of this fungus. Trisporic acids, substances with hormonal activity forming during the zygosporogenesis (e.g. the mating), have been shown to stimulate the β-carotene biosynthesis [5].

Table 1. Investigated fungal strains and their overall carotenoid content

^aThese codes were used throughout the paper for clarity. ^bStrains were cultured at 25°C under continuous light; averages were calculated measuring 3 independent extracts.

Species	Code of isolate ^a	Total carotenoid content ^b
<i>Mucor albo-ater</i>	M30	20
<i>M. bainieri</i>	M51	36
<i>M. bainieri</i>	M76	825
<i>M. circinelloides</i>	M20	378
<i>M. circinelloides</i>	M50	98
<i>M. hiemalis</i>	MH1	570
<i>M. hiemalis</i>	M18	135
<i>M. hiemalis</i>	M12	25
<i>M. hiemalis</i>	M22	105
<i>M. hiemalis</i> f. <i>hiemalis</i>	M55	24
<i>M. hiemalis</i> f. <i>luteus</i>	M57	46
<i>M. hiemalis</i> f. <i>hiemalis</i>	M59	740
<i>M. inequisporus</i>	M58	35
<i>M. mucedo</i>	M19	420
<i>M. rouxi</i>	M15	192
<i>Backusella lamprospora</i>	B1	400
<i>Rhizopus stolonifer</i>	Rh17	200
<i>Rhizopus stolonifer</i>	Rh5	57
<i>Gilbertella persicaria</i>	G10	29
<i>Gilbertella persicaria</i>	G5	28
<i>Gilbertella persicaria</i>	G6	29
<i>Gilbertella persicaria</i>	G5-G6	151
<i>Gilbertella persicaria</i>	G6-G10	127

Gilbertella persicaria produced higher amounts of pigments only if it was plated as a mixture of the opposite mating types.

Ten strains were selected for further analysis (G6 and G10 examined in mixed cultures to achieve higher carotenoid production). Effect of the growth temperature on the carotenoid production was examined (Fig. 2). In an earlier study, three-times higher carotenoid content was observed in *M. rouxii* when the culturing temperature was increased from the optimum growth temperature (28°C) to 37°C [4].

In our experiments, higher growth temperature also stimulated the production in the majority of the strains. Elevation of the growth temperature led to the highest carotenoid production in the strains M59 (*M. hiemalis*) and M19 (*M. mucedo*), where the total carotenoid contents exceeded 1 mg/g dry weight at 30 and 35°C, respectively. It is worth to mention that all fungi showed more or less restricted growth at temperatures higher than 30°C. The only exception was the mating culture of *G. persicaria* (G6-G10) retaining its growth intensity even at 38°C where it produced about 4 times more carotenoids than at 25°C. Carotenoid production of the strains M20, M79 and Rh17 (*M. circinelloides*, *M. bainieri* and *Rhizopus stolonifer*, respectively) decreased at higher temperatures.

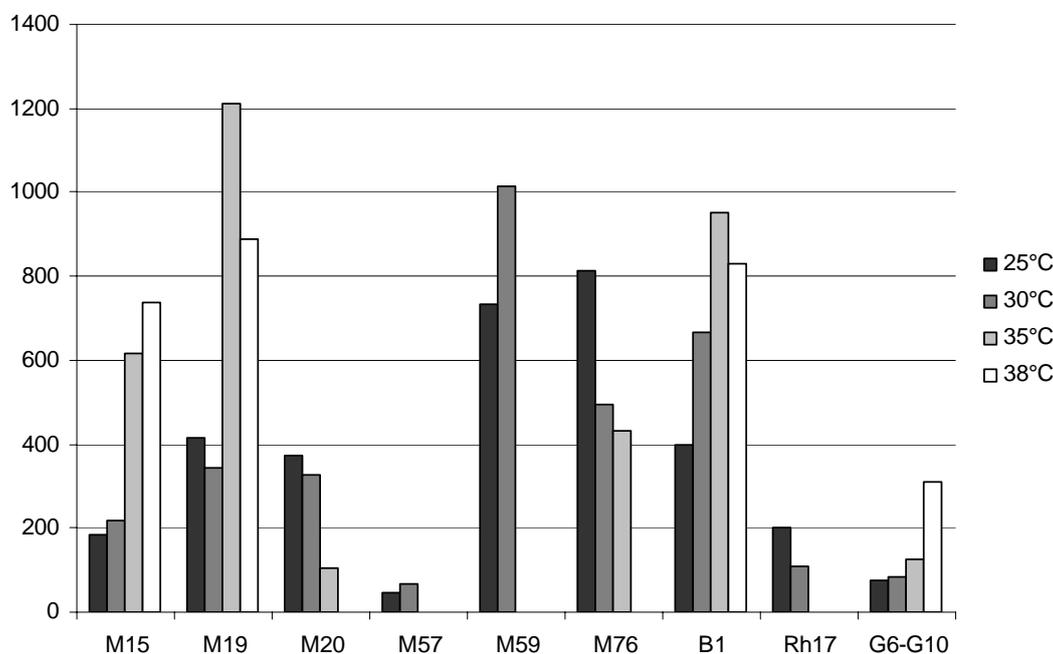


Figure 3. Total carotenoid production of Mucoralean fungi at different temperatures. The averages were calculated from 3 different measures from independently cultured mycelia.

ACKNOWLEDGEMENTS This research was supported by ETT grants (214/2006; 261/2006) and the J. Bolyai Research Scholarship.

REFERENCES

- [1] Bhosale, P. Environmental and cultural stimulants in the production of carotenoids from microorganisms. *Appl. Microbiol. Biotechnol.* 63: 351–361, 2004
- [2] Hughes, D.A. Effects of carotenoids on human immune function. *Proc. Nutr. Soc.* 58: 713–718, 1999
- [3] Lampila, L.E., Wallen, S.E., Bullerman, L.B. A review of factors affecting biosynthesis of carotenoids by the order Mucorales. *Mycopathologia* 90: 65–80, 1985

- [4] Mosqueda-Cano, G., Gutierrez-Corona, J.F. Environmental and developmental regulation of carotenogenesis in the dimorphic fungus *Mucor rouxii*. *Curr. Microbiol* 31: 141-145, 1995
- [5] Nishino, H., Murakosh, M., Ii, T., Takemura, M., Kuchide, M., Kanazawa, M., Mou, X.Y., Wada, S., Masuda, M., Ohsaka, Y., Yogosawa, S., Satomi, Y., Jinno, K. Carotenoids in cancer prevention. *Cancer Metastasis Rev.* 21: 257–264, 2002
- [6] Papp, T., Velayos, A., Bartók, T., Eslava, AP., Vágvölgyi, Cs., Iturriaga, E.A. Heterologous expression of astaxanthin biosynthesis genes in *Mucor circinelloides*. *Appl. Microbiol. Biotech.* 67: 526-531, 2006
- [7] Vágvölgyi, Cs., Magyar, K., Papp, T., Palágyi, Zs., Ferenczy, L., Nagy, Á. Value of substrate utilization data for characterization of *Mucor* isolates. *Can. J. Microbiol.* 42: 613-615, 1996



STRESS RESPONSES OF GENETICALLY MODIFIED *MUCOR CIRCINELLOIDES* STRAINS

Nikoletta KÁLMÁN¹, Ottó BENCSIK², Miklós PESTI¹,
Tamás PAPP², Csaba VÁGVÖLGYI²

¹Department of General and Environmental Microbiology, Faculty of Sciences,
University of Pécs, H-7601 Pécs, HUNGARY

²Department of Microbiology, Faculty of Science and Informatics,
University of Szeged, Közép fasor 52, H-6726 Szeged, HUNGARY

Abstract

The stress-related responses of *Mucor circinelloides* transformants altered in carotenoid production have been investigated. In zygomycetous fungi β -carotene is the predominant carotenoid, however, in transformants containing the *crtW* and *crtZ* astaxanthin biosynthesis genes from *Agrobacterium aurantiacum* new carotenoid compounds are present. *Mucor* strains with altered carotenoid content were treated with different concentrations of copper, cadmium, chromium and the oxidative stress-inducing agents, menadione, *tert*-butyl hydroperoxide and hydrogen peroxide. Results suggest that the intermediers of the β -carotene-astaxanthin pathway more efficiently increase the stress tolerance of the fungal cells as the astaxanthin, the end-product of the biosynthesis.

Keywords

astaxanthin, carotenoid biosynthesis, *Mucor circinelloides*, oxidative stress, transformation

1. INTRODUCTION

Carotenoids pigments are widely distributed in the nature. They are important, high-value additives in the cosmetic, food, and pharmaceutical industry. Their beneficial effects on human and animal health are also well documented. Among others, their antioxidant property linked to a preventive action on various types of cancer and an enhancement of the immune response makes them important in the human diet [5, 11].

Though some of these pigments could be manufactured synthetically, the demand for exploitation of natural source is continuously increasing. Microbial production is especially promising for the orange-red ketocarotenoids (e.g. astaxanthin, canthaxanthin) not available in other cheap and exploitable natural sources [2, 8, 13]. Metabolic engineering could assist for the development of commercially utilizable microbial carotene production. Recently, de novo carotenoid biosynthesis was performed in otherwise colourless organisms, such as *Escherichia coli* [17], or *Candida utilis* [10] by introduction of bacterial carotenogenic genes.

The β -carotene producer zygomycete fungus *Mucor circinelloides* is a favoured organism when fungal carotenogenesis has to be investigated. The existence of an efficient transformation system [1, 16], the capacity to express exogenous genes [6] and the ability to grow in a yeast-like form [12] are its most attractive characteristics.

Although, oxidative stress response has been extensively studied in pro- and eukaryotes, the information about filamentous fungi is fragmentary. The main objective of the present work was to investigate the stress response of various *M. circinelloides* transformants modified in their carotenoid production.

2. THE STUDY

MS12, a *leuA*-, *pyrG*-mutant of the wild-type *M. circinelloides* strain (CBS277.49) and its transformants were used in the experiments. The *crtZ* and *crtW* genes of *Agrobacterium aurantiacum* (encoding β -carotene hydroxylase and β -carotene ketolase, respectively) [9] were used for obtaining transformants with modified carotenoid content. Transformants MS12-Z, MS12-W and the co-transformants MS12-ZW, harboured heterologous *crtZ*, *crtW*, and both of them, respectively [14].

Pigment samples were obtained as described by Papp et al [14]. Measurements of the pigment contents and pigment compositions were carried out by recording the absorbance at 492 nm and with thin layer chromatography (TLC) or with high pressure liquid chromatography (HPLC) analysis, respectively [14].

Genetically modified *Mucor* strains with altered carotenoid content were treated with different concentrations of copper, cadmium, chromium and the oxidative stress-inducing agents menadione, *tert*-butyl hydroperoxide (tBOOH) and hydrogen peroxide. For oxidative stress experiments, 20 ml of YNB (glucose 1%, ammonium sulphate 0.15%, glutamate 0.15%, leucine and/or uracil 0.02%, agar 3%, pH 4.5) supplemented with the required stressor was poured in Petri dishes. Before inoculation each fungal species was grown on YNB for 10-14 days at 28°C. A disk was cut using a cork borer from the actively growing margin of the source of fungus and transferred to the centre of each study plate. Tolerance against stress conditions was analyzed by measuring the colony diameters after 5 days incubation (25°C). Minimum inhibitory concentration (MIC) values were taken as the stressor concentrations causing >95% growth inhibition. All experiments were carried out in triplicates.

3. ANALYSIS AND DISCUSSION

Misawa et al. [14] isolated a gene cluster responsible for the synthesis of astaxanthin from the marine bacteria *A. aurantiacum*. In a previous study, plasmid constructs with the genes *crtZ* (encoding β -carotene hydroxylase) and *crtW* (encoding β -carotene ketolase) used to transform *M. circinelloides*. These enzymes mediate the oxygenation reactions from β -carotene to astaxanthin thus allowing the formation of many intermediates of astaxanthin, i.e., β -cryptoxanthin, zeaxanthin, adonixanthin, phoenicoxanthin, canthaxanthin and echinenone [14].

The *Mucor* transformants with modified carotenoid content (Table 1.) were subjected to the effect of copper, cadmium, chromium and some chemical compounds (menadione, *tert*-butyl hydroperoxide and hydrogen peroxide). The toxic manifestations of heavy metals and certain chemicals are caused primarily due to imbalance between pro-oxidant and antioxidant homeostasis of the cells which is termed as oxidative stress. This oxidative stress is a disparity between free radical production and the antioxidant defence of the cell [3]. Carotenoids are well-known antioxidants and therefore a modified carotenoid content has to result an altered sensitivity of the cells against the oxidative damage.

Table 1. The relative carotenoid composition of the *M. circinelloides* MS12 strain and its transformants

Strain	astaxanthin	canthaxanthin	zeaxanthin	β -cryptoxanthin	echinenone	β -carotene
MS12	-	-	+	+	-	++
MS12-Z	-	-	++	++	-	++
MS12-W	++	+	-	+	++	++
MS12-ZW	+	++	+	++	++	++

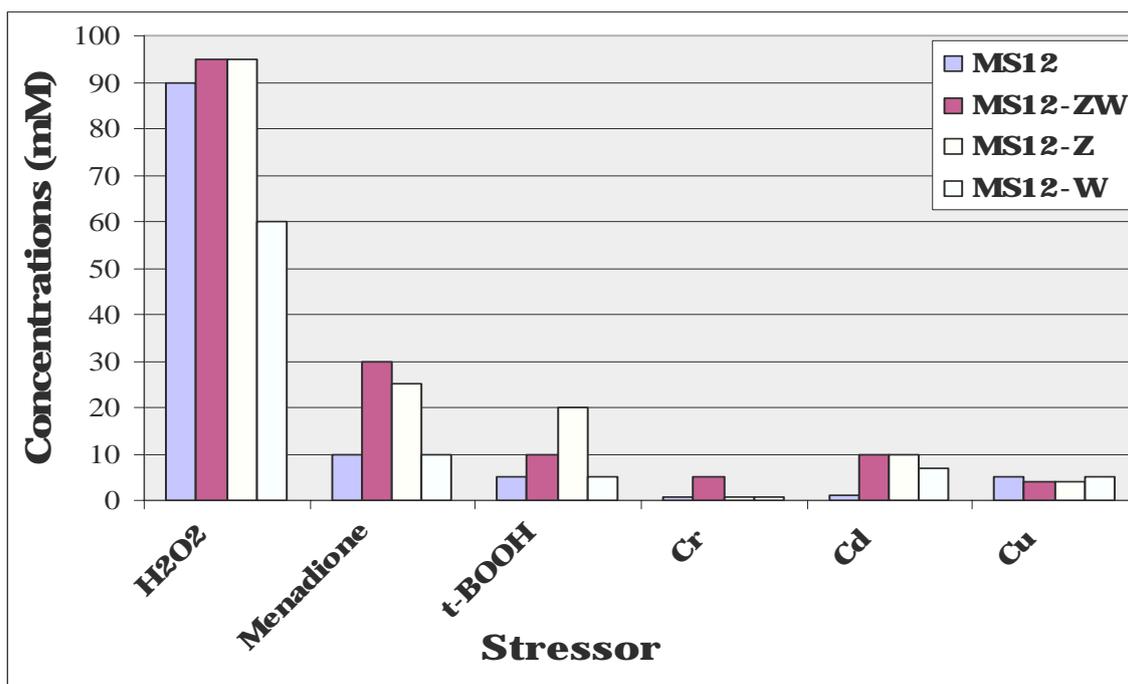


Figure 1. MIC-values against oxidative stressors for *Mucor* MS12 strain and its transformants. The values plotted represent the averages of triplicate samples. Individual values varied less than 10%.

Metal induced toxicity is very well reported in the literature [7]. One of the major mechanisms behind heavy metal toxicity has been attributed to oxidative stress [3]. Cadmium, unlike other heavy metals is unable to generate free radicals by itself, however, reports have indicated superoxide radical, hydroxyl radical and nitric oxide radicals could be generated indirectly [4]. Watanabe et al [18] showed generation of non-radical hydrogen peroxide which by itself became a significant source of free radicals via the Fenton chemistry. In the case of the investigated *Mucor* strains there were no difference detected against copper for the strain MS12 and its transformants. However, with chromium and cadmium treatment MS12-ZW (containing both of the transforming bacterial genes) revealed substantially higher MIC values than the parental strain.

When oxidative stress inducing chemicals were tested, menadione and tBOOH treatment resulted in higher MIC values for MS12-ZW and MS12-Z than for MS12. There was no such difference for hydrogen-peroxide. Surprisingly, practically for all stressors MS12-W demonstrated similar or lower MIC values than the parental strain.

4. CONCLUSIONS

Several studies have shown metals like copper, cadmium, iron, mercury, nickel, lead and arsenic possess the ability to generate reactive radicals, resulting in cellular damage like depletion of enzyme activities, damage to lipid bilayer and DNA [15]. Similarly, there are a broad range of chemicals which impair cells through similar mechanisms. Carotenoids able to "quench" singlet oxygen primarily by a physical mechanism, in which the excess energy of singlet oxygen is transferred to the carotenoid's electron-rich structure: due to this feature they are well known antioxidants. The presented results reinforce that in metabolically engineered fungal cells new carotenoids express protective effect against oxidative stress. Surprisingly, various intermediers of the β -carotene-astaxanthin pathway seem to be more important from this respect than the end-product astaxanthin.

Acknowledgements

This research was supported by ETT grants (214/2006; 261/2006) and the J. Bolyai Research Scholarship.

REFERENCES

- [1] Arnau J, Jepsen LP, Stroman P: Integrative transformation by homologous recombination in the zygomycete *Mucor circinelloides*. *Mol Gen Genet* 225, 193-198 (1991).
- [2] Dufossé L: Microbial production of food grade pigments. *Food Technol Biotechnol* 44, 313-321 (2006).
- [3] Flora SJS, Mittal M, Mehta A: Heavy metal induced oxidative stress & its possible reversal by chelation therapy *Indian J Med Res* 128, 501-523 (2008).
- [4] Galan C, Garcia BL, Troyano A, Vilaboa NE, Fernandez C, Blas DE, Aller P: The role of intracellular oxidation in death induction (apoptosis and necrosis) in human promonocytic cells treated with stress inducers (cadmium, heat, X-rays). *Eur J Cell Biol* 80, 312-320 (2001).
- [5] Hughes DA: Effects of carotenoids on human immune function. *Proc Nutr Soc* 58, 713-718 (1999).
- [6] Iturriaga EA, Díaz-Mínguez JM, Benito EP, Álvarez MI, Eslava A.P: Heterologous transformation of *Mucor circinelloides* with the *Phycomyces blakesleeanus* leu1 gene. *Curr Genet* 21, 215-223 (1992).
- [7] Leonard SS, Harris GK, Shi XL: Metal-induced oxidative stress and signal transduction. *Free Rad Biol Med* 37, 1921-1942 (2004).
- [8] Lukács Gy, Linka B, Nyilasi I: *Phaffia rhodozyma* and *Xanthophyllomyces dendrorhous*: astaxanthin-producing yeasts of biotechnological importance. *Acta Aliment Hung* 35, 99-107 (2006).
- [9] Misawa N, Satomi Y, Kondo K, Yokoyama A, Kajiwara S, Saito T, Ohtani T, Miki W: Structure and functional analysis of a marine bacterial carotenoid biosynthesis gene cluster and astaxanthin biosynthetic pathway proposed at the gene level. *J Bacteriol* 177, 6575-6584 (1995).
- [10] Misawa N, Shimada H: Metabolic engineering for the production of carotenoids in non-carotenogenic bacteria and yeasts. *J Biotechnol* 59, 169 (1997).
- [11] Nishino H, Murakoshi M, Ii T, Takemura M, Kuchide M, Kanazawa M, Mou XY, Wada S, Masuda M, Ohsaka Y, Yogosawa S, Satomi Y, Jinno K: Carotenoids in cancer prevention. *Cancer Metastasis Rev* 21, 257-264 (2002).
- [12] Orlovsky M: *Mucor* dimorphism. *Microbiol Rev* 55, 234-258 (1991).
- [13] Palágyi Zs, Linka B, Papp T, Vágvölgyi Cs: Isolation and characterization of *Xanthophyllomyces dendrorhous* mutants with altered carotenoid content. *Acta Aliment Hung* 35, 223-228 (2006).
- [14] Papp T, Velayos A, Bartók T, Eslava AP, Vágvölgyi Cs, Iturriaga EA: Heterologous expression of astaxanthin biosynthesis genes in *Mucor circinelloides*. *Appl Microbiol Biotech* 67, 526-531 (2006).
- [15] Stohs SJ, Bagchi D: Oxidative mechanisms in the toxicity of metal-ions. *Free Rad Biol Med* 18, 321-336 (1995).
- [16] van Heeswijk R, Roncero MIG: High frequency transformation of *Mucor* with recombinant plasmid DNA. *Carlsberg Res Commun* 49, 691-702 (1984).
- [17] Wang C-W, Oh M-K, Liao JC: Engineered isoprenoid pathway enhances astaxanthin production in *Escherichia coli*. *Biotechnol Bioeng* 62, 235-241 (1999).
- [18] Watanabe M, Henmi K, Ogawa K, Suzuki T: Cadmium-dependent generation of reactive oxygen species and mitochondrial DNA breaks in photosynthetic and non-photosynthetic strains of *Euglena gracilis*. *Comp Biochem Physiol C Toxicol Pharmacol* 134, 227-234 (2003).



ACOUSTICAL ARRANGEMENT OF THE URBAN ROADS

Vasile BACRIA, Nicolae HERIȘANU

Politehnica University of Timișoara, ROMANIA

Abstract

The phonic pollution on the urban roads is mainly generated by the transportation means. This affects the human being's live and activity. In this paper we presented the results obtained in the investigation and mitigation of the phonic pollution generated by the transportation means in the urban area through acoustical arrangement of the roads. Specific noise sources, characteristic levels, noxious effects, admissible limits and propagation way are identified. Description of measurements and analysis of the results are presented along with some methods concerning the decrease of the phonic pollution. The efficiency of the implementation of these methods is also discussed.

Keywords

Phonic pollution, decrease, urban roads, acoustic arrangement

1. INTRODUCTION

Noises and vibrations are generated on the urban roads by road transportation means such as trams, buses, trolleybuses, minibuses, cars, trucks, tractors or motorcycles. Sometimes, these noises and vibrations are generated also by the rail and air transportation means. This is possible when the urban roads are near the railway or the airport. The noises and vibrations generated by transportation means have characteristic spectra and levels of intensity. In this way it is possible to identify the main noise sources from the road transportation means, specifying the noxious effects, admissible limits and propagation way.

Starting from the results of the measurements, we establish some methods concerning the phonic pollution reduction in the urban area through the acoustical arrangement of the roads. The efficiency of the implementation of these methods was evaluated by new measurements. The acoustical arrangement can be applied in every practical situation concerning the urban roads.

2. NOISE SOURCES ON THE URBAN ROADS

The noise is generated on the urban roads by transportation means. This is characterized by specific frequency spectra, acoustic pressures and their variations in time. This noise depends on the intensity and composition of traffic, as well as on the speed of movement and it is generated by three basic sources: the engine, the exhaust system and the tire/road contact. The trams generate noise and vibrations due to the variation of speeds, the clearance of the rail extremity (joints), the elasticity of the rails, the conicalness, the eccentricity and the deformations of the bandages, the wheel guide on the rails and the brakes and accelerations.

3. NOXIOUS EFFECTS OF THE PHONIC POLLUTION

The phonic pollution generated by the road transportation means on the urban roads is extremely injurious for the human beings' life and activity. Thus, for the 70 dB(A) equivalent noise level during the daytime, 60% of the population on the urban roads is disturbed [8].

The phonic pollution affects human beings nervous system generating psychophysiological and blood circulation modifications, as well as sleeps disturbances. Also the visual function and endocrine gland are adversely affected. At the same time the phonic pollution generates auditory tiredness and sonorous trauma.

In order to reduce the effects of the phonic pollution on the urban roads, limit values which cannot be exceeded are established. These limits are characterized by the equivalent noise level, by the noise curves (C_z) and by percentual noise level (L_{10}). The equivalent noise level corresponds to an equivalent intensity which could be constant during the whole considered period of time and it is defined by relation

$$L_{ech} = 10 \lg \left[\frac{I}{T} \int_0^T 10^{0.1L(t)} dt \right] \quad (1)$$

where $L(t)$ is the instant acoustic level.

The noise curves (C_z) define the relation between the characteristic frequency of a sound and the proper acoustic pressure level in the conditions of a subjective equivalent intensity.

In this way, Romanian standard STAS 10009-88 “Urban acoustics” established the admissible limits of the noise level in urban environment, differentiated on zones and functional endorsements. For the noise level on the urban roads these values are presented in table 1.

Table 1

Street type (according to STAS 10144-80)	L_{eq} [dB]	C_z [dB]	L_{10} [dB]
I-main	75-85	70-80	85-95
II-linking	70	65	75
III-collecting	65	60	75
IV-local serving	60	55	70

In the same time the location of residential buildings on streets having different technical categories or at the limit of some functional areas as well as the road traffic organizing must be

made so that to be assured the admissible limits for the exterior noise level (which is 50 dB or C_z45 curve). This noise level is measured in a point located at 2m distance from the building’s wall, according to STAS 6161/1-79. In order to limit the effects generated by rail traffic noise upon the urban environment, it is stipulated that this one cannot exceed 70 dB(A) at the limit of the rail area (or C_z65 curve). For the limitation of the noise generated by the air traffic, it is recommended that this noise arising from airplanes displacement do not exceed 90 dB(A) during the daytime between 7.00-19.00 hours, 85 dB(A) during the evening between 19.00-22.00 hours and 80 dB(A) during the night between 22.00-7.00 hours.

4. PROPAGATION WAY OF THE NOISE

During the activity of different noise sources from the urban roads, rail or air transportation ways, their vibrations propagate in the surrounding environment as spherical and cylindrical waves and, at long distance, as plane waves.

The equation of spherical waves, in an elastic, homogeneous and isotropic medium with the speed potential ϕ as a parameter is

$$\phi = \frac{A_c}{r} e^{j(\omega t - kr)} \quad (2)$$

where r is the radial coordinate, A_c is the complex amplitude of the spherical wave at the frequency $f = \frac{\omega}{2\pi}$ that travels from the source with the speed c and $k = \frac{\omega}{c}$ is the wave number. If we consider $A_c = A e^{j\alpha}$, then the acoustical pressure can be determined with relation [3]

$$p = \rho_0 \omega \frac{A}{r} \sin(\omega t - kr + \alpha) \quad (3)$$

In the same time, taking into account that some parts of the sources from the transportation means have cylindrical shape, because of their vibrations, there are produced cylindrical waves.

The equation of cylindrical waves is

$$\phi = [AJ_m(kr) + jBY_m(kr)]e^{-jm\varphi}e^{-j\omega t} \quad (4)$$

where ϕ has the known signification, r and φ are the cylindrical coordinates, A and B are constants, J_m is the Bessel function of the first degree and m range and Y_m is the Bessel-Neumann function of the second degree and m range.

In case of the waves that travel uniformly, then $m = 0$ and the acoustical pressure can be written

$$p = A[J_0(z) + jY_0(z)]e^{-j\omega t} \quad (5)$$

Propagation of spherical, cylindrical and plane waves is causing the variation of the pressure in a point of the acoustical field. If we consider that a pressure at a specific moment is p , then the level of the acoustical pressure is

$$L = 20 \lg \frac{p}{p_0} \quad (8)$$

where $p_0 = 2 \cdot 10^{-5} [N/m^2]$ is the reference acoustical pressure.

5. MEASUREMENTS ACCOMPLISHMENT

Taking into consideration the huge number and variety of sources that have a part to play in generating the noise on the urban roads, as well as the nature of the acoustic produced by these ones, the acoustic field is extremely complex and its study is indicated to be of an experimental nature.

Noise level measurements were carried out in 119 measurements points which were located near some of the most noisy roads crossings from Timișoara city [1], [5]. The measurements were performed using the Brüel & Kjaer 2237 Controller Integrating Sound Level Meter and the Hand-held Analyser Brüel & Kjaer 2250. These ones allowed measuring and automatic recording of the most important parameters of the noise such as: L_{eq} (equivalent noise level), L_{AE} (exposure level), L_{max} (maximum noise level), L_{min} (minimum noise level), $L_{0,1}$, L_5 , L_{10} , L_{50} , L_{90} , L_{95} (percentage noise levels). These parameters were obtained during a continuous 8 hours period of time (7.30-15.30), divided into 1 hour time intervals. By means of these measured parameters, it was possible to compute other physical indicators which characterize the effect of phonic pollution, such as:

- the noise climate

$$N.C. = L_{10} - L_{90} \quad (7)$$

- the traffic noise index

$$T.N.I. = 4(L_{10} - L_{90}) + L_{90} - 30 \quad (8)$$

- the level of phonic pollution

$$L.N.P. = L_{ech} + L_{10} - L_{90} \quad (9)$$

In order to perform the measurements, the microphone was placed next to the urban roads border at 7,5 m distance from the axis of the first runway, at 1,30 m high from the ground.

Simultaneously with the noise data recording, the traffic composition and intensity as well as the speed of the vehicles were determined.

The results of the measurements, the intensity and composition of the traffic were centralized in a data base designed for the study of phonic pollution in Timișoara City.

6. ANALYSIS OF THE MEASUREMENTS RESULTS

From the obtained data it results that the equivalent noise level exceeds the maximum admissible value (defined by Romanian standard STAS 10009-88 concerning “Urban acoustics”) in 95 points from the total of 119 measured points, which means 79,85% of the total points.

The overtaking was included into the interval 0,5-15,5 dB. Table 2 presents the statistical distribution of the equivalent noise level (L_{eq}) in the measured points, as well as the percentage of disturbed people [8]. In the majority of the measurement points, the peak noise level was exceeded with 1-9,5 dB while the admissible noise level established to 50 dB measured at 2 meters distance from the buildings was generally exceeded with 1,3-32,9 dB(A). The average equivalent noise level for the 119 measured points was 71,03 dB(A) and the average traffic intensity was 1202,3 aut./h. The traffic intensity ranged between 9 and 2681 aut./h while the speed of vehicles ranged between 40 and 60 km/h.

Table 2

L_{eq}	No. of points	%	Percentage of disturbed people
54,3	1	0,85	8
55÷60	0	0	0
60,3÷63,5	9	7,6	25÷40
65,1÷70	37	31,1	42÷60
70,1÷74,9	51	42,8	60,1÷79,9
75,1÷79,6	18	15,1	80,1÷98
81,8	1	0,85	100
85,5÷85,9	2	1,7	100

Table 3

Transportation means	Minimum percentage	Maximum percentage
Trams	0,4	18
Buses	0,01	7,5
Trolleybuses	0,04	7,8
Microbuses	1,1	15,9
Cars	34,2	95,27
Trucks	0,3	18,1
Tractors	0,01	2,9
Motorcycles	0,01	4,1
Trains	0,08	54,7

The percentage of different transportation means is presented in table 3. The noise level generated by trains measured at the limit of the rail area exceeded the admissible value with 2,2-12,7 dB(A).

Because in the majority of the measured points the admissible limits were exceeded, it was found to be necessary to apply some measures for acoustic arrangement of the urban roads.

7. ACOUSTICAL ARRANGEMENT OF THE URBAN ROADS

In order to reduce the noise on the roads in Timișoara City, some measures for acoustic arrangement were established and implemented. In this way, the old rail system was completely changed and replaced with a modern one, more silent, with better insulating properties. All the old noisy trams were replaced with a newer generation, but unfortunately not the newest one. On many streets it was improved or replaced the superstructure of the runway. Many crossings were modernized and semaphores were installed. One-way traffic was imposed for some streets and the speed of vehicles was limited. It was eliminated the presence in traffic of heavy trucks in the central area of the City. On some roads it was allowed the access only for certain categories of vehicles. On the other side, in order to avoid the presence of heavy trucks on the urban roads, it was started the construction of a ring-road for Timișoara. Protective green zones were implanted between the runways and the residential areas.

The effect of the implementation of these measures on the noise abatement were evaluated through new measurements performed in 46 measurement points, selected near some of the most important crossings of the urban roads from Timișoara City.

From the obtained data it results that in the 46 measured points, the equivalent noise level was reduced with 0,1-12,4 dB and in 32 points (69,56%) the noise level does not exceed any more the admissible value defined by STAS 10009-88.

In the following section, we present a comparison between the situation existing in these 46 measurement points before and after the implementation of noise abatement measures.

In table 4 and 5 we present the statistical distribution of the equivalent noise level and the percentage of disturbed people in those 46 measurement points before (table 4) and after (table 5) the implementation of noise abatement measures.

Table 4

Leq [dB]	No. of points	%	Percentage of disturbed people
63,5	1	2,2	37
66,2÷69,7	10	21,7	47÷59
70,1÷74,9	28	60,9	60÷79
75,1÷78,6	7	15,2	80,1÷97

Table 5

Leq [dB]	No. of points	%	Percentage of disturbed people
60,1÷65	16	38,4	25÷44
66,1÷69,9	18	39,1	47÷60
70,4÷74,2	11	23,9	61÷78
75,1	1	2,2	80,1

The average equivalent noise level in these 46 measurement points was 71,8 dB(A) for an average traffic intensity of 1260,7 aut./h before the application of noise abatement measures and 67,3 dB(A) for an average traffic intensity of 1429 aut./h after the implementation.

Table 6

Transportation means	Minimum percentage	Maximum percentage
Trams	0,4	15,1
Buses	0,01	2,7
Trolleybuses	0,04	3,0
Microbuses	2,9	10,9
Cars	68,7	95,27
Trucks	0,4	16,4
Tractors	0,03	1,4
Motorcycles	0,01	1,7
Trains	0,1	1,7

Table 7

Transportation means	Minimum percentage	Maximum percentage
Trams	0,4	47,9
Buses	0,1	8,6
Trolleybuses	0,1	1,9
Microbuses	2,1	16,8
Cars	39,6	93,6
Trucks	0,1	15,3
Tractors	0,1	1,4
Motorcycles	0,3	10,4
Trains	0,1	1,5

Regarding the average equivalent noise level existent at 2 meters distance from buildings, this one was 67,3 dB before the application of noise abatement measures and 62,7 dB after that.

The percentage of transportation means in these 46 measurement points is presented in table 6 (before application of noise abatement measures) and in table 7 (after application of noise abatement measures).

In the same time it was proved that an important contribution to the noise generated by the road transportation means on the urban roads has the tire/road contact, which can be reduced by covering the road superstructure with rubberized asphalt or with rubber pavement. Using these measures it is expected to obtain a noise level reduction with approximate 4 dB. These methods will be also useful for an increased traffic security realized through the elimination of the vehicle skidding.

8. CONCLUSIONS

After performing the investigations described in the paper, it was possible to evaluate the degree of phonic pollution for Timișoara City. The acoustical arrangement of the urban roads leads to a diminution of the pollution degree also a diminution of the percentage of disturbed people.

The measurements performed after the acoustical arrangement of the urban roads proved its efficiency. This can be underlined by comparing the results of the measurements performed before and after the acoustical arrangement of the urban roads. Once the acoustical arrangement of the urban roads proved its efficiency, these methods can be easily applied in every practical situation concerning traffic or industrial noise.

Finally one can conclude that the acoustical arrangement of the roads implemented in Timișoara City proved its efficiency.

REFERENCES

- [1] Bacria V., Herișanu N, Investigation and reduction of the phonic pollution in urban area, Bul. St. Univ. Poli. Timișoara, Tom 53(67), Fasc.2, 2008, p.95

- [2] Darabont A., Văiteanu D, Combaterea poluării sonore și a vibrațiilor, Ed. Tehnică, București, 1975
- [3] Enescu N., Magheți I., Sârbu M.A., Acustică tehnică, Ed. ICPE București, 1998
- [4] Grumăzescu M., Stan A., Wegener N., Marinescu V, Combaterea zgomotului și vibrațiilor în tehnică, Ed. Tehnică, București, 1964
- [5] Herișanu N., Bacria V., Toader M., Popa Radovan S., Investigation of noise pollution in an urban area, WSEAS Transaction on Systems, vol.5, no.7, 2006, p.1643
- [6] Stan A., Munteanu N., Ionescu-Ghermănescu C., Ion C., Dinu I., Mehedincu S., Considerații asupra nivelului intensității zgomotului de trafic în exteriorul clădirilor din zona centrală și semicentrală a municipiului București, Construcții, nr.10, 1973
- [7] * * * Ständtebauliche Lärmfibel. Hinweise für die Bauleitplanung. Baden-Württemberg-Innenministerium, 1991.
- [8] * * * Lärmbekämpfung in Wien. Entwicklung – Stand Tendenzen. Magistratsabteilung 22 Umweltschutz



HEAT TREATMENT OPTIMIZATION OF CANNED MEATS IN TERMS OF THE RESOURCE UTILIZATION AND THE QUALITY OF THE PRODUCTS

Zoltán FABULYA, György HAMPEL, Margaret NAGY

University of Szeged Faculty of Engineering, Institute of Economy and Rural Development
Szeged, Mars tér 7. HUNGARY

Abstract:

Heat treatment of canned food products, particularly canned meat products, requires considerable energy as the cans need sterilization. A heat treatment with a long time span and with a temperature of around 120°C will consume considerable quantities of fuel.

The heat treatment is used to avert microbiological danger. The operation regulation has to be defined in a way which produces a microbiologically reliable product, without harming its organoleptic peculiarities, substance, taste and flavour with an oversized treatment. In the interest of safety we have to define the extent and the time span of the heat effect leading to the destruction of the microbiological pathogens with the use of engineering calculations, modelling and computer simulation. We also have to secure the observance of the regulations obtained this way for the sake of the higher quality and the less resource utilization. This observance ability is answered with the help of our developed model for the computer simulation of heat treatment processes.

Keywords:

autoclave, heat treatment, modelling, simulation

1. INTRODUCTION

Heat treatment provides increased shelf life and is a defensive measure against microbiological hazards. Thus, inappropriate handling and violation of the operation regulation might have serious consequences. Therefore, heat treatment is a crucial point of food safety. With longer heat treatment the risk is decreased. However, if the heat treatment is too long, the quality of the product may decrease; the smell, the taste and the substance is in danger (liver products might develop distinctive colours and meat products might drip liquids etc.). Therefore the operation regulation and the control should be designed in a way so that the operation fulfils both safety and quality.

Heat treatment of canned goods and especially of meat products requires large quantities of energy as these products require long treatment at around 120 degree Celsius. Reducing the use of natural resources is an important goal in industrial processes – a few years ago this only meant saving energy, today it includes the paradigm of environment management and the paradigm of sustainable development – the goal is to reduce the energy usage or at least to produce more products without increasing energy usage [3]. Although reduction in the use of these resources (water, electricity, heat energy) obviously decreases the cost of manufacturing and increases the economy of manufacturing, it is not trivial to implement in many production plants as the cost of these resources is not calculated or measured at all, thus wasting resources is not visible. Similarly, increased quality and nutrition parameters might also remain undetected.

Insulating the heat treatment equipment is easy, but it requires changes in the technological process which raises food safety problems. Moreover, production plants are uneager to change the technological processes. Another problem is the high initial cost of measuring equipment and the required periodical replacement of sensors. The result is that only the most important data is collected. In heat treatment, this data is the core temperature and the outer temperature. In the field of heat treatment, general heat loss was an important

field around 1970 [4, 5, 8]. Around 1980, the heat utilization and heat intake ratio were important issues [1, 6, 7]. If the insulation is changed on the equipment, the technological processes must be changed in accordance with engineering calculations. Because of the above mentioned reasons, and because of the many parameters and many different processes, modelling and simulation should be combined with engineering calculations. The intensity and the length of the heat treatment must be calculated in a way to effectively neutralize microbiological hazards, and the resulting requirements must be implemented and monitored in order to achieve a higher quality.

In this work, we demonstrate the mathematical model of the steam requirements of a heat treatment process and a simulation application which incorporates the model and is capable of determining the collective resource usage of parallel heat treatment processes.

2. THE STUDY

2.1. Heat treatment values and calculations of the length and temperature of heat treatments

The neutralization of micro-organisms with heat treatment is studied since 1920. The most important micro-organisms' neutralization with wet steam can be expressed with a negative exponential equations (the correspondence and acceptability of the kinetic description of the primary reaction is based on the biological reason that supposedly wet steam denaturises vital proteins according to the monomolecular reaction) which means that consecutive identical heat treatments leave the same proportion of the initial number of micro-organisms alive.

For a given micro-organism and a given temperature, D denotes the required time to destroy 1 log cycle (90%) of the microorganism and z denotes the heat increment required to reduce D by a magnitude. The heat treatment value is denoted with F and is the value used for the longest time. F_0 is the same as F but implies $z=10$ °C for a given heat treatment, for a micro-organism with $z=10$ °C, the temperature changes on the slowest heat point of the treated object have the same neutralizing effect as keeping the temperature on 121.1 °C for F_0 minutes. The efficiency of heat treatments can be compared using F_0 .

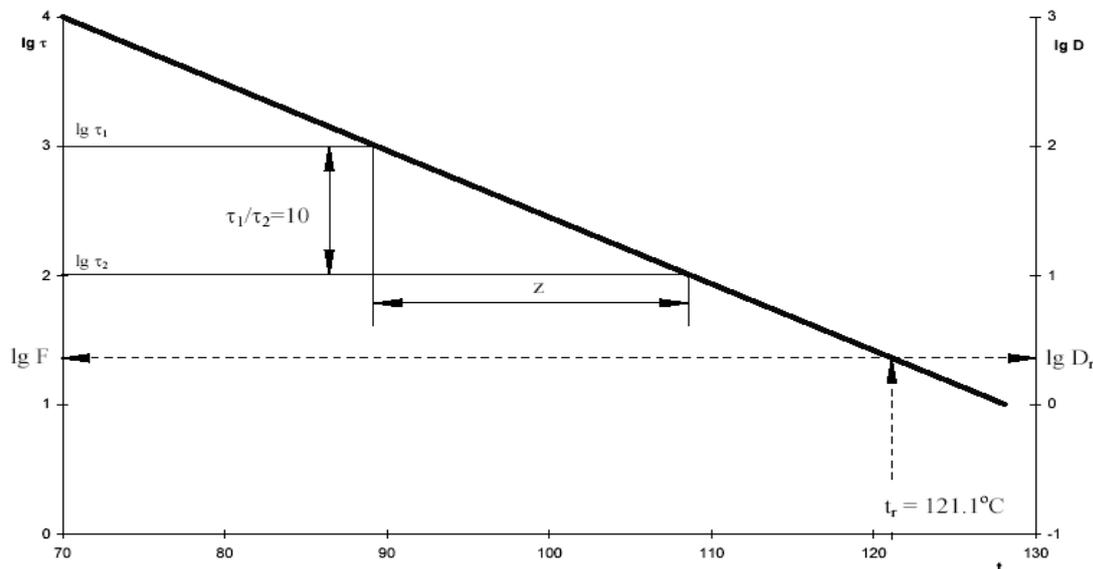


Figure 1. Neutralization of micro-organisms depending on the temperature

Figure 1 demonstrates the difference in temperature denoted by z , which reduces the thermal death time to one tenth. We might also plot a curve that is parallel with the thermal death curve with the help of the decimation times. As the decimation time measures the heat resistance of a micro-organism, this curve is referred to as heat resistance curve. We can calculate the formula of the equality of thermal death curve from the gradient and a point of the curve. A special point, according to international agreements, is the thermal death time at 121.1 °C (250 Fahrenheit) which is referred to as F-value. The D -value of the heat resistance

curve plotted with the decimation times at $121.1\text{ }^{\circ}\text{C}$ (reference temperature, t_r) is denoted by D_r .

We calculate the desired temperature of the sterilization bath (pasteurization bath, autoclave) and the desired length of the heat treatment with the help of the thermal death curve – referred to as the sterilization formula in the industry – if we know the temperature curve of the slowest heating point of the product, referred to as heat penetration curve in the industry.

The temperature of the slowest heat point of the product to be treated can be plotted against the time; this is the heat penetration curve. The curve displays the temperature change according to the three phases: heating, maintaining temperature, cooling. To design the heat treatment, the longest τ time required to destroy the required proportion of the micro-organisms relevant to the product on a feasible t temperature must be known. That is, the thermal death curve, similar to the one on *Figure 1* must be known.

We can calculate the relative neutralization speed for different t temperatures if we know the value of F and z , relative to the value of F/τ at $121.1\text{ }^{\circ}\text{C}$. To calculate the requirements of the heat treatment, the so-called sterilization curves are plotted from known heat penetration curve and the z -value from the micro-organism’s thermal death curve. Such a sterilization curve is demonstrated in *Figure 2*. On *Figure 2*, the heat penetration curve used to calculate the points of the sterilization curve is also displayed (with $z=10\text{ }^{\circ}\text{C}$).

To calculate the sterilization curve, we plot the relative thermal death speed (F/τ) instead of the temperature against the axis of heat treatment time. The integral of the sterilization curve is the sterilization value (F_0 value) which is in F -units.

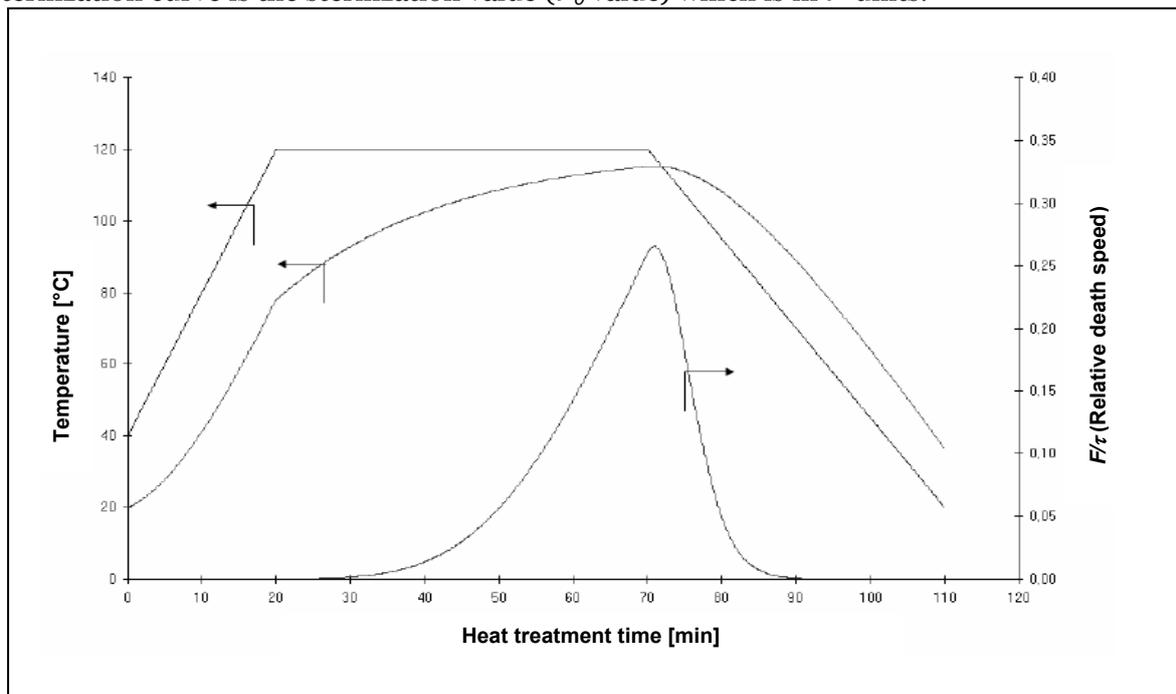


Figure 2. Plotting a sterilization curve from a heat penetration curve

As the z -value of the thermal death curve of *Clostridium botulinum* spores is between $14.7\text{--}16.3\text{ }^{\circ}\text{F}$, depending on the product, and the z -value of the thermal death curve of the internationally accepted reference spores of the putrefactive anaerobe bacteria strain *Clostridium sporogenes* P.A. 3679 is between $z=16.6\text{ }^{\circ}\text{F}$ and $z=20.5\text{ }^{\circ}\text{F}$. That is the reason of using an average value of $z=18\text{ }^{\circ}\text{F}=10\text{ }^{\circ}\text{C}$ in calculations. For *C. botulinum* spores, the highest registered D -value was 0.21 minutes on $121.1\text{ }^{\circ}\text{C}$. A worldwide standard for food products with a pH greater than 4.5 (for example, meat products) is to require a heat treatment that reduces the number of *C. botulinum* spores by twelve magnitudes. This is known as the $12D$ -concept. For that a $12 \cdot D$ minute long heat treatment is required which is $12 \cdot 0.21=2.52$ minutes on $121.1\text{ }^{\circ}\text{C}$ (so, the F -value of *C. botulinum* spores is 2.52 minutes). The required

length of the heat treatment for other temperatures can be calculated according to the information above with $z=10\text{ }^{\circ}\text{C}$.

2.2. Modelling the steam usage of a heat treatment

Heat treatment is performed in closed, pressurized units (autoclaves) from which typically 10 to 20 units are needed for treating canned food arriving from different production flows with a different flow rate and with different sizes and geometry [2]. The heat treatment in an autoclave is started when it is full with products requiring the same heat treatment. This results in a lower relative energy usage. An automated control system controls the temperature by regulating the amount of steam input (for heating and for keeping a temperature) and water input (for cooling).

On the upper part of Figure 3, the required temperature is displayed (as calculated from the sterilization curves). On the lower part of Figure 3, the required amount of steam is displayed (to be calculated later).

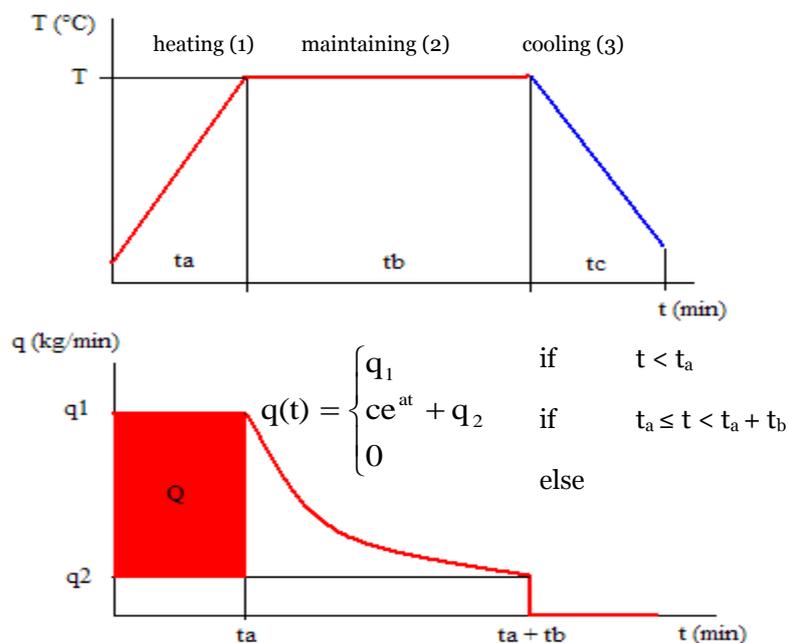


Figure 3. Development of temperature and steam mass flow in function of time
 Product-dependent data calculated from the sterilization curves:

T : required temperature ($^{\circ}\text{C}$)

t_a : heating time (minutes)

t_b : heat keeping time (minutes)

t_c : cooling time (minutes)

The parameters of the $q(t)$ steam mass flow (kg/minute) are yet to be calculated:

Q : Steam required for heating (kg), a product-independent constant

q_2 : steam mass flow loss (kg/minute), a product-independent constant

c, a : The curvature parameters of the $q(t)$ function, the first is independent of the product and the second depends on the first.

3. ANALISES, DISCUSSIONS, APPROACHES, INTERPRETATIONS

3.1. Mathematical model for steam mass flow

When modelling real-world phenomenon, considering every condition is impractical, if not impossible. For a simpler model, or even for a feasible model we must omit details that are (thought to be) less important. On the other hand, we should not over-simplify our model. We have to identify the parameters of the phenomenon and the connections between them.

In an autoclave, we have to determine the required steam mass flow, as a function of time, for a given heat treatment. The steam mass flow loss (q_2) is the amount of heat exiting on the hull of the equipment which depends on the insulation of the equipment from the

internal temperature and from the external temperature. On the other hand, individual autoclaves can be modelled as identical and all products are treated on almost the same temperature, so q_2 can be modelled as a product-independent constant during the whole heat treatment.

The amount of steam required for heating (Q) depends on the quantity of the product and from the difference of the maximum temperature and the initial temperature. As these are almost identical for every product, Q is also a product-independent constant.

Knowing q_2 , Q and t_a , the steam required for one time unit of the heating phase, the steam mass flow (q_1) can be calculated:

$$q_1 = q_2 + \frac{Q}{t_a} \quad (1)$$

In the second phase of the heat treatment, the heat keeping phase, the temperature of the cans converges to the internal temperature of the autoclave, thus the required steam mass flow is exponentially reducing from q_1 .

The curvature can be described by either the a or c parameter of the exponential arc, and the other can be calculated from the constraint that the arc starts from the value q_1 at the beginning of the heat keeping phase (at the t_a time instance). For example, for an arbitrary negative a :

$$q(t_a) = c \cdot e^{at_a} + q_2 = q_1 \Rightarrow c = \frac{q_1 - q_2}{e^{at_a}} \quad (2)$$

3.2. The adjustment of the parameter of the mathematical model

Using our results above, we can calculate the required steam mass flow for a single autoclave from three arbitrary chosen parameters (q_2 , Q , a). Now, which value combination of these parameters will result in the best model? To answer this question, we have to compare our measurements of the real process and the calculated process and find the parameter values with the smallest error. However, we do not have measurement data and the production plant is not planning to buy expensive measuring equipment to find the best model which can be simplified. As the gas usage of the furnace that produces the steam is measured, and we can calculate the gas usage of our model, we can calibrate our model based on the error in the gas usage between the simulated process and the real process. For that, we had to create a computerized simulation tool that is able to calculate the total gas usage for every minute of a 24-hour period, calculated from the total steam requirement (as in Figure 4) which is calculated from the individual steam requirements of the simulated heat treatments.

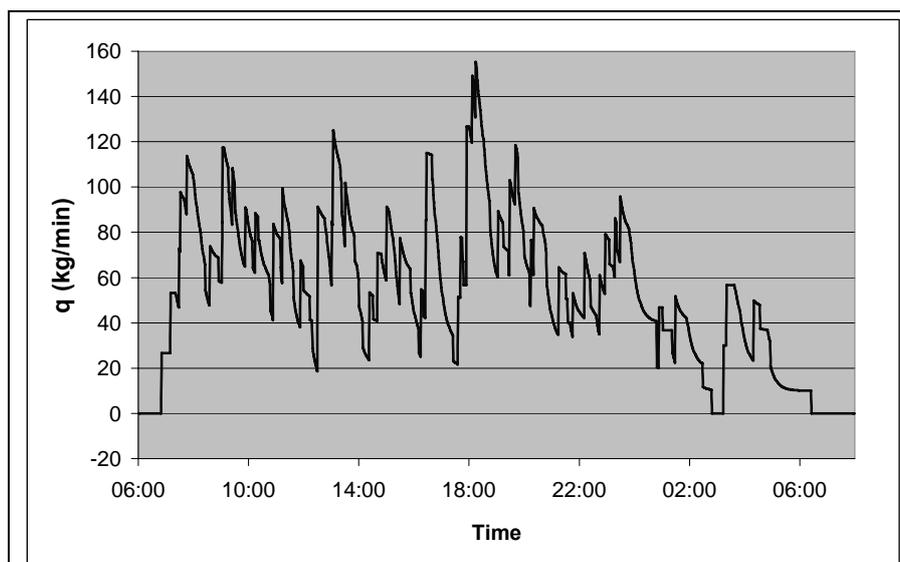


Figure 4. Total steam requirements of multiple autoclaves operating simultaneously

4. CONCLUSIONS

By comparing the simulated gas usage and the measured gas usage for the past heat treatments, the parameters of our mathematical model can be adjusted. At this point, the future gas usage can be calculated as well on a minute scale, thus we have an opportunity to prevent wasteful gas usage caused by an inefficient, unbalanced gas usage. That can be achieved by delaying some of the heat treatments in the heat treatment plan or production programming at the production lines. For this, we need adequate computer software and applications which requires further research.

REFERENCES

- [1] Bhowmik, S. R., Vichnevetsky, R., Hayakawa, K.-I. (1985): Mathematical model to estimate steam consumption in vertical still retort for thermal processing of canned foods. *Lebensmittelwissenschaft und Technologie* (18) (1) pp. 15-23.
- [2] Eszes, F., Rajkó, R., Szabó, G. (2003): Energia és vízfelhasználás csökkentés lehetőségeinek feltárása a húsiparban. 10 Symposium on Analytical and Environmental Problems, MTA Szegedi Akadémiai Bizottság Kémiai Szakbizottság Környezetvédelmi és Analitikai Munkabizottsága, Szegedi Tudományegyetem, Szeged, 2003. szeptember 29. Proceedings, pp. 169-174.
- [3] Kerekes, S., Szlávik, J. (1996): A környezeti menedzsment közgazdasági eszközei. Környezetvédelmi kiskönyvtár 2. Közgazdasági és Jogi Könyvkiadó.
- [4] Rao, M. A., Kenny, J. F., Katz, J., Downing, D.L. (1976): Computer estimation of heat losses in food processing plants. *Food Technology* (30) (3) 36.
- [5] Rao, M. A., Katz, J., Goel, V.K. (1978): Economic evaluation of measures to conserve energy in food processing plants. *Food Technology* (32) (4) 34.
- [6] Sielaff, H., Andrae, W., Oelker, P. (1982): Herstellung von Fleischkonserven und industrielle Speiseherstellung. VEB Fachbuchverlag Leipzig, 230-239.
- [7] Singh, R. P. (1986): Energy in Agriculture Volume I. Energy in Food Processing. Elsevier Amsterdam-Oxford-New York-Tokio.
- [8] Singh, R. P. (1978): Energy accounting in food process operations. *Food Technology* (32) (4) 40-43.



BLACK POPLAR (*POPULUS NIGRA*) GENE CONSERVATION IN THE SAND RIDGE REGION BETWEEN THE DANUBE AND THE TISZA

Gábor SZULCSÁN

KEFAG ZRT. Kecskemét, HUNGARY

ABSTRACT

The objective of black poplar (*Populus nigra*) gene conservation:

Black poplar is a native tree species of the Carpathian Basin. In the Danube-Tisza Mid-Region there are only some remaining scattered individual trees or population fragments at best, which are unsuitable for conducting sexual reproduction processes. Among the descendants via free-pollination of the few black poplar trees, which are situated in the crowd of hybrid poplars, we can hardly find black poplar-like descendants.

Its domestic spread, silvicultural and horticultural use as an ornamental plant shows an increasing tendency compared with the previous period, primarily because of the restrictions in nature reserve areas, the future use is expected to increase. In nature reserve areas, during forest establishment and forest regeneration it is the only possibility to afforest native tree species regardless of the previous culture.

In the Danube-Tisza Mid-Region we establish an identified ex-situ gene collection by questing the findable parent stock trees and by integrating ecotypes being conform to the environmental conditions of the region taking gene conservation and research aspects into consideration.

We carry out isoenzyme and DNA surveys on the parent stock trees marked due to the phenotypical characteristics. After receiving the laboratory results, we keep the species-identical (100% black poplar) genotypes in ex situ gene collections. We carry out monitoring of the collected material and create groups based on the characteristics as seen in order to be able to plan the further use.

We evaluate the characteristics and than we can create clone mixtures using the collected material offering the users alternative solutions, which are practicable for tree cultivation, nature preservation, gene conservation and farm or road afforestation, however natural and native.



Black poplar parent stock tree outside
Bugacpusztaháza



MORPHO-ANATOMICAL ANALYSIS OF SPIKE OF WHEAT GENOTYPES

J. LUKOVIĆ, L. ZORIĆ, Lj. MERKULOV, M. KODRANOV, B. KIPROVSKI

University of Novi Sad, Faculty of Natural Sciences,
Department of Biology and Ecology, D. Obradovića 2, 21000 Novi Sad, SERBIA

Abstract

The goal of the paper is to find, by means of an analysis of morpho-anatomical characteristics of the spike of tetraploid and hexaploid wheat genotypes, characteristics which most strongly influence the differences in yield. The hexaploid genotypes have a significantly longer spike, with a greater number and mass of grain/spike. For both groups, a normal distribution of the number and mass of grain/spikelet of a main shoot spike is notified. An analysis shows that the hexaploid genotypes have a greater cross section rachis area, and a greater number of the smaller vascular bundles, in comparison to the tetraploid ones.

Key words:

wheat, spike, morpho-anatomical analysis

1. INTRODUCTION

In different wheat cultivars, the total contribution of nonleaf green organs, including spikes and peduncles, accounts for about 40–50% of grain mass per spike, which is higher than the total contribution of the flag leaves and penultimate leaf blades [23, 1, 24]. In wheat, all parts of the spike, such as the awn, glume, lemma, palea, pericarp, and even peduncle, are capable of photosynthetic CO₂ fixation, and a considerable portion of grain mass derives from the photosynthesis of these organs [6, 18, 24]. Results of [13] suggested that awns play a dominant role in contributing to large grains and a high grain yield in awned wheat cultivars, particularly during the grain-filling stages.

To what extent will the spike realize its genetic potential depends on genetic factors and a number of physiological and biochemical processes both in the spike itself and in the whole plant. Besides by these factors, the yield is strongly influenced by environmental factors [20, 21]. The number of formed flowers per spike is higher than the number of formed grain [7]. One possible way how to affect assimilate distribution is to increase grain weight through increasing grain number [19, 8,]. Besides all other factors, flower formation is affected by the presence of adequate vascular tissue [12]. Analysing the twenty-six winter wheat varieties of different earliness and stem height [16] concluded that under conditions favourable for both a high rate of assimilate production and high sink capacity, the number and size of vascular bundles, and especially the phloem cross-sectional area, limit wheat productivity.

The goal of the paper is to find, by means of an analysis of morpho-anatomical characteristics of the spike of two tetraploid and two hexaploid wheat genotypes, those characteristics which most strongly influence the differences in final yield.

2. MATERIAL AND METHODS

The morpho-anatomical analysis of the main shoot was done in two tetraploid (NSD 3/93 and Novinka) and two hexaploid (NSO32 and NSP11) wheat genotypes. The experiment was conducted in field conditions, applying random block system with three replications, with planting density of 650-700 seedlings/m². The main shoot spikes were sampled during physiological maturity for the morphological analysis of the spike. For the anatomical analysis of the rachis, the sampling was done 10 days before full physiological maturity. For both analyses the sample was 30 spikes per genotype. Cross sections of the rachis, 20 μm thick, were made with Leica CM 1850 cryostat. Sections were observed and measurements made using Image Analyzing System Motic 2000 and included cross sections made at the 2nd, 8th and 13th internodes. The following characteristics were analysed: spike length, mass and number of grains per spike, mass and number of grains per spikelet, area of the cross section of the rachis, as well as number, height and width of central vascular bundles. The data were statistically processed using STATISTICA for WINDOWS version 8.0. The significance of differences in

mean values of measured parameters was determined using Duncan’s test, between the genotypes of the same ploidy level (means marked with the same letter do not differ) and t-test, between the genotypes that differ in ploidy level (* – significant for 0.05% and ** – significant for 0.01%).

3. RESULTS AND DISCUSSION

Yield is influenced by adequate production of photosynthetic assimilates and by the adequate capacity of the acceptor organ to accept products of photosynthesis. As the source and the acceptor of assimilates are affected by the effects of feedback, it is often difficult to determine whether it is the source or the acceptor that limits the yield in a particular case [25]. In our research, a significantly longer spike, with greater number and mass of grain/spike was found in the hexaploid genotypes (Table 1). Larger biomass, number of spikes and larger grain yield per plant in hexaploid wheat in comparison with tetraploids were found by [9].

Our results show that with the hexaploids the number of grains per spike is a more variable characteristic than grain mass or spike length, whereas with the tetraploids it is grain mass/spike which is a more variable characteristic (Table 1). The number of grains per unit area and the mass of individual grains are considered to be two main factors of yield [22]. Research has proved that the number of grains is a characteristic which has a stronger effect on the variation in grain yield, whereas the mass of grain is a more stable characteristic [10, 21]. During the period after flowering, the grain yield of wheat is either limited by the acceptor or co-limited by both the source and the acceptor, but is never limited by the source of assimilates [22].

Table 1. The spike morphological characteristics of wheat genotypes *

Genotype		Spike length (cm)		Grain number/spike		Grain mass/spike (g)	
		$\bar{x} \pm Se$ (CV%)		$\bar{x} \pm Se$ (CV%)		$\bar{x} \pm Se$ (CV%)	
T	NSD3/93	6.5 ± 0.1 (2.3)	a	29.1 ± 0.2 (1.4)	a	1.2 ± 0.1 (12.2)	a
	Novinka	6.1 ± 0.0 (0.5)	b	30.3 ± 0.6 (3.9)	a	1.3 ± 0.0 (4.6)	a
\bar{x}		6.3 ± 0.2		29.7 ± 1.6		1.25 ± 0.3	
H	NS 032	8.6 ± 0.1 (0.3)	a	41.6 ± 1.1 (2.4)	a	1.5 ± 0.0 (0.1)	a
	NSP 11	8.1 ± 0.1 (0.2)	b	39.3 ± 0.7 (1.4)	b	1.8 ± 0.0 (0.1)	b
\bar{x}		8.3 ± 0.2		40.4 ± 1.6		1.6 ± 0.1	
t- test		*		*		*	

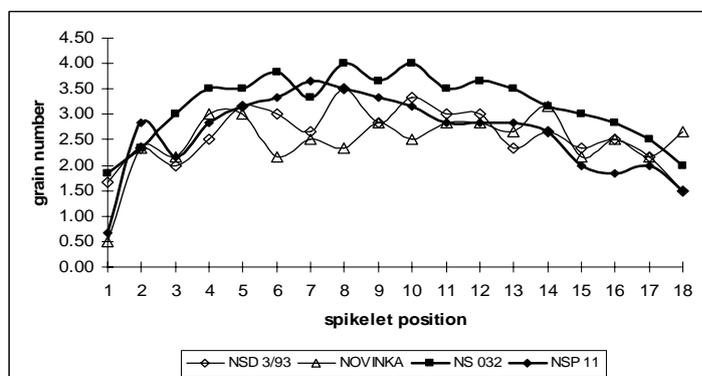


Figure 1. Distribution of grain number/spikelet for tetraploid and hexaploid genotypes

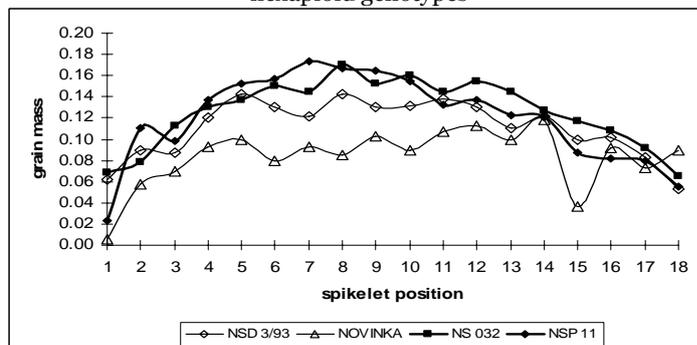


Figure 2. Distribution of grain mass/spikelet for tetraploid and hexaploid genotypes

* T-(tetraploid), H-(hexaploid), \bar{x} (means), Se (standard errors) and CV (coefficients of variation %)

The analysis of the number and mass of grain/spike of the main shoot in different positions in the spike shows greater variability and dispersion of these parameters in the tetraploid genotypes than in the hexaploid genotypes. In both groups these values rise from the basal spikelet (1st) to the more central ones, so they are highest from the 8th spikelet, and then they fall as we progress towards the 18th spikelet (Fig. 1, 2).

Miralles and Slafer [14] indicate that the mass of basal grains (grain next to the rachis) in central spikelets of the spike is larger than the mass of grains found in the same position in apical or basal spikelets. Similar findings are reported by [3], grains from the lower and middle section of the spike and the proximal floret positions were heavier than those from the upper spike section and the distal floret positions. The values for the number of grain/spike range from 0.5 (1st spikelet – Novinka)

to 4.0 (8th spikelet – NS 0.32) grains, and for the grain mass from 0.005g (1st spikelet – Novinka) to 0.173g (7th spikelet – NSP 11). Hexaploid genotypes have a greater number and mass of grains in almost all examined positions of the spikelet (Fig. 1, 2). Variability of grain mass in wheat is a result of the interaction between the potential to gather nutrients and the realization of this potential [11]. To a large extent, grain mass also depends on the speed and duration of the grain-filling period, as well as on the combination of these factors [2, 17, 4, 22, 15].

Significant differences between tetraploid and hexaploid genotypes were found in cross section rachis area for 2nd, 8th and 13th internodes level (Table 2, 3 and 4). Higher values were obtained in hexaploids. The values for number, height and width of vascular bundles of tetraploid genotypes were similar to the values of hexaploid genotypes for all internode levels.

Table 2. The anatomical 2nd internode rachis characteristics of wheat genotypes

		2 nd internode							
	genotype	cross section rachis area ($\mu\text{m}^2 \cdot 10^4$)		number of vascular bundles		height of vascular bundles (μm)		width of vascular bundles (μm)	
		$\bar{x} \pm \text{Se}$ (CV%)	a	$\bar{x} \pm \text{Se}$ (CV%)	b	$\bar{x} \pm \text{Se}$ (CV%)	a	$\bar{x} \pm \text{Se}$ (CV%)	a
T	NSD 3/93	213±18.0 (30.5)	a	17.1±1.2 (12.2)	b	176.4±2.9 (2.9)	a	151.9±2.2 (2.5)	a
	Novinka	190±6.1 (9.6)	a	23.3±0.5 (3.8)	a	172.2±5.7 (5.7)	a	150.5±5.9 (6.7)	a
	\bar{x}	201.5 ± 14.0		20.2 ± 0.9		174.3 ± 4.1		151.2 ± 5.2	
H	NS 032	315±31.2 (38.3)	a	21.8±0.3 (2.3)	a	174.7±6.1 (6.1)	a	160.9±8.7 (9.3)	a
	NSP 11	337±22.4 (25.7)	a	22.5±0.6 (4.9)	a	176.4±1.0 (1.0)	a	162.0±2.5 (2.6)	a
	\bar{x}	326.0 ± 15.6		22.1 ± 0.5		175.5 ± 2.1		161.4 ± 3.5	
t- test		*		ns		ns		ns	

Table 3. The anatomical 8th internode rachis characteristics of wheat genotypes

		8 th internode							
	genotype	cross section rachis area ($\mu\text{m}^2 \cdot 10^4$)		number of vascular bundles		height of vascular bundles (μm)		width of vascular bundles (μm)	
		$\bar{x} \pm \text{Se}$ (CV%)	a	$\bar{x} \pm \text{Se}$ (CV%)	b	$\bar{x} \pm \text{Se}$ (CV%)	a	$\bar{x} \pm \text{Se}$ (CV%)	a
T	NSD 3/93	105±5.7 (21.1)	a	12.6±0.7 (10.3)	b	166.4±4.5 (4.6)	a	150.0±2.0 (2.3)	a
	Novinka	112±6.3 (17.2)	a	17.1±0.9 (9.3)	a	159.8±7.9 (8.5)	a	134.4±7.9 (10.2)	b
	\bar{x}	108.5 ± 12.9		14.8 ± 0.7		163.1 ± 3.4		142.2 ± 3.6	
H	NS 032	199±21.0 (29.1)	b	15.0±0.3 (4.0)	a	163.9±7.6 (7.9)	a	135.4±3.7 (4.6)	b
	NSP 11	247±7.1 (17.3)	a	15.0±0.8 (8.6)	a	169.5±6.9 (7.0)	a	150.9±5.1 (5.8)	a
	\bar{x}	223 ± 8.4		15.0 ± 0.5		166.7 ± 3.4		143.1 ± 3.2	
t- test		**		ns		ns		ns	

The mass and volume of mature grain are highly correlated with the diameter of vascular bundles in the terminal internode [17]. The increase in the participation of assimilates which are transported to the spike is related to the adequate increase of phloem area, through which the assimilates are transported [6]. The variation in the development of the vascular system of the terminal internode affects the variation in the development of the seed. Pande et al. [17] think that these two factors are genetically related and that this is why wide variation of the vascular system of the terminal internode would be used to further increase the grain mass.

Table 4. The anatomical 13th internode rachis characteristics of wheat genotypes

		13 th internode							
	genotype	cross section rachis area ($\mu\text{m}^2 \cdot 10^4$)		number of vascular bundles		height of vascular bundles (μm)		width of vascular bundles (μm)	
		$\bar{x} \pm \text{Se}$ (CV%)	a	$\bar{x} \pm \text{Se}$ (CV%)	b	$\bar{x} \pm \text{Se}$ (CV%)	a	$\bar{x} \pm \text{Se}$ (CV%)	a
T	NSD 3/93	84.0±6.4 (29.1)	a	7.4±0.6 (13.5)	b	162.5±2.7 (2.8)	a	144.5±4.4 (5.3)	a
	Novinka	62.0±1.5 (7.3)	b	10.7±0.2 (3.7)	a	148.6±6.8 (7.9)	b	130.2±7.8 (10.4)	a
	\bar{x}	73.0 ± 11.9		9.0 ± 0.5		155.5 ± 6.6		137.3 ± 3.4	
H	NS 032	113±7.5 (18.9)	b	8.9±0.2 (3.4)	a	158.3±3.0 (3.3)	a	135.5±6.8 (8.7)	a
	NSP 11	159±7.1 (31.1)	a	8.6±0.5 (9.3)	a	154.1±3.1 (4.1)	a	138.1±1.7 (2.2)	a
	\bar{x}	136 ± 27.2		8.7 ± 0.3		156.2 ± 1.8		136.8 ± 2.2	
t- test		**		ns		ns		ns	

The results of this paper confirm the findings from the literature about the longer spike, larger number and mass of grain/spike of hexaploid genotypes. Higher variability and dispersion of the

number and mass of grain/spikelet of the main shoot in different positions in the spike were found in the tetraploid genotypes. The largest number and mass of grain per spikelet are detected in central spikelets in both groups. The analysis of the cross section of the rachis of tetraploid and hexaploid genotypes shows that significant differences exist only in the area of cross section of the 2nd, 8th and 13th internodes. The number and dimensions of central bundles of tetraploid and hexaploid wheat genotypes do not differ significantly. An analysis of the number and area of all vascular bundles, as well as the share of hlorenchyma in the peripheral parts of the rachis at individual levels of the rachis, will give more complete data in the anatomical analysis of the rachis.

REFERENCES

- [1] Araus JL, Brown HR, Febrero A, Bort J, Serret MD. Ear photosynthesis, carbon isotope discrimination and the contribution of respiratory CO₂ to differences in grain mass in Durum wheat. *Plant Cell Environ.* 16 (4), 383-392, 1993.
- [2] Brocklehurst PA. Factors controlling grain weight in wheat. *Nature* 266, 348-349, 1977.
- [3] Duggan BL, Fowler DB. Yield structure and kernel potential of winter wheat on the Canadian prairies. *Crop Science* 46 (4), 1479-1487, 2006.
- [4] Duguid SD, Brúlé-Babel AL. Rate and duration of grain filling in five spring wheat (*Triticum aestivum* L.) genotypes. *Can. J. Plant Sci.* 74, 681-686, 1994.
- [5] Evans LT, Dunstone RL. Some physiological aspects of evolution in wheat. *Aust. J. Biol. Sci.* 23, 725-741, 1970.
- [6] Evans LT, Rawson HM. Photosynthesis and respiration by the flag leaf and components of the ear during grain development in wheat. *Aust J Biol Sci* 23, 245-254, 1970.
- [7] Fischer RA. Number of kernels in wheat crops and the influence of solar radiation and temperature. *J. Agric. Sci.* 108, 447-461, 1985.
- [8] Frederick JR, Bauer PJ. Physiological and numerical components of wheat yield. In: Satorre EH, Slafer GA (eds): *Wheat Ecology and Physiology of Yield Determination*, Chapter No. 3, Food Products Press., 45-65, 2000.
- [9] Guzy MR, Ehdaie B, Waines JG. Yield and Its Components in Diploid, Tetraploid and Hexaploid Wheats in Diverse Environments. *Ann. Bot.* 64 (6), 635-642, 1989.
- [10] Hadjichristodolou A. Stability of 1000 grain weight and its relation with other traits of barley in the areas. *Euphytica* 51, 11 - 17, 1990.
- [11] Jenner CE. Factors in the grain regulating the accumulation of starch. *Royal Soc. Newzealand Bull.* 12, 901-908, 1974.
- [12] Langer RHM, Hanif MA. Study of Floret Development in Wheat (*Triticum aestivum*). *Ann. Bot.* 37, 743-751, 1973.
- [13] Li X, Wangm H, Li H, Zhang L, Teng N. Awns play a dominant role in carbohydrate production during the grain-filling stages in wheat (*Triticum aestivum*). *Physiologia Plantarum* 127, 701-709, 2006.
- [14] Miralles DJ, Slafer GA. Individual grain weight responses to genetic reduction in culm length in wheat as affected by source-sink manipulations. *Field Crop Research* 43, 55-66, 1995.
- [15] MÓu B, Kranstad WE. Duration and rate of grain filling in selected winter wheat populations. I. inheritance. *Crop Sci.* 34, (4), 833-837, 1994.
- [16] Nátrová Z, Nátr L. Limitation of kernel yield by the size of conducting tissue in winter wheat varieties. *Field Crops Research* 31 (1-2), 121-130, 1993.
- [17] Pande PC, Nagarajan S, Singh D, Pande HN. Some insights into differences in seed size in wheat. *Indian J. Plant Physiol.* 35 (4), 311-320, 1992.
- [18] Ram H, Singh R. Chlorophyll content, photosynthetic rates and related enzyme activities in ear parts of two wheat cultivars differing in grain yield. *Plant Physiol Biochem* 9, 94-102, 1982.
- [19] Siddique KHM, Whan BR. Ear:stem ratios in breeding populations of wheat: significance for yield improvement. *Euphytica* 73, 241-254, 1994.
- [20] Slafer GA, Andrade FH. Physiological attributes to the generation of grain yield in bread wheat cultivars released at different ears. *Field Crops Res.* 31, 351-367, 1993.
- [21] Slafer GA, Savin R. Developmental base temperature in different phenological phases of wheat (*Triticum aestivum*). *J. Exp. Bot.* 42, 1077-1082, 1991.
- [22] Slafer GA, Savin R. Source-sink relationships and grain mass at different positions within the spike in wheat. *Field Crop Research* 37, 39-49, 1994.
- [23] Thorne GN. Varietal differences in photosynthesis of ears and leaves of barley. *Ann. Bot.* 27, 155-174, 1963.
- [24] Wang ZM, Wei AL, Zheng DM. Photosynthetic characteristics of non-leaf organs of winter wheat cultivars differing in ear type and their relationship with grain mass per ear. *Photosynthetica* 39, 239-244, 2001.
- [25] Zelitch I. The close relationship between net photosynthesis and crop yield. *BioSci.* 32 (10), 797-802, 1982.



STATISTICAL EXPERIMENTAL DESIGN OF THE REMOVAL OF DIFFERENT COMPOUNDS FROM SYNTHETIC WASTEWATER BY MICELLAR-ENHANCED ULTRAFILTRATION

Szabolcs KERTÉSZ^a, Junkal LANDABURU-AGUIRRE^b, Veronica GARCIA^b,
Cecilia HODÚR^c, Eva PONGRÁCZ^{b,d}, Riitta L. KEISKI^b

^A School of Environmental Sciences, University of Szeged, Szeged, HUNGARY

^B University of Oulu, Department of Process and Environmental Engineering,
Mass and Heat Transfer Process Laboratory, FINLAND

^C Department of Mechanical and Process Engineering, University of Szeged, HUNGARY

^D University of Oulu, Thule Institute, Nortech Oulu, FINLAND

Abstract

In this study, the removal of zinc ions (Zn^{2+}) and n-butanol (n-BuOH), including salt (NaCl) from model synthetic wastewater was investigated by micellar-enhanced ultrafiltration (MEUF) using sodium dodecyl sulfate (SDS). Statistical experimental design was used in order to analyze the effect of initial concentration of Zn^{2+} , n-BuOH, SDS, NaCl on the process performance. Further, the effect of Transmembrane Pressure (TMP) and membrane nominal molecular weight limit (NMWL) were also studied. It was found that n-butanol could not be removed by using MEUF. On the contrary, Zn^{2+} was successfully removed obtaining rejection coefficients up to 99% in the most favorable conditions.

Keywords

MEUF, SDS, Zinc, MODDE, Factorial Design

1. INTRODUCTION

Heavy metal ions such as zinc are detected in the waste streams of mining operations, tanneries, electronics, electroplating and petrochemical industries, as well as in textile mill products [1]. Heavy metals toxicity in air, soil and water is a global problem and a threat to the environment and human health. Therefore, removal of heavy metals is a technological challenge with respect to industrial and environmental applications. Furthermore, volatile organic compounds (VOCs) such as n-butanol are also commonly present in industrial wastewaters. VOCs have been proven to be carcinogens and mutagens [2]. MEUF is a viable membrane-based separation technology for the simultaneous removal of heavy metals and organic compounds [3]. The principle of the process is that the surfactant monomers are aggregated to form micelles at concentrations higher than its critical micelle concentration (CMC) [4]. The solutes can be retained after being trapped by the micelles, whereas the untrapped species readily pass through the UF membranes [5]. Organic compounds are solubilised in the micelle interior and the metal ions get trapped on the surface of the oppositely charged micelles by electrostatic interaction [6]. The advantages of MEUF are low energy consumption as compared to Reverse Osmosis or Nanofiltration, relatively high fluxes and high removal efficiency. There is very few published information on the application of factorial designs by MODDE in the study of MEUF [7]. Factorial design is an efficient technique that can be applied to determine the main effects and interactions of these factors on process performance. Results of factorial design can subsequently be used to optimize and decrease the number of experiments needed. Furthermore, the use of raw material, time and natural resources will be decreased improving the efficiency of the process. This paper reports the removal of zinc ions from aqueous solutions containing n-butanol and sodium chloride by MEUF. The micelles were formed by adding the anionic surfactant sodium dodecyl sulfate (SDS) to the solutions. The main purpose was to separate zinc ions from the aqueous solutions. Additionally, the removal of n-butanol was also expected. Another goal of the present study was to screen the effect of pressure, membrane nominal molecular weight limit, the feed concentration of zinc, n-butanol, sodium chloride and SDS on the process performance.

2. MATERIAL AND METHODS

2.1. Chemicals and equipments

All chemicals involved in the experiments were of analytical reagent grade. Zinc chloride (ZnCl₂ extra pure 99.99%) and sodium dodecyl sulfate (SDS, purity > 99%) from Fisher Scientific, UK were used without further purification. SDS has a molecular weight of MW = 288.38 g/mol and its CMC equal to 8.2mM (2.36 g l⁻¹) [8].

N-butanol (obtained from Kemfine Oy, Finland) was supplied by Aldrich. The distilled water used in this study was purified by a Milli-Q plus water purification system (Millipore, USA) and had an initial resistivity of 18.2 MΩ-cm. N-butanol was determined by gas chromatography with a flame ionized detector (Agilent, 6890N). Sodium chloride (Merk, pro-analysi) was quantified.

The concentration of zinc was determined by Atomic Absorption Spectroscopy (Perkin Elmer 4100 with 3047 and 3044 flame atomization methods). The SDS content was analyzed by Total organic carbon portable analyzer (Sievers 900 Portable).

2.2. Experimental design

A set of experiments was designed by Modde 8.0 (Umetrics) using a fractional factorial design (Table 1). The factors and their respective range to be studied were pressure (P, 20 and 70 psi), SDS feed concentration (C_{SDS}, 3.5 and 20 mM), Zinc feed concentration (C_{Zn²⁺}, 0.5 and 3mM), Sodium Chloride feed concentration (C_{NaCl} 0 and 1w%), butanol feed concentration (C_{BuOH} 1 and 13 mM) and membrane nominal molecular weight limit (NMWL 3 and 10 kDa). Three centre points were included to analyze the reproducibility of the experiments.

Table 1. Experiments conducted using fractional factorial design and their respective results.

Experimental Number	Screening Part						Responses	
	Factors							
	C _{SDS} [mM]	C _{BuOH} [mM]	C _{Zn²⁺} [mM]	C _{NaCl} [mM]	Pres. [psi]	NMWL [kDa]	J [Lm ⁻² h ⁻¹]	R _{Zn²⁺} [%]
1	3.5	1	0.5	0	20	3	3.26	73.38
2	20	1	0.5	0	70	3	17.51	99.22
3	3.5	13	0.5	0	70	10	69.51	53.70
4	20	13	0.5	0	20	10	13.15	95.98
5	3.5	1	3	0	70	10	60.81	37.83
6	20	1	3	0	20	10	11.36	96.86
7	3.5	13	3	0	20	3	3.46	36.98
8	20	13	3	0	70	3	20.15	90.02
9	3.5	1	0.5	1	20	10	10.34	17.52
10	20	1	0.5	1	70	10	63.31	57.70
11	3.5	13	0.5	1	70	3	18.60	23.19
12	20	13	0.5	1	20	3	2.64	56.75
13	3.5	1	3	1	70	3	34.10	9.91
14	20	1	3	1	20	3	4.17	42.29
15	3.5	13	3	1	20	10	12.88	13.42
16	20	13	3	1	70	10	54.30	54.87
17	11.75	7	1.75	0.5	45	5	12.21	65.36
18	11.75	7	1.75	0.5	45	5	12.88	65.68
19	11.75	7	1.75	0.5	45	5	12.76	65.05

The measured responses were the rejection coefficients for zinc (R_{Zn}) and butanol (R_{BuOH}) and the absolute permeate flux (J_v), which were calculated with the following equations:

$$R = 1 - \frac{C_p}{C_r}, \quad (1)$$

where C_p and C_r are the zinc or n-butanol concentration in the permeate and retentate, respectively.

$$J_v = \frac{V}{t \times A}, \quad (2)$$

where J_v is the absolute permeate flux, V is the volume of the permeate sample collected, t is the time needed for collecting the permeate sample and A is the membrane effective area. The validity of the empirical models fitted with multiple linear regression (MLR) was tested with analysis of variance (ANOVA). The confidence level used was 95 %.

2.3. Dead-end micellar-enhanced UF experiments

All UF experiments were carried out in batch solvent resistant stirred cell (Millipore, Model 8400) with a capacity of 400 cm³. In all MEUF tests the TMP was controlled and adjusted with pressurized N₂ gas by means of a transducer. The operating temperature was 25 ± 1°C controlled by an air conditioner. The solution in the reservoir was agitated using a magnetic stirrer to provide efficient mixing at 500 rpm. This stirring speed was selected because it could lead a sufficient agitation to result

a homogenic solution without excessive vortex formation. The permeate flux was determined by measuring the first 100 cm³ (five times 20 cm³) of the feed solutions. In each experiment the first, second and the fifth permeate sample was analyzed and then integrally averaged because the compositions of the permeate varied during the experiments.

In the dead-end ultrafiltration (UF) experiments, UF flat sheet membranes of Amicon regenerated cellulose (PL series, Millipore) of different nominal molecular weight limits were used. Each membrane has a membrane effective area of 0.004m². Only the membranes with a deviation of the pure water flux, measured before and after MEUF tests, smaller than 5 % were repeatedly used. Ultra distilled water was used after each experiment test for membrane cleanings.

2.4. Experimental procedures

The initial feed volume was 200 cm³. The average permeate flux was calculated by measuring the time needed for collecting permeate samples of 20 cm³. The ultrafiltration experiments were carried out until 100 cm³ of the total sample was filtered (VCF = 2). The VCF is defined in Eq. (3):

$$VCF = V_b / V_e \quad (3)$$

where V_b and V_e are the volumes of solutions in the MEUF device at the beginning and at the end of the test, respectively. The membrane was submerged before the concentration tests for 1 h to reach equilibrium with the solution.

3. RESULTS AND DISCUSSIONS

The main purpose was the simultaneous removal of Zn²⁺ and n-BuOH by MEUF. From table 1 can be observed that butanol was not removed using micellar-enhanced ultrafiltration. The reason why the R_{BuOH} is not included in Table 1 is that, in all cases, the rejection coefficients of BuOH were very low (average 5 ± 2 %). Therefore, the research was continued in order to see the effect of the mixture of butanol and salt in the removal of zinc by micellar-enhanced ultrafiltration. In this way, the responses included in the experimental design were R_{Zn} and J_v .

3.1. Effects of factors on the absolute permeate flux

The effect of single factors on the permeate is illustrated in Fig. 1, displaying the change in the response when a factor varies from its low level to its high level while all other factors are kept at their averages. Negligible effects are those where the confidence interval includes zero.

As it can be observed from Fig. 1, pressure has a positive effect on the absolute permeate flux as expected. This means that increasing the pressure, higher permeate flux will be achieved. When pressure is increased the driving force is also increased obtaining a higher flux. NMWL has also a positive effect. Consequently, using a higher pore size membrane higher flux will be observed. Further, concentrations of SDS, BuOH, Zn²⁺ and NaCl show a negligible effect on the absolute permeate flux.

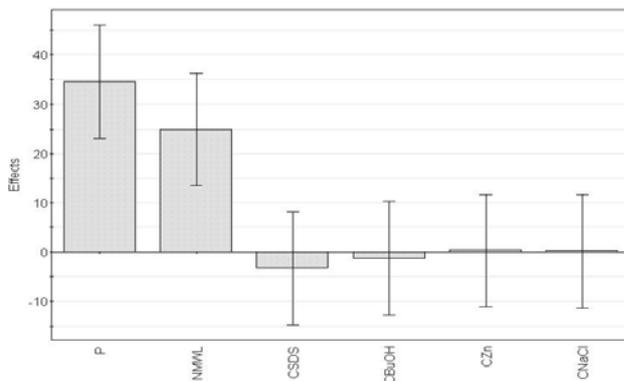


Figure 1. Effect of main factors on the absolute permeate flux varies from its low level to its high level while all other factors are kept at their averages. Negligible effects are those where the confidence interval includes zero.

As it can be observed from Fig. 2, the concentration of SDS, NaCl and the Zn²⁺ have the major effect on the rejection coefficient. Concentration of SDS has a most significant positive effect, thus, when increasing the SDS feed concentration, the rejection coefficient is also increased. This is because at higher SDS concentration, more SDS is present in micellar form. NaCl concentration of the feed has a negative effect on the rejection coefficient, therefore, increasing it will decrease rejection. This result complies with earlier study [9] reported in the literature. Since Na⁺ is a monovalent ion, it can readily bind with the negative charge head of the micelle competing with the heavy metal cations. Therefore, rejection coefficient decreases with an increase in the salt concentration. Further, zinc feed concentration also shows a negative effect on the rejection coefficient. Consequently, when increasing the zinc feed concentration rejection coefficient decreases. This shows that MEUF is more efficient for

When evaluating the validity of the fitted model with ANOVA, the regression model is statistically significant with a 95% confidence level in the range studied. The response variation percentage explained by the model, R^2 , for the permeate flux is 0.85. The response variation percentage predicted by the model, Q^2 , is 0.60. The reproducibility of the experiments is good.

3.2. Effect of factors on the rejection coefficient

The effect of single factors on the permeate is illustrated in Fig. 2, displaying the change in the response when a factor varies from its low level to its high level while all other factors are kept at their averages. Negligible effects are those where the confidence interval includes zero.

diluted heavy metal streams. Further, concentrations of NMWL, BuOH and pressure show a negligible effect on the rejection coefficient.

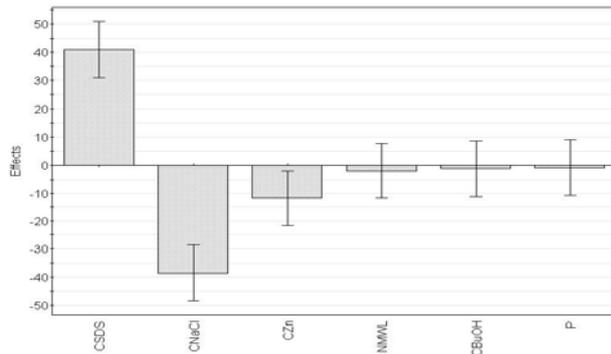


Figure 2. Effect of factors on the rejection coefficient of zinc

salt (NaCl) from model synthetic wastewater was investigated by micellar-enhanced ultrafiltration (MEUF) using an anionic surfactant agent, sodium dodecyl sulfate (SDS).

It was found that n-butanol could not be removed by using MEUF. On the contrary, Zn^{2+} was successfully removed obtaining rejection coefficients up to 99% in the most favorable experimental conditions.

A statistical experimental design (including Screening Part, SP) was used in order to analyze the effect of initial concentration of Zn^{2+} , n-BuOH, SDS, NaCl on the process performance. Further, the effect of Transmembrane Pressure (TMP) and membrane nominal molecular weight limit (NMWL) were also studied.

Pressure and NMWL have the most significant positive effects on the absolute permeate flux. Concentration of SDS has the most important positive effect, while NaCl has the most important negative effect on the rejection coefficient. Further, Zn^{2+} feed concentration has the major negative effect on the rejection coefficient.

By using fractional factorial design, the effects of 6 different factors on the MEUF process performance were evaluated in only 19 experiments. This shows the high effectiveness of experimental design for screening experiments. Further, experimental designs can now be developed as the factors with statistically no significant effect are identified.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support provided by KNRETo7/2005 Hungarian project and the Maj and Tor Nessling Foundation, the Academy of Finland and the Global Change Programme of the Thule Institute at the University of Oulu.

REFERENCES

- [1] T.G. Chuah, A. Jumariah, I. Azni, S. Katayon, S.Y.T. Choong, Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview, *Desalination* 175, 305–316, (2005)
- [2] Y. Kuo-Pin, W.M. L. Grace, W.M. Huang, W. Chihcheng, Y. Shinhao, The correlation between photocatalytic oxidation performance and chemical/physical properties of indoor volatile organic compounds, *Atmospheric Environment* 40 (2), 375–385, (2006)
- [3] D. Chandan, D. Sunando and D. Sirshendu, Prediction of permeate flux and counterion binding during cross-flow micellar-enhanced ultrafiltration, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 318, 125–133, (2008)
- [4] L. Chi-Wang, L. Chuan-Kun and Y. Wei-Shuen, Micellar-enhanced ultrafiltration (MEUF) with mixed surfactants for removing Cu (II) ions, *Chemosphere* 63, 353–358, (2006)
- [5] B.R. Fillipi, L.W. Brant, J.F. Scamehorn and S.D. Christian., Use of Micellar-Enhanced Ultrafiltration at Low Surfactant Concentrations and with Anionic–Nonionic Surfactant Mixtures, *J. Colloid Interface Sci.* 213, 68–80, (1999)
- [6] J. Lee, J.-S. Yang, H.-J. Kim, K. Baek and J.-W. Yang, Simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed surfactant, *Desalination* 184, 395–407, (2005)
- [7] X. Ioannis, J. Agnieszka and Z.-T. Grażyna, Response surface methodology for the modelling of copper removal from aqueous solutions using micellar-enhanced ultrafiltration, *J. Membr. Sci.* 321 (2), 222–231, (2008)
- [8] M. Rosen, *Micelle Formation by Surfactants*, in *Surfactants and Interfacial Phenomena*, 2nd edition, John Wiley & Sons, Inc. 122, (1989)
- [9] V.D. Karate and K.V. Marathe, Simultaneous removal of nickel and cobalt from aqueous stream by cross flow micellar enhanced ultrafiltration, *J. Hazard. Mater.* 157 (2-3), 464–471, (2008)



PLANT COVER OF THE SALINE GRASSLAND IN THE RIPARIAN ZONE OF THE OKANJ OXBOW LAKE (THE VOJVODINA PROVINCE, SERBIA)

A. KNEŽEVIĆ¹, P. BOŽA², M. STANKOV², LJ. NIKOLIĆ¹,
S. STOJANOVIĆ¹, D. DŽIGURSKI¹, B. LJEVNAIĆ¹, D. POLIĆ²

¹ University of Novi Sad, Faculty of Agriculture,
Trg D.Obradovića 8, 21 000 Novi Sad, SERBIA

² University of Novi Sad, Faculty of Sciences,
Trg D. Obradovića 3, 21 000 Novi Sad, SERBIA

Abstract

The Okanj oxbow lake is located in the alluvial flood plain of the Tisza River, north of the village of Elemir in central Banat (the Vojvodina Province, Serbia). Saline pastures predominate in the riparian zone of Okanj. The plant cover of the zone is characterized by the following floristic (182 identified taxa, i.e., 166 species, 7 subspecies, 2 varieties, 6 forms and 1 *lusus naturae*) and phytocoenological (3 classes, 5 orders, 6 alliances and 14 associations) elements. It is important to mention that out of the 174 characteristic taxa (166 species, 7 subspecies and, because of its plant-geographic and ecological significance, the Pontic-Pannonian plant species *Aster tripolium* var. *pannonicus*), 44 or 25.29% of them have the ecological index **S**₊, which defines the Okanj oxbow lake as a part of a halobiome occupying the Tisza's meander scars.

Associations *Scirpo-Phragmitetum*, *Bolboschoenetum maritimi continentale*, *Suaedetum pannonicae*, *Salsoletum sodae*, *Puccinellietum limosae*, *Pholiuro-Plantaginetum tenuiflorae*, *Hordeetum histricis*, *Camphorosmetum annuae*, *Halo-Agrostetum albae*, *Agrostio-Alopecuretum pratensis*, *Agrostio-Beckmannietum*, *Plantaginetum-Festucetum pseudovinae*, *Artemisio-Festucetum pseudovinae* and *Achilleo-Festucetum pseudovinae* are the specific phytocoenological elements of the observed halobiome.

Droughts and increasing anthropogenic influences keep degrading the ecosystem and if protective measures are not applied shortly, the rare stenovalent euhalophytes *Suaeda pannonica* and *Salsola soda* as well as the associations they predominate, *Suaedetum pannonicae* and *Salsoletum sodae*, respectively, will soon disappear.

Key words:

the Okanj oxbow lake, flora, vegetation, halobiome, protection

1. INTRODUCTION

In the region of central Banat (the Vojvodina Province, Serbia), several oxbow lakes had been formed in cut off meanders of the Tisza River by the action of ground and surface waters and precipitation. Significant among those, going from north to south, are Slano Kopovo, northeast of the town of Novi Bečej, Ostrovo, north of the village of Melenci, Rusanda, west of Melenci, and Okanj, north of the village of Elemir.

Plant covers of the riparian zones of Slano Kopovo, Ostrovo and Rusanda have been studied in considerable detail (Knežević et al. 2003, Knežević et al. 2005a, Knežević et al. 2005b). On the other hand, data on the plant cover in the riparian zone of Okanj are much scantier (Knežević 1994).

The objectives of this paper are to bring to attention the specific features of the flora and vegetation of saline pastures located in the riparian zone of Okanj, to support the

initiative for protection of the Okanj ecosystem, submitted by "Okanj", Society for Environmental Protection from Elemir, to the Directorate for Environmental Protection of Serbia, and to urge the Directorate to legislate the initiative on a short notice because the Okanj ecosystem is seriously threatened in consequence to persistent droughts and intensive negative anthropogenic influences.

2. INVESTIGATED AREA

According to Walter climodiagram made at the meteorological station in Zrenjanin, the region of central Banat which includes the village of Elemir has an average annual rainfall of 574 mm and an average annual temperature of 11.1°C. The beginning of vegetation period (April) in that region is characterized by an abrupt increase in the amount of rainfall and a considerable but gradual increase of temperature. After reaching peak discharge in June, the amount of rainfall drops abruptly. Conversely to the rainfall, the gradually increased temperatures persist through the medium part of the vegetation period and they start to go down at an increased rate only after most severe droughts in October. Because of such relationship of rainfall to temperature, the period from July to October is semidry, which is unfavorable for the vegetation of the investigated region (Knežević et al. 2003).

As a result of such climate pattern, the Okanj ecosystem has highest water level in the course of spring. During that period, the length of Okanj is up to 4.5 kilometers, the width is about 500 meters, and the depth in the middle zone is over 1 meter. Each year during the semidry period, the water level in Okanj drops down significantly. In some years, because of intensive evaporation, the entire lake runs dry.

The soil of the riparian zone of Okanj is solonchakic solonetz, but in the extensive pastures around Okanj the solonchakic solonetz soil surrounds areas under uncultivated calcareous chernozem (micellar) on the loess terrace (Nejgebauer et al. 1971).

3. MATERIAL AND METHODS

The presented data on the plant cover of the saline sites in the riparian zone around the Okanj oxbow lake include results from previous studies of saline flora of Banat (Knežević 1994) and the results of the present study.

Plants have been determined and their names used in accordance with the nomenclatures published in "Flora of SR Serbia" (Josifović, M. ed. I-X, 1970-1976), "Flora Europaea" (Tutin et al. 1960-1980, "A magyar flóra és vegetáció rendszertani-növényföldrajzi kézikönyve" (Soó I-VII, 1964-1985) and "Iconography of the Flora from the South-Eastern part of Central Europe" (Jávorka & Csapody, 1975).

Salinity values have been assessed on the basis of the ecological index of Landolt (Landolt 1977; Knežević 1994).

Syntaxonomic position of the halophytic communities occupying the sites surrounding the Okanj oxbow lake has been defined in accordance with the publications "A magyar flóra és vegetáció rendszertani-növényföldrajzi kézikönyve" (Soó V. 1973) and "Halophytic Vegetation of the Yugoslav Portion of the Banat Region" (Knežević et al. 1989).

4. RESULTS AND DISCUSSION

Following taxa have been found at sites in the riparian zone of the Okanj oxbow lake:

- | | |
|---------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| 1. <i>Achillea millefolium</i> L. /S./, | 12. <i>Arabidopsis thaliana</i> (L.) Heynh. /S./, |
| 2. <i>Achillea millefolium</i> L. subsp. <i>pannonica</i> (Scheele) Hayek /S./, | 13. <i>Artemisia maritima</i> L. subsp. <i>salina</i> (Willd.) Gams. /S+/, |
| 3. <i>Achillea setacea</i> W. et K. /S./, | 14. <i>Artemisia pontica</i> L. /S./, |
| 4. <i>Agrimonia eupatoria</i> L. /S./, | 15. <i>Artemisia vulgaris</i> L. /S./, |
| 5. <i>Agropyrum repens</i> (L.) Beauv. /S+/, | 16. <i>Aster tripolium</i> var. <i>pannonicus</i> (Jacq.) Beck /S+/, |
| 6. <i>Agrostis alba</i> L. /S./, | 17. <i>Atriplex litoralis</i> L. /S+/, |
| <i>Agrostis alba</i> L. f. <i>coarctata</i> Rchb., | 18. <i>Ballota nigra</i> L. /S./, |
| 7. <i>Allium atropurpureum</i> W. et K. /S./, | 19. <i>Beckmannia eruciformis</i> (L.) Host /S+/, |
| 8. <i>Allium vineale</i> L. /S./, | 20. <i>Bidens tripartita</i> L. /S./, |
| 9. <i>Alopecurus pratensis</i> L. /S./, | 21. <i>Bolboschoenus maritimus</i> (L.) Palla /S+/, |
| 10. <i>Althea officinalis</i> L. /S./, | <i>Bolboschoenus maritimus</i> (L.) Palla var. |
| 11. <i>Anthemis austriaca</i> Jacq. /S./, | <i>compactus</i> (Hoffm.) Jáv., |

22. *Bromus commutatus* Schrad. /S-/,
 23. *Bromus mollis* L. /S-/,
Bromus mollis L. f. *nanus* Weig.,
 24. *Bromus sterilis* L. /S-/,
 25. *Bupleurum tenuissimum* L. /S+/,
 26. *Calystegia sepium* (L.) R. Br. /S-/,
 27. *Camphorosma annua* Pall. /S+/,
 28. *Capsella bursa-pastoris* (L.) Medik. /S-/,
 29. *Carduus acanthoides* L. /S-/,
 30. *Carduus nutans* L. /S-/,
 31. *Carex gracilis* Curt. /S-/,
 32. *Carex humilis* Leysser /S-/,
 33. *Carex pseudocyperus* L. /S-/,
 34. *Carex vulpina* L. /S-/,
 35. *Centaurea banatica* Roch. ex Rchb. /S-/,
 36. *Centaurea pannonica* (Heuff.) Simk. /S-/,
 37. *Cephalaria subilvanica* (L.) Schrad. /S-/,
 38. *Cerastium dubium* (Bast.) Schwarz. /S-/,
 39. *Cerastium pumilum* Curt. /S-/,
 40. *Chartamus lanatus* L. /S-/,
 41. *Chenopodium apulifolium* Schrader /S-/,
 42. *Chenopodium glaucum* L. /S+/,
 43. *Chondrilla juncea* /S-/,
 44. *Cichorium intybus* L. /S-/,
 45. *Cirsium arvense* (L.) Scop. /S+/,
 46. *Cirsium palustre* (L.) Scop. (S-),
 47. *Consolida orientalis* (Gay.) Schröd. /S-/,
 48. *Convolvulus arvensis* L. /S-/,
 49. *Crepis foetida* L. subsp. *rhoaedifolia*
 (M. B.) Fiori et Paol. /S-/,
 50. *Crepis setosa* Hall. /S-/,
 51. *Crepis tectorum* L. /S-/,
 52. *Crypsis aculeata* (L.) Aitt. /S+/,
 53. *Cynoglossum montanum* Höjer /S-/,
 54. *Cynodon dactylon* (L.) Pers. /S-/,
 55. *Dactylis glomerata* L. /S-/,
 56. *Daucus carota* L. /S-/,
 57. *Descurainia sophia* (L.) Webb. /S-/,
 58. *Dipsacus laciniatus* L. /S-/,
 59. *Epilobium adnatum* Griseb. /S-/,
 60. *Erigeron canadensis* L. /S-/,
 61. *Erophila verna* (L.) Schevall. /S-/,
 62. *Erysimum repandum* L. /S-/,
 63. *Euclidium syriacum* /L./ R. Br. /S-/,
 64. *Euphorbia esula* L. /S-/,
 65. *Festuca ovina* L. /S-/,
 66. *Festuca vallesiaca* Sch. subsp. *Pseudovina*
 (Hack.) A. et G. /S+/,
 67. *Fragaria viridis* Duchesne /S-/,
 68. *Gagea arvensis* (Pers.) Dumort. /S-/,
 69. *Gagea pratensis* (Pers.) Dumort. /S-/,
 70. *Galium aparine* L. /S-/,
 71. *Galium molugo* L. /S-/,
 72. *Galium pedemontanum* All. /S-/,
 73. *Galium verum* L. /S-/,
 74. *Geranium columbinum* L. /S-/,
 75. *Geranium dissectum* Jusl. /S-/,
 76. *Geranium molle* L. /S-/,
 77. *Geranium pusillum* Burm. /S-/,
 78. *Glyceria maxima* (Hortm.) Holombg. /S-/,
 79. *Gratiola officinalis* L. /S-/,
 80. *Gypsophila muralis* L. /S-/,
 81. *Heleocharis palustris* (L.) R. Br. /S-/,
 82. *Helminthia echioides* (L.) Gärtn. /S-/,
 83. *Holosteum umbelatum* L. /S-/,
 84. *Hordeum maritimum* With. subsp.
gussoneanum (Parl.) A. et G. /S+/,
 85. *Hordeum murinum* L. /S-/,
 86. *Inula britannica* L. /S+/,
Inula britannica L. f. *angustifolia* Marson.,
 87. *Lactuca saligna* L. /S+/,
 88. *Juncus compressus* Jacq. /S+/,
 89. *Juncus gerardi* Lois. /S+/,
 90. *Lamium amplexicaule* L. /S-/,
 91. *Lamium purpureum* L. /S-/,
 92. *Lepidium draba* L. /S-/,
 93. *Lepidium perfoliatum* L. /S-/,
 94. *Lepidium ruderales* L. /S-/,
 95. *Lolium perenne* L. /S-/,
 96. *Lotus tenuis* Kit. /S-/,
 97. *Lycopus europeus* L. /S-/,
 98. *Lythrum salicaria* L. /S-/,
 99. *Lythrum virgatum* L. /S-/,
 100. *Malva silvestris* L. /S-/,
 101. *Matricaria chamomilla* L. /S+/,
Matricaria chamomilla L. f. *salina* (Schur) Jáv.
 102. *Matricaria inodora* L. /S+/,
 103. *Medicago lupulina* L. /S-/,
 104. *Melilotus officinalis* (L.) Pallas /S-/,
 105. *Mentha pulegium* L. /S+/,
Mentha pulegium L. l. *roseiflora* Priszter
 106. *Muscari racemosum* (L.) Mill. /S-/,
 107. *Myosotis collina* Hoffm. /S-/,
 108. *Myosurus minimus* L. /S-/,
 109. *Oenanthe silaifolia* M.B. /S+/,
 110. *Ononis spinosa* L. /S-/,
 111. *Ornithogalum umbellatum* L. /S-/,
 112. *Papaver rhoeas* L. /S-/,
 113. *Pastinaca sativa* L. /S-/,
 114. *Pholiurus pannonicus* (Host) Trin. /S+/,
 115. *Phragmites communis* Trin. /S+/,
Phragmites communis Trin. f. *stolonifera*
 (G. F. W. Meyer) Hegi,
 116. *Picris hieracioides* L. /S-/,
 117. *Plantago maior* L. /S+/,
 118. *Plantago schwarzenbergiana* Schur /S+/,
 119. *Plantago tenuiflora* W. et K. /S+/,
 120. *Poa pratensis* L. /S-/,
 121. *Podospermum canum* C.A. Mey. /S+/,
 122. *Polygonum arenarium* W. et K. /S-/,
 123. *Polygonum aviculare* L. /S-/,
 124. *Potentilla argentea* L. /S-/,
 125. *Prunus spinosa* L. (S-),
 126. *Puccinellia limosa* (Schur) Holmb. /S+/,
 127. *Pulicaria dysenterica* (L.) Gaertn. /S+/,
 128. *Ranunculus pedatus* W. et K. /S-/,
 129. *Ranunculus sardous* Cr. /S+/,
 130. *Roripa kernerii* Menyh. /S+/,
 131. *Rubus fruticosus* L. /S-/,
 132. *Rumex crispus* L. /S+/,
 133. *Salsola soda* L. /S+/,
 134. *Salvia austriaca* Jacq. /S-/,
 135. *Salvia nemorosa* L. /S-/,
 136. *Sambucus ebulus* L. /S-/,
 137. *Sambucus nigra* L. (S-),
 138. *Schoenoplectus lacuster* (L.) Palla /S-/,
 139. *Scilla autumnalis* L. /S-/,
 140. *Senecio vernalis* W. et K. /S+/,
 141. *Silene alba* (Mill.) Krause /S-/,
 142. *Silene viscosa* (L.) Pers. /S+/,
 143. *Sinapis arvensis* L. /S-/,
 144. *Sonchus arvensis* L. /S+/,
 145. *Statice gmelini* Willd. subsp. *Hungaricum*
 (Klokov) Soó /S+/,
 146. *Suaeda pannonica* Beck /S+/,
 147. *Symphytum officinale* L. /S-/,

148. *Taraxacum laevigatum* (Willd.) DC. /**S**./,
149. *Taraxacum officinale* Weber /**S**₊./,
150. *Taraxacum serotinum* (W. et K.) Poir.
subsp. *bessarabicum* (Horn.) Hand.
–Mazz. /**S**₊./,
151. *Thlaspi arvense* L. /**S**./,
152. *Thymus marschallianus* Willd. /**S**./,
153. *Trifolium angulatum* W. et K. /**S**₊./,
154. *Trifolium campestre* Schreb. (**S**-),
155. *Trifolium fragiferum* L. /**S**₊./,
Trifolium fragiferum L. f. *rigidifolium*
Hendrych.
156. *Trifolium pratense* L. /**S**./,
157. *Trifolium repens* L. /**S**./,
158. *Trifolium strictum* (L.) Jusl. /**S**₊./,
159. *Tussilago farfara* L. /**S**./,
160. *Urtica dioica* L. /**S**./,
161. *Urtica urens* L. (**S**-),
162. *Valerianella dentata* Pall. /**S**./,
163. *Valerianella locusta* (L.) Betsche /**S**./,
164. *Valerianella rimosa* Bast. /**S**./,
165. *Verbascum blattaria* L. /**S**₊./,
166. *Verbena officinalis* L. /**S**./,
167. *Veronica anagalloides* Guss. /**S**./,
168. *Veronica arvensis* L. /**S**./,
169. *Veronica hederifolia* L. /**S**./,
170. *Veronica polita* Fr. /**S**./,
171. *Vicia angustifolia* L. /**S**./,
172. *Vicia hirsuta* (L.) S. F. Gray. /**S**./,
173. *Vicia striata* M. Bieberst. /**S**./, i
174. *Xanthium spinosum* L. /**S**./.

Out of the 182 recorded taxa, 174 have been numbered as characteristic. Those were 166 species, 7 subspecies and, because of its plant-geographic and ecological significance, 1 variety (the Pontic-Pannonian species *Aster tripolium* var. *pannonicus*). Eight taxa (1 variety, 6 forms and 1 *lusus naturae*) were left unnumbered.

Of the 174 numbered characteristic taxa, 44 or 25.29% of those were labeled with the ecological index **S**₊, and 130 or 74.71% with the ecological index **S**₋.

Comparing the floras of the riparian zones of Okanj on one side and Slano Kopovo (Knežević et al. 2005a), Ostrovo (Knežević et al. 2005 b) and Rusanda (Knežević et al. 2003) on the other, we found the following.

The flora of the Okanj riparian zone (174 numbered taxa) was richer than the floras of the riparian zones of Slano Kopovo, Ostrovo and Rusanda (91, 77 and 134 numbered taxa, respectively).

The percentage of taxa labeled with the ecological index **S**₊ was lower for the flora of the Okanj riparian zone (25.29% or 44 taxa) than those for the floras of the riparian zones of Slano Kopovo, Ostrovo and Rusanda (50.54% or 46 taxa, 31.17% or 24 taxa and 31.34% or 43 taxa, respectively).

Obviously, the highest floristic richness and the lowest percentage of taxa bearing the ecological index **S**₊ in the sites around Okanj are due to a higher diversity of these sites and a higher degree of preservation of that ecosystem compared with the other analyzed ecosystems.

Rationale

The ecosystem of the riparian zone of the Okanj oxbow lake is larger (areawise) than the other ecosystems under comparison. It includes spacious pastures with the solonchakic solonetz soil. In several spots, solonchakic solonetz surrounds areas under uncultivated calcareous chernozem (micellar) on the loess terrace (Nejgebauer et al. 1971).

The ecosystem of the riparian zone of the Slano Kopovo oxbow lake covers a smaller area. It consists of a narrow riparian and inundated zone with the solonchak soil of an unusually high salinity rate (Janjatović, Kastori 1979) and adjoining pastures with the solonchakic solonetz soil (Nejgebauer et al. 1971). The calcareous chernozem soil (micellar) on the loess terrace surrounding these pastures has mostly been turned to field crop production.

The ecosystem of the riparian zone of the Ostrovo oxbow lake is made up of a system of fishponds whose construction had destroyed a considerable area under the solonchakic solonetz soil while the remaining area has been floristically impoverished by intensive anthropogenic activities. Most of the surrounding calcareous chernozem soil (micellar) on the loess terrace has been turned to field crop production (Nejgebauer et al. 1971).

The ecosystem of the riparian zone of the Rusanda oxbow lake is smallest of the analyzed ecosystems. Its narrow riparian zone under the solonchakic solonetz soil and the surrounding calcareous chernozem soil (micellar) on the loess terrace suffer intensive anthropogenic influences coming from the village of Melenci, the Rusanda spa and field crop production (Nejgebauer et al. 1971).

The actual number of taxa labeled with the ecological index S_+ in the riparian zone of Okanj is fairly high (44 taxa). This number is below than that for the riparian zone of Slano Kopovo (46 taxa) but it is higher than those for the riparian zones of Rusanda (43 taxa) and especially Ostrovo (24 taxa).

Therefore, judging by the percentage of the recorded halophytes (25.29%) and especially by their actual numbers (44 taxa), the ecosystem of the Okanj riparian zone is obviously a part of the halobiome occupying the meander scars of the Tisza River in central Banat.

Together with the other observed taxa, the recorded halophytes form numerous plant communities in the Okanj riparian zone.

The syntaxonomic position of the plant communities registered at the saline sites surrounding the Okanj oxbow lake is as follows.

Phragmitetea Tx. et Prsg. 1942

Phragmitetalia W. Koch 1926 emend. Pign 1953

Phragmition communis W. Koch 1926 emend. Soó 1947

Ass. *Scirpo-Phragmitetum* W. Koch 1926

medioeuropaeum Tx. 1941

p.p. emend. Soó 1971

Bolboschoenetalia maritimi Hejný 1967

p.p. (*Bolboschenetea maritimi* Tx. 1969, *Scirpetalia*

maritimi Borhidi 1970 p.p.)

Bolboschoenion maritimi continentale Soó (1945) 1947

emend. Borhidi 1970

Ass. *Bolboschoenetum maritimi continentale* Soó (1927)

1957

(*Scirpetum maritimi* Tx. 1937)

Thero-Salicornietea Tx. 1955, Tx. et Oberd. 1958

Thero-Salicornietalia (Br.–Bl. 1931) Tx. 1954 ex Tx. et

Oberd. 1958

Thero-Salicornion Br.–Bl. 1933 em Tx. 1950

Ass. *Suaedetum pannonicae* Soó 1927 Wendel. 1943

Ass. *Salsoletum sodae* Slavnić (1939) 1948

Festuco-Puccinellietea Soó 1968

Festuco-Puccinellietalia Soó 1968

Puccinellion limosae (Klika 1937) Wendel. 1943

Ass. *Puccinellietum limosae* (Rapcs. 1927) Soó 1930

Ass. *Pholiuro-Plantaginetum tenuiflorae* (Rapcs. 1927)

Wendel. 1943

Ass. *Hordeetum histricis* (Soó 1933) Wendel. 1943

Ass. *Camphorosmetum annuae* (Rapcs. 1916) Soó 1933

corr. Soó 1938

Halo-Agrostion albae pannonicum Knežević 1990

Ass. *Halo-Agrostetum albae* Vučković 1985

Ass. *Agrostio-Alopecuretum pratensis* Soó (1933) 1947

Ass. *Agrostio-Beckmannietum* (Rapcs. 1916) Soó 1933

Artemisio-Festucetalia pseudovinae Soó 1968

Festucion pseudovinae Soó 1933.

Halo-Festucion pseudovinae Vučković 1985

Ass. *Plantaginetum-Festucetum pseudovinae* Parabuški

1980

Ass. *Artemisio-Festucetum pseudovinae* (Magyar 1928)

Soó 1945

Xero-Festucion pseudovinae Vučković 1985

Ass. *Achilleo-Festucetum pseudovinae* (Magyar 1928)

Soó 1945.

The plant cover of the Okanj riparian zone comprises stands belonging to 3 classes, 5 orders, 6 alliances and 14 plant associations, bearing witness of a considerable diversity of the existing ecological niches.

Some of the registered plant communities cover a limited area or even are not completely formed in some parts of the vegetation period. On the shoreline of the oxbow lake that is not covered with stands of the communities *Scirpo-Phragmitetum* and *Bolboschoenetum maritimi continentale*, there are stands of the communities *Suaedetum pannonicae* and *Salsoletum sodae*. Since the oxbow lake serves as watering hole for cattle, the latter stands are frequently crushed down before *Suaeda pannonica* and *Salsola soda*, their respective characteristic species, reach the stage of full seed maturity. This practice, in combination with increasingly severe droughts, has led to a situation that only scant populations of the species *Suaeda pannonica* and *Salsola soda* could be observed in recent years. Stands of plant communities *Pholiuro-Plantaginetum tenuiflorae*, *Hordeetum histricis*, *Camphorosmetum annuae*, *Agrostio-Beckmannietum* and *Plantaginetum-Festucetum pseudovinae* develop on limited areas. Largest areas in the riparian zone of the Okanj oxbow lake are occupied by stands of the plant communities *Puccinellietum limosae*, *Halo-Agrostetum albae*, *Agrostio-Alopecuretum pratensis*, *Artemisio-Festucetum pseudovinae* and *Achilleo-Festucetum pseudovinae*. These stands cover the saline pastures which are subject to intensive cattle grazing and sheep folding and which are daily traversed by horse-drawn wagons and agricultural machines in the course of the vegetation period.

5. CONCLUSION

Distinguishing features of the plant cover of the saline pastures in the riparian zone of the Okanj oxbow lake (the Vojvodina Province, Serbia) make its floristic (182 recorded taxa,

i.e., 166 species, 7 subspecies and 2 varieties, 6 forms and 1 *lusus naturae*) and phytocoenological constituents (3 classes, 5 orders, 6 alliances and 14 associations).

It is important that out of the 174 characteristic taxa (166 species, 7 subspecies and, because of its plant-geographic and ecological significance, the Pontic-Pannonian plant species *Aster tripolium* var. *pannonicus*) 44 or 25.29% of them were assigned the ecological index **S₊** which defines the Okanj oxbow lake as a part of the halobiome that occupies the meander scars of the Tisza River in central Banat.

The following associations make this halobiome phytocoenologically specific: *Scirpo-Phragmitetum*, *Bolboschoenetum maritimi continentale*, *Suaedetum pannonicae*, *Salsoletum sodae*, *Puccinellietum limosae*, *Pholiuro-Plantaginetum tenuiflorae*, *Hordeetum histricis*, *Camphorosmetum annuae*, *Halo-Agrostetum albae*, *Agrostio-Alopecuretum pratensis*, *Agrostio-Beckmannietum*, *Plantagineto-Festucetum pseudovinae*, *Artemisio-Festucetum pseudovinae* and *Achilleo-Festucetum pseudovinae*.

Droughts and increasing anthropogenic influences keep degrading the ecosystem and if protective measures are not applied soon, the rare stenovalent euhalophytes *Suaeda pannonica* and *Salsola soda* as well as the associations they predominate, *Suaedetum pannonicae* and *Salsoletum sodae*, respectively, will disappear in near future.

ACKNOWLEDGEMENT

This work is part of the project TR - 20083 "Improving the technology of growing forage plants in the production of healthy animal feed," sponsored by the Ministry of Science and Technological Development of Serbia.

REFERENCES

- [1] Janjatović, V., Kastori, R., Sezonska dinamika anjona i katjona u nekih halofita na slatinama Vojvodine, Savez društava ekologa Jugoslavije, Drugi kongres ekologa Jugoslavije, 1245-1262, Zagreb, 1979.
- [2] Jávorka, S., Csapody, V., Iconographie der Flora des Südostlichen Mitteleuropea, Akademiai Kiado, Budapest, 1975.
- [3] Josifović, M. ed., Flora SR Srbije I-IX. SANU, Beograd, 1970 – 1976.
- [4] Knežević, A., Monografija flore vaskularnih biljaka na slatinama u regionu Banata (Jugoslavija), Matica srpska, Novi Sad, 1994.
- [5] Knežević, A., Boža, P., Butorac, B., Pekanović, V., Igić, R., Vukov, D., Halophytic Vegetation of the Yugoslav Portion of the Banat Region, Al II-lea Simpozion international, Cercetarea interdisciplinara zonala, Timisoara, Romania, 412- 419, 1998.
- [6] Knežević, A., Boža P., Milošev D., Lazić D., Specifičnost biljnog pokrivača priobalja akvatorije Slano Kopovo (Vojvodina, Srbija), Melioracije u održivoj poljoprivredi, Poljoprivredni fakultet, Departman za uređenje voda, 76-81, Novi Sad, 2005a.
- [7] Knežević, A., Boža, P., Stojanović, S., Lazić, D., Nikolić, Lj., Flora of saline sites in the riparian zone of the Ostrovo aquatorium (Melenci - the Vojvodina province), Savremena poljoprivreda, Vol. 54, 3-4, 243-247, Novi Sad, 2005 b.
- [8] Knežević, A., Boža, P., Stojanović, S., Milošev, D., Nikolić, Lj., Lazić, D., Stojšić, V., Specifičnosti i ugroženost biljnog pokrivača zaslanjenih staništa priobalja akvatorije Rusande, Zaštita životne sredine gradova i prigradskih naselja, Ekološki pokret grada Novog Sada, 289-294, Novi Sad, 2003.
- [9] Landolt, E., Ökologische Zeigerwerte zur Schweizer Flora, Veröffentlichungen des Geobotanischen Institutes der ETH, Stiftung Rübel, 64. Heft, Zürich, 1977.
- [10] Nejgebauer, V., Živković, B., Tanasijević, Đ., Miljković, N., Pedološka karta Vojvodine, Institut za poljoprivredna istraživanja, Novi Sad, 1971.
- [11] Soó, R., A magyar flóra és vegetáció rendszertani-növényföldrajzi kézikönyve I-VII, Akadémiai Kiadó, Budapest, 1964-1980.
- [12] Tutin, G., Heywood, V.H., Burges, N.A., Valentine, D.H., Walters, S.M., Webb, D.A. (ed.) Flora Europeae, 1-5, University press, Cambridge, 1964-1980.



GREEN MOULD DISEASE OF OYSTER MUSHROOM IN HUNGARY AND ROMANIA: ECOPHYSIOLOGY OF THE CAUSATIVE AGENTS

¹László KREDICS, ¹Péter KÖRMÖCZI, ¹Timea CSEH,
¹Lóránt HATVANI, ¹László MANCZINGER,
²Adrienn NAGY, ¹Csaba VÁGVÖLGYI

¹Department Of Microbiology, Faculty Of Science And Informatics,
University Of Szeged, HUNGARY

²Pilze-Nagy Ltd, Kecskemét, HUNGARY

Abstract:

The green mould disease of oyster mushroom (*Pleurotus ostreatus*) has been recently reported to cause great crop losses in Hungary and Romania. *Trichoderma pleurotum* and *Trichoderma pleuroticola*, the lately described fungal species responsible for the disease are present in both countries. The presented analysis has revealed that the growth of *T. pleurotum* shows a narrower temperature range (15-30°C) than that of *T. pleuroticola* (10-35°C). Acidic and neutral pH values and higher water activities were found to favour the growth of both pathogens. These data provide useful information for mushroom growers to optimize the ecophysiological parameters during oyster mushroom cultivation.

Key Words:

ecophysiology, green mould disease, oyster mushroom, *Pleurotus ostreatus*,
Trichoderma pleuroticola, *Trichoderma pleurotum*

1. INTRODUCTION

Following champignon (*Agaricus bisporus*) and shiitake (*Lentinula edodes*), oyster mushroom (*Pleurotus ostreatus*) is the third-most important commercially grown edible basidiomycete worldwide [1]. In the past few years severe green mould infections of cultivated *P. ostreatus* have been reported in South Korea [7], Italy [10], Hungary [4] and Romania [6], which might indicate a worldwide threat.

The two filamentous fungal species responsible for the problem proved to be different from *T. aggressivum* f. *aggressivum* and *T. aggressivum* f. *europaeum*, the causative agents of green mould disease in the case of *A. bisporus* [9]. In 2006 they were described as *Trichoderma pleurotum* S.H. Yu & M.S. Park, sp. nov. and *Trichoderma pleuroticola* S.H. Yu & M.S. Park sp. nov. [8]. Komon-Zelazowska et al. [5] used an integrated approach for the comprehensive characterization of several *T. pleurotum* strains from Hungary, Romania and Italy, as well as *T. pleuroticola* isolates from Canada, the USA, Italy, Hungary, Romania, Iran, The Netherlands, Germany and New Zealand. Both species belong to the *Harzianum* clade of *Hypocrea/Trichoderma*. Morphological studies have revealed that *T. pleuroticola* shows pachybasium-like properties characteristic of the *Harzianum* clade, while *T. pleurotum* possesses gliocladium-like conidiophore morphology. BIOLOG phenotype microarrays were used to determine the carbon source utilization profile of the isolates and the results have shown unequivocal differences between the two species, namely the growth of *T. pleurotum* was slower or impaired on the majority of the carbon sources tested as compared with *T. pleuroticola*, which showed similar growth to that of *T. aggressivum*,

indicating a closer relationship. The results suggest that the evolution of *T. pleurotum* was accompanied with the loss of the utilization ability of certain carbon sources. The phylogenetic analysis of a fragment including the internal transcribed spacer (ITS1-5.8S rRNA-ITS2) region of the ribosomal RNA gene cluster, a fragment covering the 4th and 5th introns and the last long exon of the *tefl* gene encoding for translation elongation factor 1 α , and a fragment including a portion of the 5th exon of the *chi18-5* (previously named *ech42*) gene encoding a family 18 chitinase confirmed the involvement of the two distinct species in causing the green mould disease of oyster mushroom worldwide [5]. A DNA BarCode for identification of these species based on ITS1 and ITS2 sequences was also provided and integrated in the main database for *Hypocrea/Trichoderma* (www.isth.info, [3]).

The aim of this study was to examine the effect of environmental factors (temperature, pH and water activity) on the mycelial growth of *T. pleuroticola* and *T. pleurotum*, the causative agents of oyster mushroom green mould disease, in comparison with related *Trichoderma* species (*T. harzianum*, *T. aggressivum* f. *aggressivum* and *T. aggressivum* f. *europaeum*).

2. THE STUDY

The *Trichoderma* strains included in this study are listed in Table 1. Strains were maintained on YEGK medium (0.5% glucose, 0.5% KH₂PO₄, 0.1% yeast extract, 2% agar).

Table 1. *Trichoderma* strains involved in the study

Species	Strain	Isolation source
<i>T. harzianum</i>	C8, C22	<i>Agaricus</i> compost, Hungary
<i>T. aggressivum</i> f. <i>aggressivum</i>	CBS 100527, CBS 450.95	<i>Agaricus</i> compost, Canada
<i>T. aggressivum</i> f. <i>europaeum</i>	CBS 100526, CBS 433.95	<i>Agaricus</i> compost, United Kingdom
<i>T. pleurotum</i>	A5, A11, A13, A14, A19, A26, A28, C2	oyster mushroom substrate (wheat straw), Hungary
<i>T. pleuroticola</i>	CPK 2902, CPK 2894, CPK 2897	natural substrate of wild-growing oyster mushroom, Hungary
	E10	oyster mushroom substrate (wheat straw), Romania
	CPK 230	decayed <i>Acer</i> stump, Canada
	CPK 882	Iran

The effect of temperature, pH and water activity (a_w) on linear mycelial growth was examined on synthetic minimal medium (0.5% (NH₄)₂SO₄, 0.5% KH₂PO₄, 0.1% MgSO₄·7H₂O, 1% glucose, 2% agar) and on a medium containing dried *Pleurotus* powder (0.1% glucose, 0.1% *Pleurotus* powder, 1% KH₂PO₄, 2% agar). Strains were inoculated onto the media with mycelial agar plugs cut from the edge of actively growing colonies. For studying the temperature dependence of the growth, plates were incubated at different temperatures (5, 10, 15, 20, 25, 30, 35 and 40°C). The effect of pH was examined at seven different pH values (pH 2, 2.2, 3, 4, 5, 6, 7, 8) adjusted by McIlvain buffer solutions (mixtures of 0.3 M Na₂HPO₄ x 2 H₂O and 0.1 M citric acid stock solutions in different proportions). a_w values between 0.997 and 0.922 were adjusted with NaCl according to Chirife and Resnik [2] (0.997: 0% NaCl, 0.991: 1% NaCl, 0.980: 3% NaCl, 0.968: 5% NaCl, 0.962: 6% NaCl, 0.951: 8% NaCl, 0.945: 9% NaCl, 0.922: 12% NaCl). Colony diameters were measured daily along two perpendicular axes. Growth curves were recorded with the aid of Microsoft Excel 2002, the colony diameter extension rates were expressed in mm/day.

3. ANALYSES, DISCUSSION, INTERPRETATIONS

The examined *T. pleuroticola* strains showed mycelial growth in the range of 10-35°C (Table 2). The optimum temperature for growth proved to be 30°C, while the growth rate significantly decreased at 35°C and no growth could be observed at 40°C and 5°C. The *T. harzianum* strains showed a temperature dependence similar to that of the *T. pleuroticola* strains. Based on our results, the examined *T. aggressivum* and *T. pleurotum* strains can be

characterized with a narrower temperature spectrum. In the case of *T. pleurotum* strains, no growth could be observed at 5, 10, 35 and 40°C, while the temperature optimum proved to be 25-30°C both on synthetic minimal medium and on *Pleurotus* powder medium. No significant differences in the temperature profiles could be observed between the two types of the media.

Table 2. Temperature dependence of the examined *Trichoderma* species. Colony diameter extension rates on minimal medium and *Pleurotus* powder containing medium in mm/day

Minimal medium	Temperature							
	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
<i>T. harzianum</i>	–	0.00-1.72	6.35-14.20	21.76-26.40	27.33-32.50	23.10-23.66	2.04-6.32	–
<i>T. aggressivum</i> f. <i>aggressivum</i>	–	0.00-1.68	3.58-10.84	9.91-21.42	25.66-28.00	8.35-25.33	–	–
<i>T. aggressivum</i> f. <i>europaeum</i>	–	–	0.00-16.25	14.00-30.30	18.57-36.50	18.35-25.30	–	–
<i>T. pleurotum</i>	–	–	2.50-5.93	17.71-21.23	22.69-23.46	18.42-23.76	–	–
<i>T. pleuroticola</i>	–	3.33-3.66	5.89-10.90	24.00-26.80	22.00-30.00	19.60-33.00	0.18-1.67	–
<i>Pleurotus</i> powder medium								
<i>T. harzianum</i>	–	–	0.00-1.43	9.25-13.92	21.46-26.00	27.33-31.00	2.22-10.02	–
<i>T. aggressivum</i> f. <i>aggressivum</i>	–	–	0.00-12.28	20.10-25.33	22.00-24.00	6.00-23.66	–	–
<i>T. aggressivum</i> f. <i>europaeum</i>	–	–	4.56-18.30	17.23-21.30	22.69-34.50	13.14-22.76	–	–
<i>T. pleurotum</i>	–	–	4.83-8.14	10.07-22.53	23.46-30.00	22.23-30.00	–	–
<i>T. pleuroticola</i>	–	2.36-4.31	12.30-20.60	21.00-25.10	27.50-30.00	29.00-30.50	0.29-2.07	–

Although the temperature ideal for the growth of oyster mushroom varies among strains, room temperatures of approximately 25°C, 13-15°C and 18°C are needed for spawn-run, induction of the development of fruit bodies and fruiting, respectively [11]. The substrate is exposed to green mould infection mostly during spawn-run, when the substrate temperature is elevated up to 30°C due to the generation of metabolic heat by mushroom mycelia. Based on our results, the *Pleurotus*-pathogenic *Trichoderma* species show maximal mycelial growth at 25-30°C, while limited, or no growth was observed at 10°C. Woo et al. [10] reported that the temperature optimum for the growth of *Pleurotus* was 28°C, while *Trichoderma* could grow well at a wider range (20–28°C), and exceeded the growth rate of *Pleurotus* by three times at 25°C. These findings suggest that the temperature of the growing room should be maintained between 15 and 18°C after spawn-run in order to minimize the possibility of green mould infection.

In the case of most *T. pleuroticola* and *T. pleurotum* isolates, the highest values of colony diameter extension rates were recorded in the pH range of 5.0-6.0 on synthetic minimal medium, while the pH optimum of the *T. harzianum*, *T. aggressivum* f. *aggressivum* and *T. aggressivum* f. *europaeum* isolates proved to be lower, at pH 4.0 (Table 3). Interestingly, the pH profiles were narrower on *Pleurotus* powder containing medium, with an optimum shifted to pH 4.0 in the case of the *Pleurotus* pathogenic *Trichoderma* species. Only *T. pleuroticola* was capable of growing at all examined pH values on *Pleurotus* powder containing medium. The growth of *T. pleurotum* and *T. aggressivum* f. *aggressivum* ceased at pH values above 5.0, while no growth of *T. harzianum* and *T. aggressivum* f. *europaeum* could be observed at pH values above pH 4.0. Our results suggest that the pH spectrum of mushroom pathogenic *Trichoderma* species can be narrower in the cultivation substrate than it can be expected based on data deriving from *in vitro* studies on synthetic media.

Table 3. pH dependence of the examined *Trichoderma* species. Colony diameter extension rates on minimal medium and *Pleurotus* powder containing medium in mm/day

Minimal medium	pH						
	2.2	3.0	4.0	5.0	6.0	7.0	8.0
<i>T. harzianum</i>	4.20-4.68	5.40-19.17	16.55-20.71	19.78-20.25	5.80-19.77	2.85-14.02	4.20-15.21
<i>T. aggressivum</i> f. <i>aggressivum</i>	5.10-8.34	10.05-18.94	10.15-19.10	5.60-18.62	2.60-16.30	2.20-6.41	2.40-4.32
<i>T. aggressivum</i> f. <i>europaeum</i>	5.52-6.55	14.80-25.25	18.20-25.55	16.25-17.37	3.70-12.55	3.95-8.05	3.15-9.28
<i>T. pleurotum</i>	2.90-5.21	14.08-18.78	9.50-19.65	13.75-20.08	15.28-20.27	10.27-18.74	9.40-14.45
<i>T. pleuroticola</i>	4.00-4.90	11.80-22.35	8.60-15.65	12.40-23.85	11.30-24.95	3.85-18.40	4.05-19.20
<i>Pleurotus</i> powder medium							
<i>T. harzianum</i>	12.90-15.15	10.70-16.9	20.70-21.05	–	–	–	–
<i>T. aggressivum</i> f. <i>aggressivum</i>	8.20-9.30	8.85-23.35	8.70-24.75	2.45-3.05	–	–	–
<i>T. aggressivum</i> f. <i>europaeum</i>	12.35-15.75	15.70-18.85	13.30-19.25	–	–	–	–
<i>T. pleurotum</i>	9.90-11.70	15.05-19.65	18.70-23.15	2.10-2.70	–	–	–
<i>T. pleuroticola</i>	14.25-19.05	21.90-23.20	17.35-34.75	19.35-29.00	0.45-0.80	0.35-0.55	1.20-1.80

These data are in accordance with the findings of Woo et al. [10], who reported that the pH optimum for the growth of *Pleurotus* was alkaline (pH 8.0-9.0) whereas *Trichoderma* preferred acidic-neutral conditions. Woo et al. [10] suggested that adjusting the pH of the substrate to 8.0-9.0 might slow down the growth of *Trichoderma* resulting in a reduction in the spreading of the infection. However, during the spawn-run period, the pH of the substrate decreases rapidly (within 5-6 days) from 8.0-9.0 to 4.5-5.0 due to the growth of oyster mushroom mycelia. Thus the higher pH can provide protection only in the initial phase, later the oyster mushroom itself changes the circumstances, resulting in a medium with a pH optimal for the pathogen.

 Table 4. Water activity dependence of the examined *Trichoderma* species. Colony diameter extension rates on minimal medium and *Pleurotus* powder containing medium in mm/day

Minimal medium	Water activity							
	0.997	0.991	0.980	0.968	0.962	0.951	0.945	0.922
<i>T. harzianum</i>	19.15-24.20	22.45-25.90	11.60-12.14	7.25-10.13	6.62-8.35	6.48-6.98	2.02-4.80	–
<i>T. aggressivum</i> f. <i>aggressivum</i>	23.35-25.80	19.30-24.80	14.68-20.70	8.21-14.77	7.07-14.77	3.55-7.20	1.51-4.37	–
<i>T. aggressivum</i> f. <i>europaeum</i>	19.20-34.25	19.10-25.20	10.77-18.42	5.94-9.90	5.14-7.88	2.97-3.67	0.00-2.05	–
<i>T. pleurotum</i>	18.10-19.03	9.28-19.00	5.14-13.25	4.97-6.80	2.20-5.85	0.00-5.17	0.00-1.60	–
<i>T. pleuroticola</i>	17.05-26.75	20.90-30.75	10.67-16.77	7.42-8.80	6.68-7.64	4.08-5.11	0.00-3.94	–
<i>Pleurotus</i> powder medium								
<i>T. harzianum</i>	28.50-30.00	22.40-35.00	15.67-21.20	8.95-16.97	5.42-7.97	3.68-4.14	2.42-2.54	–
<i>T. aggressivum</i> f. <i>aggressivum</i>	21.00-23.35	21.40-24.80	14.68-18.20	8.21-13.40	7.07-13.82	3.55-5.82	1.51-4.71	–
<i>T. aggressivum</i> f. <i>europaeum</i>	22.70-34.25	24.40-25.20	13.71-18.42	9.90-10.54	6.65-7.88	2.82-3.67	0.00-1.82	–
<i>T. pleurotum</i>	21.90-26.50	21.30-25.60	16.20-18.25	7.80-13.49	6.86-8.22	3.05-4.42	1.37-2.82	–
<i>T. pleuroticola</i>	29.25-33.25	31.75-34.00	16.61-25.55	11.78-15.34	8.22-9.45	3.85-5.74	0.00-3.67	–

Concerning water activity, most of the *Trichoderma* strains showed higher mycelial growth rates on *Pleurotus* powder containing medium with an optimum of $a_w=0.991$, than on synthetic minimal medium, where the optimal water activity for most of the isolates proved to be $a_w=0.997$ (Table 4). In the case of *T. pleurotum*, the presence of *Pleurotus* powder induced mycelial growth also at water activity values where no growth could be observed on minimal medium. All the examined strains showed a lowering mycelial growth rate with the decrease in water activity, while none of the strains were able to grow at $a_w=0.922$.

Yu [11] examined the effect of substrate moisture content (SMC) on the growth of *Pleurotus* and *Trichoderma*. The optimum for oyster mushroom fell into the 60-70% range, and the growth of it was inhibited at 80%. In contrast to this, the mycelial growth of the green mould isolates was proportional to SMC, reaching its maximum at 80%.

4. CONCLUSIONS

In the latest years the most severe crop losses in oyster mushroom cultivation have been caused by green mould infections worldwide. The causative agents were identified as new-to-science species of the filamentous fungal genus *Trichoderma*, and they have recently been described as *T. pleurotum* and *T. pleuroticola*. The pieces of information about the ecophysiology of these two green mould species provided in the present study might help oyster mushroom growers to prevent green mould disease of *P. ostreatus*, and thereby reduce crop losses.

ACKNOWLEDGEMENTS

This study was supported by grant OTKA F68381 (Hungarian Scientific Research Fund) and by the János Bolyai Research Scholarship (Hungarian Academy of Sciences).

REFERENCES

- [1] Chang, S.T. World production of cultivated and medicinal mushrooms in 1997 with emphasis on *Lentinus edodes* (Berk.) Sing. in China. *Int. J. Med. Mushrooms*, 1: 291-300, 1999
- [2] Chirife, J., Resnik, S. L. Unsaturated solutions of sodium chloride as reference sources of water activity at various temperatures. *J. Food. Sci.* 49: 1486-1488, 1984
- [3] Druzhinina, I.S., Kopchinskiy, A.G., Komon, M., Bissett, J., Szakács, G., Kubicek, C.P. An oligonucleotide barcode for species identification in *Trichoderma* and *Hypocrea*. *Fungal Genet. Biol.* 42: 813-828, 2005
- [4] Hatvani, L., Antal, Z., Manczinger, L., Szekeres, A., Druzhinina, I.S., Kubicek, C.P., Nagy, A., Nagy, E., Vágvolgyi, C., Kredics, L. Green mold diseases of *Agaricus* and *Pleurotus* are caused by related but phylogenetically different *Trichoderma* species. *Phytopathology* 97: 532–537, 2006.
- [5] Komon-Zelazowska, M., Bissett, J., Zafari, D., Hatvani, L., Manczinger, L., Woo, S., Lorito, M., Kredics, L., Kubicek, C.P., Druzhinina I.S. Genetically closely related but phenotypically divergent *Trichoderma* species cause worldwide green mould disease in oyster mushroom farms. *Appl. Environ. Microbiol.* 73: 7415-7426, 2007
- [6] Kredics, L., Hatvani, L., Antal, Z., Manczinger, L., Druzhinina, I.S., Kubicek, C.P., Szekeres, A., Nagy, A., Vágvolgyi, C., Nagy, E. Green mould disease of oyster mushroom in Hungary and Transylvania. *Acta Microbiol. Immunol. Hung.* 53: 306–307, 2006
- [7] Park, M.S., Bae, K.S., Yu, S.H. Molecular and morphological analysis of *Trichoderma* isolates associated with green mold epidemic of oyster mushroom in Korea. *J. Huazhong Agric. Univ.* 23: 157-164, 2004

- [8] Park, M.S., Bae, K.S., Yu S.H. Two new species of *Trichoderma* associated with green mold of oyster mushroom cultivation in Korea. *Mycobiology* 34: 11-113, 2006
- [9] Samuels, G.J., Dodd, S.L., Gams, W., Castlebury, L.A., Petrini, O. *Trichoderma* species associated with the green mold epidemic of commercially grown *Agaricus bisporus*. *Mycologia* 94: 146-170, 2002
- [10] Woo, S.L., Di Benedetto, P., Senatore, M., Abadi, K., Gigante, S., Soriente, I., Ferraioli, S., Scala, F., Lorito, M. Identification and characterization of *Trichoderma* species aggressive to *Pleurotus* in Italy. *J. Zhejiang Univ. Agric. Life Sci.* 30: 469-470, 2004
- [11] Yu, S.H. Integrated control of oyster mushroom green mould (1-5). <http://www.mushworld.com>, 2002.



CHANGES OF FLORISTIC COMPOSITION IN THE GLOŽAN CONSTRUCTED WETLAND SYSTEM (THE VOJVODINA PROVINCE, SERBIA)

Ljiljana NIKOLIĆ, Slobodanka STOJANOVIĆ, Aleksa KNEŽEVIĆ,
Dejana DŽIGURSKI, Branka LJEVNAIĆ

University of Novi Sad, Faculty of Agriculture, Novi Sad, SERBIA

Abstract

The constructed wetland system for municipal wastewater treatment in Gložan (near Novi Sad) is the first facility of its kind in Serbia. This biological purification system, whose final recipient in the Danube River, covers an area of 1 ha. Biomonitoring was conducted in the period 2004-2008 to assess the changes and dynamics of the floristic structure at the examined site. In the first year (2004), 41 vascular flora taxa were recorded. The respective figures in 2005, 2006, 2007 and 2008 were 34, 33, 21 and 25 taxa. Considering the total period (2004-2008), we recorded a total of 53 taxa of which 14 occurred in all study years. The paper presents also the changes in the biological spectrum and range of habitat types registered over the five-year period. In addition to its main function within the process of biological purification of municipal wastewaters, the constructed wetland system also plays an important role in the framework of sustainable development, since environmental protection is one of its major components.

1. INTRODUCTION

The first constructed wetland system (CWS) for municipal wastewater treatment prior to discharge into a watercourse was built in England in late 1970s and early 1980s [11]. Nowadays, this method is used worldwide but it is not universally accepted everywhere. In our country, the method was used for the first time in 2004. The EU Directive 91/271/EEC (1991), which deals with municipal wastewater treatment, strongly recommends constructed wetland systems. Within the framework of a pilot project titled „Municipal wastewater treatment by the method of constructed wetlands”, the first biological purification system in Serbia, with the Danube River as the final recipient, was constructed in the village of Gložan, near Novi Sad. The Gložan constructed wetland system was built on a site of a natural swamp, its area is 1 ha and it comprises three separately constructed cells.

This method is based on the utilization of phytofiltration and phyto-accumulation capacities of semiaquatic plants (macrophytes) which take up, retain and accumulate different substances from soil and water [1,2,8,9,13,6,10]. Furthermore, owing to well-developed rhizomes and root system, these plants provide in their rhizosphere a viable environment for microorganisms, which, together with plants, play an important role in the processes of decomposition of debris in water and its underlying soil substrate.

While conventional methods of wastewater purification are time- and energy-consuming as well as expensive, wetlands are a natural water filter that grow and purify the environment, acting as super-absorbers of phosphates, nitrates and various hazardous substances. CWSs are an example of clean technology that exploits solar energy and provides useful biomass as final product.

Monitoring of floristic structure, biological spectrum and chorological spectrum, are integral parts of permanent biological and ecological studies, which were the objectives of this paper. The obtained data may serve as indicators of course of succession of the studied anthropogenic wetland ecosystem.

2. MATERIAL AND METHODS

The floristic study in the Gložan CWS covers a five-year period (2004-2008). Plant species were determined in accordance with the publications Flora SR Srbije [7], Visügyi hidrobiologia [3] and Flora Europaea [15]. Presence of life forms was estimated on the basis of A magyar flóra és vegetáció rendszeretani növényföldrajzi kézikönyve [12], floristic elements on the basis of Pregled vrsta flore SR Srbije sa biljnogeografskim oznakama [4].

Table 1. Flora review of the Gložan constructed wetland system (2004-2008)

Floristic element	Life form	Plant species	2004	2005	2006	2007	2008
Adv.	Th	<i>Abutilon theophrastii</i> Medik.	+	+	+	+	+
Adv.	Th	<i>Amaranthus retroflexus</i> L.	+		+		
Adv.	Th	<i>Ambrosia artemisiifolia</i> L.	+	+			
Sub-M.	H (G)	<i>Aristolochia clematitis</i> L.	+				
Adv.	G(H)	<i>Armoracia lapathifolia</i> Gilib.	+				
Adv.	H	<i>Aster salignus</i> Willd.	+	+	+	+	+
Cosm.	HH-G	<i>Bolboschoenus maritimus</i> (L.) Palla.			+		
Eur.	H	<i>Calystegia sepium</i> (L.) R. Br.		+	+	+	+
Sub-CE	TH	<i>Carduus acanthoides</i> L.		+	+		
Cosm.	Th	<i>Chenopodium album</i> L.	+		+	+	+
Sub-Eur.	Th-H	<i>Conium maculatum</i> L.					+
Cosm.	H-G	<i>Convolvulus arvensis</i> L.	+		+		
Sub-Eur.	G	<i>Cirsium arvense</i> (L.) Scop.	+	+	+		
Cosm.	Th(H)	<i>Datura stramonium</i> L.	+				+
Sub-Eur.	Th-H-H	<i>Daucus carota</i> L.		+			
Adv.	Th	<i>Echinocystis lobata</i> (Michx.) Torr. et Gray.	+	+	+	+	+
Sub-Eur.	H-HH	<i>Epilobium hirsutum</i> L.		+	+		+
Adv.	Th-TH	<i>Erigeron canadensis</i> L.	+	+	+	+	
Sub-CE	H	<i>Eupatorium cannabinum</i> L.	+	+	+	+	+
Sub-CE	Th	<i>Galinsoga parviflora</i> Cav.	+		+		
Sub-M.	M	<i>Galega officinalis</i> L.	+	+			
Eur.	H(Ch-G)	<i>Glechoma hederacea</i> L.		+			
Sub-M.	TH-Th	<i>Helminthia echioides</i> (L.) Gärtn.	+				
Sub-CE	TH-H	<i>Inula britannica</i> L.	+	+	+		+
Subpont.	Th-TH	<i>Lactuca serriola</i> L.	+		+		
subca.subm							
Eur.	Th-TH	<i>Leonurus marrubiastrum</i> L.	+				
Sub-Eur.	HH	<i>Lycopus europaeus</i> L.	+	+	+	+	+
Sub-CE	Ch	<i>Lysimachia numularia</i> L.		+			
Eur.	HH	<i>Lysimachia vulgaris</i> L.		+			
Eur.	H-HH	<i>Mentha aquatica</i> L.					+
Circ.	H(G)	<i>Mentha arvensis</i> L.	+		+	+	
Adv.	Th	<i>Panicum capillare</i> L.	+	+	+	+	+
Cosm.	Th	<i>Panicum crus-galli</i> (L.) P.B.	+	+	+	+	+
Sub-M.	H	<i>Parietaria officinalis</i> Mert. et Koch	+				
Cosm.	HH	<i>Phragmites communis</i> Trin.	+	+	+	+	+
Sub-circ.	Th	<i>Polygonum lapathifolium</i> L.	+	+	+	+	+
Cosm.	Th	<i>Polygonum aviculare</i> L.	+				
Sub-Eur.	Th	<i>Pulicaria vulgaris</i> Gaert.	+		+		
Subjsib.	H-N	<i>Rubus caesius</i> L.	+	+			+
Sub-CE	H-HH	<i>Rumex hydrolapathum</i> Huds.	+	+			
Sub-Eur.	Th	<i>Setaria viridis</i> (L.) P.B.	+	+	+		
Sub-Eur.	Th	<i>Sinapis arvensis</i> L.	+				
Sub-Eur.	Ch	<i>Solanum dulcamara</i> L.		+	+	+	
Cosm.	Th	<i>Solanum nigrum</i> L.				+	+
Adv.	H	<i>Solidago serotina</i> Aiton.	+	+	+	+	+
Eur.	H	<i>Sonchus arvensis</i> L.	+	+	+	+	+
Circ.	H	<i>Stachys palustris</i> L.	+	+	+		+
Cosm.	Th-TH	<i>Stellaria media</i> L.	+	+	+		
Adv.	Th	<i>Stenactis annua</i> (L.) Nees.	+	+			
Sub-CE	H	<i>Symphytum officinale</i> L.	+	+	+	+	+
Eur.	H	<i>Urtica dioica</i> L.	+	+	+	+	+
Adv.	Th	<i>Xantium strumarium</i> L.	+		+	+	+
Adv.	Th.	<i>Xantium italicum</i> Mor.	+	+	+	+	+
Total number of species			41	34	33	21	25

Legend: Adv. – Adventive, Sub-M. – Sub-Mediterranean, Cosm. – Cosmopolitan, Eur. – Eurasian, Sub-CE - Sub-Central European, Sub-Eur. – Sub-Eurasian, Sub-Pont. sub-CA - sub-M. - Sub-Pontic-Sub-Central Asian - sub-Mediterranean, Circ. – Circumpolar, Sub-circ. – Sub-circumpolar, Subjsib. - Sub-South Siberian; Th – Therophyte, H – Hemicytrophite, HH – Hydato–helophyte, M - Microphanerophyte, G - Geophyte, TH – Hemitherophyte, Ch - Chamaephyte

3. RESULTS AND DISCUSSION

Study results include an analysis extant flora, percent presence of plant life forms and their floristic elements in the Gložan CWS. Within the framework of continual floristic studies conducted in the period 2004-2008, a total of 53 taxa were recorded, of which 14 taxa were common in all study years (Table 1). The highest floristic richness, that included 41 taxa of vascular flora, was registered in the first year (2004). The respective figures in the subsequent years, 2005, 2006, 2007 and 2008, were 34, 33, 21 and 25 taxa.

The richness of the recorded flora results from a number of factors, but primarily from favorable hydrological conditions in the Gložan CWS, which had been constructed at the site of a natural swamp. Additionally, the continual inflow of municipal wastewater resulted in profuse growth of reed (*Phragmites communis* Trin.) stands. At first, the reeds had thrived naturally and later on they were additionally planted. The reeds achieve their maximum growth and the height of about 4 m in the first cell of the CWS, which has highest moisture content in the underlying substrate. Because of very favorable ecological conditions (moisture, temperature, light, presence of nutrients in wastewater), the reeds formed a thick stand which suppressed the other species in the cell itself and pushed them to the very perimeter of this part of the system.

It seems important to mention at this point that, in spite of a relative floristic richness which was characteristic only for the perimeter of the first cell of the system, the reed was absolutely predominant in all three cells of the system and across the entire five-year period, being the main factor of phytofiltration and phyto-accumulation of a variety of substances from the wastewater coming from the village of Gložan. Only around the weirs between the system's cells, where the reeds were thinner and the light regime was better, did a hemicryptophyte *Calystegia sepium* (L.) R. Br. manage to thrive, climbing up the reed stalks and causing their partial lodging.

The analysis of the biological spectrum of recorded species indicated that therophytes (Th) predominated in all study years. Their numbers and percentages in 2004, 2005, 2006, 2007 and 2008 were 21 species (51.22%), 13 species (38.23%), 15 species (45.45%), 10 species (47.62%) and 11 species (44%), respectively. Presence of hemicryptophytes (H) was also significant. Their respective numbers and percentages were 13 species (31.71%), 12 species (35.29%), 11 species (33.33%), 8 species (38.09%) and 11 species (44%). Hydro-helophytes were present in low numbers, but here it should be mentioned that the predominant species in the Gložan CWS was the reed, a hydro-helophyte perfectly adapted to the conditions in the studied anthropogenic ecosystem. Hemitherophytes, chamaephytes, geophytes and microphanerophytes were also present in low numbers. The last two life forms were not recorded in the last two years of the study at all (Table 2).

Table 2. Review of life forms in the Gložan constructed wetland system (2004-2008)

GROUP OF LIFE FORM	LIFE FORM	SPECIES NUMBER AND PERCENTAGE				
		2004	2005	2006	2007	2008
Therophyte Th	Th	16 (39.02%)	10 (29.41%)	12 (36.36%)	9 (42.86%)	9 (36.00%)
	Th (H)	1 (2.44%)	2 (5.88%)		1 (4.76%)	1 (4.00%)
	Th -TH	4 (9.76%)	1 (2.94%)	3 (9.09%)		1 (4.00%)
	Th -TH-H					
Hemicryptophyte H	H	8 (19.51%)	8 (23.53%)	8 (24.24%)	7 (33.33%)	8 (32.00%)
	H-HH	1 (2.44%)	2 (5.88%)	1 (3.03%)		2 (8.00%)
	H (G)	2 (4.88%)		1 (3.03%)		
	H-G	1 (2.44%)		1 (3.03%)	1 (4.76%)	
	H-N	1 (2.44%)	1 (2.94%)	1 (3.03%)		1 (4.00%)
	H (Ch - G)		1 (2.94%)			
Hydato-helophyte HH	HH	2 (4.88%)	3 (8.82%)	2 (6.06%)	2 (9.52%)	2 (8.00%)
	HH-H					
	HH-G			1 (3.03%)		
Microphanerophyte M	M	1 (2.44%)	1 (2.94%)			
Geophyte G	G	1 (2.44%)		1 (3.03%)		
	G (H)	1 (2.44%)	1 (2.94%)			
Hemitherophyte TH	TH		1 (2.94%)	1 (3.03%)		
	TH-H	1 (2.44%)	1 (2.94%)	1 (3.03%)		1 (4.00%)
	TH-Th	1 (2.44%)				
Chamaephyte Ch	Ch		2 (5.88%)	1 (3.03%)	1 (4.76%)	

The analysis of the chorological spectrum indicated a predominance of species of wide distribution: **adventive** – 12 (29.27%) in 2004, 10 (29.41%) in 2005, 9 (27.27%) in 2006, 8 (38.09%) in 2007 and 7 (28%) in 2008; **Eurasian** – 9 (21.95%) in 2004, 12 (35.3%) in 2005, 9 (27.27%) in 2006, 5 (23.81%) in 2007 and 8 (42%) in 2008; **circumpolar and cosmopolitan** - 10 (24.39%) in 2004, 5 (14.7%) in 2005, 9 (27.27%) in 2006, 6 (28.57%) in 2007 and 7 (28%) in 2008. The species of wide distribution comprised over 75% of the spectrum in all study years (75.61% in 2004; 79.41% in 2005; 81.81% in 2006; 90.47% in 2007 and 88% in 2008), which is in agreement with the ecological conditions prevailing in this anthropogenic ecosystem.

The presence of species of narrow distribution (sub-Central European, Pontic-Central Asian and sub-Mediterranean) was low. The presence of Pontic-Central Asian and sub-Mediterranean species in the first three years was an indication of an intensive water release during the summer period in initial years of operation of the system (Table 3).

Table 3. Review of chorological spectrum in the Gložan constructed wetland system (2004-2008)

CHOROLOGICAL TYPE	FLORAL ELEMENT	NUMBER OF SPECIES AND CORRESPONDING PERCENTAGES				
		2004	2005	2006	2007	2008
Adventive	Adventive	12 (29.27%)	10 (29.41%)	9 (27.27%)	8 (38.09%)	7 (28%)
Eurasian	Eur.	3 (7.32%)	5 (14.71%)	3 (9.09%)	3 (14.29%)	4 (16%)
	Sub-Eur.	5 (12.19%)	6 (17.65%)	6 (18.18%)	2 (9.52%)	3 (12%)
	Sub-s. Sib.	1 (2.44%)	1 (2.94%)			1 (4%)
Circumpolar and cosmopolitan	Cosm.	7 (17.07%)	3 (8.82%)	6 (18.18%)	4 (19.05%)	5 (20%)
	Circ.	2 (4.88%)	1 (2.94%)	2 (6.06%)	1 (4.76%)	1 (4%)
	Sub-circ.	1 (2.44%)	1 (2.94%)	1 (3.03%)	1 (4.76%)	1 (4%)
Central European	Sub-CE	5 (12.19%)	6 (17.65%)	5 (15.15%)	2 (9.52%)	3 (12%)
Pontic-Central-Asian	Sub-Pont.-sub-CA.sub-M.	1 (2.44%)		1 (3.03%)		
Sub-Mediterranean	Sub-M.	4 (9.76%)	1 (2.94%)			

The plant cover formed in the Gložan CWS comprises 13 adventive plant species. Among these, invasive plant species (*Abutilon theophrasti*, *Ambrosia artemisiifolia*, *Erigeron canadensis*, *Xanthium italicum*, *Xanthium strumarium*) are of particular concern because of their negative impact on the native flora. Their aggressive expansion tends to degrade the ecological balance [16, 14]. The presence of invasive plant species in systems for purification of communal wastewater calls for their permanent monitoring because these plants may negatively affect the biodiversity of a given site, while a CWS may in itself become a focal point for further spread of these plants [14].

The analyses of floristic composition, biological spectrum and chorological spectrum made over the five-year study period indicated a succession towards a swamp ecosystem predominated by *Phragmites communis*, a cosmopolitan hydro-helophyte which plays a key role in the purification of communal wastewater in the Gložan CWS. The above data show that the reed adapted perfectly to the ecological conditions of the studied site and, due to high competitiveness and allelopathic action [5], it suppressed the other plant species, as indicated by a steady reduction in the number of plant species across the study years.

REFERENCES

- [1] Brix, H.: Functions of Macrophytes in Constructed Wetlands. Water Science Technology, 29, No.4: 71-78, 1994.
- [2] Ellis, J.B., Revitt, D.M. Shutes, R.B.E., Langley, J.M.: The performance of vegetated biofilters for highway runoff control. The Science of the Total Environment, 146/147: 543-550, 1994.
- [3] Felföldy, L.: Visugyi hidrobiologia. 18 Kotet Hinar határozou Kornyezetvedelmi es Teruletfejlesztési Miniszterium, Budapest, 1- 144, 1990.
- [4] Gajić, M.: Pregled vrsta flore SR Srbije sa biljnogeografskim oznakama. Glasnik Šumarskog fakulteta, ser. A, "Šumarstvo", Beograd, 54: 111-141, 1980.
- [5] Gopal, B., Goel, U.: Competition and allelopathy in aquatic plant communities. Bot. Rev., Vol. 59, (3) 155-210, 1993.

- [6] Greenway, M.: The Role of Macrophytes in Nutrient Removal Using Constructed Wetlands. *Environmental Bioremediation Technologies*, 331-351, 2007.
- [7] Josifović, M. (ED.): *Flora Republike Srbije*, I-X, SANU, Beograd, 1970-1986.
- [8] Mitsch, W.J., Gosselink J.G.: *Wetlands*. 3rd ed. John Wiley and Sons Inc., 2000.
- [9] Nikolić, L.J., Stojanović, S., Stanković, Ž.: Content of macro- (N,P,K) and micronutrients (Fe, Mn, Zn) in four promising emergent macrophytic species. *Fund. Appl. Limn. (Arch. Hydrobiol.)* 147/3-4, p. 297-306, 2003.
- [10] Nikolić, Lj., Stojanović, S., Lazić, D.: Uloga trske (*Phragmites australis* (Cav.) Trin. ex Steud.) u procesu prečišćavanja komunalnih otpadnih voda metodom mokrih polja (constructed wetlands systems). *Contemporary Agriculture*, Novi Sad, Vol. 51, br.3-4, 230-235, 2007.
- [11] Nuttall, P.M., Boon, A.G., Rowell, M.R.: Review of the design and management of constructed wetlands. *Construction Industry Research and Information association*, London, 1-267,1997.
- [12] Soó, R. A magyar flóra és vegetáció rendszeretani novényfoldrajzi kézikönyve I-VII, Akadémiai kiadó, Budapest. *Congress, Ecological Processes: Current Status and Perspectives*, 28, 1964-1985.
- [13] Stojanović, S., Knežević, A., Nikolić, L.J., Lazić, D.: Vaskularne makrofite u funkciji prečišćavanja otpadnih komunalnih voda – metoda constructed wetlands systems (Mokra polja), I Simpozijum biologa Republike Srpske, Banja Luka, Zbornik sažetaka, 23, 2005.
- [14] Stojanović, S., Knežević, A., Nikolić, Lj., Džigurski, D., Ljevnaić, B.: Prisustvo adventivnih elemenata flore u biljnom pokrivaču formiranom u sistemu „Mokra polja“, *Melioracije 09*, Poljoprivredni fakultet, Novi Sad, 144-151, 2009.
- [15] Tutin, G., Heywood, V.H., Burges, N.A., Valentine, D.H., Walters, S.M., Webb, D.A. (ed.): *Flora Europea*, 1-5, University press, Cambridge, 1964-1980.
- [16] Vrbničanin Sava, Karadžić, B., Dajić-Stevanović Zora: Adventivne i invazivne korovske vrste na području Srbije. *Acta Biologica Jugoslavica*, serija G: *Acta Herbologica*, Vol. 13, No. 1: 1-12, 2004.



ECOLOGICAL RECONSTRUCTION IN THE BANAT BLACK PINE SITE FROM “DOMOGLED-VALEA CERNEI” NATIONAL PARK

FRĂȚILĂ Eugeniu-Corneliu

Forest Research and Management Institute (ICAS)
Caransebeș Research Station, ROMANIA

Abstract:

The ecological reconstruction, included in the project LIFE04NAT/RO/000225, came as a result of the fact that in 2000, a forest surface over 90 ha was destroyed by fire. Following field observations and evaluations, a perimeter of 25 ha was identified, on which forestry vegetation was severely damaged at levels of trees, underbrush, shrub and seedlings. In this area it was considered necessary an ecological reconstruction through plantation of Banat black pine. The works were done between 2003 – 2007 and have included following actions: the analyse of the stationary and vegetation conditions, collecting the black pine seeds, producing seedlings with protected roots, land release and clearing and digging the hearths for plantation. Some succes evaluations of this ecological reconstruction were made in the summer and fall of the year 2007 and 2008. The averages of the survival percent were 79,56%, in 2007 and 74,80% in 2008.

Key words:

Banat black pine, producing seedlings, planting in hearths

1.INTRODUCTION

During time, karsts areas with hilly landforms were frequently affected by phenomena of destructive nature, such as fires or flooding, which lead to the disappearance of forestry and shrub vegetation on certain area. Reintroducing forestry vegetation in these areas has always been a problem, because through excessive erosion, an obvious antagonism was created between climatic and soil factors, exercised through the plants reduced possibilities, due to the humidity soil deficit, to maximum use the solar heat and light [5]

Regarding to the calcareous cliffs pine forests from Cerna Valley, information exist that they were affected by the catastrophic floods from 1910. At the time, the Austrian forestry regime attempted to teforests the surfaces with black locus and black pine, but with poor results [3].

Reforestation difficulties of such degraded field required a necessary scientific analyze of how the plantation can be realized, under the aspects of species composition and plantation technique. In this directions, several studies tested the reintroduction of black pines in areas of calcareous cliffs [2,3,5,6]

From methodological point of view these studies analyzed:

- ✚ The way in which already existent black pine forests installed and developed in this area;
- ✚ Stationary characteristics from point of experiment (geomorphology, climate, soil physical and chemical characteristics, soil erosion etc.);
- ✚ Black pine sapling development in different experimental variants of plantation (sapling pricked from different nurseries, direct plantation in hearths, plantation in saplings grown in bags of polyethylene);

2. ECOLOGICAL RECONSTRUCTION IN THE BANAT BLACK PINE SITE

The Banat black pine (*Pinus nigra* ssp. *banatica*) is an endemic subspecies with a restricted area in the south-west of Romania. It constitutes today representative forest ecosystems on the western slopes of Mehedinti Mountains, at altitudes between 500 and 1200 m, alongside the thermal rupture Baile Herculane and on the calcareous Domogled plateau. The Banat black pine ecosystems represent a priority European habitat: 9530* "Sub-Mediterranean pine forest with endemic black pine", included in the ROSCI0069 site, from "NATURA 2000" network, which overlaps on the territory of "Domogled-Valea Cernei" National Park.

This action, included in the project LIFE04NAT/RO/000225, came as a result of the fact that in 2000, a surface of over 90 ha, from the U.P. (Production Unit) IV Domogled was destroyed by fire. The forest lasted approximately 20 days and affected the forestry vegetation of Banat black pine and mixtures with different deciduous species. The burned forestry parcels were 108, 109, 112, 113, 116. Following field observations and evaluations a perimeter of 25 ha from u.a. (forestry parcel inside of production unit) 108B was identified, on which forestry vegetation was severely damaged at levels of trees, underbrush shrub and seedlings. In this area it was considered necessary an ecological reconstruction through plantation of Banat black pine. On the rest of the surface, it has been appreciated that plantation isn't possible, because in some cases the soil totally lacks from cliff, and isn't necessary where the fires produced partial damages, and forestry vegetation can regenerate in a natural manner [1, 4]

Ecological reconstruction in the project considered the previous experience of black pine plantation from calcareous cliff in Banat, both from the methodological and practical point of view, and the results of the researches in the field. Thus, before the ecological reconstruction:

- ✚ was made and analyze of the stationary and vegetation conditions in the established perimeter;
- ✚ the black pine seeds collecting was assured from seeds reservations found near the ecological reconstruction area;
- ✚ sowing material with protected roots was produced;
- ✚ a plantation scheme adequate to the hilly field conditions was established ;
- ✚ an evaluation of the success percentage was made one year after the plantation.

2.1. Stationary and vegetation conditions

The soil type that characterizes u.a. 108 B is rendsine. The horizons profile successions is Am-A/R-Rrz.

Regarding the forestry evolution older management studies proof that species proportion, in this u.a., were 50% beech, 10% Banat black pine, 10% mountain maple, 10% manna, 20% diverse strong essences. Today, the beech proportion has reduced with about 10% in favor of the Banat black pine, species that evolved through natural regenerations and by completion with saplings of local provenance.

The most important elements regarding the stationary and vegetation conditions are classified and described in the types of stations and forest (Table 1)

Table 1- Stationary and forest types in u.a. 108B

No.	Stationary type	Forest type	
		Code	Name
1.	Mountain/premountain beech forests, Bi, cliffs.	3.2.1.3.	Black pine mixture with deciduous, on limestone (i)
2.	Mountain/premountain beech forests, Bi, rendsines, little soils	2.3.2.2.	Mixed mountain beech forests

In the ecological reconstruction perimeter surface erosion is generalized, process emphasizes after the fire by the disappearance of shrubs and grass. In the future these phenomena can accentuate, leading to land slides, debris and cliffs rubbing, justifying the

ecological reconstruction. The following compensatory factors need to be considered for the success of the works:

- ✦ the altitudinal decrease of temperatures and reductions of the vegetation season are compensated by an increase of the solar radiation intensity;
- ✦ the reduced organic capacity of some soils can be compensated by extra humidity and a large useful soil volume;
- ✦ soil of sunny versants are droughty, instead the microbiological activity is more intense;
- ✦ shaded expositions have a shorter vegetation seasons, and the danger of early and late frosts is smaller;
- ✦ limestone presence reduced the adverse influence of altitudinal growth on the length on the vegetation season.

2.2. Works for land release and clearing

Following the 2000 year fires, trees from the ecologically reconstruction area were partially affected, through bark burns, in some case entirely, leading to the destruction of a large volume of trees. The land occupied by these trees was submitted to clearing works, consisting on felling, clearing, fashioning and gathering the foot-dry wood material in parcel 108B, that had to be reforested. The wood material had to be cut and evacuated from this perimeter was almost 1740 m³, corresponding to a number of 2100 trees. The wood material generated from the clearing works, was cut down and rough converted in stem wood, gathered with arms and deposited in stockpiles on knags.

2.3. Producing implantation material

According to the stationary conditions a planting plan of 1x2m was established, requiring the introduction of 5000 black pine sapling/ha. Therefore, to the 25 ha integral plantation a number of over 125000 black pine sapling was utilized, and in the next 2 years, for the completions, that in principle will represent about 12 ha, another 60000 more saplings shall be required.

Starting from these necessities, since the fall of 2003 were applied measures for obtaining this implantation material. This process consisted of: harvesting Banat black pine seeds from the nearest forest to the plantation area, showing in solariums and pricking out saplings from nurseries.

The black pine seeds harvesting was made in fall 2003 from the seed reservation PI.N-F232-1, situated in UP VI, u.a. 89, Băile Herculane Forestry Unit. In the spring of 2004, these seeds were shown in the Brăduț nursery solarium, from the Bozovici Forestry Unit on a nutritive bed formed from 60% beech humus, 20% spruce humus and 20% sand. The sowing was made manual, on gutters, the distance between them being 5 cm. The wetting of the germinative bed was done immediately after the sowing, and continued periodically, through aspersion, assuring the permanent moisture of the superior layer in which seed germinate. For the soil fertilization, 5 l/m² of ammonium nitrate, simple superphosphate and potassium salt, dissolved in water, were applied (Figure 1)



Figure 1. Banat black pine seeds sowing in the Brăduț nursery solarium

For the soil fertilization, 5 l/m² of ammonium nitrate, simple superphosphate and potassium salt, dissolved in water, were applied (Figure 1)

Weeds control in the solarium was done manually, through hand weeding. After the sapling were removed from the solarium, they were sorted, the healthy and vigorous ones, well raised, and with a rich radicular system were considered fit for pricking and temporary

deposited at ditch. In the spring of the year 2005 the pricking of 126900 sapling, in polyethylene bag of 12 cm diameter and 25 cm length, were made [6]. These sapling with protected roots were disposed on layers, and the holes between bags were filed with dirt, they being directly used in plantation in the years 2006 and 2007 (Figure 2)



Figure 2. Saplings layer disposal- Brăduț-Bozovici nursery



Figure 3. Bags with saplings, transported to the plantation area Domogled



Figure 4

The removal of plastic bag

After introducing the bowl and the roots in the special prepared hearth, followed the compression, by foot, of the soil surrounding the sapling to ensure a good contact between the roots with the nutritive environment (Figure 5).

In order to produce the saplings required for completions in the next two years, the block station nursery "Domogled" was also established, in which saplings were pricked out in layers, without root protection. In this case we can observe a good development of saplings, explained by the fact that the block station nursery, being situated near the seeds harvesting place, benefitted from climatic and soil almost similar to the trees that supplied the seeds [1,2]. A number of 53800 saplings were produced here, and are still maintained in culture.

After pricking all the saplings, the cultures were maintained trough hand weeding the saplings layers, wetting the cultures with rain water, and their fertilization with chemicals. In the fall of 2006, after a development period of about 2 years in open field, the bags contained saplings were transported from the Forestry Unit Bozovici in the plantation area Domogled. (figure 3)

2.4. Works for Planting

The effective preparation for plantation consisted of a partial land clearings from rocks and debris, arrangement of the plantation space and digging the hearths. The field's clearing from rocks and debris on about 30% of the surface, meaning 7,5 ha, and supposed the rocks removal from the soil and their storage in stacks and rows.

Following the plantation scheme of 1x2 m, the wooden scraps and litter were removed from 60x80 cm surfaces in the centre of with hearths of 30x30x30 cm were digged, corresponding to the earth bowl from the bag. The plantation was made after the removal of the plastic bag that protected the roots.(Figure 4).



Figure 5

Earth compressions after plantation, in order to assure a good contact of the pine radicular system with the nutritive environment

3. CONCLUSIONS

A first evaluation of the ecological reconstructions was made in the summer and fall of the year 2007, by determination of the plantation's success percent after one year, followed by a second similar evaluation, in 2008, after two years. Evaluating the success percent assumed the inventory, in 25 testing rectangular plots of 10/20 m, of the surviving saplings and their percent from the total saplings used. Each corners of these testing plots was materialized trough a wooden peg, for returning at inventories, in the same surfaces, until the definitive success of the plantation and closing the massive status.

The chart from figure 6 expresses the variations of the survival percent in different testing plots. Generally, it can observe that the survival percents in the first year (2007) were higher than in the second year (2008). Calculating some statistical values, one year after plantation (2007) the average of the survival percent was 79,56%, with a variation coefficient (s%) among the testing plots of 6,8%. In the second year (2008), the average of the survival percent was only 74,80%, with a variation coefficient (s%) among the testing plots, of 11,8%.

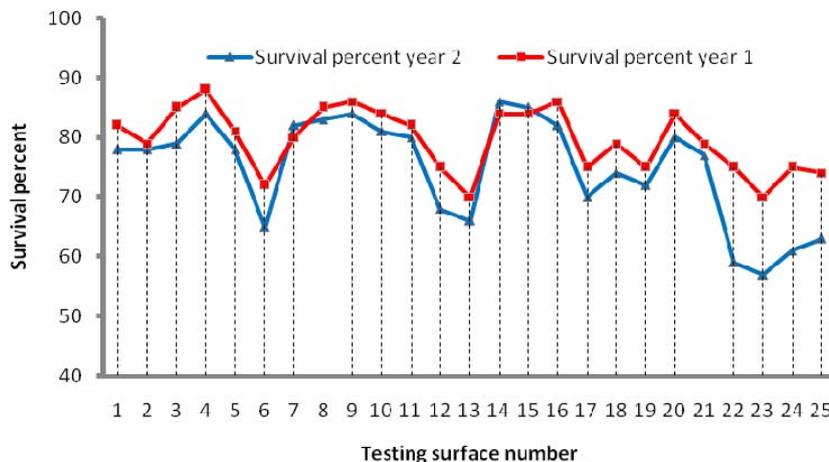


Figure 6 . Survival percent variation, one year (2007) after plantation and two year (2008) after plantation

It can, also, be observed on the graph that in 10 surfaces, the survival percents are higher than 80%. On the field, this area has been identified at the base of the versant. On the other side, in 4 plots situated in the superior parts of the versant, survival percents are under 65%.

All these data, in characteristic conditions of climate and soil of the ecological reconstruction perimeter, represent a high quality work.

REFERENCES

1. Frățilă, E.C. , *Cercetări privind răspândirea și caracteristicile ecoprotective ale pinului negru de Banat (Pinus nigra ssp.Banatica)pe teritoriul Parcului Național "Domogled-*

- Valea Cernei*”, Analele Universității din Oradea, Fascicula Silvicultură, vol IX, an 11, pag. 189-198, 2006;
2. Grigorescu, A. , *Cercetări de proveniență la pinul negru*, Anale ICAS București, vol. 37(1), pag. 19-34, 1980;
 3. Mușat, I. , *Cercetări asupra lucrărilor vechi de împădurire în zona SHEN”Porțile de Fier”* Anale ICAS București, vol26(1), pag. 147-188, 1968;
 4. Pătroescu, M et colab., *Banat black pine forests NATURA 200 SITE*, Editura Brumar, Timișoara, 2007;
 5. Popa-Costea, V et.colab., *Experimentări privind instalarea vegetației forestiere pe terenuri excesiv erodate (stâncării calcaroase)prin semănături directe cu pin negru*, Analele ICAS, 1980;
 6. Untaru, E., Mușat, I., Traci, C., *Instalarea vegetației forestiere pe terenurile degradate prin folosirea puieților de pin creșcuți în pungi de polietilenă*. Anale ICAS București, vol 37 (1), pag. 19-34, 1980;



MENTAL MAPPING IN GEOGRAPHICAL APPROACH AND REGIONAL ENVIRONMENTAL DISPARITIES AT FRONTIERS

Ildiko HORVATH GALNE¹ – Jozsef GAL²

¹NLG, Ormos E. U. 18. H-6800 Hodmezovasarhely, HUNGARY

²University of Szeged Faculty Of Engineering, Szeged, HUNGARY

ABSTRACT

Literature follows with attention the process of globalization and inter-regionalisation of environmental market. It offers and requests new possibilities and demands in agriculture too. Using of new, modern technologies in developed countries and conserve outmoded ones take difference among different less-developed and developed countries of the world. Well-known, environmental pollution does not know frontiers, so the gap between countries can be huge. What is the situation and what we can do in this area? Where to invest to win the best output?

Speaking about values we can find different measures in different countries. It takes many difficulties against how to solve problems. One is the most important factor is the disparity of short-term and long-term interests.

It has subjective and objective ways to transform and understand. People often create preconception by their mental map and connect territories and problems. It is not so simple.

We can assert reduction of over mentioned situation can be stimulated. Discrepancy and discrepancy along areas of frontiers cannot sustainable, mainly not in Central and Eastern Europe.

1. INTRODUCTION

The process of internationalization can be observed in the case of environmental programs, as well. The importance of financial funds that stimulates new technologies is increasing. This way the emphasis has been put on prevention from cleaning and controlling. It is realized differently in the case of countries on different levels, as the change to a reasonably modern technology from an undeveloped one is a significant leap forward in Eastern Europe. The problem is that the developed world appreciates only „future technologies”. The structure of environmental market in Eastern and in certain Central European countries will be similar to the earlier structure of EU, whereas a certain change in structure is proceeding towards integrated, intensive solutions in developed world. At the boundaries of regions we can often find different indexes, different measuring technologies, and significant differences in attitude (e.g. Finland and Russia) but – mainly in the case of smaller countries – the only solution is reduction of these differences and elaboration of common, harmonized solutions. The members of EU question the unification of problem management in big regions because of their disparity in measurement. Only a unified measuring technology and index system can be regarded as the basis of objective judgment of processes. An essay from Brussels confirms it. (Communication from the Commission 2003) This question is particularly problematic in the successor states of the Soviet Union, as they consider certain cases as successful ones but according to other methods these cases can be valued very modest. Placing the capital outside EU appears in this field, too, so its specific efficiency can be multiplied. Nevertheless, the process (stimulation) of abandonment of conflict between the long-term interests of environment, and the short-term interest of economy has begun in the Central and Eastern European countries-with different intensity and methods.

A kind of idea about the future is required in which different regions can develop in intensive division of labour and not in subordination to each other. The territorial inequality is lessening, the main centers of development are regions and counties, and their cooperation with other regions along the borders creates the opportunity to join the European integrating processes (Gal, J. – Valko, L. 1998). Discrepancies where countries in different state of development can be found will get more important role.

The environmental responsiveness of governments in these countries is very different. A number of enterprises deal with production, development of environmental technology and with environment protection. The role the government takes has an impact of crucial importance on them. Deriving from the nature of the market, only smaller amounts are typical that are rarely supplemented by a bigger order. This situation requires flexibility, significant capital from the enterprises; therefore a lot of them cannot survive in the rapidly changing market. From the prospect of demand the legal regulation, the lawful behavior of enterprises ensure motivation, and the pulling-impeding-moving unity of market mechanism, too, which is able to move the situation from its deadlock. The condition of its function is that it affects the whole economy including the society. In this terminology „impediment” means that we have to prevent materials, energy, products from leaving the process of production and consumption too soon. It should be realized within national frames. Regulation supporting the pull factor removes by-products from the system and it does not let it accumulate to harm the environment. Recycling, collection and managing of waste materials play important roles in this process. Most processes have regional impacts, so the role of cooperation is appraised. Only a small part of these activities can be done on purely market base, in most cases the token of effective solution is in the hand of the state. We can find both good and unacceptable examples for it in Central and Eastern Europe. For instance, Austria’s efforts prove that results can be reached in the fields of collection of paper refuse and its use as a second raw material etc., which projects have failed in other, mainly Eastern European, countries.

The judgment of environmental market is changing into a favorable direction in Central and Eastern Europe because of the accepted positive externalities of the environment protection. Its effect can be observed in the legal phase, in regional development, in manpower market and in other innovative processes, as well.

2. DISCUSSION

The above mentioned facts are supported by a study from Tubingen (Valko L. 1998), according to which 45% of the Western European environment technical enterprises can survive the first 5 years, and only 35% of them the first 10 years. It is mentioned that the condition of survival is that the given enterprise can comprehend the whole market scale from planning through analysis, consultation, execution, operation, and service to the after-care. An enterprise with only one of these activities financially runs a grave risk. Long-term situation of services with oversupply in environmental market is getting more risky comparing to firms presenting intensive environmental technique, technology. The condition of survival is adjustment to the regional and local conditions, this way the role of eco-marketing is going to be appraised. In this context the state’s role can be mentioned again, and the dynamic effect of steps that increase demand. There are regional programs not only in EU but in discrepancies, as well. Regional approach is supported by the fact that Eastern European countries that were excluded from joining in 2004 should change their environmental policy and their environment economical programs rapidly, since their backwardness is significant.

Chart no 1
National Environment Protection Program II Hungary

Source: NKP-II

TAP megnevezése	teljes költsége (mFt)	A 2003-2008 közötti időszak kp-i költségvetésből (mFt)	%
1. Quality of urban environment	1.626.561	900.647	29,3%
2. Water protection and sustainable use	1.095.875	680.100	19,7%
3. Change of climate	961.273	262.575	17,3%
4. Health and safety	682.273	386.757	12,3%
5. Use of fields	541.752	245.046	9,7%
6. Waste management	363.000	94.817	6,5%
7. Biodiversity and ecological protection	181.166	106.706	3,3%
8. Safety of environment	64.527	61.677	1,2%
9. Development of environmental awareness	40.577	32.612	0,7%
Together:	5.556.820	2.770.937	100,0%

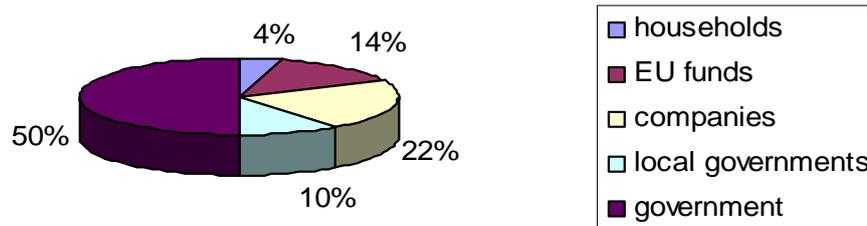
In the National Environment Protection Program II Hungary (chart no 1) has formulated a thematic action program and has planned expenses which show that harmful effects of urbanization and water protection claim the highest expense. These two problematic fields are typical of the Central and Eastern European countries. Technical-technological side of solution is ensured in these countries; the problem is the lack of financial sources. It is worth examining what distribution of sources Hungary planned in order to realize her planned obligation. I suppose that the proportions are similar in other joining countries, as well. The situation is entirely different in the case of other

countries as the rate of EU-funds is essentially smaller. The source-proportion (diagram no 1) coming from the central and municipal budgets exceeds 60%, EU makes a contribution of 13,9 % to it, and finally, there is a problematic self-share, as well.

In the early 60's American psychologists and geographers modeled a special method of cartography, which is surveying the familiarity with a place by means of the mental map. With the mental map we analyze the map formed in people's brain about their immediate environment.

Diagram no 1
Distribution of financial means in Hungary 2003-2008
(planned)

Source: NKP-II



This method helps us to see which places, flows approaching solutions are known for the inhabitants of a settlement; according to the data we can get a picture about the question that which the most interesting and the less interesting environmental impacts are, where the cardinal points of a region or a town can be found. It is worth comparing these notes with the mental maps of those who are interested in the environmental flows.

The answers to these questions help us to examine which are the questions about the areas that have aroused the people's attention and which are we have to highlight.

To serve this purpose we have to introduce the following terms: region, factors that form the region, regional development, environmental conditions. Then we show the development of the region and the immediate environment, together with the advantages and disadvantages that follow the development of the given area. If a really consistent and environmentally friendly transformation is expected, it is worth calling the attention to it.

For the sake of the efficient teaching-learning form the students should be able:

- ✚ to analyze the typical region according to different points of view,
- ✚ to recognize the typical region with the help of pictures and descriptions,
- ✚ to recognize and to name its most important features,
- ✚ to make a drawing about the region, to make a description of it,
- ✚ to try to imagine and to draw the possible future changes of the typical region,
- ✚ to inform about the rehabilitation of an environmentally destroyed region from different sources of information.

The question of the method of the process is very important here. It is the most obvious to make a task sheet where the following methodological possibilities can be exploited well:

- ✚ to draw a region on the basis of their knowledge and experience,
- ✚ to make a description of a region on the basis of lesson experiences, visual or map information,
- ✚ to analyze a region according to some given points of view,
- ✚ to make students recognize the process of a regional development with ordering pictures and drawings,
- ✚ comparative regional analysis on the basis of a written text (for example the same region in different times or different regions in the same time).

The analysis was about a region at border of Romania, Serbia and Hungary by means of which it was possible to show the connection between man and his environment, and it pointed out how the natural region became economic region.

Global problems of our environment has been revealed during decades, and at the same time the favorable counter moves have been formulated more accurately. Content of these frameworks (international organizations, contracts, financial funds etc.) depends on the responsibility taken by the region and nation. The level of environmental knowledge of nations and the available system of means move on a very wide scale. Therefore, the different short-term interests of developed and undeveloped countries have a significant impact on the international cooperation of environment protection. It

seems that the most effective way of managing global problems is the cooperation between small regions. This solution is able to handle regional disparities and discrepancies above all. In the Central and Eastern European countries the regional cooperation has been getting stronger in most regions since the 90's –after the former political alliance system had collapsed. „Visegrád countries”, Carpathian-Europe-Region, Alps-Adria or the league of Vajdasag, Transylvania and South-Eastern Hungary are good examples for it. In the field of environmental protection these cooperation could not have results that would take their environmental status closer to the Western European level. The main reason for it is the lack of financial sources.

3. CONCLUSIONS

As a result of a new attitude on both sides of discrepancies the more developed country stimulates the environmental problems, rehabilitation of the less developed one with her increased role. In the case of Austria and her Eastern neighbours the regional environmental investments can bring bigger benefit for the less developed countries but at the same time they have a positive effect on the whole region, as well. According to a certain research the economical and ecological profit of Austria's foreign environmental investments can be the triple of the same investment inside the borders of Austria.

This change means that environment political principles have new definitions, so does the principle of prevention which emphasizes the efficiency of prevention as opposed to rehabilitation of damages. The principle of the individual, who caused damage which says, that this individual has to bear the costs of rehabilitation. The principle of subsidiary, which says that adequate steps have to be taken on the most efficient institutional level. The principle of cooperation and harmonization which attempts to synchronize the environment protection policy of different countries in the interest of the most favorable output. According to the principle of compatibility the environment policy should be integrated into the work of other fields, so it has to be in harmony with the social and economical policy.

REFERENCES

- [1] Communication from the Commission [2003], Commission of the European Communities, http://europa.eu.int/comm/research/industrial_technologies/16-04-03_compenvironment_en.html
- [2] Gal Jozsef – Valko Laszlo [2000]: Environmental Education in Hungarian Higher Education, (A kornyezeti nevelés a magyar felsőoktatásban) (angol nyelven), Periodica Polytechnica, Social and Management Sciences, Vol. 8. No. 2, Budapest, p. 121-131.
- [3] Nemzeti Kornyezetvedelmi Akcioprogram-II, (kezirat), Budapest, [2002].
- [4] Valko Laszlo [1998]: Kornyezeti ipar és szabályozás, osztrak esettanulmány, OKO, IX. évfolyam, 1998. 3-4. szám, p. 50-72.
- [5] Galne Horvath Ildiko - Gal Jozsef [2009]: Some Educational and Logistic Aspects of Mental Mapping of Rural Areas, AVA Congress, Debrecen 2009.03.26-27. conf. cd



BIOSOLIDS AND VOLCANIC TUFF INFLUENCE OVER THE UPTAKE COEFFICIENT OF CADMIUM AND ZINC FROM POLLUTED SOILS IN MAIZE CULTIVATION

Smaranda MASU¹, Valeria RUS¹, N. DRAGOMIR²,
Stela URUIOC³, Mariana ALBULESCU³

¹National Research and Development Institute
for Industrial Ecology-ECOIND, Timisoara, ROMANIA

²Animal Sciences and Biotechnologies Faculty, Timisoara, ROMANIA

³ West University of Timisoara, Chemistry,
Biology & Geography Faculty, Timisoara, ROMANIA

Abstract:

Potentially toxic elements such as cadmium, lead and zinc can accumulate in cropland soils through fertilizer application. This study analyzes, comparatively, the uptake coefficient (UC) of cadmium and zinc in maize (*Zea mays* L.) destined as fodder for animals. Results indicate that the addition of biosolids can change the plant bioavailability for metals from soil. During the first phenophases of plant development, it especially accumulates cadmium into the aerial tissues. The use of the pillared volcanic tuff of type tuf-Al_n as an addition to the organic fertilizer, determines metal bioaccumulation reduction in young plants.

Keywords:

cadmium, zinc, bioaccumulation, bioavailability, soil, *Zea mays*

1. INTRODUCTION

The long application of organic fertilizers as manure, biosolids (municipal sludge anaerobic fermented) or anorganic fertilizers based on phosphatic rocks, determines both the enrichment of the agricultural land in nutritive substances, nitrogen and phosphorus, and a gradual accumulation of cadmium, lead and zinc. [5, 8, 9].

The accumulation level of heavy metals in agricultural soils reached a point which alerted the specialists from numerous countries in Europe (England, Germany, Norway), America (USA) and Australia [1, 2, 3, 4, 12]. The statistic analysis of the gathered data regarding the transfer of these metals from soil into plants, intended for human and animal consumption, is of general concern. Researches demonstrated that in plant tissues the heavy metal quantity accumulates directly proportional with the rhythmic addition of metal in soil. Accumulation rate depends on soil characteristics, plant species, plant age, hydroclimatic conditions, and type of tillage [5].

Mankind faces, in the last years, different aspects of waste storage, especially of the increasing amounts of municipal sludge. Many countries chose as solution the reuse of these as organic fertilizers for agricultural crops, due to the high content in fertilizing agents, nitrogen, and phosphorus [2, 11, 13]. Analysis of the agricultural lands fertilized with biosolids on a long period of time shows that soils can accumulate between 0.035-33.8 mg Cd/kg of D.M. and 16-5,010 mg Zn/kg of D.M., for those cultivated with wheat, and between 0.02-2.31 mg Cd/kg of D.M. and 19-429 mg Zn/kg of D.M. for those cultivated with barley [1]. Plants can also accumulate significant quantities of heavy metals. Thus, maize can accumulate in the aerial parts between 1-9 mg Cd/kg of D.M. [12]. Metal accumulation in crops represents now one of the greatest problems of the world [2]. The addition of metal immobilizing agents in soil, such as zeolites from volcanic tuffs, can significantly reduce the bioavailability of plants for certain metals [13].

To perform this study we took under consideration the following aspects: - cadmium and zinc content increase from cropland soils as a result of some anthropic activities, as is the case of the area adjacent to the mining activity from Moldova Noua, located in south-western part of Romania; - the use over long periods of some fertilizers that annually add small quantities of toxic metals, metals that accumulated in time; - crop bioavailability to accumulate metals such as cadmium and zinc in the aerial parts; - the soil addition of a metal immobilizing agent such as the modified domestic volcanic tuff, which can significantly reduce the content of the metal up-taken by plants from the soil solution.

2. MATERIALS AND METHODS

The experimental field is located at Banat's University of Agricultural Sciences and Veterinary Medicine in Timisoara (western Romania). The study was done on an experimental block comprising plots with a 13.6 m²/lot surface. Cadmium, lead and zinc salts were added to the soil, in order to obtain a pollution level similar to the one determined in the analyzed soils from Moldova Noua. Maize (*Zea mays* L.) was used as a test plant. Heavy metals were applied to soil in soluble form before seeding with maize.

The variants of the treatments of the soils on which the experiments were done are:

V1 - variant without organic fertilizer (biosolids) addition, which comprises three categories of soil (Fig.1): M - control soil with characteristics of normal soil; P - soil polluted with cadmium, zinc and lead salts; T - soil polluted with cadmium, zinc and lead salts and amended with pillared materials, of tuff-Al_n type;

V2 - variant of fertilized soil with organic fertilizer (biosolids), which also contains three categories of soil (Fig.2): FM - control soil; FP - polluted soil; FT - soil polluted and amended with pillared materials, of tuff-Al_n type.

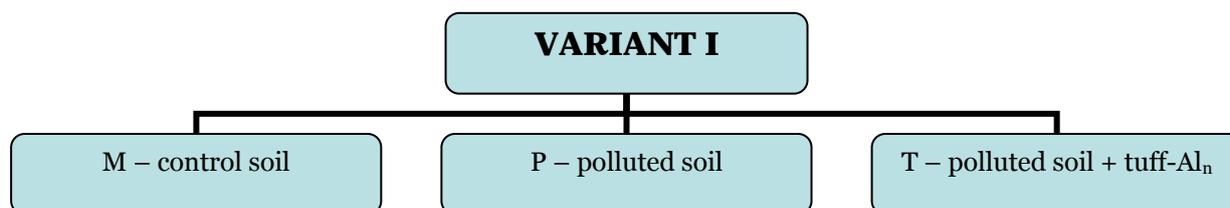


Figure.1. Variant I of treatment without biosolids addition.

M - control soil with normal soil characteristics; P- soil polluted with cadmium, zinc and lead salts; T - soil polluted with cadmium, zinc and lead salts and amended with pillared materials of the tuff-Al_n type

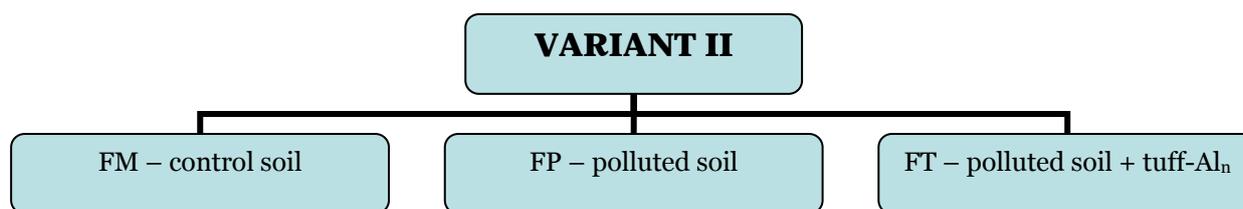


Figure.2. Variant II of treatment with biosolids addition.

MF - control soil with normal soil characteristics; FP- soil polluted with cadmium, zinc and lead salts; FT – soil polluted and amended with pillared materials of the tuff-Al_n type.

Fertilization was done with organic fertilizer (biosolids). Fertilizer dose was of 30 to of D.M./ha. Table 1 shows the characteristics of biosolids for the experiment.

Soil analysis after the artificial heavy metal pollution and fertilization, showed the following: cadmium from polluted soil was of 1-3.4 mg/kg of D.M., zinc was of 670-720 mg/kg of D.M, lead was of 58-70 mg/kg of D.M., and the stabilized pH was of 6.2-6.3.

Metal content from the polluted soils in this experiment ranks as sensitive soils and/or less sensitive, alert level, according to the effectual norms in Romania (Table 2).

Table 1. Characteristics of the biosolids used for fertilization for the experimental plots and heavy metal quantity introduced in soil for the 30 tonnes/ha dose.

Biosolids characteristics	Value	Addition of metals and other substances from biosolids (30 to of D.M./ha) in soil
pH	5.80	-
Dried matter, %	18.3	-
Humidity, %	81.7	-
Volatile substance, %	32.0	-
Extractible in ether of petroleum, mg/kg	2.11	-
Manganese, mg/kg D.M.	536.2	5.89
Zinc, mg/kg D.M.	1,575	17.9
Copper, mg/kg D.M.	481.0	5.29
Cadmium, mg/kg D.M.	76.60	0.84
Chromium, mg/kg D.M.	1,420	15.62
Nichel, mg/kg D.M.	220	2.42
Lead, mg/kg D.M.	591	6.51
N _{total} , %	0.57	0.06
P _{total} , %	0.33	0.035
Organic substance, %	34.3	3.77

Table 2. Reference values for metals in soils, according to MAPPM 756/1997, in mg/kg of D.M.

Element	Normal values	Alert level			
		Sensitive soils	Soils less sensitive	Sensitive soils	Soils less sensitive
Cadmium	1	3	5	5	10
Lead	20	50	250	100	1,000
Zinc	100	300	700	600	1,500

Soils from the T and FT categories were amended with a quantity of 2 to/ha of pillared domestic volcanic tuff, of tuff-Al_n type (ECOIND patent) [6].

After the geochemical stabilization for 30 days, the fertilized and amended polluted soils were seeded with forage maize. Analysis of plant metal accumulation from aerial tissues of plant parts (stem, leaves, and grains) was done on dried plants. Plant sampling was done accordingly to the methodology described in STAS 9597/1-74, and the sample analysis was done accordingly to STAS 9597/17-86. Plant extract analysis was done by using a spectrophotometer with atomic absorption, Varian Spectra AAS.

The comparative analysis of metal bioaccumulation from aerial tissue of plants was done through the uptake coefficient by plants, designated as UC (uptake coefficient) [7, 10]

The uptake coefficient is obtained by the ratio between the metal quantity accumulated in plant tissues that are grown on adjacent soils with anthropic activities and the metal quantity from the same part of the plant, grown on the unpolluted, control soil:

$$UC = Q_P / Q_M$$

where: Q_p – metal concentration accumulated in tissues of the plant grown on polluted soils;

Q_m – metal concentration accumulated in the tissues of the same plant grown on the unpolluted, control soil.

3. RESULTS AND DISCUSSIONS

The following tables present data regarding the accumulation level of cadmium and zinc in the aerial parts of maize (*Zea mays* L.) destined for animal forage.

From sample analysis of the aerial parts of the plants, resulted that lead was absent. Probably the two metals, cadmium and zinc, were competitively assimilated, and lead was more difficult to be accessed by plants in the presence of the other two.

Table 3 shows the cadmium and zinc quantities, periodically accumulated in the aerial parts of the forage maize (*Zea mays* L.)

Table 3. Cadmium and zinc quantities accumulated in the aerial parts of forage maize (*Zea mays L.*) in two successive phenophases

Treatment	Soil category	Zinc (mg/kg of D.M.)		Cadmium (mg/kg of D.M.)	
		First phenophase	Second phenophase	First phenophase	Second phenophase
Without fertilization with biosolids	M - control	4.20	4.20	0.025 *	0.025*
	P - polluted	14.2	10.5	0.380	0.500
	T - polluted + amended	9.65	14.7	0.320	0.380
Fertilization with biosolids	FM - control	2.80	8.63	0.570	0.700
	FP - polluted	12.8	14.50	1.300	1.470
	FT - polluted + amended	3.12	5.00	1.200	1.417

* the determined quantity of cadmium in plant tissues obtained on unpolluted soils can originate from atmospheric deposits, or from transport of the pollutant by the abundant rainfalls from the 2008 spring, from the plots with polluted soil in those unpolluted.

Zinc accumulates differently in the aerial parts, depending on the plant growth level and treatment type. In the variants without biosolids fertilization, zinc quantity remains constant (4.2 mg/kg) in plants grown on the control soil. In plants grown on polluted soil (P) the quantity of zinc in the second phenophase, at plant maturity, is lower (10.5 mg/kg) compared to the first phenophase when the plant is immature (14.2 mg/kg).

Addition of tuff- Al_n in the variant of no-biosolids soil, reduced the bioaccumulation level of zinc with 32% in the first phenophase, from 14.2 mg/kg to 9.65 mg/kg.

Addition of biosolids had a synergetic effect in the variant of the treatment with biosolids-pillared tuff to decrease bioaccumulation, up to 75%, (from 12.8 mg/kg to 3.12 mg/kg) for zinc accumulation in plant tissue.

Cadmium is introduced in soil through biosolids addition. In time, it accumulates in the aerial parts of plants. Addition of biosolids will determine the increase of cadmium accumulation in plants up to 71% in the first phenophase (from 0.38 mg/kg to 1.3 mg/kg) and up to 66% in the second phenophase (from 0.50 mg/kg to 1.47 mg/kg). Addition of the pillared tuff- Al_n in the experimental variant that doesn't use fertilization with biosolids, doesn't limit cadmium bioaccumulation in the aerial parts of plants, the quantitative values being similar (0.38 mg/kg; 0.32 mg/kg). This situation can be noticed in advanced phases of plant development, in the second phenophase, of maize harvest for forage, recording similar values ((0.50 mg/kg; 0.38 mg/kg).) When adding pillared tuff (tuff- Al_n) to the experimental plots, fertilized with biosolids, no effects on the bioaccumulation reduction could be noticed, values being similar (1.47 mg/kg in variant FP; 1.41 mg/kg in variant FT). Biosolids have components with no limitation effect for metal bioaccumulation in plant tissue.[6]. The forage maize biomass shows significant quantities of cadmium (1.2 mg/kg; 1.4 mg/kg), which makes it unusable as food for animals.

Tables 4, 5, and 6, show the values of the uptake coefficient of cadmium and zinc from polluted soils, unfertilized and fertilized with biosolids, with and without amendments that immobilize metals in soil of the Tuff- Al_n type compared to control soils.

Table 4 shows the uptake coefficient for cadmium and zinc from polluted soils compared to the unpolluted soils ($UC = Q_P/Q_M$) for forage maize in the first phenophase, when the height of plants is of 20-30 cm. The uptake coefficient (UC) is reported to the quantity of metal accumulated in plants cultivated on common soils, unfertilized, unpolluted, and non-amended.

 Table 4. Uptake coefficient of cadmium and zinc by forage maize (*Zea mays L.*), in the first phenophase

Treatment	Experimental variant	Uptake coefficients (UC)	
		Cd	Zn
Without addition of biosolids	P – polluted soil	14.4	3.80
	T – polluted soil and treated with Tuff- Al_n	12.8	2.28
	FM – normal soil	22.8	0.70
With addition of biosolids	FP – polluted soil	33.0	3.16
	FT – polluted soil and treated with Tuff- Al_n	24.0	0.65

From the data presented in table 4, we can see that when grown on soil with significant quantities of metals (cadmium and zinc), the cultivated plants, under such conditions, will uptake, in the aerial tissues, higher quantities of metals than the plants cultivated on unpolluted, normal soils.

Thus, in the case of zinc, the uptake coefficient was of 2.28 – 3.80 and for cadmium it was ten times higher (UC= 33).

Biosolids addition needed to fertilize the soil, did not modify the uptake coefficient for zinc (UC=3.80 in variant P and UC=3.16 in variant FP) in plant tissues, but it also favored a higher accumulation of cadmium.

Thus, the uptake coefficient for cadmium increases twice (UC=33.0 in the variant FP) compared to the similar variant, of polluted and unfertilized soil (UC=14.4 in variant P).

Table 5 shows the uptake coefficient for cadmium and zinc from polluted soils compared to the unpolluted soils (UC = Q_P/Q_M) for forage maize in the second phenophase, when the height of plant is of 50-70 cm.

Table 5. The uptake coefficient for cadmium and zinc by the forage maize (*Zea mays L.*), in the second phenophase

Treatment	Experimental variant	Uptake coefficient (UC)	
		Cd	Zn
Without addition of biosolids	P – polluted soil	20.0	2.50
	T – polluted soil and treated with Tuff-Al _n	15.2	3.50
	FM – normal soil	28.0	1.98
With addition of biosolids	FP – polluted soil	16.0	3.45
	FT – polluted soil and treated with Tuff-Al _n	13.0	1.25

In the second phase of plant development, when forage maize is harvested, it can be observed that zinc is taken in the same proportion as in the first phase, reporting it to the plants cultivated on the control soil. For zinc bioaccumulation, in treatment variant without addition of biosolids UC is of 2.5 – 3.5, and in the ones with biosolids UC was of 3.45.

In the case of cadmium could be observed that, along with the plant growth, the plant will uptake from the polluted soil higher quantities of metal. The accumulation level in tissues increases over 20 times compared to the accumulation in the plant tissues cultivated on unfertilized, normal soils. Biosolids addition will not determine significant changes in the UC values.

Table 6 shows the values for the uptake coefficient for cadmium and zinc in the case of domestic volcanic tuff - Tuff-Al_n, type addition to polluted soils fertilized or unfertilized with biosolids, in the two growth phenophases of plants.

Table 6. Uptake coefficient for cadmium and zinc determined for the addition of Tuff-Al_n to polluted soils, unfertilized (V1) and fertilized with biosolids (V2).

Treatment	Experimental variant	Uptake coefficient (UC)			
		First phenophase		Second phenophase	
		Cd	Zn	Cd	Zn
V1- Without addition of biosolids	T – soil polluted and treated with Tuff-Al _n *	0.84	0.66	0.76	1.34
V2- With addition of biosolids	FT – soil polluted and treated with Tuff-Al _n **	0.75	0.2	0.27	0.34

*UC = quantity of metal from plants grown on polluted soil with addition of Tuff-Al_n / quantity of metal from plants grown on polluted soil without addition of Tuff-Al_n.

**UC = quantity of metal from plants grown on polluted and fertilized soil with addition of Tuff-Al_n / quantity of metal from plants grown on polluted and fertilized soil without addition of Tuff-Al_n.

Addition of Tuff-Al_n to polluted soils, unfertilized with biosolids, determines the reduction of the uptake coefficient of metals by plants from soils polluted and treated with Tuff-Al_n, compared to those without addition of Tuff-Al_n.

It can be observed that, in the first phenophase, both cadmium and zinc accumulate to a sub-unitary level of UC= 0.66 – 0.84 in the case of plants grown on areas polluted and treated with volcanic tuff. In the second phenophase, the cadmium accumulation maintains within the same range (UC= 0.76), but increases for the accumulation of zinc (UC= 1.34).

In the second case, when the soil is polluted and fertilized with biosolids, the addition of pillared tuff determined at first the decrease of the accumulated metal quantity.

In the advanced phases of plant growth, the metal quantity uptake decreased, the uptake coefficient being only 0.27 – 0.34.

Sub-unitary value of UC demonstrates the efficiency of pillared domestic volcanic tuff - Tuff-Al_n type, as amendment of soils polluted with heavy metals and fertilized or not with biosolids. It also demonstrates the difference between plants cultivated on amended soils with Tuff-Al_n, and those grown on similar soils untreated with the metal immobilization agent based on pillared domestic volcanic tuff - Tuff-Al_n type.

4. CONCLUSIONS

The presented data are the result of an experiment regarding biosolids use as organic fertilizer and of the volcanic tuff - Tuff-Al_n type as amendment to soils artificially polluted with cadmium, lead and zinc, in order to reduce their bioaccumulation in forage maize (*Zea mays L.*).

Values of the obtained uptake coefficients (UC) for cadmium and zinc depend on the affinity of plants for a certain metal, of the metal mobility in soils and the variant of treatment compared to the control soil (unpolluted).

Addition of volcanic tuff - Tuff-Al_n type, influenced the uptake coefficient for cadmium and zinc, compared to the control soil, especially when the polluted soil was associated with biosolids.

Generally, pillared material Tuff-Al_n, reduced cadmium and zinc transfer from soil to plant tissues, both in the first and second phenophases.

REFERENCES

- [1] Adams, M.L., Zhao F.J., McGrath, S.P., Nicholson, F.A., Chambers B.J. Predicting cadmium concentration in wheat and barley grain using soil properties, *Journal of environmental quality Journal*, Vol. 33 (2): 532-541, 2004
- [2] Bhogal, A., Nicholson, F. A., Chambers, B.J., Shepherd, M.A., Effects of past sewage sludge addition on heavy metal availability in light textured soils. Implications for crop yields and metal uptakes, *Environ. Pollut*, 2,413-423, 2003.
- [3] Fries, W., Lombi E., Horak O., Wenzel W.W., Immobilization of heavy metals in soils using inorganic amendments in a greenhouse study. *Journal of Plant Nutrition and Soil Science*, 166: 191–196, 2003
- [4] Hocking, P.J., McLaughlin, M.J., Genotypic variation in cadmium accumulation by seed of lineseed, and comparison with seeds of other crop species. *Australian Journal of Agricultural Research*, 51: 427–433, 2000
- [5] Kumpiene, J. J., Lagerkvist, A., Maurice, C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review, *Waste Management* 28: 215-225, 2008.
- [6] Mășu S., Lixandru B., Trandafir G., Rechișean D., Gașpar S., Pintoi O., Study of the process of zinc bioaccumulation in corn cultivated on polluted soils., *Lucrari Zootehnie și Biotehnologii*, Vol. XXXVIII, Timișoara: 44-54, 2005
- [7] McBride, M.B, Martinez, C.E., Topp, E., Evans, L., Trace metal solubility and speciation in a calcareous soil 18 years after notill sludge application, *Soil Science*, 165 (8): 646-656, 2000
- [8] Puschenreiter, M., Horace, O., Fries, W., Hart W., Low-cost agricultural measures to reduce heavy metal transfer into the food chain – A review *PLANT SOIL ENVIRON.*, 51, (1): 1–11, 2005
- [9] Singh, B. R., Myhr K., Cadmium uptake by barley as affected by Cd sources and pH levels, *Geoderma* 84: 185-194, 1998.
- [10] Silveira, M.L.A., Alleoni, L.R.F., Guilherme, L.R.G., Biosolids and heavy metals in soils, *Scientia agricola*, 60, nr. 4: 793-806, 2003
- [11] Snyman H.G., Jong, J. M. De, Avelig T. A. S., The stabilization of sewage sludge applied to agricultural land and the effects on maize seedlings. *Water Sci. Technol.* 38 (2): 87-95, 1998
- [12] Vassilev, A., Vangronsveld, J., Yordanov I., Cadmium Phytoextraction, present state, biological backgrounds and research needs, *Bulgarian Journal of Plant Physiology.*, 28(3-4): 68-95, 2002
- [13] Vessolek, G., Fahrenhorst, C., Immobilization of heavy metals in a polluted soil of sewage farm by application of modified aluminosilicate: a laboratory an numerical displacement study, *Soil Technology*, vol. 7, ISS: 221-232, 1994



ANALYSIS OF PRECIPITATION QUANTITY IN VOJVODINA

Atila BEZDAN, Radovan SAVIC, Atila SALVAI

Faculty of Agriculture, Department of Water Management, Novi Sad, SERBIA

Abstract:

In view of the fact that the areas of arable soil in Vojvodina covered by irrigation systems are very small, and so are the possibilities to diminish the negative consequences of occasional droughts, our agricultural production is greatly dependent on the natural conditions. The natural meteorological processes, including also precipitation are of stochastic character, so that they can not be described by mathematical expressions in a simple way, and their future states can not be reliably predicted. On the example of precipitation data registered at the meteorological station R. Sancevi we demonstrated the application of several statistical methods to analyze the periodicity.

Keywords:

precipitation, changes, periodicity

1. INTRODUCTION

As a consequence of the insufficiently developed irrigation systems in Vojvodina, and relatively small areas of arable land where irrigation is possible, the atmospheric precipitation are still the major factor in providing water to the soil and crops. Lack of precipitation in one area in relation to average perennial value for specific period, leads to the occurrence of meteorological drought that can also cause substantial decrease of water quantities in aquatories and decline in ground water levels (hydrological drought), and thereafter it can also hinder proper growth and development of crops (agricultural drought). Hence, the phenomenon of droughts, as a time series of a stochastic character, deserves serious attention and thorough analyses.

The ever increasing water demands, and the simultaneously increasing danger of potential deterioration of water quality, have directed substantial research activities on the problems concerning the causes of drought occurrence. In view of the fact that in our present circumstances a decisive role in drought occurrence have the amount and time distribution of precipitation, i.e. their shortage, a need is evident for many-sided study and analyses of this complex phenomenon.

2. THE STUDY

The natural meteorological processes, including also precipitation, are of stochastic character, so that they can not be described by mathematical expressions in a simple way, and their future states can not be reliably predicted. Hence, for this purpose certain statistical methods are to be used. It is frequently the case, especially in the agricultural investigations and practice, that the description of precipitation is based only on the most elementary statistical indicators which, lacking the necessary application of all the preceding and accompanying analyses, may yield erroneous conclusions and predictions. Often, such analyses pay insufficient attention to the fact that the time series can have a certain cyclic component, so that it is of crucial importance to choose correctly the time period taken for the analysis. Depending on the nature of the variable, the duration of the period in which a process is developed and the effect of man and the environment, stochastic series can have, a more or less expressed deterministic component, which is manifested either through periodicity, abrupt changes, or trends.

It has been observed that the direct causes of hydrometeorological phenomena, solar activity, atmospheric processes, and the like, have marked elements of periodicity. Hence, it

can be expected that their consequences also exhibit a certain degree of periodicity, although it is very difficult to prove direct partial cause-consequence relations [1,2]. A certain stochastic series is to be analyzed on the basis of the results of long-term measurements and registering of all the relevant hydro meteorological quantities in the past. In order to carry out the analyses in a correct way, and thus provide a better description of the phenomenon itself, it is necessary to ensure that the analyzed sample encompasses at least two full hydrologic, or meteorological cycles, one series of dry and one series of wet years [3,4,5].

The cyclic nature of a certain phenomenon which can be represented by a stochastic time series can be analyzed using one or more of the existing numerous methods, such as autocorrelation, moving average, periodogram, integral curve of modular deviations, etc. On the example of a series of monthly and annual precipitation sums registered at the meteorological station Rimski Sancevi near Novi Sad, in the 1948-2008 period for the monthly and annual values, by the presented analysis we demonstrated the applicability of some of the above meteorological and statistical methods for the analysis of droughts.

3. ANALISES AND DISCUSIONS

After establishing that they are representative and consistent, and on proving their independence by Anderson’s autocorrelation test, the series of data on monthly and annual precipitation sums registered at the Rimski Sancevi meteorological station were analyzed for their homogeneity. For this purpose use was made of Student’s T-test and normalized Z-test. In this way it was established the significance of the differences of the mean values and standard deviations between the series of data for the 1948-1994 period and the second series for encompassing the 1995-2008 period.

On the basis of the results presented in Table 1 it is evident that at the level of annual values, a inconsiderable precipitation increases occurred (the average value is higher by 31.7 mm), whereas for the monthly sums of precipitations the situation differs from one month to another. A largest increase of monthly precipitation in the analyzed period was registered in September and October (15.1 and 15.8 mm), as well as in some the other months (5-11.4 mm), whereas in February, June, August and December insignificant decreases in precipitation (0.2-9.4 mm) were observed. In all cases, the noticed differences for the significance level of $\alpha=0.05$ and the corresponding number of degrees of freedom, there were no statistically significant differences, i.e. the series can be considered as the homogeneous ones.

Table 1. Test of the homogeneity of monthly and annual precipitation. Criterion for the hypothesis acceptance at the significance level of $\alpha=0.05$ and the corresponding number of degrees of freedom for T-test $t=0\pm 2.00$, and for Z-test $z=0\pm 1.96$.

Statist. indicat.	M o n t h l y v a l u e s												Years
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Subseries 1: Period 1948 - 1994; N=47													
Min. 1	5	3	3	15	15	20	2	8	2	0	9	3	384
Max. 1	102	113	117	90	134	204	169	148	89	113	156	150	888
Avg. 1	36	38	36	48	55	87	63	55	37	39	51	54	599
Std. 1	23	29	24	17	31	41	41	34	22	33	29	32	113
Subseries 2: Period 1995 - 2008; N=14													
Min. 2	8	1	3	9	17	28	11	0	4	1	7	16	289
Max. 2	75	64	95	156	176	237	209	125	160	143	143	138	999
Avg. 2	41	29	36	54	67	79	68	50	53	55	57	45	631
Std. 2	18	17	24	34	37	45	55	33	39	43	33	31	184
Δ Avg.	-5.0	9.2	0.2	-6.4	-11.4	8.1	-5.9	5.3	-15.1	-15.8	-6.2	9.4	-31.7
t	-0.73	1.10	0.02	-0.94	-1.13	0.62	-0.43	0.51	-1.81	-1.43	-0.68	0.97	-0.77
Z	-0.85	1.45	0.02	-0.68	-1.04	0.61	-0.37	0.53	-1.38	-1.26	-0.63	1.00	-0.61

The time variations of annual precipitation sums are presented in Fig. 1.a. However, only after carrying out the periodogram analysis (Fig. 1.b) it appeared that the most probable

durations of the identified cycles are about 14 years (maximum values of the periodogram peaks - halves of amplitude squares). The hydrological duration and the periodic sequence of dry and wet periods can be best observed on the integral curve of modular deviations. In this, the increasing values of this function denote precipitation surplus (the series of wet years) and decreases determine precipitation deficits (Fig. 1.c). On the integral curve of modular deviations is clearly evident the termination of an extremely dry and the beginning of another wetter period.

The periodicity of precipitation occurrence can also be followed on the basis of the moving average. It can be noticed that in respect of annual precipitation registered at the Rimski Sancevi meteorological station the period since 1982 to 1994 can be characterized as extremely dry. After that, started a extremely wet period (in 2001 annual precipitation sum where absolutely maximal - 999 mm)

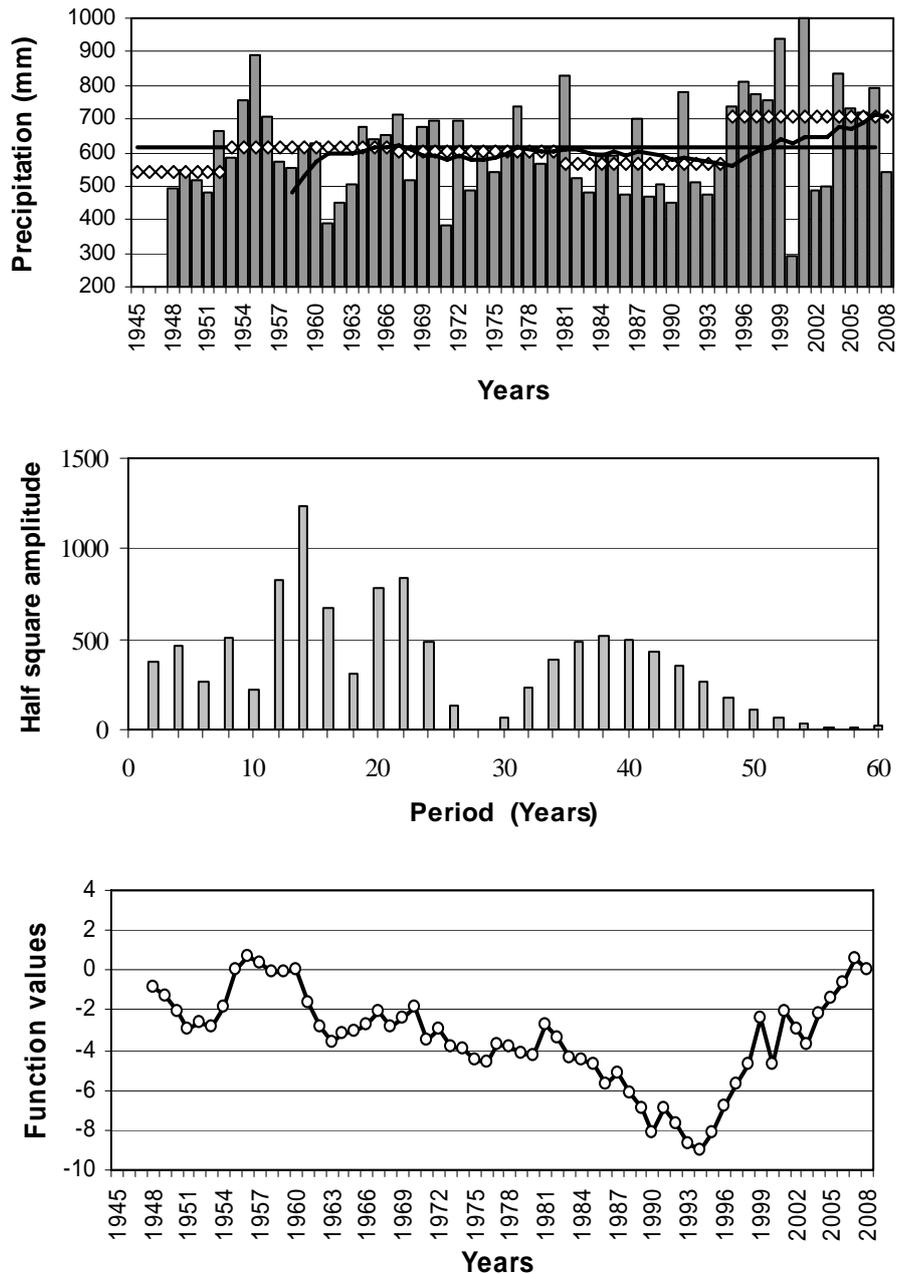


Fig. 1. a) Sum of annual precipitation, their average values and the 14-year moving average; b) Periodogram; c) Integral curve of modular deviations for the meteorological station Rimski Sancevi in the 1948-2008 period

4. CONCLUSIONS

The obtained results indicate that on the basis of data registered at the Rimski Sancevi meteorological station, a period 1982-1994 could be observed that is characterized by extreme deficiency of precipitation; in 1995 started a extremely wet period. This deficiency has been noticeably stronger than those registered in the past, but the differences are not so large to be statistically significant.

The precipitation distribution over a year has also undergone certain changes. A largest increase in precipitation has been observed for in September and October, and maximal decrease in February and June. This deficiency has been noticeably stronger than those registered in the past, but the differences are not so large to be statistically significant.

A certain regularity has been observed in the sequence of wet and dry years, so that appropriate longer or shorter cycles of changes could be noticed, as well as the termination of the one period with precipitation deficiency and the beginning of another considerable wetter period.

In view of the fact that in the previous time spans, droughts of similar character to the last one had been observed, it can be undoubtedly said that we do not deal with an unusual phenomenon. Only, the damages thus caused were this time very high because of the significant investments put into the intensification of agricultural production, and because of potentially higher yields, as well as in view of the unused possibilities to mitigate negative effects of such a drought.

REFERENCES

- [1] Yevdjevich V.: Stochastic Processes in Hydrology, Water Resources Publications, Fort Collins, Colorado, USA, 1972.
- [2] Prohaska S.: Hydrological time series analysis, Stochastic hydrology, Belgrade, Yugoslavia, (in Serbian), 1975.
- [3] Salvai A., Zelenhasic E., Savic R.: Periodicity discharge analysis of large Yugoslav rivers, Monograph Management, utilization and protection of water in Vojvodina, Faculty of agriculture, Institute for water management, pp. 25-36, Novi Sad, Yugoslavia (in Serbian), 1994.
- [4] Zelenhasic E. Salvai A, Smailagic J., Savic R.: Periodicity analysis of some meteorological variables in Serbia, Monograph Management, utilization and protection of water in Vojvodina, Faculty of agriculture, Institute for water management, pp. 49-61, N. Sad, Yugoslavia (in Serbian), 1994.
- [5] Savic R, Salvai A, Belic S.: "Precipitation - permanent reduction or periodical changes?", Eco-Conference, pp. 175-180, Novi Sad, Yugoslavia (in Serbian), 1997.



ROMANIAN STEEL INDUSTRY THE THIRD YEAR OF EU INTEGRATION ENVIRONMENTAL ISSUE TO COMPLY THE EU STANDARDS AND REGULATIONS – BADISCHE STAHL-ENGINEERING “OFF GAS” CONCEPT

¹Rodica ISTRATE, ²Manfred SCHMITH

¹BSE - BADISCHE STAHL-ENGINEERING GMBH – Representative from ROMANIA

²BSE - BADISCHE STAHL-ENGINEERING GMBH - Senior VP Sales & Marketing, GERMANY

Abstract:

This article presents Romanian steel industry production and environmental efforts in view to achieve the EU environmental standards and regulation and remain profitable. BSE – Badische Stahl Engineering - “off gas” concept means “High productivity and low emissions can go hand to hand”

Keywords:

Productivity, emissions, environmental standards, off gas,

1. INTRODUCTION

Environmental protection measures are very much shaped by the EU. The integral approach set forth in the Integrated Pollution Prevention and Control Directive (IPPC Directive) deserves special mention in this context. Best available techniques, subject to the conditions of the IPPC Directive, are described in a series of reference documents (BREF documents). The new development and improvement of available techniques also gives rise to changes in operating practice, not least as a result of new legislation and regulatory activities of the European Union and its member states

European Union has one of the most competitive steel industries of the world, Steel companies viable from an economic-financial point of view (restructured, modernized and revamped), complex fabrication structure with accent on the fabrication of high added value products; High technological level, innovation capacity, skilled labor force, organization, integration, most severe environment legislation in the world;

European Union represents the main action engine in the field of global policy of environment protection, including as concerns the climate changes.

Badische Stahlwerke GmbH (BSW), one of the most productive Mini Mills in the world, reached more than 2 million tons of good billets in 2007 operating with two conventional 90-ton electric arc furnaces (EAF). For more than 20 years BSW has been working hard to reduce their gaseous emissions with the focus on particulate matter, organic compounds and also carbon dioxide. BSE- Badische Stahl Engineering, belong to BSW, is little sister and all the research and experiment are done practically in BSW before becoming “products”.

Operation of a steel plant on a very high productivity level is the basic for high efficiency and low cost. Beside the traditional key figures of a steelmaker we realize all over the world, that the stakeholders can no longer ignore the environmental standards. Especially the off-gas has a huge impact on a “clean” production. If we look at the present debates, it is clear for the industry that one of the challenges will be the reduction of global greenhouse gases.

This paper shows which level of emissions could be reached without having any disadvantage on productivity and gives an overview of various standards and practices in Europe and worldwide.

2. ROMANIA – MEMBER OF EU(27)

Main indicators of EU 27 steel industry for 2007 are presented in Table1.

Crt. No	Indicator	Europe	Romania	%
1	Production capacities (crude steel)	244	9.1	3.73
2	Crude steel production	210	6.2	2.95
	- converter		4.4	
	- electric		1.9	
3	Continuous cast steel	200	6.1	3.05
4	Hot rolled production	172	5.5	3.20
	- flat	103	1.9	1.84
	- long	69	3.7	5.36
5	Steel tubes production	32	0.8	2.50
	- seamless	49	0.6	1.22
	- welded		0.2	
6	Domestic consumption of steel products	182	4.7	2.58

Table 1. Main indicators of EU 27 and Romania steel industry (2007)

Romanian Steel Industry in restructuring, modernizing and revamping, have the capacity to produce by two processes: converter 71% and electric 29% the structure and quantity (Table 2).

Company	Production	Process	Production
	capacities		2007
	- k tons -		- % -
ArcelorMittal	6950	Converter	75.9
- Galati	6000	Electric	71.1
- Hunedoara	950		4.8
MECHEL (Targoviste and Campia Turzii)	1015	Electric	7.8
MECHEL - DUCTIL STEEL (Otelu Rosu)	300	Electric	5.6
TMK (Resita)	450	Electric	5.6
TENARIS (Calarasi)	400	Electric	5.1
TOTAL	9115		100

Table 2. Romanian steel industry ownership and production (2007)

We must mention that 96.5 % of the weight was continuous cast steel.

European and worldwide recognition of Romanian steel industry with a capacity of 9.15 mil. Tons / year. 65.8% of capacity is converter steel making, especially for flat products. We must mentioned that all the companies have 100% capacities for continuous casting of crude steel.

The Romanian steel industry is owned by large international steel producing groups (Table 3.). ArcelorMittal and MECHEL possesses nowadays 93 % of steel making capacity and 89.3% of the crude steel production (2007).

After 1989 in the framework of restructuring process:

- were closed and dismantled over 8 mil. tons of crude steel making capacities;
- were closed and dismantled over 10 mil. tons of rolling capacities;
- the personnel number in steel industry diminished from 150 thousand persons up to 37 thousand persons in 2007;
- it increased the weight of continuous cast steel from 36.7% in 1989 up to 96.5% in 2007;
- the labor productivity was in 2007 of 326 t. steel/man

The crude steel production of Romanian steel industry, realized in the last years was of 6.2 mil. Tons, out of which cast steel production reached 6 mil. tons in 2007 and production of hot rolled products established in the last years at 5.5 mil. Tons (Figure 1.).

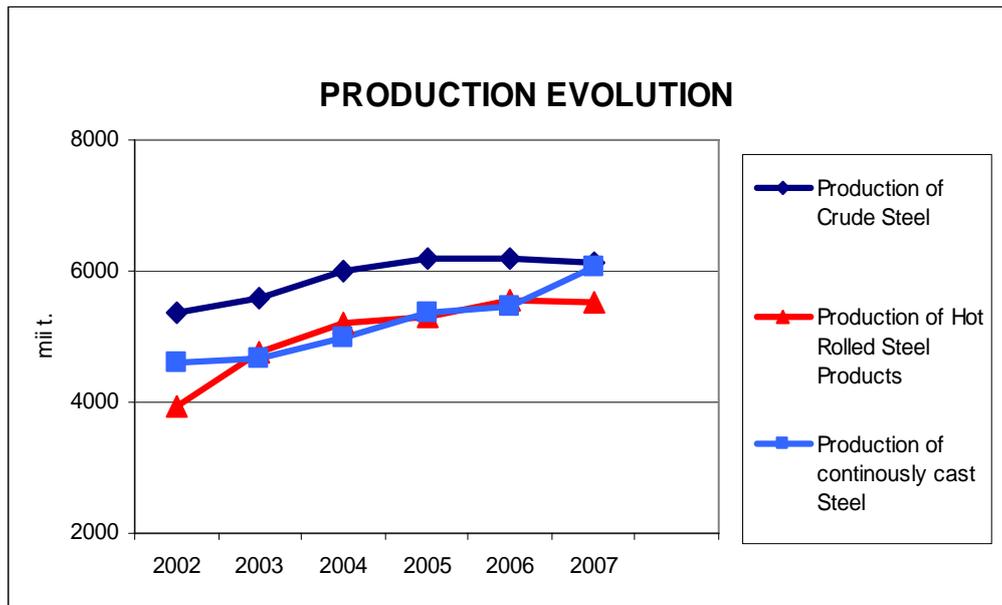


Figure 1. Main indicators of steel production

Romania transposed totally EU legislation in the field of environment. The IPPC Directive was transposed in the Romanian legislation by the GED no. 34/2002, approved by the Law no. 645/2002. Deadlines for conformation with The Romanian Steel Companies din Romania, develop investment programs to comply with IPPC requirements up to the deadline approved by the EC (IPPC Directive for the steel companies with transition periods accepted by EC between 31.12.2012-31.12.2015) inside the Conformity Programs negotiated with environment authorities

3. DESCRIPTION OF THE EXPERIMENTAL SETUP

3.1. Typical emissions from STEEL PLANTS

Emissions from EAF steel plants are linked to the input material. All organics and heavy metals are entering the process via the scrap and are therefore difficult to control.

Dust is generated during meltdown of scrap through vaporization of metals mainly in the electric arc. Inorganic gaze generation is linked to the process itself. Normally emissions from stacks are given in concentrations (mg/Nm^3). Since off-gas volume flow can vary significantly for different fume systems it is difficult to compare emissions from different installations. For this reason so called emission factors have been defined. An emission factor is the average emission rate of a given pollutant for a given source, relative to units of activity. For a steel plant this is for example the emitted weight of a pollutant per ton of steel produced like 100 g of EAF dust per ton of steel.

On the other hand the legal situation concerning limiting values for certain pollutants is very confusing. There is not a single limiting value for a pollutant which all industrialized countries in the world would have in common. The European Union is on the way to harmonize the environmental laws but is still far away from common limiting emission values.

The only way to get the full picture is to compare emission factors with the range of emission factors throughout the industry. The data basis so far is not very big but the IPPC office of the European Union is publishing emission factors in the so-called “Best available techniques reference document for the Iron and Steel industry” (BREF document).

3.2. Environmental performance and productivity of BSW

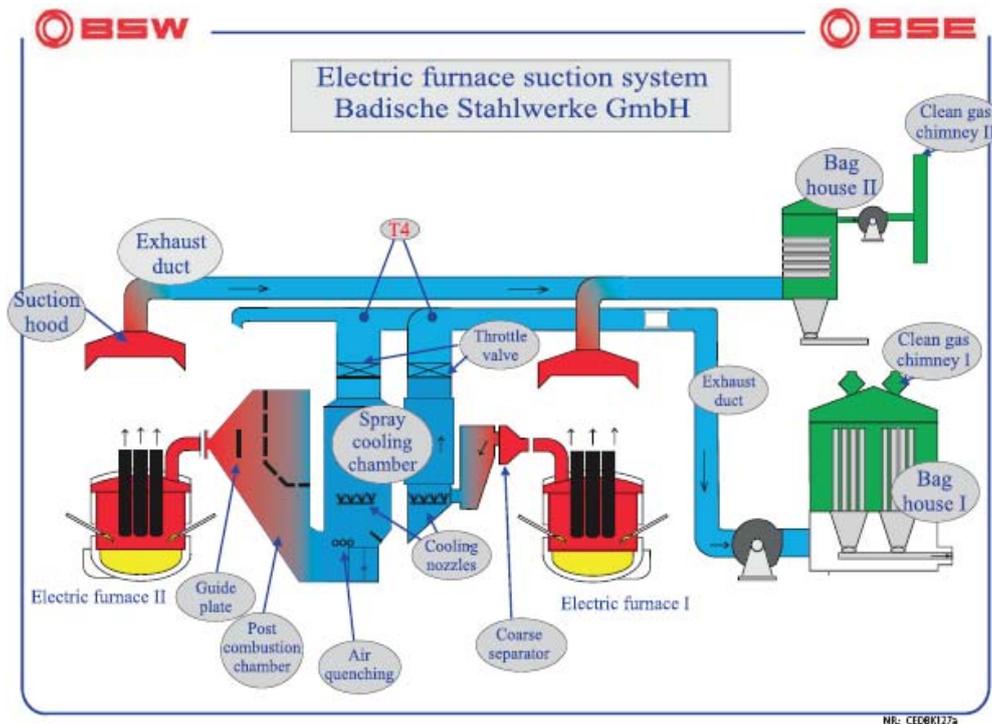


Figure 2: Schematic drawing of BSW's off-gas system

BSW – located at Kehl/Germany - is a so-called mini-mill founded 1968 by Willi Korff. The steelmaking facilities comprehend an EAF melt shop with two 90-t-EAF equipped with 90 MVA transformers, an average tap-to tap time in 2007 of 39.8 min and a productivity of 135 t/h, having produced 2.17 tons of billets in 2007. BSW is using state of the art equipment for their fume extraction systems. The generated off-gases are sucked off directly from the furnaces through the forth hole as well as by a melt shop ventilation system with a combined capacity of 1.8 million Nm³/h and cleaned in the de-dusting systems with a filter area of 38,000 m². Schematic drawing for off-gas system at BSW is shown in figure 2.

3.3. BSE “OFF GAS” concept

“OFF GAS” concept is optimal for our environment and companies efficiency, the necessary steps are:

- Analysis and optimization of shop ventilation and off-gas treatment by fluid dynamic models and Computational Fluid Dynamics (CFD)
- Concept, planning, supplier recommendation, quality control, implementation and supervision in a single source.

a). Fluid Dynamic Modeling

BSE throw this specialists, providing solution for optimal OFF-GAS treatment, making measurement in Steel Shop Melting building in representative points at different stages of steel production and with this dates analyze the emission quantity, intensity and directions, and base on fluid dynamic modeling methodology establish by Bender Corp of BSE group member (USA), establish the best concept and engineering for off gas system dedicated for each bay (Figure3. and Figure 4).



Figure 3. FLUID DYNAMIC MODELING- Charging



Figure 4. FLUID DYNAMIC MODELING –Taping

b). Computational Fluid Dynamics (CFD) - Simulation

The CFD simulation developed by BSE (Figure 5) means simulation of whole ductwork or single parts, temperature, velocity and flow parameters in view to determined the best technical solutions for off gas system. BSE developed:

“High Temperature Quenching (HTQ) System” (Figure 6):

- Most rapid off-gas cooling by atomized water
- Lower operation costs due to lowest pressure drop in the cooling system
- Low maintenance requirements
- Reduction of water-cooled ductwork

Main technological operations:

- Cooling of the gases from Direct Furnace Evacuation
- Injection of atomized water into water spray chamber
- Atomizing of the water by compressed air in spray lances
- Valve racks for water and compressed air

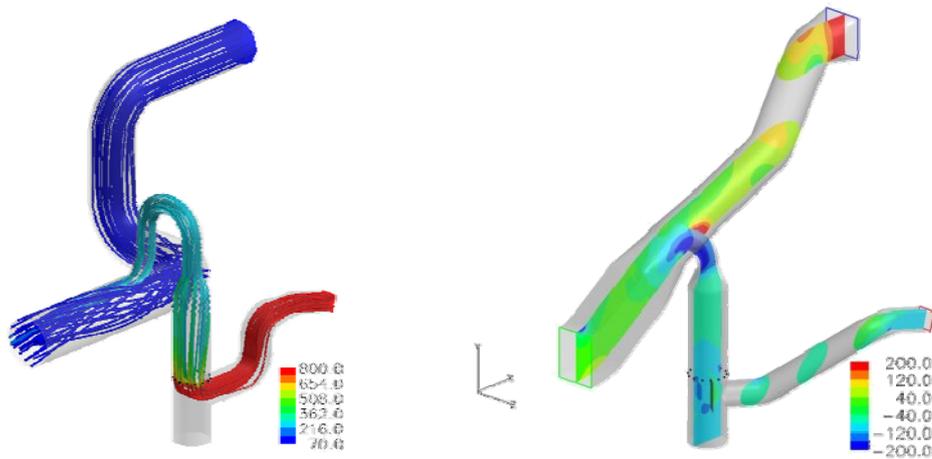


Figure 5. Simulation CFD – whole ductwork



Figure 6. High temperature quenching system

c). Filter technology

Baghouse specification is new and specific for each type of EAF and fan selection complete BSE's scope of off-gas concepts and engineering.

4.3. EMISSION OF PARTICULATE MATTER

In Germany the limiting value for dust emission for EAF plants is 5 mg/Nm³ (0,0021 gr/scf). With today's filter technology it is no problem to comply with this rule. Nevertheless BSW is measuring continuously the dust emissions on both the stacks. The results are reported to the authorities in real time. An example of the results of one year is shown in figure 9.

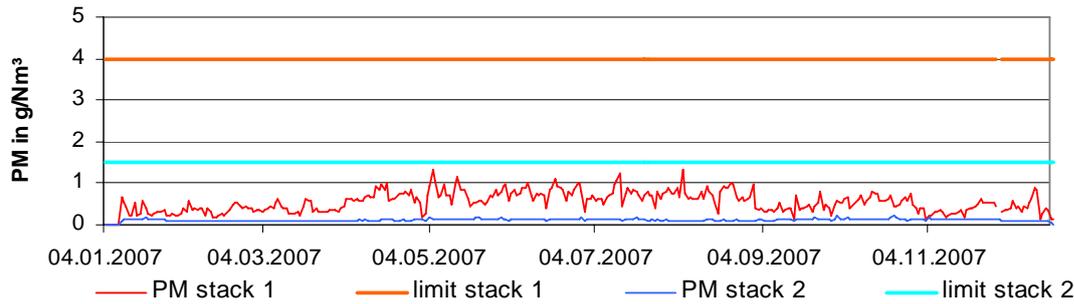


Figure 7. Continuous dust emissions of BSW at stack 1 & 2, 2007

The figures of BSW are far below any limiting values. In comparison with other steel plants BSW is again in the top flight of the emission factors. The comparison is shown in figure 10. The range of emission factors is very high. But with 0,008 mg/ton of steel BSW is very close to the minimum value.

The Romanian steel industry figures are between 20 to 30 mg/Nm³ at stack emission, but the steel workshop emission are not solved yet in any Steel shop in Romania, the dead line for this is the ending of IPPC compliance program, Table 5.

Romanian Technological and Environmental investment program, was negotiated for each Company. In Figure ... are indicators for investment between 2004-2008.

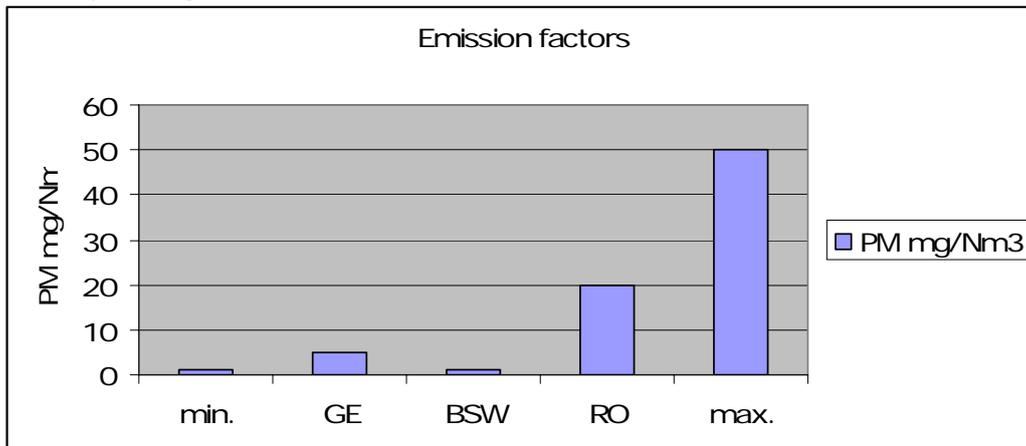


Figure 8: Comparison of emission factors for particulate matter

The Romanian Steel Companies from Romania, develop investment programs to comply with IPPC requirements up to the deadline approved by the EC, inside the Conformity Programs negotiated with environment authorities.

4. ANALYSIS OF RESULTS AND CONCLUSIONS

As shown in this paper high productivity of an EAF plant is possible without compromising on environmental performance, especially emissions. Of course some efforts and investments are necessary to operate today's technology in the right way especially in Eastern Europe. BSW is continuously investing in environment to be in compliance with latest rules and obligations. There are possibilities, however, to keep track of the costs for environmental efforts, and steel making can still be profitable in Europe.

BIBLIOGRAPHY:

- [1] Petru Ianc, Rodica Istrate, s.a. - Expansion of the European Community – Impacts and selected strategies of the Romanian steel industry to comply with the EU standards and regulations - Third International Mini-Mill Symposium, June 15-18 2008, Schluchsee, Germany.
- [2] Torsten Rummel, Dr. Jens Apfel – High productivity with low emission – Challenge for tomorrow - Stahl und Eisen No. 11 - 2008
- [3] www.bsw-kehl.de
- [4] Environmental Declaration 2008 – Badische Stahlwerke GmbH
- [5] Best Available Technique Reference Document - 2000



CATEGORIZATION OF ALLUVIAL DEPOSITS FROM THE CONTENT OF IRON AND ALKALIZATION IN TOTAL SUSPENDED SOLIDS FROM HS DTD OF SOUTHERN BANAT REGION

NEMES, K. ¹, BUGARSKI, R. ², MATAVULJ, M. ¹, BELIĆ, S. ³

¹University of Novi Sad, Faculty of Sciences, 21000 Novi Sad, SERBIA

²Hydrometeorological Service of the Republic of Serbia, SERBIA

³University of Novi Sad, Faculty of Agriculture, SERBIA

ABSTRACT

An increasingly agricultural region of Southern Banat was evaluated by the parameters of adsorption of alkaline metals and suspended particles of the rivers Tamis, Brzava, Karas, Nera and DTD canal water. Annual dynamics is categorized by statistical analyses, recognized trends of sodium adsorption ratio and a concentration of iron in total suspended solids. All these provide informational basis for irrigation, range of flood areas and transportation. Environmental protection of Carpatian waters is required because iron and sodium are present in fluvial deposits, and the sodium is gradually increasing. In the Danube-Tisza-Danube canal network in Banat region, the growing algae pointed out determination of suspended particles and changes in Ecological potential of the canalized DTD sector.

Acknowledgements

These studies were supported by the Ministry of Science and Technological development of the Republic of Serbia (project No 1945 and No 22006). We are grateful to Center for Electron Microscopy of University of Novi Sad for the SEM research.

THE INFLUENCE OF TRIBUTARIES ON LOWER RIVER TISA BASIN WATER SUPPLY NETWORK

NEMES, K. ¹, BUGARSKI, R. ², LOZANOV-CRVENKOVIĆ, Z., BELIĆ, S. ³

¹University of Novi Sad, Faculty of Sciences, 21000 Novi Sad, SERBIA

²Hydrometeorological Service of the Republic of Serbia, SERBIA

³University of Novi Sad, Faculty of Agriculture, SERBIA

ABSTRACT

The influence of dam and gates on water supply system- Danube-Tisza-Danube hydrosystem in Vojvodina province (HS DTD) in southern Banat was investigated. Annual dynamics of data represented in statistical BLOCK analyses from sulphates and alkalization (1997-2005) pointed out water supply condition of the River Tisza. The executive block is the control for conveyance system of water supply network and runoff. The obtained results from correlation matrices of SAR index was found to be in negative relation with the iron content in boundary stretch St Martonos while at the dammed stretch St Novi Becej neutral phosphatase enzyme activities were positively correlated with the iron content. The occurrence of brackish water diatom *Entomoneis paludosa* and small centric algae *Cyclotella meneghiniana* downstream the Bega River pointed to considerable problems of detailed canal network usage supplied by the impounded stretch of the river Tisa.



Figure 1. SEM magnification correlate diatom communities of Prominent diatom *Cyclotella meneghiniana* (a) of the River Tisa (b) and irrigation/drainage canals (c)

Acknowledgements

These studies were supported by the Ministry of Science and Technological development of the Republic of Serbia (project No 1945 and No 22006). We are grateful to Center for Electron Microscopy of University of Novi Sad for the SEM research.



OBTAINING INFORMATION FOR THE RIVER DANUBE ECOLOGICAL STATUS FROM THE CITY OF NOVI SAD

NEMEŠ Karolina, Uranija KOZMIDIS-LUBURIĆ

Faculty of Technical Sciences, University of Novi Sad, 21000 Novi Sad, SERBIA

Abstract

Obtaining information of the Danube River (1997-2005) pointed out degradation of four river stretches. Integrating data were represented in the block of phosphatase enzyme activities and dynamics of iron depositing bacteria. The Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) detection of bacteria *Gallionella* in water samples of alluvium and biofilm of the Novi Sad drinking water resources indicated heavy metals in groundwater. The SEM observations shows that at those groundwater where the iron increasing in oil contaminated wells the activity of alkaline ions resulted in characteristic depositional environment of the Novi Sad City. There, the potassium, aluminum, titanium and zinc are consumed in same relation, and their elemental dispersion is very similar. The biological activity pointed out stabilization of iron and phosphorus in drainage wells.

Key words:

model to study, PAI, Iron-depositing bacteria, SEM & EDS, particles, The Danube River

1. INTRODUCTION

As a step forward substantial progress in harmonization and implementation the EU water policies of The Danube River and improvement of the Ecological status of the infrastructure of the city of Novi Sad, the research of bio-activities concerning metal deposits was investigated from un-treated water samples.

2. MATERIAL AND METHODS

Hydrological network of the River Danube in Novi Sad is sustained of two small slack-water areas, small streams entering from Fruska Gora mountain, Danube-Tisza-Danube (DTD) Canal entering to the main river's channel. It also includes waste water disposal systems as well as drinking water transportation system of the Danube abstraction wells supply for the more than 200 000 citizens of Novi Sad. The research was made on four urban river stretches concerning river banks and middle current of the river when the samples were collected from the three bridges (1997-2007): stretch I from 1262 to 1259 r km (L1, R1); stretch II 1257 r km (L2, M2, R2); stretch III 1254-5 r km (L3, M3, R3), L3- municipal waste water discharges; stretch IV from 1253 to 1245 r km (L4, M4, R4). During the research, the ruining of three bridges and Oil-refinery in 1999 and the drought 2003 year unfavorably occurred. Several oil contaminated drainage wells in the vicinity of the drinking water wells and deep drainage well located at the stretch four, upstream the piezometer Danubius of the second urban river stretch (left riverbank) and biofilm of drinking water pipe represent our investigated water-deposit samples. The phosphatase enzyme reaction took place at 30°C by the use of substrate p-nitrophenylphosphate [1]. The reaction mixture contained of 3 ml of water was contained of 0.3 ml buffer solution (0.33 M Tris, 0.33 M TES), pH of un-filtered water samples was adjusted for acid (pH 5), neutral (pH 7) and alkaline (pH 9) conditions of water; 0.3 ml of 5 % w/v of substrate p-nitrophenylphosphate and 2.4 ml of untreated water sample. The concentration of p-nitrophenol was determined by measurement of absorption at 420 nm; the average values of three phosphatase activities were described as PAI index

[4]. Deposit analysis of the groundwater drainage wells was made by the use of Scanning Electron Microscope (SEM) JEOL JSM-6460 L. The EDS pattern of elemental composition (total wt %) were recorded on an OXFORD INCA Microanalyses suite and presented in diagram and categorized graph. The particule size analyses was made by MASTERSIZER 2000, Malvern instruments UK. A spatial framework for collecting, storing, and classifying information on the character of urban river network was proposed using the software Stat.soft Statistica 8.

3. RESULTS AND DISCUSSION

The implementation of the Water Framework Directives in the monitoring requirements of large rivers requires serious steps which are proposed in the Directives, and should be applied to the water remediation for the achievement of good Ecological status of protected areas [2, 6]. As an important step, the urban river network research [5] concerning changes of phosphorus availability is represented in BLOCK- (box-plot) integrating data of activity of phosphatases enzymes in season succession when we compared river banks and middle current of the river. Nevertheless, increased activities appeared from municipal waste water discharges (river stretch L III) (Figure 1).

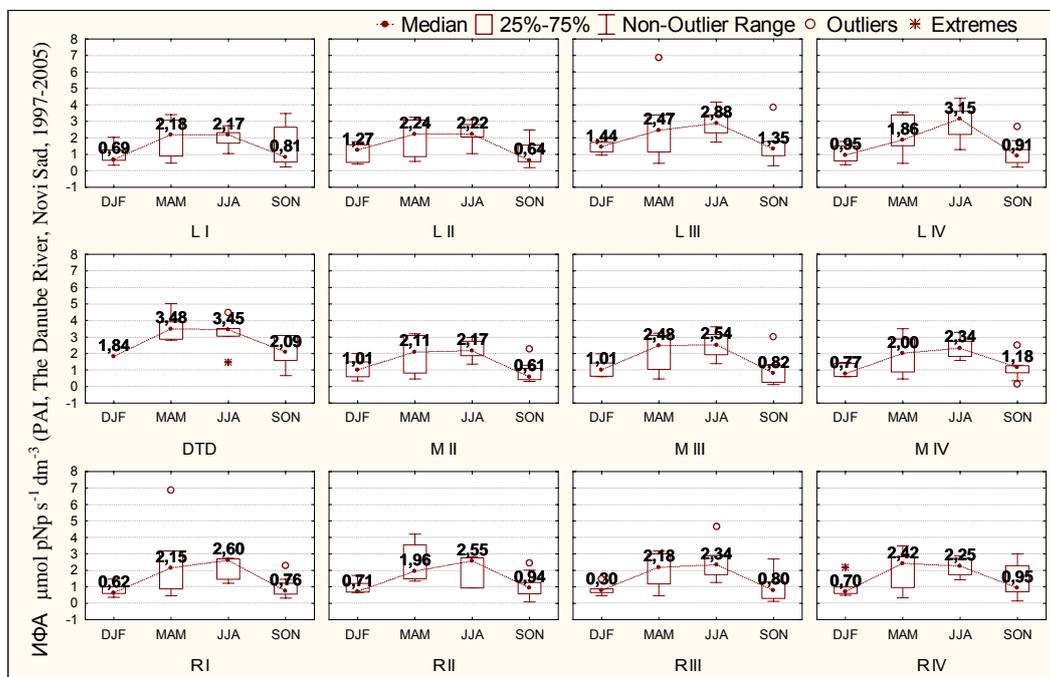


Figure 1. Box-plot: seasonal dynamics of phosphatase activity index of the surface water of The Danube in the City of Novi Sad (PAI_{NS}) (left riverbank, DTD canal, middle current, right riverbank of The Danube; river km 1262–1245).

In conformity with results of piped water, phosphatase activities after the period of closing the water suggested the sensitivity of parameter for hydrodynamic conditions of piped water (Figure 2). It was also noted that in hot water from electric boiler (>70 °C) the phosphatase enzyme activities were detected, too (sample 13). In this system, neutral phosphatase are active when they are compared with the depositional environment of the most contaminated piezometer 9 contributed by acid phosphatase enzyme activities. The acid phosphatase enzyme activity is shown in the most microbiologically contaminated ground water, where the oil and its derivatives has its highest concentration (Figure 2).

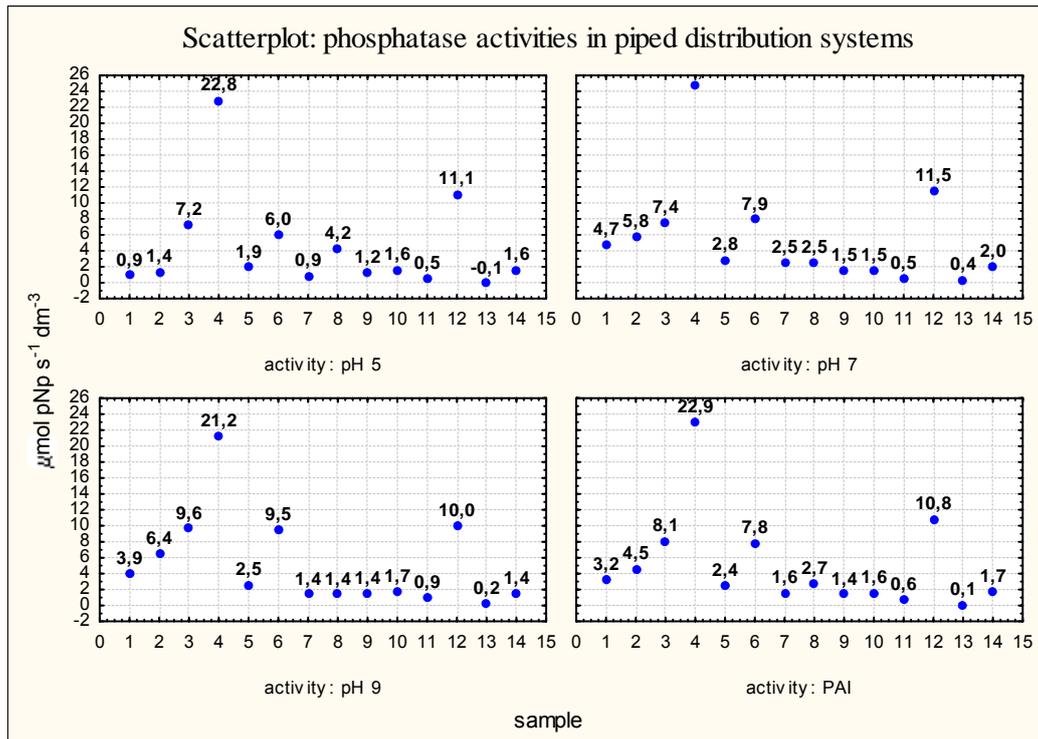


Figure 2. Scatterplot: categorization of phosphatase enzyme activities ($\mu\text{mol pNP s}^{-1} \text{dm}^{-3}$) in piped systems in Novi Sad. Water samples: 1) Danubius piezometer 7, 2) Danubius piezometer 7 unfiltered, 3) Danubius piezometer 9, unfiltered, 4) Danubius piezometer 15, unfiltered, 5) Piezometer 1 in the vicinity of river bank- stretch 4 of the Danube River, unfiltered, 6) Drainage well 5 in the vicinity of oil refinery- unfiltered, 7) Drainage well 9 filtered, 8) Drainage well 9- unfiltered, 9) Raw drinking water 1, 10) Raw drinking water 2, 11) Liman: sector I - cold water, 12) Liman residential area: sector IV- cold water- pipe deposit, 13) Liman: sector I- hot water (boiler), 14) Liman: sector IV, hot water.

The high portion of amorphous content throughout the drainage system of The Danube River alluvium reveals the growth of iron-oxidizing (iron-depositing) bacteria. Scanning electron micrographs demonstrate that Fe- depositing microbial mat sampled in oil polluted drainage wells is primarily composed of granules and several types of bacteria with the predominant species being described as *Gallionella feruginea*, *Leptothrix ochracea* and *Chrenothrix polispora* (Figure 3). Increasing mineralization [3] was a contributing factor for infrastructure degradation because of iron-depositing bacteria occurrence detected in 2004-2008 (Figure 3). The water of drainage wells located one km from the left riverbank is highly contaminated with the iron-depositing bacteria in water and there oil derivative- benzene was mostly determined in concentration of 1 $\mu\text{g/l}$ (well 8, well 9, well 10) and maximum conc. of 9.4 $\mu\text{g/l}$ was measured in November, and there was found extreme conc. (23 $\mu\text{g/l}$) in drainage well 9.

In drinking water distribution system of the Novi Sad city, the physico-chemical parameters belong to rarer unsatisfactory quality due to the 40 % of changed color, 40 % of manganese increased, 30 % of residual chlor, increased concentration of iron and chloroform in 20% [9]. Nevertheless, there has been paid attention in alkalization processes; decreasing of pH was also detected in Novi Sad [8]. It is important to mention that at the sector of The upper Danube at the river km 1300 and nearby The Novi Sad city, an increase in the concentration of aluminium and iron was followed by more or less constant values in the Danube Delta and on the way to it [7]. From the electromagnetic method geosolar for the assessment of diffuse pollutants, ammonia was continually detected at contaminated area [10], an important nutrient for movement of groundwater microorganism (in prepare).

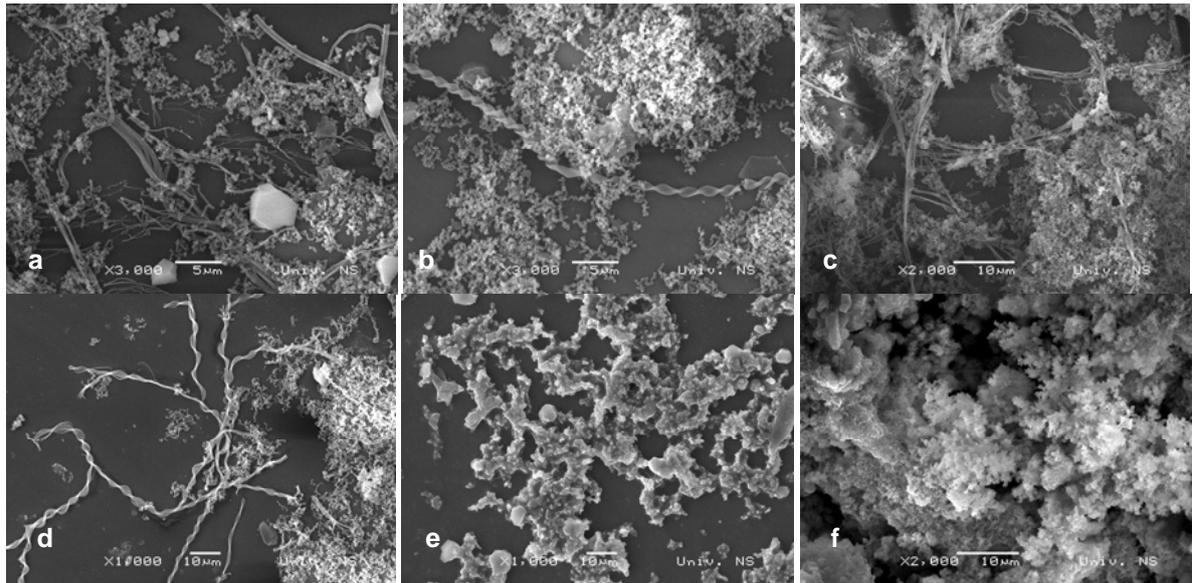


Figure 3. The SEM magnification: a-d) iron-depositing bacteria of groundwater of The Danube drainage well nearby The City of Novi Sad sampled in 2007 (left river bank, fourth river stretch), e) silted material of piezometer Danubius from the second river stretch, f) biofilm of piped drinking water.

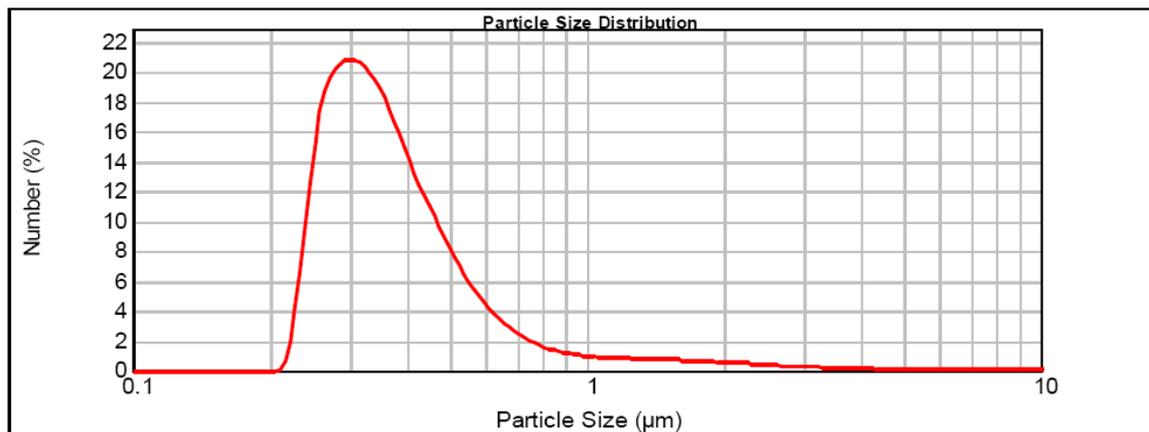


Figure 4. Particle size distribution analyses of groundwater deposit of The Danube River carried by Mastersizer 2000.

Particles of the sample of groundwater deposit are in diameter range from 0.2 µm to 8 µm. Predominant particles have diameter of about 0.3 µm (Figure 4). About 90 percent of all particles belong to range from 0.2 µm to 0.65 µm. The particle distribution is comparable to SEM research of particles size showing grains in diameter range about 160 – 196 nm, but braided stalks probably belong to larger particle size of active microorganisms.

Considering the dynamics of iron-oxidizing/depositing bacteria, similar elemental composition of the grains and stalks in drainage wells and pipes were recorded (Figure 5,6). Potassium, titanium and zinc are microbiologically consumed equally, and their elemental dynamics is similar in silicon, dependent on content of aqueous calcites and chlorides. Therefore, the movement of particles and their relative error of weight fraction indicated contamination and degradation of river sector Ecological status nearby residential areas.

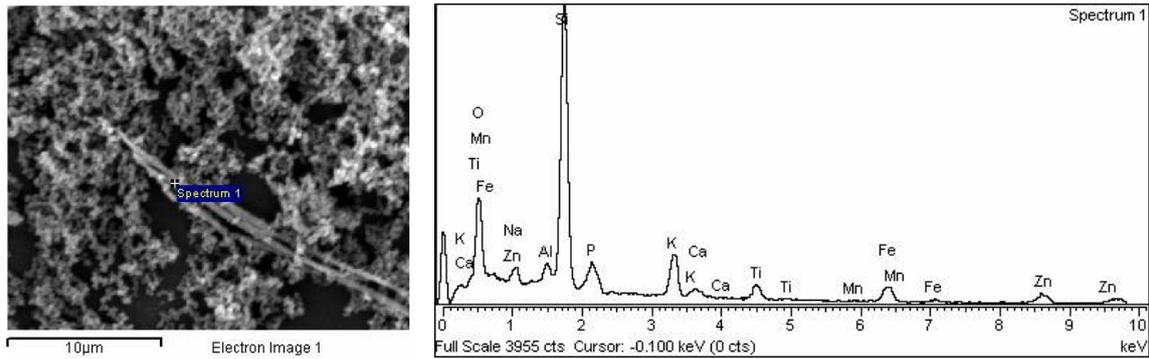


Figure 5. SEM and EDS diagram of spectrum point analyses (Oxford Instrument INCA-X-sight software) of the groundwater deposits shown by the X- ray spectra from the spectrum point of the fourth river stretch (The Danube in Novi Sad). Mineral identification of feldspar is assisted with the X- ray microanalyses by standards.

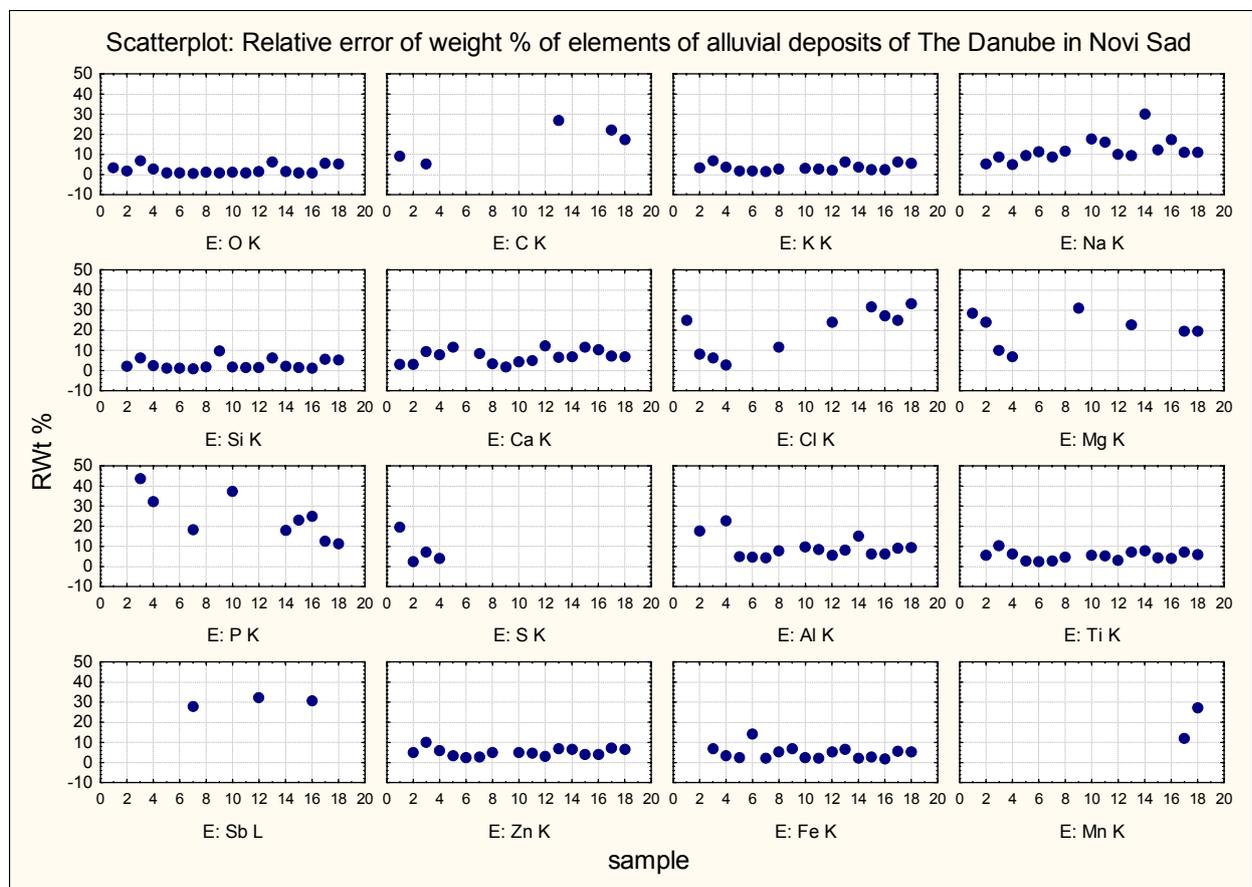


Figure 6. Categorized graphs of relative error of weight fraction (%) of different elements in groundwater drainage deposits. Relative weight (sigma weight (%)/weight (%)) was presented by the categorized scatterplot graph (Statistica 8) in order to provide systematization of EDS analyzed parameters of spectrum point analyses (Oxford Instrument INCA-X-sight software). The elemental composition analyses was carried out in piezometers Danubius located on left riverbank of second river stretch (sample 1–4) and downstream on the fourth river stretch- left riverbank in deep water well in 2007 (5-7) and the one collected from 2008 (8), drainage well 1 (9-11) sampled in 2007, drainage well 6 (12-13), drainage well 7 (14), drainage well 9 (15-16), drainage well 10 (17-18). The drainage wells are located between the Oil Refinery and Drinking water wells of The City of Novi Sad. Mineral identification of feldspar by standards is assisted from the X-ray microanalyses.

4. CONCLUSION

Obtaining information of urban river sector of The Danube, indicated that at those groundwater where the contamination with the iron-depositing bacteria occurred, the movement of phosphorus, particles and their elemental composition resulted in characteristic depositional environment of the groundwater of the Novi Sad Capital City of Vojvodina Province.

Acknowledgements

These studies were supported by the Ministry of Science and Technological development of the Republic of Serbia (Grant No 1945 and No 142 058).

REFERENCES

- [1] Flint, K. P. & Hopton, J. W. (1976): Some properties of a Neutral Phosphatase of a Bacterium Isolated from a trickling Filter Effluent. *European. J.App. Microbiology.* 3, 237-243.
- [2] Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States.
- [3] Krammers, J. W. & Rottenfusser, B. A.: Techniques for SEM and EDS characterization of oil sands. *Scanning electron microscopy/1980/IV.* SEM Inc., AMF O'Hare (Chicago), USA. (1980), pp. 97-103
- [4] Matavulj, M.: The non-specific phosphomonoester hydrolases of microorganisms and their importance in phosphorus cycle in aquatic environments. In *Serbo-Croatian. pHd thesis.* Sveučilište u Zagrebu.Croatia. (1986).
- [5] Gayin, S., Gantar, M., Matavuly, M., Petrovicy, O. (1990): The long term investigation of the River Danube water quality in the Yugoslav section according to microbial parameters.- *Wat. Sci. Tech.*, 22, 5, 39-44.
- [6] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000. *Official Journal of the European Communities.*
- [7] ICPDR- International Commission for the Protection of the Danube River.
- [8] *HYDROLOGICAL YEARBOOKS: Water quality.* Hydrological yearbooks. Water quality (in Serbian). Hydrometeorological Service of the Republic of Serbia (1998-2005).
- [9] *Ecobilten*, (2007). City of Novi Sad.
- [10] Stojiljković, D. & Rajić, M. (2009): New method for determining pollutants. Conference proceedings “Sustainable Irrigation”, Faculty of Agriculture, Novi Sad. Pp. 91-96.
- [11] StatSoft.Inc (2009): *Statistica 8.*



ENVIRONMENTAL IMPACTS OF NITRATE AND NITRITE

Gábor NAGY¹, Zoltán GALBÁCS¹

¹Department of Inorganic and Analytical Chemistry, University of Szeged
H-6720 Dóm tér 7, Szeged, HUNGARY

Abstract:

The natural nitrogen cycle is significantly influenced by the human activity – principally by agriculture and transport. The excessive fertilizing, the organic matter content of sewage waters, and the emission of nitrogen oxides to the atmosphere – caused by vehicles and industrial activities – are unsettling the biosphere's nitrogen balance. The anthropogenic nitrogen surplus in soils, water bases and atmosphere means great problem, and its indirect effect is observable in our environment and daily life. Nitrite and nitrate pollutions are important and serious risks in spite of being relegated to the background in global environmental protection.

Keywords:

nitrate, nitrite, fertilizer, eutrophication, methemoglobin

1. SIGNIFICANCE OF NITROGEN

The nitrogen is present in the environment in many various forms and considerable amount. Nitrogen compounds are especially important from environmental, ecological and physiological aspect because they are indispensable constituents of e.g. proteins, nucleic acids or humus; they can be found in the atmosphere, in soils or in any living organism. The wide interval of nitrogen's oxidation state (-3 - +5) indicates the high number of the – essential, toxic, neutral or anthropogenic - components nitrogen can form. Among these numerous compounds nitrate and nitrite mean significant environmental risk and can cause long-term natural damages.

2. THE NITROGEN CYCLE

The elemental nitrogen of the atmosphere – because of its inert structure – highly resists chemical reactions; hence the most of organisms are disable to use it for biological processes. Only some microorganisms (e. g. Rhizobium, Azotobacter, Clostridium) can fix and convert nitrogen to accessible form for plants (ammonia, ammonium). Ammonia is oxidized by Nitrosomonas and Nitrococcus bacteria to nitrite which is converted to nitrate by Nitrococcus and Nitrobacter species during the nitrification process. These nitrogen forms are also available for the flora. Nitrogen compounds of organic residues are converted to ammonia in the course of ammonification then nitrified as well. A part of nitrite/nitrate content of the soil is returned to the atmosphere as elemental nitrogen and dinitrogen oxide by the activities of e.g. Pseudomonas, Paracoccus species (denitrification) (Figure 1).

Accordingly the presence of nitrate and nitrite in the soil is evident; these forms are the main nitrogen sources of plants and indirectly animals and mankind too. However natural nitrogen cycle is significantly influenced by human activities – principally by traffic and agriculture. The biosphere's nitrogen balance is affected by the overfertilizing, the high organic matter content of sewage or nitrogen oxide emissions of traffic and industry. Anthropogenic nitrogen surplus in the soils, water bases and atmosphere are both sources of environmental problems; the impact to the nature is clearly noticeable.

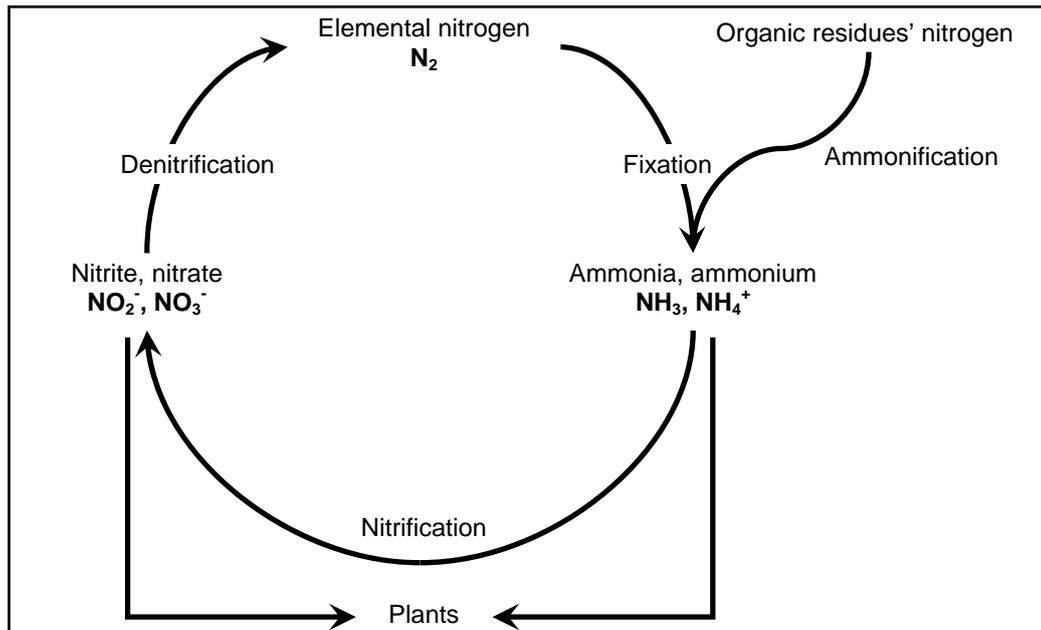


Figure 1. The nitrogen cycle

3. FERTILIZERS

Usually the nutrient content of soils does not correspond with the demands of cultivated plants; hence fertilizers are basic materials in nowadays' agriculture to increase the crop yields. However added nutrients influence the ion mobility and chemical attributes in soils and the components of soil water, the considered and responsible application of fertilizers not necessarily endangers the environment. Besides proportional nutrient supply can be ensured for the plants with fertilizers, some soil parameters can be optimized, such as alkalinity or structure.

However the irresponsible usage of fertilizers can entail serious environmental and financial risks; incorrect dosaging can disturb the existing balance of nutrients, can cause the elements' immobilization and might reduce the product's quality and yield. Soil accepts and stores nutrients only in limited rate; if it is encumbered with fertilizers beyond this limit, nutrients will concentrate in the soil solution, soil water will be polluted and even salt accumulations will evolve. The surplus of organic matter might reach the drinking water bases by erosion, leaking of groundwater or surface runoff and threatens their quality and causes eutrophication.

Nitrogen fertilizers can be especially harmful because of their possibly high solubility; leaching rate of fertilizers' nitrogen content can reach 80% depending on weather, characteristics of soil, amount of fertilizer and vegetation.

Further risk of soil's high nitrogen level is the nitrate accumulation in vegetables. Under optimal circumstances organic acids – derived from oxidation of carbohydrates – form amino acids with ammonia enzymatically reduced from nitrate. These amino acids are essential components of vegetal proteins. If the nitrogen metabolism suffers disturbance, biosynthesis of proteins will slow down and nitrates and amino acids will accumulate in the plant organism. The accumulated nitrate can worsen the vegetable's tissue attributes, lasting and even its taste. High nitrate levels can be measured in e.g. lettuce, kohlrabi, radish, colewort and spinach.

4. NITRATE IN WATERS

Eutrophication of surface waters is caused by increased organic matter content – basically nitrogen and phosphorus compounds – originated from sewage or leaking from fertilized agricultural areas. Great amount of nutrients offsets the balance between photosynthesis and plant breathing: the water's oxygen concentration rises and the flora

starts to proliferate. The multiplied species of fitoplanctons and algae further increase the nutrient amount of water however during their degradation processes the water's dissolved oxygen resource is consumed. Finally the lack of oxygen leads to almost complete disappearance of flora and fauna, decreasing biodiversity and the water loses its self-cleaning capability (Figure 2). Under natural conditions eutrophication occurs much more slowly (e.g. lake succession); the intensive organic matter input significantly speeds up the process.

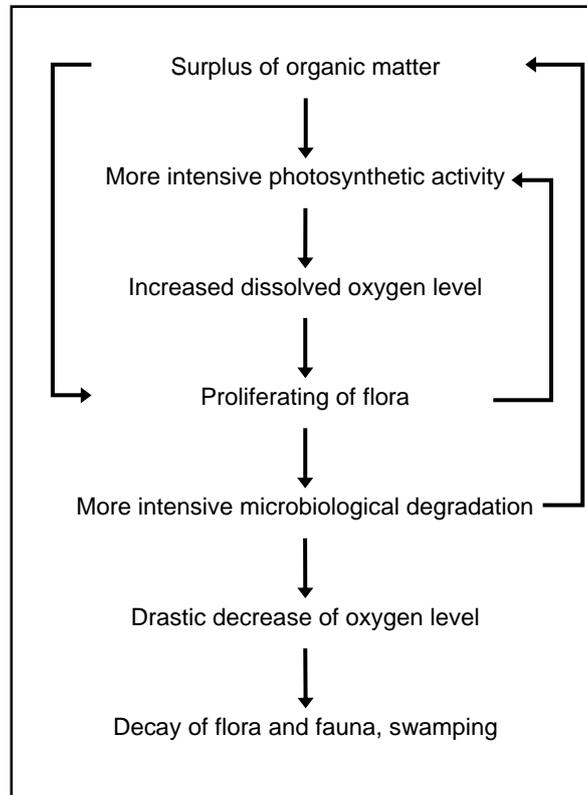


Figure 2. Process of eutrophication

High nitrite and nitrate content means direct risk where drinking water is supplied from polluted water bases. Leaked to groundwater, nitrogen compounds of fertilizers endanger the water quality of drilled wells and other water sources. The amount of nitrate ions stays unchanged during the conventional water cleaning processes; hence the nitrate content of consumed water is equivalent with the water base's.

5. NITROGEN COMPOUNDS AS AIR POLLUTANTS

Besides elemental nitrogen other nitrogen compounds are formed in the course of denitrification that harm the atmosphere. The gas phase losses of fertilizers can get to the atmosphere as nitrogen oxides (e.g. N_2O , NO_x) and take part in generating acid rains and tropospheric smog and thinning ozone layer. The great amount of organic matter can make the denitrification more intensive and considerable part of the fertilizer's nitrogen amount can get in the air. Flue gases are main sources of these types of air pollutions; the magnitude of fertilizer's impact is minor, but confirmed and not negligible.

6. NITRATES AND NITRITES IN FOODS

Nitrite and nitrate get in foods partly as a result of not suitable producing or handling processes and partly as additives. Food industry applies nitrite and nitrate components (e.g. E249 – KNO_2 , E250 – $NaNO_2$, E251 – $NaNO_3$, E252 – KNO_3) primarily with conservation purpose. Most of meat products contain added nitrate and/or nitrite preventing appearance of pathogen microorganisms and ensuring the bright color of the meat. As mentioned, some vegetables' nitrate content can be high as well such as dairy products, cheeses, wines or flour.

7. PHYSIOLOGICAL EFFECTS

Nitrate and nitrite content of foods and drinking water can induce various medical problems – however most of these components usually leave human organism fast and without evolving any deleterious effect. Nitrite – reduced from nitrate mainly in stomach and small intestine – can transform to nitrous acid that oxidizes the ferro-ion of hemoglobin and causing methemoglobinemia. In the case of methemoglobinemia blood's oxygen carrying capability decreases and even death can occur. Under normal circumstances 1-2% of human organism's hemoglobin is present in methemoglobin form; if this scale is about 10% symptoms of languor and concentration disturbance will be observable; 50% of methemoglobin is lethal. Nitrite poisoning is really rare in adult population because a special

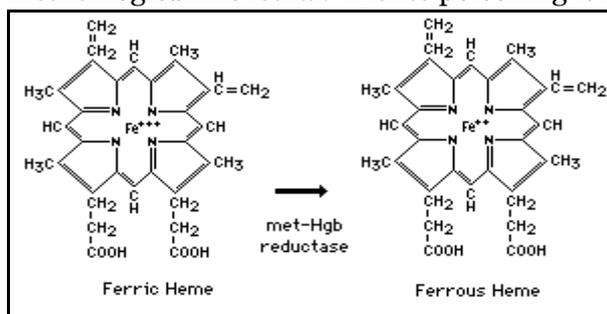


Figure 3. Structure of hemoglobin and methemoglobin [6]

enzyme transforms back the methemoglobin to hemoglobin (Figure 3); however babies are highly endangered because in early age the methemoglobin reductase is not working adequately yet. Therefore the babies' nutrients and drinking water must not include nitrate or nitrite in even trace amount because in lack of medical help anoxic state (“blue baby” disease) is probably deadly.

Another problem related with nitrite presence is the formation of nitrosamines and nitrosamides. These carcinogen N-nitroso compounds are particularly evolved in the acidic media of stomach through reactions of amides and amines with nitrite [2].

8. REGULATIONS

Because of the above environmental and physiological dangers controlling the nitrate and nitrite emissions and monitoring their concentration in foods and waters is important and required. Regulations, decrees and limit values exist to avoid the unnecessary, dangerous or harmful application of these compounds. The directives and regulations of the EU assign fertilizing parameters, limit values for drinking waters, vegetables, meat products etc., and lay emphasis on the protection of nitrate sensitive regions (areas where nitrates can easily reach drinking water bases). Unfortunately national rules not always correspond to the international requirements.

9. CONCLUSIONS

Fast and effective solving of environmental problems caused by anthropogenic nitrite and nitrate is difficult task because of its complexity. The only long-term solutions seem to be the reasonable fertilizing and the adequate wastewater treatment. The environmental and medical risk can only be reduced with controlled emissions and international co-operation. Nitrate and nitrite pollutions are critical however often hidden problems of nowadays that should be taken much more serious.

REFERENCES

- [1] Attila Kerényi, Általános környezetvédelem – globális gondok, lehetséges megoldások, Mozaik Oktatási Stúdió, 1998
- [2] Ghibu G. D., Balint M., Garban Z., Investigations concerning the effects induced by the presence of nitrites and nitrates in the feed of rabbits, Proceedings of the 14th Symposium on Analytical and Environmental Problems, 2007
- [3] N. T. Faithfull, Methods in agricultural chemical analysis, Cabi Publishing, 2002
- [4] R. F. Follett, J. L. Hatfield, Nitrogen in the environment: sources, problems and management, Elsevier, 2001
- [5] Pál Stefanovics, Talajvédelem, környezetvédelem, Mezőgazdasági Kiadó, 1981
- [6] <http://www.med-ed.virginia.edu/courses/path/innes/images/rcdgifs/enzyme3.gif>



SUPPORTING THE REASONABLE AGRICULTURAL PRODUCTION WITH A NEWLY FOUNDED ENVIRONMENTAL LABORATORY IN THE SOUTH EASTERN REGION OF HUNGARY

Gábor NAGY, Tünde NYILAS, Szilvia ÖRDÖG, Anita VOLFORD¹

¹SoilChem Laboratory - Homokkert Small-regional Integration Public Company
H-6782 Vállalkozók útja 1/b, Mórahalom, HUNGARY

Abstract:

An agricultural and environmental laboratory was founded within the framework of Baross Gábor Program in the summer of 2008 in Mórahalom, South-East Hungary, South Great Plain region. The primary aim of this initiative is making the countryside's agriculture more effective and environmentally aware, and assisting the dynamic development of the region. The laboratory helps agricultural production – the primary financial source of the region's villages – with analytical measures of soil and water samples, counseling about nutrient dosing, organized presentations, and cooperating with local enterprises and with another laboratory analyzing chemical residues in the produced crops. One significant deficiency was compensated by the establishment of SoilChem Laboratory – meeting the conditions set forth by directives of the European Union –, due to the lack of environmental laboratories in the region.

Keywords:

soil and water analyzing laboratory, agriculture, environmentally aware,
food safety and technology network

1. INTRODUCTION

With the help of the Baross Gábor Program, conducted by the Homokkert Small-regional Integration Public Company consortium a research and development network and a food safety and food technological subcenter has been set up in the South Great Plain region in Hungary. It is structured around up-to-date technological and metrological solutions and results cooperation of scientific institutions, researcher non-profit organizations and the entrepreneur sector.

The micronetwork and the soil- and water analysis laboratory – coordinated by the Homokkert Public Company – provides agro-innovative services for the cooperatives and partner organizations (DATÉSZ Rt., Mórakert Cooperative). By doing so it improves the local products' competitiveness and the standard of nutrition and quality assurance.

2. THE IMPORTANCE OF AGRICULTURE IN THE REGION

45,000 people live in the area of Mórahalom, which is considered the center of the Homokhát Small-region. Most of the people work in agriculture, thus their living is exposed to the competitiveness of the vegetable and fruit grown by them. Agriculture uses 72% of the small-region's land. The rate of forests is high, resulted by the afforestation in the beginning of the last century. The rate of lawns is also high because of the previously existing vast meadows and mowing fields. However vegetable growing is typical in arable farming and in the garden cultivation branches and its economical importance is unquestionable, it occupies relatively small area from the region's land. The volume of land used for pomology and vineyards shows the characteristics of sand farming. Non-cultivated lands and waste lands are the signs of uncertainty of farming and marketing and the disarrays about the ownership of the tenures (Figure 1).

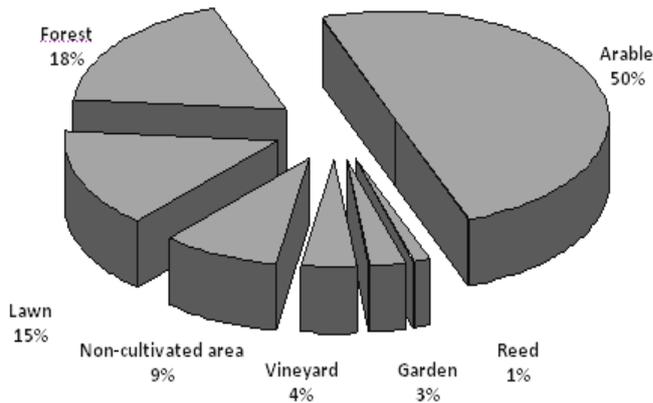


Figure 1. Distribution of cultivation branches of the small-region's area

The integrators, the cooperatives and other significant economic operators have to make sure the compliance with the market requirements, which means producing clear, healthy and high quality products. The most significant such integrator is Mórakert Cooperative founded in 1995 and declared as the first fruit and vegetable producer realizer organization by the Ministry of Agriculture and Rural Development in 2002. Its turnover and number of members has increased significantly in the last 10 years (Figure 2).

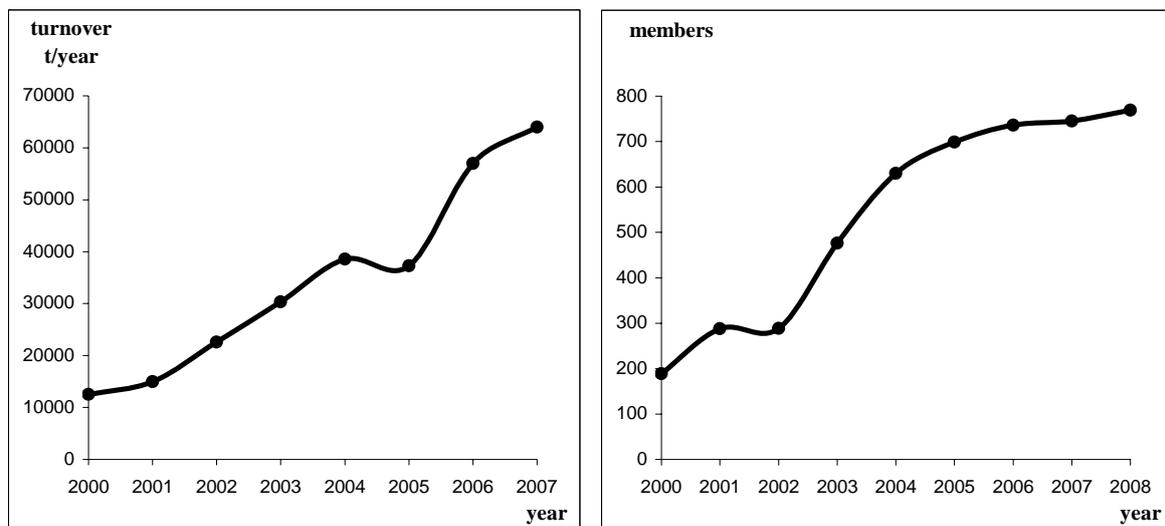


Figure 2. Growth of turnover and number of members of Mórakert Cooperative

3. HOMOKKERT PUBLIC COMPANY

The Hommokkert Small-regional Integration Public Company was corporated in 2000 by 9 agrarian cooperatives and the local authority of Mórahalom. The company was comprising producer and marketing cooperatives until the conversion in 2004 when the main profile of the company changed and two stratalgical directions were developed in connection with the agricultural priorities. These focus on the improvement of the living and income conditions of the rural population.

International connections

The Homokkert Public Company cultivates good relations with international partners. Seeking the possibility of cooperation with neighboring countries and participating in common projects are important parts of the company's activity. A recent collaboration was the establishment of a Borderland Commercial Center with Topolya and Temerin, two towns in Vojvodina, within the framework of an inter-regional project in 2008. The primary aim of this center is helping the cross-border trade of the agricultural products in the region.

Profiles of the Homokkert Public Company

On the one hand the main profile of the Company is encouraging alternative income activities – the so-called Renewable Energy Information Center was built in support of this objective – and on the other hand the research and development, innovation and innovation intermediation services. The Regional Food Safety and Technological Micronetwork needs to be highlighted here, which was set up in the framework of the Baross Program. The Network was evolved by the partnership of the Homokkert Public Company and Mórakert Cooperative

in Mórahalom, the DABIC Public Company in Szentes and the College of Kecskemét (Figure 3). Its goal is to establish an accredited institute complying with the international standards and placed near big producer-realizer cooperatives (e.g. Mórakert Cooperative).



Figure 3. Centers of the Regional Food Safety and Technological Micronetwork

Aims of regional food safety and technological micronetwork

- a) establishing a regional food safety and technological subcenter with the utilization of results and experiences of the regional center and network maintained by DABIC Public Utility Company
- b) founding an agrarian research workshop with the collaboration of acknowledged researcher-teachers with scientific degree and local experts, and developing an academic practicing section in connection with garden cultures and the safety of horticultural products
- c) establishing an experimental soil and water analyzing laboratory and the publication of results
- d) achieving experimental developments in relation with product innovation and changing production structure in vegetable, fruit and ornamental plant growing
- e) starting continuous horticultural research and development activity based on regional demands
- f) evolving a research and development and innovation micronetwork – with thousands of members - considering the specifics of producer-realizer cooperatives (TÉSZ) and the conditions of local product structure
- g) establishing a consultant network and educational activity
- h) experimental developing of analytical methods, e.g. for fast determination of chemical residues
- i) founding an agrarian research workshop that conduces to the production of high added-value or new products (bioproducts, functional foods) with developing growing methods and technologies

4. REASONABILITY OF MICRONETWORK

Directives of the EU – Food safety

Establishing and maintaining the Regional Food Safety and Technological Micronetwork is reasoned by directives and regulations of the EU. In hygienic overseeing of food producing, the European Union put emphasis on supervision of producing environment instead of the former final product checking in the last years. Therefore application of new analytical methods is required. SoilChem Laboratory – part of Regional Food Safety and Technological Micronetwork – wishes to keep pace with this continuous vocational improvement. Developing analytical procedures to support the development of new technologies – that result healthy and safe food – is one of SoilChem Laboratory’s primary goals. Nowadays food safety is number one priority of agrarian economy: organizations in agriculture and food industry must correspond to the higher and higher requirements of food safety and environmental protection, and must meet the consumers’ increasing demands.

Considering food safety regulation of the European Union, configuring quality insurance systems and helping producing activity at agrarian small and medium enterprises became indispensably necessary by now. In the interest of competitiveness of these enterprises preventive self-checking food safety systems must function effectively „from field to table”, ensuring the transparency of food chain. Successful food politic demands the absolute traceability of crops, food and their components. This enables the enterprises to

withdraw hazardous forage or food from the market in case of consumers' health is endangered. Healthy and safe food can only be ensured by continuous monitoring of critical points of the producing process and by running quality insurance systems. It is reasonable to establish and upkeep accredited food safety and technological centers and subcenters, placed near farmers in the interest of quantitative and qualitative determinations of health-damaging chemical and microbiological compounds.

Functions of centers:

Instrumental tests are indispensable to obtain knowledge of environmental factors and their impacts. Thus we can collect data that help us to intervene in the process of cultivation. Precision nutrition replenishment can be attained only in possession of the knowledge on the soil's current nutrition level. Therefore soil analysis is necessary both before and during every single cultivation process. More detailed information is needed of soil and irrigation water in case of horticultural crops (nutrient rate and quantity, harmful elements).

- a) monitoring chemical residues (pesticides, pharmaceuticals etc.) of crops and food
- b) detection of metal pollutants (lead, cadmium, mercury, arsenic, aluminium, copper, zinc, nickel) in food of plant and animal origin
- c) determination of nitrate in vegetables susceptible for nitrate accumulation
- d) complete analysis of soil and water
- e) microbiological monitoring to increase the hygiene of food processing technologies
- f) forage-safety monitoring
- g) issue accredited certificates

Economic advantages

The building up of the Micronetwork is appropriate concerning its economic advantages as well. The current international and domestic consumer habits seem to prefer products with known origin; customers appreciate the value derived from the specific circumstances of the production. Thus the quality advantages in the production lead to market advantages. With the characterization of agricultural and food industrial products grown on excellent soil, using adequate technology and defining the relating quality features and with the conscious perpetuation of these benefits these products can obtain market advantages.

5. CONCLUSIONS

The whole sector and region profits from the database of materials endangering food safety, building up and operation of preventive indication systems, meeting the requirements of identification and traceability, and applying new, conventional sampling methods. The Micronetwork's indirect economic effects can be measured in the improvement of competitiveness of the analyzed products, the prevention of the damages caused by loss of consumer trust, and the recognition of the network's trademark.

The operation of SoilChem Laboratory as a service provider, accredited institute makes the non-profit investment self-supporting in the future.

ACKNOWLEDGEMENTS

This work was supported by the Gábor Baross Program (BAROSS-3-2007-0009; OMF-01162/2007).



ARSENIC PROBLEM AND POSSIBLE SOLUTION FOR DRINKING WATER

Tamás BUJDOSÓ¹, Ágnes PATZKÓ¹, Zoltán GALBÁCS²,
István LICSKÓ³, Imre DÉKÁNY¹

¹Department of Colloid Chemistry, University of Szeged,
Aradi Vt. 1., H-6720 Szeged, HUNGARY

²Department of Inorganic and Analytical Chemistry,
University of Szeged, Dóm tér 7., H-6720 Szeged, HUNGARY

³Department of Sanitary and Environmental Engineering,
Budapest University of Technology and Economics,
Budafoki út 4., H-1111 Budapest, HUNGARY

Abstract

Aim of this research was the removal of toxic and carcinogenic arsenate (AsO_4^{3-}) ions from drinking water on different metals (Mg, Mn, Al, Fe) content layered double hydroxides (LDH). The efficiency of the MgAl LDHs in the arsenic removal is increased with increasing nitrate content in LDH. The basal spacing of LDH was decreasing with 0.085 nm after the ion-exchange. The calcinated form of each adsorbent resulted less arsenic removal, but less dissolution of metal from the oxide compared to the uncalcinated LDH. Increasing the manganese content in the MnFe LDH resulted enhanced arsenic removal efficiency.

Keywords:

arsenic removal, drinking water, layered double hydroxide, adsorption, calcination



SLAG – UTILISATION IN ROAD CONSTRUCTION – EXPERIENCE AND SOLUTIONS

¹Rodica ISTRATE, ²Adrian CALIMENTE

¹University “Politehnica” Timisoara , Faculty of Engineering Hunedoara - Associate teacher & IR Business Services Prest SRL Hunedoara - Administrator

²BSE SC SLAG PROCESING SERVICE SA - General Director

Keywords:

Steel slag, waste recycling, by-product, road construction

1. INTRODUCTION

As the world population grows, so do the amount and type of waste being generated. Many of the wastes produced today will remain in the environment for hundreds, perhaps thousands, of years. The creation of nondecaying waste materials, combined with a growing consumer population, has resulted in a waste disposal crisis. One solution to this crisis lies in recycling waste into useful products. One answer to all of these problems lies in the ability of society to develop beneficial uses for these waste products.

The road-highway construction industry can effectively use large quantities of diverse materials. The use of waste by-products in lieu of virgin materials for instance, would relieve some of the burden associated with disposal and may provide an inexpensive and advantageous construction product. Current research on the beneficial use of waste byproducts as road-highway construction materials has identified several promising uses for these materials. Some of these materials include: Blast furnace and steel slags.

2. STEEL SLAG IN EUROPE

In Europe are produced annually around 15 Mil tones of steel slag, resulting from different type of steel technology (Figure 1),

More than 75 % of steel slag was recycled in Europe (Figure 2.) in different kind of utilization in especial like raw materials.



Figure 1. Type of steel slag

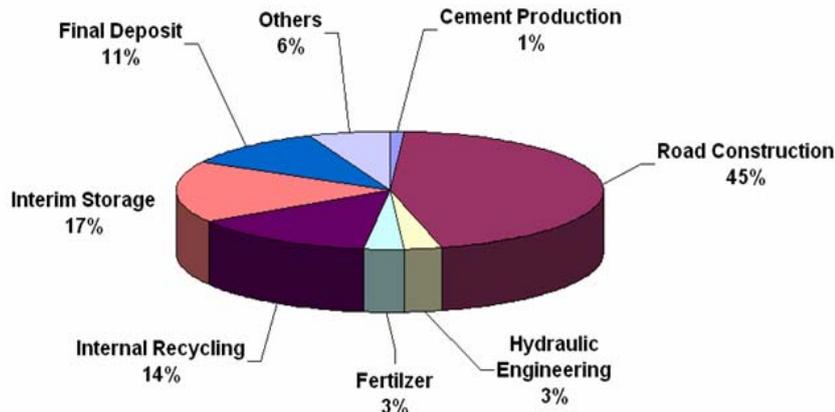


Figure 2. Slag utilization in Europe

2.1. European waste framework Directive

Present situation in the steel industry on material management give as an overview on the legal situation regarding the dealings with by-products such as slag and secondary raw materials on the basis of the European waste framework directive. Further on it describe the existing frameworks nebulous differentiation between waste and non waste (by products, when ceases waste to be waste) that lead to a flood of court procedures and to a discrimination of by-products and products made of recycled materials. Metallurgical slag is given as an example for a purposeful produced by-product in the steel industry which replaced primary raw materials and thus saving resources. Typical product criteria are described. Finally the proposal on the revision of the waste framework directive of the European Commission and those presently discussed in Parliament and Council is evaluated regarding the necessary clarification

- when a substance is excluded from the waste legislation as (by-)product, or
- when it ceases to be secondary raw material

A discrimination of by-products and products made of recycling material compared to products made of virgin material is not acceptable and contrary to the aim of sustainable management. On the contrary the usage of by-products and secondary raw-materials must have priority.

European Waste Catalogue does only name unprocessed slag as a waste, European Waste Shipment Regulation (NO 259/93) - GREEN LIST, GC 070 exclude processed slag from the waste list:

“Slags arising from the manufacture of iron and steel (including low alloy steel) excluding those slags which have been specifically produced to meet both national and relevant international requirements and standards.”

Green list substances shall be generally excluded from control procedures of the regulation since such waste should normally not present a risk to environment.

Principles of European Waste management say that steel slag has to be recycled (Figure 3.).



Figure 3. Waste management hierarchy

3. DESCRIPTION OF THE EXPERIMENTAL SETUP

3.1. Steel slag treatment process

Steel slag type	Treatment	
Hot slag from EAF	Cooling by water spraying	Quick cooling is important for technical and environmental properties (Figure 4)
Raw slag with steel	Iron separation	Steel recovery pays for the slag treatment (Figure 5)
Raw slag	Crushing and screening	Crushing and screening gives different products (Figure 5)
Slag products	Road aggregates rip rap chippings	Products differ only in grain size distribution (Figure 6.)

Table 1. Main slag processing

Main slag processing is mechanical treatment of cold slag, the principle of slag processing are in Table 1.



Figure 4. Cooling area with water spraying



Figure 5. Instalation of slag treatment SPS Hunedoara

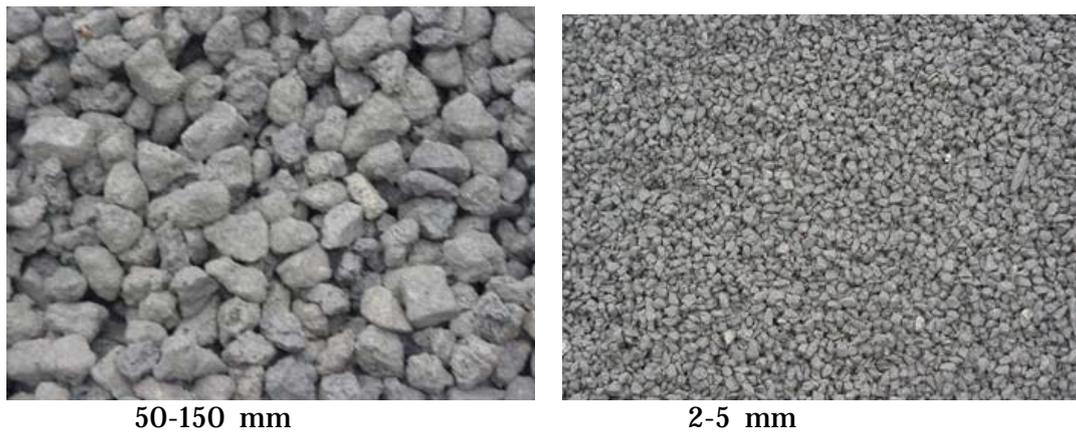


Figure 6. Slag products

3.2. Steel slag in Road construction

CLOOS Luxemburg had more than 100 years experience in utilization of slag in road construction, an examples of road layers (Figure 6.)

Slag crushing aggregates can be used in all layers of the road, in Romania; SPS homologated the shape, foundation, basic and binder layers and are in course of homologation the utilization of slag in asphalt layer. Here will be used cold slag treatment procedure for obtain good results.

Terminologie des couches et performances des matériaux utilisés

GRANDEVOIRIE (autoroutes, trafic lourd)		VOIRIE (routes, trafic léger)	
15 cm	COUCHE DE ROULEMENT ET COUCHE DE LIAISON	15 cm	Caractéristiques requises Voir C.T. 9/98 version 1.98
30-50 cm		20-30 cm	
30-50 cm	COUCHE DE BASE	20-30 cm	Matériaux utilisés Enrobés
30-50 cm	COUCHE DE FONDATION	20-30 cm	
25-40 cm	COUCHE DE FORME	20 cm	Matériaux utilisés LHF Porphyres Calcaires durs Dolomies Grès schisteux Grès dolomitique Grès de Luxembourg Matériaux de recyclage
25-40 cm	FOND DE COFFRE / REMBLAI	20 cm	
			Caractéristiques requises Matériau 0/50 type 1: VB(0/2) < 0,15 LA < 20 CS 32/40 < 18
			Caractéristiques requises Matériau 0/50 type 2: VB(0/2) < 0,40 CS 32/40 < 30
			Matériaux utilisés Déchets de carrière 0/250 ou Matériau de remblai adapté

Remarque: La couche de base en grande voirie est à mettre en oeuvre en 2 couches.
La couche de fondation est à mettre en oeuvre par couches d'épaisseur de max. 25-30 cm.
Les fuseaux granulométriques des matériaux 0/50 sont conformes aux fuseaux pour type 1 resp. type 2.

Figure 6. Slag road layers

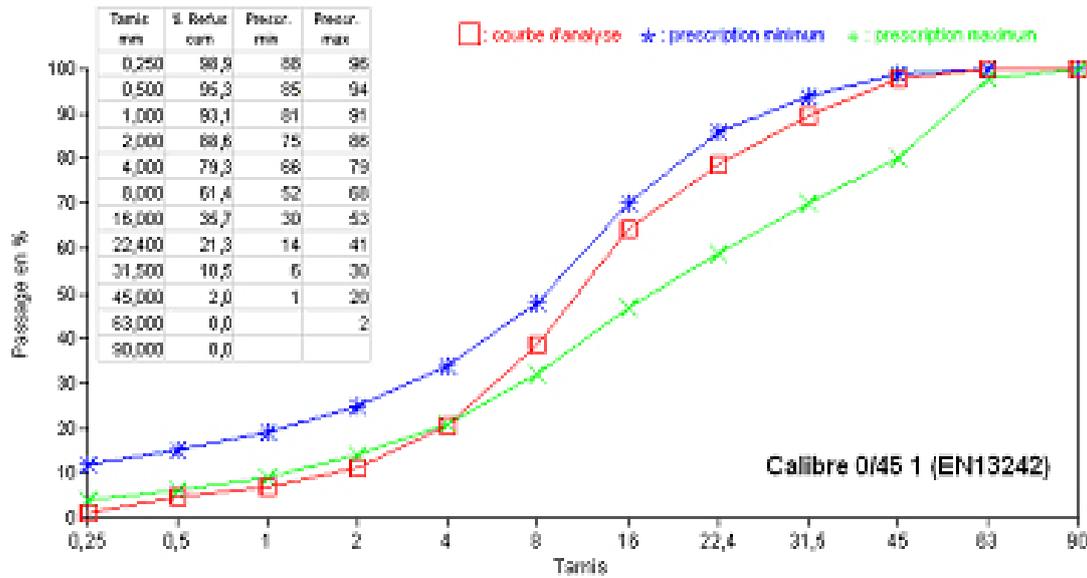


Figure 7. Slag aggregate 0/45

In Figure 7. we can see red line, property of slag product 0-45; and minimum and maximum requirement of EN 13242,

Example of slag utilization in road construction in Hunedoara is the 4 bands road between Deva and Hunedoara (Figure 8), where the basic, foundation and binder was made from slag aggregates from Buituri Slag Dump, processing by SPS. Unfortunately the Romanian road designers and constructors don't understand yet to use this waste; by-products existing in Hunedoara in Slag Dump in quantity of 70 Mill. Tones.

SPS continue the researches regarding slag utilization in road construction with University "Politehnica" Timisoara – Road Construction Department, now in researches of Slag roads compartment in different charges starting with County roads, Villages roads, technological roads, and sure Highway.



Figure 8. Slag road construction; Hunedoara - Deva

4. ANALYSIS OF RESULTS AND CONCLUSIONS

4.1. Product Certification and Quality Control

Steel slag has to undergo a quality control process like any other process (Table 2.), steel slag is an artificial stone, with the request property for road construction, and other utilizations: concrete production, fertilization, hydraulic construction, building foundation, etc.

No.	INDICATORS	VALUE
1	Bulk density according to DIN 52110	Average value: 2,06 g/cm ³ for grain size mixture 0/32 and 0/45
2	Proctor density according to DIN 18127	Average value: 2,47 g/cm ³ for grain size mixture 0/32 and 0/45
3	Fines	In grain size range 0,0 – 0,063 mm from 0,2 to 0,4 weight.-%.
4	Destruction by beating SZ 8/12	Desired value 18,0 weight-% for chippings
5	Destruction by beating SD 10	Desired value 26,0 weight-%
6	Polished stone value (PSV)	PSV 60, chippings for asphalt
7	Frost resistance	Limit value 3,0 weight.-%
8	Volume stability	Limit value 5,0 vol.-%
9	Inner angle of incline	Average value 40 °

Table 2. List of technical test

Slag Processing Service SA Hunedoara (CLOOS Luxemburg is main shareholders with 80% of shares), start the work in ArcelorMittal Hunedoara Slag Dump, with chemical and physical tests of the slag, make in Luxemburg (80 tones of samples taken from different places from slag dump was send with tracks). After this was start the treatments of old slag: crushing and screening, iron separation, aggregates rip rap chippings, with 500.000 tones/year capacity Installation.



Figure 9. Conformity Certificate

Conformity Certificate for slag aggregates utilization in Romania (Figure 5.), was obtain by SPS in 2006, was certificate that the products “Crashing Aggregates from Steel Slag” 0-4; 4-8; 8-16; 16-31,5; 31,5-63; si 0-63, produces by SPS in Slag Dump Buituri Hunedoara, are in accordance with: EN 12620/2002, EN 13242: 2002/AC:2004, Utilization domain: construction of: roads, civil and industrial buildings, hydraulic and earth construction.

4.2. Comparatives cost of slag roads and virgin materials roads

We analyze comparatives structure of road layers; classic and two alternatives for basic and foundation layers, (Figure10.) mentioned that wear layer in all three situations remain the same asphalt mixture and the existing shape also.

Thickness	Layer – CLASSIC
5 mm	Wear - asphalt mixture
20 mm	Basic - natural crash stone
30 mm	Foundation -Ballast 0-63 mm
X mm	Shape - existing

Thickness	Layer- Alternative 1	Layer- Alternative 2
4 mm	Wear - asphalt mixture	Wear - asphalt mixture
15 mm	Basic - slag 0-63 mm	Slag - optimal mixture stabilized with: 0.5 ciment and 8% water
20 mm	Foundation -Slag 0-150	
X mm	Shape - existing	Shape - existing

Figure 10. Comparative layers classic-slag roads

The comparative costs in “LEI” of all three variants (Figure 11.):

1. Classic system road (virgin materials)
2. Alternative 1 road system with slag
3. Alternative 2 road system with slag and cement

So as that the partial slag roads analyze are with 24% chipper that classic roads. If the road will be executed integrally by slag products like in Luxemburg, Germany, France, etc. the cost reduction is around 40%.

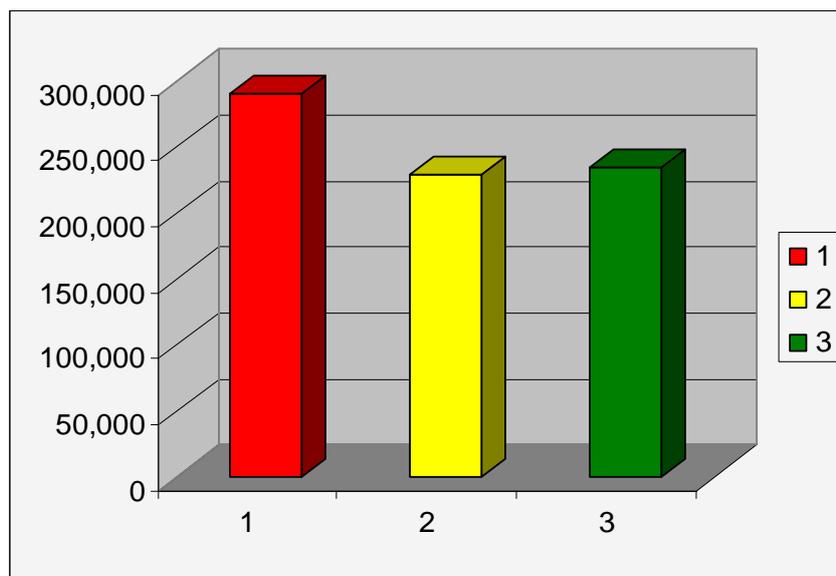


Figure 11. Comparatives cost of the roads

Conclusions: We can construct with the same amount 140% more roads.

This is not the single reason for using slag, the durability, stability of the roads is better and not the last we save virgin materials, recycling the slag and ensuring the slag dump disappear.

Use of steel slag is absolutely necessary in Europe to reduce costs and to comply with environmental laws

- Slag use in Europe has a long tradition.
- European law asks for recycling of steel slag.
- European legislation makes it sometimes difficult to bring slag products to the market.
- Process technology is known and proven.
- Slag products can be certified and have to undergo a quality control procedure.

BIBLIOGRAPHY:

- [1] Dr. Jens Apfel - Sustainable Use of Steel Slag in the European Union – 4th European Slag Conference – Madrid 2006
- [2] G Endeman – Material management in the context of the waste framework directive – 5th European Slag Conference – Luxemburg 2007
- [3] Robin L. Schroeder - The Use of Recycled Materials in Highway Construction - Autumn 1994· Vol. 58· No. 2
- [4] JTG Richardson – Slag bound materials in composite roads – 2000 Society of Chemical Industry
- [5] www.euroslag.org
- [6] www.cloos.lu



PROBLEMS IN THE PROCESS OF WASTE WATER TREATMENT ON THE SUBOTICA WASTE WATER TREATMENT PLANT (WWTP)

¹Aleksandra KURTES, ¹Bojana BURGER,
¹Imre CSEKE, ²Mirjana MILORADOV VOJINOVIC

¹Waterworks and Sewerage Public Utility Company „Waterworks and Sewerage“ Subotica
²Faculty of Technical Science, Novi Sad, SERBIA

Abstract

The waste water treatment plant (WWTP) in Subotica has continuously been operating for 33 years. The Plant was designed for mechanical and biological treatment of municipal waste waters. The major issue in the functioning of the plant is its low hydraulic capacity and the inflow of waste waters other than municipal, and not pre-treated industrial and technological effluents respectively. Massive organic matter surges, as well as waters with toxic effect have negative impact on the micro world of the active sludge, modify the character and ability of sludge sedimentation, condition oxygen deficit in aeration tanks, which aggravate the treatment process management and result in the effluent's poor quality. The aim of this paper is to present the effects of the Subotica WWTP operation, and also the quality of technological effluents by the major industries in the city, and their impact on the treatment process in 2008.

Key words:

waste water treatment process, effects of the WWTP's operation, industrial effluents.

1. INTRODUCTION

The city's WWTP is located on the southern part of the city of Subotica, while the recipient for treated wastewaters is Lake Palic. The sewage network in Subotica is built up according to a general sewage system, meaning that the same system takes off stormwater and wastewater alike. The public sewage network comprises drains of different shape, size and material. The city is divided into eight major collection point, and the whole sewage system is gravitation-based. The lowest point in the city is its WWTP. The WWTP was commissioned late 1975 and since then it has been operating continually. The reason behind building a WWTP was a special ecological disaster in Lake Palic in 1971 with a massive pestilence of fishes. Parallel with the building of the WWTP, the lake recovery was implemented as well (desiccation and desludge of the lake-bottom), whereupon the lake was divided by dikes into four sectors. The aim of dividing the lake in such a manner was to provide a more efficient and intensive process of autpurification of the water and thus to provide the highest possible quality of water in the 4th sector, i.e. the tourist part of Lake Palic. Lake Palic is an aeolic, eutrophic lake with maximum depth of about 2.5 meters. Sufficient water quantity in the lake is provided by the inflow of treated waste water from the Plant. Excess water is evacuated through lake Omladinsko jezero via a canal to Ludas Lake, from where it is taken by the Keres streamlet to the Tisa River (Fig 1).

An imperative in the Plant's operation is the best possible quality of effluent, first and foremost, due to the recipient's high sensitivity and eutrophic character. The WWTP was designed to treat municipal wastewaters with a designed hydraulic load of 30000 m³/day and 45000 m³/day respectively in times of heavy stormwater, while the designed BOD of influents is 250 mg/l O₂. Waste water undergoes primary and secondary treatment, which comprise mechanical (coarse and fine screen, aerated sand trap and primary sedimentation tank) and biological (aeration tank) treatment of waste waters (Figure 2) [4]. Biological treatment is implemented by activated sludge method. Water is taken from the aeration tanks to secondary sedimentation tanks, where sludge is separated from the treated water.

The problem in the operation of the Plant and achieving water quality, which will not impair and additionally accelerate the eutrophication process of the recipient, is the lack of tertial treatment within waste water treatment (removal of nitrogen and phosphorous compounds), massive hydraulic load of the Plant and the inflow of not treated industrial effluents.

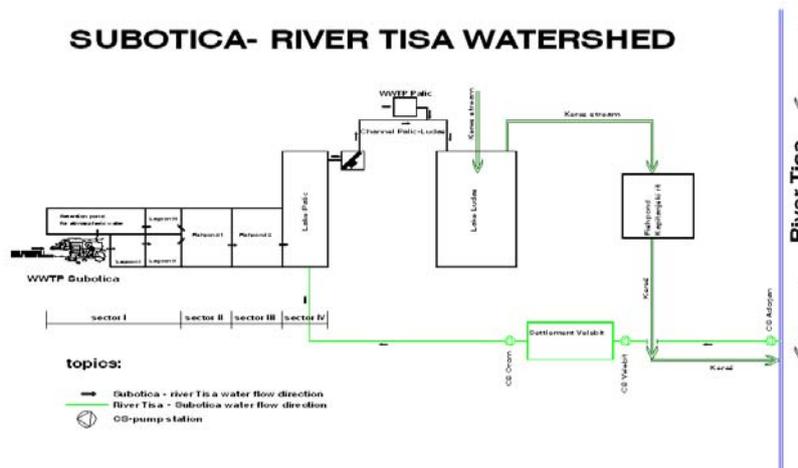


Figure 1. Subotica-River Tisa Watershed

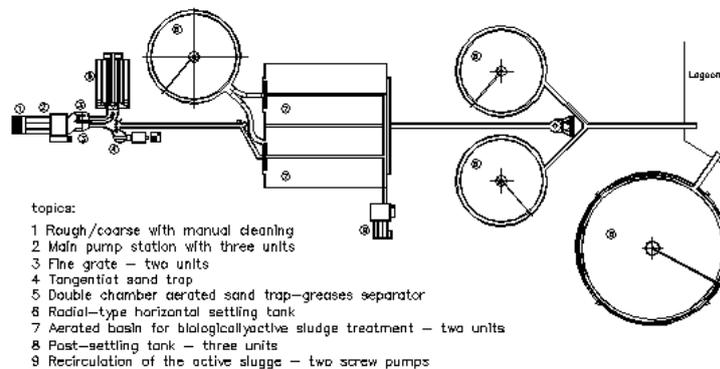


Figure 2. The Wastewater Treatment Plant of the City of Subotica

The aim of this paper is to present the effects of the Subotica WWTP operation, and also the quality of technological effluents by the major industries in the city, and their impact on the treatment process in 2008.

2. MATERIAL AND METHOD OF WORK

Analyses of the Plant's operation are permanently made by the internal laboratory for the quality control of waste and surface waters in the Subotica Waterworks PUC. The laboratory is equipped for physical, chemical and hydro biological analyses. Physical and chemical analyses cover a set of relevant parameters, first pH, organic load, oxygen concentration, total nitrogen and phosphor content in the waste and treated water, as well as dry matter content and sedimentation volume of the bioactivated sludge, and are defined by the recommended standard methodology. Instantaneous and 24-hour composite samples are processed per each treatment phase. Samples of industrial effluents are taken once or twice a month. The selection of parameter volumes for the analyses of industrial effluents is made depending on the type of industry, and mostly, it includes basic parameters.

Biological analyses include microscopic quality control of the bioactivated sludge according to the recommended methodology [3]. Analyses are made on a daily basis, while samples are taken from the aeration tanks and the recirculating sludge. Fresh, native and coloured preparations are analysed. Photos of the samples are taken daily, and data are kept in a database. Toxicological tests of industrial effluents are also made. Toxicity level is determined by standard short (24h) tests on aquarium fish *Lebistes reticuatus*. LC-50 is defined (concentration of chemicals which kills 50% of the organisms in a specific time). Results are expressed in %Tlm which is conversely proportional to toxicity level, and in Dil. Tlm indicates the number of times the water is to be diluted in order to achieve LC-50.

3. RESULTS AND DISCUSSION

The operation of the WWTP

The average quantity of intake water on the Plant was 39155 m³/day, while an average quantity of 32375 m³/day of waste waters was treated in 2008 [2].

The quality of intake water was varied over the year. Moderate content of organic matters, with time-to-time surges of organically highly loaded waters was characteristic for the raw waste water. The tendencies of average and maximum organic load values for the raw and treated waste water are shown in Table 1.

Table 1: Organic load values of influent and effluent waste waters and Sludge Volume Index

Parameters	BOD (mg/l)		BOD (mg/l)		SVI (ml/g)
	Influent average	Influent max.	Effluent average	Effluent max.	
January	228	390	16		228
Febr.	207	332	14		240
March	208	332	17		279
April	197	233	7		261
May	219	318	20		326
June	161	282	14		354
July	205	302	22		555
Aug.	211	341	11		378
Sept.	232	382	16		368
Oct.	260	352	34		519
Nov.	248	347	31		452
Dec.	203	424	15		325

From the aspect of impact on the aquatic eco-system of Lake Palic, it is essential to emphasise that there is a relatively high nitrogen and phosphor content in the city's waste waters. In the total nitrogen content its ammonium form is dominant. The average concentration of total nitrogen in inlet water was 44,2 mg/l. Thereof ammonium nitrogen made up 29,2 mg/l or 66%. The total nitrogen concentration in treated water was 30,7 mg/l, and 23,5 mg/l, or 76% of this was ammonium nitrogen. The effect of total nitrogen decrease was 30% in the Plant. The total nitrogen concentration in treated water was 6,61 mg/l, and 3,41 mg/l of this was ammonium nitrogen. The effect of total phosphor decrease was 50% in the Plant [2].

Microscopic sludge analyses serve system status assessment based on quality of floc and microorganism composition. High hydraulic load and frequent surges of high concentrations of organic matters condition system overload and oxygen drop in aeration tanks, which are reflected in the qualitative and quantitative composition of microbe community in the activated sludge [1]. Filamentation index [3] (total number of filamentous bacteria) was increased over the whole year (FI=6). *Thiothrix* spp., was dominant, and it is a sulphuric bacterium, which, with the contexture of its long and thick filaments changes sludge characteristics and aggravates sludge sedimentation and it is reflected in increased SVI over the whole year (Figure 3b). Frequent occurrence and higher number of type 1863 was recorded as well, since it grows on hydrophobic substrates (grease) and, due to its morphology, it floats up and creates foam. The size, shape, structure and stability of flocs were satisfactory most of the year, yet sludge age was constantly old with frequent occurrences of sludge decay signs (Figure 3a). Numerous low diversity colonies (as a consequence of uniform substrate) occurred during the year as well. The number of free cells in supernatant was constantly increased (indicating system overload) From the protozoa, flagellates (indicators of overload) also occurred frequently, while amoebae were recorded infrequently and in smaller number. Free-living ciliates occurred sporadically, mostly *Colpidium* spp. and *Euplotes* spp. From the crawling ciliates, *Aspidisca costata* was dominant, which was permanently present and sometimes achieved high numbers.

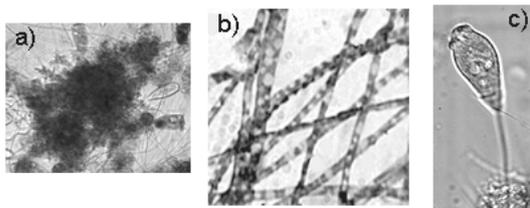


Figure 3. Activated sludge microorganisms: a) sludge floc, b) *Thiothrix* spp., c) *Vorticella microstoma*

Most frequently, the total number of fixed ciliates was higher than 20000/ml, sometimes reaching a value over 120000/ml (which also indicates sludge ageing). During May, June and July, the number of this indicator groups of organisms dropped (to below 10000/ml), due to the toxic influence of the influent water quality. Dominant were *Vorticella microstoma* (Figure 3c), *Opercularia* spp. and *Vorticella convalaria*.

Industrial Effluent Analysis

A total of 104 wastewater samples of industrial origin were analysed in the wastewater quality control laboratory. Quality incompliance of effluents to the prescribed values is determined on the base of permitted maximum concentration (PMC) set in Article 18 of the Decision on Public Sewage (the Official Journal of the Subotica Municipality no. 39/2001). The effluent quality of controlled industrial polluters deviated from the prescribed PMC values in the following parameters: low and high pH values, high organic load, grease and oil, sedimentary matters, inorganic soluble salts, total nitrogen and phosphor and AA detergents [2]. Effluents coming from process industry (milk processing, flour and fruit processing, beverage production) had the most significant negative impact on the Plant's operation. (Table 2).

About 70% of the analysed samples showed satisfactory quality in view of toxicity (atoxic or oligotoxic water levels I and II) and did not disturb the Plant's operation [2]. In average, the highest toxicity level over the year was in food processing industries, i.e. dairy and flour processing (farina production) and in the textile industry, while maximum toxicity level was also recorded in fruit processing industry and beverage production, where it amounted to %Tlm=1,41, which corresponds to mesotoxic water level V. If %Tlm value is lower (>100), the analysed sample is of higher toxicity level (Table 2).

Table 2. Demonstrated maximum values of critical physical and chemical parameters and toxicity level of dominant industries in Subotica in 2008

Sampling spot-industria Parameters	Flour Processing Industry	Milk processing Industry	Fruit Processing and Beverage Production	PMC
max. pH	6,31	7,85	10,12	8,5
min. pH	3,58	4,48	1,52	6,5
BPK ₅ (mg/l)	13900	65668	2082	-
Total N (mg/l)	334	873	28,8	50
Total P (mg/l)	142	71	1,90	12
Grease (mg/l)	-	7177	-	30
Total Sedimentary Matters (mg/l)	12520	1380	110	100
%Tlm	3,17	3,17	1,41	100
Toxicity Level	Mesotoxic Level V	Mesotoxic Level V	Mesotoxic Level V	-

4. CONCLUSION

WWTP in Subotica received higher quantities of water than the designed ones during 2008.

Unlike municipal wastewaters, which are mostly uniform in their physical and chemical composition, the character of industrial effluents significantly varies in quality and quantity. The WTP cannot treat adequately the diverse composition of industrial effluents, hence these aggravate the treatment process by making it slower and more expensive.

The lack of tertial water treatment is the cause of high total nitrogen and phosphor concentration in the effluent over the whole year.

Due to the above indicated, effluent quality during 2008 was not always satisfactory, yet treatment effects, express through the decrease in total organic load of the water, amounted to 92%.

LITERATURE

- [1] Burger, B.: Microbiological characterization of activated sludge in WWTP of Town Subotica. International conference Waste Waters, Municipal Solid Wastes and Hazardous Wastes (36; 2006; Subotica), Conference Proceedings (ISBN 86-82931-17-6) pp. 95-98. Subotica, 2006.
- [2] Database of Waterworks and Sewerage Public Utility Company „Waterworks and Sewerage“ Subotica
- [3] Jenkins, D., Richard M.G., Diagger, G.T. : Manual on the Causes and Control of Activated Sludge Bulking, Foaming and Other Solids Separations Problems, 3rd ed, Pres LLC, Co-published by IWA Publishing, London, 2004
- [4] Milic Rafai, Č., Trunzel Mešter, E., Kurteš, A., Medić, O.: Process control at WWTP of Subotica. International Conference Waste Waters and Municipal Solid Wastes, Conference Proceedings pp. 101-106. Budva, 1999.



THE METHOD OF RISK ASSESSMENT AT WORKPLACE AND WORKING ENVIRONMENT IN AN EXAMPLE OF A METAL MECHANICAL PROCESSING SECTION OF A FACTORY

Bozo NIKOLIC, Biljana GEMOVIC

Higher Education School of Professional Studies, Novi Sad, SERBIA

ABSTRACT

The aim of this work is to show, with due respect to the existing methodologies, the implementation of an original method of risk assessment at workplace and working environment. The example represented here is based on implementation of this method in a section of a factory where mechanical processing of metal is performed. The risk assessment procedure is conducted through implementation of our own method. It is ensured that the project is conducted thoroughly, from the defining of technological process – system, to implementation of measures for control of (“emergency”) risk.

The method is of quantitative character with possibility to determine and compare all risks, at every workplace and including all participants who take part in working environment on every basis.

1. INTRODUCTION

Risk assessment is based on systematic record keeping and tracking of all factors, vulnerability and hazards in a working process. Therefore, it is crucial to recognize organization of work, working process, means of work, material and raw material used in working process, means and equipment for personal protection and other relevant elements. A precondition to this has to be the recognition of existent facts. This is a basic and starting point and it is also required by the Code of Practice (1), made in compliance with Directives of the European Union. Apparently, the true answer and primary task of any method is: to determine risk arising at any workplace and regarding any worker, to determine all risks and to allocate the risks to individuals, working space and working environment.

Risk assessment methodology has to be clear and unambiguous in order to enable a complete analysis of risk assessment to be conducted. A methodological way of risk analysis, according to the method of High School from Novi Sad is the following:

Defining of system – defining assessment levels (company, facilities, floors, premises, work-rooms, workplace, work activity etc.) – identifying hazards and vulnerability – evaluation of risk – measures for elimination, prevention and reduction of risk – re-evaluation of risk – conclusion on risk – measures for maintenance of risk control.

2. THE STUDY

2.1 Input data. Technological setting

In our example, an engine hall and working process of metal processing are used as a model. In this section of a factory, steel material is processed through grinding, perforating, milling, welding etc. It is a standard section of a factory with typical and recognizable hazards.

There are N workplaces in this factory section where it is likely that hazards and vulnerability for workers at those workplaces may occur. The workers in the engine hall are exposed to shared hazards and vulnerability arising from workplaces in the environment all the time during their working hours. The workers whose workplace is not the engine hall, but who are frequently present there during their working hours (such as section managers, maintenance workers, controllers and alike) are also exposed to the same hazards. Also, all

those who every now and then enter the hall are exposed to the same hazards (directors, trainees etc.). Naturally, risks relating to each of these categories of employees are different because of their different frequency of exposure to hazards and vulnerability.

2.2 About the method

The method of the School is formed to meet the following requirements:

- ✚ to include all workplaces by making a selection of them out of technological process together with important hazards and vulnerability and to determine risks for each of them
- ✚ to determine risks at all levels (the engine hall);
By meeting the given requirements it is ensured that risks for each of the workers are determined, i.e. for all those who are present in the company (the engine hall)
- ✚ the method for all risk parameters is based on numerical, quantitative values, independent of a level at which the risk is determined, thus enabling presentation of all risks together and their uniform observation
- ✚ the measures for elimination, reduction and prevention of risks are clearly defined, as well as the measures for maintenance of risk control level. The represented system of risk management makes way to implementation of quality systems in health and safety at workplace.

Characteristics of the method:

- a) Risk calculation of a workplace based on a table determination of all risk parameters; likelihood of accidents, damage size, frequency and number of people exposed to hazards and vulnerability

$$R_i = V * F * S_i * N$$

R_i , S_i – risks and damage size for different categories of employees, depending on the frequency of their exposure to hazards and vulnerability.

- b) risk assessment of working environment based on determining likelihood of accident occurrence which is based on values of safety conditions in the working environment and accordingly developed mathematical equation

$$R_i = f(x) * F * S_i * N$$

$$f(x) = 16.46 x^{2.7}$$

$$x = n/N,$$

where

n – is the number of negative values of safety conditions

N – is the total number of evaluated values of safety conditions

The evaluated values of safety conditions have to be in compliance with legislation and technical regulations.

2.3 Output data

There are several key points in the risk assessment procedure, of which every represents an interest evaluated from various points of view. One of them is a table of remaining risk for all workplaces, working environment and for each of the workers. The significance of this table is to the advantage of an employer and, naturally, to the advantage of an employee. According to the results of this work, the table has to determine the following risks for each of the workplaces:

- ✚ the risk of a workplace
- ✚ the risk of the engine hall
- ✚ the “somebody else’s” risk

The “somebody else’s risk” relates to the activities of some other workplace, which a worker sometimes has to perform. The example is a job of a driver, a work which we sometimes have to do. The risk is considerably lower compared to a driver’s risk, since the frequency of exposure to hazards and vulnerability is also lower, but positively this risk exists.

Only a risk assessment conducted in such a way can provide answers regarding size and types of risks which a worker is exposed to during the working hours.

Table 1: Risk table

	WORKPLACE		QUANTITATIVE ASSESSMENT OF REMAINING RISK						QUALITATIVE RISK ASSESSMENT	
	Occupation (job)	Code number	Primary risk				Secondary risk			
			Company, facility	facility part, plant	Plant, working room	workplace	source	value		Source (activity, workplace, ...)
1.	Counselor	112	0	0,3	0,05			Company Headquarters		
2.	Technical secretary		0	0,5	0,32			Company Headquarters		
3.	Operational engineering							Company Headquarters		
4.	Qualified worker							Company Headquarters		
5.	Coordinator							Centre for ambrosia suppression		
6.	Section manager		2,7	0,52	0,36			Plantation		
7.	Assistant		2,7	0,52	0,36			Plantation		
8.	Non-qualified worker							Plantation		
9.	Driver					37,5	Form 4/23	Company Headquarters		

3. ANALISES, DISCUSSION, INTERPRETATIONS

3.1 The example for mechanical processing on a lathe:

IDENTIFICATION OF HAZARDS AND VULNERABILITY

1 No.	2 Code of hazards and vulnerability	3 The descriptive analysis of hazards and vulnerability including data regarding easier and more precise determination of likelihood, frequency and damage size
1	05	When grinding fragile material with low speed of cutting or with particular geometry of cutting tools, there occur torn parings whose temperature might go even up to 800°C, and which are likely to hit a worker in the eye thus causing a severe injury. As a worker does this type of work during a whole working day, it is possible that a worker sustains eye injuries often and it is more than likely that injuries occur every day

QUANTITATIVE RISK ASSESSMENT

4 Likelihood level	5 Frequency	6 Damage size	7 No. of peple – coeff.	8 Risk	9 Risk level
5	4	2	1	40	Low but present

THE MEASURES FOR REDUCTION, PREVENTION AND ELIMINATION OF RISK

10 Safetyain	11 Organizacioal	12 Constructive	13 Safety	14 Personal safety means	15 Other
Protection of eyes				Protective spectacles	

ADDITIONAL RISK ASSESSMENT

16 Likelihood level	17 Frequency	18 Damage size	19 No. of peple – coeff.	20 Risk	21 Risk level
0,033	4	2	1	0,264	Negligible

RISK MANAGEMENT

22 Who implements	23 Time frame for implementation measures	24 Procedure within quality systems	25 Conslusion	26 Measures for control of the remaining risk
Safety officer	Immediately	IQ2.f...	Risk is low and tolerated	Drawing up and strict implementation of code of personal means of protection

3.2 The example of working environment risk assessment

According to the Code of general measures for buildings whose purpose is to be used for working or subsidiary premises and Code of keeping records, values that characterize the safety conditions of the engine hall can be determined. Those values are:



-
- | | |
|--------------------------------------------------------------------|-------------------------------------------------|
| ✦ Clear height of the work-room | ✦ work at height and depth |
| ✦ Clear area of the work-room per worker | ✦ cramped, limited |
| ✦ Clear volume of the work-room per worker | ✦ hazardous space |
| ✦ floor of the work-room | ✦ wet and slippery surfaces |
| ✦ inner surface of ceiling and walls | ✦ physical instability of the work-room |
| ✦ opening of windows of the work-room | ✦ inappropriate and not adapted working methods |
| ✦ door of the work-room | ✦ contact of elements at voltage |
| ✦ lighting of the work-room | ✦ indirect contact |
| ✦ corridors, availability of staircase | ✦ thermal effect of electrical source |
| ✦ passages and access | ✦ thunderbolt |
| ✦ protective fence | ✦ electrostatic charge |
| ✦ handy warehouse | ✦ work in low/ high pressure atmosphere |
| ✦ rotating and mobile parts | ✦ radiation |
| ✦ free movement of parts | ✦ work in the open air |
| ✦ indoor transport | ✦ use of hazardous material |
| ✦ exposure to being blocked (shut), covered by something and alike | ✦ work with animals |
| ✦ hazardous surfaces | ✦ water surfaces |

In comparison with the procedure for the workplace, we determined hazards and vulnerability in this way (columns 1, 2 and 3); other columns are identical to risk assessment of a workplace

4. CONCLUSION

In compliance with the set aims of the work, the conclusions have completely met and justified the expectations. Basically, the conclusions are:

- ✦ the established methodology and formed method of risk assessment make risk analysis simple
- ✦ the method implemented in engine hall for metal processing gives completely precise answers to all arising risks
- ✦ two risk levels are distinctive: the level of engine hall and the level of workplace, evaluation within these two levels gives all information;
- ✦ quantitative nature of the method enables comparison of all obtained values;
- ✦ the method presented in this work can be completely applied to any engine hall that is basically used for mechanical processing;
- ✦ the same method, but with a change to values evaluating safety conditions, can be used for any working environment, which can differ.

REFERENCES

- [1] Bozic, V., Kosic, S., Nikolic, B. (2006). Regulation for risk assessment procedure in the work place and in the workspace – comments, VTS Novi Sad.
- [2] Harms-Ringdahl, L., (2001) Safety Analysis: Principles and Practice in Occupational Safety, CRC Press
- [3] Laban, M., Krnjetin, S., Nikolic, B. (2007). Risk management and risk assessment in the enterprise, *Symposium about occupational safety and health*, Novi Sad, pp. 44-57.
- [4] Macdonald, D., (2004). Practical Machinery Safety, Integra Software Services Pvt. Ltd, Pondicherry, India
- [5] Nikolic, B., (2007). Enactment about risk assessment, *Symposium about occupational safety and health*, Novi Sad, pp. 32-43.
- [6] Nikolic, B., Laban, M.: Occupational health and safety risk assessment method, 17th International Symposium ECOLOGY 2008, Sunny Beach Resort, Bulgaria
- [7] Risk Management: Implementation principles and Inventories for Risk Management/Risk Assessment methods and tools, Conducted by the Technical Department of ENISA Section Risk Management, June 2006
- [8] Ruzic-Dimitrijevic, Lj., Nikolic, B., (2008). Designing and building an information system for a higher education institution, InSITE 2008, Bulgaria.
- [9] Ruzic-Dimitrijevic, Lj., Nikolic, B., (2008). A way forward – correction of the risk assessment method for workplace and work environment and its wider application, Kopaonik, 2009, Serbia



METHODOLOGICAL FRAMEWORK FOR THE STRATEGIC ENVIRONMENTAL IMPACT ASSESSMENT (SEIA) OF SPATIAL PLANS IN AUTONOMOUS PROVINCE OF VOJVODINA

Dejan FILIPOVIĆ¹, Tamara ZELENOVIĆ VASILJEVIĆ²,
Mirjana VOJINOVIĆ MILORADOV³, Maja ĐOGO³, Ivana MIHAJLOVIĆ³, Milena STOŠIĆ³

¹ Faculty of Geography, University of Belgrade, Belgrade, SERBIA

² Provincial Institute of Urban Planning of Vojvodina, Novi Sad, SERBIA

³ Department of Environmental Engineering, Faculty of Technical Sciences,
University of Novi Sad, Novi Sad, SERBIA

Abstract:

This paper provides a methodological framework for conducting Strategic Environmental Assessment (SEA) of spatial plans in Autonomous Province of Vojvodina. The main objective of Strategic Environmental Impact Assessment is to ensure environmental protection and the establishment of sustainable development by integrating the basic principles of environmental protection in the process of preparation, drafting and adoption of a Plan.

Keywords:

Strategic Impact Assessment, environmental protection

1. INTRODUCTION

Planned solutions defined in the planning documentation may have some impact on certain segments of the environment, positive and negative. In planning and organizing the space, it is necessary to pay special attention to the aspect of environmental protection as an integral part of the process taking place or will take place on the areas embraced in the plan.

Such an approach is the unique optimal way for the realization of active environmental protection, monitoring and management of certain areas in accordance with the basic principles of sustainable development [6].

The realization of this approach in accordance with the tendency of harmonization legislation in the territory of the Republic of Serbia and the Autonomous Province of Vojvodina with the legislation of the European Union, Strategic Environmental Impact Assessment (SEIA) of planning documents have the important role, as a separate instrument for implementation of environmental protection in all segments of development. This instrument is an integral part of sustainable development strategy, by which a comprehensive estimate the possible impacts of the prescribed planning solutions.

In the Republic of Serbia, a Strategic Environmental Impact Assessment is an important document, which is an integral part of planning documents, that gain legal dimension by adopting a set of the Law on Protection of the Environment in December 2004. Strategic Environmental Impact Assessment is not only important measure, but an instrument that makes the plans, programmes and policies related to the area of spatial and urban planning, agriculture, forestry, water, etc.

However, after five years of application of the Law on Strategic Environmental Impact Assessment ("Official Gazette of the Republic of Serbia", no. 135/04), experts who work on these elaborats meet with a large number of problems, especially due to the lack of established methodology and insufficient definition of current state environmental indicators and indicators of effects on the territory of the Republic of Serbia and the Province of

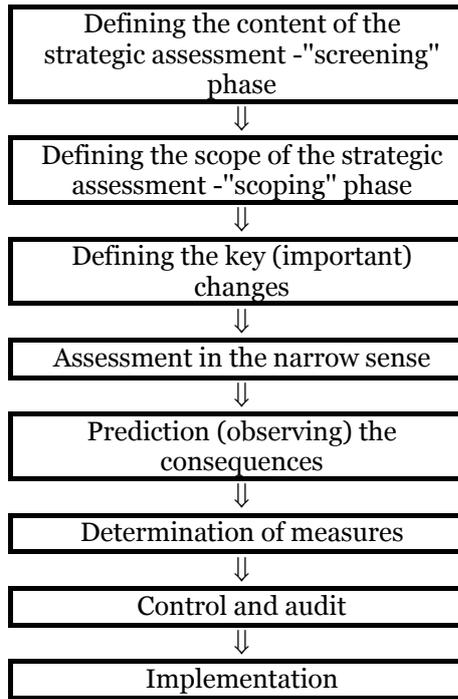


Figure 1. General methodological process of SEIA

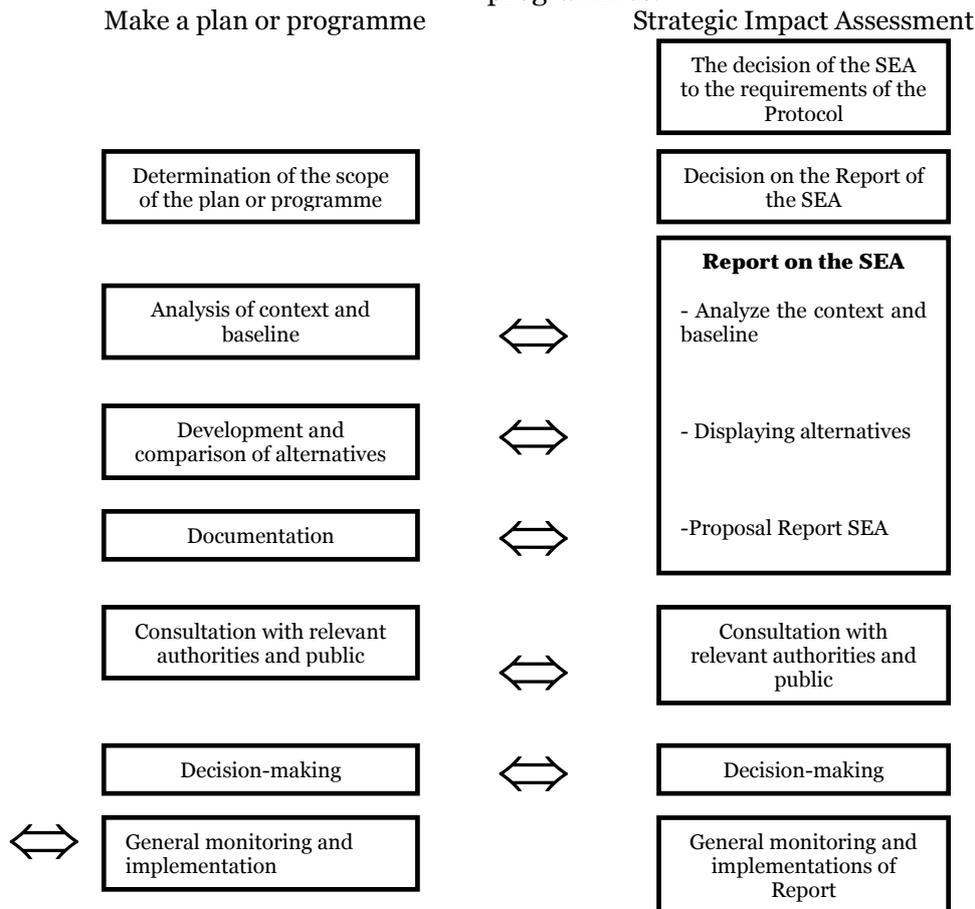


Figure 2. Links between the creating stages of plans and strategic impact assessment [5]

In terms of methodology of the Strategic Assessment Report of plans, it is necessary to note that there are several different methodological approaches regarding the way of constituting.

Vojvodina, so that today there is a great diversity and unevenness. Major problem is the fact that current state environmental monitoring in our country was established only in the last few years, and only in few locations, insufficient in number, so it's often difficult to adequately define and comment the indicators of current state of the environment because of the lack of data.

2. METHODOLOGY OF STRATEGIC ENVIRONMENTAL IMPACT ASSESMENT

Experiences of the countries, members of the European Union, point to the importance of the planning process and the process of Strategic Impact Assessment of planning documentation. Strategic Impact Assessment is partially integrated into the plans and programmes if they are made in separate stages. The general methodological procedure that is used for preparing the strategic assessment consists of several general phases, as it's showed in Figure 1.

To be completely integrated, process of SEIA should be intertwined with the procedure of plans or programmes.

The main task of the SEIA in Serbia, as a developing country, is to facilitate timely and systematic consideration of the possible environmental impact at the level of strategic decision-making in plans and programmes, considering the principles of sustainable development. Integrating the process of SIA in the process of preparation and decision making, in spatial plans, allows the efficient evaluation of the instrumentalization of the strategic environmental impact in spatial and urban planning.

Content of Strategic Assessment Report, and also the basic methodological approach are defined by the Law on Strategic Environmental Impact Assessment ("Official Gazette RS", no. 135/04) and the Law on the Environmental Protection ("Official Gazette RS", no. 135/04). Strategic evaluation became important by adoption of EU Directive 2001/42/EC on the environmental assessment effects of plans and programmes, that began to implement in 2004. in Serbia, by adoption of the Law on Strategic Environmental Impact Assessment, and has started the implementation in 2005.

The Strategic Assessment Report is the document that describes, evaluates and assesses the potential significant impact on the environment, which could result by implementation of plans and programmes. It shall also define measures for reduction of adverse effects on the environment.

Report's content is in accordance with the provisions of Article 12 of Law on Strategic Environmental Impact Assessment, and shall include the following in particular:

1. The bases of the strategic assessment;
2. The general and specific objectives of the strategic assessment and selection of indicators;
3. The evaluation of likely impact with the description of measures planned for reduction of adverse effects on the environment;
4. The guidelines for elaboration of lower level strategic assessments and Assessments of environmental impact of projects;
5. The programme of monitoring of environmental status during the execution of plans and programmes (monitoring); and programmes that have already been realized are considered qualified for elaboration of the strategic assessment report;
6. The programme of monitoring of environmental status during the execution of plans and programmes (monitoring);
7. The outline of methodology applied and difficulties encountered during the strategic assessment elaboration;
8. The outline of decision making methods, description of reasons vital for selection of the given plan and programme from the aspect of alternative solutions considered and the outline of methods in which the environmental issues have been included in plans and programmes;
9. The conclusions reached in the process of strategic assessment report elaboration presented in the way understandable for public;
10. Other data of relevance for the strategic assessment [4].

3. GENERAL METHODOLOGICAL FRAMEWORK FOR STRATEGIC ENVIRONMENTAL IMPACT ASSESSMENT

Analysis of methodological framework is useful to make a comparative analysis with the methodology used for the purpose of the strategic impact report and methodological bases, which are proclaimed in the general legal framework that regulates the issues, analyzed in the Law on Strategic Environmental Impact Assessment. The main goal is consisted in efforts for adaptation the general methodology of Strategic Environmental Impact Assessment to the specific of each analyzed plan.

Strategic assessment of impact of certain plans and programmes is a new discipline and it is the result of evaluation of the environmental impact. Environmental Impact Assessment of Projects and facilities on the environment has shown insufficiency in the system of environmental protection, so Strategic Environmental Impact Assessment was developed to examined cumulative impacts on the environment.

Strategic Environmental Impact Assessment integrate ecological, socio-economic and cumulative impacts, so that it:

1. Includes maintenance on the source of environmental problems in planning stage and reduces the consequences of rehabilitation;
2. Allows to determine the need and justification from the environmental protection point of view;
3. Processing wider importance issues, and
4. Determines the context and set policies for a hierarchical framework of future Assessment of Environmental Impact of plans and projects.

The strategic assessment procedure shall be composed of the following stages:

1. The Preparation stage that shall include:
 - a) The decision on the strategic assessment elaboration;
 - b) The selection of the strategic assessment developer;
 - c) The participation of authorities and organizations concerned;
2. The strategic assessment report;
3. The decision making procedure that shall include:
 - a) The participation of authorities and organizations concerned;
 - b) The participation of the public concerned;
 - c) The report on the results of participation of authorities and organizations;
 - d) Public concerned;
 - e) The evaluation of the strategic assessment report;
 - f) The approval of the strategic assessment report. [4]

4. METHODOLOGICAL FRAMEWORK FOR THE STRATEGIC ASSESSMENT OF SPATIAL PLANS IN AUTONOMOUS PROVINCE OF VOJVODINA

Analyzing the process of Strategic assessment Report for spatial plans consists of four phases:

1. Basic, analysis and evaluation of the present situation (Land use defined in Spatial Plan and main environmental issues);
2. Possible environmental impact assessment;
3. Environmental protection measures;
4. Environmental monitoring programme.

Without detailed consideration of any single phase, it is necessary to emphasize that each phase has its own peculiarities and should not be neglected in the integrated planning of the environment.

The way of evaluation of the possible impacts of planning decisions on the environment in the Republic of Serbia is not yet sufficiently developed and methodologically confirmed. According to the generally adopted model, the significance of the impact can be compared to assess the size, i.e. intensity of the impact and spatial scale in which the impact can be made. The following table shows that planning decisions can, according to size of their impacts, be divided into one with the: higher impact, smaller impact and non important impacts. Also planning decisions can be divided to one with: positive impacts, good impacts and very good impacts. According to the intensity, planning decisions can be presented as one with: a strong

Table 1. Size evaluation of planning decisions impact on the environment

The size of the impact	Label	Description
Critical	- 3	Strong negative impact
Larger	- 2	Larger negative impact
Lower	- 1	Minor negative impact
No impact	0	No data
Positive	+ 1	Smaller positive impact
Favorable	+ 2	Larger positive impact
Very favorable	+ 3	Strong positive impact

negative impact, a negative impact, less negative impact, less positive impact, a positive impact and a strong positive impact, and there are also some planning decisions with a lack of data in some cases, so it cannot be said how big their impact can be. [2]

On the other hand, according to the size of the impact, spatial planning solutions can be divided to the one with the: global impact, national impact and regional impact, and also to impacts that have municipal and local character (Table 2).

Table 2. Spatial scale evaluation of planning decisions impact on the environment

The importance of the impact	Label	Description
Global	G	Possible global impact
National	N	Possible impact on the national level
Regional	R	Possible impact in the region
Municipality	M	Possible impact in the municipality
Local	L	Possible impact in a zone or part of the municipality

Table 3. Probability scale for the assessment of impact

Probability	Label	Description
100%	W	Predictable impact
more than 50%	V	Probable impact
less than 50%	M	Possible impact
less than 1%	N	No probable impact

It is also possible to state the probability that some estimated impact can take place in the present, and sometimes it is an important criterion for decision-making procedure in the phases of plan creating.

Probability of impact in this case can be determined by the following scale (Table 3).

As additional criteria, by which evaluation is done in Strategic Impact Assessment, some estimation is made using the duration of impact and its consequences. In this case, a temporary-periodic (P) and long (D) effects are defined. That is how are defined the important impacts for the Plan, as well as for Impact Assessment.

It is important to consider the positive impact on the environment because the emphasis is always only on the negative impacts on the environment [3]

As already noted, there is no unique methodology for Impact Assessment, in the world and also in our country, and the decision on the usage of certain methodology framework and techniques are left to experts.

In the third phase, the appropriate measures of environmental protection are prescribed in order to decrease the negative impact and improve the environment. In this phase the guidelines for plans on different hierarchy levels are defined, as well as the guidelines for Strategic Environmental Impact Assessment and Assessment of Environmental Impact of projects.

Finally, there is the phase in which the monitoring programme is defined, which includes proposed state indicators for environmental monitoring. Also, it is very important to monitor the implementation and effectiveness of the prescribed measures of protection defined in plan, and whether defined safeguards provide relevant results.

The applied technique is based on the continuous process of harmonization of the planning process with the identification of problems, the solutions for the prevention, and proposal of measures for environmental protection in all phases of design and implementation of spatial plans.

5. ENVIRONMENTAL INDICATORS

Environmental indicators are very suitable for measuring and evaluating of planning decisions, from the possible negative impact on the environment point of view, and for the determination of negative impact that is necessary to reduce or eliminate. Environmental indicators are one of the instruments for the systematic identification, assessment and monitoring, processes and environmental conditions, and consideration of the consequences. In the process of defining of environmental indicators, Serbian experts evaluated environmental indicators of sustainable development defined by European Union [6].

6. CONCLUSIONS

Strategic Environmental Impact Assessment of plans and programmes is a complex process that considers not only the preparation of the Strategic Assessment Report, but also includes the implementation of several stages that must be integrated in the appropriate procedures of creating, decision-making and adoption of plans and programmes.

The unique methodological approach for Strategic Environmental Impact Assessment is still not defined. Content of the strategic assessment of impact of certain plans and programmes and Strategic Assessment Report is defined by law, but it is not possible to identify the content and unique methodology, because the elements that define the content of

the document should contain the way in which the methodology leads to specific goals and results [6].

Table 4. Specific objectives and environmental indicators in SEA [1]

No.	SPECIFIC OBJECTIVES SEA	INDICATORS
1.	Reduction of emissions harmful substances in the air	Emissions of particles of dust, SO ₂ , NO _x
2.	Reduce exposure of inhabitants to high noise levels	Number of buildings in the zone of increased noise
3	The development of organized water supply	Increase the capacity for water supply
4	Preservation of the quality of surface and underground water	Biological oxygen for five days BPK ₅
5	Reduce the risk of flooding	% reduction of vulnerable land area jeopardized by floods
6	Conserving arable agricultural land	Conversion of soil arable surface (%)
7	Preservation of area under the meadows and pastures	Conversion of area under the meadows and pastures (%)
8	Improvement of state forests and increase the areas under forest	Conversion of forest land area
9	Detention of erosion processes	Reduction of erosion soil (%)
10	The introduction of the collection, treatment and storage of municipal waste	% of households involved in the system % of waste that is stored
11	Conserving biodiversity - to avoid losses	% permanently lost species in relation to the region
12	Preserve and avoid damage of protected natural resources	The number of the important protected area and natural resources that are damaged
13	Reclamation of degraded areas	% recultivation area
14	Preserve and protect the cultural important areas	The number and importance of vulnerable buildings and cultural heritage
15	Raising the quality of the areas	Provide infrastructure at the area (public transport and infrastructure, public facilities, standards, etc.)
16	Preservation of population- stop emigration	% reduction of population
17	The growth of employment-creating the conditions for the return of working-age population	% of employees and unemployed
18	Promote and develop the infrastructure	The number and the quality of new infrastructure elements
19	Improve public information on environmental information issues	Amount of information about the environment

Due to the complexity and the lack of a unique methodology for the Strategic Environmental Impact Assessment, particularly the assessment of possible impact on the environment in the Strategic Assessment Report, in the Republic of Serbia is still present diversity in the manner and methodology.

REFERENCES

- [1] Center for the planning of urban development, Report on the strategic environmental impact assessment of spatial plan of special use area - nature park "Golija", Belgrade, 2005.
- [2] Filipović D, Obradović M, Strategic impact assessment in the spatial planning - tool to determine the importance of planning solutions for environmental protection and sustainable development, Gazette of Serbian geographic society, Booklet LXXXV - No. 2, Belgrade, 2005.
- [3] Filipović D, Specific features in the design and procedure of passing strategic Environmental Impact Assessment, Collection booklet from professional conference "Engineering activities and obligations in the protection of the environment", Association of Engineers and the Belgrade City Assembly of Belgrade, Belgrade, 2005.
- [4] Law on Strategic Impact Assessment ("Official Gazette of the Republic of Serbia", No. 135/04), 2004.
- [5] United Nations Economic Commission for Europe & Regional Environmental Center for Central & Eastern Europe Protocol on SEA, Resource Manual to Support Application of the UNECE Protocol on Strategic Environmental Assessment Draft Final, 2007
- [6] Zelenović-Vasiljević, T. Methodological framework for conducting Strategic Environmental Impact Assessment of spatial plans for special use areas in Serbia, Theses paper, FTN, Novi Sad, 2008.



POLYCHLORINATED BIPHENYLS (PCBs), IN SOUTH BAČKA – FROM THE ENVIRONMENT TO HUMAN MILK

Mirjana VOJINOVIĆ MILORADOV¹, Tamara VUKAVIĆ²,
Jan SUDI³, Marija JEVTIĆ⁴, Ivana MIHAJLOVIĆ¹

¹ Department of Environmental Engineering, Faculty of Technical Sciences,
University of Novi Sad, Novi Sad, SERBIA

² Institute of Child and Youth Health Care, Faculty of Medicine,
University of Novi Sad, Novi Sad, SERBIA

³ Institute of Occupational Health, Novi Sad, SERBIA

⁴ Institute of Public Health of Vojvodina, University of Novi Sad, Novi Sad, SERBIA

Abstract:

Measurements of PCBs congeners (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180, PCB 209) in 16 samples of 3rd day human colostrum were performed in 2006, using GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph for PCBs. Concentrations of PCB congeners – 52, 138, 153 and 180, measured in 2006 were 2-5 times higher than concentrations of the same congeners measured in 2003 in the same region. Human milk, was once again a mirror of environmental pollution.

Keywords:

polychlorinated biphenyls, human milk, environment

1. INTRODUCTION

Our environment is under constant influence of various human activities – seldom beneficial to it, often harmful, sometimes even highly dangerous. Many chemicals are hazardous for human health. Among these, due to their earlier extensive production and worldwide use, are organochlorine contaminants (OCC). Pesticide residues and polychlorinated biphenyls (PCB) still keep the prominent position on OCC list related to human health potential hazards.

Persistent organic pollutants (POPs), due to their persistence, long life and presence in all environmental macroecosystems (soil, water, air, and their microbiota), and in particular due to their bioaccumulation and biomagnification through the food chain, have made humans particularly exposed [9]. More than 90% of POPs daily intake in humans is via food, and of that amount, around 90% are from animal sources [4].

Breastfed human newborn, nutritionally relying only upon mothers milk, is the ultimate ring in the food chain, on our planet. As such, its level of exposure is highest for humans [12]. Therefore, continuous monitoring of POPs in human milk could point, not only to the level of exposure of very young children, but also to changes in the the environment [11].

PCBs were manufactured from 1930 around the world continued. They were extensively and broadly used in many fields of industry and it was easy for these chemicals to find their way into the environment, in the course of innumerable accidents of various levels. In spite of their restricted use which started gradually in industrialized countries since their potential hazard was anticipated, inadequate storage and disposal, even leakage and spill incidents, continued their environmental inlet. Great chemical stability, physical and chemical inertness, results in a very slow degradation, with their persistence in the environment. This, together with high mobility in the atmosphere, has put PCBs on the list of global environmental pollutants. PCBs bioaccumulated and biomagnified in a wide range of plants and animals consumed by humans, with the net effect of the greatest toxic risk for animals and humans on the end of food chain. As highly lipid soluble substances, with the $K_{ow} > 5$, PCBs are deposited primarily in adipose tissue. In mammals, the only way to excrete in significant amounts liposoluble substances, such as PCBs, is via milk, during lactation. Since milk is the only food during

the first months of life, the exposure of breastfed neonates might be the highest of all macroorganisms, with superimposed postnatal, over prenatal exposure.

Throughout fifteen years, a series of ecologically very unfavorable events [5] - possible atmospheric transport of PCBs from UN bombed targets in Bosnia and weeks of incinerations and fires after NATO bombardment of oil refinery and other industries in Serbia (e.g. 100 000 ng ITEQ/kg and 70-74 g/kg of PCBs in samples of soil on one location in central Serbia), not only soil and waters, were contaminated, but inevitably plants, animals and humans, amplifying its historical presence. UNEP task groups in summer 1999. identified four hot spots in the territory of Serbia, one of these being the city of Novi Sad [1].

PCBs are bioaccumulated in plants and animals consumed by humans. During delivery, a period of short term starvation, liposoluble substances mobilized from fat reserves into the blood reach the mammary gland. Since milk is the only way for their excretion, the neonate, relying fully on mother's milk, as the only source of nutrients, may be at greatest risk of all mammals, particularly in the earliest neonatal period. Studies on PCB in early human milk (colostrum) are few [2, 3, 7, 11].

Pollution of early human milk with POPs is being monitored in the region of South Backa since 1982 [10].

2. MATERIAL AND METHODS

Samples of colostrums

Donors of colostrum (early milk) were 16 healthy mothers living in and around the city of Novi Sad, age 28.81±4.29 years (range 23-39). They gave birth to healthy babies after a normal pregnancy and normal delivery in 2006. Questionnaires related to demographic data on mothers and their babies, as well as dietary habits, smoking and occupational and other exposure to chemicals of mothers were filled on entry into the study, when each mother consented examination of her colostrum. Mothers expressed colostrum in the amount of 21.87± 13.53 mL ($\bar{X} \pm SD$), range 7-55 mL, into specially prepared glass containers, on the 3rd postpartal day, after the 2nd morning breastfeed. Samples were frozen at -20°C until analyzed.

Preparation of samples

PCBs were extracted from human milk using modified method of Jan [6] as described earlier [10].

PCB congeners determination

All analytical determinations of 8 key PCB congeners in human milk samples were performed at the Institute of Occupational Health in Novi Sad. Samples were analyzed using GC-ECD (HP 5890 supplied with a Quadrex fused silica column 5% Ph for PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180, PCB 209)

Standards used

The system was calibrated using Pesticide Mix 33 with individual EPA standard mixture of 7 PCB congeners PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180, PCB 209 (Dr Ehrenstorfer Laboratories, Augsburg, Germany).

Statistical analysis

Statistical analyses were performed using Statistica for Windows, version 7.1, from StatSoft (Tulsa, OK, USA). Concentrations of 8 PCB congeners in human milk were summarized using arithmetic means, standard deviation, median, minimum and maximum values. Pearson correlation was used to assess association between age of mothers and of PCB congeners in their milk.

3. RESULTS

PCB congener 138 was the only one detected in all examined samples; congeners 52 and 153 and 180 were detected in all but one sample (153 and 180 in the same sample, 52 in different sample); congener 209 was detected in two samples; and 101 in only one sample; while congeners 28 and 118 were not detected in any of 16 examined samples of colostrum (Table 1). Average values of 5 PCB congeners, detected in more than one of 16 examined human colostrum samples are presented in Table 2.

4. DISCUSSION

Concentrations of 4 PCB congeners – 52, 138, 153 and 180, measured in 2006 were 2-5 times higher than concentrations of the same congeners measured in 2003 in the same region [6]. To our knowledge, no ecological accident occurred in this region at the time of pregnancy of these mothers or earlier.

Table 1. Concentrations (ng/g wet) of 8 EPA PCB congeners in 16 individual samples of human colostrum

Sample of colostrum	Age of mothers	Parity of mothers	PCB congeners						Sum of congeners
			52	101	138	153	180	209	
1	23	1	0.19	-	0.14	0.20	0.10	-	0.63
2	33	2	0.42	0.12	1.27	1.27	1.94	0.12	5.14
3	39	7	0.17	-	0.07	0.09	0.05	-	0.38
4	23	1	0.3	-	0.11	0.16	0.15	-	0.72
5	30	1	0.23	-	0.27	0.29	0.48	-	1.27
6	31	4	0.05	-	0.03	0.04	0.03	-	0.15
7	24	2	0.19	-	0.14	-	-	-	0.33
8	25	1	0.57	-	0.58	0.7	1.12	-	2.97
9	26	2	0.83	-	0.22	0.34	0.4	-	1.79
10	29	2	-	-	0.04	0.06	0.06	-	0.16
11	25	1	0.39	-	0.14	0.14	0.07	-	0.74
12	32	3	0.29	-	0.11	0.15	0.13	-	0.68
13	29	1	0.11	-	0.04	0.04	0.03	-	0.22
14	30	3	0.25	-	0.06	0.08	0.05	-	0.44
15	31	3	0.07	-	0.03	0.04	0.02	-	0.16
16	31	3	0.21	-	0.05	0.21	0.16	0.12	0.75

- not detected

 Table 2. Concentrations (ng/mL) of 5 EPA PCB congeners detected in more than 1 of 16 samples of 3rd day human colostrum. $\bar{X} \pm SD$, median value, range.

	PCB congeners					Sum
	52	138	153	180	209	
Mean	0.29	0.21	0.26	0.32	0.09	1.17
SD	0.20	0.32	0.33	0.53	0.04	1.42
Median	0.23	0.11	0.15	0.10	0.09	0.68
Range	0.05 - 0.83	0.03 - 1.27	0.04 - 1.27	0.03 - 1.94	0.07 - 0.12	0.05 - 5.43

Correlation of organochlorine contaminants in milk and age of mothers, together with higher levels in milk of primiparous than of multiparous mothers, was found by others [13]. In this study, the only correlation was found between PCB congener 153 and the age of mothers ($p=0.019$). This could be attributed to greater proportion of multiparous than primiparous mothers (10:6) than in previous study (7:11) on the same territory, in which no correlation was found [13]. Occupation and dietary habits of mothers did not imply any known exposure to chemicals.

Comparing these latest results with the results from the earlier periods [11] for the same geographic area, the fall of total PCBs in early human milk from 1982 (mean value 40.08 $\mu\text{g/L}$ whole milk) till 1993 (mean value 10.95 $\mu\text{g/L}$ whole milk), was observed. The assumed total PCBs in 2003 (10.25 ng/g whole milk) suggest that their unchanged levels in early human milk over 10 years are the result of continued inlet into the environment. These determinations in Serbia are very scarce and till now, performed only by this group of authors.

5. CONCLUSIONS

Last measurements of PCBs congeners (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180, PCB 209) in 16 samples of 3rd day human colostrum were performed in 2006, using GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph for PCBs.

PCB congener 138 (0.21 ± 0.32 , $\bar{X} \pm SD$) was detected in all examined samples; congeners 52 (0.29 ± 0.20), 153 (0.26 ± 0.33) and 180 (0.32 ± 0.53) in all but one sample; congener 209 (0.09 ± 0.04) in two samples; and 101 in only one sample; while congeners 28 and 118 were not detected in any of 16 examined samples. The only correlation found was between PCB congener 153 and the age of mothers ($p=0.019$). Mothers, donors of colostrums, did not have any known occupational or dietary exposure to chemicals.

Concentrations of PCB congeners – 52, 138, 153 and 180, measured in 2006 were 2 - 5 times higher than concentrations of the same congeners measured in 2003 in the same region. Total PCBs in human colostrums, in the same region, showed a four time decrease from 1982 till 1993; mostly

unchanged levels till 2003; followed by the rise in this last measurements. Human milk, was once again a mirror of environmental pollution.

Acknowledgements

This study was supported by Project No. 114-451-00603 of Secretariat for Science and Technology of the Province of Vojvodina.

REFERENCES

- [1] APOPSBAL Project - Assessment of the selected POPs (PCBs, PCDDs/Fs, OCPs) in the atmosphere and water ecosystems from the waste materials generated by warfare in former Yugoslavia (APOPSBAL), ICA2-CT2002-10007, The third year annual report held in Zadar, Croatia, 2002.
- [2] Czaja K, Ludwicki JK, Góralczyk K, Strunicki P, Exposure of infants to polychlorinated biphenyls and pesticides from mother's milk, *Organohalogen Compd*, 38, 109-112, 1997.
- [3] Dillon JC, Martin GB, O'Brian HT, Pesticide residues in human milk, *Fd Cosmet Toxicol*, 19, 437 - 442, 1981.
- [4] Fürst P, Contribution of diferent pathways to human exposure to PCDDs/PCDFs, *Organohalogen Compounds*, 13, 1 - 8, 1993.
- [5] Holoubek I, Kočan A, Holoubkova I, Hilscherova K, Kohoutek J, Falandysz J, Roots O, Persistent bioaccumulative and toxic compounds in the central and eastern European countries – The state of the art report – Human exposure, *Arh Hig Rada Toksikol*, 52, 182, 2001.
- [6] Jan J, Chlorobenzene residues in human fat and milk, *Bull Environ Contam Toxicol*, 30, 595 - 599, 1983.
- [7] Polishuk ZW, Ron M, Wasserman M, Cucos S, Wasserman D, Lemesch C, Pesticides in people, *Pesticid Monit J*, 10, 121 - 129, 1977.
- [8] Sudaryanto A, Kunisue T, Kajiwara N et al, Specific accumulation of organochlorines in human breast milk from Indonesia: Levels, distribution accumulation, kinetics, and infant health risk, *Environ Pollut*, 139, 107 - 117, 2006.
- [9] Van Oostdam J, Gilman A, Denailly E et al, Human health implications of environmental contaminants in Arctic Canada: a review, *Sci Total Environ*, 230, 1 - 8, 1991.
- [10] Vukavić T, Pavkov S, Čušić S, Rončević N, Vojinović M, Toković B, Pesticide residues in human colostrum: Seasonal variations, *Arch Environ Contam Toxicol*, 15, 525 - 528, 1986.
- [11] Vukavic T, Vojinovic-Miloradov M, Pavkov S, Đilas S, Pesticide residues and polychlorinated biphenyls in human colostrum - seasonal variations in Yugoslavia a decade later, *Frensen Environ Bull*, 12, 215 - 218, 2003.
- [12] Vukavić T, Vojinović-Miloradov M, Pavkov S, Nikolić Lj, Exposure of newborns to Pesticide residues and PCBs in colostrum during UN Security Council sanctions for Yugoslavia, *Prenat Neonat Med*, 2 (1 - 4), 356 - 359, 1997.
- [13] Vukavić T, Vojinović-Miloradov M, Ristivojević A, Hlpka J, PCB pollution of early milk in the province of Vojvodina, *Environ Toxicol Pharmacol*, 25, 176 - 178, 2008.



VARIABILITY OF GAS-PARTICLE PARTITIONING OF POLYCYCLIC AROMATIC HYDROCARBONS IN A PILOT AREA OF VOJVODINA

Mirjana VOJINOVIC MILORADOV, Jelena RADONIC, Maja TURK SEKULIC,
Jelena KIURSKI, Maja DJOGO

Faculty of Technical Sciences, University of Novi Sad, SERBIA

Abstract:

Polycyclic aromatic hydrocarbons consist of two to eight condensed aromatic rings and they are produced during incomplete combustion of organic materials. High atmospheric levels of polycyclic aromatic hydrocarbons are associated with industrial activities, energy production, and any type of combustion and traffic. In the atmosphere, PAHs are distributed between gaseous and particulate phase. Distribution of PAHs in the atmosphere controls removal processes and atmospheric degradation. During the June and July 2004 air sampling campaign was conducted in the region of Vojvodina, and concentration levels of 16 PAHs in gaseous and particulate phases were determined.

Keywords:

Polycyclic aromatic hydrocarbons; Gas-particle partitioning; Atmospheric distribution; Active air sampling

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are the complex group of organic compounds with planar structure, with C and H atoms organized in ring structure with at least two aromatic rings. Primary natural sources of PAHs are fires and volcanic eruptions. The most important anthropogenic sources of PAHs in the atmosphere are wood combustion, energy production, and production of aluminium, incineration, catalytic cracking and exhaust gases from vehicles. Concentration levels and behavior of polycyclic aromatic hydrocarbons in the environment have been frequently monitored because of their long-term transport, global distribution and high toxicity [1, 2, 3, 4, 5].

In the atmospheric environment, PAHs are found in the gaseous phase or sorbed at the solid particles, depending mainly on ambient temperature and vapor pressures. Gas-particle partitioning process can be described using partitioning coefficient K_p :

$$K_p = \frac{F}{K_v} = \frac{TSP}{A} \quad (1)$$

where:

K_p – partition coefficient between particle and gaseous phase in atmosphere ($m^3 \mu g^{-1}$)

K_v – partition coefficient between gaseous and particle phase in atmosphere ($\mu g m^{-3}$)

A i F – compound concentration associated with the gaseous and particle phase, respectively ($ng m^{-3}$ air)

TSP – total suspended particulate matter concentration ($\mu g aerosol m^{-3}$ air)

Atmospheric distribution of PAHs, can also be described with total amount of substance proportion sorbed on atmospheric particles, ϕ :

$$\phi = \frac{F}{A + F} = \frac{K_p \cdot TSP}{1 + K_p \cdot TSP} \quad (2)$$

During the period from June - July 2004, air sampling campaign was conducted in the region of Vojvodina, Serbia, and concentration levels of 16 US EPA PAHs were determined.

2. MATERIALS AND METHODS

Concentration levels of selected polycyclic aromatic hydrocarbons have been determined in accordance with the sampling procedure and analysis of organic pollutants in ambient air, adopted by EPA [6, 7]. Active air sampling method is realized through flowing of definite quantity of air, controlled by compressor, through the sampler. In the first step, air is released through the horizontally placed single layer filter made of glass fiber (GF), which holds atmospheric particles over 0.1 µm in diameter. Air, then, passes through the sorbent made of polyurethane foam (PUF), placed behind GF, which collects gaseous phase of PAHs molecules.

The sampler used for the active sampling of air was GV2360 Thermo Andersen TSP, made of stainless steel boxes and equipped with 20.32 x 25.4 cm filter holder and PUF holder (9 cm in diameter and 30 cm long). Air was passed through using a 1200 watt motor controlled by an inverter (Hitachi L100-015NPE) and flow was measured by a Sierra 620 fast flow insertion mass flow meter with a totaliser. The average total sampled air was 1200 m³/day. For each sampling period, per one Whatman grade G653 glass fiber filter (dimension: 20.32 x 25.4cm) and two polyurethane foam filters (dimension: 9 cm diameter and 5 cm long) were used.

Prior the sampling, glass fiber filters were burned in 400°C for 5 hours and polyurethane foam filters were Soxhlet extracted by 1:1 acetone/hexane (Merk suprasolv) by a Foss Tecator Soxtec 1045 HT-2 apparatus for 4 hours to 120°C.

After the sampling period (3 x 24h), GFs and PUFs were extracted and analyzed using GC/MS method. Analytical determination of 16 EPA PAHs in all samples was carried out in laboratories of Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Masaryk University in Brno, Czech Republic.

3. RESULTS

Three 24-hour high volume samples were collected from each of three sampling sites in in the town of Pančevo, Vojvodina, Serbia. Air sampling campaign in Pančevo was conducted during the period from 27th – 30th June, 2004. Two samplers were placed within the industrial area, in the yard of the oil refinery and petrochemical complex (localities P1 and P2, respectively). The third HiVol sampler was placed in the city center, on the top of the Pančevo city hall (locality P3). Detailed information on the three sampling spots is presented in Table 1. Concentration levels of 16 EPA PAHs are presented in Table 2.

Table 1. Detailed information on the sampling sites

Site ID	Latitude	Longitude	Elevation (m a.s.l.)
P1	N 44°49' 56.3"	E 20°41' 25.4"	82
P2	N 44°49' 57.0"	E 20°40' 17.0"	85
P3	N 44°52' 12.8"	E 20°38' 24.1"	130

Table 2. Average concentrations of PAHs in gaseous and particulate phase (ng/m³)

Sample type	PUF	GF	PUF	GF	PUF	GF
Locality	P1		P2		P3	
Sampling period	27-30th June 2004					
Nap	1.195	0.010	0.811	0.016	0.454	0.010
Acy	0.065	0.003	0.050	0.001	0.044	0.001
Ace	0.063	0.006	0.054	0.006	0.027	0.002
Flo	1.454	0.003	1.497	0.009	0.171	0.002
Phe	18.309	0.041	27.364	0.144	3.659	0.030
Ant	0.679	0.001	1.152	0.007	0.187	0.002
Flu	2.133	0.024	10.997	0.167	2.160	0.071
Pyr	1.521	0.020	3.773	0.095	1.831	0.077
B(a)A	0.023	0.008	0.017	0.018	0.070	0.028
Chr	0.120	0.018	0.146	0.066	0.206	0.088
B(b)F	0.041	0.045	0.019	0.220	0.029	0.380
B(k)F	0.022	0.030	0.010	0.122	0.012	0.144
B(a)P	0.021	0.016	0.006	0.102	0.000	0.130
I(1,2,3-cd)P	0.021	0.046	0.005	0.240	0.000	0.365
D(ah)A	0.000	0.002	0.000	0.013	0.000	0.024
B(ghi)P	0.035	0.066	0.009	0.320	0.000	0.500
Total	5.700	0.336	45.909	1.547	8.849	1.853

Estimated distribution of polycyclic aromatic hydrocarbons between gaseous and particulate phase in the ambient air of Pancevo is shown in Figures 1 – 3.

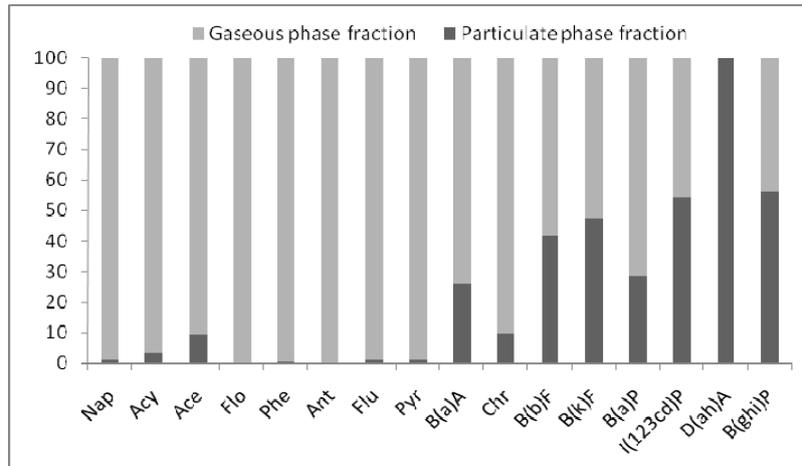


Figure 1. PAH distribution between gaseous and particulate phase at locality P1

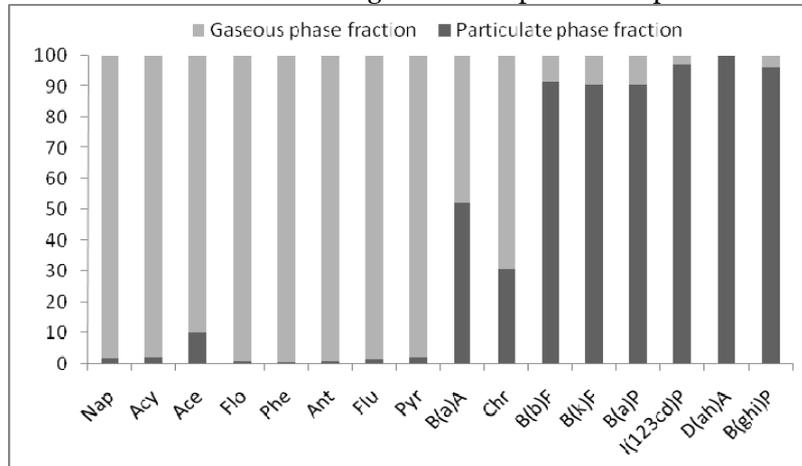


Figure 2. PAH distribution between gaseous and particulate phase at locality P2

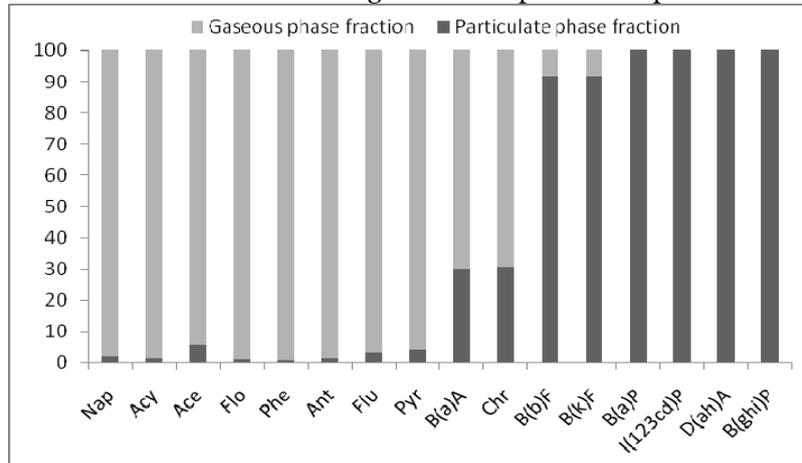


Figure 3. PAH distribution between gaseous and particulate phase at locality P3

In the city of Novi Sad, the highest total concentration level of examined PAHs was detected on the locality P2 (Petrochemical complex Pancevo) and equals $\Sigma\text{PAH}=47.456 \text{ ng/m}^3$. Total concentration of PAHs at the localities P1 (oil refinery) and P3 (city center) are $\Sigma\text{PAH}=26.036 \text{ ng/m}^3$ and $\Sigma\text{PAH}=10.747 \text{ ng/m}^3$, respectively.

In national legislation, maximum allowed concentration of examined group of persistent organic pollutants has not been defined, therefore comparison with legally adopted values was not possible. Threshold value of ambient air quality for benzo(a)pyrene for 24-hour sample, 0.1 ng/m^3 , has been

exceeded at the localities P2 and P3, with value 0.108 ng/m³ for locality P2 and 0.130 ng/m³ for locality P3.

Obtained experimental results point out on almost complete particle sorption of pollutants B(b)F, B(k)F, B(a)P, I(1,2,3-cd)P, D(ah)A i B(ghi)P, with exception of sampling site P1 (Oil Refinery Pancevo), where foregoing PAHs fractions, beside D(ah)A, are about 50%. Specific distribution of polycyclic aromatic hydrocarbons at oil refinery, does not manifest, apriory, low concentration of total suspended particles in the atmosphere. Increased concentration levels of PAHs in gaseous phase or sorbed at ultrafine particles which can not be collected at glass fibre filters, issued from refinery, are probably responsible for atmospheric distribution of PAHs at site P1.

4. CONCLUSIONS

Results of analysis point out on the presence of residual quantities of PAHs in air samples from three localities in the town of Pančevo.

The highest concentrations of examined polycyclic aromatic hydrocarbons was detected at the petrochemical complex (47.456 ng/m³).

Regulation defines limit value of ambient air quality only for benzo(a)pyrene (0,1 ng/m³ for 24-hour sample). Limit value was exceeded at two selected localities in Pančevo – petrochemical complex (0.108 ng/m³) and city center (0.130 ng/m³).

Direct influence of atmospheric distribution on wet and dry deposition processes, long-range transport, as well as potential reactions of degradation of PAHs in the atmosphere, points out on an extreme importance of examination and determination of concentration levels and partition of pollutants in the atmosphere.

LIST OF REFERENCES

- [1] Cincinelli A, Del Bubba M, Martellini T, Gambaro A, Lepri L, Gas-particle concentration and distribution of n-alkanes and polycyclic aromatic hydrocarbons in the atmosphere of Prato (Italy). *Chemosphere* 68, 2007.
- [2] Radonic J, Turk Sekulic M, Vojinovic Miloradov M, Čupr P, Klánová J, Gas-particle partitioning of persistent organic pollutants in the Western Balkan countries affected by war conflicts. *Environmental Science and Pollution Research*, Volume 16, Number 1, 2009.
- [3] Tasdemir Y, Esen F, Urban air PAHs: Concentrations, temporal changes and gas/particle partitioning at a traffic site in Turkey. *Atmospheric Research* 84, 2007.
- [4] U.S. EPA, Compendium of methods for the determination of toxic organic compounds in ambient air, Second edition, Compendium method TO-4A, Determination of pesticides and polychlorinated biphenyls in ambient air using high volume polyurethane foam (PUF) sampling followed by gas chromatographic/multi-detector detection (GC/MD), 1999., <http://www.epa.gov/ttn/amtic/airtox.html>
- [5] U.S. EPA, Compendium of methods for the determination of toxic organic compounds in ambient air, Second edition, Compendium method to-13a, Determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS), 1999., <http://www.epa.gov/ttn/amtic/airtox.html>
- [6] Vasilakos C, Levi N, Maggos T, Hatzianestis J, Michopoulos J, Helmis C, Gas-particle concentration and characterization of sources of PAHs in the atmosphere of a suburban area in Athens, Greece. *Journal of Hazardous Materials* 140, 2007.
- [7] Vojinović Miloradov M, Kovačević R, Adamov J, Krajinović S, Nedeljković B, Matić I, Assessment of POPs after accident in Serbia, Scientific reunion of the special program of the Alexander von Humboldt Foundation concerning the reconstruction of the South Eastern Europe, Sustainability for humanity and environment in the extended connection field science-economy-policy, ISBN 973-625-205-1, Timisoara (Romania), February 2005.



SNAIL MEAT, ROLE AND PLACE IN HUMANS DIET

CRISAN Dana Carolina, DANCIU Ioan

University „Lucian Blaga“ Sibiu
Faculty Of Food Technology, ROMANIA

ABSTRACT

The present study aims to establish the differences between the chemical compositions of snail meat and pork meat used for making snail pate and liver pate.

Snail meat as fish meat also is high-protein and low-fat (0,5–0,8%), low-calories (60-80 cal/100g.), high biological proteins content (12-16%), minerals (1,5%) and nitrogen (2,5%).

Chemical Composition of Snail Meat

SPECIE	COMPONENT			
	WATER (%)	PROTEIN (%)	FAT (%)	MINERALES (%)
SNAIL	79,35	16,10	1,08	1,50
CHIKEN	70,00	19,00	8,50	1,00
TURKEY	67,00	23,40	7,60	1,10
CARP	76,00	18,50	2,40	1,20
WALLER	63,50	16,80	17,40	1,10
VEAL	78,00	20,00	1,00	0,70
RABBIT	71,40	21,30	5,50	1,15
PORC	65,00	18,00	16,20	0,80
BEEF	65,50	17,90	15,70	0,90

After some laboratory tests, the results are even better for *Helix Pomatia* : water -75,09%, protein - 18,46%, fat -0,25 %, ashes – 1,62%, carbohydrates – 1,01%



ADVANTAGE OF THE SUBSTITUTION ETHYLMERCAPTAN, COMPOUND FOR ODORIZATION NATURAL GAS, WITH TETRAHYDROTHIOPHEN

Zoran ČEPIĆ¹, Jova JURIC², Mirjana VOJINOVIĆ MILORADOV³

^{1,3}Department of Environmental Engineering,
Faculty of Technical Sciences – Novi Sad, SERBIA

²Company for Natural Gas Odorization “OD – JU“ – Ruma, SERBIA

Abstract:

This paper presents the advantage of substitution ethylmercaptan, compound for odorization natural gas, with other compound for odorization, tetrahydrothiophen. The physical - chemical properties of both compounds, ecological - toxic characteristics, odorization properties and evaluation of annual consumption odorization compounds in Serbia are discussed. The comparative analysis of these two odorization compounds from the aspect of chemical stability in the system of gas installations and economic acceptability have been described.

Keywords:

Ethylmercaptan, tetrahydrothiophen, odorization, substitution

1. INTRODUCTION

Natural gas, in particular, which is distributed for consumer goods, must be odorized up to level of one fifth of the lower flammable limit for security and health safety reasons.

Odorization compound with their physical - chemical properties should ensure first of all recognizable strong smell from a small portion of evaporation, or in a low concentration level to be detected leakage of gas and prevent unwanted consequences.

In Serbia as odorant, almost exclusively, used ethylmercaptan characterized with the best ability odorization, are no longer used in most European countries.

One of the main reasons for the termination of the use of ethylmercaptan as odorant its chemical instability (in the reaction with air and iron-oxide), which causes loss of smell intensity, as well as changes characteristic strong unpleasant smell.

Most frequently used compound for odorization natural gas is tetrahydrothiophen which has recognized intensive smell. It is the most stable of all gas odorants. Tetrahydrothiophen not react with iron oxides and bases and it does not change, nor the intensity or character of smell, for the most causes of loss of smell.

Unlike ethylmercaptan, which is extremely toxic to flora and fauna biosystem and the environment, tetrahydrothiophen belongs to the middle toxic group pollutant and there is no label danger for the environment according to the German classification for surface water pollutants. [4]

2. ETHYLMERCAPTAN (EM)

Physical - chemical characteristics:

- ✚ Chemical formula: C_2H_6S
- ✚ Appearance and the smell: colourless liquid – reminiscent of the smell of garlic
- ✚ Melting point: $-148\text{ }^\circ\text{C}$
- ✚ Boiling point: $35\text{ }^\circ\text{C}$
- ✚ Density (g cm^{-3}): 0.839
- ✚ Flash point: $-45\text{ }^\circ\text{C}$
- ✚ Explosion limits: 2.8 - 18.2 %
- ✚ Water solubility: slight

Other properties of ethylmercaptan:

- ✚ In normal circumstances, a stable, but extremely flammable liquid;
- ✚ Incompatible materials: oxidans (can lead to flammable), strong acid (reaction can be violent), calcium chloride (react violently), corrosive effect on metals, reacts violently with alkaline metals;
- ✚ Classification, belongs to the 3rd group of toxins and is extremely toxic to flora and fauna and surface water;
- ✚ UN number 2363;
- ✚ Additional tag 336; [5]

Ethylmercaptan as natural gas odorant

Ethylmercaptan has a very strong and unpleasant smell reminiscent of the smell of garlic. Threshold of low sensitivity of smell defined EM, based on its odorization capacity, as the best odorization compound for the natural gas. However, the big problem is nonstability of ethylmercaptan because it easily reacts with oxides and bases giving disulfide, and in that case losing smell properties.

In addition, irreversible adsorption of ethylmercaptan on the walls of steel and polyethylene gas pipes increases ethylmercaptan consumption.

Low flammability and extreme toxicity, associate with environmental and contamination aspect are the problems, because increase the cost of transport and storage. For these reasons ethylmercaptan as odorant need to replace with other substances with a higher chemical stability and less or slightly toxicity for the environment. [4]

Assessment of consumption ethylmercaptan in Serbia

According to company for natural gas odorization “OD – JU” from Ruma, the total amount of odorized gas in 2007. year was about 517,500,000 Sm³. Total consumption of ethylmercaptan was about 6700kg, with the average achieved concentration about 12.95 mg/Sm³ of natural gas. [3]

3. TETRAHYDROTHIOPHEN (THT)

Physical - chemical characteristics:

- ✚ Chemical formula: C₄H₈S
- ✚ Physical state and appearance: Liquid.
- ✚ Odor: strong unpleasant
- ✚ Molecular Weight: 120.11 g/mole
- ✚ Color: Clear Colorless.
- ✚ Boiling Point: 284.5°C
- ✚ Melting Point: 27.4°C
- ✚ Density: 1.26 (Water = 1)

Information about toxicity:

- ✚ Acute oral LD₅₀ (in rats) 2450mg/kg
- ✚ Acute inhalation LC₅₀ (in mice) 27g/Sm³ (2 hours)

Environmental information:

Information about toxicity for aquatic organisms: No data available
Toxicity to Animals:

Acute oral toxicity (LD₅₀): 1900 mg/kg [Mouse].

Acute dermal toxicity (LD₅₀): >3800 mg/kg [Rat].

Tetrahydrothiophen as natural gas odorant

Tetrahydrothiophen has recognizable characteristic strong smell that is different from other spices impurities that may appear in the natural gas. THT shows very small deviations from own specific fragrance and is very difficult to overdose.

Tetrahydrothiophen is the most stable of all gas odorants, as a result of heterocyclic chemical structure, what is unusual for other common odorants. Tetrahydrothiophen not react with iron oxides and bases, and is imperceptible to most of the causes of pad smell.

Adsorption of tetrahydrothiophen on the walls of the new pipe is almost completely reversible so that the amount of THT is a reserve of odorant. In the case of changes in the dosage THT, dynamic equilibrium adsorption and desorption are disturbing and THT is desorbed from the wall of pipes back into the gas.

THT is in the middle group of pollutants according to the German classification of pollutants surface water (W6K2) and not wearing the label of danger for the environment, which makes it easier for packaging, storage and transport. [1, 4]

4. COMPARATIVE ANALYSIS OF ETHYLMERCAPTAN AND TETRAHYDROTHIOPHEN AS ODORANTS

Stability

The difference in stability ethylmercaptan and tetrahydrothiophen in the presence of corrosion on the walls of pipes is a significant benefit for the THT, which could be displayed in the chart (Figure 1).

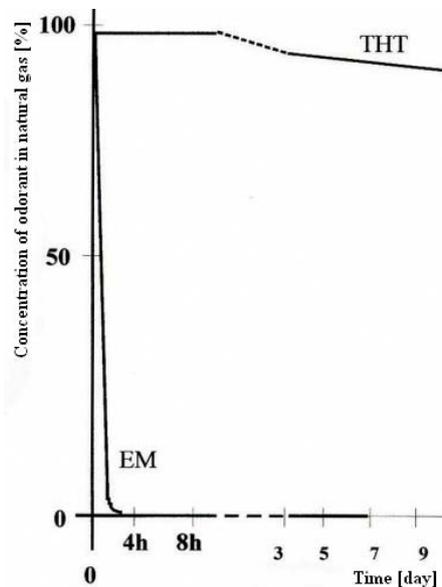


Figure 1. Graphic display depending on the concentration of odorant in function of time, in the natural gas in the presence of corrosion [4]

From the diagram it could be seen that the concentration of THT in the gas begins to decline significantly after the third day, while the concentration of EM decline in the "0" for about 2 hours. This means that the EM is totally spent in the chemical reaction of oxidation, losing completely smell in a very short time. [4]

Economic effects

Comparative analysis of the costs of the odorization with EM and THT in the following text is calculated for concentrations of odorant in the natural gas of 12.95 mg/Sm³ for odorization 517.500.000Sm³/yr, the average distance from odorants storage is about 80km.

Odorant ethylmercaptan

Total amount of required odorant is 517.500.000 Sm³/yr • 0.00001295 kg/Sm³ = 6700 kg/yr.

Price of charging for EM is 16.10 €/kg, (or 0.000241 €/Sm³).

The annual price for EM is 16.10 €/kg • 6700 kg/god = 107,850 €/yr.

Odorant tetrahydrothiophen

Total amount of required odorant is 517.500.000 Sm³/yr • 0.00001295 kg/Sm³ = 6700 kg/yr.

Price of charging for THT is 31.02 €/kg, (or 0.000465 €/Sm³).

The annual price for THT is 31.02 €/kg • 6700 kg/god = 207,850 €/yr. [3]

5. CONCLUSION

Replacement and substitution of ethylmercaptan by THT as the odorant for natural gas, is obviously required for the following reasons:

- ✚ For the protection of the environment bearing in mind its outstanding cumulative and biocumulativ toxic effect for flora, fauna, biosystem and environmental in general;
- ✚ Ethylmercaptan has unstable smell properties especially in the presence of oxide and base. This is particularly expressed in equipment and installations with compressed natural gas (LPG) for the cars;
- ✚ In Europe are generally not used ethylmercaptan for odorization natural gas.
- ✚ The harmonization between national and international (EU) laws of regulations in the field of natural gas odorization with the EU.

According to real estimation, of the replacement procedure ethylmercaptan by tetrahydrothiophen can be completed in the next 3 to 4 years. [3, 4]

REFERENCES:

- [1] DVGW Technischen Vorschriften G280-1/2004, G280/2004 und G2881
- [2] Material safety data sheet tetrahydrothiophene msds, www.sciencelab.com/xmsds-tetrahydrothiophene
- [3] OD-JU, konsolidovani finansijski izveštaj za poslovnu 2007. godinu, Ruma, 2007.
- [4] Podolšak N., Milan Fističić M., Usporedba svojstava komercijalnih kemijskih spojeva za odorizaciju plina – tetrahidrotiofena i etilmerkaptana, Stupnik, 2005.
- [5] Safety (msds) data for ethylmercaptan, msds.chem.ox.ac.uk/et/ethyl_mercaptan.html



QUANTITY AND RECYCLABILITY OF Fe - METALS AT THE END-OF-LIFE VEHICLES IN REPUBLIC OF SERBIA

Milan PAVLOVIĆ¹, Nikola KARANOVIC², Zoran ČEPIĆ³, Aleksandar PAVLOVIĆ⁴

¹Technical Faculty Mihajlo Pupin – Zrenjanin, SERBIA

^{2,3}Faculty of Technical Sciences – Novi Sad, SERBIA

⁴Jugodrvno Company – Belgrade, SERBIA

Abstract:

The growth of the world's population has determined the need for faster, simpler and easier communication. Due to such communication, along with modern social - economic and industrial development, the number of vehicles has largely increased. At the end of life, vehicles represent a potential threat to the environment. This paper gives a statistical view of the number of registered vehicles by brands in Serbia. The amount of Fe – metals by vehicle dismantling, and the possibility of their recycling is shown. It was pointed out the necessity of harmonization of our laws which regulates this area with the laws of the EU, as well as the need for implementation of appropriate ISO standard in the Republic of Serbia.

Key Words:

Statistic data, ISO standard, Fe-metals, recyclability

1. INTRODUCTION

In order to minimize the impact of vehicles disposal on the environment, the End-of-Life Vehicles Directive (2000/53/EC) aims to promote the collection, reuse and recycling of their components. Generally speaking, there are few problems if the vehicles are disposed and not recycled, like occupying the landfill space, potential leakages of fuel and motor oil into water recipient and soil, emissions of volatile compounds, and possible fires. Some of the components are classified as harmful or either hazardous to the environment. Those problems are still present in recycling operation, if the dismantling operations are not handled by regulations, and this means that all fluids (oil, fuel, windshield washer fluid, anti-freeze, brake liquids, etc), batteries, and other nonmetal parts should be extracted.

In Serbia, the recycling business is present but the most of them are recycling just one sort of material or car parts. For now, the new products are being exported and some of these parts, like batteries, are reused. Fuels are being sent to oil refinery, tires are used in cement industry in combustion processes, but shredder dust, textiles, car seats, glass and some other parts are being landfilled. [2]

2. THE STATISTICS OF REGISTERED CARS IN SERBIA

According to data from project “Razvoj integrisanog i održivog sistema reciklaže motornih vozila na kraju životnog ciklusa u Srbiji”, in Serbia are 1.534.658 registered passenger vehicles in 2008. [3]

In Serbia, almost one third of total population owns „Zastava” (31%), followed by „Opel” (18%), „Volkswagen” (16%), „Lada”, „Fiat” and „Reno” (7%). [3]

3. AMOUNTS OF FE-METALS AND RECYCLING POTENTIAL BY VEHICLE DISMANTLING

The car is a product of high complexity for whose benefit in the production is used more than hundred different technologies and that are built around 15 000 parts. Car parts are produced from different materials. The total weight of the current passenger car is represented by iron and steel.

The European Union Directive said that the acquisition of vehicles at the end of the life cycle of vehicles and parts should be organized by the state. It is necessary to provide storage and the space to be made by the treatment of spent vehicles and their components.

International Standard ISO 22628 in 2002 very clearly define the issue of recycling of passenger vehicles, which is not the case in Serbia where there is no standard for this. ISO 22628 also defines and recyclability rate (percentage by mass of the new vehicle potentially able to be recycled, reused or both), and recoverability rate (percentage by mass of the new vehicle potentially able to be recovered, reused or both), as shown in the figure 2. [2, 4]

	Recovery		Undefined residue
(Component parts) Re-use	(Materials) Recycling	(Materials) Energy recovery	(Materials)
Recyclability rate ^a			
Recoverability rate ^a			
Vehicle mass			

Figure 2. Material distribution of the total mass of vehicles for the further treatment [4]

Almost a third of passenger cars in Serbia are the brand “Zastava” (which is about 511.553 vehicles), which presents models “Koral”, “Skala” and “Florida” by one-third (approximately 170.517 vehicles). [1, 3]

Potential for recycling Fe-metals from vehicles “Zastava” is calculated by the following formula:

$$\text{Number of vehicles from particular model "Zastava"} \times \text{vehicle weight} \times \text{percentage of Fe-metals in vehicle} \times \text{rate of recyclability}$$

Table 1. Recyclability potential of Fe-metals in "Zastava" vehicles [1]

Model of Zastava car (Fiat Auto)	Number of vehicles	Vehicle weight [kg]	Percentage of Fe-metals [%]	Rate of recyclability [%]	Fe-Metals recyclability potential [kg]
Koral	170.517	807	73.6	62.0	62.792.926
Skala	170.517	835	75.0	62.0	66.207.488
Florida	170.517	950	73.6	62.0	73.919.801
Total					202.920.215

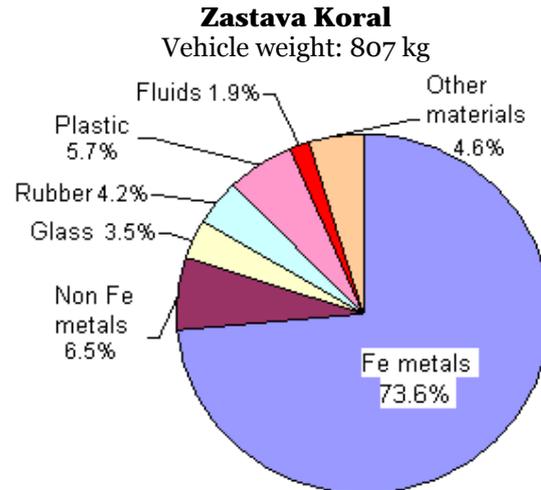


Figure 2. Participation of different types of material in the Zastava Koral [1]

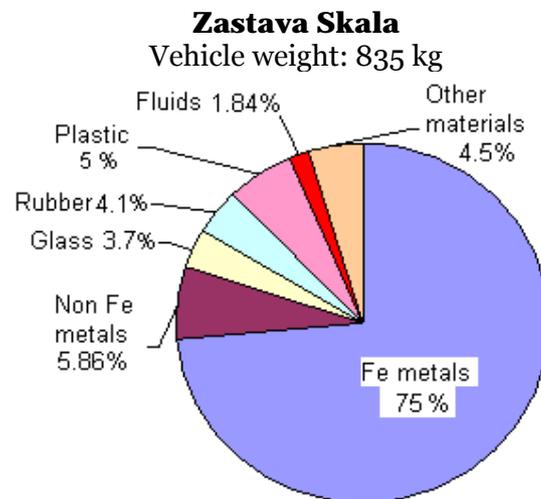


Figure 3. Participation of different types of material in the Zastava Skala [1]

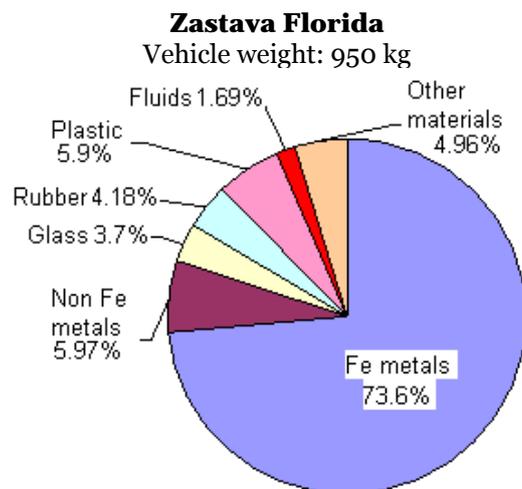


Figure 4. Participation of different types of material in the Zastava Florida [1]

4. CONCLUSION

In this analysis is shown the potential for recycling Fe-metals only from vehicles brand “Zastava”, which makes one third of the total number of registered passenger cars in Serbia (according to data for 2008. yr.). The remaining two thirds are foreign vehicle manufacturers with much greater potential for recycling, because they are more massive and have higher rate of recyclability. Serbia has significant capacity for processing Fe-metals, so vehicles for recycling are an important resource.

For accession Serbia to EU, it is necessary to enact a law that regulates this area, and harmonize it with EU legislation. [1, 3]

REFERENCES

- [1] Đorđević M., Sistem za reciklažu iskorišćenih putničkih automobila, doktorska disertacija, Mašinski fakultet, Kragujevac.
- [2] Guidebook for the Vehicle Dismantling and Recycling Industry Environmental Planning Regulation, British Columbia, July 2008.
- [3] Milan Pavlović, Izveštaj sa Nacionalnog Projekta “Razvoj integrisanog i održivog sistema reciklaže motornih vozila na kraju životnog ciklusa u Srbiji”, 2008/2009.
- [4] Road vehicles – Recyclability and recoverability, International standard ISO 22628-2002
- [5] Zastava automobili – Institut za automobile, Kragujevac, 22.09.2004.



IMPLEMENTATION VERIFICATION REQUIRED EQUIPMENT TO COMBAT PESTS AND DISEASES IN ROMANIA IN ORDER TO ELIMINATE ENVIRONMENTAL CONTAMINATION WITH TOXIC SUBSTANCES

¹S.T. BUNGESCU, ¹W. STAHLI, ²V. VLĂDUȚ, ³S.S. BIRIȘ, ⁴M.E. NAGY, ¹T. IANCU

¹Banat's University of Agricultural Sciences and Veterinary Medicine Timisoara – Department of Agricultural Machines, ROMANIA

² Research and Development National Institute for Agricultural and Food Industry Machines and Implements – INMA Bucharest, ROMANIA

³ “POLITEHNICA” University of Bucharest, ROMANIA

⁴ Research and Development National Institute for Agricultural and Food Industry Machines and Implements – INMA Cluj-Napoca, ROMANIA

Abstract:

At present, in Romania, the pest and diseases from the agricultural crops it is effected in proportion of 95 percent, by sprinkling and spraying of pesticides in the shape of liquid. These involve a very high risk of contamination of the operator and of the ambient environment with toxic substances. On that account, at present in our country, this risk has to be reduced through the introduction in our legislation of some European standards that suit with UE requirements (example: SR EN 907:2003, SR EN 13790-1:2004, SR EN 13790-2:2004 and so on). As part of this paper the authors presents the settlements that exist at present in Romania, as concerns the machinery test used for the pest and diseases control in agriculture, fruit growing and forestry and which of the European standards are applied.

Keywords:

Weed-killing equipments, the pump output, the fan output, output coefficient

1. THE CURRENT CONDITIONS IN OUR COUNTRY'S AGRICULTURE REGARDING THE AGRICULTURE SURFACE, SPRINKLED MACHINERY etc.

Romania was and is a prevalent agricultural country. The agricultural surface evolution between 1989 and 2004 is presented in the table from below.

Table 1. The agriculture surface evolution, thousands hectares

Year	Agricultural Total	Arable	Grasslands	Hay fields	Vineyards and viticulture nursery	Orchards and fruit-growing
1989	14759,0	9458,0	3257,0	1448,0	278,0	318,0
1990	14769,0	9450,0	3263,0	1465,0	277,0	131,0
1991	14798,0	9423,5	3309,8	1467,9	285,8	311,3
1992	14790,0	9356,9	3349,2	1480,6	298,6	304,8
1993	14793,1	9341,5	3362,6	1489,3	303,9	295,8
1994	14797,5	9338,0	3378,4	1493,7	298,4	289,0
1995	14797,2	9337,1	3392,4	1497,7	292,4	277,6
1996	14788,7	9338,9	3391,7	1498,5	289,0	270,6
1997	14794,0	9341,4	3409,8	1490,8	286,3	265,7
1998	14801,7	9350,8	3402,7	1503,4	281,8	263,0
1999	14730,7	9358,1	3322,8	1512,0	281,1	256,7
2000	14856,8	9381,1	3441,7	1507,1	272,3	254,6
2001	14852,3	9401,5	3421,4	1510,0	267,4	252,0
2002	14836,6	9398,5	3424,0	1513,6	259,6	240,9
2003	14717,4	9414,3	3355,0	1490,4	230,5	227,2
2004	14711,6	9421,9	3346,9	1498,4	223,3	221,1

The source: The statistical year-book of Romania, 1990-2005 issues

The main indicators bound of human potential in Romanian agriculture are presented in table 2.

Table 2. The main indicators evolution of the human potential in Romanian agriculture (1990-2004).

Year	The total population thousands persons	The rural population thousands persons	The total engaged population thousands persons	The population engaged in agriculture thousands persons	The rural population weight in total population %	The population weight engaged in agriculture in rural population %	The population weight engaged in agriculture in total engaged population %
1990	23.207	10.598	10.840	3.055	45.7	28,8	28,2
1991	23.185	10.633	10.786	3.116	45.9	29,3	28,9
1992	22.789	10.422	10.458	3.362	45.7	32,2	32,1
1993	22.755	10.349	10.062	3.537	45.5	34,2	35,2
1994	22.731	10.303	10.011	3.561	45.3	34,6	35,6
1995	22.681	10.224	9.493	3.187	45,1	31,2	33,6
1996	22.608	10.196	9.379	3.249	45,1	31,9	34,6
1997	22.546	10.141	9.023	3.322	45,0	32,8	36,8
1998	22.503	10.155	8.813	3.296	45,1	32,5	37,4
1999	22.458	10.155	8.420	3.419	45,2	33,7	40,6
2000	22.435	10.190	8.629	3.523	45,4	34,6	40,8
2001	22.408	10.164	8.563	3.456	45,4	34,0	40,4
2002	21.795	10.186	9.234	3.357	46,7	32,9	36,3
2003	21.733	10.133	9.223	3.286	46,6	32,4	35,6
2004	21.673	9.777	9.158	2.893	45,1	29,6	31,6

The source: The statistic year-book of Romania, 1991 – 2005 issues

At present, the best and diseases control in Romanian agriculture is done, in proportion of 95 % (per cent), by spraying with pesticides in liquid aspect.

In 2005, in Romania, there were 14800 (14832) sprayers for cereal crops and 5640 (5641) sprayers for vineyards and orchards.

Sprayers mealing machinery with mechanical pull park evolution and structure related at the arable surface between 1990 and 2004 is presented in the table from below:

Table 3. The sprayers and mealing machinery with mechanical pull evolution and structure

Specification	1990	1994	1998	2002	2004	2004/ 1990
Arable surface, thousands hectares	9.450,0	9338,0	9350,8	9398,5	9421,9	1,00
Arable surface that correspond on a physical tractor-hectares	74,37	57,92	56,76	55,53	54,84	0,74
Sprayers and mealing machinery with mechanical pull sprayers	14994	12099	9424	7191	6573	0,44

The source: Calculated after the statistic year-book of Romania, 1991 – 2005

2. WHAT HAS BEEN ACHIEVED UNTIL NOW:

At present, in Romania, there is not a legislative framework (lawful stipulations regarding the obligatory character), equipment and skilled staff in this domain. 13790 European Norm (EN) concerning the “Sprayers control that are in exploitation” is known by the specialists from Romania, but it is not applied because there are not structures at national level to allow its application.

The operator staff training is actually null, the spraying being inadequately made, that is in discord with the current European norms from this domain. The control measures effected with unskilled staff lead to an accented pollution of the environment.

At present, the National institute is master regarding the new equipments acceptance. The specialists are occupied with: the plant protection machinery certification from the product concordance point of view, the samples effectuation from performance point of view and work safety.

The weed-killing equipments control and verification mainly follows the technical, constructive-functional characteristic properties establishing and of the manner in which, through their engineering and working, they jeopardize the users life safety or pollute the environment.

The institute performs the following determinations:

- the constructive parameters determination;
- the equipment enfeed at the tractor verification;

- the combiner stability determination;
- the working qualitative coefficients determination;
- the power coefficients determination;
- the working coefficients determinations.

The working qualitative coefficients are established at different operating speeds of the machinery. For the optional run establishing, the tests manager has to pursue the obtaining of some qualitative coefficients with maximum values. At test the specialists establish:

- ✚ the pump output;
- ✚ the volumetrically productive capacity of the pump;
- ✚ the nozzle output;
- ✚ output coefficient;
- ✚ the transversal distribution measurement on the test stand;
- ✚ the pressure loss measurement;
- ✚ the pressure oscillation measurement at the spraying stopping on sections (apron segments);
- ✚ the substances norms;
- ✚ the fan output;
- ✚ the drops size;
- ✚ the operating pressure variation during the tanks evacuation;
- ✚ the agitation system efficiency.

The specialists from INMA, Cluj-Napoca branch have achieved two test stands of the distribution uniformity of the solution at sprayers, one of them for the sprayers in the field (uniformity on the working breadth) and the other one for the sprayers in space (for the output verification on nozzle).



Figure 1. INMA Cluj – Napoca: a) – the stand achieved by INMA Cluj for spraying in field; b) – the team from Cluj together with specialist from Germany (Photo Bungescu Cluj 2008).

3. WHAT IS IT DONE AT PRESENT IN ORDER TO INCREASE THE PROFESSIONAL QUALIFICATION OF THE SPECIALISTS FROM THE AGRICULTURE?

A few achievements that contribute to the professional qualification bettering of the specialists from agriculture:

- ❖ the “Plant Protection” section establishment at the Agricultural Science and Veterinary Medicine University of Banat – Timisoara in 2002. As part of this specialization, the students also study pest and diseases control machinery in horticulture, vegetable growing, agriculture, fruit growing – viticulture and forestry. In the 3rd year of faculty they study the discipline “Machinery and Equipments for Plant Protection” (28 hours of course and 14 hours of laboratory). The discipline is directed by Dr. eng. Walter Stahli from Germany, co-worker being Dr. eng. Sorin – Tiberiu Bungescu. The discipline has a recent bibliographical material and a modern laboratory (machinery, devices component parts, measuring and control instrumentations) this being possible due to the collaboration with the companies: Lechler, Agrotop, Hardi, albus and with Hohenheim University from Germany (Prof. dr. Siegfried Kleisinger)
- ❖ At the University from Craiova - Romania (Agriculture Faculty) there were already made the first steps for the establishment of this specialization, being, at present, under way of accreditation;
- ❖ For the operative staff with medium professional preparedness: agricultural mechanics, school leaver of agricultural high school, farmers from practice it is foreseen the establishment of a school of increasing of professional preparedness at Voiteg (Timis Country) with the support of Mechanization School from DEULA Germany, of Germany’s Government, of USAMVB Timisoara and of German forum from Romania.



Figure 2. The students attend at practical demonstrations in field with Berthoud sprayer.



Figure 3. The student attend at practical demonstrations of utilitarian aviation.



Figure 4. Demonstration in Plant Protection Machinery and Equipments discipline laboratory



Figure 5. Photo of Agricultural High School at Voiteg (Timis Country)(Photo Bungescu Voiteg 2008)



Figure 6. Pictures of the verification sprayed cars purchased from the School of Agriculture at Voiteg (Photo Bungescu Voiteg 2008)



Figure 7. Results obtained from the stand to check a Voiteg of the pest and diseases control equipment (Bungescu 2008)



Figure 8. Plaquette for periodic verification of the pest and diseases control equipment in England.(Photo Bungescu England 2008)

- ❖ Romania attended the second workshop on verification equipment sprayed organized by the European Union together with the Federal Office of Plant Protection in Germany that took place in town Straelen in Germany in 2007. At this meeting attended by almost all countries in the European Union. Romania was first entering the books in the future.



Figure 9. Photos from during the workshop in Germany (Photo Bungescu Germany 2007)

4. THE LEGISLATION THAT IA APPLIED AT PRESENT IN ROMANIA, BUT THAT IS NOT COMPULSOR

- **SR ISO 5681:1995** - Machinery and equipments for plant protection. Vocabulary;
- **STAS 9924-74** - Machinery for plant protection. The liquid tanks capacity;
- **STAS 9926-91** - Machinery for plant protection. Work protection and hygiene limitations;
- **SR ISO 6686:1999** - Machinery and equipments for plant protection. Nozzles with anti-eye dropper. Performances determinations;
- **SR ISO 6720:1999** – Agricultural machinery. Sowing machinery, fertilizer sower planting machinery and spraying equipments. Recommended working breadth.
- **STAS 12836-90** –Tractors and agricultural machinery. Methods for the conditions determination at experiments in field;
- **STAS 13042/1-91** –Agricultural machinery. Determination methods of constructive parameters;
- **STAS 13042/2-91** –Agricultural machinery. Determination methods of working coefficient;
- **SR EN ISO 12100-2:2004** – Machinery safety. Basis drafts. General principles of projection. Part 2: Technical principles.
- **SR ISO 730-1+C1:2000** - Agricultural tractors on wheels. Suspension machinery in three points mounted in the back. Part 1: The categories 1, 2, 3 and 4.
- **SR ISO 4254-6:2000** - Forest agricultural machinery and tractors. Technical devices that allow the security ensurance. Part 6: Machinery and equipments for plant protection;
- The basis European Norms used for the technical verification of the plant protection equipment in use are:
- **SR EN 13790-1:2003** - Agricultural Machinery. – Sprayers – Inspection of sprayers in use – Part 1: Field crop sprayers, CEN, 2004, Brussels;
- **SR EN 13790-2:2003** - Agricultural Machinery – Sprayers - Inspection of sprayers in use – Part 2: Air-assisted sprayers for bush and tree corps;
- **SR EN 12761-1:2002** – Agricultural and forestry machinery – Sprayers and liquid fertilizer distributors, Environmental protection. – Part 1: General;
- **SR EN 12761-2:2002** - Agricultural and forestry machinery – Sprayers and liquid fertilizer distributors, Environmental protection. – Part 2: Field crop sprayers;
- **SR EN 907:2003** – Agricultural and forest machinery. Sprayers and liquid fertilizers administer machinery. Security.
- **ISO 5681** – Equipment for crop protection – Vocabulary;
- **ISO 10625** – Equipment for crop protection – Sprayer nozzles – Colour coding for identification;
- **ISO 19732** – Equipment for crop protection – Sprayers strainers – Colour coding for identification.

5. CONCLUSIONS: WHAT ARE THE EXPECTATIONS FOR THE FUTURE?

- ❖ The staff schooling that works in this domain with skilled specialists from UE countries;
- ❖ The creation of a control network of the sprayers in use from Romania (see figure 6);
- ❖ The new European legislation implementation in this domain at national level;
- ❖ The compulsory periodical control introduction of these machinery, control that should be effected by state. Working points: Bucharest, Cluj-Napoca and Timisoara (there were chosen these three cities because at present here there is interest for this domain).
- ❖ The organization possibility in the future of a Workshop at the University from Timisoara with Plant Protection Federal Office support from Germany – BBA on control themes of sprayers with a view to implementation in Romania of the European Norms in this domain.



Figure 10. Possible verification center in Romania: a) - A possible control network of sprayers in Romania; b) - The team who can implement in Romania in the future the European legislation in this domain (Bucuresti – Cluj-Napoca – Timisoara).

REFERENCES

- [1] BOLINTINEANU Gh., VLĂDUȚ V., POPESCU M. “Orientations, directions and requirements in the equipments for phyto-sanitary protection domain in terms of Romania,s adhesion at UE” Scientific Papers INMA, INMATEH III/2006, pg. 115 – 124.
- [2] GANZELMEIER H. European Standard EN 13790 – the basis for sprayer inspections in Europe, SPISE Braunschweig Germany, 397, Berlin 2004, pag. 24 – 42.
- [3] IANCU T. “Agricultural economy”, Agroprint Publishing House, Timisoara, 2007;
- [4] STAHLI, W., BUNGESCU, S.T., “The technical testing and verification of the spraying equipments”, Agriculture Mechanization, XVII, Nr. 5/2006, pg. 27 – 31.
- [5] BUNGESCU S., STAHLI W., VLĂDUȚ V., BIRIȘ S., NAGY Mihaela – Elena, IANCU T. – “Requirements and settlements regarding the pest and deseases control equipment verification in Romania in the period of pre-adhesion at UE.”, 2nd European Workshop on Standardised Procedure for the Inspection of Sprayers in Europe – SPISE-, Landwirtschaftskammer North-Rhine/Westphalia, Second European Workshop on Standardised Procedure for the Inspection of Sprayers in Europe – SPISE 2 – Straelen, Germany, April 10 - 12, 2007, pag. 160 – 166.



EXAMINATION OF BLACK LOCUST (*Robinia pseudoacacia* L.) AFFORESTATIONS IN BÁCS-KISKUN COUNTY

Tamás BARNA, Gábor SZULCSÁN

KEFAG Zrt. 6000 Kecskemét, József A. u. 2., HUNGARY

Abstract

The traditional methods of soil examination are nowadays not sufficient any more to predetermine the productivity of the given tree species. The nutrient content analysis of the soil is also necessary. We should however know the nutrient demand of tree species, including black locust as well, more exact. Therefore examinations aiming the determination of the plants nutrient content would be necessary. In the course of these examinations the correlation between the nutrient reserves of the soil and the nutrient element content of the plant should be found. If in possession of these data we can complete the traditional soil examination to be performed before afforestations with the determination of the nutrient reserves of the soil, we will be able to prepare a much more exact forecast on the expectable growth of the planned target stand.

Key words:

Robinia pseudoacacia, black locust, afforestation, soil examination

1. INTRODUCTION

In Hungary there has been afforestations done in agricultural areas of significant extent during the recent decades. These were mainly concentrated to the sand regions of the Great Hungarian Plain. The main reason therefore is, that the traditional field plant production is on these sand-textured soils with little nutrient content the most uneconomical. Afforestation can be considered in these areas also as an activity bringing income, because due to the claimable subsidy system the subsidies cover nearly 100% of the implementation costs and the expenses arising from maintenance until the age of 5-6 years, and the subsequent maintenance costs again can be covered by the incoming revenues from selling timber. The maintenance expenses do not arise every year regularly, but from time to time about every 10 year in comparison with the yearly arising expenses in case of field plant production. Although the earning capacity of silviculture only amounts to 5-6 % even in the best case, the relatively short cutting interval of 15-30 years ensures an acceptable income even for farmers being used to yearly income.

Due to the above considerations an increasing proportion of people making their living from agriculture afforest their fields. This economic approach requires from afforestation planners as well to review traditional planning principles and to work out some new, more precise methods to make the predetermination of stand growth more accurate.

Farmers afforest yearly 2500 – 3000 ha in Bács-Kiskun County. Among the applied tree species black locust is used most frequently. The reason is that it accomodates itself well to the site extremes, the proportion of its surviving in the afforestations is good, and its timber can be used from relatively young age, at least as firewood. In case of end use at the age of 30-35 years it can be used for several reasons, it is producing timber of a high value. It was not by chance, that the black locust became, 50 years ago already, the tree of the Great Hungarian Plain. The majority of the Hungarian farmers think it is a native tree species and do not know, that it was brought in to Hungary from North-America just 250 years ago.

Since – as mentioned – the afforestations can also be considered as a business activity, the quality of the stands being established in the course of the investment really matters. The findings during exploration of the natural sites before afforestation planning determine the investments for 30-40 years. That is why we have undertaken to examine the progress of

some black locust afforestations and to compare the findings in the natural sites exploration reports with the growth data of the 6-26-year-old stands. We have tried to explain why the growth of an actual stand is good or actually poor.

In our opinion it is more so since necessary to reconsider the aspects of selecting tree species, because the currently used aspects were written down in the 1960's by Dr. Imre Babos and his associates (BABOS et al. 1966). The environmental changes, which have meanwhile taken place and the growing business requirements lead us to reconsider the methods of natural sites exploration. We expect our work to improve the planning of afforestations and as a result to lead to the establishment of better tree stands in the future.

2. INSTRUMENTS

Soil drill; soil laboratory – various examining instruments; SUUNTO for measuring tree height and slope, tape measure for measuring diameter

3. METHOD

Site exploration in 25 forest tracts, collection and examination of 71 soil samples, in an area of total 113,4 ha.

Determination of site characteristics based on laboratory test and examinations on site. Measuring the height and diameter of at least 30 trees in each forest tracts, calculating average tree measures on this basis.

Determination of stand productivity on the basis of Károly RÉDEI edit. (1997): Handbook of black locust management. (in Hungarian) ERTI, Budapest.

Short, written evaluation of the site and the stand.

Chart 1 Forest improvement model of black locust stands, seed and coppice origin (Rédei edit. 1997)

Description of improvement cutting	Remaining stand after improvement cutting					
	Age	Average height (Hm)	Basal area (G)	Average diameter (Dm)	Number of stems (N)	Average stem distance (am)
	year	m	M ²	cm	pcs	M
PRODUCTIVITY GROUP I.						
Cleaning	5-6	7	7	6	2500	2,2
Cleaning	9-10	12	14	10	1800	2,5
Selective thinning	14-15	16	14	14	900	3,6
Increment thinning	23-24	22	17	22	450	5,1
End use	35	25	30	29	450	5,1
PRODUCTIVITY GROUP II.						
Cleaning	7-8	7	8	6	2700	2,7
Cleaning	12-13	11	14	10	1800	2,5
Selective thinning	18-19	15	14	14	900	3,6
End use	30	18	28	20	900	3,6
PRODUCTIVITY GROUP III						
Cleaning	9-10	7	8	6	3000	2,0
Cleaning-like selective thinning	15-16	10	8	8	1600	2,7
End use	25	13	21	13	1600	2,7

The evaluation of the soil characteristics happened due to the following aspects (Barna 1994):

Chart 2 Determination of fertile layer thickness of the forest soils depending on climate conditions

Categories	Beech and hornbeam-oak climate	Turkey and Sessile oak - forest steppe climate
	cm	
Very shallow (ISE)	0-20	0-40
Shallow (SE)	20-40	40-60
Medium-deep (KMÉ)	40-60	60-90
Deep (MÉLY)	60-100	90-140
Very deep (IMÉ)	100-	140-

Chart 3 Specific values of physical soil types

Physical soil types	Hy (%)	Soil plasticity according to Arany	5-hour capillary water rise (mm)
Rubble (TÖ)	-	-	-
Coarse sand (DHO)	0,3	-	450-
Sand (HO)	0,3-1,0	-50	450-300
Loam (V)	1,0-5,0	30-50	300-75
Clay (AG)	5,0-6,0	50-60	75-40
Heavy clay (NAG)	6,0-	60-	-40

Chart 4 pH-value of soils

Categories	pH
Very strongly acidic	-3,0
Strongly acidic	3,0-4,0
Sour	4,0-5,0
Slightly acidic	5,0-6,8
Neutral	6,8-7,2
Slightly alkaline	7,2-8,0
Alkaline	8,0-9,0
Strongly alkaline	9,0-10,0
Very strongly alkaline	10,-11,0

Chart 5 Lime content of soils

Categories	Lime content (%)
Calciferous in patches	0-1
Low-lime	1-5
Calciferous	5-

Chart 6 Humus content of soils

Categories	Humus content (%)
Humus free	0
Low humus	1-2
Humus	2-4
High humus	4-10
Moorland	10-

4. CONCLUSIONS

In the course of the examination we have evaluated at the end 22 forest tracts. The total area amounts to 113,4 ha. The facts of the forest tracts are summarized in the chart 7/1-5.

Unfavourable soil characteristics (marked with red in the charts 7/1-5.)

1. The growth of the examined black locust stands is first and foremost influenced by the fertile layer thickness of the soil. Generally is a shallow fertile layer less than 40 cm already unfavourable.
2. This unfavourable effect is intensified, if the lime-content of the surface soil is about 5 % , and
3. straight below the sodium content reaches or exceeds 0,02%.
4. Furthermore the mechanical composition of the soil impacted also on the stand growth. The growth was further harmed, if the proportion of coarse sand in the surface soil exceeded 25%.

Among the above mentioned soil characteristics the soil drought is increased by the shallow, calciferous fertile layer of soil composed of coarse sand. The examined sites belong to the water resources management levels very dry – dry. And the sodium content of about 0,02% has already a toxic effect on the roots. The situation is aggravated thereby, that straight below the shallow – very shallow fertile layer significant sodium content can be detected!

Chart 7/1. Soil examinations

	Village, member, item									
	Császártöltés 247A		Császártöltés 247B		Császártöltés 16H			Császártöltés 81B		
Area (ha)	14,4		4,2		1,8			10,0		
Sstand	Robinia pseudoacacia		Robinia pseudoacacia		Robinia pseudoacacia			Robinia pseudoacacia		
Age in 2005 (years)	6		6		16			26		
Examined soil layers (cm):	0-70	70-200	0-80	80-200	0-60	60-100	100-200	0-20	20-140	140-200
Climate	ESZTY		ESZTY		ESZTY			ESZTY		
Hydrology	VFLEN		VFLEN		VFLEN			VFLEN		
Gen. soil type	HH		HH		HH			HH		
Thickness of fertile layer of the soil (cm):	KMÉ		KMÉ		KMÉ			ISE		
Physical soil types	HO		HO		HO			HO		
pH H ₂ O	8,1	8,5	7,9	8,5	7,9	8,0	8,4	8,0	8,3	8,5
pH KCl	7,7	8,1	7,6	8,0	7,3	7,4	7,7	7,4	8,0	8,1
CaCO ₃ (%)	10,4	12,7	10,1	11,1	3,8	23,1	31,5	10,0	9,2	11,3
Sodium (%)		0,035		0,037			0,042		0,023	0,026
Total salt (%)										
hy (%)	0,35	0,31	0,39	0,27	1,29	1,15	0,72	0,38	0,34	0,27
K _A					33	34				
5-hour capillary water rise (mm)	310	415	280	430	380	340	325	225	380	360
Humus (%)	0,39	0,16	0,49	0,14	1,40	1,21		0,60	0,35	0,16
Mechanical composition: clay	0,68	1,03	0,80	0,88	6,00	8,35	2,80	1,30	1,40	1,20
silt	2,64	2,85	3,00	2,71	14,20	18,40	20,70	2,70	2,60	1,80
fine sand	81,18	84,12	79,50	80,00	77,00	71,35	73,20	82,00	79,10	72,80
coarse sand	15,50	12,00	16,70	16,40	2,30	1,90	3,30	14,00	16,90	24,20
Average height (m)	5,0		5,0		14,0			15,0		
Average diameter (cm)	5,0		4,0		14,0			12,0		
Classification	Productivity group I.		Productivity group I.		Productivity group II.			Productivity group III.		
Notes	The medium-deep fertile layer of the soil can compensate the unfavourable effects of the high lime- and sodium content for the time being! Supplementary examinations are necessary!		The medium-deep, slightly loaming fertile layer of the soil can compensate the unfavourable effects of the high lime- and sodium content for the time being! Supplementary examinations are necessary!		The depth of the low humus content in the fertile layer of the soil can compensate the unfavourable effects of the high lime- and sodium content only on a limited scale!			The very shallow fertile layer of the soil and the high lime- and sodium-content measurable in the whole section collectively cause the poor growth!		

Chart 7/2. Soil examinations

	Village, member, item			
	Császártöltés 91B ₃	Bugac 315C	Bugac 272C	Kisszállás 73F

Area (ha)	4,4			12,1		2,2			8,8		
Target stand	Robinia pseudoacacia			Robinia pseudoacacia		Robinia pseudoacacia			Robinia pseudoacacia		
Age in 2005 (years)	27			8		6			7		
Examined soil layers (cm):	0-10	10-50	50-200	0-60	60-200	0-55	55-80	80-	0-30	30-60	60-
Climate	ESZTY			ESZTY		ESZTY			ESZTY		
Hydrology	VFLEN			VFLEN		VFLEN			VFLEN		
Gen. soil type	HH			HH		HH			HH		
Thickness of fertile layer of the soil (cm):	ISE			KMÉ		SE			ISE		
Physical soil types	HO			HO		HO			HO		
pH H ₂ O	7,6	8,5	8,7	8,1	8,6	8,1	8,5	8,6	7,7	8,3	8,3
pH KCl	7,5	7,9	8,2	7,6	8,3	7,6	7,7	7,9	7,3	7,9	7,5
CaCO ₃ (%)	9,9	10,2	8,4	4,0	11,5	3,3	12,5	15,7	1,1	7,1	17,7
Sodium (%)		0,032	0,032		0,031		0,028	0,047		0,026	0,044
Total salt (%)											0,010
hy (%)	0,50	0,27	0,22	0,46	0,20	1,00	0,59	0,37	0,61	0,30	1,08
K _a											
5-hour capillary water rise (mm)	170	390	410	300	510	390	415	465	110	435	395
Humus (%)	0,86	0,23		0,81		1,30	0,57	0,19	1,12	0,13	0,67
Mechanical composition: clay	2,52	1,50	0,62	1,35	0,95	1,80	2,90	0,95	1,70	1,50	0,10
silt	2,58	2,15	3,38	3,50	0,88	12,50	6,03	3,98	3,80	2,40	22,40
fine sand	79,50	82,65	85,60	70,85	78,37	72,25	80,77	78,67	74,20	77,90	72,10
coarse sand	15,70	13,70	10,40	24,30	19,80	13,50	10,30	16,40	20,30	18,20	5,40
Average height (m)	10,0			9,0		10,0			9,0		
Average diameter (cm)	4,0			10,0		7,0			10,0		
Classification	Productivity group III.			Productivity group I.		Productivity group I.			Productivity group I.		
Notes	The very shallow fertile layer of the soil and the high lime- and sodium-content measurable in the whole section collectively cause the poor growth!			The low humus, medium-deep fertile layer of soil can compensate the high lime- and sodium-content of the lower layers for time being!		The low humus content of the fertile layer of the soil can be classified as nearly medium-deep! This is sufficient for the primarily well growth of the black locust!			The root system of the stand has presumably not filled out fertile layer of soil yet. Supplementary data are necessary for verifying the showed well growth in contempt of the relatively poor site!		

Favourable soil characteristics (marked with green in the charts 7/1-5.)

1. At least medium-deep (deeper than 50 cm) fertile layer of soil.
2. Low lime content of fertile layer of soil (below 5%).
3. Low sodium content of the subsoil (below 0,02 %).
4. Humus content more than 1,00 %.
5. Loaming soil (silt content about 10%), and low proportion of coarse sand.

These soil characteristics should be accordingly taken into consideration to a greater extent in the course of afforestation planning. The data also show that we could classify only young, at most 10 years old stands into the productivity group I. The older stands of 26-27 years all belong due to their growth to the poorest productivity group III. *It can be accordingly expected, that the growth of the at first well growing black locust stands will later fall back thus far, as the root system fills out the lime- and sodium-free fertile layer of soil.* Since it is in the examined forest tracts generally shallow, it can be stated with certainty that this quality decrease is due to happen soon!

Abbreviations used in the Charts 7/1-5:

Climate:	ESZTY – forest steppe
Hydrology:	VFLEN – independent of the phreatic water
Genetically soil type:	HH – sandy soil with poor humus content
Thickness of infertile layer of the soil:	ISE – very shallow SE – shallow KMÉ – medium deep
Physical soil type:	HO – sand

Chart 7/3. Soil examinations

	Village, member, item			
	Kisszállás 73D	Kelebia 138C	Kelebia 169N	Kelebia 164C
Area (ha)	8,9	3,2	4,9	4,0

Target stand	Robinia pseudoacacia			Robinia pseudoacacia			Robinia pseudoacacia		Robinia pseudoacacia		
Age in 2005 (years)	7			6			8		8		
Examined soil layers (cm):	0-30	30-60	60-	0-45	45-60	60-	0-50	50-	0-30	30-60	60-
Climate	ESZTY			ESZTY			ESZTY		ESZTY		
Hydrology	VFLEN			VFLEN			VFLEN		VFLEN		
Gen. soil type	HH			HH			HH		HH		
Thickness of fertile layer of the soil (cm)	ISE			SE			SE		SE		
Physical soil types	HO			HO			HO		HO		
pH H ₂ O	8,3	8,4	8,3	7,4	7,8	8,4	7,9	8,2	7,9	8,3	8,5
pH KCl	7,8	7,9	7,4	7,1	7,4	7,9	7,6	7,8	7,6	7,9	8,1
CaCO ₃ (%)	3,3	3,2	6,0	1,6	2,6	4,2	3,8	3,2	3,0	4,4	7,2
Sodium (%)		0,025	0,014			0,033		0,012		0,021	0,022
Total salt (%)			0,010								
hy (%)	0,33	0,30	0,86	0,34	0,27	0,29	0,25	0,25	0,36	0,28	0,21
K _A											
5-hour capillary water rise (mm)	350	395	465	150	420	440	350	430	175	410	475
Humus (%)	0,22	0,17	0,43	0,46	0,22	0,18	0,19	0,19	0,58	0,22	
Mechanical composition: clay	1,70	1,80	1,30	1,80	1,50	0,90	0,80	0,50	1,30	1,30	0,70
Silt	1,70	1,10	8,40	0,90	0,80	2,80	1,10	1,30	1,80	1,20	1,60
fine sand	81,90	80,70	84,60	79,30	81,60	77,10	75,30	82,20	80,70	80,50	75,80
coarse sand	14,70	16,40	5,70	18,00	16,10	19,20	22,60	16,00	16,20	17,00	21,90
Average height (m)	7,0			6,0			9,0		9,0		
Average diameter (cm)	7,0			6,0			8,0		8,0		
Classification	Productivity group II.			Productivity group I.			Productivity group I.		Productivity group I.		
Notes	Despite very shallow fertile layer of the soil and shallow presented sodium-content the black locust shows medium growth. We have expected poorer results due to the facts! Therefore supplementary examinations are necessary for reliable evaluation!			Despite very shallow fertile layer of the soil and relatively shallow presented high sodium-content the black locust is well-grown for the time being. The examined soil characteristics do not explain it! Therefore supplementary examinations are also necessary for reliable evaluation of the site! The decreasing of the stand growth is to be expected soon!			The fertile layer of the soil nearly classifiable as medium-deep and the relatively low lime- and sodium-content enable the black locust to grow well for the present. Supplementary examinations would be still necessary!		Despite shallow fertile layer of the soil and relatively shallow presented high sodium-content the black locust is well-grown for now. The examined soil characteristics do not explain that! Therefore supplementary examinations are also necessary for reliable evaluation of the site!		

Chart 7/4. Soil examinations

	Village, member, item									
	Tompá 89D		Kisszállás 58E		Kerekegyháza 47K ₁		Kerekegyháza 47K ₂		Kerekegyháza 45F ₁	
Area (ha)	5,2		3,0		2,5		2,5		2,3	
Target stand	A		A		A		A		A	
Age in 2005 (years)	8		8		9		9		10	
Examined soil layers (cm):	0-40	40-180	0-10	10-180	0-85	85-180	0-60	60-180	0-50	50-80 80-
Climate	ESZTY		ESZTY		ESZTY		ESZTY		ESZTY	
Hydrology	VFLEN		VFLEN		VFLEN		VFLEN		VFLEN	
Gen. soil type	HH		HH		HH		HH		HH	
Thickness of fertile layer of the soil (cm):	SE		ISE		KMÉ		KMÉ		KMÉ	
Physical soil types	HO		HO		HO		HO		HO	
pH H ₂ O	7,5	8,3	7,5	8,2	8,3	8,5	8,4	8,7	8,2	8,8 8,5
pH KCl	7,0	7,9	7,0	7,9	7,7	7,9	7,9	8,2	7,9	8,3 8,6

Chart 7/4. Soil examinations (continuing)

	Village, member, item				
	Tompá 89D	Kisszállás 58E	Kerekegyháza 47K ₁	Kerekegyháza 47K ₂	Kerekegyháza 45F ₁

CaCO ₃ (%)		12,0		10,9	6,8	13,3	7,2	11,5	9,3	11,5	7,3
Sodium (%)		0,037		0,032		0,028		0,027		0,024	0,030
Total salt (%)											
hy (%)	0,89	0,35	0,92	0,38	0,41	0,43	0,36	0,25	0,37	0,22	0,46
K _a											
5-hour capillary water rise (mm)	335	390	350	500	285	480	390	415	215	425	200
Humus (%)	1,32	0,29	1,30	0,21	0,45	0,18	0,38		0,37		0,29
Mechanical composition: clay	1,60	5,80	1,60	2,30	1,80	1,60	1,70	1,30	1,80	1,40	3,80
silt	10,20	4,20	10,80	4,00	2,70	4,90	2,20	1,50	2,10	0,80	1,90
fine sand	69,00	59,90	73,10	72,10	31,00	80,10	64,70	70,40	62,60	55,00	79,60
coarse sand	19,20	30,10	14,50	21,60	26,50	13,40	31,40	26,80	33,50	42,80	14,70
Average height (m)	9,0		8,0		9,5		3,2		6,8		
Average diameter (cm)	9,0		9,0		10,0		3,0		8,0		
Classification	Productivity group I.		Productivity group I.		Productivity group II.		Productivity group III.		Productivity group III.		
Notes	The unfavourable effects of shallow fertile layer of the soil and shallow presented sodium are compensated by loaming structure and low humus content!		The unfavourable effects of shallow fertile layer of the soil and shallow presented sodium are compensated by loaming structure and low humus content!		The relatively high lime-content damages the unfavourable effects of medium-deep fertile layer of the soil! Supplementary examinations are necessary!		The above facts do not explain such poor growth of the young black locust stand! Supplementary examinations are necessary!		Despite medium-deep fertile layer of the soil because of high lime- and sodium-content in the whole section and low humus content the black locust shows poor growth. Nevertheless supplementary examinations would be necessary for reliable evaluation of the site!		

Chart 7/5. Soil examinations

	Village, member, item							
	Kerekegyháza 45F ₂		Lajosmizse 110H		Lajosmizse 110J		Lajosmizse 111E	
Area (ha)	2,3		2,3		2,6		7,5	
Target stand	A		A		A		A	
Age in 2005 (years)	10		10		10		7	
Examined soil layers (cm):	0-35	35-180	0-60	60-180	0-70	70-130	0-55	55-140
Climate	ESZTY		ESZTY		ESZTY		ESZTY	
Hydrology	VFLEN		VFLEN		VFLEN		VFLEN	
Gen. soil type	HH		HH		HH		HH	
Thickness of fertile layer of the soil (cm):	ISE		KMÉ		KMÉ		SE	
Physical soil types	HO		HO		HO		HO	
pH H ₂ O	8,2	8,9	8,2	8,5	8,2	8,4	8,2	8,5
pH KCl	7,8	8,3	7,6	7,8	7,7	7,6	7,8	7,9
CaCO ₃ (%)	7,6	17,2	3,0	24,2	6,0	3,0	2,1	1,0
Sodium (%)		0,031		0,052		0,026		0,030
Total salt (%)								
hy (%)	0,40	0,20	0,52	0,73	0,47	0,67	0,46	0,38
K _a								
5-hour capillary water rise (mm)	320	450	355	460	430	445	390	380
Humus (%)	0,51		0,66		0,40	0,57	0,31	0,32
Mechanical composition: clay	1,50	0,10	0,20	0,08	2,60	5,80	3,20	1,40
silt	2,90	1,70	5,20	9,90	2,90	3,00	2,40	2,20
fine sand	62,00	81,60	78,80	87,50	75,80	71,20	74,20	67,80
coarse sand	33,60	16,60	15,80	2,50	18,70	20,00	20,20	28,60
Average height (m)	3,7		8,0		6,0		3,0	
Average diameter (cm)	3,5		10,0		8,0		2,0	

Chart 7/5. Soil examinations (continuing)

	Village, member, item			
	Kerekegyháza 45F ₂	Lajosmizse 110H	Lajosmizse 110J	Lajosmizse 111E

Classification	Productivity group III.	Productivity group II.	Productivity group III.	Productivity group III.
Notes	The very shallow fertile layer of the soil, the high lime- and sodium-content and the soil poor in organic materials and rich in coarse sand explain properly the extremely poor growth of the black locust. Extremely dry site!	Despite high lime- and sodium-content the black locust stand shows surprisingly well growth. The well growth is due to the medium-deep fertile layer of the soil! Supplementary examinations would be necessary! Extremely dry site!	The above facts do not explain such poor growth of the black locust. Supplementary examinations would be necessary! Extremely dry site!	The above facts do not explain such poor growth of the black locust. Supplementary examinations would be necessary! Extremely dry site!

After all it has become obvious, that the afforestation planning nowadays can not be based only on these, traditional examination aspects any more. We have come namely to contradictory or unexplainable results in more cases. Glaring examples for that show the forest tracts Kelebia 169N and Kerekegyháza 47K. In these and similar cases detailed nutrient testing would be also necessary for evaluating site quality. The examinations should be extended at least to the following elements: N, P, K, Ca, Mg, Zn, Fe, Mn.

And the case Kisszállás 58E shows that the depth situation of lime and sodium should be determined more exact!

BIBLIOGRAPHY

- [1] BABOS Imre et al. 1966: Erdészeti termőhely-feltárás és térképezés. Akadémiai Kiadó, Budapest
- [2] BARNA Tamás szerk. 1994: Erdőműveléstan. Erdészeti és Faipari Egyetem, Erdőmérnöki Kar, Vadgazda Mérnöki Szak, Sopron
- [3] RÉDEI Károly szerk. (1997): Az akáctermesztés kézikönyve. ERTI, Budapest



DEPOSITIONAL ENVIRONMENT OF THE DANUBE-TISZA-DANUBE HYDROSYSTEM OF SOUTHERN BANAT OBTAINED FROM SOME PARAMETERS OF METAL ADSORPTION IN WATER

NEMEŠ Karolina¹, BELIĆ Sima², BUGARSKI Radojka³

University of Novi Sad, The Faculty of Sciences¹, Faculty of Agriculture²
Hydrometeorological Service of the Republic of Serbia³
21000 Novi Sad, SERBIA

ABSTRACT

An increasingly demand for meliorative action of Southern Banat region was evaluated by the parameters of adsorption of alkaline and heavy metals from suspended particles of the DTD canal water. Annual dynamics is categorized by statistical analyses, recognized trends of sodium absorption ratio and a concentration of iron in total suspended solids. All these provide preliminary informational basis for irrigation, flood areas and transportation determination. Environmental protection of these waters is required because iron and sodium are present in alluvial deposits, and the sodium is gradually increasing. EDS informative data pointed out metals (aluminum, titanium, zinc, iron) in alluvium of the Danube.

Key words:

SAR, Fe/TSS, adsorption, Box-plot, South Banat, DTD hydrosystem

1. INTRODUCTION

Large river transportation of loess material includes the loessification process which converts deposits. The building of dams and gates, and channelization of rivers slowly influenced on transportation of metals during sedimentation at the reduced river flow [2, 6, 7, 11, 12]. Meliorative canals could cause displacement of bio-activity of the soil of agricultural Vojvodina Province [5,9]. Therefore, in this paper, the movement of metals was observed from the assessment of metal adsorption in water from the index of sodium alkalization ratio- SAR and ratio of iron in total suspended solids- Fe/TSS.

2. MATERIAL AND METHODS

Our model to study progress of alkalization of waters in Southern Banat region from continual monitoring of the Danube-Tisa-Danube hydrosystem is represented. The SAR index- sodium adsorption ratio in miliequivalents- $SAR = Na / \sqrt{(Ca + Mg) / 2}$, was calculated according to guidelines for interpretations of irrigation water quality [1, 3] and the amount of iron in suspended material Fe/TSS from concentration in mg/l [2], and bioindicators [5, 9]. Integrating data are taken from Hydrological yearbooks [4].

Deposit analysis of the groundwater drainage wells was made by the use of Scanning Electron Microscope (SEM) JEOL JSM-6460 L. The EDS pattern of elemental composition (total wt %) were recorded on an OXFORD INCA Microanalyses suite and presented in diagram. A spatial framework for collecting, storing, and classifying information on the character of river network was proposed using the software Stat.soft Statistica 8 [13].

3. THE RESULTS AND DISCUSSION

Following categorization of indices and conductivity in suspended material in BLOCKS (Figs. 1-5), the ratio of iron in total suspended solids increased during the lowest concentration of solids estimated in rivers Tamis, Brzava and Moravica in the Tamis river basin. Hence, the tributaries of Great canal Banatska Palanka-Novi Becej were investigated and categorized with elevated suspended solids- an increased sedimentation obtained from the comparison of values with the The Danube in Southern Banat (St Pančevo- at the confluence of the Tamis river, downstream St Smederevo, St Banatska Palanka- at the confluence of canal network in Banat). Near the Botos- the gate of The Tamis and DTD hydrosystem, the movement of iron in total suspended solids was narrow. Previously, the fraction of iron in total suspended solids was obtained from The Sava River in Croatia pointed out by author- median 3 % [2], while in The Danube River it stretches through 1-3 % of median values. The integrating data of the small eutrophic Moravica river pointed out 3 % median of Fe/TSS ratio and there was the smallest fraction of the iron in suspended solids obtained from a decade of the research but comparable to acceleration of alkaline metal adsorption in 2005 of depositional environment. The sedimentation of iron is clarified in the samples of The Karas River when the concentration of suspended solids was in the range 0-10 mg/l (Figs. 1-2). From this point of view, the importance of research of sediments of residential areas is important [8].

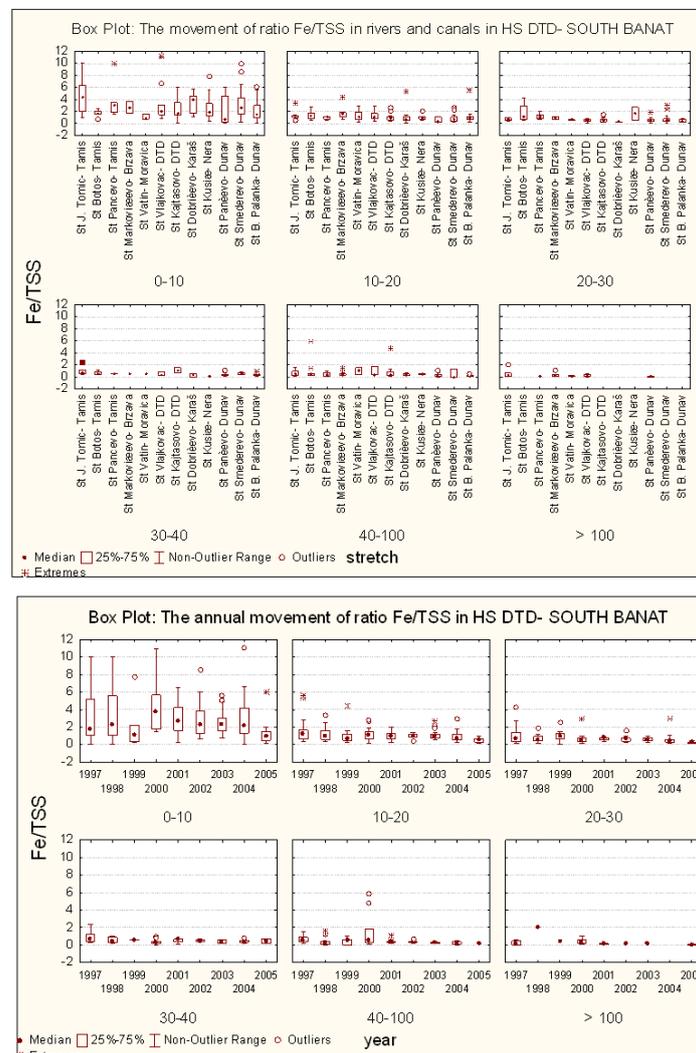


Figure 1-2. Box-plot graphs of ratio of iron in total suspended solids categorized in annual dynamics of data and stretches obtained from HS DTD of Southern Banat Region

The equality of means of metal adsorption parameters downstream the main gates of the Tamis River hydrographic unit (Tamis, Brzava and Moravica) and southern tributaries of The Danube- Karas and Nera were tested by ANOVA (Fig. 7). Obtained from standardized values of the SAR index and ratio of iron in total suspended solids, the similar values are evaluated in the rivers Tamis, Nera and The Danube River nearly The St Smederevo (correlation of the phosphates with the SAR index pointed

out the level of erosion). The confluence of phosphates, obtained from standardized values, was higher at the localities St Jasa Tomic- Tamis River, St Markovicevo- Brzava, St Kusić- Nera and St Smederevo- The Danube during the period 1997-2005. The comparison of parameters Fe/TSS and SAR index is showing the similar variability at the same localities 1997-2005 while the negative standardized values were observable at the boundary Station Jasa Tomic- Tamis River, Brzava, Nera and St Smederevo- The Danube (Figs. 1- 7).

The consequence of seasonality between November-February from weather warming generated high water because of snow melting after cold period in February of 1999 when the huge quantity of precipitation in Bega river basin contributed in high water level [10]. During the same period of high water in hydrographical basin of the Tisza and The Danube River, the weather in Ukraine triggered increasing of cesium in The Danube [7]. Taking responsible activities of Romania-Serbia engineers: hydroelectrical interventions, retention and distribution of water in Banat region are concerned for the next decade.

Integrating data of iron and alkaline metals of Danube-Tisza-Danube hydrosystem pointed out depositional environment (Figs. 1 - 8). The alteration of indices was observed in drought 2000 year. Obtained through the dynamics of metals in alluvion of Carpathian rivers entering Serbia, there was measured the highest concentration of metals and conductivity during sedimentation in DTD hydrosystem in Banat region in 2000. The concentration of copper significantly increased during the drought 2000 year, but the metal reduction gradually decreased in rainy year 2001 [4]. After the high erosion of water, the movement of metals in DTD hydrosystem could be categorized as C 3 - S 1 – good irrigation water quality of meliorative hydrosystem. The study of biodiversity of algae in southern Banat indicated good ecological potential compared with the brackish water diatoms such as *Entomoneis paludosa* and *Bacillaria paradoxa*. The prominent algae of Banat from genus *Cymbella* thrive in canals during the low iron content (Fig. 8).

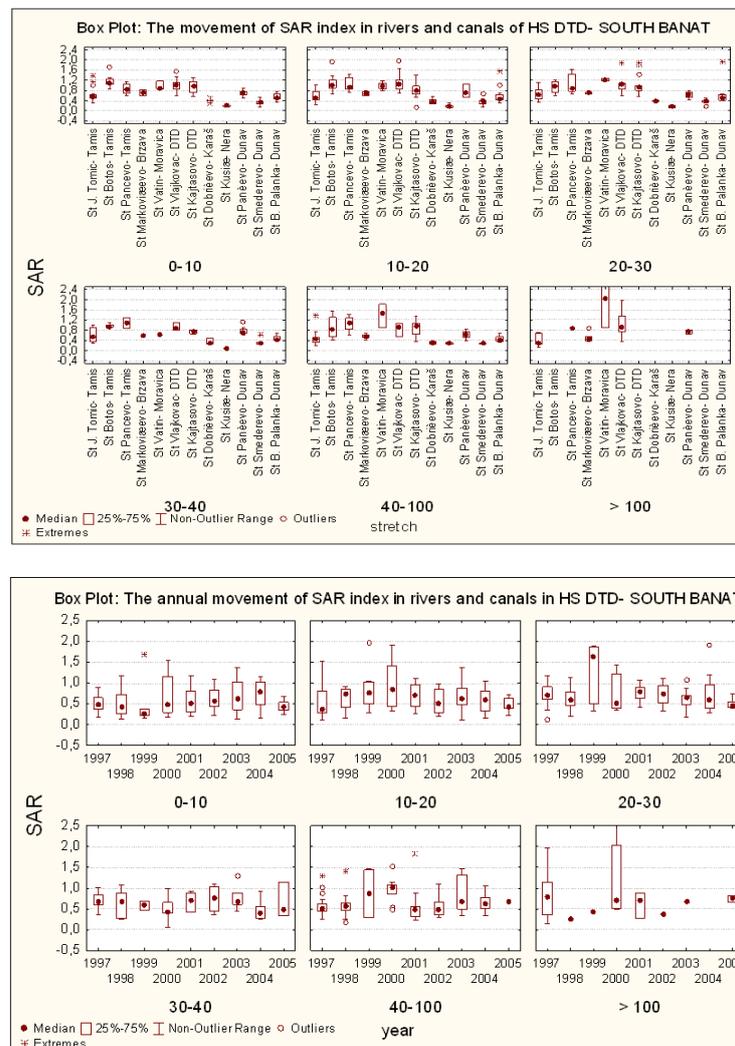


Figure 3-4. Box-plot graphs of SAR index in total suspended solids categorized in annual dynamics of data and stretches obtained from HS DTD of Southern Banat Region.

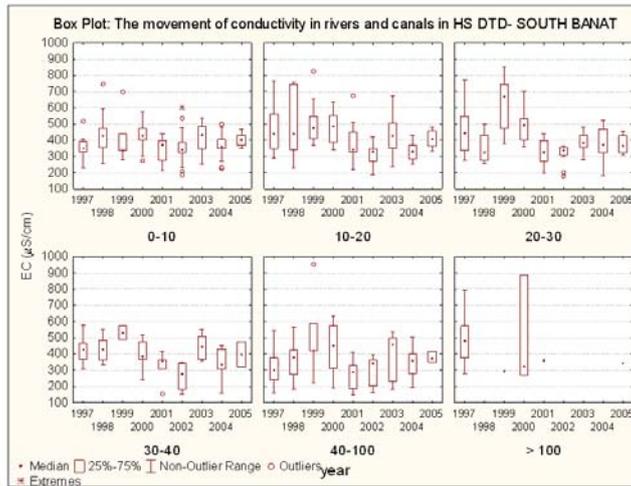


Figure 5. Box-plot graphs of conductivity in total suspended solids categorized in annual dynamics of data obtained from HS DTD of Southern Banat Region.

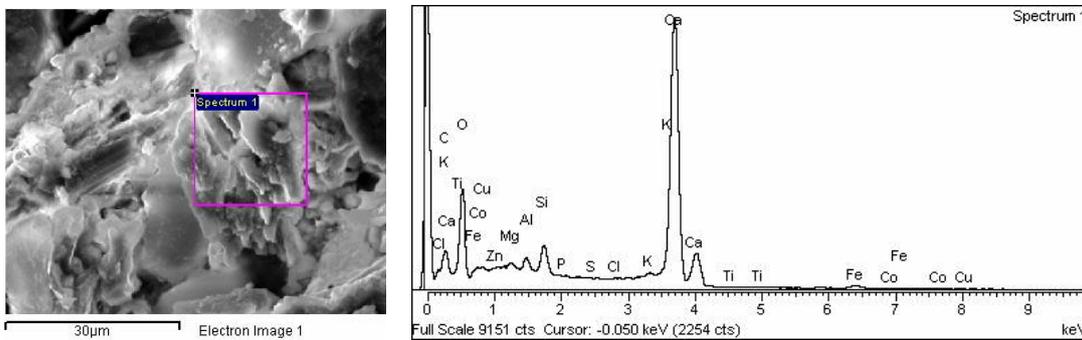


Figure 6. EDS analyses of groundwater deposits in piezometer from locality Kovin (alluvium of The Danube in Southern Banat nearby St Smederevo) (December, 2007). Elemental composition in wt %: O: 61.09, Al: 1.20, Si: 2.46, P: 0.00, K: 0.47, Ca: 33.11, Ti: 0.00, Fe: 1.05, Zn: 0.00, Cl: 0.00, Mg: 0.62, S: 0.00, Co: 0.00.

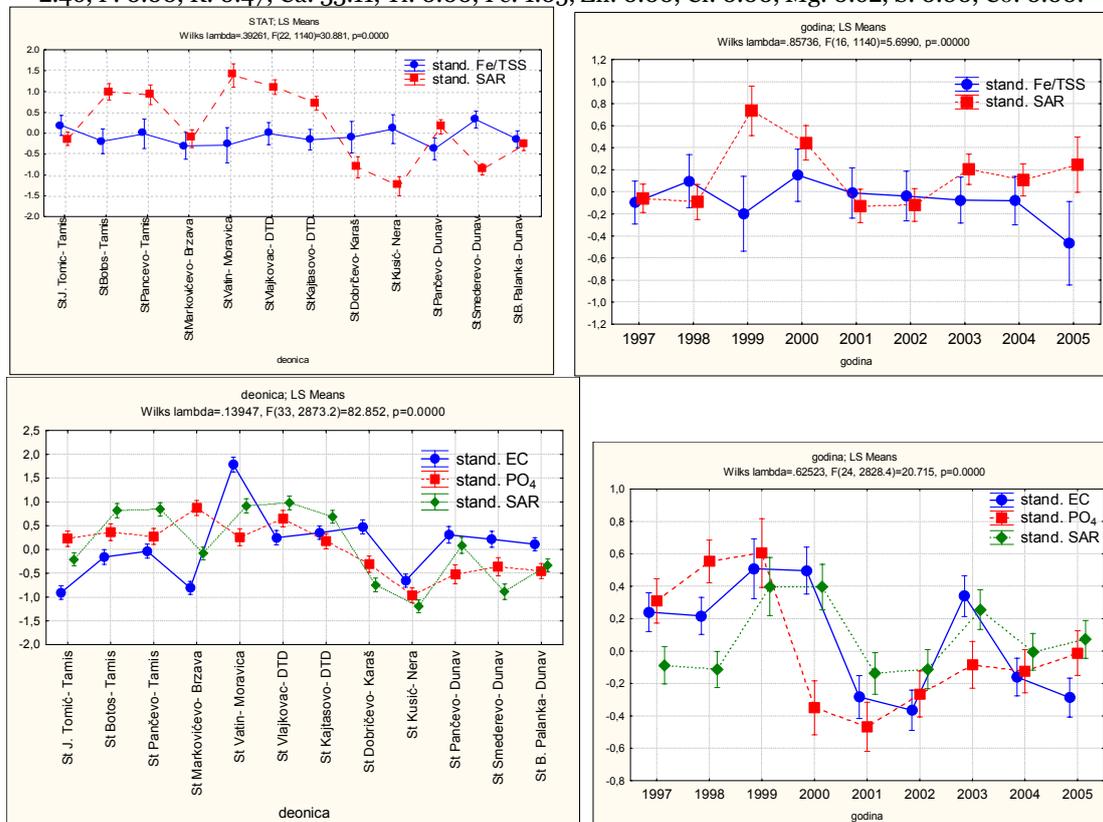


Figure 7. Equality of means was tested by ANOVA for standardized parameters: SAR index, ratio Fe/TSS, phosphate concentration and conductivity

4. CONCLUSION

In general, picture of the relations of some metals obtained through indices of alkalization and corrosion- the ratio of iron during sedimentation is represented in box-plot categorized graphs- „BLOCKS“ of rivers of Southern Banat. Because of the movement of metal adsorption in hydrosystem, considering gradual alkalization of surface and groundwater water, during the lowest concentration of suspended material, an attention is given to changes of Danube-Tisza-Danube hydrosystem water quality.



Figure 8. Scanning electron microscopy magnification of prominent diatoms of HS DTD in southern Banat region in 2004 (genus *Cymbella* with centric diatoms).
Genus *Cymbella* thrive in canals with low iron content.

Acknowledgement

These studies were supported by the Ministry of Science and Technological development of the Republic of Serbia (Grant No 22006).

REFERENCES

1. Ayers, R. S., Weskot D. W. (1985): Water quality for Agriculture, FAO Irrigation and drainage paper 29, Rev. 1. Rome.
2. Šimić, I. (1987): Korelacija koncentracije željeza, mangana i suspendovane tvari u vodi rijeke Save. Rijeka Sava- zaštita i korišćenje voda, Zbornik radova sa savjetovanja u Zagrebu. Jugoslovenska akademija znanosti i umjetnosti Zagreb. Pp. 192-197.
3. Belić, S., Škorić, M., Belić, A., Savić, R., Bugarski, R., Dragović, S., Hadžić, V., Bošnjak, Đ., Jarak M., Milošević N., Maksimović L. (1996): Upotrebljivost voda Vojvodine za navodnjavanje. The irrigation water quality. Univerzitet u Novom Sadu, Novi Sad.
4. Hydrological yearbooks, (1998-2005): Water quality. Hidrološki godišnjak. Kvalitet voda (in Serbian). Hydrometeorological Service of the Republic of Serbia.
5. Nemeš, K. (2005): Sezonska dinamika fitoplanktona Hidrosistema Dunav-Tisa-Dunav u Banatu. Magistarska teza, PMF, Univerzitet u Novom Sadu.
6. Boyeva, H. (2006): Floods in Ukraine. XXIIIth Conference of The Danubian countries on the hydrological forecasting and hydrological bases of water management. Beograd, Jun 2006. Conference Abstract book. Paper CD proceedings.
7. Kanivets, V. V. (2006): The role of suspended sediments in transportation of ¹³⁷Cs by The Danube River. XXIIIth Conference of The Danubian countries on the hydrological forecasting and hydrological bases of water management. Beograd, Jun 2006. Conference Abstract book. Paper CD proceedings.
8. Savić, R., Pantelić-Miralem, S., Belić, A. (2007): Značaj istraživanja kanalskih sedimenata pri revitalizaciji melioracionih sistema. Zbornik radova Melioracije, pp. 53-60.
9. Nemes, K., Matavuly, M., Lozanov-Crvenković, Z., Slavka, G., Dalmacija, B. (2008): Ecological Potential of Phytoplankton Communities in the Danube-Tisza-Danube Hydrosystem in Southern Banat Region (Serbia). Paper No 383. BALWOIS 2008, the third International Scientific Conference on Water Observation and Information System for Decision Support, held in Ohrid, Republic of Macedonia. CD proceedings.
10. Teodorescu, N. I. (2008): The main characteristics of high water registered in Bega River Basin during February 1999. XXIVth Conference of The Danubian countries on the hydrological forecasting and hydrological bases of water management. Bled, Slovenia 2-4. June 2008. Conference Abstract book. Paper CD proceedings.
11. Petan, S., Horvat, A., Padežnik, M., Mikoš, M., Globevnik, L., Brilly, M. (2008): Gravel bar sampling along The Sava basin. XXIVth Conference of The Danubian countries on the hydrological forecasting and hydrological bases of water management. Bled, Slovenia 2-4. June 2008. Conference Abstract book. Paper CD proceedings.
12. Bonacci, O., Oskoruš, D. (2008): The influence of three Croatian hydroelectric power plants on The Drava River sediment regime. XXIVth Conference of The Danubian countries on the hydrological forecasting and hydrological bases of water management. Bled, Slovenia 2-4. June 2008. Conference Abstract book. Paper CD proceedings.
13. StatSoft.Inc (2009): Statistica 8.