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

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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 similiar. 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 then 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).

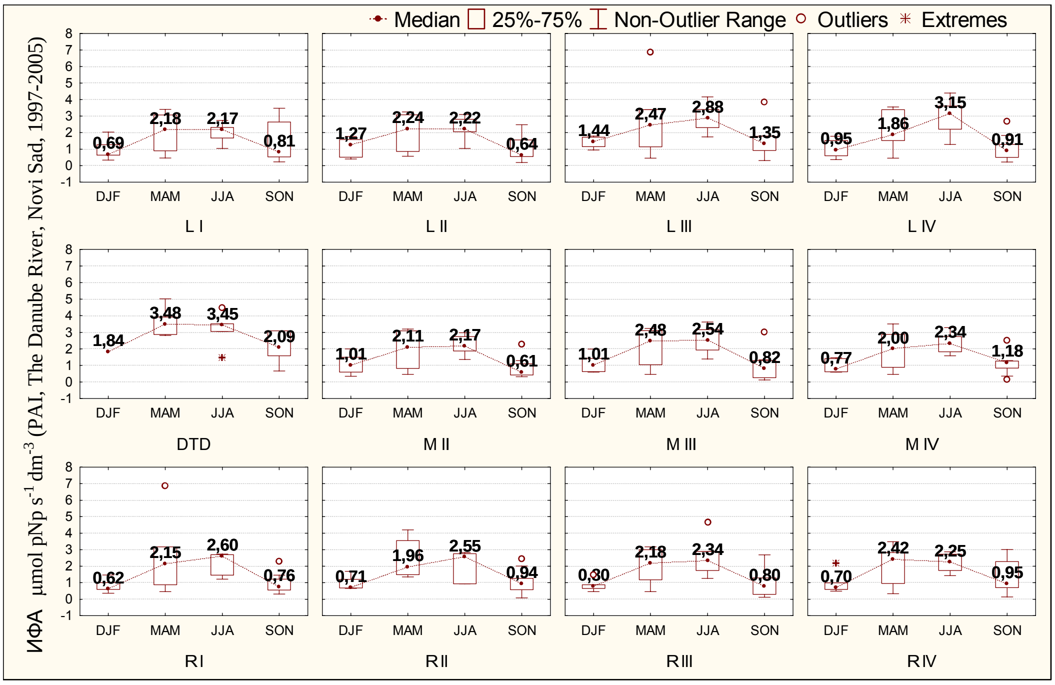

Figure 1. Box-plot: seasonal dynamics of phosphatase activity index of the surface water of The Danube in the City of Novi Sad (PAI_{NS}) (left riverbank, DTD canal, middle current, right riverbank of The Danube; river km 1262–1245).

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).

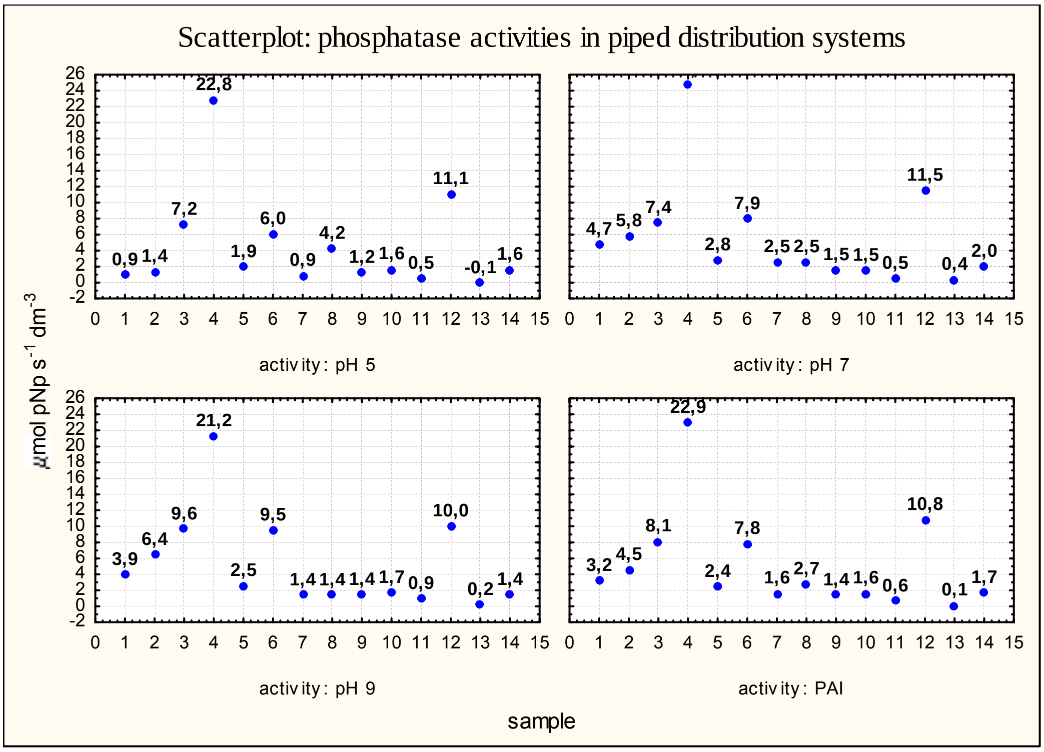

Figure 2. Scatterplot: categorization of phosphatase enzyme activities (μmol pNP s^{-1} dm^{-3}) in piped systems in Novi Sad. Water samples: 1) Danubius piezometer 7, 2) Danubius piezometer 7 unfiltered, 3) Danubius piezoemeter 9, unfiltered, 4) Danubius piezometer 15, unfiltered, 5) Piezometer 1 in the vicinity of river bank- stretch 4 of the Danube River, unfiltered, 6) Drainage well 5 in the vicinity of oil rafinery- 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 od bacteria with the predominant species being described as *Gallionella feruginea, Lepthothrix ochracea* and *Chrenothrix polispora* (Figure 3). Increasing mineralization [3] was a contributing factor for infrastructure degradation because of iron-depositing bacteria occurence 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 μg/l (well 8, well 9, well 10) and maximum conc. of 9.4 μg/l was measured in November, and there was found extreme conc. (23 μg/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 collor, 40 % of manganese increased, 30 % of residual chlor, increased concentration of iron and chloroform in 20% [9]. Neverthelless, 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).

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.

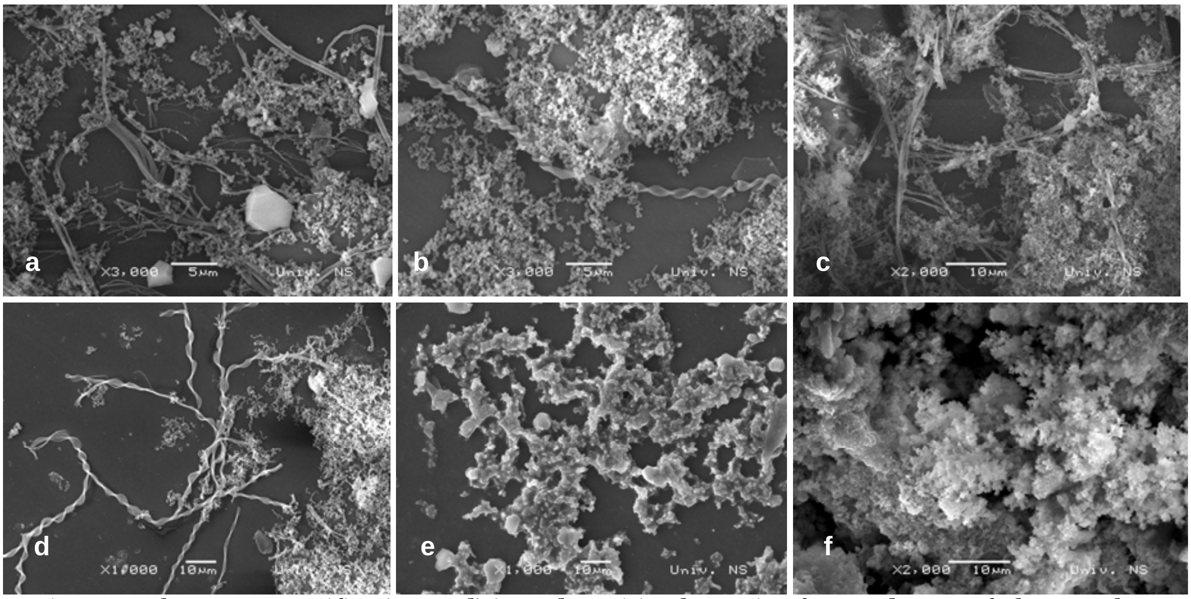

Figure 3. The SEM magnification: a-d) iron-depositing bacteria of groundwater of The Danube drainage well nearby The City of Novi Sad sampled in 2007 (left river bank, fourth river stretch), e) silted material of piezometer Danubius from the second river stretch, f) biofilm of piped drinking water.

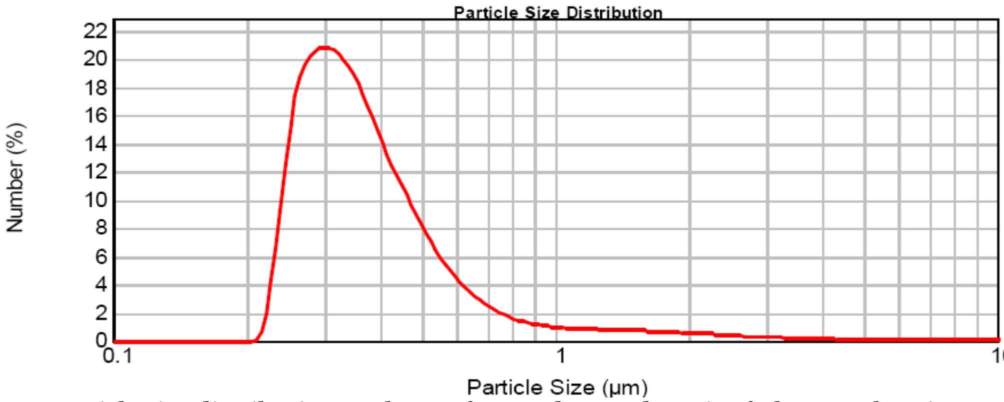

Figure 4. Particle size distribution analyses of groundwater deposit of The Danube River carried by Mastersizer 2000.

Considering the dynamics of iron-oxidizing/depositing bacteria, similiar 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 similiar 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.

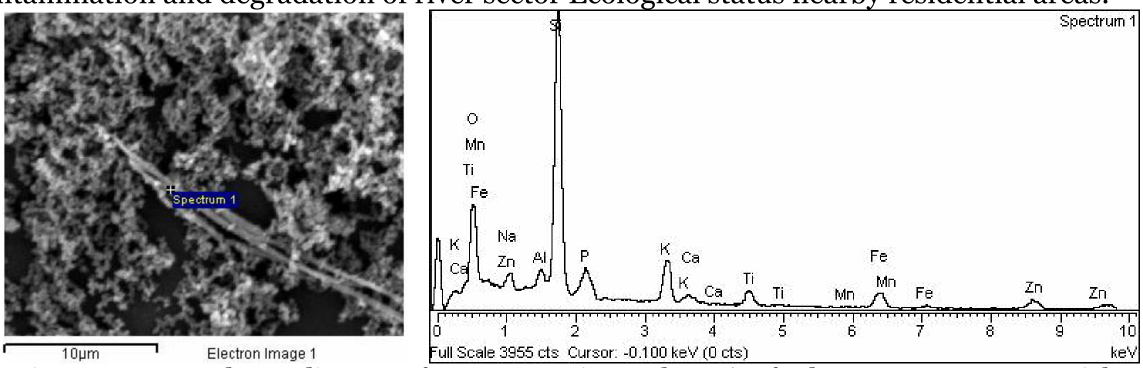

Figure 5. SEM and EDS diagram of spectrum point analyses (Oxford Instrument INCA-X-sight software) of the groundwater deposits shown by the X- ray spectra from the spectrum point of the fourth river stretch (The Danube in Novi Sad). Mineral identification of feldspar is assested with the X-ray microanalyses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

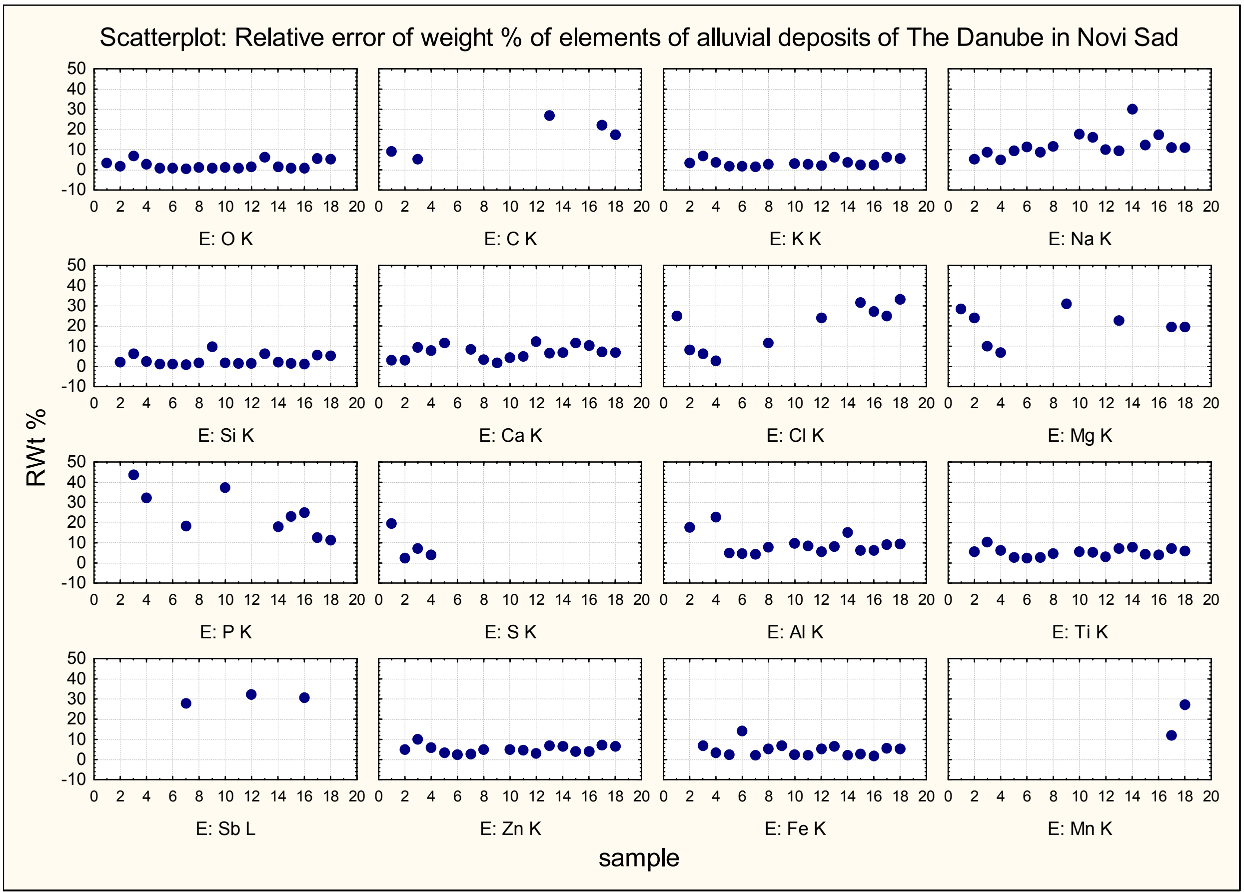

Figure 6. Categorized graphs of relative error of weight fraction (%) of different elements in groundwater drainage deposits. Relative weight (sigma weight (%)/weight (%)) was presented by the categorized scatterplot graph (Statistica 8) in order to provide systematization of EDS analyzed parameters 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 fouth 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 assested 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 occured, 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.

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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.