MONITORING OF INORGANIC CHEMICAL PARAMETERS IN RIVER DANUBE, NOVI SAD, SERBIA

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Abstract
Because of the importance Danube river has on the region and the population affected by it is essential to maintain constant monitoring. With new emerging pollutants every day and regular threats one of the crucial goals is to investigate the causes of possible contamination with the acquisition of new, until then unknown information. To be able to achieve quality investigation and to acquire new information special monitoring has been conducted, in which quantitative analysis of key physical-chemical parameters in water body was carried out with laboratory methods.

Introduction
River Danube is one of the most important rivers in Europe. It passes through 10 countries (starting from Germany then going through Austria, Slovakia, Hungary, Croatia, Serbia, Romania, Bulgaria, Moldova and Ukraine) and is basin for a large number of tributaries from 9 more countries, thus connecting 19 countries all together and around 90 million inhabitants. It represents waterway for those countries and main route from Germany to Black sea.
In many ways Danube gives life to all countries it influences. Firstly around 30 % of inhabitants affected by it use Danube water (partly purified) for drinking. Furthermore large amount of water is used in agriculture for watering crops. It is also home of more than 20 national nature parks with unique fauna and flora. Fishing industry is also very developed on Danube river and represents part of its life. Taking all of this into account we come to realization that river Danube is essential part of everyday's life for these countries as well as very influential economical factor. With wide range of usages and water circulation through various different systems but still ending up in river basin the problem of pollution emerges.
Because it represents main waterway (easier and chipper method for transportation) many factories has been build on river banks. Most of those factories directly and indirectly pollutes river (by direct discharge of pollutants in water or vicinity). Also boats used for transport directly pollute and disturbs normal river biota. Since it river represents and gives life, many big cities are build on its banks and large number of them is still disposing waste water directly into the river. Beside this one of the main emerging problems is use of pesticides for crops, and they are directly or through its tributaries in water circulation affiliated.
To be able to preserve biota and maintain sufficient quality of water constant monitoring is from crucial importance. Also, adequate monitoring provides us data about river changes and possibilities on how to improve water quality and to mitigate pollution. The aim of this paper is to monitor important physico-chemical parameters in the Danube River. Also multivariate statistical method (hierarchical cluster method) was also applied to confirm the current state of

the Danube River, as well as investigate the causes of possible contamination with the acquisition of new, until then unknown information.

Experimental

Samples of surface water for laboratory analysis were collected from six locations on river Danube in the city of Novi Sad, Serbia. Three locations are located before the discharge of wastewater (Location 1,Location 3, and Location 5) and three locations are located after the discharge of wastewater (Location 2, Location 4 and Location 6).Thirty-sixsamples were collected, six samples from each locations. Samples are poured into 1 L bottles, stored in hand refrigerator at 4 ^{0}C, and transported to the laboratory. Analyses were carried out in accredited Laboratory for monitoring of landfills, wastewater and air, Department of Environmental Engineering and Occupational Safety and Health in Novi Sad.

Chemical parameters that were monitored in surface water are: orthophosphate, sulfate, nitrite, nitrate, chromium, total chlorine, fluoride, chloride and ammonia.Concentrations of orthophosphate in samples were analyzed according to the Standard Methods of Environment Protection Agency (EPA 365.3). Chromium, sulfate, nitrite, nitrate, total chlorine, fluoride, chloride and ammoniawere analyzed according to the HACH Methods (HACH 8023 for chromium, HACH 8021 for sulfate, HACH 8507 for nitrite, HACH 8192 for nitrate, HACH 8167 for total chlorine, HACH 8023 for fluoride, HACH 8113 for chloride and HACH 8155 for ammonia). The concentrations of all parameters were measured with UV-VIS spectrophotometer (DR 5000, HACH, Germany).

Multivariate statistical method used in this research areHierarchical cluster analysis (CA). Statistical processing will be carried out using the program IBM SPSS statistic 20.

Results and discussion

Quantitative analysis of key physical-chemical parameters in water body was carried out with laboratory methods.Research monitoring of the Danube River is necessary for the development of a database that will contain physico-chemical parameters that disturb the quality of the water body.The assessment of the influence of selected inorganic parameters on the quality of the Danube River at selected locations enables us to confirm the level of contamination of the observed river.

The data obtained from the analysis of water quality will provide information about contamination of the examined surface water bodies.However, a specific problem in monitoring of surface water quality is the complexity associated with the analysis of a large number of variables and high variability due to anthropogenic and natural impacts.By applying various multivariate techniques, interpretation of complex data matrices will be simplified in order to better understand the state of water quality of the examined area. These techniques will enable identification of possible sources of pollution affecting water bodies and represent useful tools for reliable water resources management.

Cluster analysis is a statistical technique used to identify relatively similar groups of objects. Cluster analysis does not know the association of the object or the final number of groups, but the goal is to establish similar groups or clusters.The cluster analysis groupobserved location into classes so that the locations with the most similar concentrations for the examined parameters are in the same class (cluster). Grouping of locations is carried out based on the concentration for analyzed physico-chemical parameters for each location separately.

The results were presented by dendrogram graphic (Figure 1) based on cluster analysis.

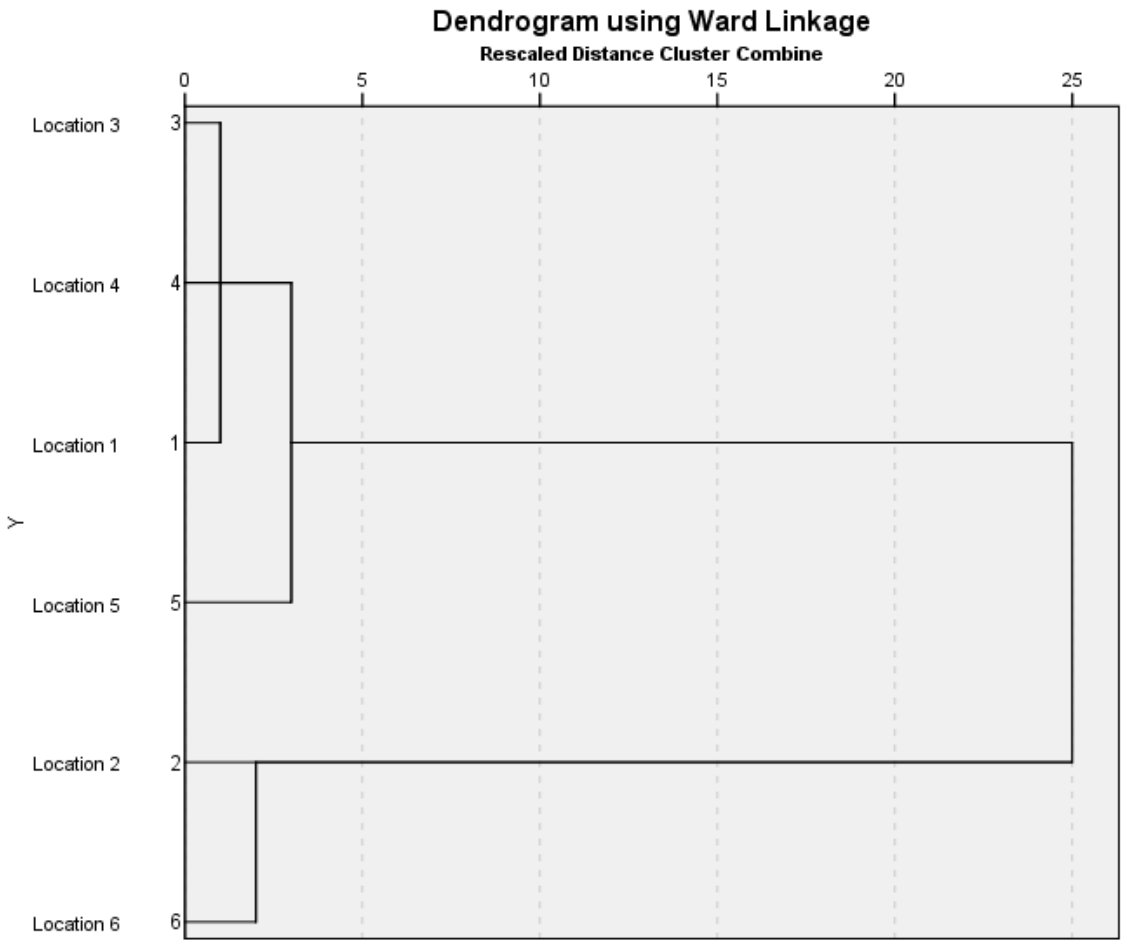

Figure 1.Dendrogram graphic for six locations

Analyses of cluster method are in full compliance with the obtained analytical results. On the dendogram, two main clusters are shown. First cluster is for locations: 3, 4, 1 and 5. Location 1, 3 and 5 are situated before the discharge of wastewater and the concentration of the parameters is approximately the similarand within the allowed limits. Location 4 is placed150 meters after the discharge of wastewater, but this location is specific in relation to other locations that are located after the discharge. The concentration of the analyzed parameters at this location depends on the time passed since wastewaters weredischarge, as well as the flow velocity.Huge flow and large distances allow dilution of wastewater, and concentrations of parameters are relatively low. In second cluster are locations 2 and 6. These locations are placed 20 meters after discharge of wastewater. Concentrations of all parameters are higher on these two locations compared to other locations. Concentrations of ammonia and orthophosphateare quite elevated and indicate that organic matter from municipal wastewater is breaks down and affectson the quality of the river Danube.

Conclusion

The river Danube is the most important river in Serbia, which is why it is of great importance to monitor the quality of the river. Level of contamination of the river is of great importance especially at locations where wastewater is discharged in river. In this paper is used multivariate statistical method which helps us to understand the processes within the river as

well as to obtain information of importance that can serve us for the planning of further monitoring. Environmental protection, especially surface water, is a multidisciplinary technique where in addition to the improvement of the monitoring system, it is necessary to use other methods (such as statistics) that will improve the quality of the environment.

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References
[1] Y. Ouyang, P. Nkedi-Kizza, Q.T. Wu, D. Shinde, C.H. Huang, Assessment of seasonal variations in surface water quality, Water Research, 2006 Vol. 40, Issue 20, pages 3800-3810
[2] C. Filik Iscen, Ö. Emiroglu, S. Ilhan, N. Arslan, V. Yilmaz, S. Ahiska, Application of multivariate statistical techniques in the assessment of surface water quality in Uluabat Lake, Turkey, Environ Monit Assess, 2008, Issue 144, Page 269.
[3] M. Vojinovic-Miloradov, I. Mihajlovic, O. Vyviurska, F. Cacho, J. Radonic, N. Milic, I. Špánik, Impact of wastewater discharges to Danube surface water pollution by emerging and priority pollutants in the vicinity of Novi sad, Serbia, Fresenius Environmental Bulletin, 2014, Issue 23, pages 2137-2145.
[4] M. Markovic, M. Vojinovic-Miloradov, Lj. Ignjatovic, B. Obrovski, A. Cavic, I. Mihajlovic, Ecological status of artificial accumulation lake Vrutci case study, Serbia Fresenius Environmental Bulletin. 2017, Vol. 26 Issue 8, pages 5184-5189
[5] V. Mićić, M. Kruge, P. Körner, N. Bujalski, T. Hofmann, Organic geochemistry of Danube River sediments from Pančevo (Serbia) to the Iron Gate dam (Serbia–Romania), Organic Geochemistry, 2010, Issue 41, pages: 971-974
[6] S. Kolarevic, J. Knezevic-Vukcevic, M. Paunovic, J. Tomovic, Z. Gacic, B. Vukovic-Gacic, The anthropogenic impact on water quality of the river Danube in Serbia: Microbiological analysis and genotoxicity monitoring, Archives of Biological Sciences, 2011, Issue 63, pages: 1209-1217
[7] B. Stanic, N. Andric, S. Zoric, G. Grubor-Lajsic, R. Kovacevic, Assessing pollution in the Danube River near Novi Sad (Serbia) using several biomarkers in sterlet (Acipenser ruthenus L.), Ecotoxicology and Environmental Safety, 2006, Vol. 65, Issue 3, pages 395-402,
[8] A. K.T. Kirschner, G. G. Kavka, B. Velimirov, R. L. Mach, R. Sommer, A. H. Farnleitner, Microbiological water quality along the Danube River: Integrating data from two whole-river surveys and a transnational monitoring network, Water Research, 2009, Vol. 43, Issue 15, pages 3673-3684
[9] B. Vrana, V. Klučárová, E. Benická, N. Abou-Mrad, R. Amdany, S. Horáková, A. Draxler, F. Humer, O. Gans, Passive sampling: An effective method for monitoring seasonal and spatial variability of dissolved hydrophobic organic contaminants and metals in the Danube river, In Environmental Pollution, 2014, Vol. 184, pages 101-112
[10] M. Djogo, J. Radonic, I. Mihajlovic, B. Obrovski, D. Ubavin, M. Turk-Sekulic, M. Vojinovic-Miloradov, Selection of optimal parameters for future research monitoring programmes on MSW landfill in Novi Sad, Serbia, Fresenius Environmental Bulletin, 2017, Vol. 26, Issue 7, pages 4867-4875