

Application of chemometrics in monitoring of spatial and temporal variations in river water quality and water classification

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Abstract: The Topčiderska River is the right tributary of the Sava River, with the length of its course of 31 km, and the catchment area of about 147 km². It represents one of the most polluted urban waters in the territory of the Republic of Serbia. Soil erosion, as well as the discharge of wastewater from certain parts of the city and from industrial zones located in its catchment, to the greatest extent cause the pollution of this river. Within this work, representative samples of Topčiderka River water sampled in different time periods and from different locations were analyzed. Over ten physico-chemical parameters were selected that best indicate the current quality of the river water. The obtained measurement results were subjected to chemometric analysis, using chemometric methods (HCA and PCA). Water quality was analyzed from two aspects, temporal and locational. Based on the results of statistical data processing, insight was gained into the variation in the water quality of the Topčiderska River and the causes of the resulting variation were revealed. Based on these conclusions, the water of this river was classified in accordance with the Regulation on limit values of pollutants in surface and underground waters and the Regulation on water classification. The obtained results show that the water of the Topčiderska River is highly polluted, and that according to the degree of pollution and purpose, it is classified as IV class.

Keywords: Topčiderska River, pollution, chemometric methods, classification

1. Introduction

The surface water quality control program in the territory of the City of Belgrade includes 24 watercourses with 30 control profiles, with water, sediment and hydrobionts (shellfish, fish) as the medium of the freshwater ecosystem. The monitoring is carried out in order to: assess the quality of watercourses, monitor the trend of pollution, the convenience of using them for the irrigation of agricultural areas, the convenience of using them for water supply, the health safety of citizens, monitoring the deposition of organic and inorganic micropollutants in the sediment, and their bioaccumulation in hydrobionts, the assessment of the ability of self-purification and eutrophication, preservation of water quality, rehabilitation, protection and improvement of watercourses.

The water of the Topčiderska River is tested in the laboratory for human ecology and ecotoxicology of the City Institute for Public Health Belgrade, once a month on the profile of the bridge near the Hippodrome, by sampling directly from the shore.

2. Material and methods

During the three-year period of monitoring the water quality of the Topčiderska River, samples from the water intake of the bridge near the Hippodrome were analyzed. Water quality and seasonal variation of quality parameters were examined, and the water class was determined according to the Regulation on limit values of pollutants in surface and underground waters [1]. 13 physico-chemical parameters were selected for regular monitoring. Samples were collected and analyzed once a month (except in January and February). The sample size was 30.

The water of the Topčiderska River was tested from the source to the mouth by sampling at 13 measuring points as shown in Figure 1.

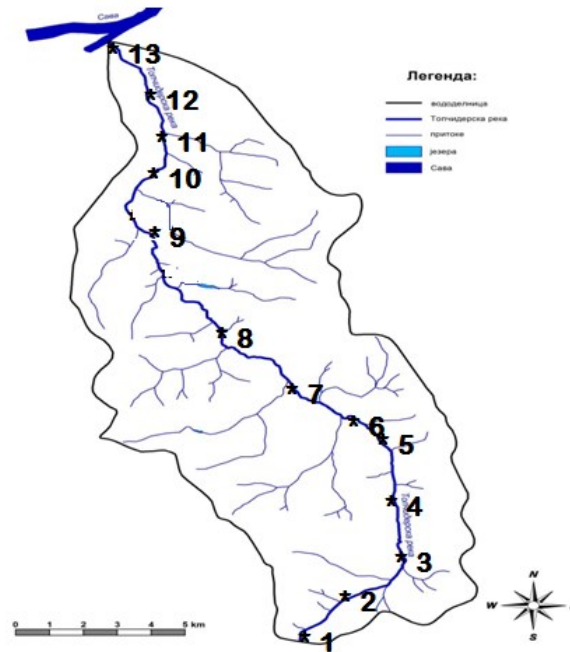


Figure 1. Description of study area – Topčiderska River basin and sampling sites.

Legend:

- | | |
|--|---|
| 1. The source of the Topčiderska River | 8. Entrance to the Rakovica engine factory |
| 2. Dućevac | 9. The exit from the Rakovica industrial zone |
| 3. Palanački potok | 10. Lisički potok |
| 4. Ripanj | 11. Topčiderski park |
| 5. Resnik (center) | 12. Topčider Barracks |
| 6. Settlement of Kijevo (Knezevac) | 13. Mouth of Topčiderska River |
| 7. Entrance to the industrial zone | |

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used in order to reveal the sources of pollution and to group locations according to the

similarity in the distribution of pollutants and to reduce the database i.e., reduced the number of variables required for monitoring.

3. Results and discussion

Basic statistical parameters were calculated for all selected parameters, and Table 1 shows the mean value, minimum and maximum value and standard deviation.

Table 1. Descriptive statistics of the results of the analysis of the physical and chemical parameters of water quality of the Topčiderska River in three years of monitoring.

Parameter	Number of samples	Max	Min	Mean	Standard deviations, %
Temperature, °C	30	26.0	5.4	16.69	6.30
pH value	30	8.5	7.8	8.1	0.18
Electrical conductivity, µS/cm	30	980	580	761.7	67.01
Alkalinity, mg/l	30	358.2	246.8	320.12	26.12
Total hardness, mg/l CaCO ₃	30	493.9	274.0	382.23	37.43
Suspended matter, mg/l	30	52	2	22.77	14.47
Total organic carbon, TOC, mg/l	30	16.2	4.85	7.63	2.79
Dissolved oxygen, mg/l O ₂	30	3.1	11.4	7.67	2.52
Chemical oxygen demand, COD, mg/l O ₂	30	75	3.5	17.89	15.02
Biochemical oxygen demand, BOD ₅ , mg/l O ₂	30	18.5	3.1	9.54	4.11
Nitrite nitrogen, mg/l N	30	0.805	0.002	0.34	0.20
Nitrate nitrogen, mg/l N	30	4.5	0.5	3.03	0.96
Total phosphates, mg/l	30	1.45	0.268	0.73	0.31

In this way, by applying multivariate chemometric methods, temporal/spatial variations in the water quality were performed. The classification and categorization of the water of the Topčiderska River at the sampling sites was carried out. The grouping of measurement sites by similarity and Euclidean distance is shown in Figure 2.

As can be seen from the dendrogram (Figure 2), 4 clusters were formed from 13 measurement locations. The first cluster includes five locations (8-12), the second, also, 5 measurement locations (2, 4-7), the third only one measuring point (3), and two locations (1,13) are grouped in the fourth cluster. The first cluster represents the measuring points next to the industrial zone and the surrounding area (8-12). The second cluster consists of populated places (2, 4-7). The third cluster represents only one location, Palanački potok (3) which is singled out as highly polluted. In the fourth cluster, they grouped samples from the source and mouth of the Topčiderska River (1 and 13), according to the measured very high values of conductivity and hardness, concentrations of chloride and bicarbonate, which indicates a high content of ionic species in the water. It is worth noting that the content of organic matter has increased in all locations, which means that this river is quite polluted because most of the parameters are above the maximum allowed concentration (MAC) parameters for water surfaces [1].

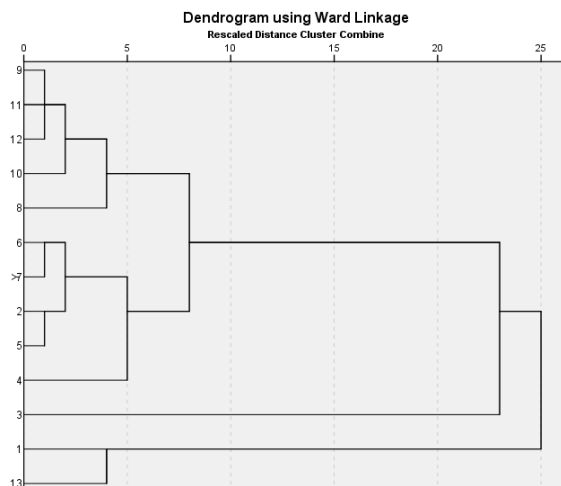


Figure 2. Dendrogram of sampling location grouping using HCA, *Ward Linkage* method.

Based on the PCA after Varimax rotation and the correlation matrix with the corresponding factors, hardness (UT), alkalinity and conductivity belong to the first component, with a very high factor loading over 0.7. The second component has the highest load of oxygen, phosphates and pH. Temperature and BOD belong to the third component, while the parameters HPK and TOC and total suspended matter, with a very high coefficient of 0.87 now belong to the fourth factor. Nitrates and nitrites are equally represented in all components.

3. Conclusions

The results obtained from this research show the great importance of multivariate statistical techniques for the analysis and interpretation of complex data sets obtained through multi-year monitoring. Using these chemometric statistical methods, the identification and distribution of pollution sources and factors responsible for the variability of parameters in water was carried out, which contributed to a better understanding of temporal/spatial variations in water quality, with the aim of more efficient management of water resources and adequate water classification [2, 3].

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