

Original Research

**MULTIVARIATE ASSESSMENT OF HEAVY METALS IN RIVER WATER FROM
NOVI PAZAR AREA**

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Abstract

Surface water pollution has become a serious global problem, particularly pollution caused by heavy metals. This study focused on ten heavy metals (Fe, Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb) in the water of the Raška River in the vicinity of Novi Pazar city, located in the southwestern part of Serbia, and on the investigation of the processes and activities governing these pollutants in the study area. Three multivariate statistical methods were applied, including principal component analysis supported by Pearson correlation analysis and hierarchical cluster analysis. The results indicated the presence of two principal components, which explained the vast majority of the variance in the dataset, accounting for 93.9%. It was determined that the occurrence of heavy metals in the study area is influenced by both natural processes, such as soil and rock weathering, and anthropogenic activities, including municipal and domestic wastewater discharge and agricultural activities. These results highlight the importance of identifying the main factors controlling heavy metal distribution in surface waters, as this provides a better understanding of water quality and supports more effective monitoring and management.

Keywords: principal component analysis, Pearson correlation, clustering, chemometric analysis, Raška River.

INTRODUCTION

Surface water represents one of the most important natural resources, as it is widely used for drinking water supply, agriculture, industry, and recreation. However, water systems are increasingly exposed to different types of pollution caused by urbanization, industrial development, agricultural activities, and inadequate wastewater management [1]. Among various pollutants, heavy metals are of particular concern because they are persistent in the environment, non-biodegradable, and may accumulate in aquatic ecosystems [2].

Heavy metals can enter surface waters from both natural and anthropogenic sources. Natural inputs are mainly related to the weathering of rocks and soils, while anthropogenic sources include municipal and domestic wastewater discharge, agricultural runoff, industrial

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activities, and traffic-related emissions [3,4]. Once released into aquatic systems, these elements may affect water quality and pose potential risks to aquatic organisms and human health.

Identifying the main processes that control heavy metal distribution in river water is essential for understanding pollution sources and improving water quality management. However, heavy metal concentrations are often influenced by several factors, which makes their interpretation complex. For this reason, multivariate statistical methods are widely used in environmental studies [5]. Pearson correlation analysis, hierarchical cluster analysis, and principal component analysis can help reveal relationships among elements, group pollutants with similar behaviour, and identify possible natural and anthropogenic sources [6].

The Raška River basin, located in the southwestern part of Serbia, is influenced by both natural geological conditions and human activities, including settlements, agriculture, and wastewater discharge. Therefore, this area represents a suitable case study for investigating the factors controlling heavy metal occurrence in surface waters. The aim of this study was to assess the relationships among selected heavy metals in river water from the Novi Pazar area and to identify the main processes affecting their distribution using multivariate statistical methods.

MATERIALS AND METHODS

Study area overview

The study area is located in the southwestern part of Serbia, in southeastern Europe. A total of 18 surface water samples were collected in the vicinity of Novi Pazar city, within the Raška River basin, as shown in Figure 1. The area is predominantly hilly to mountainous, with elevations ranging from approximately 390 to 1800 m above sea level. The climate is temperate continental, with an average annual precipitation of 750–850 mm [7]. The area is mainly covered by forests and pastures, with agricultural land occurring locally.

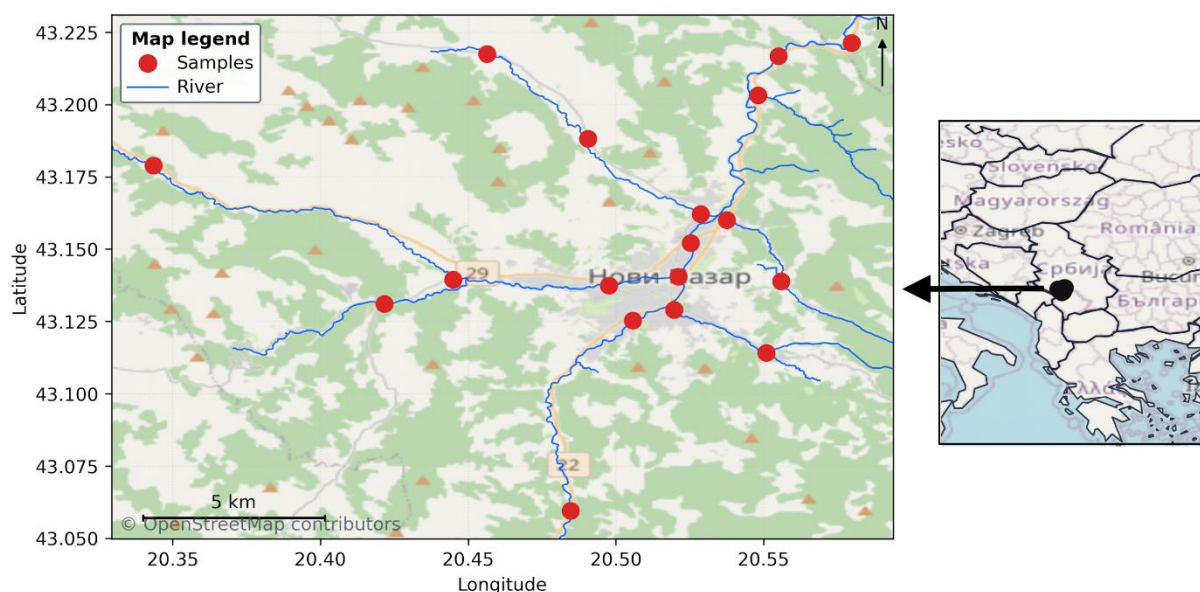


Figure 1 Overview of the study area with the locations of river water samples

Surface water sampling and heavy metal analysis

Surface water samples were collected in 1.5 L plastic bottles, which had previously been rinsed with distilled water and then with water from each sampling location. Samples were collected at approximately 20 cm below the water surface, with the bottle opening facing upstream. All samples were acidified on-site to $\text{pH} < 2$ using concentrated HNO_3 , in order to ensure that heavy metals remained dissolved in the water and to prevent their precipitation. After sampling, the samples were labelled, stored in a refrigerator, and then transported to the laboratory, where heavy metal concentrations were measured. A total of nine heavy metals were quantified in the surface water samples: Fe, Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb. The analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS; iCAP TQ, Thermo Fisher Scientific, USA). During the measurements, quality assurance and quality control procedures were followed. The instrument was regularly calibrated, reagent blanks and spiked water samples were analyzed after every six samples, and all analyses were performed in triplicate.

Multivariate statistical analysis

In this study, three multivariate analysis methods were applied. Pearson correlation analysis was used to examine the relationships among heavy metals. The strength of the correlation coefficient r was used to evaluate the degree of association between variables. Correlations were considered weak when $|r| < 0.5$, moderate when $0.5 < |r| < 0.7$, and strong when $|r| > 0.7$ [8,9].

For grouping heavy metals and metalloids according to their similarities, hierarchical cluster analysis was applied. This method is effective for revealing underlying relationships and variations in the dataset [5]. In this study, the analytes were clustered based on similarity using Ward's linkage method and Euclidean distance.

For data dimensionality reduction, principal component analysis was applied. This multivariate statistical method aims to transform a dataset containing correlated variables into a new set of uncorrelated variables. The number of principal components to be retained was determined using the Kaiser criterion, according to which only principal components with an eigenvalue greater than 1 were retained [5,6].

Before conducting multivariate analysis, the dataset was standardized in order to minimize the influence of different concentration ranges. The mentioned methods were used to determine the processes controlling the chemistry of heavy metals in the sampled surface water.

RESULTS AND DISCUSSION

Pearson correlation matrix of surface water samples is presented in Table 1, while dendrogram of heavy metals obtained via hierarchical cluster analysis is shown in Figure 2. It can be seen that a strong positive correlation was characterized for Fe and Mn ($r = 0.99$) and Fe and Cu ($r = 0.93$). Additionally, Cu showed a strong positive correlation with Mn ($r = 0.92$). These findings suggest that similar processes govern Fe, Mn, and Cu behaviour in surface water of the study area. Furthermore, another strong positive correlation was observed between Ni and Zn ($r = 0.92$) and Ni and Cr (0.77). Also, Cd showed a strong positive correlation with Zn and Pb ($r = 0.93$), while similar situation was observed for Pb with Co,

Cr, and Ni ($r > 0.82$). According to Pearson correlation matrix, it can be said that Ni, Zn, Pb, Cd, Cr, and Co share a similar origin. The results of Pearson correlation analysis were further supported by the hierarchical cluster analysis. As shown in Figure 2, all heavy metals were divided into two main clusters. The first cluster included Fe, Mn, and Cu, while the second comprised Ni, Zn, Pb, Cd, Cr, and Co. The grouping of heavy metals within the same cluster suggests that the analytes in each cluster are influenced by similar processes controlling their mobility and concentrations in surface water. In contrast, the analytes grouped in the separate cluster are likely affected by different environmental or anthropogenic processes.

Table 1 Pearson correlation matrix of surface water samples in the Novi Pazar area

Analyte	Fe	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Fe	1	0.24	0.99	0.50	0.65	0.93	0.41	0.30	0.41
Cr	0.24	1	0.17	0.81	0.77	0.37	0.82	0.72	0.82
Mn	0.99	0.17	1	0.43	0.60	0.92	0.34	0.23	0.33
Co	0.50	0.81	0.43	1	0.92	0.59	0.97	0.85	0.97
Ni	0.65	0.77	0.60	0.92	1	0.74	0.92	0.87	0.91
Cu	0.93	0.37	0.92	0.59	0.74	1	0.52	0.44	0.52
Zn	0.41	0.82	0.34	0.97	0.92	0.52	1	0.93	1.00
Cd	0.30	0.72	0.23	0.85	0.87	0.44	0.93	1	0.93
Pb	0.41	0.82	0.33	0.97	0.91	0.52	1.00	0.93	1

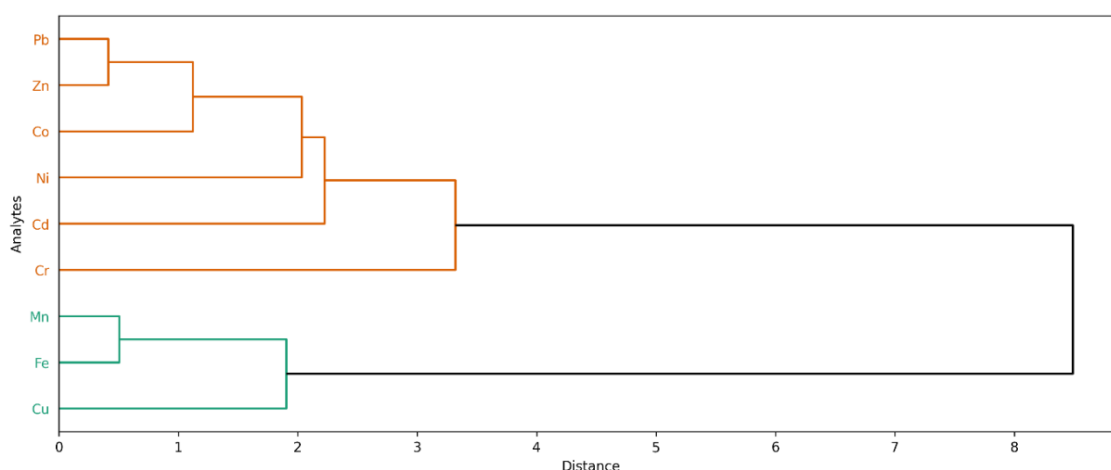


Figure 2 Dendrogram of surface water samples in the Novi Pazar area

For a more detailed determination of the processes controlling the behavior of heavy metals in the investigated water, principal component analysis was also performed. The scree plot is shown in Figure 3a, while Figure 3b presents the biplot of the first two principal components with scores and loadings. The loading values for each principal component with an eigenvalue greater than 1, together with the percentage of explained variance, are given in Table 2. The results indicate that two principal components were characterized by eigenvalues greater than 1, and therefore these two components were retained for further analysis. These two principal components explained the vast majority of the variance in the data, amounting to 93.9%.

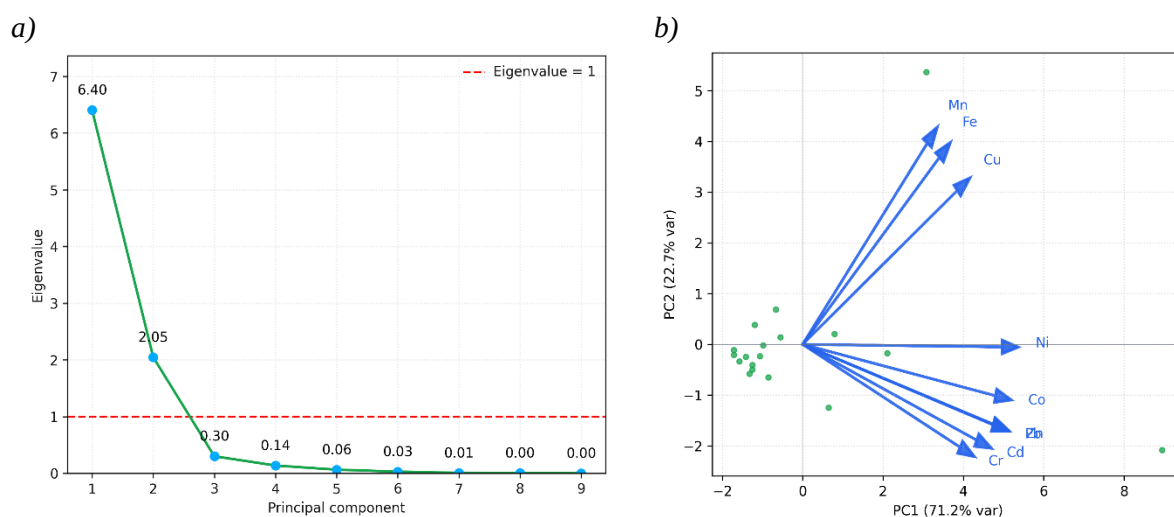


Figure 3 Scree plot of all principal components (a) and biplot of the first two principal components showing score and loading values

Table 2 Loadings of the first two principal components with eigenvalues greater than 1

Analyte	PC1	PC2
Fe	0.206	0.971
Cr	0.880	0.052
Mn	0.127	0.987
Co	0.920	0.314
Ni	0.850	0.494
Cu	0.348	0.906
Zn	0.969	0.213
Cd	0.932	0.118
Pb	0.966	0.210
Cumulative explained variance (%)	71.2	93.9

The first principal component (PC1) explained 71.2% of the variance and had strong loadings of Cr, Co, Ni, Zn, Cd, and Pb. Nickel, Cd, Pb, and Zn are metals whose presence in the environment is mostly explained as a consequence of anthropogenic activities. Namely, Ni, Cd, Pb, and Zn enter surface waters through the discharge of municipal and domestic wastewater into rivers [10,11]. Since the Raška River, where sampling was conducted, passes through a large number of villages, as well as the town of Novi Pazar, municipal and domestic wastewater can be considered one of the processes controlling the levels of heavy metals in the investigated water. Additionally, Cu, Zn, and Cd are often explained as a result of the excessive use of artificial fertilizers [12]. Therefore, PC1 can be interpreted as an anthropogenic factor.

On the other hand, the second principal component (PC2) explained 22.7% of the variance and was mainly associated with negative loadings of Fe, Mn, and Cu. In the environment, Fe and Mn are considered to be predominantly of geogenic origin, since they are common constituents of the Earth's crust [13]. High loadings of Fe and Mn suggest that these elements may be associated with Fe–Mn oxide/hydroxide phases. Fe and Mn often originate from rocks, soils, and sediments. When river turbidity increases, erosion or sediment resuspension

may occur, allowing these elements to be released into the water [14]. Copper can bind to Fe/Mn oxides and sediments, which may explain why it appears in the same principal component [15]. Hence, PC2 can be explained as natural factor.

CONCLUSION

This study examined the factors controlling heavy metal distribution in the surface water of the Raška River, in the vicinity of Novi Pazar, using Pearson correlation analysis, hierarchical cluster analysis, and principal component analysis. The obtained results indicate that the observed heavy metal concentrations are shaped by several controlling factors, including weathering of soil and rocks, municipal and domestic wastewater discharge, and agricultural practices. These findings highlight the importance of source identification for understanding the processes that influence surface water quality in the Raška River basin.

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