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Potentially toxic elements in sediments near mines – a comprehensive approach for the assessment of pollution status and associated risk for the surface water environment

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Abstract:	This research is focused on the assessment of the pollution status of river and lake sediments near Pb, Zn, and Cu mines and tailings in the most southeastern part of Serbia - Krajište area. High potentially toxic elements (PTEs) contents are detected in studied river sediments (up to 7892 mgkg-1 for Zn, 3224 mgkg-1 for Cu, 36790 mgkg-1 for Pb, 64.2 mgkg-1 for Cd, and 1444 mgkg-1 for As). Given that the contents of the studied elements in most of the river sediments exceeded the background values, values prescribed by regulations of the Republic of Serbia, as well as probable effect concentration (PEL), it is possible to conclude that sediments were heavily polluted and that detrimental effects can be expected. Contamination indices including EF, CF, Igeo, Eri, RI, PLI and ATI were used to assess the degree of pollution by PTEs. The ecological risk assessment revealed that there is a significant risk observed for toxic elements (primarily Pb, Cu, Cd and As) at this moment. The highest contamination indices (EF, Igeo, CF, PLI, ATI) are mainly associated with historical and current mining activities. The Monte Carlo analysis based on the risk assessment indices was used to evaluate the uncertainty. The most pronounced toxic risk is found for the Pb, Cu, Cd and As which assessment was in the range of high and extremely high-risk

	probabilities. The obtained results suggest that levels of toxic elements pose a significant ecological risk to the surface water environment near Pb, Zn, and Cu mines in the Krajište area. The methodology applied in this paper could be very useful for other researchers dealing with the problem of environmental pollution by toxic elements.
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Dear Editor,

We are pleased to submit an original research article entitled **"Potentially toxic elements in sediments near mines – a comprehensive approach for the assessment of pollution status and associated risk for the surface water environment"** by Sanja Sakan, Aleksandra Mihajlidi-Zelić, Nenad Sakan, Stanislav Frančišković-Bilinski, Igor Kodranov and Dragana Đorđević for consideration for publication in **Environmental Science and Pollution Research**.

We show the first results on the influence of mining activities on river sediments in Eastern Serbia, offering insight into the problem of Pb, Zn, As and Cu contamination in river systems. The impact of the mining activities in the Karamanica and Blagodat ore fields on the pollution status of river and lake sediment was estimated in this research. The main goal of this research was to evaluate the level and distribution of toxic elements (i.e., Pb, Cd, Cu, Zn, As, Mn, Ni and Cr), assess the contamination degree of sediments using contamination indices, (EF, CF, Igeo, Eri, RI, PLI and ATI) and evaluate the uncertainty associated with the risk assessment indices using Monte Carlo analysis. The methodology applied here, namely the combined use of pollution indices, geochemical background values, magnetic susceptibility, statistical analysis, and Monte Carlo analysis, gives a suitable information about contamination levels, sources of PTEs, as well as the current and future potential risks of mining activities to the downstream environments. Those methods have been used separately earlier, but their combined use is proven to be a more valuable tool for the analysis of the situation since if the several independent methods point to same result, the certainty of the obtained data is more pronounced.

We hope that our manuscript meets criteria to be published in **Environmental Science and Pollution Research**, since it deals with the ecological risk assessment and evaluation of the pollution status of surface waters, especially taking into account that the problem of surface water pollution is growing globally and that the lack of clean drinking water has been observed all over the world.

All co-authors agree with the contents of the manuscript, everyone meriting authorship in this work has been named above, and there is no conflict of interest involving this study. This manuscript has not been published before and it is not under consideration for publication anywhere else. Its publication has been approved by all co-authors. I have not submitted my manuscript to a preprint server before submitting it to **Environmental Science and Pollution Research**.

Sincerely,

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Potentially toxic elements in sediments near mines – a comprehensive approach for the assessment of pollution status and associated risk for the surface water environment

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Abstract

This research is focused on the assessment of the pollution status of river and lake sediments near Pb, Zn, and Cu mines and tailings in the most southeastern part of Serbia - Krajište area. High potentially toxic elements (PTEs) contents are detected in studied river sediments (up to 7892 $mgkg^{-1}$ for Zn, 3224 $mgkg^{-1}$ for Cu, 36790 $mgkg^{-1}$ for Pb, 64.2 $mgkg^{-1}$ for Cd, and 1444 $mgkg^{-1}$ for As). Given that the contents of the studied elements in most of the river sediments exceeded the background values, values prescribed by regulations of the Republic of Serbia, as well as probable effect concentration (PEL), it is possible to conclude that sediments were heavily polluted and that detrimental effects can be expected. Contamination indices including EF, CF, Igeo, Eri, RI, PLI and ATI were used to assess the degree of pollution by PTEs. The ecological risk assessment revealed that there is a significant risk observed for toxic elements (primarily Pb, Cu, Cd and As) at this moment. The highest contamination indices (EF, Igeo, CF, PLI, ATI) are mainly associated with historical and current mining activities. The Monte Carlo analysis based on the risk assessment indices was used to evaluate the uncertainty. The most pronounced toxic risk is found for the Pb, Cu, Cd and As which assessment was in the range of high and extremely high-risk probabilities. The obtained results suggest that levels of toxic elements pose a significant ecological risk to the surface water environment near Pb, Zn, and Cu mines in the Krajište area. The methodology applied in this paper could be very useful for other researchers dealing with the problem of environmental pollution by toxic elements.

Keywords: mining activities, toxic elements, magnetic susceptibility, contamination indices, Monte Carlo simulation, river sediments

Introduction

The dynamics of the behaviour of PTEs in freshwater environments have been one of the main focuses of environmental monitoring in the last years. High toxicity and nonbiodegradability of PTEs in the environment have raised extensive concern (Chen et al., 2019), and the presence of these elements in river systems is considered an indicator of anthropogenic influence. PTEs represent significant hazard to aquatic environment because anthropogenic sources are globally widespread and there is a fast increase in their number (Ustaoğlu et al., 2020). Natural processes, such as rock weathering can also emit toxic elements, but their contribution is small (Haris et al., 2017). One of the significant sources of environmental pollution by toxic elements are mining activities. Mine tailings, the waste material leftover after the extraction of target minerals from the ore material, frequently contain high contents of PTEs (García-Giménez and Jiménez-Ballesta, 2017). Various researchers have studied the impact of active and closed mines on aquatic ecosystems (Ayari et al., 2023; Barago et al., 2023; Lidman et al., 2023; Maftei et al., 2014; Shen et al., 2019; Shikazono et al., 2008, Yucel et al., 2018). The results of these studies indicate that all processes related to mining activities during exploitation, but also after their closure caused significant water contamination.

PTEs in the environment can have deleterious effects on the health of living biota through the food chain and water supply (Ayari et al., 2023). Sediments have a high retention capacity for PTEs which can be subsequently released into water, therefore many studies have investigated PTE levels in sediments and surface water (Haris et al., 2017). Given that PTEs are very toxic, a mere comparing their sediment content with the geochemical background values may not give the appropriate information on PTEs' adverse impacts on the ecosystems (Ustaoğlu et al., 2020). For that reason, many other additional methods are used to assess the degree of pollution in river and lake systems. According to Kowalska et al. (2018), pollution indices are crucial for the proper assessment of toxic elements contamination of soil and sediment. The most widely used indices are Contamination factor (CF), Enrichment factor (EF), Index of geoacumulation (Igeo), Potential ecological risk index (Eri), Ecological risk index (RI), and Pollution load index (PLI) (Ayari et al., 2021; Gantayat et al., 2023; Haris et al. 2017; Pujiwati et al., 2022). One of the relatively new indices, known as the Aggregative toxicity index (ATI), proved to be very significant in assessing the degree of contamination. Jamshidi-Zanjani and Saeedi (2017) developed this index and ATI was also applied in the Sakan et al. (2023). Furthermore, more accurate information on contamination levels and sources can be provided when pollution indices are applied along with geochemical background values (Maftei et al., 2014).

In addition to chemical analyses to determine levels of toxic elements and subsequent processing of data to assess the degree of pollution in soil and sediment, magnetic susceptibility (MS) is also used as a proxy for chemical methods for the assessment of soil and sediment pollution. This method is rapid, simple and non-destructive. Pollutants and magnetic particles are usually associated, enabling the use of magnetic susceptibility as an indicator of pollution; however, the intricacy of these relationships makes it hard to construct a single function to compute pollutant concentrations from MS (Paradelo et al., 2009). Combined use of magnetic susceptibility and pollution indices (Duodu et al., 2016) is a valuable tool for the assessment of sediment pollution status (Chaparro et al., 2020).

The importance of more precise determining of the uncertainties has led us to apply a Monte Carlo simulation, as it was seen in a number of manuscripts (Fakhri et al., 2018). Based on the input, as it was done in manuscript by Fakhri et al. (2018), data health risks has been defined as a mean of variability in health risk assessments and quantifying uncertainty, while the Monte Carlo simulation is applied to perform the probabilistic risk assessment.

Mine tailings represent a significant risk to the environment even after mining activities have terminated because of the presence of toxic elements (García-Giménez and Jiménez-Ballesta, 2017). The environment in Serbia, due to the long history of mining on its territory, is also affected by this threat. Taking that into account, the content of several toxic elements and their geochemical impact on the river and lake pollution status in the Krajište area (southeastern Serbia), near mines and their tailings were studied in this research. Namely, the impact of the mine tailings located in the Karamanica ore field with deposits of Pb, Zn and Cu ore, and the Blagodat ore field containing Pb and Zn ore was investigated.

Although negative effects of the flotation tailings in the Blagodat ore field, near the village of Kriva Feja, on the streams and soil in the vicinity of flotation tailings have been reported (Đokić et al., 2013; Đokić et al., 2012; Đorđević et al., 2012), data regarding the influence of the Musulj-Kekerinci dump in the Blagodat ore field on the surrounding rivers are extremely scarce, and the environmental impact of mining activities in the Karamanica ore field has not been investigated yet. For that reason, the content of several toxic elements in river sediments near the Musulj-Kekerinci dump (Blagodat ore field) and the flotation tailings pond in the Karamanica ore field and their geochemical impact on the river and lake pollution status were investigated.

The specific objectives of this study were: (1) to evaluate the level and distribution of toxic elements (i.e., Pb, Cd, Cu, Zn, As, Mn, Ni and Cr) content in sediment samples taken from the rivers and lakes near the area of mines and their tailings; (2) to assess the sediment contamination level using contamination indices, including EF, CF, Igeo, Eri, RI, PLI and ATI; 3) application of magnetic susceptibility for assessing the PTE pollution levels; (4) evaluating the uncertainty associated with the risk assessment indices using Monte Carlo analysis; and (5) to differentiate between natural and anthropogenic sources of contamination. This kind of research has not previously been conducted in this area. For detailed research, in addition to chemical methods, magnetic measurements are also included, as well as the application of statistical methods, including Monte Carlo simulation. We expect that the obtained results will be of great importance for the assessment of the ecochemical status of the examined locality and in showing the influence of (old) tailings and pilot plants on pollution with toxic elements, which is also of great importance due to the proximity of the border with Bulgaria and the possibility of transboundary pollution. We believe that the combination of applied methods will be extremely valuable for other researchers dealing with the issue of pollution with toxic elements not exclusively related to metal mining.

Materials and methods

Study area and sampling

In the period from August 13 to 14, 2020. samples of sediments were collected in surface waters in the Krajište area in southeastern Serbia (Fig. 1). GPS coordinates and the names of the localities are shown in Table 1. Eight samples of river sediment and two samples of lake sediment were taken during sampling. Sediment samples were taken with a plastic spatula.

The Karamanica ore field is located in the southeasternmost part of Serbia, on the southern slopes of the Bele Vode mountain (1829 m a.s.l.), southwest of the town of Bosilegrad and close to the border with Bulgaria and North Macedonia. The mine exploits Podvirovi and Popovica deposits of lead, zinc and copper ore located near Karamanica village. Popovska and Karamanička rivers, tributaries of the Golema river, and the Nameless stream that flows into the Karamanička river, stretch through the exploitation field. Additionally, occasional torrential tributaries of Popovska and Karamanička rivers flow through the exploitation field. The Golema river is a tributary of the Brankovačka river, which empties into the transboundary Dragovištica river. Dragovištica river in Bulgaria joins the Struma river, eventually draining into the Aegean Sea. The location of planned mines of the Karamanica ore field includes a part of the ecologically important area of the Ecological Network of the Republic of Serbia - Prime Butterfly Area – PBA. To test flotation technology for processing lead, zinc and copper ore from the Podvirovi and Popovica deposits, a pilot plant was built (Request for EIAS, 2021). The pilot facility, which includes the flotation tailings pond, is located less than 5km from the borders of Serbia with Bulgaria and North Macedonia, and was operating at the time of sampling. The Nameless stream that flows into the Karamanička river flows alongside the flotation tailings pond. The sediments analyzed in this manuscript were taken from The Nameless stream that flows into the Karamanička river (two samples, upstream and downstream of the flotation tailing dump of the Podvirovi ore deposit pilot plant), as well as from Golema and Brankovačka rivers.

Grot mine (EX Blagodat mine) is a lead-zinc mine located in the Blagodat ore field, on the southeast side of the mountain Besna Kobila, in the southeastern part of Serbia, near the village of Kriva Feja and around 20 km from the state borders with Bulgaria and North Macedonia. From the western slopes, the waters flow into the Barisavička and Jelašnička rivers towards the South Morava river and the Danube, which empties into the Black Sea. From the eastern slopes, the Musuljska and Crna rivers, tributaries of the Ljubatska river, together with Ljubatska river flow into the transboundary river Dragovištica, a tributary of the Struma river, which flows into the Aegean Sea. A part of the Ljubatska river is directed into the Lisina lake, a reservoir built on the confluence of the Lisinska and Božička rivers, and from there the water is pumped through the Božica channel into the Vlasina lake, a reservoir formed on the Vlasina river. The reservoirs of the Vlasina and Lisina lakes together with the system of channels and tunnels and four hydropower plants represent the hydropower system Vlasina. Vlasina lake is a protected natural asset (category I) of exceptional importance. In addition, the area of Vlasina is included in the internationally significant areas for birds - IBA (Important Bird Areas), for plant species - IPA (Important Plant Areas), and, as a wetland of international importance, in the list of Ramsar areas.

The Blagodat ore field includes Blagodat, Đavolja Vodenica, Vučkovo II, and Kula deposits (https://www.mindat.org/loc-62233.html). The first commercial research and ore exploitation in these areas was organised by the Italian Mining Company "Societe Comercial d'Oriente" in 1903 (Stojmenović et al., 2017). More recently, geological, geochemical and geophysical investigation of the Blagodat ore field in the 60s and 70s resulted in a mine opening, which is still active. The tailings that accompanied mining activities in the Blagodat ore field are located in two places. The oldest one, occupying 6,628 m^2, in the vicinity of which river sediment samples were taken, is located in Musulj - Kekerinci Mahala near the confluence of Krasnodolska river and Crna river, where tailing material deposited more than a century ago, together with recent mine waste material, contaminates Crna river and still prevents the development of plants in this location (Đokić, 2012; Đokić et al., 2012; Đokić and Jovanović, 2008). In this manuscript, samples were taken from Krasnodolska river, Crna river (two samples, upriver and downriver from the confluence with Krasnodolska river) and Ljubatska river (before the water intake for Lisina lake), as well as samples from Lisina and Vlasina lake. Sediment samples of the Krasnodolska and Crna rivers were taken in the vicinity of their confluence, near the Musulj - Kekerinci dump.

Research methodology

Sample analysis

After taking sediment samples in the field and arriving at the laboratory, samples were air-dried for 8 days before analysis (Arain et al., 2008). Analysis of dried sediments was performed using BCR sequential extraction (Sakan et al., 2016; Sutherland 2010). The procedure is described in more detail in the Supplementary material. After obtaining the extracts, the content of studied elements was determined using Thermo Scientific ICP-OES iCap 6500 Duo and Thermo Scientific ICP-MS iCap Q.

In this research, the contents of the following elements were determined in each sample: Pb, Cd, Cu, Zn, As, Mn, Ni, Cr, Al, B, Ba, Ca, Co, Fe, K, Li, Mg, Na, P, S, Sr, and V. The results are expressed in mg kg^{-1} dry sediment.

Within this manuscript, the presented results refer to the total contents of elements and the calculation of contamination factors and the assessment of the degree of pollution was performed using methods related to the total content of elements. The total content is represented by the sum of the extracted content of each element individually during the three steps of BCR sequential extraction and digestion using aqua regia, which represents an additional fourth extraction step that is not part of the standard BCR extraction procedure.

Magnetic susceptibility (MS)

The magnetic susceptibility was measured in the dried sample using a magnetic susceptibility meter SM30 (Sakan et al. 2022) and the mean value of three consecutive measurements was taken as a final result.

Toxic element pollution indices

For the quantification of pollution level of studied sediments the following contamination indices were calculated: Enrichment factor (EF), Contamination factor (CF), Index of geoaccumulation (Igeo), Ecological risk factor (Eri), Ecological risk index (RI), Pollution load index (PLI) and Aggregative toxicity index (ATI). Definitions and detailed explanation of the calculation of pollution indices are presented in the Supplementary material. As geochemical background contents the 75th percentiles of the frequency distribution of the data were used (Dos Santos and Alleoni, 2013).

Statistical analyses

Descriptive statistical parameters, as well as correlation analysis, were applied to investigate the distribution of studied elements. For statistical analyses, IBM SPSS 21 software was used.

Monte Carlo simulation

A Monte Carlo analysis based on mathematical statistics and probability theory was used to assess model uncertainty by random sampling of a probability distribution for each variable (Qu et al., 2018). In this manuscript, the Monte Carlo simulation was applied to estimate the distribution of the toxic element content (or Eri and HRI) in river sediments in order to determine a probability distribution (i.e., uncertainty) for the assessment metrics with a purpose of evaluation of uncertainty associated with the risk of toxic elements in the studied area.

Results and discussion

Performance of the analytical procedure

The accuracy of the obtained results was checked by analysing sediment reference material (BCR-701) for three-step sequential extraction. The average recovery values for heavy metals in the standard reference material were in the range of 77.2–121.2%. The relative standard deviations of the means of duplicate measurement were less than 10%. Expanded uncertainty of the measurement with coverage factor 2 was max. 6%.

Element content in studied river sediments

The descriptive statistics of 22 elements are shown in Table 2**.** The spatial distribution of the content of selected elements, some of which are very significant due to their toxicity, is shown in Figs. 2a and 2b.
Distribution of the element's contents by locality indicates that in locality 4 (Brankovačka river), increased content of barium was observed compared to other localities, and that the contents of Cr, V, and Sr in sediment are also increased at this locality. More depicted in Fig. 2b, sediment collected at locality 6 (Crna river) contains a much higher content of Pb than sediments in other localities.
For the preliminary risk assessment, the total content of the studied elements was compared with the: 1) limit and remediation values prescribed by the Regulation of the Government of the Republic of Serbia (2012); 2) threshold effect concentration (TEC) and probable effect level (PEL); 3) element concentrations in the continental crust (Wedepohl, 1995) and background values, and 4) as well as with data for river sediments in the world. The TEC and PEL are defined in MacDonald et al. (2000).
The obtained results show that the studied river sediments contain very high levels of PTEs. The total content of elements were up to 7892 $mgkg^{-1}$ for Zn, 3224 $mgkg^{-1}$ for Cu, 36790 $mgkg^{-1}$ for Pb, 64.2 $mgkg^{-1}$ for Cd, and 1444 $mgkg^{-1}$ for As. The mean values of Zn, Cu, Pb, Cd, and As contents are higher than the maximum allowable values (MAV) and remediation value (RV) (Government of the Republic of Serbia, 2012). The Ni content is similar to the MAV value, while the Cr content is lower, which indicates the geochemical origin of these elements. The contents of As, Cd, Cu, and Pb in river sediment were characterised by high coefficient of variation values (CV $\geq$ 100 %) (Table 2; Fig. 2). The highest value of the coefficient of variation was observed for Pb, followed by As

and Cu, while the CV for Cd has a value of 100 %. The mean values of these PTEs, as well as Zn were much higher than the geochemical background and element content in the Continental Crust (Tables 2 and 3). The content of Ni and Cr is slightly higher compared to the estimated background value (Table 3), which may be a consequence of the specific geochemistry of the investigated localities. The levels of As, Cd, Cu, Pb, Zn, and Ni exceeded PEL, which indicates that these elements pose a potential risk to aquatic life in studied rivers. Ni exceeded the TEC levels and the Cr content is similar to the TEC level, so it is possible to conclude that investigated river systems are not polluted with these elements.

The results of comparisons of the content of other elements with the crust values show that the content of Al, Ba, Ca, Co, Li, Mg, Na, Sr, and V (mean value) is lower, while the content of B, Fe, K and Mn larger than the crust values. Slightly higher content of these elements in relation to crust values is associated with specific geology in certain localities. It is known that manganese sulfides are present to a greater or lesser extent along with sulphides of lead, copper, and cadmium. The increased content of Ca and Co indicates an increased content of carbonates in the mentioned localities, i.e. specific rocks with a higher cobalt content.

Results of comparison with other studies have shown that the mean content of Pb, Cd, Zn, Cu, and As in studied river sediments were similar to data for the areas worldwide affected by the mining activities (Table 3). The mean values of Cu, Pb, Cd, and As contents in the surveyed river sediment on the territory of Krajište are higher compared to the values listed in Table 3 for the river sediment located near the mine area in Tunisia (Ayari et al., 2023), Romania (Maftei et al. 2014), Japan (Shikazono et al. 2008), UK (Wolfenden and Lewin, 1978), Spain (Oyarzun et al. 2011) and China (Shen et al., 2019). The results for stream sediment, in terms of Zn and Cd contents, in Guizhou province, China (abandoned Zn–Pb smelter, Hezhang Country), which were presented in the paper by Yang et al. (2010), are higher than the values obtained in our research, but the content of Pb is higher than in Guizhou province, even though these sediments are affected by the abandoned Zn–Pb smelter. It is possible to conclude that water originating from the area near the flotation tailings and pilot plant contains high concentrations of toxic elements.

Magnetic susceptibility (MS)

The values of magnetic susceptibility and results of the determination of anomalies (extremes and outliers) by the Box plot method are shown in Table S1. Correlations between MS and elements contents are presented in Table S2.

MS shows a very high positive correlation with Pb and P. Correlations between magnetic susceptibility and Pb are also shown in the literature (Karimi et al., 2011). Desai et al. (1989) reported some aspects of the magnetic susceptibility of ferroelectric magnesium hydrogen phosphate crystals, which may explain the existence of a relationship between phosphate and magnetic susceptibility in the investigated area.

Despite the following correlations are not statistically significant, correlations with Co, Fe and K should also be mentioned. The existence of a positive, but weak correlation of MS with Fe and K indicates that magnetic susceptibility is influenced by the high contents of iron-bearing ferromagnetic minerals, but also clays minerals (Putra et al., 2019).

Anomalies of studied elements and magnetic susceptibility (MS) have been determined, using a boxplot statistical approach. Elements with anomalies are: Cr, Pb, Al, Ba, Co, P, Sr, as well as MS.

When looking at cases (sampling locations), it was found that the most anomalous location is 6 (Crna river, upriver from the confluence with Krasnodolska river), with four extremes: Cr, Pb, P and MS. As according to correlation analysis, MS is in very good correlation with Pb and P, also in a weak correlation with Cr, it could be assumed that they form an association, probably associated with some ore occurrence.

The second anomalous location is 4 (Brankovačka river), with extremes of Cr, Ba and Sr and an outlier of Al. This could be due to the local geological composition of surrounding rocks.

Two more locations show one anomaly: 5 (Krasnodolska river) an extreme of P, and 1 (The Nameless stream) one outlier of Co, which is the result of the specific geological composition of the rocks in the aforementioned localities.

Classification values of topsoil magnetic susceptibility (Magiera, 2022) are presented in Table S3. The obtained MS values (Table S1) of the examined sediment samples were compared with the MS classification values for the soil (Table S3). The value of MS in sample 6 (Crna river) is greater than 1×10^{-3} SI units, which indicates that at least one element concentration is above the threshold value. At this site, the Pb content is extremely high and many of the contamination factors calculated for this site are extremely high.

Contamination indices

The grades of contamination and ecological risk based on the calculated factors (i.e. EF, CF, Igeo, Eri, RI, PLI, ATI) are shown in Tables S4 and S5.

Enrichment factor (EF)

Calculated enrichment factors (EF) for analyzed sediments are presented in Fig. 3a. The EF values were interpreted according to Acevedo-Figueroa (2006). EF values are calculated using Al as a normalizer. Being the main component of fine-grained aluminosilicate minerals, and as such, a good surrogate for clay particles (Donkor et al., 2005), Al has been the most frequently used tracer element in normalization calculations/models. As background values, 75 percentile of the frequency distribution (Dos Santos and Alleoni, 2013) of the element content in sediments from the Vlasina river watershed are used (Table 3). The reason for this choice of values for the background content is that the sediments of the rivers in the Vlasina region have been shown to be uncontaminated by toxic elements (Sakan et al., 2023; Sakan et al., 2022).
As shown in Figure 3a and Table S4, the sediment samples were extremely severely enriched with Zn, Cu, Pb, Cd and As, moderately severely enriched in Mn and minor enrichment was observed for Ni and Cr. The highest EF values were calculated in sediments at site 6 (Crna river) which was sampled upriver from the confluence with Krasnodolska river, close to the tailing dump.

Contamination factor (CF)

The calculated results for the contamination factors (CF) are given in Fig. 3b. In accordance with the grades of contamination factor (Table S5), CF is classified into four groups in Pekey et al. (2004) and Hakanson (1980). This investigation showed that CF values for studied elements ranged from 0.87 to 1774 (low to very high contamination). According to the analysis of the data, the order of mean CF values in sediment samples, indicating the degree of sediment contamination by the individual element, is the following: Pb >> Cd > Cu > As > Mn > Cr > Ni. Again, the highest CF values were calculated for sediments at site 6 (Crna river).

Index of geoaccumulation (Igeo)

The calculated Igeo values are shown in Figure 4a. Müller (1979) proposed seven grades or classes of pollution level (Table S4). The calculated results of Igeo indicated that investigated sediments were uncontaminated to strongly contaminated by Pb; uncontaminated to moderately contaminated with respect to Zn, Cu, Cd and As, and that the degree of contamination of sediments by Ni, Cr and Mn was in the range of uncontaminated to uncontaminated to moderately contaminated.
According to the mean values of Igeo, the pollution of studied sediments by elements is decreasing in the following order: Pb > Zn > Mn > Cd > Cu > As > Cr > Ni, which is consistent with the calculated EF values.

Ecological risk factor (Eri)

The results of the evaluation of potential risk factor (Eri) are summarized in Figure 4b. The Eri for studied elements and the associated ecological risk were as follows: Zn (1 - 106) – low to considerable; Ni (4.30- 11.13) – low; Cu (4.34- 661) - low to very high; Cr (2.98 – 9.21) – low; Pb (3.62 - 8837) - low to very high; Cd (3.91- 4189) - low to very high; and As (3.78 - 1301) - low to very high ecological risk. It was observed that the values of potential risk factor correspond to low to very high ecological risk (Cu, Pb, Cd, and As), considerable (Zn), and low ecological risk (for Ni and Cr). The mean Eri values for studied elements in descending order were: Cd > Pb > As > Cu > Zn > Ni > Cr. It should be emphasized that the high mean value of Eri for Cd compared to Pb and other elements is a consequence of the fact that the potential ecological risk factor of a single toxic element is calculated from the perspective of the biological toxicity of elements.

Ecological risk index (RI)

The RI represent the sum of individual elements risk factors. The calculated values of RI (Tables S5 and S6, Fig. S1) are in the range from 24.40 to 9637, indicating low to very high ecological risk in the investigated area (mean value is 3971). The results showed that there was low potential ecological risk for the sediment sample collected from Vlasina lake, and higher ecological risk at other localities. Fig. S2 shows the contribution of different PTEs to the average potential ecological risk index (RI). The contribution of each element to the average RI is the following: Cd (42%) = Pb (42%) > As (9%) > Cu (6%) > Zn (1%), while the contribution of Ni and Cr is 0%. As well as for EF and CF, the highest RI values were calculated for sediments at site 6 (Crna river).

Pollution load index (PLI)

The results of the PLI are presented in Table S6 and Fig. S1. The value PLI > 1 indicates the existence of pollution; otherwise, if the PLI < 1, there is no metal pollution (Tomlinson et al., 1980). In this study, the average PLI value for sediment samples was 13.78, ranging from 0.65 to 27.81, which indicated no pollution for Vlasina lake, and elevated pollution level for all other localities: high ecological risk (1,2 - the Nameless stream emptying into Karamanička river, 3 - Golema river, 5 -Krasnodolska, 6, 7 - Crna and 8 - Ljubatska rivers), considerable (9 - Lisina lake) and moderate ecological risk (4 - Brankovačka river).

Aggregative toxicity index (ATI)

In Tables S6 and Fig. S1 the results of ATI values for studied localities are shown. The parameters used to calculate the aggregative toxicity index are presented in Table S7. The proposed classification of ATI is as follows: ATI < 0.1 indicates no toxic level; 0.1 ≤ ATI < 0.3 reveals a low toxic degree; 0.3 ≤ ATI < 0.5 signifies a medium toxic degree; 0.5 ≤ ATI < 1 points to a high toxic degree, and ATI > 1 indicates an extremely high toxic degree (Jamshidi-Zanjani and Saeedi, 2017).
The highest values of the ATI parameter were observed for Crna river - site 6 (20.384), followed by the Nameless stream emptying into Karamanička river – sites 1 and 2, and Golema river – site 3 (about 10), and sites 7 and 5 (Krasnodolska and Crna rivers). These values of the ATI factor indicate an extremely high toxic degree. A high toxic degree (0.5 ≤ ATI < 1) was observed at localities 8 and 9 (Ljubatska river and Lisina lake), a medium toxic degree was registered for Brankovačka river (site 4), and for Vlasina lake (site 10) calculated ATI value indicated a low toxic degree.

Conclusion for contamination factors

Taking into account the individual contamination factors, Pb is the biggest contributor to pollution in most localities, followed by Cu, Cd and As, whose values are usually extremely severe, and sometimes moderately severe. Also, there is significant pollution by Zn, followed by Mn, and low contamination with respect to Ni and Cr was observed. Based on this result, it can be concluded that there is a high probability that Pb could cause harm to the environment in the area. Of all calculated contamination factors, only the mean value of factor Eri is higher for Cd compared to Pb. Unlike Igeo, EF and CF, which are based on environmental geochemistry, and their values show the degree of heavy metals pollution by anthropogenic activities, the calculation of the potential ecological risk factor of a single toxic element takes into account the toxicity of elements. Cd toxicity coefficient is 3 to 30 times that of other elements, and even low concentration of Cd are capable of causing severe health problems.
Contamination factors for As are higher in sites 1, 2, and 3, which are related to the Karamanica ore field, due to the higher content of arsenic in ores from this ore field (Milošević et al., 2015). Based on the obtained results, it can be concluded that the highest values of the contamination factors were observed in the river sediment at site 6, i.e. Crna river, upriver from the confluence with Krasnodolska river (in the vicinity of Musulj – Kekerinci dump located in Blagodat ore field).

Correlation analysis

Pearson's correlation analysis was performed for the contents of the examined elements (Table S8). In our study, a significant positive correlation is observed between most of the studied elements. Positive correlations were found between Zn and Cd, Ca, S, Mn; Cu and Mn, S, As; Cr and Fe, Al, V; Cd and Zn, Ca, S, Mn; Ca and Zn, S, Cd; Fe and Cr, Al; Mn and Zn, Cu, S, Cd; and As and Cu, S; also a negative correlation exists between As and Li. Obtained results confirm that hydroxides of iron play a role in the distribution of Cr and that manganese hydroxides are significant for Zn, Cu, and Cd bounding. Positive correlation of Mn with Zn, Cu, S and Cd can also point to the common origin of these elements, i.e. the source of these elements that is associated with mining activities. Sulfides of cadmium, manganese, arsenic, antimony, nickel and cobalt are present in the composition of lead-zinc or lead-zinc copper ores of the sulphide type to a greater or lesser extent (Stanojević and Filipović-Petrović, 2014). Since iron is abundant in the Earth's crust, and aluminium mainly originates from aluminosilicate minerals, positive correlations of Cr with these two elements indicate its natural, i.e. geochemical origin. Positive correlations of Zn and Cd with Ca may indicate the existence of carbonate-hosted Zn ores. The metamorphic (schist) complex which dominates both Blagodat and Karamanica ore fields includes carbonate horizons composed of marbles and calcschists, metallogenically favourable for deposition of metasomatic mineralization type. Ore deposits were formed by metasomatic reactions of marbles and calcschists induced by hydrothermal solutions of Pb, Zn and Cu (Simić, 2001; Simić, 2002; Đokić, 2012).
The existence of a positive correlation between phosphorus and lead was shown in this paper. This correlation may indicate the presence of some Pb phosphates in the area. Phosphorus (P) in the river sediment can influence the fate and transport of heavy metals (Shen et al., 2020). In soils phosphorus can be associated with Al, Fe, or Ca (Werner and Prietzel, 2015). It was already reported that calcium-rich pyromorphite [$Pb_5(PO_4)_3Cl$] can act as a main lead-bearing phase in mine-waste soils (Cotter-Howells et al., 1994.)

The absence of a greater number of positive correlations between the elements may be a consequence of a relatively small number of samples covered by this research.

Monte Carlo simulation

The assessment of the ecological risk of Ni, Zn, Pb, Cu, Cr, Cd, and As, was conducted by the Monte Carlo simulation (Fig. 5, Table S9). Ecological Risk Analysis results, arranged for each toxic element in order from highest to lowest probability, showed: Low risk for Ni and Cr; Lower > Low > Median > High risk for Zn; High > Extremely High > Median > Lower ≈ Low risk for Pb, Cu, Cd and As. It is possible to conclude that there is a high risk of Pb, Cu, Cd and As pollution in the investigated area. The most of the investigated sites possess a high and extremely high-risk probabilities for Pb, Cu, Cd and As, as it was shown in result analysis. In comparison with the assessment of the ecological risk that have been carried out so far in localities in Serbia (Sakan et. al., 2021), those results are the one with the highest estimated risk values so far. If the form of the HRI graph in the Fig. 5 is considered it could be expected that the most pronounced toxic, elements, Pb, Cu, Cd and As could also have a majority of their concentration in high mobility fractions, see (Sakan et. al., 2021).
Based on the assessment of the total HRI (Table S10), the highest probability in the examined area is for low risk, then lower and finally median risk. However, given that the individual risks of Pb, Cu, Cd, and As pollution are extremely high, there is a need for improvements in tailings management strategies and to prevent any further exploitation of ore deposits.

Conclusion

The impact of the mining activities in the Karamanica and Blagodat ore fields on the pollution status of river and lake sediment was estimated in this research. The geochemical signature of the mining activity in surface sediments in the most southeastern part of Serbia (Krajište area) was evidenced by notable contents of the PTEs associated with the Pb, Zn, and Cu mines and tailings.
Obtained results confirm that hydroxides of iron play a role in the distribution of Cr and that manganese hydroxides are significant for Zn, Cu, and Cd bounding. Positive correlation of Mn with Zn, Cu, S and Cd can also point to the common origin of these elements, i.e. the source of these elements that is associated with mining activities. The origin of Pb, Cd, As, Zn, and Cu is anthropogenic, rather than a simple crustal, whereas Ni and Cr are dominantly of geochemical origin. It is possible to conclude that water originating from the area near the flotation tailings and pilot plant contains high concentrations of toxic elements, causing the high content of these elements in the examined river sediments. The elevated levels of PTEs in sediments indicate the existence of a potential risk to the environment and health of the local population.
Taking into account the individual contamination factors, Pb is the biggest contributor to pollution in most localities, followed by Cu, Cd and As. The values of contamination factors usually indicated very high levels of contamination. Also, there is significant pollution by Zn, followed by Mn, and low contamination with respect to Ni and Cr was observed.
The highest values of the contamination factors were registered for the river sediment from Crna river, upriver from the confluence with Krasnodolska river, in the vicinity of Musulj-Kekerinci dump (Blagodat ore field). The results of MS were high for that locality and the Pb content was extremely high, indicating the existence of a high probability that Pb could cause harm to the environment. In this manuscript, the use of MS as a contamination indicator has been shown to be efficient for contamination by Pb.
Based on the Monte Carlo simulation, the individual risks of Pb, Cu, Cd, and As pollution are extremely high, and the recommendation is that additional protection measures should be taken regarding tailings and other mining activities in the investigated area, and that any further exploitation of ore deposits should be prevented. The evident potential risk of toxic elements is a strong argument for the continuous monitoring of studied sediments. The methodology applied here, namely the combined use of pollution indices, geochemical background values, magnetic susceptibility, statistical analysis, and Monte Carlo analysis, gives a suitable information about contamination levels, sources of PTEs, as well as the current and future potential risks of mining activities to the downstream environments. Those methods have been used separately earlier, but their combined use is proven to be a more valuable tool for the analysis of the situation since if the several independent methods point to same result, the certainty of the obtained data is more pronounced.

Author Contributions
S.S: conceptualization, formal analysis, methodology, data curation, supervision, validation, visualization, writing original draft. A.M.Z: investigation, validation, visualization, writing-review and editing. N.S: methodology, software, writing-review and editing. S.F.B: investigation, formal analysis, writing-review and editing. I.K: formal analysis, writing-review and editing. D.Đ: conceptualization, methodology, supervision, writing-review and editing.

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Data availability
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare no competing interests.

Appendix A. Supplementary data

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Table 1
Sampling locations with the GPS coordinates

Label	Name of locality	GPS coordinates
1	The nameless stream that flows into the Karamanička river (upstream of the flotation tailing dump of the Podvirovi ore deposit flotation pilot plant)	N 42.349999°, E 22.3384774°
2	The Nameless stream that flows into the Karamanička river (downstream of the flotation tailing dump of the Podvirovi ore deposit flotation pilot plant)	N 42.3444682°, E 22.3449898°
3	Golema river (near village Omatica)	N 42.3410672°, E 22.3668551°
4	Brankovačka river (village Brankovci, before the Gradište small hydropower plant dam)	N 42.4150061°, E 22.4915979°
5	Krasnodolska river (near the confluence with Crna river)	N 42.5171703°, E 22.248264°
6	Crna river (upriver from the confluence with Krasnodolska river)	N 42.516755°, E 22.248210°
7	Crna river (from the confluence with Krasnodolska river)	N 42.516702°, E 22.248553°
8	Ljubatska river (before the water intake for Lisina lake)	N 42.5028795°, E 22.30225°
9	Lisina lake (near the dam)	N 42.5508947°, E 22.3880402°
10	Vlasina lake (near the Božica canal)	N 42.6792604°, E 22.3519681°

Table 2

Descriptive statistics of the content of the studied elements, Crust values and Quality Guidelines [mg kg^{-1}]

	Min	Max	Mean	SD[a]	Median	CV[**]	HM[b]	GM[c]	TEC[d]	PEL[e]	MAV[f]	RV[g]	Crust[h]
Zn	74.3	7,892	3,521	2,992	4,074	85.0	403	1586	121	459	430	720	65
Ni	17.7	45.8	32.3	10.10	30.00	31.3	29.39	30.83	22.7	48.6	44	210	56
Cu	21.2	3,224	1,183	1,316	506	111	92	367	31.6	149	110	190	25
Cr	29.6	91.5	43.8	20.19	36.6	46.1	38.6	40.7	43.4	111	240	380	126
Pb	15	36,790	6,848	10,986	4,497	160	128	1,663	35.8	128	310	530	14.8
Cd	0.06	64.2	25.5	25.6	18.0	100	0.5	7.7	0.99	4.98	6.4	12	0.1
As	4.2	1,444	396	588	50	148	25	88	9.79	33	42	55	1.7
Al	9,877	33,011	17,954	6,977	16,132	38.9	16,030	16,911	nd[***]	nd	nd	nd	79,600
B	<DL*	111	24.4	45.9	0.1	188	0.1	0.8	nd	nd	nd	nd	11
Ba	34.5	431	129	110	98	85.3	89	104	nd	nd	nd	nd	584
Ca	4,388	46,397	18,869	16,410	11,311	87.0	9,227	12,945	nd	nd	nd	nd	38,500
Co	4.24	39.6	18.2	9.2	17.5	50.5	13.4	16.0	nd	nd	nd	nd	24
Fe	27,549	108,639	65,615	25,608	58,539	39.0	56,466	61,059	nd	nd	nd	nd	43,200
K	1987	94,094	39,894	40,797	27,922	102	5,242	14,478	nd	nd	nd	nd	21,400
Li	9.16	21.8	14.6	4.3	13.9	29.5	13.6	14.1	nd	nd	nd	nd	18
Mg	6,200	16,265	11,266	2,972	10,660	26.4	10,486	10,889	nd	nd	nd	nd	22,000
Mn	753	6,161	3,193	1,977	4,114	61.9	1,804	2,474	nd	nd	nd	nd	716
Na	2,431	13,558	5427	4,178	3,273	77.0	3,669	4,328	nd	nd	nd	nd	23,600
P	1,282	2,122	1,527	262	1,478	17.2	1,493	1,509	nd	nd	nd	nd	nd
S	5	13,122	5,676	5,071	7,304	89.3	47	1,443	nd	nd	nd	nd	nd
Sr	5.67	42.4	15.9	10.2	13.3	64.2	12.3	13.8	nd	nd	nd	nd	333
V	26.7	88.9	46.9	21.0	41.6	44.8	40.1	43.2	nd	nd	nd	nd	98

*bellow detection limit; ** in %; ***nd - no data

[a]SD (standard deviation); [b]HM (harmonic mean); [c]GM (geometric mean); [d]TEC (threshold effect concentration)—MacDonald et al. (2000); [e]PEL (probable effect concentration)—MacDonald et al. (2000); [f] MAV, maximum allowable value (Government of Republic of Serbia, 2012); [g]RV, remediation value (Government of Republic of Serbia, 2012); [h]Element concentrations in the Continental Crust—K.H. Wedepohl, (1995).

Table 3
Comparison with results for similar river sediments and background values [mg kg^{-1}]

		This study	RS, China[a]	SS, Tunisia[b]	RS, Romania[c]	RS, Japan[d]	RS, UK[e]	SS, China[f]	SS, Spain[g]	BV[h]
Zn	Min	74.3	46.9	nd*	50	86.8	nd	nd		
	Max	7892	325	nd	1117	7490	6,955	30,425		
	Mean	3521	113	5790	126.2	1607	nd	nd	1092.7	74.25
Ni	Min	17.7	18.4	nd	16	nd	nd	nd		
	Max	45.8	45.5	nd	48	nd	nd	nd		
	Mean	32.3	28.9	16.08	30.10	nd	nd	nd		20.57
Cu	Min	21.2	16.7	nd	17	nd	nd	nd		
	Max	3224	92.1	nd	451	nd	2,557	nd		
	Mean	1183	36.7	31.67	45.63	nd	nd	nd	122.2	24.4
Cr	Min	29.6	44.7	nd	39	nd	nd	nd		
	Max	91.5	129	nd	99	nd	nd	nd		
	Mean	43.8	68.8	31.42	71.44	nd	nd	nd		19.88
Pb	Min	15	16.1	nd	17	nd	nd	nd		
	Max	36790	192	nd	139	nd	6,411	21,850		
	Mean	6848	42.5	3542	36.35	nd	nd	nd	2708.6	20.73
Cd	Min	0.06	0.100	nd	0.11	nd	nd	nd		
	Max	64.2	0.910	nd	2.38	nd	44	97		
	Mean	25.5	0.336	16.80	0.43	nd	nd	nd	3.7	0.46
As	Min	4.2	2.46	nd	8.2	nd	nd	nd		
	Max	1444	15.0	nd	170	nd	nd	nd		
	Mean	396	5.10	81.71	24.44	nd	nd	nd	119.8	11.1

*nd – no data; [a] River sediments, China, origin of elements: natural, agricultural and industrial activities, mining, and vehicular traffic (Shen et al. 2019); [b] Stream sediments, Northern Tunisia, near abandoned Pb and Zn mine (Ayari et al. 2023); [c] River sediments, Romania, presence of many waste dumps and underground mining works (closed or still active) which cause the well-known process of acid mine drainage (Maftei et al. 2014); [d] River sediment in the Tsushima Island, Japan, Taisyu Zn–Pb mine area (Shikazono et al. 2008); [e] RS, Afon Twymyn, Wales, river bed sediments from different metal mining regions in the UK (Wolfenden and Lewin, 1978); [f] Stream sediment in Guizhou province, China (Abandoned Zn–Pb smelter, Hezhang Country) (Yang et al. 2010); [g] Stream sediments in Mazarrón Pb-(Ag)-Zn mining district (Oyarzun et al. 2011); [h] Backround values (this study): BV for Al is 1264.42 mg kg^{-1}.

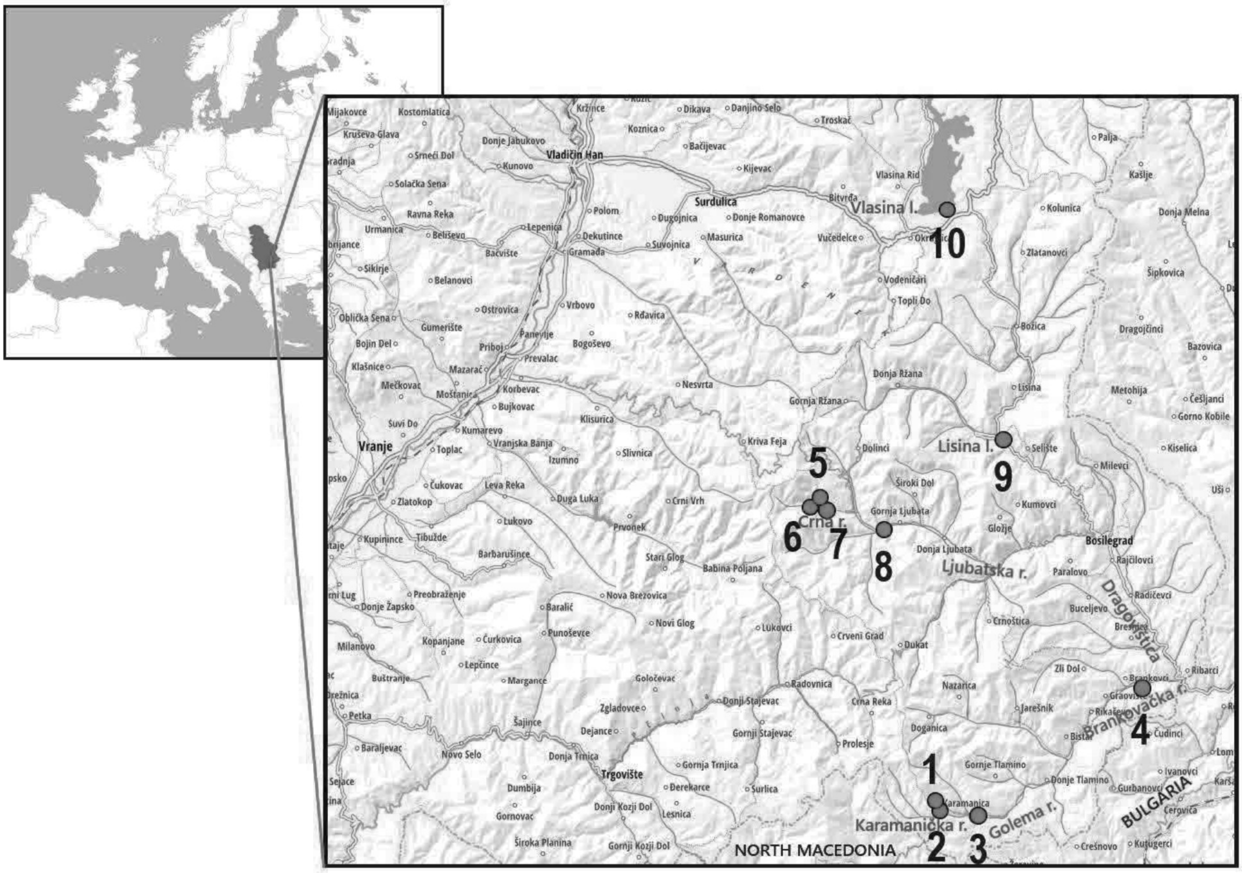

Figure 1. Map with sampling locations: (1), (2) The Nameless stream that flows into the Karamanička river; (3) Golema river; (4) Brankovačka river; (5) Krasnodolska river; (6) (7) Crna river; (8) Ljubatska river; (9) Lisina lake; and (10) Vlasina lake (adapted from https://www.serbiamap.net).

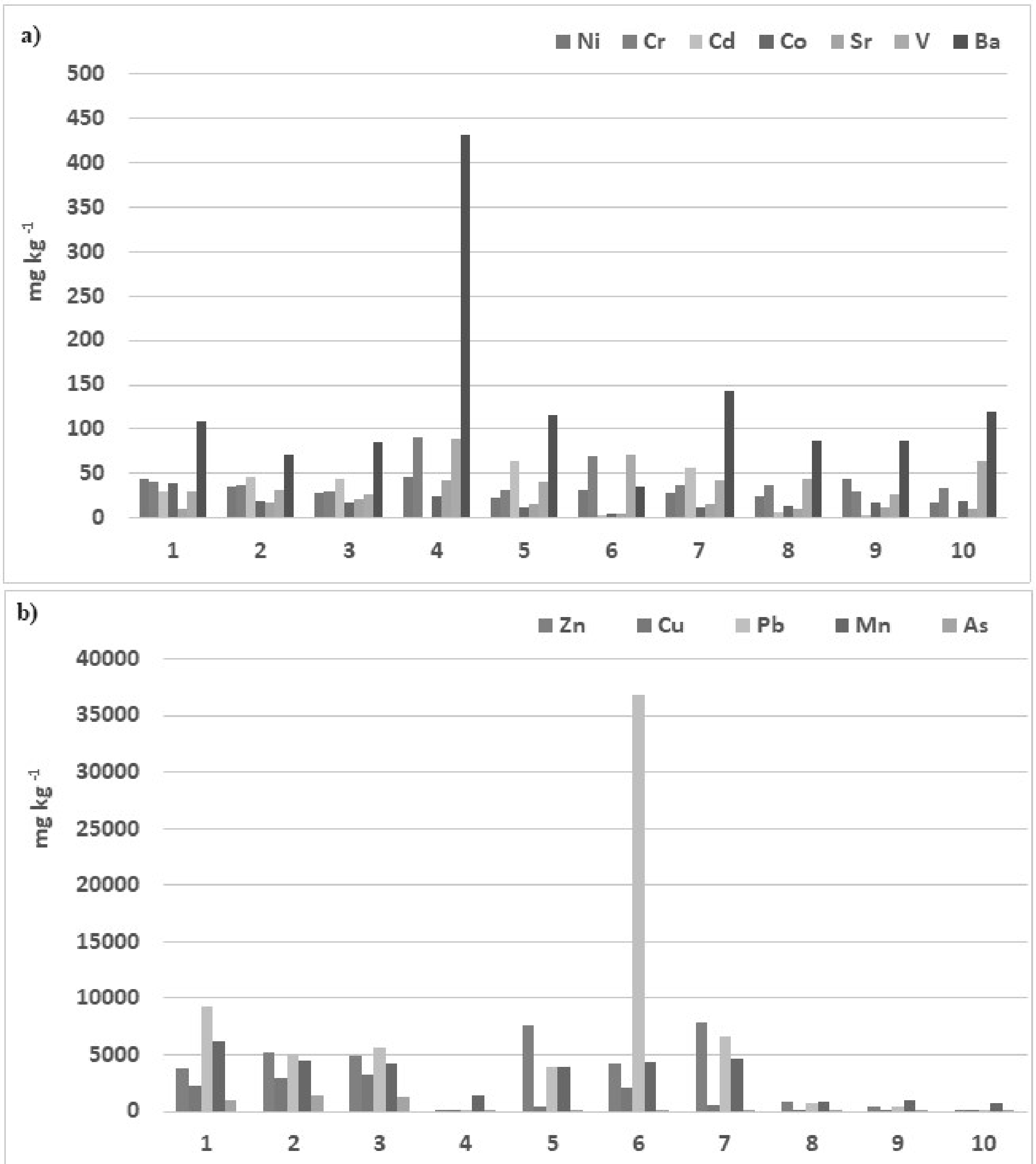

Figure 2. Total content of studied elements in river sediments: (a) Ni, Cr, Cd, Co, Sr, V, and Ba; and (a) Zn, Cu, Pb, Mn, and As.

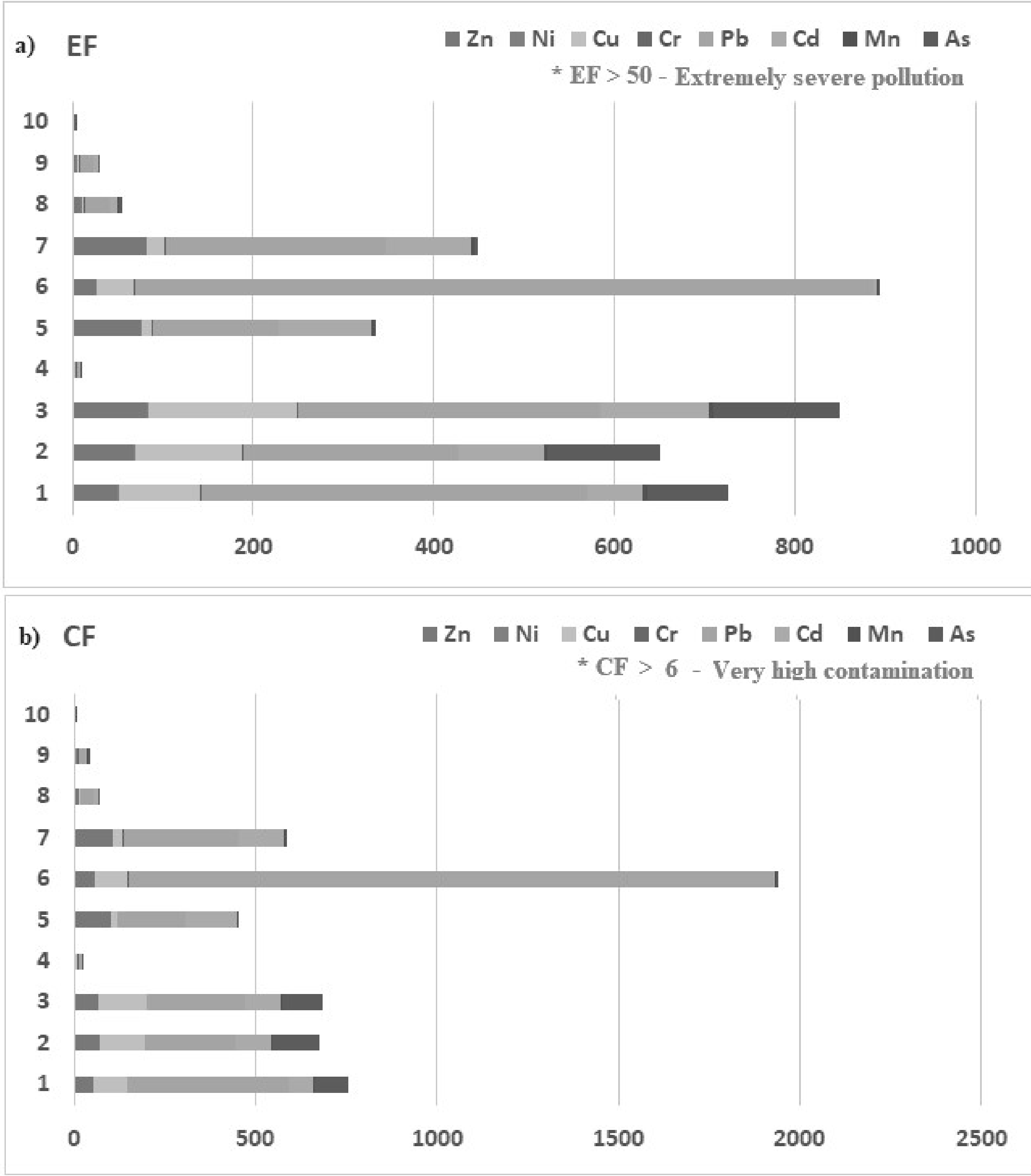

Figure 3. Contamination indexes for studied elements: a) Enrichment factor (EF), and b) Contamination factor (CF).

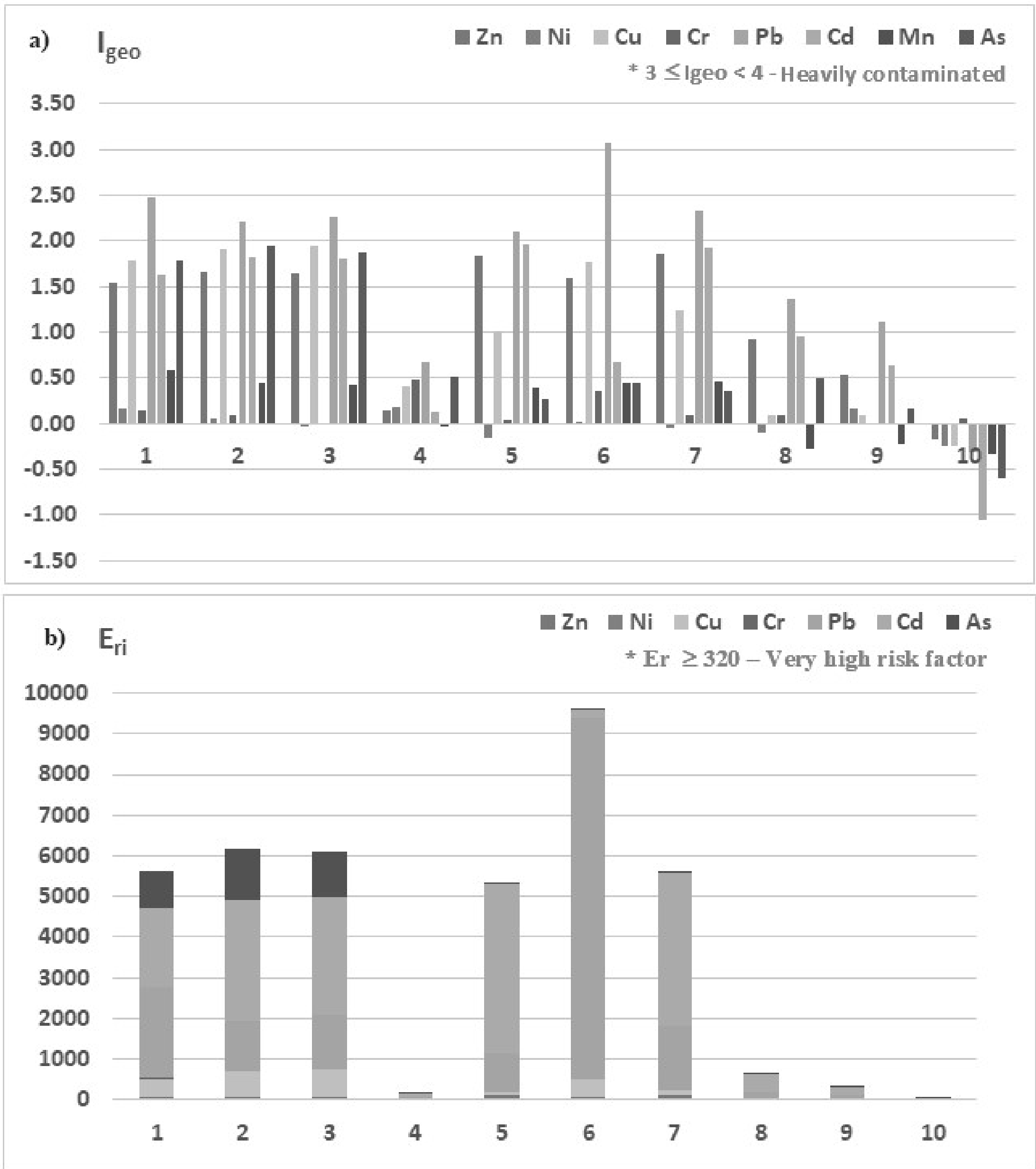

Figure 4. Contamination indexes for studied elements: a) Index of geoaccumulation (Igeo); and b) Ecological risk factor (Eri).

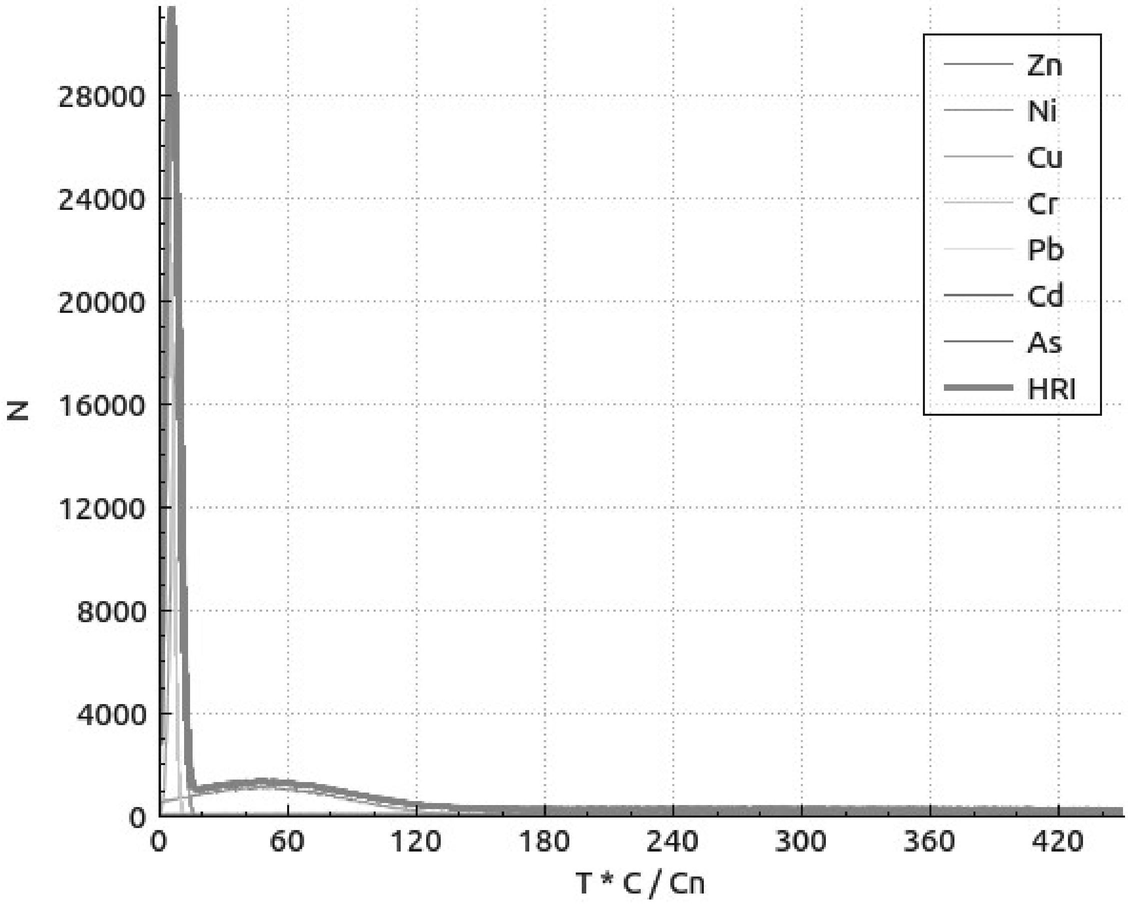

Figure 5. Distribution curve and exceedance probability curves of the risk index (RI) and total ecological risk comprehensive index HRI based on a Monte Carlo simulation run 100,000 times. Local backgrounds are the reference values for the calculation of Eri.