JOURNAL OF WATER AND LAND DEVELOPMENT
e-ISSN 2083-4535

Polish Academy of Sciences (PAN) Institute of Technology and Life Sciences – National Research Institute (ITP – PIB)

JOURNAL OF WATER AND LAND DEVELOPMENT
DOI: 10.24425/jwld.2024.151812
2025, No. 64 (I–III): 12–20

Potentially toxic elements contamination and ecological risk assessment in water and surface sediments of Bistrica River

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RECEIVED 14.07.2024 ACCEPTED 15.10.2024 AVAILABLE ONLINE 31.12.2024

Abstract: This research evaluates the quality of water and surface sediment in the Bistrica River, addressing the growing environmental challenges in Kosovo caused by extensive human activities. Contamination of these resources poses significant threats to aquatic ecosystems and human health. To assess this, we analysed the levels of potentially toxic elements (PTEs) in the samples using inductively coupled plasma optical emission spectrometry (ICP-OES). The elements examined included Fe, Pb, Ni, Mn, Cu, Zn, Al, and Co. Samples were collected from various sites along the Bistrica River during both high-flow and low-flow seasons in October 2023.

The degree of PTE contamination was assessed using several pollution indices (contamination factor (*CF*), contamination degree (*CD*), pollution load index (*PLI*), enrichment factor (*EF*), geoaccumulation index (I_{geo}) and ecological risk index (*ERI*)), indicating that both water and surface sediment exhibited moderate to high levels of contamination. Results revealed that pollution in water samples exceeded the guidelines set by the U.S. Environmental Protection Agency (EPA) and World Health Organization (WHO).

Additionally, statistical analysis and contamination clusters, primarily originating from agricultural fields and grazing areas within the catchment. To reduce these risks and safeguard both the aquatic ecosystem and human health, it is crucial to maintain regular monitoring and enforce effective management strategies.

Keywords: Bistrica River, ecological risk, heavy metals, surface sediment, water

INTRODUCTION

Kosovo, a relatively new country in Europe, is experiencing continuous industrial development. Certainly, this rapid and significant development also has negative consequences for the environment in general, due to the enormous pollution it has caused (Angello, Behailu, and Tranckner, 2020). The significant presence of heavy metals in the environment is a serious concern due to their potential for accumulation, dispersion, and integration into the food chain (Ewaid, 2017). The potentially toxic elements (PTEs) can affect the physiological and metabolic activities of organisms, posing a potential risk to the environment and also to human health through transmission and amplification in the food chains (Li, 2022; Lu, 2022). The sediment may contain PTEs from natural sources because they constitute one of the principal elements of the Earth's crust. Nevertheless, anthropogenic activity (industrial, domestic, and agricultural wastewater) has become a major source of metallic contamination in sediments (Mahlathi, Siyakatshana and Chirwa, 2016; Cao *et al.*, 2023). The PTEs are distributed between sediments and the aqueous phase. However, numerous studies have consistently shown that only a small amount of these contaminants remain dissolved in the aqueous phase, and approximately 90% become trapped in sediments by various processes, including adsorption and co-precipitation (Su *et al.*, 2023). Consequently, the principal PTE reservoir is sediment (Tian *et al.*, 2020). However, any change in ecological conditions (temperature, pH, dissolved oxygen, redox potential, and salinity) causes the desorption of

PTEs from sediments to the aquatic environment, resulting in secondary water pollution. That will increase potential ecological risks for aquatic organisms and human health (Rajeshkumar *et al.*, 2018; Sun *et al.*, 2019; Jaskuła and Sojka, 2022).

Sediments are frequently employed as an indicator for monitoring PTE contamination in aquatic ecosystems (DPMP, 2020; KAS, 2024). In recent decades, wastewater and surface runoff have been discharged into the Bistrica estuary, seriously affecting the ecosystem and aquatic life through contaminants, including PTEs. Therefore, it is crucial to evaluate the degree of pollution in its sediments.

The aim of this study was to comprehensively assess the influence of heavy metal pollution – including cobalt, aluminium, copper, iron, manganese, nickel, lead, and zinc – on the quality of water and surface sediments in the Bistrica River. Specifically, the research focused on four key objectives: 1) evaluating the distribution and bioavailability of PTEs in the surface sediments of the Bistrica estuary, 2) identifying the sources of PTEs in these sediments, 3) assessing the degree of PTE contamination using pollution indices, 4) estimating the ecological risks posed by these elements in the Bistrica River. To achieve these objectives, the study results were meticulously compared with the environmental standards recommended by the U.S. Environmental Protection Agency (EPA).

MATERIALS AND METHODS

STUDY AREA

The area is characterised by various human activities, including agriculture along the Bistrica River, recreational and artisanal fishing, and tourism. Located on the western side of the Republic of Kosovo, the study area falls within the administrative territory of the Municipality of Peja, encompassing 77.08% of its total area (Fig. 1). According to the latest population census, the Municipality of Peja has 82,299 inhabitants (KAS, 2024). The average annual rainfall is 800 mm in the plain areas and over 1,025 mm in the mountainous regions (DPMP, 2020; KAS, 2024). The main river in the study area is the Bistrica River of Peja, which represents the primary catchment with a surface area of 464.8 km^2. The Bistrica River of Peja has a length of 54 km, an average flow of 10.21 m^3·s^{-1}, an annual flow of 200.66 · 10^6 m^3, and a flow coefficient of 0.651 (DPMP, 2020; KAS, 2024). Sample collection for this study was conducted in October 2023. Water samples were gathered from three locations: M1 at the Transit Bridge, M2 in the village of Pavlan, and M3 in the village of Zahaq. At each site, samples were composited by blending water from various depths. These sites were selected to evaluate the physicochemical properties and heavy metal content in the water. Additionally, sediment samples were collected from the same points for further analysis.

SAMPLE PREPARATION

Water samples were collected from three locations, with each site providing two samples using 2 dm^3 glass bottles, filtered, and transferred to Teflon containers. The samples were treated with 1 cm^3 of HCl and 5 cm^3 of HNO_3 before undergoing microwave digestion. High-purity standard solutions (99.98%) for target elements were supplied by Merck Germany.

For the sediment analysis, 2 g of sediment were digested with 15 cm^3 of concentrated HNO_3 at 130°C for 5 h, then filtered and washed with 0.1 M HNO_3. The samples were diluted to 100 cm^3 with deionised water for metal analysis, following the U.S. Environmental Protection Agency (EPA) guidelines (U.S. EPA, 2017a; Ngatia, Kithiia and Voda, 2023).

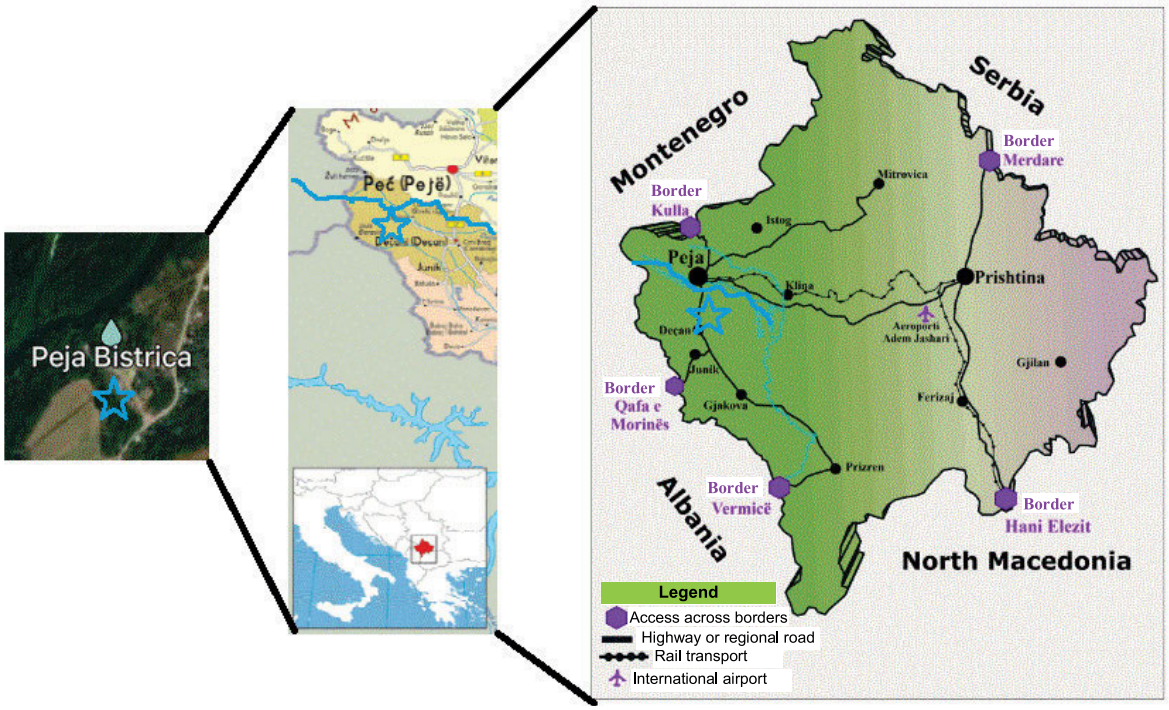

Fig. 1. Study area sampling locations – Peja (Pejë) Bistrica; source: own elaboration based on Kosovo Environmental Protection Agency (Alb.: AMMK – Agjencioni për Mbrojtjen e Mjedisit të Kosovës)

QUALITY CONTROL AND INSTRUMENTATION

For metal quantity determination, we used inductively coupled plasma optical emission spectroscopy (ICP-OES). Standard solutions (100 mg·dm^{-3}) of metals such as As, Cd, Co, Cu, Al, Fe, Mn, Ni, Pb, and Zn were prepared. The calibration curve was linear with an R^2 of 0.9996, and all reagents were of analytical grade. Heavy metal concentrations were measured using ICP-OES (DW-2100) following the methods by U.S. EPA (2017b) and Gajek *et al.* (2022). Each batch included two spiked blanks and two method blanks processed simultaneously. The argon gas used had a purity of 99.99%. The analysed elements were As, Cd, Co, Cu, Al, Fe, Mn, Ni, Pb, and Zn.

ASSESSMENT OF POTENTIALLY TOXIC ELEMENT CONTAMINATION

To assess the contamination and risk of potentially toxic elements (PTEs) in sediment, several environmental indicators were used, contamination degree (*CD*), contamination factor (*CF*), enrichment factor (*EF*), pollution load index (*PLI*), geoaccumulation index (I_{geo}), and ecological risk index (*ERI*). Numerous studies have utilised the average shale values (*ASV*) or Earth's crust as a reference baseline (Ejigu, 2021; Acharya, Muduli and Das, 2023). In this work, the *ASV* was employed as a background of PTEs (Acharya, Muduli and Das, 2023).

CONTAMINATION FACTOR AND CONTAMINATION DEGREE

The contamination factor (*CF*) and the contamination degree (*CD*) are extensively used to evaluate the PTE contamination level of different deposits (Ejigu, 2021; Acharya, Muduli and Das, 2023). The *CF* measures the level of contamination caused by an individual metal, whereas the *CD* measures the contamination degree, including the total *CF*. These indices are determined using the following formulas (Hakanson, 1980; Novita *et al.*, 2020; Yang *et al.*, 2020):

$$CF = \frac{CHM}{CBG} \tag{1}$$

$$CD = \sum_{i=1}^{n} CF \tag{2}$$

where: *CHM* = potentially toxic element concentration in sediment, *CBG* = potentially toxic element background concentration, *n* = number of studied potentially toxic elements. The *CF* values were classified according to Hakanson's classification.

POLLUTION LOAD INDEX

The *PLI* shows how often the concentration of PTEs in sediment is higher than the typical uncontaminated baseline concentration (Hakanson, 1980; Tomlinson *et al.*, 1980). Considering all PTEs collectively, the *PLI* determined each sample's pollution level. The *PLI* value gives a general indication of metal(oid) toxicity in each sample site (Hakanson, 1980; Tomlinson *et al.*, 1980). The *PLI* was calculated using the equation below:

$$PLI = \sqrt[n]{CF_1 \cdot CF_2 \cdot \ldots \cdot CF_n} \tag{3}$$

This empirical index offers a quick, easy method for determining the degree of PTE pollution. If $PLI > 1$, it indicates PTE pollution in sediment; however, if $PLI < 1$, it shows no metal pollution.

ENRICHMENT FACTOR

The enrichment factor (*EF*) was calculated to evaluate whether PTEs are elevated compared to Earth's crust values due to anthropogenic contamination (Kumar, Pandita and Setia, 2022). This index is commonly used to analyse anthropogenic impacts on the sediments by normalising the PTEs to a conservative element, such as Al (Yona *et al.*, 2018). The *EF* is calculated using the following Equation (4):

$$EF = \frac{\left(\frac{\text{Metal}}{\text{Al}}\right)_{\text{sediment}}}{\left(\frac{\text{Metal}}{\text{Al}}\right)_{\text{background}}} \tag{4}$$

where the numerator and denominator are the ratio of metal(oid) to Al in the studied sample and background respectively. Sediments are categorised into three categories (Zha *et al.*, 2018).

GEOACCUMULATION INDEX

The degree of potentially toxic element contamination in aquatic ecosystems is generally measured using the geoaccumulation index (I_{geo}) (Lee *et al.*, 2020; Novita, Firmansyah and Pradana, 2023). The latter represents a quantitative evaluation of the sediment pollution level of each metal(oid). The Equation (5) was used to calculate this index (Lee *et al.*, 2020; Novita, Firmansyah and Pradana, 2023).

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5B_n} \tag{5}$$

where: C_n = metal(oid) concentration present in studied sediment, B_n = metal(oid)'s geochemical background concentration, the correction factor (1.5) is used to compensate for possible consequences of anthropogenic impacts or alterations in sediments' lithology (Muller, 1979; Tomlinson *et al.*, 1980; Novita, Firmansyah and Pradana, 2023). Sediments are categorised according to the Tomlinson and Muller classification (Muller, 1979; Tomlinson *et al.*, 1980).

ECOLOGICAL RISK INDEX

The ecological risk index (*ERI*) considers toxicity, variations in background concentrations, and environmental migratory patterns for each specific metal. The *ERI* is utilised to evaluate the ecological risk of PTEs (Muller, 1979; Tomlinson *et al.*, 1980; Ennaji *et al.*, 2020). According to the following formula, the *ERI* was determined by Equation (6):

$$ERI = TR \cdot CF_i \tag{6}$$

where: *TR* = toxic response coefficient, *i* = of the specific element. According to Liu *et al.* (2015), such *TR* values are taken: Cd = 30, As = 10, Zn =1, Ni = 5, Co = 5, Pb = 5, Cd = 7, Cr = 2, Cu = 5. The *ERI* values are classified according to Muller (1979), Tomlinson *et al.* (1980), Liu *et al.* (2015), and Ennaji *et al.* (2020).

The soil and sediment classification with respect to ecological risk values involves five classes: *ERI* < 40 – low ecological risk; 40 < *ERI* < 80 – moderate ecological risk; 80 < *ERI* < 160 – appreciable ecological risk; 160 < *ERI* < 320 – high ecological risk, and *ERI* > 320 – serious ecological risk (Muller, 1979; Tomlinson *et al*., 1980; Liu *et al*., 2015; Ennaji *et al*., 2020).

RESULTS AND DISCUSSION

PHYSICAL AND CHEMICAL CHARACTERISTICS

The physical and chemical characteristics offer valuable indications regarding pollutant presence, water suitability for diverse purposes, and aquatic life health. Monitoring parameters like temperature, dissolved oxygen, pH, and pollutant levels enables early detection of water quality alterations, facilitating intervention when required. Therefore, the Table 1 depicts the physical and chemical parameters of water samples collected from the Bistrica River in Peja.

The physical and chemical parameters measured at three water sampling points (M1, M2, and M3) provide insight into the quality of water in the study area. The water temperature ranged from 11.7 to 13.4°C, with M1 exhibiting the highest temperature. The levels of *DO* varied from 6.8 to 8.6 mg·dm^{-3}, with M1 having the highest concentration, indicating better aeration. The *EC* ranged from 387 to 425 µS·cm^{-1}, with M3 showing the highest conductivity, indicating higher dissolved ion concentrations or pollutant levels. The pH levels ranged from 6.44 to 6.87, with M2 and M3 showing slightly higher pH values compared to M1. The *TDS* increased from 159 to 178 mg·dm^{-3} from M1 to M3. Chloride (Cl^-) concentrations were highest at M1, while *COD* and *BOD* were the highest at M3, indicating higher organic pollution levels at this site. Total phosphorus (P_{tot}) levels slightly increased from M1 to M3, while nitrate (NO_3^-) levels remained constant across all sites.

Total nitrogen (N_{tot}) and ammonium (NH_4^+) concentrations were the highest at M3, indicating greater nutrient loading. Nitrite (NO_2^-) levels were consistent across all sites. Inorganic nitrogen (N_{inorg}) levels were highest at M2, suggesting different nitrogen dynamics compared to M1 and M3. Sulphate (SO_4^{2-}) concentrations showed slight variations across sites, with M1 exhibiting the highest value. Overall, these variations suggest differing pollution levels and environmental conditions at each sampling point, highlighting the need for targeted management strategies to maintain water quality in the study area. Phosphate (PO_4^{3-}) levels appear relatively low across all points, with M3 exhibiting the highest concentration. The *TOC* levels show a discernible increase from M1 to M3, suggesting a rise in organic carbon content in the water. Transparency varies, with M3 displaying the highest transparency among the three points.

The *TMS* are notably elevated at M3, indicating a higher concentration of suspended solids. Fluoride (F^-) concentrations remain consistently low across all sampling points. Dissolved oxygen levels (*DO*) show minimal variation, while calcium (Ca^{2+})

Table 1. Water samples in the Bistrica River in Kosovo – physical and chemical characteristics

Parameter	Value in sample point			Parameter	Value in sample point		
	M1	M2	M3		M1	M2	M3
T_w (°C)	13.4	11.7	12.3	PO_4^{3-} (mg·dm^{-3})	0.035	0.055	0.069
DO (mg·dm^{-3})	8.6	8.4	6.8	*TOC* (mg·dm^{-3})	9.3	11.8	19.89
O_2 (%)	115	86.5	86	C_w	without	transp.	transp.
EC (19°C, µS·cm^{-1})	389	387	425	*TMS* (mg·dm^{-3})	21	19.9	55.3
pH	6.44	6.81	6.87	F^- (mg·dm^{-3})	0.3	0.2	0.1
TDS (mg·dm^{-3})	159	169	178	*FT* (°dH)	11.63	11.09	11.3
Cl^- (mg·dm^{-3})	3.19	1.44	2.19	F_{Ca} (°dH)	13.6	12.8	12.2
COD (mg·dm^{-3})	28.4	35.8	59.6	F_{Mg} (°dH)	17.4	13.6	15.9
BOD (mg·dm^{-3})	16.2	20.9	42.1	Ca^{2+} (mg·dm^{-3})	98.6	99.8	101
P_{tot} (mg·dm^{-3})	0.101	0.103	0.113	Mg^{2+} (mg·dm^{-3})	19.84	16.8	16.9
NO_3^- (mg·dm^{-3})	0.5	0.5	0.5	M_A (mg·dm^{-3})	14.11	10.25	10.35
N_{tot} (mg·dm^{-3})	0.221	0.231	0.259	HCO_3^- (mg·dm^{-3})	426.35	584.6	548.63
NH_4^+ (mg·dm^{-3})	0.08	0.06	0.28	*TUR* (NTU)	3.8	3.4	3.6
NO_2^- (mg·dm^{-3})	0.01	0.01	0.01	$KMnO_4$ (mg·dm^{-3})	5.69	12.352	10.43
N_{inorg} (mg·dm^{-3})	0.152	0.236	0.223	*SUR* (mg·dm^{-3})	<0.2	<0.2	<0.2
SO_4^{2-} (mg·dm^{-3})	8.64	7.62	7.99	T_a (°C)	21	23	24

Explanations: T_w = water temperature, *DO* = dissolved oxygen, *EC* = electrical conductivity, pH = potential of hydrogen, *TDS* = total dissolved solids, *COD* = chemical oxygen demand, *BOD* = biochemical oxygen demand, P_{tot} = total phosphorus, N_{tot} = total nitrogen, N_{inorg} = inorganic nitrogen, *TOC* = total organic carbon, C_w = colour of water, *TMS* = total suspended solids, *FT* = total hardness, F_{Ca} = calcium hardness, F_{Mg} = magnesium hardness, M_A = residue after evaporation, *TUR* = turbidity, *SUR* = cationic and anionic surfactants, T_a = air temperature.
Source: own study.

and magnesium (Mg^{2+}) levels exhibit slight variations across the sampling points. Alkalinity levels decrease from M1 to M3. Bicarbonate (HCO_3^-) levels are highest at M2, followed closely by M3. Turbidity levels demonstrate minimal variance across the sampling points. Potassium permanganate ($KMnO_4$) levels are the highest at M2, indicating elevated levels of oxidisable substances. Sulphate levels remain below the detection limit at all sampling points. The T_a gradually increases from M1 to M3. These findings collectively contribute to our understanding of water quality dynamics at each sampling point and aid in the assessment of potential environmental impacts.

The following figure (Fig. 2) illustrates the values of physical and chemical parameters in the water samples of the Bistrica River in Peja, specifically at the sampling points M1, M2, and M3.

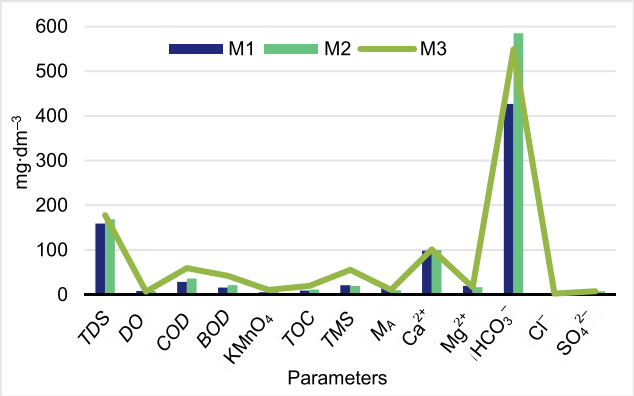

Fig. 2. Graphic presentation of physical and chemical parameters; M1–M3 = sample points, *TDS*, *DO*, *COD*, *BOD*, *TOC*, *TMS*, M_A, as in Tab. 1; source: own study

POTENTIALLY TOXIC ELEMENTS IN THE SURFACE WATER OF THE BISTRICA RIVER

The potentially toxic elements' (PTE) distribution (Co, Al, Cu, Fe, Mn, Ni, Pb, and Zn) in the surface water of Bistrica River was analysed. The measured concentration of heavy metals in the water for the Bistrica River is presented in Table 2. The results are also compared to World Health Organization (WHO) standards values (Mirza *et al.*, 2019). Total PTEs concentrations in water samples of Bistrica River followed the order: Fe > Pb > Zn > Ni > Mn > Cu > Al > Co.

The results are different from the sediment and soil samples. This could be explained by the variation over time in geochemical processes, sampling location, sediment and soil composition, weathering, and anthropogenic activities. These results show that potentially toxic elements do not strongly contaminate the Bistrica River.

According to the results that are presented in the Table 2, cobalt, manganese, and nickel demonstrate concentrations within acceptable limits, aligning closely with WHO guidelines. Cobalt's concentrations range between 0.014 to 0.019 mg·dm^{-3}, well below the WHO limit of 0.01 mg·dm^{-3} (WHO, 2021). Similarly, the levels of manganese span from 0.165 to 0.221 mg·dm^{-3}, meeting the WHO standard of 0.4 mg·dm^{-3}. Nickel, with concentrations ranging from 0.181 to 0.241 mg·dm^{-3}, also falls comfortably

Table 2. The presence of heavy metals in water samples (mg·dm^{-3}) compared to WHO standard (WHO, 2021)

Element	Value in sample point			WHO standard
	M1	M2	M3	
Co	0.018	0.019	0.014	0.01
Al	0.029	0.038	0.086	0.20
Cu	0.038	0.028	0.069	2.00
Fe	0.485	0.661	0.897	0.30
Mn	0.165	0.192	0.221	0.40
Ni	0.181	0.210	0.241	0.02
Pb	0.432	0.485	0.585	0.01
Zn	0.355	0.389	0.401	3.00
As	nd	nd	nd	0.01
Cd	nd	nd	nd	0.003

Explanations: nd = not detected.
Source: own study.

below the WHO limit of 0.02 mg·dm^{-3}. On the other hand, aluminium, copper, iron, lead, and zinc surpass WHO guidelines.

Aluminium, copper, and zinc exhibit concentrations exceeding the recommended thresholds of 0.2 mg·dm^{-3}, 2 mg·dm^{-3}, and 3 mg·dm^{-3}, respectively. Iron concentrations, ranging from 0.485 to 0.897 mg·dm^{-3}, significantly surpass the WHO standard of 0.3 mg·dm^{-3}. Lead concentrations fluctuate between 0.432 to 0.585 mg·dm^{-3}, considerably higher than the WHO (WHO, 2021) threshold of 0.01 mg·dm^{-3}. This comparison underscores the importance of monitoring these elements to ensure adherence to WHO standards, particularly for elements exceeding recommended levels, as their presence could pose potential health risks (WHO, 2021).

ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS POLLUTION RISK IN SEDIMENT

The contamination factor (*CF*) is calculated to evaluate the PTE's pollution degree in sediments. According to Hakanson's classification (Novita *et al.*, 2020), the results of *CF* indicate low contamination (*CF* < 1) in the Bistrica River sediment, except Fe and Mn, which show moderate contamination at sites M3 (Fe = 0.995) and M3 (Mn = 0.413) (Tab. 3). The highest *CF* was observed in M3 for Fe, Mn, and Ni due to urban wastewater discharges (Novita *et al.*, 2020; Tugiyono *et al.*, 2023), and in M3 and M2 for Zn, Pb and Ni, which receive potentially toxic elements from fishing hooks and other metal waste (Novita *et al.*, 2020; Tugiyono *et al.*, 2023). The *CF* changes in the following descending order: Fe > Zn > Mn > Ni > Pb > Al > Co.

The sediment shows a higher degree of contamination because of the uncontrolled anthropogenic activities in the Bistrica River, which often serves as a metal contamination source, through industrial or agricultural runoff. Moreover, it could be related to the increased flow of the river, heavily influenced by weather conditions, particularly precipitation. During rainy periods, river discharge increases significantly,

Table 3. The presence of heavy metals in sediment samples ($mg \cdot kg^{-1}$) measured compared to U.S. Environmental Protection Agency Standard

Element	Value in sampling location			EPA Standard
	M1	M2	M3	
Co	0.072	0.068	0.085	–
Al	0.064	0.089	0.095	–
Cu	0.095	0.098	0.111	<25
Fe	0.698	0.858	0.995	25
Mn	0.186	0.198	0.413	–
Ni	0.185	0.193	0.212	<20
Pb	0.158	0.187	0.143	<40
Zn	0.565	0.802	0.913	<90
As	nd	nd	nd	–
Cd	nd	nd	nd	–

Explanations: nd = not detected.
Source: own study.

increasing thus the transport of sediments and metal contaminants from upstream to downstream, at the same time increasing the concentration of heavy metals in sediment deposits (Monier, Soliman and Halani, 2023). The pollution load index (*PLI*) in Bistrica River sediment is small, suggesting no pollution in the study area.

The presence of heavy metals in the sediment samples for the Bistrica River is summarised in Table 3 and compared to U.S. Environmental Protection Agency (EPA) standards values (U.S. EPA, 2017a).

Regarding surface sediment samples, the heavy metal content values are as follows: arsenic and cadmium were reported as "nd" (not detected) across all measurements, indicating that their concentrations were below the detection limit of the analytical methods used. This suggests relatively low levels of arsenic and cadmium in the sediment samples, which is generally favourable from an environmental standpoint as these elements can be toxic at higher concentrations (Wang *et al.*, 2023). The concentrations of cobalt and aluminium show slight variations across the three measurements. The Co values range from 0.068 to 0.085 $mg \cdot kg^{-1}$, while the concentration of Al ranges from 0.064 $mg \cdot kg^{-1}$ at sampling point M1 to 0.095 $mg \cdot kg^{-1}$ at M3. Copper concentrations are under the EPA recommendation value of <25 across all measurements. Elevated copper levels in sediment can pose risks to aquatic organisms, particularly sensitive species like fish and invertebrates, and may indicate inputs from industrial or urban sources. Also, iron concentrations are lower than the EPA recommendation value by up to 25 $mg \cdot kg^{-1}$ in surface sediment samples. Elevated iron levels can result from both natural processes and human activities such as mining or industrial discharge. While iron is an essential nutrient, excessive levels can lead to sedimentation issues and potentially impact aquatic ecosystems. The concentrations of nickel, lead, and zinc are within or below the EPA recommendations (<20 for Ni, <40 for Pb, and <90 for Zn). This suggests compliance with regulatory standards and indicates lower risks of adverse effects on the environment from these elements.

ENRICHMENT FACTOR

The enrichment factor (*EF*) is largely applied to evaluate the presence of anthropogenic pollutants compared to the natural values (Wang *et al.*, 2023). The results were below 1, indicating low enrichment in the research area. Overall, the *EF* results of PTEs in the Bistrica River follow the order: Fe > Zn > Mn > Ni > Pb > Cu > Al > Co (Wang *et al.*, 2023).

GEOACCUMULATION INDEX

The results obtained for geoaccumulation index are below zero ($I_{geo} < 0$), indicating that the sediment in the Bistrica River is uncontaminated. The I_{geo} values of the studied PTEs decrease in the order below: Fe > Zn > Ni > Mn > Pb > Cu > Al > Co (Ghouma *et al.*, 2022; Wang *et al.*, 2023).

ECOLOGICAL RISK INDEX

The ecological risk index (*ERI*) results indicate a low risk (*ERI* < 40) for Co, Al and Cu at all studied sites, as well as for Ni and Pb at stations M1, M2, and M3. The *ERI* indicates a moderate risk (40 < *ERI* < 80) (Ghouma *et al.*, 2022; Wang *et al.*, 2023) for Fe and Mn at all stations M1, M2, M3 and for Zn at stations M1, M2 and M3.

STATISTICAL ANALYSIS

Multivariate statistics were used to estimate the possible sources of potentially toxic element pollution at the Bistrica River. Dendrogram analysis is critical for interpreting and understanding environmental samples, as it provides a clear and systematic method for clustering and visualising complex data. Therefore, dendrogram analysis is an indispensable tool for making sense of environmental datasets, guiding effective interventions, and enhancing our comprehension of ecological systems. The Figure 3 shows the dendrogram of the distribution of heavy metals in the surface sediment of the Bistrica River.

The research identifies two unique cluster groups, one with Co, Al, and Cu and the other one with Mn, Ni, Pb, Fe, and Zn. High positive correlations were observed between Fe, Zn, Pb, Ni, and Mn indicating a common source and spreading pattern.

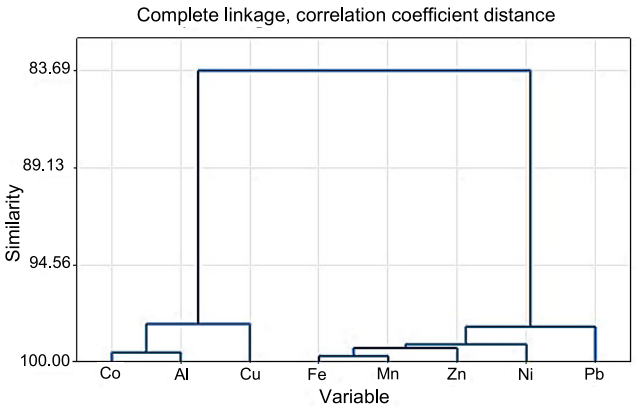

Fig. 3. The dendrogram of the distribution of heavy metals in sediment of the Bistrica River; source: own study

Previous research findings revealed that most of the chemical elements are mainly attributed to anthropogenic pollution aspects of the environment (Ghouma *et al*., 2022; Xu, Goa, and Yuan, 2022), while another part of some chemical elements (Cu, Al, and Co) might be attributed to geological aspects (Yeon, Kim and Lee, 2016; Liang *et al*., 2023). In the Figure 4, it is presented the heatmap plot of the heavy metals in water and sediment.

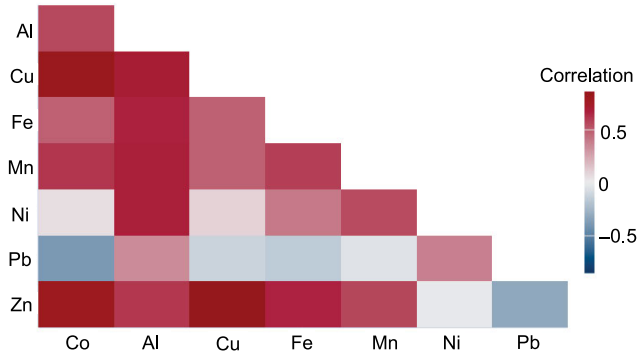

Fig. 4. Heatmap plot of the heavy metals in water and sediment samples; source: own study

Statistical data shows that the highest concentration of heavy metals (mg·kg^{-3}) is presented in the surface sediment samples (Tab. 4).

From the results we see that the highest concentration was found in Fe < Zn < Mn < Ni < Pb < Cu < Al < Co < As < Cd. These values are presented for comparison.

Table 4. Descriptive statistics of heavy metals presented in sediment samples (mg·kg^{-3})

Variable	*CV*	*SD*	Minimum	Median	Maximum
As	*	0.000000	0.000000	0.000000	0.000000
Al	19.89	0.01644	0.06400	0.08900	0.09500
Ni	7.05	0.01387	0.18500	0.19300	0.21200
Pb	13.75	0.0224	0.1430	0.1580	0.1870
Fe	17.48	0.1486	0.6980	0.8580	0.9950
Cu	8.39	0.00850	0.09500	0.09800	0.11100
Cd	*	0.000000	0.000000	0.00000	0.000000
Mn	48.08	0.1277	0.1860	0.1980	0.4130
Zn	23.39	0.178	0.565	0.802	0.913
Co	11.85	0.00889	0.06800	0.07200	0.08500

Explanations: *CV* = coefficient variation, *SD* = standard deviation.
Source: own study.

CONCLUSIONS

The study assessed the concentrations and bioavailability of potentially toxic elements (PTEs) in water and surface sediments from the Bistrica River. The highest PTE levels were found at stations M1, M2, and M3, influenced by anthropogenic activities such as urban effluents, agriculture, and fishing. The bioavailability data indicated high mobility of PTEs in water, suggesting easy assimilation by aquatic organisms. PTE concentrations followed the order: Fe > Zn > Mn > Ni > Pb > Cu > Al > Co. Contamination indices (contamination factor (*CF*), contamination degree (*CD*), pollution load index (*PLI*), enrichment factor (*EF*), geoaccumulation index (I_{geo})) indicated low to moderate contamination, but the ecological risk index (*ERI*) highlighted significant risks for Fe and Mn, particularly for aquatic life. Multivariate analysis showed that Fe, Mn, Zn, Ni, and Co were primarily from anthropogenic sources, while Cu, Al, and Pb might have multiple origins. Despite meeting WHO surface water quality guidelines, the river faces pollution from urban, industrial, agricultural, and chemical runoff.

ACKNOWLEDGEMENTS

The authors would like to thank the research and scientific explorers project for sustainable operation of surface water systems exploiting citizens for agriculture and seasonal recreation.

FUNDING

This study is independent research and did not receive financial support from the University of Pristina or any other funding opportunities.

CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

REFERENCES

Acharya, P., Muduli, P.R. and Das, M. (2023) "Assessment of heavy metal accumulation in *Penaeus monodon* and its human health implications," *Marine Pollution Bulletin*, 188, 114632. Available at: https://doi.org/10.1016/j.marpolbul.2023.114632.

Angello, Z.A., Behailu, B.M. and Tranckner, J. (2020) "Integral application of chemical mass balance and watershed model to estimate point and nonpoint source pollutant loads in data-scarce little Akaki River, Ethiopia," *Sustainability*, 12 (17), 7084. Available at: https://doi.org/10.3390/su12177084.

Cao, Y.R. *et al*. (2023) "Improved calculations of heavy metal toxicity coefficients for evaluating potential ecological risk in sediments based on seven major Chinese water systems," *Toxics*, 11(8), 650. Available at: https://doi.org/10.3390/toxics11080650.

DPMP (2020) *Development Plan of the Municipality of Peja 2020–2028*. Peja: Municipality of Peja.

Ejigu, M.T. (2021) "Overview of water quality modeling," *Cogent Engineering*, 8, 1891711. Available at: https://doi.org/10.1080/23311916.2021.1891711.

Ennaji, W.A. *et al*. (2020) "Heavy metal contamination in agricultural soil and ecological risk assessment in the northeast area of Tadla plain, Morocco," *Journal of Sedimentary Environments*, 5, pp. 307–320. Available at: https://doi.org/10.1007/s43217-020-00020-9.

Ewaid, S.H. (2017) "Water quality evaluation of Al-Gharraf River by two water quality indices," *Applied Water Science*, 7, pp. 3759–3765. Available at: https://doi.org/10.1007/s13201-016-0523-z.

Gajek, M. *et al.* (2022) "The elemental fingerprints of different types of whisky as determined by ICP-OES and ICP-MS techniques in relation to their type, age, and origin," *Foods*, 11(11), 1616. Available at: https://doi.org/10.3390/foods11111616.

Ghouma, A. *et al.* (2022) "Health risk assessment associated to heavy metal pollution levels in Mediterranean environment soils: A case study in the watershed of Sebkhet Ariana, Tunisia," *Arabian Journal of Geosciences*, 15, 716. Available at: https://doi.org/10.1007/s12517-022-09877-8.

Hakanson, L. (1980) "An ecological risk index for aquatic pollution controls a sediment logical approach," *Water Research*, 14(8), pp. 975–1001. Available at: https://doi.org/10.1016/0043-1354(80)90143-8.

Jaskuła, J. and Sojka, M. (2022) "Assessment of spatial distribution of sediment contamination with heavy metals in the two biggest rivers in Poland," *CATENA*, 211, 105959. Available at: https://doi.org/10.1016/J.CATENA.2021.105959.

KAS (2024) *Kosovo Agency of Statistics*. Available at: https://ask.rks-gov.net/ (Accessed: April 26, 2024).

Kumar, V., Pandita, S. and Setia, R. (2022) "A meta-analysis of potential ecological risk evaluation of heavy metals in sediments and soils," *Gondwana Research*, 103, pp. 487–501. Available at: https://doi.org/10.1016/j.gr.2021.10.028.

Lee, H. *et al.* (2020) "Legacy and novel flame retardants in water and sediment from highly industrialized bays of Korea: Occurrence, source tracking, decadal time trend, and ecological risks," *Marine Pollution Bulletin*, 160, 111639. Available at: https://doi.org/10.1016/j.marpolbul.2020.111639.

Li, Y. *et al.* (2022) "Water quality characteristics and source analysis of pollutants in the Maotiao River Basil (SW China)," *Water*, 14(3), 301. Available at: https://doi.org/10.3390/w14030301.

Liang, R.Z. *et al.* (2023) "Multi-index assessment of heavy metal contamination in surface sediments of the Pearl River estuary intertidal zone," *Marine Pollution Bulletin*, 186, 114445. Available at: https://doi.org/10.1016/j.marpolbul.2022.114445.

Liu, L. *et al.* (2015) "Co-occurrence correlations of heavy metals in sediments revealed using network analysis," *Chemosphere*, 119, pp. 1305–1313. Available at: https://doi.org/10.1016/j.chemosphere.2014.01.068.

Lu, J. *et al.* (2022) "Contrast analysis of flow-discharged measurement method in a wide-shallow river during ice periods," *Water*, 14(24), 3996. Available at: https://doi.org/10.3390/w14243996.

Mahlathi, C., Siyakatshana, N. and Chirwa, E. (2016) "Water quality modelling and optimisation of wastewater treatment network using mixed integer programming," *Water SA*, 42(4). Available at: https://doi.org/10.4314/wsa.v42i4.16.

Mirza, R. *et al.* (2019) "Contamination, ecological risk and source identification of metals by multivariate analysis in surface sediments of the khouran straits, the Persian Gulf," *Marine Pollution Bulletin*, 145, pp. 526–535. Available at: https://doi.org/10.1016/j.marpolbul.2019.06.028.

Monier, M.N.A.M., Soliman, A.A. and Halani, Al. (2023) "The seasonal assessment of heavy metals pollution in water, sediments, and fish of grey mullet, red seabream, and sardine from the Mediterranean coast, Damietta, North Egypt," *Regional Studies in Marine Science*, 57, 102744. Available at: https://doi.org/10.1016/j.rsma.2022.102744.

Muller, G. (1979) "Schwermetalle in den Sedimenten des Rheins: Veränderungen seit 1971 [Heavy-metals in sediment of the Rhine – Changes since 1971]," *Umschau in Wissenschaft und Technik*, 79(24), pp. 778–783.

Ngatia, M., Kithiia, S.M. and Voda, M. (2023) "Effects of anthropogenic activities on water quality within Ngong River sub-catchment, Nairobi, Kenya," *Water*, 15(4), 660. Available at: https://doi.org/10.3390/w15040660.

Novita, E. *et al.* (2020) "River water quality assessment in East Java, Indonesia," *Journal of Water and Land Development*, 47, pp. 135–141. Available at: https://doi.org/10.24425/jwld.2020.135040.

Novita, E., Firmansyah, J.W. and Pradana, H.A. (2023) "Penentuan indeks kualitas air Sungai Bedadung Kabupaten Jember menggunakan metode IP dan NSF-WQI [Determination of the Bedadung River water quality index in Jember Regency using the IP and NSF-WQI methods]," *Jurnal Ilmu Lingkungan*, 21(3), pp. 495–502. Available at: https://doi.org/10.14710/jil.21.3.495-502.

Rajeshkumar, S.Y. *et al.* (2018) "Studies on seasonal pollution of heavy metals in water, sediment, fish and oyster from the Meiliang Bay of Taihu Lake in China," *Chemosphere*, 191, pp. 626–638. Available at: https://doi.org/10.1016/j.chemosphere.2017.10.078.

Su, Q. *et al.* (2023) "Heavy metals in surface sediment of Plateau Lakes in Tibet, China: Occurrence, risk assessment, and potential sources," *Toxics*, 11(10), 804. Available at: https://doi.org/10.3390/toxics11100804.

Sun, C. *et al.* (2019) "Concentrations, speciation, and ecological risk of heavy metals in the sediment of the Songhua River in an urban area with petrochemical industries," *Chemosphere*, 219, pp. 538–545. Available at: https://doi.org/10.1016/j.chemosphere.2018.12.040.

Tian, K. *et al.* (2020) "Ecological risk assessment of heavy metals in sediments and water from the coastal areas of the Bohai Sea and the Yellow Sea," *Environment International*, 136, 105512. Available at: https://doi.org/10.1016/j.envint.2020.105512.

Tomlinson, D.L. *et al.* (1980) "Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index," *Helgoländer Meeresuntersuchungen*, 33, pp. 566–575. Available at: https://doi.org/10.1007/BF02414780.

Tugiyono, T. *et al.* (2023) "Evaluation of the water quality status and pollution load carrying capacity of Way Umpu River, Way Kanan District, Lampung Province, Indonesia, based on land use," *International Journal of Ecology*, 2023(1), 2689879. Available at: https://doi.org/10.1155/2023/2689879.

U.S. EPA (2017a) *Method 3051A (SW-846): Microwave assisted acid digestion of sediments, sludges, and oils*, Revision 1. Washington, DC: United States Environmental Protection Agency.

U.S. EPA (2017b) *Method 6010C (SW-846): Inductively coupled plasma-atomic emission spectrometry*, Revision 3, Washington, DC: United States Environmental Protection Agency.

Wang, Y. *et al.* (2023) "Assessment and simulation of water environment carrying capacity in a river basin using system dynamic model," *Polish Journal of Environmental Studies*, 32(3), pp. 2893–2907. Available at: https://doi.org/10.15244/pjoes/161326.

WHO (2021) *Guidelines for drinking-water quality*, 4th edn. Geneva: Word Health Organization. Available at: https://www.who.int/publications/i/item/9789241549950 (Accessed: May 20, 2024).

Xu, H., Goa, Q. and Yuan, B. (2022) "Analysis and identification of pollution sources of comprehensive river water quality: Evidence from two river basins in China," *Ecological Indicators*, 135, 108561. Available at: https://doi.org/10.1016/j.ecolind.2022.108561.

Yang, G. *et al.* (2020) "Heavy metals of sediment cores in Dachan Bay and their responses to human activities," *Marine Pollution*

Bulletin, 150, 110764. Available at: https://doi.org/10.1016/j.marpolbul.2019.110764.

Yeon, Y.J., Kim, D.H. and Lee, J.L. (2016) "Water quality modeling for integrated management of urban stream networks," *International Journal of Environmental Science and Development*, 7(12), pp. 928–932. Available at: https://doi.org/10.18178/ijesd.2016.7.12.906.

Yona, D. *et al.* (2018) "Distribusi dan Status Kontaminasi Logam Berat pada Sedimen di Sepanjang Pantai Barat Perairan Selat Bali, Banyuwangi [Distribution and status of heavy metal contamination in surface sediments on the Coast of Ranokomea, West Poleang, Bombana Regency]," *Journal of Fisheries and Marine Science*, 1, pp. 21–30.

Zha, D. *et al.* (2018) "Assessment of organophosphate flame retardants in surface water and sediment from freshwater environment (Yangtze River, China)," *Environmental Monitoring and Assessment*, 190, 222. Available at: https://doi.org/10.1007/s10661-018-6587-5.