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Spatial patterns and ecological significance of heavy metals in water and sediments of the Drini–Buna river system

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ABSTRACT

The Drini River Basin represents the largest river system in Albania and plays a key role in supporting freshwater resources, biodiversity, hydropower production, and human activities. This study evaluated the distribution, contamination status, and ecological risk of trace metals in water and surface sediments collected from eleven stations covering the basin of the river. Concentrations of metals were determined and interpreted using contamination indices, including the geoaccumulation index (Igeo), Nemerow pollution index (NPI), and potential ecological risk index (PERI). Trace metal concentrations exhibited significant spatial variability, with the highest enrichment observed for Ni, Cr, and Co. Geoaccumulation index results classified these metals as moderately to heavily contaminated at several stations, particularly in the upper basin and the Zalli River. In contrast, Cu, Mn, Fe, Al, Pb, Cd, and Hg generally remained within the uncontaminated or slightly contaminated categories. The NPI values for water were below 1 at all stations, indicating no significant metal pollution in the water column. PERI values ranged from low to moderate ecological risk, with no station exceeding the threshold for considerable ecological risk. The highest ecological risk was observed at the Zalli stream station, while the Bushtrica River exhibited the lowest contamination and risk levels. The spatial distribution of metals suggests that sediment contamination is controlled predominantly by geogenic factors associated with ultramafic and ophiolitic formations characteristic of northeastern Albania, although localized contributions from historical mining activities cannot be ruled out. Results indicated good water quality with respect to trace metals and low to moderate ecological risk in sediments, providing an important baseline for future monitoring and management of the Drini River Basin.

Keywords: Drini River; heavy metals; sediments; water quality; contamination indices; river pollution; Albania.

INTRODUCTION

Rivers are considered dynamic environmental systems where natural geochemical processes integrate with anthropogenic pressures occurring throughout the watershed (Allan, 2004; Vörösmarty et al., 2010). Waters and river sediments act both as transporters and sinks for contaminants, especially potentially toxic metals, which may persist in the environment for long periods due to their non-biodegradable nature (Förstner et al., 1981; Putri et al., 2025). Heavy metals are among the most important contaminants in aquatic systems because of their toxicity, persistence, bioaccumulation potential, and ecological impacts on aquatic organisms and food webs (Tchounwou et al., 2012; Ali et al., 2019). Their accumulation in sediments is of particular concern because sediments can function both as long-term reservoirs and as secondary sources of contamination when environmental conditions change, thereby influencing water quality and ecosystem health (Burton, 2002; Eggleton et al., 2004).

The Drini River is one the largest river systems in Albania and one of the most important hydrological systems in the Western Balkans. It plays an important role in regional water resources, biodiversity conservation, hydropower

production, and socio-economic development (UNDP, 2010; Skoulikidis et al., 2009). The basin is characterized by mountainous terrain, diverse carbonate and silicate geological formations, intensive hydropower infrastructure, agricultural land use, urban settlements, and localized industrial activities that may influence both water and sediment quality through natural and anthropogenic processes (Shumka et al., 2018; UNECE, 2011). The Drini River Basin includes the White Drin and Black Drin rivers, which converge near the city of Kukës before flowing toward the Adriatic Sea through the Buna River system, forming a transboundary watershed shared by several Western Balkan countries and representing one of the most significant freshwater networks in southeastern Europe (UNDP, 2010; UNECE, 2011).

The Black Drin (Drini i Zi) originates from Lake Ohrid, one of the oldest and deepest tectonic lakes in Europe, near the town of Struga (Albrecht & Wilke, 2008). From its source, the river flows northward through North Macedonia before entering northeastern Albania near the border region of Dibër. Within Albanian territory, the river traverses mountainous and valley landscapes, passing through important urban centers including Peshkopi and Kukës. Along its course, the Black Drin receives several tributaries and is strongly influenced by major hydropower reservoirs, including Fierza Reservoir, Koman Reservoir, and Vau i Dejës Reservoir, which significantly regulate its hydrological regime, flow dynamics, and sediment transport processes (UNDP, 2010; UNECE, 2011). Near Kukës, the Black Drin converges with the White Drin (Drini i Bardhë), originating from Kosovo, forming the Drin River (Drini). The combined river then flows westward through northern Albania before bifurcating near Shkodër, where one branch discharges into the Buna River and ultimately reaches the Adriatic Sea near the Albania–Montenegro coastal zone (Skoulikidis et al., 2009; UNECE, 2011).

The objectives of this study were to determine the concentrations and spatial distribution of selected heavy metals in water and sediment samples of the Drini River Basin, evaluate sediment contamination using pollution indices, assess relationships among physicochemical parameters and metal concentrations, as well as identify potential natural and anthropogenic sources of contamination.

MATERIALS AND METHODS

Study area

Water and sediment samples were collected from 11 monitoring stations along the Drini River and its tributaries during the study period, covering both upstream and downstream sectors under different anthropogenic and geological conditions. Sampling campaigns were conducted in January, 2024 to evaluate the spatial variability of metal distribution. Labeling of each station, coordinates, and description of the location are presented in Table 1. The map of sampling stations is presented in Figure 1.

Sampling methodology

Surface water samples were collected approximately 10–20 cm below the water surface

Table 1. Sample stations description

Description	Station	Latitude	Longitude
Zalli river	Zalli-00	41.5218746	20.4225285
Black Drini. Bridge of Gjorica	DRINI-01	41.5565289	20.4542901
Black Drini - Gryka	DRINI-02	41.6500972	20.3932045
Black Drini-Muhur	DRINI-03	41.6787526	20.3371339
Black Drini. Doda's Bridge	DRINI-04	41.8868885	20.3196929
Black Drini. Ujmishti Moss	DRINI-05	41.9363719	20.3626220
Black Drini-Kukes	DRINI-06	42.0688024	20.4201150
White Drini-Kukes	DRINI-07	42.1580676	20.5431168
Drini-Bachallek, Shkoder	DRINI-08	42.0421863	19.4955004
Buna river-Bridge of Buna	DRINI-09	42.0454896	19.4853715
Buna River- After confluence with Drini	DRINI-10	41.9977049	19.4178952
Bushtrica River	DRINI -11	41.9351847	20.3635702

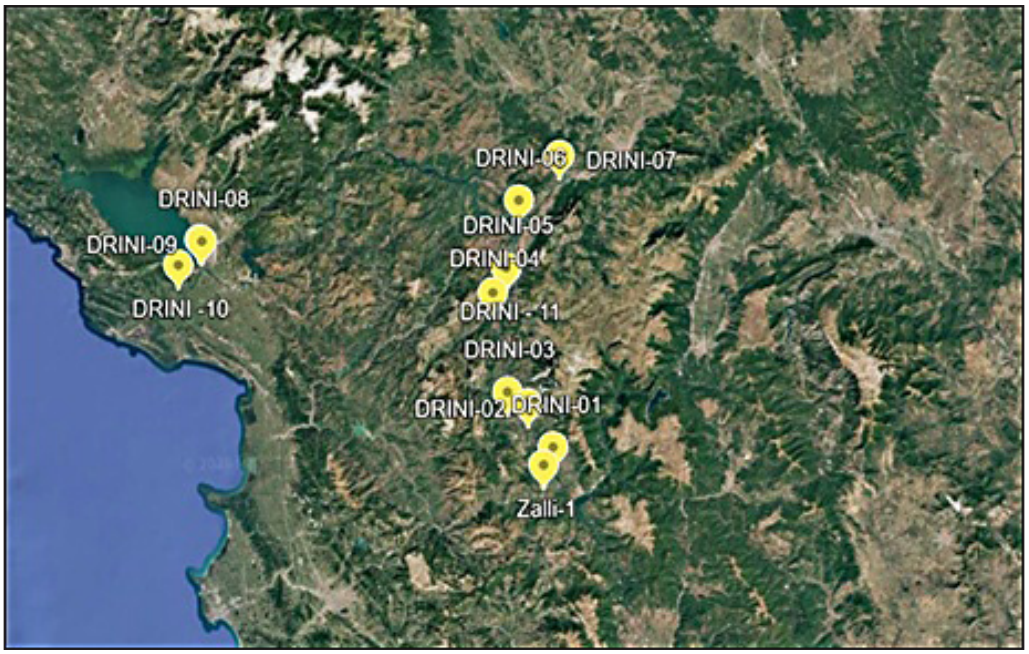

Figure 1. Map of sampling stations

using pre-cleaned polyethylene bottles following the procedures described in the Standard Methods for the Examination of Water and Wastewater (APHA/AWWA/WEF, 2023) and the guidance provided in ISO 5667-6:2014 for sampling rivers and streams.

Sediment samples were collected from the upper 0–5 cm layer using a stainless-steel grab, aiming to represent the most recently deposited material as the most environmentally relevant compartment for assessing contaminant accumulation and recent pollution inputs (Förstner et al., 1981; Burton, 2002). Sediment samples were transferred into acid-cleaned polyethylene containers, maintained at approximately 4°C during transport, and processed in the laboratory prior to analysis.

Field measurements, including temperature, pH, dissolved oxygen (DO), electrical conductivity (EC), and total dissolved solids (TDS), were performed in situ using a calibrated multiparameter probe according to APHA/AWWA/WEF, 2023. All sampling and analytical procedures were conducted under strict quality assurance and quality control (QA/QC) protocols, including instrument calibration, use of analytical blanks, certified reference materials, and replicate analyses, to minimize contamination and ensure analytical reliability and data quality (ISO/IEC 17025:2017; Magnuson et al., 2014).

Metal analysis and quality control

The water samples were filtered through 0.45 µm membrane filters and acidified with ultrapure nitric acid (HNO_3) to pH < 2 immediately after collection to prevent metal adsorption and preserve sample integrity (ISO 5667-3:2018; APHA/AWWA/WEF, 2023). Sediment samples were air-dried at room temperature, homogenized, sieved through a 63 µm mesh, and subjected to acid digestion prior to analysis. Microwave-assisted digestion of sediment samples was performed using concentrated HNO_3, HCl, and HF, according to USEPA Methods 3051A and 3052 (USEPA, 2007; USEPA, 1996). Metal concentrations were determined using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) and Flame Atomic Absorption Spectrometry (FAAS) for water and sediment samples, respectively, using the Analytik Jena 800G and 800F. Instrument calibration was performed using multi-point calibration curves prepared from certified standard solutions, while analytical quality was verified through procedural blanks, duplicate analyses, and certified reference materials (CRMs). All measurements were carried out in triplicate, and analytical precision, expressed as relative standard deviation (RSD), remained within acceptable limits for trace metal determination.

Evaluation of water and sediment quality

The evaluation of water quality due to physicochemical parameters and metals in water was based on the criteria established in Directive 2006/44/EC, which defines recommended quality requirements for freshwater bodies designated for the protection and maintenance of fish life. For metals included in the priority substances list (Pb, Cd, Ni, Hg), the Environmental Quality Standards (EQS) established under the European Union Water Framework Directive were applied. Chromium guideline values were adopted from the Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption.

Sediment quality was evaluated by comparing obtained results with the background and approximate European range of concentrations, as recommended in the Forum of European Geological Surveys, which provides harmonized continental-scale geochemical reference data derived from standardized sampling and analytical protocols across Europe (Salminen et al., 2005; De Vos et al., 2006; Videja et al., 2025). The corresponding limit and guideline values applied in this study are presented in Tables 2 and 3.

Assessment of contamination status based on environmental indices

The assessment of environmental contamination in aquatic ecosystems requires not only the direct measurement of pollutants in water and sediments, but also the application of integrated pollution indices that facilitate interpretation of complex datasets and support identification of anthropogenic impacts (Hakanson, 1980; Tomlinson et al., 1980). Such indices are particularly useful for distinguishing natural geochemical variability from contamination associated with human activities and for evaluating the overall ecological condition of aquatic environments (Sutherland, 2000). In water quality studies, the Nemerow Pollution Index (NPI) is commonly applied as a comprehensive indicator that provides a balanced evaluation of pollution intensity and potential environmental risk due to heavy metals (Nemerow et al., 1970; Al Yousif et al., 2023). NPI is calculated according to Equation (1):

$$NPI = \sqrt{\frac{PI_{max}^2 + PI_{mean}^2}{2}} \quad (1)$$

where: is the maximum pollution index and is the mean pollution index calculated for the studied parameters.

For sediment assessment, several complementary indices are widely used to characterize the degree and origin of contamination. The Geoaccumulation Index (Igeo), originally proposed by Müller (1969), assesses sediment contamination by comparing measured concentrations with geochemical background values while incorporating a correction factor for natural lithogenic variability (Loska et al., 2004; Varol, 2011). It is calculated according to the Equation (2):

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \quad (2)$$

where: is the measured concentration of the element in the sediment and is the geochemical background value, while the factor 1.5 is introduced to minimize the influence of natural variations in background values caused by lithological differences.

The Igeo classification comprises seven classes, ranging from Class 0 ($Igeo \leq 0$, unpolluted) to Class 6 ($Igeo > 5$, extremely polluted), providing a widely accepted framework for evaluating sediment contamination levels (Müller, 1969; Förstner & Müller, 1981).

The potential ecological risk index (PERI) is a widely used approach for evaluating the ecological risk posed by toxic metals in sediments by considering not only the degree of contamination but also the toxic response of each element. The method, originally proposed by Hakanson (1980), integrates contamination levels with metal-specific toxicity coefficients, thereby providing a more ecologically relevant assessment of environmental risk. The ecological risk factor for an individual metal is calculated as:

$$E_r^i = T_r^i \times CF^i \quad (3)$$

where: is the potential ecological risk factor of metal , is the toxic-response factor of the metal, and is the contamination factor.

Commonly used toxic-response factors include Cd = 30, Pb = 5, Cu = 5, Ni = 5, Cr = 2 and Zn = 1. The overall ecological risk index for a sampling site is obtained by summing the individual risk factors:

$$PERI = \sum E_r^i \quad (4)$$

The PERI classification generally interprets values below 150 as low ecological risk, 150–300 as moderate risk, 300–600 as considerable risk, and values above 600 as very high ecological risk. This index is particularly useful in sediment studies because it enables the identification of metals that contribute most significantly to ecological stress and supports prioritization of environmental management actions.

Statistical treatment of data

Principal component analysis (PCA) was applied to identify relationships among the measured variables and to explore spatial patterns among the sampling stations. Prior to analysis, the dataset was standardized using a z-score transformation to eliminate the influence of differences in measurement units and variable magnitudes. PCA was performed separately for water quality parameters and sediment trace metal concentrations using the correlation matrix. Components with eigenvalues greater than 1 were retained according to the Kaiser criterion, and the results were interpreted using score and loading plots (biplots). The analysis allowed the identification of groups of correlated variables, the recognition of potential sources of contamination, and the assessment of similarities and differences among sampling stations. All statistical analyses were performed using XLSTAT 2025.1.3 software.

RESULTS AND DISCUSSION

Physicochemical characteristics of water

Table 2 presents the physicochemical characteristics of the water samples. The obtained results indicate good water quality throughout the Drini River Basin. Water temperature (5.1–9.3°C) and pH (7.45–7.65) remained within ranges suitable for aquatic life, while dissolved oxygen concentrations (11.3–12.3 mg/L) reflected well-oxygenated conditions. Electrical conductivity values (255–420 µS/cm) indicated low mineralization and limited anthropogenic influence. Total suspended solids were generally low, except at DRINI-06 (69.6 mg/L) and DRINI-07 (12.8 mg/L), suggesting localized sediment transport. Calcium was the dominant major cation (36–96 mg/L), whereas sulfate concentrations (3.18–48.1 mg/L) showed greater spatial variability related to catchment geology. Overall, the basin was characterized by well-oxygenated waters, moderate mineralization, and low physicochemical disturbance during the monitoring period.

Heavy metals in surface water

The concentrations of trace metals in the Drini River Basin, (Table 3) indicate good chemical water quality and generally low levels of contamination. All measured metals remained below the guideline values established by Directive (EU) 2020/2184, Directive 2006/44/EC,

Table 2. Results of physicochemical analysis of water samples

Station	Temp. °C	pH	Cond. µs/cm	TSS mg/L	DO mg/L	Ca mg/L	Mg mg/L	Cl^- mg/L	SO_4^{2-} mg/L
DRINI-00	5.1	7.59	287	3.28	12.3	38	3.8	9.90	3.18
DRINI-01	5.2	7.62	369	1.44	12.1	76	6.2	12.1	27.5
DRINI-02	5.7	7.45	420	4.58	12.3	96	9	13.5	48.1
DRINI-03	7.0	7.61	409	3.55	11.8	90	8.4	11.3	45.6
DRINI-04	8.1	7.64	405	2.05	11.3	88	8.4	12.8	47.9
DRINI-05	6.0	7.56	255	5.82	12.3	52	6	11.3	26.6
DRINI-06	8.5	7.59	358	69.6	11.6	72	13.2	9.93	34.9
DRINI-07	7.2	7.49	316	12.8	11.7	64	8.4	9.93	22.1
DRINI-08	7.9	7.58	279	2.58	11.6	50	13.2	9.21	8.55
DRINI-09	9.3	7.63	277	2.54	11.5	64	6	9.93	4.38
DRINI-10	8.8	7.61	280	3.54	11.6	60	7.2	9.22	9.77
Drini -11	7.1	7.65	274	2.02	12.3	36	2.4	5.67	11.5
Recommended value[a]	25	≥6.0-≤9.0	1000	25	≥7	na	na	na	na
Recommended value[b]	25	≥6.0-≤9.0	1000	25	≥5	na	na	na	na

Table 3. Concentration of trace metals in water, (µg/L)

Station	Cr	Cu	Mn	Fe	Cd	Zn	Ni	Co	Pb	Hg
ZALLI-00	3.42	0.76	2.02	3.71	0.01	2.28	7.38	1.21	0.105	<0.02
DRINI-01	3.92	2.02	2.26	2.75	0.12	2.06	0.90	0.15	0.212	<0.02
DRINI-02	4.44	3.08	1.35	7.57	0.52	2.14	2.52	0.14	0.284	<0.02
DRINI-03	3.62	2.15	0.92	7.37	0.01	2.42	0.90	1.11	0.289	<0.02
DRINI-04	3.21	2.20	2.11	7.38	0.01	3.64	0.62	<0.1	0.303	<0.02
DRINI-05	1.97	2.24	0.32	7.49	0.01	3.66	1.37	<0.1	0.142	<0.02
DRINI-06	16.1	4.01	5.39	10.9	0.01	5.32	2.78	0.94	0.283	<0.02
DRINI-07	13.5	5.08	15.4	5.86	0.09	7.40	2.11	1.20	0.424	<0.02
DRINI-08	2.57	2.03	1.53	8.95	0.01	2.15	2.53	0.89	0.145	<0.02
DRINI-09	1.40	1.84	0.41	8.99	0.04	3.46	1.58	1.17	0.132	<0.02
DRINI-10	1.92	2.20	0.50	7.44	0.01	1.37	1.00	0.26	0.138	<0.02
DRINI- 11	1.20	1.96	1.26	2.06	0.01	1.02	1.60	<0.1	0.070	<0.02
Recommended value[c,d]	50[c]	40[d]	50[c]	200[c]	0.9	300[c]	34[e]	na	14[e]	0.07[e]

and the Water Framework Directive. Chromium (1.20–16.1 µg/L), copper (0.76–5.08 µg/L), zinc (1.30–8.30 µg/L), nickel (0.62–7.38 µg/L), lead (0.07–0.42 µg/L), and mercury (<0.02 µg/L) were present at low concentrations, indicating negligible ecological risk. Cadmium (0.01–0.52 µg/L) showed the highest relative enrichment, with the maximum value recorded at DRINI-02, but remained below relevant regulatory limits. Spatially, slightly elevated concentrations of several metals were observed at DRINI-06 and DRINI-07; however, all values remained well below threshold levels. The obtained results suggest that metal concentrations are largely controlled by natural geological and catchment characteristics, supporting a good chemical status of the basin waters. There are no known published data regarding the distribution of metals in Black Drini River. Most papers refer to White Drini, flowing across Kosovo, for which the concentration of metals in water (Haxhibeqiri et al., 2015) has resulted in more than 10 times higher concentrations compared to the results obtained in this study. For example: Cu varied from 30-37 µg/L; Cr 32-55 µg/L; Fe 410-460 µg/L, etc.).

Heavy metals in sediments

The concentrations of metals in the sediments of the Drini River Basin showed considerable spatial variability. Chromium (322.5–917.2 mg/kg), nickel (56.6–1378.1 mg/kg), and cobalt (95.9–219.4 mg/kg) consistently exceeded the upper limits of the reported European concentration ranges (95, 60, and 25 mg/kg, respectively) at all sampling stations. Therefore, these elements represent the most enriched components of the sediment geochemistry throughout the basin. In contrast, iron (11,607–25,860 mg/kg), manganese (517–1194 mg/kg), copper (20.6–51.0 mg/kg), and cadmium (0.07–0.55 mg/kg) remained within the typical European concentration ranges. Zinc concentrations ranged from 42.0 to 420 mg/kg. While most stations exceeded the upper European range value of 120 mg/kg, particularly DRINI-05, DRINI-08, DRINI-06, and DRINI-07, the highest concentrations were localized rather than basin-wide.

Lead concentrations (3.27–34.4 mg/kg) generally remained within the reported European range (5–35 mg/kg), although the maximum value at DRINI-06 approached the upper limit. Mercury concentrations varied between 0.014 and 0.079 mg/kg, with several stations exceeding the upper European range value of 0.03 mg/kg, particularly DRINI-08, DRINI-10, DRINI-03, and DRINI-11. Even for sediments, most published data refer to White Drini River. Several studies have reported similar results regarding the metal concentrations in sediments. According to Haxhibeqiri (2015), the concentration of Cd varied between 01-1.0 mg/kg while in this study, the interval of values varied between 0.07-0.55 mg/kg; Cu varied between 14.5-48.1 mg/kg, while in the presented study it reached 24.9-51.0 mg/kg; higher values for Cr, Mn, Zn, Ni were also obtained in this study.

Table 4. Results of heavy metals concentration in sediments, (mg/kg dw)

Station	Cr	Cu	Mn	Fe	Cd	Zn	Ni	Co	Pb	Hg
ZALLI-00	861.3	24.9	953.8	25258.4	0.07	95.2	1378.1	216.9	4.24	0.020
DRINI-01	656.5	34.0	1159.4	24198.5	0.28	42.0	193.7	188.3	16.7	0.036
DRINI-02	643.3	39.4	889.4	22707.9	0.16	51.8	230.1	180.4	10.1	0.027
DRINI-03	534.9	22.8	721.6	14292.8	0.18	177	318.7	115.0	5.65	0.045
DRINI-04	429.6	20.6	892.1	13659.9	0.30	213	252.1	108.0	8.1	0.038
DRINI-05	724.4	30.9	834.4	25589.1	0.53	420	398.2	205.3	21.8	0.018
DRINI-06	667.3	46.0	1193.5	25859.8	0.31	300	198.1	219.4	34.4	0.020
DRINI-07	552.4	51.0	1135.4	22198.7	0.42	268	214.4	177.2	25.4	0.014
DRINI-08	917.2	34.6	840.0	24976.5	0.45	337	477.9	216.2	14.4	0.079
DRINI-09	560.0	29.7	517.0	20962.4	0.55	215	154.0	206.0	13.4	0.038
DRINI-10	741.2	34.6	714.6	21751.6	0.36	52.6	347.9	186.9	11.2	0.052
Drini- 11	322.5	30.3	936.0	11606.9	0.16	210	56.6	95.9	3.27	0.045
European background/median	31/60	19/25	448/850	20100	0.2/0.4	60/70	28/30	8/10	15/20	0.03/0.08
Approximate European range	5-95	5-50	100-1500	5780-45280	0.05-1	20-120	5-60	1-25	5-35	<0.01-0.03

Environmental contamination assessment

The Nemerow Pollution Index (NPI) values for all monitoring stations were below 1, ranging from approximately 0.10 to 0.42, indicating that the waters of the Drini River Basin can be classified as unpolluted with respect to the investigated metals (Figure 2). According to the NPI classification (NPI < 1 = unpolluted; 1–2 = slightly polluted; 2–3 = moderately polluted; >3 = heavily polluted), none of the sampling sites exhibited evidence of metal pollution. The highest NPI value was recorded at DRINI-02 (0.42), followed by DRINI-06 and DRINI-07 (approximately 0.24), suggesting relatively higher metal concentrations at these locations, although still well below pollution thresholds. The remaining stations showed consistently low NPI values, generally around 0.10–0.16, reflecting low overall metal contamination. These results indicate that trace metal concentrations in the river water are largely controlled by natural geochemical processes and remain within acceptable environmental levels. The low NPI values are consistent with the generally low concentrations of dissolved metals observed throughout the basin and suggest the absence of significant anthropogenic metal pollution sources affecting water quality.

The geoaccumulation index (Igeo) revealed marked differences among the analyzed metals (Figure 3). Nickel, cobalt, and chromium exhibited the highest positive Igeo values, with most stations falling within the moderately to heavily contaminated and heavily contaminated categories, indicating substantial enrichment in the basin sediments. Nickel showed the strongest enrichment, reaching Igeo values close to the heavily to extremely contaminated class at some locations. Zinc displayed moderate enrichment, whereas copper showed values close to background levels. In contrast, manganese, iron, aluminum, lead, and mercury exhibited predominantly negative Igeo values, indicating uncontaminated conditions, while cadmium generally remained within the uncontaminated to slightly contaminated range. The predominance of Ni, Cr, and Co enrichment is consistent with the geological setting of the Drini River Basin, which is strongly influenced by ultramafic and ophiolitic formations that naturally contain elevated concentrations of these elements (Salminen et al., 2005; Economou-Eliopoulos et al., 2012; Hamuna et al, 2021). Similar enrichment patterns have been reported throughout the Balkan Peninsula, particularly in Greece and Albania, where weathering of ophiolitic complexes and Fe–Ni laterite deposits results in naturally elevated concentrations of Ni, Cr, and Co in soils and sediments (Kelepertzis et al., 2013; Economou-Eliopoulos, 2021). The FOREGS Geochemical Atlas of Europe identified some of the highest regional background concentrations of cobalt, nickel, and chromium in areas associated with Balkan ophiolites and ultramafic rocks (Salminen et al., 2005). Therefore, the observed Igeo pattern suggests that the enrichment of Ni, Cr, and Co

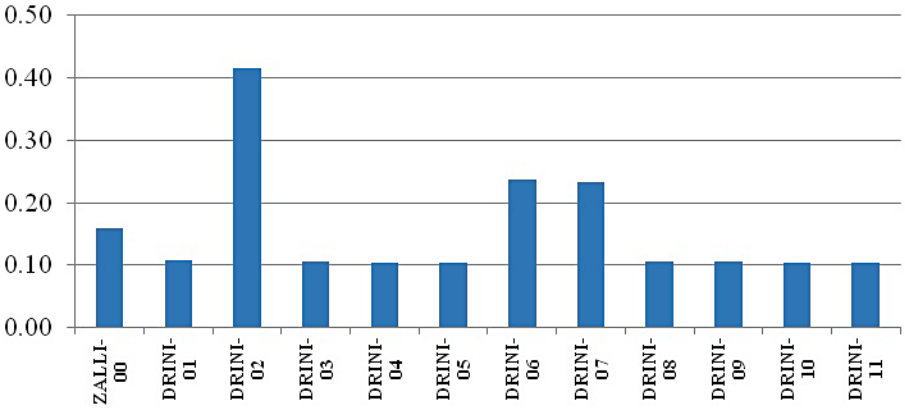

Figure 2. Spatial variation of NPI

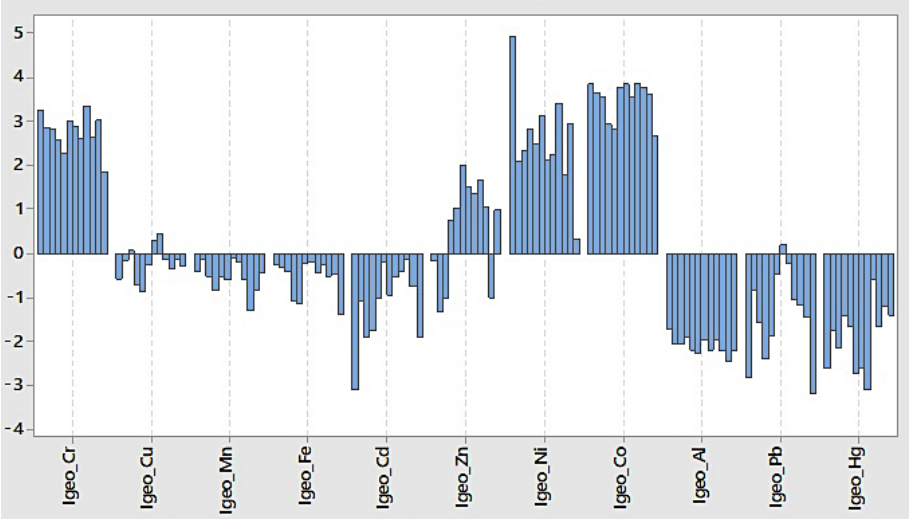

Figure 3. Igeo of metals in sediments

in the Drini River Basin is largely controlled by lithogenic sources, rather than anthropogenic inputs, whereas the remaining metals generally occur at concentrations close to natural background levels. This interpretation is further supported by the widespread occurrence of Cr–Ni–Co mineralization and ultramafic lithologies within the Albanian ophiolite belt (Çina et al., 2010; Economou-Eliopoulos et al., 2012).

The potential ecological risk index (PERI/RI) values showed moderate spatial variability across the Drini River Basin, ranging from approximately 70 to 285 (Figure 4). According to the classification proposed by Hakanson (1980), RI < 150 indicates low ecological risk, 150–300 indicates moderate ecological risk, 300–600 indicates considerable ecological risk, and RI > 600 indicates very high ecological risk. Most monitoring stations exhibited low ecological risk, with RI values below 150, suggesting limited potential adverse effects of metal contamination on aquatic ecosystems. The lowest risk was observed at DRINI-11 (RI ≈ 70), while DRINI-01, DRINI-02, DRINI-04, DRINI-06, DRINI-07, and DRINI-09 also remained within the low-risk category.

Moderate ecological risk was identified at DRINI-05, DRINI-08, and DRINI-10, with RI values ranging from approximately 150 to 200, indicating increased ecological pressure from potentially toxic metals. The highest RI value was recorded at ZALLI-00 (RI ≈ 285), placing this station near the upper limit of the moderate-risk category and suggesting a greater contribution of ecologically sensitive metals. Nevertheless, none of the investigated stations exceeded the threshold for considerable ecological risk (RI > 300), indicating that the overall ecological threat posed by sediment-associated metals in the basin remains relatively limited.

The observed spatial pattern suggests that ecological risk is concentrated at a few locations, whereas most stations are characterized by low

risk despite the elevated concentrations of geogenic elements, such as Cr, Ni, and Co. This occurs because the PERI method assigns different toxic-response factors to metals, giving substantially greater weight to highly toxic elements such as Cd and Hg than to Cr, Ni, or Co (Hakanson, 1980). Consequently, the ecological risk assessment indicates that although several stations exhibit metal enrichment, the overall potential ecological impact on the aquatic environment is generally low to moderate across the Drini River Basin.

The elevated concentrations of Cr, Ni, and Co observed at ZALLI-00 may be partly related to the geological characteristics of the catchment, which drains ultramafic and ophiolitic rocks of the Mirdita Ophiolite Belt, naturally enriched in these elements (Kierczak et al. 2021). However, the influence of the Bulqiza mining district should also be considered. The Bulqiza area hosts one of the largest chromite deposits in Europe and has been subjected to intensive chromium mining for several decades. Mining activities, waste rock disposal, erosion of mine tailings, and drainage from extraction areas have been reported to contribute to soil and surface-water contamination in the region. Studies conducted in the Bulqiza area identified significant environmental impacts associated with chromite exploitation, including increased erosion, sediment mobilization, and contamination of soils and water bodies by chromium-bearing materials. Therefore, the elevated ecological risk observed at ZALLI-00 likely reflects the combined influence of naturally metal-rich ophiolitic lithologies and historical or ongoing mining activities within the Bulqiza catchment.

Bushtrica River (DRINI-11) exhibited the lowest overall metal-related ecological risk among the investigated sites, as reflected by the lowest RI value recorded in the basin. Metal concentrations were generally low, indicating limited accumulation of potentially toxic elements in the sediments. Unlike stations influenced by ultramafic formations or mining-affected catchments, Bushtrica did not show pronounced enrichment of Cr, Ni, or Co, suggesting a weaker influence of metal-rich geological formations and anthropogenic pressures. The low contamination levels observed at this station indicate that the Bushtrica River represents one of the least impacted tributaries within the Drini River Basin with respect to trace metals, reflecting relatively natural geochemical conditions and limited sources of metal input. Consequently, the station can be considered a local reference site for assessing metal contamination within the basin.

The PCA biplot (Figure 5) of water parameters explained 57.87% of the total variance, with F1 and F2 accounting for 36.20% and 21.68%, respectively. The distribution of stations and variables indicates that water chemistry in the Drini River Basin is controlled by both geological weathering processes and trace metal inputs associated with ultramafic formations.

The positive side of F1 was characterized by elevated concentrations of major ions (Ca, Cl^{-}, SO_4^{2-}, EC) and several trace metals (Fe, Mn, Zn, Cr, Cu, and Pb), whereas the negative side was associated with higher pH and dissolved oxygen values. This separation suggests a gradient from more mineralized and metal-enriched waters to

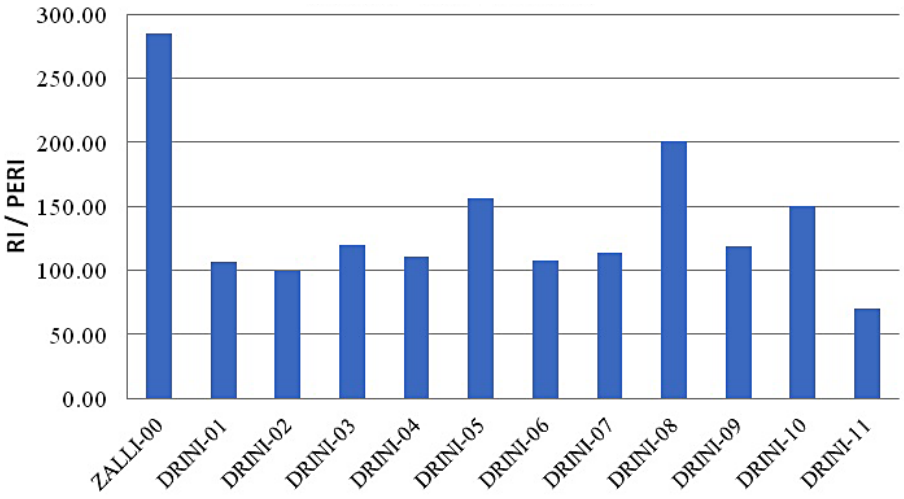

Figure 4. Variation of PERI in sediments

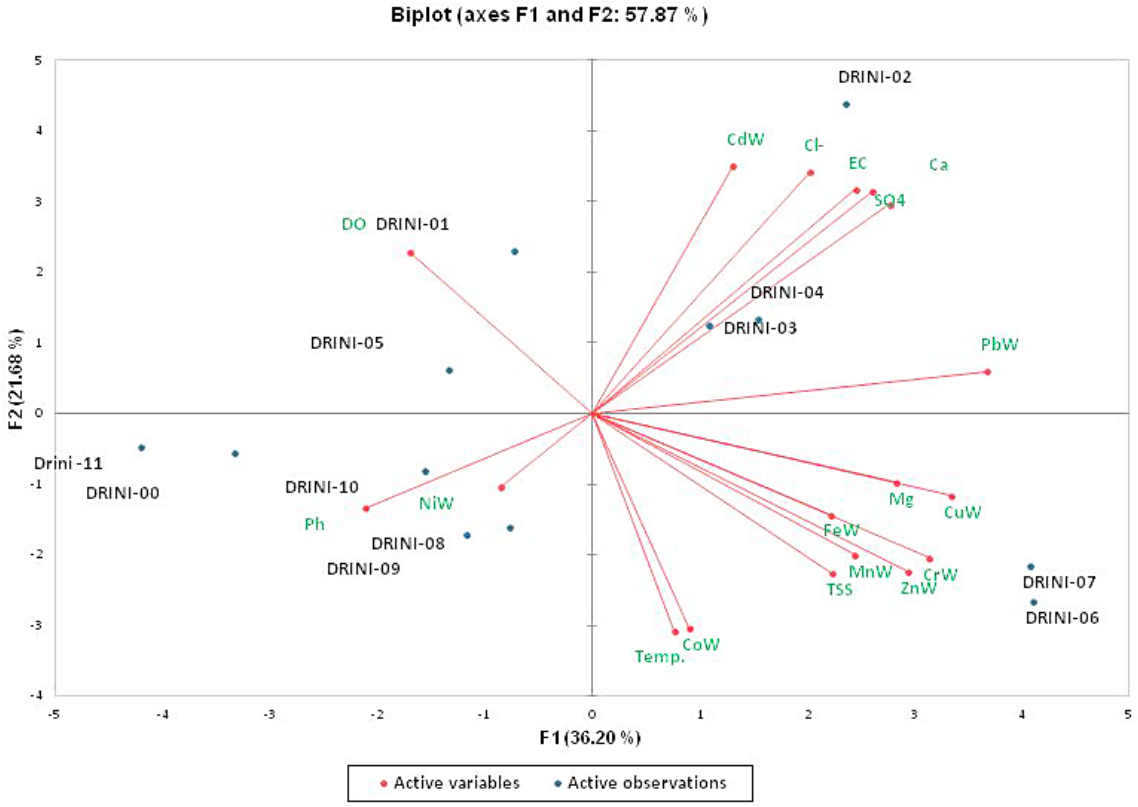

Figure 5. PCA biplot of water parameters

less mineralized and better-oxygenated waters. Stations DRINI-02, DRINI-03, and DRINI-04 clustered in the positive F1 and positive F2 quadrant and were strongly associated with EC, Ca, SO_4^{2-}, and Cl^-, indicating the influence of rock weathering and increased dissolved mineral content in the middle section of the Black Drini River. Stations DRINI-06 and DRINI-07, located near Kukës, were associated with Fe, Mn, Zn, Cr, Cu, and TSS, suggesting enhanced transport of particulate matter and metal-bearing materials. Their close grouping reflects similar hydrochemical conditions and common geological controls. The Zalli River station (DRINI-00) occupied a distinct position on the negative side of F1, separated from most other stations. Although not directly associated with the major metal vectors in the PCA space, its isolated position indicates a unique hydrochemical signature compared with the main river system. This differentiation is likely related to the influence of the Bulqiza chromite mining area and the ultramafic lithologies that dominate the Zalli catchment. The exceptionally high Cr, Ni, and Co concentrations observed in sediments at this station support the existence of a strong geogenic and mining-related influence. Stations DRINI-08, DRINI-09, and DRINI-10, located in the downstream section near the Drini–Buna confluence, clustered together and were associated mainly with pH and dissolved oxygen. Their grouping suggests that downstream mixing and dilution processes reduce the influence of localized metal and mineral inputs observed in the upstream reaches.

The PCA of heavy metals in sediments (Figure 6) showed that the first two principal components explained 62.34% of the total variance (F1 = 38.91%, F2 = 23.44%), indicating that the main patterns of sediment metal distribution were adequately represented by the PCA model. F1 appears to represent a gradient of metal enrichment, separating stations with elevated concentrations of Cr, Co, Fe, Pb, Cu, Cd, Mn, and Zn from stations with lower metal contents. Most trace metals are located on the positive side of F1, suggesting a common source and similar geochemical behavior.

F2 further differentiates stations according to the relative contribution of Ni and Cr enrichment versus Pb–Cu–Cd enrichment. Positive F2 values are dominated by Ni, Cr, Co, and Fe, whereas negative F2 values are associated with Pb, Cu, Cd, Mn, and Zn.

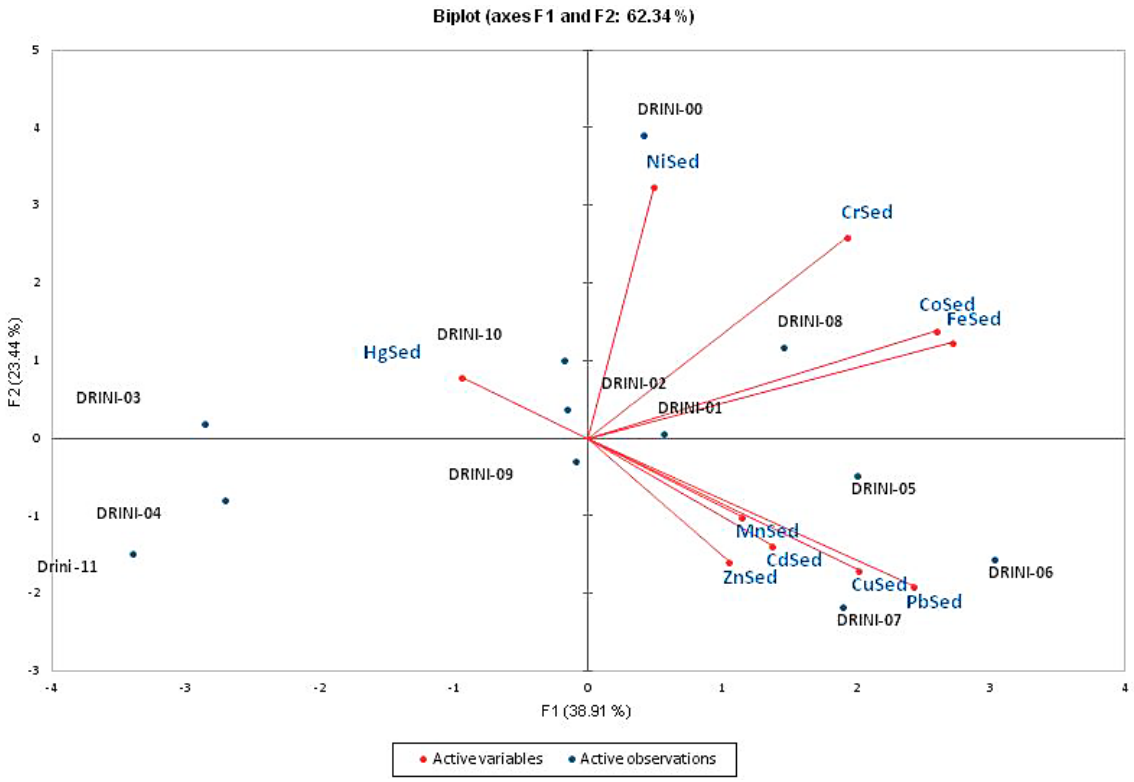

Figure 6. PCA biplot of metals in sediments

Among the selected stations, DRINI-00 is clearly isolated in the upper-right quadrant and shows a strong association with Ni, indicating a unique geochemical signature compared to all other stations. This result is consistent with the exceptionally high Ni concentration measured at this station (1378 mg/kg) and reflects the influence of the Bulqiza chromite mining district and ultramafic lithologies. The separation of DRINI-00 from the remaining stations confirms that the Zalli River is the major hotspot of metal enrichment within the basin.

DRINI-01 and DRINI-02 are located close to the vectors for Cr, Co, and Fe, indicating that these stations are influenced by the same geological source affecting the Zalli River. Their position suggests downstream transport of metals derived from ophiolitic and ultramafic formations, although at lower concentrations than those observed at DRINI-00.

Stations (DRINI-05, DRINI-06, and DRINI-07, located in the middle and lower basin) are metal-enriched, associated with Pb, Cu, Cd, Mn, and Zn. The close grouping of these metals suggests a common accumulation mechanism, likely related to fine-particle deposition and local anthropogenic inputs, although concentrations remain generally lower than those of Cr and Ni.

The downstream and tributary stations (DRINI-03, DRINI-04, DRINI-09, DRINI-10, and DRINI-11) are located on the negative side of F1 and are relatively distant from most metal vectors, indicating lower levels of contamination and weaker influence from the ultramafic source areas. Their position reflects more background-like sediment composition and the effects of dilution and sediment mixing within the river system.

CONCLUSIONS

The assessment of trace metals in the Drini River Basin demonstrated that metal distribution is predominantly controlled by natural geological conditions, particularly the widespread occurrence of ultramafic and ophiolitic formations. Elevated concentrations of Cr, Ni, and Co were mainly observed in sediments from the upper basin, especially at ZALLI-00 and at Black Drini stations, indicating strong geogenic influence with possible localized contributions from mining activities.

Sediment quality indices revealed enrichment of Cr, Ni, and Co, whereas other metals generally remained within background or low-contamination levels. Despite this enrichment, ecological

risk assessment indicated predominantly low ecological risk across the basin, with only a few stations reaching moderate risk levels.

In contrast, dissolved metal concentrations in water were consistently low. Nemerow Pollution Index values remained below pollution thresholds at all monitoring sites, confirming good water quality and the absence of significant trace-metal contamination in the water column.

Spatial patterns highlighted stronger geogenic influence in the upper catchment, while downstream sections reflected sediment transport and mixing processes. The Bushtrica River showed the lowest contamination levels and may serve as a local reference site for future monitoring.

Multivariate statistical analysis further supported these findings. The PCA of water quality parameters revealed that the hydrochemistry of the basin is primarily controlled by mineral weathering processes and trace metal transport. Stations DRINI-02, DRINI-03, and DRINI-04 were associated with elevated ionic content (EC, Ca, SO_4^{2-} , and Cl^-), whereas DRINI-06 and DRINI-07 showed stronger relationships with Fe, Mn, Zn, Cr, Cu, and suspended solids. The Zalli River station (DRINI-00) exhibited a distinct hydrochemical signature, reflecting the influence of the Bulqiza mining area and ultramafic lithologies.

Similarly, the PCA performed on sediment data confirmed the dominant role of geological factors in controlling metal distribution throughout the basin. DRINI-00 was clearly separated from all other stations and strongly associated with Ni enrichment, while DRINI-01 and DRINI-02 were closely linked to Cr, Co, and Fe. These results highlight the influence of chromite-bearing ultramafic formations and indicate that the Zalli River acts as the principal source of Cr–Ni–Co enrichment within the basin. Downstream stations showed progressively weaker metal enrichment, reflecting dilution and sediment mixing processes. Overall, the PCA results corroborate the contamination indices and demonstrate that natural geological controls are the primary drivers of trace metal occurrence in both water and sediments of the Drini River Basin.

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