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Assessments of Heavy Metal Contaminants in the Drenica River and Bioremediation by *Typha angustifolia*

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Abstract: The concentrations of cadmium, copper, lead, zinc, nickel, and chromium in samples of sediment, water, and *Typha angustifolia* plants in the stream of the Drenica River were determined to assess the level of pollution. According to sediment analysis results from seven locations, the concentrations of Cu, Ni, Zn, and Cr exceeded the permitted limits according to WHO standards from 1996. In the plant samples, the concentrations of Cd and Pb were above the allowed limits according to GD161 and ECE standards, and according the WHO standard, the water quality in the Drenica River is classified into the first, second, and third quality categories. The results of this study show the bioaccumulation coefficient in *Typha angustifolia* plants, and it was found that the most bioaccumulated of the metals is Cd, with a bioaccumulation coefficient (BAF) greater than 1. The pollution load index (PLI), enrichment factor (EF index), Geoaccumulation index (Igeo), potential ecological risk factor (Eif), and potential ecological risk index (RI) were used in combination to assess the degree of pollution and the environmental risk presented to the freshwater ecosystem of the Drenica River. The results show that the Drenica River is mainly polluted by Ni, Cu, and Cr, reflecting substantial impacts of anthropogenic activities, including sizeable industrial effects, the development of urbanism, agricultural activities, and the deposition of waste from a ferronickel factory in the area.

Keywords: heavy metals; macrophytes; contaminants; sediment; concentration; standards; pollutants; classification; water quality

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1. Introduction

The plant *Typha angustifolia* has attracted the attention of scientists for its extraordinary ability to accumulate heavy metals from the environment where it grows [1–4]. This plant, known for its characteristic shape and important ecological service in its natural habitats, is also a potential environment for monitoring soil and water pollution [5–8]. Aquatic ecosystems, which are rich in biodiversity, are a testament to the intricate balance of nature. The diversity of macrophytes, a key measure, is directly influenced by factors such as altitude, nutrient levels, and water quality [9–11]. Despite this significance, the mechanisms governing species diversity in aquatic ecosystems have often been overshadowed by research on terrestrial and benthic ecosystems. However, the tireless efforts of scientists have begun to shed light on this crucial aspect. Their research has explored species diversity across various water bodies, revealing that water quality parameters directly impact plant diversity dynamics. Anthropogenic influences tend to favor a higher diversity of non-indigenous species over indigenous ones [12]. This research is vital to understanding and preserving the delicate balance of aquatic ecosystems.

Heavy metals in water and soil are not just a concern but a significant environmental threat, endangering aquatic ecosystems, agricultural productivity, and human well-being [13,14]. As noted by various studies, their harmful properties, their long-lasting presence in the environment, and their capacity to infiltrate food webs make them a pressing issue [14,15]. They enter ecosystems through both natural processes and human activities. Heavy metals such as lead, mercury, cadmium, chromium, arsenic, and selenium are significant inorganic pollutants. Their contamination often originates from industrial processes and the use of various synthetic substances, like pesticides, paints, and batteries, although some occur naturally as well [16,17]. Many heavy metals are harmful to plants and animals and tend to bioaccumulate in the food chain, posing risks to organisms at higher trophic levels, including humans [18,19]. Although the toxic effects of certain heavy metals like lead and mercury have been recognized for centuries, our understanding of their full impact has only developed more recently. This understanding underscores the urgent need for sustainable solutions like phytoremediation [20,21].

Certain aquatic plants can extract nutrients [22,23]. Recently, many scientists have focused on macrophytes' accumulation of heavy metals. In addition, phytoremediation processes have been studied in macrophytes grown in sediments and waters contaminated by metals [23]. This innovative technique utilizes the natural abilities of certain plants to absorb, detoxify, or degrade various pollutants, including heavy metals, organic compounds, and even radioactive substances. Phytoremediation has gained widespread attention in recent years due to its cost-effectiveness, sustainability, and minimal environmental impact compared to traditional remediation methods [24]. By harnessing the power of plants, phytoremediation offers a sustainable solution to some of the most pressing environmental challenges while providing additional benefits such as habitat restoration, erosion control, and improved water quality [22,25].

The concentration of heavy metal content in *Typha angustifolia* is critical to understanding the potential effects of environmental pollution and examining the possibilities of using this plant in environmental remediation processes. These analyses elucidate the essential role of plants as environmental pollution monitors and potential resources for the rehabilitation of their natural habitats. Recent studies [26–31] on the biological assessment of rivers in Kosovo show a very concerning situation; therefore, this study aimed to analyze the concentrations of heavy metals in sediment, water, and *Typha angustifolia* plants.

Heavy metals such as lead, mercury, cadmium, chromium, arsenic, and selenium, are significant inorganic pollutants. Their contamination often originates from industrial processes and the use of various synthetic substances like pesticides, paints, and batteries, although some occur naturally as well [32]. Many heavy metals are harmful to plants and animals and tend to bioaccumulate in the food chain, posing risks to organisms at higher trophic levels, including humans [18,19]. Although the toxic effects of certain heavy metals like lead and mercury have been recognized for centuries, our understanding of their full impact has only developed more recently. This understanding underscores the urgent need for sustainable solutions like phytoremediation [20,21].

2. Materials and Methods

2.1. Study Area

The Drenica River collects the waters of the Denica Depression(Figure 1). The Drenica River catchment is located in the central part of Kosovo and has an area of 447 km^2 [33]. This watershed separates the waters from the Drini i Badhë River watershed. The southernmost point of the Drenica River catchment is on Carraleva mountain (Breshanc peak 1044 m, while the northernmost point is in Lubovec (815 m). The waters of this catchment flow from the south and north to the east and are discharged into the Sitnica River. The Drenica River is the left branch of the Sitnica River. The average annual air temperature is 10.6 °C; the coldest month is January, with an average temperature of 0.8 °C; and the hottest month is July, with an average temperature of 20.6 °C. The average annual rainfall is 670 mm. Within the Drenica River's catchment area are 34 villages, and the city of Drenas (Gllogoc) has a population of 61,145. According to [34], the water flows in the Drenica River are as follows: Qmin = 0.02 m^3/s, Qavg. = 1.52 m^3/s, Qmax = 32.80 m^3/s. The Drenica River catchment is characterized by a complex geological construction in which rocks of ages from the Paleozoic to the Quaternary take part [35]. From the hydrogeological point of view, the following three types of aquifers are distinguished in the space of this watershed: aquifers with intergranular porosity, aquafers with crack porosity, and aquifers with little water (formed mainly in Paleozoic rocks) [36].

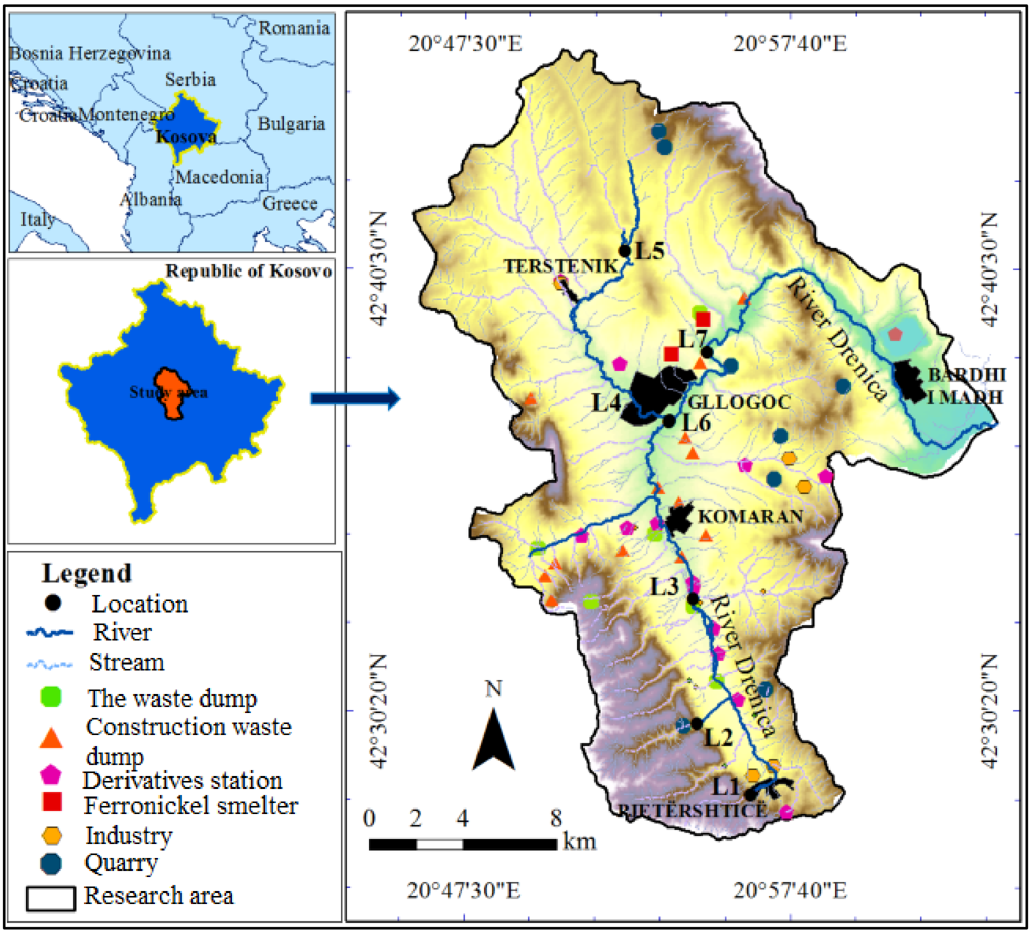

Figure 1. Location of research area and environmental hotspots.

The Drenica River is influenced by a ferronickel industrial complex that dates back to 1984. Waste is dumped in a space near the Drenica River, creating hills of slag. The landfill has an area of 24 ha, while the area of influence is 45 ha and is considered a source of air, water, and soil pollution. On average, 1 million tons of slag are generated per year, which has a chemical composition comprising SiO_2, MgO, FeO, and CaO. The municipal waste of Drenas is also dumped here; therefore, this location is considered an environmental hotspot [37].

The Drenica River originates in Bretenc (1046 m) of Caraleva Mountain and has a basin of 477 km^2 and a length of 50.5 km. In the upper part of the Drenica, from the source to the village of Pokelek, the river valley is 2–4 km wide, and the width of the riverbed is up to 4 m. North of Petershtica to Drenas (Gllogoc), there is a slight slope, with a wide riverbed and features of a lowland river. From Drenas to Bellacevc, the river has a closed bed that does not exceed 5 m wide, with a pronounced slope and depth. After exiting the gorge, the river widens and reaches a width of 8–10 m, and its slope decreases, where it takes on the characteristics of a plain river and flows into the Sitnica River. The average flow of the Drenica into the Sitnica is 2.0 m^3/s [37].

2.2. Preparation of Samples

Samples were collected along the course of the Drenica River in the summer of 2023 at seven monitoring stations. For measurement of the water's physicochemical parameters at each station, samples were collected 50 cm under the water surface using 1.5 L labeled polyvinyl bottles. The samples collected for trace metals analysis were acidified to a pH < 2 using 10% analytical-grade HNO_3 to keep the metals in a dissolved state and to prevent bacterial activity [38]. Samples were placed in refrigerator boxes (+4 °C) and transported to the laboratory [39]. Concerning the sediment samples, three replicates of bottom sediments were collected at each sampling site using a sediment sampler. The samples were emptied into polyethylene bags, stored in refrigerator boxes (+4 °C), and analyzed at the laboratory [38].

To determine the concentration of heavy metals (Cd, Cr, Cu, Pb, and Hg) in the water, EPA Method No. 1637 was used. The water samples were treated with nitric acid to reach pH = 2. A volume of 100 mL of sampled water was placed in a 400 mL volume chemical cup and treated with 3 mL of concentrated nitric acid. In addition, the chemical cup was heated to below the boiling temperature to obtain 20 mL after evaporation. Another 3 mL of concentrated nitric acid was added, covering the chemical cup, and the heating temperature was regulated to create acid reflux for the complete digestion of the sample. Samples were left to evaporate until almost dried up, then left to cool down. After cooling, 1:1 nitric acid was added, and the samples were heated again until all residue or precipitation was dissolved. Samples were centrifuged to remove any insoluble residue, then diluted up to 25 mL. Metals in the solution were determined directly by graphite furnace AAS.

To assess the levels of heavy metals in the sediments, EPA Method No. 3050 B was used. Samples were air-dried in the laboratory at room temperature and ground into a fine mixture using a mortar and pestle before being sieved through 2 mm mesh. In addition, about 0.3 g–0.5 g of the sample was added to the reference vessel. Samples were digested with added nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) [40]. Afterward, samples were mineralized in an "ETHOS ONE PRO-24" microwave digester, and the digested solution was cooled and filtered using Whatman filter paper No. 40. The filtered sample was then diluted up to 100 mL with metal-free distilled water and stored in a particular container until analysis [40]. To determine the total heavy metal concentrations in sediments, and AAS flame atomic absorption spectrophotometer (novAA 350 Series by Analytics Jena) was used [38].

The sampling sites were strategically selected to measure the impact of all potential contamination sources. Vegetation was analyzed based on the phytosociological method of the Zurich–Montpellier school. To measure the level of total nitrogen (N), we used ISO methods 7890/1, 2000, and for phosphorus (P), we used ISO-7150-1 (1984) [41].

2.3. Statistical Analysis

Statistical analyses of metal concentrations in water, sediment, and plants are reported as mg/kg dry weight, and each result is the mean value of three replicates. A one-way ANOVA was conducted using SPSS 15.0 statistical package Origin Pro 2019. Graphs were generated by Microsoft Excel 2007.

Table 1. Contamination classification indices for soil.

Index	Equation	Category and Description	References
Pollution load index (PLI)	PLI = $\sqrt[n]{CFn1\ x\ CFn2\ xCFn3X\ CFni}$, where n is the total number of heavy metals being considered and CF is the contamination factor.	PLI = 0 denotes an ideal condition of no pollution, PLI = 1 denotes the presence of merely baseline levels of pollutants, and PLI > 1 denotes the site's ongoing deterioration.	[42]
Contamination factor (CF)	Cfmetals = Cmetal/Background	The Hakanson (Hakanson, L. 1980) [11] classification method is utilized to classify metal CF. This results in the following four classes: CF < 1 (class 1), 1 ≤ CF < 3 (class 2), 3 ≤ CF < 6 (class 3), and CF ≥ 6 (class 4). These classes indicate varying degrees of contamination, namely low, moderate, considerable, and very high.	[43]
Enrichment factor (EF)	EF = $\frac{C/Cd(sample)}{C/Cd(background)}$	The enrichment factor (EF) can be generally understood as follows [44,45]: <2, minimal; 2–5, moderate; 5–20, substantial; 20–40, very high; >40, extremely high.	[44,45]
Geoaccumulation index (Igeo)	Igeo = log2[Cn/1.5 Bn], where Bn is the background value for a given metal (n), Cn is the observed concentration of that metal in the sediment, and a factor of 1.5 is applied because the background data may vary due to lithological differences.	Igeo ≤ 0, practically unpolluted; 0 ≤ Igeo ≤1, unpolluted to moderately polluted; 1 ≤ I geo ≤ 2, moderately polluted; 2 ≤ Igeo ≤ 3, moderately to heavily polluted; 3 ≤ Igeo ≤ 4, heavily polluted; 4 ≤ I geo ≤ 5, heavily to highly polluted; 5 ≤ I geo, extremely polluted.	[46,47]
Potential ecological risk factor (Eif)	According to Duodu et al. (2016), $RI = \sum Er = \sum Tr \times CF$, where Tr indicates each metal's toxicological response factor, whereas Er denotes the possible ecological danger factor of that particular metal. The contamination factor (CF) for any metal is known.	The Hakanson (1980) [11] standardized response coefficient for heavy metal toxicity was chosen as the evaluation criterion. The corresponding toxicity coefficients were Cd = 30, Cu = 5, Pb = 5, Ni = 5, Cr = 2, and Zn = 1 [47]. RI < 150, low risk; 150 ≤ RI < 300, moderate risk; 80 ≤ Er < 160, considerable risk; 160 ≤ Er < 320, high risk; Er ≥ 320 very high risk	[48,49]
Potential ecological risk index (RI)	As per the research conducted by (Hakanson, 1980) [11], the RI is determined using the following equation: Ri = $\sum_{i=1}^{n} Eri$ where Er is the ecological risk factor of a given elected at each soil sample location, RI is the integrated potential ecological risk index, calculated as a sum of the Eri for all examined heavy metals.	RI < 150, low risk; 150 ≤ RI < 300, moderate risk; 300 ≤ RI < 600, considerable risk; RI ≥ 600, high risk	[47]
Bioaccumulation coefficient	BFC = Cplant parts/Csoil	C plant parts, metal concentration in plant (mg/kg dry weight); C soil, concentration in soil (mg/kg dry weight).	[50]

3. Results and Discussions

Various studies have proven that *Typha angustifolia* is an aquatic macrophyte that can remove copper and nickel from wastewater [51,52].

Table 2 and Figure 2 present the levels of heavy metals in the soil (Cu, Cd, Ni, Pb, Zn, and Cr) at seven different locations (L1 to L7) along the main streams of the Drenica River and the side branches of the Shale River, Nekoc River, and Verboc River. If present at high levels, these metals are potential environmental pollutants that can harm people, plants, animals, and the entire ecosystem.

Table 2. The level of heavy metals in sediment along the streams of the Drenica River.

Location	**Heavy Metals Unit (mg/kg)**					
	Cu	**Cd**	**Ni**	**Pb**	**Zn**	**Cr**
L1	37.07	0.15	463.33	19.70	68.09	474.85
L2	59.55	0.33	173.96	36.97	77.30	138.18
L3	54.24	0.46	463.87	32.48	83.34	590.13
L4	33.14	0.21	92.81	12.72	47.96	207.71
L5	53.78	0.31	308.42	58.24	76.71	229.33
L6	56.58	0.27	138.78	50.83	82.35	165.17
L7	35.06	0.17	190.97	46.70	61.79	95.90
Mean ± Std	47.06 ± 4.31	0.27 ± 0.4	261.7 ± 57.7	36.8 ± 6.2	71.07 ± 4.8	271.6 ± 70.4
*** Target value of soil (mg/kg)**	36	0.8	35	85	50	100

* Target values are specified to indicate desirable maximum levels of elements in unpolluted soils [53,54].

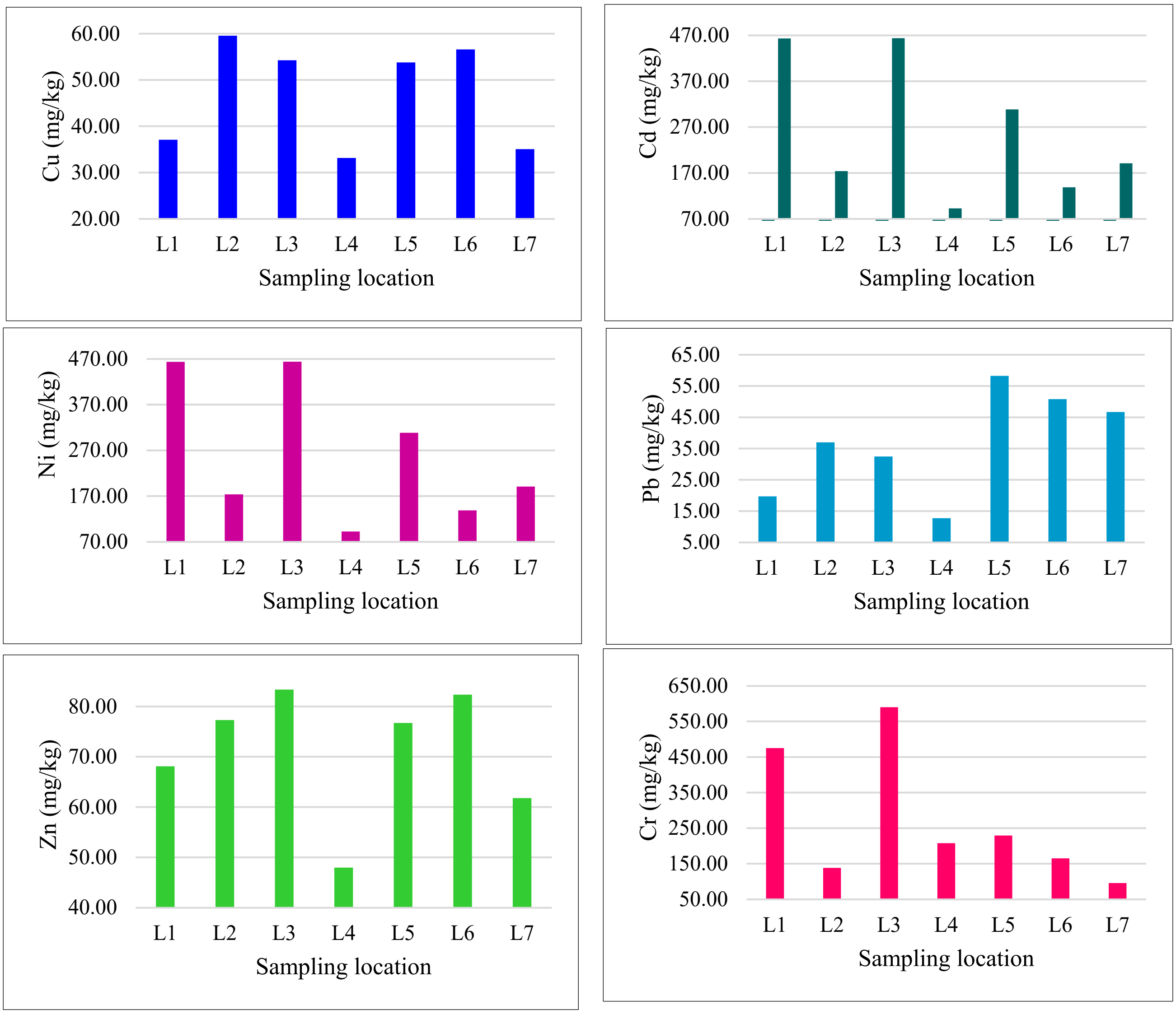

Figure 2. The levels of heavy metals in sediment along the streams of the Drenica River.

The highest level of Cu (more than 59.55 mg/kg) is in L2, while the lowest level (33.14 mg/kg) is in L4. The average and standard deviation of all locations were 47.06 ± 4.31 mg/kg (Table 2 and Figure 2). In locations L1, L2, L3, L5, and L6, the concentration of copper in sediment was above the limit (30 mg/kg) allowed by the WHO [53] (Table 2 and Figure 2). According to the WHO, excess over the permitted limit is based on the average values [53].

The highest level of Cd is 0.455 mg/kg in L3, while the lowest value is 0.148 mg/kg in L1. The mean value and standard deviation were 0.27 ± 0.4 mg/kg (Table 2 and Figure 2). According to the WHO, cadmium concentration in the sediment was within the allowed limit (0.8 mg/kg) at all sampling locations [53].

The highest level of Ni is 463.870 mg/kg in L3, while the lowest value of 92.806 mg/kg was recorded in L4. The mean value and standard deviation were 261.7 ± 57.7 mg/kg (Table 2 and Figure 2). According to the WHO, the nickel concentration in sediments was above the allowed limit (35 mg/kg) at all sampling locations [53].

The highest level of Pb is 58.24 mg/kg was recorded at L5, while the lowest value of 12.7 mg/kg was recorded at location L4 (Table 2 and Figure 2). The average value and standard deviation were 36.8 ± 6.2 mg/kg. According to WHO, the concentration of Pb in the sediment was within the allowed limit (85 mg/kg) at all sampling locations [53].

The highest level of Zn is 83.340 mg/kg in L3, while the lowest is 61.7 mg/kg at location L7. The average value and standard deviation were 71.07 ± 4.8 mg/kg (Table 2 and Figure 2). According to WHO, the concentration of Zn in the sediment was above the permissible limit (50 mg/kg) at all sampling locations except location L4 [53] (Table 2 and Figure 2).

The highest level of Cr of 590.13 mg/kg recorded at L3 is due to the industrial ferronickel operation there [53,54], while the lowest value of 95 mg/kg was recorded at location L7 (Table 2 and Figure 2). The average value and standard deviation were 271.6 ± 70.4 mg/kg. According to WHO, the concentration of Cr in the sediment was above the allowed limit (100 mg/kg) at all sampling locations except location L7 [53].

The values of Cu, Cd, Pb, and Zn in this study were lower than those reported in [55] for the Sitnica River and Trepça River in Kosovo, while the values of Ni and Cr were higher in our study. This is due to the ferronickel in our study area. Likewise, compared to those reported in [56] for the Toplluha River in Kosovo, the results for Cr and Ni metals in the Drenica River have higher values, while Cu, Cd, Pb, and Zn have lower values.

The lowest value of CF based on the average values in the sediment indicated a low level of pollution (CF < 1 Table 1) by cadmium and lead; an average level of pollution ($1 \leq CF < 3$) by copper, zinc, and chromium; and very high contamination ($CF \geq 6$) by nickel (Table 3). Whereas in [56], very high CF pollution with zinc was reported in the Toplluha River in Kosovo, in our research, high levels of CF pollution with nickel are reported, which is thought to be a consequence of the ferronickel industry located in the study area.

Table 3. Values of the contamination factor and geoaccumulation index (Igeo).

	Cu	Cd	Ni	Pb	Zn	Cr
CF	1.31	0.34	7.48	0.43	1.42	2.72
Geoacumulation index (Igeo)	0.34	−1.58	2.56	−1.17	0.49	1.43

The geoaccumulation index (Igeo) values calculated in this study show that heavy metals such as Cu and Zn belong to the 0 < Igeo < 1 class, indicating no contamination to moderate contamination (Table 3). Metals such as Cr, Cd, and Pb belong to the 1 < Igeo < 2 class, indicating moderate pollution, while Pb belongs to the 2 < Igeo < 3 class, indicating moderate to very high pollution.

The values of the PLI (Pollution Load Index) in the sediment ranged from 0.15 at location L4 to 4.40 at location L3 (Figure 3). According to [57], a PLI > 1 indicates heavy metal pollution, while a value < 1 suggests no pollution. Based on this, locations L1, L2, L3, L5, and L6 indicate pollution levels, with the highest values of this index presented at locations L3, L5, and L6. These areas are subject to significant anthropogenic pollution from household sewage, industrial and agricultural activities, and the region's geology, as in the case of location L2.

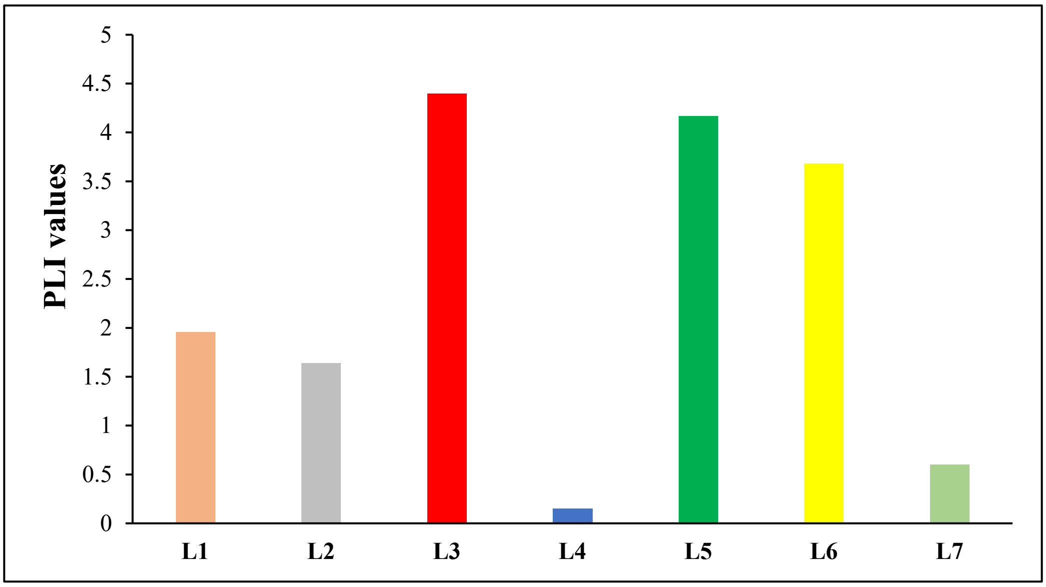

Figure 3. Pollution load index (PLI) value of heavy metals in the sediment of the Drenica river.

High values of this index in the sediment of surface waters were also presented in conducted in Kosovo [58]. The influence of industrial areas in increasing the values of this index has also been documented in many studies in the countries of the Albania region [59], North Macedonia [60], Greece [61], Serbia [62], Montenegro [63], as well as worldwide in countries like the Philippines [64], Turkey [65], Nigeria [66], Italy [67], Spain [68], and China [69].

The EF (enrichment factor) values for Cu, Ni, and Cr metals in the sediment of the Drenica River indicate their enrichment. In contrast, Pb and Zn metals had minimal values (EF < 2), with the lowest levels detected a locations L2–L6 (Figure 4). Cu had an EF value usually above 40, with agricultural activities along the course of the Drenica River being the main factor contributing to this high level (Figure 4). The EF values for Ni were significantly high (5–20) in locations L2, L4, and L6, while locations L3, L5, and L7 showed very high EF values, along with location L1, where they were exceptionally high (Figure 4). Based on this, we can conclude that the high levels of metals such as Ni, Cu, and Cr indicate substantial impacts from anthropogenic activities, including significant industrial influence, urban development, agricultural activities, and the deposition of waste by the ferronickel industry in the study area.

Compared to research conducted along the Toplluha River in Kosovo [56], the EF values in the Drenica River are higher for Ni and Cu but lower for Pb, Zn, and Cr. A similar comparison hold for a study conducted in the surface waters of Lake Badovci in Kosovo [58]. Additionally, we found higher EF values for all metals than those reported in [70] for the Drini Bardhë River.

Locations L1, L3, and L5 have higher RI values than locations L2 and L4, where there is little anthropogenic influence (Table 4). Locations with higher percentages of hazardous metals, such as Ni, Cr, and Cd, tend to have higher RI values, indicating a greater risk to aquatic ecosystems and human health in these areas. High RI values indicate the need for immediate corrective measures and the management of pollution from industrial water and sewage, as well as continuous monitoring by competent institutions to reduce the negative impact of hazardous metals in the water environments of the Drenica River.

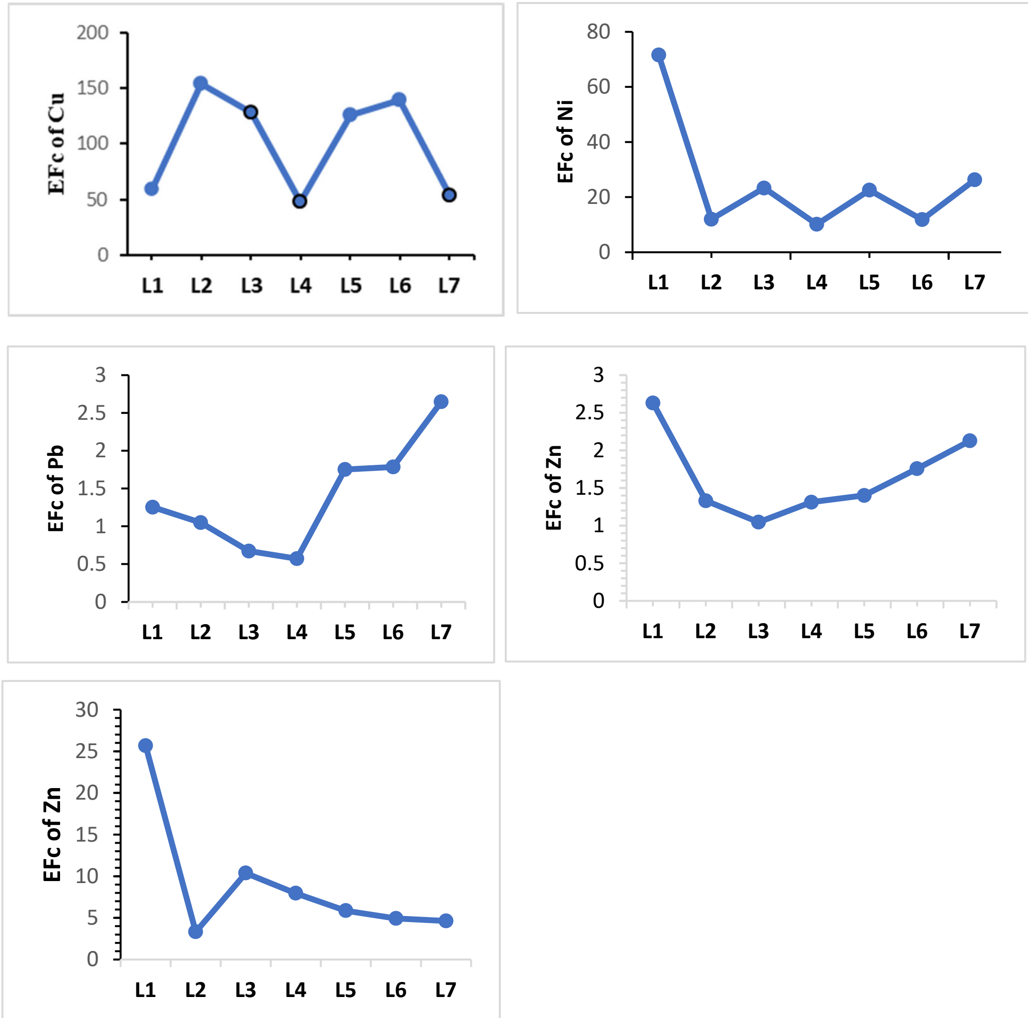

Figure 4. Enrichment factor (EF) values for heavy metals in sediment from sampling sites along the Drenica River.

Table 4. Potential ecological risk factor and possible environmental risk indices of heavy metals in sediments.

	Potential Ecological Risk Factor (Eif)						Potential Ecological Risk Index (RI)
	Cu	**Cd**	**Ni**	**Pb**	**Zn**	**Cr**	
L1	1.060328	0.034225	175.2439	0.053715	1.854499	22.54825	200.7949
L2	2.736267	0.172225	24.70232	0.189174	2.389992	1.909371	32.09935
L3	2.270044	0.323477	175.6534	0.146014	2.778222	34.82534	215.9965
L4	0.847423	0.068252	7.030983	0.022394	0.920103	4.314344	13.2035
L5	2.231704	0.153077	77.65134	0.469467	2.353954	5.259225	88.11877
L6	2.470136	0.112225	15.72145	0.357604	2.712609	2.728113	24.10214
L7	0.94846	0.043056	29.7723	0.301853	1.527202	0.919681	33.51255

Table 5 presents a Spearman correlation analysis between the concentrations of Cu, Cd, Ni, Pb, Zn, and Cr metals in the sediment. According to the analysis, they share a similar type of pollution source and distribution path; the correlation values between Cu and Ni are relatively low (correlation coefficient value of 0.107), while a positive correlation ($p < 0.05$) is observed between Cu and Zn. This may be the result of having the same type of pollution source, including pollution from the application of plant protection products in agricultural operations and urban and industrial impacts, including drainage systems, that contribute to the amount of copper and zinc in river sediments.

Table 5. Spearman correlation analysis between the concentrations of Cu, Cd, Ni, Pb, Zn, and Cr metals in the sediment.

			Cu	Cd	Ni	Pb	Zn	Cr
Spearman's rho	Cu	Correlation Coefficient	1.000	0.679	0.107	0.429	0.857 *	−0.036
		Sig. (2-tailed)	.	0.094	0.819	0.337	0.014	0.939
		N	7	7	7	7	7	7
	Cd	Correlation Coefficient	0.679	1.000	0.179	0.250	0.750	0.214
		Sig. (2-tailed)	0.094	.	0.702	0.589	0.052	0.645
		N	7	7	7	7	7	7
	Ni	Correlation Coefficient	0.107	0.179	1.000	0.036	0.393	0.643
		Sig. (2-tailed)	0.819	0.702	.	0.939	0.383	0.119
		N	7	7	7	7	7	7
	Pb	Correlation Coefficient	0.429	0.250	0.036	1.000	0.357	−0.321
		Sig. (2-tailed)	0.337	0.589	0.939	.	0.432	0.482
		N	7	7	7	7	7	7
	Zn	Correlation Coefficient	0.857 *	0.750	0.393	0.357	1.000	0.321
		Sig. (2-tailed)	0.014	0.052	0.383	0.432	.	0.482
		N	7	7	7	7	7	7
	Cr	Correlation Coefficient	−0.036	0.214	0.643	−0.321	0.321	1.000
		Sig. (2-tailed)	0.939	0.645	0.119	0.482	0.482	.
		N	7	7	7	7	7	7

* Correlation is significant at the 0.05 level (2-tailed).

This connection between these two elements with similar pollution effects was also reported in [70]. While cadmium presents the highest value of the correlation coefficient with copper (r = 0.679) and zinc (r = 0.750), a similar correlation was reported in [71]. Likewise, Nickel presents the highest value of the correlation coefficient with Cr (r = 0. 643), and the connection between these metals was also reported in [72].

A hierarchical cluster analysis was performed to identify possible sources of contamination. A hierarchical dendrogram was used to display the results (Figure 4). The results of metal concentrations (Cu, Cd, Ni, Pb, Zn, and Cr) at seven sampling locations at the mouth of the Drenica River can be grouped into the following three clusters:

First group: Locations L1 and L3, which are affected by agricultural activity (Figure 5);

Second group: Location L5, which has little anthropogenic influence (Figure 5);

Third group: Locations L4, L6, and L7, which are significantly influenced by urban and industrial development (Figure 4).

Location L2, also grouped in the third cluster, is impacted by nearby mines and quarries (Figure 5) that affect the Shale River, which flows into the Drenica River. Field observations confirmed this.

The concentration of Cu in plants varied from 0.31 mg/kg at L1 to 3.90 mg/kg at location L2 (Table 6). The average concentration and its standard deviation were 1.01 ± 0.93 mg/kg. According to the WHO, the concentration of copper in plants was within the permissible limit (10 mg/kg) at all locations [53].

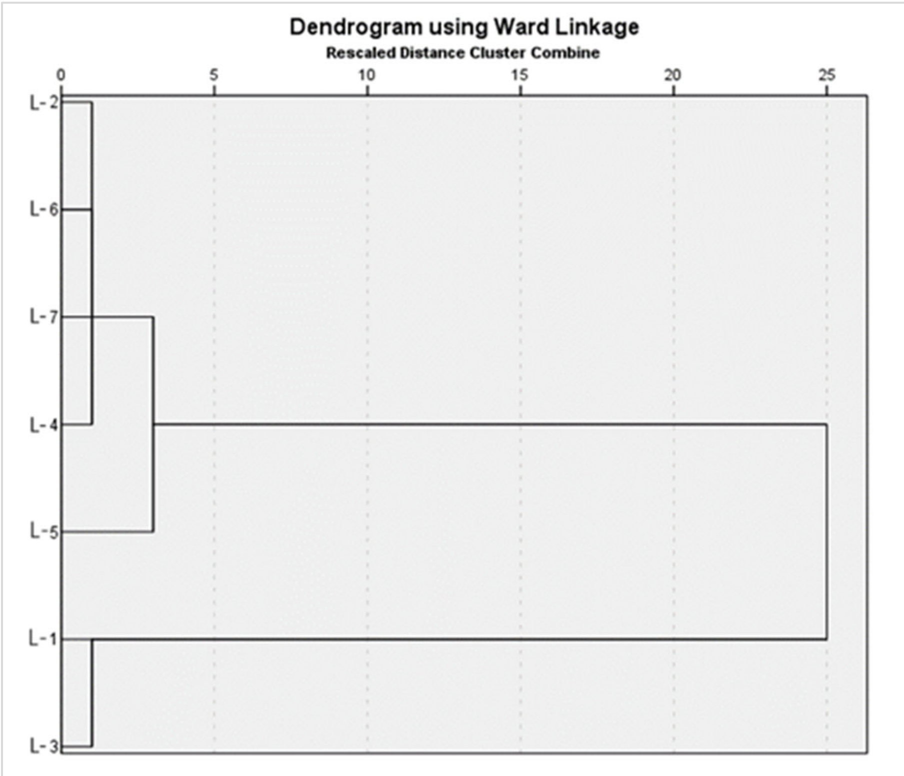

Figure 5. Hierarchical dendrogram.

Table 6. Results of concentrations of heavy metals in plants.

Location	Heavy Metals					
	Cu	**Cd**	**Ni**	**Pb**	**Zn**	**Cr**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
L1	0.31	0.830	n.d	5.90	23.848	n.d
L2	3.90	0.933	n.d	3.77	22.691	n.d
L3	0.32	1.078	n.d	0.41	18.070	n.d
L4	0.47	1.134	n.d	0.16	25.455	n.d
L5	1.16	1.302	n.d	2.86	21.814	n.d
L6	1.34	1.132	n.d	1.40	18.522	n.d
L7	0.40	1.157	n.d	0.40	13.850	n.d
Mean ± Std	1.01 ± 0.93	1.08 ± 0.14	-	2.12 ± 1.99	20.6 ± 3.7	-
** Permissible value in plants (mg/kg)	10	0.02	10	2	0.60	1.30

** Source: [53].

The highest level of Cd was 1.30 mg/kg at L5, while the lowest was 0.83 mg/kg at L1. The average and standard deviation for all locations were 1.08 ± 0.14 mg/kg (Table 6). In all places, the concentration of Cd in plants was above the allowed limit (0.02 mg/kg) according to the WHO [53].

The concentration of Pb in plant samples varied from 0.16 mg/kg at L4 to 5.90 mg/kg at L1. The average and standard deviation for all locations were 2.12 ± 1.99 mg/kg (Table 6). This average value is above the allowed limit (2 mg/kg) according to the WHO [53], with exceedances recorded at locations L1, L2, and L5.

The highest level of Zn was 24.4 mg/kg at location L4, while the lowest was 13.8 mg/kg recorded at location L7. The average and standard deviation for all locations were 20.6 ± 3.7 mg/kg (Table 6). According to the WHO, the concentration of Zn in plants was within the allowed limit (50 mg/kg) at all locations [53]. Meanwhile, the values of nickel and chromium were undetectable.

The highest concentrations of metals in *Typha angustifolia* were generally found for Zn, Pb, and Cd. However, there is no statistically significant relationship between Cd, Cu, Ni, Pb, Zn, and Cr levels in sediments and those in plants. Studies have shown that heavy metals such as Cr, Ni, Cu, Zn, and Cd can be present in sediments at different levels, affecting their accumulation in plants like *Typha angustifolia* [73]. Variability in environmental conditions, such as soil pH, organic carbon content of soil and sediments, and other factors, can affect the level and growth of plants, causing changes in the accumulation and removal of heavy metals from aquatic plants [74].

Absorption rates and accumulation in aquatic flora are generally influenced by various factors, including the type of plant, its stage of growth, and the properties of the metals [75]. Both biological (e.g., plant type, age, and generation time) and non-biological (e.g., temperature, humidity, season, and nutrients) influence metal accumulation [76]. A lack of correlation between metal values in sediment and the leaves of *Typha angustifolia* was also reported in [10], and low level of metal accumulation in plant leaves was also demonstrated in [77]. The authors of [11] concluded that, under optimized conditions, *Typha angustifolia* can potentially be used as phytoremediator for wastewater containing heavy metals such as melanoidin and phenol.

The concentrations of Cd and Zn found in *Typha angustifolia* plants in our study are higher than those reported in [78] for the same plant along the main course of the Sitnica River, whereas our reported Pb, Cu, and Cr concentrations are lower. These higher values can be attributed to the agricultural activity in the area, as well as the impact of landfills in Trepça.

Table 7 shows the bioaccumulation coefficients of heavy metals (Cu, Cd, Ni, Pb, Zn) in samples (L1 to L7) taken from *Typha angustifolia* plants and sediment from the Drenica River. Our results for the Drenica River indicate that *Typha angustifolia* plants accumulate metals at a disproportionate rate relative to their levels in the soil, as evidenced by bioaccumulation coefficients (BAF) greater than 1 for Cd. This suggests that *Typha angustifolia* in the Drenica River tends to effectively accumulate this metal, with plant levels much higher than those in the soil.

Table 7. Coefficient of bioaccumulation for values of metals in plants and soil.

Location	**Heavy Metals**					
	Cu	**Cd**	**Ni**	**Pb**	**Zn**	**Cr**
L1	0.008363	5.608108	n.d	0.299492	0.350242	n.d
L2	0.051889	2.810241	n.d	0.101975	0.293552	n.d
L3	0.0059	2.369231	n.d	0.012623	0.216823	n.d
L4	0.014182	5.425837	n.d	0.012579	0.530744	n.d
L5	0.021569	4.159744	n.d	0.049107	0.284359	n.d
L6	0.023683	4.223881	n.d	0.027543	0.224918	n.d
L7	0.011409	6.96988	n.d	0.008565	0.224146	n.d

Conversely, for metals such as Ni and Cr, where detectable levels were not found in plants (as indicated in Table 7), the BAF is zero (Table 7), indicating that plants do not accumulate these metals. This may be due to inherent resistance to these specific metals or because the soil's pH is outside the suitable range for bioaccumulation. At lower levels, it is observed that plants also bioaccumulate metals such as Cu, Pb, and Zn.

The highest level of Cu was 10.2 µg/L at L5, while the lowest was 0 µg/L at locations L1 and L2 (Table 8). The average and standard deviation for all locations were 4.95 ± 4.2. According to the standards for evaluating the ecological status of surface waters [79] based on the average values, the water belongs to the first category. According to standard [80], locations L1, L2, and L3 belong to the first category; location belongs L6 to the second category; and locations L3, L5, and L7 belong to the third category.

Table 8. Concentrations of heavy metals in water.

Location	Heavy Metals					
	Cu	Cd	Ni	Pb	Zn	Cr
	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L
L1	0	0.044	n.d	1.631	0.358	1.928
L2	0	0.181	n.d	1.482	0.232	0.475
L3	7.409	0	n.d	1.828	1.875	1.297
L4	1.257	0.061	n.d	2.075	1.454	0.986
L5	10.208	0.017	n.d	2.589	0	1.292
L6	5.621	1.167	n.d	1.167	1.465	8.605
L7	10.188	0.095	n.d	1.899	4.826	1.373
Mean ± Std	4.95 ± 4.2	0.22 ± 0.38	-	1.81 ± 0.42	1.45 ± 1.52	2.27 ± 2.61

The highest value for cadmium (1.16 μg/L) was recorded at location L6, while the lowest value was 0 at location L3 (Table 8). The average and standard deviation for all locations were 0.22 ± 0.38. According to the standard outlined in [79], monitoring points L1, L2, L3, L4, L5, and L7 belong to the first category, while monitoring point L6 belongs to the second category. According to the standard outlined in [64], locations L1, L3, L4, and L5 belong to the first category; locations L2 and L7 belong to the second category; and location L6 belongs to the third category.

The values of nickel in the water were below the detection limits. Similarly, the highest lead level in water was 2.58 μg/L at L5, while the lowest was 1.16 μg/L at location L6 (Table 8). The average and standard deviation for all locations were 1.81 ± 0.42. According to the standards for evaluating the ecological status of surface waters [79] based on average values, the water belongs to the first category. According to the standard outlined in [80], locations L2 and L6 belong to the second category, and locations L1, L3, L4, L5, and L7 belong to the third category.

For chromium, the highest value of 8.60 μg/L was recorded at location L6, while the lowest value of 0.47 μg/L was recorded at location L2 (Table 8). The average and standard deviation for all locations were 2.27 ± 2.61. According to the standard outlined in [79] based on average values, water belongs to the first category, while water belongs to the second category according to the standard outlined in [80].

4. Conclusions

In this study, the concentrations of the six studied heavy metals (Cu, Cd, Ni, Pb, Zn, and Cr) in the sediments of the Drenica River, as well as their accumulation in *Typha angustifolia* plants, were comprehensively assessed for determinations of contamination and potential environmental risk in the area. Based on the study results, several key findings emerged.

In the sediments of the Drenica River, the levels of heavy metals such as copper (Cu), nickel (Ni), and chromium (Cr) exceeded international standards set by the WHO, indicating significant pollution from various industrial and anthropogenic sources in the study area.

Regarding plant effects, the accumulation of heavy metals in *Typha angustifolia* indicates the significant ability of the investigated plants to absorb these metals from their environment. Concentration values of Cd and Pb exceeded international standards, highlighting the high bioaccumulative potential of these plants for Cd, posing potential risks to the local ecosystem and fauna.

Comparing our results to previous research conducted in Kosovo and surrounding region, higher levels of Ni and Cu were observed, reflecting their dependence on the ferronickel industry and agricultural activities impacting heavy metal levels in water and sediments.

The highest values of the contamination factor (CF) and geoaccumulation index (Igeo) were recorded for Ni, indicating very high pollution levels in the sediment. Additionally, the enrichment factor (EF) and potential ecological risk index (RI) showed very high values at locations L1, L3, L5, and L7, highlighting intense pressure from anthropogenic activities such as industrial operations, urban development, and agriculture.

Furthermore, a comparison of measured metal values with ecological status standards [63] and ECE shows that locations L1, L3, L4, L5, and L7 do not exhibit high ecological water quality.

In conclusion, we recommend the implementation of pollution management strategies based on calculated pollution indices like the Pollution Load Index (PLI) and the ecological risk factor index (RI). Continuous monitoring and integrated pollution source management are essential for the enhancement of water quality in the Drenica River area. This study serves as a crucial foundation for understanding the impact of anthropogenic activities on Kosovo's water environment, emphasizing the urgent need for actions to protect and preserve the Drenica River's environment.

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