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ASSESSING HEAVY METAL POLLUTION IN WATER AND SEDIMENTS OF THE NERODIME RIVER, KOSOVO (SIX SAMPLING SITES, JUNE–JULY 2024)

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ABSTRACT

Aim of the study

This study examines the distribution, sources, and ecological risks of heavy metal (HM) contamination in the water and sediments of the Nerodime River, located in an urbanized area of Kosovo. Acknowledging the interactions between industrial, urban, and agricultural activities, this research seeks to clarify the geographical distribution of HMs and propose sustainable management strategies and practices.

Material and methods

Water and sediment samples were collected at six sites (M1–M6) during June and July 2024, coinciding with the peak of agricultural runoff and urban discharges. Heavy metal concentrations were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) for water samples, and ICP-MS for sediments. Statistical analyses, including one-way ANOVA, Principal Component Analysis (PCA), and Cluster Analysis, were used to identify significant differences and potential sources of pollution.

Results and conclusions

For example, Zn concentrations reached up to 5.85 mg/L, surpassing the WHO safe limit of 4.0 mg/L by 46%, while Pb levels of 0.19 mg/L exceeded the limit of 0.01 mg/L by nearly 19 times ($p < 0.05$). Sediment analysis identified cadmium and lead as key contributors to ecological risk. The Geo-accumulation Index (Igeo) ranged from "unpolluted to moderate" (–0.12) up to "moderate" (2.11). In contrast, the ecological risk index (RI) values ranged from 120 to 180, indicating an overall moderate but locally significant risk from cadmium (Cd). PCA indicated strong associations among metals such as Zn, Fe, and Cu from urban and industrial runoff, with Cd linked to agricultural practices.

Keywords: the Nerodime River, heavy metals, urban runoff, ecological risk, PCA, sustainable management

INTRODUCTION

Urbanization and the development of the countryside have significantly impacted variations in river systems, resulting in substantial changes in their physical, chemical, and biological characteristics. Heavy metals (HMs) are listed among the most hazardous pollutants in river ecosystems due to their persistence in the environment, toxicological profiles, and tendency to bioaccumulate. Heavy metals generally enter river systems primarily from industrial activities, agriculture, and urban activities, which have both short-term and long-term ecological impacts (Ntini, 2018; Salem et al., 2016). Once introduced, these metals bind to sediment

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layers, acting as reservoirs and sources of pollutants that reflect past events with significant implications for the aquatic environment (Bhardwaj et al., 2019).

Rivers deliver essential ecosystem services, hence sustaining both urban and rural ecosystems. Most recent studies have portrayed the impacts of HMs on river ecosystems, primarily citing urbanization, vehicle emissions, industrial activities, and land use changes as major contributors (Kumar et al., 2022; Zhou et al., 2024). Such findings underscore the need for site-specific studies, as HM concentrations vary significantly with regional geological conditions and human activities (Huang et al., 2018).

The Nerodime River, which flows through the city of Ferizaj in Kosovo, has a unique hydrological system, forming two distinct branches that flow into two lakes. This rare bifurcation is significant not only for hydrology but also for increasing the risk of transboundary pollution, as the river ultimately flows into both the Aegean Sea and Black Sea basins. As a result, heavy metal contamination from local industrial, urban, and agricultural sources can spread across borders, emphasizing the importance of international cooperation in monitoring and mitigation (Adnan et al., 2022; Bai Yang et al., 2016). While heavy metal pollution of Kosovo's rivers has been recognized more and more, there is still a lack of comprehensive research into the Nerodime River regarding its spatial distribution of pollutants, their origins, and the ecological consequences on water quality and sediments (Demaku et al., 2022; Wu et al., 2016). In this context, the European Union Water Framework Directive (WFD) and its 2027 environmental quality targets act as key policy benchmarks, encouraging member and candidate states, including Kosovo, to reach "good chemical and ecological status" for surface waters. The importance of this study is thus aligned with these EU objectives, offering data directly relevant to regional water management and compliance efforts.

The present study tries to address this critical research gap by investigating the geographical distribution, ecological hazards, and sources of heavy metal contamination in the Nerodime River. To our knowledge, this is the first comprehensive assessment of the Nerodime River that simultaneously evaluates water and sediment quality along with ecological risk indices (Igeo, RI), providing a holistic understanding of contamination patterns and their potential consequences in terms of environmental impact.The results aim to inform urban river management practices, enhance pollution mitigation strategies, and support socio-cultural and ecological planning practices in Ferizaj City.

Study area and sampling design

The Nerodime River branches out into two different streams: one flows to the west and another to the north. This point is crucial in understanding local pollution and the interplay between natural and human factors. To distinguish the differences in pollution levels, the study area was divided into three main zones, taking into consideration human activities, the shape of the river, and proximity of pollution sources. Six sampling sites were designated (M1–M6). The exact geographic coordinates of the sampling sites were recorded with a handheld GPS (±3 m accuracy): M1 (42.3641°N, 21.1285°E), M2 (42.3608°N, 21.1347°E), M3 (42.3525°N, 21.1452°E), M4 (42.3487°N, 21.1519°E), M5 (42.3402°N, 21.1623°E), and M6 (42.3365°N, 21.1708°E). Sampling was conducted during June and July 2024, which coincided with the peak periods of agricultural runoff and increased rainfall in the Ferizaj region, maximizing the likelihood of capturing heavy metal inputs from both agricultural and urban discharges (Zhang et al., 2011).

Land use patterns surrounding the sampling points vary across different locations. Dense urban and industrial activities characterize the upstream sites M1 and M2 (Jezerc Village). Sites M3 and M4 (Nerodime e Epërme Village) are characterized by mixed land uses, including both agricultural and residential areas. The downstream locations M5 and M6 (Nerodime e Poshtme Village) are predominantly agricultural, featuring extensive crop farming fields that contribute to potential agrarian runoff. The average discharge of the Nerodime River is estimated to range between 1.8 m^3/s and 4.6 m^3/s, based on a specific runoff of 8–20 $l/s/km^2$ for the catchment area of 229 km^2. These values may vary depending on precipitation levels and other climatic factors. The river experiences its maximum flow during the spring months (March to May) due to snowmelt and rainfall, while the minimum flow is typically observed during late summer (August to September). Given that the Nerodime River bifurcates, eventually flowing into both the Black Sea and the Aegean Sea, pollutants from the river have the potential for transboundary environmental impacts.

Sample collection

Sampling was conducted in June and July 2024, coinciding with elevated agricultural activities and seasonal rainfall, increasing farm runoff and urban discharges into the river. To obtain representative data, water samples were collected at three different locations within each site: the left bank, midstream, and right bank, and then combined into a single composite sample for each site. Sediment samples (0–10 cm depth, >1000 g) were gently collected using a stainless-steel grab sampler, placed into pre-cleaned polyethylene containers, and transported to the laboratory under cooled and dark conditions in order to prevent contamination (Dević et al., 2016; Varol, 2011).

Sample preparation and analysis

Water samples were filtered through 0.45 µm membrane filters to eliminate suspended solids before analysis, ensuring the accurate determination of dissolved heavy metals.

Sediment samples were air-dried in a dust-free room, cleaned to remove any obvious debris, and then sieved using a 100-mesh nylon screen to ensure a uniform grain size. Samples were digested with the aid of microwave digestion equipment using a high-precision acid mixture of HNO_3, HCl, and $HClO_4$, ensuring complete decomposition of organic matter and accurate extraction of heavy metals. The concentrations of heavy metals were determined using ICP-MS (Agilent 7500a), which offers high sensitivity and precision. The detection limits (LOD) were as follows: As 0.0005 mg/L, Cd 0.0001 mg/L, Pb 0.0002 mg/L, Zn 0.001 mg/L, Fe 0.002 mg/L, Ni 0.0005 mg/L, Cu 0.0003 mg/L, and Cr 0.0005 mg/L. For sediments, the detection limits ranged from 0.01 to 0.05 mg/kg depending on the element.

All reagents used in this study were of analytical grade, and quality control was strictly maintained. In addition, all experiments were carried out with CRMs, blank samples, and replicate analyses to check the reliability of the experiments; recovery rates were maintained at 100 ± 10% to validate the result (Birch et al., 2001; Chen et al., 2021; Chen et al., 2009).

Quality assurance and control

The quality control techniques in this study were performed following strict international standards to ensure that the data acquired are reliable and valid. To ensure accuracy, replicate analyses of the samples and

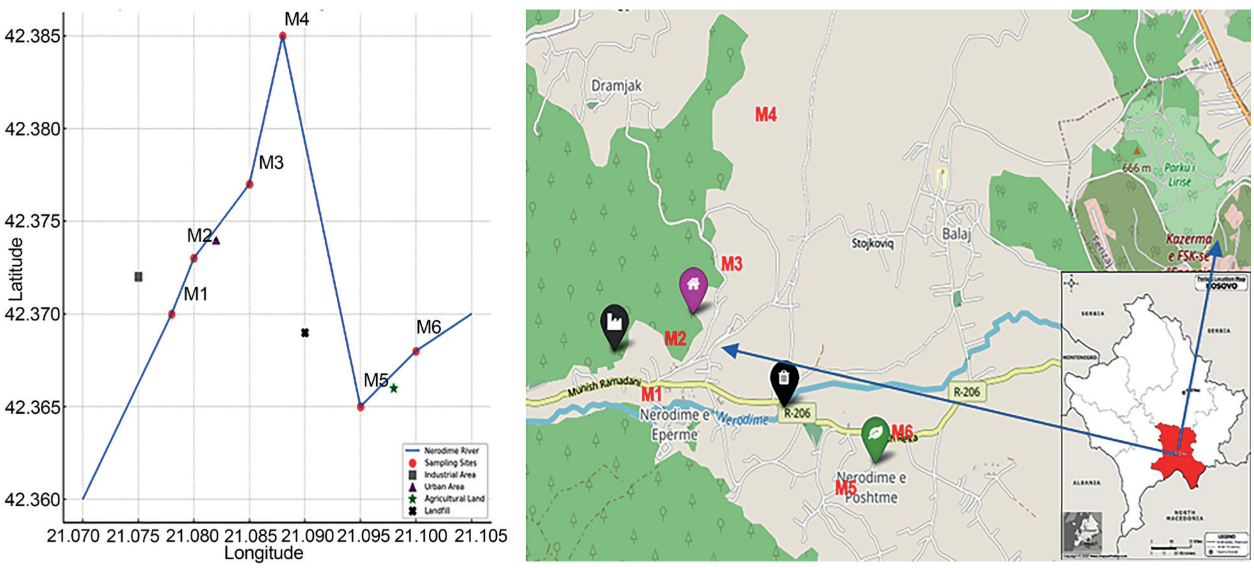

Fig. 1. Map of the Nerodime River with sampling sites (M1–M6) and potential sources of heavy metal pollution, including industrial, urban, agricultural areas, and landfill locations (Source: Authors' own elaboration)

certified reference material were conducted, along with blank samples for monitoring possible contamination at each step of the analytical procedure. The calibration of the instruments was performed using standard solutions to ensure consistency and precision in the measurements (Gayathri et al., 2021).

Data analysis

The collected data were analyzed with the help of several advanced indices to estimate the degree of pollution and the ecological risks associated with HMs in this area. Some of the leading indices being used include the following:

Nemerow Synthesis Index-Pn − an integrated index measuring the arithmetic mean and maximum values of pollution in calculating an integrated general polluting assessment

$$Pn = \frac{\sqrt{P^2 i,\,\text{ave} + P^2 i,\,\text{max}}}{2} \tag{1}$$

where Pi represents the single pollution index, calculated as:

$$Pi = \frac{ci}{si} \tag{2}$$

where Ci is the measured concentration of the heavy metal, and Si is the regulatory standard for the given pollutant (Feng et al., 2019).

Table 1. Classification of pollution degree based on PI and PN values

PI	PN	Pollution degree
≤ 1.0	≤ 0.7	Unpolluted
~1.5	0. 7~1.0	Warning line (still clean)
1.5 ~2.0	1.0 ~2.0	Unpolluted to moderate
2.0 ~2.5	2.0 ~3.0	Moderate to heavy
$Pi > 2.5$	$Pn > 3.0$	Heavy to extreme

Geo-accumulation Index (Igeo) − this metric quantifies the contribution of natural and anthropogenic sources to HM contamination. It is expressed as:

$$I_{geo} = \log 2\left(\frac{Cd}{k \cdot Cb}\right) \tag{3}$$

where Cd is the measured concentration, Cb is the background concentration, and k is a correction factor (1.5) accounting for natural variability (Ghaleno, 2015; Ilie et al., 2017). Background concentrations (Cb) were determined from regional geochemical baseline studies of uncontaminated soils and sediments in Kosovo (Demaku et al., 2022), supplemented by internationally accepted reference values when local data were not available. This approach ensured both local relevance and comparability with global research.

Ecological Hazard Index (RI) − this index evaluates the combined toxicity and environmental risks of HMs. It is computed as:

$$RI = \sum\nolimits_{i=1}^{n} E_{ri}, \text{ where } E_{ri} = T_{ri} \cdot \frac{C_d}{C_b} \tag{4}$$

where RI reflects the multifarious comprehensive potential ecological risk index, therefore representing the possible risks of all the involved contaminants. E_{ri} is the hazard index with a single factor. T_{ri} is the toxicity response coefficient, which substitutes the biological toxicity coefficient for reflecting the amount of toxicity of HM and the susceptibility of organisms to pollutants. It is ascertained in response to several elements, including the HM concentration of surface sediments, sedimentation, affinity for solids, susceptibility of water to metal pollution, and central toxicity level (Ke et al., 2017; Mamat et al., 2016). Table 3 presents a classification of ecological risk depending on E_{ri} and RI.

Table 2. Summary of the classification levels for Igeo

Igeo	≤ 0	0–1.0	1.0–2.0	2.0–3.0	3.0–4.0	4.0–5.0	≥ 5.0
Pollution degree	Unpolluted	Unpolluted to moderate	Moderate	Moderate to heavy	Heavy	Heavy to extreme	Extreme

Table 3. Classification of potential ecological risk coefficient

E_r^i	RI	Risk
< 40	< 150	Low
40–80	150–300	Moderate
80–160	300–600	Considerable
160–320	600–1200	High
> 320	> 1200	Significantly high

RESULTS AND DISCUSSION

Water contamination analysis

Table 4 shows triplicate measures of HM levels in water samples collected at each of the six sites along the Nerodime River. Among the analyzed samples, Zn and Fe were classified as the most abundant pollutants. Zn concentrations ranged from 3.44 to 5.85 mg/L; however, all M4–M6 samples exceeded the maximum WHO regulatory limit of 5.0 mg/L for drinking water (WHO, 2011). This limit represents the maximum permissible concentration established to protect human health and aquatic ecosystems (Edition, 2011). Additionally, iron concentrations exceeded the limit of 0.2 mg/L, with a peak of 0.41 ± 0.069 mg/L at M4. Pb presents a maximum value of 0.19 ± 0.024 mg/L at M2, higher than the limit of 0.01 mg/L. Mn presented concentrations of 0.04 ± 0.007 mg/L, detected in M2, to 0.07 ± 0.006 mg/L, detected in M6, but exceeding only the WHO limit of 0.05 mg/L by just a slight amount. The nickel values ranged from 0.02 mg/L to 0.03 mg/L, with higher levels detected in samples from M4 and M5. Cd, Cu, As, and Cr showed values lower than the limits corresponding to each one in WHO for stations M4 and M5.

There are clear trends in the HM distribution, whereas the highest concentrations are observed at the upstream stations, M1 and M2, which are heavily affected by industrial activities and untreated urban runoff. For example, zinc ranged from 3.44 ± 0.329 mg/L at M1 to the maximum value of 5.85 ± 0.415 mg/L at M6, while iron ranged from 0.22 ± 0.023 mg/L at M2 to the maximum value of 0.41 ± 0.069 mg/L at M4. This, therefore, indicates increased concentrations upstream due to the substantial impact of industrial and urban sources.

Notably, the upstream area contains several industrial facilities, including small-scale manufacturing units and metal processing workshops, as well as untreated discharges from municipal sewage systems and stormwater drains. These factors significantly contribute to the elevated levels of heavy metals. On the other hand, the downstream sites, M5 and M6, recorded lower levels due to the natural effects of dilution and sedimentation, which further reduce pollutant concentrations.

Table 4. Concentration of heavy metals in water samples with experimental deviations [mean/std] based on triplicate measurements from the Nerodime river sampling site

Element	M1 [Mean/Stdv]	M2 [Mean/Stdv]	M3 [Mean/Stdv]	M4 [Mean/Stdv]	M5 [Mean/Stdv]	M6 [Mean/Stdv]	Water (WHO-standard)
As	0.006/0.001	0.005/0.001	0.003/0.001	0.004/0.001	0.003/0.001	0.005/0.001	0.01
Ni	0.02/0.001	0.02/0.004	0.02/0.003	**0.03/0.002**	**0.03/0.002**	0.02/0.002	0.02
Zn	3.44/0.329	3.39/0.436	3.59/0.412	**5.04/0.472**	**5.43/0.77**	**5.85/0.415**	4.00
Fe	**0.31/0.029**	**0.22/0.023**	**0.3/0.036**	**0.41/0.069**	**0.38/0.03**	**0.29/0.037**	0.2
Cu	0.19/0.026	0.15/0.009	0.21/0.03	0.14/0.011	0.16/0.01	0.2/0.038	0.2
Cd	0.002/0.001	0.003/0.001	0.001/0.001	0.002/0.001	0.004/0.001	0.005/0.001	0.003
Cr	0.047/0.003	0.039/0.005	0.044/0.002	0.048/0.009	0.05/0.004	0.049/0.007	2.0
Pb	**0.1/0.01**	**0.19/0.024**	**0.1/0.013**	**0.1/0.008**	**0.11/0.021**	**0.09/0.015**	0.01
Mn	0.06/0.011	0.04/0.007	0.06/0.008	0.05/0.009	0.04/0.003	0.07/0.006	0.05

Generally, Zn and Fe are the dominating pollutants in this area, and their concentrations in all samples exceeded the permissible limit value. Table 4 summarizes the results of this study, highlighting the need for close attention to pollution control in upstream areas to protect the Nerodime River ecosystem from further industrial and urban impacts. To effectively combat ongoing contamination, it is essential to adopt the following: improved wastewater treatment practices, stricter industrial regulations, enhanced control over industrial activities, and more effective agricultural practices. To assess whether the differences in heavy metal concentrations across sites were statistically significant, a one-way ANOVA was conducted. Prior to ANOVA, normality was confirmed using the Shapiro–Wilk test and homogeneity of variances with Levene's test ($p > 0.05$), verifying that the assumptions for parametric testing were satisfactorily met. The results indicated that the concentrations of Zn, Fe, and Pb exhibited significant differences ($p < 0.05$) between upstream (M1, M2) and downstream sites (M5, M6), confirming the impact of localized pollution sources. To better visualize spatial variability, Figure 2 shows boxplots of Zn, Fe, Pb, and Mn concentrations across all sampling sites (M1–M6). The boxplots emphasize the higher concentrations at upstream sites compared to downstream locations, reinforcing the statistical differences observed in ANOVA.

These results represent conditions during June–July 2024, coinciding with peak agricultural runoff and seasonal rainfall. Seasonal variability is anticipated, with potentially lower HM levels in winter due to reduced runoff and higher variability during spring floods. Therefore, while the observed patterns are typical of the summer agricultural season, long-term monitoring is needed to understand year-round trends. Interestingly, Zn concentrations at the downstream site, M6 (5.85 mg/L), remained high despite the expected dilution effects. This anomaly may indicate localized downstream sources, such as agricultural runoff enriched with Zn-containing fertilizers, small-scale waste disposal sites, or leaching from soils with high Zn levels. These localized inputs could explain the persistent high Zn levels at M6.

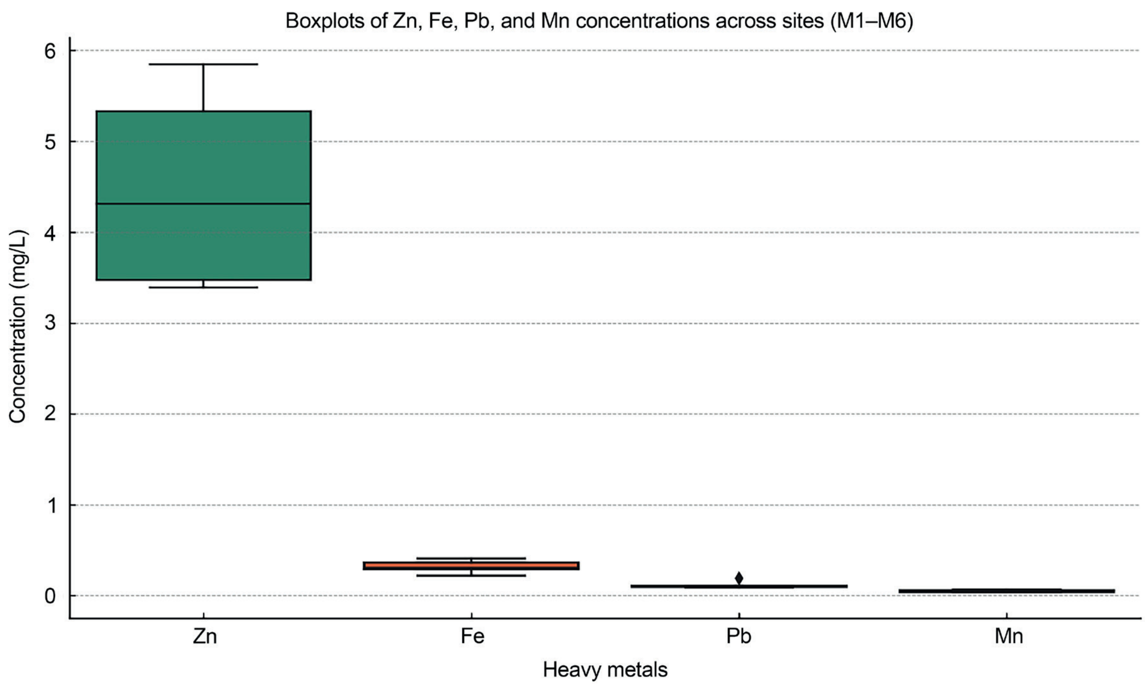

Fig. 2. Boxplots of Zn, Fe, Pb, and Mn concentrations across sampling sites (M1–M6) (Source: Authors' own elaboration)

Comparative analysis of heavy metals in water

The quantities of heavy metals (HMs) in the water samples from the Nerodime River were compared with those reported in other rivers in Kosovo (Table 5). The maximum concentrations of Mn, Ni, Zn, Fe, Cu, Cd, Cr, Pb, and As from this investigation were compared with corresponding values reported for the Lepenc, Sitnicë, Graçanica, and Drini Bardh Rivers (Pejman et al., 2015).

In this investigation, Zn showed the highest concentration (i.e. 5.85 mg/L), exceeding EU and WHO acceptable limits. Mn and Fe levels were also noticeably raised, but they remained lower compared to values observed in the Sitnica River. Cd and Cr values were much lower than in other rivers, especially Graçanica. These variations represent the specific pollutant profiles influenced by local industrial, agricultural, and urban activities (Hao et al., 2021). For comparison, WHO (2011) and EU (Directive 98/83/EC; 2000/60/EC Water Framework Directive) limits were used as reference environmental standards. In Table 5, some river datasets display missing values ("/"), indicating either unreported parameters in the original studies or non-detectable levels in those rivers. For comparison, WHO (2011) and EU (Directive 98/83/EC; 2000/60/EC Water Framework Directive) limits were used as reference environmental standards. These gaps should be considered when comparing datasets, as the absence of data does not imply the absence of contamination.

Sediment contamination analysis

Table 6 summarizes the concentrations of heavy metals in the sediments of the Nerodime River, including means and standard deviations for stations M1–M6 and comparisons with USEPA reference values [mg/kg] (Burgess, 2008).

Table 5. Comparison of heavy metal concentrations in rivers across Kosovo [mg/L]

River	Mn	Ni	Zn	Fe	Cu	Cd	Cr	Pb	As
This study (max conc.)	0.07	0.03	5.85	0.41	0.21	0.005	0.050	0.21	0.006
Lepenc River	0.06	0.09	0.19	0.58	0.18	/	/	0.09	/
Sitnica River	> 0.7	0.10	< 5.0	> 0.3	< 0.2	0.09	0.19	> 0.5	/
Graçanice River	/	3.77	/	6.39	9.97	4.17	/	10.0	/
Drini i Bardh River	n.d.	0.013	0.39	0.87	0.02	n.d.	0.032	n.d.	n.d.

Note: n.d. – not detected

Table 6. Concentration of heavy metals in sediment samples with experimental deviations [mean/std] based on triplicate measurements from the Nerodime river sampling sites

Element	M1 [Mean/Stdv]	M2 [Mean/Stdv]	M3 [Mean/Stdv]	M4 [Mean/Stdv]	M5 [Mean/Stdv]	M6 [Mean/Stdv]	Reference Value (USEPA, [mg/kg])
As	1.04/0.013	1.06/0.013	1.08/0.025	1.09/0.013	1.09/0.025	1.10/0.025	15
Ni	1.28/0.025	2.35/0.062	3.33/0.088	2.43/0.037	3.46/0.075	3.61/0.100	20
Zn	1.44/0.037	0.00/0.000	0.96/0.013	1.43/0.025	1.43/0.037	1.85/0.050	90
Fe	3.31/0.062	2.22/0.050	3.30/0.075	3.41/0.088	5.38/0.112	5.29/0.100	30000
Cu	0.19/0.013	0.15/0.013	0.21/0.013	0.14/0.013	0.17/0.013	0.22/0.025	35
Cd	0.02/0.001	0.03/0.001	0.01/0.001	0.02/0.001	0.11/0.001	0.15/0.001	0.5
Cr	0.33/0.013	0.33/0.025	0.44/0.013	0.48/0.025	0.50/0.025	0.49/0.025	50
Pb	3.21/0.125	3.19/0.112	3.30/0.150	5.13/0.175	0.50/0.188	5.93/0.200	25
Mn	0.20/0.013	0.24/0.025	0.16/0.013	0.25/0.025	0.24/0.013	0.27/0.025	600

Note: The units for Fe and Mn concentrations have been thoroughly verified to ensure accuracy.

The maximum Pb concentrations reached 5.93 mg/kg at M5 and M6, which is far below the reference value of 25 mg/kg, suggesting that there is no substantial ecological risk. However, the relatively high values indicate a potential signal for local pollution from anthropogenic sources. Generally, cadmium presented low values, ranging up to 0.15 mg/kg at M6, which is very close to the reference value of 0.5 mg/kg. However, it is considered a critical contaminant due to its high toxicity, even at low concentrations. Conversely, the concentrations of Fe and Zn are significantly lower than the reference values, indicating a minimal ecological impact. However, under certain environmental conditions, such as low pH or high organic matter, their bioavailability could increase, necessitating ongoing monitoring. It should be noted that values reported as 0.00 (e.g., Zn at M2) indicate concentrations below the instrumental detection limit rather than a complete absence of the element.

HM potential ecological risk in rivers

The potential ecological risk of heavy metals (HMs) in water and sediment samples was assessed using the hazard index (RI) in Tables 7 and 8.

The ecological risk of the measured heavy metals in the collected water samples from the Nerodime River is presented in Table 8, calculated from their measured concentrations, their respective reference values (U.S.E.P.A., 2003), and their metal toxicity coefficients. Hence, Pb and Zn were the major contributors to the ecological risk with the Ervalue of 95.0 and 19.50, respectively. Thus, the exceptionally high Pb concentration of 0.19 mg/L was greater than the allowable limit of 0.025 mg/L. Similarly, the high amount of zinc, with a concentration value of 5.85 mg/L was greater than the permissible limit of 0.120 mg/L, and its presence is principally attributed to farming and industrial activities in the upstream areas of the river.

Although iron was detected at a relatively high concentration of 0.41 mg/L, it contributes little to the ecological risk as reflected by its low Ecological Risk (Er) value of 1.37. The metals such as Mn and Ni showed even less than Er value of 0.70 and 7.50, respectively, suggesting minimal ecological risk. Furthermore, their detected concentration was either at or below the permissive limit, indicating that their presence in the water is due to both natural and anthropogenic factors, with a negligible impact on water quality. To visualize spatial patterns, a risk distribution map was created, showing that upstream sites (M1–M2) have the highest ecological risk index (RI > 150, moderate risk), while downstream sites (M5–M6) show lower risk (RI < 120, low risk). This spatial map highlights localized hotspots of Pb and Cd contamination.

Table 8 presents the ecological risk of heavy metals in the sediments of the Nerodime River. As shown in the table, cadmium (Cd) and lead (Pb) are the primary contributors to the ecological risk. Though cadmium has a low concentration of 0.15 mg/kg, the value of Er reaches 4.00 due to its very high toxicity response coefficient (Tr = 30). This may develop into a greater ecological risk to the aquatic ecosystem. Therefore, the value of the lead, with a relatively high concentration of 5.93 mg/kg, amounts to 0.83. The prevalence of these elements is related to pollution from automo-

Table 7. Ecological risk assessment for heavy metals in water samples from the Nerodime River

Metal	Concentration [mg/L]	RfD [mg/kg/day]	Exposure [mg/kg/day]	Hazard quotient [HQ]	Toxicity response [Tr]	Reference concentration [mg/L] USEPA	Ecological risk [Er]
Zn	5.85	0.30	0.17	0.56	1.00	0.120	19.50
Fe	0.41	0.14	0.01	0.08	1.00	1.0	1.37
Pb	0.19	0.00	0.01	1.36	5.00	0.025	95.00
Ni	0.03	0.02	0.00	0.04	5.00	0.052	7.50
Mn	0.07	0.14	0.00	0.01	1.00	Not established	0.70

Abbreviations: HQ – Hazard quotient; Tr – Toxicity response coefficient; Er – Ecological risk; RfD – Reference dose

Table 8. Ecological risk assessment for heavy metals in sediment samples from the Nerodime River

Metal	Concentration [mg/kg]	RfD [mg/kg/day]	Exposure [mg/kg/day]	Hazard quotient [HQ]	Toxicity response [Tr]	Reference concentration [mg/kg]	Ecological risk [Er]
As	1.11	0.00	0.00	2.64	10.00	7.24	1.53
Ni	3.61	0.02	0.00	0.13	5.00	16	1.13
Zn	1.85	0.30	0.00	0.00	1.00	120	0.02
Fe	5.38	0.14	0.00	0.03	1.00	30000	0.00
Cu	0.22	0.04	0.00	0.00	5.00	31.6	0.03
Cd	0.15	0.00	0.00	0.11	30.00	0.99	4.55
Cr	0.55	0.00	0.00	0.13	2.00	43.4	0.03
Pb	5.93	0.00	0.00	1.06	5.00	35.8	0.83
Mn	0.29	0.14	0.00	0.00	1.00	460	0.00

Abbreviations: HQ – Hazard quotient; Tr – Toxicity response coefficient; Er – Ecological risk; RfD – Reference dose

bile exhaust and industrial emissions. When comparing classifications across indices (Pn, Igeo, RI), there is general agreement that Pb and Cd pose the highest risk. However, Igeo for Cd suggests "moderate" pollution, whereas RI highlights its ecological importance due to toxicity. Pb, with Er = 95, clearly indicates a high risk, while Cd, with Er = 4.55, represents a moderate but still concerning risk. The consistency across indices strengthens the conclusion that Pb and Cd are the priority contaminants for mitigation.

The metals Fe, Zn, Cu, and Mn exhibited very low values of Er index (<1), signifying their minimal contribution to ecological risk. This suggests that their concentrations are either too low or within normal background, and therefore they do not substantially contribute to the environmental risk of sediments (Burgess, 2008; EPA, 2014; Hübner et al., 2009; Persaud et al., 1993). Beyond ecological concerns, heavy metal contamination also presents potential risks to local communities. Pb in particular can enter the food chain through contaminated irrigation water and bioaccumulate in crops. At the same time, Cd may build up in sediments and then in benthic organisms that fish eat. Local residents who rely on river water for farming or recreation could therefore be indirectly exposed, highlighting the need for ongoing monitoring and stricter wastewater management to reduce human health risks.

Cluster and PCA analysis (Figures 3 and 4) identified three sources of contamination: Fe, Cr, Zn, and Cu linked to industrial and urban runoff; As, Ni, and Cd of geological origin; and Mn, Pb linked to vehicular emission. These findings reveal the complex interplay between human and natural causes in sediment HM concentration levels (Sojka and Jaskuła, 2022).

The dendrogram (Fig. 3) depicts the cluster analysis of heavy metals in sediments based on similarities in their distribution patterns and sources. Arsenic and nickel group together because they show low concentrations, probably originating from natural or mixed sources, hence a slight ecological risk. Cadmium clusters with As and Ni, but is somewhat separated, which is in line with high toxicity and moderate contribution from human activities.

Iron and chromium represented one cluster, which may indicate the natural geochemical origins of the elements and their low ecological risk. Zinc and copper are grouped in one cluster, suggesting that these metals have the same anthropogenic sources, such as runoff from farmlands. Lead and manganese fell into a different cluster, indicating specific behaviors under the influence of human activities, particularly emissions from traffic and industrial sources.

These cluster patterns further confirm the results presented in the tables, indicating a significant ecological impact of Pb and Cd, while suggesting a minimal

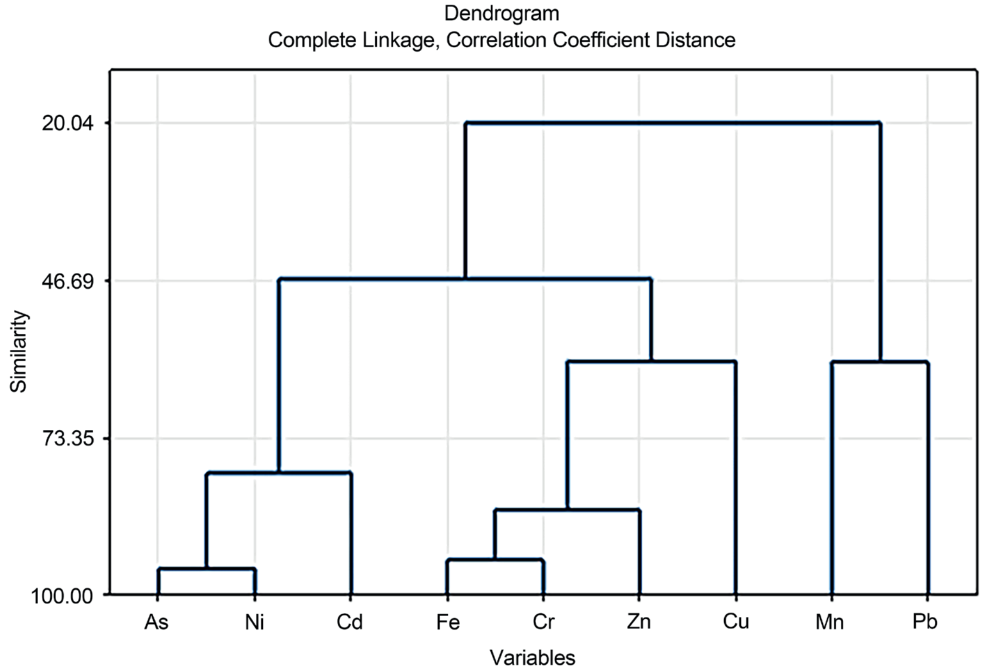

Fig. 3. The clustering analysis dendrogram of HMs (Source: Authors' own elaboration)

influence of Fe and Cr. It also reveals other relationships, such as that of Mn and Pb, which warrant further consideration. These PCA and cluster groupings align with the surrounding land use: Zn, Fe, and Cu cluster with upstream sites influenced by industrial areas and untreated sewage; Cd corresponds with downstream agricultural zones where phosphate-based fertilizers are used; Pb and Mn are closely associated with traffic emissions near urban crossings. This direct link between statistical results and land use patterns strengthens the interpretation of both human and natural sources.

Figure 4 presents a PCA loading plot showing the contributions of heavy metals (As, Mn, Ni, Pb, Fe, Cu, Cd, Cr, Zn) to the first two principal components, PC1 and PC2.

Cd has the highest loading on PC2, indicating its distinct behavior. This behavior aligns with the agricultural land use surrounding downstream sites (M5, M6), where phosphate-based fertilizers, often containing trace amounts of Cd, are commonly used. Most likely, the runoff from these farmlands contributes to the localized accumulation of cadmium in sediments. Mn and Zn load positively on PC1 and negatively on PC2, indicating their similar behavior across all sampling sites. The magnitude of the loading vectors further depicts the influence of metals such that Cd, Fe, and Pb, with longer vector lengths, are highly variable in the dataset, while Cu, due to its shorter vector length, depicts much more minor apparent variations (Dai et al., 2018; Chabukdhara and Nema, 2012).

The Principal Component Analysis showed that PC1 accounted for 96.69% of the total variance, whereas PC2 represented 3.31%. Together, they cumulatively explained nearly 100% of the overall variability in heavy metal concentrations across the sampling sites.

Groupings in the plot reflect either common origins or geochemical tendencies. Metals such as Ni, Cr, Pb, and Fe all exhibit strong relationships that can represent familiar sources, ranging from industrial emissions to natural rock weathering. In contrast, the independent vector of Cd suggests another independent source, likely associated either with site-specific conditions or agricultural input, such as fertilizers (Zhang et al., 2018).

PC1 explains the main variability, which is dominated by metals such as Mn, Zn, As, and Cr, possibly

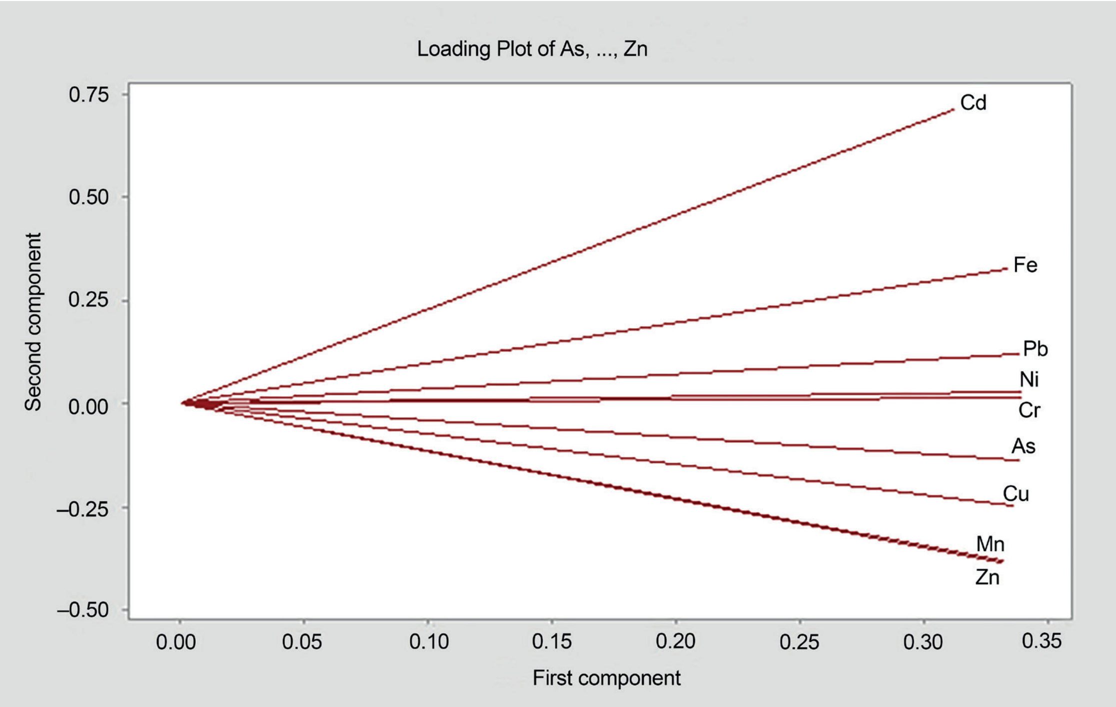

Fig. 4. Loading plot of heavy metal contributions to principal components in sediment samples (Source: Authors' own elaboration)

from industrial and/or urban runoff. The dominance of Cd in PC2 explains the secondary variability, which is assumed to be from agricultural sources. The grouping of metals such as Ni, Cr, Pb, and Fe implies the exact source of the impact, while the marked behavior of Cd shows regional pollution, thus requiring further study.

These findings have practical relevance for detecting pollution hotspots and targeting mitigation efforts. High scores of PC1 represent high values of Mn, Zn, and Cr, while high scores in PC2 are triggered by Cd concentration and further assist focused environmental management efforts (Singh et al., 2005).

CONCLUSIONS

In this study, the presence of heavy metals was investigated in detail in the water and sediments of the Nerodime River in Ferizaj, Kosovo. The results indicated significant differences in the distribution of heavy metal concentrations, driven by both human-induced sources − including industrial wastewater and runoff from agricultural activities − and natural geological factors. While sediment samples generally complied with international standards, water samples showed values exceeding the regulatory limits of some important contaminants, such as Zn, Fe, and Pb, in all samples, reflecting intense localized pollution with heightened ecological risk. Quantitatively, Zn concentrations at the downstream site M6 (5.85 mg/L) exceeded the WHO permissible limit of 4.0 mg/L by approximately 46%, indicating that Zn levels need to be decreased by at least 40% to comply with drinking water standards. Pb concentrations (0.19 mg/L) were nearly 19 times higher than the WHO limit of 0.01 mg/L, requiring urgent mitigation.

The risk assessment delineated a pronounced contrast between the heavily contaminated upstream sites and the downstream areas, which received natural dilution and sedimentation. Considering the potential toxicity of each contaminant, cadmium (Cd) and lead (Pb) were the elements of most significant concern. This was supported by PCA and cluster analysis, which revealed three primary sources of pollution:

industrial and urban runoff contributed to high values of Zn, Fe, and Cu, geological sources contributed to the presence of As, Ni, and Cd, whereas vehicle emissions accounted for the most variance in Pb and Mn. If left unaddressed, these contamination patterns could increase ecological risks, including the bioaccumulation of Pb and Cd in aquatic organisms, loss of biodiversity, and potential socio-economic impacts such as reduced agricultural productivity and public health issues for local communities.

The present work has highlighted the urgent need for immediate and synchronized action to address heavy metal pollution of the Nerodime River, focusing on improving wastewater treatment facilities, stricter control of industrial discharges, and sustainable farming practices that reduce runoff. To ensure effective mitigation, we recommend implementing a systematic monitoring program with sampling at least quarterly, including water and sediment analyses for Zn, Pb, Cd, Fe, and Mn, along with calculating ecological risk indices (Igeo, RI) to track trends and identify emerging hotspots. The pollution trends and the overall effectiveness of these interventions should be followed through the institution of ongoing monitoring programs.

The study revealed a distinct geographical distribution of heavy metal contamination, with upstream sites (M1, M2) showing the highest levels of pollution due to industrial discharges and untreated urban runoff. Downstream sites exhibited lower concentrations, affected by natural dilution and sedimentation processes. Implementing these measures could significantly reduce ecological risks and align local water quality management with the EU Water Framework Directive 2027 targets. To improve pollution mitigation, we recommend implementing advanced wastewater treatment facilities, enforcing stricter industrial effluent regulations, and adopting sustainable agricultural practices to reduce runoff. Regular monitoring programs are essential for tracking the effectiveness of these measures and ensuring environmental health of the Nerodime River.

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Ocena zanieczyszczenia metalami ciężkimi wody i osadów rzeki Nerodime w Kosowie (sześć miejsc poboru próbek, czerwiec–lipiec 2024)

ABSTRAKT

OCENA ZANIECZYSZCZENIA METALAMI CIĘŻKIMI W WODZIE I OSADACH RZEKI NERODIME W KOSOWIE (SZEŚĆ LOKALIZACJI POBORU PRÓBEK, CZERWIEC–LIPIEC 2024 R.)

Cel badania

Niniejsza praca ma na celu zbadanie rozmieszczenia, źródeł pochodzenia, a także zagrożeń ekologicznych związanych z zanieczyszczeniem metalami ciężkimi (HM) w wodzie i osadach rzeki Nerodime, położonej na zurbanizowanym obszarze Kosowa. Uwzględniając interakcje między działalnością przemysłową, urbanizacyjną i rolniczą, niniejsze badania mają wyjaśnić rozmieszczenie geograficzne metali ciężkich (HM) oraz pomóc wypracować strategię i praktyki zrównoważonego zarządzania.

Materiał i metody

Próbki wody i osadów do badań pobrano w sześciu lokalizacjach (M1–M6) w czerwcu i lipcu 2024 r., w okresie odpowiadającym szczytowi spływu wód z terenów rolniczych i zrzutów z terenów zurbanizowanych. Stężenia metali ciężkich analizowano metodą spektrometrii emisyjnej z plazmą sprzężoną indukcyjnie (ICP-OES) w przypadku próbek wody oraz metodą ICP-MS w przypadku osadów. Do identyfikacji istotnych różnic i potencjalnych źródeł zanieczyszczeń wykorzystano analizy statystyczne, w tym jednokierunkową analizę wariancji (ANOVA), analizę głównych składowych (PCA) i analizę skupień.

Wyniki i wnioski

Przykładowo, stężenia Zn sięgały 5,85 mg/l, przekraczając bezpieczny limit określony przez Światową Organizację Zdrowia, wynoszący 4,0 mg/l o 46%, podczas gdy poziom Pb wynoszący 0,19 mg/l przekraczał limit 0,01 mg/l prawie 19-krotnie ($p < 0,05$). Analiza osadów wykazała, że kadm i ołów stanowią główne czynniki ryzyka ekologicznego. Wskaźnik geoakumulacji (Igeo) wahał się od „niezanieczyszczonego” (–0,12) do „umiarkowanego” (2,11). Natomiast wartości wskaźnika ryzyka ekologicznego (RI) wahały się od 120 do 180, co wskazuje globalnie na umiarkowane, ale lokalnie na istotne ryzyko spowodowane przez zanieczyszczenie kadmem (Cd). Analiza PCA wykazała silne powiązania między metalami takimi jak Zn, Fe i Cu pochodzącymi ze zrzutów z terenów miejskich i przemysłowych; natomiast Cd wiązał się z praktykami rolniczymi.

Słowa kluczowe: rzeka Nerodime, metale ciężkie, zrzut z terenów miejskich, ryzyko ekologiczne, PCA, zrównoważone zarządzanie