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ASSESSMENT OF WATER AND SEDIMENT QUALITY OF DOBERÇAN THERMAL BATH, GJILAN, KOSOVO

This study evaluates the quality of water and surface sediment, ecological risk, and potential pollution sources at the Doberçan Thermal Bath (Gjilan, Kosovo) during 2025. Physicochemical parameters, nutrients, major ions, and trace metals were analyzed, and contamination was assessed using the contamination factor (*CF*), the geoaccumulation index (I_{geo}), the pollution load index (*PLI*), and the ecological risk index (*ERI*). The results indicate slightly alkaline conditions with increased mineralization and pronounced eutrophication pressure. Trace metal analysis indicates moderate concentrations of Fe and Zn, while Pb, Ni, Cd, As, and Cr exceed EU and WHO guideline values at selected sites. The applied indices indicate predominantly low to moderate contamination levels; however, localized hotspots of elevated ecological risk were identified, particularly associated with Cd and Pb enrichment. Spatial differences among sampling sites suggest localized pollution sources and variable accumulation patterns in sediments. The findings highlight the vulnerability of thermal and recreational waters to diffuse pollution, underscoring the importance of long-term monitoring and improved wastewater management to protect ecosystem integrity and public health.

1. INTRODUCTION

Water resources are vital for ecosystem functioning, biodiversity, and human health [1]. Globally, freshwater systems are increasingly threatened by anthropogenic pollution, in-

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cluding industrial discharges, agricultural runoff, and urban effluents, which alter physicochemical properties and ecological integrity [2, 3]. Nutrient enrichment and heavy metal contamination can trigger eutrophication, habitat degradation, and bioaccumulation of toxic substances, posing significant ecological and public health risks [4, 5].

Key water quality indicators, such as pH, electrical conductivity, total dissolved solids (*TDS*), and nutrient concentrations, are commonly used to assess pollution levels. Elevated *TDS* and phosphate levels often signal eutrophication and deteriorating water quality [1–6]. Persistent trace metals, including lead (Pb), nickel (Ni), iron (Fe), and zinc (Zn), accumulate in sediments and can impact aquatic ecosystems and human health over time [7, 8].

Integrated approaches combining physicochemical measurements, trace metal analysis, and statistical correlations are essential to identify pollution sources and assess ecological effects [1–4]. In the Western Balkans, water quality is challenged by legacy industrial activities, inadequate wastewater treatment, and weak regulatory enforcement [9]. Regional studies indicate heavy metal contamination in rivers and lakes, often exceeding safety thresholds [10, 11]. In Kosovo, both urban and rural water bodies show elevated trace metal levels, highlighting the need for systematic monitoring and management [12, 13]. Despite these efforts, thermal and recreational waters, such as the Doberçan bath, remain understudied [3].

Thermal water sites are particularly vulnerable due to recreational use and mixed pollution inputs. Contaminants in water and sediments necessitate detailed investigations to understand pollution dynamics, ecological impacts, and human health risks [2–4]. Toxic metals may enter the human body through ingestion, dermal contact, or food consumption, leading to neurological, renal, and cardiovascular effects [4–9]. Hazard index-based assessments provide quantitative estimates of these risks and guide regulatory and remediation measures.

This study addresses these gaps by offering an integrated assessment of water and surface sediment quality at the Doberçan thermal bath (municipality of Gjilan) during 2025. By combining physicochemical analyses, trace metal profiling, ecological indices, and health risk assessment, the research identifies key pollution sources, evaluates ecological status, and quantifies potential risks to both the environment and public health [14, 15]. The results provide a scientific basis for targeted remediation and sustainable water management in vulnerable water bodies.

2. MATERIALS AND METHODS

In 2025, surface water and sediment samples were collected from three stations at the Doberçan thermal bath, Gjilan, Kosovo, with three replicates per sample type. Water samples were collected approximately 20 cm below the surface in polyethylene and dark glass bottles, filtered, acidified with HCl and HNO_3, and stored at low temperature until analysis. Sediments (2 g) were digested with 69% HNO_3 at 130 °C for 5 h, filtered, washed, and diluted for metal analysis following U.S. EPA guidelines [16, 17]. High-purity standards (99.98%, Merck, Germany) ensured calibration accuracy.

2.1. STUDY AREA

Sampling locations were georeferenced using GNSS technology (KOPOS, Kosovo Positioning System) to capture spatial variability. Physicochemical parameters, including pH, electrical conductivity (*EC*), total dissolved solids (*TDS*), salinity, ammonium ions (NH_4^+), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), and nitrate (NO_3^-), were measured following standard methods (APHA, 2021; ISO 11885:2007). Trace metals (Fe, Zn, Pb, Ni, As, Cd, Co, Cr, Cu, and Mn) were analyzed after microwave-assisted digestion using ICP-OES. Quality control included replicates, blanks, and standard solutions to ensure analytical reliability [16, 18].

The study was conducted at the Doberçan thermal bath, located in the municipality of Gjilan, eastern Kosovo. This site is a natural thermal water source historically used for recreation and local water supply. The surrounding area comprises a mixture of agricultural land, small settlements, and natural vegetation, exposing the site to potential anthropogenic pressures such as agricultural runoff, domestic wastewater, and minor industrial discharges [18].

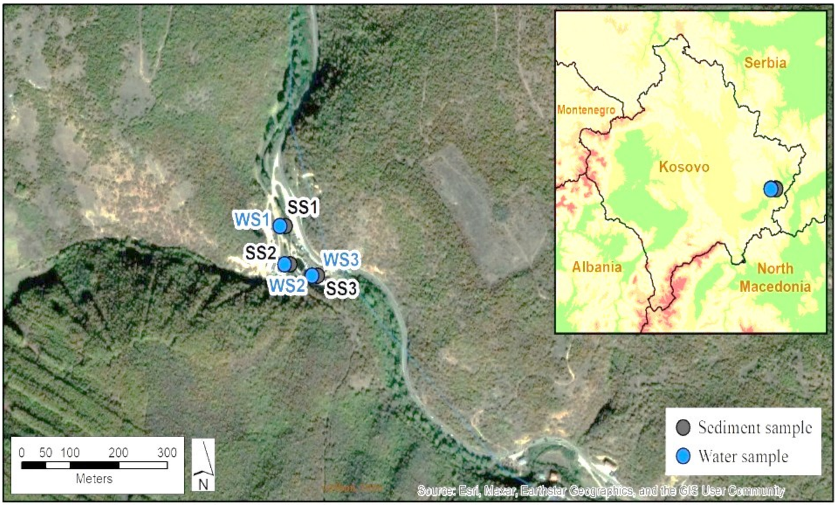

Fig. 1. Study area and sampling locations in Doberçan bath, Gjilan, Kosovo. Water sample sites (WS1–WS3) are shown as circles, and sediment sample sites (SS1–SS3) as triangles

The sampling points were strategically selected to assess both surface water and sediment quality, representing the most frequently used water sources and potential contamination gradients. The thermal bath's ecological and social significance, combined with its accessibility and historical use, makes it a suitable site for evaluating pollution dynamics, ecological status, and human health risks. Water and sediment samples were collected at three different sites, designated as representative sampling locations. Water samples were labeled WS1, WS2, and WS3, while sediment samples were designated SS1, SS2, and SS3, as presented in Fig. 1.

2.2. POLLUTION AND ECOLOGICAL RISK ASSESSMENT

To evaluate the contamination level and potential ecological risks of heavy metals in sediments, several established environmental indices were employed, including the contamination factor (*CF*), geoaccumulation index (I_{geo}), pollution load index (*PLI*), and potential ecological risk index (*RI*). These indices provide a comprehensive framework for quantifying sediment contamination and assessing associated ecological risks.

The contamination factor (CF_i) is an index used to evaluate the contamination level of a specific element in sediments according to Hakanson [19]

$$CF_i = \frac{C_i}{B_i} \tag{1}$$

where CF_i is the contamination factor for a given pollutant, C_i is the concentration of the heavy metal in the sediment sample, mg/kg, and B_i is its background concentration, mg/kg.

CF values are classified into four categories: $CF < 1$ corresponds to low contamination, $1 \le CF < 3$ to moderate contamination, $3 \le CF < 6$ to considerable contamination, and $CF \ge 6$ to very high contamination [19].

The geoaccumulation index (I_{geo}) was used to assess metal enrichment in sediments relative to background values [20]. I_{geo} is calculated as:

$$I_{geo} = \log_2\left(\frac{C_i}{1.5B_i}\right) \tag{2}$$

where C_i is the concentration of the metal, and B_i is the geochemical background concentration, and the constant factor 1.5 accounts for potential variations in background values.

I_{geo} indices are classified as follows: $I_{geo} < 0$ indicates uncontaminated, $0 \le I_{geo} < 1$ uncontaminated to moderately contaminated, $1 \le I_{geo} < 2$ moderately contaminated, $2 \le I_{geo} < 3$ moderately to strongly contaminated, $3 \le I_{geo} < 4$, strongly contaminated, $4 \le I_{geo} < 5$: strongly to extremely contaminated, $I_{geo} \ge 5$ extremely contaminated conditions [20].

The pollution load index (*PLI*) was calculated to estimate the level of heavy metal contamination in sediments [21, 22]:

$$PLI = \left(CF_1 CF_2 CF_3 \ldots CF_n \right)^{1/n} \tag{3}$$

where n is the number of analyzed metals and CF_i is the contamination factor of each metal [23]. *PLI* values are interpreted as follows: $PLI < 1$: no pollution; $PLI = 1$: baseline pollution level; $PLI > 1$: polluted [21].

The potential ecological risk index (RI) was used to assess sediment pollution by considering both the contamination level and the toxic response of individual metals [19, 23]. The ecological risk of each metal (E_r^i) and the risk index (*RI*) are calculated as:

$$E_r^i = T_r^i \, CF_i \tag{4}$$

$$RI = \sum_i E_r^i \tag{5}$$

where CF_i is the contamination factor of the metal and T_r^i is its toxic response coefficient. Typical T_r values for Fe, Mn, Cd, and Pb were considered as 1, 1, 30, and 5, respectively [19, 24]. *RI* values were interpreted according to the Hakanson classification [19] as: $RI < 150$: low risk, $150 \leq RI < 300$: moderate risk, $300 \leq RI < 600$: considerable risk, $RI \geq 600$: very high risk.

2.3. MULTIVARIATE STATISTICAL ANALYSIS

Hierarchical cluster analysis (HCA) using Ward's method was applied to group sampling sites based on similarities in heavy metal concentrations and physicochemical parameters. The analysis revealed clear clustering patterns, indicating that certain sites share comparable contamination profiles and environmental conditions.

This grouping facilitates the identification of areas potentially influenced by similar sources of pollution, whether natural geochemical background or localized anthropogenic inputs. The HCA results thus provide a robust visualization of spatial relationships among sampling points and help target monitoring and remediation efforts effectively [22, 23].

Principal component analysis (PCA) was conducted to identify potential sources of heavy metals in the sediment. PCA reduced the dimensionality of the dataset and highlighted the main factors controlling metal distribution. The first few principal components accounted for the majority of variance, distinguishing between metals predominantly influenced by natural geological processes and those likely associated with anthropogenic activities, such as wastewater discharge or agricultural runoff. This multivariate approach allows a clearer understanding of complex interactions among metals and physicochemical parameters, providing insights into both the origin of contamination and the relative contribution of different sources [20, 24]. The combination of HCA and PCA offers a powerful framework for interpreting spatial and compositional patterns, supporting evidence-based decision-making for environmental management and pollution mitigation.

3. RESULTS AND DISCUSSION

3.1. PHYSICOCHEMICAL CHARACTERISTICS AND WATER QUALITY ASSESSMENT AT DOBERÇAN THERMAL BATH

The physicochemical analysis of surface water from the sites WS1–WS3 provides a comprehensive assessment of water quality, reflecting both natural geochemical conditions and potential anthropogenic influences (Table 1). Water temperatures ranged from 25.9 °C (WS1) to 27.6 °C (WS2), indicating stable thermal conditions typical of geothermal springs. Such temperatures can influence microbial metabolism, chemical reaction rates, and dissolved oxygen solubility.

Dissolved oxygen (*DO*) levels were critically low (1.16–1.24 mg/dm^3, corresponding to 8.93–16.8% saturation), suggesting potential organic enrichment, limited water circulation, or stagnant conditions. Hypoxic conditions of this magnitude may stress aquatic organisms and enhance anaerobic processes, potentially leading to increased nutrient release from sediments.

Electrical conductivity (*EC*) was increased (1175–1450 μS/cm), with high total dissolved solids (*TDS*: 10.13–18.19 mg/dm^3) and increased salinity (3.91–18.64 mg/dm^3). These values indicate that water chemistry is influenced by both natural mineral dissolution and localized anthropogenic inputs, with the highest values observed at WS3 reflecting cumulative effects.

Nutrient concentrations exhibited significant spatial heterogeneity. Phosphate (PO_4^{3-}) levels were exceptionally high at WS2 (20.11 mg/dm^3), strongly indicating localized eutrophication, potentially driven by agricultural runoff or point-source pollution. Nitrate (NO_3^-) and ammonium (NH_4^+) were generally low, whereas nitrite (NO_2^-) equal to 0.58 –0.69 mg/dm^3 was moderately elevated, suggesting partial nitrogen transformation and incomplete nitrification, likely exacerbated by low *DO* levels.

Organic load indicators, including chemical oxygen demand (COD 15.6–19.1 mg/dm^3) and biochemical oxygen demand (BOD 11.2–16.1 mg/dm^3), reflect moderate pollution consistent with observed hypoxia. Alkalinity (HCO_3^- 121.31–154.59 mg/dm^3) and total hardness (15.36–18.21 °dH) suggest sufficient buffering capacity and moderate mineral content, stabilizing pH and influencing metal solubility and mobility.

Additional parameters, including TOC, TMS, and trace fluoride (F^- 0.1–0.2 mg/dm^3), support the characterization of mineral-rich waters typical of thermal systems. Water color and transparency indicate low turbidity, although moderate TMS values (13–23.3) may reflect suspended particulate matter or dissolved organic content.

Table 1

Physicochemical properties of water samples
collected from Doberçan Thermal Bath, Gjilan, Kosovo

Parameter	WS1	WS2	WS3	Parameter	WS1	WS2	WS3
Water temperature, °C	25.9	27.6	26.8	SO_4^{2-}, mg/dm^3	11.31	51.3	48.0
DO, mg/dm^3	1.24	1.16	1.19	PO_4^{3-}, mg/dm^3	0.41	20.11	4.21
O_2, %	11.9	16.8	8.93	TOC, mg/dm^3	6.2	7.4	8.5
EC, µS/cm	1190	1175	1450	Water color	without	transp.	transp.
pH	7.3	7.5	7.8	TMS	13	19.7	23.3
Salinity, mg/dm^3	3.91	5.56	18.64	F^-, mg/dm^3	0.1	0.2	0.2
TDS, mg/dm^3	10.19	10.13	18.19	ORP, mg/dm^3	35	4.65	6.44
Cl^-, mg/dm^3	0.21	0.23	0.22	Total hardness, °dH	15.36	18.21	16.65
COD, mg/dm^3	18.3	15.6	19.1	Ca, mg/dm^3	3.6	2.2	1.9
BOD, mg/dm^3	11.2	14.9	16.1	Mg, mg/dm^3	19.9	21.6	19.8
P_{tot}, mg/dm^3	0.41	0.19	0.21	MA	11.4	12.8	13.1
NO_3^-, mg/dm^3	0.01	0.015	0.011	HCO_3^-, mg/dm^3	121.31	154.59	140.28
N_{tot}, mg/dm^3	0.24	0.29	0.31	TUR, NTU	2.1	4.5	3.9
NH_4^+, mg/dm^3	0.04	0.08	0.07	$KmnO_4$	2.39	3.98	3.39
NO_2^-, mg/dm^3	0.58	0.64	0.69	SUR	< 0.1	< 0.2	< 0.1
N inorganic, mg/dm^3	0.16	0.28	0.26	Air temperature, °C	21	23.3	23

TMS – total mineral solids, ORP – oxidation-reduction potential, MA – mineral alkalinity, SUR – surfactant residues, transp. – transparent.

3.2. THE PRESENCE OF HEAVY METALS IN WATER

The concentrations of selected heavy metals (As, Mn, Ni, Fe, Cu, Zn, Cd, Pb, and Cr) in water samples collected from the sites WS1–WS3 indicate generally low to moderate contamination levels, with clear spatial differences among the sampling points (Table 2). The concentrations of heavy metals in water samples collected from the three investigated sites indicate moderate contamination with evident spatial variability. Among the analyzed elements, arsenic (As), nickel (Ni), cadmium (Cd), lead (Pb), and chromium (Cr) exceeded the EU–WHO health-based guideline values, whereas manganese (Mn), iron (Fe), copper (Cu), and zinc (Zn) remained within the recommended limits. Lead showed the greatest deviation from permissible concentrations, followed by Ni, Cd, and Cr, indicating that these elements represent the main chemical concern in the investigated thermal water system. The observed distribution patterns suggest that, although part of the elemental composition reflects the natural mineralized character of the thermal source, the elevated concentrations of As, Ni, Cd, Pb, and Cr indicate localized anthropogenic influence, likely associated with untreated wastewater discharge, agricultural runoff, and intensive recreational use of the surrounding area. These findings underline the need for continuous monitoring and targeted mitigation measures to protect both environmental quality and public health.

Table 2

Concentrations of heavy metals in water samples collected from Doberçan Thermal Bath, Gjilan, Kosovo

Element	WS1	WS2	WS3	St. Dev.	Min	Mean	Max	EU–WHO limit [mg/dm^3]	Health-based guideline	Status
As	0.016	0.020	0.014	0.0025	0.014	0.017	0.020	0.01	yes	EL
Mn	0.23	0.19	0.27	0.033	0.19	0.23	0.27	0.4*	no	WL
Ni	0.33	0.41	0.30	0.046	0.30	0.35	0.41	0.07	yes	EL
Fe	0.05	0.06	0.04	0.008	0.04	0.05	0.06	0.3*	no	WL
Cu	0.27	0.33	0.22	0.045	0.22	0.27	0.33	2.0	no	WL
Zn	1.10	0.92	1.18	0.109	0.92	1.07	1.18	3.0	no	WL
Cd	0.013	0.011	0.016	0.0021	0.011	0.013	0.016	0.003	yes	EL
Pb	0.37	0.44	0.29	0.061	0.29	0.37	0.44	0.01	yes	EL
Cr	0.08	0.06	0.10	0.016	0.06	0.08	0.10	0.05	yes	EL

EL – exceeds limit, WL – within limit.

To further explore the relationships among the detected metals, multivariate statistical analyses including hierarchical clustering and principal component analysis were performed, as presented in Figs. 2 and 3 [22, 23].

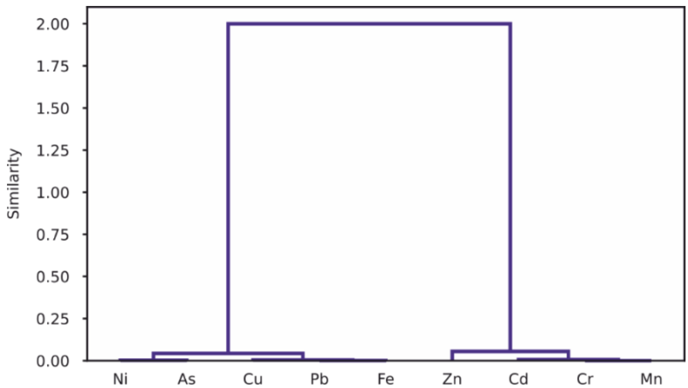

Fig. 2. The dendrogram of the distribution of heavy metals in the water resources

The scree plot in Fig. 3 shows the eigenvalues of each principal component, indicating that the first few components account for the majority of variance in the dataset. This information facilitates the interpretation of the distribution and relative influence of different elements on the water quality of the study area. By identifying the main contributing metals and their groupings, the analysis supports understanding of potential natural versus anthropogenic sources and guides targeted monitoring and management strategies [22, 23].

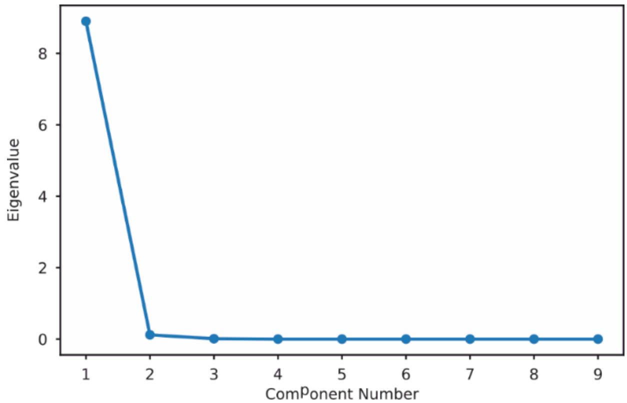

Fig. 3. Scree plot of eigenvalues from PCA of heavy metals in water samples from the Doberçan Thermal Bath

3.3. THE PRESENCE OF HEAVY METALS IN SEDIMENT

The concentrations of heavy metals in surface sediments from the investigated sites reveal pronounced spatial variability and heterogeneous accumulation patterns (Table 3).

Table 3

Concentrations of heavy metals in sediment samples [mg/kg]

Element	SS1	SS2	SS3	St. Dev.	Min	Mean	Max	EPA sediment standard	Status
As	26.00	42.95	12.53	15.28	12.53	27.16	42.95	33	EL (SS2)
Cd	1972.30	7.26	2.55	1137.79	2.55	660.70	1972.30	3	EL (all SS1–SS3)
Co	0.42	8.27	1.91	3.74	0.42	3.53	8.27	40	WL
Cr	16.28	43.36	29.09	13.42	16.28	29.58	43.36	90	WL
Cu	13.74	30.05	19.96	8.14	13.74	21.25	30.05	35	WL
Fe	5255.81	16,039.52	8,020.81	5574.87	5255.81	9642.71	16,039.52	50,000	WL
Mn	191.97	397.66	244.85	104.37	191.97	278.83	397.66	500	WL
Ni	37.42	37.31	31.85	2.97	31.85	35.53	37.42	50	WL
Pb	80.55	353.10	86.01	159.50	80.55	173.22	353.10	91	EL (SS2)
Zn	91.12	462.59	102.78	201.38	91.12	218.83	462.59	121	EL (SS2)

EL – exceeds limit, WL – within limit.

Iron (Fe) exhibited the highest absolute concentrations, followed by cadmium (Cd), zinc (Zn), lead (Pb), and manganese (Mn), indicating marked differences in sediment enrichment among the sampling points. Cadmium showed exceptionally elevated values at SS1, whereas Zn and Pb reached their maximum concentrations at SS2, suggesting localized anthropogenic contamination hotspots.

Copper, chromium, nickel, cobalt, and arsenic were detected at comparatively lower concentration ranges and displayed less pronounced spatial dispersion. According to the applied EPA sediment quality standards, Cd exceeded guideline values at all sites, while As, Pb, and Zn surpassed threshold limits at specific sampling points. These findings confirm that sediment contamination in the Doberçan Thermal Bath is spatially heterogeneous and controlled by both natural geochemical background and site-specific anthropogenic inputs.

3.4. ASSESSMENT OF HEAVY METAL CONTAMINATION IN SURFACE SEDIMENTS OF THE DOBERÇAN THERMAL BATH

The contamination factor (CF_i) values reveal varying levels of metal contamination across the sediment sampling sites (SS1–SS3), as illustrated in Fig. 4. Among the analyzed metals, Fe, Cd, Mn, and Pb exhibit elevated CF_i values, indicating moderate to very high contamination, whereas Zn, Cr, Cu, Ni, Co, and As generally show low to moderate contamination levels.

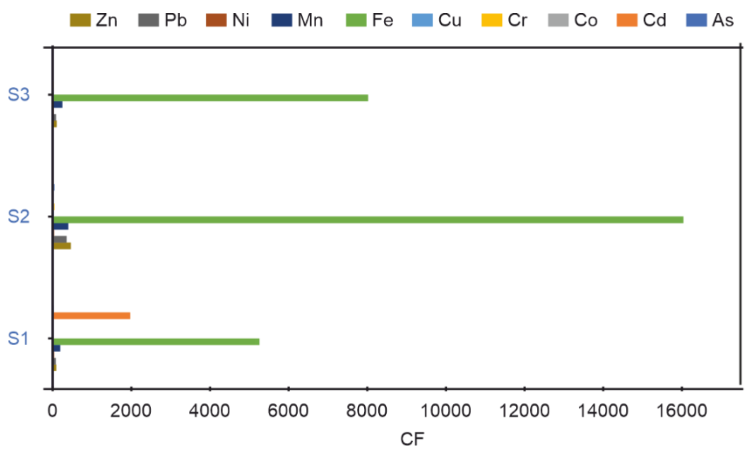

Fig. 4. Contamination factors of heavy metals in the sediment from Doberçan Thermal Bath, Gjilan, Kosovo

Iron demonstrates moderate contamination, with the highest CF_i observed at site SS2, reflecting primarily natural contributions enhanced by sediment accumulation. Cadmium shows the highest contamination at site SS1, where extremely elevated concentrations correspond to very high contamination, while sites SS2 and SS3 present considerably lower CF_i values. Manganese exhibits moderate contamination, with the peak CF_i at SS2, suggesting site-specific accumulation influenced by both natural geochemistry and anthropogenic inputs. Lead shows high contamination at SS2, indicating localized enrichment likely associated with human activities, whereas SS1 and SS3 display moderate contamination levels [26, 27]. Chromium, copper, nickel, cobalt, zinc, and arsenic generally present low to moderate contamination across all sites, suggesting limited anthropogenic influence and predominance of natural background levels [26, 27].

The spatial distribution of CF_i values identifies SS2 as the most contaminated site, followed by SS1, with SS3 representing the least impacted location. These findings demonstrate that sediment contamination in the Doberçan Thermal Bath is controlled by a combination of natural geochemical background and localized anthropogenic inputs, with significant enrichment occurring at specific sites.

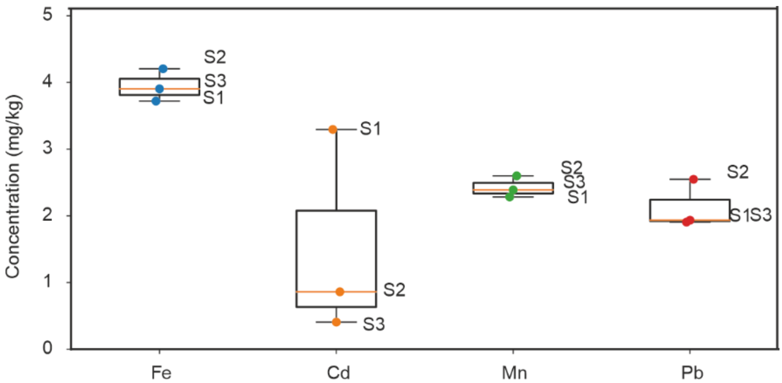

Fig. 5. Boxplots of heavy-metal concentrations (Fe, Cd, Mn, Pb) in sediment samples from Doberçan bath (Gjilan), shown on a logarithmic scale; individual points represent measured values at sampling sites SS1–SS3, illustrating within-element variability and the influence of extreme values

Figure 5 illustrates the distribution of heavy metal concentrations in the sediment samples from the investigated area. Among the analyzed elements, Fe exhibited the highest absolute concentrations, ranging from 5255.81 to 16,039.52 mg/kg, followed by Cd, Zn, Pb, and Mn, indicating marked differences in accumulation among the sampling sites. Cadmium showed particularly pronounced variability, with an exceptionally elevated value at SS1, whereas Zn and Pb reached their maximum concentrations at SS2, suggesting localized anthropogenic enrichment. Copper, chromium, nickel, cobalt, and arsenic were detected at comparatively lower concentration ranges and showed less pronounced spatial dispersion. The logarithmic presentation clearly demonstrates the heterogeneous distribution of metals within the sediment matrix and confirms that SS1 and SS2 represent the most impacted locations. These findings indicate that heavy metal accumulation in the Doberçan Thermal Bath sediments is controlled by both natural geochemical background and site-specific anthropogenic inputs.

The statistical summary of the calculated values of potential ecological risk (Er_i), pollution load index (*PLI*), and risk index (*RI*) for sediment samples from the Doberçan Thermal Bath reveals clear spatial variability among the investigated sampling sites (SS1–SS3) (Table 4). Although Fe exhibited the highest absolute concentrations in the sediment matrix, its ecological interpretation should be considered with caution because iron is largely controlled by natural geogenic background and has a substantially lower toxicological significance than more hazardous trace metals.

Table 4

Statistical summary for sediment samples from Doberçan bath, Gjilan, Kosovo

Parameter	Fe	Cd	Mn	Pb	*PLI*	*RI*
Min	1.05	153.00	0.38	20.14	1.70	174.57
Max	3.21	118,338.00	0.80	88.28	10.74	118,361.60
Mean	1.95	39,642.00	0.56	43.31	5.83	39,688.02
St. Dev.	1.12	6,8181.13	0.22	38.93	4.52	68,145.98

Cadmium represents the principal contributor to potential ecological concern due to its extreme concentration variability and elevated toxic response, making it the most environmentally relevant pollutant in the investigated area. Lead and manganese also contribute to localized ecological pressure, whereas the remaining analyzed metals show comparatively lower ecological influence.

The combined *PLI* and *RI* results further confirm that the sediment contamination pattern is mainly governed by localized anthropogenic enrichment, particularly at SS1 and SS2, indicating that ecological risk is not controlled solely by absolute metal abundance but also by metal toxicity and site-specific accumulation behavior [26, 27]. The spatial distribution of the calculated pollution load index for the analyzed sediment samples is illustrated in Fig. 6.

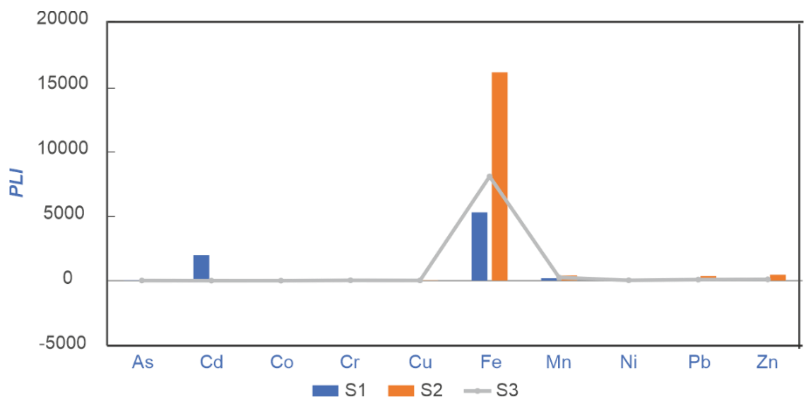

Fig. 6. Pollution load index (*PLI*) values for sediment samples from the Doberçan bath

The potential ecological risk distribution of the analyzed heavy metals in sediment samples is presented in Fig. 7. Cadmium emerges as the principal contributor to ecological concern due to its pronounced spatial variability and elevated toxicological relevance, particularly at SS1 [26–29]. Lead and manganese also show localized ecological influence, whereas iron, despite its high absolute abundance, should be interpreted mainly as a geogenic component with comparatively lower environmental significance [26–29].

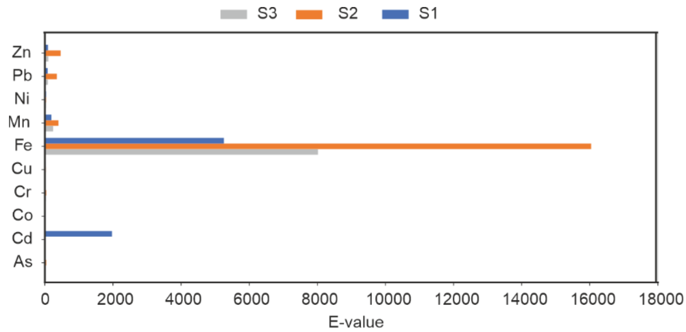

Fig. 7. Individual ecological risk values (*ERI*) of analyzed metals in sediment samples from the Doberçan bath

Arsenic, cobalt, chromium, copper, nickel, and zinc exhibit substantially lower ecological contributions, indicating limited risk to the sediment environment. The observed distribution patterns confirm that localized anthropogenic activities play a major role in controlling heavy metal accumulation and ecological pressure within the Doberçan Thermal Bath sediments [26–29].

Table 5

Spearman correlations between physicochemical parameters and heavy metals in the water of the Doberçan Thermal Bath

Correlation	*r*-value	*p*-value
EC–Cu	0.92	< 0.05
EC–Zn	0.85	< 0.05
Cu–Cd	0.67	< 0.05
Zn–Cd	0.71	< 0.05

Spearman correlation analysis of physicochemical parameters and heavy metals in the Doberçan Thermal Bath revealed significant relationships among the measured variables, indicating that water chemistry may influence the mobility and distribution of trace metals. Electrical conductivity showed strong positive correlations with Cu ($r = 0.92$, $p < 0.05$) and Zn ($r = 0.85$, $p < 0.05$), while Cu was moderately correlated with Cd ($r = 0.67$, $p < 0.05$). These associations suggest partially shared anthropogenic and hydrogeochemical sources.

In parallel, the individual ecological risk values (*ERI*) confirmed cadmium as the dominant ecological risk contributor, with additional localized influence from Pb and Mn, whereas Fe displayed high absolute abundance but comparatively lower ecological significance due to its geogenic background. The remaining analyzed metals exhibited minor ecological contributions, supporting the interpretation of spatially heterogeneous but site-specific sediment contamination within the Doberçan Thermal Bath area [26–29].

The observed relationships indicate that physicochemical water composition plays an important role in controlling the transport and distribution of trace metals in the investigated thermal system. Electrical conductivity (*EC*) shows strong positive correlations with copper and zinc, while moderate positive associations among Cu, Zn, and Cd suggest partially shared mobility patterns and localized contamination inputs. These findings confirm that heavy metal behavior in the Doberçan Thermal Bath water is influenced by both mineralization processes and anthropogenic contributions [26–29].

Table 6

Spearman correlations between heavy metals in sediment samples of the Doberçan Thermal Bath

Metals	Cd	Zn	Pb	Cu	Fe	Mn
Cd	1	0.84	0.91	0.65	0.48	0.50
Zn	0.84	1	0.88	0.70	0.52	0.55
Pb	0.91	0.88	1	0.60	0.51	0.53
Cu	0.65	0.70	0.60	1	0.79	0.73
Fe	0.48	0.52	0.51	0.79	1	0.94
Mn	0.50	0.55	0.53	0.73	0.94	1

Strong positive correlation $r \geq 0.75$.
Moderate positive correlation: $0.50 \leq r \leq 0.74$.

Spearman correlation analysis among heavy metals in Doberçan bath sediments reveals clear co-accumulation patterns, as presented in Table 6. Cadmium shows strong positive correlations with lead (r = 0.91) and zinc (r = 0.84), together with a moderate positive association with copper (r = 0.65), suggesting partially shared contamination sources and similar accumulation behavior. Lead and zinc are also strongly positively co rrelated (r = 0.88), whereas copper exhibits strong positive relationships with iron (r = 0.79) and a moderate positive relationship with manganese (r = 0.73). In addition, iron and manganese display the strongest positive correlation (r = 0.94), indicating a pronounced geogenic co-enrichment pattern. These correlation patterns suggest that Cd, Pb, Zn, and Cu are mainly influenced by localized anthropogenic inputs, while Fe and Mn variability is more strongly controlled by natural geological background [26, 29].

Table 7 provides a concise framework for interpreting sediment contamination and ecological risk in the Doberçan Thermal Bath. I_{geo} differentiates uncontaminated from extremely contaminated sediments, CF_i identifies metals contributing most to pollution, *PLI* reflects the sediment contamination level, and *ERI* integrates both metal concentration and toxic response to highlight potential ecological threats. Together, these indices allow a comparative assessment of sediment quality and support targeted monitoring and management decisions [26, 29].

Table 7

Pollution ecological indices: Classification and interpretation

Index	Classification	Interpretation
I_{geo}	$I_{geo} < 0$	uncontaminated
	$0 \le I_{geo} < 1$	uncontaminated to moderately contaminated
	$1 \le I_{geo} < 2$	moderately contaminated
	$2 \le I_{geo} < 3$	moderately to heavily contaminated
	$3 \le I_{geo} < 4$	heavily contaminated
	$4 \le I_{geo} < 5$	heavily to extremely contaminated
	$I_{geo} \ge 5$	extremely contaminated
CF_i	$CF_i < 1$	low contamination
	$1 \le CF_i < 3$	moderate contamination
	$3 \le CF_i < 6$	considerable contamination
	$CF_i \ge 6$	very high contamination
PLI	$PLI < 1$	baseline level / no pollution
	$PLI = 1$	reference baseline
	$PLI > 1$	contaminated
Er_i	$ERI < 40$	low risk
	$40 \le ERI < 80$	moderate risk
	$80 \le ERI < 160$	considerable risk
	$160 \le ERI < 320$	high risk
	$ERI \ge 320$	very high risk

4. CONCLUSIONS

The physicochemical analysis of water from the Doberçan Thermal Bath revealed slightly alkaline pH, variable electrical conductivity, and moderate organic matter content, indicating moderately impacted water quality.

Although several physicochemical parameters remain within acceptable limits, concentrations of heavy metals such as Pb, Cd, As, Ni, and Cr exceed EU and WHO guideline values, suggesting potential concerns for human health.

Sediment analysis identified iron as the most abundant element, largely of geogenic origin, while cadmium exhibited extremely elevated concentrations and represents the primary contributor to potential ecological risk. Lead and zinc showed localized enrichment, indicating site-specific anthropogenic influence.

The integrated pollution indices (CF, I_{geo}, PLI, and RI) indicate generally low to moderate contamination levels; however, localized areas with elevated ecological risk were observed, particularly at SS1 and SS2. Correlation analysis suggests that Cd, Cu, and Zn may share common anthropogenic sources, including wastewater discharge and agricultural activities. These findings highlight the importance of continuous monitoring and targeted environmental management measures to mitigate localized contamination and ensure the sustainable use of thermal water resources.

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