

Spatial distribution of dissolved trace metals and metalloids in the Sitnica–Llap–Ibar river system, Kosovo

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ABSTRACT

This study aimed to determine the spatial distribution of dissolved trace metals and metalloids in the Sitnica–Llap–Ibar river system in Kosovo and to identify pollution patterns relevant to environmental assessment and river-basin management. A dry-season monitoring campaign was conducted at ten surface-water sampling sites distributed along the investigated river system. Water samples were filtered, acidified, and analysed for Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Co, and Mo using inductively coupled plasma mass spectrometry (ICP-MS). The contamination status was evaluated using the contamination factor (CF), and the measured concentrations were compared with international environmental guideline values. The highest mean concentrations were recorded for Fe (595.00 µg/L), Mn (324.61 µg/L), and Al (202.50 µg/L), whereas Cd and Co occurred at comparatively lower levels. The highest individual concentrations were observed mainly at site W2, including Al (760 µg/L), Fe (1620 µg/L), Mn (615 µg/L), and Ni (23.1 µg/L). Pb reached its maximum concentration at W7 (13.2 µg/L), while Zn was highest at W3 (120 µg/L). CF values indicated considerable contamination for Mn and Pb, moderate contamination for Cd, Ni, and Al, and low contamination for the remaining analysed elements. Overall, the results confirmed pronounced spatial heterogeneity, with higher contamination indicators at W2, W3, and W7 and comparatively lower levels at W9 and W10. The study was limited to a dry-season campaign; therefore, seasonal variability and hydrological effects should be addressed in future monitoring. These findings provide useful baseline data for pollution control, environmental monitoring, and integrated river-basin management in Kosovo. The study offers original site-specific evidence on dissolved trace metal and metalloid contamination in the Sitnica–Llap–Ibar river system and supports future risk assessment and water-quality management.

Keywords: surface water quality, dissolved trace metals, metalloids, spatial distribution, contamination factor, Sitnica–Llap–Ibar river system.

INTRODUCTION

Surface water quality is a fundamental component of ecological integrity, agricultural sustainability, and public health, particularly in regions where river systems support irrigation, domestic uses, and ecosystem services. At the global scale, rapid urbanization, industrial development, agricultural intensification, and insufficient

wastewater treatment continue to increase pollutant inputs into freshwater environments (WHO, 2022; UN Environment, 2021). Among the major contaminant groups, trace metals and metalloids are of particular concern because of their persistence, non-biodegradability, and potential accumulation in aquatic environments and food chains (Tchounwou et al., 2012). In addition, recent studies have demonstrated that particulate

matter generated from industrial and urban activities can act as a carrier of toxic trace metals, thereby contributing to increased environmental and health risks in exposed populations (Eghomwanre and Ojoka, 2025). Elements such as lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), and manganese (Mn) may affect aquatic ecosystems and human health even at relatively low concentrations, particularly under continuous or repeated exposure (Kabata-Pendias and Mukherjee, 2007; Jaishankar et al., 2014). Recent studies further confirm that trace metals remain important chemical stressors in freshwater systems because of their toxicological relevance and long-term environmental behaviour (Singh et al., 2023).

In the Western Balkans, including Kosovo, river systems are affected by pressures related to historical and ongoing mining, coal-fired energy production, metallurgical processing, agriculture, urbanization, and untreated municipal wastewater. In Kosovo, several studies have reported degradation of surface waters under combined pollution sources. Elevated concentrations of minerals, trace metals, and metalloids have been reported in the Drin i Bardhë and Ibar Rivers under industrial and municipal influence (Dreshaj et al., 2022), while streams in the municipality of Dragash have shown deterioration associated with sewage discharge and inadequate waste management (Ibrahimi et al., 2021). In addition to metal contamination, persistent organic pollutants have been detected in the White Drin River (Camaj Isa et al., 2024), and plant bioindicators have indicated physiological stress in industrial areas such as Drenas and Mitrovica (Bajra-Brahimaj et al., 2024). These findings show that Kosovo's surface waters are exposed to complex environmental pressures and require spatially detailed assessment.

Within this regional context, the Sitnica–Llap–Ibar river system represents an environmentally pressured river network in Kosovo. The system receives inputs from lignite-fired thermal power plants, mining and metallurgical facilities, industrial zones, intensively cultivated agricultural areas, and densely populated urban settlements. Recent investigations have documented water-quality degradation and complex pollutant patterns in the Sitnica River using physicochemical monitoring, wireless-sensor datasets, and toxicological bioassays (Kelmendi and Aliu, 2023; Ahmedi and Makolli, 2023). However, existing studies have

generally focused on specific river sections, selected contaminants, or particular monitoring approaches. Consequently, a system-wide evaluation of dissolved trace metals and metalloids across the interconnected Sitnica–Llap–Ibar river network is still lacking. Moreover, recent studies in environmental health and occupational safety emphasize that industrial and mining regions in developing countries require integrated monitoring approaches that combine environmental and occupational risk perspectives rather than relying only on isolated pollutant assessments. This approach is consistent with recent findings highlighting the need for integrated environmental health and occupational safety assessments in industrial regions of developing countries (Ayeleso et al., 2024). As a result, information on the spatial distribution of dissolved trace metals and metalloids across the Sitnica–Llap–Ibar river system remains limited, especially regarding dissolved-phase contamination across multiple sampling locations.

Inductively coupled plasma mass spectrometry (ICP-MS) provides high sensitivity and multi-element capability and is widely used for trace-metal determination in environmental monitoring (US EPA, 2017; Skoog et al., 2014). In this context, recent studies have highlighted the usefulness of integrated spatial monitoring approaches for identifying pollution patterns, environmental gradients, and pollution hotspots in anthropogenically impacted regions (Amaechi et al., 2026). In addition to direct concentration measurements, contamination indices such as the contamination factor (CF) are useful for comparing measured concentrations with reference values and identifying spatial differences among sampling sites (Hakanson, 1980; Tomlinson et al., 1980). Such approaches support the identification of localized contamination patterns and provide a basis for interpreting site-specific environmental pressure.

Unlike previous investigations that focused on individual river segments, specific contaminants, or isolated monitoring approaches, this study provides the first integrated spatial assessment of dissolved trace metals and metalloids across the Sitnica–Llap–Ibar river system using harmonized sampling and ICP-MS analysis. By combining multi-element determination, contamination factor evaluation, and multivariate statistical analysis, the study identifies spatial contamination gradients and potential pollution

hotspots associated with different anthropogenic pressures, including mining, thermal power generation, agriculture, and urban activities. The approach contributes new baseline information on dissolved-phase metal contamination within one of the most environmentally pressured river systems in Kosovo and supports future river-basin monitoring and management strategies.

The objectives of this study were to quantify concentrations of selected dissolved trace metals and metalloids in surface waters at ten monitoring locations along the Sitnica–Llap–Ibar river network, assess their spatial distribution across the investigated sites, compare measured concentrations with relevant international water-quality guideline values, and evaluate contamination levels using the contamination factor approach. Given the limited availability of spatially distributed dissolved-metal data for this river system, this study establishes a baseline dataset for dissolved trace metals and metalloids and identifies locations exhibiting elevated contamination signals. The generated dataset may serve as a reference framework for future temporal monitoring, ecological risk investigations, and watershed-management programs in Kosovo.

MATERIALS AND METHODS

Study area

The study was conducted along the Sitnica–Llap–Ibar river system, located in central and northern Kosovo. This watershed is exposed to substantial anthropogenic pressure, including dense urban settlements, intensively cultivated agricultural land, major road infrastructure, and industrial facilities such as lignite-fired thermal power plants and mining–metallurgical complexes. The Sitnica River flows through the municipalities of Fushë Kosovë/Kosovo Polje, Obiliq/Obilić, and Vushtrri/Vučitrn, receiving inputs from urban and industrial areas. The Llap River joins the Sitnica upstream of Mitrovica, while the Sitnica subsequently discharges into the Ibar River in the Mitrovica area, forming an important hydrological network that ultimately drains towards the Danube basin. Previous studies have identified this river system as one of the most affected in Kosovo, with pollution hotspots associated with untreated municipal wastewater, agricultural runoff, and industrial effluents (Ferati et

al., 2015; Kadriu et al., 2021; Kelmendi and Aliu, 2023).

Surface water samples were collected at ten sampling sites (W1–W10), selected to represent upstream–downstream variation and areas potentially influenced by major urban, agricultural, and industrial pressures. W1 (Sllatina) represents an upstream reach of the Sitnica River influenced mainly by rural settlements and agricultural activities. W2 (Palaj), also located on the Sitnica River, lies in the Obiliq area, near lignite-fired power plants and associated industrial facilities, and therefore reflects strong industrial and urban pressure. W3 (Prelluzha) is located further downstream on the Sitnica River, integrating inputs from mixed agricultural land and upstream settlements from both the Sitnica and Llap sub-catchments. W4 (Millosheva), located on the Llap River, drains predominantly rural and agricultural areas but is also influenced by nearby road infrastructure along the Prishtina–Mitrovica transport corridor.

Further downstream, W5 (“Pestova intro”) and W6 (Pestova) are situated within an intensively cultivated agricultural plain near Vushtrri, where arable land and local food-processing activities may contribute both diffuse and point-source inputs. W7 (Nedakove) lies on a lower-reach section of the Sitnica River and reflects the combined influence of upstream urban discharges, agricultural activities, and industrial pressures across the Kosovo Plain. W8 (Shupkovac) is located on the lower course of the Sitnica River, close to the city of Mitrovica and the surrounding mining and metallurgical area, immediately upstream of its confluence with the Ibar River. Finally, W9 (Suhodoll) and W10 (Mitrovica) are positioned along the Ibar River in the Mitrovica area, representing sections potentially influenced by urban wastewater and mining-related activities. The sampling stations, their coordinates, river sections and main nearby anthropogenic pressures are presented in Table 1.

To illustrate the spatial context, Figure 1 presents the distribution of the ten surface water sampling sites (W1–W10) along the Sitnica, Llap, and Ibar rivers in central and northern Kosovo, together with nearby municipalities and major road infrastructure. This provides geographical context for interpreting spatial variation in dissolved trace metal and metalloid concentrations across the investigated river system.

Table 1. Sampling stations along the Sitnica River and main nearby anthropogenic pressures

Station	Latitude	Longitude	River section	Main nearby pressure
W1 – Slatine	42.614060	21.073770	Upstream	Agricultural area
W2 – Palaj (Mining Obiliq)	42.861150	21.062927	Upstream	Mining activities
W3 – Prelluzhe	42.729113	21.014419	Midstream	Agricultural area
W4 – Milosheve	42.726816	21.078047	Midstream	Urban discharge
W5 – Pestova (Entrance)	42.779633	20.990030	Midstream	Agricultural area
W6 – Pestova (Exit)	42.782815	20.992115	Midstream	Agricultural runoff
W7 – Nedakovc (Sitnica Bridge)	42.797710	20.990690	Midstream	Traffic and urban influence
W8 – Shupkovac	42.877529	20.874912	Downstream	Agricultural and urban influence
W9 – Suhodoll	42.884903	20.850760	Downstream	Urban discharge
W10 – Mitrovica (Ibar Bridge)	42.890746	20.862622	Downstream	Industrial and transport influence

Note: The stations are grouped according to their relative position along the river course and the dominant nearby anthropogenic pressure.

In situ observations and basic physico-chemical parameters were recorded during the sampling campaign to characterize field conditions at each site. Sampling location, sampling time, water temperature, odor, pH, electrical conductivity, and visual appearance are summarized in Table 2.

Sampling sites and sample collection

Surface water samples were collected during a single dry-season sampling campaign in October 2024 from ten sampling sites (W1–W10) distributed across seven river sections/locations along the

Sitnica–Llap–Ibar river system. The sampling sites were selected to represent spatial variation along the river network and areas potentially influenced by urban wastewater discharges, agricultural activities, industrial zones, and tributary confluences. At each site, surface water was collected from approximately 20–30 cm below the water surface using pre-acid-washed polyethylene bottles.

Before sampling, the bottles were rinsed three times with river water from the respective site to minimise the risk of cross-contamination (Bogdanowicz et al., 2021). Approximately 500 mL of water was collected at each site. All samples were filtered in situ through 0.45 µm membrane filters.

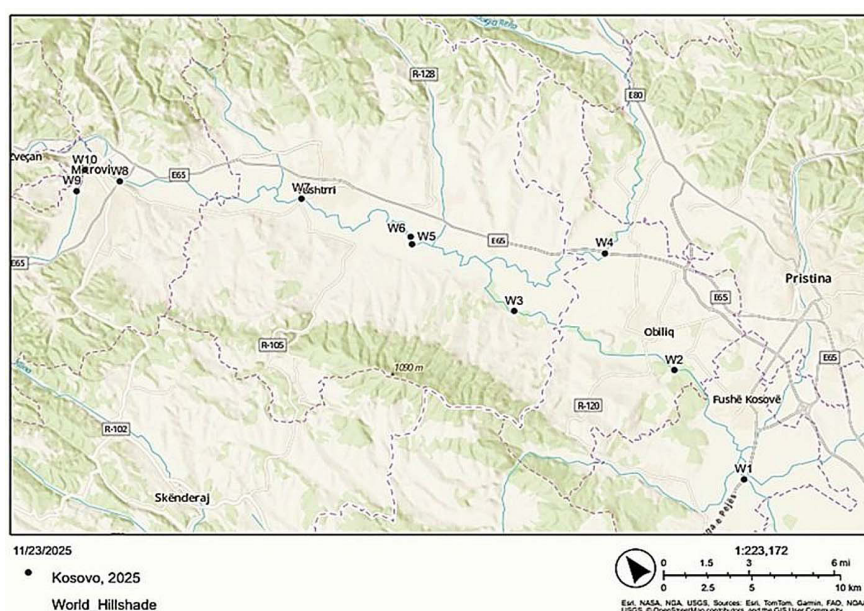


Figure 1. Distribution of surface water sampling sites (W1–W10) along the Sitnica, Llap and Ibar rivers in central and northern Kosovo, with reference to nearby municipalities and road infrastructure

Table 2. Field observations and physicochemical parameters recorded at the sampling sites

Parameter	Unit	Standard method	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10
Sampling location	–	ISO 5667-3; ISO 5667-6	Slatina	Palaj	Prelluzhë	Millosevë	Pestova (Inlet)	Pestova (Outlet)	Nedakovc	Shupkovac	Suhodoll	Mitrovica (Ibar Bridge)
Sampling time	h	–	14:00	15:10	16:55	17:45	08:10	08:30	09:20	10:40	11:15	12:30
Water temperature	°C	DIN 38404-C4	21	20	20	18	19	19	20	19	18	17
Odor	–	DEV B 1/2	No odor	Strong odor	Strong odor	Strong odor	Strong odor	Strong odor	Strong odor	Strong odor	No odor	No odor
pH	–	ISO 10523:2008	8.50	7.90	8.10	8.38	8.11	8.10	8.30	7.67	8.10	8.09
Electrical conductivity	µS cm ⁻¹	ISO 7888:1985	490	810	815	450	765	760	780	790	323	310
Visual appearance	–	ISO 7027:1999	Clear	Turbid	Turbid	Turbid	Turbid	Turbid	Turbid	Turbid	Clear	Clear

Note: Field observations and physicochemical parameters were recorded during the dry-season sampling campaign.

Immediately after filtration, the samples were acidified to pH < 2 with ultrapure nitric acid (HNO₃, trace-metal grade) to preserve dissolved metal species and prevent adsorption onto container walls, following US EPA recommendations for trace-metal monitoring in natural waters (US EPA, 2017).

Sampling was carried out under dry-season conditions to reduce short-term hydrological variability and to obtain spatially comparable measurements of dissolved trace metal and metalloid concentrations along the investigated river system. Because sampling was conducted during a single dry-season campaign, the results should be interpreted as a spatial snapshot of dissolved trace metal and metalloid concentrations rather than as a seasonal or long-term assessment of water quality.

Sample handling, preservation, and transport

After filtration and acidification, the samples were stored in insulated, light-protected cooling containers and maintained at approximately 4 °C during storage and transport to the accredited analytical laboratory, Actlabs, Canada. The samples were transported under refrigerated conditions to preserve sample integrity and minimise potential chemical alteration before analysis. The analysis was performed within the recommended holding time for acid-preserved water samples intended for dissolved trace-metal and metalloid determination.

The sampling bottles used for sample collection complied with ISO 5667 requirements for water sampling and preservation. Since the sampling campaign was based on a single dry-season monitoring event, the dataset was interpreted as a preliminary spatial assessment of dissolved trace

metal and metalloid concentrations across the investigated river system, rather than as a seasonal or long-term assessment of water quality.

Chemical analysis using ICP-MS

Concentrations of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Co, and Mo were determined by inductively coupled plasma mass spectrometry (ICP-MS), following the procedures described in US EPA Method 6020B (US EPA, 2017). ICP-MS was selected because of its high sensitivity, low detection limits, and multi-element capability, which make it suitable for the determination of dissolved trace metals and metalloids in natural waters (Skoog et al., 2014).

Instrument calibration was performed using multi-element standard solutions prepared at five concentration levels covering the expected concentration range of the analysed elements. Internal standards, including In, Rh, and Bi, were added to all standards and samples to correct for potential matrix effects and instrumental drift. Analytical precision and accuracy were controlled through the accredited laboratory's standard QA/QC procedures, including calibration verification, internal standards, blanks, duplicate analyses, and certified reference materials. The reported concentrations were used for descriptive statistical analysis, spatial interpretation, and contamination-factor calculation.

Quality assurance and quality control (QA/QC)

Quality assurance and quality control (QA/QC) procedures were applied to ensure the

accuracy, precision, and reliability of the analytical data. QA/QC was performed according to the accredited laboratory procedures reported in Actlabs Analytical Report No. A24-15550. Method blanks were analysed to check potential contamination during sample preparation and instrumental analysis, while field blanks were used to evaluate possible contamination introduced during sampling, handling, and transport.

Duplicate analyses were performed to assess analytical precision, and relative percent deviation (RPD) values below 10% were considered acceptable. Certified reference materials for trace metals in water, together with calibration verification standards, were used to verify analytical accuracy. Recovery values within the range of 85–115% were accepted. Limits of detection (LOD) and limits of quantification (LOQ) were established for each element in accordance with EPA-based analytical protocols. Instrumental drift and matrix effects were monitored and corrected using internal standards.

All analytical procedures were conducted under ISO/IEC 17025 accreditation, ensuring the traceability and reliability of the laboratory data.

The LOD for each element was provided by the analytical laboratory (Actlabs, Canada). The LOQ was calculated using the standard formula $LOQ = 10 \times LOD$, following established analytical chemistry protocols.

Quality assurance and quality control (QA/QC) procedures were implemented throughout the analytical process. Instrumental LOD were provided by the analytical laboratory, whereas LOQ were calculated as ten times the corresponding LOD values. The LOD and LOQ values for the analyzed dissolved trace metals and metalloids are presented in Table 3.

Analytical precision was assessed through duplicate analysis of the water sample W10. For each element, the relative percent difference (RPD) between the original and duplicate measurements was calculated to evaluate analytical repeatability. The obtained RPD values are reported in Table 4.

Analytical accuracy was evaluated using a certified reference material (CRM). Recovery values were calculated for each element as the ratio of the measured concentration to the certified concentration and are also presented in Table 5.

Table 3. Limits of detection (LOD) and limits of quantification (LOQ) for dissolved trace metals and metalloids determined by ICP-MS

Element	LOD (µg/L)	LOQ (µg/L)	Method
Al	2.0	20.0	ICP-MS
As	0.03	0.30	ICP-MS
Cd	0.01	0.10	ICP-MS
Co	0.005	0.050	ICP-MS
Cr	0.5	5.0	ICP-MS
Cu	0.2	2.0	ICP-MS
Fe	10	100	ICP-MS
Mn	0.1	1.0	ICP-MS
Ni	0.3	3.0	ICP-MS
Pb	0.01	0.10	ICP-MS
Zn	0.5	5.0	ICP-MS
Mo	0.1	1	ICP-MS

Statistical analysis

Descriptive statistics, including minimum, maximum, mean, median, standard deviation (SD), and coefficient of variation (CV), were calculated to summarize the concentration ranges and spatial variability of the analysed dissolved trace metals and metalloids. Statistical processing was performed using IBM SPSS Statistics, version 26, and the Python programming language.

Pearson correlation analysis was applied as an exploratory tool to evaluate potential relationships among the analysed elements and to identify possible common sources or similar geochemical behaviour. Principal Component Analysis (PCA) was also performed as an exploratory multivariate approach to support the interpretation of

Table 4. Duplicate precision (RPD%) for the W-10 water sample

Element	Original	Duplicate	RPD (%)
Al	23	23	0
Cr	1.7	1.8	5.71
Mn	47.4	47.8	0.84
Fe	80	80	0
Co	0.17	0.176	3.47
Ni	2.1	2.2	4.65
Cu	1.2	1.2	0
Zn	9.2	9.3	1.08
As	0.82	0.83	1.21
Cd	0.1	0.11	9.52
Pb	1.35	1.36	0.74

spatial patterns in dissolved trace metal and metalloid concentrations. Given the limited number of samples, the PCA results were interpreted cautiously and used only as supporting evidence for spatial interpretation.

To support the interpretation of contamination levels, the contamination factor (CF) was calculated for each element by dividing the measured concentration by the corresponding reference value (Tomlinson et al., 1980; Arora et al., 2025). CF values were used to compare contamination intensity among elements and sampling sites and to identify locations with relatively elevated dissolved metal and metalloid concentrations. The CF results were interpreted as indicators of relative contamination intensity and not as a complete ecological risk assessment.

Measured concentrations were compared with selected international water-quality guideline values, including NOAA SQuRTs, WHO drinking-water guideline values, and relevant EU Water Framework Directive environmental quality standards, in order to contextualize the observed concentrations and identify potential exceedances. Figures and statistical visualizations were prepared from the authors' original numerical data using Python, Matplotlib, and related scientific libraries.

RESULTS AND DISCUSSION

Measured concentrations and descriptive statistics of dissolved trace metals and metalloids

Dissolved trace metal and metalloid concentrations measured at the ten sampling sites (W1–W10) are presented in Table 6. The analysed elements included aluminium (Al), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), arsenic (As), cadmium (Cd), and molybdenum (Mo). These values represent laboratory-reported concentrations obtained from Actlabs Analytical Report No. A24-15550. The concentration patterns showed clear differences among both elements and sampling sites, providing the basis for evaluating the spatial distribution of dissolved trace metals and metalloids across the investigated river system.

The results presented in Table 6 show marked differences in dissolved trace metal and metalloid concentrations among the investigated sampling sites. The highest concentrations were generally

Table 5. Recovery (%) of certified reference material (CRM) for the analyzed dissolved trace metals and metalloids

Element	Measured	Certified	Recovery (%)
Al	148	142	104.23
Cr	20.9	20	104.5
Mn	41.1	39	105.38
Fe	100	98	102.04
Co	27.9	27	103.33
Ni	64.2	62	103.55
Cu	23.5	23	102.17
Zn	80.5	79	101.9
As	62.4	60	104
Cd	7.29	7	104.14
Pb	21.1	20	105.5

recorded for Fe, Mn, and Al, with particularly elevated values at W2 and W7. In contrast, the downstream sites W9 and W10 showed comparatively lower concentrations for most of the analysed elements. These spatial differences indicate an uneven distribution of dissolved trace metals and metalloids across the investigated river sections.

To further characterize the concentration dataset, descriptive statistical analysis was performed, and the obtained parameters are summarized in Table 7.

Table 7 summarizes the descriptive statistics of dissolved trace metals and metalloids in the analysed surface water samples, including mean, standard deviation, minimum, maximum, and percentile values. Fe, Mn, and Al showed the highest mean concentrations, whereas Cd and Co were present at comparatively lower levels. The relatively high standard deviation values observed for Pb, Zn, Fe, Mn, and Al indicate marked spatial variability among the sampling sites, suggesting an uneven distribution of these elements within the investigated river sections. This pattern may reflect site-specific inputs or local hydrochemical conditions.

To further examine relationships among the analysed elements, Pearson correlation analysis was applied as an exploratory tool. The results are presented in Figure 2 and were used to support the interpretation of possible similarities in element behaviour or spatial distribution patterns.

Figure 2 presents the Pearson correlation matrix for selected dissolved trace metals and metalloids in the analysed surface water samples. Strong positive correlations were observed among

Table 6. Dissolved trace metal and metalloid concentrations in surface water at sampling sites W1–W10

Site	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	As	Cd	Mo
W1	80	2.5	189	480	0.886	7.2	6.1	15.3	2.05	3.64	0.35	0.70
W2	760	6.2	615	1620	2.420	23.1	11.6	71.0	8.86	6.14	0.09	0.60
W3	180	4.2	580	690	1.090	10.6	1.1	120.0	6.79	4.39	0.17	0.40
W4	117	8.8	131	470	0.548	9.2	4.4	25.3	1.41	3.80	0.08	0.30
W5	39	2.8	362	330	0.863	11.5	2.5	25.6	0.92	4.83	0.03	1.30
W6	56	4.2	329	330	0.852	11.4	1.9	13.8	1.13	5.52	0.05	2.00
W7	708	7.4	427	1350	2.300	19.8	4.9	39.6	13.20	5.90	0.09	1.10
W8	25	2.8	520	480	0.885	11.0	1.5	13.6	1.08	6.54	0.02	1.50
W9	37	3.0	45.5	120	0.206	3.0	1.2	7.4	0.36	0.71	0.04	0.20
W10	23	1.8	47.6	80	0.173	2.1	1.2	9.3	1.36	0.83	0.11	0.05

Note: Concentrations are expressed in µg/L. Al – aluminium; Cr – chromium; Mn – manganese; Fe – iron; Co – cobalt; Ni – nickel; Cu – copper; Zn – zinc; Pb – lead; As – arsenic; Cd – cadmium; Mo – molybdenum.

Table 7. Descriptive statistics of dissolved trace metals and metalloids in surface water samples

Statistic	Pb	Cd	Cr	Ni	Cu	Zn	Fe	Mn	Al	As	Co
Count	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Mean	3.72	0.10	4.37	10.89	3.64	34.09	595.00	324.61	202.50	4.23	1.02
SD	4.37	0.10	2.34	6.54	3.31	35.64	505.86	213.47	284.50	2.06	0.77
Min	0.36	0.02	1.80	2.10	1.10	7.40	80.00	45.50	23.00	0.71	0.17
25%	1.09	0.04	2.80	7.70	1.28	13.65	330.00	145.50	37.50	3.68	0.62
50%	1.39	0.09	3.60	10.80	2.20	20.30	475.00	345.50	68.00	4.61	0.87
75%	5.61	0.11	5.70	11.48	4.78	36.10	637.50	496.75	164.25	5.81	1.04
Max	13.20	0.35	8.80	23.10	11.60	120.00	1620.00	615.00	760.00	6.54	2.42

Note: Concentrations are expressed in µg/L. SD – standard deviation; Pb – lead; Cd – cadmium; Cr – chromium; Ni – nickel; Cu – copper; Zn – zinc; Fe – iron; Mn – manganese; Al – aluminium; As – arsenic; Co – cobalt.

Al, Fe, Ni, and Pb, particularly between Al and Fe ($r = 0.96$), Al and Pb ($r = 0.92$), Fe and Ni ($r = 0.93$), Fe and Pb ($r = 0.89$), and Al and Ni ($r = 0.87$). These relationships suggest similar spatial distribution patterns and may indicate common geochemical behaviour or potential shared anthropogenic sources. Manganese showed moderate to strong positive correlations with Ni ($r = 0.79$), Fe ($r = 0.70$), Pb ($r = 0.58$), and Al ($r = 0.54$), indicating partial association with the main metal group. Chromium displayed moderate correlations with Al, Fe, Ni, and Pb ($r = 0.55$ – 0.61), but a weaker relationship with Mn ($r = 0.21$). In contrast, Cd showed weak or negative correlations with most analysed elements, including Cr ($r = -0.15$), Ni ($r = -0.14$), and Mn ($r = -0.11$), suggesting a distinct distribution pattern or different controlling factors. Given the limited number of samples, these correlations should be interpreted cautiously and used as exploratory evidence.

The numerical Pearson correlation matrix corresponding to Figure 2 is presented in Table 8.

Strong positive correlations were observed among Al, Fe, Ni, and Pb ($r = 0.872$ – 0.965), indicating that these elements are likely controlled by similar geochemical processes or share common sources. Moderate positive correlations were found between Cr and the other major elements ($r = 0.545$ – 0.611), while Mn showed moderate to strong correlations with Fe ($r = 0.700$) and Ni ($r = 0.787$). In contrast, Cd exhibited weak or negative correlations with most elements ($r = -0.154$ to 0.108), suggesting different geochemical behavior or a distinct source compared with the remaining dissolved elements.

The exploratory PCA score plot presented in Figure 3 illustrates the distribution of sampling sites based on dissolved trace metal and metalloid concentrations. The first principal component (PC1) explained 65.61% of the total variance, indicating

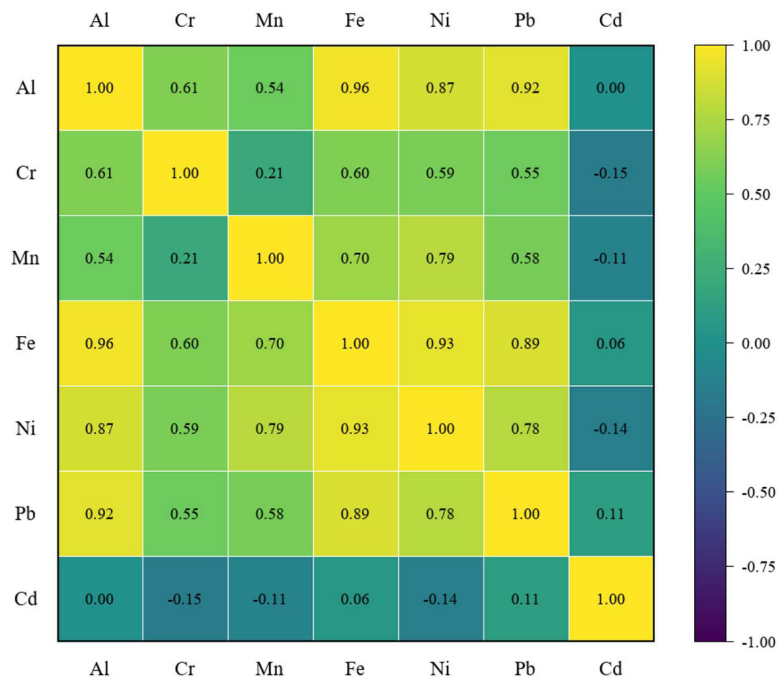


Figure 2. Pearson correlation matrix of selected trace metals and metalloids in water samples

Table 8. Numerical Pearson correlation matrix of dissolved trace metals and metalloids in the Sitnica–Llap–Ibar River System

Element	Al	Cr	Mn	Fe	Ni	Pb	Cd
Al	1.000	0.611	0.541	0.965	0.872	0.918	0.000
Cr	0.611	1.000	0.206	0.604	0.589	0.545	-0.154
Mn	0.541	0.206	1.000	0.700	0.787	0.581	-0.110
Fe	0.965	0.604	0.700	1.000	0.934	0.891	0.061
Ni	0.872	0.589	0.787	0.934	1.000	0.778	-0.142
Pb	0.918	0.545	0.581	0.891	0.778	1.000	0.108
Cd	0.000	-0.154	-0.110	0.061	-0.142	0.108	1.000

that most of the variability among samples was associated with a dominant concentration gradient.

Sites W5–W8 showed relatively similar characteristics, whereas W1 and W10 were clearly separated from the remaining sites. This separation suggests distinct hydrochemical conditions or localized differences in dissolved metal and metalloid concentrations across the investigated river sections.

While the PCA score plot (Figure 3) shows the spatial distribution and relative grouping of sampling sites based on dissolved trace metal and metalloid concentrations, the PCA loading plot (Figure 4) provides additional information on the contribution of individual elements to the principal components and their possible associations.

The PCA loading plot (Figure 4) illustrates the contribution of individual dissolved trace

metals to the first two principal components. Cadmium (Cd) exhibited a strong positive loading on PC2, indicating that its distribution pattern differed from that of the other analyzed elements. In contrast, Al, Fe, Ni, and Pb showed strong negative loadings on PC1, suggesting that these elements were closely associated and contributed substantially to the overall variability explained by the first principal component. Chromium (Cr) and Mn also contributed to the PCA structure but displayed different loading patterns, reflecting moderate associations with both principal components. Overall, the PCA loading pattern indicates that the analyzed elements do not exhibit a uniform distribution among the sampling sites and suggests the presence of different geochemical controls or potential sources influencing their

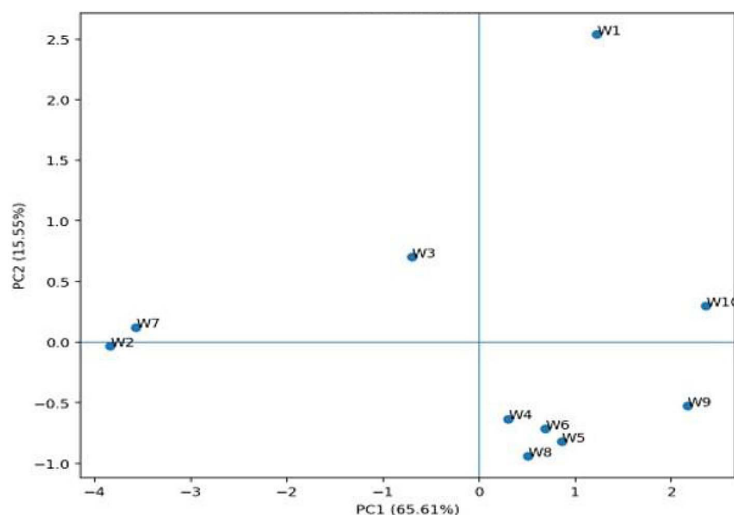


Figure 3. PCA score plot of water samples based on trace metal and metalloid concentrations

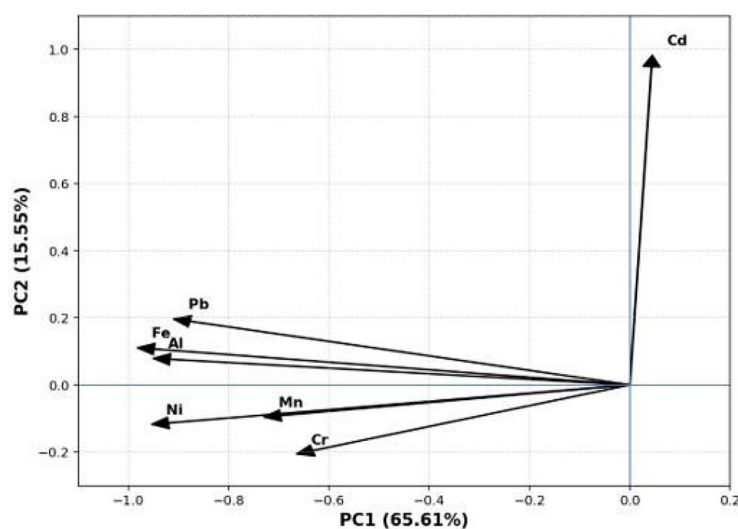


Figure 4. PCA loading plot of trace metals and metalloids in water samples

occurrence. Considering the limited number of sampling sites, these results should be interpreted as exploratory. The PCA results are presented in Table 9.

The first principal component (PC1) explained 65.61% of the total variance, suggesting that it represents the dominant factor governing the spatial distribution of dissolved trace metals and metalloids in the investigated river system. The second principal component (PC2) accounted for a further 15.55% of the variance, whereas the third principal component (PC3) contributed 11.73%. Collectively, the first three principal components explained 92.89% of the total variance, indicating that the extracted components provide a robust representation of the variability within the dataset.

The PCA loading matrix (Table 10) indicates that Al, Fe, Ni, and Pb exhibit high absolute loadings on PC1 (−0.911 to −0.983), suggesting that these elements are strongly associated and likely controlled by similar geochemical processes. Chromium and manganese show relatively stronger contributions to PC3, reflecting secondary variability within the dataset. In contrast, Cd displays a dominant positive loading on PC2 (0.983), indicating a distinct geochemical behavior and suggesting that its distribution may be influenced by different sources or environmental processes compared to the other analyzed elements.

Table 11 presents the contamination factor (CF) and ecological risk factor (Er) values calculated for the analysed trace metals and metalloids. Based on mean concentrations, Mn and Pb

Table 9. Eigenvalues, explained variance and cumulative variance of principal components

Principal Component	Eigenvalue	Explained Variance (%)	Cumulative Variance (%)
PC1	4.5927	65.61	65.61
PC2	1.0884	15.55	81.16
PC3	0.821	11.73	92.89
PC4	0.3214	4.59	97.48
PC5	0.1433	2.05	99.53
PC6	0.0315	0.45	99.98
PC7	0.0017	0.02	100

showed considerable contamination levels, while Cd, Ni, and Al were classified within the moderate contamination category. The remaining elements were classified as low contamination. All calculated Er values were below 40, corresponding to the low-risk category according to Hakanson's classification. However, these Er values should be interpreted cautiously, as the present study is based on a single dry-season sampling campaign and does not represent a complete ecological risk assessment.

The spatial distribution of contamination indicators shows that W2, W3, and W7 had relatively elevated multi-element contamination within the Sitnica–Llap–Ibar river system, whereas W9 showed consistently low CF values for all analysed metals and W10 showed generally low contamination, except for Cd. This pattern, characterized by a limited number of sites with elevated contamination values against a broader background of lower contamination, suggests that dissolved trace metal and metalloid contamination is spatially heterogeneous rather than uniformly distributed along the investigated river continuum.

W2 (Palaj/Obiliq) was among the sites with the highest contamination indicators. This site is located in an area influenced by lignite-fired power plants, open-pit mining activities, ash-disposal areas, and urban pressures. The elevated

values observed for Al, Mn, Pb, and Cd may be associated with a combination of coal-combustion residues, runoff from disturbed areas, wastewater inputs, and local industrial activities. Further downstream, W3 (Prelluzha) integrates potential inputs from the Llap sub-catchment and the urban corridor of Fushë Kosovë–Obiliq–Vushtrri. The elevated indicators for Mn, Ni, Pb, and Cd at this site are consistent with cumulative urban, industrial, and diffuse agricultural influences reported in the wider area. At W7 (Nedakovec), increased values for Al, Fe, Mn, Ni, Pb, and Cd suggest that this reach may reflect the combined influence of upstream urban, agricultural, and industrial inputs.

Metal-specific patterns provide further insight into possible source-related influences. The enrichment of Al, Fe, and Mn at W2 and W7 is compatible with geochemical and anthropogenic processes commonly associated with lignite-bearing and industrially affected areas. In contrast, elevated values for Ni, Pb, and Cd at selected sites may indicate stronger anthropogenic influence, including possible contributions from coal combustion, vehicular emissions, small-scale industrial activities, wastewater discharge, and agricultural inputs. Since Ni, Pb, and Cd are environmentally relevant priority substances, their elevated concentrations at selected sites indicate potential environmental

Table 10. PCA loadings of dissolved trace metals and metalloids in the Sitnica–Llap–Ibar River

Element	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Al	-0.9515	0.0791	0.1233	-0.2432	0.1032	0.052	0.0273
Cr	-0.6655	-0.206	0.6377	0.3199	-0.0742	0.0133	0.0034
Mn	-0.7308	-0.0958	-0.6133	0.2528	-0.1213	0.0439	0.0097
Fe	-0.9832	0.1107	-0.0166	-0.0307	0.1098	0.084	-0.0283
Ni	-0.9547	-0.1177	-0.1341	0.0925	0.1786	-0.1276	-0.0011
Pb	-0.9112	0.1967	0.0576	-0.2377	-0.2605	-0.0567	-0.0069
Cd	0.0447	0.9827	0.0383	0.1733	0.0255	-0.0105	0.0039

Table 11. Contamination factor and ecological risk factor values of trace metals and metalloids in surface water samples

Element	Mean concentration (µg/L)	Reference value (µg/L)	Toxicity factor	CF	Er	CF class	Er class
Pb	3.72	1.20	5	3.10	15.50	Considerable	Low
Cd	0.10	0.08	30	1.25	37.50	Moderate	Low
Cr	4.37	11.00	2	0.3973	0.7945	Low	Low
Ni	10.89	4.00	5	2.7225	13.6125	Moderate	Low
Cu	3.64	9.00	5	0.4044	2.0222	Low	Low
Zn	34.09	120.00	1	0.2841	0.2841	Low	Low
Fe	595.00	1000.00	1	0.5950	0.5950	Low	Low
Mn	324.61	80.00	1	4.0576	4.0576	Considerable	Low
Al	202.50	87.00	1	2.3276	2.3276	Moderate	Low
As	4.23	150.00	10	0.0282	0.2820	Low	Low
Mo	0.815	34.00	1	0.0240	0.0240	Low	Low

Note: CF – contamination factor; Er – ecological risk factor. Reference values are expressed in µg/L.

concern, particularly under low-flow conditions when dilution capacity is reduced.

By comparison, Cu and Zn displayed lower CF values overall, with localized enrichment mainly at W2 and W3. This pattern may reflect mixed urban–agricultural influences and the partly particle-reactive behaviour of these elements, which can promote attenuation through sorption to suspended particles and sediments. Similar spatial contrasts, with stronger Ni–Pb–Cd signals near industrial or urban pressure zones and more moderate Cu–Zn patterns, have been reported in other impacted river systems.

At the downstream Ibar sites, W9 and W10, CF values were below 1 for most analysed metals. This may reflect dilution, reduced local inputs, or partial retention of particle-reactive metals within upstream sediments and floodplain deposits. The contrast between sites with elevated contamination indicators and downstream sites with lower values supports the interpretation of localized dissolved metal pressure within the investigated river sections, rather than continuous contamination along the entire river system.

Although all calculated Er values remained within the low-risk category, the relatively elevated CF values observed for selected elements indicate that low overall Er values should not be interpreted as an absence of contamination. Instead, the results suggest that contamination is concentrated at specific pressure-influenced sites. Therefore, the CF and Er results should be considered complementary indicators: Er values provide a general risk classification, whereas CF values

highlight element-specific contamination signals that may require closer environmental attention.

From a monitoring perspective, the results support a spatially differentiated approach within the investigated river system. Sites W2, W3, and W7 may be considered priority locations for follow-up monitoring, including repeated seasonal sampling and complementary sediment or biological assessment. Such monitoring would help determine whether the elevated dissolved metal concentrations observed during this dry-season campaign represent persistent contamination patterns or short-term spatial variability.

Overall, this study extends the current understanding of dissolved trace metal and metalloid contamination within the Sitnica–Llap–Ibar river system by providing a system-wide spatial assessment across multiple river sections exposed to different anthropogenic pressures. Unlike previous investigations that focused on individual river reaches or specific pollution sources, the present study demonstrates that dissolved metal contamination is spatially heterogeneous, with elevated contamination signals concentrated at selected locations rather than uniformly distributed throughout the river network.

The combined interpretation of ICP-MS measurements, contamination factors, correlation analysis, and PCA results indicates that sites affected by mining, thermal power generation, urban activities, and agricultural pressures exhibit distinct contamination signatures. In particular, the identification of W2, W3, and W7 as locations with elevated contamination indicators provides

new evidence of localized dissolved-phase metal enrichment within the river system. These findings highlight the importance of spatially resolved monitoring approaches, as basin-scale assessments may overlook local contamination hotspots.

The study therefore contributes a baseline dissolved-metal dataset for the Sitnica–Llap–Ibar watershed and provides a reference framework for future seasonal monitoring, source-apportionment studies, and river-basin management programs in Kosovo.

CONCLUSIONS

The results of this study demonstrate that the initial research objective was achieved, as a spatially resolved dataset of dissolved trace metals and metalloids across the Sitnica–Llap–Ibar river system was successfully established and systematically analysed.

The findings confirm that dissolved trace metal contamination is not uniformly distributed along the river network but is instead spatially heterogeneous, with clearly identifiable hotspots of elevated concentrations. In particular, sites W2, W3, and W7 consistently exhibited higher contamination indicators compared with downstream locations, indicating localized environmental pressure.

A key outcome of this study is the identification of distinct spatial contamination patterns associated with different anthropogenic influences, including mining activities, thermal power generation, urban wastewater inputs, and agricultural runoff. This demonstrates that dissolved metal behaviour in the studied river system is strongly controlled by site-specific human pressures rather than basin-wide background conditions.

The study fills an important research gap by providing one of the first system-wide, multi-element assessments of dissolved trace metals and metalloids for this interconnected river network in Kosovo. Previous studies have typically focused on individual river segments or limited pollutant groups, whereas this work integrates multi-site ICP-MS analysis with contamination factor evaluation to reveal spatial variability at the river-system scale.

Although ecological risk factors indicated low overall risk classification, contamination factor analysis revealed moderate to considerable enrichment for selected elements (particularly

Mn, Pb, Cd, Ni, and Al), highlighting that low-risk classifications may mask localized contamination signals. This emphasizes the importance of spatially resolved monitoring approaches in complex river systems.

This study provides a baseline dataset for future environmental monitoring and establishes a reference framework for temporal trend analysis, source apportionment studies, and watershed management strategies in the Sitnica–Llap–Ibar river system.

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