EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology, 2026, 27(9), 303–321
https://doi.org/10.12912/27197050/226466
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Received: 2026.07.09
Accepted: 2026.08.03
Published: 2026.08.15

Water pollution in the Klina River caused by urban discharges and other pollution sources

Sadija Kadriu[1], Mensur Kelmendi[1*]

[1] Faculty of Food Technology, University Isa Boletini of Mitrovica, Str. Ukshin Kovaçica, 40000, Kosovo
* Corresponding author's e-mail: mensur.kelmendi@umib.net

ABSTRACT

This study evaluates the water quality of the Klina River in Kosovo in relation to urban discharges and other anthropogenic pollution sources. Water samples were collected from eight monitoring sites during summer and autumn 2025. The analysis included pH, dissolved oxygen (DO), BOD_5, COD, NH_4-N, NO_3, total nitrogen (TN), PO_4-P, total phosphorus (TP), and the heavy metals Fe, Cu, Mn, Cd, Zn, Pb, Cr and Ni. Results were compared with the ecological-status criteria of Administrative Instruction MESP-AI 16/2017 and with reference values for heavy metals. The analytical framework additionally included paired Wilcoxon tests with false-discovery-rate adjustment, Pearson correlation analysis, an adapted water quality index (WQI), heavy metal pollution index (HPI), metal index (MI), contamination factors (CF), a reference-based pollution load index (PLI_{ref}), and exploratory principal component analysis (PCA) and hierarchical cluster analysis (HCA). The results show a clear deterioration in water quality in sections influenced by urban and agricultural pressures. The most critical conditions occurred in the Skenderaj urban-influenced section, especially at M_3 and M_4, where DO reached extremely low values and BOD_5, COD and nutrient concentrations indicated substantial organic and nutrient pollution. Cd, Mn and Fe exceeded reference values at several sites, while Ni exceeded the reference value only at selected downstream sites during summer. The paired analysis showed significantly higher DO and significantly lower pH, BOD_5, COD, NH_4-N, NO_3, PO_4-P and TP in autumn. M_3 had the highest adapted WQI in both campaigns, and Cd was the most persistent metal concern. PCA and HCA consistently distinguished M_1 as the least-affected station and M_3–M_4 as the principal monitored pollution hotspots. Using the lowest-category approach for the assessed physicochemical quality elements, M_1 showed moderate conditions, whereas each of M_2–M_8 had at least one result below the displayed moderate range; this does not constitute a complete ecological-status classification. The findings support improved wastewater treatment, stricter control of untreated discharges and continuous seasonal monitoring before the river joins the White Drin River. Because the dataset comprises only two seasonal campaigns and no independent field replicates, the findings characterize the monitored 2025 conditions rather than a complete annual assessment or definitive source attribution.

Keywords: Klina River, urban discharges, water quality, ecological status, heavy metals, wastewater treatment.

INTRODUCTION

The Klina River is one of the medium-flow rivers of Kosovo. Along its 69 km course, the river passes through the municipalities of Skenderaj and Klina before joining the White Drin River. Published studies identify Kuçicë as the upper-course/source area, while a recent diatom-based assessment reports a river length of 69 km and places the Klina River within the White Drin River Basin (Bytyçi et al., 2022; Fetoshi et al., 2025).

Throughout its course, the Klina River is affected by urban wastewater from settlements located along both banks, as well as by runoff from agricultural activities. Previous biological assessments identify untreated sewage, agricultural runoff and other anthropogenic activities as major pollution pressures on the river (Bytyçi et al., 2022; Fetoshi et al., 2025).

Previous assessments of the Klina River have mainly emphasized biological indicators. Macrophyte-based indices showed a downstream decline in ecological status, while a recent diatom-based assessment demonstrated relationships between biological indices and physicochemical pollution indicators (Bytyçi et al., 2022; Fetoshi et al., 2025). A recent spatial-seasonal assessment that jointly evaluates physicochemical parameters, multiple heavy metals, integrated indices and national classification criteria remains insufficiently documented.

Urban, agricultural and industrial pressures on surface waters have also been documented in other river systems in Kosovo. Studies of the Sitnica and Morava e Binçës rivers reported substantial deterioration of physicochemical quality and poor ecological conditions in sections affected by wastewater and other pollution sources (Kelmendi and Aliu, 2023; Sadiku and Kadriu, 2022). Similar water-quality concerns have been reported for wells and springs in Kosovo, showing that contamination affects both surface-water and drinking-water resources (Kadriu et al., 2020).

Due to its geographical position and relief, Kosovo's rivers drain into three major basins: the Black Sea, the Adriatic Sea and the Aegean Sea. Combined with limited water reserves and increasing anthropogenic pressure, this setting makes the protection of surface waters a particularly important environmental priority (Bytyçi et al., 2022).

The limited availability of water resources and the uncontrolled pollution of several rivers in Kosovo, particularly the Klina River, motivated this study to generate reliable data on the degree and spatial distribution of pollution.

The increase in population, commercial activities and the irresponsible use of water resources have contributed to the deterioration of river and lake ecosystems, mainly through the discharge of organic matter, nutrients, suspended matter and other pollutants into surface waters (Kelmendi and Aliu, 2023).

In addition to organic and nutrient pollution, the presence of heavy metals in aquatic environments represents another important concern. Heavy metals may originate from natural geological formations, industrial activities, urban runoff, agricultural inputs and other anthropogenic sources. Once introduced into aquatic ecosystems, some heavy metals may persist, accumulate in sediments or aquatic organisms and pose risks to biodiversity and human health (Malik et al., 2010; Kelmendi et al., 2024).

The importance of maintaining good water quality is further emphasized by epidemiological evidence associating contaminated water resources and inadequate infrastructure with the occurrence of waterborne diseases (El Morabet et al., 2023).

The relevance of heavy metal monitoring in Kosovo has been highlighted by research conducted in the Shala of Bajgora mountain massif, where the presence of Pb, Zn, Cd and Ni beyond reference values was identified in several water sources (Kelmendi et al., 2024). That study also emphasizes that water quality may be affected both by anthropogenic activities and by the geological composition of the area, indicating the need to include heavy metal analysis in broader water quality assessments (Kelmendi et al., 2024).

The scientific novelty of the present study lies in integrating the 2025 spatial-seasonal dataset with paired seasonal testing, integrated water and metal indices, and separate PCA/HCA models for physicochemical parameters and fully quantified metals. This combined approach supports the identification of pollution hotspots and co-variation patterns while retaining Kosovo's statutory ecological-status framework.

Therefore, this study aims to evaluate the water quality of the Klina River through selected physicochemical parameters and heavy metals, in order to determine the level of pollution, identify the most affected sections of the river and provide scientific evidence for future environmental management and protection measures.

MONITORING OF THE KLINA RIVER WATERS

To obtain a representative spatial overview of water quality in the Klina River, eight sampling sites were selected along the river course. The first site, M_1 in Kuçicë, represents the upper course and is the least affected by direct urban discharges, whereas M_2–M_8 were selected in sections exposed to urban, agricultural or cumulative downstream pollution pressures. The network was designed to provide a spatial upstream-to-downstream overview of the monitored river section rather than a probabilistic representation of the entire catchment.

The establishment of a monitoring network along the river course is essential for identifying pollution gradients and distinguishing between less-impacted upstream sections and downstream segments affected by human activities. Previous studies in Kosovo likewise used purposively selected monitoring points to evaluate river sections affected by urban and industrial discharges or water sources exposed to geogenic heavy-metal pressures (Kelmendi and Aliu, 2023; Kelmendi et al., 2024).

The selection of M_1 as an upstream reference point enables comparison with downstream locations and allows assessment of spatial changes in water quality along the river course. This comparison is important because it supports interpretation of patterns associated with settlements, wastewater discharges and agricultural activities, without by itself establishing source causation.

Monitoring was carried out during two seasonal campaigns: August and October 2025. These campaigns are referred to as summer and autumn, respectively; river discharge and precipitation were not measured directly.

Seasonal monitoring is particularly important in river water quality assessment because pollutant concentrations may vary depending on water flow, temperature, precipitation, runoff intensity and the level of wastewater dilution. Therefore, the comparison between summer and autumn provides a more complete interpretation of the ecological condition of the river than a single sampling campaign.

The geographic coordinates of the eight stations were obtained from Google Earth and processed in QGIS 3.40 Bratislava. The station layer and monitoring map are presented in WGS 84 (EPSG:4326), with coordinates reported in decimal degrees to improve reproducibility.

The monitoring network with sampling sites is presented in Figure 1, while the coordinates of the monitoring points are presented in Table 1:

- M_1 is located in the upper course of the river in the village of Kuçicë. Although livestock farming and other agricultural activities may contribute runoff, the site was selected as the least directly urban-influenced station in the monitoring network.
- M_2 represents the sampling site located at the entrance to the town of Skenderaj, where the station was selected to characterize conditions at the entrance to the urban reach.
- M_3 is located within the urban reach of Skenderaj, where several potential discharge sources are present, including households, food-service activities and local industry.
- M_4 represents the sampling site located approximately 70 m downstream of the existing wastewater treatment plant located in the village of Llaushë in this municipality.
- M_5, located near the village of Rezallë, was selected to assess conditions in a section potentially influenced by agricultural runoff.
- M_6, located near the village of Ujëmirë, represents a less densely populated hilly-mountainous section where agricultural activity remains a potential pressure.
- M_7 is located at the entrance to the town of Klina and was selected to characterize river conditions before the main urban-influenced section.
- M_8 is located downstream of the town of Klina, after the principal urban reach. It is located approximately 300 m upstream of the confluence with the White Drin River. The site was selected to assess the cumulative downstream condition immediately before the confluence.

MATERIALS AND METHODS

To characterize the ecological and chemical conditions observed during the monitored 2025 campaigns, sampling, preservation, transportation and laboratory analysis were performed according to internationally recognized water-quality standards. The sampling design included eight

Table 1. Sampling points and their coordinates

Sampling site	Latitude (DMS)	Longitude (DMS)	Latitude (DD)	Longitude (DD)	Altitude (m)
M_1 – Kuçicë	42°49’34.73”N	20°45’46.87”E	42.82631389	20.76301944	689
M_2 – Skenderaj	42°46’16.74”N	20°47’31.44”E	42.77131667	20.79206667	627
M_3 – Skenderaj	42°44’5.64”N	20°47’32.29”E	42.73490000	20.79230278	602
M_4 – Llaushë	42°43’17.02”N	20°45’52.36”E	42.72139444	20.76454444	589
M_5 – Rezallë	42°41’35.60”N	20°44’21.44”E	42.69322222	20.73928889	558
M_6 – Ujëmirë	42°37’21.57”N	20°40’27.55”E	42.62265833	20.67431944	453
M_7 – Klina	42°37’28.77”N	20°35’52.49”E	42.62465833	20.59791389	392
M_8 – Klina	42°36’48.93”N	20°34’9.18”E	42.61359167	20.56921667	381

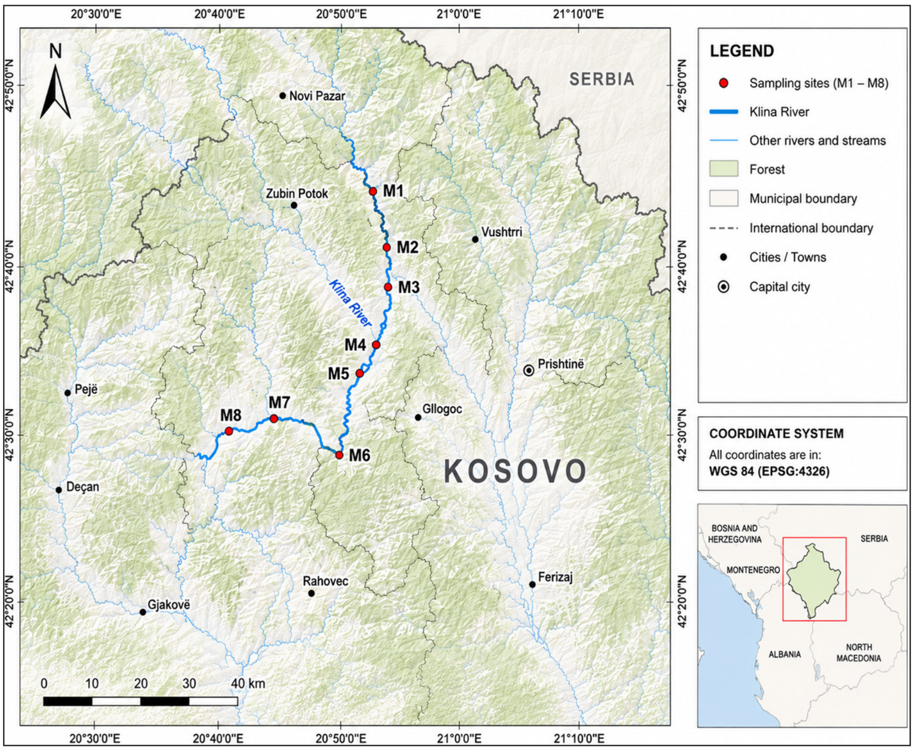

Figure 1. Location of the eight monitoring stations along the Klina River

sites distributed along the river course, from the upper section in Kuçicë to the lower section near the confluence with the White Drin River.

The methodological approach was designed to compare spatial differences among the eight sites and campaign-related differences between August and October 2025. The sites covered a less urban-influenced upstream section, urban and peri-urban reaches, agricultural areas and the cumulative downstream section; this design supports assessment of spatial patterns but not definitive source attribution.

Water samples were collected during two seasonal campaigns: summer, in August 2025, and autumn, in October 2025. These two periods were selected because seasonal changes in temperature, precipitation and river flow may influence pollutant concentrations, dilution capacity and the transport of nutrients, organic matter and metals.

Because river discharge and precipitation were not measured directly, the August and October campaigns are described as summer and autumn sampling periods, respectively, without assigning confirmed low-flow or high-runoff conditions. The comparison represents two seasonal campaigns rather than a complete annual characterization.

Water sampling followed ISO 5667-6 for rivers and streams, ISO 5667-1 for sampling-program design and techniques, and ISO 5667-3 for preservation and handling (International Organization for Standardization, 2006, 2012, 2014). At each site, samples were collected in clean, appropriately prepared containers and labelled for traceability. The retained documentation does not specify the container material, volume or whether every container was rinsed before collection.

During sampling, special attention was paid to avoiding contamination from the riverbank, sediments or external materials. The bottles were clearly labelled with the sampling code, date, location and season. After collection, the samples were transported to the laboratory under refrigerated conditions, approximately 4 °C, and submitted for analysis promptly to minimize changes before measurement. Exact holding times for the individual analytes were not available in the retained documentation.

The physicochemical parameters analyzed in this study included pH, dissolved oxygen (DO), five-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), ammonium nitrogen (NH_4-N), nitrates (NO_3), total nitrogen (TN), orthophosphate phosphorus (PO_4-P) and total phosphorus (TP). These parameters were selected because they are widely used indicators for evaluating organic pollution, nutrient enrichment, oxygen depletion and the ecological status of surface waters.

The determination of each physicochemical parameter was performed using standard analytical methods. The pH was determined according to ISO 10523:2008; dissolved oxygen according to ISO 5814:2012; BOD_5 according to ISO 5815-2:2003; COD according to ISO 15705:2002; ammonium nitrogen according to ISO 7150-1:1984; nitrates according to DIN 38405-9:2011; total nitrogen according to ISO 11905-1:1997; and phosphate and total phosphorus according to ISO 6878:2004.

Where applicable, potentiometric and spectrophotometric techniques were used for the determination of physicochemical parameters. Kelmendi and Aliu (2023) report a comparable set of standard physicochemical methods for a Kosovo river study, providing regional methodological context; direct analytical comparability additionally depends on equivalent instrumentation, reagents, calibration and quality-control procedures.

In addition to physicochemical parameters, selected heavy metals were analyzed in the water samples, including Fe, Cu, Mn, Cd, Zn, Pb, Cr and Ni.

For heavy-metal analysis, according to the available laboratory documentation, samples were preserved following Standard Methods (American Public Health Association et al., 2005). However, the preservative, target pH, container material and holding time were not recorded in the retained documentation. Samples were then digested by microwave-assisted acid digestion (U.S. Environmental Protection Agency, 2007a), and metal concentrations were determined by inductively coupled plasma mass spectrometry (U.S. Environmental Protection Agency, 2007b).

This analytical procedure is suitable for determining trace metal concentrations in water samples and allows detection at low concentration levels. A similar EPA 3015A/6020A approach was applied in a previous Kosovo water-quality study, providing regional methodological context; nevertheless, direct comparability depends on equivalent sample preparation, calibration and quality-control conditions (Kelmendi et al., 2024).

Physicochemical results were compared with the criteria of Administrative Instruction MESP No. 16/2017 on the classification of surface water bodies in Kosovo (Ministry of Environment & Spatial Planning, 2017). Physicochemical status was evaluated using the relevant type-T2 river thresholds. The reported class is therefore based on the analyzed physicochemical parameters and should not be interpreted as a complete ecological-status assessment incorporating biological and hydromorphological quality elements.

Within the analyzed physicochemical parameter set, the overall class at each site was assigned from the parameter with the lowest status, following the one-out, all-out principle.

The results of heavy metal concentrations were compared with the relevant reference values for surface waters. The selected benchmarks were taken from Kosovo's national water-status report (Ministry of Environment and Spatial Planning & Kosovo Environmental Protection Agency, 2015). Concentrations above these values were treated as exceedances of the selected reference benchmarks; the exceedances alone were not considered proof of a specific pollution source.

For exploratory interpretation, the results were evaluated both spatially and seasonally. Spatial comparison was performed among sampling sites M_1–M_8, while seasonal comparison was made between the summer and autumn campaigns. This approach supported identification of the most affected monitored sections and campaign-related patterns, while source attribution and catchment-wide generalization remained outside the study design.

Quality assurance and quality control

Heavy metals were measured at the Hydrometeorological Institute of Kosovo using an Agilent Technologies 7700 ICP-MS. Each reported concentration was calculated as the mean of three consecutive instrumental readings of the same sample; these readings indicate instrumental repeatability and are not independent field or sample-preparation replicates. A blank was included for each calibration curve, a quality-control sample was analyzed after every ten samples, and recovery/spike-recovery testing and a certified reference material were used as quality-control measures. The laboratory reported calibration coefficients of determination (R^2) ranging from 0.9997 to 1.0000. Method-specific LOD and LOQ ranges are provided in Supplementary Table S2. The calibration-standard concentration range, certified-reference-material identification, numerical recovery values, run-specific precision data and original ICP-MS instrument files were not available in the retained documentation.

Statistical analysis

Data processing and statistical analyses were performed in Python 3.13. Data organization and descriptive calculations were conducted using pandas 2.2.3, while the Wilcoxon signed-rank tests and Pearson correlation analyses were performed using SciPy 1.17. The integrated pollution indices, PCA, HCA and the corresponding graphical outputs were generated within the Python environment. The complete dataset was organized in CSV format. The eight stations were treated as paired spatial units because every station was sampled in both campaigns. Seasonal differences in physicochemical parameters and in the fully quantified metals Fe, Mn, Cd and Ni were evaluated using two-sided Wilcoxon signed-rank tests. This non-parametric paired test was selected because only eight site pairs were available and normality of seasonal differences could not be assumed. p-values were adjusted across parameters with the Benjamini–Hochberg false-discovery-rate procedure (Wilcoxon, 1945; Benjamini & Hochberg, 1995). The false-discovery-rate adjustment was applied separately to the nine physicochemical comparisons and the four fully quantified-metal comparisons. Pearson coefficients and two-sided p-values were calculated for selected a priori relationships among organic-pollution, oxygen and nutrient indicators. The Wilcoxon results are interpreted as exploratory paired-site evidence. Pearson correlations were calculated from the 16 pooled site-season observations and are interpreted as exploratory associations because repeated observations from the same sites are not fully independent and within-site field variability was not measured.

Integrated water-quality and heavy-metal indices

An adapted weighted-arithmetic WQI was calculated from pH, DO, BOD_5, COD, NH_4-N, NO_3, TN, PO_4-P and TP using the high-status thresholds for type T2 rivers in MESP No. 16/2017: pH = 8.6; DO = 7.0 mg/L; BOD_5 = 4.0 mg/L; COD = 4.0 mg/L; NH_4-N = 0.10 mg/L; NO_3 = 1.00 mg/L; TN = 1.5 mg/L; PO_4-P = 0.05 mg/L; and TP = 0.10 mg/L. The quality rating was calculated as $q_i = 100(V_i - V_{ideal})/(S_i - V_{ideal})$, the unit weight as $W_i = K/S_i$, and $WQI = \Sigma(q_iW_i)/\Sigma W_i$ (Horton, 1965; Brown et al., 1970). The ideal values were 7.0 for pH, 14.6 mg/L for DO and 0 for all other parameters. Quality ratings were not capped; values above 100 were retained, and no negative q_i values occurred in the dataset. Because the national instruction does not prescribe an official WQI, the index is used only for comparative ranking and not as a substitute for statutory ecological classification.

HPI_4, MI_4, CF and PLI_{ref} were calculated only for Fe, Mn, Cd and Ni, which had complete quantitative values in all 16 site-season observations. Reference values of 0.20, 0.05, 0.005 and 0.020 mg/L were used. $CF_i = C_i/S_i$; $HPI_4 = \Sigma(WiQi)/\Sigma Wi$, where $W_i = 1/S_i$ and $Q_i = 100(C_i/S_i)$; $MI_4 = \Sigma(C_i/S_i)$; and $PLI_{ref} = (CF_1 \times CF_2 \times CF_3 \times CF_4)^{(1/4)}$ (Mohan et al., 1996; Tamasi and Cini, 2004). Cu, Zn, Pb and Cr were excluded because censored values require a predefined treatment rule. PLI_{ref} is a standards-based exceedance index, not a geochemical enrichment index. The four reference values were taken from Kosovo's national water-status report (Ministry of Environment and Spatial Planning & Kosovo Environmental Protection Agency, 2015). HPI_4 and MI_4 follow the cited methodological approaches, whereas CF and $PLI_{(ref)}$ are used here as explicitly defined, standards-based adaptations. No numerical substitution was applied to censored Cu, Zn, Pb or Cr results.

An Ecological Risk Index was not calculated because catchment-specific background concentrations and a defensible set of toxic-response factors for the selected metal set were unavailable. Human Health Risk Assessment was not performed because exposure pathways, intake rates and population-exposure data were outside the study design.

Multivariate statistical analysis

Exploratory PCA and HCA were applied separately to the nine physicochemical parameters and the four fully quantified metals. The 16 site-season observations were standardized to z-scores. PCA was performed on the correlation matrix, and the first two components were retained for interpretation. HCA used Ward's linkage and Euclidean distance (Jolliffe, 2002; Ward, 1963). Because only two campaigns and no independent field replicates were available, the multivariate analyses identify co-variation and relative grouping rather than definitive pollution-source apportionment. The resulting HCA solutions were evaluated descriptively using silhouette coefficients. Owing to the small number of site-season observations relative to the number of variables, both PCA and HCA were treated as exploratory analyses and no confirmatory source attribution was inferred.

RESULTS AND DISCUSSION

Water samples from the Klina River were collected during August and October 2025. The study focused on pH, DO, BOD_5, COD, NH_4-N, NO_3, TN, PO_4-P and TP. These parameters were used to characterize oxygen conditions, organic-matter pollution, nutrient enrichment and the condition of the assessed physicochemical quality elements.

The results were examined across the eight monitoring stations and between the two seasonal campaigns to identify spatial pollution gradients and seasonal changes. Potential pollution sources are discussed as interpretations of the observed patterns rather than as directly confirmed causes.

Physicochemical parameters and physicochemical status assessment

Although pH values were generally within or close to the acceptable range, pH remains an important supporting parameter because it can influence the mobility and toxicity of nutrients and heavy metals in aquatic environments.

The results show a clear deterioration of water quality after the river enters urban and peri-urban areas. Sampling site M_1, located in the upper course of the river, generally shows lower pollution pressure compared with downstream sites. In contrast, M_3 and M_4 show the most critical values for several parameters, which are consistent with substantial urban-wastewater influence and this pattern may reflect treatment-related or other nearby inputs; however, the available data do not permit the contribution of the wastewater-treatment plant to be separated from other local sources.

The physicochemical measurements and their assigned status categories are presented in Table 2. The results were compared with the indicative values for physicochemical river-quality elements provided in Administrative Instruction MESP No. 16/2017. The thresholds used in the present physicochemical assessment are presented in Table 3.

In this study, the lowest category among the assessed physicochemical parameters was used to summarize the condition of each site. This summary should not be interpreted as a complete ecological-status classification because biological and hydromorphological quality elements were not assessed.

Based on the displayed type-T2 thresholds, M_1 showed a moderate physicochemical condition in both campaigns, whereas M_2–M_8 had at least one result outside the displayed moderate range and was therefore classified as below moderate for the assessed physicochemical quality elements.

Under the lowest-category approach used here, the overall physicochemical condition of each site is determined by the least favorable assessed parameter. This comparative summary does not replace the complete statutory ecological classification of the water body.

The findings indicate that good physicochemical conditions were not achieved across the monitoring network. The least favorable categories were driven mainly by oxygen depletion, high BOD_5 and COD values, and elevated nutrient concentrations. Similar findings were reported for the Sitnica River, where several physicochemical parameters exceeded reference values and the river was classified as having poor ecological status (Kelmendi and Aliu, 2023).

Phosphorus compounds, including PO_4-P and TP, also indicate anthropogenic pressure along the river course. Elevated TP values in downstream sections are consistent with possible inputs from domestic wastewater, detergents, organic residues and agricultural runoff; however, these sources were not directly traced in the present study. Together with nitrogen compounds, phosphorus may accelerate eutrophication processes and reduce ecological quality.

The increase in nitrogen compounds is important from an ecological perspective because excessive nitrogen input can contribute to eutrophication, algal growth and deterioration of aquatic habitats. In surface waters, nitrogen and phosphorus concentrations above reference values are commonly linked with nutrient enrichment and changes in river trophic conditions (Kelmendi and Aliu, 2023).

The high BOD_5 values indicate that a considerable amount of biodegradable organic matter is present in the water and can be decomposed by microorganisms, consuming dissolved oxygen during the process. At the same time, elevated COD values indicate a broader load of organic and inorganic oxidizable substances. The simultaneous increase of BOD_5 and COD, combined with low

Table 2. Results of physicochemical parameters (mg/L) and status assessment of the physicochemical quality elements of the Klina River

Site	pH	DO	BOD_5	COD	NH_4-N	NO_3	TN	PO_4-P	TP	Final class
Summer season (02.08.2025)										
M_1	8.66	5.25	2.1	4.9	0.34	2.9	0.53	0.006	0.07	Md
M_2	8.42	3.09	27.3	60.3	0.281	8.7	2.31	0.018	0.78	BM
M_3	8.25	0.02	50.2	102.5	1.527	6.1	4.94	0.125	1.53	BM
M_4	8.96	0.18	42.7	77.1	0.882	27.6	3.46	0.072	1.27	BM
M_5	8.59	3.85	35.4	69.6	0.831	18.9	3.16	0.065	1.06	BM
M_6	8.62	4.42	22.5	40.7	0.658	11.7	2.03	0.061	0.69	BM
M_7	8.15	4.76	12.8	25.6	0.626	7.8	1.51	0.055	0.41	BM
M_8	8.37	4.05	23.1	48.2	1.031	5.9	2.65	0.081	0.73	BM
Autumn season (22.10.2025)										
M_1	8.48	5.75	1.6	4.5	0.028	2.7	0.70	0.004	0.05	Md
M_2	7.83	3.28	23.7	51.6	0.259	8.4	3.02	0.015	0.68	BM
M_3	8.13	0.03	45.1	94.2	1.386	5.8	3.41	0.113	1.38	BM
M_4	8.67	0.21	35.2	66	0.712	27.2	8.30	0.063	1.05	BM
M_5	8.24	5.1	27.6	62.6	0.650	18.5	5.96	0.052	0.82	BM
M_6	8.37	5.99	16.4	34.5	0.591	11.4	4.21	0.048	0.59	BM
M_7	7.58	6.77	9.6	19.4	0.556	7.5	3.09	0.038	0.31	BM
M_8	8.01	4.68	19.9	39.8	0.830	5.8	3.67	0.063	0.34	BM

Note: MESP-AI 16/2017. DO = dissolved oxygen; BOD_5 = five-day biochemical oxygen demand; COD = chemical oxygen demand; TN = total nitrogen; TP = total phosphorus. The status categories used here are H = high, G = good, Md = moderate and BM = below moderate. The final classification summarizesonly the assessed physicochemical quality elements and does not represent a complete ecological-status classification.

Table 3. Indicative values of physicochemical river-quality elements according to MESP-AI 16/2017

Type	Status	pH	DO	BOD_5	COD	NH_4-N	NO_3	TN	PO_4-P	TP
T1	H	7.0–8.6	>8.0	<1.50	<4.0	<0.10	<1.50	<2.0	<0.05	<0.09
T1	G	<7.0; >9.0	8.0–7.0	1.50–5.00	4.0–7.0	0.10–0.20	1.50–3.00	2.0–3.5	0.05–0.10	0.09–0.15
T1	Md	<7.0; >9.0	7.0–5.0	5.00–6.00	7.0–12.0	0.20–0.80	3.00–6.00	3.5–10.0	0.10–0.20	0.15–0.30
T2	H	7.0–8.6	>7.0	<4.0	<4.0	<0.10	<1.00	<1.5	<0.05	<0.10
T2	G	<7.0; >9.0	7.0–6.0	4.0–6.0	4.0–7.0	0.10–0.25	1.00–2.00	1.5–3.0	0.05–0.10	0.10–0.20
T2	Md	<7.0; >9.0	6.0–5.0	6.0–8.0	7.0–12.0	0.25–0.70	2.00–5.00	3.0–10.0	0.10–0.20	0.20–0.40

Note: Type T1 = small mountain river and medium river; T2 = small, medium and large lowland river. H = high; G = good; Md = moderate. The displayed threshold table does not define numerical ranges for poor or bad status; values outside the moderate range should therefore be described transparently as below moderate unless an additional statutory rule is cited.

DO, is consistent with strong organic-pollution pressure. Untreated or insufficiently treated urban wastewater is a plausible contributor, but the available measurements do not establish a single source.

The very low dissolved oxygen values at M_3 and M_4 suggest that the river section passing through and downstream of Skenderaj is under strong organic pollution pressure. When dissolved oxygen decreases to very low levels, the aquatic environment becomes unsuitable for many organisms, and the self-purification capacity of the river is significantly reduced. Similar interpretations have been reported in previous studies on the Sitnica River, where high BOD_5 and COD values were associated with low oxygen content and poor ecological status (Kelmendi and Aliu, 2023).

Heavy metal concentrations

Overall, the physicochemical results indicate that the main pollution pressure in the Klina River is related to organic matter and nutrient enrichment. The most affected section is the urban-influenced part of the river around Skenderaj, while downstream sections continue to reflect cumulative pollution before the river reaches Klina.

Selected heavy metals (Fe, Cu, Mn, Cd, Zn, Pb, Cr and Ni) were evaluated to complement the physicochemical assessment of the Klina River.

The concentrations presented in Table 4 were compared with the maximum permitted values reproduced in the 2015 Kosovo water-status report from Legislative Decree No. 152/1999 (Ministry of Environment & Spatial Planning, 2015).

The data presented in Table 4 show exceedances of the reference values for Cd, Mn and Fe at several sampling sites in both seasons, while Ni exceeded the reference value only in August at M_7 and M_8. The concentrations of the other analyzed metals were within the reference values or below the detection limits. Figures 2–5 present the metals that exceeded reference values in at least one sample.

Previous research in the Shala of Bajgora mountain massif reported Pb, Zn, Cd and Ni above reference values in several water sources, demonstrating the regional relevance of heavy-metal monitoring (Kelmendi et al., 2024).

Fe and Mn were descriptively higher in autumn, but the paired differences were not statistically significant after adjustment for multiple testing (Table 11). Runoff, sediment remobilization, redox conditions and geological inputs remain plausible explanations, but no source-specific measurements were available to distinguish among them.

Cd was the most persistent exceedance, occurring above the adopted value in 15 of 16 site-season measurements (Table 9). This pattern warrants priority monitoring and targeted investigation of potential sources.

The inclusion of heavy metals provides a more complete assessment of the chemical pressure affecting the Klina River. While physicochemical parameters mainly reflect organic and nutrient pollution, heavy metals may indicate additional pollution sources, including urban runoff, industrial influence, agricultural inputs, natural geological background or sediment remobilization.

Previous studies have documented heavy-metal contamination in water bodies and bioaccumulation in fish tissues, supporting the

Table 4. Concentration of heavy metals (mg/L) according to sampling sites in the Klina River

Parameter	Method	MPL	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
Summer season (02.08.2025)										
Fe	EPA 6020A	0.2	0.075	0.079	0.108	0.125	0.297	0.212	0.339	0.143
Cu	EPA 6020A	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Mn	EPA 6020A	0.05	0.028	0.041	0.086	0.105	0.129	0.0119	0.054	0.049
Cd	EPA 6020A	0.005	0.006	0.013	0.021	0.024	0.025	0.024	0.026	0.025
Zn	EPA 6020A	3	0.001	0.002	0.002	<LOD	<LOD	0.005	0.003	0.004
Pb	EPA 6020A	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	EPA 6020A	0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ni	EPA 6020A	0.02	0.008	0.007	0.009	0.008	0.007	0.008	0.021	0.022
Autumn season (22.10.2025)										
Fe	EPA 6020A	0.2	0.021	0.297	0.497	0.344	0.289	0.3	1.288	0.135
Cu	EPA 6020A	1	<0.001	0.008	0.011	0.007	0.006	0.004	0.004	0.005
Mn	EPA 6020A	0.05	0.006	0.344	0.299	0.277	0.127	0.199	0.052	0.049
Cd	EPA 6020A	0.005	0.005	0.022	0.025	0.023	0.025	0.019	0.026	0.023
Zn	EPA 6020A	3	0.008	0.004	0.001	<0.001	<0.001	0.00416	0.00216	0.00416
Pb	EPA 6020A	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cr	EPA 6020A	0.05	<0.001	0.003	0.006	0.004	0.003	0.004	0.005	0.016
Ni	EPA 6020A	0.02	0.009	0.007	0.008	0.007	0.006	0.004	0.001	0.003

Note: MPL = maximum permitted levels for selected heavy metals in surface waters. <LOD = below the method detection limit.

environmental relevance of continued monitoring (Malik et al., 2010; Kadriu et al., 2021).

From an environmental management perspective, these findings indicate the need for regular monitoring, identification of direct discharge points, evaluation of the existing wastewater treatment plant and implementation of additional treatment measures before the Klina River joins the White Drin River.

Environmental implications and pollution sources

The environmental interpretation of the results indicates that the Klina River is affected by a combination of point and diffuse pollution sources. Urban wastewater discharges appear to represent an important pressure in the Skenderaj and Klina sections, while agricultural runoff and local surface inputs may contribute to nutrient enrichment and the transport of suspended and dissolved contaminants. The repeated exceedance of selected heavy metals also indicates the need to investigate possible local sources, sediment remobilization and natural geological contributions within the river catchment.

Because no source-specific tracers, sediment chemistry or discharge samples were analyzed, source statements are interpreted as hypotheses supported by spatial co-variation rather than direct source confirmation.

From an environmental-management perspective, the findings support strengthening wastewater-treatment infrastructure, evaluating the performance of the existing treatment plant, preventing direct untreated discharges, investigating potential heavy-metal sources and establishing regular seasonal monitoring. Priority should be given to the M_3–M_4 section around and downstream of Skenderaj, while the lower course before the confluence with the White Drin River should remain under regular monitoring because it receives the cumulative upstream pollution load.

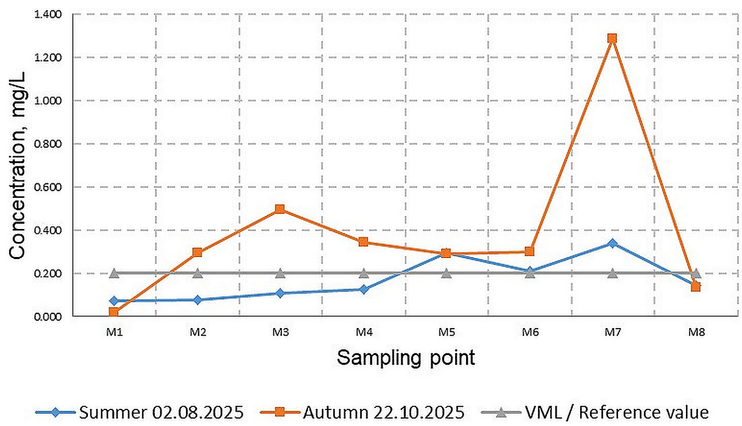

Figure 2. Fe concentrations by sampling site and season

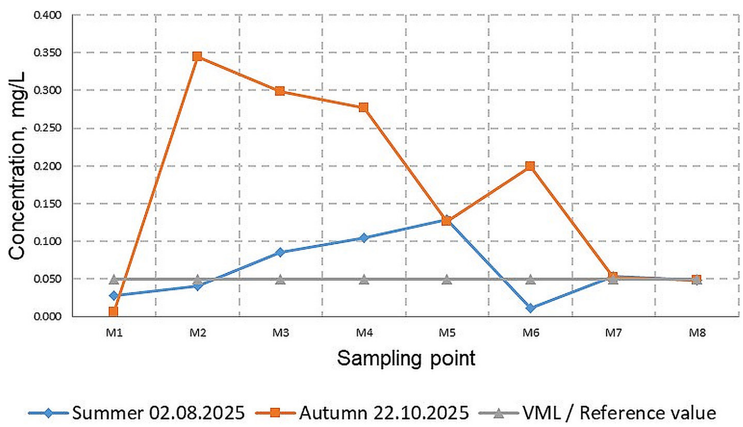

Figure 3. Mn concentrations by sampling site and season

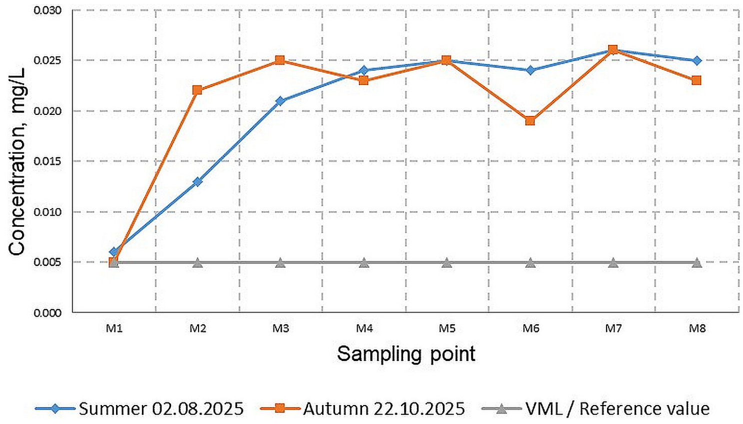

Figure 4. Cd concentrations by sampling site and season

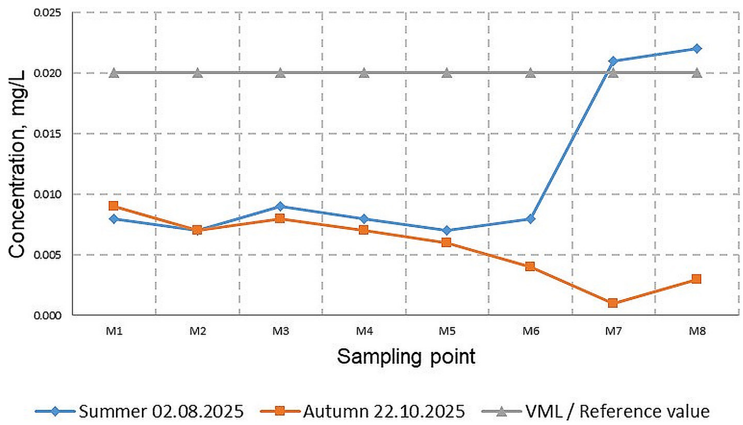

Figure 5. Ni concentrations by sampling site and season

Statistical interpretation of water quality data

To provide a structured interpretation of the dataset, the following analyses include seasonal descriptive statistics, critical-value screening, selected Pearson correlations, paired Wilcoxon tests with Benjamini-Hochberg adjustment, adapted water- and metal-quality indices, and exploratory PCA and HCA. Because the dataset comprises eight stations sampled in two campaigns without independent field replicates, the inferential and multivariate results are interpreted as exploratory.

Seasonal means, ranges, standard deviations and percentage changes for the physicochemical parameters are summarized in Table 5.

The descriptive statistics show that mean dissolved oxygen increased from summer to autumn, while BOD_5, COD, NH_4-N, PO_4-P and TP decreased. This pattern is consistent with partial seasonal improvement in several parameters, but river flow was not measured and dilution cannot be confirmed. The autumn increase in TN may reflect runoff-related nutrient transport, although the source was not directly assessed. The most critical physicochemical values recorded across the two campaigns are identified in Table 6.

The critical values identify M_3 and M_4 as the main pollution hotspots. M_3 records the most critical organic pollution indicators, including the lowest DO and the highest BOD_5, COD, NH_4-N, PO_4-P and TP values. M_4 records the highest NO_3 and TN values, indicating strong nutrient pressure downstream of the Skenderaj section.

These results highlight the dominance of the Skenderaj-affected section, especially M_3 and M_4. These sites should be prioritized for pollution-source identification and wastewater management measures. The selected a priori Pearson correlations and their corresponding two-sided p-values are presented in Table 7.

The selected correlations show coherent co-variation among organic-load, nutrient and oxygen indicators. The very strong positive correlation between BOD_5 and COD shows that biodegradable and chemically oxidizable loads increase together. The negative correlations between DO and both BOD_5 and COD indicate that organic pollution is associated with oxygen depletion. All selected correlations were statistically significant ($p < 0.001$), but correlation alone does not identify a specific pollution source. Seasonal descriptive statistics for Fe, Mn, Cd and Ni are presented in Table 8.

Heavy metal statistics show that Fe and Mn were descriptively higher during autumn, while Cd remained almost constant and above the reference value in most measurements. Ni decreased in autumn and exceeded the reference value only in selected summer sites. These results indicate that chemical contamination is not uniform, but varies by metal, season and sampling location.

The autumn Fe and Mn increases were descriptive and did not remain significant after Benjamini-Hochberg adjustment (Table 11); therefore, possible explanations such as runoff or sediment remobilization require additional data. Persistent Cd exceedances warrant continued monitoring. The frequency with which Fe, Mn, Cd and Ni exceeded the adopted comparison values is summarized in Table 9.

Cadmium represents the most persistent heavy metal concern, exceeding the reference value in 15 out of 16 measurements. Manganese and iron also show frequent exceedances, while nickel exceeded the reference value only in two summer measurements. These findings support the conclusion that the river is affected not only by organic and nutrient pollution, but also by chemical contamination.

Cd, Mn and Fe should be prioritized in future monitoring, while Ni appears to be a localized and season-specific concern in this dataset.

Because the statistical dataset is based on two seasonal campaigns, the results should be interpreted as supportive descriptive evidence. Future studies should include more frequent sampling, replicate laboratory measurements and hydrological data, such as river flow rate, to allow stronger

Table 5. Seasonal descriptive statistics of physicochemical parameters in the Klina River (n = 8 per season)

Parameter	Summer mean	Summer min-max	Summer SD	Autumn mean	Autumn min-max	Autumn SD	Change (%)
pH	8.50	8.15-8.96	0.259	8.16	7.58-8.67	0.355	-4.0
DO	3.20	0.02-5.25	2.02	3.98	0.03-6.77	2.59	+24.2
BOD_5	27.01	2.10-50.20	15.64	22.39	1.60-45.10	13.87	-17.1
COD	53.61	4.90-102.50	30.70	46.57	4.50-94.20	28.35	-13.1
NH_4-N	0.772	0.281-1.53	0.399	0.627	0.028-1.39	0.401	-18.8
NO_3	11.20	2.90-27.60	8.19	10.91	2.70-27.20	8.11	-2.6
TN	2.57	0.53-4.94	1.33	4.04	0.70-8.30	2.25	+57.2
PO_4-P	0.060	0.006-0.125	0.037	0.050	0.004-0.113	0.033	-18.0
TP	0.817	0.07-1.53	0.466	0.652	0.05-1.38	0.431	-20.2

Table 6. Critical physicochemical values recorded in the Klina River during the monitoring campaigns

Parameter	Indicator	Critical value	Site	Season	Interpretation
DO	Minimum	0.02	M_3	Summer	Severe oxygen depletion in the Skenderaj urban-influenced section.
BOD_5	Maximum	50.20	M_3	Summer	Highest biodegradable organic load.
COD	Maximum	102.50	M_3	Summer	Highest chemically oxidizable pollution load.
NH_4-N	Maximum	1.53	M_3	Summer	Highest ammonium concentration, typical of wastewater influence.
NO_3	Maximum	27.60	M_4	Summer	Highest nitrate concentration, indicating nutrient pressure.
TN	Maximum	8.30	M_4	Autumn	Highest total nitrogen, likely influenced by runoff and nutrient transport.
PO_4-P	Maximum	0.125	M_3	Summer	Highest orthophosphate concentration.
TP	Maximum	1.53	M_3	Summer	Highest total phosphorus and eutrophication pressure.

Table 7. Pearson correlation coefficients between selected physicochemical parameters in the Klina River (n = 16) and corresponding two-sided p-values

Relationship	Pearson r	p-value	Interpretation
BOD_5-COD	0.991	<0.001	Very strong positive relationship
BOD_5-TP	0.986	<0.001	Very strong positive relationship
COD-TP	0.977	<0.001	Very strong positive relationship
DO-BOD_5	-0.872	<0.001	Strong negative relationship
DO-COD	-0.842	<0.001	Strong negative relationship
NH_4-N-PO_4-P	0.983	<0.001	Very strong positive relationship

Table 8. Seasonal descriptive statistics of selected heavy metals in the Klina River

Metal	Reference value	Summer mean	Summer min-max	Summer SD	Autumn mean	Autumn min-max	Autumn SD	Change (%)
Fe	0.2	0.172	0.075–0.339	0.100	0.396	0.021–1.288	0.387	+130.1
Mn	0.05	0.063	0.0119–0.129	0.040	0.169	0.006–0.344	0.129	+168.5
Cd	0.005	0.0205	0.006–0.026	0.0072	0.0210	0.005–0.026	0.0068	+2.4
Ni	0.02	0.0113	0.007–0.022	0.0064	0.0056	0.001–0.009	0.0027	–50.0

inferential statistical testing and more detailed source apportionment.

Paired seasonal tests

The paired Wilcoxon results for the physicochemical parameters are presented in Table 10. The paired analysis showed a consistent autumn increase in DO and decreases in pH, BOD_5, COD, NH_4-N, NO_3, PO_4-P and TP. These differences remained significant after BH adjustment (adjusted p = 0.0088). TN increased at six sites and its mean rose by 57.2%, but the paired difference did not reach the adjusted significance threshold (adjusted p = 0.0547). These findings remain exploratory because only eight paired sites and two campaigns were available.

The corresponding paired seasonal tests for the four fully quantified metals are presented in Table 11.

None of the seasonal differences for Fe, Mn, Cd or Ni remained significant after correction for multiple testing. The descriptive autumn increases in Fe and Mn should therefore not be presented as statistically confirmed seasonal effects. Cu, Zn, Pb and Cr were not tested because censored observations were not replaced by zero.

Integrated pollution indices

The adapted WQI values for each monitoring site and season are presented in Table 12. M_3 had the highest adapted WQI in both campaigns (881.31 in summer and 797.10 in autumn), followed by M_4. M_1 had the lowest values. Mean WQI decreased from 473.31 to 388.93, and all eight paired sites had lower autumn values (Wilcoxon W = 0.0, p = 0.0078). The adapted index is used only for comparative ranking and does not replace a complete statutory ecological-status assessment.

Table 9. Exceedance frequency of selected heavy metals in the Klina River

Metal	Reference value	Summer exceedances (n=8)	Autumn exceedances (n=8)	Total (n=16)	Main interpretation
Fe	0.2	3	6	9	Marked autumn increase; possible runoff/ sediment influence.
Mn	0.05	4	6	10	Frequent exceedance, especially in autumn.
Cd	0.005	8	7	15	Most persistent exceedance across the river course.
Ni	0.02	2	0	2	Exceedance only in selected summer downstream sites.

Table 10. Seasonal descriptive statistics and paired Wilcoxon comparison of physicochemical parameters (n = 8 paired sites)

Parameter	Summer mean ± SD	Autumn mean ± SD	Change (%)	Wilcoxon W	Raw p	BH-adjusted p	Interpretation
pH	8.50 ± 0.259	8.16 ± 0.355	-4.0	0.0	0.0078	0.0088	Significant decrease
DO	3.20 ± 2.02	3.98 ± 2.59	+24.2	0.0	0.0078	0.0088	Significant increase
BOD_5	27.01 ± 15.64	22.39 ± 13.87	-17.1	0.0	0.0078	0.0088	Significant decrease
COD	53.61 ± 30.70	46.57 ± 28.35	-13.1	0.0	0.0078	0.0088	Significant decrease
NH_4-N	0.772 ± 0.399	0.627 ± 0.401	-18.8	0.0	0.0078	0.0088	Significant decrease
NO_3	11.20 ± 8.19	10.91 ± 8.11	-2.6	0.0	0.0078	0.0088	Significant decrease
TN	2.57 ± 1.33	4.04 ± 2.25	+57.2	4.0	0.0547	0.0547	Not significant
PO_4-P	0.060 ± 0.037	0.050 ± 0.033	-18.0	0.0	0.0078	0.0088	Significant decrease
TP	0.818 ± 0.466	0.653 ± 0.431	-20.2	0.0	0.0078	0.0088	Significant decrease

Note: BH = Benjamini-Hochberg false-discovery-rate adjustment. Statistical significance was defined as adjusted $p < 0.05$.

The HPI_4, MI_4 and PLI_{ref} results for the four fully quantified metals are summarized in Table 13.

HPI_4 exceeded 100 at all sites except M_1 in both seasons. The highest summer HPI_4 occurred at M_7 (408.21), while the highest autumn value occurred at M_3 (418.92). MI_4 exceeded 1 at every site, and PLI_{ref} exceeded 1 at five sites in summer and six sites in autumn. These results emphasize persistent Cd pressure and localized Fe and Mn hotspots. Site-specific contamination factors for the summer campaign are presented in Table 14. The corresponding contamination factors for the autumn campaign are presented in Table 15.

Cadmium was the dominant contamination factor in most site-season combinations. Autumn Fe and Mn increases were spatially heterogeneous: CF_{Fe} was highest at M_7 (6.44), while CF_{Mn} was highest at M_2 (6.88). The metal signal therefore was not controlled by one uniform spatial pattern.

Exploratory PCA and HCA

The explained variance and parameter loadings for the physicochemical PCA are presented in Table 16.

The first two components explained 81.0% of standardized variance. PC1 represented the organic-pollution and oxygen-depletion gradient, with strong positive loadings for BOD_5, COD, NH_4-N, PO_4-P and TP and a strong negative loading for DO. M_3 in both seasons had the highest positive PC1 scores, while M_1 occupied the most negative positions. The corresponding PCA biplot and Ward dendrogram are shown in Figure 6.

The Ward HCA clusters derived from the physicochemical dataset are summarized in Table 17. The four-cluster solution had an exploratory silhouette coefficient of 0.386. M_1 formed the least-impacted cluster, M_3 the strongest organic-pollution and oxygen-depletion cluster, and M_4–M_5 a high organic and nutrient-pressure cluster. The concordant exploratory patterns in PCA and HCA are consistent with M_3–M_4 as the principal monitored hotspots, but they do not establish pollutant origin.

The explained variance and metal loadings for the heavy-metal PCA are presented in Table 18. The first two metal components explained 70.6% of standardized variance. PC1 was associated with Fe, Cd and Mn, while PC2 was dominated by Ni. M_7 in autumn reflected the exceptional Fe

Table 11. Paired seasonal comparison of Fe, Mn, Cd and Ni (n = 8 paired sites)

Metal	Summer mean ± SD	Autumn mean ± SD	Change (%)	Wilcoxon W	Raw p	BH-adjusted p	Interpretation
Fe	0.172 ± 0.100	0.396 ± 0.387	+130.1	6.0	0.1094	0.2188	Not significant
Mn	0.063 ± 0.040	0.169 ± 0.129	+168.5	6.0	0.2031	0.2708	Not significant
Cd	0.0205 ± 0.0072	0.0210 ± 0.0068	+2.4	10.0	1.0000	1.0000	Not significant
Ni	0.0113 ± 0.0064	0.0056 ± 0.0027	-50.0	1.5	0.0469	0.1875	Not significant after adjustment

Table 12. Adapted weighted-arithmetic water quality index by site and season

Site	Summer WQI	Autumn WQI	Seasonal change (%)	Main interpretation
M_1	111.42	30.80	-72.4	Lowest integrated pollution
M_2	303.64	270.17	-11.0	Elevated integrated pollution
M_3	881.31	797.10	-9.6	Highest integrated pollution
M_4	662.42	563.35	-15.0	Elevated integrated pollution
M_5	571.08	459.28	-19.6	Elevated integrated pollution
M_6	414.99	363.02	-12.5	Elevated integrated pollution
M_7	322.30	265.58	-17.6	Elevated integrated pollution
M_8	519.33	362.10	-30.3	Elevated integrated pollution

Table 13. Integrated heavy-metal indices based on Fe, Mn, Cd and Ni

Site	HPI_4 summer	HPI_4 autumn	MI_4 summer	MI_4 autumn	PLI_{ref} summer	PLI_{ref} autumn
M_1	99.30	81.97	2.53	1.68	0.56	0.27
M_2	202.14	379.10	4.16	13.11	0.74	1.99
M_3	327.13	418.92	6.91	13.86	1.15	2.33
M_4	372.77	384.33	7.92	12.21	1.26	1.98
M_5	391.46	390.19	9.41	9.28	1.61	1.53
M_6	360.02	311.67	6.50	9.48	0.83	1.46
M_7	408.21	398.36	9.02	12.73	1.78	1.15
M_8	392.06	345.63	7.80	6.40	1.40	0.82

Table 14. Standards-based contamination factors during summer.

Site	CF Fe	CF Mn	CF Cd	CF Ni	Dominant exceedance
M_1	0.37	0.56	1.20	0.40	Cd
M_2	0.39	0.82	2.60	0.35	Cd
M_3	0.54	1.72	4.20	0.45	Cd
M_4	0.62	2.10	4.80	0.40	Cd
M_5	1.48	2.58	5.00	0.35	Cd
M_6	1.06	0.24	4.80	0.40	Cd
M_7	1.70	1.08	5.20	1.05	Cd
M_8	0.71	0.98	5.00	1.10	Cd

concentration, whereas M_7 and M_8 in summer were distinguished by elevated Ni. The corresponding PCA biplot and Ward dendrogram are shown in Figure 7. The exploratory Ward HCA patterns for the heavy-metal dataset are summarized in Table 19.

The five-pattern solution had an exploratory silhouette coefficient of 0.517 and separated low-metal observations, summer downstream Ni enrichment, an autumn Fe-Mn group and the unique M_7 autumn Fe hotspot. These patterns are compatible with multiple controls and require validation using additional seasons, field replicates, sediment chemistry and potential source samples.

Study limitations

The study is limited by two seasonal campaigns and the absence of independent field replicate samples. Three consecutive ICP-MS readings support instrumental repeatability but do not quantify field or sample-preparation variability. LOD and LOQ were supplied as ranges rather than run-specific values. The calibration concentration range, detailed CRM identification, numerical recovery percentages and original ICP-MS files were unavailable. Analyses conducted outside the regular state monitoring network are not always archived in the institute's software. The calculated

Table 15. Standards-based contamination factors during autumn

Site	CF Fe	CF Mn	CF Cd	CF Ni	Dominant exceedance
M_1	0.10	0.12	1.00	0.45	Cd
M_2	1.48	6.88	4.40	0.35	Mn
M_3	2.48	5.98	5.00	0.40	Mn
M_4	1.72	5.54	4.60	0.35	Mn
M_5	1.44	2.54	5.00	0.30	Cd
M_6	1.50	3.98	3.80	0.20	Mn
M_7	6.44	1.04	5.20	0.05	Fe
M_8	0.68	0.98	4.60	0.15	Cd

Table 16. Explained variance and correlation loadings for the physicochemical PCA

Parameter / component	PC1	PC2	Interpretation
Explained variance (%)	64.0	17.0	Cumulative: 81.0%
pH	+0.237	+0.738	Strong association with PC2
DO	-0.873	-0.096	Strong association with PC1
BOD_5	+0.980	-0.019	Strong association with PC1
COD	+0.960	-0.084	Strong association with PC1
NH_4-N	+0.824	-0.445	Strong association with PC1
NO_3	+0.527	+0.750	Strong association with PC2
TN	+0.658	+0.231	Moderate association
PO_4-P	+0.849	-0.392	Strong association with PC1
TP	+0.974	-0.007	Strong association with PC1

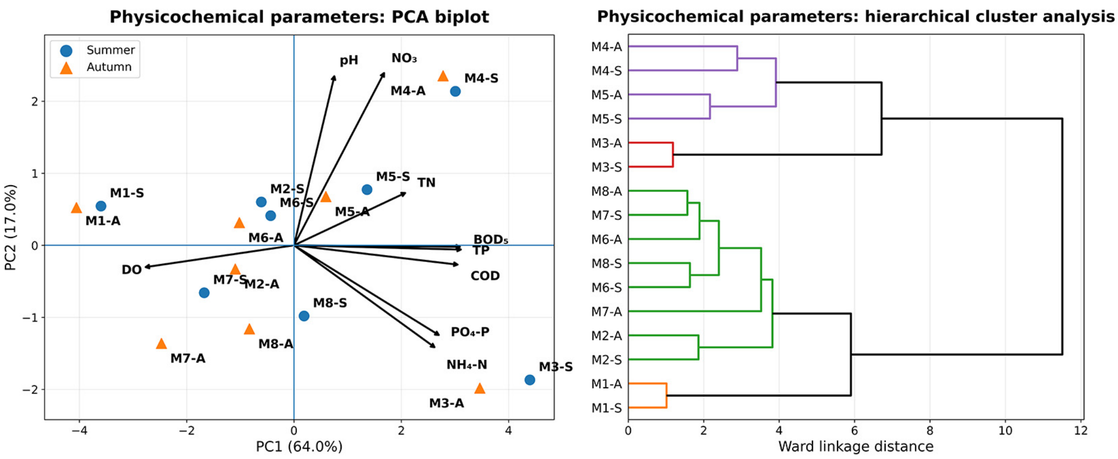

Figure 6. PCA biplot and Ward hierarchical clustering of standardized physicochemical parameters: S – summer; A – autumn

Table 17. Exploratory physicochemical clusters obtained using Ward's HCA

Cluster	Site-season observations	Main pattern
1	M_1-S, M_1-A	Least-impacted upper-course observations.
2	M_2-S, M_6-S, M_7-S, M_8-S, M_2-A, M_6-A, M_7-A, M_8-A	Intermediate pollution profile.
3	M_3-S, M_3-A	Strongest organic pollution and oxygen depletion.
4	M_4-S, M_5-S, M_4-A, M_5-A	High organic and nutrient pressure.

Table 18. Explained variance and correlation loadings for the heavy-metal PCA

Metal / component	PC1	PC2	Interpretation
Explained variance (%)	43.0	27.6	Cumulative: 70.6%
Fe	+0.794	-0.086	Strong association with PC1
Mn	+0.629	+0.013	Moderate association
Cd	+0.720	+0.587	Strong association with PC1
Ni	-0.418	+0.867	Strong association with PC2

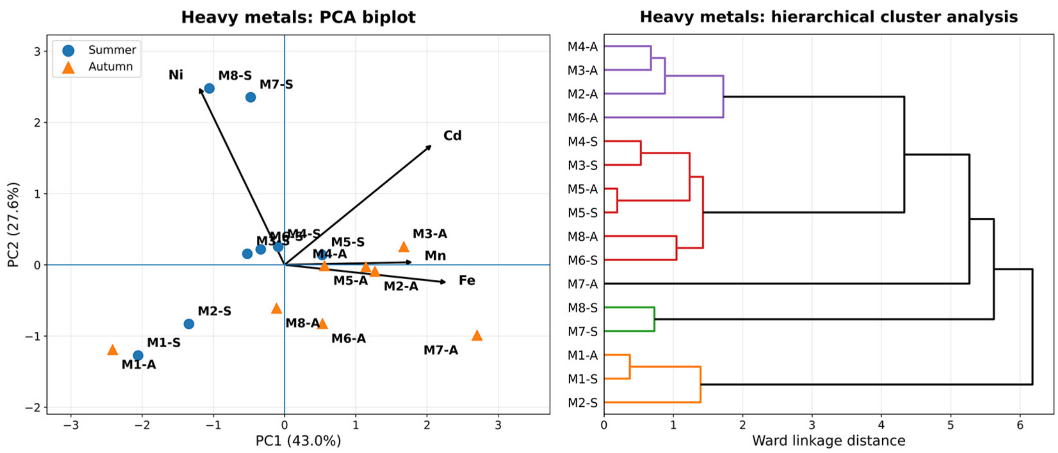

Figure 7. PCA biplot and Ward hierarchical clustering of standardized Fe, Mn, Cd and Ni concentrations. S=summer; A=autumn

Table 19. Exploratory heavy-metal patterns identified using Ward's HCA

Pattern	Site-season observations	Main characteristics
1	M_1-S, M_2-S, M_1-A	Lowest combined metal concentrations.
2	M_7-S, M_8-S	Summer downstream group characterized by elevated Ni.
3	M_3-S, M_4-S, M_5-S, M_6-S, M_5-A, M_8-A	Moderate multi-metal profile with persistent Cd influence.
4	M_2-A, M_3-A, M_4-A, M_6-A	Autumn group with increased Fe and Mn.
5	M_7-A	Distinct Fe hotspot.

indices depend on the selected reference values, and PCA/HCA cannot provide definitive source attribution. Future work should include sampling across additional seasons and hydrological conditions, field duplicates, flow measurements, sediment analysis and source-specific sampling.

CONCLUSIONS

The results of this study indicate that the Klina River is under persistent anthropogenic pressure consistent with urban wastewater discharges, agricultural runoff and other local pollution sources along its course. The most critical sections are located downstream of urban settlements, particularly after the river passes through Skenderaj and before it reaches the lower course near Klina.

The analyzed physicochemical parameters showed unfavorable conditions in the assessed physicochemical quality elements, particularly very low dissolved oxygen and elevated BOD_5, COD, nitrogen and phosphorus concentrations. Together, these findings are consistent with organic pollution, nutrient enrichment and reduced self-purification capacity in the most affected sections.

Cd, Mn and Fe exceeded the adopted comparison values at several sites, while Ni exceeded its comparison value only at M_7 and M_8 in summer. Cadmium was the most persistent concern, exceeding the adopted value in 15 of 16 site-season observations.

The unfavorable conditions at M_4, approximately 70 m downstream of the Llaushë wastewater-treatment plant, are consistent with substantial pressure in this section; however, the available design cannot separate treatment-plant performance from other nearby discharges.

The paired tests, integrated indices and multivariate analyses consistently distinguished the least-affected upper-course station from the principal urban-influenced hotspots. Nevertheless, the conclusions apply to the two monitored 2025 campaigns and should not be interpreted as a complete annual assessment or definitive source apportionment.

Overall, the study provides scientific evidence that can support local and national environmental institutions in planning protection measures, reducing pollution pressure and supporting targeted pollution-control measures and a stronger long-term monitoring program for the Klina River.

The complete machine-readable site-season dataset is provided as Supplementary Data S1 in CSV format and includes sampling dates, seasons, WGS 84 coordinates, altitude, physicochemical results and heavy-metal concentrations. Supplementary Tables S1 and S2 are provided in a separate Supplementary Material file. Original ICP-MS instrument files were not available in the retained documentation.

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