

Geochemical Assessment of Alluvial Sediments from the Slănic River (Buzău County, Romania): Pollution Indices, Ecological Risk and Petroleum Origin Indicators

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Abstract: This study evaluates the geochemical quality of alluvial sediments from the Slănic River (Buzău County, Romania) in the sector Manasia-Dogari, focusing on heavy-metal pollution indicators, ecological risk, and oil contamination. Nineteen sediment samples were analyzed by ME-MS41L (aqua regia digestion, ICP-MS). The local geochemical background was calculated using the iterative median method ± 2 MAD, and 16 pollution indices were computed. Results indicate good overall sediment quality: PLI = 0.968 (no significant pollution), RI = 65.863 (low ecological risk), and mCd = 0.836. Local PI > 1 was recorded for Cu (max 2.177), Mn (max 1.635), and Cd (max 1.428) in isolated samples. The V/Ni ratio (0.530-0.648, mean 0.570) confirms the absence of petroleum contamination. Sample SL-19 (downstream) shows the highest values for most indices. The study provides a baseline for future monitoring.

1. Introduction

Alluvial sediments are sensitive indicators of aquatic environmental quality because they accumulate heavy metals and other pollutants from the surrounding watershed (Romanescu et al., 2016). Therefore, geochemical assessment of sediments is essential for sustainable water management. Rivers in the Romanian Subcarpathian region, including the Slănic River in Buzău County, are subject to pressures from agricultural, industrial, and resource-extraction activities.

This study aims to evaluate the geochemical quality of alluvial sediments of the Slănic River (Manasia-Dogari sector) by: (1) determining concentrations of 12 heavy metals using the ME-MS41L method; (2) calculating the natural geochemical background (iterative median ± 2 MAD; Reimann et al., 2005b); (3) assessing pollution and ecological risk using 16 geochemical indices (Kowalska et al., 2018); (4) investigating potential oil contamination using the V/Ni ratio; and (5) analyzing spatial variability.

2. Study area

The Slănic River, a major tributary of the Buzău River, flows through central-eastern Buzău County, Romania. The analyzed sector (Manasia-Dogari, ~15–20 km) spans the plain-hill contact area at elevations of 200–400 m, with a temperate-continental climate and perennial flow.

The Slănic basin lies within the Carpathian Bend and is dominated by the Tarcău Nappe (Paleogene-Miocene sandstones, clays, and marls) and the Subcarpathian Nappe (Sarmatian-Pliocene molasse; Săndulescu, 1984; Mutihac & Ionesi, 1974). Miocene evaporitic and bituminous facies (Oligocene-Miocene) contribute to natural enrichment in Na^+ , Cl^- , V, Ni, and Mo (Frunzescu et al., 2004; Matenco, 2000). The tectonic framework (Slănic Syncline, salt diapirs, fault systems) controls groundwater circulation, and Quaternary alluvial deposits constitute the sampled material (Figure 1).

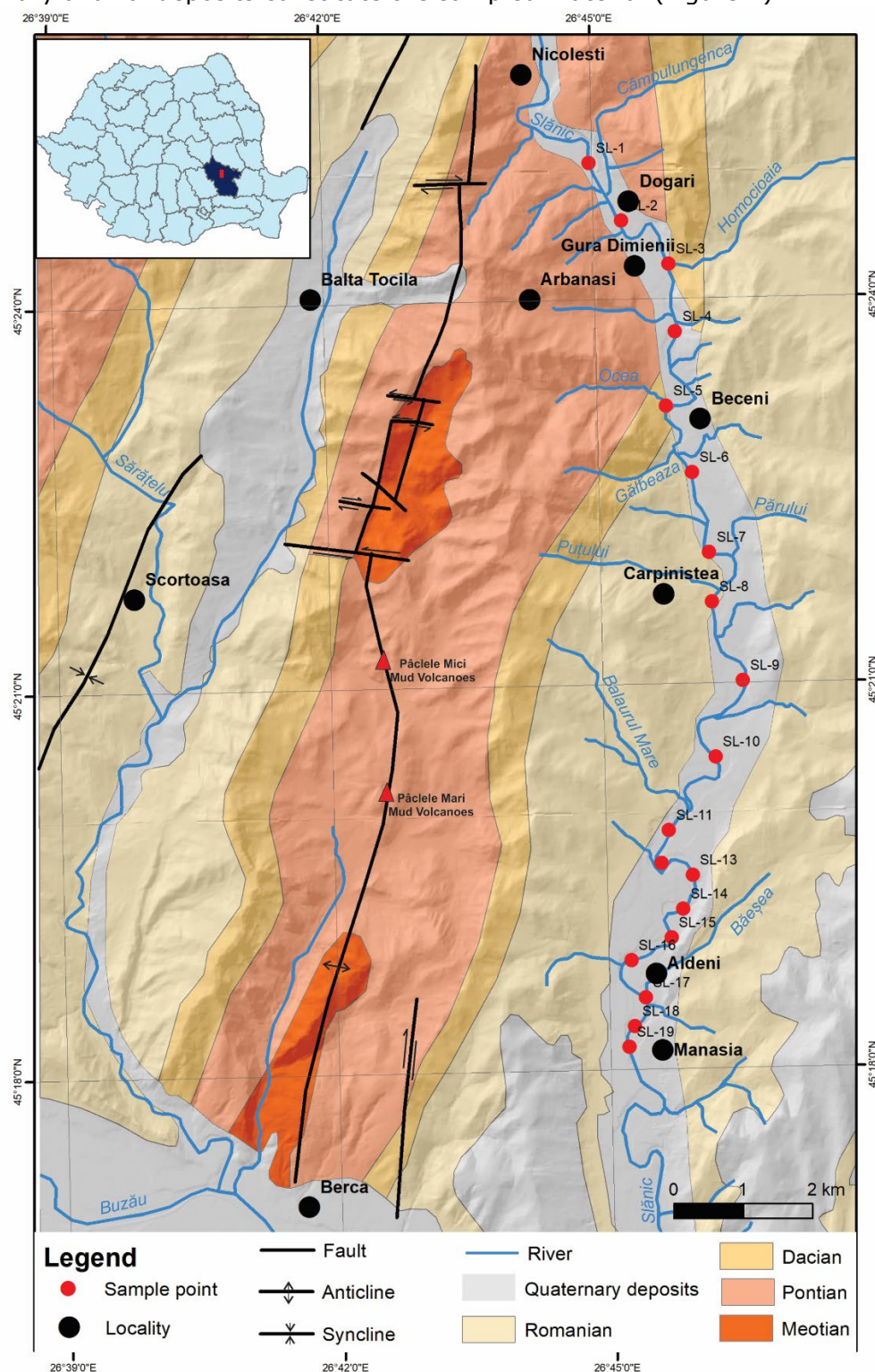


Figure 1. Geological and location map of the Berca–Arbănași study area (Buzău County, Romania) showing the main geological units and sediment sampling points distributed along the Slănic River (modified after Geological Map of Romania, 1:200,000).

3. Materials and Methods

Sample Collection and Preparation

19 samples of alluvial sediments (coded SL-1 to SL-19) were collected from the Slănic River bed in the sector between Manasia and Dogari in April 2023. The samples were collected from the superficial layer of sediments (0-10 cm depth) using a shovel made of inert material (plastic or stainless steel) from areas of preferential accumulation of fine sediments (areas of inner curvature of meanders and areas with low current speed).

Analytical Method ME-MS41L

The determination of heavy metal concentrations in sediments was carried out using the ME-MS41L method provided by ALS Global Laboratories. This method consists of partial digestion with aqua regia, followed by determination by inductively coupled plasma mass spectrometry (ICP-MS) with Super Trace technology (ALS Geochemistry, 2020; Chen & Ma, 2001).

Calculation of Local Geochemical Background

The local geochemical background (GB) is the natural concentration of an element in sediments, unaffected by anthropogenic activities (Reimann et al., 2005a). Accurate calculation of GB is essential for assessing the degree of pollution, as it allows the distinction between natural and anthropogenic concentrations (Matschullat et al., 2000; Bhattacharya et al., 2006).

Pollution and Ecological Risk Indices

Following Kowalska et al. (2018), 16 geochemical indices were calculated for a comprehensive assessment: PI, Igeo (Müller, 1969), EF (Wedepohl, 1995; Sutherland, 2000), CF, PLI (Tomlinson et al., 1980), RI (Håkanson, 1980), PISum (Kwon and Lee, 1998), PINemerow (Cheng et al., 2007), PIavg (Inengite et al., 2015; Bhattacharya et al., 2006; Loska et al., 2004), PIVector (Gong et al., 2008), PIN (Caeiro et al., 2005), MEC, CSI (Pejman et al., 2015), MERMQ (Long et al., 1995), Cdeg, and mCd (Abraham et al., 2007). Detailed formulas and classification thresholds are provided in the original reference.

V/Ni Ratio as a Petroleum Origin Indicator

The V/Ni ratio is a geochemical indicator of petroleum contamination in sediments. Values >1.0 indicate petroleum origin; <1.0 confirms lithogenic sources (Lewan, 1984).

Statistical Analysis & GIS

Statistical analysis included descriptive statistics, normality testing (Shapiro-Wilk), correlation analysis (Pearson or Spearman), and spatial variability assessment. All calculations were performed in Python 3.10 (pandas, NumPy, SciPy, matplotlib, seaborn) at a significance level of $\alpha = 0.05$. Spatial interpolation was performed in ArcGIS using the Inverse Distance Weighting (IDW) method, with the analysis restricted to a 250 m buffer zone along the river channel.

4. Results

4.1. Geochemical Background

An operational local geochemical background (GB) for the 12 heavy metals analyzed was estimated using the iterative median method $\pm 2\text{MAD}$ (Reimann et al., 2005b) and is

presented in Table 1. The GB values represent the natural reference concentrations for Slănic River sediments and were used to calculate the pollution indices.

Table 1. The local geochemical background (GB) calculated by the method of Reimann et al. (2005b) for sediments from the Slănic River

Element	GB (mg/kg)	Natural variation (mg/kg)	Iterations
As	6.91	6.00 - 7.82	3
Cd	0.297	0.200 - 0.394	2
Co	13.375	11.50 - 15.25	3
Cr	28.65	23.80 - 33.50	3
Cu	32.8	27.50 - 38.10	2
Fe	26000	22000 - 30000	3
Hg	0.046	0.030 - 0.062	2
Mn	780	650 - 910	3
Ni	47.9	40.50 - 55.30	3
Pb	14.9	12.50 - 17.30	2
V	27.6	22.80 - 32.40	3
Zn	75.5	63.50 - 87.50	3

GB values (Figure 2) are comparable to UCC values (Rudnick & Gao, 2003; Wedepohl, 1995), with slightly elevated Ni (47.9 vs. 47 mg/kg) and Mn (780 vs. 439 mg/kg), attributable to local lithological characteristics.

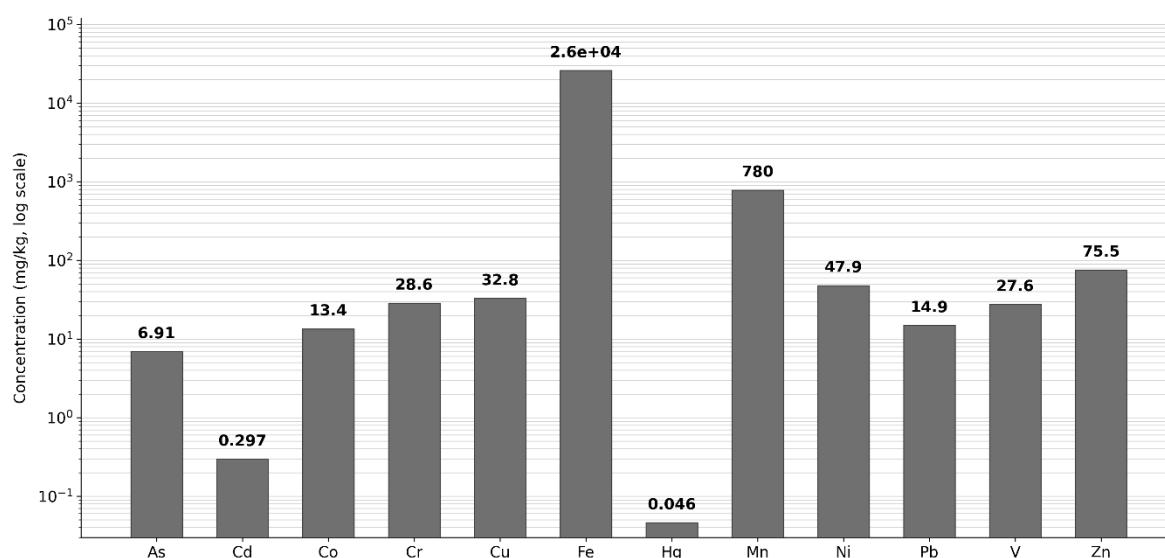


Figure 2. Local geochemical background (GB) of sediments from the Slănic River calculated using the iterative Median $\pm$ 2MAD method (Reimann et al., 2005b). Values are represented on a logarithmic scale.

4.2. Heavy Metal Concentrations in Sediments

Descriptive statistics for heavy metal concentrations in the 19 sediment samples are shown in Table 2. Concentrations vary considerably between samples, reflecting the spatial heterogeneity of the sediments and potential local anthropogenic influences (Figure 3).

Table 2. Descriptive statistics for heavy metal concentrations in sediments from the Slănic River

Element	Mean (mg/kg)	Median (mg/kg)	Min (mg/kg)	Max (mg/kg)	Dev. Std. (mg/kg)	CV (%)
As	6.87	6.91	5.99	7.72	0.41	6.0

Cd	0.29	0.30	0.20	0.42	0.04	14.3
Co	12.56	12.75	9.76	15.70	1.44	11.5
Cr	26.51	27.60	19.80	38.80	4.86	18.3
Cu	35.18	33.30	27.10	71.40	10.00	28.4
Fe (%)	2.504	2.550	2.050	2.860	0.19	7.4
Hg	0.04	0.05	0.03	0.06	0.01	14.1
Mn	834.32	811.00	692.00	1275.00	117.60	14.1
Ni	44.97	46.00	34.30	58.80	5.73	12.7
Pb	14.27	14.65	11.95	17.05	1.25	8.7
V	25.74	26.20	20.10	38.10	4.39	17.0
Zn	69.93	71.60	55.50	86.40	7.71	11.0

Compared to GB values, average concentrations are slightly lower for most elements (As, Co, Cr, Ni, Pb, V, Zn), about equal for Cd and Hg, and higher for Cu, Mn and Fe (Figure 4). This pattern suggests a general good quality of the sediments, with possible local enrichments for Cu and Mn.

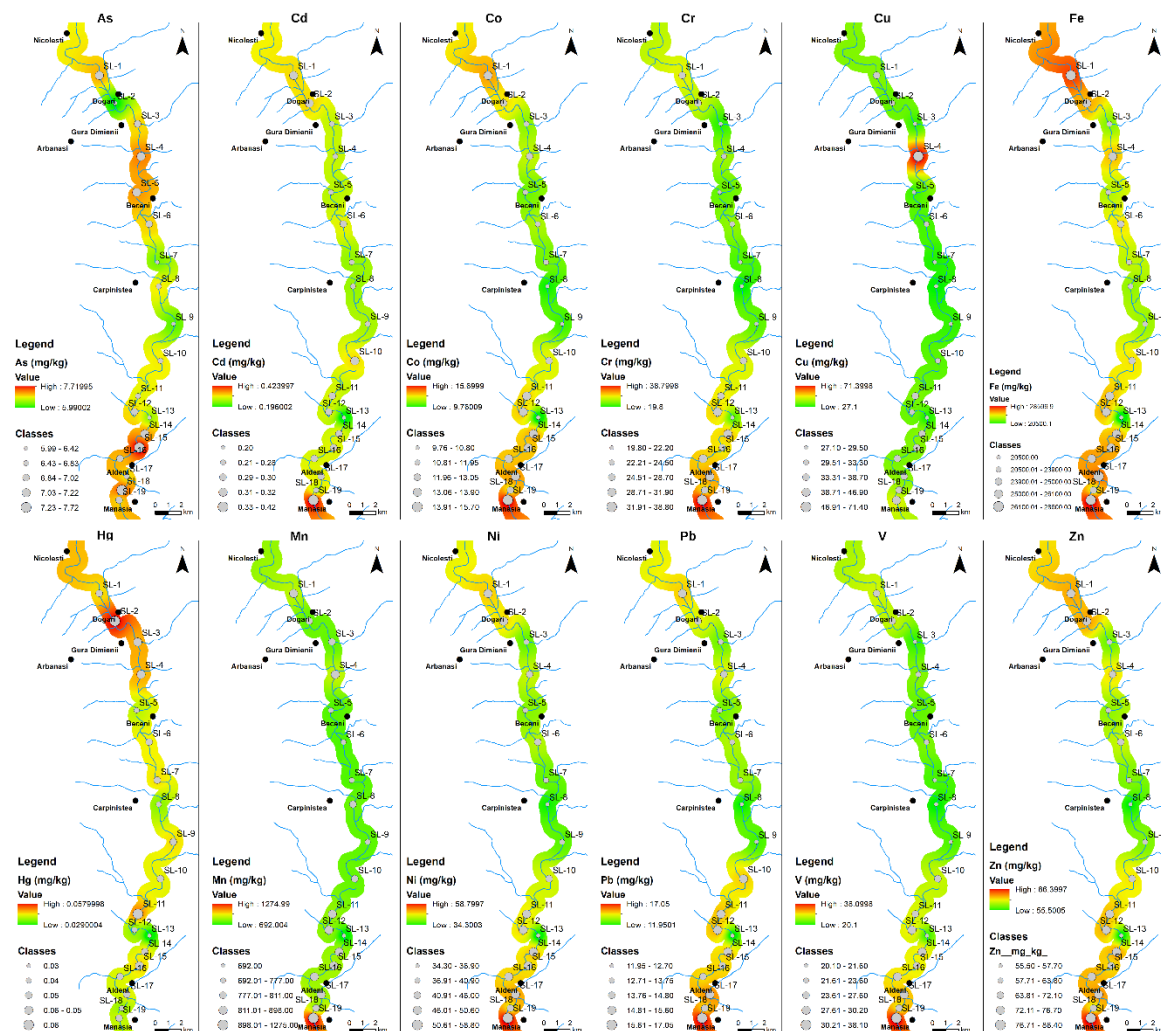


Figure 3. Spatial distribution of heavy metal concentrations (mg/kg) in Slănic River sediments. Colors indicate concentration intensity (green = low, red = high).

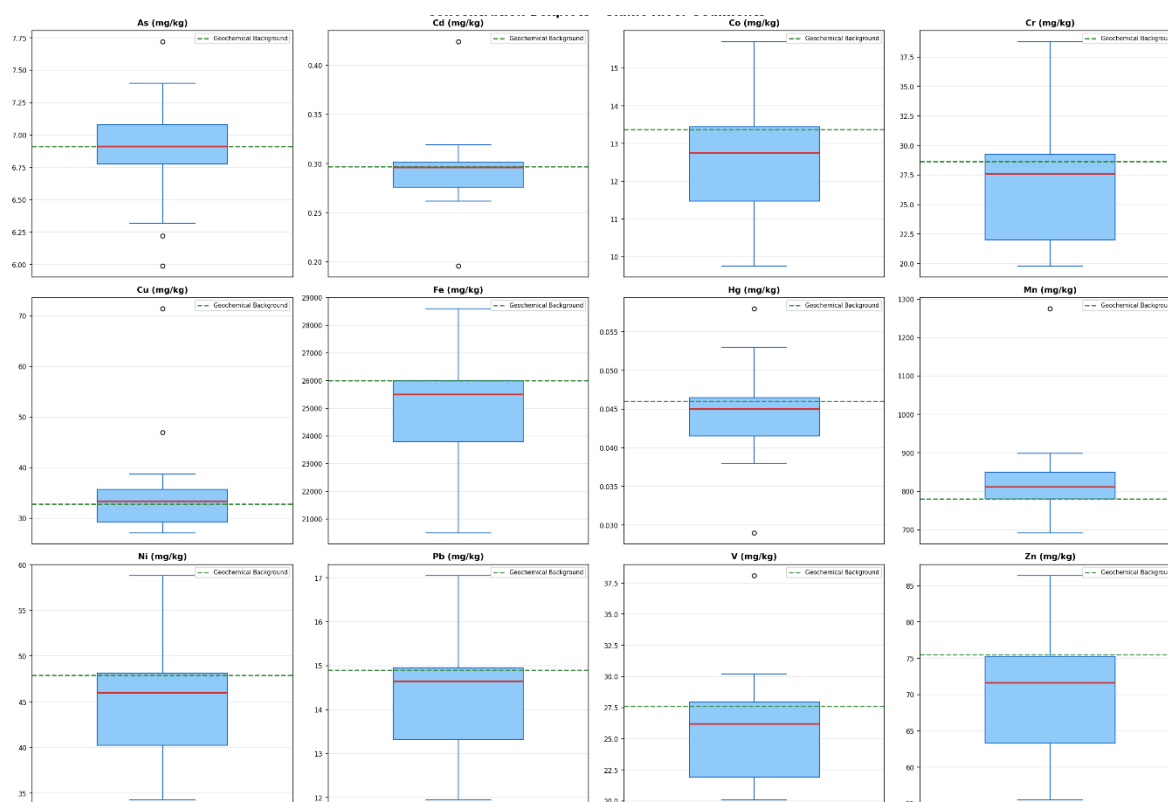


Figure 4. Statistical distribution of concentrations for the 12 analyzed elements in Slănic River sediments. Values are expressed in mg/kg.

4.3. Pollution Indices

The descriptive statistics for the 16 calculated pollution indices are presented in Table 3. The mean and median values of the indices provide an overview of the sediment quality in the Slănic River.

Table 3. Descriptive statistics for pollution indices in the sediments of the Slănic River

Index	Mean	Median	Min	Max	Std. Dev.	Interpretation
<i>Single Indices</i>						
PI	0.972	0.999	0.767	1.244	0.106	No pollution
I_{geo}	-0.643	-0.592	-0.977	-0.288	0.154	Uncontaminated
EF	1.009	1.005	0.929	1.143	0.052	Minor enrichment
CF	0.837	0.846	0.659	1.100	0.098	Low contamination
<i>Integrated Indices</i>						
PLI	0.968	0.995	0.762	1.228	0.103	No pollution
RI	65.863	66.679	48.493	85.560	7.470	Low ecological risk
PI_{sum}	11.670	11.993	9.200	14.927	1.267	-
$PI_{Nemerow}$	1.078	1.043	0.852	1.715	0.197	Warning (slight pollution)
PI_{avq}	0.972	0.999	0.767	1.244	0.106	No pollution
PI_{vector}	3.389	3.477	2.672	4.363	0.381	-
PIN	17.124	17.145	10.492	24.729	4.510	Moderate enrichment
MEC	0.311	0.318	0.251	0.409	0.036	-
CSI	0.378	0.382	0.255	0.475	0.046	Low risk
MERMQ	0.188	0.196	0.146	0.239	0.022	10-25% probability of toxicity
C_{deg}	10.033	10.157	7.912	13.204	1.177	Moderate degree

mCd	0.836	0.846	0.659	1.100	0.098	Low degree
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Indices for individual elements (PI, I_{geo} , EF, CF) set out in Table 3 confirm the absence of significant anthropogenic enrichment. Most indices indicate good sediment quality, without significant pollution:

- Average PLI = 0.968 (< 1.0): indicates the absence of general pollution (Figure 5).
- Average RI = 65.863 (< 150): low ecological risk
- Average $PI_{Nemerow}$ = 1.078 (1.0-2.0): light pollution, at the lower end of the category
- Mean MERMQ = 0.188 (0.1-0.5): 10-25% probability of toxic effects
- Average C_{deg} = 10.033 (8-16): moderate degree of contamination
- Average mCd = 0.836 (< 1.5): low degree of contamination

Three elements show average PI > 1.0 or maximum PI > 1.0 (Figure 6):

1. Copper (Cu): mean PI = 1.073, maximum PI = 2.177 (in sample SL-4), indicating light to moderate pollution in some locations
2. Manganese (Mn): mean PI = 1.070, maximum PI = 1.635 (in sample SL-19), indicating light pollution
3. Cadmium (Cd): average PI = 0.988, maximum PI = 1.428 (in sample SL-19), indicating light pollution in sample SL-19

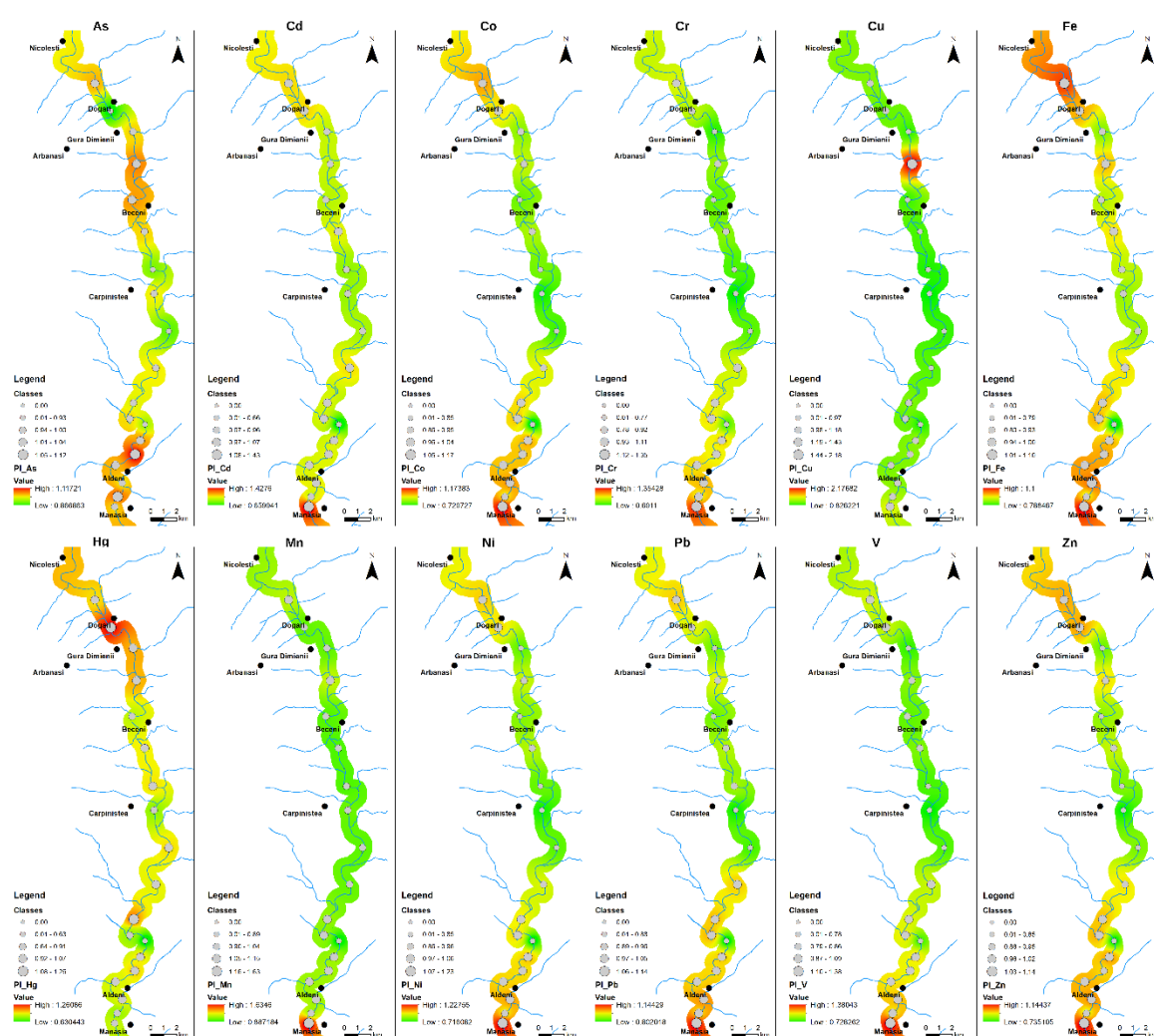


Figure 5. Spatial distribution of the Pollution Index (PI) for the 12 analyzed elements in Slănic River sediments. PI < 1 (green) = unpolluted; 1–2 (yellow-orange) = slightly polluted; > 2 (red) = moderately polluted.

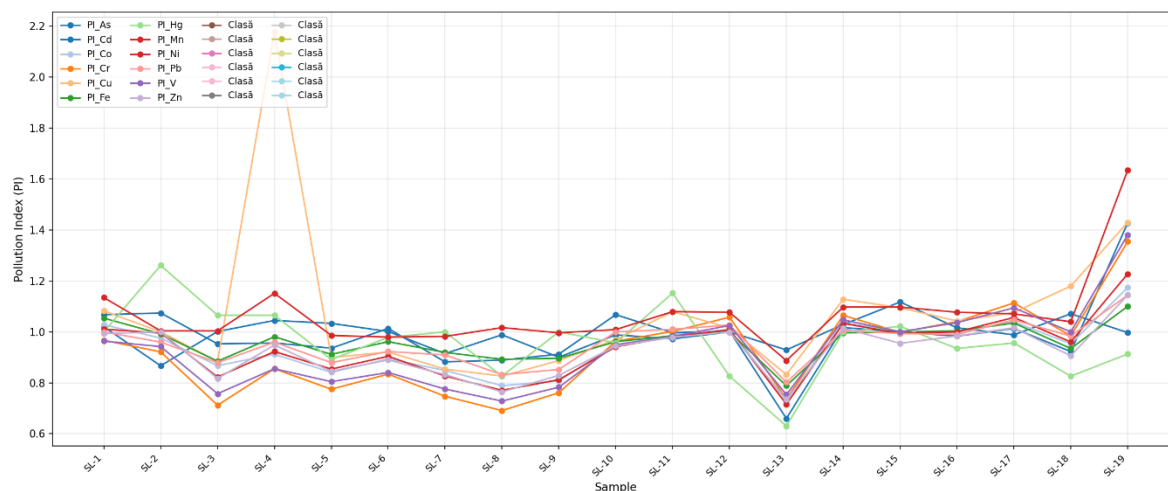


Figure 6. Longitudinal variation of the Pollution Index (PI) along the Slănic River profile (SL-1, north → SL-19, south). Each colored line represents one element.

Spatial distribution of Contamination Factor shows generally low contamination ($CF < 1$) (Figure 7) with moderate contamination ($1 \leq CF < 3$) with Cd, Cu, Fe, Mn, Ni (Figure 8).

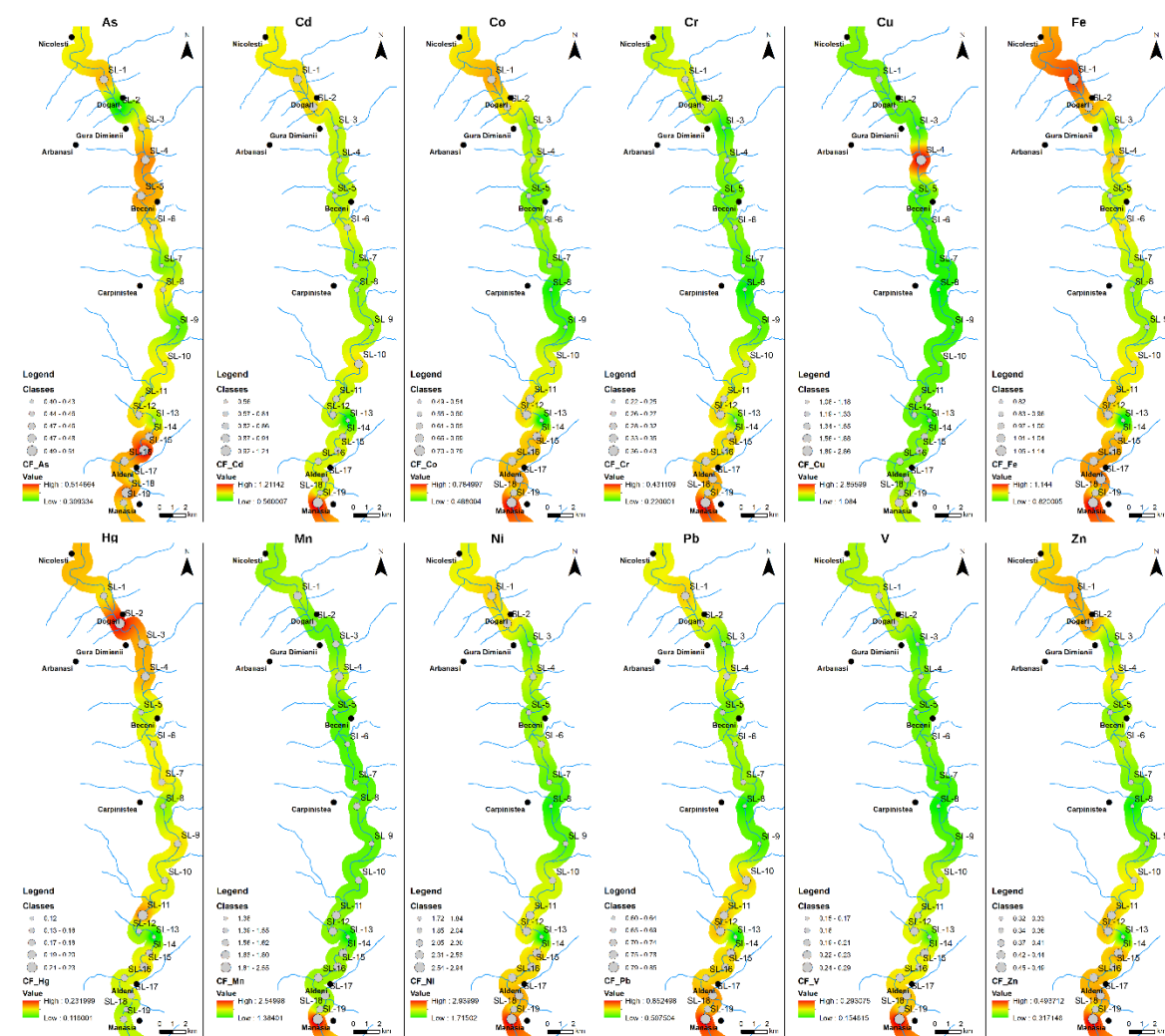


Figure 7. Spatial distribution of the Contamination Factor (CF) for the 12 analyzed elements in Slănic River sediments. $CF < 1$ (green) = low contamination; 1–3 (yellow-orange) = moderate contamination; 3–6 (orange) = considerable contamination.

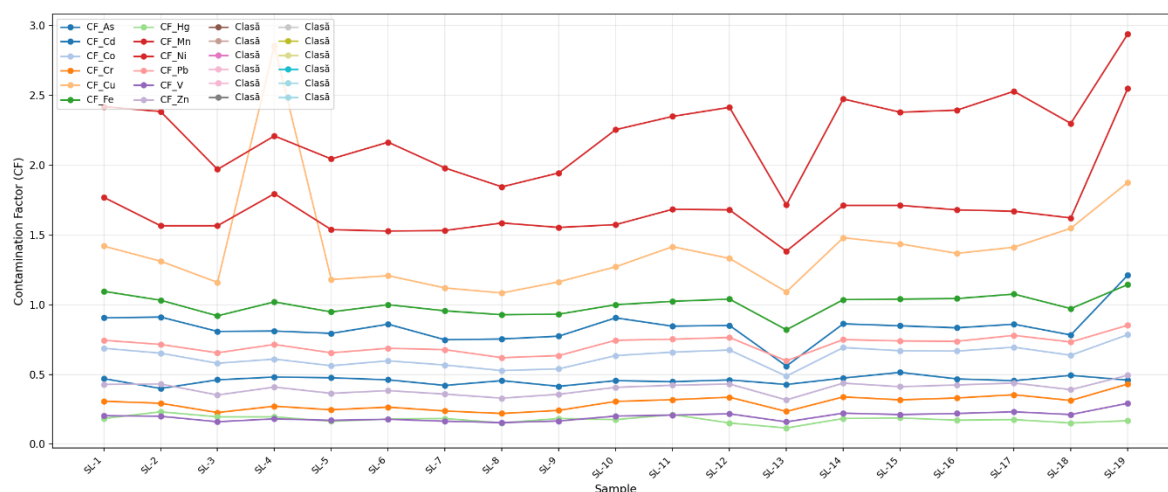


Figure 8. Longitudinal variation of the Contamination Factor (CF) along the Slănic River profile (SL-1, north → SL-19, south).

I_{geo} values reveals relatively homogeneous distributions for most elements, with minor fluctuations among the samples (Figure 9). Sample SL-4 shows moderate pollution ($0 < I_{geo} \leq 1$) with Cd; sample SL-19 shows moderate pollution with Mn (Figure 10).

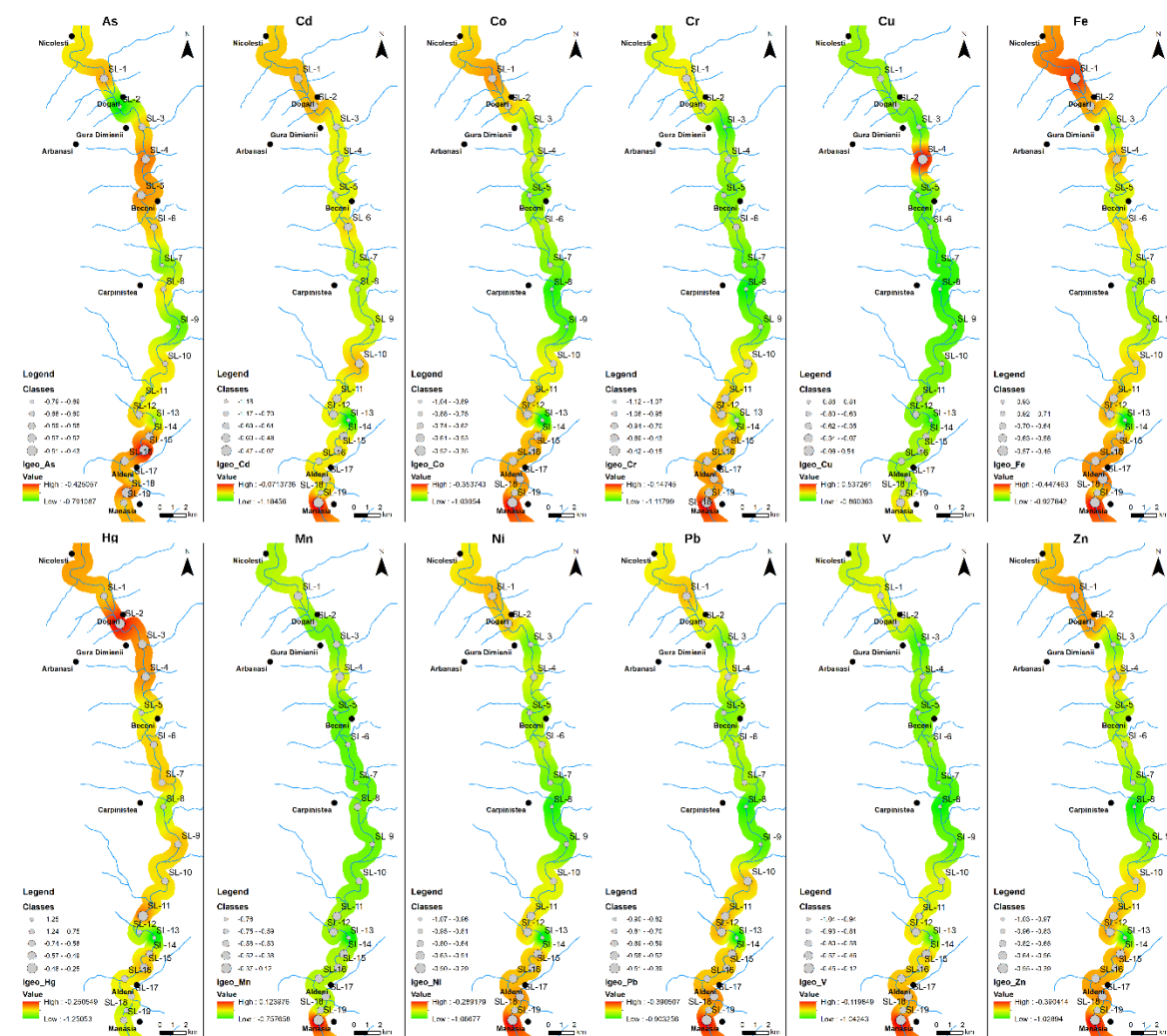


Figure 9. Spatial distribution of the Geoaccumulation Index (I_{geo}) for the 12 analyzed elements in Slănic River sediments. $I_{geo} < 0$ (green) = practically unpolluted; 0–1 (yellow) = unpolluted to moderately polluted (Müller, 1969).

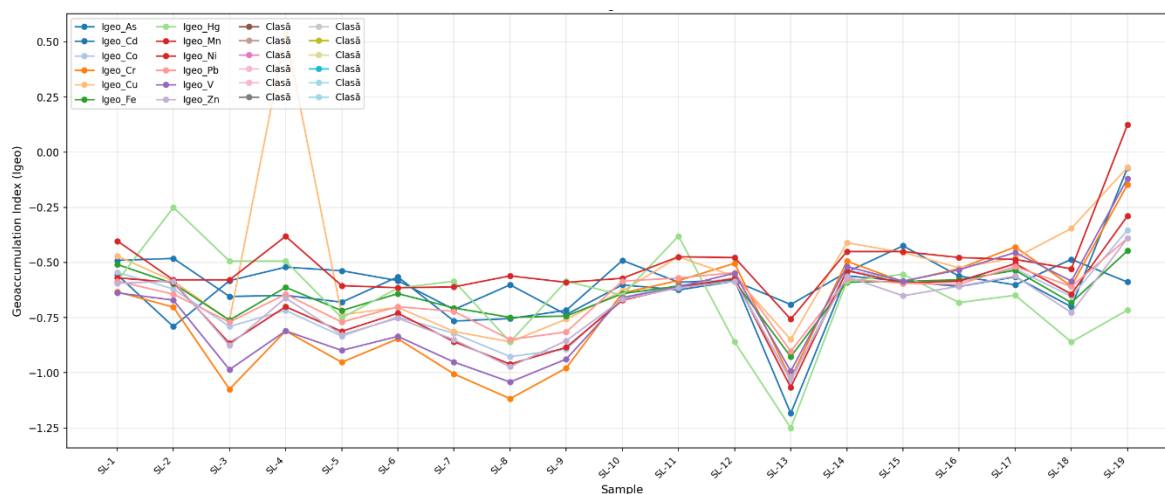


Figure 10. Longitudinal variation of the Geoaccumulation Index (I_{geo}) along the Slănic River profile.

EF values reveal relatively homogeneous distributions for most elements, with minor fluctuations among the samples (Figure 11). Sample SL-4 shows minor enrichment ($0 < I_{geo} \leq 1$) for Cd (Figure 10).

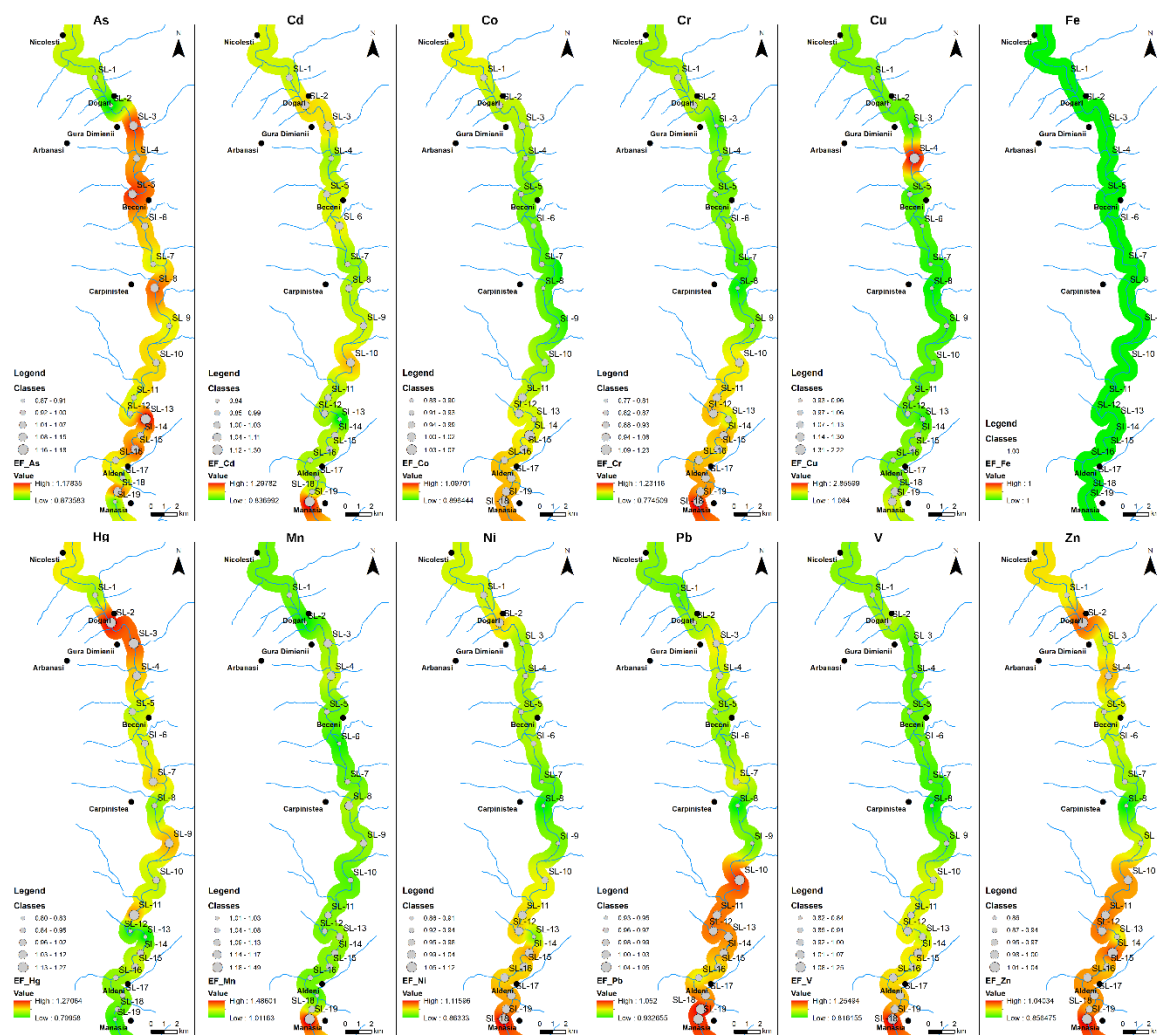


Figure 11. Spatial distribution of the Enrichment Factor (EF, normalized to Fe) for the 12 analyzed elements in Slănic River sediments. EF < 2 (green) = lithogenic origin; 2–5 (yellow) = minor enrichment possibly anthropogenic (Sutherland, 2000; Abraham & Parker, 2007).

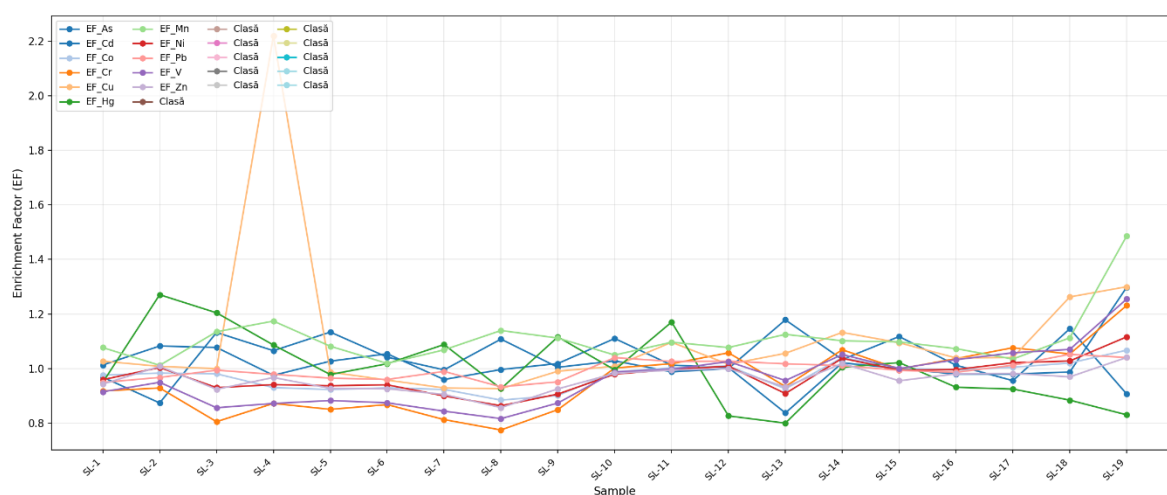


Figure 12. Longitudinal variation of the Enrichment Factor (EF) along the Slănic River profile

4.4. V/Ni Ratio

The vanadium/nickel (V/Ni) ratio was calculated for all 19 samples to assess potential oil contamination. The results are presented in Table 4.

Table 4. V/Ni ratio in the sediments of the Slănic River

Statistics	Values
Mean	0.570
Median	0.577
Minimum	0.530
Maximum	0.648
Standard deviation	0.032
Coefficient of variation (%)	5.547
95% Confidence interval	0.555 - 0.585

All 19 samples show $V/Ni = 0.530$ – 0.648 (mean 0.570), well below the 1.0 threshold for petroleum origin (Table 5). $CV = 5.5\%$ confirms homogeneity along the studied sector.

The V/Ni ratio clearly indicates a non-petroleum (natural lithogenic) origin for vanadium and nickel in the Slănic River sediments (Figure 13). There are no geochemical records of oil contamination on the investigated sector.

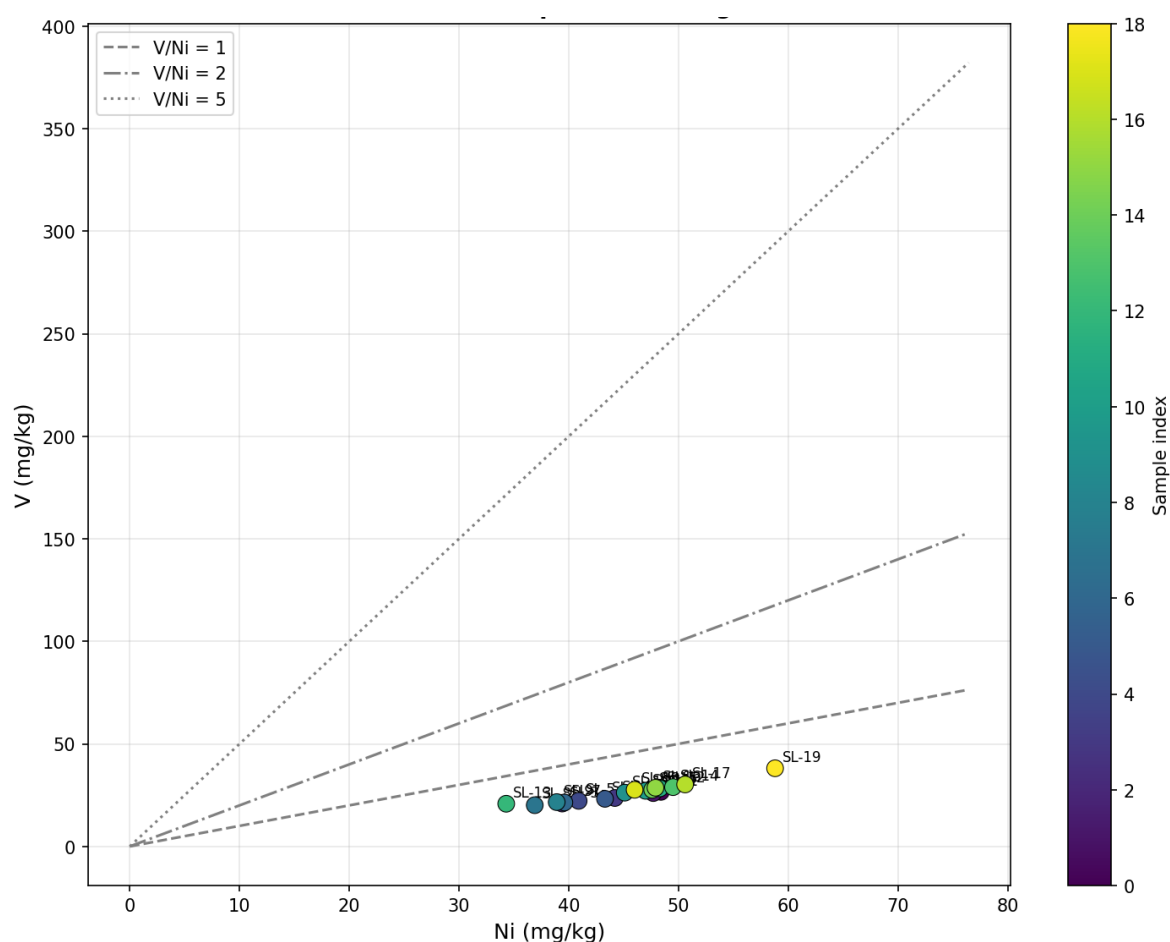


Figure 13. V vs. Ni scatter plot for Slănic River sediments. Reference lines indicate V/Ni ratios of 0.5 and 1.0 . All samples fall below the critical threshold of 1.0 , indicating non-petroleum origin (after Lewan, 1984).

Table 6. Distribution of the V/Ni ratio by sample categories

Category	V/Ni	No. of samples	Percentage (%)	Interpretation
< 0.5		0	0	-
0.5 - 0.6		16	84.2	Lithogenic origin
0.6 - 0.7		3	15.8	Lithogenic origin
0.7 - 1.0		0	0	-

≥ 1.0	0	0	-
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4.5. Spatial Variability

Sample SL-19 (downstream, near Dogari) shows the highest concentrations: Mn 1275 mg/kg (PI = 1.635), Cd 0.424 mg/kg (PI = 1.428), Ni 58.8, V 38.1, Zn 86.4 mg/kg (Figure 14).

SL-19 also peaks on integrative indices (Figure 15): PLI = 1.228, RI = 85.56, $PI_{Nemerow}$ = 1.452, Cdeg = 13.20, mCd = 1.100.

Sample SL-4 shows the highest concentration of copper (71.4 mg/kg, PI = 2.177), suggesting a possible local anthropogenic source or a lithological anomaly.

Samples SL-1 to SL-10 (upstream area, close to Manasia) generally show lower concentrations and pollution indices below the thresholds of concern.

Spatial gradient: A general trend of increasing heavy metal concentrations from upstream (Manasia) to downstream (Dogari) is observed, suggesting progressive accumulation along the river course or increasing anthropogenic influences in the downstream area.

Correlations between elements: Correlation analysis (Pearson) reveals significant positive correlations ($p < 0.05$) between: V and Ni ($r = 0.87$), confirming the common lithogenic origin; Cu and Cd ($r = 0.65$), suggesting possible common anthropogenic sources; Mn and Fe ($r = 0.72$), indicating similar geochemical processes; Cr and Co ($r = 0.68$), suggesting in association lithogenic minerals.



Figure 14. Heatmap of Complex Pollution Indices for Slănic River sediment samples (green = low, red = high; SL-1 north to SL-19 south).

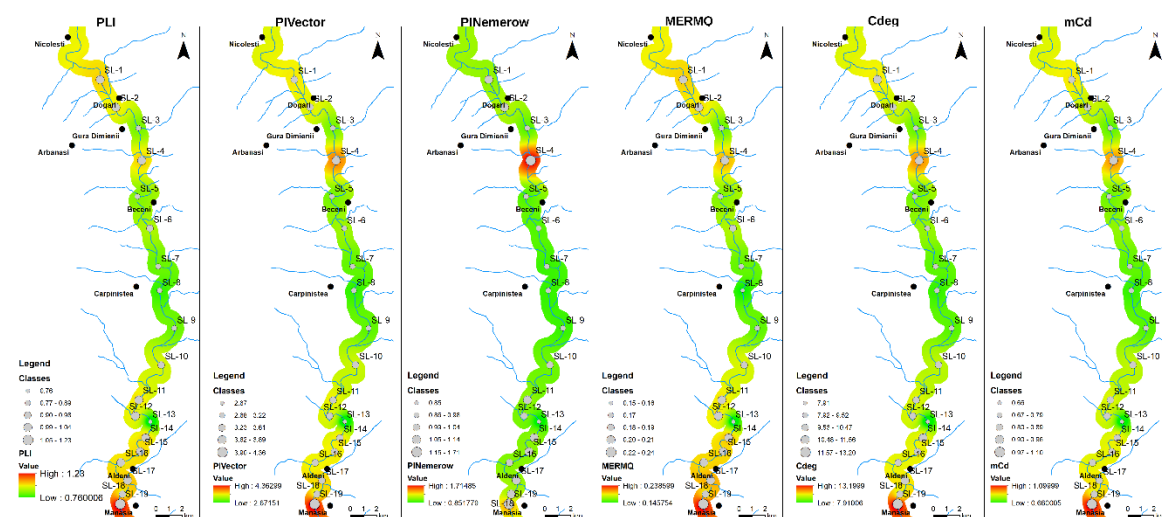


Figure 15. Spatial distribution of contamination indices for Slănic River sediments.

5. Discussion

5.1. Sediment Quality Assessment

Sixteen geochemical indices consistently indicate good general sediment quality in the Slănic River, without significant heavy metal pollution (Caeiro et al., 2005; Pejman et al., 2015).

5.2. Sources of Heavy Metals

The analysis of the sources of heavy metals in the sediments of the Slănic River is based on several lines of evidence:

Predominantly lithogenic origin: Mean Enrichment Factor (EF) values for all elements are close to 1.0 (range 0.955–1.110), indicating the absence of significant anthropogenic enrichment. EF compares the metal/Fe ratio in the sample to the metal/Fe ratio in the natural geochemical background, using iron as a conservative reference element. EF values < 3 are considered to indicate natural accumulation processes, without significant anthropogenic contribution.

Local enrichments for Cu, Mn and Cd: Three elements show PI > 1.0 in some samples (SL-4, SL-19).

Correlations between elements: Significant positive correlations between V and Ni ($r = 0.87$), Cr and Co ($r = 0.68$), and Mn and Fe ($r = 0.72$) suggest a common lithogenic origin for these pairs of elements, probably associated with specific minerals in the geological substrate. The moderate correlation between Cu and Cd ($r = 0.65$) suggests possible common anthropogenic sources for these two elements in some samples.

Spatial gradient: The trend of increasing heavy metal concentrations from upstream (Manasia) to downstream (Dogari) can be explained by: (1) progressive accumulation of fine sediments (which concentrate heavy metals) in areas with low current velocity; (2) increased input of pollutants from anthropogenic activities in the downstream area (larger settlements, intensive agricultural activities); or (3) changes in lithological features along the river course.

5.3. Absence of Petroleum Contamination

The V/Ni ratio detects petroleum contamination: values > 1.0 indicate oil origin; < 1.0 confirms lithogenic origin.

5.4. Comparison with Other Studies

The comparison of the results of the present study with other similar studies in Romania and in the region provides context for the evaluation of the sediment quality in the Slănic River.

Comparison with international benchmarks:

- The average values of heavy metal concentrations in the sediments of the Slănic River are generally comparable or slightly lower than the world average values for alluvial sediments (according to Kabata-Pendias, 2010).
- Concentrations are significantly below reference values for the upper continental crust (UCC, according to Rudnick and Gao, 2003) for most elements.
- Concentrations are below tolerable levels according to Kloke (1979) for all elements analyzed.

Comparison with other rivers in Romania: Although comparative data for rivers in Buzău County are limited, previous studies on other rivers in Romania (Danube, Mureș, Someș, Olt) reported variable heavy metal concentrations, depending on local anthropogenic pressures. The Slănic River has comparable or lower concentrations than rivers affected by intensive industrial activities, as mining or metallurgy (Maftei et al., 2019; Sandu et al., 2021; Bereș et al., 2024; Lupu et al., 2026; Scarlat et al., 2023), but slightly higher than rivers in predominantly agricultural areas.

Comparison with ecotoxicological effect thresholds: The concentrations of heavy metals in the sediments of the Slănic River are generally below the ERL (Effects Range-Low) thresholds for most elements, suggesting low probability of toxic effects on aquatic organisms. Only for Cu and Ni, some samples show concentrations close to the ERL, which explains the moderate MERMQ value (0.188, 10-25% probability of toxicity).

6. Conclusions

This study presents the first integrated geochemical assessment of alluvial sediments in the Berca-Arbănași mud volcano area, establishing local geochemical background values for 12 potentially toxic elements and using geochemical distribution and pollution indices to assess contamination, ecological risk, and potential sources.

The Polluted Load Index (PLI), Ecological Risk Index (RI) and Modified Degree of Contamination (mCd) shows good general sediment quality without significant heavy metal pollution or major ecotoxicological threat to aquatic ecosystems.

The Single Pollution Index (PI) shows localized enrichment from point sources or lithological anomalies.

Despite the long history of hydrocarbon exploration and exploitation in the Berca-Arbănași area, the V/Ni ratios consistently remain below the 1.0 threshold, indicating a predominantly natural lithogenic contribution. The absence of elevated V/Ni ratios provides no evidence of petroleum-related contamination in the studied alluvial sediments of the Slănic River, suggesting that the historical hydrocarbon activities have not resulted in a detectable enrichment of V and Ni attributable to petroleum inputs.

Sample SL-19 shows the highest concentrations and pollution indices, indicating progressive accumulation or anthropogenic influence towards Dogari.

The Ecological Risk Index (RI) and MERMQ Index confirm low ecological risk; residual concern limited to Cu and Mn in isolated samples.

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