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Contamination Assessment of Toxic Elements in River Sediments from Baia Mare, Romania—Extreme Pollution from Mining Activities

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Abstract: Sediment samples from the Săsar River and its main tributaries were analyzed for their potentially toxic elements at the site of the Romplumb metallurgical company and near the well-known Pb-Zn-Cu epithermal deposit of Baia Sprie located in the Neogene volcanic chain of the Eastern Carpathians, Romania. The average metal concentrations arranged in order of decreasing abundance are as follows ($mg \cdot kg^{-1}$): Mn (4098) > Zn (2093) > Pb (918) > Cu (489) > As (160) > Cr (37.51) > Ni (30.25) > Co (28.13) > Cd (9.72) > Hg (1.81). Several pollution indices were successfully used to assess the degree of contamination and ecological risk. The majority of sampling sites indicate high degrees of pollution, with two major hotspots identified. There are further sources, such as the Șuior (Pb-Zn-Au) and Săsar (Au-Ag) epithermal deposits, Cuprom company, and Bozânta tailing ponds, identified as contaminants. The Baia Mare mining district is causing a serious threat to the aquatic systems in the region, and it can be taken as a reference area for the human impact derived from the mining of mineral deposits of Au-Ag-Cu-Pb-Zn. It is imperative to reduce ecological risks and thereby protect the population living within this abandoned mining area.

Keywords: toxic elements; river sediments; pollution; ecological risk; mining; ore deposits

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1. Introduction

River sediments and waters play an essential role in the natural environment, and their quality necessitates careful global monitoring to prevent ecological and human health concerns [1–3]. Mining is considered as one of the most major sources of potentially hazardous compounds, which are widely present in aquatic systems and have a severe impact on ecosystem living [4–8]. These metals are released into groundwater and surrounding water columns, impacting several environmental parameters [9]. Metals do not naturally decompose like organic pollutants and have the potential to heavily accumulate in the surrounding media [10].

Pollutants that infiltrate into stream sediments can easily be transferred to aquatic living species and subsequently to the human body via the food chain, posing major health risks [11–13]. The harmful elements contained in stream sediments mostly originate from tailing ponds and waste dumps left over after the shutdown of mining operations [6,14–16]. Toxic metal emissions from mining activities can contaminate surface water, groundwater, agricultural soils, and food crops, causing health dangers to the population via a variety of pathways including the mouth (with food and drinking water or from the soil or sediments to the mouth via the hands), respiratory tract, and skin [17,18]. Some elements, such as Zn,

Cr, Ni, and Mn, are known as micronutrients essential for the welfare of human being in trace amounts, whereas Cd, As, Pb, and Hg that are frequently associated with them in the same ore deposits are extremely poisonous metal(loid)s and even in small quantities, can cause acute and even chronic health impacts, some of which are not fully understood [7,19].

Although most of the mining activities in Romania were closed in 2006, the sites within the mining zones remained unrestored with serious environmental repercussions. The mine residues from the ore-processing plants were dumped in tailings easily accessible to wind and water, causing the metals to spill into surface and groundwater, infiltrate the topsoils, and thereby become part of the human nutrition cycle with a non-calculable risk potential to populated areas in the vicinity. Săsar, Herja, Baia Sprie, and Șuior are some known gold mineralizations that belong to the Baia Mare district, which is located in the northwestern region of Romania in Maramureş county. Even though mining has ceased, the resulting slurries from ore processing plants of gold, silver, sulfides, sulfosalts, sulfates, and silicates are stored in several tailing ponds and waste dumps across the area. The primary water body receiving the discharge of contaminated water from mining waste is the Săsar River. This river is supplied by various tributaries and springs that maintain contact with ore minerals in the subsurface. Subsequently, the contaminated water flows into the Lăpuș and Someș rivers [20].

Considering the previously mentioned issues, the current study aims to evaluate the toxicity level of stream sediments and the environmental impact on aquatic life using various pollution indices as well as to identify the source (geogenic or anthropogenic) using spatial and multivariate statistical approaches. Different contamination indices are commonly used in the quality assessment of diverse surroundings, such as soils, water, and sediments [6,21–24]. These pollution indices are an objective tool for assessing the contamination degree of several toxic metals. They can provide valuable information about the level of enrichment in sediments by classifying the samples or concentrations as functions of the severity of pollution. The results obtained can also be used to develop remediation methods in the components of the analyzed areas based on knowledge of the intensity of pollution and the mobility of pollutants. The results from this investigation provide a quantitative measure of several pollution indices indicating the presence of certain toxic elements in high concentrations.

2. Geological Setting

The Săsar river basin runs through the southern central area of the Baia Mare mining district, which is situated in the Neogene volcanic chain of the Eastern Carpathians. The main ore-bearing structure in this metallogenic district exhibits an east–west trend and is a direct result of the deep-seated faulting along the Dragoş-Vodă crustal lineament [25]. The study area is located north of the town of Baia Mare, with the volcanic landscape characterized by the interplay of Neogene volcanic activity and deep linear erosion during phases of quiescence into the lava plateaus and volcanic cones, rarely exceeding an altitude of 1000 m (a.m.s.l) [26].

In more detail, the geological units in the Săsar River watershed are made up of Neogene magmatic rocks belonging to the Igniș-Gutâi Volcanic Mts. (Figure 1). The Baia Mare gold and base metal deposits are hosted by the northwestern part the Eastern Carpathian Mts., which is a Neogene volcanic arc that was derived from the continental collision of the African and European plates [27,28]. The magmatic activity in the Baia Mare area was enhanced by crustal spreading during the subsidence of the Transcarpathian Basin [29].

Several ore deposits have been exploited in the study area and hence have been considered as sources of contamination: Săsar, Herja, Baia Sprie, and Șuior. The Săsar deposit is a complex mineralized structure zone made up of several veins. These veins are enriched in Au and Ag accommodated into the lattice of sulfides, sulfosalts, sulfates, and silicates, such as pyrite, sphalerite, galena, marcasite, arsenopyrite, chalcopyrite, tetrahedrite, and pyrargyrite, which are accompanied by carbonates (calcite, rhodochrosite, and siderite),

sulfates (baryte and gypsum), and silicates (quartz) [30]. The Herja deposit is located in the northeast edge of Baia Mare and dominated by Pb-Zn minerals, the common sulfides of which are associated with several sulfosalts as well as carbonates, sulfates, and silicates [31]. In the Baia Sprie deposit located near the southern edge of the volcanic massif, the following ore and gangue minerals have been observed: pyrite, chalcopyrite, sphalerite, galena, wolframite, scheelite, stibnite, realgar, orpiment, arsenopyrite, tetrahedrite, bournonite, semseyite, proustite-pyrargyrite, andorite, felsobanite, szmikite, dietrichite, quartz, calcite, dolomite, chlorite, and baryte [32–34]. The Șuior deposit, which is approximately 25 km from Baia Mare, is another vein-type deposit where fine-grained quartz was impregnated with pyrite and followed in order of decreasing abundance by sphalerite, galena, arsenopyrite, chalcopyrite, marcasite, tetrahedrite, and the proustite-pyrargyrite solid solution series [32].

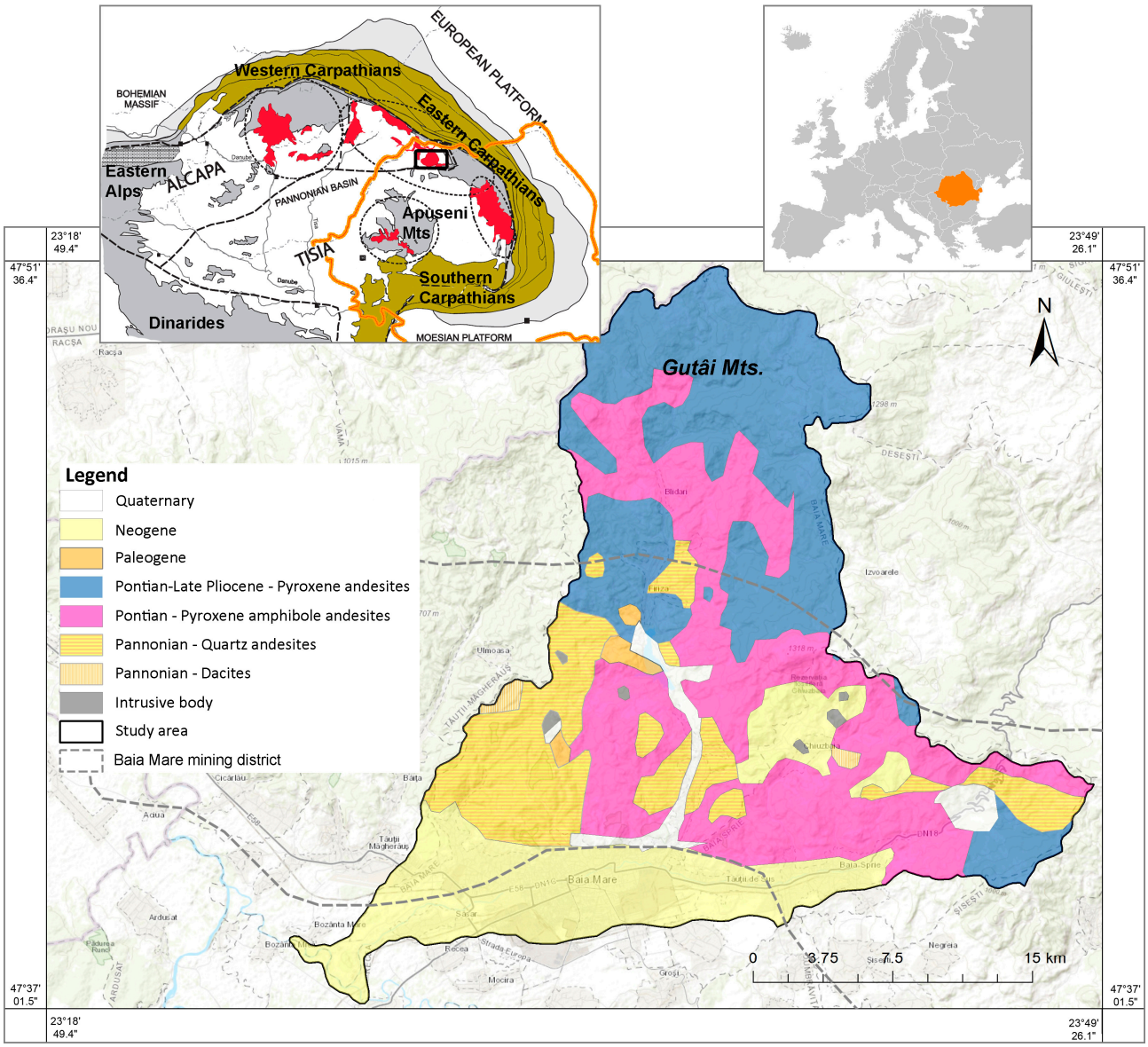

Figure 1. Simplified geological map showing the location of the study area (upper left inset: Carpathian-Pannonian region showing the Neogene volcanism of the Carpathians in red color; upper right inset: location of Romania within Europe—orange color).

In the watershed system of the River Săsar, numerous waste dumps, tailing ponds, and abandoned processing and metallurgical plants are found where former mining operations

were carried out, and their mineralogical compositions mirror the host rock lithology and mineral assemblages of the mined-out mineral deposits. These mining and processing residues have been undergoing a pervasive supergene alteration, leading to a great variety of post-mining "mineral" products [35].

In the Baia Mare area, there were two metallurgical platforms that processed copper (Cuprom, formerly known as Phoenix) and lead (Romplumb). The Romplumb Society is a lead-producing company whose main activity was obtaining lead cut from selective lead concentrates through the pyrometallurgical processing of lead concentrates. The metallurgical waste (slag) was deposited in the vicinity of the plant and was subject to wind and rain erosion [36]. The company operated until 2012, when all activity was stopped.

The Cuprom company has produced copper and copper wires, as well as gold and silver ingots, from raw materials in the Romanian market since 1925. The industrial activity resulted in a large amount of metallurgical slag, which was partially processed to obtain copper concentrates [36]. The company operated until 2009.

3. Materials and Methods

3.1. Sampling Sites and Chemical Analysis

A total of 40 stream sediment samples were collected from the main-stream Săsar River (RS) and from six other tributaries (Firiza River—RF, Lăpuș River—RL, Borcut Valley—VB, Chiuzbăii Valley—VC, Usturoi Valley—VU, and Roșie Valley—VR). The samples were taken from the bedforms of the active drainage systems from a depth of 5–25 cm using a stainless-steel shovel and a plastic scoop. A sample consists of at least 5–10 sampling points that are spread out over an area of about 10 m^2 upstream and downstream of the chosen point. The obtained samples with an initial weight between 3 and 3.5 kg were properly stored and labeled in plastic zip-lock bags for further investigations. The sampling locations are shown in Figure 2, and the network was established based on accessibility and human activities—particularly mining explorations that have a negative impact on the studied area.

In the laboratory, the collected samples were dried at room temperature and organic debris was removed. Each sample was sieved and a fraction of less than 63 μm was used in this study, as recommended by the European Commission in "Sampling strategy for chemical monitoring in sediment" (Guidance on chemical monitoring of sediment and biota under the Water Framework Directive—Document no. 25) to avoid the effects of grain-size variability between samples. Moreover, the related Romanian legislation (Directive no. 161/2006) provides threshold values for certain metals in sediments for fractions less than 63 μm.

A total of 10 potential toxic elements (Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Hg and Pb) were selected to be determined by Inductively Coupled Plasma Mass-spectroscopy (ICP-MS). The sieved dry sample sediments (0.5 g) were digested using the *aqua regia* method. The quality assurance and the quality control of the samples were assessed by the ALS Global company with certificate number RM21169673.

3.2. Contamination Assessment

3.2.1. Geochemical Distribution

To enhance data interpretation and visualization, GIS methods (Geographic Information System) were employed using the ESRI ArcGIS 10.2 software. Statistical interpolation maps were generated using the Inverse Distance Weighting (IDW) interpolation method for quantifying the probability of variables that exceed or do not exceed the threshold. The following IDW parameters were used: cell size = 55; power = 2; and variable search radius with number of points = 4.

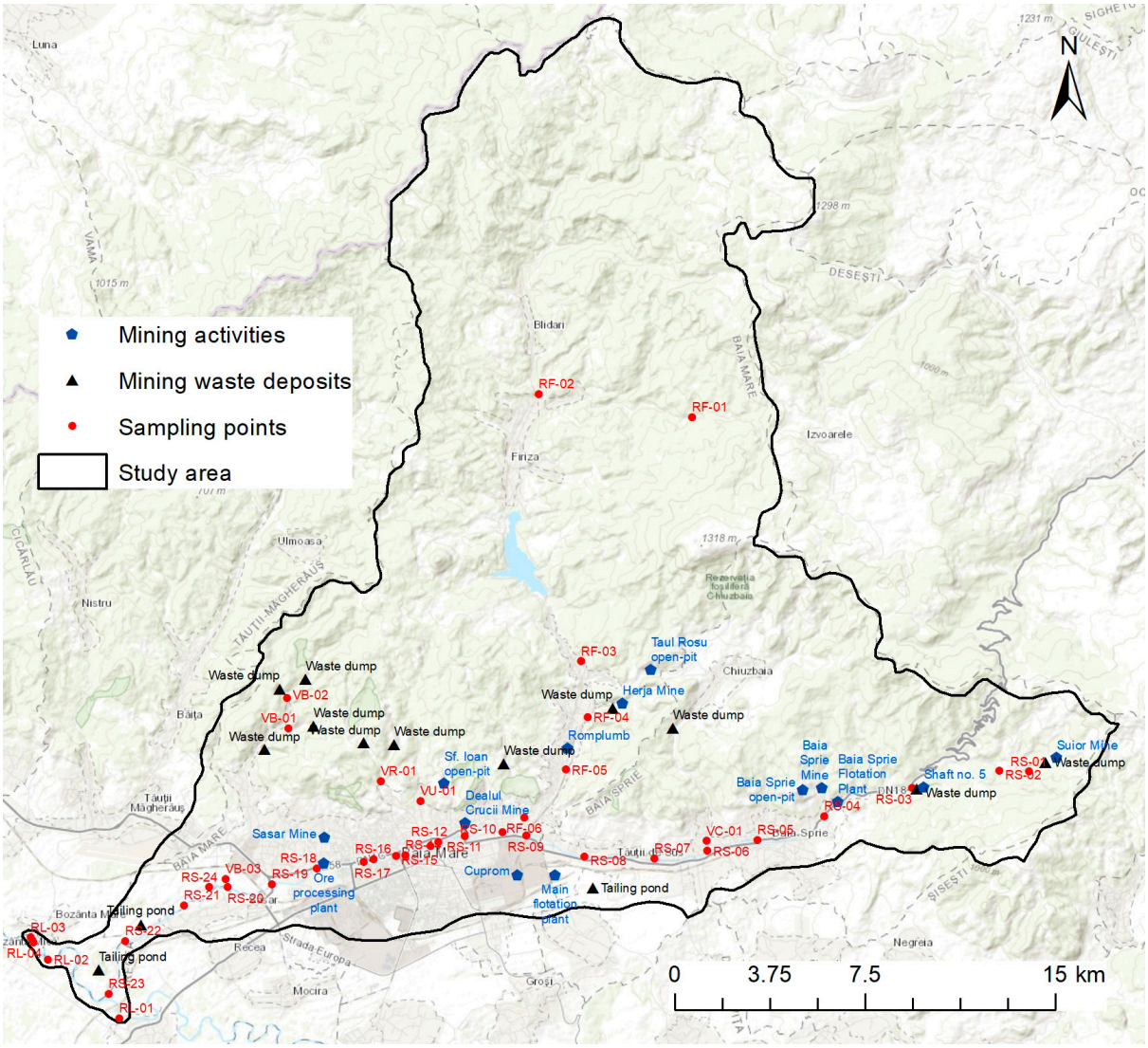

Figure 2. Locations of sampling sites and potential contamination sources from mining activities within the study area.

3.2.2. Pollution Indices

Several indicators such as the geo-accumulation index (I_{geo}), enrichment factor (EF), contamination degree (CD), potential ecological risk index (RI), and environmental toxicity quotient (ETQ) were used for the first time in the Săsar River catchment area to assess the status of river sediment pollution with some potential toxic elements. The selected indices are explained below.

Geo-Accumulation Index (I_{geo})

The I_{geo} was proposed by Müller [37] to quantify pollution intensity in the environment using the following mathematical formula [11]:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right)$$

where C_n is the measured concentration of metal(loid), n, in sediment, B_n is the geochemical background concentration of metal(loid), n, and 1.5 is the background matrix correction factor due the changes that may occur in lithology. Based on I_{geo}, the sediments can be classified as follows: unpolluted ($I_{geo} \leq 0$ = Class 0); unpolluted to moderately polluted

($0 < I_{geo} \leq 1$ = Class 1); moderately polluted ($1 < I_{geo} \leq 2$ = Class 2); moderately to heavily polluted ($2 < I_{geo} \leq 3$ = Class 3); heavily polluted ($3 < I_{geo} \leq 4$ = Class 4); heavily to extremely polluted ($4 < I_{geo} \leq 5$ = Class 5); extremely polluted ($I_{geo} \geq 5$ = Class 6).

Enrichment Factor (EF)

The EF is an indicator often used to evaluate anthropogenic contributions and is obtained based on the following relationship:

$$EF = \frac{\left(C_{metal(loid)}/C_{Fe}\right)_{Sample}}{\left(C_{metal(loid)}/C_{Fe}\right)_{Background}}$$

where $C_{metal(loid)}$ represents the concentrations of an element in the sample and in the average sediment. Fe was chosen as a normalizing element in this study since it is a stable element [38,39]. The results can be expressed as follows: EF < 1 (no enrichment), 1 < EF < 3 (minor enrichment), 3 < EF < 5 (moderate enrichment), 5 < EF < 10 (moderately severe enrichment), 10 < EF < 25 (severe enrichment), 25 < EF < 50 (very severe enrichment), and EF > 50 (extremely severe enrichment).

Contamination Degree (CD)

The contamination degree (CD) proposed by Hakanson [40] can assess the overall contamination in a specific area, considering the sum of all the individual contamination factors (CFs). The CD index is calculated according to the following formula:

$$CD = \sum_{i=1}^{n} CF$$

$$CF = C_{ielement}/C_{ibackground}$$

where CF is the contamination factor, $C_{i\ element}$ represents the concentration of the metal(loid) in the sample, and $C_{i\ background}$ is the concentration of the metal(loid) in the selected reference background. The obtained results are categorized as follows: CD < 6 (low contamination), $6 \leq CD < 12$ (moderate contamination), $12 \leq CD < 24$ (considerable contamination), and $CD \geq 24$ (very high contamination).

Potential Ecological Risk Index (RI)

This index is a mechanism for assessing the impact of potentially harmful components on aquatic behavior. The RI is obtained using following formula:

$$RI = \sum_{1}^{M} E_r^i = \sum_{1}^{M} T_r^i \times \frac{C^i}{C_n^i}$$

where E^i_r is the ecological risk factor for metal(loid)—M, T^i_r is the toxic-response factor for a metal(loid), which is defined for Cr = 2, Mn = Zn = 1, Co = Ni = Cu = Pb = 5, As = 10, Cd = 30, and Hg = 40. C^i is the concentration of elements in the sample, and C^i_n is the background value of the element.

Four risk levels were classified [40] based on the RI results: <150 (low ecological risk), $150 \leq RI < 300$ (moderate ecological risk), $300 \leq RI < 600$ (considerable ecological risk), and RI > 600 (very high ecological risk).

Environmental Toxicity Quotient (ETQ)

The impact of hazardous compounds on human life can be assessed through the ETQ. This indicator was proposed by Ali et al. [41] in order to determine the elemental toxicity of sediments [17]. The US Agency for Toxic Substances and Disease Registry (ATSDR) has published the total score (TS) of the hazard intensity of each element [42].

The equation is as follows:

$$\mathrm{ETQ} = \frac{\sum_{i=1}^{n} \mathrm{TS_i} \times \mathrm{C_i} / \mathrm{TS_{As}}}{n}$$

where C_i is the measured concentration of the specific elements. and n is the number of analyzed elements. TS_i and TS_{As} are the total scores of each element and arsenic, respectively, published by US Agency for Toxic Substances and Disease Registry [42]. Each element's score used in this study is provided in the order below:

As—1675, Cr—892, Mn—799, Co—1015, Ni—994, Cu—807, Zn—916, Cd—1317, Hg—1455, and Pb—1531.

The toxic level of ETQ is classified as follows: <10 = low, 10–50 = moderate, 50–100 = high, 100–300 = very high, and >300 = extremely high.

3.3. Statistical Analysis

The statistical distribution of the studied elements in the Săsar River sediments was assessed using descriptive statistics parameters such as minimum, maximum, mean, median, standard deviation, kurtosis, skewness, and variance. Also, a correlation analysis of Pearson coefficients and hierarchical cluster analysis (HCA) were applied in order to identify clusters or groups of variables with common sources.

Since no core samples could be collected and no pre-historical sediments could be excavated, the local geochemical background was estimated using the formula proposed by Reimann et al. [43]:

$$\text{Geochemical background} = \text{Median} \pm 2\text{MAD},$$

where MAD = median absolute deviation.

4. Results

4.1. Concentrations and Spatial Distribution

The concentrations of toxic elements in the Săsar River stream sediments are listed in Table 1 using descriptive statistical parameters. The high standard deviation values for Mn, Cu, Zn, and Pb suggest a significant dispersion in relation to the mean. The skewness parameter mostly shows positive values, indicating a high degree of right asymmetry specific to lognormal distributions. However, for Ni and Cd, the data are symmetrical, suggesting a normal distribution. The kurtosis indicates a leptokurtic tendency for most of the studied elements, except for Ni, Cd, and Zn where the values are close to zero.

Table 1. Descriptive statistics of the studied elements' concentration ($mg \cdot kg^{-1}$) and geochemical background in Săsar River catchment (N = 40).

	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Minimum	12.35	983	11.50	8.07	89.60	264	10.45	0.26	0.09	90.20
Maximum	109	11,050	84.80	58.3	2060	5770	640	25.20	20.50	3920
Mean	37.51	4098	28.13	30.25	489	2093	160	9.72	1.81	918
Median	32.50	4010	25.95	33.00	428	1723	135	8.16	0.88	782
Standard deviation	19.54	2223	13.00	12.65	349	1271	125	6.08	3.31	786
Kurtosis	3.86	1.80	8.23	−0.76	9.54	0.50	5.11	−0.19	27.32	6.26
Skewness	1.71	1.25	2.25	−0.15	2.49	0.85	1.87	0.60	4.90	2.32
Variance	382	4,941,200	169	160.12	122,054	1,615,854	15,628	36.92	10.95	618,100
Geochemical background	15.7–49.3	1090–6930	10.85–41.05	14.9–51.1	127.5–727.5	128.5–3316.5	0–282.35	1.2–15.12	0–1.79	118–1446
Geochemical threshold	49.3	6930	41.05	51.1	727.5	3316.5	283.35	15.12	1.79	1446
Background mean	30.53	3526	25.11	29.53	358	1642	134	7.37	0.73	677

The spatial distribution of the river sediment compositions in metal(loid)s is shown in Figures 3 and 4. The results show a strong variation of concentrations among all samples. The mean concentrations were found to be in the following sequence: Mn (4098 mg·kg^{-1}) > Zn (2093 mg·kg^{-1}) > Pb (918 mg·kg^{-1}) > Cu (489 mg·kg^{-1}) > As (160 mg·kg^{-1}) > Cr (37.51 mg·kg^{-1}) > Ni (30.25 mg·kg^{-1}) > Co (28.13 mg·kg^{-1}) > Cd (9.72 mg·kg^{-1}) > Hg (1.81 mg·kg^{-1}) (Table 1). The highest concentrations were predominantly observed in the samples collected from the Săsar River for elements such as Cr, Mn, Co, Ni, As, Cd, and Hg. On the other hand, Cu, Zn, and Pb showed their highest values in the samples from the Firiza River. Sample RS07 has the maximum content of Cr (109 mg·kg^{-1}) and Ni (58.3 mg·kg^{-1}). The elements Mn (11,050 mg·kg^{-1}) and Co (84.8 mg·kg^{-1}) displayed the highest values in sample RS22, while a neighboring sample (RS24) showed the highest concentrations of As (640 mg·kg^{-1}) and Cd (25.2 mg·kg^{-1}). One sampling point from the Firiza River (RF05) revealed extremely high levels of Cu (2060 mg·kg^{-1}), Zn (5770 mg·kg^{-1}), and Pb (3920 mg·kg^{-1}). The highest concentration of Hg (20.5 mg·kg^{-1}) was found in sample RS05.

The correlation matrix of the potentially toxic element concentrations from this study (Table 2) shows two distinct clusters of elements that strongly correlate: Cr-Ni and Cu-Pb-Zn-As-Cd, which may suggest two different sources for these two groups of elements. The Pearson correlation coefficient of Cr-Ni is r = 0.804, while other strong correlations were observed for Cu-Zn (r = 0.838), Cu-Pb (r = 0.834), Zn-Pb (r = 0.791), Cu-Cd (r = 0.707), Zn-Cd (r = 0.876), and As-Cd (r = 0.725). The hierarchical cluster analysis (HCA) reveals a more detailed image on the fine associations between the studied elements (Figure 5). The same two groups are observed, Cu-Pb-Zn-As-Cd and Cr-Ni, but with a stronger correlation between Cd-Zn and Cu-Pb. While there is a partial association between these two clusters, Co and Mn show a low correlation with them. Hg is poorly associated with the rest of the elements.

Table 2. Pearson correlation matrix of the studied elements in Săsar River sediments.

	Cr	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Hg**	**Pb**
Cr	1									
Mn	0.313	1								
Co	0.198	0.745	1							
Ni	0.804	0.218	0.170	1						
Cu	0.421	0.469	0.167	0.317	1					
Zn	0.566	0.565	0.276	0.479	0.838	1				
As	0.174	0.271	0.314	0.137	0.435	0.580	1			
Cd	0.461	0.423	0.204	0.406	0.707	0.876	0.725	1		
Hg	0.029	−0.036	−0.041	0.114	0.205	0.291	0.153	0.288	1	
Pb	0.195	0.399	0.128	0.146	0.834	0.791	0.415	0.634	0.308	1

The geochemical background was estimated for each element, and its values are shown in Table 1. The geochemical threshold represents the upper limit of the background interval. This threshold is exceeded by 22.5% of the samples in the case of Hg (9 samples) and by 20% for Cu and Cd (8 samples). Zn and Cr concentrations are above the geochemical background in 7 samples (17.5%). Fewer samples were observed to be above the geochemical threshold for Pb (12.5%), Mn, Co (10%), As (7.5%), and Ni (2.5%).

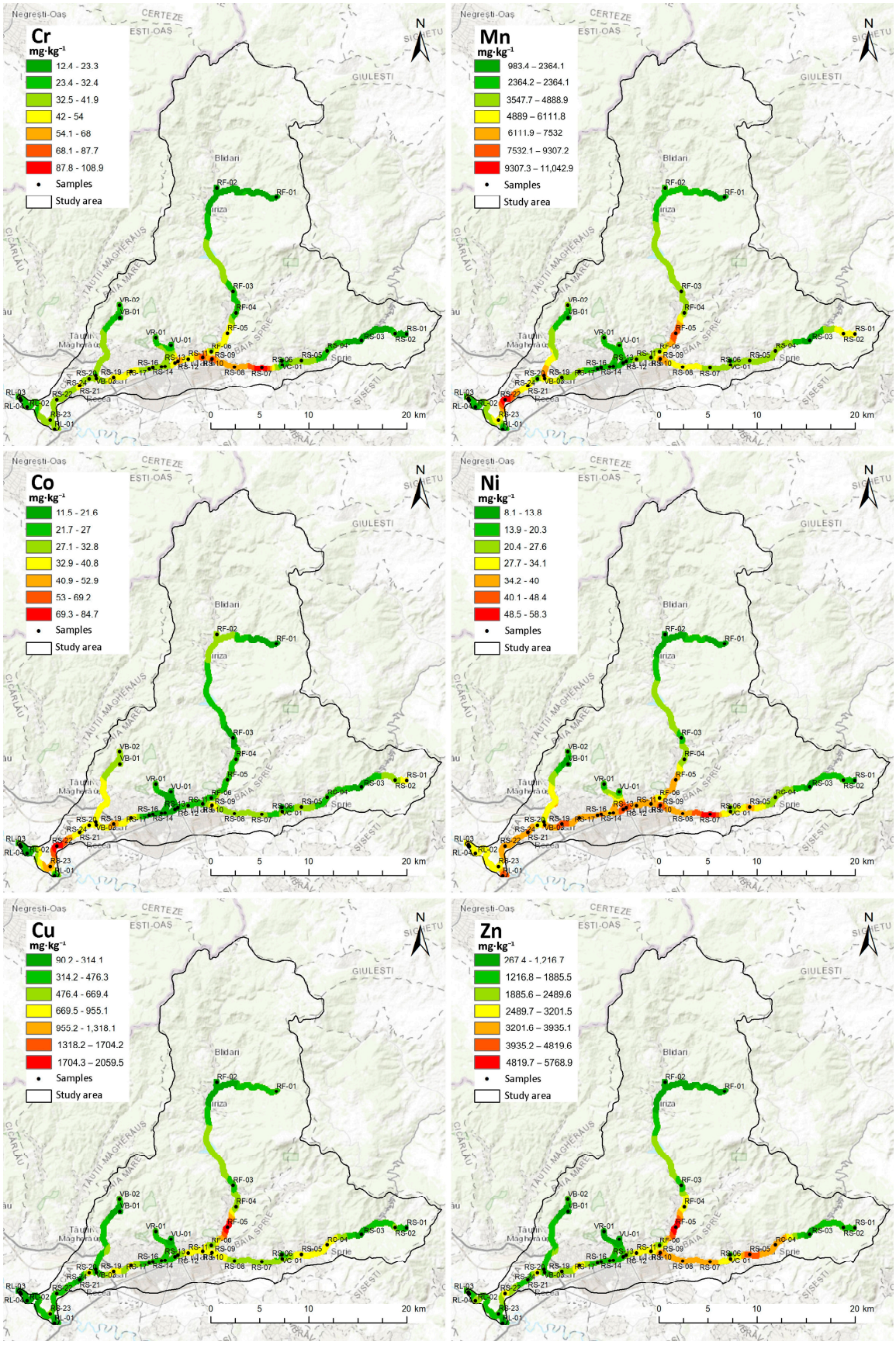

Figure 3. Distribution maps of Cr, Mn, Co, Ni, Cu, and Zn concentrations in sediments from Săsar River catchment.

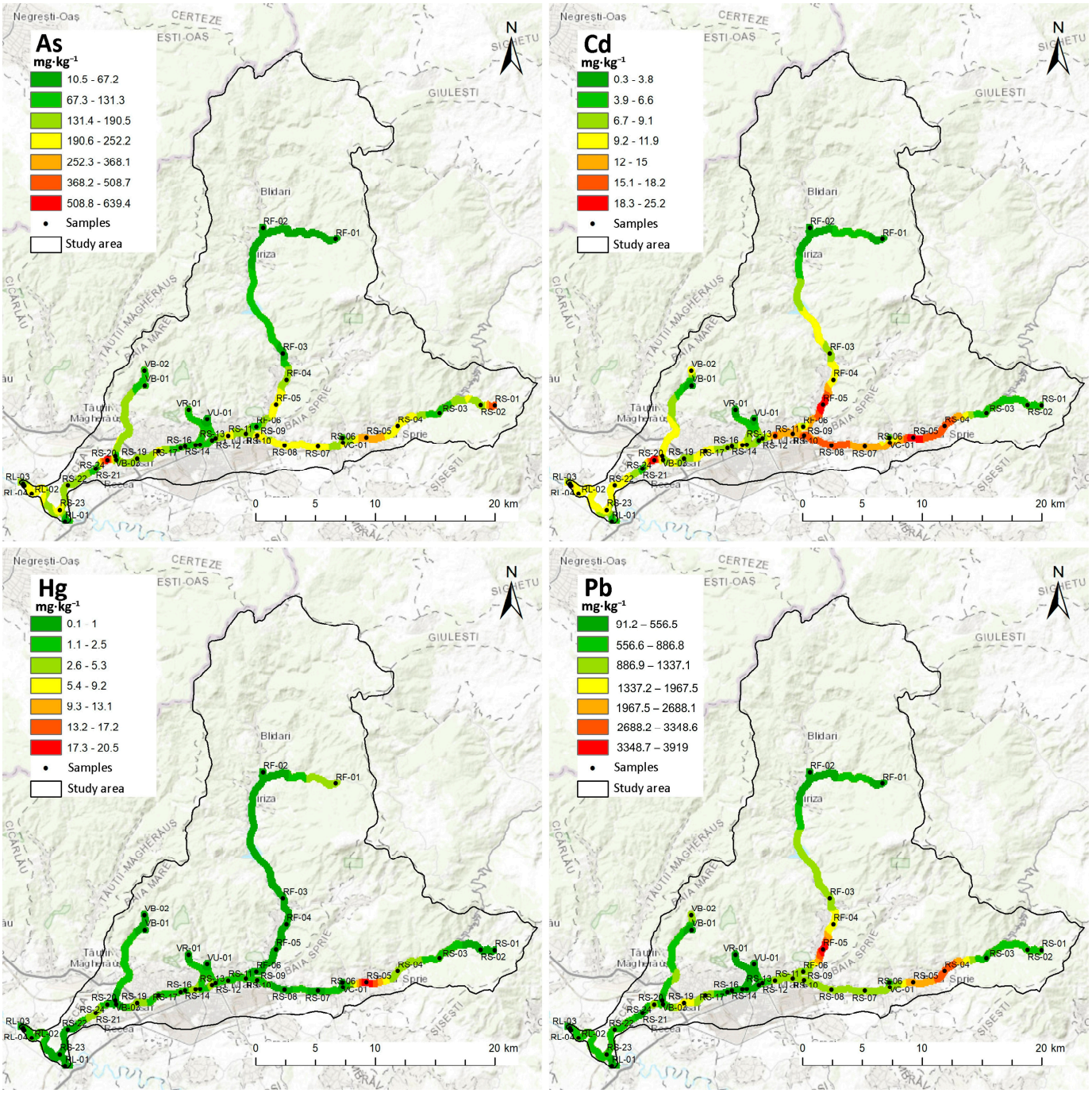

Figure 4. Distribution maps of As, Cd, Hg, and Pb concentrations in sediments from Săsar River catchment.

Although the geochemical background should be a measure to distinguish between natural concentrations and anthropogenic inputs in a specific area [44,45], the calculated values of the geochemical background appear to be quite high and do not accurately reflect the natural environment. Even when compared with the mean concentrations from the upper continental crust (UCC) [46], it can be observed that the results from the Săsar River catchment are significantly higher for almost all the studied elements, except for Cr and Ni (Table 3). This should be expected since the area is strongly affected by mining activities, and sources of contamination can be found across the entire length of the river (waste dumps, tailing ponds, and ore processing plants—Figure 2). Therefore, the estimated geochemical background, which is a statistical parameter, is influenced by the majority

of samples that show high concentrations from anthropogenic activities instead of actual natural contents.

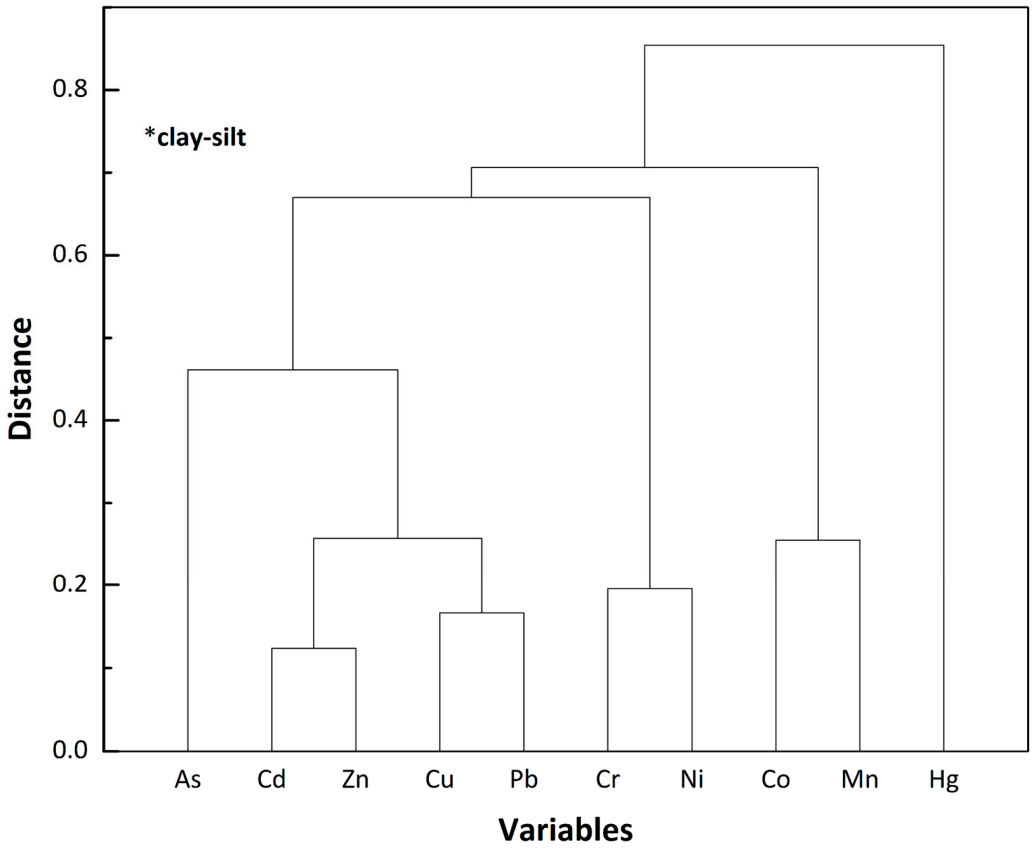

Figure 5. HCA dendrogram of PTEs analyzed from Săsar basin stream sediments.

Table 3. Comparison of toxic element concentrations in Săsar River sediments to Romanian sediment quality guidelines and to similar areas around the globe.

	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
This study:	mg·kg^{-1}									
Mean	37.51	4098	28.13	30.25	489	2093	160	9.72	1.81	918
Median	32.5	4010	25.95	33	428	1723	135	8.16	0.88	782
Romanian sediment quality guidelines *	100	-	-	35	40	150	29	0.8	0.3	85
Other Regions:										
Lom River, Cameroon [47]	65.9	331.5	-	141.9	212	33.1	5.2	-	-	15.6
Taojiang River, China [48]	38.94	-	-	-	43.09	156	15.95	9.09	1.7	48.72
Dagang River, China [8]	118	-	-	52.53	873	1204	99.14	48.28	0.34	271
Mura and Kimpulande Rivers, Democratic Republic of the Congo [49]	55.8	-	1401	43.71	3739	192	33.65	1.24	0.25	41.95
San Pedro River, Mexico [50]	-	1592	-	-	64.57	3802	533	30.43	-	1922
Anka area, Nigeria [51]	111	-	19.74	39.20	320	42.55	15.46	0.10	2.12	2234
Asprolakkas basin, Greece [52]	107	4705	-	95.84	89.63	1233	677	4.73	-	853
Arieș River, Romania [53]	15.8	290	-	17.3	58.3	72.7	10.7	0.47	0.16	20.3
Upper continental crust (UCC) [46]	92	1000	17.3	47	28	67	4.8	0.09	0.05	17

* Romanian Minister of Environment—Directive no. 161/2006.

The mean concentrations of toxic elements in sediments from the Săsar River catchment area exceed the threshold values imposed by the local legislation on sediment quality (Romanian Minister of Environment—Directive no. 161/2006) for the elements Cu, Zn, As, Cd, Hg, and Pb (Table 3). The contents of Cr and Ni are below this threshold, while Mn and Co are not included in the legislation. This implies that authorities should promptly take measures to halt and reduce contamination in the Baia Mare area, preventing potential threats to the health of the local population from these potentially toxic elements.

4.2. Estimation of Sediments Quality

The chemical compositions of Săsar River sediments were evaluated by using different pollution indices such as the geo-accumulation index (I_{geo}), enrichment factor (EF), contamination degree (CD), potential ecological risk index (RI), and environmental toxicity quotient (ETQ).

Cd, Hg, Pb, and As are highly toxic pollutants that pose potential risk to biological organisms and even to human life [19,54,55]. Therefore, data simulation is required to estimate the anthropic influence on biological ecosystems and human existence. In this case, the CD index was used in order to evaluate the degree of sediment contamination, while the RI and ETQ were applied to predict biological and human risk.

4.2.1. Geo-Accumulation Index (I_{geo})

Based on its maximum values, the I_{geo} shows unpolluted sites (Class 0) for Cr and Ni, unpolluted to moderately polluted sampling sites (Class 1) for Co and Mn, moderate contamination (Class 2) for As, Cu, and Zn, and moderately to heavily polluted samples (Class 3) in the case of Cd, Hg, and Pb. The mean I_{geo} values follow a descending order of Cd (1.73) > Pb (1.43) > Zn (1.22) > As (1.21) > Hg (1.10) > Cu (0.98) > Mn (0.38) > Co (0) > Ni (−0.42) > Cr (−0.61). Three sampling points were observed to be the most contaminated sites showing the highest values of the I_{geo}: RS05 (Hg = 2.44), RS24 (Cd = 2.27, As = 1.95) and RF05 (Pb = 2.19, Zn = 1.76, Cu = 1.69). Out of the entire data set (N = 40), the majority of samples fall into Class 2 for Cu (52.5%), Zn (82.5%), As (77.5%), Pb (85%), Cd (67.5%), and Hg (55%). Pb had only two samples (5%) that fit into Class 3 of contamination, while Hg had only one sample (2.5%). In the case of Cd, 11 samples (27.5%) were found in Class 3.

4.2.2. Enrichment Factor (EF)

The enrichment factor (EF) analysis shows a similar trend for the studied elements of Săsar River sediments. The average EF values indicate extremely severe enrichments with Cd (118) and Pb (57.57) followed by very severe enrichments with Hg (41.62), As (34.54), and Zn (34.08). Cu and Mn are enriched severely (Cu = 18.93) and moderately (Mn = 4.57), respectively, whereas Co is minorly enriched (Co = 1.83). The EF for Ni and Cr shows no anthropogenic input (Ni = 0.76, Cr = 0.47). The highest EF values are observed in the same samples as those regarding the I_{geo}: RS05 for Hg (364), RS24 for As (88.77) and RF05 for Cu (60.19), Pb (199), and Zn (70.46), except for Cd that showed higher values in samples RS09 and RS15. Cd seems to be the most enriched element in the analyzed sediments, with 85% of the samples showing EF values higher than 50 (extremely severe enrichment), while for Pb, 50% of sampling locations have EFs above 50. Zn and Cu show less samples in the extremely severe enrichment category (EF > 50: Zn—17.5%; Cu—2.5%), but most of the sampling points still suggest at least a severe enrichment (EF > 10: Zn—92.5%; Cu—82.5%).

4.2.3. Contamination Degree (CD)

Figure 6 shows the contamination degree (CD) in each sampling site for the sediments of the Săsar catchment area. The level of anthropogenic activity is very high especially in the two samples collected from the Săsar (RS05) and Firiza rivers (RF05). The very high CD index in sample RS05 is mostly represented by a local accumulation of Hg as indicated by the individual contamination factors (CFs), while sample RF05 is anthropogenically contaminated with Pb, Cu, and Zn.

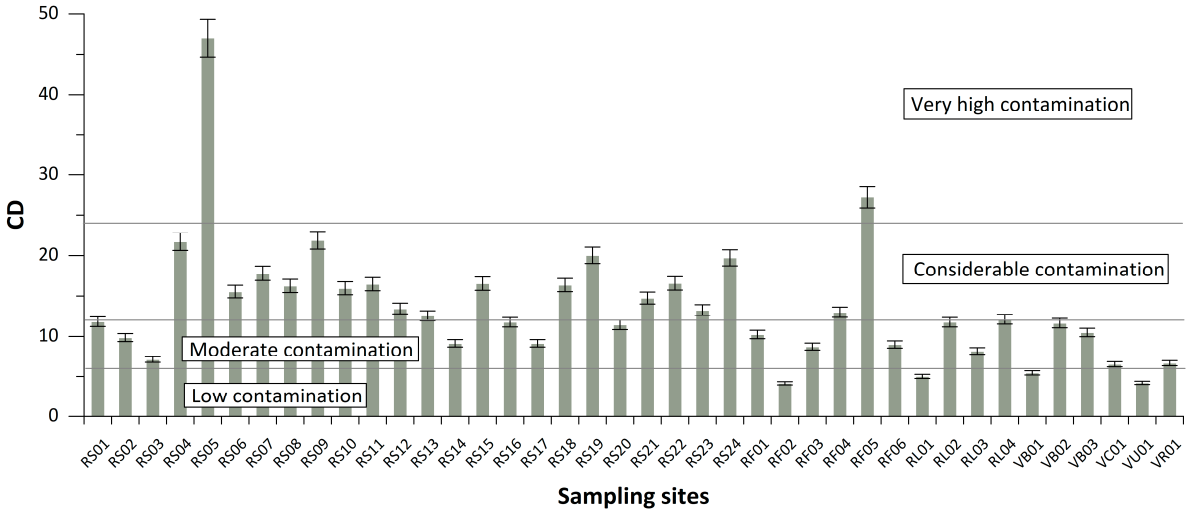

Figure 6. Contamination degree (CD) risk of PTEs in Săsar River sediments (CD < 6—low contamination, 6 ≤ CD < 12—moderate contamination, 12 ≤ CD < 24—considerable contamination, and CD ≥ 24—very high contamination).

Based on the CD results, 45% of the total number of sampling sites are considerably contaminated and 40% of samples show moderate contamination. Only 10% of the analyzed sites indicate low contamination levels.

4.2.4. Potential Ecological Risk Index (RI)

The same local accumulation of Hg in sample RS05 also contributes to an extreme RI value, suggesting a very high ecological risk in the aquatic environment (Figure 7). The potential ecological risk index is calculated based on a toxic-response factor for each metal(loid), which is substantially greater for Hg and Cd compared with the other toxic elements (see Section 3.2.2). Therefore, the RI assesses the ecological risk by mainly taking into account the Hg and Cd concentrations in a sampling location. Cd contribution was noticed in samples RS09, RS24, and RF05. In the last sample, Pb, Zn, and Cu also contributed significantly to the RI value.

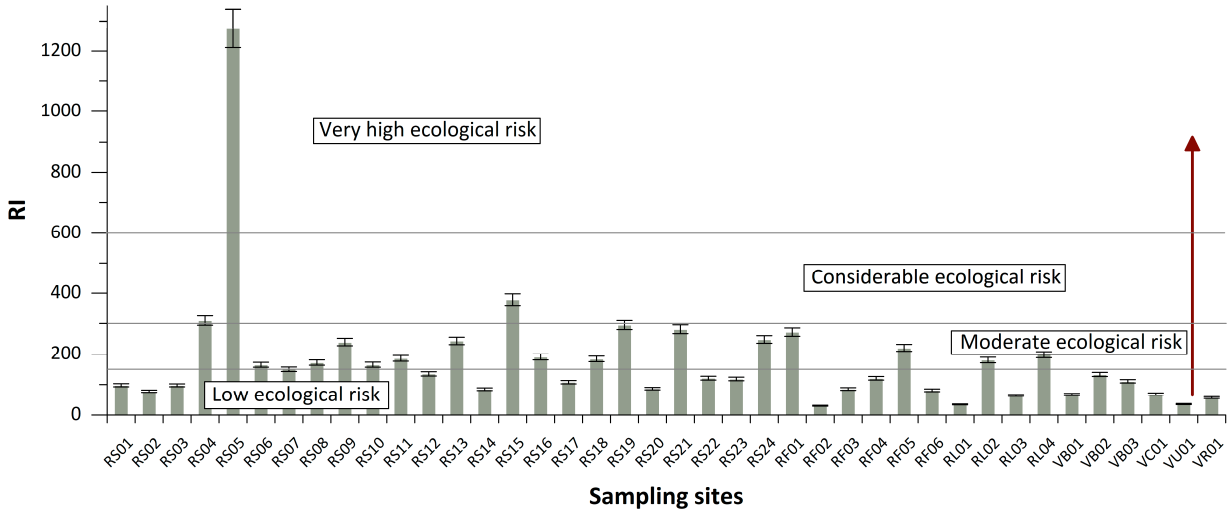

Figure 7. Potential ecological risk index (RI) in Săsar River sediments (RI < 150—low ecological risk, 150 ≤ RI < 300—moderate ecological risk, 300 ≤ RI < 600—considerable ecological risk, RI > 600—very high ecological risk).

The results show that 52.5% of the sampling points indicate a low ecological risk, while 40% show a moderate risk. Only two samples are classified to pose a considerable risk in the studied sediments.

4.2.5. Environmental Toxicity Quotient (ETQ)

The ETQ index provides a better overview of the sediments' quality concerning the impact of these hazardous compounds on human life by taking into account absolute metal toxicities. The results suggest very high (100–300) and extremely high (>300) levels of toxicity for all the sampling locations from the studied area (Figure 8). A percentage of 67.5% of samples are considered to present extremely high toxicity (ETQ > 300). The highest value was observed in sample RF05, where ETQ = 1245, with major contributions from Cu, Pb, Zn, and Mn. Significantly high values were also noticed in samples RS04, RS05, RS09, and RS22.

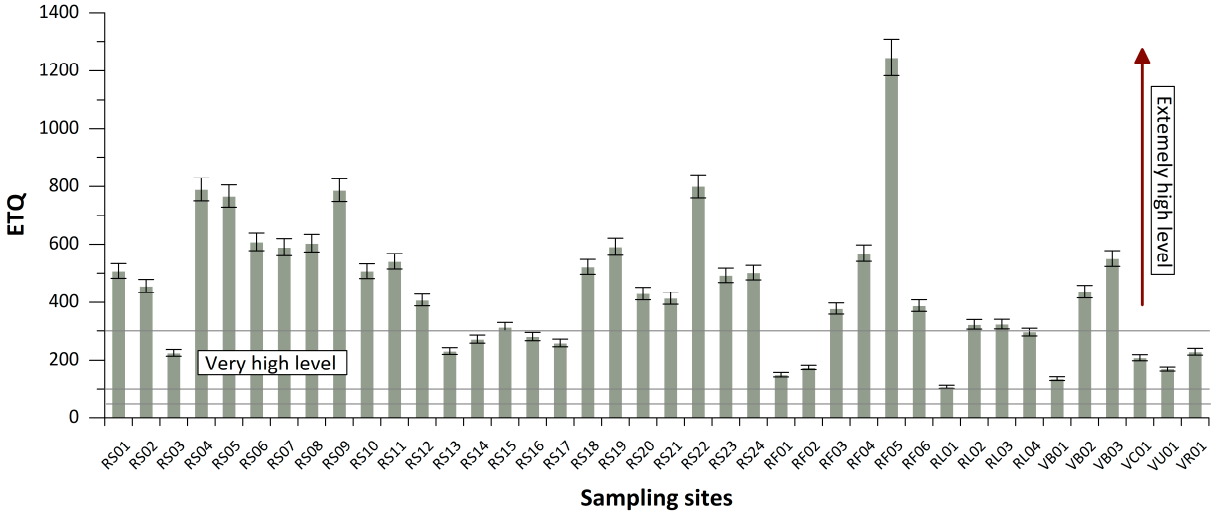

Figure 8. Environmental toxicity quotient (ETQ) in Săsar River sediments (toxic level: ETQ < 10—low, 10 ≤ ETQ < 50—moderate, 50 ≤ ETQ < 100—high, 100 ≤ ETQ < 300—very high, and ETQ > 300—extremely high).

5. Discussion

Sources of Sediment Contamination

The Săsar River crosses through one of Eastern Europe's most well-known ore deposit systems—the Baia Mare metallogenetic district, where polymetallic mineralizations (Cu-Pb-Zn-Au-Ag) have been intensively mined since ancient times. Therefore, multiple contamination sources of river sediments should be considered.

Extremely high concentrations were also observed in other river sediments from different mining sites around the globe (Table 3). In a recent study, Moldovan et al. [53] reported the concentrations of toxic elements in stream sediments of the Arieș River, Romania. Although this river drains an important area where intensive mining activities took place since Roman times, the concentrations were very low (Table 3).

The correlation matrix and hierarchical cluster analysis (Table 2 and Figure 5) reveal the sources of the studied elements from a mineralogical perspective. The Cu-Pb-Zn-As-Cd elements have their origin in ore deposits minerals, where pyrite (FeS_2), chalcopyrite ($CuFeS_2$), galena (PbS), sphalerite ($Fe_xZn_{1-x}S$), and arsenopyrite (FeAsS) are the most common sulfides. Arsenic can be also found in pyrite and sulfosalts, while Cd substitutes for Zn in the sphalerite structure [56,57]. The strong correlation between Cr and Ni suggests that these elements have a common source that might be the basaltic-andesitic rocks in the northern part of the study area. The maximum concentrations of these two elements are observed in the same sample (RS07). The association between Co and Mn suggests that their contents can be attributed to gangue minerals. Although cinnabar (HgS) is often

found in several deposits from the studied area and should be the most common source of Hg, the HCA (Figure 5) shows that Hg concentrations are not related to the other elements and might have a different source, such as gold ore processing.

The analysis of pollution indices indicates that the elements that pose higher risks to the environment are Hg, Cd, Pb, Zn, As, and Cu, which are considerably enriched in the sediments from the Săsar River catchment area. The spatial distribution maps and the pollution indices reveal two main hotspots of contamination represented by samples RF05 and RS05 (Figures 3 and 4).

Six sediment samples (RF01-RF06) were collected from the Firiza River, a major tributary of the Săsar River (Figure 2). The obtained concentrations in RF01 and RF02 are among the lowest of all the samples, as they are located in a natural area unaffected by the presence of ore deposits or mining activities. The concentrations start to rise with sample RF04, which is probably influenced by the Herja mine, and reach the maximum values in sample RF05. This sample shows the maximum contents of Pb, Zn, and Cu and relatively high contents of Cd, As, and Mn (Figures 3 and 4). All indices, with the exception of RI, highlighted RF05 as being the most contaminated sample by Pb, Zn, and Cu (±Cd): I_{geo}—moderate pollution for Zn and Cu, and a moderate to heavy contamination for Pb; EF—extremely severe enrichment for Pb, Cu, Zn, and Cd; CD—very high degree of toxicity; ETQ—extremely high degree of toxicity; RI—moderate ecological risk (Figures 6–8). The main source of such high contamination in sample RF05 is Romplumb, a metallurgical company located upstream of the sampling site (Figure 2). The company activity was lead processing from concentrated ore, which resulted in hazardous metallurgical wastes.

The concentrations of toxic elements in the Săsar River are relatively low in the first samples (RS01-RS03)—except for As that reached 488 $mg \cdot kg^{-1}$ in RS01, a sample located near a waste dump from the Șuior mine (Figure 2). The contents increase with sample RS04 and reach even higher values in RS05 (Figures 3 and 4). Even if most of the studied elements show significant concentrations in sample RS05, the pollution indices revealed that Hg is the most toxic element in this location (maximum CD and RI). The pollution source for samples RS04 and RS05 is the Baia Sprie ore deposit, an important mineralization that was intensively mined through underground work using open pits since the beginning of the 14th century [33,56]. Moreover, the Baia Sprie flotation plant is located in the same area, where ores from several mines were processed. Here, there was also an important center for Au processing through amalgamation in the past, which explains the extremely high concentration of Hg in sample RS05.

Another significant industrial activity in Baia Mare was conducted by the Cuprom company, which processed copper, resulting in the production of a substantial amount of metallurgical slag while obtaining copper concentrates. The nearby sample RS09 and to a lesser extent, the samples downstream (RS10-RS11), show high values of pollution indices (Figures 6–8) due to high contents of Cu, Zn, Cd, As, Co, and Mn.

Two other samples were highlighted by the pollution indices analysis as being contaminated: RS22 (I_{geo}, EF, and ETQ) and RS24 (I_{geo}, EF, CD, and RI). In these samples, the maximum concentrations of Co-Mn and As-Cd were observed. Sample RS22 is located near two big tailing ponds from Bozânta (Figure 2), while RS24 was collected from the upper terrace of the Săsar River, potentially indicating historical contamination from mining activities in the Baia Mare district.

One other area in the sampling map where concentrations were observed to start rising is from samples RS18 and RS19 (Figures 3 and 4). Here, a possible influence could be the Săsar mine and an ore processing plant that operated in the nearby area (Figure 2).

It is a fact that the Săsar River sediments are strongly contaminated by several sources mainly from mining activities. The final argument is supported by the concentrations observed in samples collected from the Lăpuș River, into which the Săsar River discharges. Samples RL01 and RL02 are situated upstream and downstream, respectively, of the Săsar River discharge. The concentrations of all studied elements (except Cr and Ni) are

notably higher in sample RL02 compared to RL01, indicating a substantial impact on the geochemistry of the river sediments.

6. Conclusions

Stream sediments from the Săsar River basin were analyzed for 10 potential toxic elements: Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Hg, and Pb. The geochemical distribution and pollution indices were successfully used for the first time to assess the degree of contamination in the selected area and to identify the pollution sources. This study presents novel data on the concentrations of toxic elements in river sediments from intensively mined areas. The findings are valuable for comparisons with similar polymetallic epithermal deposits worldwide.

The results suggest no contamination of Cr and Ni and a moderate enrichment of Co and Mn. Instead, the Cu, Zn, As, Cd, Hg, and Pb elements show increased overall concentrations with various levels of contamination for specific locations.

Two major hotspots were identified in the samples from the Săsar and Firiza rivers. Sample RS05 revealed very high values for all the pollution indices, suggesting an extreme degree of contamination due to the increased contents of Pb, Zn, Cu, Cd, As, and Hg. The primary source for such elevated concentrations was identified as the Baia Sprie exploitation, where both mining operations and the nearby flotation plant severely polluted the area. Moreover, gold processing by amalgamation is responsible for the high contents of Hg. In sample RF05, high values, especially of Pb, Zn, and Cu, were recorded due to the Romplumb metallurgical company whose main activity was lead processing. As expected, various other potential sources of contamination in the area significantly impacted the concentrations of river sediments, including the Cuprom company (RS09), Șuior mine (RS01), Săsar mine (RS18-RS19), and Bozânta tailing ponds (RS22).

Nevertheless, the overall concentrations of toxic elements in the Săsar River catchment area show enriched values compared with the natural background. The Baia Mare region is clearly affected by severe pollution due to intensive mining activities over the past centuries. Therefore, it is imperative to implement specific measures aimed at enhancing environmental parameters and reducing ecological risks in the area.

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