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Assessment of contamination and origin of metals in mining affected river sediments: a case study of the Aries River catchment, Romania

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Abstract: The study presents the current status of contamination with metals (Cu, Cr, Cd, Pb, Ni, Zn and As) and their anthropogenic or natural origin in the sediments of the Aries River Basin, Romania, affected by mining activities. The results indicated an enrichment of metals in the sediments. Different contamination levels of the Aries River and its tributaries were identified. According to sediment quality guidelines and contamination indices, the sediments from the Aries River were found to be highly contaminated with Cd, Cu and As, considerably with Zn and moderately with Pb and Ni. The right-bank tributaries were found to be more contaminated than the left-bank effluents, where only contamination with As of geogenic origin was identified. Principal Component Analysis enabled the identification of five latent factors (86 % total variability), reflecting the anthropogenic and natural origins of the metals. Arsenic, Cd and partially Pb were found to have a common anthropogenic origin, different from that of Cu. The statistical approach indicated also the geogenic origin of Pb due to its association with Ca, K, Na and Sr. Chromium and Ni were attributed to natural sources through their association with Mn, Fe, Al and Mg.

Keywords: river sediment; sediment quality guideline; contamination index; multivariate statistics.

INTRODUCTION

Although an important branch of the economy, mining has a negative reputation for polluting surface water and sediments with solid wastes and acidic or circumneutral mine drainage that may contain significant metal levels.[1–3] Considering their toxicity and high bioaccumulation capacity, metals are among the

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most common pollutants of soil, water and biota. Sediments are preferred in regular environment monitoring as they represent a major sink for contaminants, have higher metal concentrations than water and lower temporal variability.[4–9]

Romania has a long mining history of precious (Au and Ag) and base metals (Cd, Cu, Pb and Zn), but the inappropriate management of wastes has generated long-term pollution and even accidents with transboundary effects.[10–15] These events were the starting point for studies on water and sediment quality in mining affected catchments.[16–18] There are several studies regarding the impact of the opencast mining of porphyry Cu deposits and underground mining of auriferous pyrites on the Aries River Basin, but the origin and distribution of the contaminants in the area are still under debate.[19–25] The aim of this study was to assess the contamination level in relation to Romanian Sediment Quality Guidelines (RSQGs),[26] Consensus-Based Sediment Quality Guidelines (CBSQGs) of freshwater ecosystems[27] and several contamination indices, as well as to identify the origin of several metals (Cu, Cr, Cd, Pb, Ni, Zn and As) in the sediments of the Aries catchment, Romania.

MATERIALS AND METHODS

Site description

The Aries River (164 km in length) springs from the Bihorului Mountains and collects its tributaries on an area of around 3000 km^2. The River crosses two towns (Campeni and Baia de Aries) and several villages with a total population of 40000 inhabitants. The riverbed is surrounded by forested hills at an altitude of 1000–1200 m. The Aries Basin is of high economic importance because of the large reserves of gold and base metals and also has outstanding tourism potential through its natural reservations and caves.[20,28] The mining activities in the area encompassed the extraction of auriferous pyrite (Baia de Aries), Cu and Au ores (Rosia Montana), porphyritic Cu (Rosia Poieni) and Fe and Mg ores (Masca Baisoara). The ores were processed by flotation, while Au was extracted by the cyanide leaching procedure in Baia de Aries. Tailings and wastewaters were stored in several tailing ponds in the floodplain of the Aries River and its right-bank tributaries. Some of the mining and ore processing facilities were demolished, while others were conserved or have been abandoned. Currently, the opencast Cu mine at Rosia Poieni is in operation and the exploitation of gold and silver ores at Rosia Montana is planned to start. Although remediation measures have been undertaken, the centuries of mining activities and the poor management of the resulting wastes have led to deterioration of the ecosystem.[21,23]

Sampling

Fifteen spot samples from the sediment top layer (about 0–10 cm) were collected along the Aries riverbed over a distance of 92 km (Fig. 1). Sediment samples were also collected from tributaries in order to evaluate their possible contribution to the pollution of the main stream. Thus, samples were collected from 8 right-bank tributaries (Abrud, Stefanca, Muscani, Sesei, Harmaneasa, Cioara, Morilor and Rimetea), exposed in different extents to pollution by mining activities, and from 7 left-bank tributaries (Bistra, Valea Mare, Lupsa, Posaga, Ocolis, Ocolisel and Iara), situated outside the mining area. The sediment samples were collected using plastic shovels and transported to laboratory in polyethylene bags. The bulk sediment samples were oven dried at 105±5 °C, homogenized and sieved to pass through a 63-μm sieve.

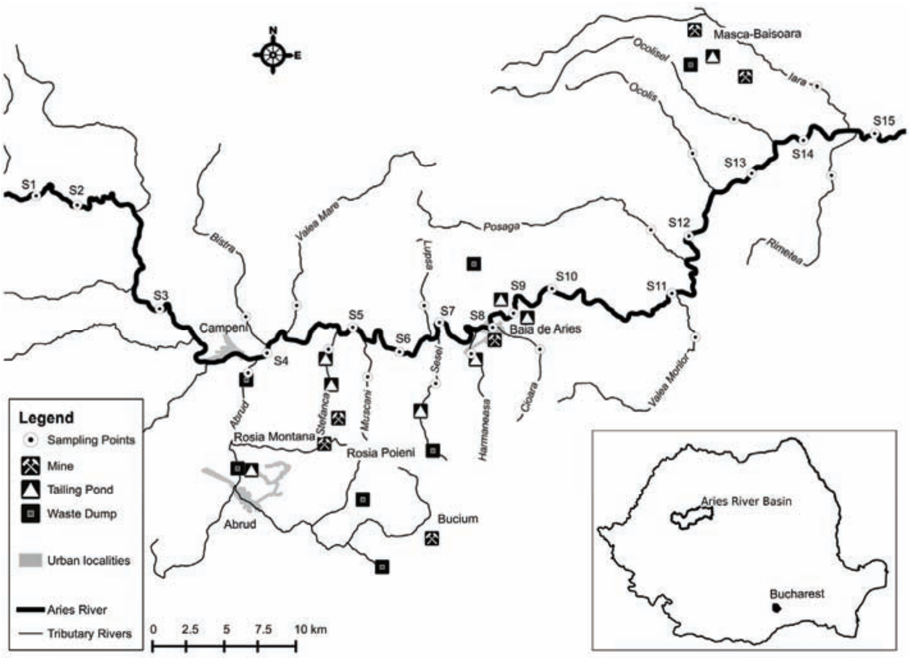


Fig. 1. Map of the sampling points and mining facilities in the Aries catchment.

Sample preparation and instrumentation

The mineral composition of the river sediments was characterized by recording X-ray powder diffraction patterns employing a high-resolution Bruker D8 Advance diffractometer (Bruker-AXS, Karlsruhe, Germany) using the CuK_α line. The metal contents in the sediments were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using OPTIMA 5300DV multichannel spectrometer (Perkin–Elmer, Norwalk, CT, USA), after *aqua regia* digestion according to ISO 11466:1995.[29] Thus, 1 g of sediment sample was subjected to digestion with 21 mL of 37 % HCl and 7 mL of 65 % HNO_3. The mixture was allowed to react overnight at room temperature, and then boiled under reflux for 2 h. After cooling, the mixture was filtered and diluted to 100 mL with ultrapure water.

Accuracy of metals determination

The accuracy of metals determination by ICP-OES was tested by analyzing two certified reference materials (CRMs), namely BCR 701 Freshwater sediment and NCS DC 78301 River sediment purchased from LGC Promochem (Wessel, Germany). In accordance with Table I, the accuracy and precision for the determination of metals in the CRMs by ICP-OES were in the range of 92–105 % and 2.0–5.5 %, respectively.

Sediment quality guidelines and contamination indices

In order to screen sediments contamination, the metal contents were compared with the threshold values in RSQGs[26] complying with EU legislation. For the assessment of ecotoxicological risk and to predict the potential effects of metals on sediment dwelling organisms, the metal concentrations were compared with the CBSQGs for freshwater ecosystems.[27] For assessment of the extent of contamination in the catchment, several indices were calculated for the metals: the enrichment factor (*EF*, Eq. (1)) according to Sinex and Helz,[30] the geoaccumulation index (*I*geo, Eq. (2)) introduced by Muller,[31] and the contamination factor (*CF*, (Eq. (3)) and contamination degree (*CD*) according to Hakanson.[32] The background level used to calculate the indices was the elemental composition of the continental crust according to Taylor and McLeenan:[33] Pb 20, Cu 25, Zn 71, As 1.5, Cd 0.098, Ni 20, Cr 35 and Fe 35000 mg kg^{-1}. Considering that Fe in sediments results mainly from natural weathering processes, it was used for the geochemical normalization of the metals:[34]

$$EF = \frac{([\mathrm{Me}]/[\mathrm{Fe}])_{\mathrm{sample}}}{([\mathrm{Me}]/[\mathrm{Fe}])_{\mathrm{background}}} \tag{1}$$

where [Me]/[Fe] refers to the metal-to-Fe ratio in the sediment sample or background.

TABLE I. Comparison of the found content of metals (mg kg^{-1}, n = 3 parallel samples) with the indicated/certified values in the certified reference materials

Element	BCR 701 Freshwater sediment		NCS DC 78301 River sediment		Average recovery %	Pooled *SD* %
	Certified[a]	Found[a]	Certified[a]	Found[a]		
As	–[b]	56±6	56±5	59±5	105	4.0
Cd	11.7±1.0	10.3±1.5	2.45±0.2	2.35±0.3	92	5.5
Cr	272±20	280±12	90±4	88±5	100	2.0
Cu	275±13	276±15	53±3	52±3	99	2.3
Mn	–[b]	675±45	975±17	920±40	94	2.3
Ni	103±4	100±8	32[c]	30±3	95	3.6
Pb	143±6	140±6	79±6	83±8	102	3.0
Zn	454±19	458±14	251[c]	245±25	99	3.0

[a]Mean±*U*, where *U* expanded uncertainty for 95 % confidence level; [b]not certified; [c]indicative value

Values of *EF* < 1 indicate no enrichment, while values >1 indicate different degrees of enrichment.

Geoaccumulation index resulted from comparing the current concentration of the elements in the sediments with their background values:

$$I\mathrm{geo} = \log_2\left(\frac{c_\mathrm{n}}{1.5B_\mathrm{n}}\right) \tag{2}$$

where c_n is the concentration of metal examined in sediments and B_n is the geochemical background concentration of metal (n). Based on the *I*geo values, seven pollution classes were defined, ranging from unpolluted to extremely polluted.

Contamination factor of a metal was computed by dividing its concentration in sediment by its background concentration. According to *CF* values, sediments contamination was classified as low, moderate, considerable or very high:

$$CF = \left(\frac{c_\mathrm{n}}{B_\mathrm{n}}\right) \tag{3}$$

Summation of *CF* values for seven metals (As, Cd, Cr, Cu, Ni, Pb and Zn) gave the contamination degree (*CD*) describing, according to Hakanson,[32] the quality of the sediments. Based on the *CD* values, the sediments were classified into four classes corresponding to: low ($CD \leq 8$), moderate ($8 < CD \leq 16$), considerable ($16 < CD < 32$) and very high contamination ($CD > 32$).

Statistical analyses

The normality of all data was assessed by the Shapiro–Wilk test, while the Mann–Whitney U test was used to assess significant differences between the metal contents in the main stream and its tributaries.

Multivariate exploratory techniques, such as principal component analysis (PCA), hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) are widely applied to evaluate water and sediment quality through data reduction and classification.[35-37] These techniques can be used to obtain relationships between parameters and sampling sites, or to identify the important factors and sources influencing sediment quality.[38] PCA was used to outline the anthropogenic or natural origin of contaminants and to assess their specific input from tributaries to the main stream. A previous study revealed that tailings deposited in the Aries River Basin pose high contamination risk for the sediments, especially by As, Cd, Cu and Pb.[39]

HCA and LDA were used to group the sediments (sites) in relation to their degree of metal contamination. The statistical approach is useful in case of complex systems such as sediment as it offers the possibility to establish correlations or differences between multiple parameters or sites considered in a study.[40,41] Given the complexity of real field circumstances, the study took into consideration seven metals likely to be of anthropogenic origin and metals normally present in sediments from natural sources (Na, K, Ca, Mg, Ba, Sr, Al, Fe and Mn). For the multivariate statistical analysis, all parameters were *z*-scale standardized (mean = 0; variance = 1) in order to avoid misclassifications arising from the different orders of magnitude of the studied parameters.[42] In order to define the geogenic and anthropogenic origin of the contaminants, PCA was applied on the standardized data, as this method is considered very efficient for this purpose. According to the Kaiser criterion, only the PCs with eigenvalue higher than 1.0 were retained and subjected to varimax rotation. Factor loadings used to determine the relative importance of a variable as compared to other variables in a PC were classified as "strong", "moderate" and "weak" corresponding to absolute loading value of >0.75, 0.50–0.75, and 0.30–0.50, respectively.[43] Positive values on each component are related to important inputs, whereas negative values correspond to low input. Hierarchical Cluster Analysis (HCA) and LDA allow the grouping of sampling sites based on their similarities. HCA was realized by means of the Ward linkage method using squared Euclidian distance as a measure of similarity. LDA in the standard mode was applied to construct the discriminant function for an adequate classification of sediments/sites sharing similar pollution levels.[41] The statistical analysis was performed using Microsoft Office Excel 2007 with XLSTAT plug-in (Addinsoft).

RESULTS AND DISCUSSION

Mineralogical composition of the sediments

The X-ray diffraction analysis emphasized the presence of silicates (quartz, SiO_2 and albite, $NaAlSi_3O_8$) as the major class of minerals (20–50 %) in all sediments. However, differences in the mineralogical composition of sediments were observed. Muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) was found as the major constituent (20–50 %) in all tributaries and as a minor constituent (5–20 %) in the Aries River sediments. Orthoclase ($AlKSi_3O_8$) and illite ($KAl_2(Si_3Al)O_{10}(OH)_2$) were identified as minor minerals (5–20 %) in the sediments of the tributaries, while in those from the Aries River, they were present only in traces (<5 %). In contrast, feldspar ($Al_2CaO_8Si_2$) and clinochlore ($(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$) were identified as minor minerals (5–20 %) in the Aries River sediments and in traces (<5 %) in the tributaries. Traces of cuprite (Cu_2O) and calcopirite ($CuFeS_2$) were found in the sediments of the Muscani and Sesei Tributaries, respectively. Effenbergerite ($BaCu(Si_4O_{10})$) was identified as a minor mineral (5–20 %) in the Muscani, Sesei and Cioara Tributaries. Anglesite ($PbSO_4$) was identified in traces (<5 %) in the sediments from sampling points S6–S10, situated in the area with maximum pollution. Minerals from the carbonate group, such as dolomite ($CaMg(CO_3)_2$) were identified as a minor component (5–20 %) in the sediments of the Aries River upstream from the pollution sources (S1–S3), while calcite ($CaCO_3$) was identified in some of sediments of the right side tributaries.

Metal contents and sediment quality

The metal concentrations in the sediments from the Aries River and its tributaries are presented in Tables II and III. Although strictly speaking, As is a metalloid, the term metal will be used in this paper to include all the elements under discussion. Examination of data revealed high variability of the Cu, Zn, Cd and Fe content in the sediments collected from the main stream. Differences among metal concentrations in sediments from the left-side tributaries were small, while sediments from the right-bank exhibited a much larger variability for As, Cd, Cu, Pb and Zn. The Shapiro–Wilk test showed that the metal contents in the sediments did not follow a normal distribution ($p < 0.05$). Thus, to evaluate the similarity or difference in the contents of each metal between the main stream and its right/left side tributaries, the non-parametric Mann–Whitney *U*-test was applied. According to this test, the main stream was differentiated ($p < 0.05$) from the left side tributaries, situated outside the mining area, with respect to the Pb, Cu, Zn, As and Cd contents, and from the right side tributaries that drain the mining area with respect to the Pb, Zn, Cd, Ni and Cr contents.

The guideline values for metals used for the characterization of sediment quality are presented in Table IV. According to Romanian legislation, sediments are considered unpolluted if the metal content is lower than the corresponding threshold value. According to the CBSQGs, sediments are predicted to be non-toxic if the metal concentration is lower than the corresponding threshold effect concentration (*TEC*), while those with a metal content exceeding the probable effect concentration values (*PEC*) are predicted to be toxic. Sediments with a metal concentration between the *TEC* and *PEC* values are predicted to be neither

TABLE II. Concentration (mg kg^{-1}) of metals in the sediments of the Aries River

Site	Pb	Cu	Zn	As	Cd	Ni	Cr	Mn	Fe	Al	Ca	K	Mg	Na	Sr	Ba
S1	21.2	8.69	84.7	8.23	0.256	12.3	16.2	542	14256	9945	9170	1536	6706	214	11.9	68.4
S2	17.6	7.80	77.2	9.12	0.100	13.3	14.0	305	13197	9544	9034	1484	7067	151	10.0	54.1
S3	26.6	21.2	136	14.2	0.343	16.4	20.1	589	17431	16058	7988	2604	9869	208	14.0	65.1
S4	23.2	37.2	250	13.4	0.845	53.4	33.1	1110	15173	14364	5072	1674	8146	153	14.3	86.7
S5	27.6	40.6	229	16.4	0.777	32.0	24.5	761	14247	17017	3871	2232	6380	179	16.8	86.7
S6	25.7	54.9	275	12.5	1.15	20.4	21.1	1164	13457	15396	5181	1871	8705	153	17.0	69.6
S7	25.4	180	153	13.2	0.376	18.6	15.3	486	10895	13531	2727	1755	5592	155	12.5	65.9
S8	37.3	120	179	14.0	0.818	19.3	17.7	697	11279	13417	4419	1904	7085	156	13.9	57.8
S9	33.6	195	233	16.4	0.981	19.2	14.7	789	10411	12527	3454	1550	6177	164	10.5	39.6
S10	32.1	534	594	18.2	1.57	24.3	20.6	1858	33200	22341	4516	2430	8090	187	14.7	62.4
S11	17.8	320	240	12.4	0.900	26.8	18.6	733	10593	13468	4888	2547	6588	228	22.4	71.6
S12	21.0	187	228	14.6	0.968	27.1	19.8	705	11159	15935	3853	2587	6977	189	14.8	62.3
S13	15.3	188	116	16.4	0.510	29.3	23.8	937	37900	21000	9000	3400	9150	118	15.0	54.0
S14	22.6	163	228	16.4	0.939	26.9	20.6	795	10950	15870	5536	2590	7283	166	17.6	61.8
S15	41.5	347	338	23.0	1.87	42.1	32.0	1159	40300	25204	7362	3049	8556	199	23.9	113
Min.	15.3	7.80	77.2	8.23	0.100	12.3	14.0	305	10411	9544	2727	1484	5592	118	10.0	39.6
Max.	41.5	534	594	23.0	1.87	53.4	33.1	1858	40300	25204	9170	3400	9869	228	23.9	113
Average	25.9	160	224	14.6	0.827	25.4	20.8	842	17630	15708	5738	2214	7491	175	15.3	68.0
SD	7.5	149	126	3.59	0.479	10.9	5.67	373	10375	4329	2189	588	1209	29.5	3.88	17.3

TABLE III. Concentration (mg kg^{-1}) of metals in the sediments of the tributaries of the Aries River

Site	Pb	Cu	Zn	As	Cd	Ni	Cr	Mn	Fe	Al	Ca	K	Mg	Na	Sr	Ba
Right-bank tributaries																
Abrud	2.84	10.7	734	3.05	0.305	3.30	2.07	1168	39102	20812	4950	3045	6015	285	2.90	7.50
Stefanca	13.4	68.0	69.4	11.7	0.133	18.7	10.9	416	9459	9899	4641	1711	4806	243	22.3	57.8
Muscani	95.1	581	186	12.8	0.832	12.1	10.2	513	12495	15215	2807	2646	5342	390	53.5	192
Sesei	19.8	167	59.3	10.4	0.219	5.10	6.30	109	16614	10199	2697	1614	4473	141	6.50	28.9
Harmaneasa	189	33.0	139	23.2	1.54	19.7	16.5	1523	9649	12575	52495	3510	5402	264	36.0	72.3
Cioara	37.9	19.7	108	14.5	0.268	20.2	13.2	530	9875	10489	16677	3590	5563	188	23.3	67.4
Morilor	16.1	21.0	64.0	6.08	0.205	20.8	18.7	596	9596	15133	17878	2804	5374	267	12.9	67.7
Rimetea	57.1	10.8	65.2	4.90	0.154	14.7	14.2	1480	34365	17945	54530	3533	5655	480	78.6	103
Min.	2.84	10.7	59.3	3.05	0.133	3.30	2.07	109	9459	9899	2697	1614	4473	141	2.89	7.50
Max.	189	581	734	23.2	1.54	20.8	18.7	1523	39102	20812	54530	3590	6015	480	78.6	192
Average	53.9	114	178	10.8	0.457	14.3	11.5	792	17644	14033	19584	2807	5329	282	29.5	74.6
SD	62.2	196	229	6.43	0.491	6.93	5.41	527	12092	3970	21777	788	485	108	25.7	55.5
Left-bank tributaries																
Bistra	15.4	17.0	80.6	9.26	0.095	21.0	22.7	468	11939	12842	2489	1114	7375	151	12.5	50.8
Valea Mare	30.5	21.4	62.4	6.68	0.210	8.04	14.2	282	10136	8574	3664	1212	3435	179	17.3	23.1
Lupsa	13.7	19.4	89.0	11.1	0.141	19.9	22.3	369	10621	13892	6887	2367	7123	196	22.0	60.4
Posaga	11.6	13.3	56.9	6.80	0.180	16.1	21.6	357	10461	12448	5737	1708	8180	190	12.5	45.3
Ocolis	13.4	14.2	80.4	9.00	0.120	19.5	14.6	448	9881	15711	7344	3300	8378	207	36.3	79.9
Ocolisel	16.6	17.5	67.3	12.3	0.201	16.3	18.7	324	9707	13408	7754	2567	5965	139	18.2	84.8
Iara	21.4	12.5	68.4	15.2	0.184	18.4	16.2	576	8795	13811	7977	3245	4549	146	21.2	66.1
Min.	11.6	12.5	56.9	6.68	0.095	8.04	14.2	282	8795	8574	2489	1114	3435	139	12.5	23.1
Max.	30.5	21.4	89.0	15.2	0.210	21.0	22.7	576	11939	15711	7977	3300	8378	207	36.3	84.8
Average	17.5	16.5	72.1	10.0	0.162	17.0	18.6	403	10220	12955	5979	2216	6429	173	20.0	58.6
SD	6.53	3.30	11.5	3.06	0.043	4.36	3.67	100	965	2194	2138	900	1869	27.0	8.11	21.2

TABLE IV. Guideline values for metals for characterization of sediment quality

Element	RSQGs[a]	CBSQGs[b]	
	Threshold value, mg kg^{-1}	*TEC*[c], mg kg^{-1}	*PEC*[d], mg kg^{-1}
Pb	85	35.8	128
Cu	40	31.6	149
Zn	150	121	459
As	29	9.79	33.0
Cd	0.8	0.99	4.98
Ni	35	22.7	48.6
Cr	100	43.4	111

[a]Romanian Sediment Quality Guidelines[26]; [b]consensus-based Sediment Quality Guidelines[27]; [c]threshold effect concentration; [d]probable effect concentration

toxic nor non-toxic. The status of metal contents in the sediments according to the RSQGs and CBSQGs associated to relative frequency of occurrence (%) are exhibited in Fig. 2. Sediments in the main stream were found to be polluted with Cu, Cd and Zn. Sediments from the left-side tributaries exhibited values below

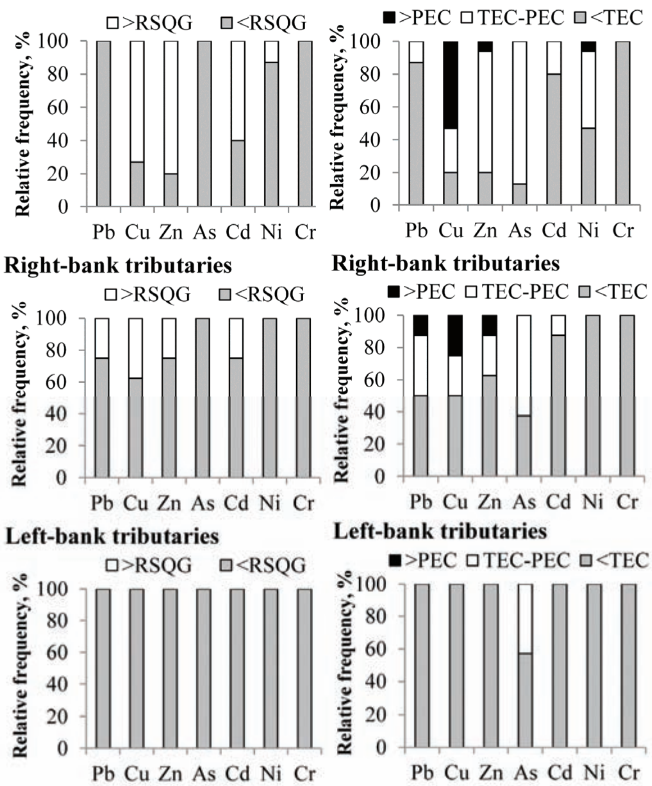
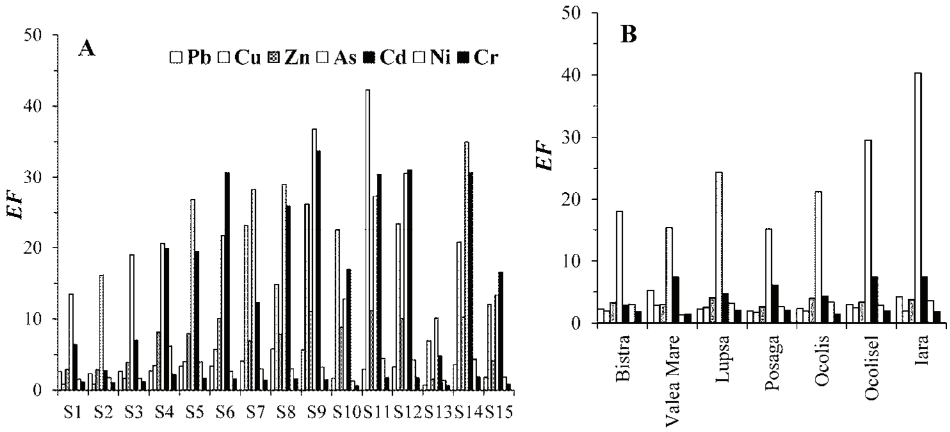


Fig. 2. Status of metal contents in the sediments of the Aries River and its tributaries in relation to the RSQGs and CBSQGs values and the relative frequency of occurrence.

the RSQGs for Pb, Cu, Zn, As, Ni, Cd, and Cr, while the *TEC* value for As was exceeded in 3 tributaries. Sediments from the right-bank tributaries revealed differences in terms of pollution and toxicity in relation to a particular contaminant. Differences in sediments ranking according to the two guidelines are because the RSQGs set the threshold values for the polluted or unpolluted status assessment, while the CBSQGs provide a basis for toxicity or non-toxicity prediction. However, good agreement between the rankings of sediments by the two guidelines was observed for Cu, Zn, Pb and Cr, while differences appeared in the case of As, Cd and Ni.

The classification of the sediments from the Aries River and its tributaries of different pollution levels according to contamination indices are presented in Figs. 3–6. Figure 3 shows the enrichment of the metals in the sediments of the Aries River and the increase in pollution from upstream to downstream, which supports the role of the river in collecting contaminants from its tributaries. Values of the *EF* < 1.5 indicate a lithological source of the element, while values



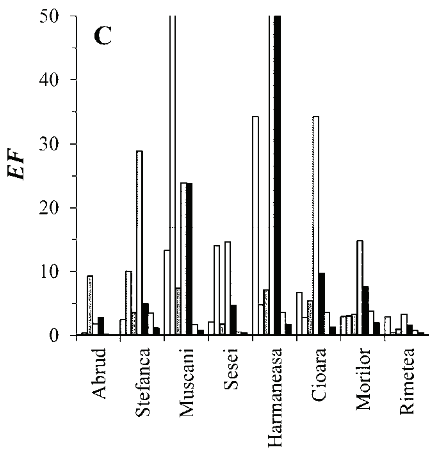
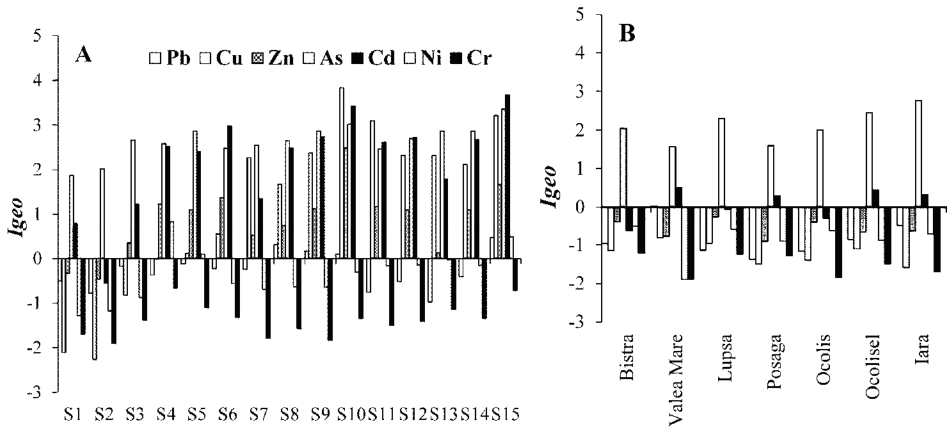


Fig. 3. Metal enrichment factor (*EF*) in the sediments: a) Aries River, b) left-bank tributaries, c) right-bank tributaries. No enrichment (*EF* < 1), minor (1 ≤ *EF* < 3), moderate (3 ≤ *EF* < 5), moderately severe (5 ≤ *EF* < 10), severe (10 ≤ *EF* < 25), very severe (25 ≤ *EF* < < 50) and extremely severe (*EF* > 50) enrichment.[30]

of the *EF* > 10 suggests an anthropogenic origin.[44] Values of the *EF* > 10 were found for As, Cd and Cu in sediments from the Aries River, for As, Cd, Cu and Pb in the right bank tributaries and As in the left bank tributaries, suggesting anthropogenic origins of these elements.



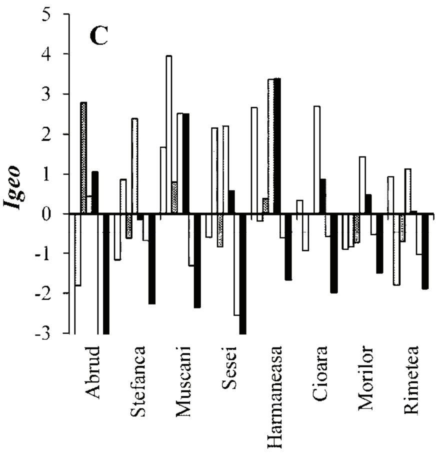


Fig. 4. Metal geoaccumulation index (*I*geo) in the sediments: a) Aries River, b) left-bank tributaries, c) right-bank tributaries. Practically unpolluted (*I*geo ≤ 0), unpolluted to moderately (0 < *I*geo ≤ 1), moderately (1 < *I*geo ≤ 2), moderately to heavily (2 < *I*geo ≤ 3), heavily (3 < < *I*geo ≤ 4), heavily to extremely (4 < *I*geo ≤ 5) and extremely (*I*geo > 5) polluted.[31]

Figure 5 shows that the enrichment of metals in the sediments followed the order: Cr < Ni < Pb < Zn < Cu < Cd < As, which corresponded to different levels of contamination: very high for Cu, Cd, As (10 < *CF* < 11), considerable with Zn (*CF* =3.8), moderate with Pb and Ni (*CF* =1.4) and no contamination with Cr. Results indicated also the existence of local peaks, of which the most representative was S10 site with a *CF* values of 21 (Cu), 16 (Cd), 12 (As) and 8.4 (Zn) and an overall *CD* of 61. The sediments of the right-bank tributaries were found to exhibit moderate to very high degrees of contamination. The data showed different index pattern of right-bank tributaries with respect to As, Cu, Cd and Pb (Harmaneasa, Muscani, Sesei, Cioara and Stefanca). The Abrud River differentiated itself from the other tributaries by the high Zn content in the sediment. After the confluence of the right-bank tributaries with the Aries River, an increase of the metal loading in the sediment was observed (sites S4–S7), corresponding to a considerable contamination with Cu and Zn and very high contamination with Cd and As. Sediments from the left-bank tributaries showed moderate degrees of contamination and lower metal loadings. Their classification as moderately to heavily polluted according to *I*geo and very high contaminated according to *CF* was mainly due to As. Interestingly, the contamination of sediments with As was found to increase from west to east (Posaga, *CF* = 4.5; *I*geo = = 1.6; *EF* = 15; Ocolis, *CF* = 6.0; *I*geo = 2.0, *EF* = 21; Ocolisel, *CF* = 8.2, *I*geo = = 2.5, *EF* = 30; Iara, *CF* = 10; *I*geo = 2.8 and *EF* = 40) and the same was true for the main stream. In the absence of anthropogenic sources on the valley of the left-bank tributaries, the presence of As was attributed to the mineralogy of the local bedrock.

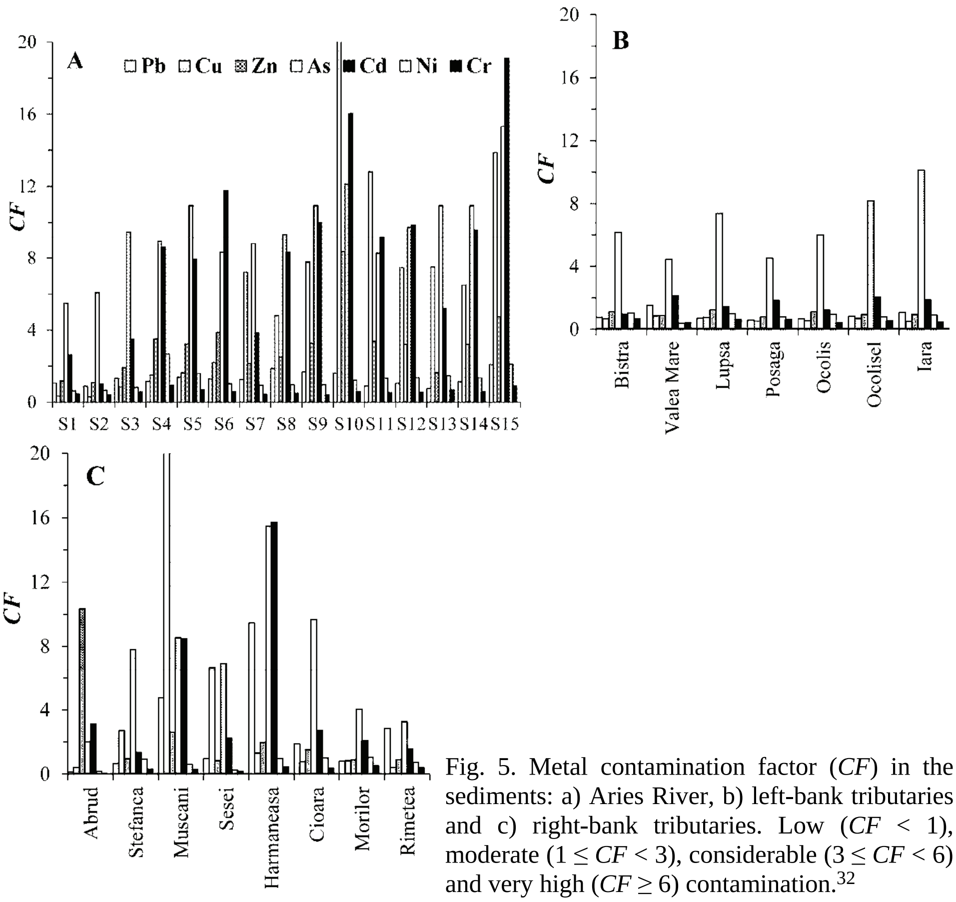


Fig. 5. Metal contamination factor (*CF*) in the sediments: a) Aries River, b) left-bank tributaries and c) right-bank tributaries. Low (*CF* < 1), moderate (1 ≤ *CF* < 3), considerable (3 ≤ *CF* < 6) and very high (*CF* ≥ 6) contamination.[32]

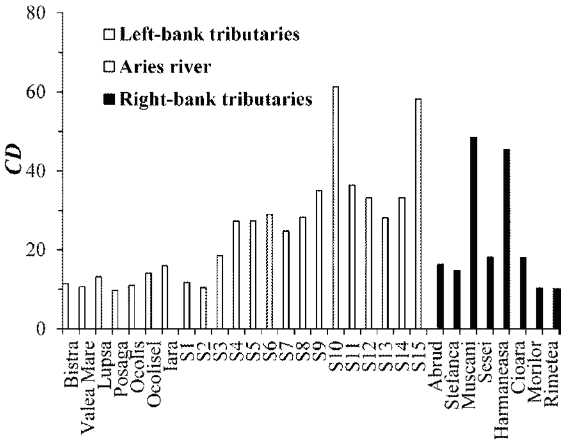


Fig. 6. Contamination degree (*CD*) of the sediments in the Aries River and its tributaries. Low ($CD \leq 8$), moderate ($8 < CD \leq 16$), considerable ($16 < CD < 32$) and very high ($CD > 32$) contamination degree.[32]

Multivariate statistics

The varimax rotated loadings of the five PCs with eigenvalues higher than 1 of the metal contents in sediments are presented in Table V. Five latent factors cumulated 86 % of the total variance and described different sources for the metals in the sediments. The first latent factor explaining 32 % represents sediment pollution with As and Cd (strong influence) and Pb and Cu (moderate influence) of anthropogenic origin, as suggested by the lack of correlation with naturally occurring metals, such as alkaline and alkaline earth elements. This factor was ascribed to the right-bank tributaries with very highly contaminated

TABLE V. Varimax rotated factor loadings of significant PCs; * – strong influence on the latent factor; ** – moderate influence on the latent factor

Metal	PC1	PC2	PC3	PC4	PC5
Pb	0.630**	0.612**	–0.123	–0.156	0.246
Cu	0.571**	–0.412	0.351	–0.081	0.502**
Zn	0.301	–0.197	0.821*	–0.135	–0.155
As	0.809*	0.075	0.037	0.414	–0.004
Cd	0.825*	0.025	0.382	0.267	0.068
Ni	0.292	–0.035	0.117	0.834*	0.069
Cr	0.163	–0.044	0.025	0.924*	0.009
Mn	0.405	0.433	0.686**	0.154	0.018
Fe	–0.068	0.110	0.872*	0.067	0.061
Al	0.111	0.027	0.851*	0.335	0.197
Ca	0.038	0.945*	0.027	–0.077	0.152
K	0.032	0.570**	0.384	0.079	0.282
Mg	–0.071	–0.140	0.381	0.699**	–0.053
Na	–0.140	0.463	0.241	–0.371	0.651**
Sr	–0.039	0.557**	0.017	–0.067	0.755*
Ba	0.232	0.056	–0.045	0.216	0.889*
Variability, %	32	22	14	10	8

sediments, namely Harmaneasa (Pb, As and Cd), Muscani (As, Cd and Cu), Sesei (As and Cu) and Cioara and Stefanca (As). The second PC with 22 % of total variance was correlated with the natural input of Pb (moderate influence), as shown by the positive loadings with alkaline and alkaline earth elements of geogenic origin. The third factor exhibiting 14 % of the total variance was indicative for the natural origin of Zn (strong influence) in the sediments, confirmed by the concomitant positive loadings with Mn, Fe and Al. The most probable source of Zn was the Abrud River, as shown above. The fourth factor accounting for 10 % of the total variance had positive loadings with Ni and Cr of geogenic origin, since most sediments exhibited minor enrichment/low contamination with these metals. The natural source of Ni and Cr is consistent with the moderate influence of Mg on PC4, as its minerals act as host-rocks for Ni and Cr.[45,46] In the Aries Basin, Mg minerals are associated with those belonging to the silicate and carbonate group, which explains the presence of Al in this factor, albeit with a weak influence on this factor.[45] The last PC explaining 8 % of the total variance is associated with anthropogenic contamination of sediments by Cu, especially through the Muscani and Sesei Tributaries as their sediments were found to be very high contaminated with Cu. The results are in good agreement with the mineralogical analysis. The presence of Ba in this factor is related to wastes from the processing of Cu ores.[47] The results of the HCA are displayed in Fig. 7. The cluster C1 groups the elements of geogenic origin (Pb, Ca, K, Na and Sr) and supports the idea that the natural input of Pb from bedrock in sediments is more significant than the anthropogenic source identified by PCA. The association of Zn with Mn, Fe and Al in the cluster C2 confirmed the natural origin of Zn. The cluster C3 is divided in two sub-clusters, one of which confirms the natural origin of Cr and Ni following the correlation with Mg, and the other proving the anthropogenic origin of As, Cd and Cu. A similar origin of Ni and Cr was also found in the case of mine tailings deposited in the Aries River basin.[39] This shows the greater influence of the anthropogenic origin of As from the right-bank tributaries compared with the natural source of the left-side tributaries on the sediments in the main stream. The natural origin of Cr, Ni, Zn and the anthropogenic origin of As, Cd and Cu identified by the PCA and CA is in accordance with that suggested by their enrichment factors.

The clustering of the sampling sites according to their contents of metals is presented in Fig. 8. The sampling sites were clustered in two groups according to the contamination degree: moderate to considerable (C1) and considerable to very high contamination (C2). This grouping is in agreement with the contaminant distribution in the studied sites and was confirmed by LDA with a 90 (C1) and 85 % (C2) prediction, respectively.

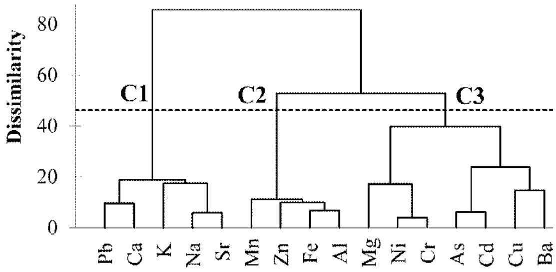


Fig. 7. Dendrogram showing the clustering of the metals in the sediments from the Aries River catchment.

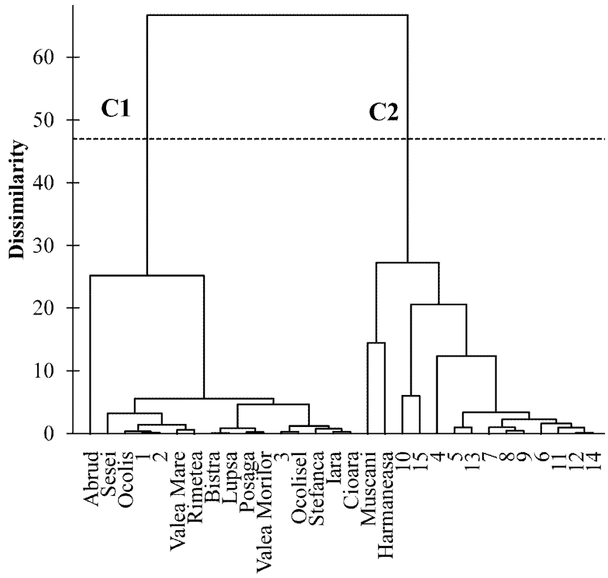


Fig. 8. Dendrogram showing the clustering of the sediments sampling sites from the Aries River catchment considering their metals contents.

CONCLUSIONS

A comprehensive insight of the current status of sediment contamination with metals and the potential origin of contaminants in the Aries River catchment has been provided. Guidelines and contamination indices were used to evaluate the contamination of the sediment, while multivariate statistical approaches allowed for the clarification of the anthropogenic or natural origin of seven metals. The obtained results indicated metal enrichments in sediment in the order Cr<Ni<Pb<Zn<Cu<Cd<As. The enrichment factors of the metals and the degree of contamination of the sediments in the Aries River increased from upstream to downstream with local peaks, demonstrating that the River remained a collector for pollutants coming mostly from the mine-affected right-side effluents. Sedi-

ments of the Aries River were found to be very highly contaminated with Cd, Cu and As, considerably with Zn, moderately with Pb and Ni, and low with Cr. The right-bank tributaries were found to be very highly contaminated with Pb, As and Cd (Harmaneasa), As, Cd and Cu (Muscani), Cu and As (Sesei), As (Cioara and Stefanca) and Zn (Abrud). In contrast, the sediments from most of the left-side effluents were classified as very high contaminated only because of As. The PCA, HCA and LDA brought increased knowledge and contributed to a better understanding of the sediment pollution phenomena in the Aries River basin. The anthropogenic origin of As, Cd, Cu and some Pb in the main stream and the right-side tributaries was established. However, the anthropogenic source of Cu was found to be different from that of As, Cd and Pb. The geogenic input of Pb was confirmed by its association with Ca, K, Na and Sr in a common PC and cluster. The anthropogenic loading of As in the sediments from the right-side tributaries was much higher as compared to the geogenic one from the left-bank tributaries. Zinc occurred especially from natural source due to its retention on minerals containing Mn, Fe and Al and came mainly from the Abrud River. Nickel and Cr were found to be of natural origin according to their association with Mg.

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И З В О Д

ПРОЦЕНА ЗАГАЂЕЊА И ПОРЕКЛА МЕТАЛА У РЕЧНИМ СЕДИМЕНТИМА ПОГОЂЕНИХ РУДАРСТВОМ: СТУДИЈА СЛУЧАЈА ЗАХВАТА НА РЕЦИ *ARIES* У РУМУНИЈИ

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Ова студија представља тренутни статус загађења металима (Cu, Cr, Cd, Pb, Ni, Zn и As) и њиховог антропогеног порекла у седиментима базена реке *Aries* у Румунији, који је погођен рударским активностима. Резултати указују на обогаћење седимената металима. Идентификовани су различити нивои загађења у реци *Aries* и њеним притокама. Према упутствима за квалитет седимената и индекса загађења, нађено је да су седименти из реке *Aries* високо загађени са Cd, Cu, As, значајно са Zn и умерено са Pb и Ni. Нађено је да су десне притоке више загађене него леве, у којима је нађен само As геолошког порекла. Статистичком PCA методом је идентификовано пет латентних фактора (са укупном варијабилношћу од 86 %), што одражава антропогено и природно порекло метала. Нађено је да As, Cd и делимично Pb имају заједничко антопогено порекло, различито од Cu. Статистички приступ је такође указао на геолошко порекло Pb, због своје повезаности са Ca, K, Na и Sr. Хром и Ni су приписани природном извору, на основу њихове повезаности са Mn, Fe, Al и Mg.

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