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Assessment of minor elements contamination in Bistriţa River sediments (upstream of Izvorul Muntelui Lake, Romania) with the implication of mining activity

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ABSTRACT

This study is based on the distribution and risk assessment of pollution with minor elements in the surface sediments of the Bistriţa River, Romania (upstream Izvorul Muntelui Lake).

The concentrations for the elements Cr, Co, Ni, Cu, Zn, Cd, Pb and As were measured by X-ray fluorescence and the results vary between 39 and 99 $mg \cdot kg^{-1}$ for Cr, 11.2 to 38.5 $mg \cdot kg^{-1}$ — Co, 16 to 48 $mg \cdot kg^{-1}$ — Ni, 17 to 451 $mg \cdot kg^{-1}$ — Cu, 50 to 1117 $mg \cdot kg^{-1}$ — Zn, 0.11 to 2.38 $mg \cdot kg^{-1}$ — Cd, 17 to 139 $mg \cdot kg^{-1}$ — Pb and 8.2 to 170 $mg \cdot kg^{-1}$ — As.

Several indicators of contamination as pollution load index (PLI), contamination factor (CF), ecological risk index (RI), geoaccumulation index (I_{geo}) and priority index (P_{index}) were used to assess the degree of minor element pollution. The contribution of each chemical element in PLI for the entire length of the river, is the following: As (15.6%) > Cu (14.9%) > Zn (13.6%) > Cd (12.2%) > Pb (11.8%) > Co (10.7%) > Ni (10.6%) = Cr (10.6%). P_{index} confirms the very high contamination with Cd, As and Cu in a single sampling point. CF for each element indicates only a local high contamination for Cu, Pb, Zn, As and Cd.

1. Introduction

The heavy metal concentration in sediments is in close relation with the geological setting, as well as with some anthropogenic activity (Wijaya et al., 2013). The minor element contamination in sediments can affect the water quality and has drawn attention due to their toxicity, persistence and biological accumulation (Li et al., 2013). These toxic elements can be introduced into aquatic environments by anthropogenic sources and therefore it is critical to assess the contamination in sediments and to understand the river pollution status (Jiang et al., 2013). Different pollution indices such as the enrichment factor (EF), pollution load index (PLI), ecological risk index (RI), geoaccumulation index (I_{geo}) and priority index (P_{index}) have been successfully used to estimate the impact of human activities on sediment quality (Jiang et al., 2013; Kabir et al., 2011; Mohiuddin et al., 2010; Olubunmi, 2010; Wijaya et al., 2013; Yang et al., 2009). Besides all of these, another way to assess the contamination level more accurately is by using the geochemical background. Moreover, the use of the pollution indices together with the geochemical background values, can give more suitable information about contamination levels and sources. The integration of geochemical background for the same river in the pollution indices analysis helped to eliminate any errors in establishing the possible contamination sources.

The hydrographic basin of Bistriţa River has a great importance mainly in upstream of Izvorul Muntelui Lake, where manganese deposits, polymetallic ore deposits, native sulfur and uranium ore have been extracted. In this paper the attention is focused on Bistriţa River upstream of Izvorul Muntelui Lake, an area which is affected by the presence of many waste dumps and underground mining works (closed or still active) which cause the well-known process of acid mine drainage. These sources contribute to an increasing level of contamination of waters, soils and river sediments.

The purposes of the present study can be described as follows: (1) to determine the spatial distributions of certain minor elements (Cr, Co, Ni, Cu, Zn, Cd, Pb, As) in the stream sediments of Bistriţa River; (2) to assess the contamination degree of sediments using pollution indices together with the geochemical background values; and (3) to differentiate between geogenic and anthropogenic sources of contamination.

2. Geological setting and mining activity

The Bistriţa hydrographic basin (upstream of Izvorul Muntelui Lake) is superimposed on three geological units (Fig. 1), known as Crystalline–Mesozoic (or Median Dacides), Carpathian and Transcarpathian flysch

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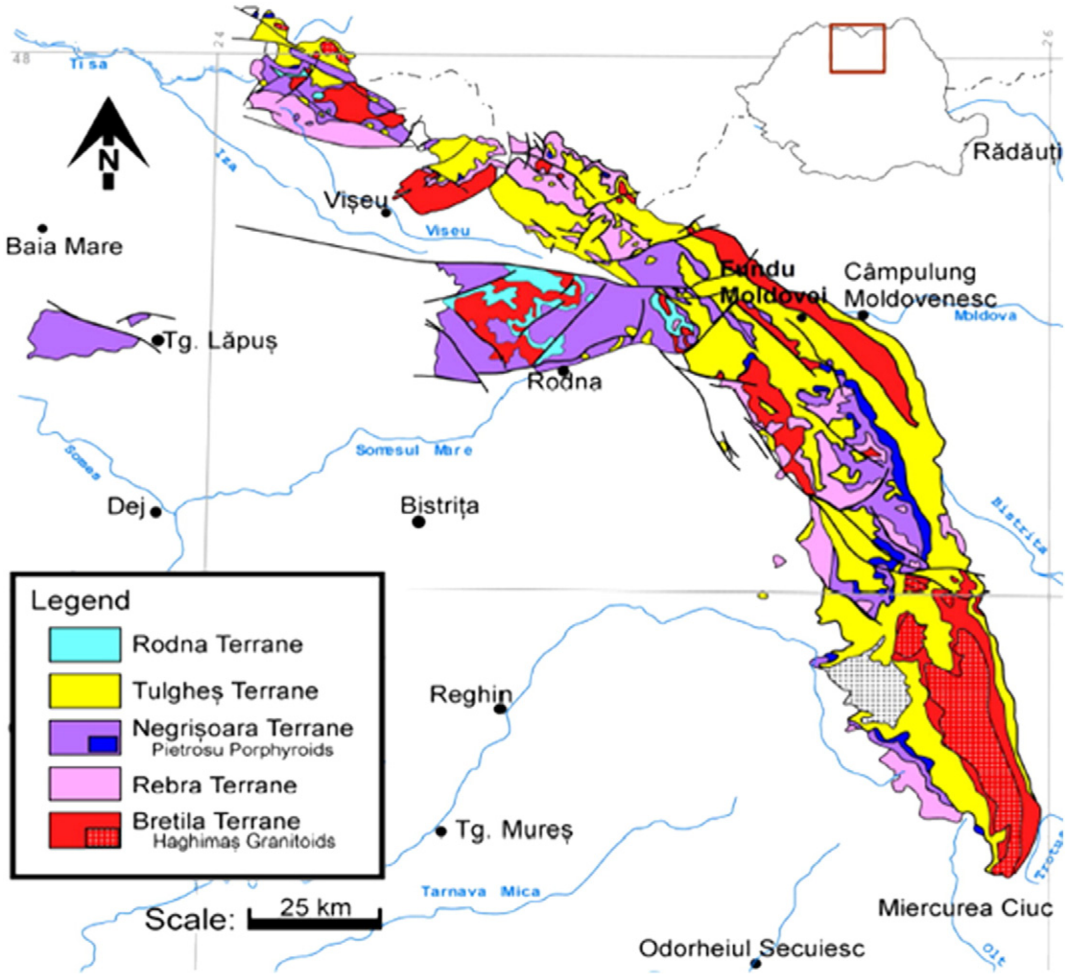

Fig. 1. Geological map of the studied area (Balintoni, 2010).

zones. The Median Dacides are composed of alpine tectonic units of Infrabucovinian, Subbucovinian and Bucovinian nappes. The upper part of the studied area comprises a variety of rocks such as black quartzites, metabasites, paragneiss, microcline gneiss, amphibolites, mica–schists and porphyroids (Balintoni, 2010).

The Crystalline–Mesozoic zone has complex mineralogical and metallogenic features due to the Fe, Mn, U and polymetallic sulfides accumulations (Rusoaia, Fluturica Cîrlibaba, Dadu, Orata, Colacu, Oiţa, Mestecăniş, Tolovanu, Iacobeni, Căprăria, Arşiţa, Argestru, Fagu, Crucea, Leşul Ursului, Valea Leşului, Isipoaia, Holdiţa and Broşteni). These deposits are found on the Eastern and Western alignments along Bistriţa River (Fig. 2) and they have a major impact on the environment. The mining activities from this area were mostly closed, but modern rehabilitation methods have not been applied so far.

The Mn deposits are placed in black quartzites belonging to the Tulgheş group (Munteanu and Dumitraşcu, 2010) and belong to the following districts: Cîrlibaba (Rusoaia, Fluturica Cîrlibaba, Dadu and Orata ore deposits), Ciocăneşti (Colacu, Oiţa, Tolovan and Mestecăniş deposits) and Iacobeni (Arşiţa, Argestruţ and Căprăria) (Ionce, 2010). The syngenetic sulfide mineralizations were exploited at Leşul Ursului, Valea Leşului, Isipoaia, Crucea and Fagu mining sites. They are composed of black quartzites in the deepest parts, on top of which are developed sericite schists and porphyric rocks, and sulfide-bearing schists in the upper parts (Petrescu, 2007). The genetic type of the mineralizations from Bistriţa area is metamorphosed volcano-sedimentary. They occur as lenses along the rock schistosity (Rusoaia, Dadu, Oiţa, Iacobeni), massive lenses and stratiform disseminations (Arşita, Fagu, Crucea, Lesul Ursului, Valea Leşului, Isipoaia), and veins (Mestecaniş).

The mineralogy is very complex, the main minerals being rhodochrosite, rhodonite, tephroite, spessartine, manganogrunerite and Fe–Mn oxyhydroxides. The Mn sulfide either represents 10% from Mn ore or appears as constituent in massive Fe–Cu–Zn sulfides ores such as Holdiţa, Broşteni, Lesul Ursului, Valea Leşului, and Isipoaia. The Ni, Co, Bi and As sulfides appear as accessory minerals associated either with the Mn ore or with massive sulfides ores (chalcopyrite, pyrite, pyrrhotite, bornite, and sphalerite) (Hîrtopanu, 2004). From the geochemical point of view, the major elements are Fe, Mn, U, Pb, Cu and Zn, and the elements Ca, Mg, Al, Cd, Ag, Bi, As, Sb, Ni and Co are present as minor elements.

The U ore from Crucea contains sulfides and sulfosalts together with gangue minerals such as ankerite, calcite, siderite, dolomite, quartz, hematite and clay minerals. The U ore is hydrothermal and appears as lenses, veins or massive textures (Murariu, 2005).

The mining activity of the East Carpathians manganese deposits started since the 18th century, first for the iron and later for the manganese. About 10,000,000 t of manganese ore have been extracted so far from this area (Munteanu et al., 2004), resulting in more than 1.7×10^6 m^2 of waste dumps all over the region (Popescu and Popescu, 2009). The uranium deposits are exploited since 1962 and over 1,200,000 t of uraninite ore were mined until today. The intensive mining activity created over 30 radioactive waste dumps in Crucea–Botuşana area, disposed next to the mining facilities in piles of variable sizes that are spread over an area of 364,000 m^2 (Petrescu et al., 2010).

From the climatological point of view, the studied area has a transition temperate-continental climate. The mean annual temperatures are of 6–9 °C and the annual rain falls are abundant (600–800 mm/year).

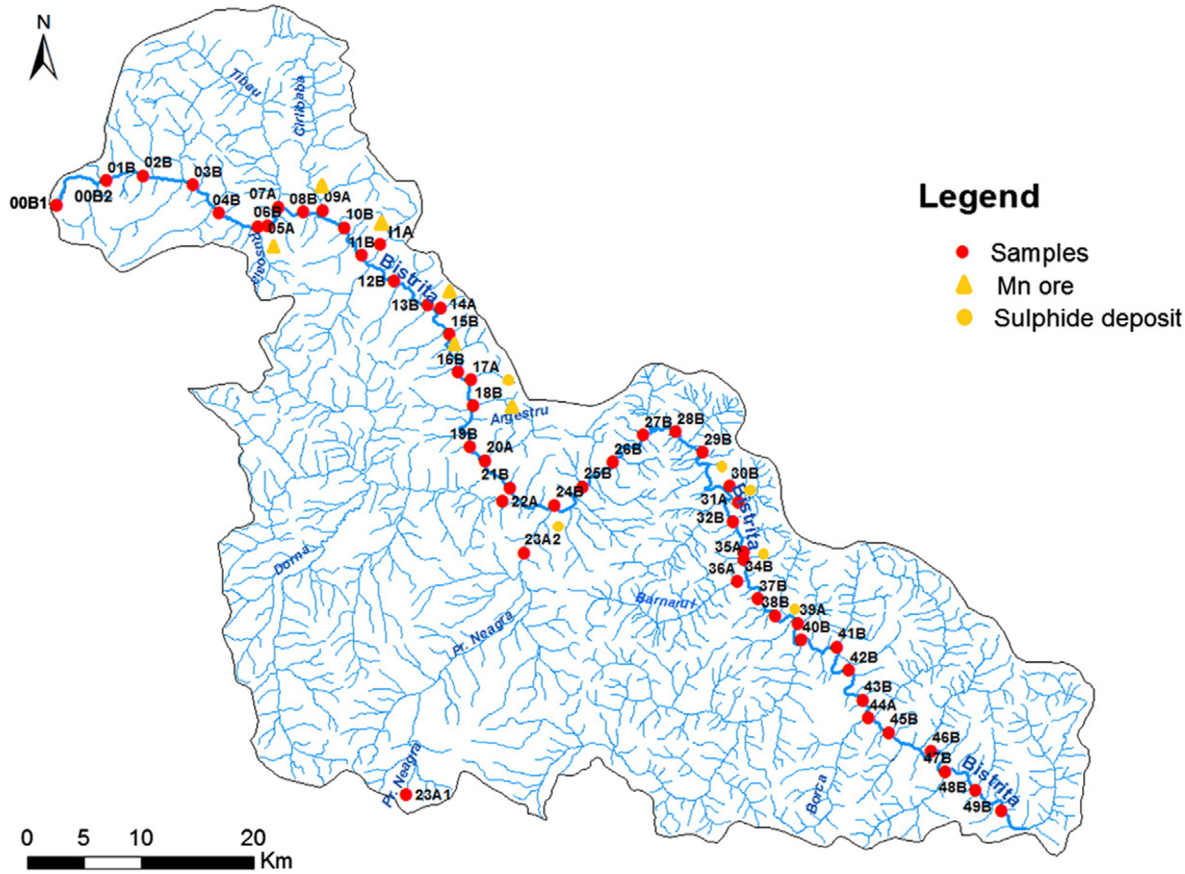

Fig. 2. Sampling sites of Bistrița River (upstream of Izvorul Muntelui Lake).

3. Material and methods

3.1. Sediment sampling and analysis

A number of 52 stream sediment samples were collected in June 2012 from Bistrița River (upstream of Izvorul Muntelui Lake) with an equidistance of about 3–4 km, depending on accessibility and pollution sources. The sampling sites are shown in Fig. 2. The samples, with a weight of about 2 kg, were placed into plastic bags. At the laboratory, each sample was dried and sieved at room temperature. The fraction of less than 0.16 mm diameter was homogenized in a mill. For chemical analysis, the powder pressed samples were prepared using a sediment/binding agent ratio of 5:1 and 20 t/cm^2 pressure. For each sediment sample two powder pressed samples were prepared, each of them weighing 9 g.

The chemical analysis of Cr, Co, Ni, Cu, Zn, Cd, Pb and As was done using an EDXRF Epsilon 5 Spectrometer. It has the following characteristics: Gd anode, Be window (300 μm), rating 25–100 kV, 0.5–24 mA, maximum power 600 W, Ge-X-ray detector, 30 mm^2, 5 mm thick, Be window (8 μm), resolution ≤ 140 eV, polarizing optics with 3-dimensional design, secondary targets Al, Ti, Fe, Co, Cu, Zn, Ge, Zr, Mo, Ag, Ce_2O_3, Al_2O_3, BaF_2, CsI and KBr. The standardization was performed using 24 CRM ($LKSD_{1–4}$, $STSD_{1–4}$, $Till_{1–4}$ $SO_{1–4}$, $JLk_{1–3}$, RT, RTH, GSD etc.). The exposure time was 50 s, with the exception of As and Cd, in which case the exposure time was 100 s. The lower limit of detection for measured elements is cca 2 mg·kg^{-1} (Cr, Co, Ni, Cu, Zn, Pb), 1 mg·kg^{-1} for As and 0.1 mg·kg^{-1} for Cd. Quality control and quality assurance were assessed using the SO-4 certified reference material. The standard was measured after each 10 sample measurements. The results for Cr, Co, Ni, Cu, Zn, Pb and As indicated an analytical precision better than 5% relative standard deviation (RSD) and accuracy was within 4%. For Cd the results were slightly higher (precision 21% RSD and accuracy 13%) due to the low concentrations of this element in CRM (0.34 mg·kg^{-1}) very close to the detection limit of the instrument (0.1 mg·kg^{-1}).

3.2. Pollution assessment in the sediments

3.2.1. Geochemical maps

The data set was managed by GIS methods (Geographic Information Systems) which allows a very fast and good visualization of element distribution in the river sediments. The statistical interpolation maps were made for each analyzed chemical element. The maps were obtained using the Inverse Distance Weighting interpolation method.

3.2.2. Geochemical background

The geochemical background was calculated as Reimann et al. (2005) suggested:

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

where MAD is the median absolute deviation.

3.2.3. Pollution indices

Pollution load index (PLI) was calculated for all analyzed elements using the following equation:

$$\text{PLI} = \sqrt[n]{\text{CF}_1\,x\,\text{CF}_2\,x\,\text{CF}_3\,x\ldots\text{CF}_n}$$

where, n is the number of elements and CF = $C_{element}/C_{background}$. Contaminant factor (CF) is used for monitoring and evaluating pollution for a single element (Abdel Ghani et al., 2013). Contamination assessment is made as follows: if PLI > 1 = polluted and PLI value < 1 = unpolluted (Abdel Ghani et al., 2013; Chen et al., 2012; Kalender and Uçar, 2013; Lim et al., 2013; Usero et al., 2000; Wijaya et al., 2013).

Ecological risk index (RI) was calculated using the formula:

$$RI = \sum_{m=1}^{n}\left(T_m\, x\, \frac{C_m}{C_b}\right)$$

where, n is the number of element contents (in this situation have been taken into account 7 elements: Cr, Ni, Cu, Pb, Zn, Cd and As) and T_m is the response coefficient for the toxicity of each element (Cd = 30, As = 10, Cr = 2, Zn = 1, and 5 for Pb, Cu and Ni) (Kabir et al., 2011; Lim et al., 2013; Wijaya et al., 2013; Yang et al., 2009). The results are interpreted as follows: RI < 300 — low to moderate; between 300 and 600 — high; and RI > 600 — extremely high. C_m is the $\boldsymbol{m}$ minor element content in the sample and C_b represents the background value of the element $\boldsymbol{m}$.

The geo-accumulation index (I_{geo})

$$I_{geo} = \log_2\left(\frac{C_x}{1.5 \times B_x}\right)$$

where C_x is the concentration of the element in sediment, B_x is the geochemical background value, and 1.5 is a correction factor due to changes that may occur in lithology (Audry et al., 2004; Jiang et al., 2013; Mohiuddin et al., 2010; Moore et al., 2009; Müller, 1969; Olubunmi, 2010; Wijaya et al., 2013; Zhang et al., 2009). The results are divided into six different classes of quality ranging from unpolluted to extremely polluted.

The priority index (P_{index}) is determined by combining the following items such as PLI, RI and I_{geo} (Kabir et al., 2011; Wijaya et al., 2013) applying the relationships:

$$P_{index} = \sum PLI^N, RI^N, sI_{geo}^N$$

$$0 \le P_{index} \le 3$$

PLI^N can be determined by dividing the value of the pollution load index which was calculated for each sediment sample to the maximum value calculated for a set of sediment samples ($PLI^N = PLI/PLI_{max}$). The situation is similar to the case of ecological risk index ($RI^N = RI/RI_{max}$) and geoaccumulation index ($sI_{geo}^N = sI_{geo}/sI_{geo\ max}$).

Kabir et al. (2011) and Wijaya et al. (2013) suggested a simplified relationship for I_{geo}:

$$sI_{geo} = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{I_{geoi}}{\left(I_{geoi}\right)_{max}}\right]$$

where, n is the total number of elements, I_{geoi} are the I_{geo} values of the heavy metal. The values obtained by normalization were applied in the P_{index} relationship.

4. Results and discussion

4.1. Descriptive statistics

Statistical analysis showed different variations of the Cr, Co, Ni, Cu, Zn, Cd, Pb and As contents in the sediments of Bistriţa River (upstream of Izvorul Muntelui Lake). Central tendency parameters such as arithmetic mean and median, indicate higher values for Zn and Cr. The skewness parameter suggests a high degree of positive asymmetry to the right, with a lognormal distribution (one exception, Cr). The variance shows a very high degree of dispersion only for Zn (Table 1).

4.2. Assessment of contamination

The spatial distribution of As, Cr, Ni, Co, Zn, Cd, Cu and Pb in Bistriţa River sediments (upstream of Izvorul Muntelui Lake) is shown in Figs. 3–5 (the last one containing interpolation maps).

The content variation of trace elements is closely related to the geological features, alteration and transport processes which play a role in the mobilization and deposition of the material along the hydrographic basin. The increase of heavy metal concentrations in river sediments can be a result of leaching metals from the waste material (Förstner, 1998) and changes in pH and Eh values which lead to changes of oxidation states (Petrescu, 2007). In the case of Bistriţa River, the pH shows a wide range of value from 3.67 to 8.37 (average 7.68). The lowest values were recorded on tributaries that drain the mining sites.

The obtained values for the geochemical background and geochemical threshold are shown in Table 2. The geochemical threshold shows exceeding values of minor element content in several sampling points, but the pollution indices indicate that these exceedings are minimal and do not involve a high degree of pollution.

The geochemical background of As is situated between 27 $mg \cdot kg^{-1}$ and 5.1 $mg \cdot kg^{-1}$. An arsenic enrichment was observed in the sample 23A2 which is placed on Neagra Valley tributary. The values of Co geochemical background vary between 16 $mg \cdot kg^{-1}$ and 12 $mg \cdot kg^{-1}$.

The As and Co values exceed the geochemical threshold in 00B2 sampling point, but these contaminations do not have an anthropogenic source. In the Ştiol Lake area (spring of the river), a peat bog was identified (Tanţău et al., 2011). A peatland environment retains chemical elements from ground waters and atmospheric-dust pollutants and therefore the concentrations of some trace elements can reach very high values (Smieja-Król et al., 2010). Due to this capacity of peat bogs to retain some trace elements and to prevent streams and water pollution (Yoon et al., 2012), the As and Co contamination in the case of 00B2 sample is local.

Table 1
Statistical parameters for the Bistriţa River (upstream of Izvorul Muntelui Lake).

Statistical parameter	Cr	Co	Ni	Cu	Zn	Cd	Pb	As
	$mg \cdot kg^{-1}$							
No. of samples (n)	52	52	52	52	52	52	52	52
Minimum	39	11.2	16	17	50	0.11	17	8.2
Maximum	99	38.5	48	451	1117	2.38	139	170
Arithmetic mean	71.44	14.90	30.10	45.63	126.19	0.43	36.35	24.44
Geometric mean	70.26	14.61	30.87	34.76	102.91	0.37	33.36	18.93
Median	71.5	14.6	29	31	98.5	0.37	32	16.1
Module	75	14.7	–	–	82	0.27	–	10.6
Standard deviation	12.77	3.80	6.82	62.91	151.24	0.32	19.92	26.00
Kurtosis	2.86	30.09	3.17	34.84	37.14	27.14	16.87	20.56
Skewness	−0.11	4.78	0.19	5.47	5.71	4.42	3.48	3.89
Quartile 1	64.25	13.32	26	23.25	79	0.27	27	11.82
Quartile 3	78	15.2	35	42	116.5	0.51	38.75	24.97
Interquartile ranges	13.75	1.88	9	18.75	37.5	0.24	11.75	13.15
Variance	163.19	14.41	46.56	3957.41	22872.55	0.10	396.94	676.12

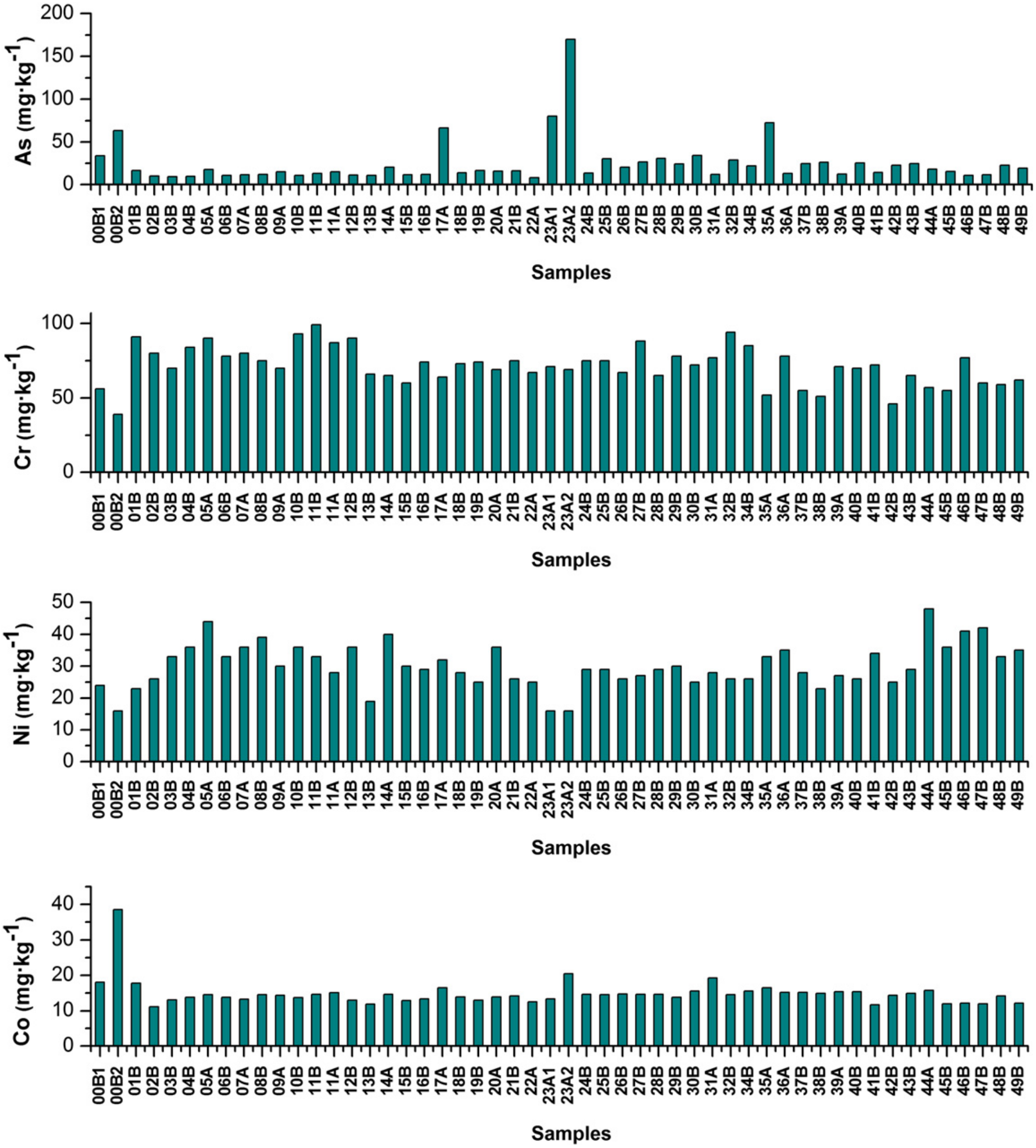

Fig. 3. As, Cr, Ni and Co distribution in the Bistriţa River (upstream of Izvorul Muntelui Lake).

The As contamination risk is relatively low in 25B, 28B, 30B and 32B sampling sites. The Co content is also high in samples 01B and 31A, but with no anthropogenic effects since the values showed by RI, PLI and I_{geo} are in the admitted limits. The situation is quite different in the case of samples 17A, 23A2 and 35A, where the high concentration values suggest an anthropogenic source.

The geochemical background of Cr is in the range 84 $mg \cdot kg^{-1}$ and 58 $mg \cdot kg^{-1}$ and the geochemical threshold is slightly exceeding in the sampling points 01B, 05A, 10B, 11B, 11A, 12B, 27B, 32B and 34B. For the 01B sample, the Cr concentrations exceed the geochemical threshold values, but neither the pollution indices indicate high contamination.

The Cd, Cu, Pb and Zn contents point out a high ecological risk for the sampling points 11A, 19B and 35A, where the concentrations exceed the geochemical threshold and pollution indices also point out a higher degree of contamination. Ni does not indicate any pollution risk although the concentration values are slightly exceeding than those of the geochemical threshold in 05A, 08B, 14A, 44A, 46B and 47B sampling points.

In the contamination assessment of Bistriţa River by means of pollution indices, background values from the same river were used, and not an average of the values in the crust because the lack of similarity between the texture, chemistry and sediment mineralogy (Lim et al., 2013).

The PLI values in the sediments from Bistriţa River (upstream Izvorul Muntelui Lake) range between 0.73 and 3.16 with an average of 1.12 (Table 3). The very high values are caused by the presence of anthropogenic sources, in this case the uranium exploitation from Crucea area, Suceava County. The percentage contribution of each element in PLI of the entire length of the river is the following: As (15.6%) > Cu (14.9%) > Zn (13.6%) > Cd (12.2%) > Pb (11.8%) > Co (10.7%) > Ni (10.6%) = Cr (10.6%).

The P_{index} values calculated for each location are listed in Table 4. The P_{index} values in the Bistriţa River sediments (upstream of Izvorul Muntelui Lake) are found to be in the 0.40 to 2.90 interval (with an average of 0.93). The mean contribution of each element to the P_{index} values is the following: Cd (49.32%) > As (20.92%) > Cu (10.01%) > Pb (7.94%) > Ni (7.12%) > Cr (2.86%) > Zn (1.83%). The high values of Cd

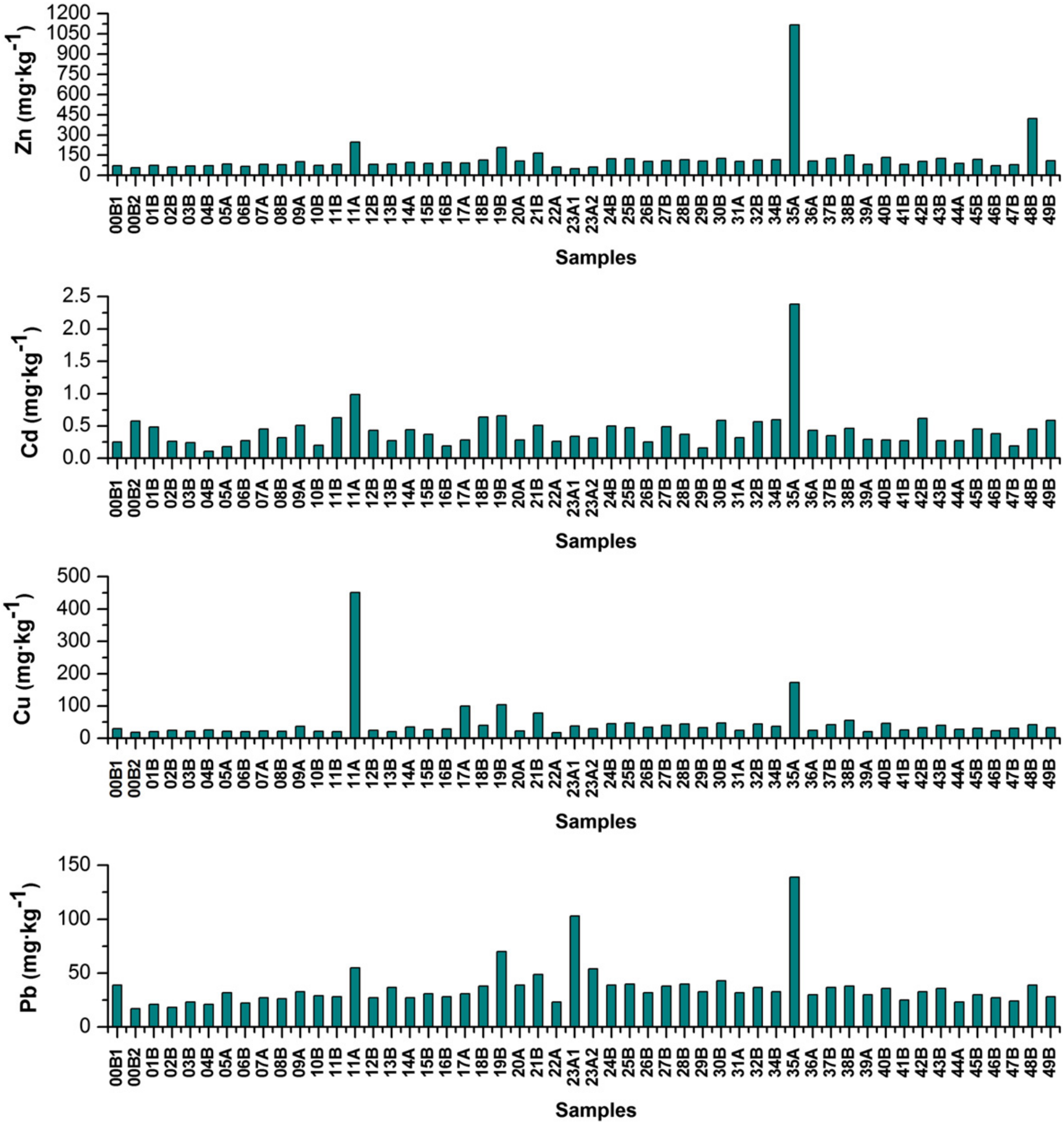

Fig. 4. Zn, Cd, Cu and Pb distribution in the Bistriţa River (upstream of Izvorul Muntelui Lake).

are strongly associated with anthropogenic pollution. The highest value of Cd was found at the sampling point 35A which is located near the uranium mines area (Crucea, county Suceava) (Fig. 6).

The levels of Zn, Pb and Cd indicate an anthropogenic intake with a strong degree of pollution in point 35A (Fig. 4). Geochemical background values of Cu in the studied area ranged from 13 $mg \cdot kg^{-1}$ to 49 $mg \cdot kg^{-1}$. The maximum value is 452 $mg \cdot kg^{-1}$ in the sample 11A. Mining and industrial wastewaters have a high contribution to elements such as As, Zn, Cd and Pb.

The natural background indicates a Cr content between 84.5 $mg \cdot kg^{-1}$ and 58.5 $mg \cdot kg^{-1}$ and the geochemical threshold is slightly exceeding in the sampling points 01B, 05A, 10B, 11B, 11A, 12B, 27B, 32B and 34B. According to the analysis of the pollution indices, the sediments of the Bistriţa River (upstream of Izvorul Muntelui Lake) do not have a Cr contamination. The situation is similar to Ni content. The values of the Ni content are situated slightly above the geochemical threshold but the pollution indices do not suggest any contamination produced by anthropogenic sources.

The Co concentration in the sampling point 00B2 (Fig. 3) is over the geochemical threshold and this fact would be explained by the peat bog environment, as it was discussed above. Sample location does not indicate any source of anthropogenic pollution.

The maximum value of As (170 $mg \cdot kg^{-1}$) was recorded in 23A2 sampling point, located on Neagra Valley tributary which drains the Călimani-Negoiu Românesc sulfur open-pit. The geo-accumulation index (I_{geo}) suggests a moderate contamination in this case, and in the other samples I_{geo} shows a low contamination degree. The high content of only As in sample 23A2 is not due to the mining works from Călimani-Negoiu Românesc, but more likely to the presence of realgar (AsS), orpiment (As_2S_3) and yellow arsenic sulfide layer in Şaru Dornei compartment which lead to an enrichment of water and sediments in As (Mihalca and Alexe, 2013).

The element concentrations in sediment samples from Bistriţa are shown in Table 5 compared with the available Romanian legislation of sediments quality and with other similar environments reported in literature. The concentrations of all elements, except for Cr, exceed the

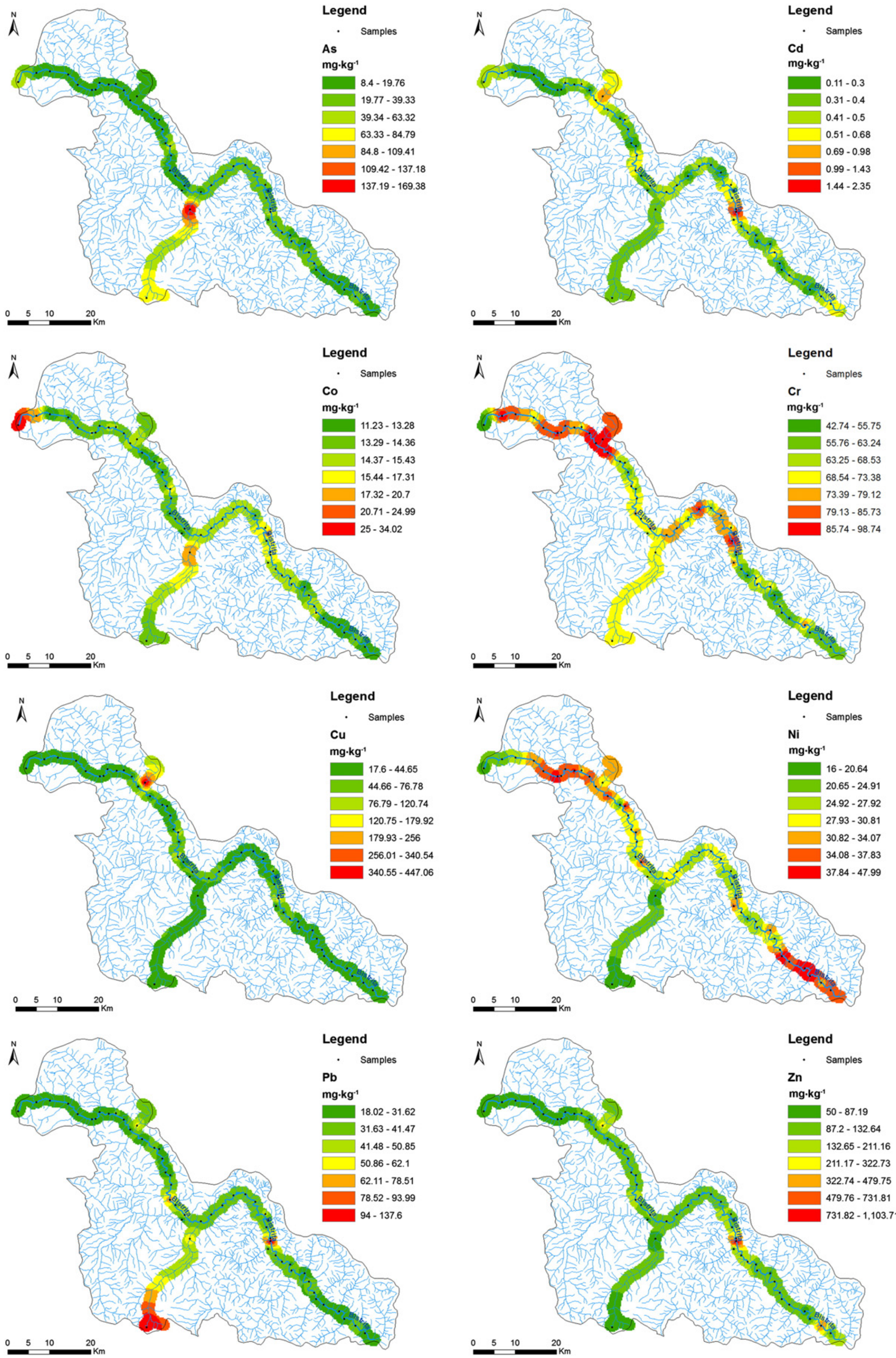

Fig. 5. Distribution maps of the studied elements in the Bistriţa River (upstream of Izvorul Muntelui Lake).

Table 2
Determination of geochemical background for the Bistriţa River (upstream of Izvorul Muntelui Lake).

Element	Geochemical background	Geochemical threshold	Mean content
	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$
Cr	84–58	84	67
Co	16–12	16	14
Ni	37–21	37	28
Cu	49–13	49	31
Zn	136–60	136	92
Cd	0.59–0.15	0.59	0.35
Pb	44–20	44	31
As	27–5.1	27	16

threshold values of Romanian Sediment Quality Guidelines but just locally in the above mentioned sampling points (indicated by the pollution coefficients as well). The median values are in admissible limits for all elements (Table 5). By comparing the results with the concentrations from the rivers of Europe (Salminen et al., 2005) it can be observed that the median values from Bistriţa are slightly higher for As, Co, Zn, Cu and Pb, suggesting an anthropogenic source for these elements. The concentrations reported by Salminen et al. (2005) represent data from unpolluted rivers across Europe and can be considered natural values for such environments. The median values obtained on Bistriţa are lower or approximately equal with concentrations reported by Singh et al. (2013) on Ganga river, India, in industrial/urban centers. In comparison with river Meža, Slovenia, affected also by an intensive mining

Table 3
PLI, RI and I_{geo} for minor elements content along the Bistriţa River (upstream Izvorul Muntelui Lake).

Sample	PLI	RI	I_{geo}							
			As	Cd	Co	Cr	Cu	Ni	Pb	Zn
00B1	1.03	60.37	0.51	−1.09	−0.21	−0.85	−0.62	−0.83	−0.25	−0.95
00B2	1.02	99.66	1.42	0.13	0.88	−1.37	−1.35	−1.42	−1.45	−1.31
01B	0.96	65.56	−0.51	−0.15	−0.23	−0.15	−1.13	−0.89	−1.14	−0.93
02B	0.77	42.91	−1.26	−1.03	−0.90	−0.34	−0.88	−0.72	−1.36	−1.16
03B	0.80	42.03	−1.38	−1.15	−0.68	−0.53	−1.07	−0.37	−1.01	−1.03
04B	0.78	32.70	−1.28	−2.27	−0.60	−0.27	−0.82	−0.25	−1.14	−0.95
05A	0.98	46.37	−0.44	−1.56	−0.52	−0.17	−1.07	0.04	−0.53	−0.72
06B	0.83	45.19	−1.17	−0.98	−0.60	−0.37	−1.20	−0.37	−1.07	−1.07
07A	0.97	63.07	−1.05	−0.24	−0.65	−0.34	−1.00	−0.25	−0.78	−0.76
08B	0.93	52.33	−1.00	−0.73	−0.52	−0.43	−1.07	−0.13	−0.83	−0.81
09A	1.10	72.36	−0.68	−0.06	−0.54	−0.53	−0.32	−0.51	−0.49	−0.46
10B	0.88	41.83	−1.16	−1.41	−0.61	−0.12	−1.07	−0.25	−0.68	−0.91
11B	1.05	79.09	−0.88	0.25	−0.51	−0.03	−1.13	−0.37	−0.73	−0.76
11A	2.00	185.98	−0.66	0.90	−0.47	−0.22	3.29	−0.61	0.25	0.84
12B	0.98	61.81	−1.09	−0.30	−0.69	−0.17	−0.88	−0.25	−0.78	−0.76
13B	0.82	45.22	−1.16	−0.98	−0.81	−0.62	−1.13	−1.17	−0.32	−0.72
14A	1.11	70.29	−0.21	−0.27	−0.51	−0.64	−0.40	−0.10	−0.78	−0.55
15B	0.93	56.07	−1.04	−0.52	−0.70	−0.75	−0.77	−0.51	−0.58	−0.66
16B	0.89	41.24	−0.99	−1.48	−0.64	−0.45	−0.67	−0.56	−0.73	−0.53
17A	1.39	95.76	1.49	−0.92	−0.34	−0.66	1.12	−0.42	−0.58	−0.59
18B	1.16	84.04	−0.77	0.27	−0.59	−0.47	−0.20	−0.61	−0.29	−0.28
19B	1.53	103.37	−0.54	0.31	−0.69	−0.45	1.18	−0.77	0.60	0.57
20A	1.01	53.32	−0.58	−0.92	−0.59	−0.55	−1.00	−0.25	−0.25	−0.40
21B	1.35	82.52	−0.57	−0.06	−0.56	−0.43	0.76	−0.72	0.08	0.24
22A	0.73	40.78	−1.53	−1.03	−0.74	−0.59	−1.44	−0.77	−1.01	−1.16
23A1	1.26	108.12	1.76	−0.64	−0.64	−0.51	−0.28	−1.42	1.15	−1.47
23A2	1.32	153.35	2.85	−0.78	−0.03	−0.55	−0.62	−1.42	0.22	−1.16
24B	1.17	73.16	−0.82	−0.09	−0.51	−0.43	−0.03	−0.56	−0.25	−0.19
25B	1.30	81.79	0.35	−0.18	−0.52	−0.43	0.03	−0.56	−0.21	−0.16
26B	1.01	52.34	−0.23	−1.09	−0.50	−0.59	−0.44	−0.72	−0.53	−0.42
27B	1.24	79.40	0.15	−0.12	−0.51	−0.20	−0.20	−0.66	−0.29	−0.37
28B	1.22	72.62	0.37	−0.52	−0.51	−0.64	−0.07	−0.56	−0.21	−0.27
29B	1.01	48.18	0.02	−1.73	−0.60	−0.37	−0.48	−0.51	−0.49	−0.39
30B	1.35	93.95	0.52	0.15	−0.42	−0.49	0.03	−0.77	−0.11	−0.15
31A	1.00	52.24	−0.99	−0.73	−0.12	−0.39	−0.88	−0.61	−0.53	−0.43
32B	1.30	88.19	0.28	0.10	−0.52	−0.10	−0.07	−0.72	−0.32	−0.30
34B	1.22	84.45	−0.11	0.18	−0.42	−0.25	−0.32	−0.72	−0.49	−0.27
35A	3.16	317.76	1.62	2.16	−0.34	−0.96	1.91	−0.37	1.59	3.01
36A	1.04	63.10	−0.88	−0.30	−0.46	−0.37	−0.88	−0.29	−0.63	−0.39
37B	1.15	66.02	0.06	−0.60	−0.46	−0.88	−0.13	−0.61	−0.32	−0.14
38B	1.22	77.64	0.13	−0.21	−0.49	−0.99	0.26	−0.89	−0.29	0.10
39A	0.90	48.45	−0.93	−0.87	−0.44	−0.51	−1.13	−0.66	−0.63	−0.78
40B	1.16	61.06	0.09	−0.92	−0.44	−0.53	0.00	−0.72	−0.36	−0.06
41B	0.91	49.23	−0.72	−0.98	−0.84	−0.49	−0.82	−0.33	−0.89	−0.76
42B	1.09	84.55	−0.06	0.22	−0.54	−1.14	−0.48	−0.77	−0.49	−0.42
43B	1.12	59.21	0.06	−0.98	−0.49	−0.64	−0.20	−0.56	−0.36	−0.15
44A	0.99	53.53	−0.41	−0.98	−0.41	−0.83	−0.72	0.17	−1.01	−0.66
45B	1.04	66.91	−0.64	−0.24	−0.80	−0.88	−0.57	−0.25	−0.63	−0.25
46B	0.93	57.46	−1.16	−0.48	−0.78	−0.39	−0.94	−0.06	−0.78	−0.97
47B	0.86	42.34	−1.04	−1.48	−0.80	−0.75	−0.57	−0.03	−0.95	−0.81
48B	1.40	77.82	−0.06	−0.24	−0.56	−0.78	−0.13	−0.37	−0.25	1.61
49B	1.11	81.05	−0.32	0.15	−0.78	−0.71	−0.48	−0.29	−0.73	−0.37
Min.	0.73	32.70	−1.53	−2.27	−0.90	−1.37	−1.44	−1.42	−1.45	−1.47
Max.	3.16	317.76	2.85	2.16	0.88	−0.03	3.29	0.17	1.59	3.01
Mean	1.12	74.19	−0.32	−0.51	−0.52	−0.52	−0.41	−0.54	−0.47	−0.43

Table 4
Analysis of priority index (P_{index}).

Sample	PLI^N	RI^N	sI^N_{geo}	P_{index}
00B1	0.33	0.19	0.60	1.12
00B2	0.32	0.31	1.00	1.64
01B	0.30	0.21	−0.06	0.45
02B	0.24	0.14	0.09	0.47
03B	0.25	0.13	0.33	0.72
04B	0.25	0.10	0.11	0.45
05A	0.31	0.15	0.09	0.55
06B	0.26	0.14	0.20	0.60
07A	0.31	0.20	0.20	0.71
08B	0.29	0.16	0.30	0.76
09A	0.35	0.23	0.35	0.93
10B	0.28	0.13	−0.01	0.40
11B	0.33	0.25	−0.08	0.50
11A	0.63	0.59	0.13	1.34
12B	0.31	0.19	0.05	0.55
13B	0.26	0.14	0.29	0.70
14A	0.35	0.22	0.51	1.09
15B	0.29	0.18	0.53	1.00
16B	0.28	0.13	0.24	0.65
17A	0.44	0.30	0.51	1.25
18B	0.37	0.26	0.29	0.92
19B	0.48	0.33	0.28	1.09
20A	0.32	0.17	0.40	0.89
21B	0.43	0.26	0.26	0.94
22A	0.23	0.13	0.32	0.68
23A1	0.40	0.34	0.22	0.96
23A2	0.42	0.48	0.27	1.17
24B	0.37	0.23	0.27	0.87
25B	0.41	0.26	0.28	0.94
26B	0.32	0.16	0.37	0.85
27B	0.39	0.25	0.05	0.69
28B	0.39	0.23	0.46	1.07
29B	0.32	0.15	0.20	0.67
30B	0.43	0.30	0.31	1.03
31A	0.32	0.16	0.21	0.69
32B	0.41	0.28	−0.04	0.65
34B	0.39	0.27	0.08	0.73
35A	1.00	1.00	0.90	2.90
36A	0.33	0.20	0.24	0.77
37B	0.36	0.21	0.66	1.23
38B	0.39	0.24	0.72	1.35
39A	0.28	0.15	0.29	0.73
40B	0.37	0.19	0.33	0.89
41B	0.29	0.15	0.31	0.75
42B	0.35	0.27	0.87	1.48
43B	0.36	0.19	0.45	0.99
44A	0.31	0.17	0.71	1.19
45B	0.33	0.21	0.70	1.24
46B	0.29	0.18	0.27	0.75
47B	0.27	0.13	0.59	1.00
48B	0.44	0.24	0.63	1.31
49B	0.35	0.26	0.54	1.15
Min.	0.23	0.10	−0.08	0.40
Max.	1.00	1.00	1.00	2.90
Mean	0.36	0.23	0.34	0.93

activity, the medians from Bistriţa are higher just for Cr and Co, and much lower for Zn, Cd and Pb (Gosar and Miler, 2011). Although such comparisons can give an idea about the degree of pollution in different areas, sometimes it can be misleading since it does not take into account the differences in lithological context which may have a great influence on the background concentrations of certain elements.

5. Conclusions

The geochemical background values instead of the average crust were used to calculate the pollution indices, because there is no similarity between the texture, chemistry and sediment mineralogy. Relationships between elements and geogenic and/or anthropogenic sources were explained by assessing pollution indices like I_{geo} (geo-accumulation index), PLI (pollution load index), CF (contamination factor), RI (ecological risk index) and P_{index} (priority index). Geological formations have an effect on the minor elements concentrations and could explain the higher values where sample locations are not indicating a source of anthropogenic pollution (e.g. 00B1, 00B2, and 23A2 sampling points).

The CF indicates a high As contamination in this 23A2 sample, which is caused by the lithologic substrate (presence of realgar (AsS), orpiment (As_2S_3) and yellow arsenic sulfide layer in Şaru Dornei deposits). P_{index} indicates the very high contamination with As in the point 35A. In this case the source of contamination is the U ore as this sample is located near uranium mines (Crucea, Suceava County).

According to the analysis of the pollution indices, the sediments of the Bistriţa River (upstream of Izvorul Muntelui Lake) do not have a Cr and Ni contamination.

The Co concentration is high in samples 01B and 31A, but with no anthropogenic effects since the values showed by RI, PLI and I_{geo} are in the admitted limits. The situation is quite different in the case of samples 17A, 23A2 and 35A, where the high concentration values suggest an anthropogenic source. The high concentration in the sample 00B2 is local and it is produced by the presence of peat bogs.

The elements Cd, Cu, Pb and Zn show a high ecological risk for the sampling points 11A, 19B and 35A, where the concentrations exceed the geochemical threshold and also the pollution indices show a high degree of contamination. The CF for each element indicates a high contamination for Cu in 11A point, and for Cd, Pb and Zn in sample 35A. PLI has a very high value in the sampling point 35A (PLI = 3.16) which indicates a contamination from anthropogenic sources. High values have also been recorded in points 11A, 17A and 43B. P_{index} confirms the very high contamination with Cd, As and Cu in the point 35A. The concentrations of all elements, except for Cr, exceed the threshold values of Romanian Sediment Quality Guidelines but just locally in the above mentioned sampling points (indicated by the pollution coefficients as well). The median values are in admissible limits for all elements.

The use of pollution indices proved to be very useful in the assessment of certain minor element contamination in river sediments. These indices

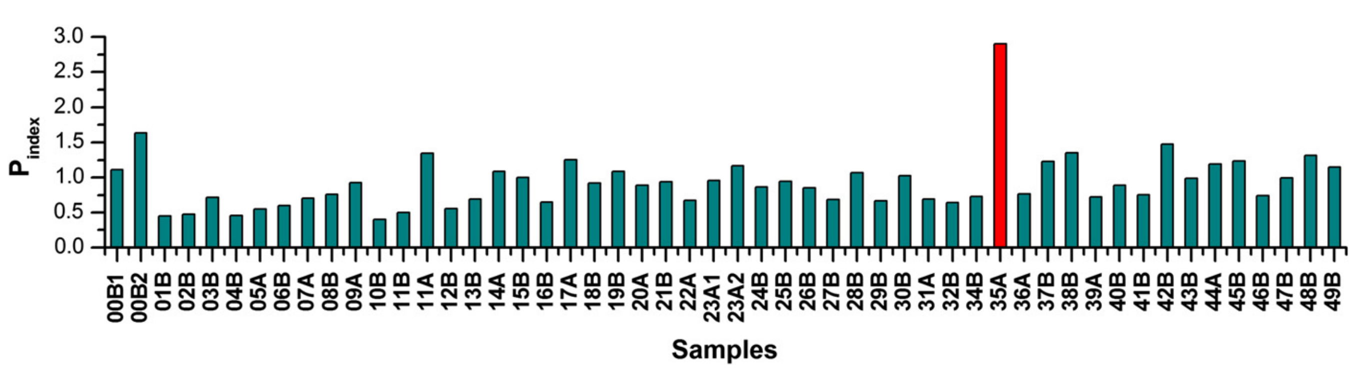

Fig. 6. Evaluation of P_{index} of minor elements content for the Bistriţa River (upstream of Izvorul Muntelui Lake).

Table 5
The minor elements concentration in Bistriţa samples compared with the national guidelines and with similar environments.

Element	Bistriţa River, Romania		Romanian sediment quality guidelines	Ganga River, India (Singh et al., 2013)	Meža River, Slovenia (Gosar and Miler, 2011)	Europe stream sediments (Salminen et al., 2005)
$mg \cdot kg^{-1}$	Min.–max.	Median		Median	Median	Median
As	8.2–170	16.1	29	–	16	6
Cr	39–99	71.5	100	157.66	53.90	63
Ni	16–48	29	35	50.33	20.40	21
Co	11.2–38.5	14.6	–	20.33	7.65	8
Zn	50–1117	98.5	150	103.66	1188	71
Cd	0.11–2.38	0.37	0.8	0.67	6.80	0.28
Cu	17–451	31	40	56.66	24.40	17
Pb	17–139	32	85	19	1223.50	20.5

gave suitable information regarding the degree of contamination and also helped to distinguish between natural and anthropogenic sources. The integration of geochemical background for the same river in the pollution indices analysis upholds to eliminate any errors in establishing the possible contamination sources.

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