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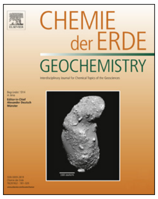

Chemical and mineralogical composition of fluvial sediments (Bistrita River, Romania): Geogenic vs. anthropogenic input into rivers on its way through mining areas

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ABSTRACT

The upper reaches of the Bistrita drainage system were selected as a natural test site to determine the geogenic and anthropogenic input into fluvio-lacustrine systems in humid mid-latitude morphoclimatic zones. The reason for this selection lies in the complex geology and its metallogenic evolution leading to a great variety of Fe, Mn, U, and polymetallic sulfides ore deposits. It sparked an intense mining activity during the past centuries with a strong impact on the drainage system similar to many mineralized sites in the world which are still under exploitation. Sediment samples from Bistrita River were analyzed by means of X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), near-infrared (NIR) and micro-Raman spectroscopy (μ-Raman).

Our results revealed that the chemical and mineralogical built-up of the stream sediments is mainly geogenic, with most of the trace elements accumulated in the river sediments derived from the source rocks exposed in catchment area of the River Bistrita. A strong input by man has been detected in the drainage system near abandoned mining sites. The trace elements are mainly accommodated in the structure of detrital minerals representative of the clastic aureole around the source rocks, and to a lesser extent adsorbed onto the surface of clay minerals. The REE incorporated into muscovite furnish evidence of having derived from the source rocks, prevalently mica schists exposed by supergene processes in the provenance area and rule out a neoformation of clay minerals on transport and deposition.

1. Introduction

Several trace and major elements, especially those supposed to be rather immobile such as Al, Fe, Ti, Th, Sc, Zr and REE are used as a tool to establishing the origin of river sediments and determining the geochemical processes of concentration (Bhuiyan et al., 2011; Um et al., 2013; Wu et al., 2013). The mineralogical composition of the fluvial sediments is decisive studying their response to weathering as exemplified by some stable minerals among the heavy minerals such as zircon that can retain certain elements, whereas others, predominantly forming part of the light minerals, e.g., feldspars very swiftly mechanical disintegrate and chemical decompose being exposed to weathering (Dill, 2017a,b; Dill et al., 2012; Marques et al., 2014). Decomposition in an aquatic environment such fluvial drainage system causes differentiation of chemical elements due to the different mobilities and stabilities of minerals and thus gives rise to a pattern of dispersion governed by nature and man.

Currently, during investigation of the mineralogy and geochemistry of fluvial sediments, emphasis is placed upon toxicity of some elements in this continental environment (Chabukdhara and Nema, 2012; Cuvier et al., 2016; Dalai et al., 2004; Das and Krishnaswami, 2007; Di Leonardo et al., 2014; Dou et al., 2013; Gaillardet et al., 1999; Maftei et al., 2014; Wu et al., 2013). Toxic afore-mentioned metals contained in stream sediments can affect the water quality and they are introduced into aquatic systems to a great deal by anthropogenic processes, such as mining (Dalai et al., 2004; Di Leonardo et al., 2014; Maftei et al., 2014) superimposed on what has been accumulated by natural processes during weathering, erosion, transport and deposition (Duman et al., 2012; El-Sayed et al., 2015; Oliveira et al., 2016; Sindern et al., 2016; Singh et al., 2013; Šmuc et al., 2015). Trace elements are

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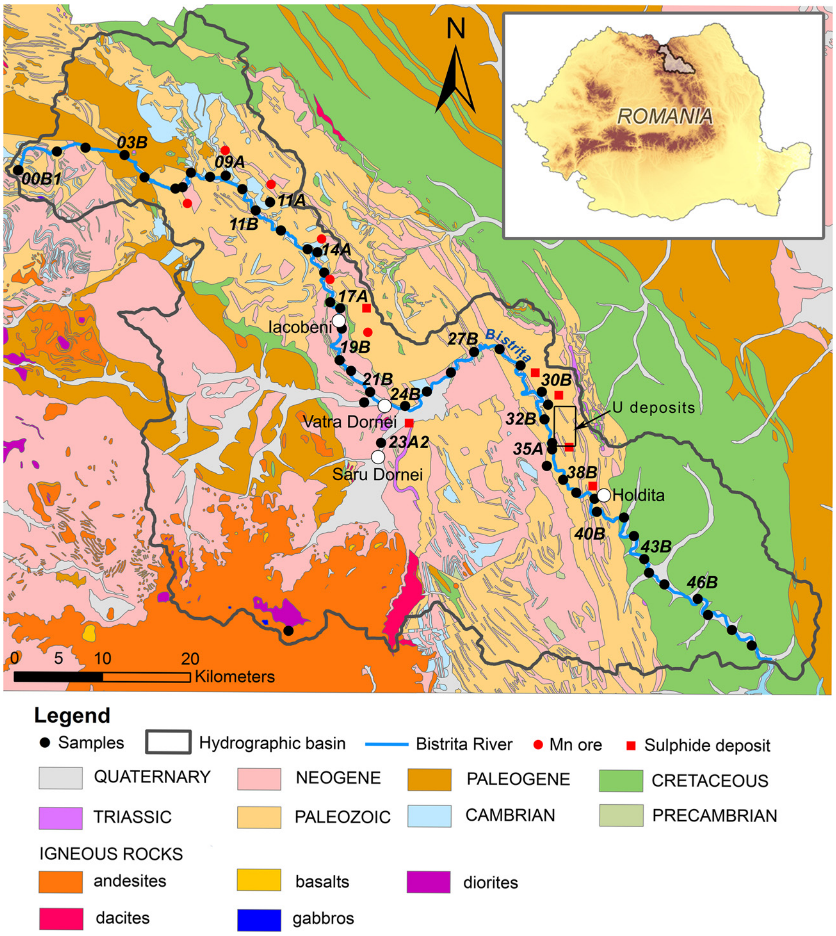

Fig. 1. Geological map of the Bistrita River basin and the location of sampling sites.

concentrated in the detrital fraction of stream sediments or adsorbed onto the surface of fine-grained particles. Previous studies have mainly focused on the association of certain elements with the clay-sized material of fluvial sediments (Chen et al., 2016; Duman et al., 2012; El-Sayed et al., 2015; Oliveira et al., 2016; Silva et al., 2016; Sindern et al., 2016; Tansel and Rafiuddin, 2016).

The upper reaches of the Bistrita fluvial drainage system has been taken as a natural test site to delineate the input by nature and man into the fluvio-lacustrine systems in humid mid-latitude morphoclimatic zones. The upstream part of the Bistrita hydrographic system (upstream of Izvorul Muntelui Lake; Fig. 1) represents a case in point for similar areas affected by mining elsewhere in the world, due its great variety and many ore deposits in the East Carpathians that have been under exploration as early as the 18th century (Maftei et al., 2014; Munteanu et al., 2004). From the metallogenic point of view, the Fe, Mn, U, and polymetallic sulfide ore deposits have to be highlighted. As a result of this long-lasting mining activity numerous waste dumps and tailing ponds litter the area, including radioactive ones which have been derived from the still active uranium exploitation in the Crucea Mining Area, Suceava County (Fig. 1). All these factors are a great impact on the stream sediments, reflected by a strong variation in their geochemical and mineralogical composition.

The principal goal of the current study is to establish the evolution of the river sediments, i.e., their formation, source, and anthropogenic influences based on geochemical and mineralogical dataset. The study aimed in detail

(1) to determine the concentrations of certain major and trace elements in sediments and to identify the major and minor mineral phases;
(2) to establish the geogenic or anthropogenic nature of the sediments, especially the contribution ratio of these two sources;
(3) to identify the degree of adsorption processes or concentrations of trace elements in detrital material; and
(4) to identify the sediments provenance source and evolution regarding the mineralogical aspects and weathering processes.

2. Geomorphological – climatological setting

The climate regime of the study area is described according to Köppen-Geiger climate classification scheme and its types labeled as *Dfb* (warm summer), and *Dfc* (cold summer) (Koppen, 1936; Peel et al., 2007). The average temperature exceeds 10 °C in the warmest months and the coldest month has an average below −3 °C. The average annual temperatures lie in the 6–9 °C (Maftei et al., 2014). Precipitation reaches in all seasons an annual value of 600–800 mm (Maftei et al., 2014). The temperature of the warmest month is averaging below 22 °C, with at least four months of above 10 °C for the warm summer continental climate (*Dfb* – warm summer) and three or less months of above 10 °C for the continental subarctic climate (*Dfc* – cold summer) (Koppen, 1936; Peel et al., 2007).

Based upon their geomorphological investigations of the Bistrita River System Rădoane et al. (2003) concluded that the hydrographic has been rather stable and evolved without any hiatuses and changes in style in the same way since the Sarmathian age (Miocene), in other words during the last 13.5 million years. This is all the more astounding since the region is tectonically very instable heralded by a constant vertical uplift of up to 5–6 mm/year. From the human impact point of view, it has to be noted that the construction of the Izvorul Muntelui Dam in this drainage system provides an anthropogenic threshold that will influence the future evolution of the river (Rădoane et al., 2003).

The Bistrita hydrographic crosses three major geological units, known as Median Dacides (or Crystalline-Mesozoic), Carpathian, and Transcarpathian flysch zones (Fig. 1). The Median Dacides are composed of Alpine tectonic units of Infrabucovinian, Subbucovinian, and Bucovinian nappes (Balintoni, 2010; Berbeleac, 1998).

According to Mutihac (2010) the central-eastern Carpathian unit is composed of meso- and epi-metamorphic crystalline schists. As potential source rocks mica-schists, quartzitic schists with biotite, black quartzites with amphibolite intercalations, crystalline limestones and chloritic schists have to be mentioned. The heavy minerals from Bistrita sediments reveal the metamorphic source: garnet, pyroxene, Mn- and Fe-oxides, ilmenite, rutile and pyrite (Ciortescu et al., 2014).

Balintoni (1997) identified within Tulghes lithogroup different lithozones. The Holdita lithozone stands out for its black color caused by high graphite contents and for being hosts to pre-metamorphic Fe-Mn and barite ore deposits. The Crystalline-Mesozoic zone is very complex and interesting from the mineralogical and metallogenic point of view, due to the Fe, Mn, U and polymetallic sulfides ore accumulations. These deposits crop out along the banks of the Bistrita River where they provoked large mining activities resultant in elevated concentrations of a wide range of elements in the stream sediments. The consequences of these mining operations has widely been discussed in Maftei et al. (2014). Among the several manganese and sulfide ore deposits located in Bistrita River basin some areas were identified to have a great impact on the chemical composition of sediments (Maftei et al., 2014, Fig. 2): The peatland environment from Bistrita River springs, Neagra Valley tributary that drains Călimani-Negoiu Românesc sulfur open-pit, the arsenic-rich layers in Saru Dornei mineralization, and intensive uranium exploitation in the Crucea mining area, Suceava County. The Eastern Carpathians mining activity started since the 18th century and it is estimated that more than $1.7 \times 10^6\,\mathrm{m}^2$ of waste dumps were resulted all over the region (Maftei et al., 2014). The uranium material was extracted since 1962 and over 1.2 million tons of uraninite ore mined until the present time. As a consequence of this, over 30 radioactive waste dumps are known in Crucea mining district spreading across an area of more than $364.000\,\mathrm{m}^2$ (Petrescu et al., 2010).

3. Samples and methods

3.1. Sampling and analytical procedure

Fifty-two stream sediment samples were collected from Bistrita trunk river and some of its main tributaries, at an equidistant spacing of 3–4 kilometers. The big-pack samples of up to about 2 kg in weight were collected in plastic bags and dried at room temperature. Each sample was sieved and the fraction less than 0.16 mm diameter was used for analysis. During incipient study those samples with highest concentrations of certain toxic elements were singled out to assess the degree of contamination and identify the sources of pollution. The detailed results of this pre-stage were presented in Maftei et al. (2014). A number of 19 samples out of this study were taken for the present study, based on the degree of contamination and position (Fig. 1). The samples were analyzed by X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), near-infrared (NIR) and micro-Raman spectroscopy. The XRF, XRD and NIR measurements were carried out at the Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany. The micro-Raman spectra were acquired at Earth Science Institute of the Slovak Academy of Sciences from Banská Bystrica, Slovakia.

The chemical analysis of Na, Mg, K, Ca, Ti, b, Cs, Sr, Ba, Zr, Nb, La, Ce, Nd, Sm and Th was carried out with a Philips PW2400 (WD-XRF) spectrometer. The measurements were done on fused samples in order to ensure a homogenous distribution of the elements. A quantity of 1 g from each finely ground sample was annealed in a muffle furnace in porcelain crucibles at a temperature of 1030 °C (10 min) for determination of volatile compounds (water, organic carbon, CO_2, SO_2). The annealed samples were mixed with 25 mg of lithium bromide and 5 g of lithium metaborate and heated in platinum crucibles at 1200 °C for 20 min. The device was calibrated using certified reference materials (CRMs). The lower limits of detection are: 0.01% for Na, Mg; 0.005% for K, Ca; 0.001% for Ti; 0.05% for Al; 2–3 $\mathrm{mg\,kg^{-1}}$ for Rb, Cs, Sr, Zr, Nb; 5 $\mathrm{mg\,kg^{-1}}$ for Ba, Nd, Sm, Th; and 20 $\mathrm{mg\,kg^{-1}}$ for La and Ce. The analytical precision was better than 5% relative standard deviation (RSD).

The X-ray diffraction spectra were obtained using a PANalytical MPD Pro diffractometer. The instrument uses a Cu anode and is equipped with a double detector. The samples were measured in the scanning range of 2–85°. The diffractograms were semi-quantitatively evaluated by Rietveld refinement using the Bruker Topas 2.1 software package.

The near-infrared spectra were acquired using a Portable Infrared Mineral Analyzer (PIMA) from Integrated Spectronics Pty Ltd. The device operates in the wavelength region from 1.3 to 2.5 μm. The infrared radiation penetrates the sample to about 2–3 mm and the measured area is 10 mm in diameter. The spectra acquisition and manipulation was done using PimaView 3.1 software package.

Certain samples were analyzed by means of micro-Raman spectrometry. For this purpose, the grain minerals were sorted by hand-picking from the sediment samples using a binocular magnifier. The measurements were carried out with a Horiba-Jobin Yvon spectrograph – LabRam HR 800, with CCD detector and equipped with an Olympus microscope with 100× magnifying objective. The device uses two laser sources, at 532 nm and 633 nm. The sorted crystals from the sediment samples were measured using both lasers together with several density filters in order to avoid samples deterioration and fluorescence effect. The micro-Raman spectra were acquired using an exposure time of 40–150 s, 2–4 acquisitions, within the 65–1100 $\mathrm{cm^{-1}}$ spectral range.

3.2. Statistical analysis

The descriptive statistics were obtained for the concentrations of Na, Mg, K, Ca, Ti, Rb, Cs, Sr, Ba, Zr, Nb, La, Ce, Nd, Sm and Th in the Bistrita River stream sediments (upstream of Izvorul Muntelui Lake). The Pearson correlation coefficient was used to determine the variables association for a normal distribution dataset. The relationships between the results were identified by means of hierarchical cluster analysis (HCA) applied on the standardized dataset after calculating the Euclidian distance and using the complete-linkage method.

The cluster analysis performed on Bistrita river sediments (upstream of Izvorul Muntelui Lake) follows the next steps: 1) variables standardization of the dataset; 2) recalculation of the correlation matrix; 3) identifying the similarity degree by means of Euclidian distance; 4) merging the clusters through hierarchical agglomerative analysis using the complete linkage method; and 5) dendrogram representations (Davis, 2002; Forina et al., 2002; Milligan and Cooper, 1988). In the present study the standardization was done using the method suggested by Shannon et al. (2003) applied on the sediment samples from Bistrita River (upstream of Izvorul Muntelui Lake).

Since the river sediments represent products derived from weathering of the continental crust, the element concentrations was normalized to the average values of the upper continental crust (UCC), which is common practice to assessing the mobility of elements during weathering and transport processes (Dalai et al., 2004). In the case of Bistrita River samples, the normalization was conducted using the values reported by Rudnick and Gao (2003) for the UCC.

4. Results

4.1. Geochemical distribution

The chemical analysis showed variable results for the studied elements in the different sampling sites and demonstrated a strong

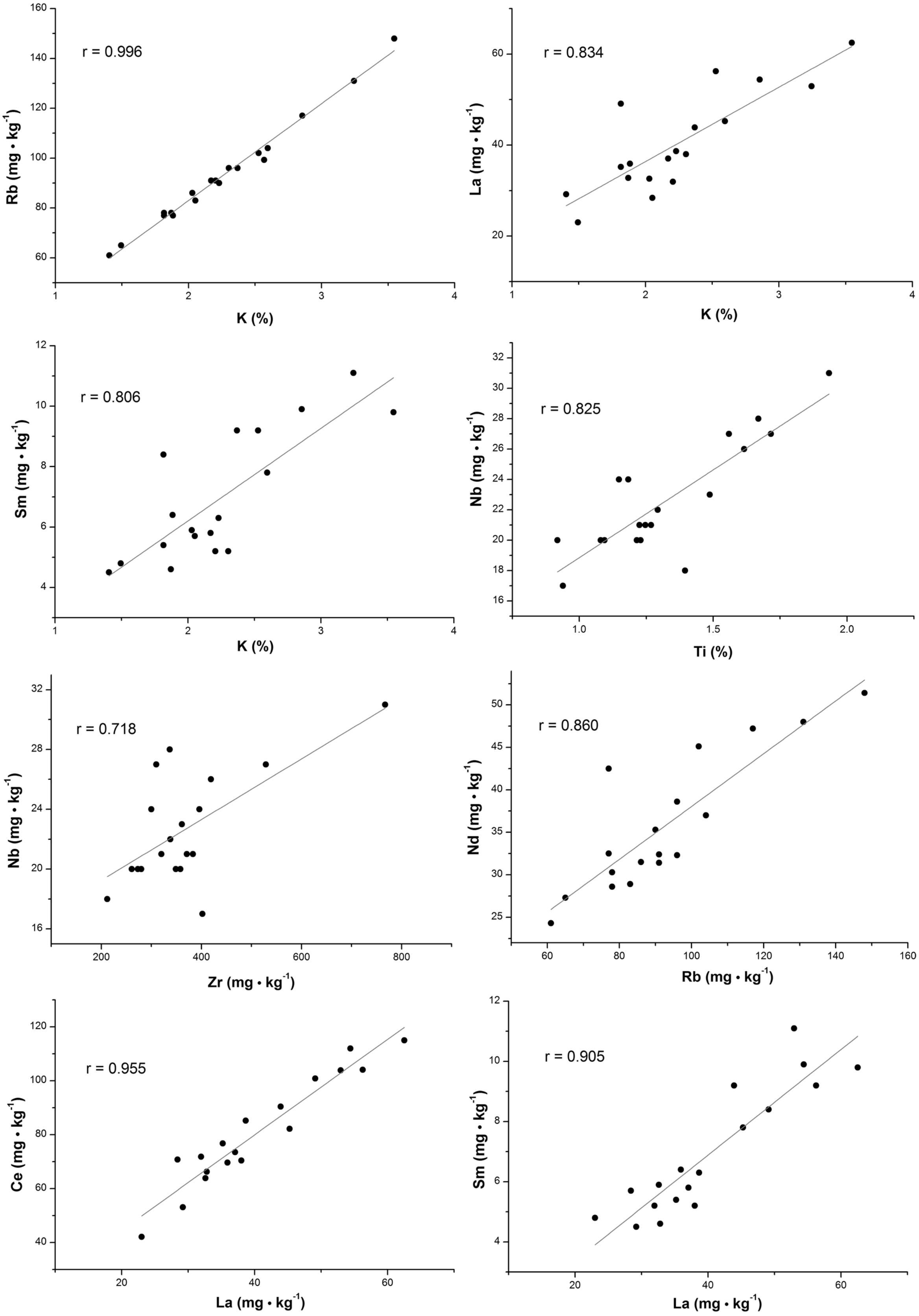

Fig. 2. Correlation plots of trace elements concentration in stream sediments of Bistrita River.

correlation with the environmental conditions of each sample. The results are shown in Table 1.

The chemical concentrations of Na and K in Bistrita River sediments (upstream of Izvorul Muntelui Lake) were identified in the range of 1.25–2.14 wt%, and 1.41–3.55 wt%, respectively, with average values of 1.87 wt% for Na and 2.26 wt% for K. The contents of Mg, Ca and Ti were

Table 1
Geochemical distribution of the studied elements in sediment samples (XRF results).

Sample	Na	Mg	K	Ca	Ti	Rb	Sr	Zr	Nb	Cs	Ba	La	Ce	Nd	Sm	Th
	(wt%)					(mg kg^{-1})										
00B1	1.93	1.28	2.53	0.61	1.18	102	118	396	24	6.4	486	56.2	104.1	45.1	9.2	23
03B	1.72	1.25	1.41	0.89	1.15	61	90	300	24	2.7	260	29.2	53.1	24.3	4.5	13
09A	2.14	1.83	2.57	0.84	1.67	99	73	337	28	n.a.	535	n.a.	n.a.	n.a.	n.a.	11
11B	1.83	2.26	2.17	1.84	1.25	91	86	371	21	3.9	428	37	73.5	31.4	5.8	20
11A	2.13	1.89	3.24	0.45	1.27	131	70	383	21	3.7	685	52.9	103.9	48	11.1	23
14A	1.85	1.75	2.59	0.98	1.08	104	79	273	20	4	606	45.2	82.1	37	7.8	18
17A	1.49	1.56	2.86	0.67	1.62	117	72	419	26	4.7	583	54.4	112	47.2	9.9	24
19B	2.09	1.67	1.82	1.61	1.93	77	94	767	31	3.7	445	49.1	100.8	42.5	8.4	27
21B	2.04	1.8	2.37	1.28	1.56	96	90	529	27	3.5	533	43.9	90.4	38.6	9.2	22
23A2	1.25	2.6	1.49	2.16	1.39	65	139	212	18	3.7	925	23	42.1	27.3	4.8	17
24B	1.92	1.69	2.30	1.26	1.09	96	93	349	20	4	503	38	70.4	32.3	5.2	20
27B	1.89	1.72	2.03	1.41	1.21	86	103	358	20	3.8	491	32.6	63.9	31.5	5.9	19
30B	1.75	1.89	2.05	1.45	1.23	83	103	261	20	4	511	28.4	70.7	28.9	5.7	17
32B	1.92	1.81	1.87	1.54	1.29	78	105	338	22	3.6	476	32.8	66.3	28.6	4.6	18
35A	1.63	1.74	3.55	0.44	0.92	148	78	280	20	5.1	752	62.5	115	51.4	9.8	27
38B	2.02	1.85	1.88	1.47	1.72	77	101	310	27	3.3	475	35.9	69.6	32.5	6.4	20
40B	2.02	1.91	2.23	1.41	1.49	90	106	361	23	4	521	38.6	85.2	35.3	6.3	21
43B	1.97	1.96	2.21	1.64	1.22	91	108	320	21	4	517	31.9	71.8	32.4	5.2	20
46B	1.91	1.27	1.82	2.55	0.94	78	112	402	17	3.6	340	35.2	76.7	30.3	5.4	18

n.a. = not analyzed.

observed between 1.25 wt% and 2.60 wt% with a mean value of 1.78 wt% for Mg, 0.44 wt% and 2.55 wt% – average of 1.29 wt% for Ca, and 0.92–1.93 wt% (average concentration of 1.33 wt%) for Ti (Table 1).

The average concentration of Rb in the studied sediments is of 93.17 mg kg^{-1} and it ranges from 61 to 148 mg kg^{-1}, while the mean content of Sr is of 95.78 mg kg^{-1} and varies between 70 and 139 mg kg^{-1} (Table 1). The highest contents of Rb were identified in sample 35A. In the case of Sr the greatest values were observed in sample 23A2. The Zr concentration was found to be between 212 and 767 mg kg^{-1} with an average of 366.63 mg kg^{-1}. The variance and standard deviation suggest for Zr a great degree of dispersion (Table 2).

The concentrations of Nb and Cs in Bistrita River sediments (upstream of Izvorul Muntelui Lake) showed values between 17 and 31 mg kg^{-1} for Nb and in the range of 2.7–6.4 mg kg^{-1} for Cs (Table 1). The average contents were calculated as 22.63 mg kg^{-1} and 4 mg kg^{-1}, respectively. Ba is a very abundant trace element in the studied samples. It ranges from 259.8 to 925.3 mg kg^{-1} with a mean value of 530.24 mg kg^{-1} (Table 1).

The concentrations of the studied REE (La, Ce, Nd, and Sm) are presented in Table 1. The abundance of these elements in the Bistrita River sediments is given by the following order of abundance: Ce > La > Nd > Sm. The mean concentrations of La and Ce were observed to be of 40.39 and 80.66 mg kg^{-1} respectively. La ranges from 23 to 62.5 mg kg^{-1} and Ce varies from 42.1 to 115 mg kg^{-1}. Nd and Sm concentrations were observed between 24.3 and 51.4 mg kg^{-1} (average of 35.8 mg kg^{-1}) and 4.5–11.1 mg kg^{-1}, respectively (average of 7 mg kg^{-1}). The Th concentration from the Bistrita river sediments ranges from 10.67 to 27 mg kg^{-1} with an average of 19.88 mg kg^{-1}.

The overall mean concentration of the discussed elements in the stream sediments of Bistrita River (upstream of Izvorul Mnutelui Lake) are listed in the order of decreasing abundance: K (2.26 wt%) > Na (1.86 wt %) > Mg (1.77 wt%) > Ti (1.33 wt%) > Ca (1.29 wt%) > Ba (530.24 mg kg^{-1}) > Zr (366.63 mg kg^{-1}) > Sr (95.78 mg kg^{-1}) > Rb (93.17 mg kg^{-1}) > Ce (80.66 mg kg^{-1}) > La (40.39 mg kg^{-1}) > Nd (35.81 mg kg^{-1}) > Nb (22.63 mg kg^{-1}) > Th (19.88 mg kg^{-1}) > Sm (6.96 mg kg^{-1}) > Cs (3.98 mg kg^{-1}).

4.2. Mineralogy

The most reliable results are those provided by the XRD analyses which give the bulk mineralogical composition of the sediment samples.

Table 2
Descriptive statistics.

Element	N	Mean	Minimum	Maximum	Median	St. dev.	Skewness	Variance	UCC
	(wt%)								
Na	19	1.86	1.25	2.14	1.92	0.22	−1.24	0.05	3.27
Mg	19	1.77	1.25	2.60	1.80	0.32	0.48	0.10	2.48
K	19	2.26	1.41	3.55	2.21	0.55	0.68	0.30	2.80
Ca	19	1.29	0.44	2.55	1.41	0.56	0.30	0.32	3.59
Ti	19	1.33	0.92	1.93	1.25	0.27	0.54	0.07	0.64
	(mg kg^{-1})								
Rb	19	93.17	61	148	91	21.39	0.94	457.78	82
Sr	19	95.78	70	139	94	17.67	0.47	312.21	320
Zr	19	366	212	767	349	119	2.08	14171	193
Nb	19	22.63	17	31	21	3.71	0.63	13.80	12
Cs	18	3.98	2.7	6.4	3.85	0.78	1.63	0.62	4.9
Ba	19	530	259	925	510	144	0.91	20868	628
La	18	40.39	23	62.5	37.52	10.94	0.47	119.65	31
Ce	18	80.66	42.1	115	75.15	20.26	0.11	410.58	63
Nd	18	35.81	24.3	51.4	32.45	7.93	0.59	62.93	27
Sm	18	6.96	4.5	11.1	6.1	2.12	0.56	4.49	4.7
Th	19	19.88	10.67	27	20	4.11	−0.25	16.87	10.5

*UCC = Upper continental crust concentrations (Rudnick and Gao, 2003).

Table 3
Semi-quantitative mineralogical composition of stream sediments of Bistrita River obtained by means of XRD.

Samples	Main minerals (wt%)			Accessory minerals
	Quartz	Feldspar	Muscovite-Illite	
00B1	38.3	32.5	26.7	Chlorite, ± hornblende
03B	59.5	19.2	16.1	Chlorite, ± hornblende
09A	41.3	32.8	21.8	Chlorite
11B	46.5	28.3	22.0	Chlorite, dolomite
11A	37.1	30.2	30.8	Chlorite
14A	45.9	26.7	26.1	Chlorite
17A	45.5	23.8	27.4	Chlorite
19B	49.8	26.6	19.1	Chlorite, dolomite, ± hematite
21B	46.5	25.6	24.2	Chlorite, ± dolomite
23A2	52.7	24.3	19.8	Chlorite, ± dolomite
24B	37.4	40.0	19.1	Chlorite, ± dolomite
27B	44.6	31.4	21.9	Chlorite, ± dolomite
30B	42.1	35.6	17.9	Chlorite, ± dolomite
32B	46.1	31.8	18.9	Chlorite, ± dolomite
35A	44.2	16.5	36.2	–
38B	46.4	31.1	20.7	Chlorite, ± dolomite
40B	37.3	38.3	20.2	Chlorite, ± dolomite
43B	46.3	25.3	23.1	Chlorite, ± dolomite
46B	53.9	22.4	19.3	Chlorite, calcite

The XRD results obtained from analysis of the Bistrita River sediments are illustrated in Table 3. The following main minerals were identified: quartz – SiO_2, muscovite – $KAl_2(Si_3Al)O_{10}(OH,F)_2$, illite – $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, feldspar ($KAlSi_3O_8$, $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$), together with the accessory minerals: chlorite – $(Mg,Fe,Li)_6AlSi_3O_{10}(OH)_8$ hornblende – $Ca_2(Mg,Fe^{2+},Fe^{3+},Al)_5(Si,Al)_8O_{22}(OH)_2$, dolomite – $CaMg(CO_3)_2$, hematite – Fe_2O_3, calcite – $CaCO_3$. The Rietveld semi-quantitative analysis revealed the following mineralogical composition of the sediment samples (Table 3): quartz – 16–40 wt%; feldspar – 16–40 wt%; muscovite-illite – 16–36 wt%; and chlorite – 1–5 wt%.

The near-IR results are in good agreement with the diffraction data, except for the main minerals quartz and feldspars. The PIMA device operates in the near-infrared (NIR) range between 1.3 and 2.5 μm. Only those minerals respond as being excited by NIR that contain certain molecules and ions such as H_2O, OH^-, NH_3, CO_3^{2-}, SO_4^{2-}, and cation-OH bonds (Fe-OH, Al-OH, Mg-OH) (Bowitz and Ehling, 2008; Cloutis et al., 2006). Therefore, this method is suitable especially for the study of sulfates, carbonates and clay minerals. In the case of Bistrita River sediments the NIR spectra revealed the presence of muscovite and illite, but also of several trace minerals present in very low amounts, such as: kaolinite – $Al_2Si_2O_5(OH)_4$; epidote – $Ca_2Al_2(Fe,Al)(SiO_4)(Si_2O_7)O(OH)$; and vermiculite – $(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2{\cdot}4(H_2O)$.

The micro-Raman measurements are an additional tool and helped identifying certain minor minerals in the sediment samples from Bistrita River, especially heavy minerals and ferromagnesian silicates. The following minerals were observed in the micro-Raman spectra: quartz, muscovite, calcite; anatase – TiO_2; goethite – $FeO(OH)$; hematite – Fe_2O_3; pyrolusite – MnO_2; diopside – $CaMgSi_2O_6$; and pargasite – $NaCa_2(Mg,Fe)_4Al(Si_6Al_2)O_{22}(OH)_2$.

4.3. Statistical analysis

4.3.1. Descriptive statistics

The central tendency parameters show high values for Ba, Zr, Sr, Rb, and Ce concentrations (Table 2). The degree of symmetry shows that the dataset is skewed towards the right (positive), except for Na. The concentrations reveal a normal distribution and the variance indicates a high dispersion only for Ba and Zr.

4.3.2. Cluster analysis and correlations

The correlation matrix of the studied elements is presented in Table 4 and representative correlation plots in Figs. 2 and 3. The matrix was calculated using the standardized values. Positive and statistically significant correlation coefficients were observed for the following pairs of elements: Ti – Nb, K – Rb, K – La, K – Ce, K – Nd, K – Sm, Rb – La, Rb – Ce, Rb – Nd, Rb – Sm, Zr – Nb, La – Ce, La – Nd, La – Sm, La – Th, Ce – Nd, Ce – Sm, Ce – Th, Nd – Sm, Nd – Th, Sm – Th. High negative correlations were identified for: K – Sr, Ca – Rb, Ca – La, Ca – Ce, Ca – Nd, Ca – Sm, and Rb – Sr (Table 4).

The hierarchical cluster analysis was applied on a set of 16 chemical elements (Na, Mg, K, Ca, Ti, Rb, Cs, Sr, Ba, Zr, Nb, La, Ce, Nd, Sm, and Th) and the results are presented in the form of a dendrogram shown in Fig. 4. Three main clusters were identified: i) K – Rb – Cs – La – Nd – Ce – Sm – Th; ii) Na – Ti – Nb – Zr; and iii) Mg – Ba – Ca – Sr.

5. Discussion

5.1. Geogenic vs. anthropogenic impact

There is a dual impact on the chemical composition of the stream sediments which may depicted as follows: (i) geogenic impact caused, e.g., by detrital minerals indicative of the source or provenance lithologies, and (ii) anthropogenic contaminants which have been derived from agriculture, and household or industrial waste dumps, or taken to the extreme, from mining activities (Sindern et al., 2016; Singh et al., 2013; Šmuc et al., 2015).

The geogenic contribution is directly related to the geological setting of the riverś catchment area. The trace elements concentrated in stream sediments are a mirror image of what is (was) at outcrop in the

Table 4
Correlation matrix of the elements of stream sediments of Bistrita River.

	Na	Mg	K	Ca	Ti	Rb	Sr	Zr	Nb	Cs	Ba	La	Ce	Nd	Sm	Th
Na	1.000															
Mg	−0.297	1.000														
K	0.082	−0.075	1.000													
Ca	−0.052	0.329	**−0.720**	1.000												
Ti	0.172	0.216	−0.237	0.082	1.000											
Rb	0.047	−0.072	**0.996**	**−0.703**	−0.261	1.000										
Sr	−0.223	0.238	**−0.648**	**0.637**	0.008	**−0.644**	1.000									
Zr	**0.497**	−0.277	−0.024	0.040	**0.599**	−0.025	−0.204	1.000								
Nb	0.350	−0.228	−0.060	−0.259	**0.825**	−0.083	−0.250	**0.718**	1.000							
Cs	−0.128	−0.195	**0.570**	−0.439	−0.209	**0.563**	0.038	−0.014	−0.037	1.000						
Ba	−0.496	**0.641**	0.422	−0.175	0.005	0.431	0.088	−0.317	−0.281	0.272	1.000					
La	0.180	−0.355	**0.834**	**−0.709**	0.030	**0.833**	**−0.593**	0.377	0.333	**0.642**	0.195	1.000				
Ce	0.253	−0.346	**0.812**	**−0.615**	0.126	**0.803**	**−0.583**	0.467	0.377	**0.606**	0.128	**0.955**	1.000			
Nd	0.128	−0.194	**0.862**	**−0.682**	0.121	**0.860**	**−0.538**	0.363	0.313	**0.627**	0.366	**0.964**	**0.951**	1.000		
Sm	0.169	−0.187	**0.806**	**−0.693**	0.195	**0.791**	**−0.586**	0.385	0.372	0.490	0.337	**0.905**	**0.899**	**0.947**	1.000	
Th	0.226	−0.044	**0.668**	−0.395	0.338	**0.677**	−0.373	**0.579**	**0.447**	**0.539**	0.294	**0.836**	**0.866**	**0.888**	**0.777**	1.000

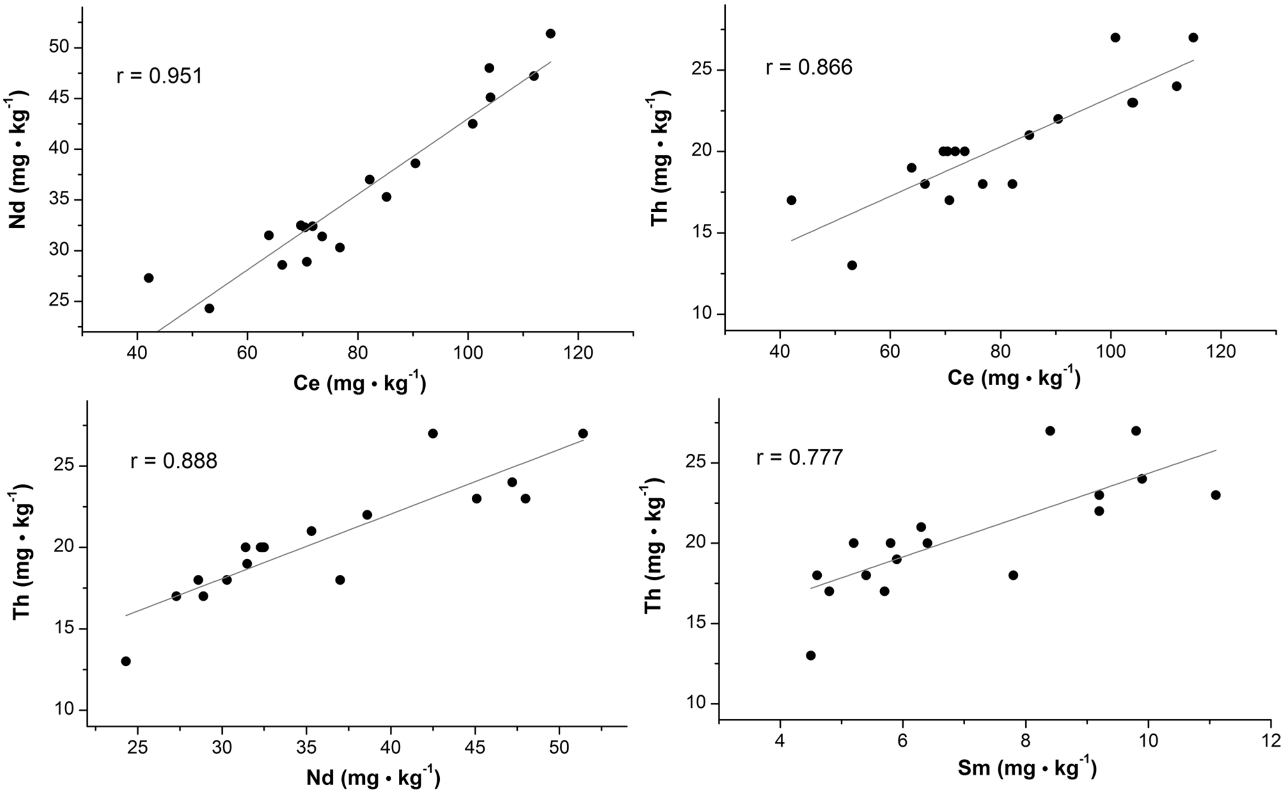

Fig. 3. Trace elements correlations datasets from stream sediments of Bistrita River.

source area. They are released by weathering which is governed by different factors, among others the regional climate (temperature, precipitation) and the geology (host rock lithology, ore and gangue mineralization) (Schneider et al., 2016; Zhao and Zheng, 2015). This sort of chemical composition controlled by lithology is known as the geochemical background (Reimann et al., 2005).

The anthropogenic part of sediments composition is derived from several human activities, such as urban and industrial discharges, agriculture, mining exploitation (Duman et al., 2012; El-Sayed et al., 2015; Sindern et al., 2016; Singh et al., 2013; Šmuc et al., 2015). The river sediments act as an important storage sink for the anthropogenic input of trace elements, as well as carriers for contaminants due to their remobilization that might appear as a result of physicochemical changes in the environment (Oliveira et al., 2016; Sindern et al., 2016; Singh et al., 2013; Šmuc et al., 2015). The anthropogenic fraction consists in pollutants adsorbed to geogenic material, especially fine-grained particles, such as argillaceous terrestrial components, due to their sorptive nature (Gibbs, 1973; Sindern et al., 2016; Singh et al., 2013). Although the source of trace elements that enter the environment is of geogenic nature, the contaminants derive following anthropogenic activities that implies large volumes of rocks being exposed to an accelerated and intensive alteration on surface conditions. This weathering leads to increased acidity in water streams and groundwater, and therefore to an enhanced metals mobility.

To establish the anthropogenic input of trace elements into the fluvial sediments aggravating the geogenic contamination, especially in

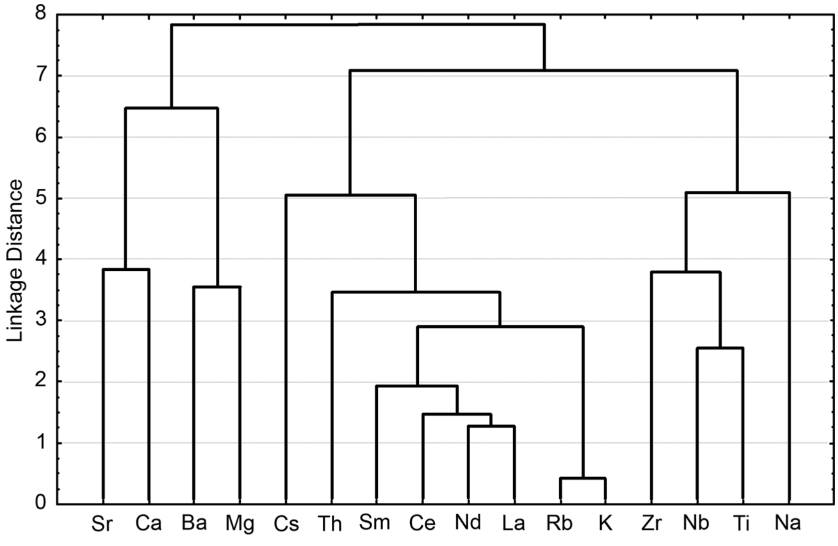

Fig. 4. Dendrogram of hierarchical cluster analysis to illustrate the element concentrations under study in stream sediments of Bistrita River.

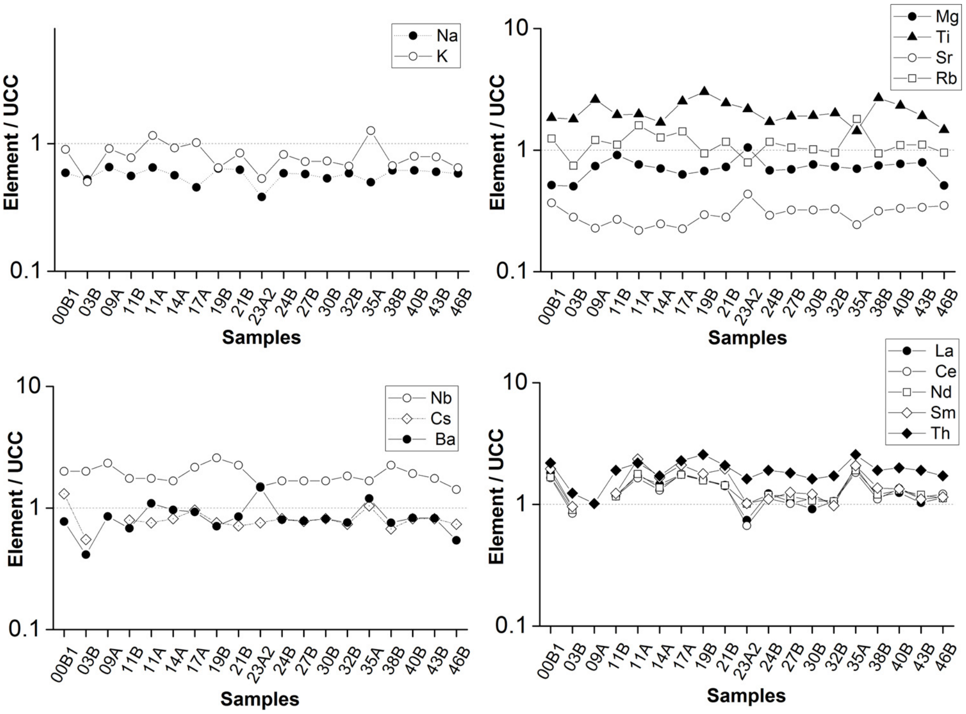

Fig. 5. Elements under study in stream sediments of Bistrita River normalized to the average values of the upper continental crust (UCC).

areas affected by mining activities (i.e. Bistrita river basin) is a major environmental issue and forms a key element of the present study.

An efficient way to assess the geogenic and anthropogenic contribution is by comparing the concentrations obtained to the mean values from the upper continental crust – UCC (Schneider et al., 2016; Wu et al., 2013). The geology of Bistrita drainage basin is made up prevalently of metamorphic rocks and includes mica-schists, quartzitic schists, black quartzites, and chloritic schists. Locally, several Fe, Mn, U and sulfides deposits are emplaced into these rocks and found at outcrop along River Bistrita. On normalization these sediments to the UCC standard, the concentration of the Bistrita sediments reveal a slight depletion in Mg, Ca, Na and K (Fig. 5). This depletion is striking for the Ca concentration. The elements mentioned above are the most soluble ones in aquatic systems (Wu et al., 2013). The Ti contents when normalized to the UCC show a moderate enrichment, whereas values of Rb and Sr from the Bistrita sediments show moderate enrichments for Rb, especially in the sampling points *11A*, *14A*, *17A* and *35A* and a depletion for Sr in all samples (Fig. 5). In case of Zr and Nb, the normalization suggests a high enrichment for both elements in the sediments (Fig. 5). The normalization of Ba and Cs concentrations shows slightly similar values with those from the upper continental crust (Fig. 5), with local enrichments for Ba in certain sampling points. In the case of Cs a moderate depletion regarding the UCC was observed. Positive anomalies can be observed in certain sampling points for Rb, Sr, Ba and Cs. In the area of Călimani sulfur open-pit (sample *23A2*) noticeable enrichments are indicated for Sr and Ba, while near the Crucea U mines (sample *35A*) the anomalies are observed for Rb, Cs and Ba. This suggests a significant anthropogenic contribution in Bistrita sediments composition which is due to the local mining activities. Nevertheless, the geogenic and anthropogenic components contribute in different proportions to the sediments formation, the latter one having a greater share in areas where mining exploitations were/are active.

5.2. Adsorption vs. detrital concentration of trace elements

Trace elements can either be accommodated in the lattice of the detrital minerals or included as tiny accessory minerals such as zircon and monazite in mica. Moreover, these elements are found also adsorbed onto the surface of fine-grained particles, e.g., clay minerals which commonly resulted from supergene alteration. Clay minerals incorporate elements in their lattice or by adsorption on particles surface, especially in the case of expansive clays (i.e. montmorillonite) (Chen et al., 2016; Silva et al., 2016). This dualism is debated in the succeeding paragraph.

Apart from clay minerals, other such as Fe and Mn oxy-hydroxides, or organic matter have also a high adsorption capacity (Oliveira et al., 2016; Sindern et al., 2016). Several factors can influence adsorption, such as adsorption properties of material, surface heterogeneity of sediments, particle size and shape (Tansel and Rafiuddin, 2016). Several previous studies have outlined the association of trace elements with the finer fractions. In the bottom sediments of Qaroun Lake, Egypt, it was observed that increased metals concentrations are associated with an increased silt and clay-sized grains content (El-Sayed et al., 2015). In the shelf sediments from northern Cyprus it was shown that high metals levels were correlated with regions that have high contents of muddy sand and clay (Duman et al., 2012).

In sediments of Bistrita river, the fine-grained fraction is present only in subordinate amounts, suggesting the main source of the studied trace elements to be bound to detrital minerals (Table 3).

The correlation matrix of the studied elements (Table 4) in samples from Bistrita River supports substitution and association mechanisms discussed above. A strong correlation was observed between K and Rb (r = 0.996, Fig. 2), suggesting the substitutions of these two elements in alkali-feldspars and potassium micas (muscovite) from the sediments (Sharma et al., 2013). Another substitution is indicated by the good correlation of Ca with Sr (r = 0.637) showing at least part of the Ca to be replaced by Sr in the carbonate minerals calcite and dolomite. Although Nb shows up in mafic minerals such as pyroxenes, amphiboles, biotite at elevated quantities (Das and Krishnaswami, 2007), the strong correlations between Ti, Zr and Nb indicate that they are concentration not only in the above mafic minerals but also in ultrastable heavy minerals such as zircon and TiO_2 polymorphs. The preference of Nb for zircon and rutile is underscored by the strong positive correlation of the couple Nb – Ti (r = 0.825) and the couple Nb – Zr (r = 0.718) (Fig. 2).

These results prove that the trace elements under study are mainly accommodated in the crystal lattice of rock-forming accessory transported as bed load material from the source rocks to the depocenter, with only a smaller quantity bound to the clay-sized material through adsorption mechanisms. Only in sample *35A* from Crucea U mine adsorption to the clay minerals is likely (Table 4).

5.3. Provenance analysis

Due to their low mobility in aquatic supergene environments, the elements Al, Fe, Ti, Th, Sc, Zr and rare earth elements (REE) are valuable markers to pinpoint the sediment source of the river, where they used to be concentrated in the finer fractions of the sediments (Bhuiyan et al., 2011). The REEs are the most immobile elements and are highly resistant to solution-and-precipitation processes under near ambient conditions (Um et al., 2013; Wu et al., 2013). In river sediments the REEs are in general strongly associated with the clay minerals.

The studied light and medium REEs (La, Ce, Nd, Sm) and Th contents from the Bistrita River show similar values, with a moderate level of enrichment, compared with the UCC values (Fig. 5). The host sediments have been derived from metamorphic and granitic rocks which tend to contain high REE concentrations (Šmuc et al., 2015). The most elevated values were observed at the sample site *35A*, which is located in environs of the uranium mines, near Crucea. The U ore deposits have high concentrations in radioactive elements such as U and Th and in addition contain minerals rich in REEs, Ca and other elements that substitute for the cations in the crystalline structure (Laidlow, 2013).

The studied REEs (La, Ce, Nd, Sm) and Th concentrations are strongly correlated in Bistrita River, showing Pearson coefficients of r = 0.77–0.96 (Fig. 3). These minor elements present high correlation coefficients also with K and Rb suggesting their association with potassium micas (especially muscovite). Strong correlation coefficients between Sr, Ca, REEs, Th, Cs, Rb, K and Nb, Zr, Ti were obtained by the cluster analysis (Fig. 4). Other sampling points that show relatively high REEs concentrations are *11A*, *14A*, *17A*, *19B* and *21B* (Table 1 and Fig. 5). All of these points are located nearby several Mn and sulfide deposits (Fig. 1). Since REEs are associated with muscovite, the main source in the samples under study might be the mica-schists and syngenetic sericitic alteration of various types of ore deposits in the catchment area.

In addition to the use of REEs, another way to establish the source of the sediments can be gone by studying the mineralogy of host rocks and sediments. The mineralogical analysis of the fluvial sediment samples yielded as major constituents quartz, feldspars and muscovite. As minor minerals illite, chlorite, dolomite, calcite, hornblende, kaolinite, epidote, vermiculite, anatase, hematite, goethite, pyrolusite, diopside and pargasite were determined. This mineral assemblage well agrees with the chemical data obtained (Tables 3 and 5).

After performing a Rietveld analysis on the studied samples and obtaining the mineralogical composition (Table 4), a very strong correlation between K concentration and muscovite content was observed (r = 0.916) (Table 5), which shows that K accumulated mostly in muscovite. Potassium feldspar is found in lower amounts in sediment samples than suggested by the lack of correlation between K and feldspar content. This might be due to the source rocks of the sediments that have a lower content in K-feldspar and are richer in acid plagioclase feldspar. No correlation was observed between Ca and feldspar content, either, and a poor correlation for Na – feldspar (r = 0.439), that indicates only albite to be present in the sediment which slightly more resistant to weathering than anorthite (Ca-plagioclase) (Sak et al., 2004). The presence of plagioclase in the sediments in a significant amount (16.5–40 wt% – Table 3) shows an incipient stage of weathering. Plagioclase has a faster rate of alteration, even faster than K-feldspar (Campodonico et al., 2014). The composition of sediments has clearly been inherited from the parent material and, hence, the low degree of weathering led to a mineralogical immature sediment.

Table 5
Correlation coefficients between chemical composition and mineralogical assemblage of stream sediments of Bistrita River.

	Quartz	Muscovite	Feldspar	Chlorite
Na	−0.403	−0.066	**0.439**	0.014
Mg	−0.108	−0.021	0.146	−0.129
K	−0.619	**0.916**	−0.073	−0.374
Ca	0.451	−0.647	0.030	0.309
Ti	−0.023	−0.229	0.194	0.075
Rb	−0.575	**0.933**	−0.13	−0.366
Sr	0.234	−0.471	0.125	0.152
Zr	0.034	−0.057	−0.025	0.207
Nb	−0.016	−0.072	0.050	0.134
Cs	−0.529	**0.584**	0.080	−0.255
Ba	−0.258	0.529	−0.105	−0.392
La	−0.420	**0.821**	−0.203	−0.336
Ce	−0.459	**0.749**	−0.136	−0.180
Nd	−0.471	**0.861**	−0.187	−0.332
Sm	−0.410	**0.812**	−0.194	−0.398
Th	−0.277	**0.576**	−0.159	−0.201

Another correlation was observed between Rb and muscovite content, supporting the K – Rb substitution. The muscovite content from the Bistrita River is correlated also with REEs, Th and Cs concentrations (Table 5) indicating the geochemical associations of these elements in river sediments. The REEs incorporation in muscovite structure proves that the sediments contain primary muscovite which originated from mica-schists and not from alteration during weathering.

6. Conclusions

The chemical composition, particularly of trace elements, and the mineralogical composition of stream sediments of Bistrita River provide valuable information on the source of the sediments. Both datasets allow for establishing the geogenic and anthropogenic contribution to the built-up of stream sediments and moreover how the chemical compounds are related to the minerals in the various grain size fractions. Different solubilities and mobilities of the chemical compounds on transport from the source to the fluvial depocenter are accountable for the element concentration, either in the more arenaceous detrital fraction or adsorbed onto the surface of clay minerals. This is an important environmental issue in an ever increasing globalization, particularly in areas affected by active or abandoned mining operation in the area under consideration as well as elsewhere in the world in metallogenic provinces attractive in terms of base metals and radioactive elements to satisfy the needs of an ever increasing population.

The parameter of geochemical distribution among the trace elements under study were successfully assessed using of statistical methods, including the hierarchical cluster analysis (HCA) and correlation matrix. The identified three main clusters were:

1) K – Rb – Cs – La – Nd – Ce – Sm – Th
2) Na – Ti – Nb – Zr
3) Mg – Ba – Ca – Sr

The current results normalized to the average values of the upper continental crust (UCC) show a slightly enrichment for the Ti, Rb, Nb, La, Ce, Nd, Sm, and Th. This enrichment is caused by the weathering whereas due to their elevated mobility, alkaline and earth alkaline elements Na, Mg, Ca, and K demonstrate a depletion in comparison with the UCC. A conspicuous regional influence of the geology on the sediments was observed in one site where the REE and Th underwent strong enrichment provoked by active mining operations of uranium ore deposits which account for the spill-over of minerals abundant in REE and radioactive elements into the fluvial drainage system. Nevertheless, this influence on the environment shows great international significance, since the deposits from Bistrita basin are classic mineralizations with well-known genetic type models. The sulfide deposits are volcanogenic-sedimentary massive sulfides of Kuroko type (VMSK) associated with metamorphic rocks (Berbeleac, 1998). The genetic model of U mineralization from Crucea is represented by Schwartzwalder deposit, Front Range, USA, with similar ore deposits at Rožná, Bohemian Massif, Czech Republic, or Arjeplog-Arvidsjaur deposits from Sweden (Murariu, 2005). Similar environmental impact of uranium exploitations was reported also in different parts of the world, where stream sediments act as storage bodies for trace elements. For instance, at Bertholène uranium mining site, France, it was observed that stream conditions contribute to trace elements re-mobilization and transportation, enhancing their potential availability (Cuvier et al., 2016).

The mineral assemblage of the stream sediments allowed for a better understanding of evolution of the fluvial sediment load and corroborates the strong geogenic impact, mainly from various units made up of metamorphic rocks. Correlating the mineralogical and chemical datasets attests to the abundance of plagioclase s.s.s and, hence, a moderate degree of chemical weathering. With this in mind a classification of the Bistrita River drainage system and its sediments can be achieved. It of Quaternary age, and from the mineralogical as well as mineralogical point of view immature. This is especially true for the phyllosilicates and its main representatives of the mica group. The close association of REE and muscovite is typical of a clay mineral of primary origin still hosting the REE minerals unlike secondary phyllosilicates newly developed during weathering alongside with detrital REE carriers.

Further research studies on a more detailed scale near the mining sites to assess the magnitude of the impact, especially of toxic elements into the ecological cycle are necessary to solutions and implement measures of remediation for this sort of environments in Romania and across the globe.

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