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The anthropic impact on the geochemistry of sediments of the river Bistrița (upstream of Izvorul Muntelui lake), Romania

DOCTORAL THESIS

ABSTRACT

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INTRODUCTION

The river sediments in the aquatic environment are responsible for minor elements concentration and play an important role in the transport and storage of toxic elements. The sediments are heterogeneous assemblages consisting of a variety of absorbent phases (i.e. organic matter, oxides, carbonates, sulfides, clays) whose abundance is subject to hydrological, pH and redox conditions (Zhang et al., 2014).

In the last years, the contamination with certain minor elements has become a worldwide problem, due to their toxicity, persistence and abundance of these elements in the environment.

Large quantities of dangerous chemicals, mainly with high concentrations of heavy metals were discharged into rivers around the world, due to the rapid growth of the global population, but also due to the expansion of industrial and agricultural production (Islam et al., 2015).

In the permissible concentrations the minor elements play an essential role in functioning of organism processes, but overcoming these values can lead to serious consequences.

In addition to anthropic activity, the concentration of heavy metals in sediments is closely related to geological formations (Wijaya et al., 2013). Contamination of sediments with minor elements can affect water quality and therefore this represents an international concern for toxicity and bioaccumulation of these metals (Li et al., 2013). To identify the degree of contamination in sediments, a series of pollution indices were applied, such as enrichment factor (EF), pollution index (PLI), ecological risk index (RI), geo-accumulation index (I_{geo}) and index priority (P_{index}) (Yang et al., 2009, Mohiuddin et al., 2010, Olubunmi, 2010, Kabir et al., 2011, Jiang et al., 2013, Wijaya et al., 2013, Maftei et al., 2014).

Bistrita River is a tributary of the Siret River, one of the most important hydrographic basins in Romania and is located in the central-eastern part of the Eastern Carpathians (Romania). It has many important hydrotechnical developments resulting in one of the biggest lakes, Izvorul Muntelui. Bistrita river basin is of major importance upstream of Izvorul Muntelui Lake, where manganese ore, polymetallic sulfides, native sulfur and uranium were extracted.

This study presents an analysis of sediments in Bistrita river upstream of Izvorul Muntelui Lake, since this area is affected by the presence of numerous waste dumps and underground mining works (closed or still active) which contributes to acid mine drainage process. These sources lead to an increasing level of water, soil and river sediment contamination.

The main objectives of the study were: (1) determining the concentrations of major and minor elements in Bistrita River sediments (upstream of Izvorul Muntelui Lake); (2) identification of spatial distribution of minor elements (Cr, Co, Ni, Cu, Zn, Cd, Pb, As) in Bistrita river sediments; (3) assessing the degree of contamination of sediments by pollution indices and geochemical background values; (4) correlation of chemical and mineralogical aspects through cluster multivariate analysis; (5) identifying the sediment source by comparing the contents with the average values of the upper continental crust.

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I. GEOLOGY OF THE BISTRIȚA BASIN (UPSTREAM OF IZVORUL MUNTELUI LAKE)

I.1. Lithostratigraphy

Bistrita river basin (upstream of Lake Izvorul Muntelui) crosses three major geological units known as the Crystalline-Mesozoic (or Median Dacides), and Carpathian flysch and Transcarpathian flysch. The Median Dacides consist of Alpine tectonic units such as Infra-Bucovinean, Sub-Bucovinean and Bucovinean Nappes (Balintoni, 2010). The composition of Median Dacides consists also in crystalline schists which forms pre-alpine crystalline massifs and sedimentary deposits. The geology of the studied area is shown in Figure 1.

According to Mutihac (2010), the central-eastern Carpathian unit includes the pre-Hercynian crystalline schists complex with a wide expansion and into which two groups can be distinguished according to the degree of metamorphism: the meso-metamorphic crystalline schists and epi-metamorphic schists.

Balintoni (1997) identified within the Tulgheș group the following lithozones: Holdița, Leșu Ursului and Arșița Rea. The Holdița lithozone is of black color due to the presence of graphite, and it hosts pre-metamorphic mineralizations of Fe-Mn and barite.

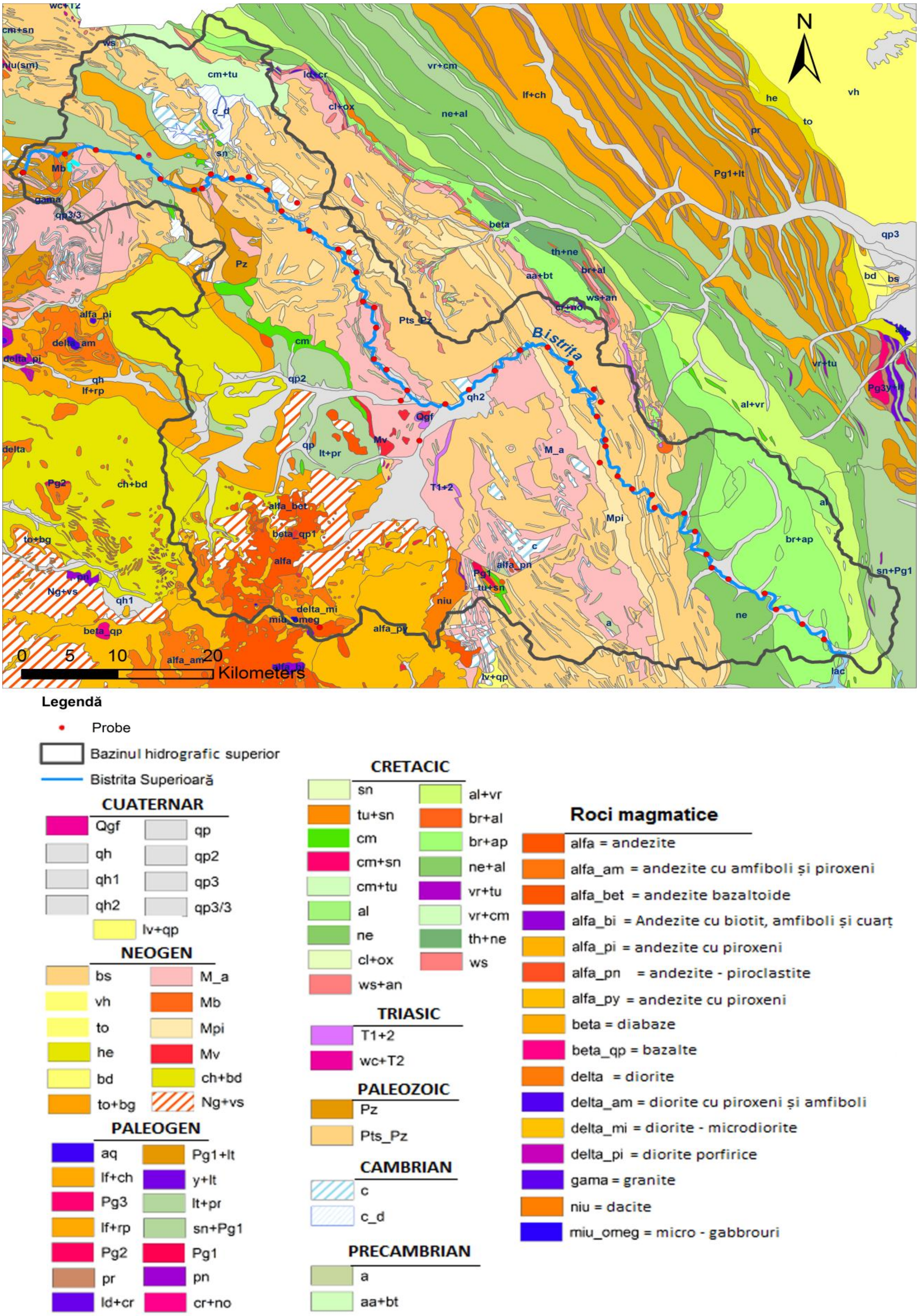

Figure 1. *Geological map of Bistrița hydrographic basin (upstream of Izvorul Muntelui Lake), modified after Ianovici et al. (1968a), Ianovici et al. (1968b)*

I.2. Metallogeny

The Crystalline-Mesozoic area is very complex regarding the mineralogy and metallogeny due to the Fe, Mn, U and polymetallic sulfides accumulations. These deposits can be found on the eastern and western alignment of Bistrița river and they have a strong impact on the environment (Rusoaia, Fluturica Cîrlibaba, Dadu, Orata, Colacu, Oița, Mestecăniș, Tolovanu, Iacobeni, Căprăria, Arșița, Argestru, Fagu, Crucea, Leșu Ursului, Valea Leșului, Isipoaia, Holdița and Broșteni). The mining activities in the area are mostly ceased, but modern methods of rehabilitation have not been applied so far.

As an overview, the genetic ore type is given by the hydrothermal metamorphosed-sedimentary character (Dadu, Oița, Rusoaia, Tolovanu, Iacobeni, Broșteni and Holdița ore deposits) from Proterozoic and Cambrian. The mineralizations of Fagu, Crucea, Leșu Ursului, Valea Leșului, and Isipoaia are of Kuroko type with Cambrian ages. The ore is shaped as lenses consistent with the rock schistocity (Rusoaia, Dadu, Oița, Iacobeni), massive ore lenses and stratiform dissemination (Arșița, Fagu, Crucea, Leșu Ursului, Valea Leșului, Isipoaia), and as veins in the case of Mestecăniș deposit.

II. SAMPLES AND ANALYTICAL METHODS

II.1. Studied area

The studied area is represented by the hydrographic basin of Bistrița river (upstream of Izvorul Muntelui Lake), located in the central-eastern part of the Eastern Carpathians (Figure 2).

II.2. Sampling

A total number of 52 sediment samples were collected along the river Bistrița at an equidistance of about 3-4 kilometers depending on the accessibility and potential sources of pollution. Some of the sampling points were located downstream of the confluence with its major tributaries (Rusoaia, Țibău, Cîrlibaba, Argestrul, Dorna, Pr. Neagra, Crucea, Barnarul, Holdița, Borca) (Figures 3 and 4).

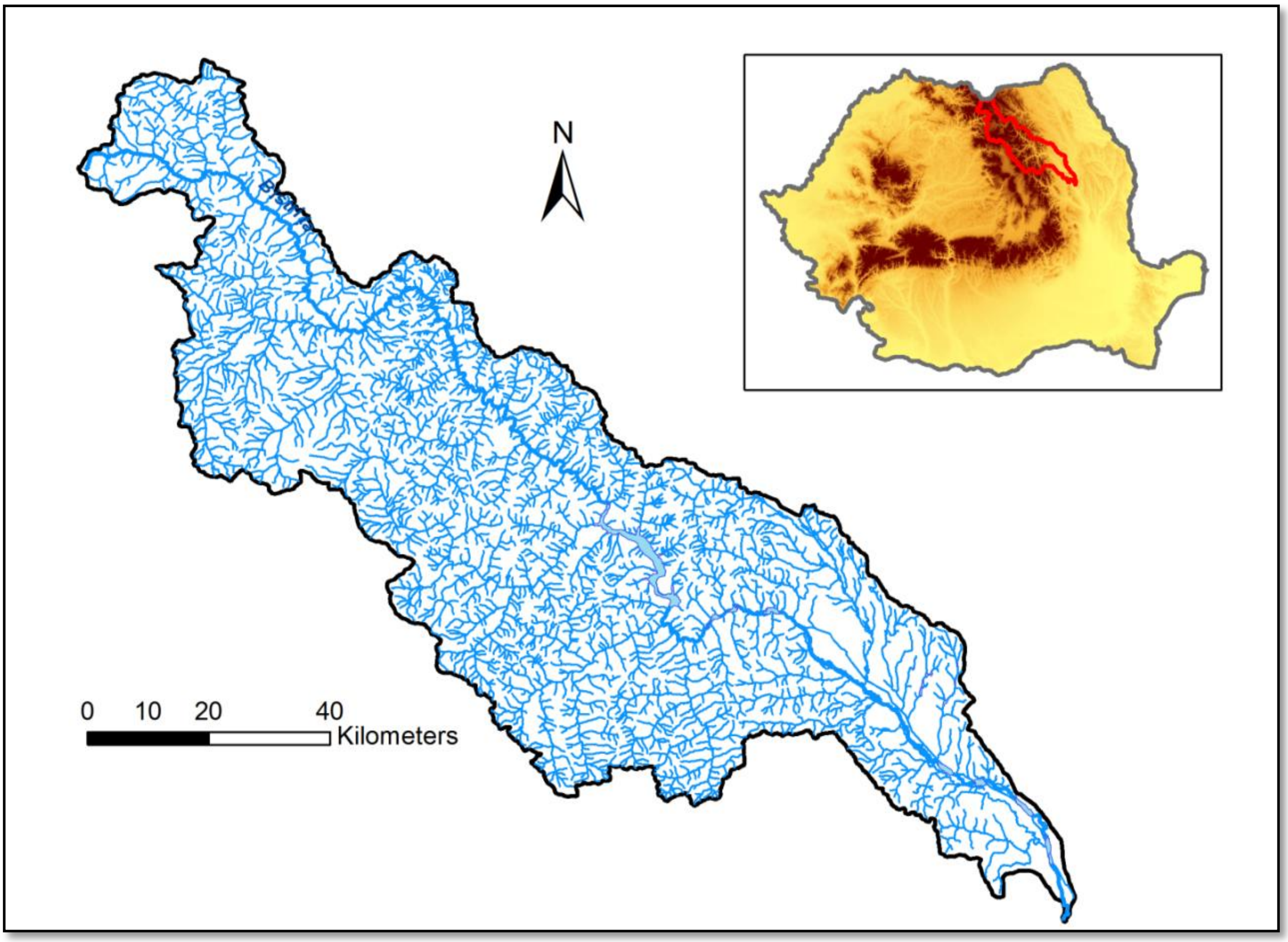

Figure 2. *Hydrological map of Bistrița river basin*

For each sample were collected about 2 kg of stream sediment and stored in self sealed plastic bags. At the sampling point were determined the basic physico-chemical parameters of water, such as pH, temperature (°C), dissolved oxygen - LOD (mg/L) and total dissolved salts - TDS (mg/L).

The sediment samples were dried in the electric oven (70°C) and separated into two fractions by sieving at a particle size of 0.16 mm. Only the fine fraction < 0.16 mm was used for the analysis.

II.3. Analytical methods

II.3.1. X-ray fluorescence (XRF)

The analyses were carried out at the Department of Geology, Faculty of Geography and Geology, "Alexandru Ioan Cuza" University of Iasi and also at the Federal Institute for Geosciences and Natural Resources from Hannover, Germany.

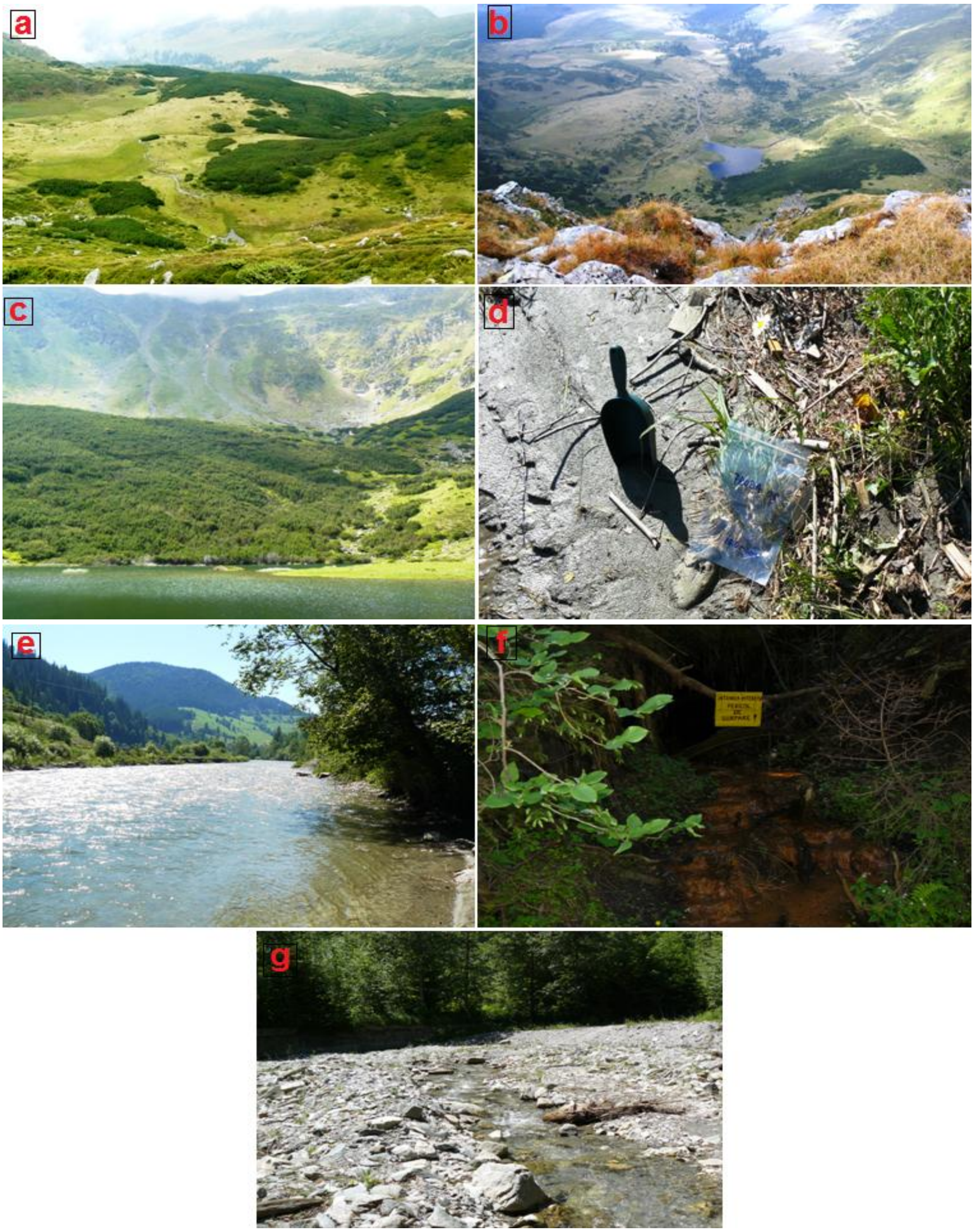

Figure 3. a - *Bistrița Aurie Springs (Rodnei Mountains),* **b** - *Știol Lake (view from Gărgălău peak),* **c** - *Știol Lake (sampling point 00B1),* **d** – *Sampling at the 04B point, Bistrița river*, **e** - *Bistrița river,* **f** – *Tributary that drains the Ciocănești area (Suceava county), ceased mining activity (sampling point 14A),* **g** – *Sampling point 35A, mining activity from Crucea (Suceava county).*

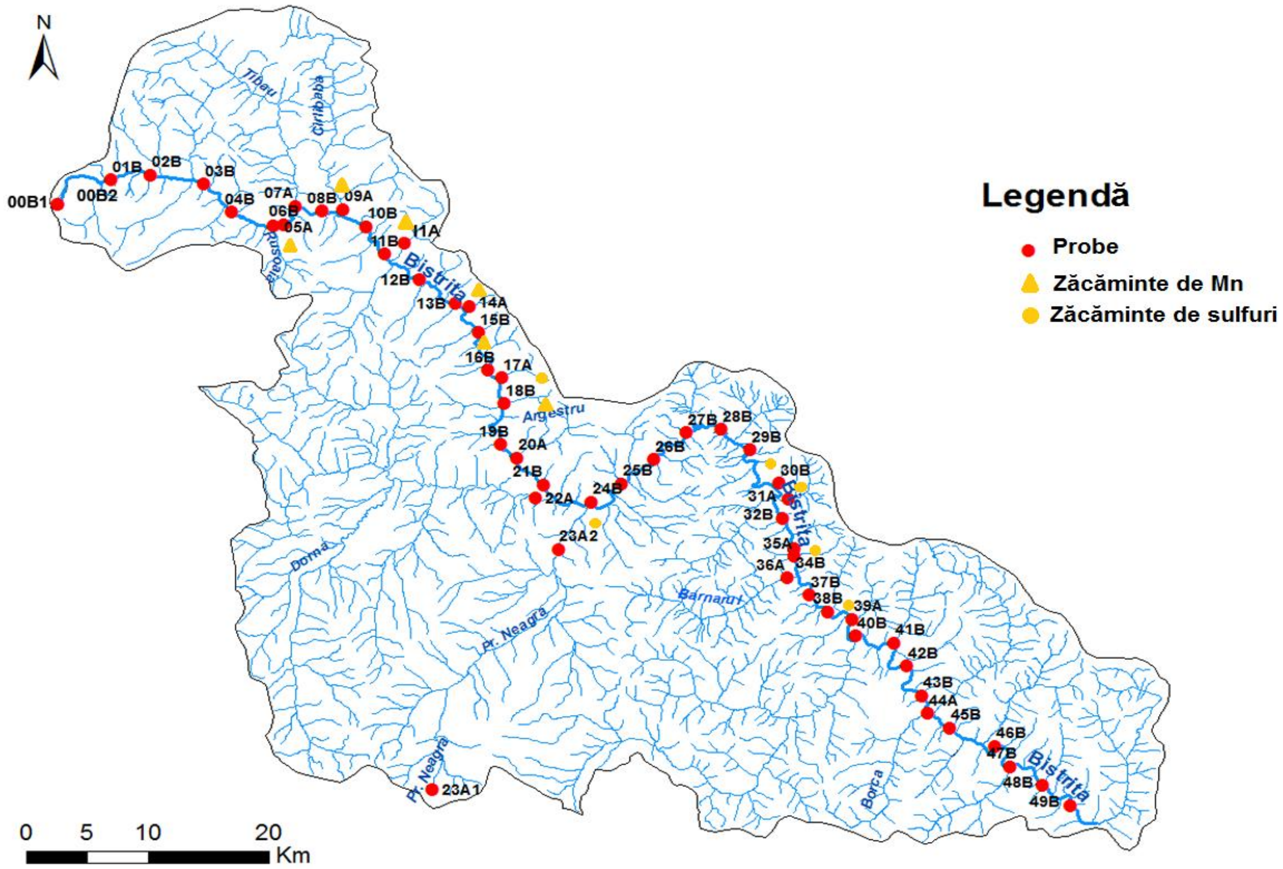

Figure 4. *Sediment sampling map (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

The chemical analysis of the elements Ti, Mg, Ca, Na, K, Cs, Sr, Rb, Ba, Zr, Nb, La, Ce, Nd, Sm and Th was performed using a Philips PW2400 Spectrometer (WD-XRF) at the Federal Institute for Geosciences and Natural Resources from Hanover, Germany.

II.3.2. X-ray diffraction (XRD)

The XRD analysis was performed within the Federal Institute for Geosciences and Natural Resources from Hanover, Germany, by using a PANalytical MPD Pro with Cu anod and double detector. Scanning range was between 2 and 85 degreees.

II.3.3. Infrared Spectrometry (PIMA)

The infrared measurements were carried out with a Portable Infrared Mineral Analyzer (PIMA) from Integrated Spectronics Pty Ltd. The device operates in the wavelength region from 1300 to 2500 nm. This technique allows non-destructive and in-situ analysis in a very short time. The sample has to be placed in front of the optical port where the infrared radiation passes into the sample. The radiation penetrates the sample to about 2-3 mm, and it is reflected back to a monochromator. At the end an absorption spectrum is obtained. The measured area of a sample is 10 mm in diameter. The spectra are acquired with the help of PimaSP Acquisition v2.1 software and the spectra interpretation is made with PimaView 3.1 software.

II.3.4. Micro-Raman spectroscopy

The micro-Raman spectra were obtained with an unpolarized Raman spectrograph Horiba - Jobin Yvon - Labrie, equipped with an Olympus microscope (using the lens with 100x magnification factor). The 633 nm line of a He-Ne laser was used for excitation, with a holographic diffraction grating 600 lines/mm and a CCD detector. The laser power was controlled by a series of density filters to prevent degradation of the sample. However, some samples have not been identified using the red laser, due to the fluorescence phenomenon present in some of the crystals. In this case, the samples were analyzed using the 532 nm green laser.

The sediment samples were treated with distilled water in several steps and separated from the clay fraction using the 0.10 mm sieve. The samples were dried in an oven at a temperature of 40 °C. The sediment grains were sorted using a binocular magnifier and identified by micro-Raman spectroscopy at the Geological Institute in Banská Bystrica, Slovakia.

III. GEOCHEMICAL ANALYSIS OF MAJOR AND TRACE ELEMENTS AND MINERALOGY OF THE SEDIMENTS FROM BISTRITA RIVER (upstream of Izvorul Muntelui Lake)

III.1. STATISTICAL INTERPRETATION

III.1.1. Descriptive statistics

The statistical analysis of elements Na, Mg, K, Ca, Ti, Rb, Sr, Zr, Nb, Cs, Ba, La, Ce, Nd, Sm and Th in sediments of Bistrita River (upstream of Izvorul Muntelui lake) was achieved using Statistics 12.0 software. Several statistical parameters were determined, such as minimum and maximum, arithmetic mean, median, skewness values (asymmetry), variance and standard deviation.

The association between variables was identified using the Pearson's correlation coefficient applied to a series of data with a normal distribution.

The relationship between variables was determined using the cluster analysis (HCA) after standardizing the data set, calculating the Euclidean distance and using the complete linkage method. Thereby, a new data matrix was obtained and the significant correlations were identified.

III.1.2. Hierarchical cluster analysis (HCA) and Pearson correlation coefficient

The cluster analysis is a method for identifying groups or clusters based on the similarity between classes of variables (Chabukdhara and Nema, 2012).

The hierarchical cluster method is the most often used because it identifies clusters with similar variables and then joining successively the following similar data (Davis, 2002, Forina, 2002).

The calculation principle consists in the determination of the variables in a data matrix of *n* x *n* with similarity between pairs. The pairs of data which show the highest similarities will be merged. The matrix is recalculated and it represents the average similarities between variables combined with other variables. The process continues until the similarity matrix is reduced to a 2 x 2 form (Davis, 2002). The objects are gradually united into groups to a final cluster containing all variables. The larger groups are obtained by merging the smaller ones (Forina, 2002).

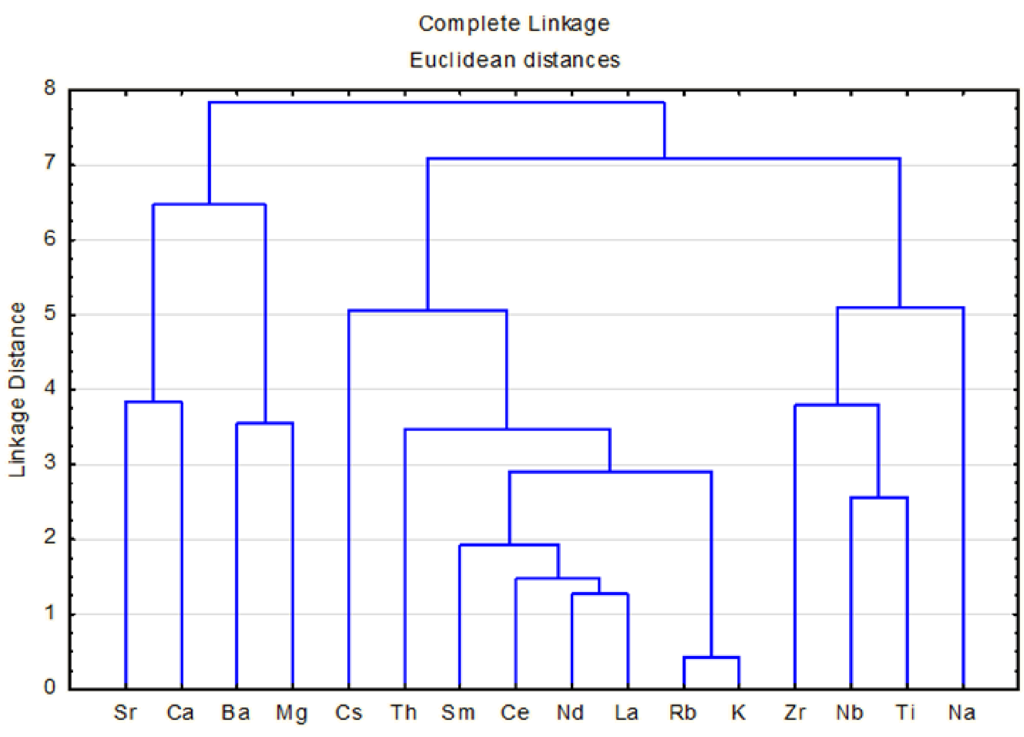

Figure 5. *Dendrogram showing the cluster representations of the variables*

Measurements are made on each object in the data set and at *n* objects and *m* features the observations are given as *n* x *m*, X matrix.

The standardization of the data set is an important step in cluster analysis. This method is required in those cases in which the Euclidean distance from the dissimilarity matrix (or matrix of distances between variables) shows high sensitivity to differentiate between the size or scale of the variables (Milligan and Cooper, 1988). This method is used to smooth the data set, to eliminate the differences between values and to bring the variables at closer scales.

A strong positive correlation is observed between the elements Rb and K (r = 0.995). This suggests a control of the alkali feldspar and potassium micas on these elements in sediments (Sharma et al., 2013).

The Sr concentration in Bistrita river sediments (upstream of Izvorul Muntelui Lake) is positively correlated with Ca concentration (r = 0.591) suggesting a Ca substitution by Sr, due to the similarity of the ionic radii (Salminen, 2005), especially in carbonate minerals from Bistrita river sediments (calcite and dolomite).

Ba and Mg are positively associated (r = 0.651) due to retention of Ba in clay minerals (Das and Krishnaswami, 2007). Nb concentrates in mafic minerals such as pyroxenes, amphiboles and biotite (Ranasinghe et al., 2008). The strong positive correlations of Nb with Ti (r = 0.818) and Zr (r = 0.722) indicates its concentration in the heavy minerals from sediments. The presence of Nb in rutile and zircon is indicated by the correlations Nb-Ti and Nb-Zr, respectively (Salminen, 2005).

The correlation matrix shows a significant association, but with a negative trend, of the elements Ca – K (-0704), Ca – Rb (-0695), Ca – La (-0.707), Ca – Ce (-0614), Ca – Nd (-0682), Ca – Sm (-0692), which suggests that the ratio carbonate / potassium silicates, mainly orthoclase and micas (muscovite, biotite), is controlling the concentration in sediments of Rb, La, Ce, Nd and Sm. The negative correlation between K and Ca is determined by the sediment mineralogy (high carbonate content occurs at the expense of silicates).

III.2. MINERALOGY OF THE SEDIMENTS

In the Bistrita river sediments (upstream of Izvorul Muntelui lake) were identified the following main minerals by X-ray diffraction (XRD): quartz - SiO_2, muscovite - $KAl_2(Si_3Al)O_{10}(OH,F)_2$, illite - $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, potassium and plagioclase feldspar ($KAlSi_3O_8$, $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$), chlorite - $(Mg,Fe,Li)_6AlSi_3O_{10}(OH)_8$ and accessory minerals: 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 - $CaCO_3$.

From the results given by infrared spectroscopy on Bistrita River sediments (upstream of Izvorul Muntelui Lake), the following compositions were obtained (Figure 6):

Muscovite (38.37%) > plagioclase (29.26%) > potassium feldspar (26.88%) > quartz (2.31%) > kaolinite (2.18%) > illite (0.43%) > epidote (0.35%) > vermiculite (0.31%).

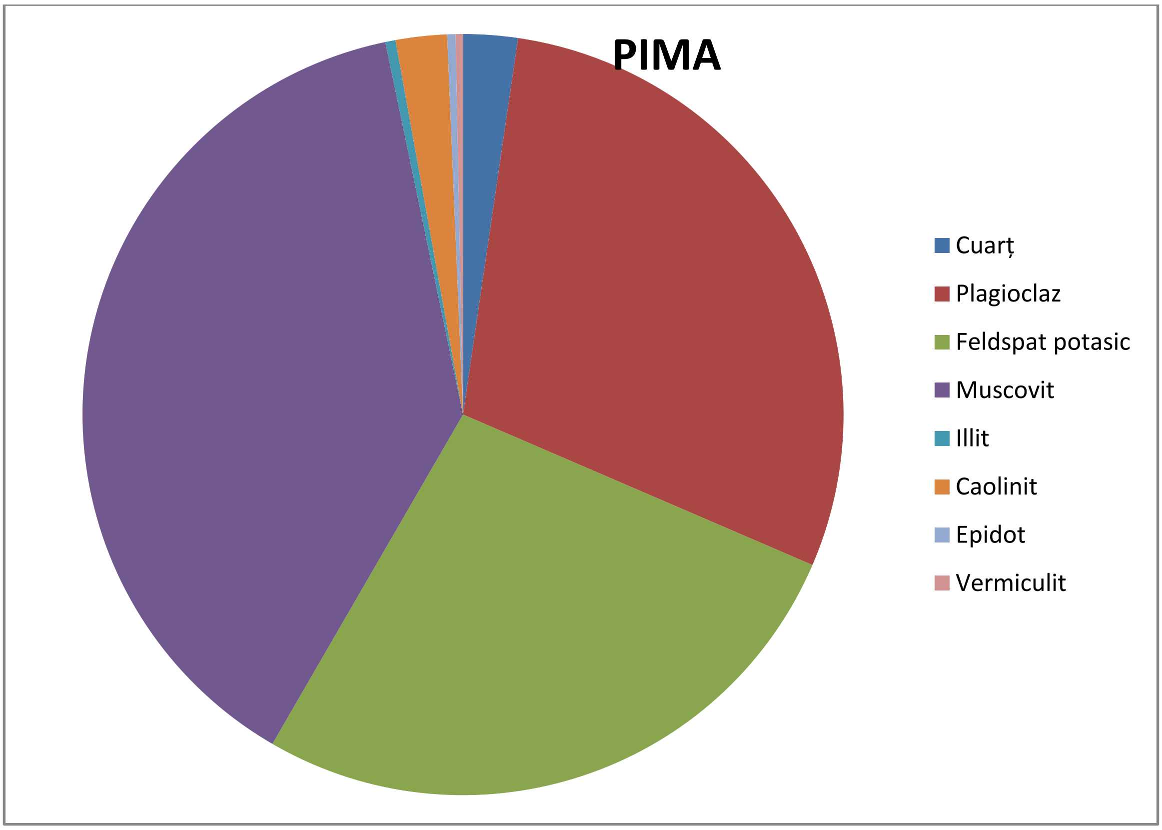

Figure 6. Mineralogical distribution in Bistrita River sediments (upstream of Izvorul Muntelui Lake) based on the results obtained by IR spectroscopy

By using the micro-Raman spectroscopy the following minerals have been identified in the sediments of Bistrita river (upstream of Izvorul Muntelui Lake),: anatase - TiO_2 (Figure 7), calcite - $CaCO_3$ (Figure 8), quartz - SiO_2 (Figure 9), diopside - $CaMgSi_2O_6$ (Figure 10), goethite - $FeO(OH)$, hematite - Fe_2O_3, muscovite - $KAl_2(Si_3Al)O_{10}(OH,F)_2$, pargasite - $NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}(OH)_2$ and pyrolusite - MnO_2.

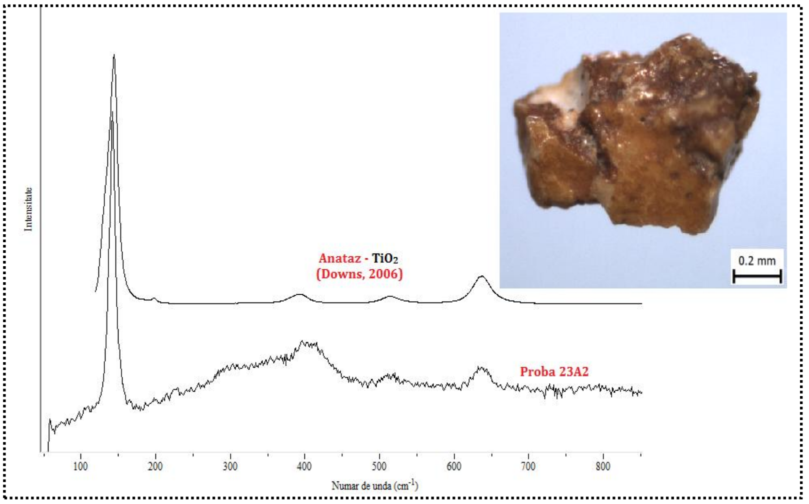

Figure 7. *Micro-Raman spectrum of anatase compared with reference spectrum after Downs (2006)*

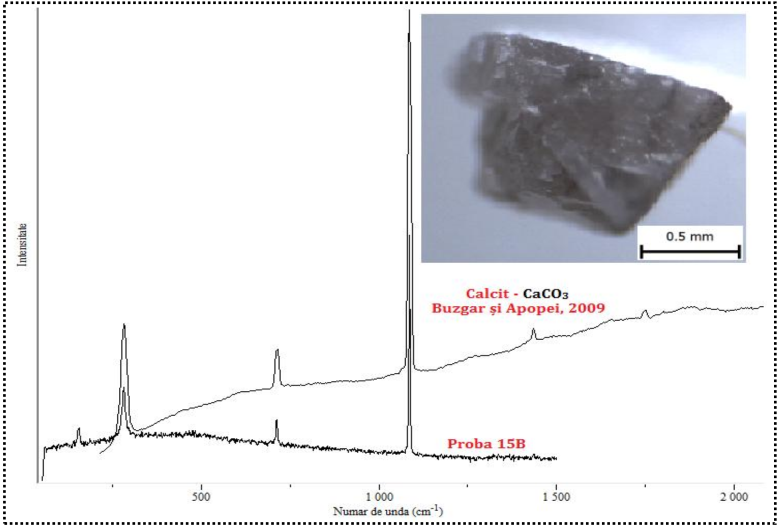

Figure 8. *Micro-Raman spectrum of calcite compared with reference spectrum after Buzgar and Apopei (2009)*

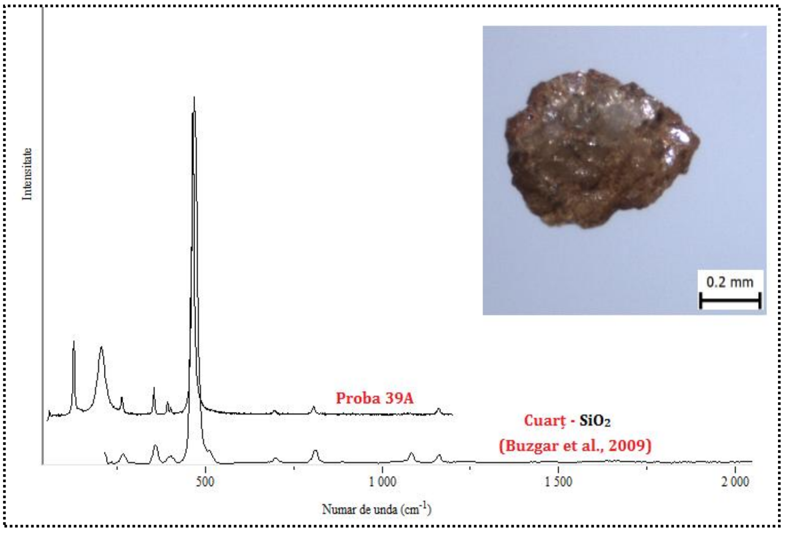

Figure 9. *Micro-Raman spectrum of quartz compared with reference spectrum after Buzgar et al. (2009)*

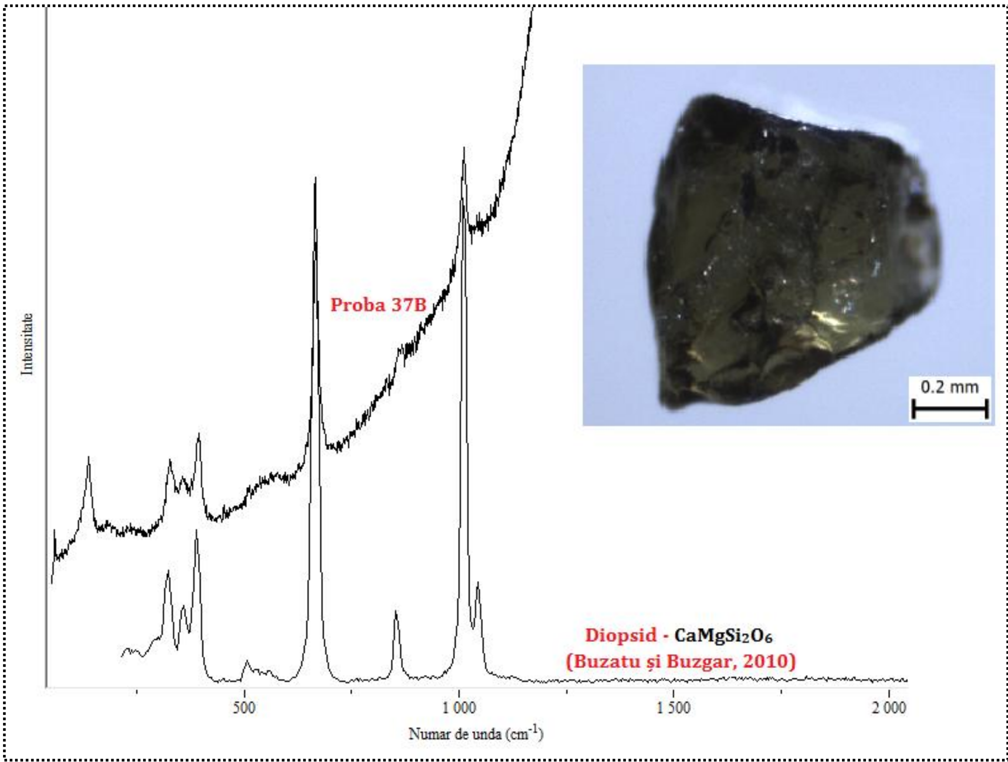

Figure 10. *Micro-Raman spectrum of diopside compared with reference spectrum after Buzatu and Buzgar (2010)*

III.4. SEDIMENTS GEOCHEMISTRY

The concentration of major and minor elements determined in Bistrita river sediments (upstream of Izvorul Muntelui Lake) is given in descending order by the series: K (2.23 %) > Na (1.84 %) > Mg (1.75 %) > Ca (1.31 %) > Ti (1.28 %) > Ba (524 mg·kg^{-1}) > Zr (365.16 mg·kg^{-1}) > Sr (98.16 mg·kg^{-1}) > Rb (92.47 mg·kg^{-1}) > Ce (81.56 mg·kg^{-1}) > La (40.41 mg·kg^{-1}) > Nd (36.07 mg·kg^{-1}) > Nb (22.21 mg·kg^{-1}) > Th (20.37 mg·kg^{-1}) > Sm (7.03 mg·kg^{-1}) > Cs (4.17 mg·kg^{-1}).

III.4.1. Sodium (Na), Magnesium (Mg), Potassium (K), Calcium (Ca) and Titanium (Ti)

The Na, Mg, K, Ca, and Ti contents in the sediments of Bistrita River (upstream of Izvorul Muntelui Lake) are within the ranges 1.25% to 2.13% (average 1.84%) - Na, 1.25% and 2.60% (with an average of 1.75%) - Mg, 1.41% and 3.55% (average 2.23%) - K, 0.44% and 2.55% (average 1.31%) – Ca, and 0.87% and 1.93% (with an average of 1.28%) for Ti, respectively (Figure 11).

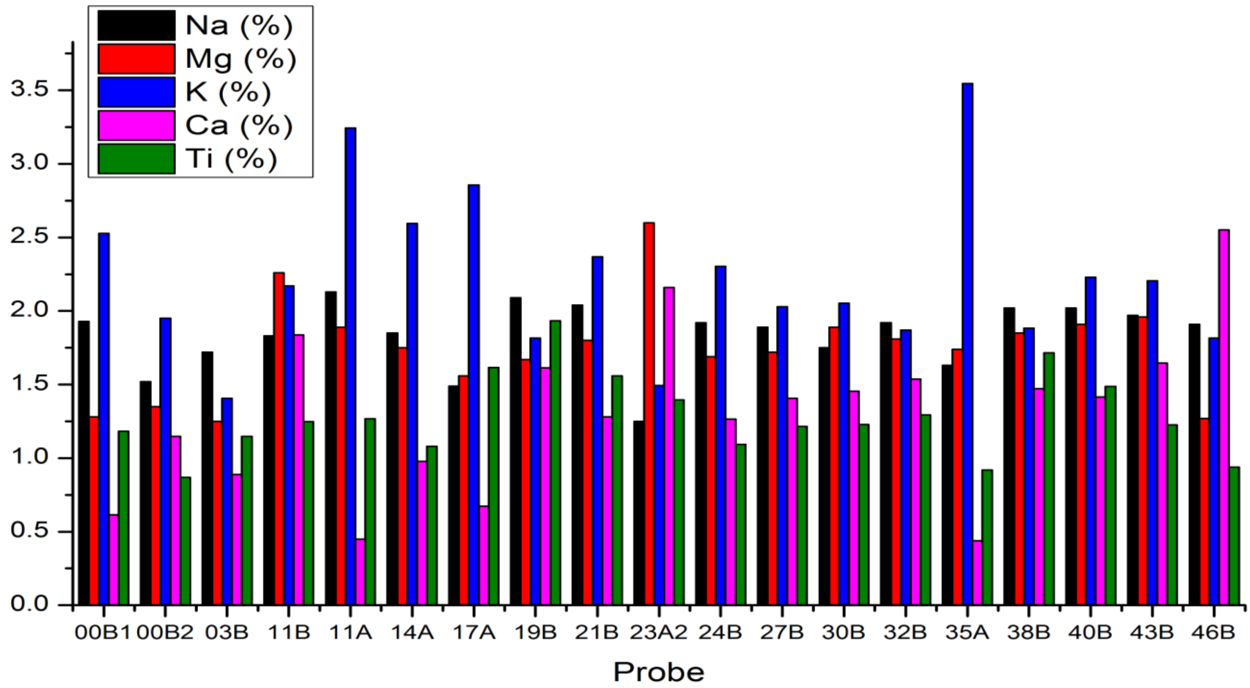

Figure 11. *The distribution of Na, Mg, K, Ca and Ti (%) in sediments of Bistrita River (upstream of Izvorul Muntelui Lake)*

In the Bistrita river sediments (upstream of Izvorul Muntelui Lake) is observed a decrease in concentrations of the mobile elements Mg, Ca, Na and K (Figures 12, 13, 14 and 15). The lowest Ca contents were recorded in the sampling points 00B1, 11A and 35A (Figure 22). The Mg and K contents are constant, with relatively slight increases for K in sampling points 11A and 35A and for Mg in sampling points 11B and 23A2.

The normalization of Ti content from Bistrita River sediments (upstream of Izvorul Muntelui lake) to the upper continental crust suggests a moderate increase (Figure 16). The highest concentrations of Ti were identified in the sampling points 17A, 19B, 21B and 38B.

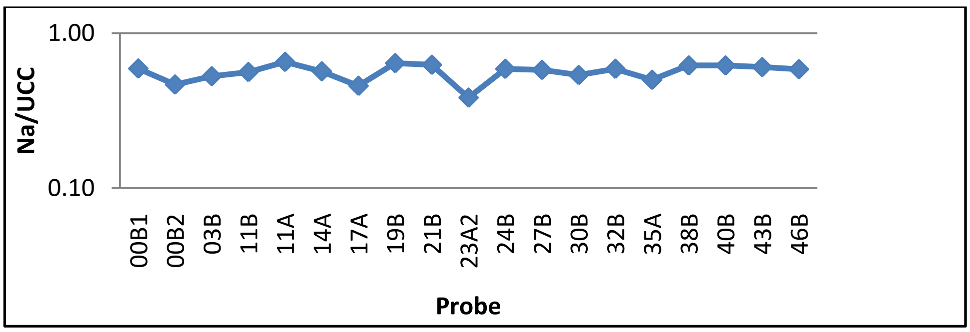

Figure 12. *The Na content (%) normalized to UCC*

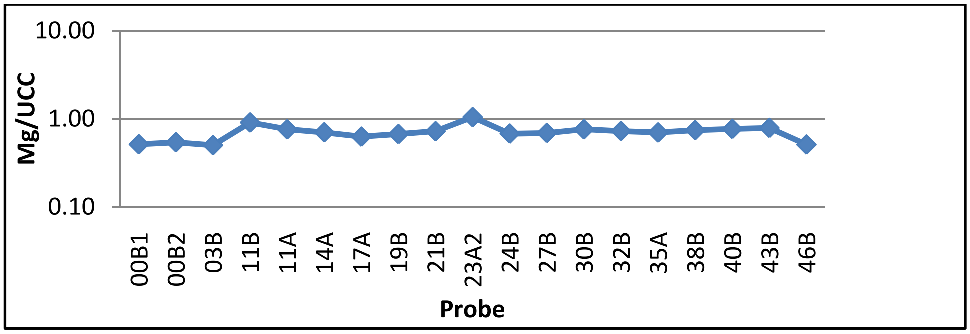

Figure 13. *The Mg content (%) normalized to UCC*

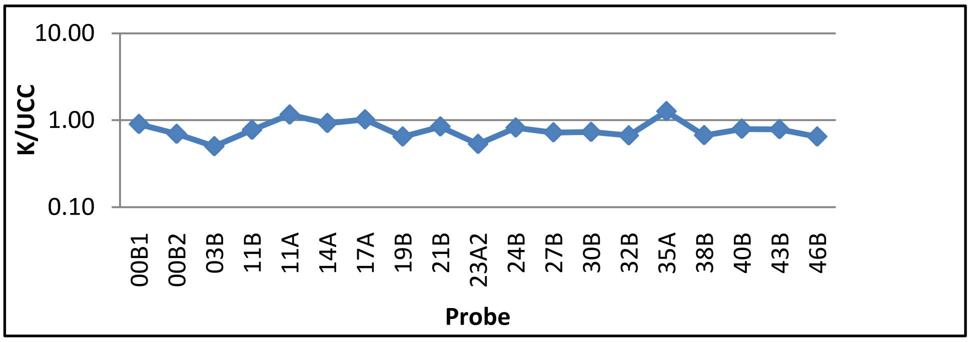

Figure 14. *The K content (%) normalized to UCC*

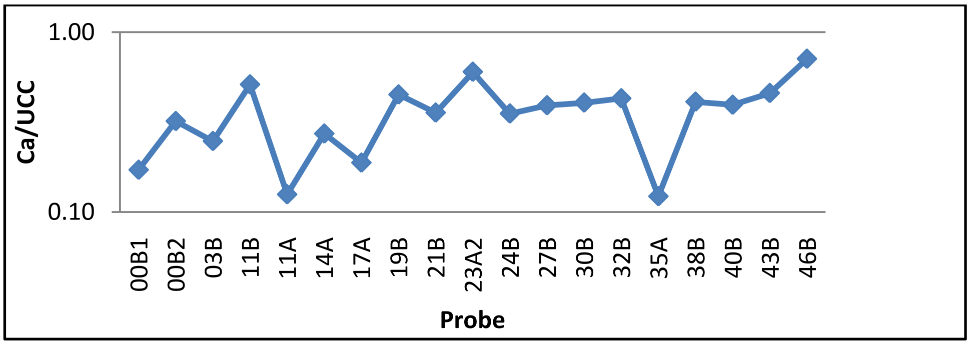

Figure 15. *The Ca content (%) normalized to UCC*

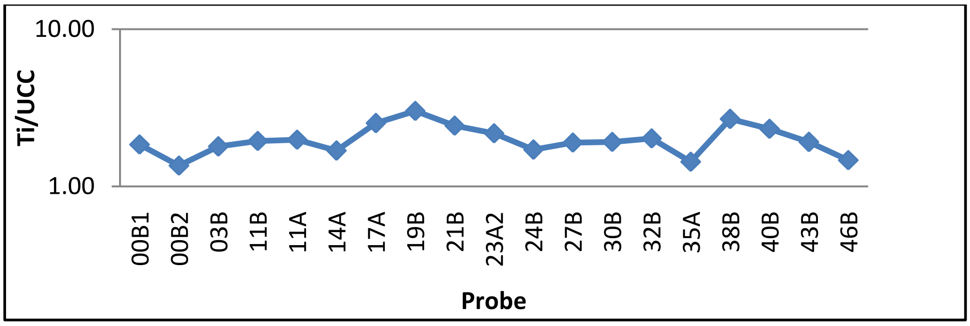

Figure 16. *The Ti content (%) normalized to UCC*

III.4.2. Rubidium and Strontium (Rb and Sr)

The content of Rb in Bistrita river sediments (upstream of Izvorul Muntelui Lake) is in average of 92.47 mg·kg^{-1} and it ranges from 61 mg·kg^{-1} to 148 mg·kg^{-1}. The average content of Sr is 96.18 mg·kg^{-1} and it ranges from 70 mg·kg^{-1} to 139 mg·kg^{-1}.

The normalization of Rb and Sr contents from Bistrita river sediments to the upper continental crust values indicates a sharp increase in Rb concentration in the sampling points 11A, 14A, 17A and 35A (Figure 17) and a progressive decrease of Sr content in all sampling points (Figure 18).

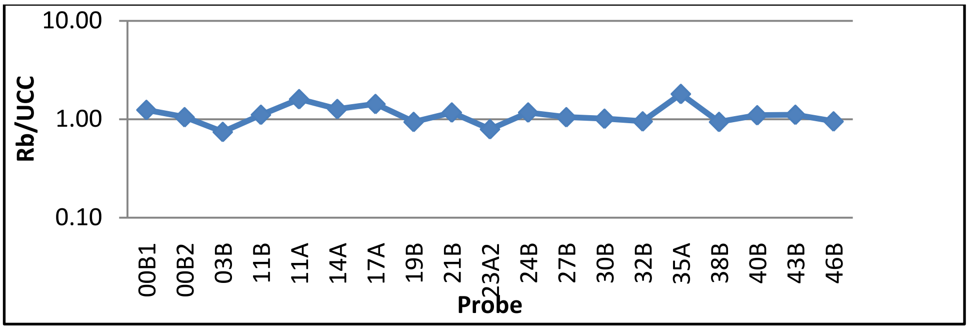

Figure 17. *The Rb content (mg·kg^{-1}) normalized to UCC*

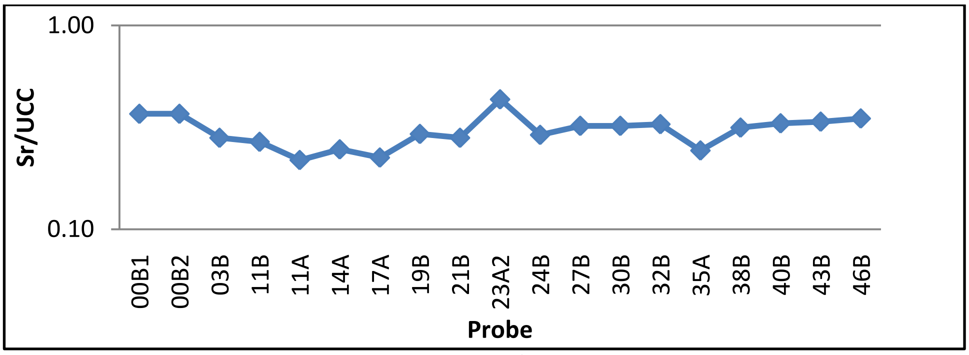

Figure 18. *The Sr content (mg·kg^{-1}) normalized to UCC*

III.4.3. Zirconium and Niobium (Zr and Nb)

The Zr content in the sediments of Bistrita River (upstream of Izvorul Muntelui Lake) is on average of 356.16 mg·kg^{-1} and it ranges from 212 mg·kg^{-1} to 767 mg·kg^{-1} (Figure 19). The Nb concentration ranges from 17 mg·kg^{-1} to 31 mg·kg^{-1}, with a mean value of 22.21 mg·kg^{-1} (Figure 20).

III.4.4. Cesium and Barium (Cs and Ba)

The contents of Cs and Ba in the sediments of Bistrita River (upstream of Izvorul Muntelui Lake) range from 2.70 mg·kg^{-1} to 7.60 mg·kg^{-1} with an average value of 4.17 mg·kg^{-1} (Cs) and from 259.80 mg·kg^{-1} to 925.30 mg·kg^{-1} with an average of 524.86 mg·kg^{-1} (Ba), respectively (Figure 20 and 31).

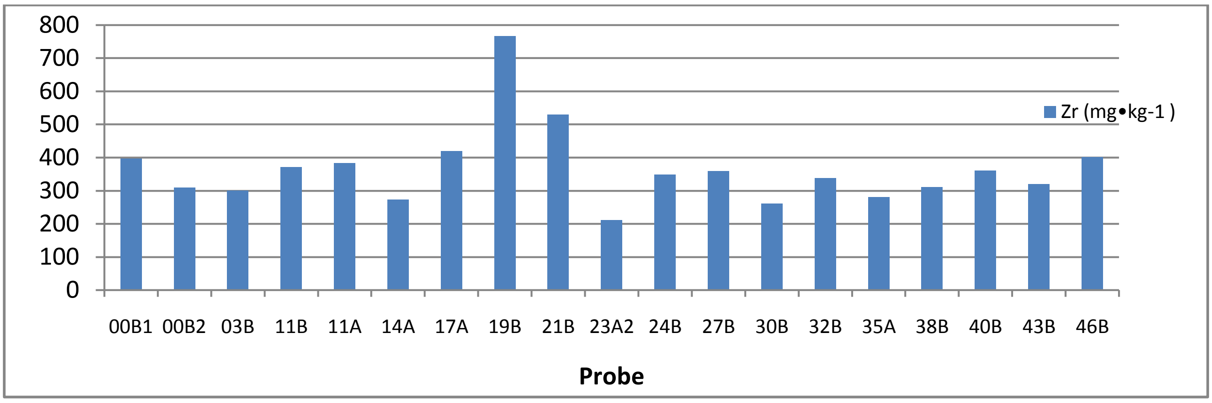

Figure 19. *The Zr distribution (mg·kg^{-1}) in sediments of Bistrita river (upstream of Izvorul Muntelui Lake)*

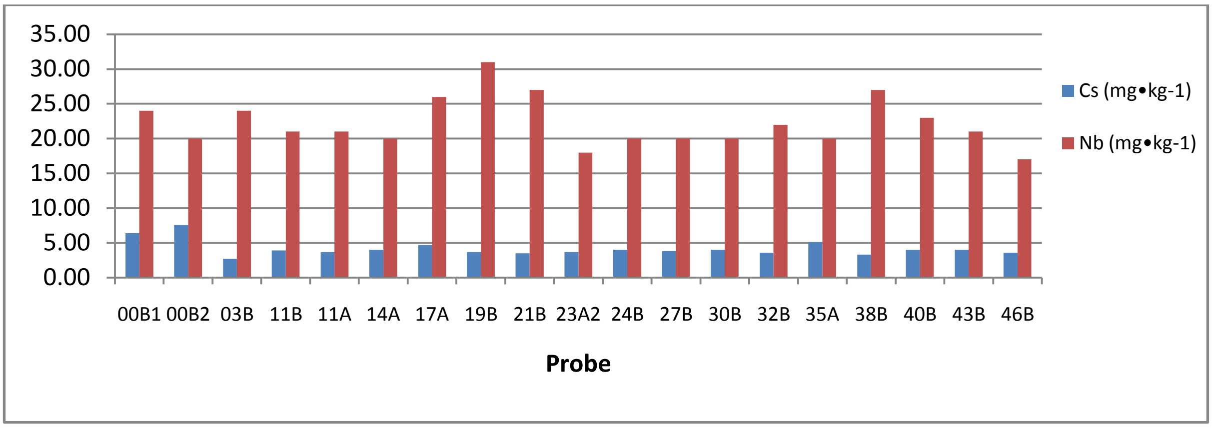

Figure 20. *The Nb and Cs distribution (mg·kg^{-1}) in sediments of Bistrita river (upstream of Izvorul Muntelui Lake)*

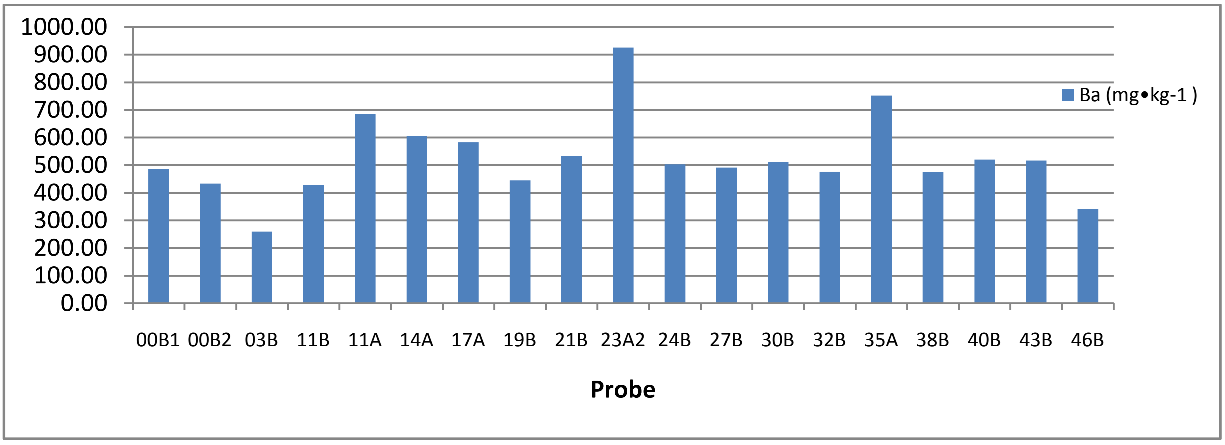

Figure 21. *The Ba distribution (mg·kg^{-1}) in sediments of Bistrita river (upstream of Izvorul Muntelui Lake)*

III.4.5. Lanthanides and Thorium ((La, Ce, Nd, Sm) and Th)

The average concentration of lanthanides in Bistrita river sediments (upstream of Izvorul Muntelui Lake) is given by the series: Ce > La > Nd > Sm (Figure 22). The Th concentrations show an intense decrease compared with the values of the upper continental crust.

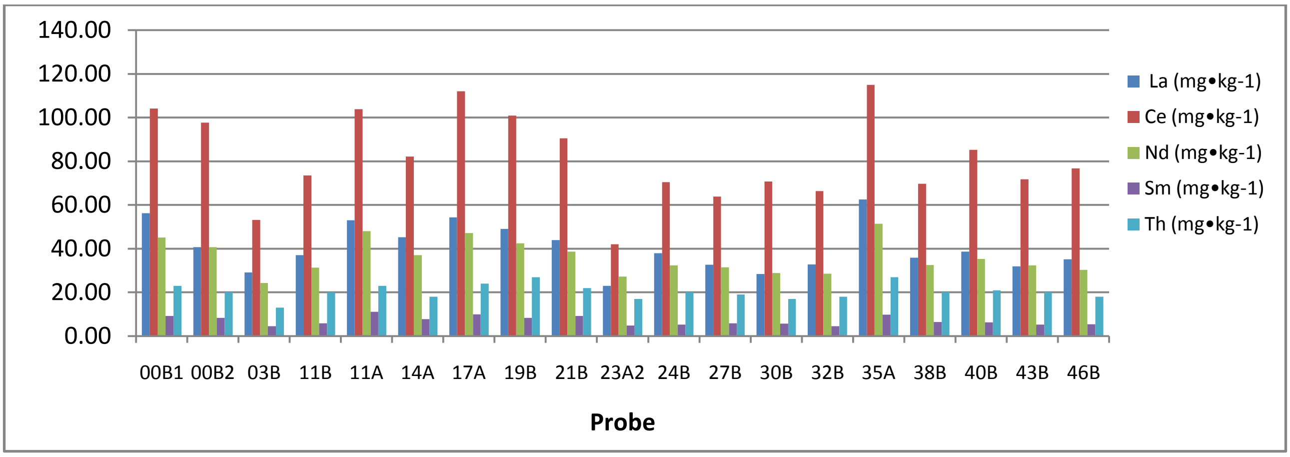

Figure 22. *The lanthanides and Th distribution (mg·kg^{-1}) in sediments of Bistrita river (upstream of Izvorul Muntelui Lake)*

IV. ASSESMENT OF THE GEOCHEMICAL RISK PRODUCED BY MINOR ELEMENTS POLLUTION IN THE SEDIMENTS OF BISTRITA RIVER (upstream Izvorul Muntelui Lake)

IV.1. STATISTICAL PARAMETERS

IV.1.1. Descriptive statistics

Several statistical parameters were determined for the elements Cr, Co, Ni, Cu, Zn, As, Cd and Pb, such as: number of samples (n), the minimum and maximum values, arithmetic mean, geometric mean, median, module, standard deviation, Skewness (asymmetry), Kurtosis curve, quartiles 1 and 3, interquartile range, and variance.

IV.1.2. Geochemical background

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

$$Geochemical\ background = Median \pm 2MAD$$

where, *MAD* is the median absolute deviation.

IV.1.3. Pollution indices

The priority index (P_{index})

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

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

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

where, n is the total number of elements, I_{geoi} are the I_{geo} values of each elements.

P_{index} was used by several authors (Kabir et al., 2011, Wijaya et al., 2013) to combine the ecological risk level determined by the concentration of minor elements in the sediments of a river.

In the Bistrita river sediments (upstream of Izvorul Muntelui Lake), the priority index was determined for the following eight elements: Cr, Co, Ni, Cu, Zn, As, Cd and Pb.

The highest values were found in the sampling point 35A, located near the uranium mining activity (Crucea, Suceava County) (Figure 23).

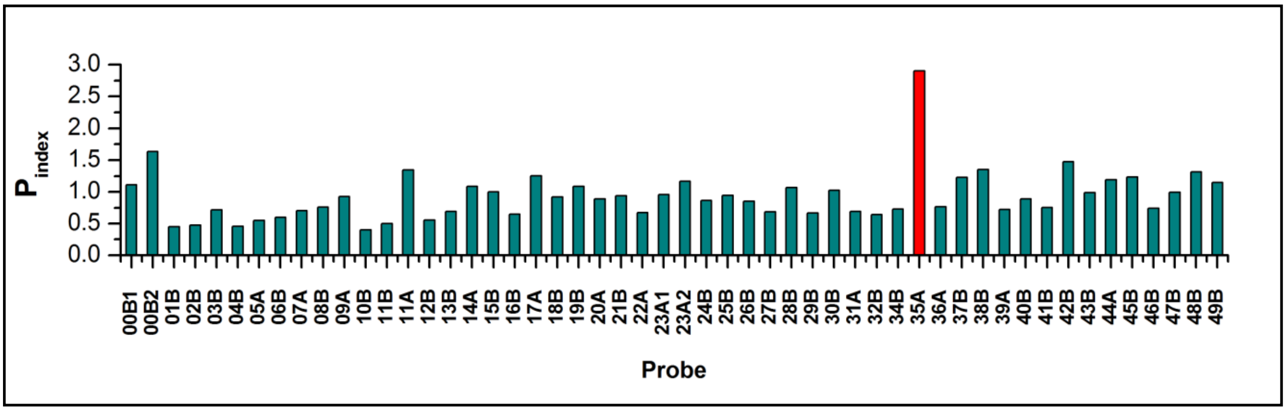

Figure 23. *The priority index evaluation for the minor elements content in sediments of Bistrita River (upstream of Izvorul Muntelui Lake)*

IV.2. DISTRIBUTION OF THE ELEMENTS

The natural background of **Cr** indicates concentrations between 84.5 mg·kg^{-1} and 58.5 mg·kg^{-1}. For the studied samples, the geochemical threshold is easily exceeded in the sampling points 01B, 05A, 10B, 11B, 11A, 12B, 27B, 32B and 34B (Figure 24).

Although the Cr concentrations exceed the geochemical threshold values, the pollution indices do not indicate high contamination in the Bistrita river sediments (upstream of Izvorul Muntelui Lake).

The **Co** concentration estimated above the threshold in sample **00B2** (Figure 25) could be explained by the presence of peat bogs. 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-Krol et al., 2010).

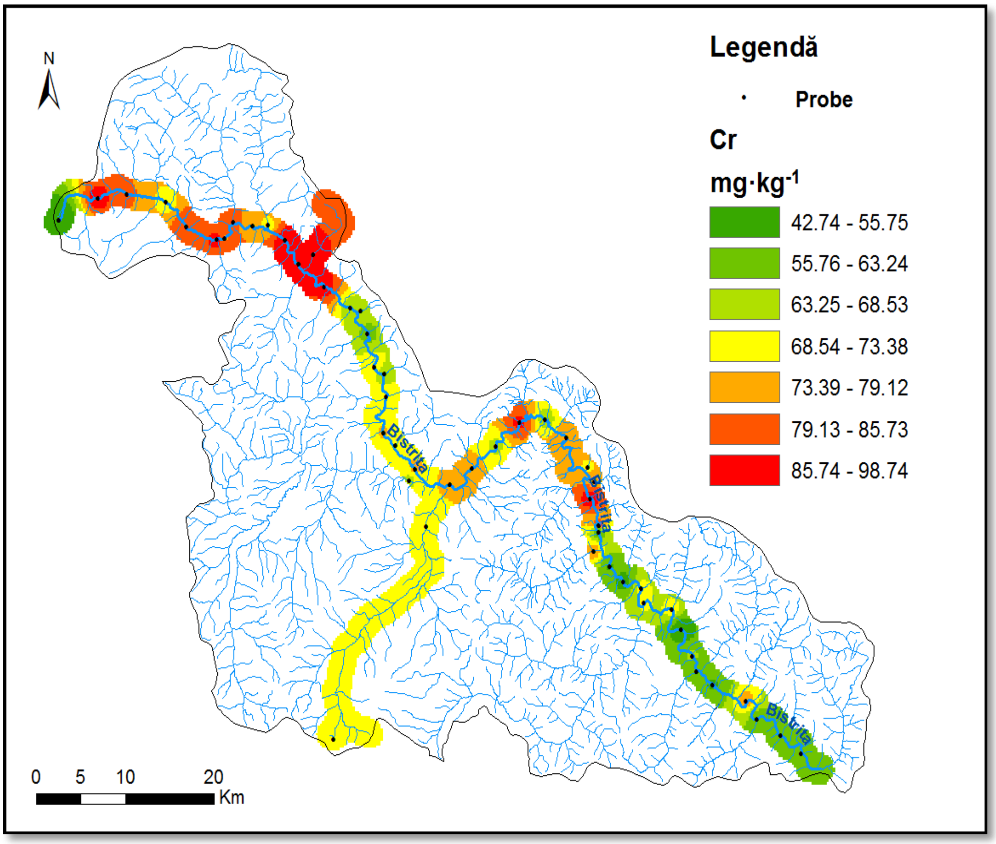

Figure 24. *Distribution map of Cr (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

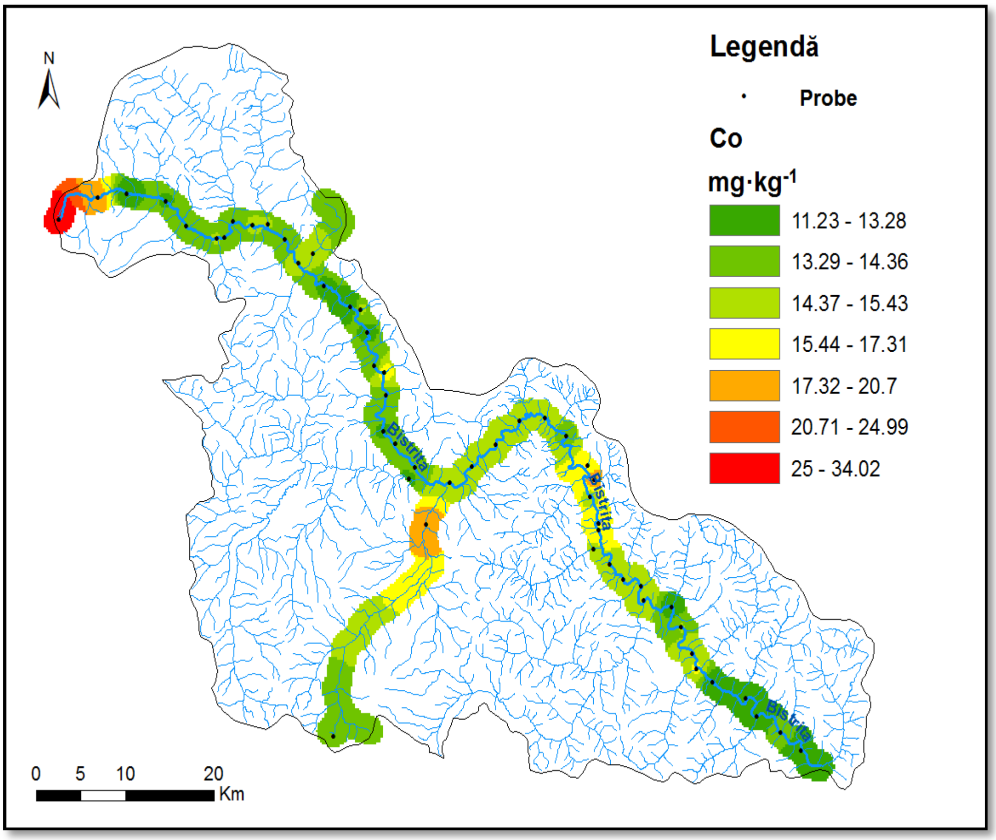

Figure 25. *Distribution map of Co (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

In Bistrita river sediments (upstream of Izvorul Muntelui Lake), the **Ni** concentration ranges from 16 mg·kg^{-1} to 48 mg·kg^{-1}, with an average of 30.10 mg·kg^{-1} (Figure 26). As well as for Cr, the Ni contents do not exceed with much the geochemical threshold. The pollution indices show no degree of contamination.

The geochemical background of **Cu** is situated between 13 mg·kg^{-1} and 49 mg·kg^{-1}. The maximum value in this study is 452 mg·kg^{-1} in the sample 11A (Figure 27).

In the present study on the Bistrita River (upstream of Izvorul Muntelui Lake) were observed **Zn** concentrations in the range 50 mg·kg^{-1} and 1117 mg·kg^{-1}, with an average of 126.19 mg·kg^{-1}. The value from sample 35A which exceeds the geochemical threshold suggests a strong degree of anthropogenic pollution.

Also the geo-accumulation index confirms this fact for the sample 35A (heavy contamination) and for the sample 48B (moderate contamination) (Figure 28).

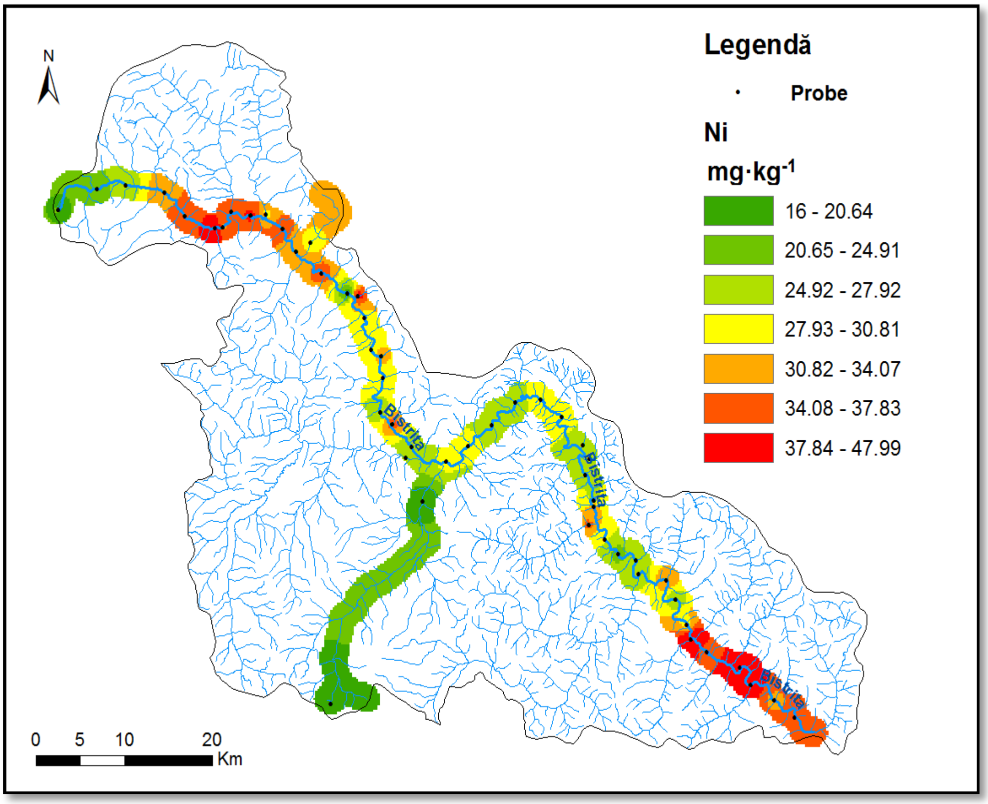

Figure 26. *Distribution map of Ni (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

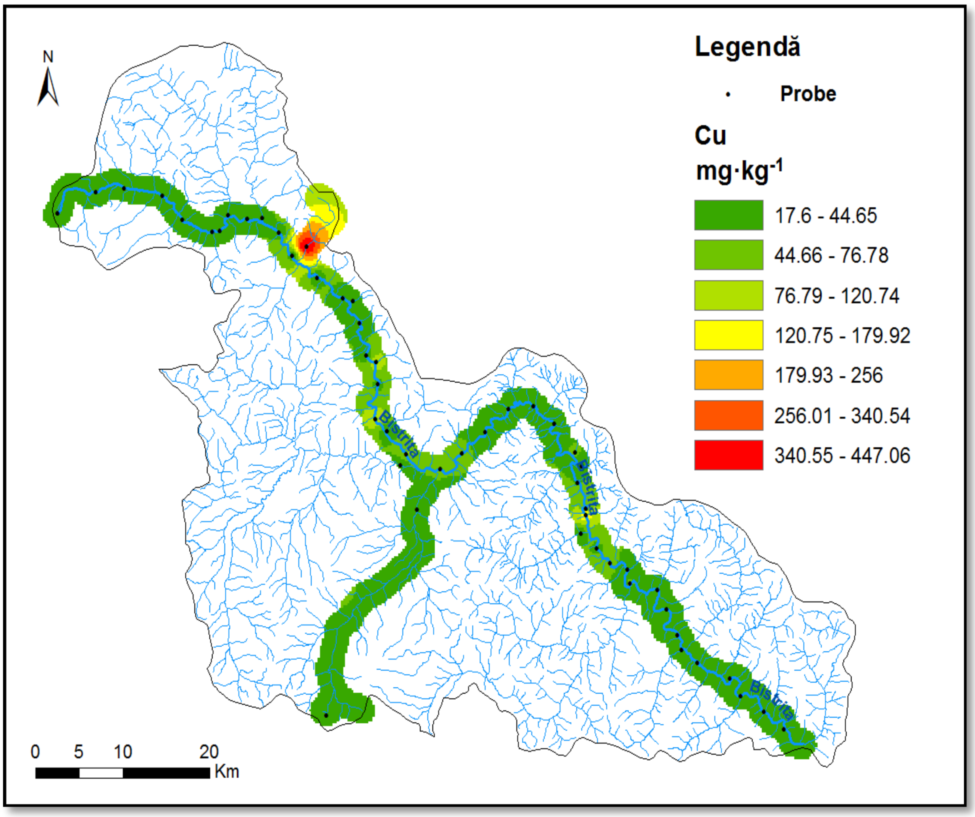

Figure 27. *Distribution map of Cu (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

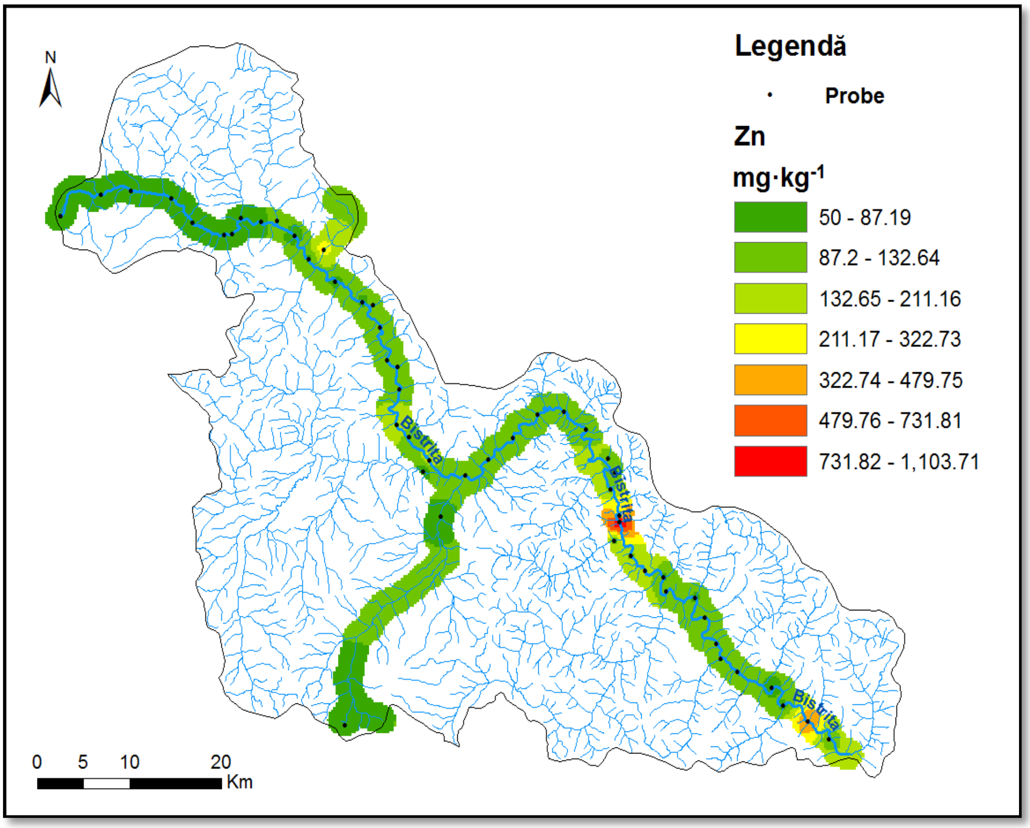

Figure 28. *Distribution map of Zn (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

The geochemical background of **As** is situated between 27.1 and 5.1 mg·kg^{-1}. An arsenic enrichment was observed in the sample **23A2** which is placed on Neagra Valley tributary. Contamination indices suggest a high degree of pollution in the sample 23A2 (Igeo = 2.85) (Figure 29).

The natural background of **Cd** indicates concentrations between 0.15 and 0.59 mg·kg^{-1}, the geochemical threshold being exceeded in the sampling points **11B, 11A, 18B, 19B, 34B, 35A** and **42B** (Figure 30). The geo-accumulation index indicates a moderate contamination in sample **35A**, while other samples show no degree of pollution.

The geochemical background of **Pb** ranges from 20 mg·kg^{-1} to 44 mg·kg^{-1}. Although the concentrations showed an exceeding of geochemical background, this is minimal and does not indicate an advanced degree of pollution, the values being significantly lower than the threshold imposed by the national legislation. This is revealed also by the geo-accumulation index, where the estimated values are below zero for almost all the samples, indicating no contamination of the river sediments, except for samples 23A1 and 35A, where the index is higher than 1 (I_{geo} = 1.15 and I_{geo} = 1.59, respectively) suggesting a moderate contamination.

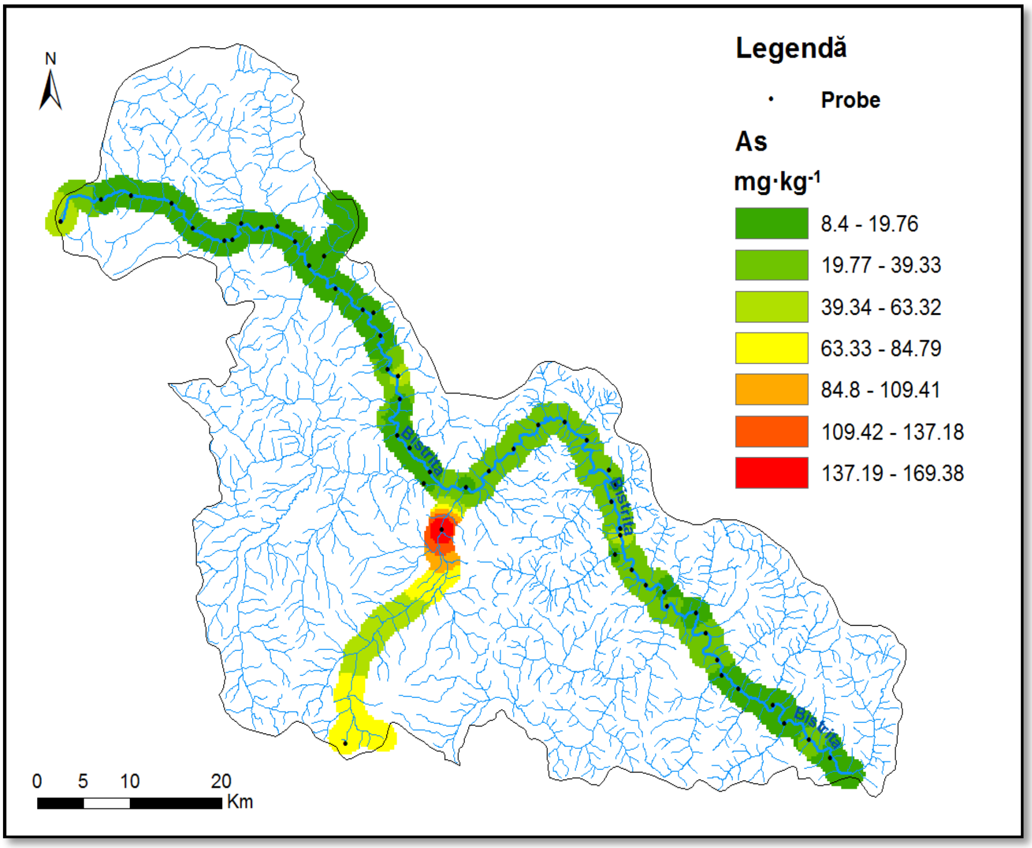

Figure 29. *Distribution map of As (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

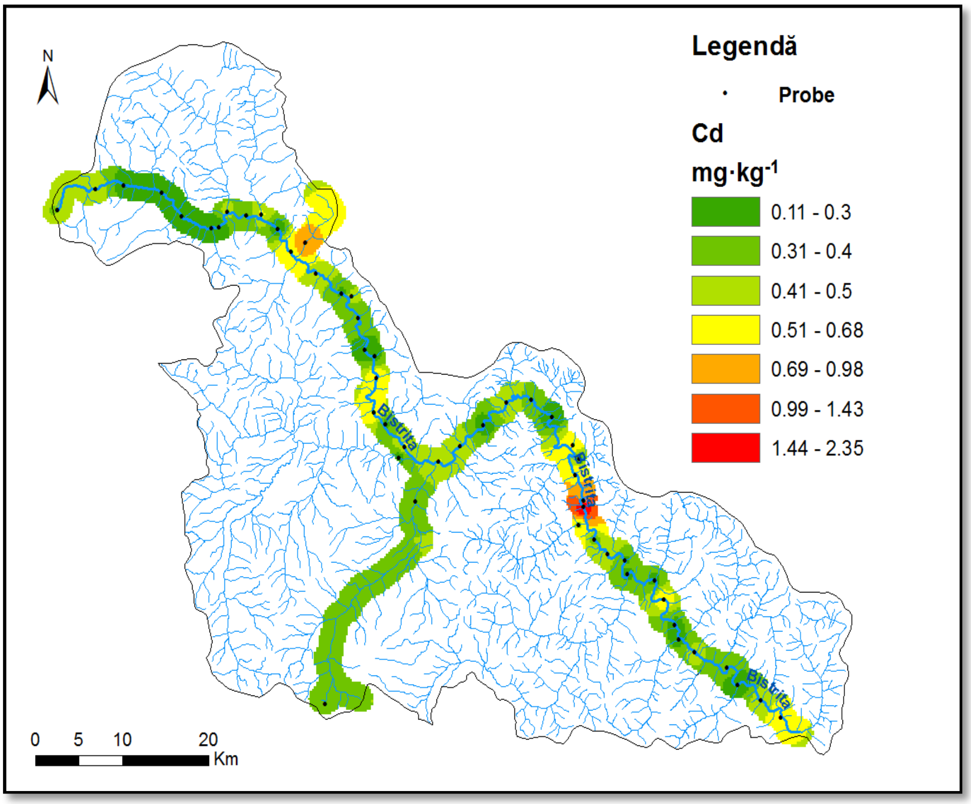

Figure 30. *Distribution map of Cd (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

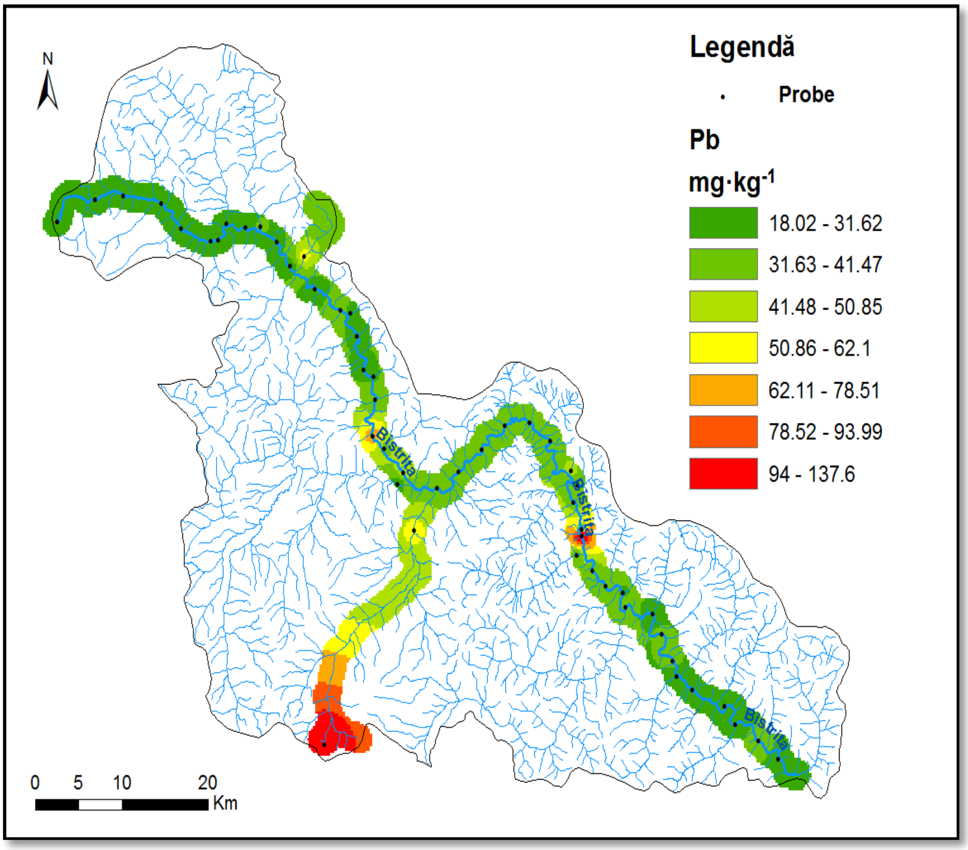

Figure 31. *Distribution map of Pb (mg·kg^{-1}) in sediments of Bistrita River (upstream of Izvorul Muntelui lake) (Maftei et al., 2014)*

CONCLUSIONS

In the present study the chemical and mineralogical composition of the Bistrita River sediments (upstream of Izvorul Muntelui Lake) was determined. The chemical and mineralogical results were correlated through multivariate cluster analysis. The source was identified by comparing the results with the average contents of the upper continental crust. The spatial distribution of minor elements Cr, Co, Ni, Cu, Zn, As, Cd, Pb was performed and the risk of contamination was evaluated through pollution indices and geochemical background.

The hierarchical cluster analysis groups the values into three series. The first group includes the elements: K - Rb - Cs - La - Nd - Ce - Sm - Th, the second group consists of: Na - Ti - Nb - Zr, and the third group includes Mg - Ba - Ca - Sr. The first group (K, Rb, La, Nd, Ce and Sm) is strongly negative correlated with the third group (Ca and Sr). The strong positive correlation between Rb and K ($r = 0.995$) suggests an alkali feldspar control in sediments.

The contents of Na, Mg, K, Ca, and Ti in the sediments of Bistrita river (upstream of Izvorul Muntelui Lake) are within the range 1.25% and 2.13% (average

1.84%) - Na, 1.25% and 2.60% (with an average of 1.75%) - Mg, 1.41% and 3.55% (average of 2.23%) - K, 0.44% and 2.55% (average 1.31%) - Ca and 0.87% and 1.93% (with an average of 1.28%) for Ti concentration, respectively. The lowest Ca contents were recorded in the sampling points 00B1, 11A and 35A. The Mg and K contents are constant, with relatively slight increases for K in sampling points 11A and 35A and for Mg in sampling points 11B and 23A2.

The normalization of the elements from Bistrita river sediments to the upper continental crust values indicates a sharp increase of the rare earth contents in sampling point 35A. Within this area is localized the U ore deposit from Crucea (Suceava). Within this area is localized the U ore deposit from Crucea (Suceava). The uranium deposits usually contain radioactive elements such as radium (Ra), thorium (Th) and lead (Pb) and minerals often associated with REE, calcium and other elements that substitute the cations in the crystal structure.

Using pollution indices proved to be very useful in assessing the risk of contamination with minor elements in sediments of the river. These indices have provided information on the extent of contamination and also helped to distinguish between natural and anthropogenic sources.

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