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GEOCHEMISTRY OF RECENT SEDIMENTS AT CONFLUENCE OF THE BLAŠTICA RIVER INTO TIKVEŠ LAKE

Ivan Boev[1], Dalibor Serafimovski[2], Goran Tasev[1]

Faculty of Natural and Technical Sciences, Institute of Geology, "Goce Delčev" University in Štip,
Blvd. "Goce Delčev" 89, 2000 Štip, Republic of North Macedonia
[2]Faculty of Electrical Engineering, University "Goce Delčev" in Štip,
"Krste Misirkov" 10A, 2000 Štip, Republic of North Macedonia
ivan.boev@ugd.edu.mk

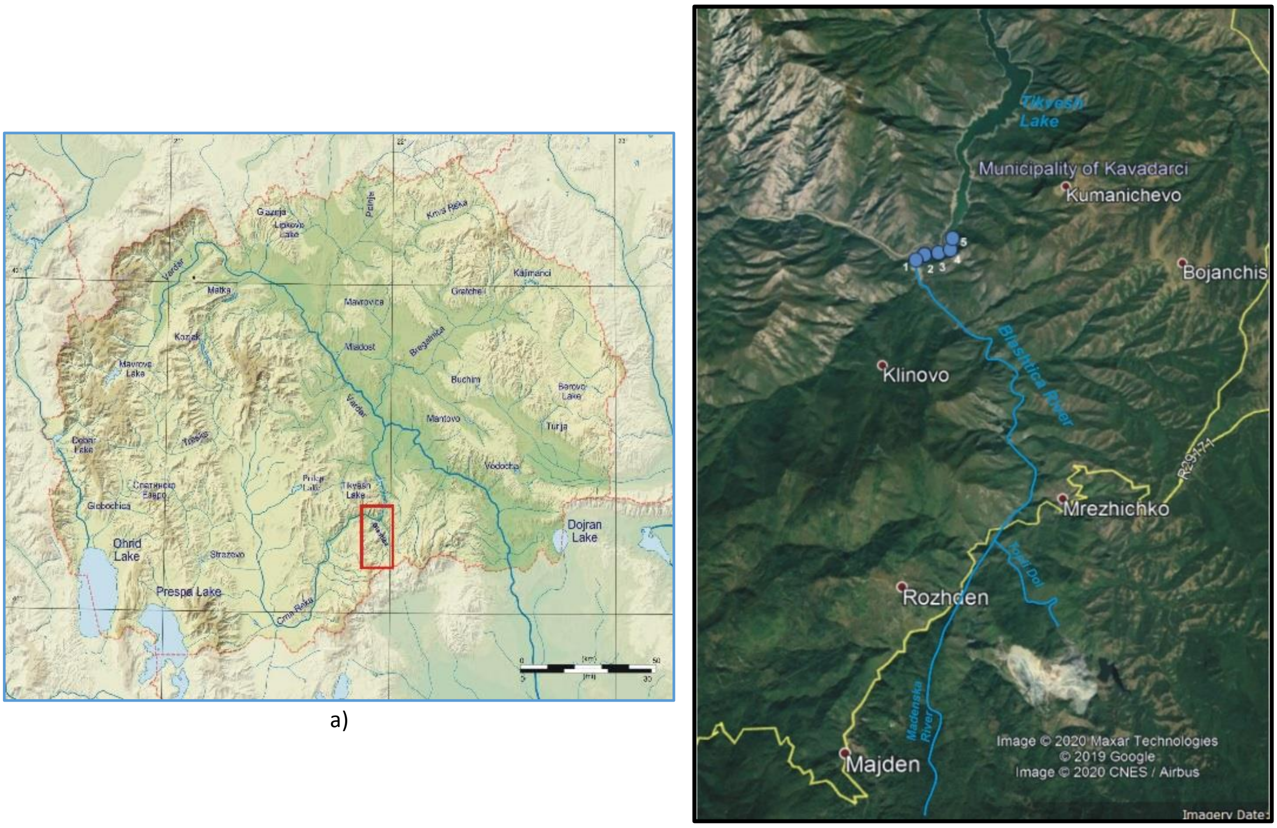
Abstract: The paper presents the results of the latest geochemical study of the sediments of the lower parts of the Blaštica river at its confluence with Tikveš Lake, i.e. the connection with the Crna Reka rivsr. Complete analyses of 58 elements were performed at FUS-ICP to allow observation of the individual anomalous contents of individual elements and the contaminant elements of the mud sediments. Statistical processing of these results gave characteristic results. Calculation of the so-called geo-accumulation index in general was within the Class 0, Class 1 and Class 2 or it was showing uncontaminated to moderately contaminated state of the setting, except the silver (Class 6) that showed extremely contaminated level of I_{geo}. In regards to contamination factor, almost for all analyzed elements it ranged from low to very high (Class 1 to Class 4), although as the most common occurred moderate to considerable (Class 2 and Class 3), while the pollution load index ranged from 1.59 to 3.20, which indicates progressive deterioration in regards of pollution at studied sites. The factor loadings were calculated after the Varimax rotation statistical processing and we obtained four factors (F1–F4) of which the F1 suggests slight anthropogene input. Also, rare earth elements were determined and the results were processed statistically. The europium anomalies showed values between 0.6933 and 0.7670 (average 0.7232) indicating negative anomaly.

Key words: geochemistry; geo-accummulation index; contamination factor; pollution index; Tikveš Lake; rare earth elements; schlich minerals

INTRODUCTION

After more than a year of dry period here in the Republic of North Macedonia the water level of the Tikveš Lake decreased significantly. Wide belt of lake sediments became exposed at the surface along the whole lake perimeter. That was a fine opportunity to try to test some scientific as well as practical hypotheses. Namely, the aim of this research was to study the concentration of some toxic elements in sediments formed at the confluence of the Blaštica river into Tikveš Lake (Figure 1), focusing on the identification of eventual natural and anthropogenic element sources that could originate from the well known Kožuf metallogenic district.

The westernmost parts of the Kožuf metallogenic district reach the river of Blaštica (right tributary of the Crna Reka river) and the north-western side stretches in a line, from the Mrežičko village via the village Konopište, through the course of the Bošavica river to the city of Demir Kapija. Through these water-ways the entire area is drained into the river of Vardar. As a result of past mining activities within the area of interest there are unreclaimed dumps with anomalous concentrations of antimony, arsenic, lead, mercury and thallium at abandoned, but world-known Alšar mine, that represent a significant environmental and health hazards. Other known ore deposits/mineral occurrences are Majdan (arsenic), Dudica (copper-gold) and Arničko (antimony). Other ore deposits are supposed to have existed here but have remained unknown due to the lack of exploration, which may imply lack of awareness of potential risks (Kahuda et al., 2014).



a)

b)

Fig. 1. Overview geographic map of the Republic of North Macedonia with position of the studied area (a) and position of sampling locations at the confluence of Blaštica into Tikveš Lake (b)

GEOLOGICAL SETTING OF THE TERRAIN OF INTEREST

An intermediary to acidic igneous rocks of the Kožuf volcano-intrusive complex developed in a basement composed of Triassic sediments, Jurassic ophiolite formations (gabbro-peridotitic) and Cretaceous carbonates and clastic sediments (Figure 2). Magmatic activity took place during the Miocene-Pliocene (6.5 to 1.8 Ma; Boev 1988, Kolios et al., 1980). Rocks are dacite-quartzlatitic to trachy-rhyolitic composition and were mainly enriched in LIL (Large Ion Lithophile) elements (Boev, 1988). Extrusive magmatic activity was intense and represented by various types of tuff, breccia and lacustrine volcanic-sediments. The intrusive phase of the magmatic activity is represented by subvolcanic bodies, which were entirely hydrothermally altered by later hydrothermal processes. Below we are explaining in more details the most important geological units of the complex.

Plagioclase within these rocks are strongly altered and weathered into oligoclase and andesine, which are associated with epidote, coisite, sericite and albite.

Precambrian eye-like two-mica gneiss (*Gmb*) occur as product of intensive K-feldspar alteration of the adjacent porphyry granodiorite rocks ($\delta\gamma$). These rocks as main minerals contain quartz, K-feldspar, plagioclase, muscovite and biotite, while as accessory minerals occur garnet and epidote. Lenticular muscovite gneiss (*Gm*) of the Precambrian age too, occur on the contact with the previously described eye-like two-mica gneiss as well as with the micaschist (*F*) and rocks of the marble series. These rocks are characterized by grey to grey-white color, while as main minerals occur quartz, microcline, plagioclase (oligoclase), muscovite, biotite and phengite. Precambrian grey to grey-white dolomite marbles (*Md*) were developed in the lower part of the marble series.

The whole mass is homogenous and mainly built by dolomite and rarely dolomite-calcite marbles (in the southern parts). Porphyry granitoides ($\delta\gamma$) of Precambrian age occur as grey to dark-grey coarse-grained rocks with porphyry structure and massive texture. They were built mainly by plagioclase, K-feldspar, quartz and biotite, while as accessory minerals occur sphene, garnet, apatite and zircon.

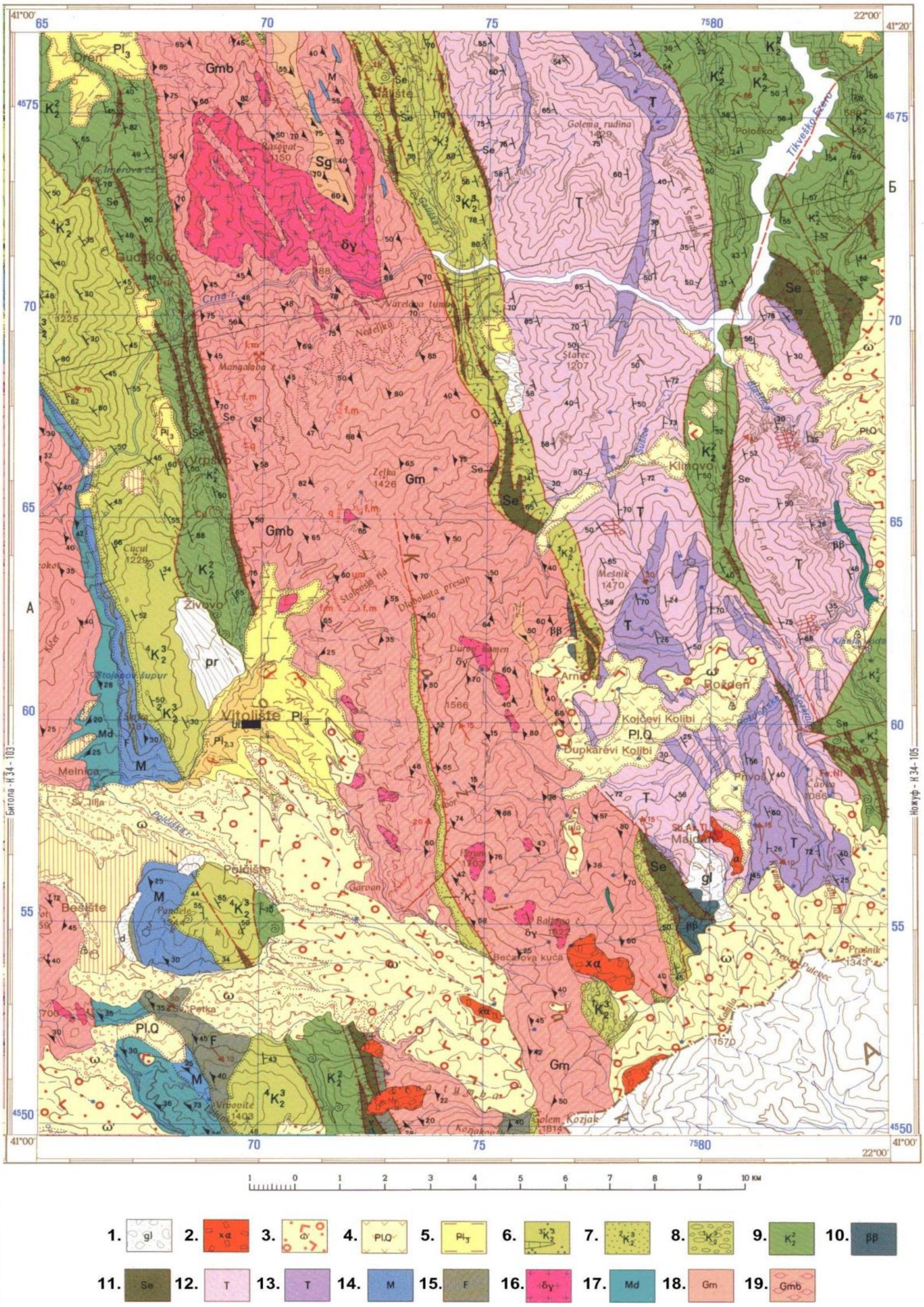


Fig. 2. Excerpt from basic geological map 1 : 100 000 with position of Tikveš Lake (upper right corner)
1. *gl* – Quaternary glacial sediments; 2. $x\alpha$ – Quaternary quartz latite; 3. ω' – Pliocene quartz latite breccia; 4. *Pl,Q* – Pliocene volcano terrigenous products; 5. Pl_3 – Pliocene gravel, sand and sub-clay; 6. ${}^3K^3_2$ – Cretaceous flysch, sandstone, alevrolite, clay, limestone and layered limestone; 7. ${}^2K^3_2$ – Cretaceous sandstone, clay and conglomerate; 8. ${}^1K^3_2$ – Cretaceous conglomerate and sandstone; 9. K^2_2 – Cretaceous sandstone, clay, clayschist and conglomerate; 10. $\beta\beta$ – Jurassic diabase; 11. *Se* – Jurassic peridotite and serpentinite; 12. $T_{(light\ purple\ color)}$ – Triassic marbleized limestone and dolomite; 13. $T_{(dark\ purple\ color)}$ – Triassic clayschist and sandstone; 14. *M* – Cambrian marble; 15. *F* – Cambrian phyllite micaschist; 16. $\delta\gamma$ – Precambrian porphyry granodiorite; 17. M_d – Precambrian grey to grey-white dolomite marble; 18. *Gm* – Precambrian lenticular muscovite gneiss; 19. *Gmb* – Precambrian eye-like two-mica gneiss

Cambrian phyllite micaschist (*F*) occur as several varieties mainly differentiated by the minerals present within them. These rocks in thick stripes interchange vertically and horizontally while being characterized by their schistosity and plate-like forms. Mineral composition ranges from garnet, graphite and albite in quartz-muscovite-sericite schist up to epidote, chlorite and amphibole in the green micaschist. Cambrian marbles (*M*) occur as thick masses with grey to grey-white and dark grey color. Rarely are occured plate-like forms of these marbles.

Triassic marbleized limestone and dolomite ($T_{light\ purple\ color}$) and clayschist and sandstone ($T_{dark\ purple\ color}$) are characterized by grey, grey-white and rarely blue color. The most common form of occurrence is massive and plate-like. Jurassic serpentinite and peridotite (*Se*) mainly are present within the ophiolite areas. Serpentinite rocks dominate within the complex and are characterized by dark-green color. The main minerals are serpentine with olivine and pyroxene relics. As accessory minerals occur chlorite, talc, magnetite and chromite. Peridotites are characterized by dark-green color and built mainly by rhombic pyroxene and partly serpentinized biotite, chlorite, magnetite and chromite.

Jurassic diabase ($\beta\beta$) is characterized by green color, schistose and massive texture. Their composition is dominated by plagioclase and amphibole, while as secondary minerals occur epidote, chlorite, calcite, sericite and albite.

Cretaceous sandstone, clay, clayschist and conglomerate (K^2_2) interchange in thick layers. Conglomerate layers are thick up to 3 m and heterogenous in their composition (quartz, quartzite, gneiss, schist and claystone). Sandstones interchange with conglomerate and are thick up to 1 m. They are characterized by purple, grey-green and grey-brown color and built by quartz, quartzite, mica and feldspar cemented by clay-sericite-limonite mixture. Cretaceous conglomerates and sandstone (${}^1K^3_2$) mainly occur in the area of Majdan, Tribor and Sokol. They are characterized by gneiss pieces (75%) followed by green rocks and marbles. Conglomerates dominate over the sandstone within this type of facies. Cretaceous sandstone, clay and conglomerate (${}^2K^3_2$) are dominated by sandstone (quartz and arcose varieties with carbonate cement).

Clay and conglomerate occur rarely than sandstone. Cretaceous sandstone, claystone, alevrolite and limestone (${}^3K^3_2$) facies are dominated by sandstone, while alevrolite, claystone and limestone, although present, are not that common. All the facies members are finely layered with some repetition of particular members.

Pliocene gravel, sand and sub-clay (Pl_3) are deficiently developed and stratified sediments. They are represented by yellowish gravel, gravel sands, sands and sub-clay as continuance of the lower Pliocene facie. Pliocene volcano-sedimentary products (*Pl, Q*) in the area of interest were developed around the Majdan, Rožden and Mrežičko. They are developed with limestone and clay sandstone, clay, loosely cemented sandstone and conglomerate that interchange vertically with tuffaceous sand, sandstone, tuff and diatomite earth. Pliocene quartzlatite breccias (ω‘) were formed during the volcanic activity at the Kožuf mountain, which resulted with relatively thick cover of volcanic breccia and limited flows of quartzlatite.

Quaternary quartzlatites ($x\alpha$) are grey to dark-grey, very compact and hard rocks. They are built of fine-grained quartz and feldspar matrix with phenocrystals of sanidine and plagioclase. Rarely they occur biotite, pyroxene, amphibole, sphene, magnetite, epidote, apatite and opal nests. Quarternary glacial sediments (*gl*) are formed in high mountainous areas. By the intensive erosion sediments were transported and only preserved near the Majdan village within one large mass.

MATERIAL AND METHODS

Sediment samples at the confluence of Blaštica into Tikveš Lake were collected from five sampling sites. Samples of 15–25 kg were taken depending on the availability of material (Figure 1). All samples were collected as representative and transferred to the laboratory as soon as possible for analysis. One part of samples intended for chemical analysis was dried in an oven for 48 h at 80°C, and finally ground in a total mortar, sieved to < 63 µm sediment fraction and homogenized before each weighing, while the other part was used for the so-called schlich-analysis. The applied the schlich method as usual focused on concentration of heavier minerals. Samples were flushed and the schlich obtained was subjected to further processing. First, magnetic separation of minerals was performed and both fractions were observed under stereomicroscope Optika Microscopes Italy, LAB series with maximal magnification of ×40 times and paired with high quality digital camera and adequate software.

The Rare Earth Elements (REE) were analyzed at the Actlabs' facility in Ontario, Canada. As we already know that REEs are among the most difficult elements to analyze properly, it was crucial that the samples were ground so that 95% of the material passed through 200 μm mesh sieve, to ensure the resistate minerals will undergo the complete fusion. The analysis required a lithium metaborate/tetraborate fusion with subsequent analysis by ICP-OES and inductively coupled plasma mass spectrometry (ICP-MS). Although the lithium metaborate-tetraborate fusion dissolution procedure has long been recognized as the best technique for ensuring that geological samples go into solution, historically it has not been proven to be highly compatible with ICP-MS sample-introduction systems. However, research and development conducted by Actlabs into sample introduction into the ICP-MS has solved this shortfall. A robotic fusion process ensures very reproducible results, which was not possible with a manual fusion process, and highly accurate results can now be obtained in a cost-effective and rapid manner. The advantage of this procedure over XRF for major oxide analysis is that it is more matrix-independent and any rock type (including sulphide-bearing samples) can be analyzed without special calibration or pre-treatment. A mass balance was required as an additional quality control technique and elemental totals of the oxides should be between 98 and 101%. Geochemical analysis was performed by the ICP-MS technique using an Agilent 7500 (Babington type atomizer) instrument. The power of the plasma was set at 1500 W with a pump speed of 0.1 rps, an integration time of 0.3 s, and a total acquisition time of 8.0 s (Agilent Technologies, 2005).

RESULTS AND DISCUSSION

As we already mentioned 5 sediment samples were analyzed with FUS-ICP method and total of 58 elements were identified (Table 1).

Table 1

Chemical composition of the sediments at the inflow of the Blaštica river into Tikveš Lake (mg/kg), FUS-ICP method

	Average	Min	Max	Mean	Stand. dev
Al	83232.52	77693.38	88357.82	83154.60	3591.82
Fe	53231.52	46407.50	57303.25	53067.18	4106.52
Ca	58109.87	44169.07	73659.69	57231.01	10079.36
Mg	28502.53	24682.06	37197.37	28182.58	4517.11
Na	13571.63	11313.34	14472.95	13516.79	1172.65
K	26932.07	24526.32	29498.20	26883.58	1618.22
Ti	5035.01	4438.09	5672.69	5015.60	441.56
Mn	1105.44	943.07	1200.00	1101.38	92.61
P	2345.96	1403.91	3243.78	2266.07	587.20
Sr	1212.66	1026.45	1351.00	1207.13	113.64
Ba	562.58	544.43	584.17	562.42	13.61
Rb	117.77	111.46	124.00	117.68	4.63
B	83.71	61.40	97.14	82.75	11.95
V	123.93	115.47	130.21	123.76	6.43
Zn	286.88	224.74	373.71	281.41	56.25
Pb	44.16	20.88	64.91	41.47	14.15
Cd	0.56	0.40	0.82	0.55	0.15
Cu	49.42	35.68	63.40	48.60	8.90
Cr	185.06	148.16	221.73	183.53	23.60
Ni	152.16	72.56	217.34	142.30	50.31

Table 1 – continue

	Average	Min	Max	Mean	Stand. dev
Co	66.37	55.26	77.13	66.00	6.99
Li	26.36	21.82	30.45	26.19	2.96
Be	2.78	1.98	3.61	2.69	0.67
Ga	20.20	18.20	24.07	20.10	2.08
Ge	1.66	1.26	2.26	1.62	0.37
As	24.65	19.49	28.00	24.44	3.08
Se	3.81	2.81	4.67	3.76	0.63
Sb	7.21	3.23	10.92	6.68	2.56
Tl	3.34	3.10	3.70	3.33	0.22
Bi	11.88	7.87	15.72	11.52	2.89
Sn	4.91	4.00	7.18	4.80	1.16
Cs	6.41	5.80	6.78	6.40	0.33
Mo	1.61	0.94	2.19	1.54	0.45
In	0.28	0.08	0.87	0.18	0.30
Sc	14.35	12.40	17.80	14.24	1.82
Y	28.50	26.51	32.41	28.43	2.09
La	49.54	46.80	52.93	49.49	2.11
Ce	100.31	94.72	104.00	100.24	3.71
Nd	42.18	40.14	43.12	42.17	1.07
Sm	8.09	7.80	8.75	8.09	0.34
Eu	1.72	1.56	1.80	1.72	0.09
Gd	6.53	5.66	7.00	6.51	0.57
Tb	0.99	0.90	1.15	0.98	0.09
Dy	5.36	5.00	6.14	5.35	0.41
Ho	1.17	1.00	1.41	1.16	0.14
Er	3.06	2.81	3.65	3.05	0.30
Tm	0.52	0.46	0.62	0.52	0.06
Yb	2.75	2.46	3.16	2.74	0.23
Lu	0.40	0.32	0.50	0.40	0.06
Hf	1.95	1.67	2.36	1.94	0.23
Th	17.69	16.72	18.20	17.68	0.53
U	6.98	5.12	8.06	6.89	1.09
Pd	21.84	17.50	26.50	21.54	3.60
Ag	2248.55	1450.00	3561.77	2127.71	767.12
Au	0.51	0.50	0.54	0.51	0.02
Te	0.58	0.56	0.61	0.58	0.02
Nb	29.90	17.99	47.11	28.21	10.26
W	3.10	2.10	3.63	3.05	0.52

The table above shows that analysis of the lake sediments by the FUS-ICP was determined presence of 58 elements, the results of which are shown through statistical clustering of minimum and maximum values, average, mean and standard deviation (Table 1), but there is still a possibility to see that the anomalous values of individual elements in the analyzed samples trials are far beyond background values. More specific statistical data processing with factor analysis are given in the following chapters.

Statistical analysis of the analytical results

The objectives of the current study, definition of the metal pollution in sediments at the confluence of the Blaštica river into Tikveš Lake, were performed through the definition of degree of contamination and pollution using pollution indicators as geo-accumulation index (I_{geo}), metal contamination factor (CF), and pollution load index (PLI). Also, we tried give an answer about the eventual origin of material found in sediments through the REE analysis. To our knowledge our study is the first of this kind for the aforementioned locality.

Index of geo-accumulation (I_{geo})

Geo-accumulation index is used to assess the anthropogenic impact. This index for the first time was introduced by Müller (1979). It is calculated using the following equation:

$$I_{geo} = \log_2 \frac{Cn}{1.5Bn},$$

where *Cn* is the measure of the particular metal concentration in the sediment, while *Bn* is the background concentration of the element (average shale concentration that has been given by Turekian and Wedepohl, 1961), and 1.5 is the factor compensating background data (correction factor) due to the lithogenic effect (Taylor, 1964). The I_{geo} factor is not comparable to other indices of metal enrichment due to the nature of the I_{geo} calculation; it involves a log function and a background multiplication of 1.5. The factor itself is composed of seven grades (0–6) indicating various degrees of metal enrichment above the average shale value ranging from unpolluted to very high polluted sediment quality. Class 0 (uncontaminated): $I_{\text{geo}} \leq 0$; Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated sediment): $1 < I_{geo} < 2$; Class 3 (moderately to strongly contaminated): $2 < I_{geo} < 3$; Class 4 (strongly contaminated): $3 < I_{geo} < 4$; Class 5 (strongly to extremely contaminated): $4 < I_{geo} < 5$; Class 6 (extremely contaminated): $5 < I_{geo}$. Class 6 is an open class and comprises all values of the index higher than class 5. Geo-accumulation index was calculated for the 5 samples from the same number of sampling locations at the vicinity of the Blaštica river inflow into Tikveš Lake.

As we can see from Table 2 the geo-accumulation index in general was within the Class 0, Class 1 and Class 2 or it was showing uncontaminated to moderately contaminated state of the setting, except for the silver (Class 6) that showed extremely contaminated level of I_{geo}.

Table 2

Geo-accumulation index at 5 sampling locations at the Blaštica river inflow into Tikveš Lake.

Element	I_{geo}		Class	Level of pollution
	Min	Max		
Li	–1.51	–1.18	0	Uncontaminated
Be	–0.82	–0.22	0	Uncontaminated
Na	–0.24	0.01	1	Uncontaminated to moderately contaminated
Mg	0.09	0.50	1	Uncontaminated to moderately contaminated
Al	–0.43	–0.31	0	Uncontaminated
P	0.29	1.13	1–2	Uncontaminated to moderately contaminated
K	–0.49	–0.30	0	Uncontaminated
Ca	0.29	0.80	1	Uncontaminated to moderately contaminated
Ti	–0.44	–0.20	0	Uncontaminated
V	–0.52	–0.40	0	Uncontaminated
Cr	0.09	0.50	1	Uncontaminated to moderately contaminated
Mn	–0.30	–0.06	0	Uncontaminated

T a b l e 2 – continue

Element	I_{geo} Min	I_{geo} Max	Class	Level of pollution
Fe	–0.42	–0.21	0	Uncontaminated
Co	0.66	1.00	1	Uncontaminated to moderately contaminated
Ni	–0.34	0.76	1	Uncontaminated to moderately contaminated
Cu	–0.64	–0.06	0	Uncontaminated
Zn	0.46	0.96	1	Uncontaminated to moderately contaminated
Ga	–0.45	–0.17	0	Uncontaminated
Ge	–0.64	–0.06	0	Uncontaminated
As	0.00	0.36	1	Uncontaminated to moderately contaminated
Rb	–0.63	–0.53	0	Uncontaminated
Sr	0.82	1.10	1-2	Uncontaminated to moderately contaminated
Cd	–0.12	0.60	0-1	Uncontaminated to moderately contaminated
Cs	–0.26	–0.10	0	Uncontaminated
Ba	–0.47	–0.40	0	Uncontaminated
Tl	0.39	0.57	1	Uncontaminated to moderately contaminated
Pb	–0.36	0.77	0–1	Uncontaminated to moderately contaminated
U	–0.08	0.37	0-1	Uncontaminated to moderately contaminated
Se	1.14	1.65	2	Moderately contaminated
Th	–0.07	0.01	0–1	Uncontaminated to moderately contaminated
Sb	0.36	1.58	1–2	Uncontaminated to moderately contaminated
Sc	–1.80	–0.58	0	Uncontaminated
Y	–0.39	–0.19	0	Uncontaminated
Ag	9.53	10.43	6	Extremely contaminated
Sn	–0.81	–0.23	0	Uncontaminated
Mo	–1.42	–0.58	0	Uncontaminated
La	–1.08	–0.96	0	Uncontaminated
Ce	0.07	0.16	1	Uncontaminated to moderately contaminated
Nd	0.11	0.18	1	Uncontaminated to moderately contaminated
Sm	–0.21	–0.09	0	Uncontaminated
Eu	0.04	0.18	1	Uncontaminated to moderately contaminated
Gd	–0.53	–0.32	0	Uncontaminated
Tb	–0.51	–0.27	0	Uncontaminated
Dy	–0.32	–0.12	0	Uncontaminated
Ho	–0.59	–0.24	0	Uncontaminated
Er	–0.29	–0.03	0	Uncontaminated
Tm	0.43	0.73	1	Uncontaminated to moderately contaminated
Yb	–0.46	–0.21	0	Uncontaminated
Lu	–1.19	–0.74	0	Uncontaminated
Hf	–0.92	–0.58	0	Uncontaminated
W	–0.25	0.30	0–1	Uncontaminated to moderately contaminated

Metal contamination factor (CF)

Contamination factor was calculated by comparing the mean of trace metal concentration with average shale concentration given by Turekian and Wedepohl (1961), which is used as global standard reference for unpolluted sediments. CF for each metal was determined by the following equation:.

$$Contamination\ factor\ (CF) = \frac{Mean\ metal\ concentration\ at\ contaminated\ site}{Metal\ average\ shale\ concentration}$$

Hakanson (1980) classified CF values into four grades, i.e., CF < 1 in class 1 with low CF, 1 ≤ CF < 3 in class 2 with moderate CF, 3 ≤ CF < 6 under class 3 with considerable CF, and CF ≥ 6 kept in class 4 with very high CF. Our findings in the regards to the metal contamination factor are given in Table 3.

Table 3

Metal contamination factor in sediments at the Blaštica river inflow into Tikveš Lake

Element	Min$_{CF}$	Max$_{CF}$	Class	Level of contamination factor
Li$_{Contam.fact.}$	0.33	0.46	1	Low
Be$_{Contam.fact.}$	0.66	1.20	1–2	Low to moderate
Na$_{Contam.fact.}$	1.18	1.51	2	Moderate
Mg$_{Contam.fact.}$	1.65	2.48	2	Moderate
Al$_{Contam.fact.}$	0.97	1.10	1–2	Low to moderate
P$_{Contam.fact.}$	2.01	4.63	2–3	Moderate to considerable
K$_{Contam.fact.}$	–0.49	–0.30	1	Low
Ca$_{Contam.fact.}$	2.00	3.33	2–3	Moderate to considerable
Ti$_{Contam.fact.}$	0.96	1.23	1–2	Low to moderate
V$_{Contam.fact.}$	0.89	1.00	1–2	Low to moderate
Cr$_{Contam.fact.}$	1.65	2.46	2	Moderate
Mn$_{Contam.fact.}$	1.11	1.41	2	Moderate
Fe$_{Contam.fact.}$	0.98	1.21	1–2	Low to moderate
Co$_{Contam.fact.}$	2.91	4.06	2–3	Moderate to considerable
Ni$_{Contam.fact.}$	1.07	3.20	2–3	Moderate to considerable
Cu$_{Contam.fact.}$	0.79	1.41	1–2	Low to moderate
Zn$_{Contam.fact.}$	2.37	3.93	2–3	Moderate to considerable
Ga$_{Contam.fact.}$	0.96	1.27	1–2	Low to moderate
Ge$_{Contam.fact.}$	0.79	1.41	1–2	Low to moderate
As$_{Contam.fact.}$	1.50	2.15	2	Moderate
Rb$_{Contam.fact.}$	0.80	0.89	1	Low
Sr$_{Contam.fact.}$	3.42	4.50	3	Considerable
Cd$_{Contam.fact.}$	1.33	2.73	2	Moderate
Cs$_{Contam.fact.}$	1.16	1.36	2	Moderate
Ba$_{Contam.fact.}$	0.94	1.01	1–2	Low to moderate
Tl$_{Contam.fact.}$	2.21	2.64	2	Moderate
Pb$_{Contam.fact.}$	1.04	3.25	2–3	Moderate to considerable

Table 3 – continue

Element	Min$_{CF}$	Max$_{CF}$	Class	Level of contamination factor
U$_{Contam.fact.}$	1.38	2.18	2	Moderate
Se$_{Contam.fact.}$	4.68	7.78	3–4	Considerable to very high
Th$_{Contam.fact.}$	1.39	1.52	2	Moderate
Sb$_{Contam.fact.}$	2.15	7.28	2–4	Moderate to very high
Sc$_{Contam.fact.}$	0.25	0.84	1	Low
Y$_{Contam.fact.}$	1.02	1.25	2	Moderate
Ag$_{Contam.fact.}$	20714.29	50882.43	4	Very high
Sn$_{Contam.fact.}$	0.67	1.20	1–2	Low to moderate
Mo$_{Contam.fact.}$	0.36	0.84	1	Low
La$_{Contam.fact.}$	0.51	0.58	1	Low
Ce$_{Contam.fact.}$	1.61	1.76	2	Moderate
Nd$_{Contam.fact.}$	1.67	1.80	2	Moderate
Sm$_{Contam.fact.}$	1.22	1.37	2	Moderate
Eu$_{Contam.fact.}$	1.56	1.80	2	Moderate
Gd$_{Contam.fact.}$	0.88	1.09	1–2	Low to moderate
Tb$_{Contam.fact.}$	0.90	1.15	1–2	Low to moderate
Dy$_{Contam.fact.}$	1.09	1.33	2	Moderate
Ho$_{Contam.fact.}$	0.83	1.18	1–2	Low to moderate
Er$_{Contam.fact.}$	1.12	1.46	2	Moderate
Tm$_{Contam.fact.}$	2.30	3.10	2–3	Moderate to considerable
Yb$_{Contam.fact.}$	0.95	1.22	1–2	Low to moderate
Lu$_{Contam.fact.}$	0.46	0.71	1	Low
Hf$_{Contam.fact.}$	0.60	0.84	1	Low
W$_{Contam.fact.}$	1.17	2.02	2	Moderate

Analysis of data obtained as contamination factor, from table above, gave us an information that in general for almost all analyzed elements the metal concentration factor ranged from low to very high (Class 1 to Class 4), although as the most common occurred as moderate to considerable (Class 2 and Class 3).

Pollution load index (PLI)

Pollution load index for each site was determined by the method proposed by Tomlinson et al. (1980). The PLI for a single site is the nth root of *n* number multiplying the factors (CF values) together. PLI for each site was determined by the following equation:

$$PLI = \sqrt[n]{(CF1 * CF2 * CF3 * \ldots\ldots..CFn)},$$

where *CF* is contamination factor and *n* is number of parameters. According to Mohiuddin et al. (2010), PLI = 0 indicates a perfect state of pollution; PLI = 1 points indicate only baseline levels of pollutants present, and PLI > 1 would indicate progressive deterioration of sites.

For ours 5 samples, from 5 different locations, we have calculated pollution load index that ranged from 1.59 to 3.20, which puts this parameter (for all five samples) in category PLI > 1. This PLI trend indicates progressive deterioration in regards of pollution at studied sites. Performed factor analysis of elemental concentrations (rotated factor loadins – Varimax) did not proved any logical correlated/associated elemental pairs (Table 4).

Table 4

Factor loadings after Varimax rotation

	F1	F2	F3	F4		F1	F2	F3	F4
Al	0.823	–0.339	–0.294	0.347	Bi	0.248	–0.627	–0.732	0.098
Fe	0.987	–0.069	–0.112	–0.095	Sn	0.366	–0.825	0.127	0.411
Ca	–0.544	0.632	0.526	–0.167	Cs	–0.331	–0.225	0.281	0.872
Mg	–0.278	–0.089	–0.951	–0.105	Mo	0.609	–0.646	–0.240	–0.394
Na	0.661	–0.348	–0.617	–0.248	In	0.582	–0.708	0.169	0.363
K	0.850	–0.426	–0.178	0.253	Sc	0.249	–0.934	0.166	0.195
Ti	0.961	–0.253	0.082	0.076	Y	0.561	–0.717	–0.094	0.402
Mn	0.948	–0.017	–0.298	0.114	La	–0.224	0.349	–0.890	–0.188
P	0.855	–0.450	–0.226	0.128	Ce	0.309	0.346	–0.743	–0.483
Sr	–0.076	0.959	0.142	–0.234	Nd	0.527	–0.128	–0.758	–0.363
Ba	–0.351	0.238	–0.822	–0.380	Sm	0.423	–0.890	0.079	0.150
Rb	0.824	0.198	0.014	–0.530	Eu	0.806	–0.032	–0.556	0.202
B	0.078	0.291	0.951	–0.063	Gd	0.969	0.035	0.005	–0.245
V	0.943	0.136	0.253	–0.169	Tb	0.436	–0.887	0.142	–0.051
Zn	0.914	–0.311	0.260	0.033	Dy	0.543	–0.683	–0.007	0.488
Pb	–0.138	0.013	0.990	0.008	Ho	0.532	–0.525	–0.034	0.663
Cd	0.830	–0.420	0.337	0.149	Er	0.586	–0.788	0.107	0.155
Cu	0.876	–0.461	–0.131	0.056	Tm	0.879	–0.301	0.174	0.327
Cr	–0.475	0.378	–0.757	–0.244	Yb	0.839	–0.499	0.021	0.217
Ni	–0.216	0.560	–0.766	–0.232	Lu	0.100	–0.991	0.085	–0.014
Co	0.832	–0.522	–0.181	–0.043	Hf	–0.650	0.544	0.524	0.077
Li	0.962	–0.268	–0.044	0.031	Th	0.645	0.085	–0.744	0.151
Be	0.957	–0.141	0.242	–0.077	U	0.883	–0.256	–0.165	–0.358
Ga	0.268	–0.925	–0.011	0.270	Pd	–0.272	–0.676	0.410	0.548
Ge	0.901	–0.362	0.220	0.093	Ag	0.324	–0.923	–0.193	0.072
As	0.006	0.770	–0.366	–0.523	Au	0.503	–0.776	0.233	0.300
Se	–0.528	0.737	0.389	–0.162	Te	–0.040	0.348	–0.413	–0.841
Sb	0.938	–0.320	–0.099	0.091	Nb	0.846	–0.399	0.345	0.075
Tl	0.682	–0.298	0.126	0.656	W	–0.300	–0.928	0.022	–0.217

The first group, within the strongest Factor 1, consists of 21 elements (Al, Fe, K, Ti, Mn, P, Rb, V, Cd, Cu, Co, Li, Be, Ge, Sb, Eu, Gd, Tm, Yb, U and Nb, which are slightly affected by anthropogenic activities. The existence of the group is confirmed by factor analysis results (Table 4). Factor 1 is the strongest factor, contains high values of mentioned chemical elements loadings, explaining 36% of total variability within the data. As suggested elsewhere (Bačeva et al., 2014), such association of chemical elements is probably naturally distributed. The contents of these elements mostly depend on the basic geological structure being reflected from the natural processes. The fact that many toxic metals such as arsenic, lead, nickel, cadmium, copper, mercury, zinc and chromium present in untreated or allegedly treated industrial effluents can be carried by rivers in variable amounts (Singare et al., 2011) was confirmed in ours study with Cd, Cu, Co and U present within the Factor 1 array of elements. Factor 2 consisted of elements Sr, As and Se, Factor 3 of B and Pb, while the last Factor 4 enclosed only Cs.

The absence of some significant pollution in sediments at the inflow of the Blaštica river into Tikveš Lake is in full accordance with the findings that despite heavy loads of metals in soil as well in sediments of surveyed catchments of the upper parts of Blaštica, in the area of the well-known Alšar deposit (Bačeva et al., 2014), migration of As, Tl etc., in surface and ground water is limited by presence of carbonate buffer zone, that exist widely in the area of interest (Kahuda et al., 2014). The measured concentrations of REE from the 5 samples in surficial sediments from Tikveš Lake are presented in Table 5, together with basic descriptive statistics and concentrations of REE in upper continental crust, adopted by Taylor and McLennan (1995), Wedepohl (1995) and the average concentrations from the nearby Kožuf Mountain (Boev, 1988; Janković et al., 1997; Boev and Yanev, 2001; Boev et al., 2019). All statistical analyses and plotting were performed using software packages such are Petrograph and Excel + XLStat.

Table 5

Measured concentrations of REE in 5 samples in surficial sediments from Tikveš Lake (mg/kg)

	BL-1	BL-2	BL-3	BL-4	BL-5	Average	Min	Max	Mean	Stand. dev
La	46.8	52.93	47.86	50.1	50	49.54	46.80	52.93	49.49	2.11
Ce	97.11	103.42	94.72	102.3	104	100.31	94.72	104.00	100.24	3.71
Nd	42.35	43.12	40.14	42.3	43	42.18	40.14	43.12	42.17	1.07
Sm	8.75	8.04	7.87	7.8	8	8.09	7.80	8.75	8.09	0.34
Eu	1.78	1.75	1.56	1.8	1.7	1.72	1.56	1.80	1.72	0.09
Gd	6.98	6.03	5.66	7	7	6.53	5.66	7.00	6.51	0.57
Tb	1.15	0.96	0.93	0.9	1	0.99	0.90	1.15	0.98	0.09
Dy	6.14	5.32	5.04	5.3	5	5.36	5.00	6.14	5.35	0.41
Ho	1.41	1.16	1.07	1.2	1	1.17	1.00	1.41	1.16	0.14
Er	3.65	2.95	2.81	2.9	3	3.06	2.81	3.65	3.05	0.30
Tm	0.62	0.47	0.46	0.56	0.5	0.52	0.46	0.62	0.52	0.06
Yb	3.16	2.63	2.46	2.8	2.7	2.75	2.46	3.16	2.74	0.23
Lu	0.5	0.41	0.39	0.32	0.4	0.40	0.32	0.50	0.40	0.06
ΣLREE	195.01	207.51	190.59	202.5	205	200.12	190.59	207.51	200.02	6.34
ΣHREE	23.61	19.93	18.82	20.98	20.6	20.79	18.82	23.61	20.73	1.59
ΣREE	218.62	227.44	209.41	223.48	225.6	220.91	209.41	227.44	220.81	6.46
ΣLREE/ΣHREE	8.26	10.41	10.13	9.65	9.95	9.68	8.26	10.41	9.65	0.75
% LREE	89.20	91.24	91.01	90.61	90.87	90.59	89.20	91.24	90.58	0.72
% HREE	10.80	8.76	8.99	9.39	9.13	9.41	8.76	10.80	9.39	0.72

The ΣREE concentrations in surficial lake sediments varied between 209.41 and 227.44 mg/kg while ΣLREE ranged from 190.59 to 207.51 mg/kg and ΣHREE were significantly lower ranging 18.82 to 23.61 mg/kg.

LREE accounted for 89.20% to 91.24% of the total REE in the studied surficial lake sediments, while HREE accounted for 8.76% to 10.80% of total REE. This correlates well with the percentage of LREE in the upper continental crust (Taylor and McLennan, 1995; Wedepohl, 1995) and also agrees with the conclusions of Tyler (2004), that LREEs are usually more abundant than HREE in the Earth's crust. The salic minerals (feldspars, quartz) preferentially concentrate LREE, which also explains the high percentage of LREE in surficial sediments from Tikveš Lake (Figure 3). Slightly elevated contents of HREE in surficial lake sediments could be explained by the contribution of the mafic and ultramafic rocks in the nearby area, which contain HREE rich minerals: potassium feldspars, amphiboles and pyroxenes (Boev, 1988; Jankovic et al., 1997; Boev and Yanev, 2001; light colored shadow patterns in the upper part of the REE plot on Figure 3).

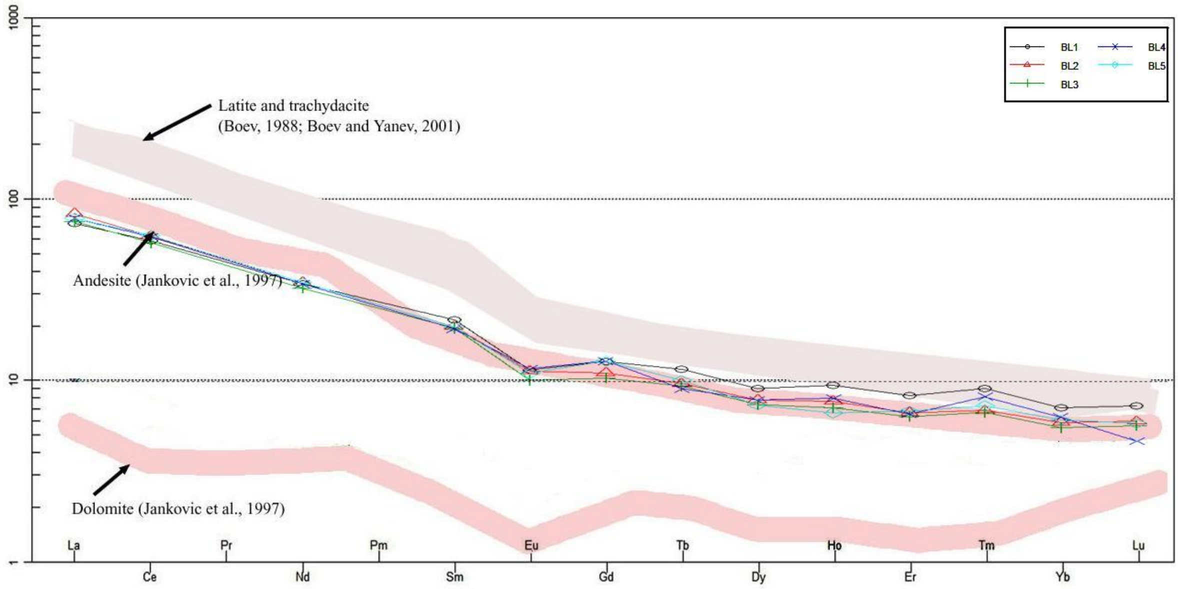


Fig. 3. Normalized REE values pattern from the Blaštica River confluence into Tikveš Lake compared with normalized REE values patterns of the Kožuf/Alšar area

As we may see from the Figure 3 above, normalized REE values pattern in samples from Tikveš Lake strongly reflect the magmatic rocks REE patterns (Kožuf/Alšar area) from where the Blaštica river originates.

The average ratio LREE/HREE was within the range 8.26 to 10.41 mg/kg. The LREE/HREE ratio and Eu anomaly, as suggested Mao et al. (2011), can be used to trace weathering intensity. It is wellknown that chemical weathering affects the chemical composition of rocks in the order: plagioclase feldspars > K-feldspar > quartz. The weathering residues of all feldspars are different clay minerals. However, the chemistry of bed rocks often does not reflect the exact source before weathering, because a lot of minerals (e.g., feldspars) become progressively depleted, thus new sediments become less representative of the source rock (Nesbitt et al., 1996). That is why the abundance and patterns of REE are reasonably well preserved during weathering, as they are far less mobile during sedimentary processes (Vrhovnik et al., 2012).

Eventual Eu anomalies were calculated, using directions given in Rollinson (1993), as:

$$Eu^{*} = \frac{Eu_N}{\sqrt{Sm_N \cdot Gd_N}},$$

where:

Eu^{*} – calculated Eu anomaly,
Eu_N – normalized Eu value,
Sm_N – normalized Sm value,
Gd_N – normalized Gd value.Obtained values for calculated Eu^{*} anomalies are given in Table 6.

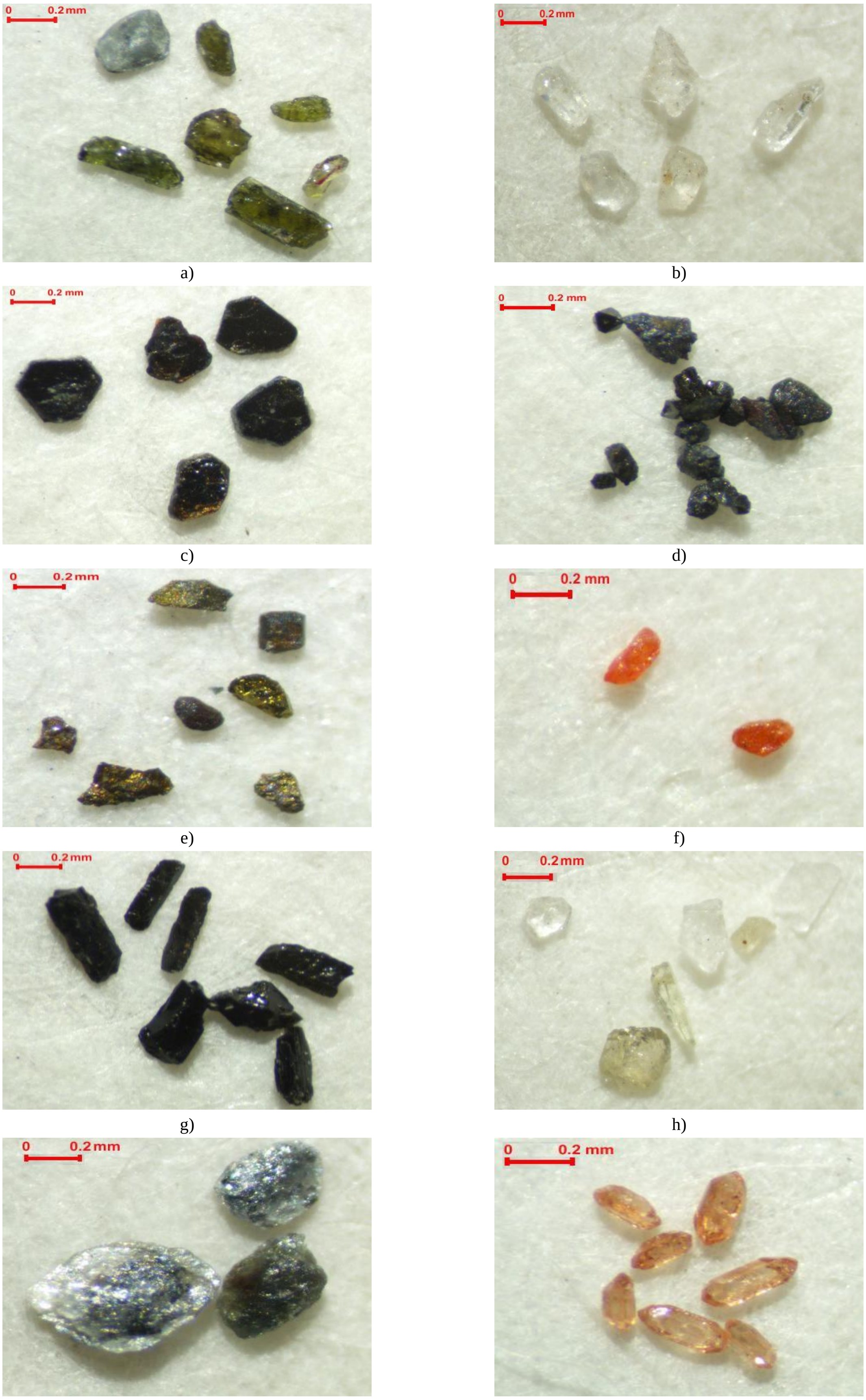
Table 6

Calculated Eu anomalies in samples from the Tikveš Lake sediments

Sample	Sm_N	Eu_N	Gd_N	Eu*
BL-1	21.35	11.56	12.83	0.6985
BL-2	19.80	11.36	11.08	0.7670
BL-3	19.38	10.13	10.40	0.7135
BL-4	19.21	11.69	12.87	0.7435
BL-5	19.70	11.04	12.87	0.6933

As it can be seen from the Table 6, Eu shows a weak negative anomaly. Namelly, Eu anomaly showed values between 0.6933 and 0.7670 (average of 0.7232), which is very similar to findings of Boev (2013) for the rocks of the Kožuf volcanic area.

In the present study LREE/HREE ratios and a significant Eu anomaly are detected in the lake sediments and also in the vulcanites from Kožuf Mountain (Alšar area), which provides powerful evidence to support the hypothesis that REE in the lake sediments originate mainly from "nearby" rocks and are not implying exact information that they were under the influence of the former mining activities at the Alšar and Ržanovo mines.



a) b) c) d) e) f) g) h) i) j)

Fig. 4. Schlich mineral fractions found in sediment samples at the confluence of the Blaštica river into Tikves Lake
a) amphibole; b) apatite; c) biotite; d) magnetite; e) pyrite; f) realgar; g) pyroxene; h) plagioclase; i) mica; j) zircon

These former findings (by the REE analyses) were confirmed by the results of schlich analysis of the Tikveš Lake sediment samples (Table 7).

The observed minerals in the form of monomeral fractions, recorded under a binocular microscope, are illustrated in Figure 4 in accordance to the individual mineral grains given in Table 7. It is indicative that in addition to the presence of petrogenic minerals in the order of amphiboles, pyroxenes, mica, feldspars and other representative for volcanic rocks, presence of metallic minerals such as magnetite and hematite, while especially interesting were pyrite and realgar that have been identified in the primary ore at the Alšar ore deposit.

It should be noticed predomination of milky-white to transparent-white minerals. Colored minerals are relatively rarer.

Table 7

Results from the schlich study of grinded samples from Tikveš Lake*

Mineral	Representation
Magnetite	••
Plagioclase	•••
Pyroxene	•••
Amphibole	•••
Biotite	••••
Muscovite	••••
Quartz	••••

*schlich – The finer portion of crushed ore, as of gold, lead or tin, separated by the water in certain wet processes. Symbols meaning: •••• very present; ••• present; •• poorly present; • rare

CONCLUSION

Results of geochemical study of sediments from the Blaštica river confluence in Tikveš Lake showed a geological connection between the studied material in the sediments of this river estuary in the Tikveš Lake and the parent rocks through which Blaštica river flows on its way into the Tikveš Lake. The analyses of the geological background of the terrain and the observed mainly volcanic rocks give a pattern of the minerals found in the processed schlich materials of the studied area. Feldspar, mica, zircon, plagioclase, titanite are also characteristic of the primary volcanic rocks from which they were extracted. The magnetite, pyrite and realgar found in the schlich unambiguously link to the primary origin at Alšar where they were liberated and transported to the waters of the Blaštica river. The increased geochemical presence of arsenic, antimony, silver, bismuth, gold, uranium and others is another confirmation of the leaching of these elements from primary "contaminated" rocks and ores from the Alšar mine. The identified contamination factors explicitly indicate the high share of silver as one of the contaminants identified in the sediments examined. On the other hand, the values determined for europium, between 0.6933 and 0.7670, give the anomalous value which coincides with the contents of europium in the volcanic rocks of these areas and also indicates increased concentrations of the rare elements found in the studied sediments from the Blaštica river, especially Eu, Gd, Tm and Yb.

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Резиме

ГЕОХЕМИЈА НА СОВРЕМЕНИТЕ СЕДИМЕНТИ ВО ВЛИВОТ НА РЕКАТА БЛАШТИЦА ВО ТИКВЕШКО ЕЗЕРО

Иван Боев[1], Далибор Серафимовски[2], Горан Тасев[1]

[1]*Институт за геологија, Факултет* за *природни и технички науки, Универзитет „Гоце Делчев“ во Штип,*
бул. „Гоце Делчев“ 89, 2000 Штип, Република Северна Македонија
[2]*Институт за геологија, Факултет* за *природни и технички науки, Универзитет „Гоце Делчев“ во Штип,*
„Крсте Мисирков“ 10А, 2000 Штип, Република Северна Македонија
ivan.boev@ugd.edu.mk

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Во трудот се прикажани резултатите од најновите истражувања и проучувања на геохемиските карактеристики на седиментите од крајните долни делови на реката Блаштица, на нејзиното влевање во Тиквешко Езеро, односно поврзаноста со Црна Река. На FUS-ICP се извршени комплетни анализи на 58 елементи, кои овозможија согледување на индивидуалните аномални содржини на одделни елементи и елементи загадувачи на миловитите седименти. Нивната статистичката обработка даде карактеристични резултати. Пресметката на таканаречениот индекс на геоакумулација обично беше помеѓу Класа 0, Класа 1 и Класа 2 или покажуваше неконтаминирана до умерено контаминирана средина, освен за среброто (Класа 6) кое покажа екстремно високо ниво на контаминација I_{geo}. Факторот на контаминација речиси за сите анализирани елементи се движеше во опсег од низок до многу висок (Класа 1 до Класа 4), иако најчесто се манифестираше како умерен и значаен (Класа 2 и Класа 3), додека индексот на контаминациска оптоваре-ност се движеше од 1.59 до 3.20, што укажува на прогресивно влошување во однос на контаминација на проучуваните локации. Факторот на оптоварување е пресметан со статистичката обработка од типот Варимакс-ротација и се добиени четири фактори (F1–F4) од кои F1 сугерира мало антропогено влијание. Исто така, извршено е определување на елементите на ретки земји, резултатите се обработени статистички, а се добиени и аномалиите на еуропиумот, кои покажаа вредности помеѓу 0.6933 и 0.7670, што укажува на негативна аномалија.