Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia with a grant from the CEI-ES Know How Programme organize

CENTRAL EUROPEAN INITIATIVE
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1st INTERNATIONAL WORKSHOP ON THE PROJECT

Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)

PROCEEDINGS

Edited by:
T. Serafimovski & B. Boev
Kavadarci, 10th October 2013

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WATER AND SOIL ANALYSES OF SOME PARTS IN THE KOZUF AREA, R. MACEDONIA

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Abstract
The present study of pollution of water and soils, was an integral part of the CEI funded project "Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)" and was performed at particular parts of the famous Kožuf metallogenic district. Our compilation study have shown that the major pollution suffered stream sediments, soil and mine waste related to former Alšar exploration and exploitation with significantly increased concentrations of heavy metals (6÷8098 mg/kg Sb; 25÷32000 mg/kg As; 1÷922 mg/kg Cd; 5÷569 mg/kg Cr; 2÷20 mg/kg Pb; 4÷154 mg/kg Ni; 1÷775 mg/kg Tl). The latest study of water samples from the Alšar drainage area have not shown some significant pollution, although it was expected (0.00025÷0.00254 mg/l Cr; 0.013÷0.061 mg/l Fe; 0.00015÷ 0.00043 mg/l Co; generaly <0.0005mg/l Ni and three samples ranging 0.00112 ÷ 0.00217 mg/l Ni; 0.00058÷0.0011 mg/l Cu; 0.000272÷0.02731mg/l As, with an exception of one sample (A10-hot water well) where it was recorded value of 0.196469 mg/l As; <0.0005mg/l Cd; 0.000251÷0.009026 mg/l Sb; 0.000102÷0.00061 mg/l Tl; 0.000258 ÷0.001482 mg/l Pb). Our latest findings in regards to the Stara Reka (Dudica) area, where solid samples are still in the stage of laboratory processing, we determined concentrations of heavy metals in water samples: 0.000219÷0.0024 mg/l As; 0.000512÷0.0065 mg/l Pb; 0.00079÷0.0008mg/l Cd; 0.003275÷0.1108mg/l Zn; 0.0000995 ÷0.0002mg/l Co; 0.00136÷0.0043mg/l Ni; 0.0000578÷0.0004mg/l Cr; 0.009053÷0.0348mg/l Fe; 0.000437÷0.0017mg/l Cu; 0.000232 to 0.0004 mg/l Sb; 0.0000656÷0.0001mg/l Tl, with all of them bellow the MDK values.

Key words: pollution, Kozuf, heavy metals, water, soil, sediments, mine waste

Introduction
The Kozuf magmato-metallogenic area is situated in the Serbo-Macedonian-Anadolian metallogenic province. Spatially, it is situated along the western margin of the Vardar zone and the Pelagonian Mass. Latites, quartz-latites and trachytes predominate in the magmatic complexes of the Kozuf area. Unlike most Oligo-Miocene calc-alkaline complexes in the Vardar zone and the Serbo-Macedonian Massif, the volcanics of Kozuf are very young (Pliocene age, between 12 and 1.8 Ma). Volcanic facies are widespread, whereas intrusive facies occur sporadically as subvolcanic intrusions.

The Kozuf district displays many specific features because of its metallogeny. Based on available knowledge and the degree of investigations carried out several mineralization styles and metal associations such as: volcanogenic epithermal replacement mineralization of Sb-As-Tl association, Carlin-type gold mineralization, high sulphidation enargite vein-type mineralization accompanied by gold mineralization as well, porphyry copper mineralization, epithermal Sb-As-Fe mineralization of vein-lense type related with fractures in the crystalline schists and solfataric products represented by native sulphur and marcasite, sporadically associated with galena (Boev, 1988; Janković et al., 1997). The Sb-As-Tl-Au is the predominating mineralization.

Magmatism of calc-alkaline suites and structures, both volcanic ring-radial and regional fractures are the principal factors controlling distribution of mineralization in time and space. Magmatic complexes are the principle source of ore metals and/or the source of heat energy for the formation of hydrothermal ore-bearing solutions that mobilized ore minerals from ultimate sources and transported them to the site of precipitation of mineral parageneses. The distribution pattern of mineralization is characterized by both lateral and vertical zoning. The central part of the district contains copper mineralization, surrounded by Sb-As ± Tl±Au deposit and occurrences (e.g. Alsar and Smrdliva Voda).

From the environmental point of view here we would like to give an accent to two deposits, Alshar and Dudica, as eventual contaminants of their adjacent regions and different kinds of natural medias. Alšar as deposit of As, Sb and Tl and its open adit waste dumps could easily serve as major contamination sources of Madenska river that is a tributary to the Blašnica river, which inflows into the Tikveš Lake. The second locality of interest is vicinity of the Stara Reka, which is within the Dudica deposit drainage system and passes through the watersheds of the Lukar and Kosmatec water supply localities that provide with drinking water Kavadarci and Negotino municipalities. There we have found our major goals within the CEI funded project "Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)" where we aim to make a review of all data regarding the solid and fresh water medias from those two particular drainage systems. We believe that our latest field and laboratory studies will contribute significantly in the determination of the degree of contamination by natural contaminants within the area of interest.

General geological features

The Dudica ore field is located about 2 km far from the Macedonian border with Greece, in the western margin of the Vardar zone, within its contact with the Pelagonian massif, where regional dislocation structures as well as the geotectonically labile zones associated with Jurassic peridotitic complex were developed (Hiessleintner, 1945; Ivanov, 1965 and Janković, 1967). The immediate surroundings of the deposit, covering an area of several square kilometers, consist of Paleozoic formations (phyllite, schists, sandstones, green schists, etc.) and Mesozoic crystalline limestones sporadically transformed into marble. These rocks have been intruded and/or overlain by the products of magmatic activity during Pliocene (dacite-andesite-quartz rhyolite subvolcanic intrusions). Within the broader area around Dudica, several occurences are known of ore mineralization of pyrite, copper (enargite, chalcopyrite), lead (galena), as well as the occurences of native sulphur. The mineralization is dominantly fracture controlled and occurs as a small sulphides (quartz-pyrite-enargite, pyrite-enargite, etc.) filling in veins and small fractures, or as disseminations in the sheared zones (Ivanov, 1961).

The Alšar igneous complex formed on a basement composed predominantly of the Triassic sediments, the Jurassic ophiolites (gabbro-peridotites prevails), and the Cretaceous sediments. Volcano-intrusive activity took place from 7 to 1.8 m.y. (andesitic-quartz latite to rhyolite and trachyte). The Mesozoic rocks are unconformably overlain by late Pliocene cover, and glacial till. The earliest Tertiary rocks are tuffaceous dolomites locally intercalated with sequence of tuff, waterlain ash and volcanic glass. The felsic tuffs unconformably overlies the tuffaceous dolomite, and locally the Mesozoic basement rocks. The subvolcanic latite intrusions cross cut both Mesozoic and Tertiary rocks. Mineralization is hosted by the Triassic carbonates (dolomites and marbles), the Tertiary magmatic rocks and volcano-sedimentary sequence (tuffaceous dolomite). The mineralisation generally consists of antimony, arsenic and thallium minerals associated with iron suplhides (stibnite, realgar, orpiment, and numerous Tl-minerals: lorandite, vrbaite, parapierrotite, bernardite). The later discovered fine grained disseminated gold mineralization (to 10µm in size) is found in silicified zones or in microquartz veinlets. Special attention has been given to the gold mineralization in the southern parts of the Alšar ore deposit. The epithermal ore is of disseminated replacement-type. Gold mineralization occurs in Mesozoic dolomite, in jasperoids along faults and in an unconformity between the pre-Tertiary age rocks, and micro-quartz veinlets, disseminations and silica replacement bodies in Tertiary tuffaceous dolomite and overlying Tertiary tuffs.

Sampling and methodology

Within this paper are enclosed numerous former and present solid (stream sediment, mine waste and soil) and water samples that were analyzed for a range of toxic metals to determine the level and extent of eventual contamination at Alshar and Dudica drainage areas. The latest sampling locations are given at Figure 1.

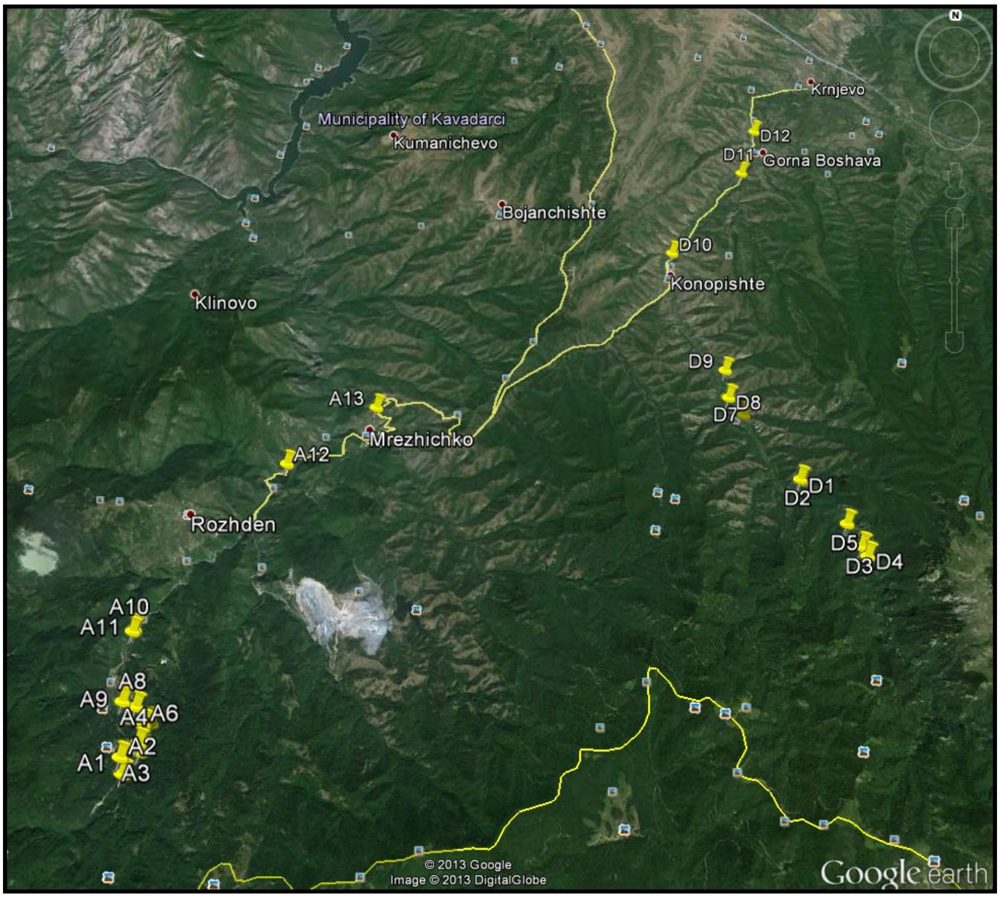

Fig. 1. Sampling locations map of the Alshar and Dudica localities

Near surface (0-20 cm) soil samples were collected because in general was not possible to distinguish A, B and C horizon. These samples were taken using plastic spatula. Solid samples were air dried at 20^{O}C for a week and sieved through 2 mm sieve to remove plant debris, pebbles and stones. They were then ground in a mechanical agate grinder to a fine powder for further geochemical analyses. Water samples were taken using medical syringe. After that water was transfered to a sterile plastic bottles through a 45 µm filter paper it was acidified with 0.4 ml of 50% nitric acid. Further preparations of water samples before the analysis were not necessary. All the analyses were performed both on ICP-AES and ICP-MS (the later for determination of particular metals present at lower concentrations detectable by ICP-AES). The accuracy and precision were better than ±5%. This was indicated by the results of duplicate measurements. It is very important to point out out that there is chronology in sampling and analysis of the area of interest. Namely, area of interest was sampled several times in a row, Hill and Warren (1997), Boev et al (2001), Boev and Lepitkova (2002; 2005) and ours April, 2013 sampling campaigne.

Results and discussion

The westernmost parts of the Kozuf Mt. reach the river Blasica (right tributary of Crna river) and the north-western side stretches in a line, from the Mrezicko village via the village Konopiste, through the course of Bosavica river to the city of Demir Kapija. Through these waterways the entire area is drained into the river 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 Alsar mine, that represent a significant environmental and health hazards. Other known ore deposits/mineral occurrences are Majdan (arsenic), Dudica (copper-gold) and Arnicko (antimony). Many other ore deposits are supposed to have existed here but have remained unknown due to the lack of exploration. The lack of exploration implies lack of awareness of potential risks.

Shallow groundwater aquifers formed in alluvial sediments of Crna and Bosavica rivers and their tributaries, that are draining the territory of project interest, represent an important source of drinking water for local municipalities (Kavadarci and Negotino) and settlements. These aquifers are typically exploited with use of individual shallow dug wells and therefore relevant water treatment prior to water supply is very complex issue for reasonable implementation. At the Kozuf Mt. has been formed karstic formations (Mesozoic carbonate) and groundwater is drained through a number of karstic sources. Main karstic sources are Lukar with capacity 400 *l/s* and sources Konjska and Babuna with capacity between 10 and 90 *l/s*. Approximate population that may be affected by negative impacts in downstream area is about 60 000 people.

Over the longer term and repeatedly localities Alshar and Dudica has been sampled and studied by several researchers in terms of environmental issues. The latest one being within the frame of the current CEI project "Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)".

As it was mentioned before, the Alsar area is characterized by natural increased concentrations of arsenic, antimony and thallium. Also, increased arsenic and thallium concentrations have also been found in some plants such as Thimus and Viola (Boev and Lepitkova, 2002). It is of note that earlier mining waste dumps with large amounts of waste material that resulted from mining activities have been found in the riverbed of Majdanska. Increased concentrations of trace elements have been determined in the material and in the river sediments (Table 1).

Table 1. Geochemical analyses of the mine waste, soils and stream sediments (in *mg/kg*; Hill and Warren, 1997; Boev and Lepitkova, 2005)

Sample	Sb	As	Cd	Cr	Pb	Ni	Tl
Stream sediment							
1	6	150	<1	97	9	156	<1
2	280	356	1	20	9	31	<1
3	18	186	<1	26	8	31	<1
4	57	296	1	18	7	26	<1
6	260	256	<1	22	3	22	<1
7	155	602	4	16	6	18	<1
8	70	277	1	15	2	19	<1
9	123	677	3	18	4	22	<1
10	85	813	4	24	4	25	<1
11	129	829	5	22	6	26	<1
12	58	315	<1	98	7	92	<1
13	33	70	<1	569	6	675	<1
14	24	25	<1	353	2	360	<1
Mine waste							
1	514	>32000	261	4	17	6	478
2	1288	8514	45	10	9	26	100
3	4481	7613	39	16	20	6	716
4	12	153	<1	5	3	11	<1
5	146	8477	922	9	19	4	775
Soil							
1	1731	3602	22	32	6	46	107
2	8098	1182	5	92	6	123	92
3	2116	672	3	130	7	154	<1

As can be seen from the table above, the chemical test results indicate that the mine waste tips present in the Alsar valley are very heavily contaminated with antimony, arsenic, cadmium and thallium. The mine waste from the adit below the *823 m* mine (sample S6) contained the highest concentrations of arsenic (32000 mg/kg), along with very high levels of cadmium (261 mg/kg) and thallium (478 mg/kg). The mine waste from adits 37 and 39 (sample S20), located north of the village of Majdan, contained the highest concentrations of thallium and cadmium at 775 mg/kg and 922 mg/kg respectively. This material also contained very high levels of arsenic (8477 mg/kg).

The soil between the waste tips from the *800 m* and *823 m* mines (sample S8, Plates 3 and 4) is very heavily contaminated with antimony, arsenic and thallium. Samples of soil taken on the western side of the stream, opposite the *800 in* and *823 m* mines were also heavily contaminated with antimony (SI 1, 8098 mg/kg and S12, 2116 mg/kg), as well as showing elevated levels of As and Tl.

Stream bed samples were found to be heavily contaminated with antimony and very heavily contaminated with arsenic, but thallium concentrations were below the screening level (1 mg/kg). The metal contamination in the stream bed extends from the ford at the border marker post (sample SI) (Plate 9), downstream as far as the confluence with the discharge from the FeNi mine (sample SI 7) (Plate 10). Samples taken downstream of the

FeNi mine (samples SI 8 and S20) were found to contain elevated levels of chromium and nickel but only slightly elevated levels of arsenic.

The analysis results of solid media samples from the Alšar area, as well as samples from the Dudica area, taken during the April, 2013 sampling campaign are still not available, since they are in analytical procedure. We hope that we will have an opportunity to present them at our next Project Workshop planned for the first half of 2014.

Water

The increased arsenic, antimony and thallium concentrations could pose risk for the human environment along the River Majdanska, the river flowing through the Alsar valley, which is an upstream tributary of the River Blašnica. The Blašnica flows in a general northwards direction past Majden and then Rozden to the west, before forming a confluence with the Kozamik. The Kozamik receives surface water discharges from the FeNi mine, and is visually contaminated with a high suspended solids load. The Blašnica flows through a series of limestone gorges, before entering Lake Tikves 7 km downstream of Mrezicko. Lake Tikves forms a nationally-important water resource. However it should be stressed that any contamination entering Lake Tikves from the Blašnica river is likely to be small in comparison with inputs from the Crna river. The latter drains a much larger basin than the Blasica, receiving municipal and industrial effluents from large towns such as Prilep, and trans-boundary pollutants from northern Greece (Hill and Warren, 1997; Boev and Lepitkova, 2005).

These facts were of enough significance to initiate several water studies of the Alšar’s drainage system. The last studies of water (Hill and Warren, 1997; Boev and Lepitkova, 2005), performed in the ICP-AES equipped analytical facility, found that arsenic is above maximally allowed concentrations (MDK) of 0.05 *mg/l* As (for both, class I-II and class III-IV) only in one sample characterized by 0.075 *mg/l* As. Cadmium in all samples have shown concentrations bellow 0.0005 *mg/l* Cd, which is below the MDK for both, class I-II (0.0005 *mg/l* Cd) and class III-IV (0.001*mg/l* Cd). The very similar pattern was followed by chromium concentrations with only one concentration of 0.002 *mg/l* Cr and all others bellow 0.001 *mg/l* Cr, which is however below the MDK for both, class I-II (0.05 *mg/l* Cr) and class III-IV (0.01*mg/l* Cr) and by nickel concentrations with only one concentration of 0.046 *mg/l* Ni and all others bellow 0.001 *mg/l* Ni, which is below the MDK for both, class I-II (0.05 *mg/l* Ni) and class III-IV (0.1*mg/l* Ni). Nothing changed significantly when were analyzed lead, with all the concentrations bellow 0.002 *mg/l* Pb that is is below the MDK for both, class I-II (0.05 *mg/l* Pb) and class III-IV (0.5*mg/l* Pb) as well as in the case of antimony where beside mainly concentrations lower than 0.003 *mg/l* Sb, where were recorded values of 0.006 and 0.01 *mg/l* Sb, which even for the highest one is five times lower than the MDK for both, class I-II (0.05 *mg/l* Sb) and class III-IV (0.05 *mg/l* Sb). The thallium concentrations, except one (0.002 *mg/l* Tl), were bellow 0.001 *mg/l* Tl, which at the upper limit of the allowed range of thallium concentrations by World Health Organization-WHO of 0.001 *mg/l* Tl (IPCS, 1996).

In the spirit of latest scientific and technical development, within this CEI-ENIGMA project, we made an effort to sample and analyze Alšar’s water drainage system. Water samples were analyzed in the ICP-AES and ICP-MS equipped analytical facility. The latest findings in this regard are given in the Table 2, bellow. From the table are imposed several facts. Namely, chromium concentrations were in the range of 0.00025÷0.00254 *mg/l* Cr while some samples have shown concentrations even bellow 0.00025 *mg/l* Cr, which is far bellow the MDK values of 0.05 *mg/l* Cr and 0.1 *mg/l* Cr for class I-II and class III-IV, respectively. The iron concentrations that were in the range 0.013÷0.061 *mg/l* Fe were several times bellow the MDK standards of 0.3 *mg/l* Fe for class I-II and 1.0 *mg/l* Fe for class III-IV (Figure 2a).

Table 2. Geochemical analyses of the water drainage system of the Alšar area (in *mg/l*)

	A1	A2	A4	A5	A8	A9	A10	A11	A12	A13
Cr	0,00027	0,00255	0,00218	0,00049	0,00027	0,00053	0,00089	<0.00025	<0.00025	0,00025
Fe	0,0135	0,03935	0,01629	0,03953	0,01412	0,02604	0,03803	0,01807	0,05531	0,06096
Co	0,00018	0,00044	0,00025	0,00042	0,00019	0,00022	0,00026	0,00015	0,00041	0,00039
Ni	<0.0005	0,00217	0,00149	0,00112	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Cu	0,00070	0,00089	0,0008	0,00087	0,00089	0,00078	0,00059	0,00066	0,00079	0,00110
As	0,00027	0,00072	0,00840	0,00101	0,00138	0,00395	0,19647	0,00667	0,00095	0,02731
Cd	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Sb	<0.00025	0,00042	0,00025	<0.00025	0,00103	0,00075	0,00903	0,00035	0,00039	0,00037
Tl	0,00011	0,00017	0,00061	0,00018	0,00022	0,00065	0,00139	0,00018	0,00011	0,00010
Pb	0,00059	0,00039	0,00148	0,00046	0,00027	0,00039	0,00052	0,00026	<0.00025	<0.00025

Note: A1-Alšar's the southernmost part (confluence of Provalska River into Madenska River); A2-left confluence to Madenska river (road overhang); A4-Smal water stream confluence to Madenska river from the left; A5-Smal water stream confluence to Madenska river from the left (300-350 m from downstream from A4); A8-From the Madenska river near the sawmill; A9-Source of drinking water by the dirt road to Majdan village (on the left side of Madenska River); A10-Hot water source Toplec; A11-Draw well, 20-25 m northern from Toplec (with three taps); A11-Tap on the road from Majdan Village to Mrezicko village; A12-Water source from rock in the vicinity of Mrezicko village.

Very similar pattern was shown by cobalt and nickel, where cobalt concentrations from 0.00015*mg/l* Co to 0.00043*mg/l* Co were several hundred times bellow the MDK values of 0.2 *mg/l* Co for class I-II and 2.0*mg/l* Co for class III-IV while nickel with its majority of values being bellow 0.0005*mg/l* Ni and three samples ranging from 0.00112 to 0.00217*mg/l* Ni is quite far below the MDK values for class I-II and class III-IV, which were set at 0.05 *mg/l* Ni and 0.1*mg/l* Ni, respectively. Something similar is with copper concentrations in sampled water samples from the Alšar vicinity, where concentrations ranged from 0.00058 up to 0.0011 *mg/l* Cu, which is more than a hundred times below the MDK values set at 0.1 *mg/l* Cu for both classes (I-II and III-IV).

In regards to arsenic concentrations we would like to stress that in general they were below the MDK values for class I-II and class III-IV (0.05*mg/l* As) with a range of 0.000272÷0.02731*mg/l* As, with an exception of one sample (A10) where it was recorded value of 0.196469*mg/l* As which is significantly above the MDK values (Figure 2b).

Within all samples cadmium concentrations were below the 0.0005*mg/l* Cd, which is at least ten times lower than the lowest value set by MDK (0.005*mg/l* Cd class I-II) or even more when we consider the MDK value for class III-IV of 0.01*mg/l* Cd. Although unexpected, antimony with its range of concentrations of 0.000251÷0.009026*mg/l* Sb as well as several below 0.00025*mg/l* Sb was way too below the MDK value of 0.05*mg/l* Sb set for both classes (I-II and III-IV, See Figure 2c). Once again surprisingly, thallium, as distinctive element of the Alšar area showed relatively low concentrations in water samples (0.000102÷0.00061*mg/l* Tl) that is below the upper limit of WHO value set at 0.001 *mg/l* Tl, except in one sample (A10) where the recorded value of 0.00138*mg/l* Tl is just above the WHO limit of 0.001*mg/l* Tl (Figure 2d). In regards to lead, as it was expected, concentrations ranging 0.000258÷0.001482 *mg/l* Pb were below MDK values set at 0.05*mg/l* Pb for class I-II and 0.1*mg/l* Pb for class III-IV.

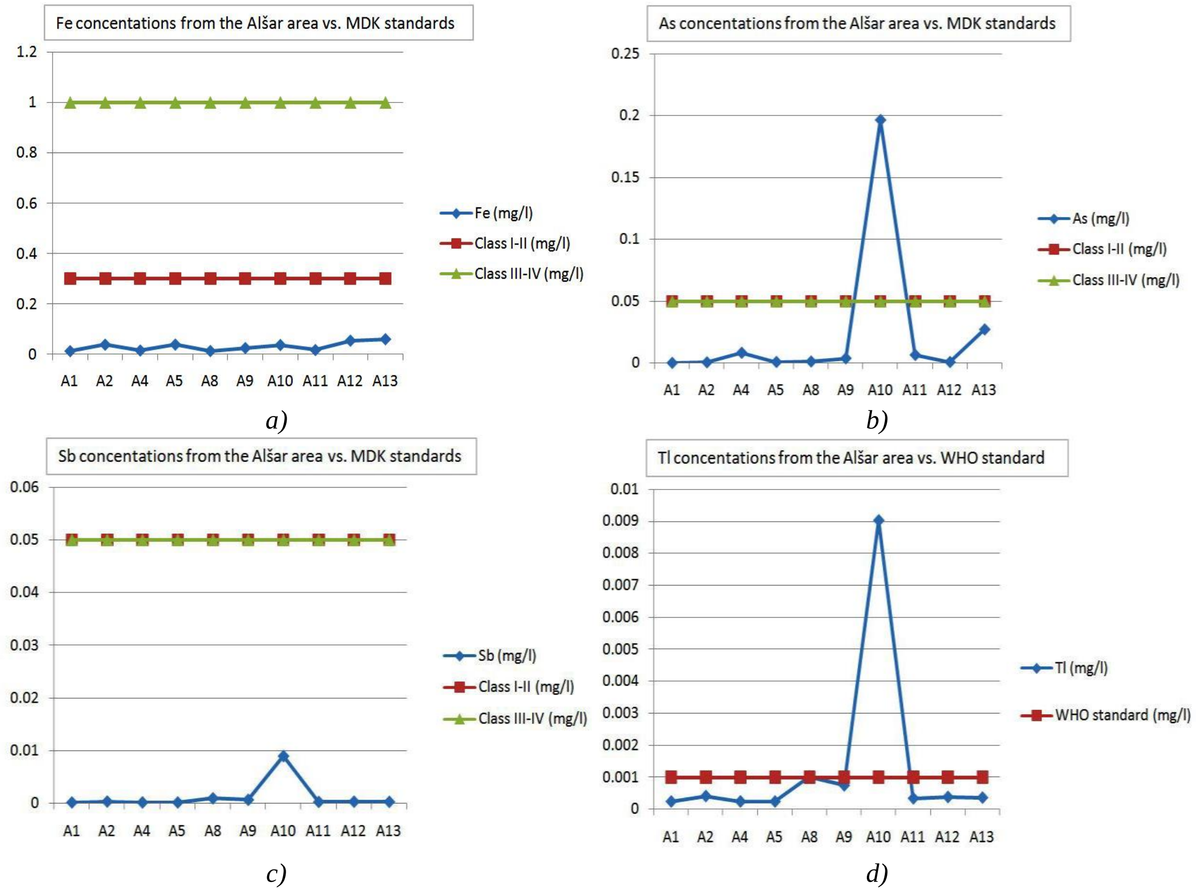

Fig. 2. Concentrations of particular metals in water samples from the Alšar area

As it was the case with the Alšar area, the Dudica area and its drainage water basin were studied several times, especially because the importance of this area as main drinking water source for the citizen of both municipalities, Kavadarci and Negotino, with more than 60 000 habitants. During one of the latest studies of the region, Boev et al (2001), there were analyzed four principal zones, the Lukar1, Lukar 2, Kosmatec and Stara Reka.

At Lukar 1, arsenic has shown values below 0.01 mg/l As, which is below 0.05 *mg/l* As, limit set as MDK (for both classes I-II and III-IV). There we would like to stress out that lead has shown elevated values in almost all of the samples (0.013÷0.074 *mg/l* Pb) while in one sample (sample 7; 0.074 *mg/l* Pb) it was slightly above the MDK standard for class I-II. Generaly, cadmium has shown concentrations within the range 0.001÷0.003*mg/l* Cd, which was below the MDK values for both classes (I-II and III-IV) with upper limits set to 0.005 and 0.01 *mg/l* Cd, respectively. Either it was expected higher presence of zinc, this element within the Lukar 1 sampling area has shown opposite with more than an hundred times lower concentrations (0.0008÷0.002*mg/l* Zn) compared to the MDK values, for class I-II of 0.2*mg/l* Zn and 1*mg/l* Zn for class III-IV. Both, cobalt and nickel, has shown lower concentration ranges, 0.001÷0.067*mg/l* Co and 0.001÷0.012*mg/l* Ni than those allowed by MDK, class I-II (0.2*mg/l* Co and 0.05*mg/l* Ni) and class III-IV (2*mg/l* Co and 0.1*mg/l* Ni). The very same pattern was followed by chromium and iron, which has shown lower concentration ranges, 0.001÷0.003*mg/l* Cr and 0.001÷0.048*mg/l* Fe than those allowed by MDK, class I-II (0.05*mg/l* Cr and 0.3*mg/l* Fe) and class III-IV (0.02*mg/l* Cr and 1*mg/l* Fe).

Quite similar results were recorded for Lukar 2 and Kosmatec localities as it given below. Namely, within the Lukar 2 sampling area, arsenic has shown values below 0.01 mg/l As, which is below 0.05 *mg/l* As, limit set as MDK (for both classes I-II and III-IV). Once again, as is it was the case with the Lukar 1, lead has shown elevated values in almost all of the samples (0.01÷0.053 *mg/l* Pb) while in one sample (sample 5; 0.074 *mg/l* Pb) it was slightly above the MDK standard for class I-II. Generaly, cadmium has shown concentrations within the range 0.001÷0.004*mg/l* Cd, which was below the MDK values for both classes (I-II and III-IV) with upper limits set to 0.005 and 0.01 *mg/l* Cd, respectively. Either it was expected higher presence of zinc, this element within the Lukar 2 sampling area has shown opposite with more than an hundred times lower concentrations (0.001÷0.002*mg/l* Zn) compared to the MDK values, for class I-II of 0.2*mg/l* Zn and 1*mg/l* Zn for class III-IV. Both, cobalt and nickel, has shown lower concentration ranges, 0.001÷0.008*mg/l* Co and 0.001÷0.003*mg/l* Ni than those allowed by MDK, class I-II (0.2*mg/l* Co and 0.05*mg/l* Ni) and class III-IV (2*mg/l* Co and 0.1*mg/l* Ni). The very same pattern was followed by chromium and iron, which has shown lower concentration ranges, 0.0÷0.001*mg/l* Cr and 0.001÷0.076*mg/l* Fe than those allowed by MDK, class I-II (0.05*mg/l* Cr and 0.3*mg/l* Fe) and class III-IV (0.02*mg/l* Cr and 1*mg/l* Fe).

Several analyses of the Kosmatec area have shown the following findings. Arsenic has shown values below 0.01 mg/l As for all the analyzed samples, which is below 0.05 *mg/l* As, limit set as MDK (for both classes I-II and III-IV). Here as is it was the case with the Lukar 1 and Lukar 2, lead has shown elevated values in almost all of the samples (0.01÷0.053 *mg/l* Pb) while in two samples (sample 4 and 6; 0.06 *mg/l* Pb and 0.061*mg/l* Pb, respectively) were slightly above the MDK standard for class I-II. Generaly, cadmium has shown concentrations within the range 0.001÷0.004*mg/l* Cd, which was below the MDK values for both classes (I-II and III-IV) with upper limits set to 0.005 and 0.01 *mg/l* Cd, respectively. Either it was expected higher presence of zinc, this element within the KOsmatec sampling area has shown opposite with more than an hundred times lower concentrations (0.001÷0.0027*mg/l* Zn) compared to the MDK values, for class I-II of 0.2*mg/l* Zn and 1*mg/l* Zn for class III-IV. Both, cobalt and nickel, has shown lower concentration ranges, 0.001÷0.01*mg/l* Co and 0.001÷0.028*mg/l* Ni than those allowed by MDK, class I-II (0.2*mg/l* Co and 0.05*mg/l* Ni) and class III-IV (2*mg/l* Co and 0.1*mg/l* Ni). Once again, as it was for Lukar 1 and Lukar 2, the very same pattern was followed by chromium and iron, which has shown lower concentration ranges, 0.0÷0.001*mg/l* Cr and 0.001÷0.745*mg/l* Fe (exept in sample 4 with recorded 0.745 *mg/l* Fe) than those allowed by MDK, class I-II (0.05*mg/l* Cr and 0.3*mg/l* Fe) and class III-IV (0.02*mg/l* Cr and 1*mg/l* Fe).

Bearing in mind that the water drainage and basin of the Stara Reka is quite important for the water supply of the Tikveš area, we are giving complete table of the geochemical analyses of it (Table 3). As it can be seen from the table, the analyses of the Stara Reka adjacent area have shown the following. Arsenic has shown values below 0.01 mg/l As for all the analyzed samples, which is five times below 0.05 *mg/l* As, limit set as MDK (for both classes I-II and III-IV). Here as is it was the case with the Lukar 1, Lukar 2 and Kosmatec, lead has shown elevated values in almost all of the samples (0.01÷0.056 *mg/l* Pb) while in one sample (sample 3 and 0.056*mg/l* Pb) it was slightly above the MDK standard for class I-II. Generaly, cadmium has shown concentrations within the range

0.001÷0.062*mg/l* Cd, which with an exclusion of sample 2 (0.062*mg/l* Cd), were below the MDK values for both classes (I-II and III-IV) with upper limits set to 0.005 and 0.01 *mg/l* Cd, respectively.

Table 3. Geochemical analyses of samples from the Stara Reka river basin (Boev et al., 2001)

	1	2	3	4	5	6	7	8	9
As	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	0,033	0,046	0,056	0,024	0,03	0,02	0,02	0,02	0,01
Cd	0	0,062	0,001	0,001	0	0,001	0,003	0,001	0,001
Zn	0,01	0,001	0,001	0,012	0,001	0,001	0,001	0,014	0,001
Co	0,001	0,002	0,006	0,007	0,001	0,008	0,001	0,001	0,001
Ni	0,001	0,001	0	0,009	0,006	0,011	0,001	0,001	0,001
Cr	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001	0,001
Fe	0,024	0,009	0,009	0,021	0,017	0,012	0,017	0,014	0,02

Either it was expected higher presence of zinc, this element within the Stara Reka sampling area has shown opposite with more than an hundred times lower concentrations (0.001÷0.014*mg/l* Zn) compared to the MDK values, for class I-II of 0.2*mg/l* Zn and 1*mg/l* Zn for class III-IV. Both, cobalt and nickel, has shown lower concentration ranges, 0.001÷0.008*mg/l* Co and 0.001÷0.011*mg/l* Ni, than those allowed by MDK, class I-II (0.2*mg/l* Co and 0.05*mg/l* Ni) and class III-IV (2*mg/l* Co and 0.1*mg/l* Ni). Once again, as it was case with Lukar 1 and Lukar 2, the very same pattern was followed by chromium and iron, which has shown lower concentration ranges 0.0÷0.001*mg/l* Cr and 0.009÷0.24*mg/l* Fe (exept in sample 4 with recorded 0.745 *mg/l* Fe) than those allowed by MDK, class I-II (0.05*mg/l* Cr and 0.3*mg/l* Fe) and class III-IV (0.02*mg/l* Cr and 1*mg/l* Fe).

The geochemical analyses results of the samples taken from the Dudica water drainage system during our sampling campaign in April, 2013 are given in the Table 4 below.

Table 4. Geochemical analyses of the Dudica's water drainage system

	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13
Cr	0,00006	0,0002	0,0003	<0.00025	0,0003	<0.00025	0,0003	<0.00025	0,0004	<0.00025	<0.00025
Fe	0,02473	0,022	0,0327	0,0181	0,0162	0,0194	0,0126	0,0091	0,0348	0,0122	0,0217
Co	0,00019	0,0002	0,0002	0.0001	0,0002	0,0002	0,0002	0,0002	0,0002	0,0002	0,0002
Ni	<0.0005	<0.0005	<0.0005	0,0018	0,0018	0,0043	0,0028	<0.0005	<0.0005	0,0014	<0.0005
Cu	0,00061	0,0008	0,0004	0,0008	0,0009	0,0012	0,0017	0,0011	<0.0005	0,0015	0,0006
As	0,00039	0,0002	0,0011	0,0006	0,0017	0,0004	0,001	0,0005	0,0024	0,0005	0,0021
Cd	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0,0008	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Zn	0.02891	0.0241	0.0164	0.0209	0.0204	0.0869	0.0312	0.0345	0.0033	0.1108	0.0197
Sb	0,00036	<0.00025	<0.00025	<0.00025	0,0003	<0.00025	<0.00025	<0.00025	<0.00025	0,0002	<0.00025
Tl	0,00011	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001	0.0001	0.00007	0,0001	0,0001
Pb	<0.00025	0,0007	<0.00025	0,0031	0,0006	0,0065	0,0028	0,0014	<0.00025	0,0017	0,0005

Note: D3-Kosmatec (water sorce from rock catchment; D4-Stara Reka, (above capture); D5-Locality called Bogorodica (near the Kosmatec, sample taken from Stara Reka); D6-Ground water source from hose; D7-From well in Stara Reka river bank; D8-Sample taken from the Stara Reka, close to the D7; D9-Vojo's rock (Gorska bottling company water catchment); D10-From the Boshavica river, at the exit from Konopište village; D11-Bozankina's tap; D12-Small bridge at the entrance of Gorno Bošava village; D13-Lukar 2 water source.

As we may see from the data in the table above, arsenic has shown values within the range 0.000219÷0.0024, which is tventy to two hundred times below 0.05 *mg/l* As, limit set as MDK (for both classes I-II and III-IV). Lead has shown relatively low values in almost all of the samples (0.000512÷0.0065 *mg/l* Pb) that are several times lower than upper limits allowed by the MDK for class I-II (0.05*mg/l* Pb) as well as for class III-IV (0.1*mg/l* Pb). Generaly, cadmium has shown concentrations within the range 0.00079÷0.0008*mg/l* Cd, which is below the MDK values for both classes (I-II and III-IV) with upper limits set to 0.005 and 0.01 *mg/l* Cd, respectively. The zinc concentrations within the Stara Reka sampling area has shown approximately ten times lower concentrations (0.003275÷0.1108*mg/l* Zn) compared to the MDK values, for class I-II of 0.2*mg/l* Zn and 1*mg/l* Zn for class III-IV. Both, cobalt and nickel, has shown lower concentration ranges, 0.0000995÷0.0002*mg/l* Co and 0.00136÷0.0043*mg/l* Ni, than those allowed by MDK, class I-II (0.2*mg/l* Co and 0.05*mg/l* Ni) and class III-IV (2*mg/l* Co and 0.1*mg/l* Ni). Once again, as it was case with former analyses (Boev et al, 2001), the very same pattern was followed by chromium and iron, which has shown lower concentration ranges 0.0000578÷0.0004*mg/l* Cr and 0.009053÷0.0348*mg/l* Fe than those allowed by MDK, class I-II (0.05*mg/l* Cr and 0.3*mg/l* Fe) and class III-IV (0.02*mg/l* Cr and 1*mg/l* Fe). Copper didn't differ much, with its concentrations range 0.000437÷0.0017*mg/l* Cu, all the concentrations were at least a hundred times lower than those for class I-II (0.1*mg/l* Cu) as well as for class III-IV (0.1*mg/l* Cu). Antimony concentration values of 0.000232 to 0.0004 *mg/l* Sb, even for the highest one, are at least a hundred times lower than the MDK for both, class I-II (0.05 *mg/l* Sb) and class III-IV (0.05 *mg/l* Sb). The thallium concentrations (0.0000656÷0.0001*mg/l* Tl), were bellow 0.001 *mg/l* Tl, which at the upper limit of the allowed range of thallium concentrations by World Health Organization-WHO of 0.001 *mg/l* Tl (IPCS, 1996).

Here we would like to stress out that particular sampling points within this latest study are involved in the drinking water supply chain (municipality drinking water system /sample D3 and D13/ and water bottling company, water catchment D9). None of the samples, for analyzed elements, didn't show concentrations above the drinking standards, also.

Also, here we must to mention that during the sampling campaign the level of surface and ground water was extremely high due to abundant precipitation and snowmelt in the high mountain peaks. Probably there we should seek an answer for relatively low concentrations of metals of interest in both areas.

Conclusions

The major pollution in both studied areas within the Kozuf metallogenic district (Alšar and Dudica) have been determined in solid samples (stream sediments, soil and mine waste) in the Alšar area and is directly related to the former exploration and exploitation when prolonged deposition of heavy metals took place. Increased concentrations of particular metals such are Sb, Tl, As and some others at the sampling point A10 (hot water well called Toplec) can be attributed to the hot water that leached and mobilized former metals and transported them to the surface. In all other water samples from both areas metal concentration levels were below MDK values, in one part probably due to high water levels (ground and surface) in April 2013, when our latest sampling campaign occurred, resulting with certain possibility of quick removal of metals from the sampled media.

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