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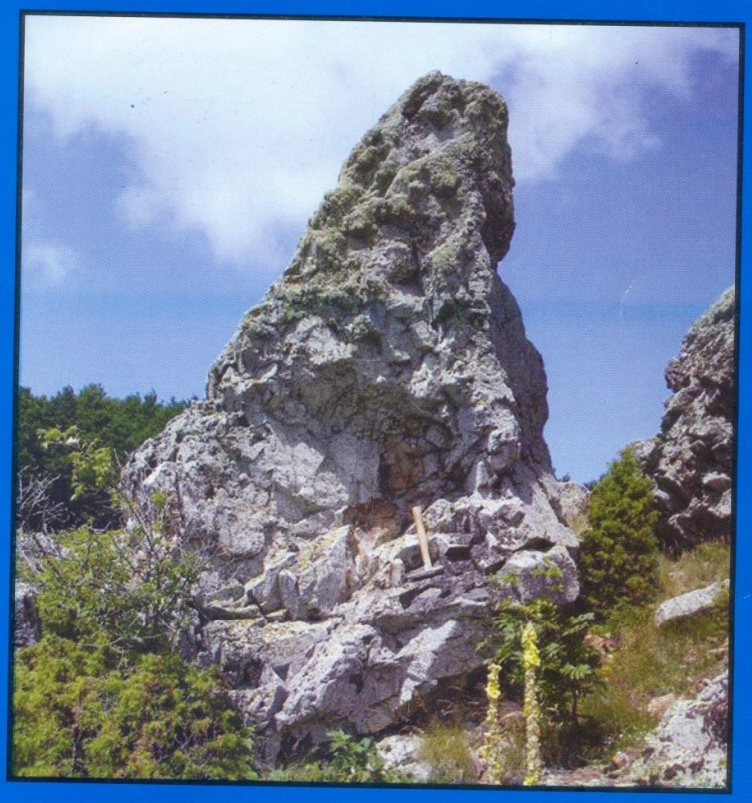

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Original scientific paper

HEAVY METALS IN SEDIMENTS AND SOILS ALONG THE BREGALNICA RIVER IN THE PART OF HYDROACCUMULATION KALIMANCI TO KOČANI

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A b s t r a c t: In frame of this paper are given the results and findings from the research performed for determination of metal pollution in the flow of the Bregalnica River. After the analysis and interpretation of data were confirmed the assumptions for increased values of the following metals: Zn, Pb, Cd, In, Cu, Fe, Mn, As, Ag and Ni. Since in the near vicinity is Sasa Mine for lead and zinc exploitation, especially interesting were the results for Pb that reached 331.2 mg/kg, Zn that reached 321.1 mg/kg, Cd that reached 2.0 mg/kg in sediments and Pb that reached 112.98 mg/kg, Zn that reached 613.71 mg/kg, Cd that reached 4.85 mg/kg in soils. The increase of metal concentration was determined in all of the analyzed medias: sediment and soil. Increased concentrations of metals quite often were of several times magnitude over the maximal allowed standards. The increase of metals concentration was highest in the area of the hydroaccumulation Kalimanci, and downwards through the flow of the Bregalnica River the concentrations decreased.

Key words: metals; pollution; lead; zinc; sediments; soils; maximal allowed concentrations

INTRODUCTION

Waste materials which are contained in the tailing of the hydro dump Sasa through the Kamenička River are bring in the hydroaccumulation Kalimanci. Water of the hydroacumulation Kalimanci is used for irrigation, and part of it flow into the Bregalnica River. Waste waters of the Kameička River, hydroaccumulation Kalimanci and the Bregalnica River contaminate the land (sediments and soils), and also the underground waters accumulated in the wells which are located on the flow of the Bregalnica River.

The tailing which is disposed in the hydrodump Sasa is waste derived from the process of selective flotation concentration in which concentration of the lead and zinc minerals are concentrated. The composition of the waste materials is directly connected with the type and the quantity of the flotation reagents, characteristics of the processed ore, process of enrichment, and also pH value of the pulp. The liquid phase of the flotation tailing is composed of highly mineralized waste water with increased concentrations of sulphates, heavy metals, phenols and other toxic materials.

According to the geographical position of the investigated terrain and the direction of the waste waters, there is possibility of contamination of the underground waters and the land (sediments and soils).

Preliminary investigation results of this type can be found in the publications from Mirčovski and Spasovski, 2003; Mirčovski, Spasovski at al. 2004; Serafimvovski et al. 2005.

GEOLOGICAL AND HYDRO-GEOLOGICAL CHARACTERISTICS OF THE TERRAIN

The moving of the waste waters underground depends of the hydro-geological characteristics of the terrain, which will be further present more detailed.

On the investigated terrain there are Quaternary alluvial sediments of the Bregalnica River and Neogene sediments in the vicinity of Kamenica and on the left side of the Bregalnica River in the vicinity of Kočani.

Alluvial sediments of the Bregalnica River consists of sands, gravel, and on some places sandy

clays. This composition of the alluvial sediments made it possible accumulation of significant quantities of waste water with possibility of contamination of the sediments and soils.

Neogene sediments in the vicinity of Kamenica and on the left side of the Bregalnica River in the vicinity of Kočani are made of marly clays and Quaternary alluvial sediments presented by clays, sandy clays, sands and gravels.

There are open type wells on the investigated terrain with free level in which the level of underground water is near the surface. Good filtration coefficient and direct hydraulic connection with the Bregalnica River shows the possibility of contamination of the underground waters, sediments and soils with the waste waters from the hydrodump of the Sasa mine.

MATERIALS AND METHODS

For the purpose of this study were collected 13 sediment and 6 soil samples from sampling sites shown on Figure 1. These samples were taken using plastic spatula. Both, soil and sediment samples were air dried at 20°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.

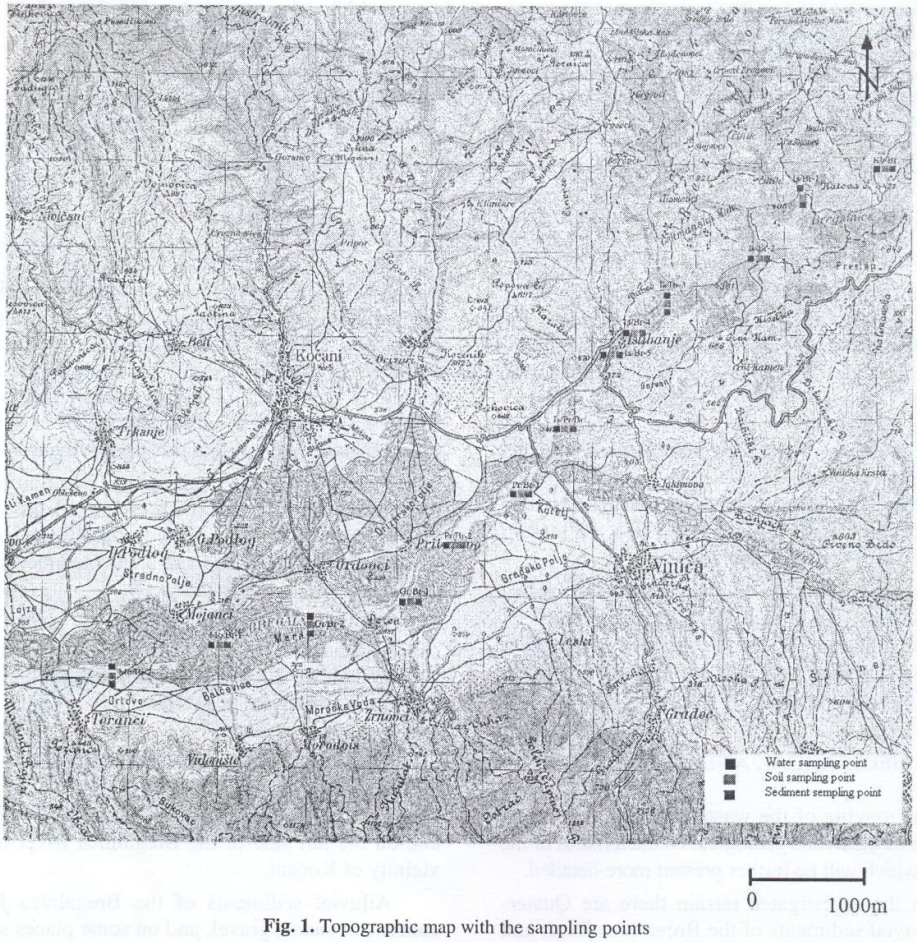

Fig. 1. Topographic map with the sampling points

All the analyses were performed both on ICP-AES (Faculty of Mining, Geology and Polytechnic, Štip). The accuracy and precision were better than ±5 %. This was indicated by the results of duplicate measurements. It is very important to point out that there is chronology in sampling and analysis of the area of interest.

RESULTS AND DISCUSSION

The results are given by certain river flows and adjacent area. This was done with a reason to clarify the contamination going along from near the mine and further. Since we have obtained the results from analyses we have proceeded to their interpretation, calculation of correlation factors, construction of particular diagrams etc.

Sediment samples

Similar to the water sampling and analysis programme in the area of interest was performed programme of sampling and analysis of sediments. The results are given below in Table 1.

As a summary from the analysis of sediments taken along the watercourses of the Bregalnica River, including both programme, we would like to point out the following facts:

Al – increased concentrations of this element (over MAC – maximal allowed concentrations) are present all over the sampled area.

Zn – in all the samples were determined anomalously increased concentrations of Zn in comparison with the MAC. This results from the presence of Zn as a major element in the mineral association in the Sasa Mine.

Pb – all the samples show increased values over the MAC, especially in the sediments from near village Istibanja and on the road Kalimanci Dam – Village Istibanja.

Co – as well as other elements, Co is determined in increased concentrations.

Cd – this very toxic metal shows high values only in some samples, in other is near to the maximal allowed concentrations.

V – only some samples has increased concentrations, in other samples the concentrations are in the range of normal values.

As – it very high concentrations over the standard values were determined in all samples, except in two. This is because of its presence in the mineral association and its low solubility and migration in mediums with a ceratin pH values.

Ag – the concentrations over MAC were determined only in two samples. All other samples has concentrations of Ag lower than standard values.

Ni – this element was determined in increased concentrations and over the standard values. Its maximum was determined in the sample Is/Br/S-3.

Cr – in all samples were determined increased values (over the standard values) of this element. In some samples the concentration is three times over the standard value.

Fe – in alll samples concentration of Fe is within the MAC.

Mn – in all samples is present with an increased concentrations above the MAC.

Cu – in all the samples were determined increased concentrations, two – three times over the MAC.

Sr – in all samples is in low concentrations except in one sample where the concentration is over the standard value.

After the analyses and interpretation of results we have constructed few diagrams with an intent to emphasize some of the facts determined during the interpretation of data (Figures 2–10).

Soil samples

Results from sampling programmes of water and sediments from the watercourses of Bregalnica River gave us a clue to proceed with a sampling programme of soils around those watercourses. During the sampling we have sampled the area in the vicinity of Bregalnica River, in the part of hydroaccumulation Kalimanci to Kočani. The sampling programme was realized along profiles that were established normaly to the watercourse. Samples were taken approximatelly from 25 meters from the watercourse on both sides. After the sampling the samples followed the same procedure as it was mentioned in the Materials and methods part of the text.

The results that were obtained with an analysis of soil samples are given in Table 2.

Table 1

Concentration of some metals in the sediments

	Kb/Br/S	Is/Br/S-1	Is/Br/S-2	Is/Br/S-3	Is/Br/S-4	Is/Br/S-5	Is/Pr/Br/S	Pr/Br/S-1	Pr/Br/S-2	Gr/Br/S-1	Gr/Br/S-2	Mo/Br/S-1	Mo/Br/S-2
							%						
Al_2O_3	2.70	2.79	4.73	4.93	4.56	2.60	5.12	1.84	1.67	1.91	2.21	2.23	2.41
FeO	4.15	3.35	6.11	6.70	3.74	4.41	6.66	3.11	2.72	2.83	2.85	3.26	3.36
CaO	0.91	0.55	0.40	0.45	0.43	0.70	0.78	1.09	0.56	0.74	0.97	0.81	0.74
MgO	0.88	0.89	2.11	2.22	2.12	1.13	1.64	0.90	0.72	0.77	0.74	0.77	0.80
TiO_2	0.17	0.12	0.17	0.18	0.14	0.09	0.12	0.07	0.09	0.11	0.18	0.12	0.09
MnO	0.08	0.09	0.07	0.08	0.08	0.06	0.30	0.05	0.04	0.05	0.05	0.07	0.09
Na_2O	0.02	0.01	0.02	0.02	0.02	0.08	0.02	0.01	0.01	0.02	0.02	0.02	0.01
K_2O	0.21	0.29	0.65	0.65	0.60	0.32	0.55	0.22	0.19	0.20	0.20	0.20	0.26
P_2O_5	0.18	0.13	0.19	0.19	0.20	0.22	0.14	0.18	0.13	0.14	0.16	0.20	0.21
							mg/kg						
Sr	40.6	23.3	15.4	17.2	15.1	36.8	91.0	27.9	20.8	34.6	48.50	33.40	20.7
Ba	75.3	130.1	83.5	94.3	84.7	148.5	291.9	84.7	68.7	75.8	76.31	138.3	96.5
Ni	16.9	22.9	55.7	60.7	55.1	26.8	30.7	16.5	16.0	12.4	10.98	19.3	23.4
Stand	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9
Cr	32.7	32.2	33.0	34.2	31.7	28.9	44.1	21.1	18.6	18.1	18.44	22.4	23.3
Stand	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
V	63.1	40.4	41.4	46.6	39.6	37.9	65.0	30.8	28.6	32.3	41.05	37.7	32.1
Stand	50	50	50	50	50	50	50	50	50	50	50	50	50
Mo	1.7	0.9	22.0	41.5	29.4	6.9	17.1	20.9	0.8	2.8	9.71	7.0	12.3
Zn	61.9	268.5	298.0	321.1	317.3	96.6	115.9	56.4	49.1	54.0	46.74	147.3	230.9
Stand	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5
Cu	23.5	24.0	75.6	79.9	77.7	26.9	36.2	18.9	14.5	13.7	13.07	18.4	21.1
Stand	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
Pb	22.6	39.1	324.9	330.9	331.2	23.6	34.5	13.6	17.2	12.9	19.17	19.4	32.3
Stand	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Co	14.3	12.2	29.4	32.8	31.2	13.3	21.3	9.8	8.2	8.9	9.05	9.5	12.7
Stand	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Cd	0.00	1.9	2.0	1.8	1.9	0.2	0.4	0.2	0.2	0.1	0.06	0.8	1.6
Stand	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
As	33.1	22.6	16.1	34.9	33.4	21.6	44.5	0.4	23.7	20.0	1.81	22.3	15.6
Stand	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Ag	0.2	0.5	0.2	0.6	0.1	0.7	1.2	0.0	0.7	0.2	0.4	0.1	0.4
Stand	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49

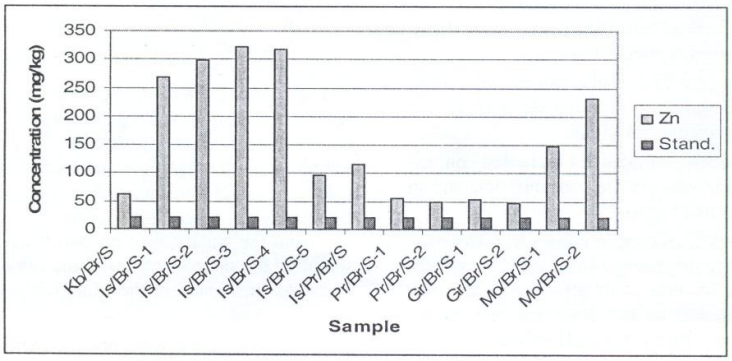

Fig. 2. Distribution of Zn in sediments of the Bregalnica River 2007

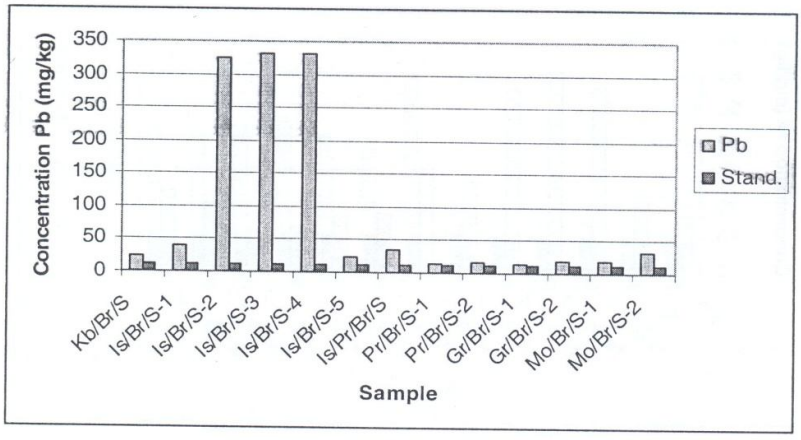

Fig. 3. Distribution of Pb in sediments of the Bregalnica River 2007

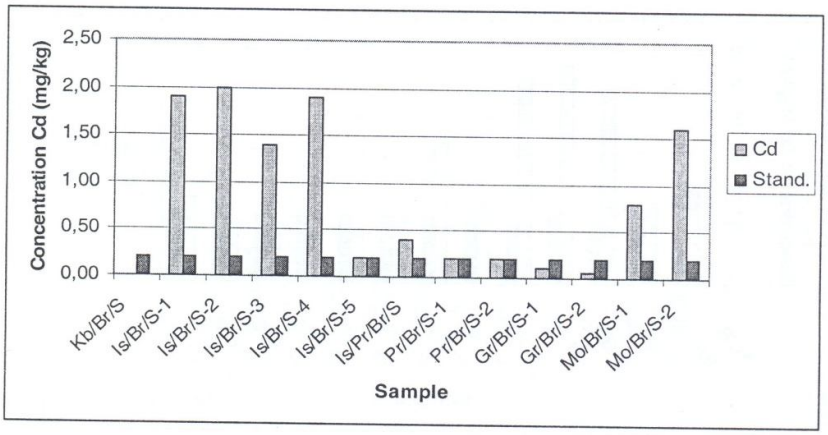

Fig. 4. Distribution of Cd in sediments of the Bregalnica River 2007

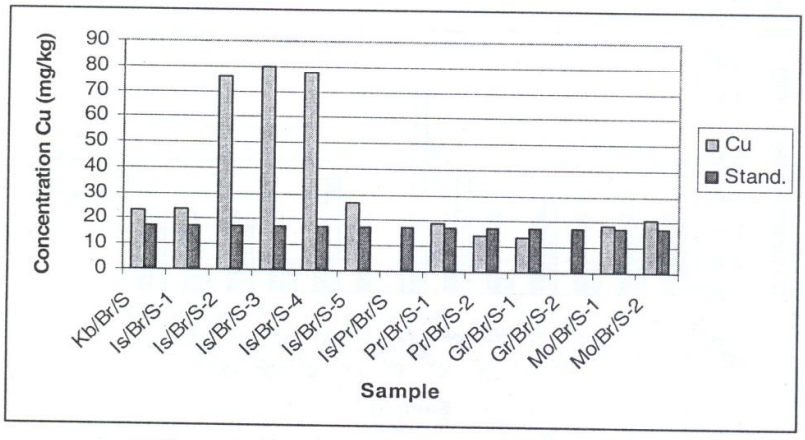

Fig. 5. Distribution of Cu in sediments of the Bregalnica River 2007

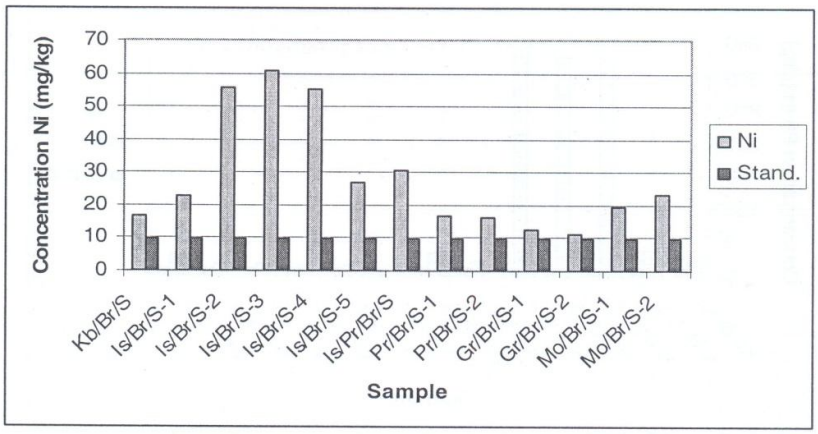

Fig. 6. Distribution of Ni in sediments of the Bregalnica River 2007

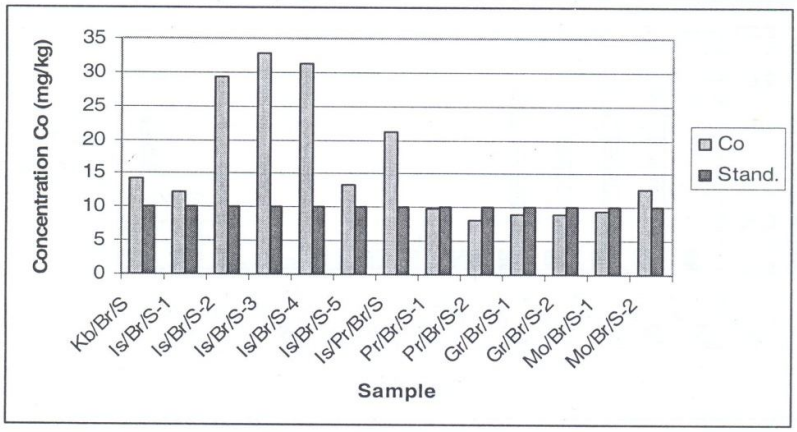

Fig. 7. Distribution of Co in sediments of the Bregalnica River 2007

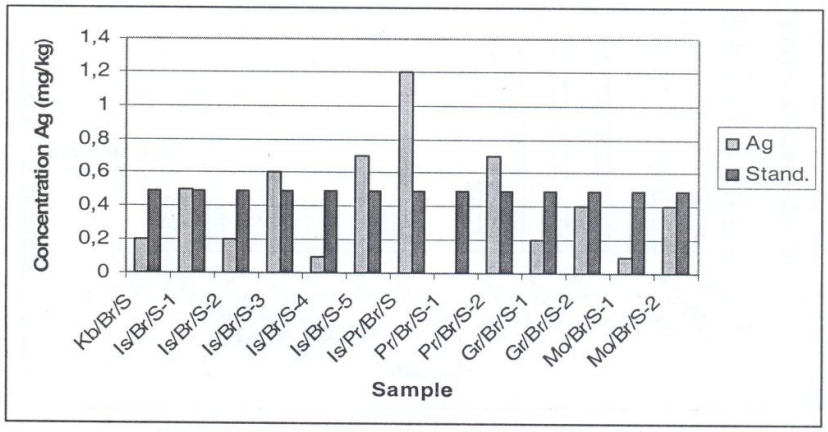

Fig. 8. Distribution of Ag in sediments of the Bregalnica River 2007

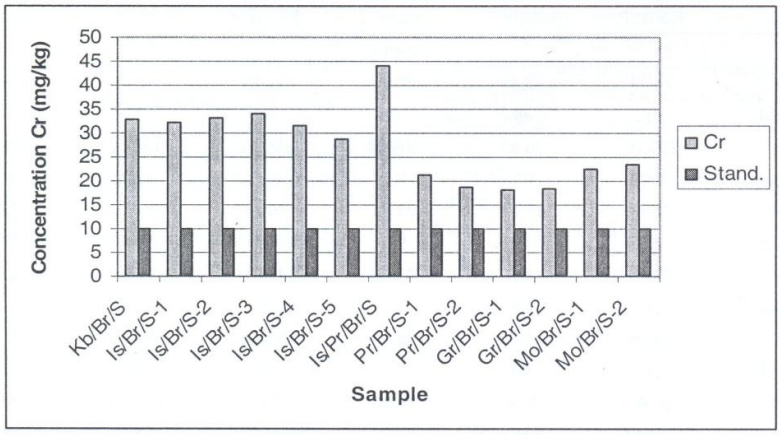

Fig. 9. Distribution of Cr in sediments of the Bregalnica River 2007

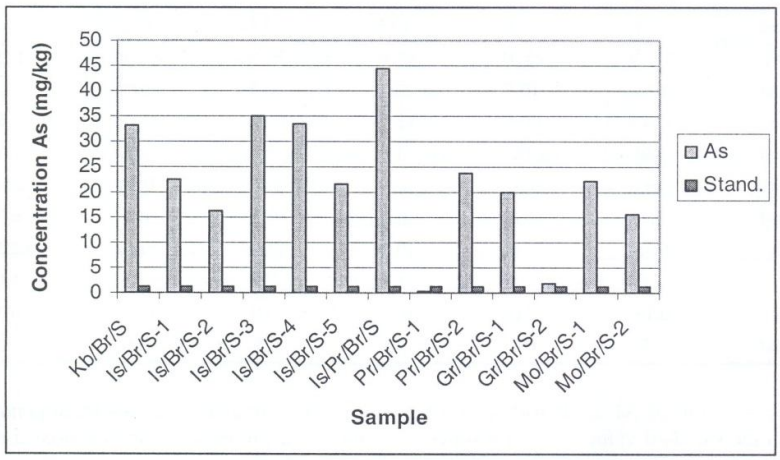

Fig. 10. Distribution of As in sediments of the Bregalnica River 2007

Table 2

Concentration of some metals in the soils

	Kb/Br/P	Is/Br/P-1	Is/Br/P-2	Is/Br/P-3	Is/Br/P-1	Is/Br/P-2
			%			
Al_2O_3	3.22	3.12	2.77	4.63	4.01	2.59
FeO	3.92	4.67	3.67	4.97	5. 35	4.48
CaO	0.61	0.96	1.40	0.60	1.15	0.85
MgO	0.90	0.89	0.86	1.11	1.42	1.06
MnO	0.16	0.09	0.11	0.14	0.08	0.48
Na_2O	0.02	0.02	0.02	0.02	0.02	0.02
K_2O	0.30	0.22	0.29	0.45	0.54	0.30
P_2O_5	0.18	0.22	0.17	0.20	0.21	0.25

	Kb/Br/P	Is/Br/P-1	Is/Br/P-2	Is/Br/P-3	Is/Br/P-1	Is/Br/P-2
			mg/kg			
Sr	24.49	43.88	34.66	31.48	35.11	31.21
Stand	49	49	49	49	49	49
Ba	139.19	76.83	108.69	190.42	132.37	225.62
Stand	0.7	0.7	0.7	0.7	0.7	0.7
Ni	22.79	19.58	23.32	30.01	36.73	34.02
Stand	9.9	9.9	9.9	9.9	9.9	9.9
Cr	27.48	38.10	23.46	35.01	39.27	31.91
Stand	10	10	10	10	10	10
V	40.66	77.55	38.45	52.54	50.13	48.11
Stand	50	50	50	50	50	50
Mo	10.85	3.26	–2.90	2.11	0.88	–6.98
Zn	512.42	70.01	307.14	613.71	135.16	452.55
Stand	22.5	22.5	22.5	22.5	22.5	22.5
Cu	26.22	24.68	27.95	32.81	42.87	33.18
Stand	17.5	17.5	17.5	17.5	17.5	17.5
Pb	53.49	25.04	57.49	74.48	66.98	112.98
Stand	10.5	10.5	10.5	10.5	10.5	10.5
Co	12.97	15.96	12.75	15.27	17.95	17.55
Stand	10	10	10	10	10	10
Cd	3.93	0.04	3.20	4.85	0.10	2.54
Stand	0.2	0.2	0.2	0.2	0.2	0.2
As	6.53	27.66	10.83	40.68	34.52	62.31
Stand	1.1	1.1	1.1	1.1	1.1	1.1
Ag	0.16	–0.09	0.34	0.04	0.37	–0.03
Stand	0.5	0.5	0.5	0.5	0.5	0.5

Al – concentration of Al in all soil samples was lower than the standard values, which resulted from the geological composition of the area.

Zn – because of the presence of Sasa mine and the geology of the area Zn has been determined in anomalously high concentrations in all samples taken near the mine.

Pb – as well as for the Zn, Pb is present in increased concentrations than the standard values in all samples.

Fe – in all samples iron showed higher concentrations than standard values. Its highest values were determined in samples Is/Br/P-1 and Is/Br/P-3.

Mn – this element have shown concentrations that are near the value allowed by standards.

Cu – copper have shown concentrations higher than standard values in all samples. Maximum concentration was determined in sample Is/Br/P-1.

Sr – in analyzed samples was not determined increased presence of Sr that exceeds the standard value.

Ba – in all samples the concentration of this element is higher than the value allowed by standard.

Ni – its presence is in very high concentrations in analyzed samples. Its concentrations are 2–3 times over the standard values.

Cr – as well as Ni, Cr concentrations are also 2–3 times over the standard values..

Co – in all samples was determined increased presence of this element, above the standard values. The maximum value was detrmined in sample Is/Br/P-1.

Cd – the very toxic cadmium showed very high values almost in all samples, except in two. All of them are few times above the standard values. This fact point out to a very serious contamination with this metal.

V – is present in concentration whish are in the nge of maximal allowed values, except in two sam-es where the concentration of V is over the MAC.

As – as a direct consequence of geology of e sampled area arsenic was determined in con-ntrations higher than standard values. The high-t concentration of arsenic was determined in mple Is/Br/P-3.

Ag – its concentrations are lower than stan-rd values.

The main reasons for increased pollution of soils in the area of interest should be the geology and composition of rocks and mineralizations, organic fertilizers used on arable soils, etc. [Younger, 2002a, 2002b] After the analyses and interpretation of results we have constructed few diagrams with intent to emphasize some of the facts determined during the interpretation of data from both programme (Fig's. 11–18).

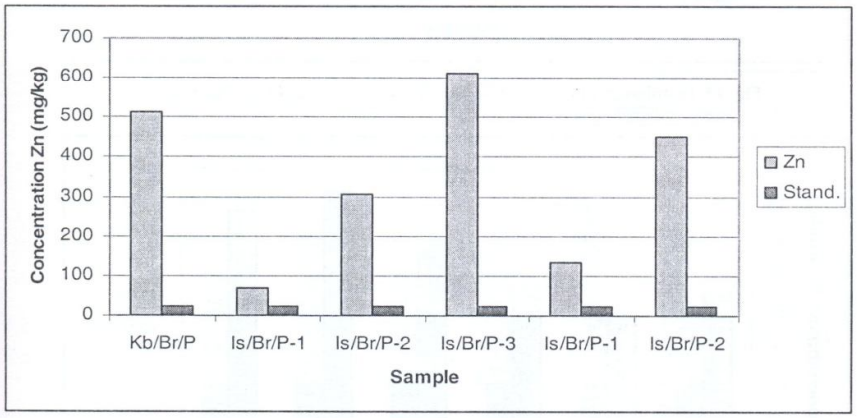

Fig. 11. Distribution of Zn in soils in the vicinity of the Bregalnica River 2007

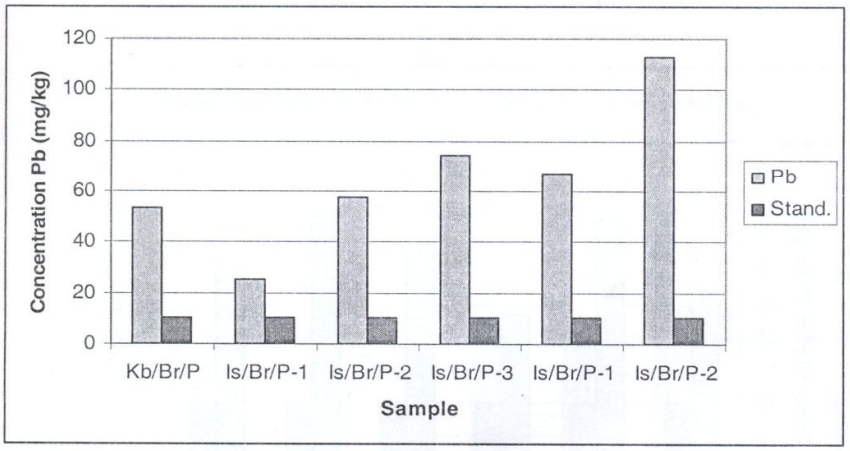

Fig. 12. Distribution of Pb in soils in the vicinity of the Bregalnica River 2007

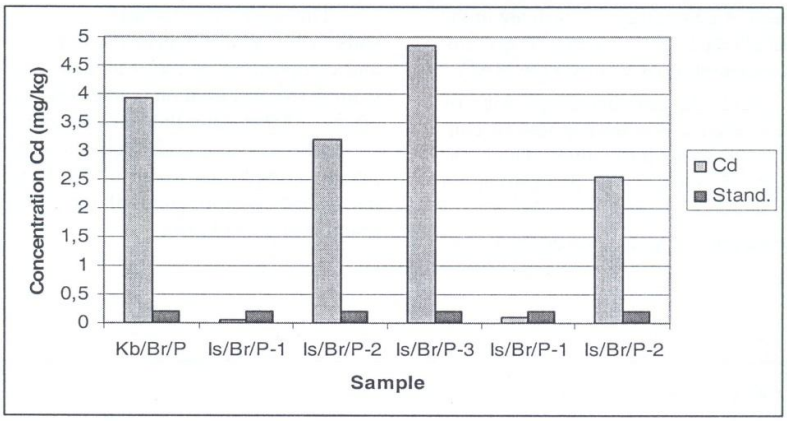

Fig. 13. Distribution of Cd in soils in the vicinity of the Bregalnica River 2007

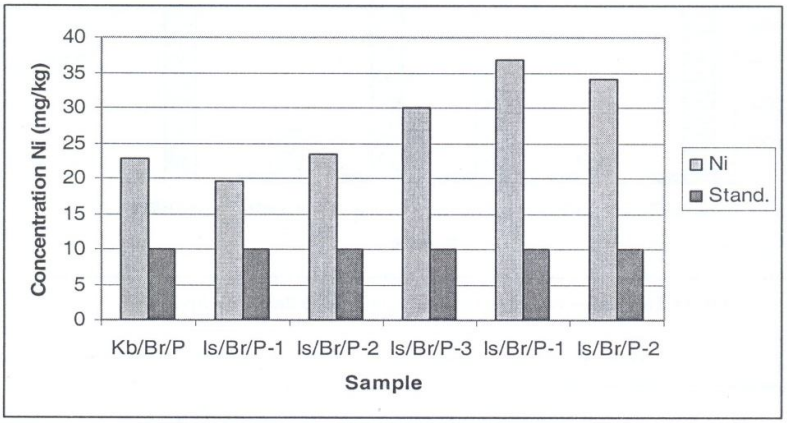

Fig. 14. Distribution of Ni in soils in the vicinity of the Bregalnica River 2007

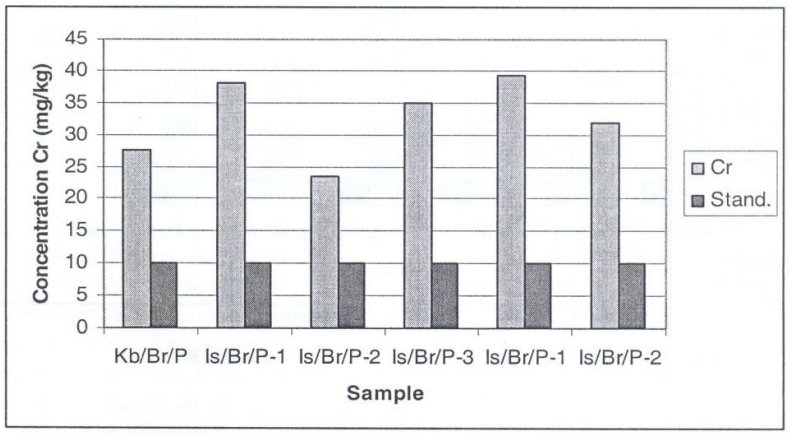

Fig. 15. Distribution of Cr in soils in the vicinity of the Bregalnica River 2007

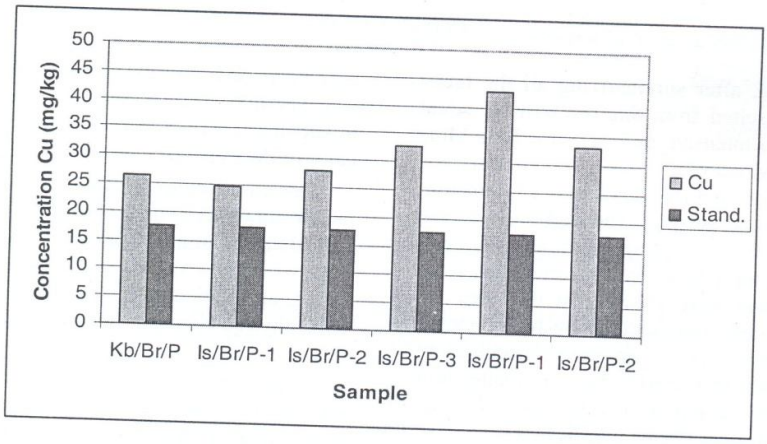

Fig. 16. Distribution of Cu in soils in the vicinity of the Bregalnica River 2007

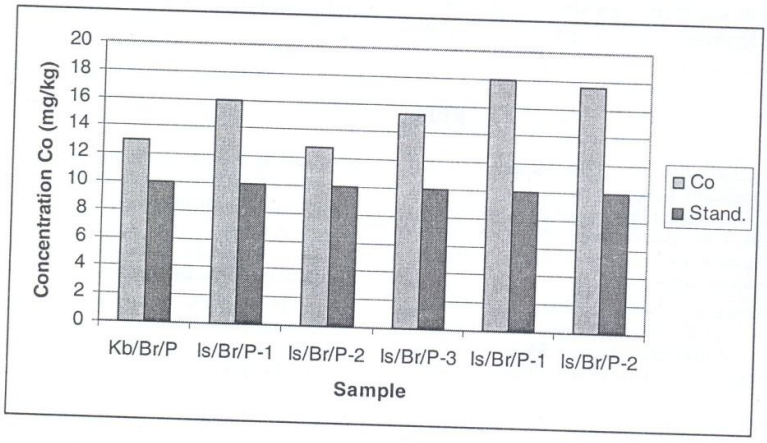

Fig. 17. Distribution of Co in soils in the vicinity of the Bregalnica River 2007

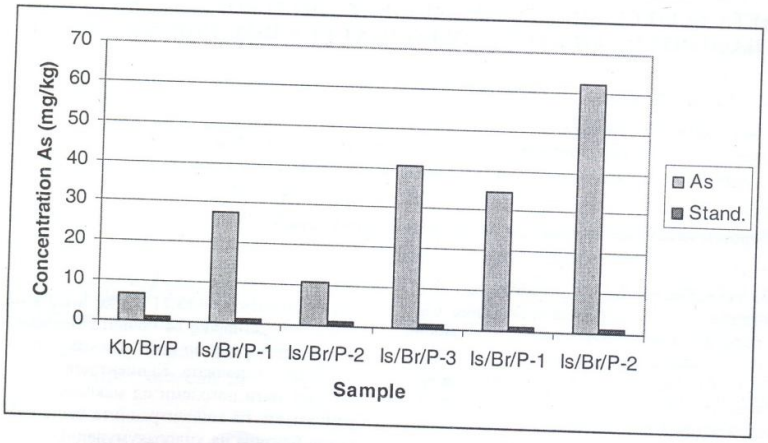

Fig. 18. Distribution of As in soils in the vicinity of the Bregalnica River 2007

CONCLUSION

In general, after summarizing all the facts, which have resulted from this research we could say that, due to intensive mining in the Sasa Mine during the previous years, was determined serious disturbance of the natural metal balance in medias such as sediments and soils. The analysis results of samples taken from sampling points along Bregalnica River, in the part of hydroacumulation Kalimanci to Kočani have shown that this area has been significantly contaminated by heavy metals and trace elements. The determined concentrations of metals shown increased values, no matter how high they were in comparison with maximal values allowed by standards (MAC and NOAA).

It can be seen that the concentrations of many of the elements in sediments are significantly bigger close to the hydroaccumulation Kalimanci and they decreased with the distance. In the soils, the concentration of the elements is variable from site to site and it shown increased values with the distance of the hydroaccumulation Kalimanci.

Increased concentrations of heavy and toxic metals are direct consequence of few factors: geological composition of the area, anthropogenic influences such as mining, railing and deposition of tailing, application of organic fertilizers on arable soils, physico-chemical features of waters (pH, Eh etc.).

After all the results and conclusions that came out from this analysis of the close proximity of the Sasa Mine it remains the open question the bioavailability of determined metals and metaloids and possibility of their inclusion into the food chain.

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Резиме

ТЕШКИ МЕТАЛИ ВО СЕДИМЕНТИТЕ И ПОЧВИТЕ ПО ТЕКОТ НА РЕКАТА БРЕГАЛНИЦА НА ДЕЛОТ ОД ХИДРОАКУМУЛАЦИЈАТА КАЛИМАНЦИ ДО КОЧАНИ

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Клучни зборови: метали; загадување; олово; цинк; седименти; почви; максимално дозволени концентрации

Во трудот се дадени резултати од истражувањата на загадувањето со метали по текот на реката Брегалница. Со анализата и интерпретацијата на податоците се потврди претпоставката за зголемени вредности на следните метали: Pb, Zn, Cd, In, Cu, Fe, Mn, As, Ag и Ni. Бидејќи во непосредна близина на испитуваниот терен се наоѓа рудникот за олово и цинк Саса, од посебен интерес се резултатите за Pb кои достигнаа вредности до 331,2 mg/kg, Zn кои дистигнаа вредности до 321,1 mg/kg и Cd кои дистигнаа вредности до 2,0 mg/kg во седиментите, и Pb кои достигнаа вредности до 112,98 mg/kg, Zn кои достигнаа вредности до 613,71 mg/kg и Cd кои достигнаа вредности до 4,85 mg/kg во почвите. Зголемени концентрации беа констатирани во сите анализирани примероци од седиментите и почвата. Концентрациите на металите беа за неколку пати поголеми од максимално дозволените. Зголемувањето на концентрациите беше најголемо во непосредна близина на хидроакумулацијата Калиманци, додека одејќи надолу по текот на реката Брегалница концентрациите постепено опаѓаат.