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# HEAVY METALS IN WATERS ALONG THE RIVER BREGALNICA IN THE PART OF HYDROACUMULATION KALIMANCI TO KOCANI

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## ABSTRACT

*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 river Bregalnica. After the analysis and interpretation of data were confirmed the assumptions for increased values of the the following metals: Zn, Pb, Cd, Cu, As and Ag. Since in the near vicinity is Sasa Mine for lead and zinc exploitation, especially interesting were the results for Pb that reached 0,019 mg/l, Zn that reached 0,029mg/l, Cd that reached 0,005mg/l, Ag that reached 0,056mg/l, As that reached 0,110 mg/l in waters. 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 hydroacumulation Kalimanci, and downwards through the flow of the river Bregalnica the concentrations decreased.*

**Key words:** heavy metals, pollution; lead; zinc; waters; Bregalnica River, Sasa Mine, maximal allowed concentrations.

## INTRODUCTION

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

The tailing which is disposed in the hydro dump 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.

Preliminary investigation results of this type can be found in the publications from (Mircovski, Spasovski at al. 2004, [1]; Spasovski at al. 2007, [2]; Spasovski, Doneva, 2007, [3][4]).



## 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 river Bregalnica and Neogene sediments in the vicinity of Kamenica and on the left side of the river Bregalnica in the vicinity of Kocani.

Alluvial sediments of the river Bregalnica 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 river Bregalnica in the vicinity of Kocani 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 river Bregalnica shows the possibility of contamination of the underground waters, sediments and soils with the waste waters from the hydro dump of the Sasa mine.

### Materials and methods

Preliminary field investigations were carried out in order to obtain essential data in the terrain. It included data on the Bregalnica River water courses selected as possible station for sample collection.

Samples from water flows and spring were collected in order to obtain data on the most critical points in terms of heavy metal contamination and how to direct future sampling and analyses.

Water samples were collected below the flotation tailing pond whose drainage waters flow into the Bregalnica River (fig. 1). The aim was to determine the effect that the mining activities and tailing pond have on the distribution of heavy and toxic metals in waters.

Water sampling was done with plastic syringe from the middle part of the water flow. The 50 ml of water from the syringe was transferred into a plastic vessel. It is of note when the water is transferred from the syringe to the vessel it is filtered through a paper filter the openings 45  $\mu\text{m}$ . Acidizing with 0.4 ml of 50% nitric acid is done before closing the vessel. This is done to avoid settling of metals on the wall and bottom of the vessel.

The samples were taken to laboratory for chemical analysis for heavy metal determination with AES-ICP.

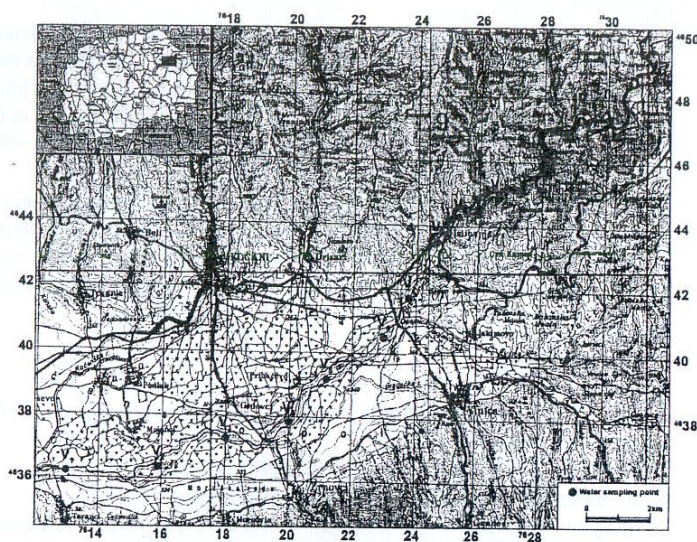


Fig. 1. Topographic map with the sampling points

## Results and discussion

The results obtained from flowing water samples are given in Table 1, with comparison between maximum allowable (MAC) concentration of heavy and toxic metals for III – IV classes.

Data shown in Table 1 make it possible to define the amount of heavy metals in the Bregalnica River water and its tributaries and the reasons for their occurrence.

Table 1. Results of chemical analysis of sediments taken from the Bregalnica River and corresponding standards (mg/l), year 2007

	Pb	Zn	Cu	Cd	As	Ag	Fe	Mn
V <sub>1</sub>	0,005	0,001	0,005	0,001	0,036	0,005	0,090	0,007
V <sub>2</sub>	0,007	0,001	0,005	0,002	0,064	0,003	0,088	0,007
V <sub>3</sub>	0,005	0,013	0,005	0,001	0,017	0,011	0,082	0,005
V <sub>4</sub>	0,005	0,002	0,009	0,002	0,043	0,003	0,087	0,007
V <sub>5</sub>	0,010	0,003	0,015	0,002	0,031	0,002	0,179	0,089
V <sub>6</sub>	0,015	0,012	0,016	0,002	0,098	0,002	0,084	0,007
V <sub>7</sub>	0,015	0,112	0,018	0,005	0,076	0,007	0,084	0,008
V <sub>8</sub>	0,012	0,114	0,019	0,002	0,042	0,005	0,075	0,006
V <sub>9</sub>	0,017	0,124	0,010	0,002	0,060	0,002	0,095	0,110
V <sub>10</sub>	0,017	0,127	0,048	0,003	0,057	0,002	0,083	0,094
V <sub>11</sub>	0,019	0,118	0,039	0,002	0,072	0,008	0,077	0,009
V <sub>12</sub>	0,018	0,128	0,015	0,002	0,110	0,001	0,024	0,009
V <sub>13</sub>	0,019	0,129	0,019	0,001	0,099	0,056	0,029	0,015
Standard	0,01	0,1	0,01	0,0001	0,05	0,002	0,3	0,05



Based on the data presented in Table 1, certain constants can be given concerning the presence of particular hard metals in the waters of the river Bregalnica in a distance between the hydroaccumulation Kalimanci to Kocani, as well as an opinion for the reasons which can contribute for the increased contents of particular metals.

The data for the concentration of zinc (Table 1) indicate its increased presence in most of the samples which were analyzed. The greatest concentrations of zinc are found in the sample  $V_{13}$ , which are 0.129 mg/l. The increased concentrations of zinc are also found in the samples:  $V_{12}$ ,  $V_{11}$ ,  $V_{10}$ ,  $V_9$ ,  $V_8$ ,  $V_7$  and  $V_6$ . In the remaining samples the concentration of zinc is present in amounts less than the standard ones. Generally, it can be concluded that the entire research area is contaminated with zinc. The increased concentrations of zinc are a result of the active working of the Mine for lead and zinc Sasa.

The increased concentration of lead are noticed in the samples  $V_{13}$  (0.019 mg/l),  $V_{12}$  (0.018 mg/l),  $V_{11}$  (0.019 mg/l),  $V_{10}$  (0.017 mg/l),  $V_9$  (0.017 mg/l),  $V_8$  (0.014 mg/l),  $V_7$  (0.015 mg/l) and  $V_6$  (0.015 mg/l). It is obvious that increased concentrations of lead are found in most of the samples, but the great sample concentrations of lead are found in those samples where increased concentrations of zinc were also found, which confirms the statement of the great influence of the hydro-waste dump and the active working of the Mines Sasa for the pollution of the environment with these metals.

In all the samples cadmium is found in extremely larger concentrations compared to maximum allowed concentration. The great sample concentrations of cadmium are noticed in the samples  $V_7$  (0.005 mg/l) and  $V_{10}$  (0.003 mg/l). This behavior of the cadmium is due to its geochemical characteristics (easily soluble, low mobility). The increased concentrations of cadmium follow the parts which are contaminated with zinc because it geochemically follows the minerals in the zinc.

The increased concentrations of copper are found in most of the samples, but the great sample concentrations of copper found in the samples  $V_{10}$  (0.048 mg/l) and  $V_{11}$  (0.039 mg/l), while in the remaining samples the concentrations of copper are close or less than in maximum allowed concentration. The presence of the copper in the waters of river Bregalnica is a result of the occurrence of chalkopyrite in an association with the minerals of the lead and zinc.

Arsenic is present in larger concentration in most of the analyzed samples, but especially larger concentration are noticed in the sample  $V_{12}$  (0.110 mg/l). The increased concentrations of arsenic are a consequence of the occurrence of arsenic together with the minerals of the copper.

The received data for the silver (Table 1) points that the silver represents a contaminant for the entire drainage system of the river Bregalnica. The presence of silver is a result of the occurrence of native silver and minerals of silver in the Mines of lead and zinc Sasa.

Iron is present in concentrations lower than maximum allowed concentration and is not a significant contaminant of the drainage system of the river Bregalnica.

Attention should be paid for the high concentrations of the manganese in the samples:  $V_9$  (0.110 mg/l),  $V_{10}$  (0.094 mg/l) and  $V_5$  (0.089 mg/l). The reason for the occurrence of the manganese in high concentrations in the waters of the river Bregalnica is

a permanent hydro- waste dump in the direct environment of the hydroaccumulation Kalimanci as a presence of the waste waters from the Mines Sasa.

## CONCLUSION

After summarizing all the facts which were received from this research, we could say that, due to the intensive mining in the Mine Sasa in the past few years, a serious disturbance of the natural metal balance was determined in mediums like waters. The results from the analysis of the samples taken from different points along river Bregalnica in a distance between the hydroaccumulation Kalimanci to Kocani showed that this area is significantly contaminated with heavy metals and trace elements. The concentrations of the most of the elements in the waters are significantly larger closer to the hydroaccumulation Kalimanci and they decrease with the distance.

The increased concentrations of the heavy and toxic metals are direct consequence of the following factors: geological composition of the area, anthropogenic influences such as mining, railing and deposition of tailing, physical-chemical features of waters (pH, Eh, etc.).

With the results and conclusions received from this analysis in the direct environment of the Mine Sasa the question remains open for the bioavailability of the determined metals and metalloids and the possibility of their inclusion in the food chain.

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