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Impacts of Pb-Zn mining on Lake Kalimanci and Human Health in Eastern Macedonia

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Abstract. Mining is very important economic activity. However, mining and related industries presents the main threat for environment. Pollution with heavy metals is a significant problem in Eastern Republic of Macedonia. In year 2003 great environmental disaster happened near small town Makedonska Kamenica, when the Sasa tailings dam collapsed and caused an intensive flow of mining waste material through Kamenica River valley and was discharged into Lake Klaimanci. Water from lake is used for irrigation, thus, the pollution assessment of the Lake Kalimanci sediments was made. The major, trace and rare earth element contamination in surficial lake sediments was studied to assess the effects of metalliferous mining activities. The mean concentrations of major elements [wt %] Si 23.5, Al 7.9, Fe 6.6, Mg 1.3, Ca 3.8, Na 1.1, K 2.3, Ti 0.4, P 0.2, Mn 0.6 and trace elements ranged within: Mo 1.0-4.6 mg kg^{-1}, Cu 144.4-1162 mg kg^{-1}, Pb 1874-16300 mg kg^{-1}, Zn 2944-20900 mg kg^{-1}, Ni 21.7-79.3 mg kg^{-1}, Cd 16.5-136 mg kg^{-1}, Sb 0.6-3.6 mg kg^{-1}, Bi 3.0-24,3 mg kg^{-1} and Ag 1.4-17.3 mg kg^{-1}. Results of rare earth elements (REE) in surficial lake sediments indicated that are tightly related to the catchment geology. The results of the sequential extraction procedure revealed the majority (Cd, Zn, Pb, Ni, Cu and Cd) of investigated toxic metals and all REEs to be strongly bonded to the exchangeable fraction and the rest (As and Mo) to the oxidizable fraction. Regarding to results is evident that heavy metals and REEs are highly bioavailable for living organisms and can seriously affect human health.

Key words: Pb-Zn mine, heavy metals, tailing dam failure, bioavailability.

Introduction

Heavy metals and some REE are essential for living organisms, although many of them are toxic at high concentrations and can affect aquatic organisms, as well as adversely affect human health (Nor, 1987; Timmermans, 1992; Silva et al., 2000; Kumar Das et al., 2008). These elements usually have dynamic distribution and behaviour in lake sediments and their sources can be natural or anthropogenic. Lakes can receive all studied elements from precipitation, snowmelt, atmospheric deposition and geologic weathering. Flushed lakes are also supplied with these metals through the discharge of industrial wastes by river waters (Demirak et al., 2006; Dawson and Macklin, 1998). Their input is also dependent on complex weathering, leaching and reactions in the vicinity of the lake (Baralkiewicz et al., 2008). Lakes can also be easily contaminated by human activity when there is any kind of industry in their vicinity, especially where mining activity is widespread near the lake. Then its ecosystem is even more vulnerable. Elevated major, trace and rare earth element content in fauna and flora in lakes may impart a very important impact on human health, reproduction and, consequently, our survival (Wright and Mason, 1999).

The total concentration of metals and REEs in sediments is generally not sufficient to assess environmental impact and thus an estimation of the bio-available fraction is necessary. The bio-available fraction is defined as the amount of element which is bound to wastes (easily exchangeable ions, metal carbonates, oxides, sulphides, organometallic compounds, ions in crystal lattices of minerals, etc.) that can be exchanged with organisms and be incorporated into their structures (Vangronsveld and Cunningham, 1998; Weisz et al., 2000; Yu et al., 2001). In this sense, sequential extraction therefore permits us to precisely identify the origin of element and to better understand their geochemical cycles and mobility.

In this study we present comprehensive data on pollutant characteristics and elimination of the environmental and health risks associated with Pb-Zn mining.

Materials and Methods

STUDY AREA Situated in eastern Macedonia, Lake Kalimanci lies in the vicinity of the small town of Makedonska Kamenica, about 5 km from the Sasa-Toranica ore district. With a length of 14 km and width of 0.3 km, the lake covers an area of 4.23 km^2 and contains approximately 127 million m^3 of water. The basic purpose of Lake Kalimanci is the storage of water which is used to irrigate around 30,000 hectares of mainly rice fields in the Kočani Valley and Ovce Pole. As a result the lake is characterized by large changes in water level, with dry season levels occasionally decreasing to only a few centimetres in inner (deeper) areas.

SAMPLING Seven surface sediment samples were collected from Lake Kalimanci in September 2007, with sample pH values ranging from 5.5 to 7.5. Sampling was carried out during a dry period (no precipitation – summer season) when the lake water levels were lower and the sediment exposed to oxidation processes. Samples were collected using a plastic spade, transferred to pre-cleaned plastic bags and then stored in the laboratory at 4 ^{o}C. After collection, samples were oven dried before undergoing dry sieving at a temperature of 50 °C for 48 hours until a constant weight was attained. After being sieved through a 0.315 mm polyethylene sieve to remove plant debris, samples were finally homogenized to a fine powder in a mechanical agate grinder for subsequent analysis.

ANALYSES Sediment samples were analyzed for complete of 53 element concentrations at a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd – Ontario, Canada) using a variety of different analytical methods. After extraction of sub-samples for 1h with 2-2-2-HCl-HNO_3-H_2O at 95 °C, trace elements such as Mo, Cu, Pb, Zn, Ni, As and Cd were analyzed via ICP-MS. Co was determined by ICP-MS after fusion with a mixture of lithium/tetraborate and dissolution in nitric acid. According to official laboratory reports, the accuracy and precision of the surface sediment analyses were assessed via the use of an international reference material such as USGS standard MAG-1 (sediment). The analytical precision and accuracy were better than ± 6%, as indicated by the results of duplicate measurement of 3 lake samples and of the MAG-1 standard.

The trace metal and REE content of different chemical fractions of the samples was determined via various extractions of lake sediment components. In order to estimate pollutant speciation and bioavailability in the sediment samples, a sequential extraction method devised by ACME laboratories was applied. The most commonly-isolated phases in such sequential extraction schemes include a water-soluble fraction (leaching stage 1), an exchangeable + carbonate fraction (leaching stage 2), an oxidizable - organic fraction (leaching stage 3), an Fe–Mn oxide bound - reducible fraction (leaching stage 4) and a residual + reducible fraction (leaching stage 5).

Results and Discussion

Approximately 80% of surficial lake sediments are represented by Si-Al-Fe assemblage, whereas Ca, Mg, Na and K contents are below 10%. This reflects that the background rocks are mainly made up of acidic intermediate vulcanites, with extremely low content of carbonates.

The trace contamination of Lake Kalimanci surface sediments is far above the crustal average as seen from other researches, owing to active mining activities in the vicinity of the Kalimanci Lake. However, the possible contamination from atmospheric deposition, transport and other industrial activities should also be taken into account. Consequently, as a result of the metal analyses of surficial lake sediments, it was determined that metals such as lead, zinc, cadmium, arsenic and copper have extremely high contents.

The REE concentrations in the surficial sediments were studied to establish their occurrence and their enrichment in Lake Kalimanci. Results indicate that REE from Lake Kalimanci are strongly related to the catchment geology of the acidic and intermediate igneous rock lithologies from the Osogovo Mountains.

The results of a sequential extraction procedure revealed Pb, Cd, Zn, Cu and Mo to be highly mobile in the water soluble and exchangeable fraction, which undoubtedly represents an increased environmental risk. Sequential extraction procedure of REE show that high percentages of REE were bound to the exchangeable fraction and a low percentage of REE was extracted in the residual fraction.

The extremely high concentrations of the studied metals and their comparatively high bioavailability could have a potentially huge impact on the surrounding ecosystem, and if no remediation or other lake

environment cleaning processes are carried out in the area, the situation could also be of great concern for human health.

Conclusion

Due to all presented results, the Lake Kalimanci surficial sediments are strongly polluted with heavy metals and REEs. Sequential extraction procedure also revealed high bioavailability of toxic elements.

Therefore, strongly polluted environment can seriously affect human health in adjacent area. Acquired results are valuable for informing the public and government about existent situation in the wide Sasa mine area to reduce mining impacts.

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