Assessment of the heavy metal contamination in the surficial sediments of Lake Kalimanci (Macedonia): a preliminary study

Ocena onesnaženosti recentnega sedimenta iz Kameniškega jezera (Makedonija) s težkimi kovinami – preliminarni rezultati

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Received: October 23, 2009 **Accepted:** November 23, 2009

Abstract: A major disaster happened in the eastern Macedonia (Europe), when part of the Sasa Mine tailings dam collapsed and caused an intensive flow of tailings material which ended up in Lake Kalimanci. The aim of this study was to assess the heavy metal contamination (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) of the surficial sediments from Lake Kalimanci. The pollution status of the sediments was evaluated by application of two environmental indices: the enrichment factor and a geoaccumulation index. The enrichment factor values (Cd 735; Pb 386; Zn 151; Ag 146; As 48; Cu 21; Sb 10 and Mo 2) revealed extremely elevated heavy metal concentrations in the investigated samples. The geoaccumulation index indicated that surficial sediments of Lake Kalimanci can be treated as moderately to strongly polluted with Pb and Cd, moderately polluted with Zn and Ag, unpolluted to moderately polluted with Cu and As and unpolluted with Mo and Sb.

Izvleček: Na območju vzhodne Makedonije se je v deponijskem predelu rudnika Sasa zgodila huda ekološka nesreča. Del jalovinskega nasipa se je zrušil in tako povzročil silovit tok flotacijsko-jalovinskega materiala, ki je zgrmel v dolino reke Kamenice, vse do jezera Ka-

Original scientific paper

menica. Namen študije je bil oceniti onesnaženje površinskega sedimenta iz jezera Kamenica s težkimi kovinami (antimon, arzen, baker, cink, kadmij, molibden, srebro in svinec). Stopnjo onesnaženja smo določili z uporabo dveh okoljskih indeksov: faktorja obogatitve in geoakumulacijskega indeksa. Izračunane vrednosti faktorja obogatitve v raziskovanih vzorcih so bile zelo visoke (Cd 735; Pb 386; Zn 151; Ag 146; As 48; Cu 21; Sb 10 in Mo 2). Rezultati indeksa geoakumulacije so razkrili podobne vrednosti in označili površinske sedimente iz jezera Kamenica kot srednje do visoko onesnažene z Pb in Cd, srednje onesnažene z Zn in Ag, neonesnažene do srednje onesnažene s Cu in As ter neonesnažene z Mo in Sb.

Key words: heavy metals, surficial sediments, enrichment factor, geoaccumulation index, Lake Kalimanci

Ključne besede: težke kovine, površinski sedimenti, faktor obogatitve, indeks geoakumulacije, jezero Kalimanci

Introduction

Tailings dams are a special type of dam built to store mill and tailings material from mining activities. Currently, thousands of tailings dams worldwide contain billions of tonnes of waste material from mineral processing activity at mine sites. They are supposed to last forever, but since 1970 there have been 35 major failures reported around the world (Diehl, 2001; Göransson et al, 2001; Grimalt et al, 1999; UNEP/OCHA, 2000).

A major environmental disaster also happened in the eastern Republic of Macedonia. In the afternoon of 30 August 2003, part of the Sasa Mine tailings dam collapsed and caused an intensive flow of tailing materials through the Kamenica River valley. The estimated height of the tailings flow was around ten metres and the length of the flow was approximately 12 km. Some 70 000–100 000 m^3 of tailings material was discharged and spread through the Kamenica River valley, down to the city of Kamenica and into Lake Kalimanci. The damaging tailings flow comprised a large amount of heavy metals (Dolenec et al, in press) and seriously affected the surrounding environment, especially Lake Kalimanci.

When heavy metals enter an aquatic environment, they are redistributed throughout the water column, deposited or accumulated in sediments and consumed by biota (Long et al, 1996; Fichet et al, 1998; Linnik & Zubenko, 2000; Singh et al, 2005; Ghrefat & Yusuf, 2006 and

Khaled et al, 2006). A fundamental characteristic of heavy metals is their lack of biodegradability and lake sediments usually operate as pollutant storage tanks that reflect long-term impacts (Maltby, 1992 and Schmitt et al, 2003). Therefore it is important to assess the extent of heavy metal accumulation in lake sediment and to determine its environmental threat.

Our objective in the preliminary study was to define the total heavy metal contamination (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) of the surficial sediments from Lake Kalimanci and to evaluate enrichment factor (EF) and geoaccumulation index (I_{geo}) values for the heavy metals present in the sediment samples.

Materials and methods

Study area

Kalimanci artificial lake is located in eastern Macedonia, in the 2000 m high Osogovo Mountains, near the city Makedonska Kamenica and the Sasa mine (Figure 1). The surface of the lake is 42 km^2, the maximum depth is 85 m and it encompasses around $120 \cdot 10^6$ m^3 of water. It is supplied by two tributaries: the Bregalnica and the Kamenica River, which flows directly from the Sasa mine and drains a large amount of mining effluents and tailings material which have discharged into Lake Kalimanci.

Figure 1. Geographical map of the investigated area (merilo 1 : 625 000)

The sediment samples from Lake Kalimanci are dominated by: quartz, plagioclases, K-feldspars, muscovite, illite and clinochlorite. Subordinate minerals are hornblende, gypsum, bassanit, calcite, dolomite, smithsonite, pyrite, marcasite, haematite, goethite and diaspor (Dolenec et al, unpublished).

The Sasa-Toranica ore district is situated 10 km N of Lake Kamenica in the Osogovo Mountains and occupies an area of about 200 km (Figure 1). It is established as one of the largest ore districts within the Besna Kobila Osogovo Tassos metallogenetic zone. The important Pb and Zn ore bodies are usually found in quartz-muscovite-graphitic schists and also in greenschists and marbles. The ore bodies are always accompanied by variable amounts of Cu, Au, Ag, Mo and Sb. The Sasa mine has been in production for over 45 years, yielding 90 000 t of high quality Pb-Zn concentrate annually and numerous tons of tailings material (Serafimovski et al, 2005).

The tailings material from the Sasa mine is made up of quartz, pyrite, galenite, gypsum, hornblende, actinolite, albite, anortite, biotite and orthoclase. The geochemical analysis of tailings material indicated an average range of Ag 0.004 μg/g, As 69.2 μg/g, Cd 84.3 μg/g, Cu 279.3 μg/g, Mo 2.9 μg/g, Pb 5595.2 μg/g, Sb 4.2 μg/g and Zn 6970.2 μg/g (Dolenec et al, unpublished).

Sampling and analysis

Seventeen surficial sediment samples from Lake Kalimanci were taken in September 2007, three years after the tailings dam accident happened. The surficial sediments were composed of silt. The chosen sampling locations were formed into eight profiles (Figure 2), covering the area around the River Kamenica tributary in the northern site of the lake which was mostly affected by the tailings flow.

The samples were collected with the plastic corers (tube 20 cm long with a 10 cm internal diameter), tightly packed into plastic bags and stored in the laboratory at 4 ºC. The sediment samples were dried at 50 ºC for 48 h. They were then sieved through a 0.315 mm polyethylene sieve to remove plant debris and homogenised by a mechanical agate grinder to a fine powder for subsequent analysis.

The mineralogy of the sediment samples was determined at the Department of Geology, Ljubljana (Slovenia) by X-ray powder diffractometry with a Philips PW 3710 diffractometer and CuKa radiation. The diffraction patterns were identified with the data from Powder Diffraction File (1977) – JPDS system.

The geochemical analysis of the following heavy metals, Ag, As, Cd, Cu, Mo, Pb, Sb and Zn, was obtained in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd.) and 0.5 g of samples were leached in hot (95 ºC) Aqua Regia and analysed by ICP Mass Spectrometry. The analytical precision and the accuracy were better than ±5 % for the analysed elements.

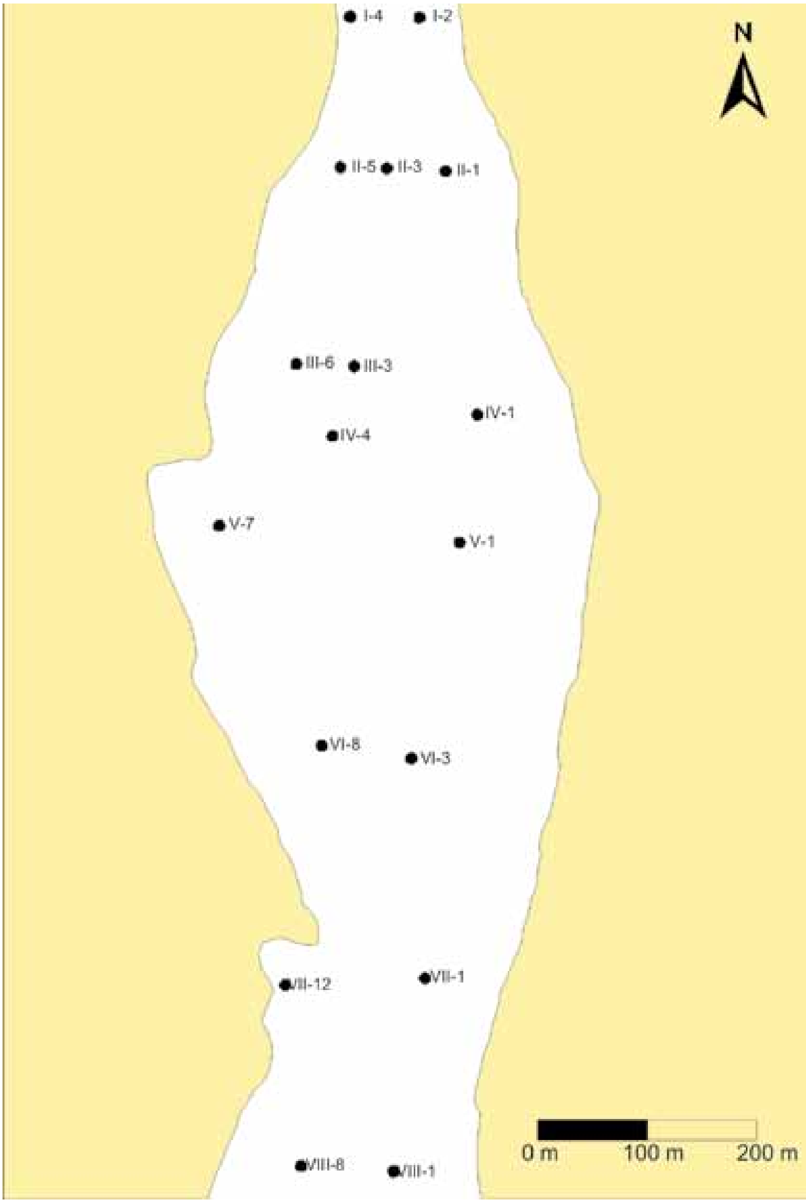

Figure 2. Sampling locations in the Lake Kalimanci

Statistical analysis

Basic statistical analysis of data was performed by use of the original statistical software program Statistica 6. Pearson multiple correlation analysis was also applied to all results.

Results and discussion

Heavy metals (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) were examined for their abundance in the surficial sediments from Lake Kalimanci.

When the accident occured, the damaging tailings flow mostly affected the northern part of the Kalimanci Lake. Consequently, the maximum concentrations of all heavy metals were determined in the northern part of the basin (Table 1, Figure 2). The maximum level of the Zn (20 900 μg/g), Pb (16 300 μg/g), Cu (1 162 μg/g), Cd (136 μg/g), Ag (17.3 μg/g), Mo (4.6 μg/g), and Sb (3.6 μg/g) was recorded in location II-3 and the highest amount of As was found in location II-1 (Table 1, Figure 2).

Table 1. Concentrations *c*/(μg/g) of the heavy metals in the investigated samples

Element *c*/ (μg/g)	Ag	As	Cd	Cu	Mo	Pb	Sb	Zn
Location								
I-2	2	54.8	48.1	238	2.2	2721	1.4	5913
I-4	10.3	68.8	74	627.3	2.9	9357	2.4	10700
II-1	3.6	86.7	77.2	415	3.1	4461	2.2	9596
II-3	17.3	77.2	136	1162	4.6	16300	3.6	20900
II-5	15.2	70.1	111.6	928.7	4.2	13800	3.2	17600
III-3	11.1	73.2	89.6	723	3.7	10900	2.7	14000
III-6	10.4	57.6	86.8	692.5	3.3	9800	2.1	14000
IV-1	5.1	66.1	59	413.1	3	6695	1.7	8105
IV-4	4.2	61.6	47.6	341.4	2.3	5343	1.6	6734
V-1	3.6	61.6	40	303.2	2.4	4447	1.3	5677
V-7	8.1	66	81.1	595.7	3.7	9472	2	12600
VI-7	5.6	128.2	54.2	315.4	3.6	7885	3.3	7181
VI-11	7.1	58.6	77.6	545.7	2.5	7557	1.6	11600
VII-1	3.6	77.8	61.3	372.5	1.9	4575	1.1	10400
VII-12	4.5	66.4	53.5	398.1	2.7	5144	1.2	9326
VIII-1	3.8	69.8	47.9	311.9	2.2	5091	1.4	7224
VIII-8	4.1	61.5	46.8	327.6	2.3	4893	1.4	7056

Basic statistical information are given in the Table 2.

Correlation analysis

A Pearson correlation matrix was used to assess element associations and metal origins (Table 3). The correlation matrix presents a significantly positive correlation between Ag, Cd, Cu, Mo, Pb, Sb and Zn, demonstrating possible co-contamination from similar sources: in our case, that would be tailings material from the Sasa mine. Conversely, no correlations were noted between As and the other elements (except Sb), suggesting that As contamination might be from a different source or it had a natural origin but was not from the same pollution source or had a different depositional nature.

Table 2. Descriptive basic statistics of the heavy metals in the surficial sediments of Lake Kalimanci

Element	Valid N	Mean	Minimum	Maximum	Std. Dev.
Ag	17	7.04	2.000	17.30	4.414
As	17	70.94	54.800	128.20	16.859
Cd	17	70.14	40.000	136.00	25.773
Cu	17	512.42	238.000	1162.00	250.845
Mo	17	2.98	1.900	4.60	0.775
Pb	17	7555.35	2721.000	16300.00	3664.172
Sb	17	2.01	1.100	3.60	0.783
Zn	17	10506.59	5677.000	20900.00	4248.268

Table 3. Pearson correlation matrix showing inter-elemental relationship (n = 17)

	Ag	As	Cd	Cu	Mo	Pb	Sb	Zn
Ag	1.00							
As	0.03	1.00						
Cd	0.93*	0.06	1.00					
Cu	0.98*	–0.03	0.97*	1.00				
Mo	0.85*	0.34	0.84*	0.83*	1.00			
Pb	0.99*	0.14	0.91*	0.96*	0.90*	1.00		
Sb	0.80*	0.55*	0.76*	0.74*	0.91*	0.84*	1.00	
Zn	0.94*	–0.00	0.98*	0.98*	0.80*	0.92*	0.69*	1.00

*$p < 0.05$

Enrichment factor

The enrichment factor (*EF*) is a useful indicator reflecting the condition of environmental contamination. It was employed to evaluate possible anthropogenic input of metals to observed sediment (Brady, 1984), calculated according to the equation:

$$EF = (M/Al)_{sample} / (M/Al)_{crust} \qquad (1)$$

where M_{sample} and M_{crust} are the levels of the investigated metals (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) in the sediment samples and in the uncontaminated crust material, respectively, and Al_{sample} and Al_{crust} are the values of the Al in the sediment samples and in the uncontaminated crust material. Metal to aluminium ratios are widely adopted, presumably because the concentration of Al in weathering products and their parent materials are generally comparable. Al is also the normalising element assumed not to be enriched owing to local contamination. Baseline values for M_{crust} were adopted from Taylor and McLennan (1985).

EF–values lower than and around 1.0 indicate that the element in the sediment originates predominantly from the crustal material and/or weathering processes (ZHANG & LIU, 2002), whereas EF–values much greater than 1.0 display the anthropogenic origin of the element (SZEFER et al, 1996). According to Chen et al (2007), *EF* < 3 indicates minor enrichment (anthropogenic impact), *EF* = 3–5 moderate enrichment, *EF* = 5–10 moderately severe enrichment, *EF* = 10–25 severe enrichment, *EF* = 25–50 very severe enrichment, and *EF* > 50 extremely severe enrichment.

The calculation of enrichment factors showed that all studied heavy metals were enriched in surficial sediments of Lake Kalimanci. Cd had the highest average *EF*–value (735) among the investigated heavy metals, which represents extremely severe enrichment. *EF*–values of Pb, Zn and Ag (average value 387, 151 and 146, respectively) also signified extremely severe enrichment. Calculated *EF*–values for As, Cu and Sb determined very severe enrichment (average value 48) with As and severe enrichment with Cu and Sb (average values 21 and 10, respectively). Mo exhibited the lowest *EF*–values among the heavy metals studied (average value 2) and displayed moderate enrichment (Table 4).

Geoaccumulation index

The geoaccumulation index (I_{geo}) was also used to assess heavy metal pollution in surficial sediments of Lake Kalimanci. It is expressed by the following equation (MÜLLER, 1969):

$$I_{geo} = \log_2 (C_n/1.5\ B_n) \qquad (2)$$

where C_n is the measured concentration

Table 4. Enrichment factors (EF) values (average) in surface sediments of Lake Kalimanci

Element	Ag	As	Cd	Cu	Mo	Pb	Sb	Zn
EF values (average)	146	48	735	21	2	387	10	151

Table 5. I_{geo} values (average) in surface sediments of Lake Kalimanci

Element	Ag	As	Cd	Cu	Mo	Pb	Sb	Zn
I_{geo} values (average)	1.8	0.6	2.2	0.9	–0.1	2.4	–0.05	1.9

of the heavy metal (n) in the sediments, B_n is the geochemical background value in the average shale of element n, and 1.5 is the background matrix correction factor owing to lithogenic effects (Loska et al, 1997; Ghrefat & Yusuf, 2006; Gonzáles-Macías et al, 2006; Chen et al, 2007).

According to Loska et al (1997) and Gonzáles-Macías et al (2006), the geoaccumulation index (I_{geo}) can be categorised in a scale ranging from 1 to 6: $I_{geo} \leq 0$ unpolluted, $I_{geo} \leq 1$ unpolluted to moderately polluted, $I_{geo} \leq 2$ moderately polluted, $I_{geo} \leq 3$ moderately to strongly polluted, $I_{geo} \leq 4$ strongly polluted, $I_{geo} \leq 5$ strongly to very strongly polluted, and $I_{geo} > 5$ very strongly polluted.

The results (average values of the I_{geo}) revealed that surficial sediments of Lake Kalimanci were moderately to strongly polluted with Pb (2.4) and Cd (2.2), moderately polluted with Zn (1.9) and Ag (1.8), unpolluted to moderately polluted with Cu (0.9) and As (0.6) and unpolluted with Mo (-0.1) and Sb (–0.05) (Table 5).

The heavy metals in sediments are derived from two sources: natural and anthropogenic. In Lake Kalimanci, however, extremely elevated concentrations of Cd, Pb, Zn, Ag, As, Cu, Sb, Cu, Sb, and Mo in the surficial sediments clearly represent anthropogenic impact originating from the mining activities (mining effluents and tailings material) and the tailings dam accident in the Sasa mine. This anthropogenic influence was also evaluated and confirmed by the calculation of enrichment factors and the index of geoaccumulation.

Conclusion

In the present study we applied two ecological indices, enrichment factor and index of geoaccumulation, to assess and evaluate the distribution of heavy metals (Ag, As, Cd, Cu, Mo, Pb, Sb and Zn) in surficial sediments from Lake Kalimanci (Macedonia). The results indicate that all heavy metals were enriched in the sediment samples studied. According to the calculated values of I_{geo} the surficial sediments were strongly polluted with Pb and Cd and unpolluted with Mo and Sb. This pollution impact clearly originates from the mining activities (acid mine drainage) of the Sasa mine and from the Sasa tailings dam accident.

Acknowledgments

The research was financially supported by the Slovenian Research Agency (ARRS), contract number 1000-05-310229.

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