Pol. J. Environ. Stud. Vol. 22, No. 5 (2013), 1525-1538

Original Research

The Occurrence of Heavy Metals and Metalloids in Surficial Lake Sediments before and after a Tailings Dam Failure

Petra Vrhovnik[1]*, Tadej Dolenec[1], Todor Serafimovski[2], Matej Dolenec[1], Nastja Rogan Šmuc[1]

[1]Faculty of Natural Sciences and Engineering, University of Ljubljana, Department of Geology,
Aškerčeva cesta 12,1000 Ljubljana, Slovenia
[2]Faculty of Mining, Geology and Polytechnics, University "Goce Delčev-Štip,"
Goce Delčev 89, 2000 Štip, Macedonia

Received: 26 June 2012
Accepted: 16 April 2013

Abstract

Tailings dam failures are relatively rare but can cause extremely high and long-term impacts on the environment. The Sasa tailings dam collapsed in August 2003 and caused an intensive flow of tailings material through the Kamenica River all the way to Lake Kalimanci, where most of the tailings material discharged. This study deals with the characterization of surficial lake sediments from Lake Kalimanci in eastern Macedonia. Mineralogical, geochemical, and statistical analyses of surficial sediments in two sampling years, before and after the Sasa tailings dam failure, were carried out. To determine the pollution status of surficial lake sediments, two environmental indexes were calculated for 2001 and 2007. Spatial distribution of the analyzed heavy metals and metalloids shows that the highest concentrations were measured on the northern part of the lake, where the Kamenica River enters.

Keywords: tailings dam failure, heavy metals and metalloids, pollution, spatial distribution, environmental factors

Introduction

Input of heavy metals and metalloids in fresh waters has been increasing in recent decades. Their occurrence in the environment results from different anthropogenic activities, though natural processes like geological weathering of nearby rocks and soils can also increase the amount of heavy metals and metalloids in lakes. The other important source of heavy metals and metalloids is the aforementioned anthropogenic input from farming, traffic, mining, combustion emissions, and other industrial manufacturing activities [1, 2], from which the dusts are subsequently deposited onto the drainage basins of rivers and lakes.

Tailings dams are a special type of dam built to store mill and waste tailings from mining activities. Currently, thousands of tailings dams worldwide contain billions of tons of waste material from mineral processing activity at mine sites. Tailings dams should be constructed to achieve a safe, stable post-operational tailings impoundment [3, 4], and to contain waste materials indefinitely. Therefore, they are supposed to last forever, but since 1970 there have been 35 major mine tailings dam failures reported around the world [5]. In 2000 alone there were a total of 5 reported accidents (China, Romania, Sweden, and the USA).

---

*e-mail: petra.vrhovnik@gmail.com
petra.vrhovnik@ntf.uni-lj.si

When the Aznalcollar accident (SW Spain) occurred in April 1998, the channels and floodplains of the lower Agrio and the middle/lower Guadiamar rivers were completely overwhelmed by 4,106 m^3 of acidic water and 2 million m^3 of toxic mud containing large amounts of heavy metals and metalloids [6].

A major disaster also happened in the eastern Republic of Macedonia (Europe). During the afternoon on 30 August 2003 one part of the Sasa Mine tailings dam collapsed and caused an intensive flow of tailing materials through the Kamenica River Valley. The height of tailing flow was around 10 meters and was more at some localities, and the length of the flow was 12 km. 70,000-100,000 m^3 of tailings was discharged and expanded through the Kamenica River Valley, up to the city of Kamenica and into Lake Kalimanci. The damaging tailings flow material comprised a large amount of heavy metals and metalloids [7], and probably seriously affected Lake Kalimanci.

When potentially heavy metals and metalloids enter into the aquatic environment they are redistributed throughout the water column, deposited or accumulated in sediments and consumed by biota [8]. A fundamental characteristic of heavy metals and metalloids is their lack of biodegradability, and lake sediments are usually operating as pollutant storage tanks that are reflecting long-term impacts [9]. For this reason it is important to assess the abundance of these heavy metals and metalloids accumulated into lake sediments and to determine the environmental risk.

Consequently, we investigated the toxic metal contamination of the surficial sediments from Lake Kalimanci. Therefore, a geochemical study of the surficial sediments in Lake Kalimanci (eastern part of the Republic of Macedonia) was carried out to determine their elemental compositions before and after the accident in 2003. To evaluate the pollution status of lake sediments before and after the accident, an enrichment factor (EF) and index of geoaccumulation (I_{geo}) were applied.

Experimental Procedures

Study Area

Lake Kalimanci is located in eastern Macedonia, in the 2000 m high Osogovo Mountains near the city of Makedonska Kamenica (Fig. 1). The origin and development of Lake Kalimanci are closely related to the deficiency of the water for irrigation purposes in the Kočani Field area. Therefore, it has an artificial origin and it is supplied by two rivers: the Bregalnica River and Kamenica River on the north side, which flows directly from the Sasa Mine. The surface of the lake is 4.23 km^2, its longest length is 14 km, and greatest width 0.3 km; the maximum depth is 85 m and it encompasses around 120 million m^3 of water.

The rocks underlying the Lake basin are dismembered into a few lithostratigraphic units, which are the parts of the Serbo-Macedonian Massif and Tertiary sediments.

Fig. 1. Geographical setting of the studied area.

The metamorphic rocks of the Serbo-Macedonian Massif are distinguished into the lower and upper metamorphic complex. The lower complex of Precambrian metamorphic rocks is introduced by gneisses, micas, amphibolites, and schists. The upper Paleozoic metamorphic and magmatic complex contains quartz-graphitic, chlorite-quartz, muscovite-chlorite schists, and layers of cipolines and marbles. The Tertiary sediments are composed of Neogene clay, sand and gravel sediments, and sandstones [10].

According to the XRD analyses in our previous research [7, 11], the sediment samples from Lake Kalimanci are dominated by the following minerals: quartz, plagioclases, K-feldspars, muscovite, illite, and clinochlorite. Subordinate minerals are hornblende, gypsum, bassanit, calcite, dolomite, smithsonite, pyrite, marcasite, hematite, goethite, and diaspor.

The Osogovo Mountains have two main ore deposits: the Sasa-Toranica and Zletovo-Kratovo, which are connected by the same geology catchment. The Sasa Ore District is situated 10 km N of Lake Kalimanci, in the Osogovo Mountains, and occupies an area of about 200 km (Fig. 1). It is established as one of the largest ore districts within the Besna Kobila Osogovo Tassos Metallogenetic Zone. The Sasa Mine has been in production for over 45 years, yielding 90,000 tons of high-quality Pb-Zn concentrate annually.

The Sasa deposit geological composition is represented by three metamorphic complexes cross-cut by the Strumica Diorite Formation, leucocratic gneisses, and Tertiary magmatites. The metamorphic complex consists of Precambrian high crystalline metamorphic rocks, Pre-Silurian greenschists, and Silurian-Devonian quartz-muscovite-graphytic schists, calc schists, marbles, and phyllites [11]. The Strumica Diorite Formation includes gabbro, diorite, and plagiogranite [11]. Tertiary magmatites are mostly presented by the quartz-latites and rhyodacites with sanidine dacites and latite-andesite porphyrites. Important Pb and Zn deposits were formed, always accompanied by variable amounts of Cu, Au, Ag, Mo, and Sb. The ore in the studied area can be found in quartz-muscovite-graphitic schsists and also in greenschists and marbles.

The composition of the tailings material is mostly dependent on the content of flotation reagenses, features of the ore, applied process of the ore enrichment, and pH values of the pulp etc. The tailings material from the Sasa mine is made up of quartz, pyrite, galenite, gypsum, hornblende, actinolite, albite, anortite, biotite, and orthoclase. The geochemical analyses of tailings material in 2003 showed an average range of Mo 3.0 mg/kg, Cu 982, Pb 6,496 mg/kg, Zn 5,121 mg/kg, Ni 31 mg/kg, As 111 mg/kg, Cd 152 mg/kg, Ag 21 mg/kg, Au 0.0 mg/kg, and Sb 5.6 mg/kg [11].

Sampling

17 surficial sediment samples from Lake Kalimanci were taken before the accident, in August 2001. The sampling collection was resumed in September 2007, four years after the accident. In these years 31 samples were taken (Fig. 2). The chosen sampling locations were formed into 8 profiles through the northern part of Lake Kalimanci and referred mostly to the area around the River Kamenica tributary on the northern site of the lake, which is directly connected to the Sasa Mine area (Fig. 3a and 3b). In 8 profiles there were 48 samples collected altogether in both sampling years; meanwhile in both years there are only 6 common locations (I-2, II-5, III-2, IV-1, V-7, VI-1). The sediment pH ranged between 5.5 and 7.5, and redox potential ranges between -325 mV and +180 mV.

The samples were collected with plastic corers (tube 10 cm long with a 7 cm internal diameter), and were tightly packed into self-locking polyethylene bags. The use of metal tools was avoided, and a plastic spatula was used for sample collection. The surficial sediment samples were stored at 4ºC and in the laboratory the sediment samples were dried at 50ºC for 48 hours. They were then sieved through a 0.315 mm polyethylene sieve to remove plant debris and homogenized by mechanical agate grinder to a fine powder for subsequent mineralogical and geochemical analyses.

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

The complete chemical analyses were obtained at the commercial ACME Laboratories in Vancouver, Canada. Several minor elements were analyzed by ICP-emission spectrometry followed by a lithium metaborate/tetraborate fusion and dilute nitric digestion (Acme Labs). In addition,

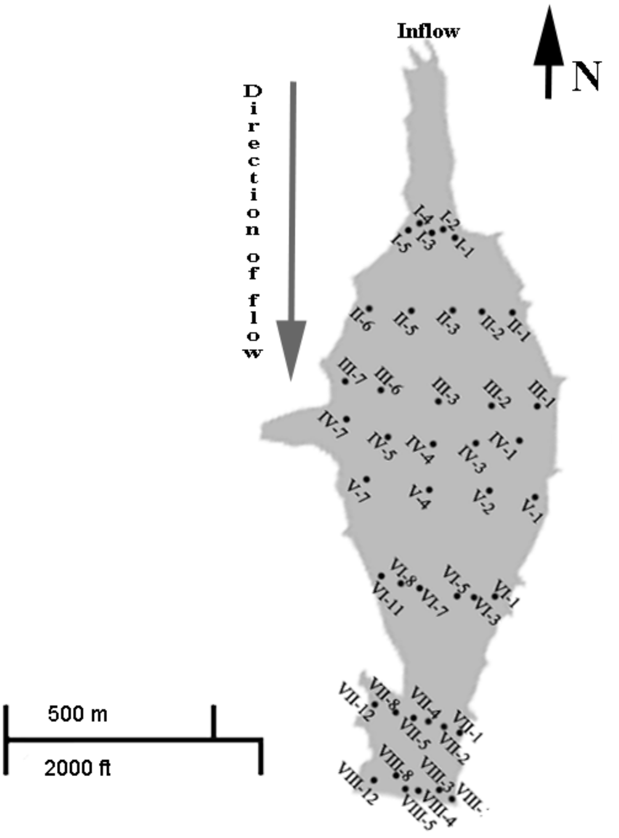

Fig. 2. Sampling locations on Lake Kalimanci.

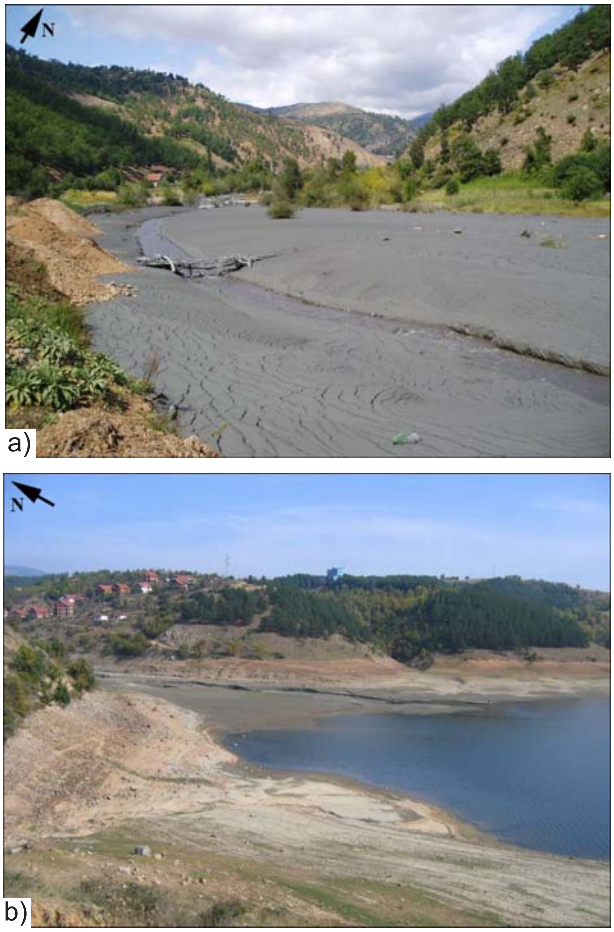

Fig. 3. a) Part of the Kamenica River after the Sasa tailings dam failure, b) part of Lake Kalimanci between the second and third profile, where the Kamenica River stream ends.

ICP mass spectrometry was applied using the same solution in the ICP ES procedure. Furthermore a separate split was digested in hot (95ºC) Aqua Regia and analyzed by ICP MS to identify precious and base metals. The quality of the analyses was monitored by comparison with the standard materials STD SO-18, STD CSC, STD DS7, STD OREAS76A, and STD R3A provided by ACME and repeated measurements of five of our samples (I-5, II-1, II-3, V-4, VIII-1).

Basic statistical parameters for each element were performed using the original statistical software program Statistica 8. Spatial distribution was carried out with Golden Software Surfer 8.

To evaluate the surficial sediments contamination with potentially heavy metals and metalloids, two environmental factors were applied.

The concept of an enrichment factor (EF) was developed in the 1970s to evaluate anthropogenic contribution in sediments and soils. Acording to Aubakar [12] it is expressed as follows:

$$EF= (M_s/Al_s)/(M_c/Al_c)$$

...where the numerator stands for the ratio of the concentration of the examined element (M_s) to the reference element (Al_s) in a sample. The denominator represents the ratio of the concentration of the examined element (M_c) to the reference element (Al_c) in a reference material. Metal to Al ratios are widely adopted due to its crustal dominance and high immobility, and the concentration of Al in weathering products and their parent materials are generally comparable. Al is also the normalizing element assumed not to be enriched due to local contamination. Baseline values for Mc were as follows [mg/kg]: Ag 0.05, As 1.5, Cd 0.098, Cu 25, Mo 1.5, Pb 20, Sb 0.2, and Zn 71 [13]. The enrichment factor values are interpreted as the levels of heavy metals and metalloids pollution that were suggested by Birth [14], and the assessment criteria are generally based on the EF values.

The Geoaccumulation Index (I_{geo}) has been widely used since the 1960s in all kinds of trace metal studies [2, 15, 16]. It was originally used for bottom sediments [15] and it enables the assessment of pollution by comparing current concentrations with unpolluted levels. It can be calculated by the following equation:

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

...where C_n is the measured concentration of the examined metal or metalloid in the sediment and B_n is the geochemical background concentration of the metal or metalloid. The factor 1.5 is used because of possible variations in background values due to lithological variability.

Results and Discussion

Mineralogy of Surficial Lake Sediments

Sediment samples of the investigated area were found to consist of sand, silt, and clay. Detailed x-ray diffraction analysis of surficial sediments from Lake Kalimanci revealed that sediments are mainly composed of quartz, pyrite, clinochlore, dolomite, muscovite, calcite, and albite, but we also detected in traces hornblende, smithsonite, goethite, gypsum, and bassanite. Quartz is a very stable mineral, and thus is present in local metamorphic and magmatic rocks near Lake Kalimanci, and also in the hydrothermal veins that contain ore minerals. The quantity of quartz can decrease the concentrations of heavy metals and metalloids.

Statistics and Geochemistry

The basic statistics of the obtained data in the Kalimanci Lake surficial sediments and their concentrations for the year 2001 are presented in Table 1; and those for 2007 after the tailings dam failure are in Table 2.

In order to assess element associations and metal origins, the Pearson correlation matrixes between the heavy metals and metalloids from 2001 and 2007 are listed in Table 3, which shows the strong positive correlation among the studied elements Mo, Cu, Pb, Zn, Cd, Ag, and Sb in both sampling years, demonstrating the possible co-contamination from similar sources such as acid mine drainage

Table 1. Concentrations of studied metals in surficial lake sediments and their descriptive statistics before the Sasa tailings dam failure (year of sampling 2001).

Sample	S (TOT)	Mo	Cu	Pb	Zn	As	Cd	Ag	Sb
	%	mg/kg							
DL	0.02	0.1	0.1	0.1	1.0	0.5	0.1	0.1	0.1
I-2	**0.6**	**1.0**	**56**	**985**	**1407**	**27**	**9.8**	**0.5**	**0.9**
II-2	0.5	1.0	79	1358	1415	53	11	0.8	1.0
II-5	**2.3**	**2.7**	**298**	**6734**	**7707**	**82**	**69**	**4.4**	**2.9**
III-2	**0.5**	**1.2**	**72**	**1050**	**1331**	**34**	**10**	**0.6**	**0.8**
III-7	0.3	1.7	205	3195	5040	100	30	2.2	2.1
IV-1	**0.2**	**1.2**	**115**	**2276**	**2813**	**68**	**23**	**1.5**	**1.9**
IV-3	0.6	1.1	57	789	1144	29	7.9	0.5	0.8
IV-5	0.7	2.1	242	4135	5106	71	41	3.1	1.8
V-2	1.5	2.2	269	4946	5792	62	52	3.9	2.1
V-7	**0.2**	**1.1**	**98**	**1572**	**1887**	**20**	**13**	**1.1**	**0.8**
VI-1	**0.5**	**2.1**	**241**	**4636**	**6169**	**55**	**44**	**3.1**	**1.8**
VI-3	0.4	0.8	60	752	1005	31	6.5	0.5	0.7
VI-8	0.3	1.4	182	3485	4418	42	30.4	2.2	1.6
VII-2	0.4	1.0	78	1257	1358	40	11	0.7	0.9
VII-5	0.6	2.3	279	4906	7301	65	47	3.5	1.7
VIII-3	0.6	0.8	94	426	917	66	5.5	0.5	0.7
VIII-5	0.5	1.9	211	3596	4942	51	40	2.7	1.4
Mean	0.6	1.5	155	2711	3515	53	26	1.9	1.4
Minimum	0.2	0.8	56	426	917	20	5.5	0.5	0.7
Maximum	2.3	2.7	298	6734	7707	100	69	4.4	2.9
Std.Dev.	0.5	0.6	89	1892	2397	22	19	1.4	0.6

*bold locations are the same in sampling years 2001, 2007.

and mine waste effluents from the Sasa lead-zinc ore deposit. Because the correlations are entirely the same for years 2001 and 2007, we can conclude that the Sasa tailings dam failure did not change the correlation of those elements, but it has only increased their concentrations in surficial sediments from Lake Kalimanci. On the contrary, the associations of arsenic with other elements were generally weak. The Pearson correlation matrixes for both studied years indicate that arsenic is not correlated like all other metals, but it withdraws from the aforementioned explanation. Its origin is most likely connected with bedrocks from the surrounding area or has a different depositional nature and has no connection with the Sasa tailings dam.

Spatial Distribution of Heavy Metals and Metalloids

Concentrations of all studied heavy metals and metalloids are presented in Fig. 4, for both sampling years 2001 and 2007.

Concentrations of molybdenum in major rock-forming silicates are around 1 mg/kg [13, 17]; the average content of Mo in surficial lake sediments in the sampling year 2001 was 1.5, with maximum value 2.7 (II-5), and in the year 2007 the average content was 2.7 mg/kg and maximum value 4.6 mg/kg, also on the second profile (II-3). After the Sasa tailings dam failure, the content of Mo was approximately two times higher than before the accident. Next to the Sasa tailings dam failure are high contents of Mo due to sulphides like pyrite, galena, and sphalerite. In view of Fig. 4, the abundance of Mo is equally distributed through the lake before the accident occurred, and comparing this to the year 2007 on Fig. 4 the highest concentrations of Mo are arranged in decreasing order from second to fifth profile. On the other hand, there are higher concentrations of Mo in the year 2007 on the southern part of the lake (profile VII and VIII), which are comparable with concentrations of Mo before the accident occurred. Presumably this is because of very strong inflow of the Sasa tailing material, when the failure occurred in 2003. The average crustal content of

Table 2. Concentrations of studied metals in surficial lake sediments and their descriptive statistics after Sasa taigs dam failure (year of sampling 2007).

Sample	S (TOT)	Mo	Cu	Pb	Zn	As	Cd	Ag	Sb
	%	mg/kg							
DL	0.02	0.1	0.1	0.1	1.0	0.5	0.1	0.1	0.1
I-1	**0.4**	**1.9**	**195**	**2272**	**2944**	**54.2**	**17**	**1.8**	**1.1**
I-2	1.4	2.2	238	2721	5913	54.8	48	2.0	1.4
I-3	0.5	1.7	167	1931	2949	62	21	1.5	1.1
I-4	1.5	2.9	672	9357	9200.00	68.8	74	10	2.4
I-5	1.1	2.9	540	7980	8627	45.5	61.1	8.9	2.4
II-1	1.6	3.1	415	4461	9596	86.7	77.2	3.6	2.2
II-3	2.1	4.6	1162	16300	20900	77	136	17	3.6
II-5	**1.9**	**4.2**	**929**	**13800**	**17600**	**70**	**112**	**15**	**3.2**
II-6	0.6	2.6	345	5066	6335	53	42	4.5	1.6
III-1	2.1	3.1	478	7595	10800	63	80	6.9	1.7
III-2	**1.9**	**4.1**	**514**	**9880**	**11900**	**62**	**71**	**7.2**	**2.1**
III-3	2.0	3.7	723	10900	14000	73	90	11	2.7
III-6	3.3	3.3	693	9600	14000	58	87	10	2.1
IV-1	**1.7**	**3.0**	**413**	**6695**	**8105**	**66**	**59**	**5.1**	**1.7**
IV-4	2.0	2.3	341	5343	6734	62	48	4.2	1.6
IV-7	1.1	3.0	343	4755	6641	69	43	3.9	1.3
V-1	1.3	2.4	303	4447	5677	62	40	3.6	1.3
V-4	3.2	1.8	144	2564	3052	78	23	2.0	1.6
V-7	**2.9**	**3.7**	**596**	**9472**	**12600**	**66**	**81**	**8.1**	**2.0**
VI-1	**0.5**	**1.0**	**162**	**1874**	**4587**	**68**	**28**	**1.4**	**0.7**
VI-5	1.5	2.6	288	4776	5188	70	39	3.8	1.7
VI-7	4.5	3.6	315	7885	7181	128	54	5.6	3.3
VI-11	1.8	2.5	546	7557	11600	59	78	7.1	1.6
VII-1	0.9	1.9	373	4575	10400	78	61	3.6	1.1
VII-4	1.5	2.6	293	4510	5965	71	41	3.5	1.4
VII-8	3.7	1.8	147	2598	3376	74	25	1.9	1.5
VII-12	1.9	2.7	398	5144	9326	66	54	4.5	1.2
VIII-1	1.7	2.2	312	5092	7224	70	48	3.8	1.4
VIII-4	3.2	2.4	270	4991	5553	95	40	3.9	1.9
VIII-8	1.6	2.3	328	4863	7056	62	47	4.1	1.4
VIII-12	1.0	1.2	225	2463	4501	28	31	2.3	0.6
Mean	1.8	2.7	415	6176	8372	68	57	5.6	1.8
Minimum	0.4	1.0	144	1874	2944	28	17	1.4	0.6
Maximum	4.5	4.6	1162	16300	20900	128	136	17	3.6
Std.Dev.	1.0	0.9	233	3491	4291	17	27	3.9	0.7

*bold locations are the same in sampling years 2001, 2007.

Table 3. Pearson correlation matrix for 2001 and 2007.

	Mo-01	Cu-01	Pb-01	Zn-01	As-01	Cd-01	Ag-01	Sb-01
Mo-01	1.00							
Cu-01	**0.98**	1.00						
Pb-01	**0.98**	**0.99**	1.00					
Zn-01	**0.98**	**1.00**	**0.99**	1.00				
As-01	0.76	0.78	**0.81**	0.80	1.00			
Cd-01	**0.98**	**0.98**	**1.00**	**0.99**	**0.84**	1.00		
Ag-01	**0.98**	**1.00**	**1.00**	**0.99**	0.81	**0.99**	1.00	
Sb-01	**0.87**	**0.88**	**0.92**	**0.90**	**0.96**	**0.94**	**0.92**	1.00
	Mo-07	Cu-07	Pb-07	Zn-07	As-07	Cd-07	Ag-07	Sb-07
Mo-07	1.00							
Cu-07	**0.87**	1.00						
Pb-07	**0.94**	**0.97**	1.00					
Zn-07	**0.90**	**0.99**	**0.98**	1.00				
As-07	0.16	0.50	0.46	0.45	1.00			
Cd-07	**0.90**	**0.99**	**0.96**	**0.98**	0.37	1.00		
Ag-07	**0.83**	**1.00**	**0.96**	**0.98**	0.53	**0.98**	1.00	
Sb-07	**0.90**	**0.97**	**0.96**	**0.97**	0.32	**0.99**	**0.97**	1.00

copper is 25 mg/kg [13], while the average concentration in surficial sediments from Lake Kalimanci before the dam failure was 155 mg/kg. The reason for such high amounts of Cu is probably the occurrence of sulphide minerals in the Sasa-Toranica and Zletovo-Kratovo ore deposits [18], and also the acid mine drainage from Sasa, which is stored on top of the tailings dam. The amounts of copper in surficial lake sediments after the dam collapse were more than 2.5 times higher than before the failure. The measured average value of copper in 2007 was 415 mg/kg. In view of the geochemical charts (Fig. 4) it is obvious that the lowest contents of Cu were in the middle and southern parts of the lake, and the highest contents were in the NW part of the lake (II-3, II-5) in both sampling years. The difference before and after the tailings dam failure is that the NW part of Lake Kalimanci (between II and III profile) had increased contents of Cu because it was there that most of the collapsed tailings dam material was deposited. Lead and zinc have the highest contents in surficial sediments from Lake Kalimanci among all studied metals, due to the Pb-Zn ore deposit near the Osogovo Mountains. The difference before and after the tailings dam failure shows that the content of those two metals in 2007 was more than 2.3 times higher than in 2001. The maximum value of Pb in 2001 was 6,734 mg/kg (II-5) and the average value was 2711 mg/kg. In the sampling year 2007 the maximal measured value was 16,300 mg/kg (II-3) and its average content was 6,176 mg/kg. Zn had maximum value in year 2001, measured at sampling location II-2, of 7,707 mg/kg, and had average content of 3,542 mg/kg; meanwhile, after the dam failure its maximum value increased to 20,900 mg/kg (also on the second profile, II-3), and its average concentration after the accident was 8,372 mg/kg. With regards to different case studies [19] the average concentrations of Pb and Zn in recent lacustrine sediments is 100 mg/kg and 205 mg/kg.

While the Former Yugoslavian Republic of Macedonia has no sediment quality criteria, we made a comparison with the Belgian Sediment Quality Criteria [20], which has second limit values for Pb 350 mg/kg and for Zn 500 mg/kg. In this respect, the concentrations of Pb and Zn, which are also major elements in Sasa production, are their levels according to averages of recent lacustrine sediments and Belgian sediment quality criteria, incomparably higher. Besides the mining activity and the tailings dam failure, the increased values of Pb and Zn also are due to weathering of galena, sphalerite, and other sulphide minerals that occurred in the Sasa-Toranica ore deposition. In view of distribution diagrams (Fig. 4), both metals increased in the NE part of Lake Kalimanci between the second and third sampling profiles, due to the entering of the Kamenica River, which caused the deposition of the greatest amounts of Sasa tailings dam material in the lake after the failure in 2003. While the Sasa-Toranica ore deposit contains great amounts of sphalerite (ZnS), consequently there also is increased cadmium, which is the secondary product from the sphalerite mineral. Next to Zn ores it also is a frequent element inside Pb ores, and in oxidazing zone is mostly found in smithsonite, hemimorphite, Mn oxides, and Fe

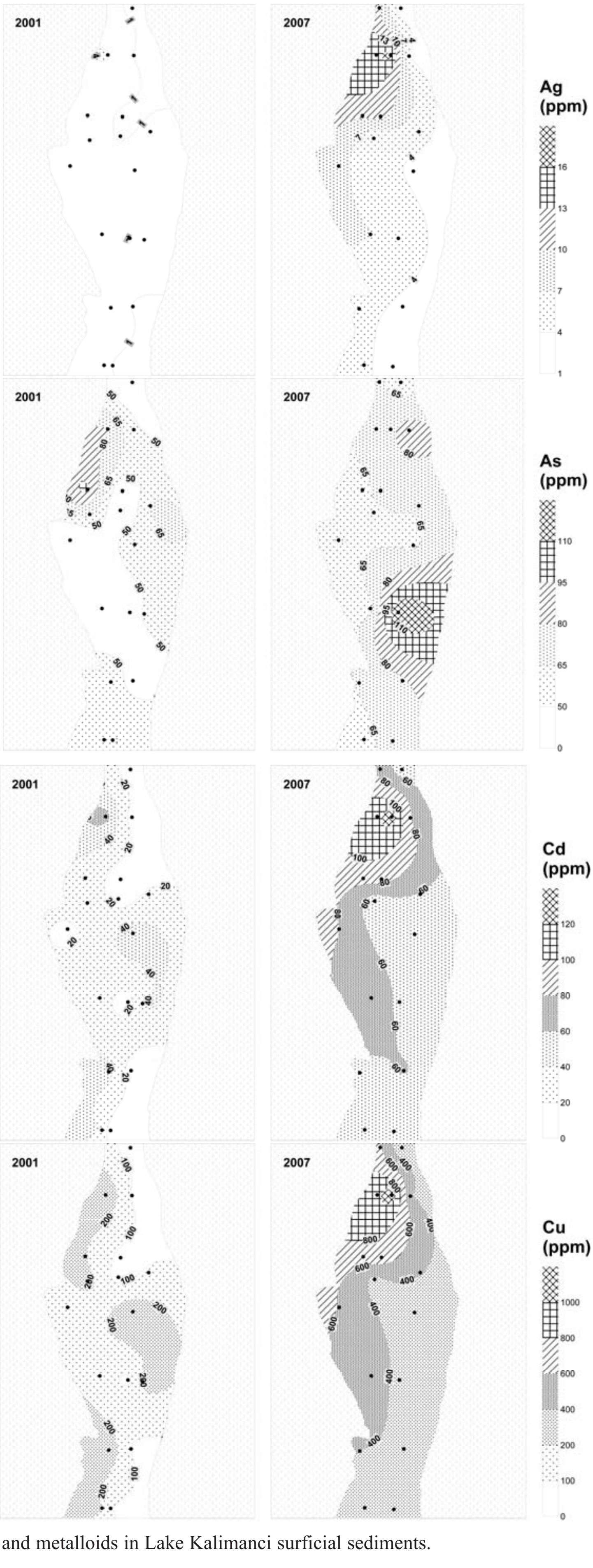

Fig. 4. Distribution of metals and metalloids in Lake Kalimanci surficial sediments.

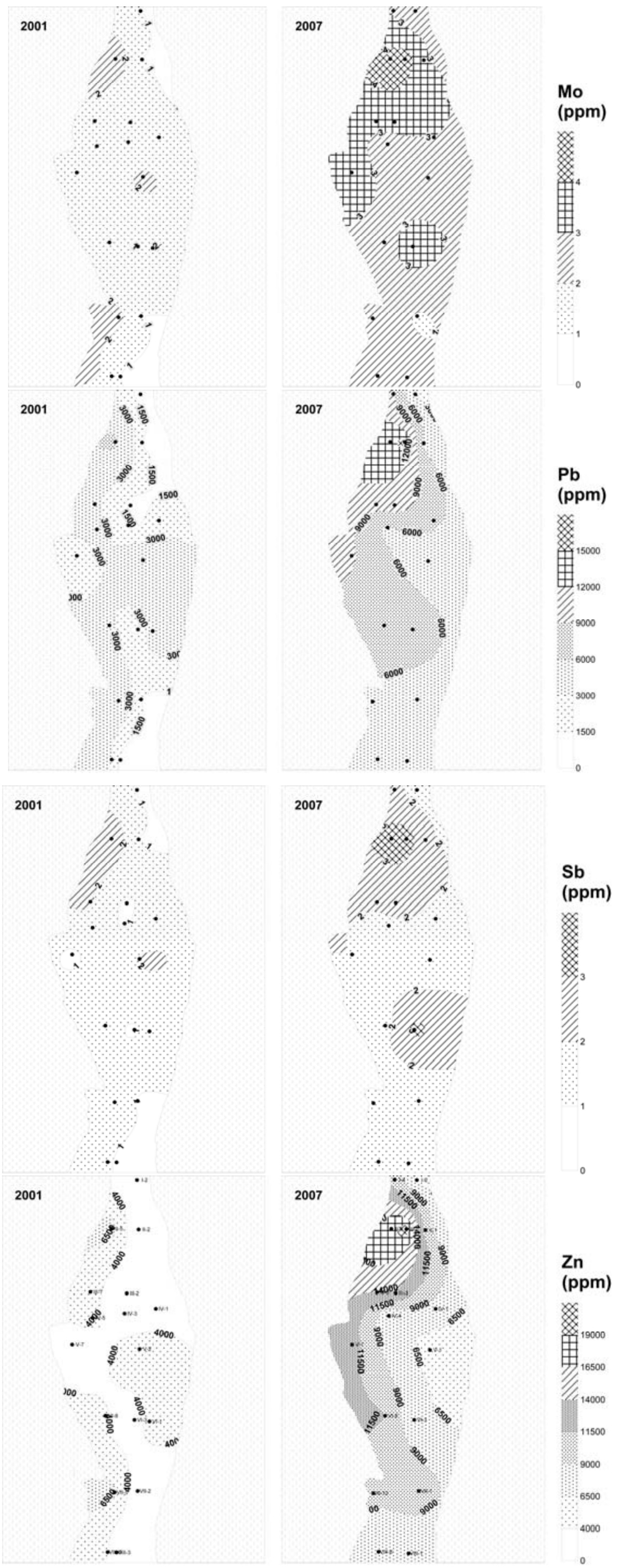

Fig. 4. Continued.

hydroxides [21]. The maximum and average concentrations of Cd in surficial sediments from Lake Kalimanci before the dam failure were 69 mg/kg (II-5) and 26 mg/kg, and after the failure 136 mg/kg (II-3) and 57 mg/kg. Spatial distribution shows the highest contents of Cd were measured on the second profile of the NW part of the lake (Fig. 4).

Silver can be found in nature, such as native silver or in combination with sulphides, sulphosalts, and other elements like S, Sb, Se, Pb, As, Bi, Cu, and Au [21]. Ag had average concentration in surficial lake sediments in 2001 of 1.9 mg/kg and its maximum was 4.4 mg/kg. After the Sasa tailings dam failure its average content rose to 5.6 mg/kg, and its measured maximum in 2007 was 17 mg/kg. The maximum value in 2007 was almost four times higher than before the accident occurred. The location of increased Ag was the same as with the aforementioned metals, and is in the NW part of the lake between the second and third sampling profiles.

Antimony is a relatively rare element in nature. It typically occurs in the vicinity of the hydrothermal deposits of galena and sphalerite, where it can be found in concentrations above 3.0 mg/kg [22]; thus higher concentrations are also expected in the region of the Sasa ore deposit. The average concentration of Sb in surficial sediments from the lake before the dam collapse was 1.4 mg/kg, and the maximum was measured at 2.9 mg/kg. Average and maximum concentrations in 2007 were not as increased in comparison with 2001 (as for all the other studied metals and metalloids), and these values were 1.8 mg/kg and 3.6 mg/kg. Even the maximum value of Sb, measured on the NW part of the lake (II-3), coincides with the values adopted in the geochemical atlas of Europe [22].

Among aforementioned metals, antimony and arsenic are the only metalloids which, according to spatial distribution diagrams, increased concentrations in 2001, before the dam failure, and in the year after the accident they both have two locations where they are enriched. Sb is enriched on the NW side of the lake (like other elements), but also at the mid-eastern part of the lake on the sixth profile (VI-3). Meanwhile, arsenic has major enrichment on the SE part of the lake (VI-3) and lower enrichment on the NE part of the lake. The average value of As before the failure was 53 mg/kg and its maximum content was 100 mg/kg; and the respective values after the dam failure were 68 mg/kg and 128 mg/kg. According to Aksentijević [23] the average concents of As in rivers and lakes are around 100 mg/kg. Its increased concentrations in the studied area are due to sulphide minerals such as galena, sphalerite, and arsenopyrite, and also to hydrothermal processes, which cause enrichment of As because of felsic and mafic igneous rocks in the surrounding area. The reason for the different locations of composition of Sb and As, compared with other studied metals, must be due to strong adsorption on clays, which "travel" farthest in suspension [24].

Sources of sulphur compounds to natural waters include solubilization from imminent rocks, fertilizers, and atmospheric precipitation, and also dry deposition. In this particular study the concentrations of sulphur have sources connected greatly by the mining industry and the environmental accident in the year 2003, when the Sasa tailing dam collapsed. After the failure, the average amount of total sulphur increased from 0.6 [wt %] to 1.8 [wt %], which is almost three times higher than before the accident. Sulphur also is released during geochemical weathering from nearby rocks and soils containing sulphides, which are oxidized in the presence of the water. Afterward they form sulphuric acid, which tends to lower the pH and Eh [25] and consequently affects the oxidative weathering reactions of other present minerals.

In sampling year 2001, before the Sasa tailings dam failure, there was no extreme exceeding studied heavy metals and metalloids (Fig. 4) in surficial sediments from Lake Kalimanci. Only As and Sb resign out between the second and third sampling profiles. All studied metals and metalloids show significant variation in their concentrations in lake surficial sediment with increasing distance from the northern part of the lake, where the Kamenica River enters the lake. In 2003, when the major environmental accident occurred, between 70,000 and 100,000 m^3 of Sasa tailings dam material was transmitted through the Kamenica River Valley into Kalimanci Lake. Thus, next to the geological weathering and increased traffic circulation, because of mining activity the collapse of the dam is a major factor for exceeded concentrations of heavy metals and metalloids in the lake. According to Fig. 4, all studied metallic elements such as Mo, Cu, Pb, Zn, Cd, Ag, and Sb, except As, have highest concentrations on the western side of the lake between the second and third sampling profiles. This coincides with the place where the Kamenica River enters. The course of the river finishes exactly between the second and third profiles, where there is increased sedimentation (Fig. 3b).

Environmental Indexes EF and I_{geo}

Environmental indexes for eight studied metals (Cd, Mo, Cu, Pb, Zn, As, Ag, and Sb) were calculated by the aforementioned equations and the data is summarized in Table 4. For evaluation of EF and I_{geo} only the locations (I-2, II-5, III-2, IV-1, V-7, VI-1) that were the same at both sampling years (2001, 2007) were chosen because of better comparison.

The enrichment factors for surficial sediments from Lake Kalimanci are presented in Table 4. EF values lower and around 1 indicate that the element in the sediment originates predominantly from the crustal material and/or weathering processes [26], whereas EF values that are much greater than 10 display the anthropogenic origin of an element [17]. Birth [14] interpreted EF values as follows: EF values of less than 1 indicate no enrichment; values of 1-3 indicate minor enrichment; 3-5 show moderate enrichment; values between 5 and 10 indicate moderately severe enrichment; from 10 to 25 enrichment is severe; values ranging from 25 to 50 indicate severe enrichment; and values over 50 indicate extremely severe enrichment.

Among all studied metals and metalloids, the EF values are the highest on the second profile (II-5) of the lake in both sampling years. Results (Table 4, Fig. 5) also revealed

Table 4. Enrichment factor (EF) and Index of geoaccumolation in surfical sediments from Lake Kalimanci.

	Mo	Mo	Cu	Cu	Pb	Pb	Zn	Zn	As	As	Cd	Cd	Ag	Ag	Sb	Sb
Sampling year	2001	2007	2001	2007	2001	2007	2001	2007	2001	2007	2001	2007	2001	2007	2001	2007
EF																
I-2	0.8	1.4	2.7	9.4	58	134	24	82	21	36	119	483	12	39	5.3	6.9
II-5	1.8	3.1	11.6	41	327	755	106	271	53	51	684	1246	86	333	14	18
III-2	0.9	2.6	3.3	20	61	474	22	161	26	39	119	697	14	138	4.6	10
IV-1	0.8	2.0	4.7	16	116	327	40	111	46	43	239	588	31	100	9.7	8.3
V-7	0.6	2.5	3.0	24	59	479	20	180	10	45	100	838	17	164	3.0	10
VI-1	1.2	0.6	8.4	6.2	202	90	76	62	32	44	391	275	54	27	7.8	3.4
Average	1.0	2.0	5.6	19	137	377	48	145	32	43	275	688	35	133	7.4	9.4
Max	1.8	3.1	12	41	327	755	106	271	53	51	684	1246	86	333	14	18
Min	0.6	0.6	2.7	6.2	58	90	20	62	10	36	100	275	12	27	3.0	3.4
I_{geo}																
I-2	-0.6	0.6	1.2	3.3	5.6	7.1	4.3	6.4	4.2	5.2	6.6	8.9	3.3	5.3	2.2	2.8
II-5	0.9	1.5	3.6	5.2	8.4	9.4	6.8	8.0	5.8	5.6	9.5	10.2	6.5	8.3	3.9	4.0
III-2	-0.3	1.5	1.5	4.4	5.7	9.0	4.2	7.4	4.5	5.4	6.7	9.5	3.6	7.2	2.0	3.4
IV-1	-0.3	1.0	2.2	4.1	6.8	8.4	5.3	6.8	5.5	5.5	7.9	9.2	4.9	6.7	3.3	3.1
V-7	-0.5	1.3	2.0	4.6	6.3	8.9	4.7	7.5	3.8	5.5	7.0	9.7	4.5	7.3	2.0	3.3
VI-1	0.5	-0.6	3.3	2.7	7.9	6.6	6.4	6.0	5.2	5.5	8.8	8.2	6.0	4.8	3.2	1.8
Average	-0.1	0.9	2.3	4.0	6.8	8.2	5.3	7.0	4.8	5.4	7.8	9.3	4.8	6.6	2.7	3.1
Max	0.9	1.5	3.6	5.2	8.4	9.4	6.8	8.0	5.8	5.6	9.5	10.2	6.5	8.3	3.9	4.0
Min	-0.6	-0.6	1.2	2.7	5.6	6.6	4.2	6.0	3.8	5.2	6.6	8.2	3.3	4.8	2.0	1.8

that all EF values from the year after the tailings dam collapse in 2007 are much higher than for the year 2001, before the accident occurred. According to the range plot (Fig. 5), Cd had the highest calculated EF values and it shows extremely severe enrichment in both sampling years; in 2001 its average value was 275 and in 2007 it was 688. The same extreme severe enrichment also was indicated for Pb in both sampling years, with average values of 137 (2001) and 377 (2007). Among other elements, Zn and Ag also had extreme severe enrichment in the year after the dam failure, and these also show severe enrichment in the year before the dam collapse. As had severe enrichment in both sampling years, with average values of 32 in 2001 and 43 in 2007. Cu had an average calculated EF of 19 in 2007, which indicates severe enrichment. In 2001 Cu shows moderately severe enrichment (average 5.6). The same enrichment also was exhibited by Sb in both years: 7.4 (2001) and 9.4 (2007). Mo had minor enrichment before (average 1.0) and after (average 2.0) the dam failure.

EF also revealed that Cd, Pb, Zn, Ag, As, Sb, and Cu have anthropogenic origin; meanwhile, Mo most likely originates from the weathering processes of the background rocks.

Müller [27] introduced the index of geoaccumolation (I_{geo}) to study the pollution levels of heavy metals and metalloids in sediments. Based on the calculated index of geoaccumolation values, we can decipher sediment quality and also degree of pollution with heavy metals and metalloids. In 1981 Müller [27] proposed seven grades of contamination as follows: values under 0 show that sediments are unpolluted; I_{geo} values ranging from 0 to 1 indicate unpolluted to moderately polluted sediments; in the third class from 1 to 2 are sediments that are moderately polluted; I_{geo} between 2 and 3 shows moderately to strongly polluted sediments; the fifth class, ranging from 3 to 4, indicates a strong pollution of sediments; the next class is between 4 and 5 and presents strong to very strong polluted sediments; and the last class adopted by Müller [27], with calculated values over 5, exhibits very strongly polluted sediments. Calculated I_{geo} for six sampling locations (I-2, II-5, III-2, IV-1, V-7, VI-1), which are the same for both sampling years, are presented in Table 4. Regarding the range plot (Fig. 6) of the calculated maximum, average, and minimum values of I_{geo} it is seen that Lake Kalimanci surficial sediments were very strongly polluted with Cd, Pb, and Zn in both sampling years, and with As and Ag in 2007 after the Sasa tailings dam failure. The values for Ag and As in 2001 and Cu in 2007 show that surficial sediments were strongly to very strongly polluted with these metallic elements. In sampling year 2007, Sb reached the pollution intensity of fourth class, which indicates strong pollution, and in the year being studied that was before the accident (2001) surficial lake sediments were moderately to strongly polluted with Sb. In the same pollution class as Sb in year 2001 was Cu, in the same sampling year. Among all studied metallic elements, Mo had the lowest pollution intensity. The calculated I_{geo} indicate that before the Sasa tailings dam collapse (2001) the surficial sediments from Lake Kalimanci were unpolluted with Mo and after the accident the pollution increased from first to second class, which indicates that surficial sediments were then unpolluted to moderately polluted with Mo.

Ghrefat et al. [28] compared calculated EF and I_{geo} results, whereas the indexes showed different contamination status of studied sediments. If we compare both calculated environmental indexes we can conclude that the EF

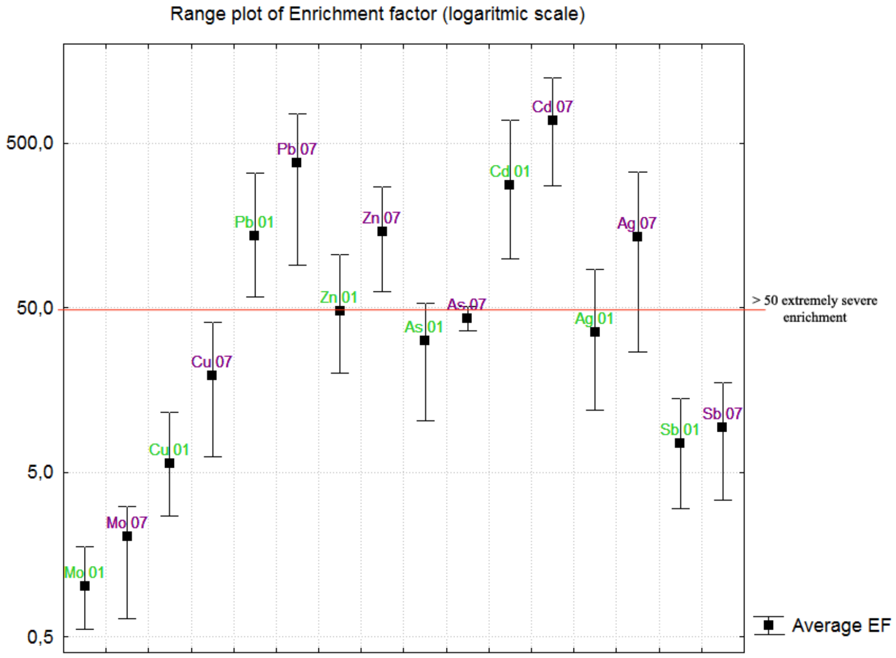

Fig. 5. Range plot of calculated enrichment factor for sampling years 2001 and 2007, with logarithmic scale.

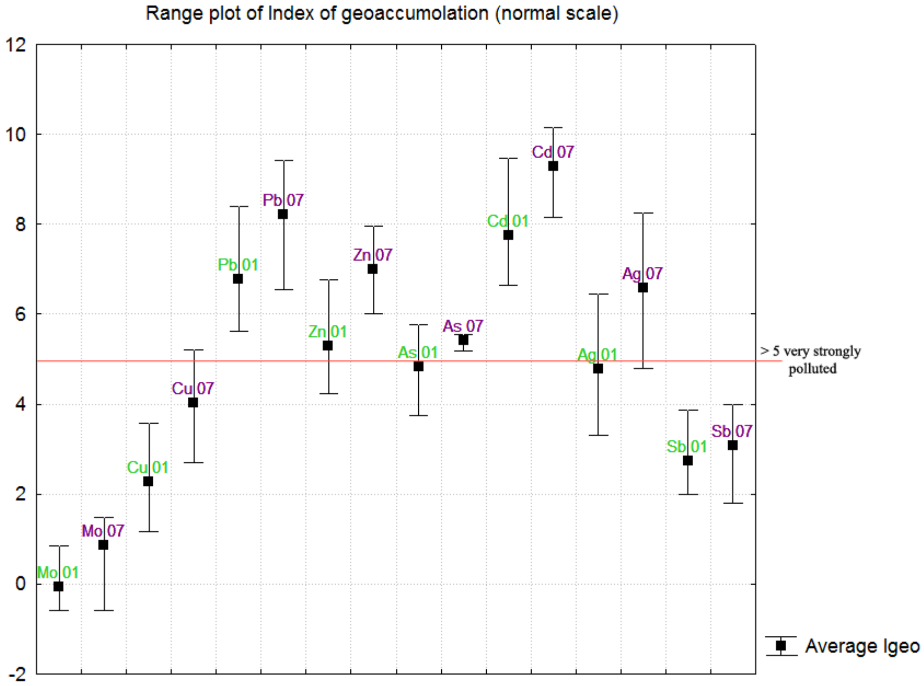

Fig. 6. Range plot of calculated index of geoaccumolation for sampling years 2001 and 2007, with normal scale.

results agree quite well with the I_{geo} results. It is again apparent that Pb, Zn, and Cd contamination of surficial sediments from Lake Kalimanci are the most pronounced among all of the investigated metals.

The pollution of the investigated area strongly increased after the dam failure. And the contamination status, is compared to other case studies [29-31], incomparably high. According to the results, the situation for all living organisms at this area is concerning.

Conclusions

A detailed study of metal and metalloid enrichments above natural concentrations in surface sediments from Lake Kalimanci before (2001) and after (2007) the Sasa tailings dam failure was the main goal of this work. Geochemical analysis shows that surficial sediments from Lake Kalimanci had higher concentrations of all eight studied heavy metals and metalloids (Mo, Cu, Pb, Zn, As, Cd, Ag, and Sb) before the dam failure occurred, compared to averages in the upper continental crust. After the accident in 2003, when the Sasa tailings dam collapsed, and the Kamenica River transported tailings dam material and discharged it in Lake Kalimanci, the content of the aforementioned heavy metals and metalloids in sampling year 2007 drastically increased. All heavy metals and metalloids, except As, show the highest measured values on the second sampling profile, most likely because on the northern part of Lake Kalimanci, the Kamenica River enters and it has a strong stream all the way to the second profile. Between the second and third profiles the energy of the Kamenica River decreases, so this is the place where most tailings material from Sasa discharged in 2003. The content of elements decreases through Lake Kalimanci exactly like the stream of the Kamenica River leads: from north to south on the western part of the lake. From the sudden increase of toxic elements after the dam failure we can conclude that the pattern of metal enrichment is dominantly related to this accident and also, consequently, to geological weathering of ore deposits in the adjacent area.

The calculated EF values define the anthropogenic origins of Ag, As, Cd, Cu, Pb, Sb, and Zn, and natural influence of Mo values in the sediment samples. The EF values for the surficial sediment samples from 2007 are much higher than the EF values from 2001 for all toxic elements. This signifies a strong anthropogenic impact on the investigated surficial sediments from Lake Kalimanci. Much the same results were revealed in the calculated I_{geo}. Considering both environmental indexes, we can conclude that surficial sediments from Lake Kalimanci are contaminated with most of the analyzed heavy metals and metalloids.

Even though all examined elements are serving as important micronutrients for living organisms, they can be very toxic when they are present in lake sediments at such high concentrations. Due to this research, a lot of work needs to be done in this area, so that the circumstances for living organisms, especially people who live there, can improve.

Acknowledgements

Our research was financially supported by the Slovenian Research Agency (ARRS), contract No. 1000-09-310079.

References

1. OCHIENG E.Z., LALAH Ć. S. O. Analysis of Heavy Metals in Water and Surface Sediment in Five Rift Valley Lakes in Kenya for Assessment of Recent Increase in Anthropogenic Activities Wandiga Bull Environmental Contamination and Toxicology, doi: 10.1007/s00128-007-9286-4. **2007**.
2. RUZHONG L., KUN S., YUEYING L., YONG S. Assessment of heavy metal pollution in estuarine surface sediments of Tangxi River in Chaohu Lake Basin. Chinese Geographical Science, **20**, (1), doi: 10.1007/s11769-010-0009-0. **2010**.
3. National Environemnt Protection Council (South Australia) Act **1995**.
4. DAVIES M. P., MARTIN T. E. Upstream constructed tailings dams – A review of the basics. Tailings and Mine Waste 00. Colorado, USA, A.A. Balkema, Rotterdam, pp. 3-15, **2000**.
5. DIEHL P. World Information Service on Energy (WISE) Uranium project [online]. Available from: http://www.antenna.nl/wise/uranium/ **2001**.
6. GRIMALT J. O., FERRER M., MACPHERSON, E. The mine tailing accident in Aznalcollar. Sci. Total Environ., **242**, 3, **1999**.
7. ROGAN ŠMUC N., VRHOVNIK P., DOLENEC T., SERAFIMOVSKI T., TASEV G., DOLENEC M. Assessement of the heavy metal contamination in the surficial sediments of Lake Kalimanci (Macedonia): a preliminary study. RMZ – Materials and Geoenvironment, **56**, (4), 437, **2009**.
8. MOHAN M., DEEPA M., RAMASAMY E.V. THOMAS A.P. Accumolation of mercury and other heavy metals in edible fishes of Cochin backwaters, Southwest India. Environ. Monit. Assess., **184**, 4233, **2012**.
9. MALTBY L. The use of the physiological energetics of Gammarus pulex to assess toxicity: a study using artificial streams. Environ. Toxicol. Chem., **11**, 79, **1992**.
10. DUMURDZANOV N., SERAFIMOVSKI T., BURCHFIEL B. C. Evolution of the Neogene-Pleistocene basins of Macedonia: Geological Society of America Digital Map and Chart Series 1 (accompanyingnotes), pp. 20, **2004**.
11. VRHOVNIK P., ROGAN ŠMUC N., DOLENEC T., SERAFIMOVSKI T., TASEV G., DOLENEC, M. Geochemical investigation of Sasa Tailing dam material and its influence on the Lake Kalimanci surficial sediments (Republic of Macedonia) – preliminary study. Geologija, **54**, (2), 169, **2011**.
12. ABUBAKR M. I. Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast. Microchem J., **90**, (2), 159, **2008**.
13. TAYLOR S. R., MCLENNAN S. M. The geochemical evolution of the continental crust. Rev. Geophys., **33**, (2), 241, **1995**.
14. BIRTH G. A scheme for assessing human impacts on coastal aquatic environments using sediments. In: Woodcoffe C.D., Furness R.A. (Eds.), Coastal GIS 2003. Wollongong University Papers in Center for Marinetime Plicy, Australia, **2003**.

15. MÜLLER G. Index of geoaccumulation in sediments of the Rhine River. Geojurnal, **2**, (1), 108 (vol. **21**). Springer-Verlag, Berlin. pp. 107-109, **1969**.
16. CHEN C. W., KAO C. M., CHEN C. F., DONG C.D. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere, **66**, (8), 1431-40. Epub 2006 Nov 17, **2007**.
17. WEDEPOHL K.H. The composition of the continental crust. Geochim. Cosmochim. Ac., **59**, 1217, **1995**.
18. SERAFIMOVSKI T., DOLENEC T., TASEV G. New data concerning the major ore minerals and sulphosalts from the Pb-Zn Zletovo Mine, Macedonia. RMZ, Materials and Geoenvironment, **52**, (3), 535, **2006**.
19. ZHANG X., YANG L., LI Y., LI H., WANG W., YE B. Imapcts of lead/zincmining and smelting on the environment and human health in China. Environ. Monit. Assess., **184**, 2261, **2012**.
20. MULLIGAN C., FUKUE M., SATO Y. Sediments contamination and sustainable Remediation. Boca Raton; London: CRC Press, Taylor & Francis Group: IWA Pub. pp. 305, **2010**.
21. SMITH K.S. Metal sorption on mineral surfaces: An overview with examples relating to mineral deposits. In The Environmental Geochemistry of Mineral Deposits. Part B: Case Studies and Research Topics. Vol. 6B, Chapter 7. Filipek L., Plumlee G. (Eds). Reviews in Economic Geology. Society of Economic Geologists, Inc., Chelsea, MI. pp. 161-182, **1999**.
22. DE VOS W., TARVAINEN T. (Chief-editors). Geochemical atlas of Europe. Part 2, Interpretation of geochemical maps, additional tables, figures, maps, and related publications. Espoo : Geological Survey of Finland, pp. 690, **2006**.
23. AKSENTIJEVIĆ S., KIURSKI J., VUČINIĆ VASIĆ M. Arsenic distribution in water/sediment system of Sevojno. Environ. Monit. Assess., **184**, 335, **2012**.
24. REIMANN C., SIEWERS U., TARVAINEN T., BITYUKOVA L., ERIKSSON J., GILUCIS A., GREGORAUSKINE V., LUKASHEV V.K., MATINIAN N.N., PASIECZNA A. Agricultural soils in Northern Europe: A Geochemical Atlas. E Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, pp. 279, **2003**.
25. NARIAGU J. O. Sulfur metabolism and sedimentary environment: Lake Mendota, Wisconson. Limnol. Oceanogr., **23**, 53, **1968**.
26. ZHANG J. L., LIU C. L. Riverine composition and estuarine geochemistry of particulate metals in China – Weathering features, anthropogenic impact and chemical fluxes. Estuar. Coast. Shelf S., **54**, 1051, **2002**.
27. MÜLLER G. The heavy metal pollution of the sediments of Neckars and its tributary: A stocktaking. Chem. Zeit., **105**, 157, **1981**.
28. GHREFAT H.A., ABU-RUKAH Y., ROSEN M.A. Application of geoaccumolation index and enrichment factor for assessing metal contamination in the sediments of Kafarin Dam, Jordan. Environ. Monit. Assess., **178**, 95, **2011**.
29. AUGUSTSSON A., PELTOLA P., BERGBÄCK B., SAARINEN T., HALTIA-HOVI E. Trace metal and geochemical variability during 5,500 years in the sediment of Lake Lehmilampi, Finland. J. Paleolimnol, **44**, 1025, **2010**.
30. SHUMILIN E., GORDEV V., RODRÍGUEZ-FIGUEROA G., DEMINA L., CHOUMILINE K. Assessement of Geochemical Mobility of Metals in Surface Sediments of the Santa Rosalia Mining Region, Western Gulf of California. Arch. Environ. Con. Tox., **60**, 8, **2011**.
31. TAYLOR H.E., ANTWEILER R.C., ROTH D.A., ALPERS C.N., DILEANIS P. Selected Trace Elements in the Sacramento River, California: Occurrence and Distribution. Arch Environ Con. Tox., **62**, 557, **2012**.