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ORIGINAL ARTICLE

An evaluation of trace metal distribution and environmental risk in sediments from the Lake Kalimanci (FYR Macedonia)

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Abstract Pollution from mining activities is a significant problem in several parts of the Republic of Macedonia. A geochemical study of the surficial sediments of Lake Kalimanci in the eastern part of the Republic of Macedonia was carried out to determine their elemental compositions and to evaluate the pollution status of lake sediments by employing an enrichment factor (EF). The major and trace 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 144.4–1,162 mg kg^{-1}, Pb 1,874–16,300 mg kg^{-1}, Zn 2,944–20,900 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}. The EF ranged within 0.12–590.3. Among which, Cd, Pb, Zn and As have extremely severe enrichment. The data indicate that trace elements had extremely high concentrations in Lake Kalimanci surficial sediments owing to the anthropogenic addition of contaminants.

Keywords Metal contamination · Lake sediment · Enrichment factor · Lake Kalimanci

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Introduction

Major and trace elements are necessary micronutrients 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 trace metals 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 trace metal 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).

Lakes are important sedimentological environments. They are usually very calm only when a river enters into lake the section area become rough. After the flow velocity of the running water is reduced, particles suspended in the water end up in a much calmer environment where they can settle down. Thus, sediments are important sinks for various pollutants such as heavy metals (Ho et al. 2003; Ikem et al. 2003) and also play a very useful role in the assessment of heavy metal contamination (Gangaiya et al. 2001). In general, high levels of contaminants have, as mentioned before, an anthropogenic origin, and their distribution and accumulation are influenced by sediment texture, mineralogical composition, reduction/oxidation state, adsorption and desorption processes, as well as their physical transport (Manahan 2000; Buccolieri et al. 2006). Most of the heavy metals in the fluvial environment are bound to fine-grained solid particles, which are transported as a suspended load and deposited as contaminated sediments along watercourses (Förstner 2004).

Trace metal studies have been mostly researched in deep lakes with a permanent anoxic deep layer (Seyler and Martin 1989; Viollier et al. 1995; Mogollon et al. 1996; Brown et al. 2000; Widerlund et al. 2002). These studies provide a basis for the examination of changes of lake sediments under redox conditions. Changes in sediment oxidation/reduction state and pH influence the solubility of metals (Miao et al. 2006). Some elements are mobilized under reducing conditions, but they form insoluble oxyhydroxides in oxic environments (e.g. Fe and Mn) or are adsorbed onto surfaces of such hydroxides (e.g. V and Co; Heggie and Lewis 1984). On the other hand, some elements tend to be more soluble under oxic conditions owing to greater particle reactivity in a reduced valence state or through the formation of insoluble sulphides in reducing sediments (Klinkhammer and Palmer 1991; Crusius et al. 1996; Rosentahl et al. 1995).

However, trace metals are natural constituents of lake waters and sediments, but they occur in low concentrations. The swift expansion of human activities has sped up the environmental pollution with heavy metals—in particular, mining activities. Several studies all over the world have evaluated trace concentrations in lake sediments as highly toxic and potentially dangerous for the surrounding ecosystem (Adams et al. 1992; Burton and Scot 1992; Aysegül et al. 2010; Tylmann et al. 2011). Such studies are very rare in the Republic of Macedonia, which is why the present study was conducted to determine the total concentrations of major and trace elements in Lake Kalimanci's surficial sediments, in the vicinity of the Sasa lead–zinc (Pb–Zn) mine.

Materials and methods

Study area

Lake Kalimanci is located in the east of the Republic of Macedonia (Fig. 1). It is an artificial lake, with its longest length 4 km and greatest width 0.3 km, and lake a maximum depth of 80 m (Fig. 2). The surface area of the lake is

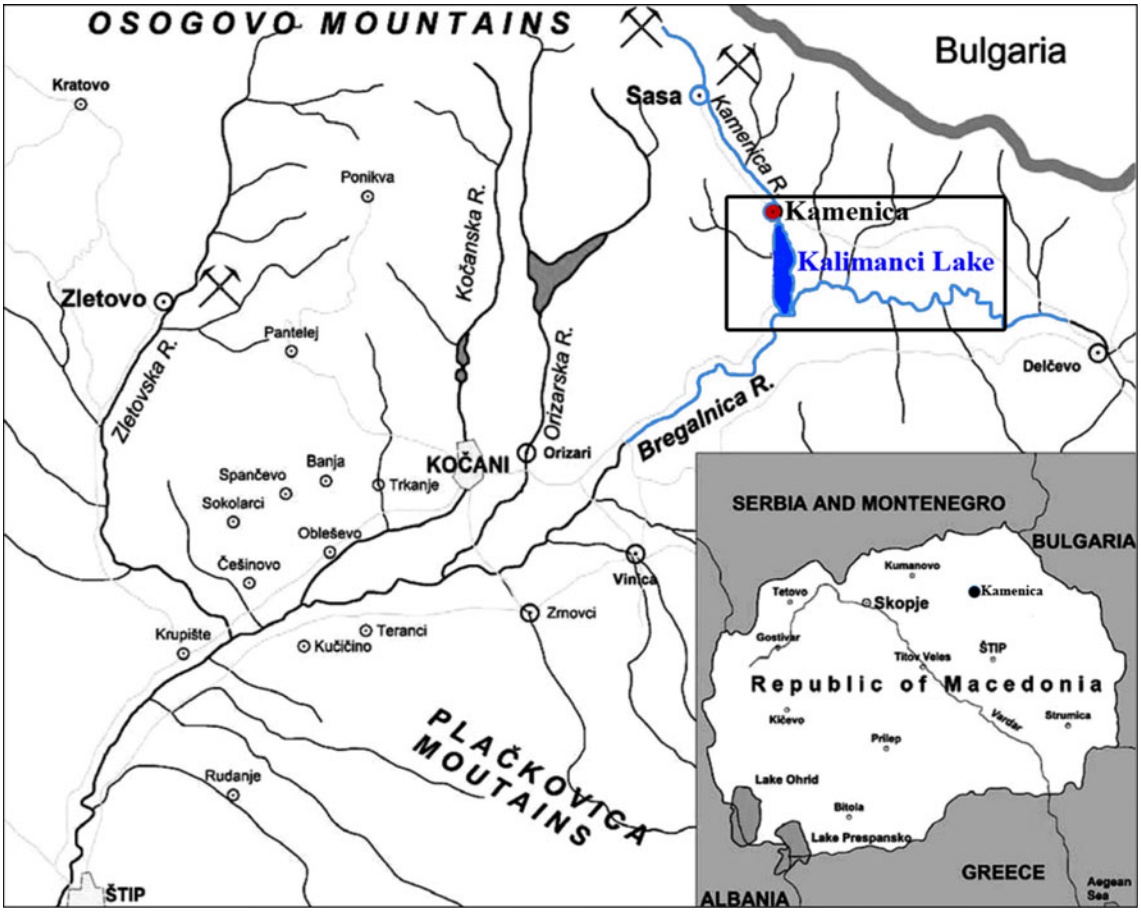

Fig. 1 Map of the study area. *Blue colour* indicates Rivers

4.23 km^2 and it accumulates approximately 127 million m^3 of water. The basic purpose of Lake Kalimanci is to irrigate about 30,000 ha, mainly rice fields in Kočani valley and Ovce Pole. The lake has two channels, the left is 36-km long and it irrigates Kočani field and the right is 98-km long and carries water to Ovce Pole. Lake Kalimanci is on the eastern side surrounded by uncultivated ground with no industry or households. Meanwhile, in the western part, a main road runs parallel to the lake and serves as the main connection between the agriculturally important Kočani Field, Sasa Mine and the Bulgarian border (Fig. 1). In the northern part, the River Kamenica enters the lake, and nearby on the northeast side lies the city of Makedonaska Kamenica. Approximately 5,000 people live in the city centre and another 3,000 in the surrounding villages. The domestic sewage system is still not well developed, and therefore many households located directly along the lake side releases waste waters into the lake.

Lake Kalimanci is characterized by large changes in water level. Sometimes during the dry season, the water level decreases by a few centimetres in the inner (deeper) parts of the lake. So, the surficial lake sediments are exposed to oxic conditions. In winter and spring, the maximum depth of the lake reaches up to 80 m with the exception of the northern margin of the lake, where the Kamenica River enters. This part is very shallow and swampy; consequently, there are the greatest contents of the Sasa tailings dam material here.

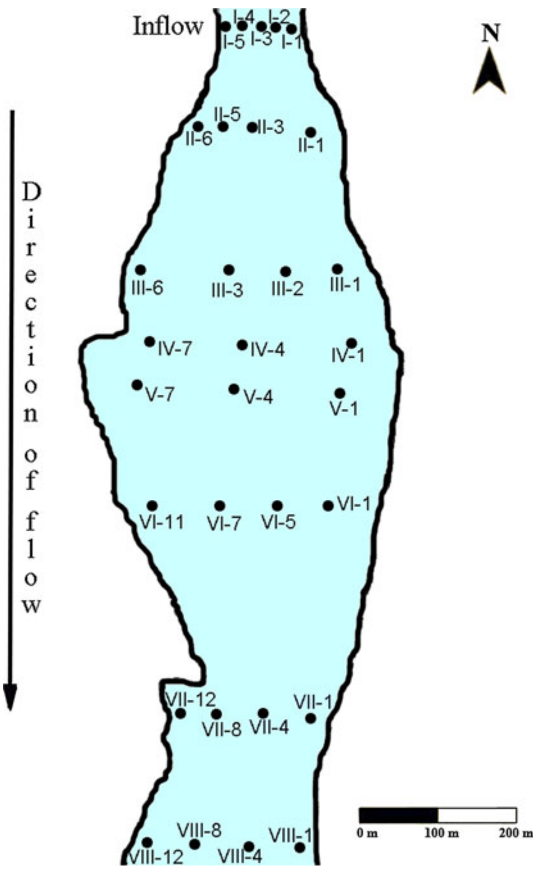

Fig. 2 Sampling locations on Lake Kalimanci

The Lake Kalimanci surface sediment samples represent fine-grained, predominantly clay and silt-sized lake sediment (>0.0063 mm) deposited after the construction of the artificial dam. Lake sediments generally reflect the mineralogical composition and the presence of ore in surrounding area and bedrocks. According to Pivko (2004), the lake sediments' main mineral phases are quartz, plagioclases, K feldspars and clay minerals and Lake Kalimanci occasionally also contains hornblende, pyrite, dolomite, smithsonite and diaspor, as well as authigenic minerals goethite, hematite and pyrite.

The Sasa Pb–Zn mine is located approximately 12-km north of Lake Kalimanci. The Sasa mine and Lake Kalimanci are connected by the Kamenica River (Fig. 1). Since 1954, exploitation of the Sasa Mine Pb–Zn deposit has caused the surrounding area, including Lake Kalimanci to become polluted with suspended substances (Vrhovnik et al. 2011b). The Sasa mine is located at an altitude of 2,000 m in the Osgovo Mountains, near the small town of Makedonska Kamenica north of the Lake Kalimanci in eastern Macedonia (Fig. 1). This area is part of the Serbo-Macedonian Massif and comprises highly metamorphic rocks containing gneiss, micas, amphibolites ilvaite skarns and schists. Typical mineral assemblage around the Sasa Mine area is represented by ore minerals: pyrite, galena, sphlareite, sometimes chalcopyrite and traces of cerussite, anglesite and malachite (Tasev et al. 2005). The tailings material from the Sasa mine is located between the Sasa mine and Lake Kalimanci, near the Kamenica River. Therefore, there is a severe threat of trace metal pollution in the surrounding area and further downstream, towards both the river and the lake. Sasa tailings material contains ground minerals (fraction under 0.315 mm) from the surrounding rocks and the residue from flotation processes (Vrhovnik et al. 2011a, b) as well as quartz, calcite, mica, cordierite, epidote, clinochlore, sphalerite, clinopyroxene, pyrite, magnetite, galena, hematite and chlorite (Vrhovnik et al. 2010, 2011a, 2012a). Surficial Sasa tailings dam material (from dam no. 4—which has been in use recently) contains on average (mg kg^{-1}): Mo 2.9, Cu 279, Pb 3,975, Zn 5,320, Ni 30, As 69, Cd 84, Sb 4.2 and Ag 4.1 (Vrhovnik et al. 2011a). In 2003, a major environmental disaster happened in the eastern Republic of Macedonia, when part of the Sasa mine tailings dam (dam no. 3 and part of no. 4) collapsed and caused an intensive flow of tailings material through the Kamenica River valley. Between 70,000 and 100,000 m^3 of tailings material was discharged into Lake Kalimanci (Rogan Šmuc et al. 2009).

Sampling and analysis

Thirty-one surficial sediment samples from Lake Kalimanci were taken in September 2007, when the lake had almost dried up because of high water consumption for irrigation in nearby Kočani field. Two days before sampling, the rest of the water was released from the artificial lake, when the dam was opened for repair, before winter. Sampling locations were arranged throughout the lake as shown in Fig. 2. The selected sampling points were located in areas of 10 × 10 m^2. The samples were collected using 10-cm long plastic corers with 10-cm internal diameter. They were than packed into plastic bags and stored in the laboratory at 4 °C. The collected lake sediment samples were dried at 50 °C for 48 h, sieved through a 0.315-mm polyethylene sieve to remove plant debris and homogenized using mechanical agate grinder to a fine powder (<63 μm) for subsequent geochemical analysis. The measured pH in lake sediments ranged from 5.5 to 7.5.

The chemical analyses were obtained at the commercial ACME Laboratories in Vancuver, Canada. Determination of abundances required 0.5 g of sampled material and were thereupon leached in hot (95 °C) Aqua Regia and afterwards conducted by ICP Mass Spectrometry. The quality of the analyses was monitored by comparison to 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 and VIII-1). Repeated analyses of different sample aliquots indicated a relative standard deviation ± 5 %.

Basic statistical analyses were performed by the Statistica 8 software. Pearson multiple correlation analysis was also applied to assess major- and trace element associations and metal origins. Pearson correlation analysis was carried out for the whole data set of element concentrations in the surface sediment of Lake Kalimanci.

Spatial distribution was carried out by means of Golden Software Surfer 8.

Enrichment factor

Potential contamination with heavy metals in the environment can be assessed by means of enrichment factors (EFs) (Sinex and Helz 1981). It is a good tool to differentiate the metal sources between anthropogenic ones and those occurring naturally (Nolting et al. 1999; Rubio et al. 2000). The concept of enrichment factor was developed in the 1970s to evaluate the anthropogenic contribution and is expressed with:

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

The numerator stands for the ratio of the concentration of the examined element to the reference element in a sample.

Table 1 Assessment criteria suggested by Birth (2003)

$\mathrm{EF} < 1$	Indicated no enrichment
$1 < \mathrm{EF} < 3$	Minor enrichment
$3 < \mathrm{EF} < 5$	Moderate enrichment
$5 < \mathrm{EF} < 10$	Moderately severe enrichment
$10 < \mathrm{EF} < 25$	Severe enrichment
$25 < \mathrm{EF} < 50$	Very severe enrichment
$\mathrm{EF} > 50$	Extremely severe enrichment

The denominator represents the ratio of the concentration of the examined element to the reference element in a reference material (Abubakr 2008). The reference element in our study was aluminium because ratios between metal and aluminium are widely adopted supposedly because the concentration of Al in weathering products and their parent materials are generally comparable (Rogan Šmuc et al. 2009). In addition, Al is the normalizing element assumed not to be enriched owning to local contamination. Baseline values for $\mathrm{M}_{\mathrm{crust}}$ reference material were adopted from Taylor and McLennan (1995). The enrichment factor values are interpreted as the levels of heavy metal pollution that were suggested by Birth (2003) and the assessment criteria are generally based on the EF values (Table 1).

Results and discussion

Statistics

The lack of a positive correlation of Si with most of the elements, except Na ($r = 0.862$, $p = 0.000$) and Ti ($r = 0.494$, $p = 0.005$), suggests no preferred association of Si with other elements. Si has a highly significant negative correlation with other major elements ($-0.41 \leq r \geq -0.88$; $0.000 \leq p \geq 0.021$) and the same correlation with the remaining trace elements ($-0.42 \leq r \geq -0.87$; $0.000 \leq p \geq 0.036$). It is also important to expose highly positive correlations of Mg ($0.44 \leq r \geq 0.89$; $0.000 \leq p \geq 0.007$) and Ca ($0.49 \leq r \geq 0.77$; $0.000 \leq p \geq 0.007$) with P, Mn, Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi and Ag. It can be explained that they are bound on ore deposition in ilvaite skarns and have no connection with the carbonate fraction. A significantly high correlation coefficient between K and Al ($r = 0.92$; $p = 0.000$) suggests that these two elements may have similar input sources and/or they have a close association, predominantly in K-feldspars and illite-muscovite assemblages of the lake sediments. Also, as the Pearson correlation matrix shows that there is a significantly high correlation between Fe and Mn ($r = 0.89$; $p = 0.000$), this could be the matter of Mn–Fe oxides in the surficial Lake Kalimanci sediments on which presumably most of trace elements could be bounded. Table 2 shows the strong positive correlation coefficients between the following trace elements Mo, Cu, Pb, Zn, Ni, Cd, Sb, Bi and Ag. These presumably originate from the Pb–Zn ore deposit from imminent Osogovo mountains or/and from the Sasa mine tailings dam (Serafimovski and Aleksandrov 1995). Arsenicum is an exception among trace elements, as it has no correlation within this group, but is strongly correlated with the majority of major elements. Its origin is probably from the bed rocks of the surrounding area without any connection to the Sasa mine. The same explanation can be given for Co and Ga, which are also better correlated with major elements Fig. 3.

Geochemistry

Major and trace metal contents of the lake sediment samples are shown in Table 3.

Major elements concentrations in surficial lake sediments

Nearly 80 % of the macrochemical components account for Si–Al–Fe assemblage in terms of the present major elements in the surficial Lake Kalimanci sediments. This compositional relationship reflects a relatively high proportion of quartz, feldspars and chlorite in surficial lake sediments which was also suggested by X-ray Diffraction (XRD) analysis in previous research (Pivko 2004; Vrhovnik et al. 2010). The aforementioned minerals are mostly associated with the acidic to intermediate igneous rocks of the Osogovo Mountains (Serafimovski and Aleksandrov 1995; Stojanov et al. 1995). The absence of carbonate minerals nearby is reflected in the low Ca and Mg contents (approximately 10 % of all components), which could be related to the presence of feldspars, chlorite and pyroxenes. The Na and K concentrations (~7 % of all components) are most likely related to the feldspar illite-muscovite content and the presence of amphiboles (hornblende). Relatively high concentration values of Mn (1,780–13,300 mg kg^{-1} range) are possibly a result of oxic conditions during sampling or the low surface area of bottom sediments in some sampling points.

Trace element concentrations in surficial lake sediments

In this research, the concentrations of trace elements in the surficial lake sediments were compared with average crustal contents (Taylor and McLennan 1995), the UK Ministry of Agriculture, Fisheries and Food (MAFF) (1998) Action Levels, the US Environmental Protection Agency (EPA) (1997) Threshold levels for sediment contaminated with heavy metals and with other studies (Pradit et al. 2010; Tylmann et al. 2011; López et al. 2010; Rognerud and Fjeld 2001).

Cobalt Native cobalt does not occur in high amounts in nature. Its average crystal content is 10 mg kg^{-1}. Rarely some cobalt can be found in granitic and metamorphic rocks (Wedepohl 1995), which are also the background rocks of the area around Lake Kalimanci. Reasons for such high amounts (11.7–27.7 mg kg^{-1}) of cobalt are the different ore deposits in the nearby area (Sasa-Toranica, Zletovo-Kratovo). Tailings disposal is discharged into the Kamenica River, which flows into Lake Kalimanci, where cobalt is easily solubilised.

Gallium Gallium is a widespread element in the natural environment. Its average occurrence in the crust is approximately 17 mg kg^{-1} (Taylor and McLennan 1995). The gallium concentrations in Lake Kalimanci's surface sediments ranged from 15 to 26.3 mg kg^{-1} dry weight, compared with the concentrations (Table 4) in Norwegian lakes (Rognerud and Fjeld 2001), and the content of gallium is up to 4 times higher in Lake Kalimanci. Notwithstanding that both lakes are located in magmatic to metamorphic rock background, presumably the enhancement of gallium is connected with the nearby lead–zinc ore deposit.

Molybdenum Molybdenum concentrations in the major rock-firming silicates and quartz are approximately 1 mg kg^{-1} in the crust, and measured content of molybdenum in surficial lake sediments is ranged from 1 to 4.6 mg kg^{-1}. Molybdenum occur naturally in oxidation states and is most stable under oxidizing conditions, otherwise it is expected to be found in sulphide species molybdenite (MoS_2) which is a common ore mineral and was also detected with XRD analysis in our previous research (Vrhovnik et al. 2010). Wedepohl (1978) explains that Mo can be coprecipitated with fine-grained sulphides such as FeS, ZnS, PbS and CuS, and all these minerals were also detected with XRD analysis. High concentrations of Mo can be also explained with pegmatite and pneumatolytic deposits in the vicinity of the Lake Kalimanci, which were changed by pneumatolitic and hydrothermal activity (Serafimovski and Aleksandrov 1995). Cook (2000) explains that molybdenum could be transported to lake basins with surface waters prior to complexing by organic-rich sediments. In his research in Central British Columbia, Cook (2000) found concentrations of molybdenum with much higher (median values ranged within 8–42 mg kg^{-1}) due to adjacent quartz-molybdenite veins and their remnants in soil and till.

Copper High amounts of copper in sulphide minerals often occur together with sphalerite and galenite minerals, while high amounts of copper minerals in the Sasa ore district were found (Serafimovski et al. 2006). Therefore,

Table 2 Pearson correlation coefficients for elements in surface lake sediments

Element	Si	Al	Fe	Mg	Ca	Na	K	Ti	P	Mn	Co
Si	1.000										
Al	−0.279 ($p = 0.129$)	1.000									
Fe	**−0.414** ($p = 0.021$)	**−0.439** ($p = 0.013$)	1.000								
Mg	**−0.845** ($p = 0.000$)	−0.035 ($p = 0.852$)	**0.493** ($p = 0.005$)	1.000							
Ca	**−0.710** ($p = 0.000$)	**−0.446** ($p = 0.012$)	**0.678** ($p = 0.000$)	**0.805** ($p = 0.000$)	1.000						
Na	**0.862** ($p = 0.000$)	0.021 ($p = 0.909$)	**−0.741** ($p = 0.000$)	**−0.766** ($p = 0.000$)	**−0.794** ($p = 0.000$)	1.000					
K	−0.175 ($p = 0.346$)	**0.915** ($p = 0.000$)	**−0.566** ($p = 0.001$)	0.007 ($p = 0.971$)	**−0.474** ($p = 0.007$)	0.191 ($p = 0.304$)	1.000				
Ti	**0.494** ($p = 0.005$)	**0.454** (0.010)	**−0.522** ($p = 0.003$)	**−0.591** ($p = 0.000$)	**−0.773** ($p = 0.000$)	**0.707** ($p = 0.000$)	**0.458** ($p = 0.010$)	1.000			
P	**−0.884** ($p = 0.000$)	−0.061 ($p = 0.746$)	**0.563** ($p = 0.001$)	**0.900** ($p = 0.000$)	**0.815** ($p = 0.000$)	**−0.888** ($p = 0.000$)	−0.104 ($p = 0.578$)	**−0.708** ($p = 0.000$)	1.000		
Mn	**−0.504** ($p = 0.004$)	**−0.401** ($p = 0.025$)	**0.894** ($p = 0.000$)	**0.640** ($p = 0.000$)	**0.725** ($p = 0.000$)	**−0.782** ($p = 0.000$)	**−0.463** ($p = 0.009$)	**−0.656** ($p = 0.000$)	**0.697** ($p = 0.000$)	1.000	
Co	**−0.805** ($p = 0.000$)	**0.522** ($p = 0.003$)	0.148 ($p = 0.428$)	**0.472** ($p = 0.007$)	0.305 ($p = 0.095$)	**−0.642** ($p = 0.000$)	0.335 ($p = 0.66$)	−0.231 ($p = 0.212$)	**0.583** ($p = 0.001$)	0.233 ($p = 0.207$)	1.000
Ga	**−0.688** ($p = 0.000$)	**0.800** ($p = 0.000$)	0.047 ($p = 0.803$)	**0.455** ($p = 0.010$)	0.070 ($p = 0.709$)	**−0.476** ($p = 0.007$)	**0.686** ($p = 0.000$)	0.075 ($p = 0.690$)	**0.426** ($p = 0.017$)	0.108 ($p = 0.565$)	**0.702** ($p = 0.000$)
Mo	**−0.556** ($p = 0.001$)	−0.121 ($p = 0.518$)	0.206 ($p = 0.267$)	**0.824** ($p = 0.000$)	**0.596** ($p = 0.000$)	**−0.414** ($p = 0.021$)	0.087 ($p = 0.641$)	**−0.486** ($p = 0.006$)	**0.661** ($p = 0.000$)	**0.379** ($p = 0.036$)	0.186 ($p = 0.315$)
Cu	**−0.597** ($p = 0.000$)	−0.070 ($p = 0.709$)	−0.022 ($p = 0.908$)	**0.749** ($p = 0.000$)	**0.591** ($p = 0.000$)	**−0.381** ($p = 0.035$)	0.085 ($p = 651$)	**−0.538** ($p = 0.002$)	**0.642** ($p = 0.000$)	0.160 ($p = 0.389$)	0.334 ($p = 0.066$)
Pb	**−0.620** ($p = 0.000$)	−0.174 ($p = 0.351$)	0.153 ($p = 0.410$)	**0.840** ($p = 0.000$)	**0.704** ($p = 0.000$)	**−0.475** ($p = 0.007$)	−0.024 ($p = 0.898$)	**−0.592** ($p = 0.000$)	**0.720** ($p = 0.000$)	0.322 ($p = 0.077$)	0.250 ($p = 0.175$)
Zn	**−0.694** ($p = 0.000$)	−0.008 ($p = 0.966$)	0.010 ($p = 0.956$)	**0.772** ($p = 0.000$)	**0.615** ($p = 0.000$)	**−0.459** ($p = 0.009$)	0.100 ($p = 0.591$)	**−0.530** ($p = 0.002$)	**0.705** ($p = 0.000$)	0.194 ($p = 0.296$)	**0.488** ($p = 0.005$)
Ni	**−0.870** ($p = 0.000$)	0.243 ($p = 0.187$)	0.208 ($p = 0.260$)	**0.757** ($p = 0.000$)	**0.566** ($p = 0.001$)	**−0.720** ($p = 0.000$)	0.172 ($p = 0.355$)	**−0.521** ($p = 0.003$)	**0.794** ($p = 0.000$)	0.350 ($p = 0.054$)	**0.841** ($p = 0.000$)
As	−0.258 ($p = 0.162$)	**−0.463** ($p = 0.009$)	**0.784** ($p = 0.000$)	**0.439** ($p = 0.013$)	**0.486** ($p = 0.006$)	**−0.468** ($p = 0.008$)	**−0.511** ($p = 0.003$)	−0.307 ($p = 0.093$)	**0.470** ($p = 0.008$)	**0.716** ($p = 0.000$)	0.091 ($p = 0.628$)
Cd	**−0.674** ($p = 0.000$)	−0.027 ($p = 0.844$)	0.036 ($p = 0.849$)	**0.781** ($p = 0.000$)	**0.613** ($p = 0.000$)	**−0.441** ($p = 0.013$)	0.108 ($p = 0.564$)	**−0.511** ($p = 0.003$)	**0.679** ($p = 0.000$)	0.227 $p = 0.219$)	**0.476** ($p = 0.007$)
Sb	**−0.419** ($p = 0.019$)	**−0.468** ($p = 0.008$)	**0.395** ($p = 0.028$)	**0.771** ($p = 0.000$)	**0.727** ($p = 0.000$)	**−0.424** ($p = 0.017$)	−0.291 ($p = 0.112$)	**−0.623** ($p = 0.000$)	**0.610** ($p = 0.000$)	**0.523** ($p = 0.003$)	0.044 ($p = 0.816$)

Table 2 continued

Element	Si	Al	Fe	Mg	Ca	Na	K	Ti	P	Mn	Co
Bi	**−0.663** ($p = 0.000$)	−0.219 ($p = 0.236$)	0.319 ($p = 0.080$)	**0.890** ($p = 0.000$)	**0.771** ($p = 0.000$)	**−0.583** ($p = 0.001$)	−0.112 ($p = 0.548$)	**−0.643** ($p = 0.000$)	**0.785** ($p = 0.000$)	**0.485** ($p = 0.006$)	0.294 ($p = 0.108$)
Ag	**−0.565** ($p = 0.001$)	−0.179 ($p = 0.334$)	0.058 ($p = 0.757$)	**0.764** ($p = 0.000$)	**0.659** ($p = 0.000$)	**−0.403** ($p = 0.025$)	−0.024 ($p = 0.896$)	**−0.582** ($p = 0.001$)	**0.649** ($p = 0.000$)	0.231 ($p = 0.211$)	0.241 ($p = 0.192$)

Element	Ga	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Ag
Si											
Al											
Fe											
Mg											
Ca											
Na											
K											
Ti											
P											
Mn											
Co											
Ga	1.000										
Mo	0.206 ($p = 0.267$)	1.000									
Cu	0.201 ($p = 0.279$)	**0.826** ($p = 0.000$)	1.000								
Pb	0.189 ($p = 0.309$)	**0.899** ($p = 0.000$)	**0.961** ($p = 0.000$)	1.000							
Zn	0.267 ($p = 0.146$)	**0.824** ($p = 0.000$)	**0.967** ($p = 0.000$)	**0.928** ($p = 0.000$)	1.000						
Ni	**0.558** ($p = 0.001$)	**0.576** ($p = 0.001$)	**0.740** ($p = 0.000$)	**0.687** ($p = 0.000$)	**0.830** ($p = 0.000$)	1.000					
As	−0.081 ($p = 0.664$)	0.298 ($p = 0.104$)	0.027 ($p = 0.884$)	0.171 ($p = 0.358$)	0.085 ($p = 0.650$)	0.195 ($p = 0.294$)	1.000				
Cd	0.266 ($p = 0.147$)	**0.839** ($p = 0.000$)	**0.959** ($p = 0.000$)	**0.920** ($p = 0.000$)	**0.985** ($p = 0.000$)	**0.813** ($p = 0.000$)	0.127 ($p = 0.496$)	1.000			
Sb	−0.048 ($p = 0.798$)	**0.855** ($p = 0.000$)	**0.773** ($p = 0.000$)	**0.868** ($p = 0.000$)	**0.721** ($p = 0.000$)	**0.476** ($p = 0.007$)	**0.491** ($p = 0.005$)	**0.766** ($p = 0.000$)	1.000		
Bi	0.209 ($p = 0.260$)	**0.897** ($p = 0.000$)	**0.881** ($p = 0.000$)	**0.956** ($p = 0.000$)	**0.876** ($p = 0.000$)	**0.697** ($p = 0.000$)	0.341 ($p = 0.061$)	**0.871** ($p = 0.000$)	**0.895** ($p = 0.000$)	1.000	
Ag	0.134 ($p = 0.472$)	**0.828** ($p = 0.000$)	**0.982** ($p = 0.000$)	**0.979** ($p = 0.000$)	**0.930** ($p = 0.000$)	**0.674** ($p = 0.000$)	0.067 ($p = 0.720$)	**0.922** ($p = 0.000$)	**0.826** ($p = 0.000$)	**0.917** ($p = 0.000$)	1.000

Bold numbers are significant

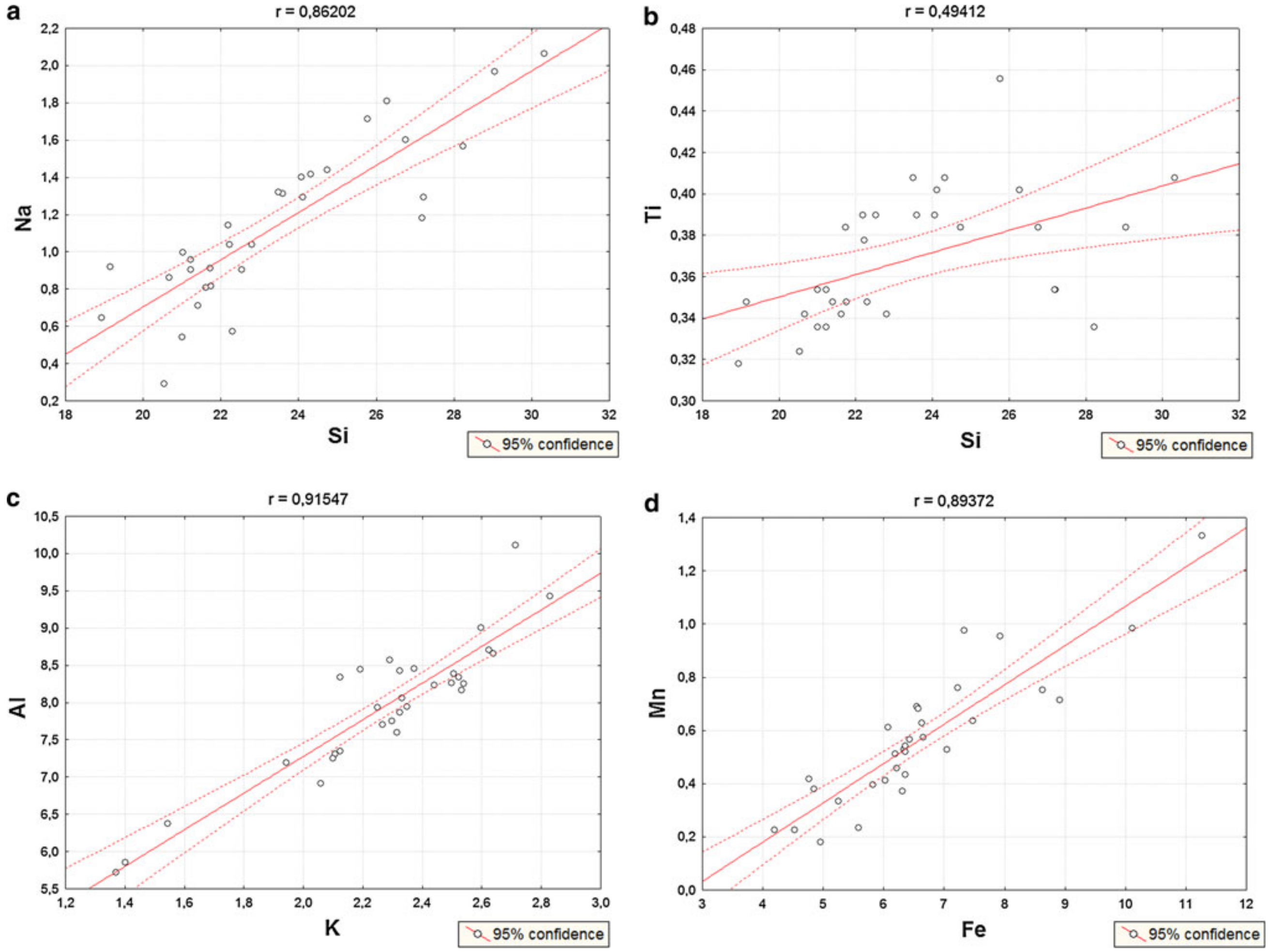

Fig. 3 Scatterplots of major elements with significantly high correlation

local and minor mobilization of copper into Lake Kalimanci is expected. This explains such high concentrations of copper in the lake sediments (144–1,161 mg kg^{-1}). Compared to other lake sediments in Table 4, Lake Kalimanci sediments have up to 15 times higher contents of copper due to the aforementioned Pb–Zn Sasa ore deposit. Also, the copper content in natural waters and their sediments is a result of the adsorption of copper on clay minerals and iron oxides (Wedepohl 1978). Regarding other investigations (Table 4), Lake Kalimanci surface sediments undoubtedly have the highest concentrations of copper.

Lead The main mineral of lead is galena and many other sulphide minerals. Galena near surface conditions can be easily mobilized, therefore has extremely high concentrations in the Lake Kalimanci surficial sediments, 1,873–16,300 mg kg^{-1}. Owing to Table 4, concentrations of lead are more than 40 times higher than in other investigated lakes. According to Langston (1990), uncontaminated sediments might be expected to contain <6 mg kg^{-1} Pb, and GESAMP (1985) also indicates that estuary sediments of polluted rivers typically show <10–50 mg kg^{-1} and up to 850 mg kg^{-1}.

Zinc According to Heide and Singer (1954), water which is highly polluted with zinc can cause contamination of river or lake sediments by adsorption on clay suspension at distance of about 15 km. Because of acid mine water from sulphide leaching, industrial wastes from flotation processes and also dust from the Sasa Mine 12 km away, high concentrations of zinc are found in the Lake Kalimanci sediments (2,944–20,900 mg kg^{-1}). According to our previous research, where XRD analysis of the surrounding area was done, we can conclude that chlorite and magnetite are the main zinc carriers (Vrhovnik et al. 2010). Oxidation of minor sphalerite proportions in certain rocks can cause local anomalies so the nearby Pb–Zn ore deposit is the main reason for the extremely high Zn content in Lake Kalimanci surficial sediment. Compared to other lakes in Table 4, Lake Kalimanci sediments have the greatest content of Zn.

Table 3 Descriptive basic statistics of the elemental contents of Lake Kalimanci sediments

Element	Mean	Min	Max	SD
Si (wt%)	23.47	18.94	30.32	2.902
Al (wt%)	7.95	5.72	10.11	0.931
Fe (wt%)	6.61	4.19	11.27	1.541
Mg (wt%)	1.35	0.74	2.21	0.345
Ca (wt%)	3.82	1.19	7.50	1.599
Na (wt%)	1.14	0.29	2.06	0.427
K (wt%)	2.28	1.37	2.83	0.346
Ti (wt%)	0.37	0.32	0.46	0.031
P (wt%)	0.16	0.09	0.23	0.038
Mn (wt%)	0.57	0.18	1.33	0.255
Co (mg/kg)	19.89	11.70	27.70	4.04
Ga (mg/kg)	21.13	15.00	26.30	2.46
Mo (mg/kg)	2.69	1.00	4.60	0.85
Cu (mg/kg)	415.1	144.4	1,162	233.5
Pb (mg/kg)	6,059	1,873	16,300	3,437
Zn (mg/kg)	8,420	2,944	20,900	4,309
Ni (mg/kg)	40.00	21.70	79.30	12.64
As (mg/kg)	67.69	27.90	128.2	16.54
Cd (mg/kg)	56.58	16.50	136.0	27.23
Sb (mg/kg)	1.77	0.60	3.60	0.71
Bi (mg/kg)	10.08	3.00	24.30	5.17
Ag (mg/kg)	5.58	1.40	17.30	3.93

Nickel Nickel often occurs together with cobalt, and like cobalt has no rock firming minerals (Wedepohl 1978). Nickel is usually associated with different metal ore deposits and in lower amounts is found in some major basaltic igneous rock units, originated under hydrothermal and metasomatic conditions. Olivine was determined by XRD analysis in our previous research (Vrhovnik et al. 2011a, b) and is a major host mineral of nickel. According to Wedepohl (1978), olivine can contain around 3 mg kg^{-1} so these high amounts of nickel (21–79 mg kg^{-1}) in Lake Kalimanci surficial sediments are due to Sasa ore deposits. Nickel is (like cobalt) easily mobilized during bedrock weathering. Compared to other studies (Table 4), the nickel content is not higher than the amount of other elements. The background basaltic rocks are probably the major source of nickel with some influence from the Sasa ore deposits.

Arsenic Measured arsenic concentrations are between 27 and 128 mg kg^{-1}. Lake sediments can accumulate a significant abundance of arsenic owing to its migration in anoxic ground waters (Subramanian et al. 1997). Such a high content of arsenic in oxic conditions (when Lake Kalimanci dried up for almost 3 months and the samples of surficial sediments were taken) indicates that when there are anoxic conditions in the lake bottom then the content of arsenic is even higher. Arsenic leaching from the Sasa tailings dam can be transported by the Kamenica River and contaminate lake sediments (Lackovic and Nikolaidis 1997). Compared to other investigations (Table 4), the amount of arsenic is incomparably higher in surficial sediments from Lake Kalimanci due to large amounts of magnetite from the Sasa ore deposit (Vrhovnik et al. 2010), which shows relatively high concentrations of arsenic.

Table 4 Trace metal concentrations in sediment samples from Lake Kalimanci and other study areas and guidelines (concentration unit is in mg kg^{-1})

Location	Co	Ga	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Ag
Lake Kalimanci	19.89	21.13	2.69	415.1	6,059	8,420	44.99	67.69	56.58	1.77	10.08	5.58
Average crustal[a]	10.00	17.00	1.50	25.00	20.00	71.00	20.00	1.50	0.10	0.20	0.12	0.05
Songkhla Lake[b]	13.05	/	/	84.00	146.0	539.0	38.00	25.00	2.50	/	/	/
Northeastern Polish Lakes[c]	/	/	/	48.60	80.50	306.0	36.10	/	0.90	/	/	/
Lake Hope[d]	20.30	/	/	22.50	17.30	129.0	39.55	/	0.39	/	0.74	/
Norwegian Lakes[e]	16.70	5.00	/	40.40	99.40	131.0	18.00	12.80	0.86	0.29	/	/
MAFF action kevels[f]	/	/	/	40.00	40.00	200.0	100.0	/	2.00	/	/	/
EPA treshold levels[g]	/	/	/	136.0	132.0	760.0	132.0	/	31.00	/	/	/

[a] Taylor and McLennan (1995)

[b] Pradit et al. (2010)

[c] Tylmann et al. (2011)

[d] López et al. (2010)

[e] Rognerud and Fjeld (2001)

[f] UK Ministry of Agriculture, Fisheries and Food (MAFF) Action Levels (1998)

[g] US Environmental Protection Agency (EPA) (1997)

Cadmium Cadmium usually replaces other elements in their minerals, most commonly zinc. Cadmium originates mainly from weathering of Cd-bearing zinc minerals which are the most frequent minerals in the Sasa ore deposit (Vrhovnik et al. 2010; Serafimovski and Aleksandrov 1995). As a result, the concentrations of cadmium are relatively high in surficial lake sediments and range from 16.5 to 136 mg kg^{-1} and are much higher than those in Table 4 from other sampling sites around the world.

Antimony The average amount of antimony in the upper continental crust is 0.2 mg kg^{-1} (Taylor and McLennan 1995), but in surficial lake sediments concentrations measured up to 3.6 mg kg^{-1}. Antimony is a major constituent of antimonides, sulphides and others minerals (Wedepohl 1978). So, we infer that increased levels of antimony are a result of waste material from the Pb–Zn ore deposit, especially because of major ore firming minerals.

Bismuth Bismuth's crystal and chemical nature is close to arsenic, antimony and lead, and it occurs only as a trace element (Wedepohl 1978). Bismuth is widely distributed in hydrothermal sulphidic and pneumatolytic ore deposits and their oxidation zones (Wedepohl 1978; Wedepohl 1995). While nearby Lake Kalimanci is a large Pb–Zn ore deposit, which was formatted in aforementioned conditions, most likely bismuth has high concentrations in surficial lake sediments and ranges between 3 and 24.3 mg kg^{-1}. Bismuth is not widely researched, but compared to Lake Hope (Table 4), the content of bismuth in surficial sediments from Lake Kalimanci is more than ten times higher.

Silver Silver is not an essential or major rock-firming mineral, often occurs in high levels in sulphide minerals (such as galena, sphalerite, pyrite, etc.), and is most frequently associated with lead ore deposits and other chalcophile elements (Wedepohl 1978). Silver in analysed surficial Lake Kalimanci sediments ranged from 1.4 to 17.3 mg kg^{-1}. Prevailing high contents of silver are due to sulphide ore minerals (especially galena) in the Sasa ore district (Serafimovski and Aleksandrov 1995), which is also the main reason for such high contents compared to average crustal concentrations (Table 4).

Other features that influence the metal burdens in the lake sediment

Table 5 Calculated values of enrichment factor in Lake Kalimanci surficial sediments

EF	Max	Min	Average
Co	2.69	1.21	2.01
Ga	1.56	1.09	1.26
Mo	3.40	0.64	1.84
Cu	51.54	6.24	17.02
Pb	903.7	90.36	312.9
Zn	326.4	43.03	121.1
Ni	4.40	1.19	2.28
As	107.8	17.79	46.92
Cd	1,538	174.7	590.3
Sb	20.80	2.39	9.27
Bi	0.21	0.02	0.08
Ag	0.38	0.03	0.12

Lake Kalimanci, like any lake, serves as the repository for materials carried into it by water, wind, ice and the activities of living organisms. Trace metal concentrations in Kalimanci Lake water have also increased, according to our previous research (Vrhovnik et al. 2012b) and lie in the following ranges (μg L^{-1}): Cd 2.25–8.25, Cu 1,934–96,849, Mo 1.06–147, Ni 0.49–915, Pb 0.79–98.5, Sb 0.12–0.59 and Zn 24.3–2,271. Rogan et al. (2010) published mean concentrations of waters from the vicinity of Lake Kalimanci (from Kočani Field, Bregalnica River and Zletovska River), where they are not directly contaminated with metals from Sasa mine or tailings dam, and the bed rocks are much the same. Nevertheless, the concentrations of trace metals from Lake Kalimanci water are highly enriched in comparison with waters presented by Rogan et al. (2010). Next to increased levels of trace metals in lake water, a minor part of trace metal contamination is probably a result of atmospheric deposition, where particles from the Sasa tailings dam are carried by strong winds from the mountains through the valley. However, according to Nicholson et al. (2003), the European average deposition rates are (g/ha/year): Zn 227, Cu 34, Ni 10, Pb 38, Cd 1.9 and As 2. These materials include fine particles of minerals and rock fragments. Nevertheless, mining activity in the vicinity of Lake Kalimanci is considered to be the main reason for the decreasing quality of lake water and sediments caused by the movement of ground Sasa tailings dam material in suspension (Heide and Singer 1954) in the Kamenica River.

Organic matter is an important controlling factor in the abundance of trace metals (Tessier et al. 1994). According to our previous study (Vrhovnik et al. 2012b), the organic matter content lay in the following ranges (%): C_{org} 0.05–2.70, N_{org} 0.00–0.34, H_{org} 0.29–5.97 and S_{org} 0.00–2.13, and had almost homogeneous concentrations of compounds through the lake. Vrhovnik et al. (2012b) presents the correlation matrix obtained for trace elements and organic matter (C_{org}, N_{org}), where the data show that the majority of trace elements (Ga, Co, Cu, Pb, Zn, Ni, Cd, Ag and Hg) are significantly correlated with C_{org} and N_{org}, indicating that organic matter plays a major role in controlling metal concentrations in surficial sediments from

Lake Kalimanci. According to Rubio et al. (2000), fine-grained sediments tend to have high metal contents due to the high specific surface of smaller particles, and therefore surface adsorption and ionic attraction are higher. Furthermore, coatings of organic matter are prevalent in the fine-grained sediments, and therefore they bind a variety of trace elements (Rubio et al. 2000). The inter-relationships among trace elements (Ga, Co, Cu, Pb, Zn, Ni, Cd, Ag, Hg and C_{org}, N_{org}) show that they are all strongly correlated, which indicates a common source of these elements or a similar enrichment mechanism in the surficial lake sediments.

Analysis indicates that trace metal concentrations (Mo, Cu, Pb, Zn, Ni, Cd, Sb, Bi and Ag) in surface sediments from the second profile (II) are consequently higher than those from the other locations (Fig. 4), except for Au, As, Ga and Co. The second profile (II) near the Kamenica River discharge has the highest values: Mo 1.0–4.6 mg kg^{-1}, Cu 144.4–1,162 mg kg^{-1}, Pb 1,874–16,300 mg kg^{-1}, Zn 2,944–20,900 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}. This part of Lake Kalimanci is under the influence of the untreated wastewaters and Kamenica River inflow coming from the nearby mining activities. With regard to different authors, who recently investigated lake sediments (López et al. 2010; Pradit et al. 2010; Rognerud and Fjeld 2001; Tylmann et al. 2011), concentrations of trace elements in Lake Kalimanci are inconceivably higher, presumably because of weathering of bedrocks and the nearby tailings dam from Sasa Mining activity. The concentrations were, from highest to lowest: Zn > Pb > Cu > As > Cd > Ni > Ga > Co > Bi > Ag > Mo > Sb. Figure 4 presents a space distribution of metals in Lake Kalimanci. As mentioned before, the majority of metals are concentrated in the western part of the lake. From the second profile (Fig. 4), a dispersion plume, rich with metals, moved on the western part of Lake Kalimanci to the dam, in the southern part of the lake. Its track coincides with the Kamenica River stream, which can be observed when Lake Kalimanci is completely empty (during sampling). Furthermore, the local road could also be the reason for the increase in metal in the western part of the lake. The road is an important connection between the agriculturally important Kočani Field, the mines and the border with Bulgaria, which tends to be the biggest exporter of agricultural and metal products. In addition, WHO (2009) reports that FYR Macedonia still allows the use of petrol with high levels of lead, which may also contribute to higher lead contents in the western part of the lake. Meanwhile, the eastern part of the Lake Kalimanci has increased levels of the studied metals, according to Fig. 4, with the exception of Co and Ga. On the eastern side of the lake, there are no roads, industry or households, just uncultivated ground.

Comparison of the measured contents of the studied metals with average contents in the Sasa tailings dam material (dam no. 4) (listed in section "Study area") shows that the surficial sediments of Lake Kalimanci had higher contents of potentially toxic metals. Among the studied elements in both sites, only As and Cd had higher contents in Sasa tailings dam material. Presumably, the reason for the aforementioned condition could be changes in the ore cultivation processes, and thus the remnants of Pb and Zn in the tailings dam had decreased over the years. Therefore, when Sasa tailings dam no. 3 and part of dam no. 4 (which has been in use recently) collapsed (Vrhovnik et al. 2011a), the material from the older dam (no. 3) caused an increase of the studied metals in surficial sediments from Lake Kalimanci.

Enrichment factor (EF)

In this study, EF was used for the assessment of mining activity in order to understand the difference in composition in terms of natural and anthropogenic elemental sources (Chester et al. 1992).

Median values of calculated EF ranged between 0.1–590.3 in surficial Lake Kalimanci sediments (Table 5). According to the published data from 23 lakes situated in the Mazurskie and Suwalskie lakelands in northern Poland, where a lack of significant local sources of pollution was expected and EF's ranged from 0.9 to 1.6 (for Cd, Cu, Ni, Pb and Zn) (Tylmann et al. 2011), we can see that EF values are incomparingly higher in the Macedonian lake. Enrichment factors are close to 1 point to a crustal origin, while those with a factor above 10 are considered to have a non-crustal source (Nolting et al. 1999), most likely anthropogenic. So, we can conclude with certainty that cadmium, lead, zinc and arsenic originate from the Sasa ore deposit, while rock disintegration is the main reason for the existence of other elements. EF values lower than 0.5 can reflect mobilization and loss of these elements reactive to Al or indicate an overestimation of the reference metal contents (Zhang 1995).

The calculation of EF showed that mainly all studied trace metals were enriched in surficial sediments of Lake Kalimanci. Cadmium has the highest mean value of EF (590.3) and represents extremely severe enrichment. The highest values of enrichment factor (signified extremely severe enrichment) were calculated for cadmium, lead, zinc and arsenic, as well as for the other trace elements, as follows: Cd > Pb > Zn > As > Cu > Sb > Ni > Co > Mo > Ga > Ag > Bi. EF also shows the highest amounts of metals in the second profile of Lake Kalimanci (sampling location II-3 and II-5), exceeding locations at III-3, I-4, I-5, VI-7 and V-7. The calculated EF values coincide well with Fig. 4, where metal distributions are presented.

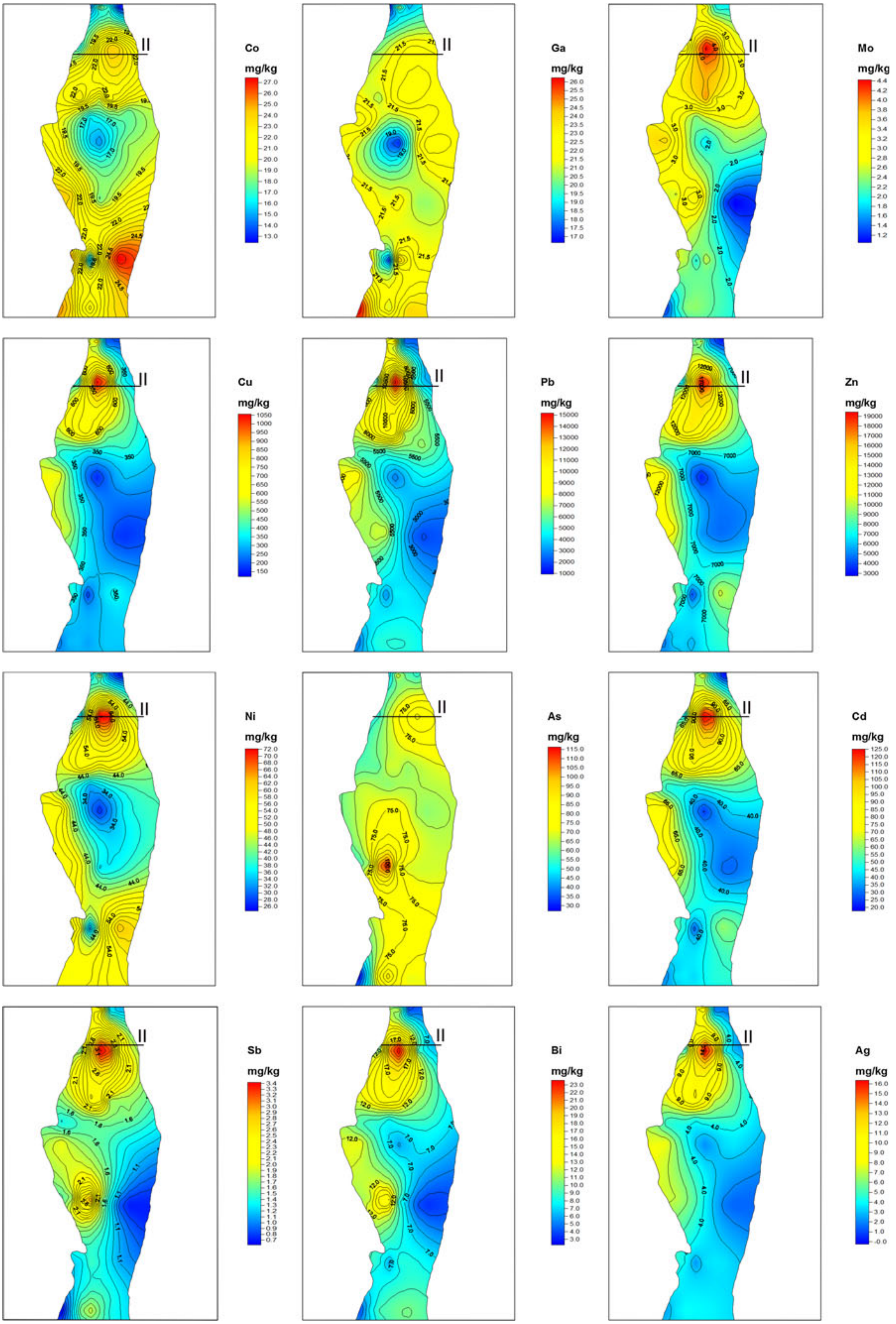

Fig. 4 Spatial distribution of trace elements in Lake Kalimanci surficial sediments (II indicates second profile)

Therefore, it could be concluded that at the northern part of the lake, where the Kamenica River enters, there is enormous pollution, which extends into the central part of Lake Kalimanci towards the dam (Fig. 4).

Conclusions

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 Lake Kalimanci. 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.

Enrichment factors are good methods for evaluating the contamination of sediments because they give a first impression of contamination. Enrichment factor values revealed that Lake Kalimanci surficial sediments have extremely severe enrichment from cadmium, lead, zinc and arsenic.

We can conclude that Lake Kalimanci's surficial sediments contain very high values of toxic trace metals. Therefore, further investigation is needed to assess the environmental risk related to the load of pollutants of the lake sediments and the surrounding area.

The failure of Sasa tailings dam had a great impact on the surrounding environment. The present study shows that discharged Sasa tailings material caused an increase in the amount of metals in surficial sediments from Lake Kalimanci. Not only the background rocks from the vicinity but also the tailings dam failure, the mining industry and consequently heavy traffic are the major reasons for the recent conditions in Lake Kalimanci. After this study, many questions remain unanswered. A detailed study of all four tailings dams is needed to clarify the metal contents during their history. A study of the lake sediments from greater depths is also necessary to evaluate the historical impact of the mining industry on the lake environment. The questions about untreated household wastes also remain unanswered, and, most importantly, an assessment of the impact of pollution on human and animal health must be provided. All the missing information will be the focus of our future work.

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