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DEPOSITION OF METALS IN GLACIAL LAKE SEDIMENT

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Abstract. The aim of this research was to find the relationship between metals content and age of the sediment and to estimate the contamination level. For the research of sediment, samples were taken from the glacial Lake Prokosko. Concentrations of eight elements (Ca, Mg, Fe, Cd, Pb, Zn, Cu and Mn) were determined. The age was determined with usage of C^{14}. For statistical evaluation of the results, we used basic statistical tools, correlation, and PCA. The results showed that all of investigated metals have natural origin. Sediment core from this research was around 18,000 years old and the results revealed characteristics of metals deposition in the process of sedimentation. Concentrations of metals were compared with age (depth) of sediment. Maximal concentrations for iron, calcium, magnesium and manganese are found in the period of Alleröd oscilation. Differences in Mn/Fe ratio and organic matter content are showing changes through history. These results show metal deposition characteristics in different climate periods, and these characteristics could be used as another proof of climate change.

Keywords: sediment, correlation, PCA, age, Mn/Fe ratio

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INTRODUCTION

Lake sediments are used to track environmental change during historical periods. The main objective of this study is to investigate the vertical distribution of selected metals in the Lake Prokosko sediment core, to determine a correlation between metals and to explore deposition (sedimentation) characteristics of metals in Prokosko Lake sediment trough history (Fe, Mn, Ca, Mg, Cd, Cu, Pb). Lake Prokosko is not deep, it has high deposit thickness, and development of this kind of lakes is sometimes influenced by human activity (Bałaga *et al*. 2002). For this reason, the study concerns the pollution of lake sediment by heavy metals (Cd, Pb, Cu, Zn). Lake Prokosko is situated in central Bosnia and Herzegovina in the Vranica mountains. It is a glacial lake, and sediments of such lakes can be the source of knowledge about climate change. During Pleistocene cold phases, higher elevations of the Dinaric Alps were covered by ice. The Vranica massif, that reaches altitudes above 2,000 m a.s.l., was ice-covered during the cold phases of Pleistocene (Dörfler 2013).

Metal distribution in a sediment is an important indicator of the nature of metals and the relationship between them (Cohen 2003). Isotopic, elemental, or molecular composition of a lake and its sediments are delivered from both external chemical inputs and internal biogeochemical processes. When interpreting chemical data, it is very important that it is placed in the paleontological context. Elemental distributions in lakes are closely linked to climatic and watershed processes. Solute concentrations regulate precipitation or dissolution of mineral phases. Minerals leave sedimentary archives and aspects of ancient water chemistry can be interpreted on the basis of these records. These records help us to understand paleoclimate (Becker *et al*. 2001, Davis *et al*. 2001). Flow conditions in the lake and suspended matter concentrations can change rapidly in meltwater streams during the higher temperature. Years of higher than average temperatures, with greater glacial melting, normally yield greater amounts of sediment (Perkins and Sims 1983). The end of Pleistocene was marked by a series of abrupt, decadal to century-scale warming and cooling events. First strong pulse of glacial melting happened between 14700 and 12800 BC (Bölling-Alleröd interstadial). This period of higher temperature was immidiately followed by significant cooling. Both seasonal and long-term melting of glacial ice released extremely large quantities of boulders, gravel, and sand, which can be discharged into lake (Cohen 2003). Mobility of manganese and iron greatly increases when redox change takes place. Therefore, Mn/Fe ratios can show the amount of dissolved oxygen in lake waters.

Study area

Prokosko Lake (Fig. 1) is a glacial lake situated in central Bosnia and Herzegovina in the Vranica mountains (43°57'26"N; 17°45'17"E). This lake is the highest mountain lake in Bosnia and Herzegovina situated at an altitude of 1,635 m above the mean sea level. It is located 22 km west of the town of Fojnica (Fig. 2). The air distance from the Adriatic Sea is 90 km (Fig. 3). It is 426.0 m long and 191.3 m wide. The surface area is around 48,000 m^2. The lake volume varies, depending on the season.

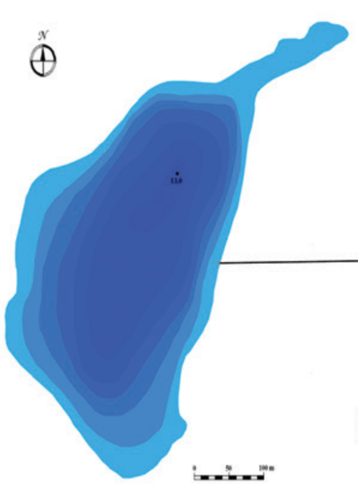

Fig. 1. Prokosko Lake (Spahić 2001)

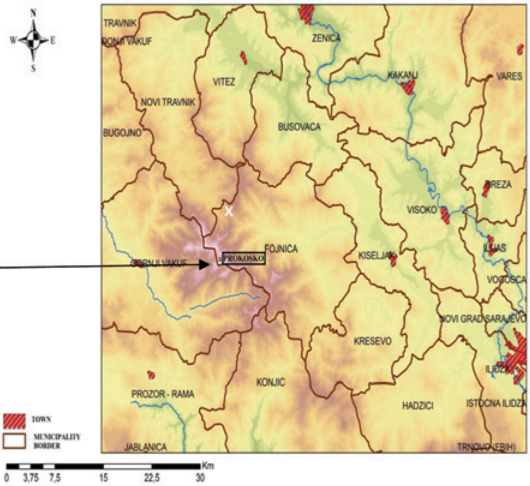

Fig. 2. Prokosko Lake with surroundings

Fig. 3. Map of Bosnia and Herzegovina with the Prokosko Lake location

Geology

The area of Lake Prokosko is part of the Middle Dinarides that are mainly built up of Paleozoicclastic rocks, Jurassic-Cretaceous flysch, Mesozoic carbonate and Neogene molasses. The Lake Prokosko terrain consists of Devonian-Carboniferous rhyolite, dolomite, meta-sandstone with veins of quartzite, marble, Lower to Middle Devonian limestone, chert and graphite schist and as a third unit of Middle Dinarides, Silurian-Devonian chlorite-sericite-quartzite and graphite schist, quartzite, meta-sandstone, dolomite, limestone and marble (Čičić 2002).

Climate

Lake Prokosko is very close to the Adriatic coast (Fig. 3). Because of that, the region experiences the transitional climate, which is influenced by the presence of the Mediterranean Sea and Dinaric Alps. It is a typical Mediterranean-subalpine to alpine climate with a very high yearly precipitation rate taking place mainly in the winter term (Dörfler 2013).

MATERIALS AND METHODS

Sampling

The lake sediment was taken at the deepest point in the lake (12 m), determined by a sonar device (Plastimo Echotest II). The aluminum platform, attached to the lake bank at five spots, was used. To remove a lake sediment core, a drive-operated surface corer with clear polycarbonate of 1-m long tubes, was used. Sediment of an overall length of 11.44 m was extracted. Because of the pressure that the corer makes, sediment core was compressed for a 0.5 m. Each tube consisted of two halves, divided along the length, which permitted division of the core sample into two halves as well (Fig. 4). For the purpose of this study, one half was subjected to the analysis. The sediment material in Lake Prokosko was made by gradual deployment of the material. The sediment has a distinctive color ranging from dark grey and black in the upper layer to pale gray and almost white at the bottom of the sediment. In the laboratory, the core was split into subsamples according to their texture and color. Splitting the sample into subsamples resulted in 95 subsamples.

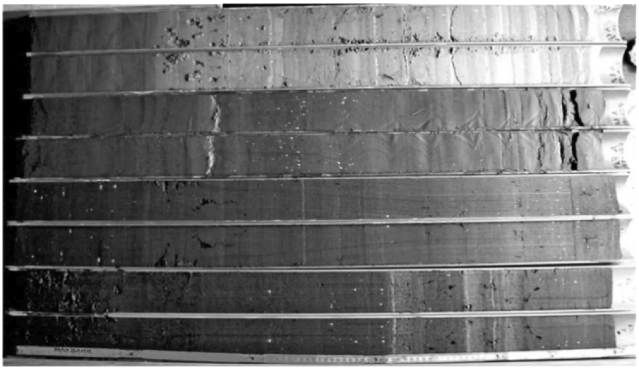

Fig. 4. Tubes with the sample

Preparation of sediment samples

The samples were air dryed, powdered and sieved trough the 2-mm sieve. The digestion of samples was performed in a microwave oven using digestion (extraction) in *aqua regia* ($HCl:HNO_3 = 3:1$) EPA 3051 (1994) (Lacort and Camarero 2004). Every fifth sample was prepared in parallel. So, in the end, 113 samples with digestion in *aqua regia* were made.

Analysis

This study presents the results of the measurement of concentrations of iron (Fe), calcium (Ca), magnesium (Mg), manganese (Mn), copper (Cu), lead (Pb) and cadmium (Cd), measurement of free moisture, and organic matter. Concentrations of selected metals were measured using FAAS technique (Fe, Ca, Mg, Mn, Zn) and GFAAS technique (Cu, Pb, Cd). Analyses were made at the Faculty of Agriculture and Food Sciences, University in Sarajevo. Concentrations were determined using a calibration curie (Harvey 2000, Broekaert 2002).

RESULTS

Age of the sediment core

Dating of sediment core that was used in this research was made at the Institute of Pre- and Protohistoric Archeology in Kiel. In order to date the sediment core, botanical macro remains were selected from the sediment and the age of sediment was determined with ^{14}C isotope. The surface sediment cores were cut lengthwise and examined, and dark layers were dissected. By this method, seven leaf fragments could be used for AMS dating. OXACAL calculation was used with a P_Sequence and a k-value of 0.5. Results from the measurements of ^{14}C are shown in Figure 5. After application of date modelling we got around 1,000 date points.

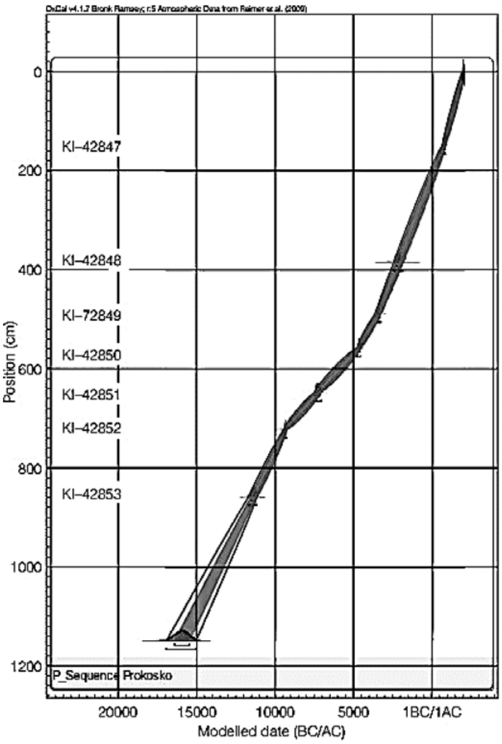

Fig. 5. Modelled date (BC/AC) – time-depth diagram

Results of the measurement of chemical and physical parameters of samples are shown in Table 1.

Table 1. Results of the measurement of chemical and physical properties of samples

	Mean	Maximum	Minimum	Median
Moisture content (%)	66.59	86.42	29.85	70.51
Organic matter (%)	8.29	15.94	0.36	10.07
Amount of iron (%)	3.68	13.39	1.21	3.18
Calcium (mg/kg)	3183.31	34100.14	10302.21	8171.42
Magnesium (mg/kg)	4923.12	17657.04	1239.31	3994.27
Manganese (mg/kg)	1761.02	8443.12	0.38	185.26
Zinc (mg/kg)	0.06	0.16	0.02	0.06
Lead (mg/kg)	2.11	24.84	0.21	1.61
Copper (mg/kg)	4.22	8.70	1.53	3.84
Cadmium (mg/kg)	0.18	0.65	0.06	0.16

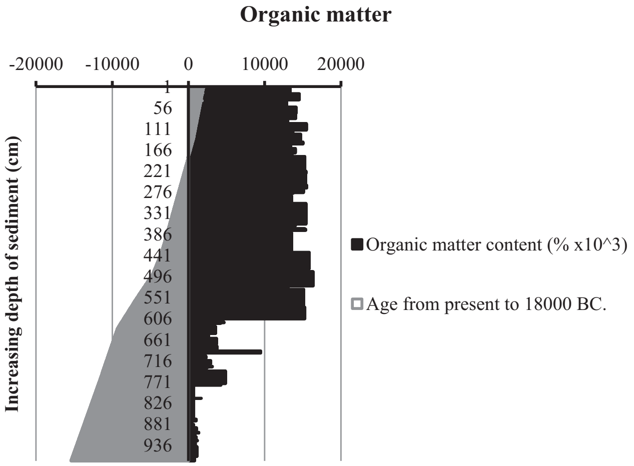

Fig. 6. Organic matter – depth (time) diagram

Metals concentrations

Vertical distribution of metals in sediment of Lake Prokosko is shown in Figures 7–14.

Note: the amount of metals in sediment samples is very different (from the percentage value in case of iron to ppb values in case of cadmium). Presentation of metals in relation to age (approximately 18,000 years) could be done only if we multiply concentrations for certain parameters (organic matter, zinc, copper, lead and cadmium).

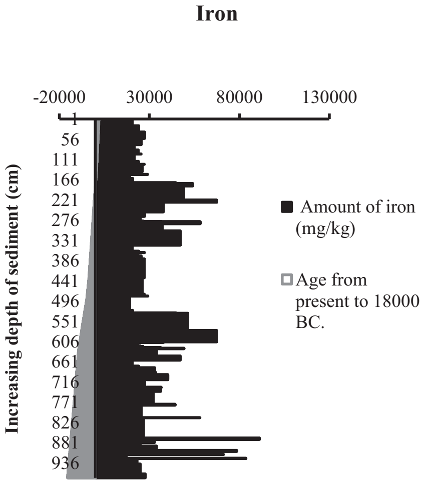

Fig. 7. Concentration – age diagram of iron

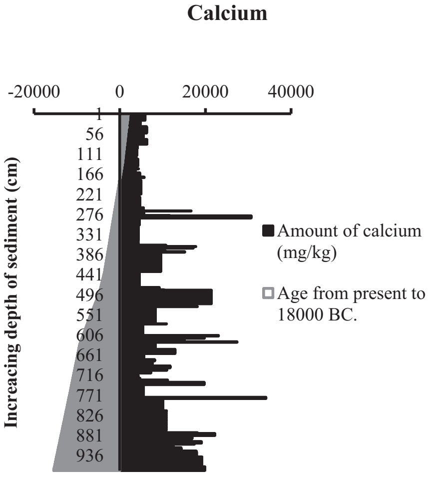

Fig. 8. Concentration – age diagram of calcium

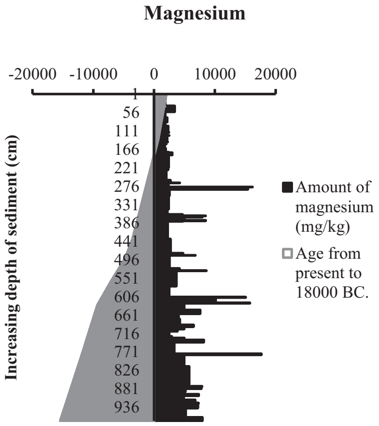

Fig. 9. Concentration – age diagram of magnesium

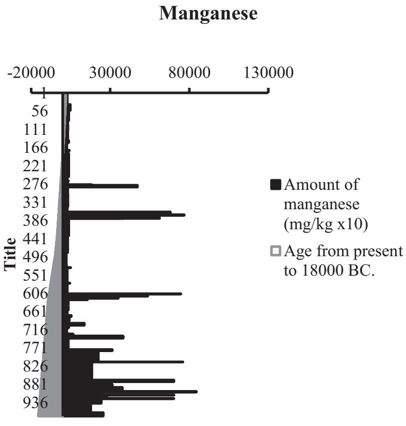

Fig. 10. Concentration – age diagram of manganese

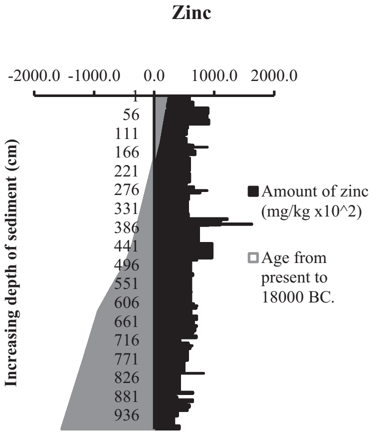

Fig. 11. Concentration – age diagram of zinc

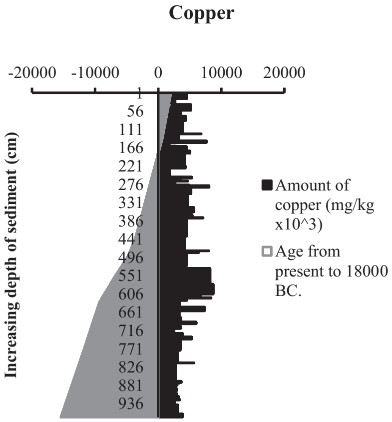

Fig. 12. Concentration – age diagram of copper

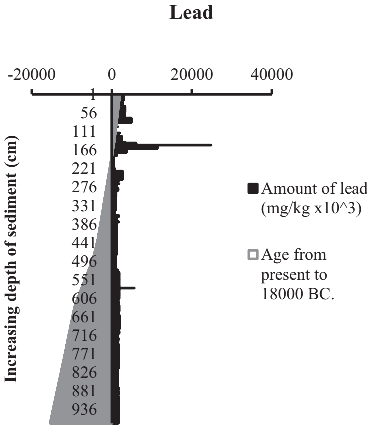

Fig. 13. Concentration – age diagram of lead

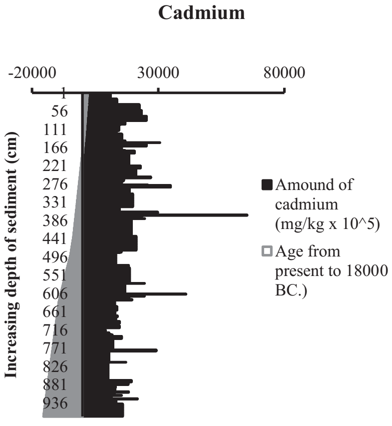

Fig. 14. Concentration – age diagram of cadmium

DISCUSSION

Age of the sediment core

Determination of sediment age was made. The results from ^{14}C show the continous accumulation of sediment with a slow increase in growth rate, without interruptions. The bottom part of the sediment (below 860 cm) provided no material for ^{14}C dating, the modelled age of this part is extrapolated with high errors. Average growth rate was 15 years per cm for the sediments below 720 cm. Between 720 and 560 cm there is a relatively slow growth, 1 cm in 28 years.

In the upper parts of the core, the sedimentation rate is faster – 1 cm per 11 years. The resolution is decreased to 450 years per sample because of higher growth rate. For younger part of sediment, resolution is 8 cm. Because of that, the time interval between the samples increases to 224 years for the section between 6200 BC and 4750 BC (610–560 cm). The resolution increases to 144 years for period from 4750 BC and 3500 BC (560–492 cm), and to 88 years for last 5,500 years (492–0 cm). The record of Lake Prokosko dates back some 18,000 years into the late glacial of the Weichselian (Dörfler 2013).

Basic parameters

Sediment of Prokosko Lake is made mainly of clastic material, organic debris, chemical precipitates, or combinations of these. The relative abundance of each depends upon the nature of the drainage basin, the climate, and the relative age of a lake. Lake Prokosko is the lake of glacial origin, this kind of lake will first receive coarse clastics, then finer clastics, chemical precipitates, and then increasingly large amounts of biological material, including peats and sedges. The content of moisture in the sediment samples was higher in the upper parts of the sediment, gradually decreasing with increasing the sediment depth. Such a result was expected because mineral matter content rises with the increase of the sediment depth. Organic matter content decreased with the sediment depth is shown in Figure 6.

The organic matter suddenly drops at the depth of 625 cm and age of 6,600 years BC. The organic matter content is in line with the change of paleoclimate, because it corresponds to the warmer period in climate which causes higher organic matter deposition in sediments.

Variation of investigated metals and age of the sediment

Of all the elements that were determined, iron had the highest concentration (maximum concentration, 13.39%; minimum concentration, 1.21%) (Fig. 7). Maximal concentration of iron was at the sediment depth of around 961 cm, and age of around 130,000 years BC. Minimum value for iron was at the sediment depth of around 900 cm, and age of around 10,000 years BC. Iron deposition in lake sediments can be difficult to interpret because of the large number of processes that precipitate, deliver, or deposite iron (Engstrom and Wright 1984). In the upper layers of the sediment, iron is in highly insoluble forms (oxides) and we do not expect lower amounts of iron in the upper layers. In our case, distribution of iron showed lower concentrations in the upper layer of the sediment profile. Some of iron is dissolved in the water with the sediment coming into contact with the lake water. Dissolution of iron in the upper layers is the result of different physical and chemical properties. In the upper layer of the soils, iron is in the oxidized state (Fe^{3+}). Migration of iron and manganese is the result of the erosion or weathering and sedimentation (Tessier and Turner 1995). If the migration of iron, in case of Lake Prokosko, had only been directed by the erosion, the results would have shown the similarity with the results for the soils, and that was not the case (lower amounts of iron in the upper layer as a result of dissolution) – iron naturally occurs in the sedimentation.

The calcium content in the sediment samples was quite high (maximum value, 34100.1 mg/kg; minimum value, 3183.3 mg/kg) (Fig. 8). Maximal concentration of calcium was at the sediment depth of around 781 cm, and age of around 11,800 years BC. At a sediment depth of around 300 cm, and age of around 1,000 years BC, we found minimal concentration of calcium. The high content of calcium comes from the sediment composition ($CaCO_3$). The concentration of calcium was lower in the upper parts of the sediment where the amount of mineral matter was lower.

The values for magnesium are much lower than the calcium values (maximum value, 17657.0 mg/kg; minimum value, 1239.3 mg/kg) (Fig. 9). Maximal concentration of magnesium was at the sediment depth of around 900 cm, and age of around 11,800 years BC. At the surface layer of the sediment we found minimal concentration of magnesium. Similar to calcium, magnesium showed lower values in the surface layer than in the depth, due to the low content of mineral substances. Magnesium showed similar behavior to calcium ($r = 0.827$, Table 3). They build similar minerals (carbonates).

The highest concentration of manganese was positioned at the 9–10 m of the sediment depth (maximum value, 8443.1 mg/kg; minimum value, 1761.0 mg/kg) (Fig. 10). Maximal concentration of manganese was at the sediment depth of around 1,000 cm, and age of around 14,000 years BC. Minimum value for manganese was at the sediment depth of around 800 cm, and age of around 11,000 years BC. The increased concentrations of manganese at this depth is the result of the larger presence of the manganese salts. The manganese inside the sediment behaves similarly to iron ($r = 0.690$, Table 3). Iron and manganese are the main particulate matters in the sediments, together with the organic matter.

The zinc concentration was rather low (maximum value, 163.2 mg/kg; minimum value, 63.0 mg/kg) (Fig. 11). Maximal concentration of zinc was at the sediment depth of around 400 cm, and age of around 2,700 years BC. Minimum value for zinc was at the sediment depth of around 800 cm, and age of around 10,500 years BC. The concentrations of copper in the sediment samples were also low (maximum value, 8.70 mg/kg; minimum value, 4.22 mg/kg) (Fig. 12). Maximal concentration of copper was at the sediment depth of around 650 cm, and age of around 7,500 years BC. At the sediment depth of around 800 cm, and age of around 10,500 years BC, we found the minimal value. Although the content of copper showed regularity in the deepest part of the sediment, in general, we can say that this was a very unbalanced distribution of copper.

Concentration of lead was low in the sediment samples (maximum value, 24.84 mg/kg; minimum value, 2.15 mg/kg) (Fig. 13). Maximal concentration of lead was found at the sediment depth of around 171 cm, and age of around 450 years BC. Minimum value for lead was found at the sediment depth of around 430 cm, and age of around 2,700 years BC. Although we found increased concentrations of lead in the surface areas of the sediment, it did not exceed the maximum value permissible for soils.

Cadmium is an element that is quite rare in the Earth's crust so that the concentration of cadmium in the samples was very low (maximum value, 0.65 mg/kg; minimum value, 0.06 mg/kg) and did not exceed the maximum permissible value (Fig. 14). Maximal concentration of cadmium was at the sediment depth of around 400 cm, and age of around 2,700 years BC, whereas the minimum value for cadmium was at the sediment depth of around 800 cm, and age of around 10,500 years BC.

It is significant that maximal concentrations of iron, manganese, magnesium and calcium were found at the similar depth (between 900 and 1,000 cm) and age (between 14,000 BC and 11,800 BC). The maximal values for these elements roughly correspond to the Alleröd period (warm period at the end of glacial age). This result can be explained by the fact that the sedimentation rate is higher at higher temperatures, and by higher amount of mineral and organic matter that comes to lake (ice melting).

Minimal concentrations for iron, zinc, copper and cadmium were found in very short part of the sediment sample (4 cm), at the depth of around 800 cm and age of around 10,500 BC. This result can be explained by the nature of iron oxides, since they are one of most important particulate matter for heavy metals adsorption. Lower amount of iron causes low amount of some heavy metals. This low amount of iron is probably due to reduction characteristics of sediment.

Similarities among metals in the sediment

The sources of selected metals in the sediment profile were investigated by using the principal component analysis (PCA) and the Pearson's correlation coefficients. The PCA method can be used in geochemical investigation because of its ability to reduce large data sets in a smaller number of principal components

(Yusoff *et al.* 2015). Principal components can explain a different nature of metals correlating with each other. The PCA results are shown in Table 2. The eigenvalues higher than one were only extracted. After the PCA, we got three eigenvaules higher than one. The first component explains 36.157% of variance and it was built by variances of Mn, Fe, Mg, Ca, and Cd. This means that these metals showed similar behavior in the sediment and might originate from natural sources. The second component explains 21.374% of variance and was built mainly by Zn. The main characteristics of the second component were similar to negative results attached to Mg and Ca. It means that Mg and Ca were very similar in behavior. They are part of the mineral matter. Since other metals from the second component showed positive variance, they were probably attached to the organic matter. The third component showed 14.193% of variance which was loaded mainly from Pb. It means that Cu and Pb showed different behavior among all of the metals investigated here, and there were large differences even between themselves.

Table 2. Component matrix extracted from the principal component analysis

Component matrix

	Component		
	1	2	3
Mn	0.846	-0.028	0.146
Fe	0.748	0.257	0.013
Mg	0.746	-0.420	0.006
Ca	0.722	-0.510	0.090
Cd	0.645	0.583	0.181
Zn	0.212	0.723	-0.157
Cu	0.211	0.340	-0.772
Pb	-0.184	0.477	0.672
Total variance	2.893	1.710	1.135
% of variance	36.157	21.374	14.193
Cumulative variance (%)	36.157	57.531	71.724

Interelemental correlations

The correlations are shown in Table 3. Iron shows a high correlation with manganese (r = 0.689). High concentrations of iron and its correlation with manganese are explained by the fact that iron oxides with oxides of manganese are primary particulate matters in the sediments (Pansu and Gautheyrou 2006).

The high correlation between calcium and magnesium (r = 0.826) was expected because these two elements are similar in nature, occur together, and participate in the construction of carbonate rocks, such as dolomite (Bauer and Velde 2014). The lower calcium content in the surface areas of the sediments is explained by the lack of minerals (e.g. carbonates) in these layers. Because of their similar nature, magnesium showed a high correlation with calcium (r = 0.826). This high correlation between them occurs because they form dolomite together (magnesium and calcium carbonate). Magnesium is highly bonded to dolomite and not to magnesite ($MgCO_3$). Table 3 gathers all of interelemental correlations.

Table 3. Interelemental correlations

	Fe	Ca	Mg	Mn	Zn	Pb	Cu	Cd
Fe	1.000							
Ca	0.225*	1.000						
Mg	0.257**	**0.827****	1.000					
Mn	**0.690****	0.538	0.487	1.000				
Zn	0.134	-0.128	-0.017	0.144	1.000			
Pb	-0.155	-0.167	-0.192*	-0.147	0.171	1.000		
Cu	0.137	0.021	0.087	-0.004	0.284**	-0.150	1.000	
Cd	0.608	0.185	0.249**	0.427**	0.398**	0.233*	0.204	1.000

* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

Mn/Fe ratio

Iron and manganese oxides are the main particulate matter and they are simmilar in nature in case of sediments which is shown even in this research (r = 0.690). Depostition of manganese and iron is regulated by changes in oxygen content in the water of lake. So, their ratio can reflect variations in redox conditions in water phase (Yusoff *et al.* 2015). Reducing conditions are result of O_2 consuption during organic matter reminaralisation, which leads to the release of Fe and Mn. After oxygenation at the chemocline due to partial or total mixing of the water column, Fe and Mn precipitates are deposited in the lake sediment (Alhonen 1986, Naeher *et al.* 2013). Because of the fact that iron is oxidised more easily than Mn, parts of sediment with higher Mn/Fe ratio have higher amounts of dissolved oxygen. Results for the Mn/Fe ratio are shown in Figure 15.

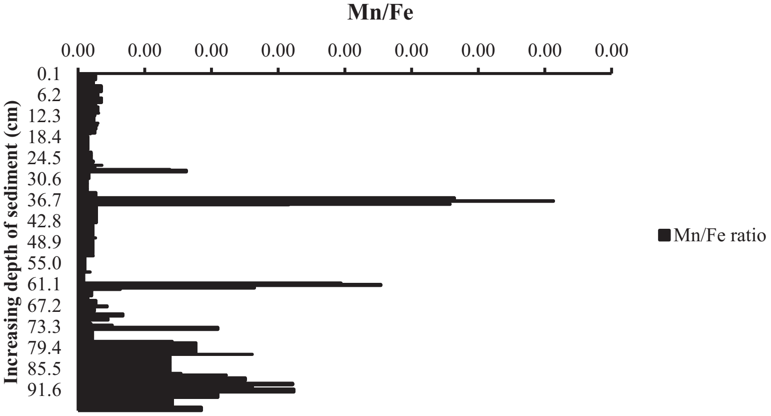

Fig. 15. Mn/Fe ratio

Results for the Mn/Fe ratio show two distincitive parts of the sediment which have the biggest ratio (amount of dissolved oxygen). Maximal Fe/Mn ratio was found at the sediment depth of around 370 cm and age of 2,600 years BC. Minimal value was found at the depth of 550 cm and age of 6,500 BC. In the Mn/Fe ratio, there is the second maximum at the depth of 612–615 cm and age between 8,600 and 8,800 years BC. It is significant that the second minimum is just before the second maximum. Another specific is one, guite long, minimum value, between two high values, at the depth of from 745 to 886 cm and ages from 11,200 to 11,800 BC, which roughly corresponds to the Alleröd oscillation, which is a warm and moist global interstadial that occured at the end of the last glacial period (Naeher 2013). Low Mn/Fe ratio mean slow amount of dissolved oxygen. Higher temperatures in this historical period at the end of the glacial age, could cause low dissolution of oxgen and usage of oxygen by organic matter during this warm period.

Estimation of anthropogenic metal enrichment

"Enrichment factor" (EF) calculation is based on Fe normalized values. The enrichment factor is defined as: EF = (Met/Fe) sample / (Met/Fe) background. The world average shale and the world average soil are among the materials often used to provide a background level. The EF values between 0.5 and 1.5 indicate that the metal is entirely made of crustal materials or natural sources (Zhang and Liu 2002). In this study, we found that the enrichment factor for lead is higher in the upper parts of the sediment. However, it is still not lead-enriched sediment, and lead entirely originates from natural sources. In one case, cadmium showed enrichment factor of 1.72 which could mean that cadmium is not entirely made of crustal material, but concentrations of cadmium are below the maximum permissible value.

Table 4. Enrichment factor

Metal / EF	Mean	Maximum	Minimum
Pb	0.16	0.59	0.06
Cu	0.14	0.23	0.07
Cd	0.91	1.72	0.40

CONCLUSIONS

1. All investigated metals originate from natural resources.

2. Maximal concentrations for iron, calcium, magnesium and manganese are found in the period of the Alleröd oscillation, this is probably due to the

higher sedimentation rate and higher amount of mineral and organic matter that comes to lake (ice melting) in this period of higher temperature.

3. The Mn/Fe ratio shows diferent oxydation reduction environment in the sediment during sedimentation. Minimal Mn/Fe (minimal amount of dissolved oxygen) ratio roughly corresponds to the Alleröd oscillation (warm period at the end of the glacial age), which is probably due to lower solubility of gases at higher temperatures.

4. There is no contamination ragarding lead and cadmium.

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