

## Distribution of metals and trace elements in sediments of three Alpine lakes

### Kovine in elementi v sledovih v sedimentih treh visokogorskih jezer

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#### Kratka vsebina

V globinskih profilih talnega sedimenta smo v treh izbranih visokogorskih alpskih jezerih: Jezero na Planini pri Jezeru, v Krnskem jezeru in Jezeru v Ledvicah z uporabo multielementne instrumentalne nevtronske aktivacijske metode ( $k_0$ -INAA) določili več kot 30 kovin in drugih elementov v sledovih. Analizirali smo sedimente do globine 16 cm (Jezero v Ledvicah), 19 cm (Krnsko jezero) in 32 cm (Jezero na Planini pri Jezeru). Z meritvami radioaktivnega Pb (Pb-210) smo določili starost sedimentov.

Ugotovili smo, da se glede na koncentracije prvih redkih zemelj in nekaterih drugih litofilnih elementov, predvsem Sc, Cr, Th in U, Krnsko jezero bistveno razlikuje od ostalih dveh jezer. Poleg tega smo ugotovili, da se v vseh treh jezerih koncentracije praktično vseh kovin in elementov v sledovih spreminjajo z globino in da pri tako imenovanih antropogenih elementih, kot so As, Br, Cd, Co, Cr, Hg, Mo, Sb in Zn, lahko ločimo tri obdobja jezerske zgodovine, ki so vezana na povečano industrializacijo v 19. in v sredini 20. stoletja. Predvsem v Krnskem jezeru smo opazili tri izrazite depresije pri 3-3,5 cm, 6-6,5 cm in 8 cm. Prvi dve depresiji lahko glede na ocenjeno starost sedimentov povežemo s potresoma leta 1976 in 1942, tretjo pa s prvo svetovno vojno. Vpliv potresov na porazdelitev elementov v profilih sedimentov ostalih dveh jezer je nekoliko manj izrazit.

#### Abstract

In three Alpine lakes (Jezero na Planini pri Jezeru, Krnsko jezero and in Jezero v Ledvicah) the distribution of some metals and trace elements was determined in sediment cores using multielemental instrumental neutron activation analysis. Sediments were analysed to depths of 32 cm, 19 cm and 16 cm, respectively. Dating of sediments was done on the basis of <sup>210</sup>Pb measurements.

It was found that the levels of rare earth elements and some other lithophilic elements such as Sc, Cr, Th and U in Krnsko jezero were significantly lower than those found in the other two investigated lakes. In all three lakes changes with depth were noticed for practically all anthropogenic elements, namely As, Br, Cd, Hg, Mo and Zn. Three periods of lake history can be distinguished which reflect industrial activities in the 19<sup>th</sup> and 20<sup>th</sup> century.

In the sediment profile of lake Krnsko jezero three well expressed lows of all investigated elements were found at depths of 3-3.5 cm, 6-6.5 cm and 8 cm which can be linked to two earthquakes in 1976 and 1942 and the First World War. The influence of earthquakes on the distribution of trace elements in the other two lakes was less evident.

## Introduction

The main source of pollutants in high mountain lake sediments is long range transport (Birch et al., 1996, Nriagu & Davidson, 1986). For trace elements as well as for other pollutants which originate from incomplete high temperature fossil-fuel combustion in power plants, the steel industry, other industry and traffic, it is known that they can be transported attached to fine aerosols hundreds of km away from the original source. From the atmosphere the pollutants are washed out to the lake catchments during precipitation events. They can then enter the lake water column from surface runoff and ultimately end in the sediment. As sediments represents a time capsule for events occurring within the lake and its surroundings, analysis of sediment cores can help us to reconstruct their pollution history.

In some regions earthquakes can play an important role in causing environmental changes. They can cause changes in lake bathymetry or increases in tropic level as a result of landslides, in-wash of allochthonous material or tectonic movements. The Julian Alps lie in a seismically very active part of Slovenia and there are records of a number of relatively strong earthquakes having occurred there, most recently in 1976 and 1997, and in 1942 and 1895 (Ribarič 1982, Vidrih et al., 1995).

The main aim of the present paper is to present results of the distribution of some selected trace metals in the sediment cores of three Alpine lakes, namely Krnsko jezero, Jezero v Ledvicah and Jezero na Planini pri Jezeru, with an attempt to reconstruct the lake histories in the last 100–150 years and to show the influence of seismic activity on the elemental levels.

### Environmental setting

Lakes Jezero na Planini pri Jezeru, Krnsko jezero and Jezero v Ledvicah are located in the Triglav National Park at altitudes of 1430, 1383 and 1830 m a.s.l. with maximal depths of 10.0, 17.6 and 15 m and surfaces of 17600, 49600 and 23700 m<sup>2</sup>, respectively. They are of glacial origin and are in different states of ontogenetic development (Gabršček et al., 1997, Brancelj, 2002). None of the lakes has a permanent surface

inflow. The hinterland of all three lakes is composed predominantly of carbonate, mostly limestone. The lakes are more or less sheltered against wind influences; however, storm events can result in enhanced mixing of the water and an increased input of terrestrial material, especially into Krnsko jezero. Their sediments can be characterised as organic-rich clay silts with a carbonate component ranging between approximately 50 to more than 99 % and an organic carbon content ranging between less than 2 (lake Krnsko jezero) and more than 10 % (Jezero na Planini pri Jezeru) (Lojen et al., 2000).

## Materials and methods

### Sampling

Sediment sampling in all three lakes was performed in 1996. In each lake several sediment cores for various analyses (Brancelj et al., 2000) were taken from the deepest part of the lake using a gravitational corer equipped with a Plexiglas tube with an inner diameter of 6 cm. Samples were of length between 30 and 38 cm, depending on the lake. On the shore the cores were sliced and subsamples prepared for different analyses. For dating of sediments and determination of animal remains the uppermost 10 cm of the sediment cores from all three lakes were sliced into 0.5 cm intervals and the rest of the core into 1 cm intervals. They were stored in clean polyethylene bags and immediately transferred to a refrigerator. In the laboratory sediments were freeze dried and homogenized. In the upper sediment slices of the lakes Krnsko jezero and Jezero v Ledvicah trace elements were also determined. However, another sediment core from lake Jezero na Planini pri Jezeru was taken for trace element determination in 1999 and sliced into 2 cm segments.

### Sediment dating

For dating sediments cores the <sup>210</sup>Pb method was used. Lyophilised and homogenised sediments were weighed into 10 mL plastic containers and <sup>210</sup>Pb, <sup>226</sup>Ra and <sup>137</sup>Cs were measured using an Ortec high purity germanium (HPGe) well-type detector connected to a Maestro multichannel analyser. <sup>210</sup>Pb

was determined via its gamma emissions at 46.5 keV, and  $^{226}\text{Ra}$  from the 295 keV and 352 keV  $\gamma$ -rays emitted by its daughter nuclide  $^{214}\text{Pb}$  following 3 weeks storage in sealed containers to allow radioactive equilibration.  $^{137}\text{Cs}$  was measured by its emission at 662 keV. On the basis of  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  measurements the radiometric chronology was determined using the so-called Constant Rate Supply (CRS) model of Shukla (1997).

### Trace element determination

$k_0$ -instrumental neutron activation analysis ( $k_0$ -INAA) was used for multielemental determination of sediments from lakes Krnsko jezero and Jezero v Ledvicah, while samples from lake Jezero na Planini pri Jezeru were analysed at ACTLAB Canada using ICP MS (Pb, Zn, Cd) and instrumental neutron activation analysis for other elements.

For  $k_0$ -INAA about 200 mg of lyophilised sediments were weighed into high purity polyethylene containers (SPRONK system) and irradiated together with an Al-(0.01%) Au alloy disc of 5 mm diameter, serving as a fluence rate monitor, for 20 hours in the TRIGA Mark II reactor of the Jožef Stefan Institute, Ljubljana, Slovenia, at a thermal neutron fluence rate of  $1.1 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ .

Gamma spectrometric measurements were carried out with High Purity Germanium (HPGe) detectors connected to the Maestro multichannel analyser.

Each sample was measured twice; for 1 h after 3 days and for about 16 hours after 8 days of cooling time. The gamma spectra were then evaluated by a PC version of the Hypermet program Ver.5, and the final elemental concentrations were calculated using the KAYZERO/SOLCOI program (KAYZERO/SOLCOI, 1996).

## Results

Radiometric chronology calculated on the basis of  $^{210}\text{Pb}$  activity levels using the CRS model of Shukla (1997) is presented in Fig 1. It showed that at the depth of 18–19 cm all the investigated lake sediments reach the age between 120 (lake Jezero v Ledvicah) and 140 years (lake Krnsko jezero). Higher sedimentation was found in lake Jezero na

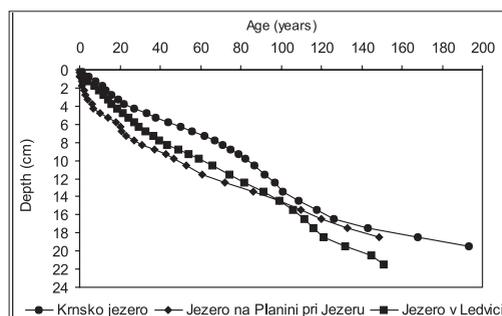


Figure 1: Radiometric chronology of three high-mountain lakes (Krnsko jezero, Jezero v Ledvicah and Jezero na Planini pri Jezeru).

Slika 1: Starost sedimentov v treh visokogorskih jezerih (Krnsko jezero, Jezero v Ledvicah in Jezero na Planini pri Jezeru).

Planini pri Jezeru than in other two lakes, especially in the first 10 cm of core. Although the sedimentation rates were relatively uniform in all investigated lakes, they were interrupted by episodes of rapid sedimentation. It is interesting to note that the turning points in all lakes are found at different depths, which all correspond to the same age of the sediment and which could be linked to the earthquakes in this region in 1895, 1942 and 1975/76. For example; in lake Jezero pri Planini pri Jezeru at the depth of 6–6.5 cm (1976), 10–10.5 cm (1942) and 14–14.5 cm (1895); in lake Krnsko jezero these points were at depths of 3–3.5 (1976), 6–6.5 (1942) and 12–13 cm (1895).

By  $k_0$ -INAA more than 30 elements were determined in each sample, namely As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Dy, Eu, Fe, Gd, Hf, Hg, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Te, Th, Tm, U, W, Yb, Zn and Zr. In Table 1 the means and their standard deviation calculated for each sediment core are presented. From these results it is easily seen that the elemental composition of the sediments of the lakes Ledvice and Jezero na Planini pri Jezeru are very similar to each other, and that the average values of these two lakes are about a factor 2–4 higher than those found in the lake Krnsko jezero. There is every indication that the geological composition of the bottom sediment of lake Krn differs from the other two lakes.

A detailed insight in the distribution of some so-called anthropogenic elements (As, Br, Cd, Co, Cr, Hg, Mo, Sb Zn and Pb (only in lake Jezero pri Planini pri Jezeru) along

the sediment cores is presented graphically on Fig. 2a-c. Only in lake Jezero na Planini pri Jezeru were heavy metals and other trace elements determined to the depth of 35 cm. In the other two lakes 19 cm (Krnsko jezero) and 16 cm (Jezero v Ledvicah) profiles were analysed. As seen from Fig. 2a-c, changes with depth are obvious for all presented elements; however, an irregular decrease is noticed which is especially pronounced in the sediment profile of lake Krnsko jezero, and much less in the other two lakes. It seems

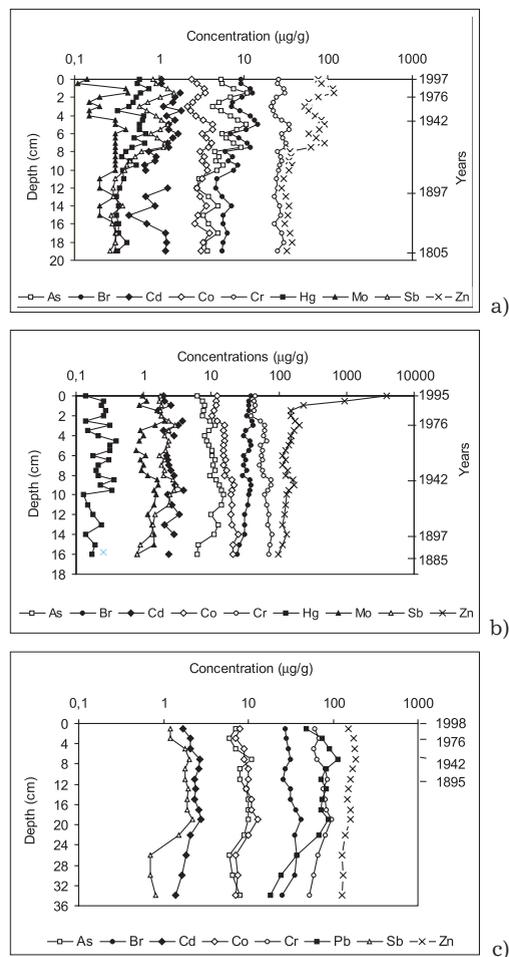


Figure 2: Distribution of trace elements in sediment profiles of lakes a) Krnsko jezero, b) Jezero v Ledvicah, c) Jezero na Planini pri Jezeru. The years of earthquakes are also marked on the Figures.

Slika 2: Porazdelitev elementov v sledovih v jezerih a) Krnsko jezero, b) Jezero v Ledvicah, c) jezero na Planini pri Jezeru. Na sliki so označene so tudi letnice potresov.

that natural events such as earthquakes played an important role in the environment of these small lakes. What really happened during the earthquake in the lake itself is very difficult to say. However, Figs. 2a-c show that a dilution of elemental concentrations is observed in all lake cores, followed by increased sedimentation rates and higher concentrations. Brancelj et al. (2000) presumed that the effect of earthquakes was to trigger slope collapse on the land which then affected sediment resuspension rather than sediment slumping within the lake itself. A detailed examination of the sediment profile of lake Krnsko jezero shows that although the concentrations in the upper 8 cm of the core are higher than below this depth, the distribution is irregular and is interrupted with 3 well expressed lows of all investigated elements at depths of 3.0-3.5 cm, 6-6.5 cm and 8 cm. It is interesting to note that at these depths an increase in ash level was observed which could be a proof of resuspension of sediments. The first two lows could be linked to the two earthquakes in this region in 1976 and 1942, and the third could be understood as the starting point of industrialisation after the First World War. Between 8 and 18 cm elemental concentrations are relatively constant, but on average lower than in the upper section, with only two smaller lows at depths of 9 and 11-12 cm. The first one can be connected to the First World War, since it is known that there were huge detonations at this region during this war (the Soča Front), which could have caused slope collapse, while the second one again can be related to the earthquake in 1895. It is also found that after the late eighties the levels of practically all elements tend to decrease.

In the sediment from lake Jezero na Planini pri Jezeru three periods of lake history can be distinguished. Elemental levels increase from the top down to 7 cm which covers the last 25 years. The decrease from this peak level to the top of the sediment core is especially noticeable for Pb and Cd, and can be connected to the use of lead-free fuels in Western Europe from the late seventies. A similar trend is also observed for As and Sb. Between 7-19 cm relatively constant elemental levels are observed in the sediment profile, reflecting the period of highest industrial emissions in the mid 20<sup>th</sup> cen-

Table 1: Mean elemental levels ( $\mu\text{g g}^{-1}$ ) with standard error in the sediment profiles of three Alpine lakes.Tabela 1: Povprečne vrednosti ( $\mu\text{g g}^{-1}$ ) elementov s standardnim odklikom v globinskem profilu sedimentov treh visokogorskih jezer.

Elements	Krnsko jezero 0 – 19 cm		Jezero v Ledvicah 0 – 16 cm		Jezero na Planini pri Jezeru 0 – 20 cm	
	mean	std	mean	std	mean	std
As	5,81	2,17	9,99	2,46	8,7	
Ba	41,9	4,9	111,9	16,2	135,0	19,0
Br	8,48	2,77	33,90	4,14	30,9	5,0
Cd	1,16	0,36	2,59	0,60	2,36	0,33
Ce	11,53	1,42	41,55	9,74	26,6	5,0
Co	3,25	0,56	16,62	3,70	9,8	1,7
Cr	27,10	3,51	59,78	11,35	75,3	12,0
Cs	2,00	0,20	3,63	0,71	3,4	0,7
Eu	0,22	0,03	0,97	0,24	0,6	0,1
Fe	8571	1569	18432	3840		
Ga	3,21	0,43	7,97	1,48		
Hf	0,69	0,08	1,77	0,39	1,4	0,3
Hg	0,48	0,13	0,23	0,07		
La	5,87	0,71	26,05	6,66	18,3	3,3
Nd	5,55	0,86	23,24	6,15		
Rb	18,9	2,6	48,7	9,4	47,2	15,0
Sb	0,70	0,37	2,00	0,56	1,8	
Sc	2,44	0,32	7,77	1,87	6,3	1,2
Sm	0,99	0,11	4,16	0,90	2,9	0,5
Tb	0,14	0,02	0,55	0,13		
Th	1,84	0,21	5,38	1,13	4,6	0,9
Tm	0,14	0,02	0,41	0,10		
U	1,15	0,06	1,66	0,22	1,3	0,4
Yb	0,46	0,06	1,60	0,43		
Zn	57,57	26,21	313,48	745,44	164,2	13,0
Zr	38,8	11,0	82,6	18,7	59,4	8,0

tury. From the depth of 19 – 35 cm concentrations decrease rapidly with depth and show the influence of the industrial revolution in the 19<sup>th</sup> century.

The distribution of elements in lake Jezero v Ledvicah is similar to that in lake Jezero na Planini pri Jezeru, with the exception of the zinc level which is extremely high in the first 1 cm of the core and may be connected with some human activity in the lake. Concentrations of other elements in the sediment slightly increase to a depth of 3 cm, are relatively constant between 3 and 13 cm, and decrease to a depth of 16 cm. After this depth further decrease in elemental content is expected in this lake as well as also in lake Krnsko jezero. Some further analyses of deeper cores would be needed to obtain the background levels before the industrial revolution in 19<sup>th</sup> century.

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