

Speciation of elements in sediment samples collected at lakes Volvi and Koronia, N. Greece

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Abstract

A five-step sequential extraction procedure was applied for the determination of the distribution of seven elements (Cd, Pb, Cr, Cu, Mn, Zn, Fe) in sediment samples collected at two lakes, Volvi and Koronia, located in N. Greece. Samples were taken in two seasons, and the average concentration of the elements was calculated. The accuracy evaluated by comparing total trace metal concentrations with the sum of the five individual fractions proved to be satisfactory. Based on the results determined at one sampling point in Koronia and two sampling points along the lake Volvi, it seems that the two lakes have not yet been polluted. There were no significant changes in the individual seasonal concentrations of elements in this monitoring period. Cd, Pb, Cu and Cr are associated with the oxidizable, carbonates and residual fractions. Zn and Fe are associated with residual and reducible fractions. The metals that we most easily extracted in the samples analysed in both lakes are Pb, Cr, Cd, Cu and also Mn in the case of Koronia lake.

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1. Introduction

It is now widely accepted that the role of aquatic sediments as a sink or as a source of pollutants cannot fully be assessed by measuring total metal concentrations. In addition, determination of total elements does not give an accurate estimate of the likely environmental impact. Instead, it is desirable to have information on the potential availability of metals (whether toxic or essential) to biota under various environmental conditions. Since the mobility of trace metals, as well as their bioavailability and related ecotoxicity to plants, critically depends upon the chemical form in which a metal is present in the sediment, considerable interest exists in trace element speciation (Davidson et al., 1994).

Chemical speciation can be defined as the identification and quantification of the different species, forms or phases present in a material, or the description of these. However, the determination of specific chemical species or binding forms is difficult and often hardly possible (Loska and Wiechula, 2002). Therefore, determinations of broader

forms, e.g. so-called mobile or carbonate bound forms, depending on operationally defined procedures can be a good compromise to give information on environmental contamination risks. As a result of this practicality, single and sequential extraction schemes have been designed for the determination of binding forms of trace metals in sediments and increasingly used over the last 10 years (Quevauviller et al., 1994; Lima et al., 2001).

A large number of sequential extraction methods have been reported, many of which are variants on the Tessier procedure (Tessier et al., 1979) in which the exchangeable metals and those nominally associated with carbonate, Fe–Mn oxides, organic material and silicate residues were extracted with different reagents (Alvarez et al., 2001; Sobczynski and Siepak, 2001). Although the reagents used in sequential extraction procedures may be insufficiently specific to dissolve exclusively the “target” phases, and results obtained can vary widely when different extraction schemes and experimental conditions are used, useful information has been gained from such studies (Dollar et al., 2001; Gumgum and Ozturk, 2001).

The objectives of the present study were to investigate, using a five-step sequential extraction procedure, the different trace elements forms present in the sediments of two

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lakes and to obtain information on the mechanisms of retention of metals in the Lakes sediments.

2. Materials and methods

2.1. Study area

The studied lakes, the meso-to-eutrophic Volvi and the hypertrophic Koronia, are located in N. Greece, about 11.5 km NE of the city of Thessaloniki (Fig. 1). The data and selected chemical characteristics of the studied lakes are shown in Table 1. The whole area is protected by the Ramsar Convention as a site of international importance for the value of the wetland habitat. The wetland includes important natural complex habitat types such as fresh water marsh, lacustrine and riverine forests, scrublands, as well as agricultural landscapes. The major sources that affect the water quality and the trophic status of the lakes are agricultural runoff, animal husbandry effluents, untreated or semitreated domestic effluents and industrial wastewaters mainly from food, dairy and dyer industries. Other important sources are resuspended stream sediments and eroded bank materials.

Volvi with a surface area 69 km² and mean depth 13.5 m has been classified on the basis of chemical and biological water parameters, as meso- to eutrophic lake. Koronia Lake with a surface area 42 km² and a mean depth 2 m has been classified as hypertrophic (Kaiserli et al., 2002). The surface area has been significantly shrunk during the last years due to overexploitation of water for agricultural and industrial purposes.

2.2. Sediment sampling and analysis

Sediment samples were collected using an Eckman sampling device from the top 20-cm layer of the bottom from one sampling site of the lake Koronia (K) and two sampling sites

Table 1
Main characteristics of the studied lakes

	Lake Volvi	Lake Koronia	
Surface area (km ²)	69	42	
Mean depth (range) (m)	13.5 (10–24)	2 (1–4)	
Altitude (m)	37	75	
Natural trophic status	Lower mesotrophic level	Mesotrophic level	
	V ₁	V ₂	
pH	8.87	8.95	8.95
Conductivity (μS/cm)	1145	1134	5080
DO (mg/l)	8.1	8.2	7.8
COD (mg/l)	84	40	61
TOC (mg/l)	16.3	18.2	17.2
TC (mg/l)	94.5		
IC (mg/l)	78.26	76.50	195
TP (μg P/l)	218	44	262
NO ₃ (μg N/l)	152	105	232
Fe (μg/l)	126	134	147
Mn (μg/l)	52	56	64

from the lake Volvi (V₁, V₂) in two seasons. Samples taken were immediately taken to the laboratory and air-dried. Then stones and plant fragments were removed by passing the dried sample through a 2-mm sieve. The sieved sample was powdered and finally passed through a 75-μm sieve (silt/clay fraction) and 75–150 μm (sand fraction) and stored in glass bottles.

Analysis of the fraction <63 μm is recommended in sediment studies because clay and silt particles generally contain the highest concentrations of pollutants, and are most readily transported in suspension in natural waters.

Analytical reagent-grade solutions were used without further purification. The sequential leaching procedure was carried out with three replicates. The flame atomic absorp-

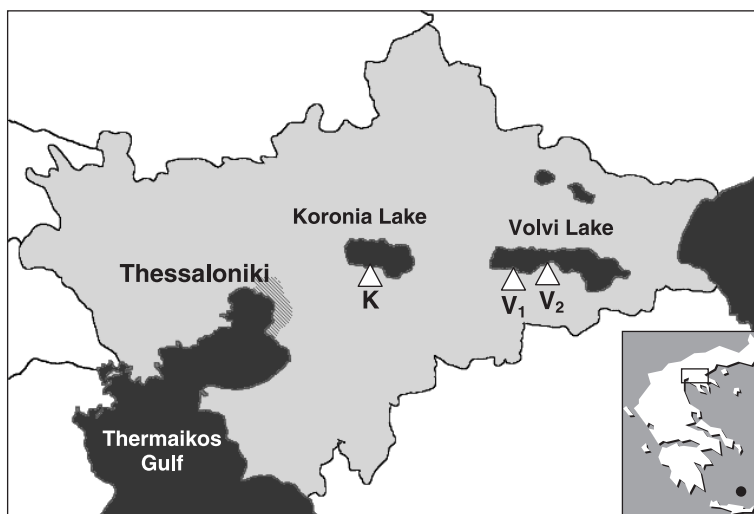


Fig. 1. Map of the studied area.

tion spectrometry (FAAS) was used for the determination of Fe, Mn, and Zn. Cu, Pb, Cd and Cr were determined by Electrothermal Atomic Absorption Spectrometry (ETAAS) with a Perkin-Elmer 2380 atomic absorption spectrometer equipped with an HGA 400 furnace programmer.

The precision of the metal analysis was controlled by including triplicate samples in analytical batches, blanks and the method of standard additions. The relative standard deviations of means of triplicate measurements were less than 5% which was regarded as a satisfactory precision. The results are expressed as a dry weight basis. The analytical procedure for the determination of total concentrations was checked by means of analysis of certified material of lake sediment (CRM 280, BCR) (Mossop and Davidson, 2003).

The sequential extraction method followed is shown in Fig. 2 and was developed principally by Tessier et al. (1979).

Fraction 1. Exchangeable. Metals in the fraction are bound to the sediments by weak adsorption onto sediments particles. Changes in ionic strength of the water are likely to affect the adsorption–desorption or ion exchange process resulting in the uptake or release of metals at the sediment/water interface.

Fraction 2. Carbonate bound. Metals bound to carbonates are sensitive to pH changes with the lowering of pH being associated with the release of metal cations.

Fraction 3. Iron/manganese oxide bound. Metals bound to iron/manganese oxide fraction are unstable under reducing (anoxic) conditions. These conditions result in the release of metal ions to the dissolved fraction.

Fraction 4. Organic bound. Degradation of organic matter under oxidizing conditions can lead to the release of soluble metals bound to those materials.

Fraction 5. Residual. This fraction should contain naturally occurring minerals which may hold trace metals within their crystalline matrix.

For the determination of heavy metals associated (chelated or adsorbed) with humic and fulvic acids, the sediments were treated with 0.1 N NaOH for 10 h. Leaching with 0.5 N HCl has also been used for the evaluation of the pollution of the areas examined. This extraction removes the “anthropogenic” trace element fraction from the sediment (Agemian and Chau, 1976; Abu-Rukah and Ghrefat, 2001).

3. Results and discussion

Comparing the total concentrations in sediments between Koronia and Volvi lakes (Table 2), we conclude that metal pollution in sediments of the Koronia Lake is considerably higher. No significant differences in heavy metal concentrations were observed in the sediments from the two stations in Lake Volvi due to the short distance between them.

Median metal concentrations in Koronia and Volvi Lakes decrease in the order Fe>Mn>Zn>Cr>Pb>Cu>Cd.

The grain size influence was also studied. Sediment samples were divided into grain size fractions (<75, [75–150] μm). The heavy metals were found mostly in the very fine grain size fraction (<75 μm). The rate of increasing or decreasing concentrations was very small and no peak concentrations were found to be associated with a particular range of grain sizes.

The concentrations in percent (%) of the elements determined at each extraction step in the sediment samples are illustrated in Figs. 3 and 4.

In the majority of cases, the sums of the extracted fractions agree to within 10% with the independently determined total metal concentrations, supporting the overall accuracy of the extraction procedure. The total concentrations of the examined heavy metals as well as the percentage (%) of anthropogenic and humic–fulvic acids fractions are also given in Table 2.

The Cu content of samples ranged between 9.5 and 18 μg/g for all sampling sites and for both lakes. The highest concentration values (~40%) for Cu were observed at the fourth stage of the extraction procedure. This indicates that Cu occurred in the forms of stable organic complexes and metal sulfides. As expected from a number of previous studies on polluted sediments (Pardo et al., 1993; Samanidou and Fytianos, 1987; Marin et al., 1997), extractable copper is mainly associated with the oxidizable phase, where it is

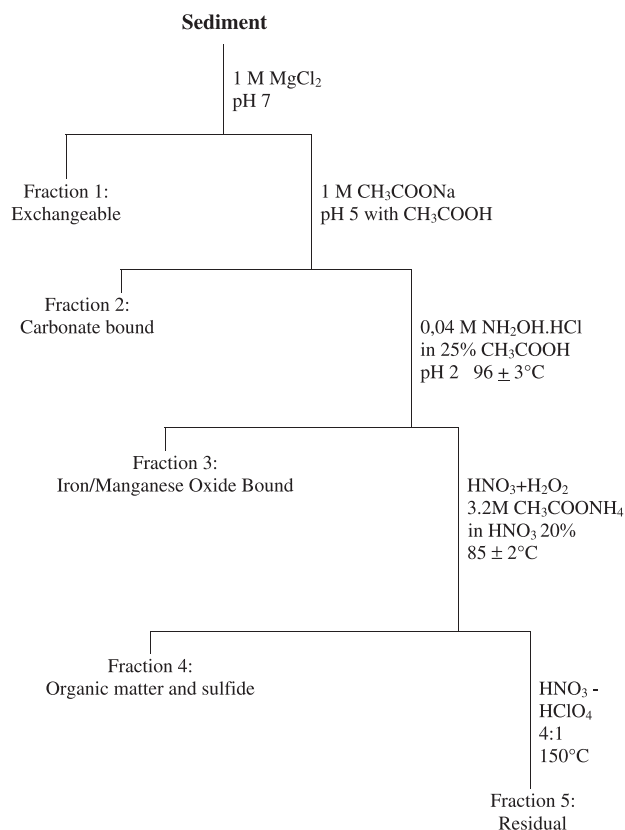


Fig. 2. Sequential extraction method followed in the present study.

Table 2

Mean total content of heavy metals in sediments and partitioning range (%) of heavy metals associated with humic and fulvic acids and the “anthropogenic” fraction

	Pb	Zn	Cu	Mn	Fe	Cr	Cd
<i>Lake Koronia</i>							
Total	20.38 (16.30–24.46)	85.86 (72.12–99.60)	16.76 (14.76–18.77)	631.8 (581.3–682.3)	5.46 (5.24–5.68)	32.20 (27.27–37.03)	0.99 (0.97–1.01)
Anthropogenic	55.45 (50.45–60.45)	42.94 (37.84–48.04)	41.25 (37.40–45.10)	51.95 (47.05–56.85)	30.47 (28.27–32.67)	20.86 (17.66–23.06)	63.02 (61.05–64.99)
Humic	10.09 (9.59–10.59)	4.38 (4.07–4.69)	1.88 (1.66–2.10)	0.24 (0.21–0.27)	1.97 (1.79–2.15)	3.32 (2.77–3.87)	5.19 (4.31–6.07)
<i>Lake Volvi (V₁)</i>							
Total	12.46 (10.52–14.40)	53.43 (47.93–58.93)	15.20 (14.00–16.22)	145.3 (133.4–157.23)	3.65 (3.53–3.77)	23.12 (20.92–25.32)	0.75 (0.74–0.76)
Anthropogenic	46.32 (41.32–51.32)	37.85 (35.01–40.69)	46.90 (45.02–48.78)	17.05 (16.54–17.56)	27.22 (26.29–28.15)	23.45 (12.78–14.12)	48.40 (45.45–51.35)
Humic	12.28 (11.89–12.67)	7.84 (7.62–8.06)	12.09 (11.68–12.50)	1.56 (1.53–1.59)	3.67 (3.56–3.78)	4.02 (3.86–4.18)	3.15 (3.04–3.26)
<i>Lake Volvi (V₂)</i>							
Total	13.56 (12.75–14.37)	69.31 (64.11–74.51)	13.14 (12.42–13.86)	91.16 (83.87–98.45)	2.91 (2.86–2.96)	20.40 (19.58–21.22)	0.98 (0.97–0.99)
Anthropogenic	45.55 (43.05–48.05)	40.68 (38.48–42.88)	47.49 (44.64–50.34)	45.82 (43.02–48.62)	39.75 (37.48–42.02)	15.88 (15.24–16.42)	49.52 (46.00–53.04)
Humic	12.48 (12.08–12.88)	14.54 (13.96–15.12)	13.68 (12.98–14.38)	0.53 (0.52–0.54)	2.80 (2.74–2.86)	3.33 (3.32–3.43)	5.60 (5.35–5.85)

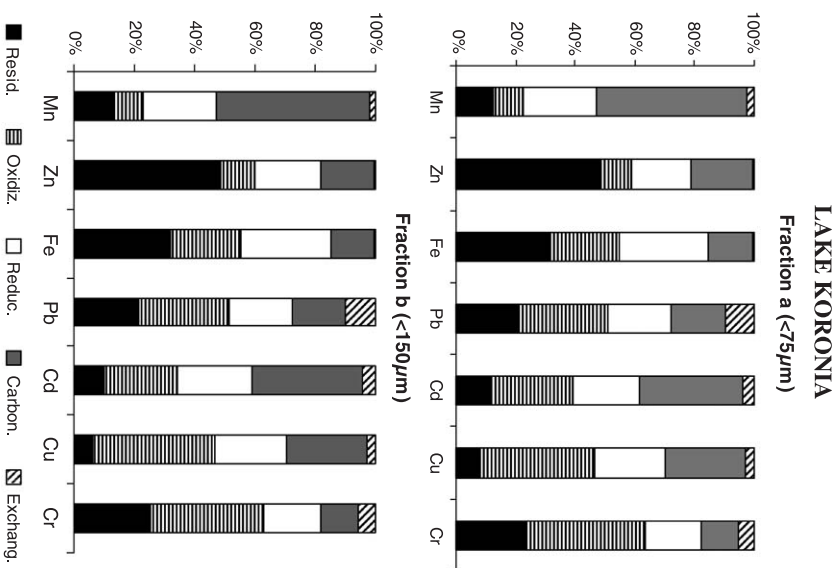


Fig. 3. Speciation of heavy metals in the sediments of the lake Koronia for the fraction <75 µm and <150 µm.

likely to occur as organically complexed metal species. This behaviour can be explained by the well-known high affinity of Cu to humic substances, which are a fraction of natural organic matter chemically very active in complexing such metals (Pempkowiak et al., 1999).

Under an oxic water column, a significant fraction (up to 40%) of the Cu reaching the sediment surface may be returned to the overlying water column by mineralization of the host organic material at the surface and in the oxic upper layers of the sediment. A smaller fraction of sediment Zn may be remobilized for the same reason (Peterson et al., 1995). With continuing diagenesis further Cr, Cu and Zn will be released, as a result of microbial oxidation of the organic substrate (Jones and Turki, 1997).

In the sediment samples, the concentration of Cd was less than 1 µg/g. Cadmium was found to be most frequently associated with sulfur (40%) for lake Volvi and it is reported that thermodynamic calculations also suggested the formation of Cd (Sahuquillo et al., 1999). However, in lake Koronia, carbonate-bound fraction becomes more important and represents for Cd the major fraction (35%); a result which has also been reported (Samamidou and Fytianos, 1987).

Zn and Fe, the two most abundant of the metals analysed, are distributed in a similar manner, with the residual the reducible and to a lesser extent the oxidizable

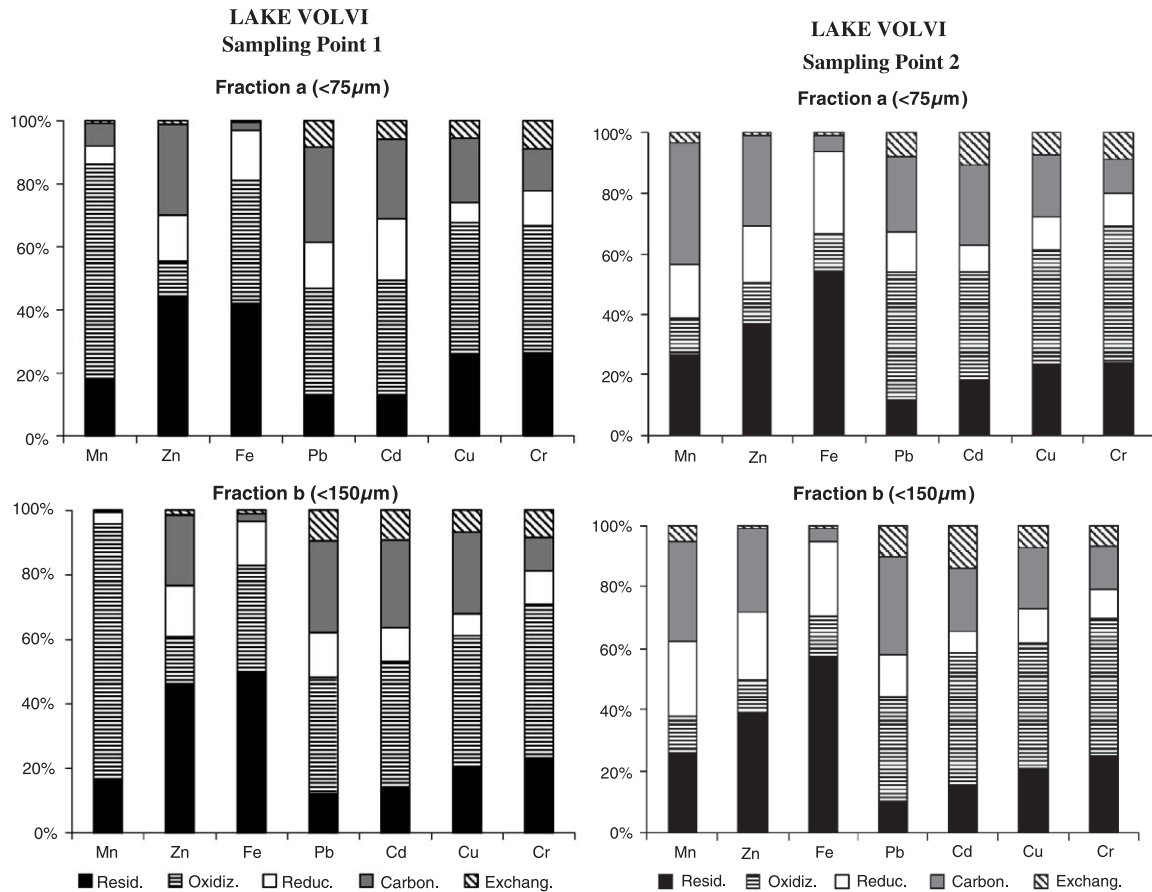


Fig. 4. Speciation of heavy metals in two sited sediments of the lake Volvi.

fractions being of greatest significance. The residual fraction is the dominant Zn host in all analysed samples and this phase carried approximately 45% of the total Zn concentration.

However, manganese which is also abundant behaves in a different way in the two lakes. In sampling site V₁, the dominant fraction is the oxidizable phase; in V₂ and K, the extractable manganese is located principally in the carbonate fraction (40% and 50%, respectively). This is probably related to the abundance of Mn in the earth's crust, including soil (Tokalioglou et al., 2002).

Our observations that Cd, Cr and Pb are distributed primary in the reducible (Iron/Manganese oxides), residual and oxidizable (organic matter and sulfides) phases, that Cu occurs in oxidizable and residual phases, are in excellent agreement with metal speciation studies of sediment from other rivers and lakes (Calmano and Forstner, 1983). Metals bound to these different phases will behave differently in the sedimentary and diagenetic environment, and thus have different potentials for remobilization and for uptake by biota.

The chromium content (total) within the sediment fraction varies from 20 to 34 µg/g.

The speciation scheme of the present study indicates its dominant presence with the oxidizable fraction of the

sediment which is previously reported (Galvez-Cloutier and Dubé, 1998; Davidson et al., 1994). However, a smaller percentage is also associated with residual fraction. The sum of these two fractions contained more than 65% of the total amount of Cr (Hlavay and Polyák, 1998). Sedimentation of the detrital chromium complex via chromite and mangetite has contributed to the chromium content and thereby resulted in the enrichment of chromium in sediments Fe–Mn oxide grain coatings transport nondetrital chromium to bottom sediments, which in turn also causes enrichment of chromium within them (Baruah et al., 1996).

In sediment samples, the concentration of Pb ranged between 10 and 21 µg/g. Lead speciation is known to be very variable, perhaps due to the relatively large proportion of the element which enters the aquatic environment through atmospheric deposition (Marin et al., 1997; Davidson et al., 1994). Lead shows no significant variation in the lake sediments. The speciation of lead suggests that a major portion is bound to the organic matter fraction with moderate amounts associated with the carbonate and residual fractions (Hlavay and Polyák, 1998).

Iron is the most abundant metal in all sediments because it is one of the most common elements in the Earth's Crust. The analysis of the distribution of Fe showed that most of it is

associated with the residual phase. The remaining fractions of Fe were distributed among the reducible and the oxidizable phases. The percentage of Fe in these two fractions was, however, variable. The variability probably results from competition between Fe organic complexes and hydrous Fe oxide forms. This situation is complicated because hydrous Fe oxides themselves can complex with organics, especially humic substances in sediments (Smith and Milne, 1979; Nembrini et al., 1982). The fractions generally vary from higher to lower concentrations for the metals Cu, Cr and Pb in the following order:

Organic fraction > residual fraction > carbonates fraction
> reducible fraction > cation exchangeable,
for the two lakes.

The anthropogenic heavy metals in sediments follow the order:

Cd > Pb > Mn > Zn > Cu > Fe
> Cr for Koronia Lake and Cd ≈ Cu > Pb > Zn > Mn
> Fe > Cr for Volvi Lake.

4. Conclusions

From the results of the present investigation, the following conclusions can be drawn.

Concerning the total concentrations in sediments, Koronia lake is considerably more polluted than Volvi lake, especially with the metals Fe, Mn, Zn and Pb. Although the sediment levels in the lake sediments are elevated, their distribution within the sediment phases are typical of background metal distribution (Izquierdo et al., 1997). Besides, more than 30% of the majority of the metals studied were associated with the residual fraction. The metals associated with this fraction cannot be remobilized under the conditions normally encountered in nature.

The sum of the metals associated with the first three fractions (exchangeable ions, carbonates and reducible) is considerably high. This is extremely important because it represents the proportion of heavy metals than can be easily remobilized by changes in environmental conditions such as pH, salinity, etc.

The metals that are most easily extracted in the samples analysed in both lakes are Pb, Cr, Cd, Cu and also Mn in the case of Koronia lake.

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