

Article

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Depth Profile Of Trace Elements In a Sediment Core Of a High-Altitude Lake Deposit At The Pyrenees, Spain

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Abstract Depth concentration profiles of 26 elements, i.e. trace elements (As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Rb, Sr, V and Zn), lithophiles (Si, Al, Fe, Mn, Na, K, Mg, Ca and Ti) and nutrients (C, P, N, S) have been established in a sediment core collected at the Respomuso Lake (Pyrenees, Spain). This high altitude lake of glacier origin was transformed into reservoir in the fifties of last century. Correlations among the depth profiles of the above elements were established. HCl-extractable elements, which are better related to bioavailability, followed the profiles of total contents. Principal component analysis was applied to establish the binding behaviour of trace elements in the sediment matrix and, in turn, to search for their anthropogenic or natural sources. It was seen that Cu, Ni, Pb, Sr and Zn clustered together, and with exception of Sr, they were not clearly associated with any major component of the sediment. Their depth profiles correlate well with each other, hence indicating their presence as a result of atmospheric pollution. Redox-sensitive elements such as Fe and Mn follow a similar trend along the vertical profile. Depth profiles of As and Co correlate well with those of Fe and Mn. Principal component analysis showed that As, Co, Fe and Mn clustered together, which confirms the close association of As and Co with Fe-Mn oxyhydroxides. As concentrations in many strata exceed the ERM value, and therefore, significant biological effects are expected. Dissolution of minerals such as pyrite, chalcopyrite and galena taking part in the mineralogy of this area accounts for the As concentration found. Ba, Cr, Rb and V were associated with the sediment matrix (aluminosilicates), hence showing low mobility.

Key words trace elements - sediments - depth profile - Respomuso Lake - extractable contents - principal component analysis

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DEPTH PROFILE OF TRACE ELEMENTS IN A SEDIMENT CORE OF A HIGH-ALTITUDE LAKE DEPOSIT AT THE PYRENEES, SPAIN

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Keywords: trace elements, sediments, depth profile, Respomuso Lake, extractable contents, principal component analysis

1. Introduction

Despite Lakes containing less than 0.02% of the water in the hydrosphere, their geological significance is much greater than this value suggests (Talbot, 1996). Lakes used as reservoirs, besides their environmental relevance they have become important sources of water and energy. In this context, Respomuso is a lake of glacier origin situated at the central Pyrenees (Spain) that was transformed into reservoir in the fifties.

Pyrenean Glaciers were declared nature monuments in 1989 (BOE, 1989), being subjected to protection since then. In an attempt to limit the ecological impact over glaciers and their peripheral protection zones, regulations have established limitations concerning waste spoils, building activities, and even flying over the area (with exception of emergency situations, scientific missions and provision of mountain refuges). However, it has been shown that enlargement of lakes addressed to their transformation in reservoirs can give rise to significant impact on these ecosystems (Prats, 1998).

Although several studies have been performed on pollution assessment in Pyrenees lakes, mainly in the framework of European projects, such as the Mountain Lake Research (MOLAR) 1999 (Mosello *et al.*, 2002), they have mostly focused on the Redó Lake, one among the few lakes that has not been altered for its conversion into reservoir. Principally, environmental control in the Redó Lake has targeted radionuclides, organochlorine compounds, polycyclic aromatic hydrocarbon and lead in the different environmental compartments (Camarero *et al.*, 1998; Carrera *et al.*, 2002; Appleby *et al.*, 2002; Grimalt *et al.*, 2004). Despite heavy metals being ubiquitous and persistent pollutants, information on their presence in Pyrenees Lakes is scarce. Some reports have pointed out enrichment factors (EF) up to 5 in several Pyrenean Lakes, thereby revealing the deposition of atmospheric pollutants in mountain areas (Camarero, 2003). Lake sediments act as a major sink for metals and hence, differentiation between natural metal enrichment in zones of mineralizations and anthropogenic effects is especially well suited by sediment cores. Sediment core analysis provides a historical record of the natural background and the man induced accumulation of metals (Ahumada and Rudolph, 2004). In remote sites, such as high altitude lakes, pollution originates principally from atmospheric deposition (Yang *et al.*, 2002). Variations in metal concentrations along the vertical profile should also take into account geogenic processes occurring in the own lake. Therefore, metal fluxes can be influenced by a large number of factors (Boyle and Birks, 1999).

The aim of this work is to investigate the variation in metal concentration throughout the vertical profile of Resposuso Lake deposits since the time it was transformed into reservoir. Distribution of trace metals in different geochemical phases of the sediment core is discussed bearing in mind their geogenic or anthropogenic sources. Potential biological risk displayed by the trace metals in the deposit is outlined on the basis of the sediment quality guidelines (USEPA).

2. Materials and Methods

2.1. DESCRIPTION OF THE STUDY AREA

The Resposuso Lake of glacial origin is located at the central-axis of Pyrenees (Tena Valley, Sallent de Gallego, Spain) and it has an altitude of 2121 m (coordinates: 428490 N, 08170 W, about 2200 m above sea level), being among the

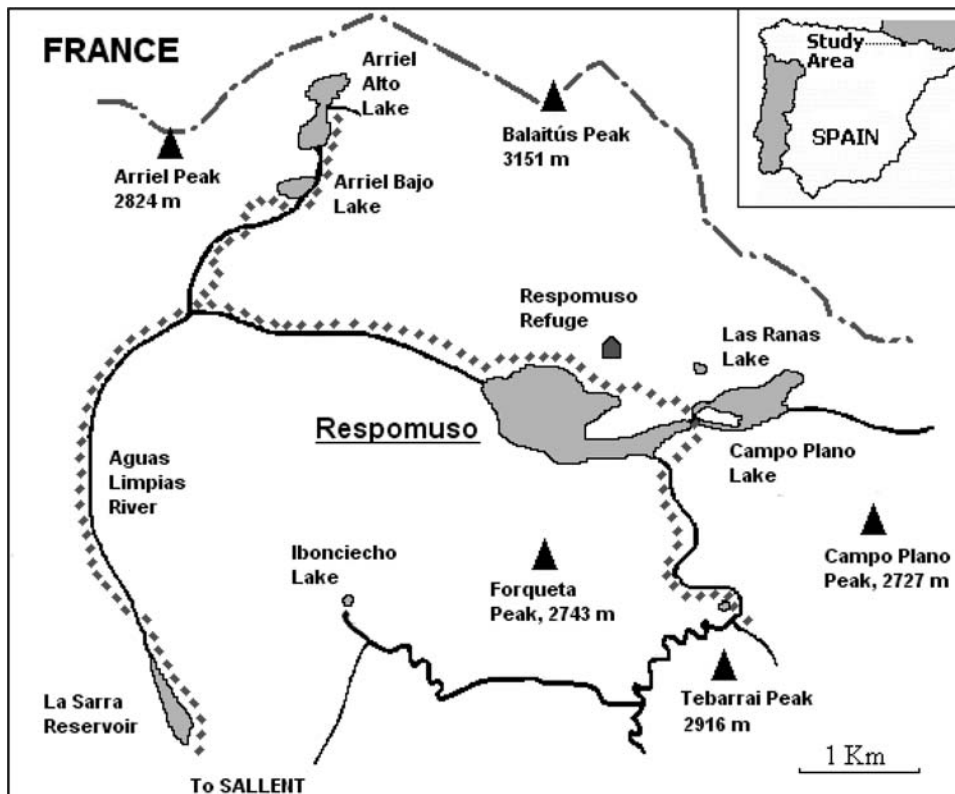


Figure 1. Map showing the study area.

highest lakes at this mountain chain. The map showing the location of the Respomuso Lake is depicted in Figure 1. The lake is surrounded by the following peaks: Forqueta (2743 m), Tebarrai (2916 m), Campoplano (2727 m), Balaitús (3151 m) and Arriel (2824 m). The lake is only accessible on foot (2.5 h from the nearest road) or by helicopter. Close to the lake there is the Respomuso refuge, which has been open from ca. 1993. Its building was started in 1980, lifting the required materials by helicopter, which flew over the lake for several times a day. This information is relevant, since activities carried out during the building period can be considered as potential sources of pollution.

The granitic massif is shaped by precambrian and Palaeozoic materials that crop out in this region of Pyrenees. Mineralogy is mainly formed by pyrite, chalcopyrite, galena, siderite, green fluorite and white fluorite. Generally, pyrite, chalcopyrite and galena contain large amounts of As. Tebarrai occurrences are remarkable within the mineralization of this area. Tebarrai occurrences are low-temperature hydrothermal veins related to sedimentary rocks in the Hercynian basement, which can be considered as polymetallic deposits with abundant fluorite. Zn-F-(Pb) mineralizations

have been prospected, although apparently none has been mined (Subías *et al.*, 1997).

Hydroelectric use of the Respomuso Lake was started in 1954. Its artificial barrage meant a noticeable increase of the basin area, *ca.* 20%. The capacity of the reservoir is about 17.3 Hm³ and the total area 55.2 Ha (IAEST, 2002). Average rainfalls are in the range 1800–2000 mm year⁻¹. Water composition corresponds to weak mineralization that is common in the whole Pyrenees area; pH ranges from 6.4 to 7.9. Trace element concentrations are quite low or undetectable with exception of As, which displays significantly high concentrations (13–26 µg/L) in some spring waters of the Tena valley, generally fountains situated at an altitude between 1300 and 3200 m (Subías and Fernández Nieto, 1995). International organizations such as the world health organisation (WHO) and the US environmental protection agency (USEPA) have given limits for As in drinking water. Until 2001, most International legislations recommended 50 ppb of Arsenic as a standard for drinking water. In 2001, EPA adopted a new standard at 10 ppb, replacing the old standard and its full applicability will start on January 2006. (<http://www.epa.gov/safewater/ars/implement.html>). This anomalous As concentration in the spring waters of this region has been attributed to dissolution processes of pyrite, chalcopyrite and skarn deposits (i.e. deposits occurring at the contact of granites with limestones) (Subías and Fernández Nieto, 1995; Garrido *et al.*, 2001). Arsenic contribution to natural water composition as a consequence of geochemical processes is well documented and, unlike anthropogenic sources, resulting pollution can spread over large areas (Chakraborti *et al.*, 2001; Rahman *et al.*, 2005).

2.2. SAMPLING

A 63 cm sediment core was collected at a side of the lake during the summer of 2002, which had been emptied with the aim of assessing the effect of a weak earthquake occurring in that period. The depth of the core selected was expected to comprise a record from the time when the Respomuso Lake was transformed into reservoir. Samples were at the centre of the Respomuso reservoir, which corresponds to the edge of the old glacier basin. Boulders found at the bottom gives exactly the depth from which the new deposit was formed. As a preliminary study, *in situ* inspection of the depth profile allowed to directly observe sediment stratification from the top up to the boulders of the old basin. Strata showed a continuous record of sedimentation and no textural evidence of erosion. An interpretable chronology was visible, so the whole core included the history of the last 42 years. Several studies (Allen, 1986; Renberg, 1986, Santschi *et al.*, 1984; Mecray, 2001) have documented that, in the absence of significant changes in sediment texture, downcore variations in trace metal concentrations and accumulation rates reflect historical variations in metal inputs.

The core was sub-sampled at 1.5 cm intervals. Sub-samples were placed into PET bags and transported to the lab at 4 °C. Sediments consisting of interlaminated sandy and clayey silts were air-dried for 15 days inside a laminar flow-chamber to avoid

contamination. Then, the dried samples were sieved through nylon sieves (50 μm meshsize), homogenised and stored in polyethylene vessels in a dry atmosphere.

2.3. ANALYTICAL METHODS

All reagents were of analytical grade. Ultrapure water from a Milli Q system (Millipore, Molsheim, France) was used throughout.

Concentrations of As, Ba, Co, Cr, Cu, Sr, Rb, Zn and V was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin-Elmer, model Optima 4300, Überlingen, Germany); Concentrations of Cd and Pb were determined by electrothermal-atomic absorption spectrometry (ETAAS) (Unicam, model Solaar 939, Cambridge, UK); concentration of Hg was determined by cold vapour-atomic absorption spectrometry (CV-AAS) (Perkin-Elmer, model FIMS 400). Sediment samples were firstly subjected to microwave-assisted digestion (CEM, model MDS-2000, Matthews, USA) using Teflon PFA vessels and a multi-stage programme based on the procedure established elsewhere (Filgueiras *et al.*, 2004). 5 mL of 65% mass/mass HNO_3 and 2 mL of 48% mass/mass HF were employed. Acid digestion was validated against CRM GBW 07302 and CRM GBW 07311 stream sediments from the National Research Center of China.

Bioavailable element contents in the sediment samples were obtained upon extraction with 1 M HCl according to the procedure recommended by the ASTM D3974-81 Practice B (ASTM, 1990; Carral *et al.*, 1995). This standard practice indicates that the metals, which are released from the sediment upon acid extraction, are bound as hydroxides, carbonates, sulphides, oxides and organic materials. The use of lower HCl concentrations, despite being a common practice, may be ineffective since acidity can be neutralized by carbonates present in the sediment (Luoma and Bryan, 1981; Snape *et al.*, 2004). On the other hand, higher HCl concentrations can lead to the attack of residual sediment phases. 1 M HCl corresponds well with ecotoxicity data (Luoma and Bryan, 1981; Ying *et al.*, 1992). Extractions were carried out in 50 mL capacity polyethylene tubes using a 0.5 g sample mass and a 20 mL extractant volume. After agitation for 2 h, the extract was separated by centrifugation (2100 rpm, 20 min). Both digestions and extractions were carried out in triplicate.

Major components were characterised by X-ray fluorescence spectrometry (XRF) (Siemens; model SRS 3000, Hannover, Germany). A portion of 5–6 g of sediment was prepared as lithium tetraborate melts for the determination of major components (SiO_2 , Al_2O_3 , Fe_2O_3 , MnO, TiO_2 , CaO, MgO, K_2O , Na_2O , P_2O_5 , S and Cl). Fusions were performed in Pt-Au crucibles. Calibration was carried out using certified Reference materials from National Research council of Canada, NRCC (SO-3, SO-4, HISS-1, MESS-3 and PACS-2, soils and sediments) and from South Africa Bureau of Standards, SACCRM (SARM 52, stream sediment).

Carbon and nitrogen determinations were carried out by elemental analysis with an automatic analyser (LECO, model CN2000, St. Joseph, USA). Calibration was performed using LECO soil standards (502–309 Soil).

Element recoveries of 93–105% obtained with certified reference materials (CRMs) pointed out that analytical methods were adequate for all elements in the samples of the Respomuso Lake. Found concentration values were in all cases within the certified ranges. All concentration values reported in this work were well above the corresponding quantification limits. Relative standard deviations were below 10% for determination of trace elements.

Factor analysis (principal components analysis, PCA) was applied as a chemometric approach to detect the latent information within the element concentration data. PCA was performed for different subsets of data as described in the 'results and discussion' section using the software StatView for Apple Macintosh.

3. Results and Discussion

3.1. DEPTH PROFILES OF MAJOR COMPONENTS IN THE RESPOMUSO SEDIMENT CORE

Analytical results for major components of the sediments are shown in Table I. Mineralogy of the Respomuso sediments is predominantly quartz, but also reflects the lithological and hydrochemical influences. Typical endogenic and authigenic formations such as Fe-Mn oxides, Ca-Mg minerals or phosphorus compounds and sulphides display a large variability as pointed out by the coefficients of variation (CV). The correlation coefficients (CC) of Pearson ($p < 0.05$) for the major elements point out that lithophiles (i.e. alkaline, alkaline-earth and aluminium) are generally well correlated. Al, the safest indicator of erosion, remains almost constant along the sediment core profile (CV: 4.4%), which means that a uniform sedimentation rate has occurred. Other erosion indicators such as K and Mg display also minimal variations. This confirms the similar physical characteristics observed for the segments of the sediment core. Ca has been included in this work within lithophiles. Nevertheless, this element can be included in different groups in aquatic systems. Thus, it has been included in the alkaline type elements that are precipitated by increased pH (Cd, Mg, Sr, Mn, Fe, Cu, Zn and Pb) and within the

TABLE I
Major components in subsamples from the Respomuso sediment core (% mass/mass)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	MgO	CaO	TiO ₂	C total	Organic matter	P ₂ O ₅	N	S
Mean	53.9	17.6	6.5	0.22	1.0	2.8	2.0	2.8	0.9	2.8	2.7	0.4	0.23	0.09
Min.	51.6	16.1	5.5	0.13	0.8	2.3	1.7	2.0	0.8	0.5	0.4	0.2	0.06	0.01
Max.	58.3	19.2	9.2	0.57	1.4	3.2	2.4	4.4	1.0	8.6	8.5	0.5	0.58	0.16
C.V (%)	2.0	4.4	12.7	45.4	12.6	6.7	8.6	18.8	7.5	60.9	61.2	18	48.6	44

sulphate-carbonate type (Ba, Sr, Ca) that are precipitated by increased sulphate or carbonate (Salomons and Förstner, 1984). The Ca geochemistry is strongly influenced by the $\text{CO}_2\text{-HCO}_3^- \text{-CO}_3^{2-}$ system, which is different for the other lithophiles (Talbot, 1996).

Additionally, Ca shows the largest CV among this group of elements (CV: 18%). Fe and Mn, two redox-sensitive metals, are significantly correlated with each other along the sediment core. A larger CV is observed for Mn (45%) than for Fe (13%). Mn concentration peaks at a depth between 15 and 31.5 cm. Mn and Fe enrichments have been reported under conditions of diagenetic metal remobilisation (Hornberger *et al.*, 1999). The Fe/Mn ratio has been commonly employed as a variable to describe sediment redox conditions and, in turn, to reveal changes in the sedimentation environment (Vaalgamaa, 2004). A significant increase in the Fe and Mn contents in the sediment core was observed at a depth between 15 and 24 cm (Figure 2). It is reasonable to ascribe the observed change to the formation and precipitation of

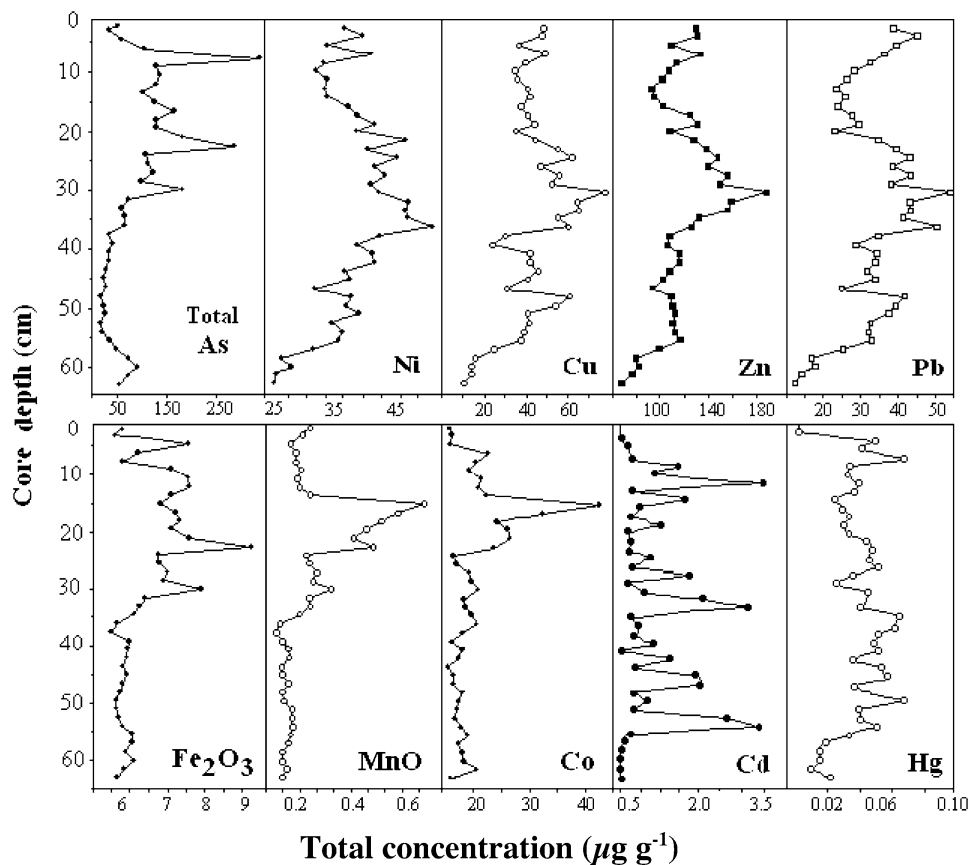


Figure 2. Depth profiles for total element concentrations (Fe_2O_3 and MnO contents are expressed as % mass/mass).

Fe and Mn oxyhydroxides. In lake waters, a redissolution of iron and manganese takes place, which diffuses upward and precipitates at the oxic/anoxic interface in the lake. The resulting hydrous iron and manganese particles are able to remove dissolved metals (Salomons and Förstner, 1984). Similar depth profiles for Fe and Mn to those observed in this work have been reported elsewhere (Chandrajith *et al.*, 1995). This profile for Mn is classified as case III (Salomons and Förstner, 1984) that corresponds to mildly reducing conditions allowing the development of well defined oxic zone where remobilised metals may be trapped and greatly concentrated over natural levels. According to this, there is an increase in Mn and Fe contents at the top layer of these sediments as occurs in the Respomuso core. The concretions and nodules of Fe/Mn oxyhydrates are autochthonous phases, for which diagenetic effects are assumed to occur in Lakes. Apart from Fe and Mn, redox processes involve the elements C, N, O, S and H. No significant correlation between Fe/Mn and those elements was found. An explanation for the maximum observed in the core above 15 cm depth could be based on the relationship between organic matter and Fe(III) precipitation in the sediments. Dissolved organic matter can significantly alter the distribution between oxidised and reduced forms of Fe and Mn (i.e. Fe (II) stabilization is a function of the concentration of organic matter). A diminished organic matter content can facilitate oxidation of Fe(II) into Fe(III), and precipitation of the latter in the sediments. This hypothesis is supported by the minimum in the C/N ratio that is observed at *ca.* 15 cm depth.

Elements belonging to the nutrient group (C, P, N, S) are also correlated with each other in the sediment core. A large variability is observed for this element group along the depth profile (CV 40–60%) except for P (CV 18%). Sediments collected at a depth between 30 and 57 cm showed a significant increase in nutrient element concentrations. The C/N ratio has been employed to establish the origin of organic matter in sediments (Meyers, 1994). A ratio between 5 and 8 suggests that the organic matter was originated in the own lake. On the other hand, a C/N ratio above the upper limit does not mean an external source of organic matter since N-containing compounds can be lost (Vaalgamaa, 2004). A C/N ratio between 25 and 35 is associated with land-derived organic matters. In the sediment core of the Respomuso Lake, the C/N ratio ranges from 7 to 14 (mean value: 11) (Figure 3), hence suggesting that organic matter is perhaps originated in the own lake. Inorganic C contents are quite low, in the range 0.02–0.05%, so total C corresponds almost exclusively to organic C. Cl concentrations were around 0.14% in the sediment core.

3.2. DEPTH PROFILES OF TOTAL TRACE ELEMENTS

Total concentrations ($\mu\text{g/g}$) of trace elements along the depth profile are shown in Table II. Mean, minimum and maximum values for each metal were: As (mean 87.3, min. 15.3, max. 339.5); Ba (mean 423, min. 387, max. 456); Cd (mean 0.83, min. <LD); Co (mean 20, min. 15.9, max. 42); Cr (mean 84.4, min. 74.72, max.

TABLE II
Total trace metal concentrations along the depth profile of the Resposmuso sediment core

Depth (cm)	As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	Rb	Sr	V	Zn
1.5	54.7±0.5	415±5	<LQ	15.9±0.7	79.4±0.7	48.2±0.7	<LQ±	37.6±0.7	38.7±1.4	107.10±0.11	154.4±0.8	111.7±1.5	129.48±0.10
3.0	33.0±0.9	409±6	<LQ	16±1	76.1±1.4	47.42±0.18	0.050±0.003	40.0±0.8	44.9±0.2	105.32±0.06	163.5±0.8	109.3±0.6	130.2±0.6
4.5	58.8±0.9	412±3	0.17±0.01	16.2±0.5	76.2±0.8	36.59±0.03	0.041±0.002	35.3±0.5	39.6±1.1	108.5±0.3	139.43±0.12	113.7±0.6	109.6±0.6
6.0	105.3±2.3	427.7±1.2	0.26±0.02	22.6±0.7	81.5±0.9	48.93±0.23	0.067±0.005	41.1±0.5	36.5±0.7	113.59±0.06	139.7±0.9	121.3±1.5	133.22±0.21
7.5	339±6	410±3	1.39±0.08	20.4±0.6	76.2±0.3	39.76±0.05	0.033±0.001	34.7±0.6	32.2±0.3	113.83±0.11	126.10±0.21	109.7±1.5	113.5±1.1
9.0	128.3±1.2	406±4	0.84±0.06	19.3±0.9	77.9±0.7	35.0±0.3	0.039±0.002	33.6±0.6	28.2±1.1	107.9±0.4	134.6±0.4	111.0±1.7	106.83±0.17
10.5	135.3±3	402±3	3.54±0.06	21.3±0.3	86.4±1.4	36.1±0.4	0.039±0.003	35.2±0.4	26.3±0.4	111.92±0.10	126.6±0.7	120.0±1.0	102.0±0.7
12.0	127.0±1.0	412.1±1.0	0.34±0.02	20.9±0.7	83.3±0.9	40.76±0.23	0.036±0.002	34.8±0.3	23.4±0.6	112.8±0.6	124.41±0.10	129.0±1.0	93.64±0.13
13.5	100.4±1.0	410±3	1.65±0.09	22.4±0.9	83.3±0.3	42.1±0.4	0.022±0.002	35.2±0.8	25.8±1.3	110.5±0.3	133.4±0.3	124.3±0.6	95.8±0.4
15.0	126.3±1.1	423.3±0.6	0.45±0.03	42±1	80.7±0.7	38.0±0.5	0.028±0.002	38.2±0.6	23.8±0.4	107.9±0.4	132.3±0.3	115.7±0.6	102.9±0.9
16.5	165.0±1.0	418.3±0.6	0.31±0.03	32.4±0.4	82.6±0.5	40.8±0.3	0.031±0.003	39.4±0.5	27.5±0.8	105.7±0.3	143.6±0.4	114.7±2.1	124.6±0.4
18.0	128.0±1.7	408.7±1.5	0.92±0.05	24±1	84.0±0.6	43.9±0.4	0.029±0.003	41.5±0.4	29.3±0.4	106.66±0.10	141.50±0.12	123.0±1.0	130.4±0.3
19.5	128.3±2.1	426.3±1.5	0.21±0.02	26.0±0.3	83.8±0.5	35.4±0.4	0.031±0.003	39.1±0.3	23.0±1.1	113.6±0.4	124.7±0.3	128.3±0.6	107.9±0.7
21.0	183±3	436.7±1.5	0.24±0.01	26.5±0.4	87.8±1.5	44.7±0.3	0.044±0.004	45.51±0.06	34.7±1.5	113.6±0.3	128.8±0.5	135.7±0.6	127.82±0.15
22.5	288±4	401.0±1.0	0.22±0.02	23.8±0.7	81.5±0.9	54.8±0.7	0.048±0.003	40.7±0.5	39.5±0.4	101.81±0.09	148.5±0.4	123.3±0.6	138.1±0.4
24.0	107.7±0.6	417±3	0.78±0.04	16.7±0.5	85.2±0.9	62.5±0.6	0.045±0.002	44.50±0.11	42.9±1.2	103.92±0.17	159.01±0.12	131.0±1.0	148.1±0.5
25.5	111±3	421.1±2.0	0.29±0.02	16.90±0.15	86.8±0.9	46.80±0.17	0.051±0.003	41.6±0.5	38.60±0.06	103.78±0.06	167.02±0.17	131.0±2.0	139.2±0.7
27.0	123.3±1.2	409±3	1.77±0.06	19.3±0.8	84.2±1.1	55.7±0.4	0.035±0.002	43.2±0.4	43.3±2.1	105.9±0.4	181.5±0.5	129.0±1.0	156.5±0.7
28.5	99.6±1.6	409±3	0.20±0.03	19.9±0.3	83.9±1.0	51.8±0.5	0.023±0.002	41.1±0.4	38.04±0.21	101.90±0.10	163.4±0.4	126.7±1.5	150.1±0.3
30.0	181±3	387.0±1.7	0.64±0.04	20.9±0.7	77.1±0.3	77.52±0.15	0.046±0.003	42.14±0.21	54.0±0.5	87.9±0.3	164.8±0.3	116.0±1.0	188.1±0.4
31.5	71.2±0.8	415±4	2.08±0.05	18.4±0.6	83.8±1.0	64.6±0.4	0.043±0.003	46.1±0.8	43.0±0.8	98.0±0.3	161.3±0.5	129±3	159.47±1.2
33.0	60.1±1.4	423±3	3.23±0.03	19±1	87.2±1.2	65.3±0.3	0.040±0.003	45.5±0.7	43.2±0.4	102.5±0.6	162.6±0.8	131.3±2.1	155.9±0.7
34.5	62.8±1.7	426.3±1.5	0.26±0.05	19.8±0.8	85.6±0.5	55.2±0.3	0.065±0.004	45.8±0.5	41.1±0.6	104.3±0.3	153.53±0.06	136.7±0.6	132.1±0.3
36.0	62.8±1.0	445±3	0.46±0.05	20.8±0.5	89.5±0.5	60.6±0.3	0.063±0.003	49.3±0.7	50.3±1.2	114.5±0.3	137.8±0.3	144.0±1.0	125.71±0.21
37.5	33.3±0.7	434.3±1.1	0.33±0.04	18.1±0.6	89.0±0.3	30.4±0.8	0.052±0.003	42.2±0.4	34.7±0.9	111.4±0.3	130.2±0.3	140.7±0.6	108.5±0.4
39.0	40.4±1.3	427±8	0.78±0.03	16±1	89.2±1.3	24.47±0.11	0.049±0.004	39.32±0.08	28.4±0.3	108.3±0.3	128.51±0.17	139.7±1.5	105.4±0.3
40.5	31.5±0.9	433.3±1.5	<LQ	18.3±0.6	91.2±0.6	42.2±0.6	0.051±0.004	41.2±0.9	34.4±0.5	110.2±0.3	134.5±0.5	137.3±0.6	115.4±0.3
42.0	32.0±1.8	431±5	1.18±0.05	17.5±0.8	90.1±0.8	42.03±0.15	0.035±0.002	41.50±0.09	34.1±0.3	110.00±0.11	135.3±0.3	138±3	115.94±0.15

(Continued on next page)

TABLE II
(Continued)

Depth (cm)	As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	Rb	Sr	V	Zn
43.5	27.3±0.6	456±4	0.39±0.02	16±1	91.4±0.9	45.9±0.3	0.053±0.003	37.73±1.0	31.8±1.1	110.2±0.5	134.0±0.7	137.3±0.6	108.3±0.5
45.0	21.7±1.5	425.9±1.7	1.938±0.03	16.6±0.3	92.8±0.7	41.0±0.6	0.057±0.003	38.4±0.3	33.9±0.8	110.09±0.21	135.8±0.6	140±3	102.82±0.12
46.5	27±3	418.2±1.0	1.88±0.03	16.5±0.5	85.0±0.7	31.3±0.5	0.036±0.002	33.5±0.6	24.62±0.21	107.91±0.06	133.4±0.3	131±3	94.6±0.4
48.0	15.3±0.6	442±8	0.29±0.02	18.21±0.11	90.7±1.2	60.8±0.3	0.045±0.002	38.5±0.6	41.5±0.3	112.30±0.12	135.1±0.8	140.0±1.0	108.9±0.3
49.5	22.7±0.6	435±3	0.66±0.02	17.6±0.8	88.09±0.10	53.5±0.8	0.067±0.003	37.8±0.5	39.2±0.4	112.6±0.4	141.18±0.21	135.7±0.6	110.3±0.7
51.0	24.3±1.2	438±4	0.34±0.03	17.4±0.3	87.1±0.3	41.2±0.8	0.039±0.003	39.59±0.08	37.5±0.7	112.4±0.5	149.3±0.4	130.7±1.5	112.10±0.11
52.5	16±3	423±3	2.70±0.04	16.93±0.21	86.3±0.8	41.6±0.13	0.040±0.002	35.7±0.7	32.82±1.1	104.6±0.6	139.79±0.10	133.0±1.0	109.8±0.3
54.0	19.3±1.1	426.3±1.5	3.48±0.05	17.9±0.5	86.5±0.4	39.3±0.6	0.051±0.004	37.3±0.7	31.9±0.7	107.0±0.8	140.9±0.21	132.7±0.7	112.1±0.5
55.5	35±4	421±4	0.30±0.03	19.2±0.8	86.3±0.9	37.9±0.6	0.031±0.001	36.7±0.4	32.9±0.6	106.8±0.4	136.1±0.06	136.7±0.6	116.3±0.7
57.0	48.7±0.9	431±3	0.12±0.02	17.6±0.5	95.5±1.6	24.8±0.4	0.016±0.001	33.4±0.6	25.0±0.4	110.0±0.6	132.62±0.06	134.7±1.2	99.59±0.08
58.5	72.5±1.0	447±3	0.08±0.03	18.3±0.4	76.58±0.06	16.0±0.3	0.016±0.001	29.30±0.12	16.9±0.5	110.8±0.6	125.58±0.06	124.3±2.1	79.6±0.5
60.0	92±3	443.3±2.0	0.05±0.02	18.5±0.5	80.1±0.4	14.3±0.3	0.016±0.002	30.48±0.20	17.80±1.1	109.42±0.06	122.9±0.7	126.7±0.6	81.1±0.6
61.5	72±3	418±4	0.06±0.02	20.8±0.6	82.0±0.6	13.9±0.4	<LQ	28.6±0.4	14.4±0.6	104.4±0.6	126.0±0.7	120.3±1.6	76.5±0.3
63.0	54.3±1.2	426±4	<LQ	16.1±0.7	74.72±0.17	10.50±0.15	0.022±0.002	28.2±0.4	12.4±0.8	109.1±0.7	129.8±	110.3±1.5	67.9±0.3

($\mu\text{g g}^{-1}$) Average value \pm standard deviation ($n = 3$).

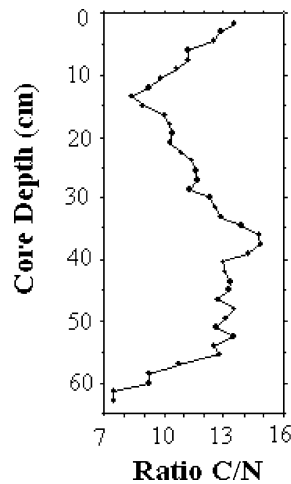


Figure 3. Depth profile of the C/N ratio.

95.5); Cu (mean 42.47, min. 10.50, max. 77.52); Hg (mean 0.039, min. <LD, max. 0.067); Ni (mean 38.6, min. 28.2, max. 49.3); Pb (mean 33.1, min. 12.4, max. 54.0); Rb (mean 107.8, min. 87.9, max. 114.5); Sr (mean 141.0, min. 122.9, max. 181.5); V (mean 127.5, min. 109.3, max. 144.0); Zn (mean 117.3, min. 67.9, max. 188.1). Depth profiles of As, Ni, Cu, Zn, Pb, Fe, Mn, Co, Cd and Hg are displayed in Figure 2.

The coefficients of variation (CV) corresponding to total element concentrations along the depth profile were: As (80%); Ba (3.3%); Cd (118%); Co (24%); Cr (6%); Cu (34%); Hg (40%); Ni (13%); Pb (28%); Rb (4.7%); Sr (10%); V (7.7%); Zn (21%).

Ba, Cr, Rb and V display CVs less than 10% so they can be considered as conservative in respect to geochemistry of the Respomuso Lake, and therefore, of natural origin. The remaining elements display a significant variability in their depth concentration profiles. No correlation between metal concentration and depth is found in the sediment core. Depth profiles of Ni, Cu, Zn and Pb are well correlated among them (CC: 0.8), which may suggest a common origin. These metals, specially Cu and Zn, are commonly used as indicators for anthropogenic influence, and in general, it has been reported that their profiles correlate with the loading history (Vaalgamaa, 2004). The importance of atmospheric input of trace metals in lakes is clear (Salomons and Förstner, 1984). Atmospheric loading of trace metals in lakes is especially important for Pb and it is also a significant source of Zn, Cu, Cd and Mn. The correlation between total Pb and extracted Pb found in our study is very high, hence demonstrating its anthropogenic origin. A noticeable increase in Pb concentration occurs in sediment collected at the upper core corresponding to recent years, despite many studies in Europe showing a decline (Camarero *et al.*,

1998; Yang *et al.*, 2002). The reason for the increase in Pb content in the upper section of the core is unclear.

The depth concentration profile of Sr is well correlated with those of Zn and Pb, and to a lesser extent, with those of the other elements. Variability of Sr concentration along the sediment core is lesser than for the above elements (CV 10.2 %). Mean Sr concentration in fluorite deposits of Tebarrai, close to Respomuso, is about 162 $\mu\text{g/g}$ (Subías *et al.*, 1988), being in good agreement with the mean Sr concentration found in our study. Sr belongs to the sulphate-carbonate type and also to the alkaline type elements. In the latter group, Sr is accompanied by Ca, Mg, Mn, Fe, Cu, Zn, Pb and Cd (Salomons and Förstner, 1984). This may relate Sr to Pb and Zn.

The depth profile of Co is very homogeneous. Only the high concentration at a 15 cm depth corresponding to the stratum of 1992 stands out. The depth profile of Co is well correlated with that of Mn (CC: 0.86), which also peaks at that depth. This behaviour could be related to a change in the redox conditions occurring in the lake. Thus, when Mn oxidation takes place, many trace elements can be removed from the water as a result of adsorption onto freshly formed surface of Mn oxyhydroxides. Adsorption ability of different elements onto Mn oxyhydroxides increases in the order: $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{Ni} < \text{Zn} < \text{Mn} \leq \text{Co}$ (Murray, 1975). The depth profile of As is characterised by a large variability (CV 80%). For As, its variability along the core can be successfully explained through its association with Fe-Mn oxyhydroxides. The occurrence of As-rich pyrites in the area together with the affinity of Fe oxides toward As(V) may account for this association. At a depth between 7.5 and 30 cm, an increase in the As concentration is clearly observed. As concentration peaks at 7.5, 22.5 and 30 cm. The depth profile of Cd is correlated neither with that of Fe and Mn nor with those of nutrient elements and major components. Cd concentrations appear to have the largest variability along the sediment core (CV 118%). The depth profile of Hg significantly correlates with nutrients (CC < 0.65). The correlation between depth and Hg concentration has been found as a result of enhanced sorption of Hg by plant debris originated from plant decomposition (Yang *et al.*, 2002).

3.3. PRINCIPAL COMPONENT ANALYSIS

By applying principal component analysis (PCA) to the matrix of 26 features (total concentration of trace element, MnO, Fe₂O₃, C, N, P, S, Al₂O₃, TiO₂, Na₂O, K₂O, SiO₂, MgO and CaO) and 42 sub-samples of the sediment core, 5 factors (F1-F5) were extracted. The first two factors accounted for 64% of the total variance (33 and 31%, respectively). The third, fourth and fifth factors only described 9, 7 and 4% of the total variance. A factor loading was considered significant when it was higher than 0.6. Major elements, i.e. P, S, C y N display very high loadings in the first component (0.9). Fe y Mn load F2 and F3, being closer to F3 with orthogonal or oblique rotation (Varimax) (loadings of 0.7 and 0.9, respectively). The rest of major

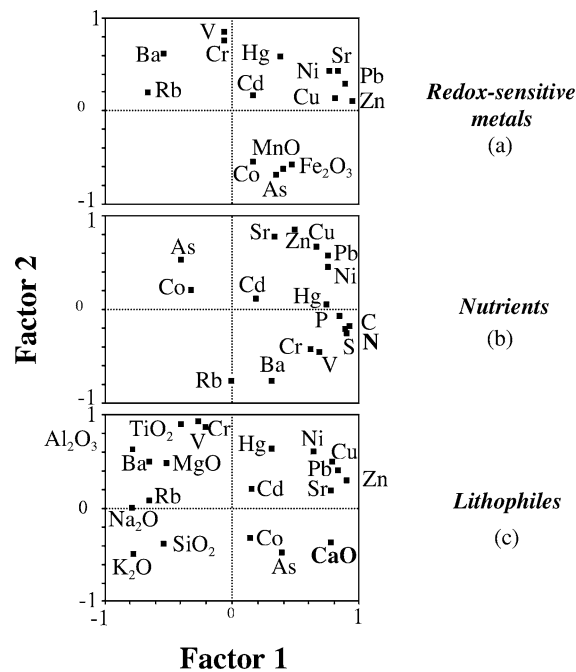


Figure 4. Loading plots of trace metal binding fractions: (a) trace metals and redox sensitive metals; (b) Trace metals and nutrients; (c) trace metals and lithophiles.

elements (Na, Mg, Al, Si, K, Ca y Ti) called lithophiles because they are major constituents of common silicates (Vaalgama, 2004) load factors 2 and 4 (with and without matrix rotation). Trace element loadings are distributed among different components, mainly F1 and F2.

Three separate PCAs were performed on the following subsets of data for a better interpretation: trace elements and redox sensitive elements, trace elements and nutrients and trace elements and lithophiles. Figure 4 shows the loading plots of factor 1 (F1) vs. factor 2 (F2) when PCA is applied to trace elements together with: i) Fe-Mn (redox sensitive elements); ii) nutrients; iii) lithophile elements including Si and Ti. For the first PCA, F1 describes 35% of the common variance, Factor 2 describes 27% and each one of the remaining factors account for less than 10% of the total variance. For the second PCA, Factor 1 describes 41%, factor 2 describes 26% and each one of the remaining factos describe less than 8% of the total variance. For the third PCA, Factor 1 describes 38%, factor 2 describes 27% and each one of the remaining factors account for less than 10% of the total variance.

As can be noted in Figure 4 (a), As, Co, Mn and Fe cluster together, thereby confirming that As and Co are preferably bound to Fe-Mn oxyhydroxides. Adsorption/coprecipitation processes are responsible for their presence in the oxides. This means that the binding behaviour of As and Co with Fe-Mn oxyhydroxides

is more dependent of the sensitive redox elements than the other trace elements. Therefore, As and Co concentration in the sediment core increases with increasing concentration of Fe and Mn, which explains the above correlation found among their depth profiles. This type of preferential affinity of trace elements to a particular mineralogical phase has also been revealed for other elements (e.g. Pb, Cu with organic matter) using PCA (Filgueiras *et al.*, 2004). Likewise, Cu, Ni, Sr, Pb and Zn cluster together but their data point in the loading plot are far from the cluster formed by As, Co, Mn and Fe meaning a different binding behaviour and likely, a different origin in the lake. The loading plot for trace elements and nutrients shows an identical cluster for Cu, Ni, Sr, Pb and Zn as above (Figure 4 (b)). However, with the exception of Hg, no clear association of trace elements with nutrients (C, N, S, P) is seen. This could be explained through the high affinity of plant debris for Hg (Yang *et al.*, 2002). Figure 4 (c) shows that the data points of V and Cr are close to that of TiO₂ and MgO. Likewise, elements such as Rb and Ba seem to be related to some matrix components such as NaO₂ and Al₂O₃, hence being geogenic.

3.4. ASSESSMENT OF ELEMENT MOBILITY

Extractable element concentrations along the depth profile are shown in Table III. Depth concentration profiles of extractable As, Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V and Zn in the Resposuso sediment core are shown in Figure 5. Mean values for each element were ($\mu\text{g/g}$ dry weight): As, 39.4; Ba, 15.3; Co, 3.7; Cr, 1.2; Cu, 22.9; Fe, 2044; Mn, 160; Ni, 4.1; Pb, 22; Sr, 5.8; V, 4.8; Zn, 12.6.

Percentages of metal extracted throughout the vertical profile are related to their ability to mobilize. Extraction percentages fall within the following ranges for the elements studied: As (23–91%); Ba (1.9–7.6%); Co (12–29%); Cr (1.1–2.4%); Cu (37–68%); Fe (1.4–13%); Mn (3.4–18%); Ni (5–19%); Pb (52–74%); Sr (3.1–6%); V (1.6–5.8%); Zn (7.1–16%). According to these values, mobility of the different elements decreases in the following order: Pb > As \approx Cu > Co > Zn \approx Ni > Fe \approx Sr \approx Mn \approx V \approx Ba > Cr. The low mobility of Ba, Cr and V confirms its association with the major components of the sediment (i.e. aluminosilicates), which remain insoluble after extraction with 1M HCl. Correlation between extractable and total content along the depth profile of the sediment core is particularly high for Mn and Fe (e.g. Mn, CC: 0.96). This correlation has also been observed for marine sediments (Tanner and Leong, 2000). Extractable contents of Mn and Fe also correlate well with each other. Extractable As correlates well with total As (CC: 0.91) and also with extractable Fe (CC: 0.80), thereby confirming its association with Fe-Mn oxyhydroxides. For other elements, significant correlation between extractable and total contents along the vertical profile is also seen for Cu (CC: 0.92), Pb (CC: 0.97), Zn (0.80), Co (CC: 0.71), Ni (CC: 0.60). It is remarkable to observe the correlation existing between extractable Ni and Zn contents with depth, which is in agreement with increased anthropogenic inputs in recent years.

TABLE III
Extractable metal contents along the depth profile of the Resposumo sediment core

Depth (cm)	As	Ba	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	V	Zn
1.5	28.51±0.12	10.6±0.2	3.72±0.07	1.04±0.01	25.5±0.9	2147±53	154±4	5.2±0.29	24.5±0.3	6.49±0.19	3.90±0.09	21.3±0.1
3.0	13.58±0.21	14.3±0.3	3.30±0.04	0.808±0.06	28.5±0.4	1601±48	71.3±0.9	6.67±0.10	30.6±0.7	5.54±0.08	4.28±0.10	18.9±0.7
4.5	25.2±0.3	14.3±0.2	3.49±0.05	0.836±0.003	21.7±0.4	1956±8	86.9±1.1	5.59±0.10	27.3±0.4	5.06±0.02	3.74±0.12	13.5±0.4
6.0	55.7±0.3	17.1±0.3	5.12±0.05	1.17±0.15	28.2±0.4	2066±20	104.0±2	6.43±0.15	25.4±0.2	5.39±0.09	4.14±0.05	17.2±0.6
7.5	131±3	14.8±0.5	4.66±0.12	1.13±0.08	19.1±0.7	5259±1	125.0±3	5.00±0.16	19.8±0.2	4.79±0.14	3.06±0.10	11.9±0.7
9.0	50±3	15.2±1.2	4.86±0.21	1.12±0.00	17.2±0.4	4472±10	133.0±6	5.34±0.47	17.8±0.5	4.54±0.06	3.34±0.20	10.8±0.5
10.5	51.80±0.22	13.1±0.7	5.20±0.32	1.10±0.20	16.0±0.1	4550±6	144.0±10	4.63±0.74	16.2±0.7	4.43±0.16	3.05±0.25	10.1±0.6
12.0	43±1	12.5±0.2	5.19±0.11	1.06±0.05	17.3±0.3	4024±1	162.0±3	3.74±0.24	15.1±0.2	4.43±0.04	2.81±0.14	10.0±0.6
13.5	35.9±0.4	11.8±0.1	6.10±0.04	0.934±0.022	19.7±0.2	3799±16	188.0±1	3.86±0.25	15.4±0.1	4.14±0.06	2.95±0.03	10.2±1.0
15.0	43.1±0.9	14.9±0.2	8.15±0.37	1.22±0.15	15.9±0.3	3756±75	694.0±26	4.62±0.23	14.9±0.3	4.09±0.08	3.17±0.10	13.6±0.2
16.5	50.6±0.8	14.4±0.2	5.49±0.14	1.44±0.04	16.1±0.3	3720±74	606.0±9	5.15±0.08	16.9±0.1	4.85±0.16	3.42±0.02	17.1±0.2
18.0	45.0±0.7	14.8±0.3	3.16±0.08	1.36±0.04	19.8±0.1	3357±51	502.0±8	6.49±0.04	18.4±0.1	5.60±0.04	3.56±0.01	16.7±0.4
19.5	51.8±0.8	16.1±0.1	4.90±0.10	1.28±0.00	15.6±0.2	3356±16	539.0±4	5.42±0.01	14.8±0.1	6.56±0.39	3.47±0.04	14.4±0.1
21.0	72±1	21.7±0.4	5.00±0.20	1.57±0.10	22.6±0.3	3870±72	493.0±22	8.52±0.71	22.70±0.5	6.58±0.22	4.41±0.16	16.7±0.5
22.5	67.5±0.3	17.8±0.7	3.32±0.00	1.18±0.03	21.8±0.4	4059±25	456.0±55	4.65±0.00	26.30±1.1	5.02±0.20	3.92±0.38	16.3±2.0
24.0	51.6±0.8	17.7±0.2	2.49±0.05	1.21±0.05	33.8±0.2	1732±24	159.0±2	5.48±0.30	30.50±0.8	6.47±0.14	5.28±0.09	15.7±0.2
25.5	52.2±0.5	16.1±0.1	2.87±0.08	1.07±0.02	24.2±0.2	1872±6	150±4	4.31±0.08	26.40±0.3	5.96±0.15	4.73±0.02	13.9±0.4
27.0	51.6±0.8	16.4±0.1	3.35±0.06	1.21±0.06	27.1±0.2	1992±8	136±2	3.60±0.29	29.30±0.4	5.72±0.08	4.79±0.08	17.7±0.4
28.5	49.1±0.6	15.6±0.1	3.51±0.03	1.24±0.04	25.7±0.1	2242±8	142±1	3.19±0.04	27.30±0.5	5.57±0.19	4.73±0.06	17.2±0.1
30.0	66.32±0.11	17.1±0.1	3.95±0.03	1.44±0.00	39.3±0.5	2990±26	160±0	3.75±0.17	39.0±0.6	5.76±0.0	5.44±0.07	21.2±0.2
31.5	41.4±0.5	18.7±0.1	2.98±0.0	1.16±0.0	38.0±0.3	1828±12	87.2±0.6	4.93±0.35	28.10±0.2	6.75±0.04	5.22±0.01	16.4±0.1
33.0	35.8±0.4	17.0±0.3	3.07±0.05	1.12±0.00	38.0±0.3	1828±15	75.5±0.6	4.31±0.06	26.6±0.0	6.30±0.13	5.51±0.06	14.4±0.1
34.5	39.6±0.3	17.2±0.1	3.04±0.07	1.17±0.02	34.6±0.3	2101±26	83±1.9	4.34±0.16	25.6±0.2	6.34±0.09	6.62±0.02	12.2±0.4
36.0	35.0±0.4	22.4±0.3	4.06±0.08	1.20±0.07	39.0±0.4	1751±28	104±1.0	6.66±0.12	30.7±0.3	7.23±0.11	8.35±0.06	14.5±0.2
37.5	20.10±0.23	18.7±0.1	3.09±0.02	1.33±0.14	18.8±0.8	1416±24	86.6±0.4	5.26±0.34	21.7±0.1	6.41±0.06	7.14±0.03	11.3±0.3

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TABLE III
(Continued)

Depth (cm)	As	Ba	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	V	Zn
39.0	26.7 ± 0.8	14.1 ± 0.0	2.49 ± 0.06	1.03 ± 0.05	13.7 ± 0.1	1664 ± 10	65.5 ± 1.2	3.89 ± 0.75	18.20 ± 0.2	5.68 ± 0.04	5.35 ± 0.08	9.47 ± 0.39
40.5	21.12 ± 0.14	13.4 ± 0.2	2.33 ± 0.02	1.20 ± 0.07	26.6 ± 0.6	1245 ± 20	63.9 ± 0.6	3.22 ± 0.09	23.6 ± 0.3	6.34 ± 0.09	5.75 ± 0.06	9.38 ± 0.24
42.0	19.4 ± 0.4	32.7 ± 0.4	2.10 ± 0.05	1.08 ± 0.00	28.5 ± 0.3	1167 ± 20	64.1 ± 0.7	2.98 ± 0.12	21.6 ± 0.3	6.53 ± 0.21	5.34 ± 0.09	8.23 ± 0.21
43.5	19.0 ± 0.6	13.4 ± 0.0	2.28 ± 0.04	1.08 ± 0.00	25.1 ± 0.6	1118 ± 15	84.2 ± 2.3	3.32 ± 0.04	23.2 ± 0.3	7.02 ± 0.20	7.11 ± 0.08	8.63 ± 0.14
45.0	19.7 ± 0.3	12.0 ± 0.1	2.08 ± 0.04	1.03 ± 0.02	15.7 ± 0.1	1475 ± 17	68 ± 1.1	2.24 ± 0.08	17.6 ± 0.2	5.75 ± 0.14	5.62 ± 0.06	7.82 ± 0.43
46.5	20.61 ± 0.13	10.4 ± 0.2	2.15 ± 0.02	1.08 ± 0.04	17.2 ± 0.5	1122 ± 10	53.8 ± 1.4	1.91 ± 0.12	17.0 ± 0.2	5.50 ± 0.06	5.48 ± 0.10	7.94 ± 0.16
48.0	12.90 ± 0.21	17.7 ± 0.5	2.57 ± 0.04	1.28 ± 0.08	40.8 ± 0.3	696 ± 33	77.2 ± 1.6	3.52 ± 0.05	29.3 ± 0.4	8.1 ± 0.24	8.10 ± 0.14	9.72 ± 0.15
49.5	18.8 ± 0.6	15.6 ± 0.2	2.39 ± 0.05	1.08 ± 0.00	35.1 ± 0.4	763 ± 10	75.1 ± 1.5	3.22 ± 0.47	27.2 ± 0.2	7.34 ± 0.17	6.73 ± 0.09	9.52 ± 0.23
51.0	15.9 ± 1.0	15.7 ± 0.3	2.19 ± 0.05	1.16 ± 0.00	26.7 ± 0.4	634 ± 15	60.9 ± 1.9	2.44 ± 0.07	26.5 ± 0.4	7.06 ± 0.09	5.99 ± 0.10	9.80 ± 0.53
52.5	10.0 ± 0.5	14.9 ± 0.2	2.24 ± 0.04	1.15 ± 0.02	27.4 ± 0.1	551 ± 10	51.0 ± 0.8	2.70 ± 0.17	24.1 ± 0.3	7.39 ± 0.16	6.04 ± 0.02	13.0 ± 3.4
54.0	14.9 ± 0.3	15.2 ± 0.1	2.49 ± 0.05	1.21 ± 0.02	25.8 ± 0.3	673 ± 11	58.7 ± 1.7	2.51 ± 0.14	23.7 ± 0.4	7.09 ± 0.18	5.88 ± 0.04	11.2 ± 0.3
55.5	26.0 ± 0.3	14.2 ± 0.3	3.07 ± 0.17	1.42 ± 0.10	23.8 ± 0.4	926 ± 51	64.2 ± 1.3	2.36 ± 0.23	23.9 ± 0.2	7.12 ± 0.06	6.92 ± 0.08	12.0 ± 0.8
57.0	33.0 ± 0.4	10.3 ± 0.1	3.26 ± 0.03	1.20 ± 0.06	10.2 ± 0.2	922 ± 28	43.2 ± 1.7	1.66 ± 0.03	16.0 ± 0.5	4.96 ± 0.11	5.32 ± 0.17	9.31 ± 0.03
58.5	49.8 ± 1.1	12.5 ± 0.2	4.95 ± 0.01	1.86 ± 0.61	6.72 ± 0.17	1109 ± 17	42.5 ± 0.7	2.05 ± 0.29	11.4 ± 0.2	4.59 ± 0.11	3.10 ± 0.02	8.50 ± 0.12
60.0	68.9 ± 0.7	10.0 ± 0.1	5.34 ± 0.05	1.73 ± 0.06	6.4 ± 0.1	1396 ± 26	56.3 ± 0.1	2.32 ± 0.52	11.3 ± 0.2	4.98 ± 0.02	3.41 ± 0.03	9.12 ± 0.29
61.5	44.8 ± 1.4	8.1 ± 0.0	6.09 ± 0.22	1.39 ± 0.06	5.1 ± 0.1	953 ± 26	54.8 ± 1.8	1.44 ± 0.06	9.23 ± 0.24	4.43 ± 0.13	1.93 ± 0.12	6.21 ± 0.20
63.0	28.2 ± 0.9	10.9 ± 0.2	4.84 ± 0.18	2.13 ± 0.08	4.6 ± 0.1	1815 ± 116	114.0 ± 4	2.37 ± 0.17	8.61 ± 0.21	5.02 ± 0.19	2.97 ± 0.10	7.24 ± 0.28

($\mu\text{g g}^{-1}$). Average value \pm standard deviation ($n = 3$)

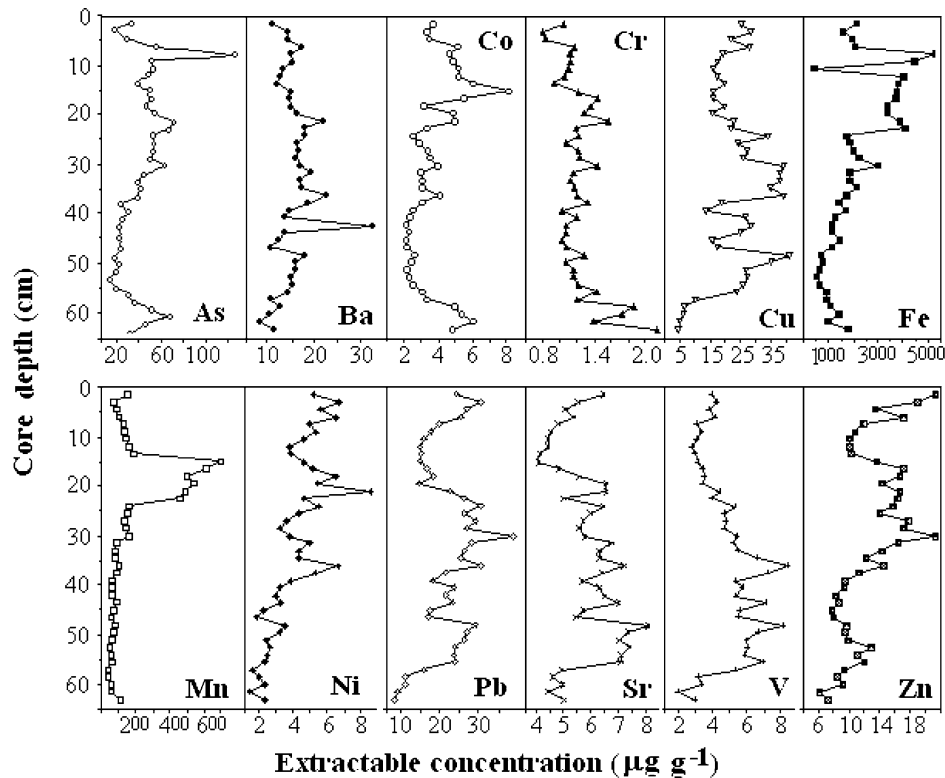


Figure 5. Depth profiles for extractable element concentrations.

3.5. TRACE ELEMENTS AND BIOLOGICAL EFFECTS

A preliminary assessment of biological effects relative to the total metal concentrations found can be made on the basis of the sediment quality guidelines (SQGs) for the National Status and Trends (NS&T) Program (www.epa.gov/waterscience/cs/guidelines.htm).

The SQGs were not promulgated as regulatory criteria or standards; they were not intended as cleanup or remediation targets. Based on chemical and biological effect measures, two values were derived for each substance: the “Effects Range-Low” (ERL) and the “Effects Range-Median” (ERM).

The ERL was the 10th percentile and meant the concentration below which adverse effects rarely occur. The ERM was the 50th percentile and meant the concentration above which effects frequently occur.

When concentrations exceeded ERL values but were lower than the ERM values, the incidence of effects increased to 20–30% for most trace metals (As, Cd, Cr, Cu, Pb, and Zn). For the above elements, when concentrations exceeded the ERM values, the incidence of adverse effects increased to 60–90%. However, the

incidence of ERM's for Ni and Hg were much lower (17 and 42% respectively) (Sediment Quality Guidelines, 1999).

In the case of As, for which the ERL and ERM values are fixed at 8.2 and 70 $\mu\text{g/g}$, respectively, the first value is exceeded throughout the vertical profile, while the second one is even exceeded in many segments of the vertical profile. This finding brings about at least an 11.1% of incidence effects and up to a 63% in cases where the ERM is exceeded, which highlights the potential environmental risk associated with these sediments. As contents beyond the ERM value were located between 6 and 31.5 cm from the upper sediment core. High As concentrations measured in sediment core samples of Respomuso Lake are due to geogenic rather than anthropogenic inputs, as demonstrated above. For the remaining metals included in the SQG (Cd, Cr, Cu, Pb, Zn, Ni y Hg), the ERM values are never exceeded, meaning a low environmental risk. For Hg, concentration values are below the corresponding ERL value. On the contrary, Ni concentrations are above the ERL value throughout the vertical profile, although this fact is only associated with a 16.7% of possible biological effects. Cd, Cr, Cu, Pb and Zn display concentrations exceeding the ERL value in many segments of the sediment core.

It seems that the high As concentrations found at some strata could have represented an environmental problem in the area under study. Waters contaminated by As as a result of mobility from As-rich sediments are well documented in areas such as Bangladesh, Nepal, China, Hungary, India, Argentina, Mexico, Rumania, Taiwan and USA. However, the occurrence of As-enriched sediments is not sufficient itself to cause water contamination. Factors such as dilution, contact time between the water and the soil/sediment and the occurrence of reducing conditions in ground water are also relevant factors. Moreover, water can suffer from As contamination in regions related to hydrothermal processes and mineral deposits. Both phenomena have been described in locations of central-axis of Pyrenees such as Tebarrai or Panticosa, nearby to Respomuso Lake (Garrido *et al.*, 2001).

In general, As mobility is explained on the basis of the redox conditions and pH occurring in the aquatic medium. A well-established mobilisation mechanism for As assumes the oxidation of As-rich pyrite to scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), the decomposition of scorodite into a Fe-hydroxide or oxide and the desorption/release from Fe(III) hydroxides. This mechanism has been mostly employed to explain As mobility in Bangladesh or Italy (Chakraborti *et al.*, 2001; Frau and Arda, 2004), and given the geochemical characteristics at Pyrenees, it could also be applied to this case study.

According to the As extractable contents, mobility of As throughout the sediment core displayed a large variability. In the Respomuso sediment core, depth is neither correlated with total As (CC -0.50) nor with extractable As (CC -0.38), but a significant positive correlation exists between depth and percentage of extracted As (CC 0.76). A possible explanation for this finding could be the enhanced reduction of As(V) into As(III) in the deep strata of the sediment core under anoxic conditions. As(III) species are weakly bound to sediment particles because As(III)

is predominantly H_3AsO_3^0 at environmental pH values and has a first pK_a of 9.2 (Kinniburgh and Smedley, 2001). On the contrary, As(V) is present as anionic forms (H_2AsO_4^- and HAsO_4^{2-}), which strongly bind sediment surfaces.

4. Conclusions

In the Respomuso Lake, a remote site at the Pyrenees mountains, it is demonstrated that anthropogenic metal inputs are derived from atmospheric deposition. Relationships found between trace metal contents and matrix components of the sediment allowed to establish the more likely explanations for variability in the depth profile of the deposit. The high concentrations of As found throughout the depth profile could make advisable further studies in the area including a close control of nearby spring waters so that poisoning episodes can be prevented.

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