



Trace elements in lake sediments measured by the PIXE technique

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Abstract

Lakes are ecosystems where there is a great potential of metal accumulation in sediments due to their depositional characteristics. Total concentration of trace elements was measured on a 50 cm long sediment core from the Infernão Lake, that is an oxbow lake of the Moji-Guaçu River basin, in the state of São Paulo, Brazil. Dating of the core shows up to 180 yrs old sediment layers. The use of the PIXE technique for elemental analysis avoids the traditional acid digestion procedure common in other techniques. The multielemental characteristic of PIXE allows a simultaneous determination of about 20 elements in the sediment samples, such as, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Ba, and Pb. Average values for the elemental composition were found to be similar to the bulk crustal composition. The lake flooding pattern strongly influences the time series of the elemental profiles. Factor analysis of the elemental variability shows five factors. Two of the factors represent the mineralogical matrix, and others represent the organic component, a factor with lead, and another loaded with chromium. The mineralogical component consists of elements such as, Fe, Al, V, Ti, Mn, Ni, K, Zr, Sr, Cu and Zn. The variability of Si is explained by two distinct factors, because it is influenced by two different sources, aluminum-silicates and quartz, and the effect of inundation are different for each other. The organic matter is strongly associated with calcium, and also bounded with S, Zn, Cu and P. Lead and chromium appears as separated factors, although it is not clear the evidences for their anthropogenic origin. The techniques developed for sample preparation and PIXE analysis was proven as advantageous and provided very good reproducibility and accuracy. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The concentrations of heavy metals in several lacustrine environments are increasing due to the industrialization process and the increase in pop-

ulation density around the lakes. Several industrial and agricultural activities generate liquid effluents, solids and gaseous emissions containing a wide range of heavy metals that contaminate soils, rivers and lakes. In some lakes the flux of anthropogenic heavy metals surpasses the natural fluxes, bringing long-term changes in the cycling of heavy metals in the lake-sediment system.

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Several heavy metals such as Zn, Mn, Cu, Cr, Ni, Co and Mo are considered essential elements to life, while others like Hg, Pb, Cd, Ag and Sn, do not have a defined biological function and they are, generally, toxic to a great variety of organisms. Even the essential metals, if present in high concentrations, can be toxic to the biota. The different ecosystem compartments have limited capacity to receive those metals, without toxic effect [1].

Lakes have two components that can serve as heavy metal storage and transport, the suspended particulate matter and the bottom sediment. Generally, the suspended particulate in the water column of a lake is rich in organic matter. It has a fundamental role in the distribution of heavy metals in the ambient. The fate of the adsorbed metals in the suspended particles is the deposition in the sediment at the bottom of the lake [2]. Lacustrine ambient associated to rivers (lakes and marginal ponds) present a special characteristic that differentiates them from the lakes of high lands. They are flooded annually by water generally rich in dissolved materials and particulate matter originated in the main river. The distribution of heavy metals in lakes and in marginal ponds reflects the type of weathering rocks of its basin, regional and local, as well as the different land use in the region.

This study explores the use of the multi-elemental capability of the PIXE technique to study trace elements and heavy metals in Lake Sediments. A 180 yr old sediment core of an industrialized region in Brazil was analyzed for their elemental composition and factor analysis was applied to study the co-variability of the trace elements. The main objective was to investigate the possibility of recent increase in heavy metals due to the fast and strong industrialization process in the region of the São Paulo State, Brazil.

2. Sediment collection and analysis

Three 50 cm long bottom sediment cores were collected at the Infernão Lake, in Southern Brazil. The three cores were sectioned into samples of 1 cm intervals. The corresponding samples were mixed in order to minimize the spatial variability

in the elemental composition and obtain a better average for the elemental composition of the sediment in this lake. The composite sample was sieved in a 63 μm nylon sieve with the use of Milli-Q water and dried for 3–4 days in a controlled environment. They were crushed and sieved again in the 63 μm sieve to reduce grain size. The traditional methodology for elemental analysis of sediment samples involves the acid digestion followed by atomic absorption analysis. This procedure produces several labor-intensive steps and potential for introducing contamination in the sample. To avoid these laborious steps, a procedure involving the resuspension of sediment was developed.

The sieved sediment was resuspended in a closed plastic bag and collected in a Nuclepore filter as an atmospheric aerosol, following a procedure developed by Cruvinel et al. [3]. Fig. 1 shows a schematic of the experimental arrangement used to prepare the sediment samples for PIXE analysis. Clean air was used as a carrier gas to produce a relatively homogeneous aerosol. The resuspended sediment material is deposited on a 25 mm diameter 0.4 μm pore size Nuclepore filter. The thin and homogeneous deposit produced by this technique is ideal to be analyzed by the PIXE method (average thickness 50 $\mu\text{g cm}^{-2}$), although some particle size effects and self-absorption could influence the concentrations of Al and Si. The

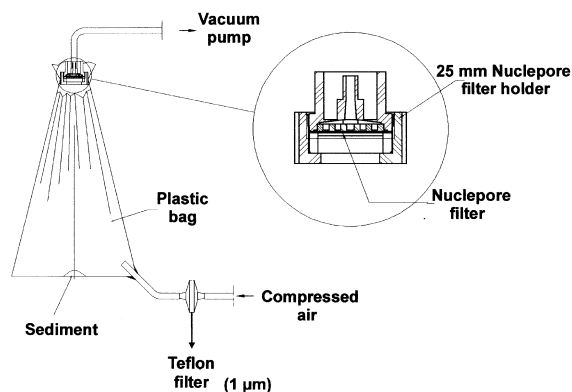


Fig. 1. Schematic on the experimental arrangement used to prepare the sediment samples for PIXE analysis. The sediments are resuspended and collected as an aerosol onto a Nuclepore filter.

gravimetric analysis of the filters was done in a electronic microbalance, and electrostatic charges were controlled by means of ^{210}Po radioactive source. The sample is then irradiated directly in the PIXE system. This sample preparation system is similar to the one proposed by Sarver [4], who have compared XRF analysis by this sample preparation system with total acid digestion procedure followed by ICP–AES analysis, with very good results.

Elemental concentrations were measured with the particle-induced X-ray emission (PIXE) method [5]. It was possible to determine the concentrations of up to 20 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Ba, and Pb). A dedicated 5SDH Pelletron accelerator facility, Laboratório de Análise de Materiais por Feixes Iônicos (LAMFI), from the University of São Paulo was used for the PIXE analysis [6]. Two Si (Li) detectors are used in the PIXE system, one optimized for low Z elements and the second has a thick absorber to detect elements heavier than Ca. The arrangement with two Si (Li) detectors provide better detection limits and avoids some of the pile-up and dead time corrections. The two Kevex detectors have 12 μm Be window and 138 eV resolution for the Mn $K\alpha$ line. Irradiation time is 10 minutes at a count rate of 2500 cps for the low Z detector and 500 cps for the high Z detector. Detection limits were in the range of 1 to 5 ppm for most of the elements. The precision of the elemental concentration measurements is typically in the range of 4 to 10%. A total of 16 standard reference material samples prepared from National Institute of Standards and Technology (NIST), USA, International Atomic Energy Agency (IAEA) and Canada Center for Mineral and Energy Technology (CANMET) standards, were prepared in a similar way to the sediment samples. The IAEA standards are SL-1 (Lake Sediment), IAEA 356 (Polluted Marine Sediment) and SOIL-7. The NIST standard is BRS (Buffalo River Sediment) and the CANMET is LKSD-3 (Lake Sediment). Fig. 2 shows the results of the quality assurance test. The standard deviation of all elements measured in these reference material standards was 17%, a very satisfactory value. Reproducibility was checked irradiating the same

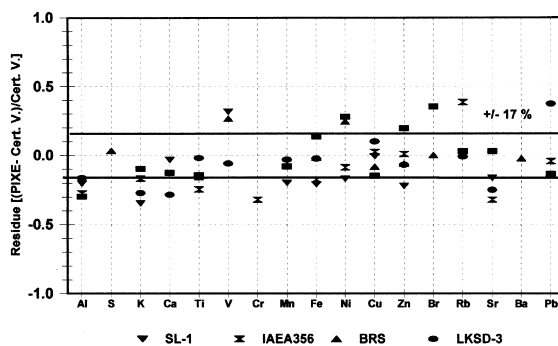


Fig. 2. Relative residuals for soil and sediment reference materials analyzed for PIXE. The average residue is about $\pm 17\%$.

sample 62 times during the irradiation of the sediment sample (this special sample is a 3 μm thick Mylar film with several metals evaporated over it). The average standard deviation in this reproducibility checking was between 4.8% and 7.7% depending on the element. All sediment samples were prepared and irradiated in duplicates and average results were taken for each centimeter of the core.

The total organic carbon was measured with a Shimadzu TOC 5000 analyzer. The dating of the sediment was determined through the ^{210}Pb method [7] and it was found that 180 yr old corresponds approximately to a sediment depth of 50 cm.

To separate the different components in the time series of the sediment elemental composition, absolute principal factor analysis (APFA) was used [8]. APFA can provide a quantitative elemental loading profile, instead of just a qualitative factor loading matrix as in traditional factor analysis. The absolute elemental source profiles help in the identification of the factors, and can be used to quantitatively compare the factor composition with assumed sources. The APFA provides the elemental mass contribution of each identified component by calculating the absolute principal factor scores (APFS) for each sample. The software package SPSS for Windows version 8.0 was used in the factor analysis calculations.

3. Results and discussion

The elemental concentrations as a function of sediment depth are shown in Fig. 3 for the In-

fernão Lake. The vertical line in some of the plots shows the average composition of sedimentary rock [9]. For several elements, such as TOC, Ca, S,

Cr, Zn and Cu, it is possible to observe an increase of elemental concentration in the first 10 cm core corresponding to about 10 yr old. This enrichment

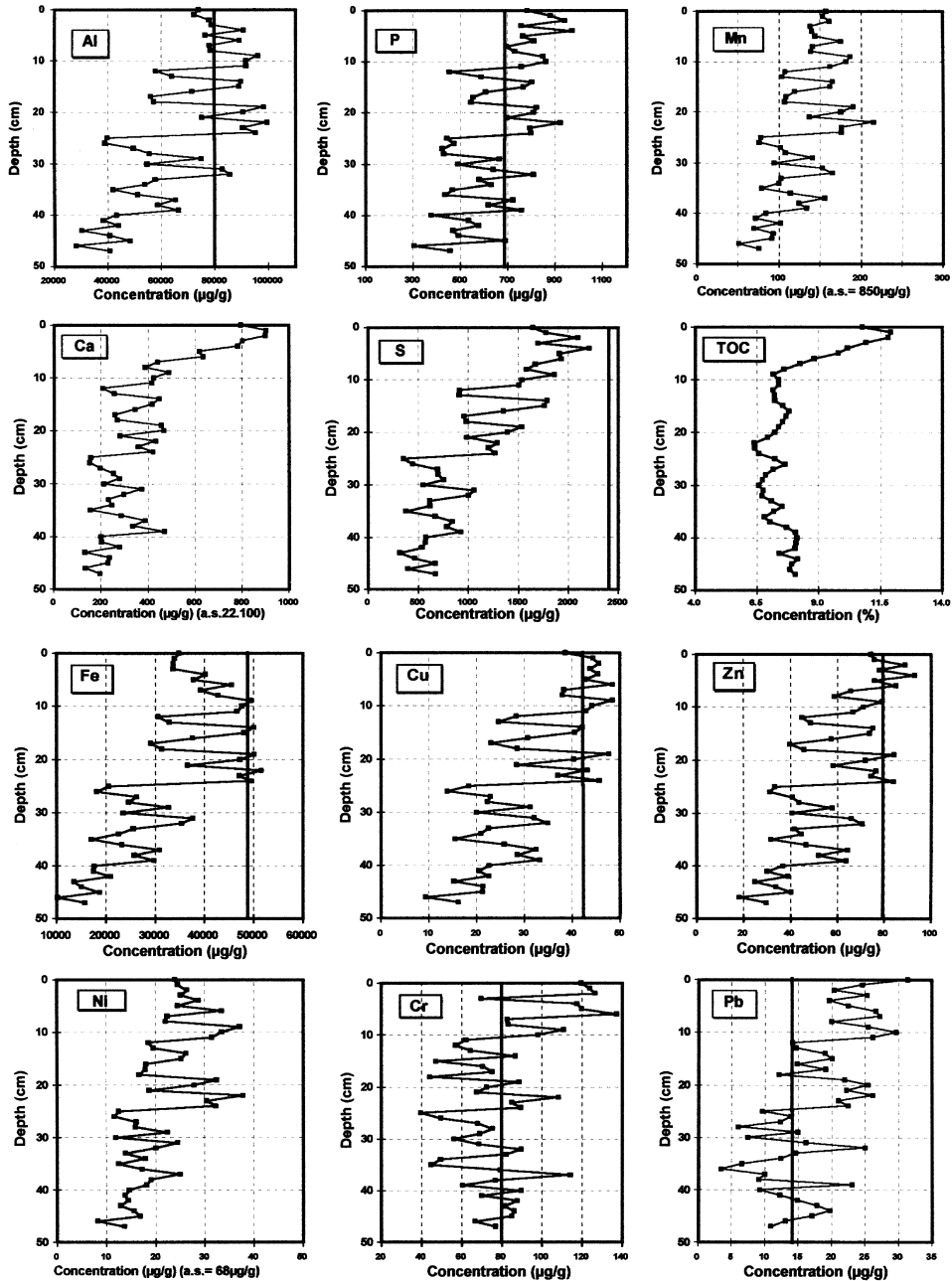


Fig. 3. Depth profiles of the concentration of metals in Infernção Lake's sediment core. The line is the distribution of the elements of the Earth's Crust in Shale's Sedimentary Rocks [9].

could be caused because these elements have association with organic matter, which increases in the first 10 cm of the core. Other elements such as Cu, Zn and Pb shows increased concentrations in the first 20 cm, corresponding to about 30 yr old. This enrichment could be caused by the increased anthropogenic influences in the Moji Guaçu River basin. The recent destruction of riparian forest of the river could also cause this enrichment. A pronounced structure of the concentration profile was observed for elements such as Al, Fe, Ti, Cu, Zn, Mn, K, V, Sr, P and Rb, that can be caused by the annual flood pattern in the lagoon (for example, at the 25 cm depth occur a drastic decrease).

Table 1 shows the comparison of observed elemental composition in $\mu\text{g/g}$ for the Infern o sediment core with different kind sedimentary rock composition [9]. The measured values in general agree with the shale composition values, indicating the absence of significant enrichment caused by anthropogenic activities for most of the elements. In addition, it is possible to observe that for elements indicative of anthropogenic activities such as Pb, Cr, Cu and Zn, the observed average composition is well within normal expected values.

Factor analysis was performed in the data set to investigate the common variability of the measured elements. Only elements that were measured in all the samples were included in the factor analysis calculations to avoid problems with estimation of missing values. The elements included in the factor analysis were: Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, S, Pb, and TOC. Table 2 shows the factor matrix of the five factors retained for the Infern o lake sediment data set. The five factors explain 96% of the original data variability. The first factor is explaining 55.8% of the data variability and is loaded with Fe, Al, Ti, V, Mn, Ni, K, Sr, Cu, Zr, Zn, S, P and Rb. This factor represents the mineralogical matrix, because it comprises the majority of the elements typically of the aluminum-silicates compounds. Si is associated with the third factor. The second factor is loaded with TOC, Ca, S and Cr, and is associated with the organic matter present in the sediment. Factor 4 has high loading only for Pb and the last is loaded mostly with Cr. The last column of Table 2 shows the communalities for each variable

that are high for most of the elements. The last two lines in Table 2 shows the eigenvalue of each factor and the percentage of variance explained by each retained factor.

Table 3 shows the absolute amounts in $\mu\text{g/g}$ apportioned by APFA to each element for the Infern o Lake sediment core. The analysis of Table 3 should be done together with Table 2, the first gives the mass associated to each variable within the factor and the second provides the variability of the elements for retained factors. Although, the first component explains 56% of the data variability, it is only responsible for 17% of the total sediment mass. The elements associated with this component suggest that it represent the mineralogical matrix, with the exception of Si. Silicon is present in two major minerals: quartz and aluminum-silicates, and the inundation scheme can bring different amounts of these minerals from year to year due to different size distribution and density. Si is present in factor 3, which accounts for 45% of the sediment mass. The elements associated with factor 3 are very similar to the ones associated with factor 1, but they appear with lower factor loading. This suggests that factor 3 represents also the mineralogical matrix, but with a higher percentage of quartz. Previous geological studies performed in this lake indicate that minerals of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) group (clay – mineral) and quartz (SiO_2) are the predominant components [10]. The kaolinite group comprises aluminum-silicates containing different metals in their structure.

The second components is loaded with organic carbon associated with Ca and S. This components represent the organic matter, accounting for 27.5% of the mass and 51% of the TOC is associated with this second factor. The fourth and fifth components represent Pb and Cr, respectively. Pb and Cr also have significant amounts associated with the second factor (the organic matter). The fourth and fifth factors would be associated with anthropogenic activities, but the APFA results do not support this possibility. The depth profile for Pb in $\mu\text{g/g}$ apportioned to each factor is showed in Fig. 4. From Fig. 4 it is not possible to observe any recent enhancement in the absolute concentration of Pb apportioned to factor 4. Pb apportioned to factor

Table 1

Elemental composition in $\mu\text{g/g}$ for trace elements in Infernão Lake sediment. The average concentrations in the Earth Crust for sedimentary rock are also listed [9]

Elements	Infernão lake sediment			Shales
	Average	Minimum	Maximum	
Al	66 947	28 104	99 444	80 000
Si	91 966	52 921	129 162	73 000
P	654	304	971	700
S	1 089	315	2 207	2 400
Cl	88.5	31.5	178	180
K	2 976	1 308	4 649	26 600
Ca	371	131	901	22 100
Ti	4 342	1 829	6 650	4 600
V	155	49.9	251	130
Cr	80.7	39.5	137	90
Mn	129	50.9	215	850
Fe	32 274	10 136	51 616	47 200
Ni	21.3	8.23	37.8	68
Cu	31.3	9.33	48.4	45
Zn	56.9	18.3	93.1	95
Rb	58.1	21.8	95.6	140
Sr	37.4	13.3	61.7	300
Zr	60.3	23.5	93.9	160
Pb	17.7	3.44	31.4	20

Table 2

VARIMAX rotated factor loading matrix of Infernão sediment core trace elements^a

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Comm.
Fe	0.96	0.08	0.15	0.20	0.03	0.99
Al	0.91	0.15	0.31	0.17	0.08	0.99
Ti	0.91	0.09	0.34	0.14	0.14	0.99
V	0.90	0.23	0.26	0.11	0.13	0.97
Mn	0.87	0.12	0.32	0.17	0.28	0.97
Ni	0.86	0.16	0.17	0.19	0.33	0.94
K	0.84	-0.03	0.48	0.06	0.17	0.96
Sr	0.82	0.09	0.29	0.40	0.12	0.94
Cu	0.82	0.41	0.25	0.16	0.19	0.97
Zr	0.82	0.18	0.17	0.45	-0.07	0.94
Zn	0.80	0.42	0.36	0.09	0.16	0.98
S	0.72	0.62	0.12	0.18	0.06	0.96
P	0.68	0.39	0.43	0.28	0.19	0.92
Rb	0.61	0.31	0.58	0.19	-0.25	0.90
TOC	-0.15	0.96	0.03	0.12	0.11	0.98
Ca	0.44	0.81	0.24	0.10	0.21	0.97
Si	0.43	0.18	0.79	0.18	0.29	0.96
Pb	0.48	0.31	0.21	0.76	0.16	0.97
Cr	0.24	0.49	0.17	0.12	0.75	0.90
Eigenv.	11.2	3.1	2.3	1.4	1.2	
% Var.	55.8	15.7	11.4	7.1	5.9	

^aThe five retained factors explain 97% of the total data variability. The row "Eigenv." shows the eigenvalue for each retained factor. The row "% Var." indicates the percentage of the variance explained by each factor. TOC is the total organic carbon.

Table 3

Absolute amounts in $\mu\text{g/g}$ apportioned to each factor for each element in the Infern ao lake sediment

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Sum	Ratio Sum/Mea
Al	20 177	12 862	25 585	4750	1963	65 337	0.98
Si	10 911	15 605	54 409	3872	5574	90 372	0.98
P	129	189	240	55.3	27.9	642	0.98
S	391	727	–	98.9	–	1216	1.12
K	817	245	1594	78.5	178	2913	0.98
Ca	88.2	328	–	–	–	416	1.12
Ti	1312	686	1766	255	223	4242	0.98
V	53.6	40.4	43.0	8.01	6.64	152	0.98
Cr	7.58	33.7	16.5	3.5	17.9	79.2	0.98
Mn	36.7	22.4	46.6	8.45	11.87	126	0.98
Fe	11 935	5661	9694	3315	729	31 334	0.97
Ni	6.76	4.72	4.85	1.82	2.67	20.8	0.98
Cu	9.50	11.6	6.08	2.00	1.59	30.8	0.98
Zn	16.6	20.5	15.4	1.56	1.94	56.0	0.98
Rb	12.5	14.6	32.5	3.63	–	63.2	1.09
Sr	12.0	5.17	11.8	6.21	1.58	36.7	0.98
Zr	18.8	13.3	16.4	11.9	–	60.4	1.00
Pb	3.56	5.03	2.42	5.71	0.80	17.5	0.99
TOC	–	38 235	28 883	4821	2923	74 861	0.96

4 appears significantly at higher depth, with ages more than 100 yr. Therefore this factor could not be associated with anthropogenic activities. Similar features are observed for chromium in factor 5. On the other hand, Pb and Cr do increase in recent layers associated with factor 2 (the organic matter). These metals could present chemical complexation and adsorption with organic matter. Both elements could have a different sedimentation process relative to elements from the mineralogical

matrix or other chemical or physical process that binds these elements differently the others metals in the sediment.

4. Conclusions

This study demonstrates the feasibility of trace element measurements in sediments using PIXE technique. The advantages of PIXE are sensitivity, multielemental capability and minimal sample preparation. In PIXE analysis the use of acid digestion is not required. Quality control through the analysis of sediments and soil reference materials using an innovative and simple sample preparation procedure indicates that with the PIXE technique high accuracy and precision can be achieved.

A 180 yr old and 50 cm long lake sediment core shows that the region is not affected by anthropogenic activities, as initially thought. Factor analysis of the trace element concentration provided a powerful tool in analyzing the trace element variability. The factor analysis of sediment trace element data indicates five factors. Two of

Distribution of total Pb in Infern ao lake's Sediment for at retained factor.

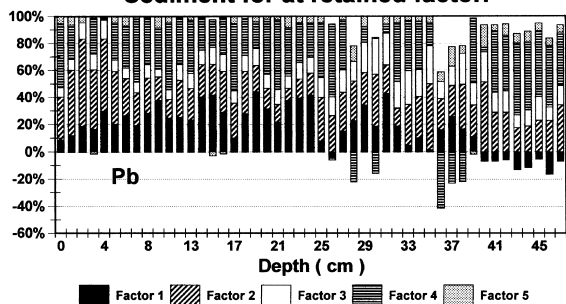


Fig. 4. Depth profiling for Pb in $\mu\text{g/g}$ apportioned for each factor for the sediment core of Infern ao Lake.

them are linked to the mineralogical matrix. A second factor is linked to the organic content and two other factors are associated with Pb and Cr, but no anthropogenic influences could be clearly identified and quantified.

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