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Comparison of metal analysis in sediments using EDXRF and ICP-OES with the HCl and Tessie extraction methods

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Abstract

The work presents an investigation on metal availability in sediments during 13 months using the dispersive-energy X-ray fluorescence (EDXRF) and atomic emission spectrometry with induced argon plasma (ICP-OES) techniques and single extraction ($0.1\,\mathrm{mol\,l^{-1}}$ HCl) and Tessie's sequential speciation methods. The EDXRF technique could yield essentially the same profile as ICP-OES for the seasonal variation of metals in sediments, but in a more practical way. The sequential extraction procedure (SEP) was more efficient in metal dissolution than single extraction. The Pb, Ni, Al, Cr, and Fe elements were less efficiently extracted with single extraction in relation to sequential extraction. For Co both methodologies were equivalent, but for Cu and Mn the extraction was higher with single extraction. Single extraction does not mobilize Pb, Ni, Al, Cr, and Fe adsorbed on oxides and bound to organic matter. However for Cu and Mn, not only extracted these metals from the four fractions, but it also dissolved part of the fifth fraction (residual). Principal Component Analysis discriminated seasonal variations in the content of several metals, mainly Fe, Co, Ni, and Zn. The mobility of metallic ions in the sediments is conditioned to the seasonal flow of organic and inorganic material coming from the river or by the erosion of adjacent soils.

Keywords: Sequential extraction; Single extraction; ICP-OES; EDXRF; Sediment

1. Introduction

Sediments are highly complex mixtures of minerals and organic compounds in which ions are associated by adsorption, absorption, or complexation.

The ecotoxicity and mobility of heavy metals in the environment depend strongly on their specific chemical forms or types of binding [1]. Determinations of total contents in the sediments of natural aquatic ecosystems are not sufficient to reveal mobilization capacities. In this sense, trace metal extraction methods with a single extractor have been applied with the use of, for example, $0.1\,\mathrm{mol\,l^{-1}}$ HCl [2,3]. The goal of using such a method is to evaluate potentially bioavailable metals. On the other hand, procedures based on sequential extractions [4–7] provide an estimate of the different ways (changeable, bound to carbonates, adsorbed in Fe and Mn oxides, bound to organic matter, and residual) in which trace metals exist besides assessing their bioavailability.

The goals of this study were to compare the metal concentrations in sediments determined by atomic emission spectrometry with induced argon plasma (ICP-OES) and dispersive-energy X-ray fluorescence (EDXRF) for 13 samples, taken from June/1999 to June/2000 and to carry out a comparison of the HCl and Tessie extraction methods to determine metal availability in sediments.

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Principal component analysis (PCA) and hierarchical cluster analysis (HCA) [8] were used to investigate the occurrence of meaningful seasonal variations in the metal concentrations and to determine those with a higher discriminating capabilities for the months sampled.

2. Experimental

2.1. Description of the study area

The upper Paraná hydrographic basin occupies a vast area, over 802,150 km^2, in Brazil. The present study was carried out on Ipê Lake, MS, Brazil, belonging to the Paraná River basin, on the right bank of the Curutuba Channel. Lake Ipê is in constant communication with the Curutuba Channel by means of a small, narrow channel and its maximum depth varies from 1.5 to 3.0 m (low and high waters). The lake area measured approximately 10,700 m^2 by GPS equipment. The samples were collected from the deepest part at an altitude of 270 m, located at 22°45′57″S and 53°26′38″W.

2.2. Materials and methods

The plastic (polyethylene) and porcelain utensils and glassware, used in the collections, storage and analytical determinations were kept in 20% HNO_3 for 48 h for decontamination, rinsed several times in distilled water and finally in deionized water and dried in an oven at 60 °C until dry. The reagents (Merck) were used without further purification.

2.2.1. Samplings

The sediments of Lake Ipê were obtained in 13 campaigns, with monthly samplings from June/1999 to June/2000.

2.2.2. Sample collection

The sediments were collected always at the same position, in a gravity-type cylindrical collector, composed of a 9.0 cm diameter, 50 cm long acrylic tube, called a gravity corer. At the point sampled, 20 cm-deep testimonies were collected, transferred to a tray, homogenized with the help of a spoon, both made of plastic, stored in completely filled polyethylene flasks and closed with polyethylene stoppers to prevent air contact. The flasks containing the samples were kept in an isothermal box with ice for transport to the laboratory where they were kept at 4 °C.

2.2.3. Sample treatment

The sediment samples were dried in an Edwards lyophilizer at 50 °C and 10^{-1} mmHg pressure, ground with a porcelain pestle and mortar with the help of a pistil, both in porcelain, immediately after being dried and sieved in a 2 mm nylon sieve. The samples obtained were separated, into a total of 33 sub-samples used for ICP-OES, EDXRF, single extraction and sequential extraction studies.

These sub-samples were stored in closed plastic flasks, closed with plastic film and stored at 4 °C until chemical analyses. The weighing of the sub-samples was anticipated to avoid error in the determination of the dry sediment mass due to humidity absorption.

2.2.4. pH determination

The pH values were determined (Hanna model HI 9321) with 1 g of sediment to 2.5 ml of ultra-pure (Milli-Q) water [9].

2.2.5. Determination of total nutrient (C, N, and P)

Total carbon and nitrogen were determined with a Perkin-Elmer model 2400 CHN Elementary Analyzer. The total phosphorus digestion was carried out according to Andersen's method [10]. The molar concentration of orthophosphate was determined by ascorbic acid reduction [11].

2.2.6. Determination of potentially available metals by single extraction (extraction with 0.1 mol l^{-1} HCl)

The fraction of potentially available metals in the sediment is defined in operational terms as the fraction extracted by moderate acid attack [12]. The sub-samples (1.0000 ± 0.0001 g dry sediment) were transferred to erlenmeyers and 25 ml standard 0.1 mol l^{-1} HCl were added. The mixtures were submitted to mechanical agitation (200 rpm) for 2:30 h at environmental temperature. The contents were filtered in a Sterifil Holder (Millipore)-type of filtration dispenser, through a 0.45 μm (Millipore) cellulose ester filter. The filtrate was stored in polyethylene bottles at 4 °C until metal determination by ICP-OES (Spectroflame Spectro Analyical Instrument—ICP). All the extractions were carried out in triplicate, including the analytical blanks, processed simultaneously with the samples.

2.2.7. Chemical studies of metals in sediments by sequential extraction [13]

Sequential extractions were applied to the samples collected in July/1999, August/1999, January/2000, March/2000, and April/2000.

2.2.7.1. First extraction (changeable fraction). The sub-samples were transferred to three erlenmeyers, 10 ml of 1 mol l^{-1} $MgCl_2$ pH 7 were added and agitated at room temperature for 1 h. The mixtures were filtered (0.45 μm filter) and the filtrate stored in polyethylene flasks at 4 °C until the analysis was carried out.

2.2.7.2. Second extraction (fraction bound to carbonates). To the residues from the first extraction 10 ml of 1 mol l^{-1} NaOAc acidified with 25% (v/v) HOAc were added until pH 5 and agitated at room temperature for 5 h. The mixtures were filtered (0.45 μm filter) and the filtrates stored in polyethylene bottles at 4 °C until the analyses were carried out.

Table 1
Concentrations of potentially available metals (mg kg^{-1}) in 20 cm sediment layers of Lake Ipê, between June/1999 and June/2000

Element	Months/years												
	June/1999	July	August	September	October	November	December/1999	January/2000	February	March	April	May	June
Concentrations (mg kg^{-1})													
Mg	71 (1)	112 (2)	83 (2)	47 (2)	40 (1)	90 (3)	123 (2)	114 (2)	92 (3)	118 (3)	80 (1)	100 (1)	174 (2)
Al	1348 (31)	1313 (25)	473 (15)	391 (14)	521 (17)	698 (32)	1056 (10)	756 (21)	609 (19)	753 (23)	396 (28)	789 (10)	1176 (14)
Cr	10.1 (2.2)	13.5 (2.0)	12.7 (0.7)	7.6 (2.8)	8.3 (2.9)	6.2 (3.5)	13.1 (0.2)	10.7 (3.6)	9.8 (1.2)	14.0 (3.1)	9.8 (2.9)	6.0 (4.1)	12.5 (1.8)
Mn	82 (1)	144 (1)	67 (1)	22.0 (0.2)	36 (1)	91 (4)	167.0 (0.2)	118 (3)	88 (4)	121 (1)	66 (3)	116 (1)	181 (1)
Fe	8872 (32)	7884 (112)	5091 (161)	2299 (92)	3359 (26)	4712 (78)	8176 (170)	5601 (122)	4699 (116)	5618 (196)	3340 (179)	5718 (1)	8550 (13)
Co	5.7 (0.1)	6.3 (0.1)	2.9 (0.1)	2.8 (0.1)	2.6 (0.1)	3.9 (0.1)	5.8 (0.1)	4.3 (0.1)	3.2 (0.1)	4.4 (0.2)	3.0 (0.2)	4.4 (0.1)	6.1 (0.2)
Ni	11.3 (1.2)	12.9 (0.5)	7.8 (0.6)	6.2 (0.3)	5.5 (0.4)	7.5 (0.7)	10.8 (0.1)	7.9 (0.5)	6.8 (0.7)	8.4 (0.1)	5.6 (0.3)	8.1 (0.2)	11.8 (0.5)
Cu	14.2 (0.3)	14.4 (0.2)	16.4 (0.2)	18.5 (0.1)	6.1 (0.1)	8.8 (0.2)	15.1 (0.1)	10.2 (0.2)	8.6 (0.6)	11.4 (0.1)	9.9 (0.5)	10.7 (0.1)	15.4 (0.2)
Zn	41 (4)	41 (4)	25 (4)	9 (2)	19 (0)	30 (5)	49 (11)	39 (5)	30 (4)	39 (2)	23 (2)	40 (2)	52 (1)
Cd	2.5 (0.2)	2.3 (0.1)	1.5 (0.1)	0.7 (0.1)	1.0 (0.1)	1.4 (0.1)	2.3 (0)	1.7 (0)	1.5 (0.1)	1.7 (0.1)	1.1 (0)	1.7 (0.1)	2.4 (0)
Pb	9.8 (0.6)	9.6 (1.2)	6.6 (1.2)	4.8 (0.5)	3.2 (0.4)	5.6 (0.5)	7.7 (0.3)	5.6 (0.5)	5.1 (0.4)	5.7 (0.8)	3.4 (0.4)	6.3 (0.9)	8.7 (0.1)

Extractor: 25 ml of 0.1 mol l^{-1} HCl. Duration of agitation: 2 h 30 min. Values in parenthesis are standard deviation of three determinations.

2.2.7.3. Third extraction (fraction bound to Fe and Mn oxides). To the residues from the second extraction 20 ml of 0.04 mol l^{-1} $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc were added and kept in a Dubnoff-type bath at 96 ± 3 °C under intermittent agitation for 6 h. After cooling, the mixtures were filtered (0.45 μm filter) and the filtrates stored in polyethylene bottles at 4 °C until analyses were carried out.

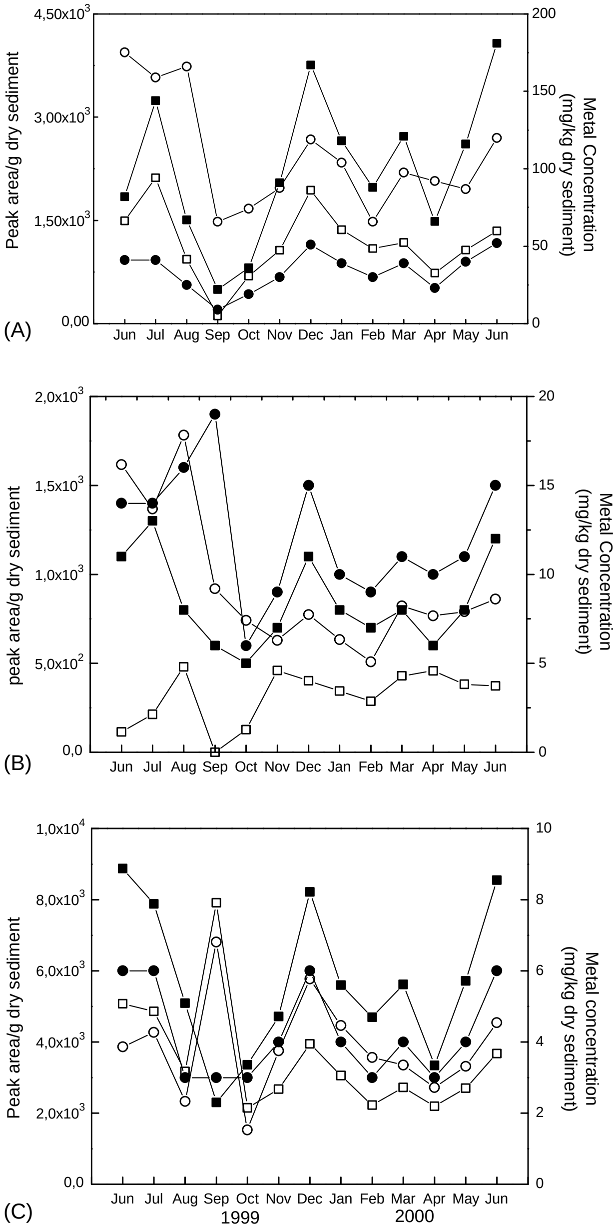

Fig. 1. Distribution of Mn, Zn, Ni, Cu, Fe, and Co in 20 cm sediment layers from Lake Ipê between June/1999 and June/2000. Axis *y* on the left: peak areas of metals obtained by EDXRF. Axis *y* on the right: concentrations (mg kg^{-1}). (A) Mn (□) and Zn (○) areas and Mn (■) and Zn (●) concentration. (B) Ni (□) and Cu (○) areas and Ni (■) and Cu (●) concentration. (C) Fe (□) and Co (○) areas and Fe (■) and Co (●) concentration.

2.2.7.4. Fourth extraction (fraction bound to organic matter). To the residues from the third fraction 3 ml of 0.02 mol l^{-1} HNO_3 and 8 ml of 30% H_2O_2 were added. The erlenmeyers were transferred to the Dubnoff-type bath at 85 ± 2 °C for 5 h and continuously shaken. After cooling, 5 ml of 3.2 mol l^{-1} NH_4OAc and 4 ml of ultra-pure water were added and shaken in a water-bath at 85 ± 2 °C for 30 min.

The residues were washed in 20 ml ultra-pure water after each extraction phase and totally transferred to the erlenmeyer. The analytical blanks, in triplicate, were processed simultaneously with the extractions of each sample fraction. The filtrates of each fraction were analyzed by ICP-OES.

2.2.8. Semi-quantitative determination of metals

Semi-quantitative metal determinations of sediment samples were obtained by EDXRF (model PW 1830 Phillips). With this technique, solid sample analysis was performed without chemical digestion and the peak areas, relative to the sediment mass, are proportional to the concentrations of the detectable elements. The EDXRF analyses were carried out using 1.000 g of the lyophilized (dried) samples and the concentrations were expressed as peak area g^{-1} dry sediment. The following irradiation conditions were used: tube voltage: 25 kV, tube current: 10 mA, and irradiation time: 300 s in vacuum, Si(Li) detector with a 30 mm^2 beryl window. The data were stored on disks and analyzed by the International Agency of Atomic Energy's AXIL/QXAS computer program.

2.2.9. Multivariate statistical analyses

The ARTHUR computer program, adapted for microcomputers [8], was used in the application of multivariate statistical techniques. Results of the physicochemical analyses and concentrations of potentially available metals extracted with 0.1 mol l^{-1} HCl were organized as columns (variables) of a data matrix whereas the rows corresponded to the months (samples). The columns were autoscaled to obtain values with a zero average and a unit variance, and PCA and HCA were applied to the resulting matrix. Correlations between all metals extracted with 0.1 mol l^{-1} HCl (listed in Table 1), pH, C, N, and P were carried out at 95% confidence limit.

3. Results and discussion

3.1. Potentially available metals using HCl method and ICP-OES technique

Total concentrations of metals in the sediments provide information regarding the accumulation rate of such metals, but do not mean they could be transferred totally to the biota, that is, its availability potential.

Nevertheless, according to Bevilácqua [14], metal extraction in 0.1 mol l^{-1} HCl permits estimation of that potential. Table 1 shows the metals obtained by ICP-OES technique that in an operational way were identified as potentially available.

3.2. Metals identified by EDXRF technique

An EDXRF study was carried out and the relative concentrations (peak areas g^{-1} dry sediment) for the chemical elements were related to the seasonal variation obtained

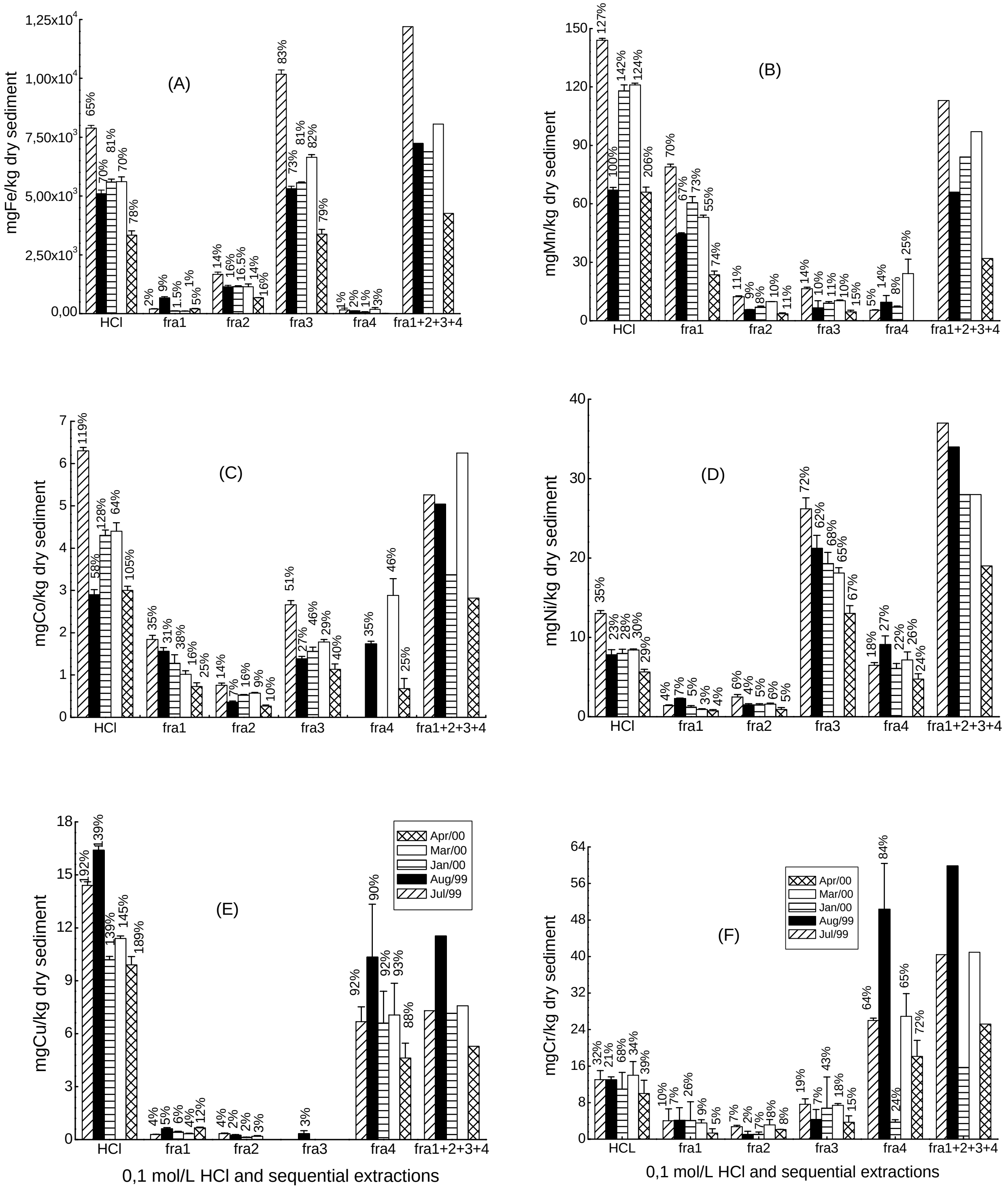

Fig. 2. Fe (A), Mn (B), Co (C), Ni (D), Cu (E), and Cr (F) concentration (mg kg^{-1}), extracted with 0.1 mol l^{-1} HCl and by sequential extraction in sediment samples collected in July/1999, August/1999, January/2000, March/2000, and April/2000. Fra $1 + 2 + 3 + 4$ is the sum (Σ) of the metal concentrations in each fraction of sequential extraction, and relates to 100%. The percentages over the bars are related to Σ.

using the wet chemical method (ICP-OES). The comparison of the seasonal distribution of Mn, Zn, Cu, Ni, Fe, and Co in the sediments by the ICP-OES and EDXRF techniques is presented in Fig. 1A–C. The profile is quite similar for the distribution of Mn, Zn, Cu, and Ni during the 13 months. However, an accentuated difference was observed between the two techniques for Fe and Co in September/1999. The justification for such discrepancies may owe to the fact that the material analyzed by the wet chemical method contains Fe and Co in the non-available mineral form and cannot be extracted with 0.1 mol l^{-1} HCl, possibly a mixed oxide due to the coincidence of the concomitant occurrence. The VisualMINTEQ program [15] was used to identify a probable composition of such a mineral. Thus, the precipitation of the mineral $CoFe_2O_4$ was anticipated, at a reduced concentration of 10^{-12} mol l^{-1}, considering the physicochemical properties and the set of metals identified in the water column in July, August, and September/1999.

3.3. Sequential speciation of the metals in the sediments using the Tessie methodology

The seasonal variation for metal distribution in different forms of environmental aggregation was investigated, since there are two different types of material entry into Lake Ipê, corresponding to periods with low and high waters, and also to compare results obtained with the single method (0.1 mol l^{-1} HCl). Samples collected in July/1999 and August/1999 (low waters), January/2000 (beginning of high waters), and March/2000 and April/2000 (high waters) were chosen. In this study the residual fractions (fifth fraction), defined as those that contain especially primary and secondary minerals capable of maintaining metals in their crystalline structures were not considered. Thus, the presence of such metals in the water column is not expected. According to Kersten and Förstener [16], metals associated with these minerals do not take part in recent environmental processes and they are not classified as potentially available. In Figs. 2 and 3, the numbers over the bars refer to the metal percentages for each fraction in the samples collected in July/1999, August/1999, January/2000, March/2000, and April/2000 regarding the sum of fractions 1 (changeable), 2 (bound to carbonates), 3 (bound to Fe and Mn oxides), and 4 (bound to organic matter). One hundred percent was attributed to that summed value (last set of bars in Figs. 2 and 3). The percentages described in the text correspond to the arithmetic averages of the 5 months, with their respective standard deviations.

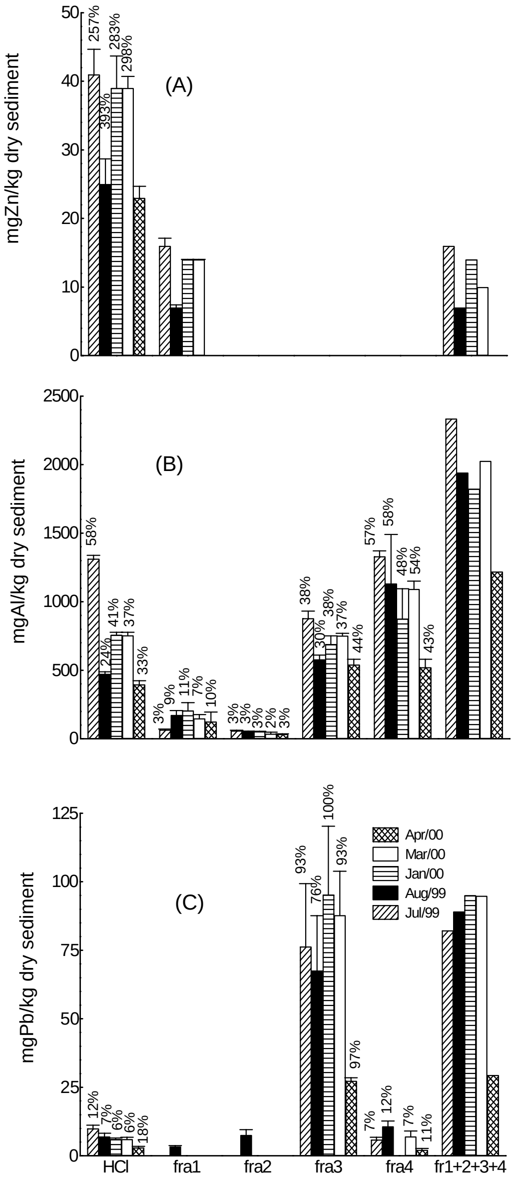

Fig. 3. Zn (A), Al (B), and Pb (C) concentration (mg kg^{-1}), extracted with 0.1 mol l^{-1} HCl and by sequential extraction in sediment samples collected in July/1999, August/1999, January/2000, March/2000, and April/2000. Fra 1 + 2 + 3 + 4 is the sum (Σ) of the metal concentrations in each fraction of sequential extraction, and relates to 100%. The percentages over the bars are related to Σ.

At first sight, in Figs. 2 and 3, it may be observed that, for a determined metal, the concentrations in the different months are grouped in the same fraction; for instance, Mn and Fe in the first and third fractions, respectively. Seasonality in the content of several metals may also be observed. For Fe (fraction 3), Co (fraction 3), Mn (fraction 1), and Zn (fraction 1), the collection made in July/1999 presented the highest levels 10,174 ± 184, 2.66 ± 0.10, 78.90 ± 1.50, and 15.90 ± 1.10 mg kg^{-1} in comparison with the collection carried out in August/1999: 5315 ± 104, 1.38 ± 0.06, 44.60 ± 0.50, and 7.10 ± 0.40 mg kg^{-1}, respectively. The flood pulse at the beginning of July/1999 (Fig. 4) may explain the highest concentrations for those metals. In general terms, the collection made in April/2000 presented the lowest levels for all the metals analyzed, indicating that there was a great mobility in the sediment–water column interface. The cause of this accentuated decrease is not associated with the pH or pE variation in the water column, but with the

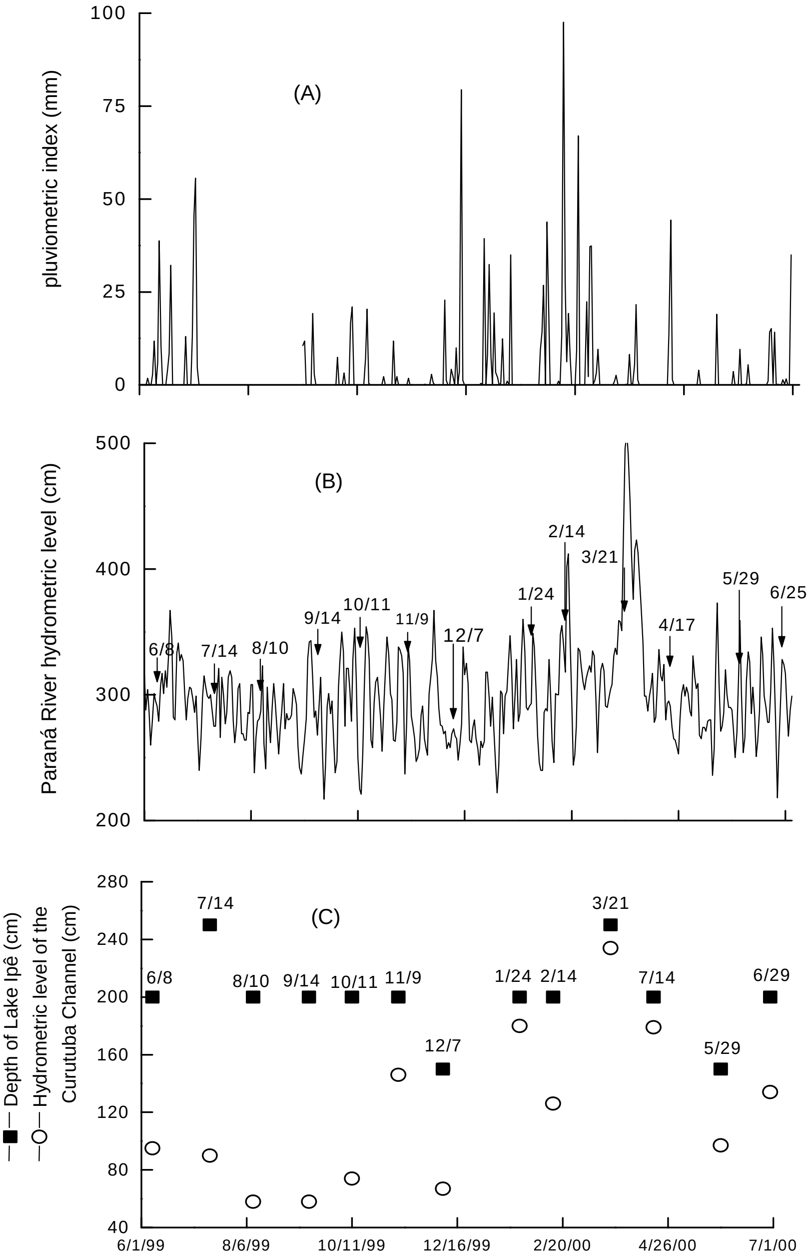

Fig. 4. Hydrometric levels and pluviosity indexes. (A) Daily pluviometric index (mm) from June/1999 to June/2000. (B) Daily hydrometric levels (cm) of the Paraná River in Porto São José city, between June/1999 and June/2000. (C) Depth of the Ipê Lake (cm) when the collections were made and at the sampling point, and hydrometric levels of the Curutuba Channel at the entrance of Lake Ipê on the date the sampling was carried out.

accentuated increase in organic matter in the water column during that period. This may be observed for lead, Fig. 3C, which, in theoretical terms, should be the ion with the highest tendency to complex with the organic matter present in the water column. In July/1999, August/1999, and January/2000 Pb [$80 \pm 14\,\mathrm{mg\,kg^{-1}}$ ($n = 3$)] was found in the third fraction (>70%), that is, adsorbed in oxides. In April/2000, the concentration was drastically reduced to $17\,\mathrm{mg\,kg^{-1}}$, indicating the solubility of the metal in the water column. The same may be verified for nickel, whose concentration was reduced between July/1999 and August/1999 and January/2000 from 23 ± 3 to $13\,\mathrm{mg\,kg^{-1}}$. Cu, besides being the metal with the highest complexation tendency, second to lead, did not suffer any accentuated variations during the 5 months. Fig. 2E shows that 91 ± 2% of copper is complexed with the sediment organic matter, that is, extracted in fraction 4. That organic fraction, probably with high molar mass, appeared less soluble and more strongly linked to copper, retaining it in the sediment independently of the increase in organic matter concentration in the column water.

3.4. Comparison between Tessie and single method ($0.1\,\mathrm{mol\,l^{-1}}$ HCl)

The concentrations obtained by the sequential method were compared to those obtained through extraction with $0.1\,\mathrm{mol\,l^{-1}}$ HCl to verify the correlation between both methods and the fraction extracted preferentially by acid. Figs. 2 and 3 show that $0.1\,\mathrm{mol\,l^{-1}}$ HCl extracted only 10 ± 5, 29 ± 4, 38 ± 11, 39 ± 17, and 73 ± 7% of Pb, Ni, Al, Cr, and Fe, respectively, against 90 ± 9% of Pb in fraction 3; 67 ± 4% of Ni in fraction 3; 52 ± 6% of Al in fraction 4; 62 ± 22% of Cr in fraction 4; and 79 ± 4% of Fe in fraction 3 for sequential extraction. For Co (95 ± 32%), the extraction with $0.1\,\mathrm{mol\,l^{-1}}$ HCl was equivalent to the sequential technique considering the sum of the four fractions, while for Cu (161 ± 24%) and Mn (140 ± 40%) it was higher.

The different results of these two methodologies may be explained considering that, in the extraction with $0.1\,\mathrm{mol\,l^{-1}}$ HCl, there was no Pb, Ni, Al, Cr, and Fe mobilization since they were predominant in fractions 3 and 4, that is, they were strongly adsorbed on the oxide surfaces or linked to organic matter. For Cu and Mn, extraction with $0.1\,\mathrm{mol\,l^{-1}}$ HCl was more efficient, but it dissolved part of the fifth fraction (residual). On the other hand, the extraction carried out with $0.1\,\mathrm{mol\,l^{-1}}$ HCl presents lower contamination risks, since only one reagent is necessary in a single execution phase, while sequential extraction uses several reagents and sample manipulations with longer execution times, 3 h compared to 48 h. Nevertheless, the results showed that the HCl extraction might lead to erroneous conclusions about metal associations and lability in the sediments. Therefore, careful planning is necessary regarding the extraction methodology used and the information that is sought based on it.

3.5. Interpretation of seasonal variations

3.5.1. PCA analysis

Multivariate statistical techniques were used to explore the relations among all the variables investigated: metals extracted with $0.1\,\mathrm{mol\,l^{-1}}$ HCl (listed in Table 1), pH, C, N, and P. Fig. 5 show the results obtained from a statistical study using PCA. PC1 and PC2 explained 72.17 and 13.20% of the total variance. There were three groups discriminated on PC1. Group A clusters samples collected in June/1999 (1), July/1999 (2), December/1999 (7), and June/2000 (13); group B, samples collected in October/1999 (5), April/2000 (11), and September/1999 (4); and group C clusters the samples collected in the remaining months. The variables with the highest loadings for PC1, setting the samples collected in June/1999 (1), July/1999 (2), December/1999 (7), and June/2000 (13) apart from the others, were Fe (0.29829), Cd (0.29829), Co (0.29642), Ni (0.29431), and Zn (0.28031). However, it is worthwhile mentioning that, except for the pH, Cu, and Cr variables, the other variables were also relevant in this discrimination. On PC2, Cu (−0.58045) was the most important variable in the discrimination of the samples collected in July/1999 (2), August/1999 (3), and especially in September/99 (4) from the others, discriminated by pH (0.66075). The discrimination in three groups was confirmed by HCA, using Euclidean distances, Fig. 6.

Fig. 5 shows that April/2000 (11) was the only month in the period of high water (from January to April/2000) (Fig. 4) that was not included in the central group. That may be explained by inspection of the concentration values in Table 1. In that month, a meaningful decrease in the concentrations of all potentially available metals was verified. Barreto et al. [17] observed, however, a large increase in

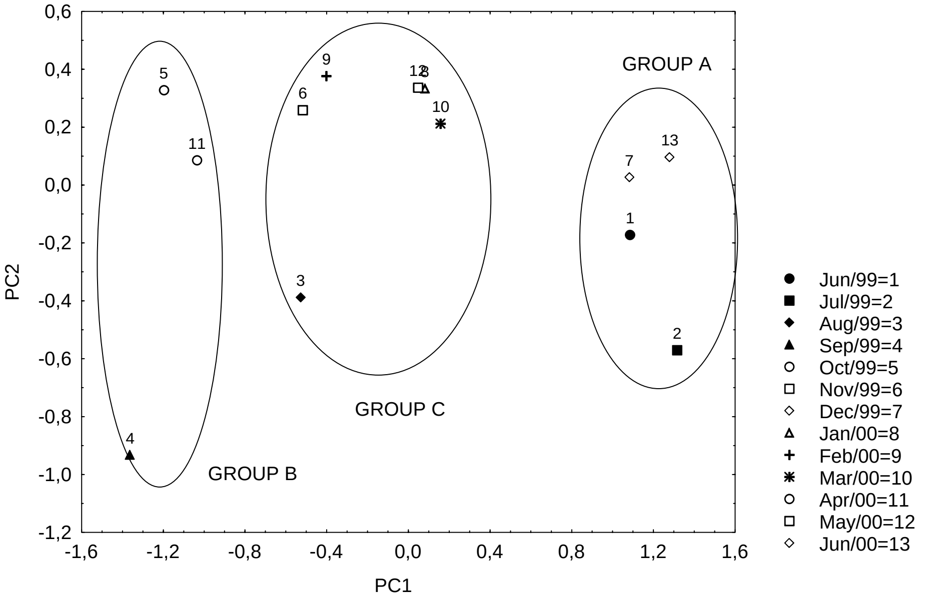

Fig. 5. Scores of the first two principal components (PC1 and PC2) of Lake Ipê between June/1999 and June/2000. PC1 and PC2 explained 72.17 and 13.20% of the total variance.

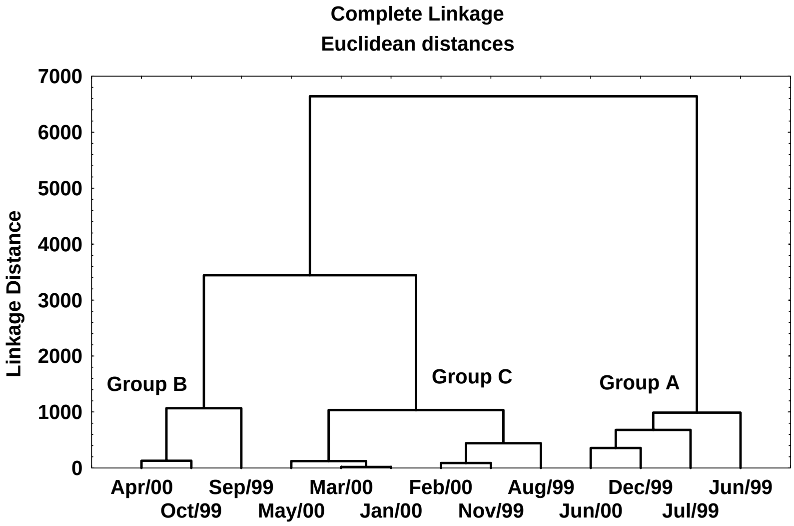

Fig. 6. Hierarchical clustering of the sediment samples of Lake Ipê between June/1999 and June/2000.

the concentrations of dissolved organic carbon (DOC) and metals [18] in the water column in April/2000. The concentration ratios in mg l^{-1} DOC (April/2000)/DOC (December/99) were equal to 7, that is, there was a 572% increase in April/2000. The dissolved iron and manganese concentrations, for instance, increased from December/1999, $[Fe] = 0.775 \pm 0.047\,mg\,l^{-1}$ and $[Mn] = 4.0 \pm 0.5\,\mu g\,l^{-1}$, to April/2000, $[Fe] = 9.262 \pm 0.324\,mg\,l^{-1}$ and $[Mn] = 21 \pm 10\,\mu g\,l^{-1}$. Theoretical calculations using the VisualMINTEQ program [12] showed that a fraction of the metallic ions may be complexed with dissolved organic matter in $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$ sequence. Therefore, this increase in the DOC concentration may have contributed to the complexation and solubility of some of the metals present in the sediment.

4. Conclusions

The comparison of the seasonal distribution of Mn, Zn, Cu, Ni, Fe, and Co in the sediments, using the ICP-OES and EDXRF techniques, showed that the profiles obtained are very similar for the Mn, Zn, Cu, and Ni distributions. The study indicated that the EDXRF technique could yield essentially the same results for the seasonal variation of metals in sediments, but in a more practical way.

The sequential extraction method was more efficient in metal dissolution than the 0.1 mol l^{-1} HCl. The Pb, Ni, Al, Cr, and Fe elements were less well extracted with 0.1 mol l^{-1} HCl than with sequential extraction. For Co, extraction with 0.1 mol l^{-1} HCl was equivalent to sequential extraction but for Cu and Mn, it was higher. Single extraction does not mobilize Pb, Ni, Al, Cr, and Fe adsorbed on oxides or when they are organically linked. For Cu and Mn, 0.1 mol l^{-1} HCl, not only extracted these metals from the four fractions, it also dissolved part of the fifth fraction (residual). Therefore, extraction with HCl may lead to erroneous conclusions about the association and lability of metals in sediments.

PCA separated the sampling months into three groups. This means that this ecosystem presented seasonality in the content of several metals. Most of them contributed to this discrimination, with emphasis on Fe, Co, Ni, and Zn. In general terms, the mobility of metallic ions in the sediments is conditioned by the seasonal fluxes of inorganic and organic matter that enter the lake directly through the river or by bank lixiviation. Metal origin and accumulation in the sediment may be explained by these two types of processes. The organic matter present in the water column has a fundamental regulator role in the increase of metal flux towards the sediment.

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