

Evaluation of metal availability in sediments of the Mogi-Guaçu and Pardo hydrographic basins

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ABSTRACT *Assessment of continental sediment has become increasingly important over the past several years. The assessment must be predictive of metal transport of potential bioavailability of metals from sediments. The concentration and possible chemical association of Al, Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn, and Pb in fluvial sediments from 10 sites in the northwest state of São Paulo, Brazil were studied using the US EPA Method 3051 and hydrochloric acid 0.1 mol L⁻¹. The ratio of elements leached by 0.1 mol L⁻¹ HCl to those from the US EPA 3051 represents an interesting tool to evaluate the liability of metals in sediments with different compositions, showing a ratio range from 0 to 0.2 (Al, Cd, Fe, Pb, Co, and Mg) and a ratio range from 0.5 to 1.1 (Cu, Mn, Ba, and Ca). Both procedures applied have shown a similar leaching profile in this work. The elements Cu, Mn, Ba, and Ca showed to be more available in the studied sediments.*

KEYWORDS

*sediment; availability; metal; hydrochloric acid;
US EPA Method 3051*

Introduction

Environmental pollution is one of the most important factors adversely affecting the biosphere. Metals are believed to be of specific ecological, biological and health significance. The occurrence and cycles of trace elements in the environment as well as the pathways in plants, food and animals is the subject of intensive investigation. This is particularly true for heavy metal content in sediments, soils, and sludge because of the potential for contamination of the human food chain. As a result, the importance and the number of environmental studies are growing.

An understanding of metal in sediment requires knowledge of its mineral phase, the association pattern way and the strength of binding among metals in sediment. Leaching techniques use a variety of reagents with different chemical behavior to release metals bound to the various fractions of sediment.

The analysis of metals in sediments has been a difficult task because of the complex nature of the sediments. However, to perform any monitoring or research project on heavy metal pollution, it is necessary to choose a method, which is inexpensive, rapid and quantitative for the level of element required.

Several techniques have been proposed for the analysis of metals in sediment (Gonzales *et al.* 1994, Daus *et al.* 1995, Krause *et al.* 1995, Bevilacqua 1996, Urasa *et al.* 1996, Gatti 1997, Rauret 1998). The majority of them deal with strong acid mixtures, which release metals from labile and non-labile fractions, although it was well recognized that only labile metal species play an important role in the environment (Förstner 1977, Förstner and Wittmann 1981, Fiszman 1984, Lemes *et al.* 2003).

According to the United States Environmental Protection Agency (USEPA 2003), the metals bound to clay minerals and humic material by cation exchange processes are also considered relatively available in the environment. The common chemical binding of metals occurs in the following sediment phases: carbonates; oxides and hydroxides; adsorbed on, or occluded with iron oxides; strongly adsorbed, or chelated, with humic materials and precipitated as sulfides (Florian 1998).

In addition, the European Community Bureau of Reference (BCR) (Ure *et al.* 1993) of the Commission of the European Communities has established analytical protocols for determination of metal bioavailable concentration by sequential

extraction scheme for sediments. The common chemical forms of metals achieved by the BCR procedures are exchangeable, bound to carbonates, easily reducible, and bound to organic matter and sulfide.

The application of sequential extractions procedures, commonly reported in the literature (Fiszman *et al.* 1984, Sutherland and Tolosa 2000, Lemes *et al.* 2003, Silva *et al.* 2002, Tessier *et al.* 1979), are able to release metals from different phases of the sediment that can hold information about the physical-chemical distribution and the availability of these metals within the bulk sediment.

Tessier *et al.* (1979) were one of the first groups to report an analytical procedure involving sequential chemical extractions. They have been developed for the partitioning of particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn) into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. The results obtained for phase 3 and 4 (Fe-Mn oxides and organic matter) indicate that these phases have a scavenging action for trace metals. In addition, as these fractions constitute important sources of potentially available trace metals, they should be considered explicitly when estimating the bioavailability of a particular metal. Sutherland *et al.* (2001) showed that nitric acid is an oxidizing agent that is not as powerful in its attack on aluminum-silicates as HF, therefore the extraction with HNO₃ conc. tends to extract metal from the exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter fractions, and not from the residual fraction, representing a partial digestion fraction and, it may represent a partial digestion of a potential toxic fraction of the sediments.

Fiszman *et al.* (1984) reported a comparison study about methods used for metal extraction in sediments, using solutions with different concentrations of hydrochloric acid, nitric acid and sequential chemical extraction (Daus *et al.* 1995, Urasa and Macha 1996, Rauret 1998, Förstner and Wittmann 1981, Silva *et al.* 2002, Tessier *et al.* 1979, Aualiita and Pickering 1988, Vicent-Beckett *et al.* 1988, Ure *et al.* 1998).

Fiszman's procedure applies four steps of extraction to Cd, Cr, Cu, Fe, Pb and Zn. In the first step uses 0.1 mol L⁻¹ hydroxylamine-hydrochloride and 0.01 mol L⁻¹ HNO₃ at pH 2. In the second step uses 30% hydrogen peroxide. In the third step uses sodium citrate (20 g) and sodium (2 g) in 120 mL

of deionized water. In the final step uses nitric acid and hydrofluoric acid mixture (5:2). They found out that 0.1 mol L^{-1} HCl was an efficient extraction procedure which presents no statistically significant difference from sequential extraction procedure (steps 1+2+3) for metals, and represents well the availability of metals in sediments.

Silva *et al.* (2002) compared 0.1 mol L^{-1} HCl to BCR sequential protocol for sediments (Cd, Cr, Cu, Ni, Pb and Zn) and the results obtained in their study were similar for both procedures.

Sutherland and Tolosa (2000) used dilute HCl to leach the sediment because it approximates the bioavailable portion of some metals in sediments.

According to the literature discussed above it is possible to observe that the extraction with diluted HCl has been suggested to represent the availability of metal in the sediments as well. Therefore, the present work aims to evaluate the metal availability in sediments combining single and rapid metal extraction technique (0.1 mol L^{-1} HCl) and US EPA Method 3051.

Methods and materials

Study area – The study has been carried out along the Pardo and Mogi-Guaçu Rivers in the northwestern of São Paulo State, Brazil. This area is approximately $23,000 \text{ km}^2$ and has been mainly used for agriculture (Oliveira *et al.* 1995, Katsuóka 2001).

The area is described in details in Lemes *et al.* (2003). In brief, close to the study area there are mining sites of zirconium, aluminum, uranium and thorium. The uranium and thorium mines are located in Poços de Caldas region, which are located 700 m upstream from the studied sites. Locations

of sampling stations are shown in Figure 1. The stream sediment samples (IG60, IG61, IG63, IG64, IG65, IG66, IG67, IG68, IG72 and IGVGS) were collected in February 1999 close to the water catchments area for water supply.

Sediment sampling, leaching procedures and analysis techniques – Sediment samples ($\sim 1 \text{ kg}$) were collected using a dredge and stored in a polyethylene bag at 4°C until analysis. Sediments were dried in an oven at 60°C for 24 h, desegregated, and sieved through a $63 \mu\text{m}$ sieve (Gatti 1997, Fiszman *et al.* 1984, Lemes *et al.* 2003).

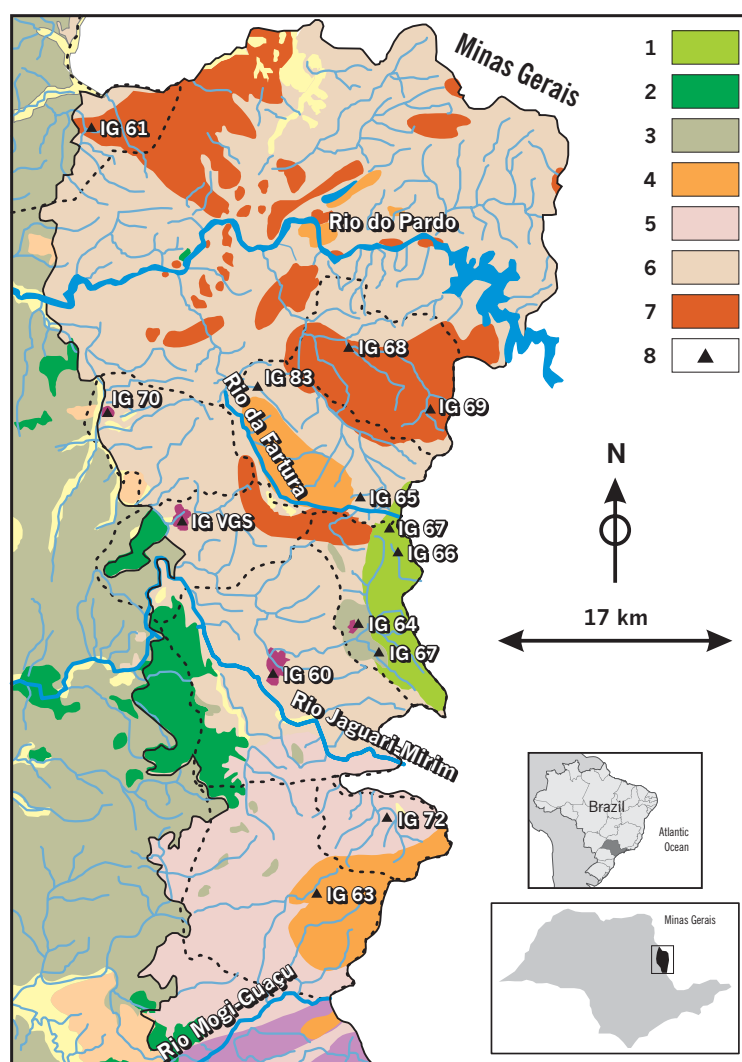


Figure 1 – Location of the catchments area and sampling points. 1. Alkaline rocks (intrusive and pyroclastic); 2. Diabase sills; 3. Sediment (diamictite and siltite); 4. Porphyritic and granite; 5. Migmatite, including anatexites and porphyritic granites; 6. Migmatite with granulite, calcosilicatic rock, amphibolite, schist and quartzite layers; 7. Granolitic rocks; 8. Catchment station

Hydrochloric acid 0.1 mol L⁻¹ extraction – Sediments (~2.5 g) were extracted with 50 mL HCl 0.1 mol L⁻¹; mechanically shaken for 2 h at 150 rotations per minute (rpm), and filtered through a filter paper (3µm).

US EPA Method 3051 – This method was chosen taking into account its widespread use in many studies (Lemes *et al.* 2003, Florian *et al.* 1998, Nagourney *et al.* 1997, Nagourney *et al.* 1999, Bettinelli *et al.* 2000). The sediment (0.5 g) was digested using the microwave system MARS 5 (CEM) using 10 mL concentrated nitric acid for 5 min at 175° C as outlined in the US EPA Method 3051. After leaching the sediment, the residue was filtered through a filter paper (3µm).

Standard Reference Material 2704 – It was analyzed for both methods (0.1 M HCl and EPA 3051) in order to validate; the relative standard deviation for all the elements were less 10 % (Lemes 2001).

Inductively-coupled plasma optical emission spectrometry – All leaching solutions were analyzed in triplicate, using an inductively coupled plasma-optical spectrometer axial Spectro Flame M 120 model (Spectro Analytical Instruments GmbH, Kleve, Germany) for Al, Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn and, Pb. A multielement standard solution was applied to establish calibration curves; typical detection limits (determined by analyzing eight replicates of the lowest standard solution and calculate at a confidence level of 99%) are in the range of 0.2-72 ng mL⁻¹.

Mineral analysis – Air-dried samples were lightly disaggregated, homogenized and then sieved to the same size class (63µm) before organic carbon analyses. Sediment texture was analyzed using the pipette method following dispersion after 2 h with Na₄P₂O₇ (Lemes *et al.* 2003). Minerals were identified by powder X-ray diffraction (XRD) under standard conditions; Ni filter was applied for CuKα radiation and by observation of thin sections. Chemical compositions (oxides) of sediments were identified by wavelength dispersive X-ray fluorescence spectrometer RIX3000 (Rigaku Co, Osaka, Japan).

Organic matter analysis – The analysis of organic matter was performed using the Walkley-Black wet oxidation method (Walkley and Black 1933).

Principal components analysis (PCA) was used with the purpose of facilitating the interpretation of the data, and Varimax rotation was applied to obtain a factorial matrix for an easy interpretation.

Results and discussion

Despite of the different lithologies in the study area (Fig. 1), the HCl extraction and US EPA method show a similar profile of metal concentration for all catchment's sediment areas (Fig. 2). With the information from Figure 2, which shows the leachate concentrations for each site, it was possible to note that IG 64 has high concentration range for about 80% of the studied elements and the site IG 72 has low concentration range for about 85% of the studied elements. Other sites elements did not show large differences of each other.

The high concentration range of the elements in IG 64 site has unusual characteristics; this site shows high organic matter (6.92%), kaolinite and illite (present level), SiO₂ (32%), Al₂O₃ (25%), Fe₂O₃ (17%), and MnO (1%). The low concentration range of elements in IG 72 site is caused by their low organic matter (0.52%), kaolinite (abundant level), illite (present level), SiO₂ (90%), Al₂O₃ (4%), Fe₂O₃ (1.5%) and, MnO (0.06%) compared to the other ones. These different types of sediments have different profiles, so the IG 64 profile shows lower value in SiO₂ and higher values in Al₂O₃, Fe₂O₃, MnO and OM that tends to increase the metal retention capacity. The site IG 72 profile, composed of pure quartz sand, is different in that it shows higher value in SiO₂ and lower values in

Table 1 – Organic matter contents of the sediment samples

Site	Predominant group	Organic matter (%)
IG 60		2.95
IG 61		1.03
IG 63		2.53
IG 64		6.92
IG 65		4.55
IG 66		5.40
IG 67		0.59
IG 68		2.64
IG 72		0.52
IG VGS		0.19

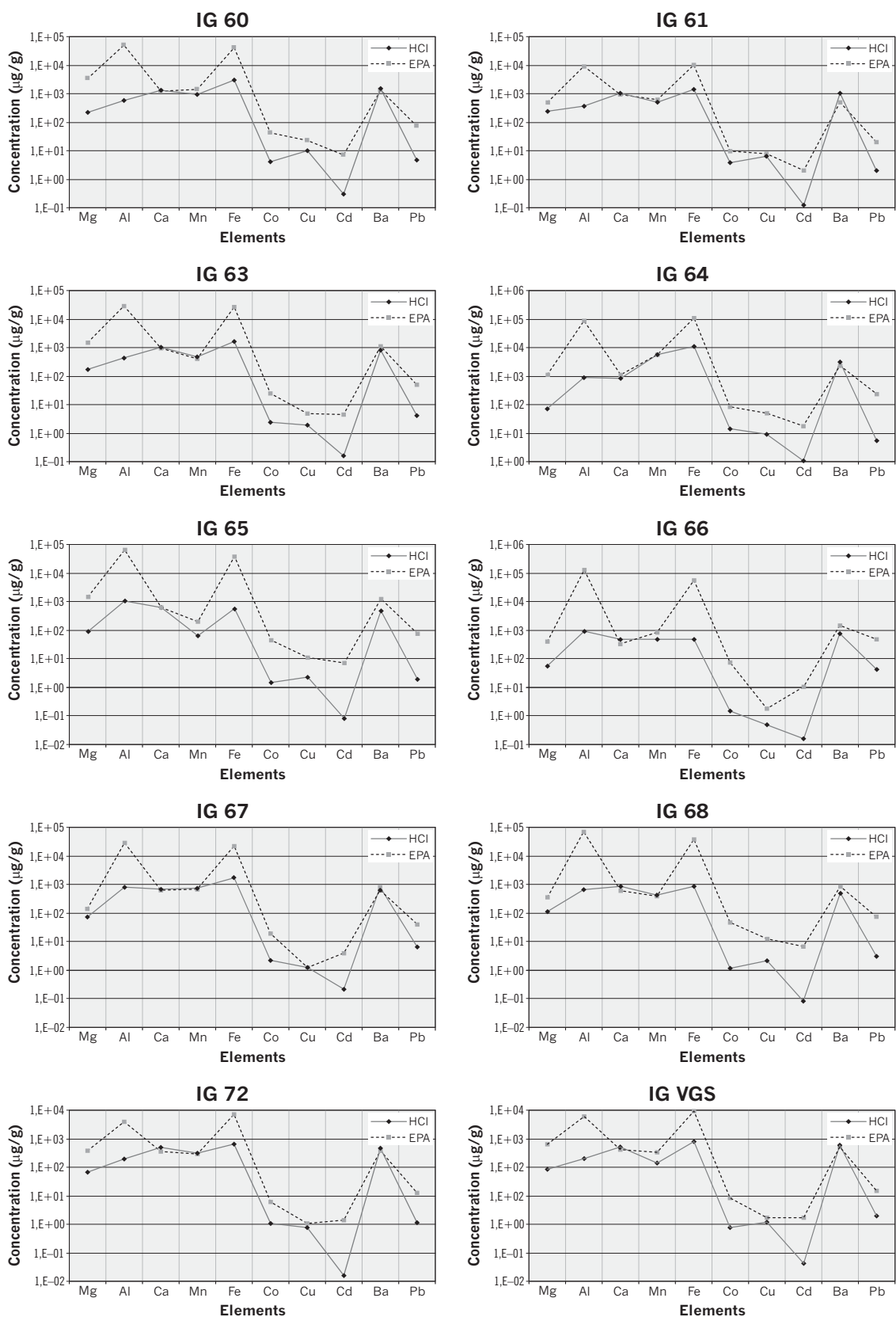


Figure 2 – Metal concentrations of leaching using 0.1 mol L⁻¹ HCl and US EPA Method 3051 method in sediment at different sites

Al₂O₃, Fe₂O₃, MnO and OM, which tends to decrease the metal retention capacity as described previously (Lemes *et al.* 2003). The remaining sites were in close agreement of their elemental concentrations as their sediment characteristics are similar.

The high organic matter, Al₂O₃, Fe₂O₃, MnO content in the sediment, increase the probability of metal sorption on it (Förstner and Wittmann 1981). The sediments chemical composition could help to explain the elements concentration of sites IG 64 and 72. IG 64 has less available metal than site IG 72, due to the high organic matter (Tab. 1).

In order to investigate the influence of different leaching procedures for ten sediment-sampling sites, the concentrations of Al, Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn, and Pb were determined applying the US EPA Method 3051 and 0.1 mol L⁻¹ HCl procedures, for which results are presented in Figure 2. The application of US EPA method 3051 yielded higher concentrations for Al³⁺ Fe > Mn = Ba = Ca = Mg elements. These metals are considered macro elements in sediments and also are in soil.

According to Ure *et al.* (1993), concentrated HNO₃ tends to leach metals that are exchangeable, bound to carbonates, easily reducible, bound to organic matter, and occluded in fractions of Fe and Mn oxides. However, the diluted HCl leach tends show greater concentration of metals bound to soluble and exchangeable fractions.

The ratio ([metal]_{HCl}/[metal]_{EPA}) of the metals was calculated with the data of Figure 2. This method suggests an indication of the metals availability in sediments. To visualize the availability of the several metals in sediments, a ranked *box-plot* was developed (Fig. 3). As expected, the acid reagent used by US EPA Method 3051 procedure is more extracting than the diluted hydrochloric procedure, showing a ratio < 0.5 for the major metals

Table 2 – Principal component analysis (PCA) of the values of US EPA and HCl procedures

Element/Method	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Al _{EPA}	0.32	0.01	0.86	-0.03	0.34
Al _{HCl}	0.32	-0.09	0.47	-0.23	0.69
Ba _{EPA}	0.96	0.23	0.12	0.03	-0.01
Ba _{HCl}	0.97	0.21	0.11	0.05	-0.02
Ca _{EPA}	0.19	0.93	-0.16	-0.13	0.00
Ca _{HCl}	0.19	0.93	-0.18	-0.03	-0.04
Cd _{EPA}	0.42	-0.35	-0.07	0.75	-0.28
Cd _{HCl}	0.98	0.09	0.13	-0.01	0.07
Co _{EPA}	0.89	-0.09	-0.05	0.39	-0.14
Co _{HCl}	0.99	0.15	0.05	-0.03	0.05
Cu _{EPA}	0.65	0.69	-0.03	0.22	0.01
Cu _{HCl}	0.65	0.70	-0.02	0.18	0.02
Fe _{EPA}	0.75	-0.21	-0.10	0.58	-0.19
Fe _{HCl}	0.99	0.10	0.00	0.04	0.05
Mg _{EPA}	0.13	0.76	0.17	0.50	0.24
Mg _{HCl}	-0.13	0.90	-0.18	-0.02	-0.21
Mn _{EPA}	0.99	-0.02	0.04	-0.01	0.04
Mn _{HCl}	0.99	-0.01	0.04	-0.04	0.05
Organic Matter	0.57	0.06	0.55	-0.08	0.56
Pb _{EPA}	-0.12	-0.33	0.90	0.04	-0.17
Pb _{HCl}	-0.09	-0.20	0.94	-0.19	-0.07
Pct of Variance	45.50	21.80	13.40	8.30	6.20

Bold-italic numbers mean high coefficient correlation

analyzed in this study. Observing Figure 3, it is possible to divide the elements into two groups:

- (a) The first group has average ratio of 0.5 to 1.1 (Cu, Mn, Ba, and Ca) showing that these metals should be preferentially bound to the soluble and exchangeable fractions of the sediments. It is possible to note that Ba, Mn and Ca yielded [HCl/HNO₃] greater than 1 in Figure 3. Ratio close to 1 suggests that these elements showed to be bound on the available fractions of the sediments.

Calcium is well known as very available element in soils and sediments and the availability is approximately 100% (Brady, 1989), therefore, the

results presented here may be taken with caution due to possible analytical error either in the acid extraction or in ICP-OES measurement. Some works have found reduction of signal on ICP-OES for some elements (ex. Ca and Ba) using high concentration ($\sim 3\text{--}4 \text{ mol L}^{-1}$) of HNO_3 for digestion of soil/sediment. Canals *et al.* (2002) and Tighe's papers (Tighe *et al.* 2004), for instance, show that nitric acid at 3.9 mol L^{-1} may show a 50% reduction signal and also a significant deterioration of limit of detection.

The final concentration of nitric acid used in this work was 3.2 mol L^{-1} , that is according to Tighe's papers. The elements Mn, Ca, and particularly Ba showed lower concentration to EPA method than HCl method and the Ca limit of detection was much higher than other elements. Canals (2002) studied the elimination of nitric acid interference in ICP-OES. They observed a 10% reduction signal reduction for nitric concentration of (0.9 and 3.9 mol L^{-1}), and some cases, a reduction of 50%. The nitric concentration at 3.9 mol L^{-1} has induced a deterioration of detection limit. The limit of detection for calcium was 179 ng g^{-1} in their study. Tighe (2004) reported comparison of four digestion methods (microwave aqua-regia, open aqua-regia, microwave nitric acid, and open nitric) of soil by ICP-OES. The microwave nitric acid applied in their study is compared with US EPA Method 3051. They found lower recoveries for Ca amount and other elements studied because these elements are usually associated with aluminosilicate phases and also they showed in their study that for microwave nitric acid digestion 8 out of 18 elements analyzed showed lower concentration in comparison with other digestion methods. Calcium result showed a ratio (open/microwave) 1.1. The possible explanation for those differences could be the matrix-elemental interferences, or temperature/pressure differences between open method and microwave method.

(b) The second group has an average ratio of 0 to 0.20 (Al, Cd, Fe, Pb, Co, Mg). In the present study, this ratio range is suggested as an

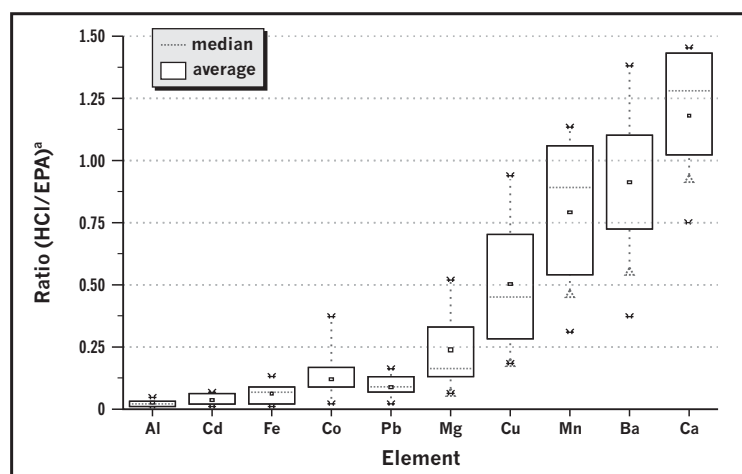
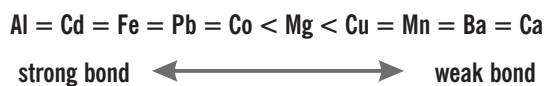


Figure 3 – Box-plot of the ratio $K = ([\text{metal}]_{\text{HCl}}/[\text{metal}]_{\text{EPA}})$ of the metals in 10 sediment samples

indication that these metals should not be preferentially bound to the soluble and exchangeable fractions of sediments. Analyzing these data, it is possible to write a bond sequence of these elements in the sediments:



Principal components analysis was applied to the concentration data of both extractions (Table 2). The PCA explained 95% of the total variability with 5 factors. A Varimax rotation was applied to obtain a factorial matrix for an easy interpretation. The higher weight of the variable is characterized by showing a lower difference between nitric and hydrochloric acid procedures. The factors 1, 2 and 3 showed higher weight variables, explaining 81% of the total variability, which is represented by Ba, Ca, Cu, Fe, Mg, and Mn. It means that these elements do not show statistically significant difference between both types of procedures each element. This is confirmed by the *Student t-test* ($p < 0.05$).

Comparing the data of factors 1 and 2 (Tab. 2) with Figure 3, it is possible to observe that the sequence of the elements in Figure 3 shows strong correlation for the elements Ca, Ba, and Mn, and medium correlation for Mg, Co, Cu and Fe for both procedures. The element Pb shows a strong correlation between both procedures, but it appears in the factor 3. The elements Al and Cd do not show any correlation. This is possibly because most

of the metals were not extracted using the treatment with HCl and HNO₃; these elements might be in crystalline structure.

The factors 1 and 2 explain 67.3% of the total variability, suggesting that these elements could come from geological formation of the region (Lemes *et al.* 2003, Ure *et al.* 1998). The factor 3 explains 13.4% of the total variability. In this factor Pb is the unique element represented. The possible explanation could be the existence of lead ore nearby the neighborhood, by association with alkaline rocks.

This region (Poços de Caldas Complex) is located 700 m upstream the study area. The Pb could run off to lower areas, explaining the high concentration observed in sites IG 64 and IG 66.

Conclusion

The ratio of the US EPA Method 3051 and the hydrochloric acid 0.1 mol L⁻¹ methods applied in this study has shown to be a very interesting tool in order to evaluate the availability of the metals in the sediments of different composition.

Among the studied elements Ba, Mn and Ca showed average ratios [HCl/HNO₃] closed to 1, suggesting that these elements are present in the more available fraction of the sediments to be bound on the more available fractions of the sediments. While Al, Cd, Fe, Pb, Co, Mg showed ratios lower than 0.2 suggesting that these elements were not preferentially bound to the soluble and exchangeable fractions of sediments.

In spite of the different composition of the sediments, it is possible to observe the same sequence of the metal lability: Al = Cd = Fe = Pb = Co < Mg < Cu = Mn = Ba = Ca.

The high concentration range of the elements found in sediment from the IG 64 site is related to the sediment composition that shows high contents of SiO₂, Al₂O₃, Fe₂O₃, MnO, and organic matter whereas these contents are very low in sediments from the IG 72 site.

The application of PCA tool showed that the elements (Ba, Ca, Cu and Mn) in the factor 1 and 2 possibly came from a geological formation in the region. The statistics also indicates that the composition of IG 64 and IG 66 sampling sites might have been influenced by a lead anomaly probably associated with the Poços de Caldas alkaline complex.

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