



The Role of the Humic Substances in the Fractioning of Heavy Metals in Rodrigo de Freitas Lagoon, Rio de Janeiro - Brazil

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ABSTRACT

One of the main results of the processes related to urbanization is the contamination of the adjacent water bodies. Inserted in this context, the Rodrigo de Freitas lagoon is situated in the south zone of the city of Rio de Janeiro. This ecosystem receives several inputs containing all sorts of pollutants, including heavy metals. The present work aimed to study the partitioning of heavy metals in the sediments of Rodrigo de Freitas and the influence of organic matter in this fractionation dynamic. The results of these analyses presented the contents of organic matter as an important metal-capturing agent. Fractionation of organic matter resulted in a predominance of humine. Heavy metal partitioning showed that the metals bound by the water-soluble phase have no significant concentrations. Special features such as, reducing sediment, high levels of organic matter and fine grain size have transformed this ecosystem in an effective deposit of pollutants, where heavy metals are not available in easily reactive fractions.

Key words: Brazil, Rio de Janeiro, Rodrigo de Freitas lagoon, heavy metals, humic acids.

INTRODUCTION

Coastal lagoons in the Brazilian Rio de Janeiro metropolis are located in littoral zones that are situated between the sea and the mainland. Increased urbanization, recreational and tourist facilities in areas around the lagoons have increased pollution levels in these water bodies. Due to their dynamic nature and to those processes occurring in transition

environments, coastal lagoons are ecosystems extremely complex and poorly understood. They are temporary sinks for the majority of metals that accumulate as a result of sedimentation and metal loading. They retain materials supplied by sources such as rivers, atmospheric deposition, urban run-off, shipping and industrial processes. Their mixtures of fresh and saline waters can generate sharp gradients regarding physical-chemical parameters and cause suspended materials that

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contain high concentrations of trace metals to aggregate and settle out in the bottom sediments of the lagoons (Eisma 1986, Hill 1998).

Metal accumulation within sediments depends directly on parameters such as pH, ionic strength, the type and concentration of inorganic and organic “ligands” plus the availability of adsorption surfaces such as clay minerals and organic matter (Davies et al. 1991). The presence of saline water enhances metal export, especially those that are soluble under anoxic conditions and those forming stable chloro-complexes. Organic compounds that result from partial decomposition of organic matter under anoxic conditions also form complexes. These processes eventually result in the export of some metals to adjacent waters where they may have an impact on living organisms (Brown 1988, Wang et al. 2004).

Anthropogenic pollutants enter coastal lagoons mainly through fluvial pathways. These pathways provide the highest concentrations of pollutants, where the major toxic metals originate from fuel combustion, non-ferrous metal smelting, iron and steel plants and sewage discharge (Brown 1988). How long these metals remain in solution will depend on their potential to form complexes with both organic and inorganic “ligands”. Humic substances form metal chelates and therefore influence the cycling of most metals in coastal lagoons. However, most organic-metal complexes can release their adsorbed metals in the presence of more abundant ions such as Ca since these cations out-compete trace metals for organic binding sites. This can cause a temporary enrichment of metals that may lead to metal toxicity within the water column (Campbell and Evans 1987).

Diagenetic processes in sediments, where the latter constitutes one of the main deposits for metals and other pollutants (Chapman 1990, Bryan and Langston 1992), can also change and redistribute these contaminants between various solid phases present within the sediments, where

they become bound (Hanson et al. 1983). However, there is confusion in the literature as to how metal concentrations should be assessed regarding environmental pollution studies. This is due to the fact that any metal present within the matrix may be bound within a relatively soluble phase or be so securely held within a silica (residual) phase that only the most extreme environmental conditions would cause its release. In order to understand the environmental impact of metals, their relative availability must be understood. Bioavailability refers to the proportion of total metals in the sediment available for uptake by biota (Meyer 2002, Naidu et al. 2003). Therefore total element analysis, where samples are completely dissolved in mixed solutions that contain hydrofluoric acid, provides a poor assessment of the environmental impact of metals in sediments. With these facts in mind, the present work aimed to study the fractioning of heavy metals in the sediments of Rodrigo de Freitas, as well as investigate the influence of some variables on the partitioning of the metals among their different chemical phases. Despite some limitations (Nirel and Morel 1990, Saeki et al. 1993, Guo et al. 1997, Ngiam and Lim 2001), selective extraction of operationally defined phases that are present within a sediment has proved to be an effective way to ascertain metal mobility, availability and their potential impact on biota (Tessier et al. 1979, Ure et al. 1993, Quevauviller et al. 1994, Cobelo-Garcia and Prego 2004). The importance of humic compounds that are composed mainly of carbohydrates, proteins, lipids, lignins, tannins and melanins (Burdon 2001) as complexing agents for metals is also studied using oxidizable organic carbon and extraction of humine, humic and fulvic acids. Statistical analysis using Spearman Correlation for these parameters plus pH, Eh and temperature was also carried out. Significant plus very significant correlations were designated at $p \leq 0.05$ and $p \leq 0.01$ respectively.

MATERIALS AND METHODS

STUDY AREA

The Rodrigo de Freitas lagoon, located in the southern area of Rio de Janeiro ($22^{\circ}57'02''$ S; $043^{\circ}11'09''$ W - Figure 1) has a perimeter of 7.5 km. Over the past twenty years this lagoon has reduced in area by 1.4 km^2 (present water mirror surface is 2.4 km^2) and by approximately 3 m in depth during the last century (SEMADS 2001). The greatest depth was recorded as 11 m (Andreata 1997). The Rodrigo de Freitas is the most urbanized lagoon in Rio de Janeiro and its only connection with the sea is via the 850 m Jardim de Alah Channel that frequently becomes silted with marine sediments. The lagoon is a semi-confined system making water renewal complex and the marine water flux

is superficial, leaving deeper layers unaffected (Torres 1990). Drainage is mainly by the Macacos River but a smaller amount escapes via the Cabeça and Rainha Rivers as well (Andreata et al. 1997). Extreme reducing conditions within the lagoon exist due to high concentrations of organic matter and low currents. Exchanges with the sea are limited, creating ideal conditions for accumulation of pollutants (Bryan and Langston 1992). This coastal lagoon represents a transition between fresh and salt water and this leads to a gradual variation in the amount of dissolved salt flocculation. Pollutants adsorbed to suspended matter tend to settle out and become deposited in the bottom sediments, whereas other more stabilized compounds may be formed as a result of, for example, complexation reactions.

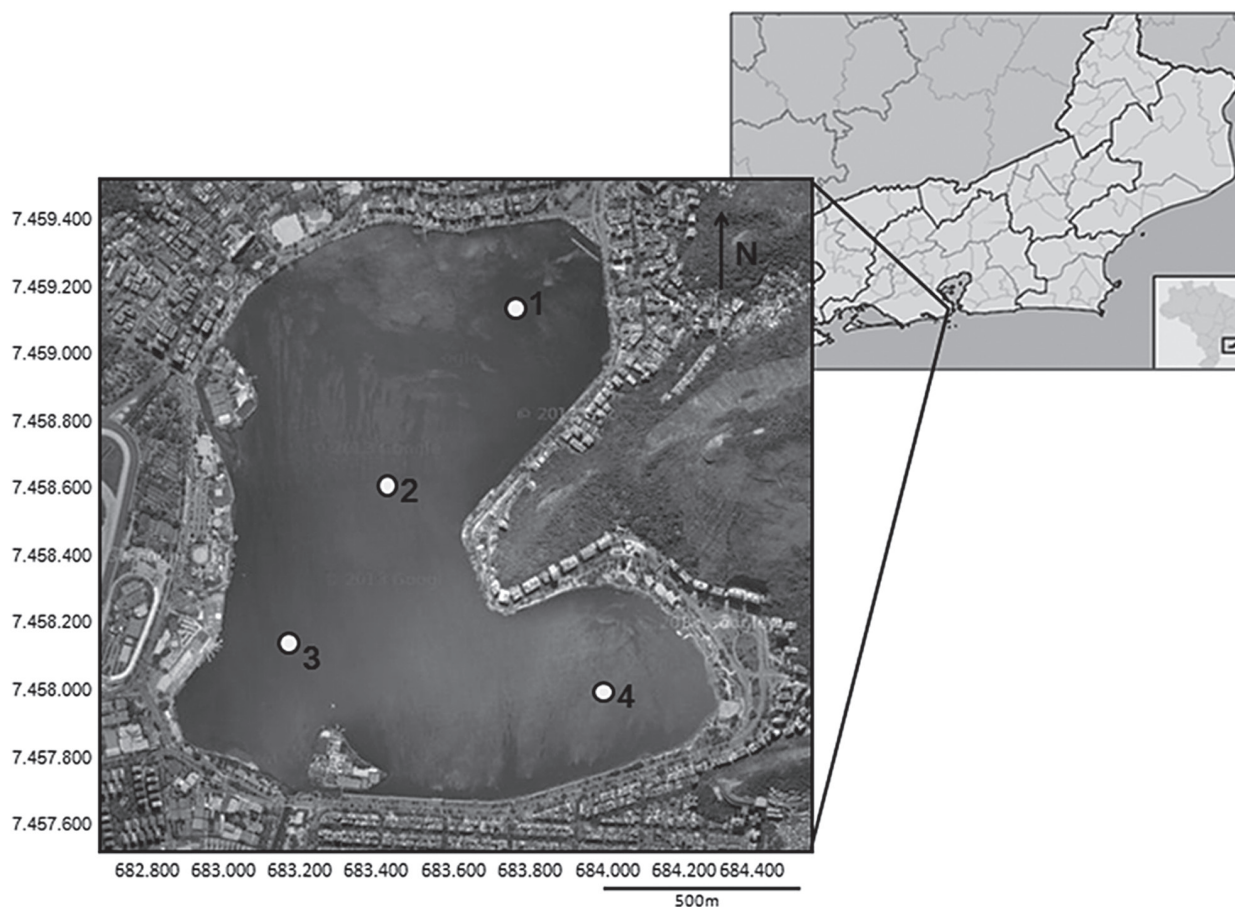


Figure 1 - Map of the studied area with the location of the sampling stations.

SAMPLE ANALYSIS

Core samples (1 m length) were collected from four different stations using PVC tubes. Both ends of the tubes were sealed under water before removal to avoid oxidation of the sample. The tubes had holes drilled at 10 cm intervals and hermetically sealed to avoid oxidation reactions. Electrodes to measure pH, temperature (Metrohm 744 meter) and Eh (Analion, ROX 673) were inserted into the sampling holes and results were recorded in the field. The cores were immediately transported to the laboratory and frozen. Opening of the cores was carried out in a glove box under an inert atmosphere of nitrogen prior to analysis. Samples were freeze dried and passed through a 2 mm diameter nylon mesh sieve. The <63 μm fraction was collected by further sieving a representative portion of the < 2 mm fraction through a nylon mesh. This size fraction was analyzed as it is relatively undiluted by coarser sizes and allows a more accurate prediction of the threat to an ecosystem by heavy metals (Forstner and Whittmann 1983).

Particle size analysis of the < 63 μm fraction taken 20 cm from the top of each core was carried out using a Malvern 2600LC (USA) laser analyzer after removing organic matter. Organic carbon employed the Walkley and Black (1934) method. Humic and fulvic acid fractions were separated using a differential solubility method established by the International Society of Humic Substances (Kononova 1996, Dabin, 1976) and later adapted by Benites et al. (2003). Humic acid was extracted using an alkaline solution, that was separated from the residue by centrifugation. Fulvic acid was extracted by acidifying this solution to pH 1.0 using H_2SO_4 (20%v/v) and allowing the suspension to settle for 18 hours. It is important to use H_2SO_4 since HCl would interfere with the determination of organic carbon (Benites et al. 2003). Carbon analysis in the form of humine was carried out on the residue from the alkaline extracts.

The selective extraction protocol (McAlister et al. 2005) is shown in Table I. In this study the extraction of the organic phase was modified. This technique offers a differential approach, whereby those operationally defined solid phases that bind these metals is examined. It provides a better understanding of metal retention and bioavailability under different environmental conditions, as well as providing additional information to enhance analytical interpretation (Tessier et al. 1979, Ure et al. 1983, Rauet 1989, McAlister et al. 2005, McAlister et al. 2008).

TABLE I
Methodology of analysis of heavy metals.

| Phase/Extractant | Ratio | Time | Conditions |
|--|--------|----------------------------------|------------------------|
| Water-Soluble Deionised Water | 1:20 | 2 hrs (leave overnight) | Shaking |
| Exchangeable/ carbonate 1M $\text{NH}_4.\text{OAc}$ (pH 5) | 1:50 | 6 hrs | Shaking |
| Amorphous Fe/Mn 0.25M $\text{NH}_2.\text{OH}.\text{HCl}$ / 0.25M HCl | 1:50 | 2hr | 600°C |
| Crystalline Fe/Mn 1M $\text{NH}_2.\text{OH}.\text{HCl}$ /25% CH_3COOH | 1:50 | 3hr | 90°C |
| Organic HNO_3/HCl (3:1) | 1:50 | 1hr | 90°C |
| Residual/ Siliceous $\text{HNO}_3/\text{HF}/\text{HCl}$ (3/1/0.5) | 0.1:25 | 20min | Microwave Digestion |

Samples were weighed into acid washed polypropylene tubes and all extracts were collected in acid washed high-density polyethylene (HDPE) containers prior to analysis. Reference material is not available to allow quality control monitoring of selective extraction. Reproducibility was monitored by including sample blanks and repeating sample analysis at regular intervals. Analytical standards were prepared by diluting a 1,000 mg.L^{-1} BDH Ltd. stock solution that is traceable to the Institute of Standards and Technology (NIST). All standards

were diluted to volume in the extracting solutions used for the selective extraction analysis so that both samples and standards were matrix matched.

Cu, Cr, Ni, Pb, Zn, Fe and Mn concentrations were analyzed using a Perkin Elmer AAnalyst 200 (USA) atomic absorption spectrophotometer. The residual phase was dissolved using a Perkin Elmer microwave digestion system and analytical accuracy was monitored using a certified reference material (I.G.G.E., stream sediment, China).

Spearman statistical analysis was used to test correlations between the several physical-chemical parameters. Correlations were considered significant for $p \leq 0.05$ and very significant for $p \leq 0.01$. Correlations between heavy metals concentrations in each phase in all of the samples and humine, humic and fluvic acids were also examined.

RESULTS AND DISCUSSION

Partitioning of metals between various phases within a sample matrix and properties such as mobility, reactivity, bioavailability, bioaccumulation and toxicity are all controlled by pH (Warren and Haack 2001). In this study, pH values for interstitial waters range between 7.14 and 8.38 and no significant variations were observed with depth. These values correlate with those recorded by Berner (1981) and Burton et al. (2004) for marine and estuarine sediments.

A positive correlation was observed between pH and humine concentrations ($p=0.0228$), where the latter was found to be the predominant fraction among the humic compounds in these sediments. Solubility and production of dissolved organic carbon is also affected by pH due to its influence on the density of the charges present on humic compounds, as well as its positive or negative influence on bacterial activity (Anderson and Nilsson 2001).

The behavior of heavy metals in a sediment matrix may be influenced either directly or indirectly by oxi-reduction conditions. Changes in oxi-reduction potentials may lead to the

decomposition of certain mineral species such as amorphous Fe oxy-hydroxides or Fe sulfides that can adsorb trace metals (Burton et al. 2004). Eh values recorded for all the profiles (Figure 2) showed an overall anoxic environment, where values decreased to between -305 and -345mV for sediments at Station 2. Similar oxi-reduction conditions were also observed in another research studies Sposito (1989). With the exception of Station 1, a decrease in Eh with an increase in depth was observed for all the samples. This direct relationship between Eh and humine concentrations ($p=0.0078$) would suggest its association with organic matter in these sediments.

Temperature is an important factor controlling the partitioning of metals between different phases since it influences the kinetics of relevant reactions (Allard et al. 1987, Tessier et al. 1989). In this study, values varied between 22.1 and 24.5°C and no defined temperature variation pattern between the four cores was observed. Statistical analysis showed a significant inverse correlation between temperature and total organic carbon ($p = 0.0043$). A higher temperature favors the production of bacteria and therefore, faster degradation of organic matter (Glud and Middelboe 2004). Other studies have shown increases in bacterial production despite small temperature variations like the one shown in this study (Gsell et al. 1997). On the other hand, De Souza et al. (2000) suggested that temperatures equal to, or below 20°C are critical for the reproduction of sulfate reducing bacteria. Therefore, further detailed studies are necessary to investigate the relationship between organic matter, bacterial activity and temperature within this lagoon.

Particle size analysis revealed the predominance of silt. Sediments with a high silt/clay content adsorb greater concentrations of heavy metals and hydrocarbons (Singh et al. 2004). In this study, however, particle size analysis showed no significant correlation with any of the other parameters analyzed. Results would suggest that

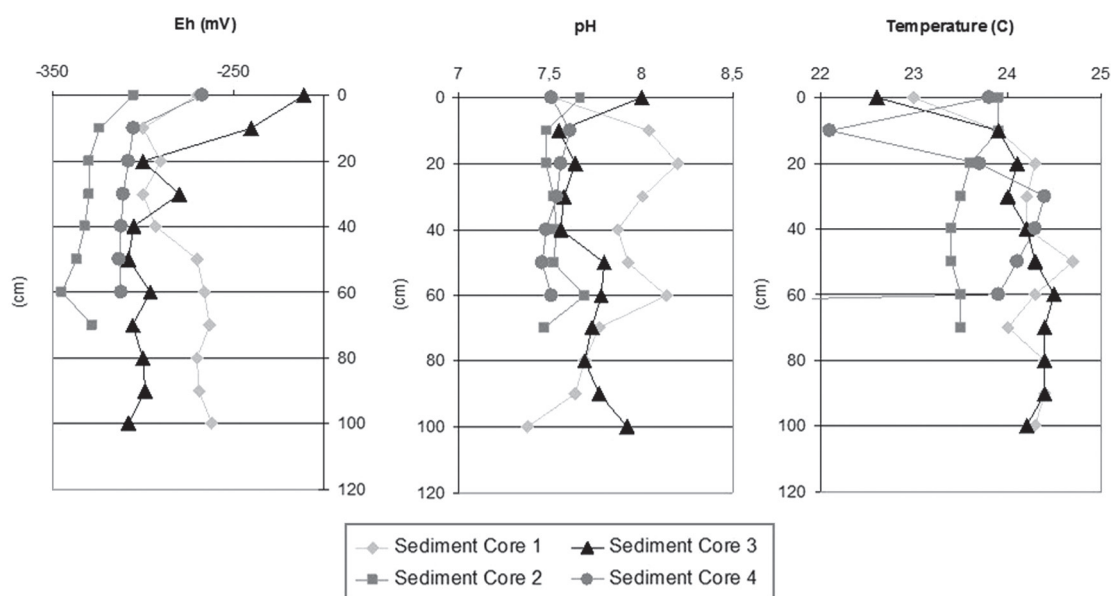


Figure 2 - Physico - Chemical parameters variation through sampling core.

the size distribution pattern of this area could be the result of not only one, but a synergy of several different parameters despite the small number of samples analyzed.

Organic matter influences the main physical, chemical and biological parameters in soils and sediments, determining their chemical behavior and fertility (Coleman et al. 1989). It is therefore fundamentally important to quantify those fractions that make up this organic matter matrix (Warren and Haack 2001). Organic carbon concentrations reached values that varied between 12.06 and 15.59%, with the highest concentrations being present in the surface samples at most stations. The only exception was recorded at Station 2 which is located in the middle of the lagoon and, since the main source of organic carbon to water bodies comes from the decomposition of animal and vegetal matter (Bentivegna et al. 2004), the highest sources would probably be found close to the water margins. Fractionation of organic matter resulted in a predominance of humine with concentrations varying between 32.9 and 82.6 g.kg⁻¹ (Figure 3). Fulvic and humic acid concentrations varied from

between <D.L. to 7.13 and 7.09 g.kg⁻¹ respectively. Both humic and fulvic acid showed variations within the core, where concentrations gradually increased up to the surface, whereas, humine showed no significant variation. This higher vertical homogeneity of humine concentrations may be associated with the fact that it represents the most refractory fraction of humic compounds, whereas other humic compounds have lower concentrations in the deeper layers, due to their degradation.

Besides the high input of organic material from domestic sewage and vegetal matter, other characteristics of the sediments in this lagoon help the adsorption and accumulation of heavy metals. Particle size analysis showed a predominance of fine particulate material in this ecosystem and its large specific surface area plus the negative charges present on this fraction, make it a very effective sink for the retention of pollutants (Ellis and Revitt 1982, Xanthopoulos and Augustin 1992, Sansalone and Buchberger 1996, Milligan and Loring 1997, McAlister et al. 2003). Another important feature of this lagoon is the reducing capacity of its sediments and in this anoxic environment, anaerobic bacteria

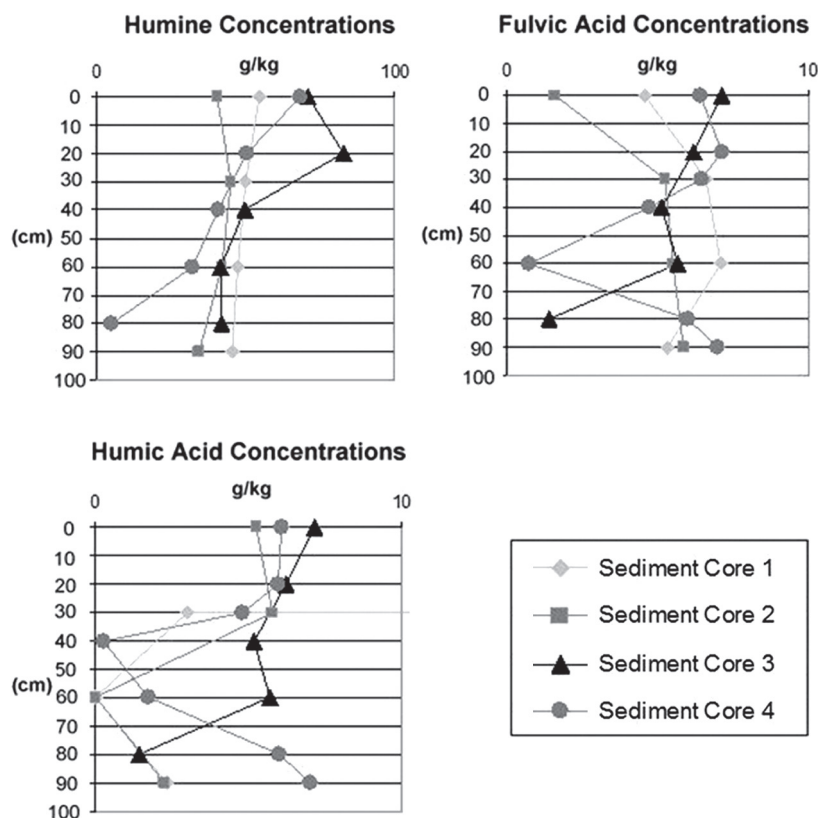


Figure 3 - Humic Acids concentrations variations through sapling core.

promotes a slow degradation of organic matter. Due to the negative charge on the surface of organic molecules, they tend to attract heavy metals and decrease their mobility. Therefore, a combination of low current speed, high organic matter concentration and fine sediments make this lagoon a favorable environment for the accumulation of contaminants, especially heavy metals.

Total Cu concentrations showed values between 25 mg.kg⁻¹ and 122.5 mg.kg⁻¹ (Figure 4) with the highest values occurring at Stations 3 and 4, and the lowest at Station 2. These results may be correlated with the source of the contaminant, which is mainly from urban discharge and traffic and the fact that Station 2 is located in the middle of the lagoon and Stations 3 and 4 are close to the margins. Total Cu shows a vertical variation where enrichment was observed towards the top of the core and this would suggest more recent pollution.

Total Pb showed a minimum value of 10.5 mg.kg⁻¹ at Station 2, and a maximum of 201.4 mg.kg⁻¹ at Station 1. Although the same pattern of enrichment with a decrease of depth was observed, Station 1 was the most contaminated and again Station 2 showed the least with respect to this metal.

Total Zn showed a similar pattern with a minimum concentration of 60.5 mg.kg⁻¹ recorded at Station 2, whereas the highest concentration of 453 mg.kg⁻¹ occurred at Station 4 and enrichment occurred towards the top of the cores. Significant correlations between Cu, Pb and Zn (p=0.0001) would suggest a common source for these elements entering the Rodrigo de Freitas Lagoon.

Total Cr showed concentrations between 18.5 and 89 mg.kg⁻¹, however, no enrichment occurred towards the surface of the core, and Station 1 was the least contaminated. The same pattern was observed for total Ni, with concentrations between 37.5 and

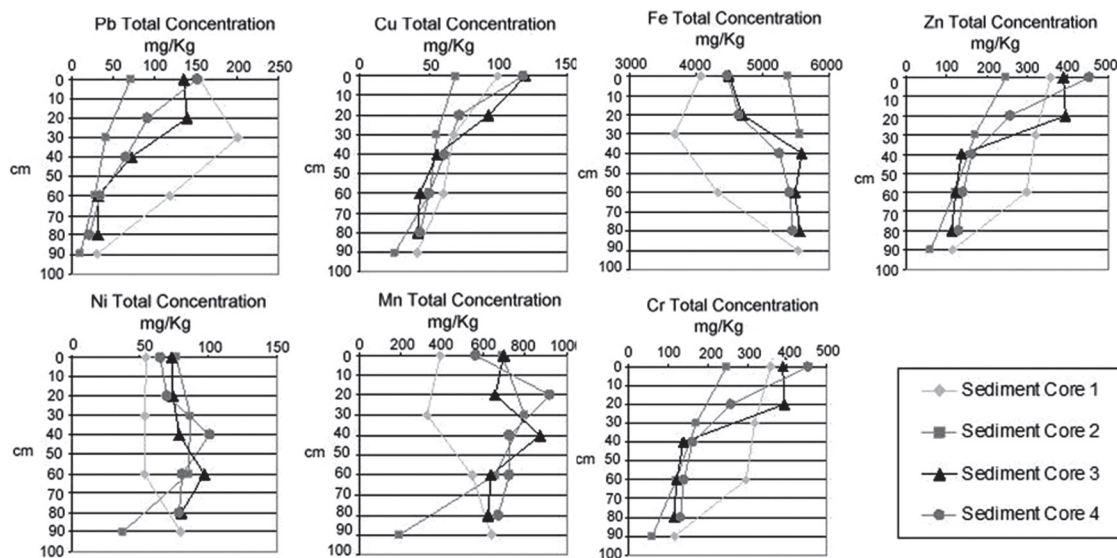


Figure 4 - Heavy metal total concentrations through sampling core.

100.5 mg.kg⁻¹ and vertical variation was random. Again Station 1 showed the least contamination. This pattern for Cr and Ni may be associated with their sources and according to statistical analysis a significant correlation ($p=0.001$) may suggest that these metals are from the same source.

ELEMENT PARTITIONING

Water-soluble phase

Metal concentrations in this phase are important regarding their bioavailability and toxicity to benthic organisms. Bioavailability and toxicity of free hydrated ions is higher than those complexed by other “ligands” (Luoma 1983, Dzombak et al. 1986, Lovgren and Sjoberg 1989). This would appear to be the situation of Rodrigo de Freitas Lagoon as results showed that the metals bound by the water-soluble phase have no significant concentrations (Figure 5).

Exchangeable/Carbonate phase

Selective extraction results (Figure 5) showed the carbonate phase to adsorb a higher percentage of Pb and Zn compared to the other metals analysed and a similar pattern was also found for sediments

from different origins (Chartier et al. 2001). In Station 2 this phase was not detected. The lowest concentrations of Cu and consequently the lower availability of this metal for trapping agents, together with its higher affinity for other matrices may explain this result, since Cu concentrations in this point were similar to the others. The exchangeable/carbonate phase was the most representative in the surface layers, reaching more than 50% of total concentration for Zn, suggesting a higher affinity with the exchangeable/carbonate phase.

Reducing Phase

Results from this study correspond with other data in the literature, showing the high affinity of amorphous Fe and Mn oxides for heavy metals, especially Cu and Pb (Kiekens 1983), whereas, crystalline Fe and Mn oxide have a high affinity for Cr and Ni (Figure 5). Despite the fact that it is an extremely reducing environment, Cu was detected in the reducing phase indicating its stability when complexed by these mineral oxides. Another explanation for the coexistence between the reducing and oxidant phases may be the interaction of oxides with hydroxides and organic matter,

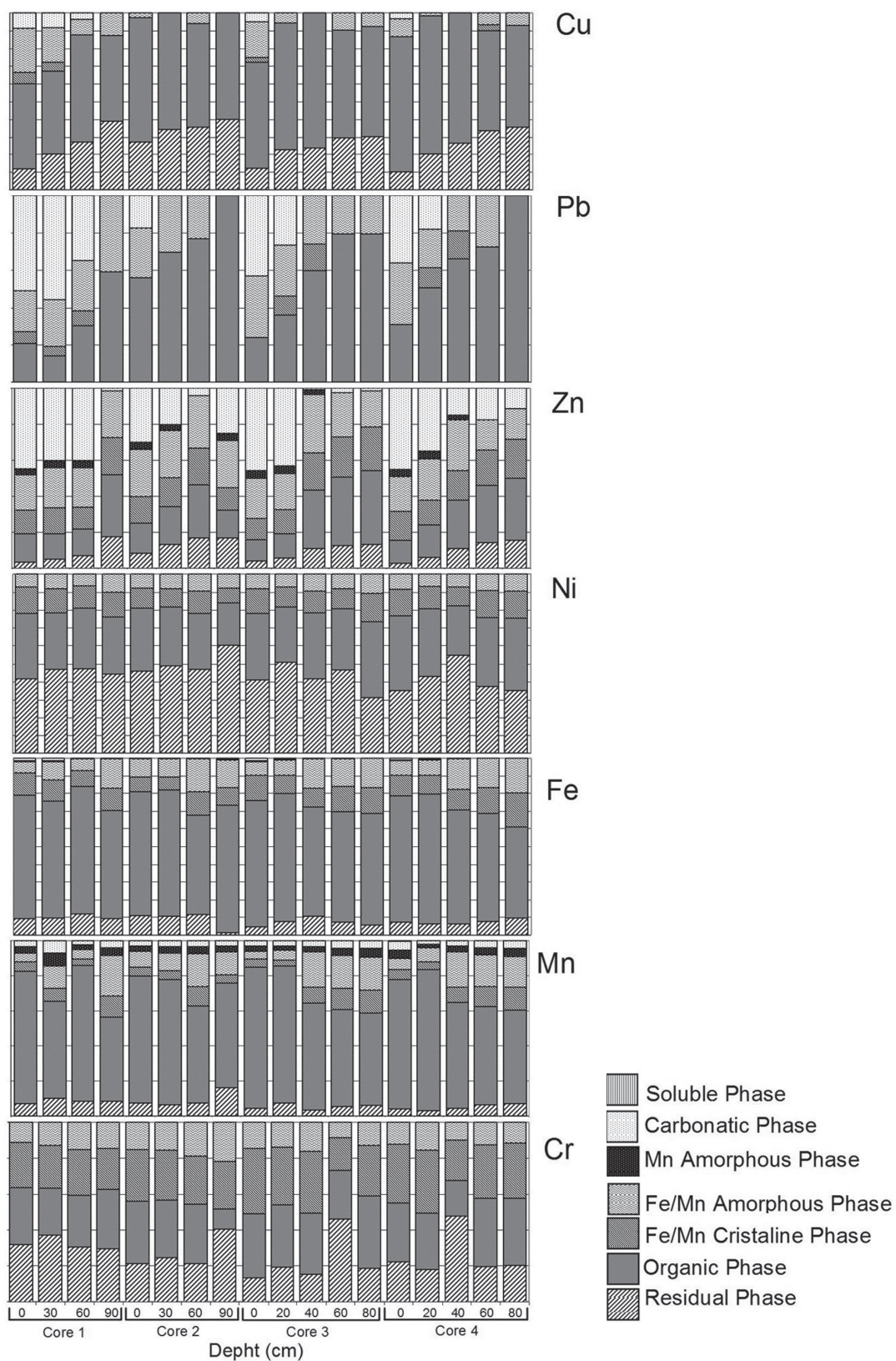


Figure 5 - Heavy metal fractionation through sampling core.

when the surface of the mineral is covered by a film of Fe and Al hydroxides (Warren and Haak 2001). Results also show that even in an anoxic environment, Zn is also significantly bound by Fe and Mn oxy-hydroxides and this phase is also a very important binding matrix in the superficial layers of the cores. However, as the depth of sample down the cores increases, the organic phase becomes more important with respect to complexing metals.

Organic Fraction

This fraction is shown to be an important binding matrix for Cu, Fe and Mn and this trend, especially for Cu which forms a stable organic complex (Stumm and Morgan 1996). Costa (2001) has been recorded in a series of studies (Pardo et al. 1990, Lopez-Sanchez et al. 1996, Chartier et al. 2001, Galan et al. 2003). Spearman analysis showed a significant correlation between Cu bound by the organic phase, humine ($p=0.0009$) and humic acid ($p=0.03$) and these results are similar to those recorded by Costa (op cit.). Up to 100% of the total Pb is bound by this phase at depth down the cores showing the influence of anoxic conditions on the degradation of oxides and the ability of organic matter to complex Pb in this type of environment. This affinity of the organic phase for Pb is verified by Spearman statistics, where significant correlations with humine ($p=0.016$) and humic acids ($p=0.00675$) were recorded.

The affinity of organic matter for some metals, especially Cu and Pb, and to a lesser extent Ni, in anoxic environments has also been shown (Hansen et al. 1990, Warren and Zimmerman 1994, Logan et al. 1997, Lin and Wang 1998, Tipping et al. 1998, Gao et al. 1999, Taka'cs et al. 1999). Ni concentrations of anthropic origin alternated between oxidant and reducing phases. Alloway (1993) suggests that, under anaerobic conditions, this metal tends to form insoluble sulfides. However, statistical analysis showed no significant correlation.

Some authors consider the organic matrix to be an important "ligand", and state that the interaction

of this matrix with heavy metals may influence the nature of both (Taka'cs et al. 1999). According to Warren and Haak (2001), the bond established between functional organic groups and metals in anoxic environments are stronger than those established with Fe and Mn oxi-hidroxi-des, making this combination chemically more reactive.

Residual Phase

The residual phase binds metals to crystalline structures, making them unavailable to affect biota (Tessier et al. 1979). In non-contaminated sediments, metal concentrations in this phase are used to describe the background of an area, when studying anthropogenic metal enrichment (Sutherland et al. 2000). In this study, enrichment of all the metals analyzed was observed. With an increase in depth down the cores, Cu and Zn are similar to their natural values, resulting in an increase of their concentrations in the lithogenic phase. This enrichment pattern was not observed for Cr and Ni, where almost 50% of the total concentration of Ni was bound by the residual phase. Morillo et al. (2004) also recorded high concentrations of these metals in this phase, suggesting stronger bonds of these elements with the sediments.

Lead concentrations were mainly below their detection limit in this phase, suggesting a low affinity of the siliceous matrix for this metal in all the samples.

CONCLUSION

Urbanization of coastal lagoon areas in the Brazilian Rio de Janeiro metropolis has caused serious impacts on the ecosystems of these areas in many ways. One of the main problems is the contamination of water bodies by pollutants that have originated from several sources. The Rodrigo de Freitas lagoon fits this context, representing a completely urbanized and intensely polluted coastal area. Both physical and chemical analysis results show Rodrigo de Freitas lagoon to have

an extremely reducing environment. Particle size distribution plus high organic matter content strongly influence the degree of heavy metal contamination. The binding patterns observed for Cu, Pb and Zn, reflect a common origin for these metals, whereas, those for Cr and Ni would indicate a different source. The small percentage of the total metals bound by the more soluble phases would suggest the high binding capacity of the organic and inorganic matrices in this lagoon for trace elements, making the sediments in this Lagoon an efficient sink for heavy metals.

The affinity of the exchangeable/carbonate phase for Pb, Cu and Zn makes these metals potentially available under a more acidic environment that may occur due to changes in pH as a result of, for example, channel dredging.

Results would indicate that the nature of the "ligand" matrices and their interactions with metals are more important than the physical-chemical parameters. Despite a extremely reducing environment, the Fe/Mn oxy-hydroxide phases were very significant, especially in the case of Zn in which they bound higher concentrations of this total metal than the organic phase in the superficial layers. However, in the deeper layers, the organic and reducing phases predominate in the speciation of the metals analyzed.

The most refractory phase of organic matter, humine, predominated with its concentration increased with depth. A correlation was observed with most of the metals studied. More detailed studies are necessary to identify the importance of metal sources and other pollutants to this ecosystem, as well as the bioavailability of heavy metals and their effects on biota.

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RESUMO

Um dos principais resultados dos processos relativos da urbanização é a contaminação de corpos d'água adjacentes. Inserida neste contexto, a Lagoa Rodrigo de Freitas está situada na zona sul da cidade do Rio de Janeiro. Este ecossistema recebe uma série de descargas contendo todos os tipos de poluentes incluindo metais pesados. O presente trabalho estudou o fracionamento dos metais pesados nos sedimentos da Lagoa Rodrigo de Freitas assim como identificou a influência da matéria orgânica na dinâmica de partição. Os resultados das análises indicaram a matéria orgânica como um importante agente ligante. Características peculiares como sedimentos redutores, altas concentrações de metais pesados e granulometria fina transformaram este ecossistema em um depósito efetivo de metais pesados, onde os mesmos não se apresentam em frações facilmente remobilizáveis.

Palavras-chave: Brasil, Rio de Janeiro, Laguna Rodrigo de Freitas, metais pesados, ácidos húmicos.

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