DA FONSECA, ESTEFAN M.; BAPTISTA NETO, JOSÉ A.; MCALISTER, JOHN; SMITH, BERNARD;
FERNANDEZ, MARCOS A.; BALIEIRO, FABIANO C.

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

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

ESTEFAN M. DA FONSECA[1], JOSÉ A. BAPTISTA NETO[1], JOHN MCALISTER[2],
BERNARD SMITH[2], MARCOS A. FERNANDEZ[3] and FABIANO C. BALIEIRO[4]

[1]Departamento de Geologia/LAGEMAR, Universidade Federal Fluminense,
Av. Litorânea, s/n, Gragoatá, 24210-340 Niterói, RJ, Brasil
[2]School of Geography, Queen's University Belfast, BT7 1NN, Belfast, Northern Ireland, United Kingdom
[3]Departamento de Oceanografia, Universidade do Estado do Rio de Janeiro,
Rua São Francisco Xavier, 524, Maracanã, 20550-013 Rio de Janeiro, RJ, Brasil
[4]Embrapa Solos, Rua Jardim Botânico, 1024, Jardim Botânico, 22460-000 Rio de Janeiro, RJ, Brasil

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

---

Correspondence to: Estefan Monteiro da Fonseca
E-mail: oceano25@hotmail.com

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°57'02' S; 043°11'09' W - Figure 1) has a perimeter of 7.5 km. Over the past twenty years this lagoon has reduced in area by 1.4km^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.
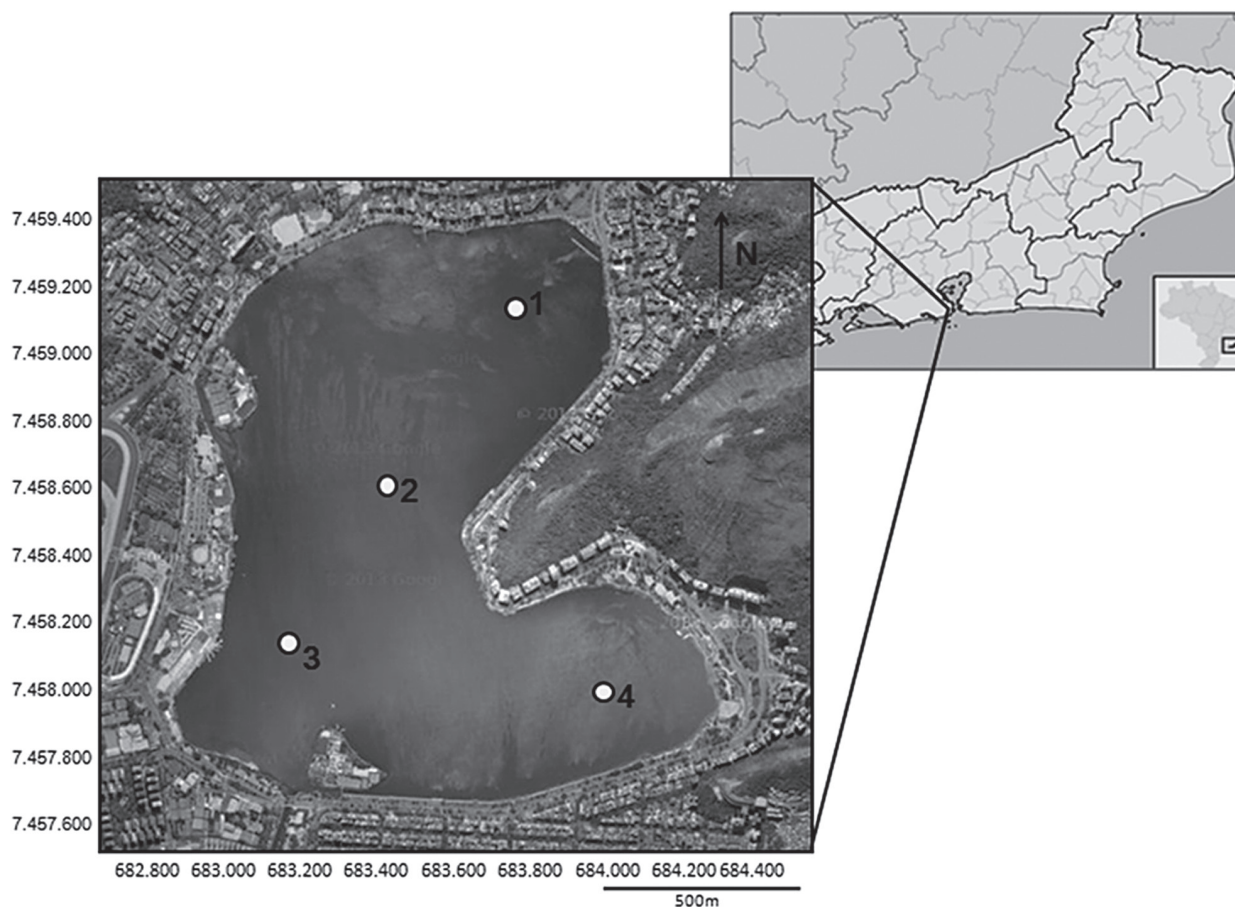

Figure 1 - Map of the studied area with the location of the sampling stations.

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 < 63μm 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 $NH_4.OAc$ (pH 5)	1:50	6 hrs	Shaking
Amorphous Fe/Mn 0.25M $NH_2.OH.HCl$/ 0.25M HCl	1:50	2hr	600°C
Crystalline Fe/Mn 1M $NH_2.OH.HCl$/25% CH_3COOH	1:50	3hr	90°C
Organic HNO_3/HCl (3:1)	1:50	1hr	90°C
Residual/ Siliceous HNO_3/HF/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
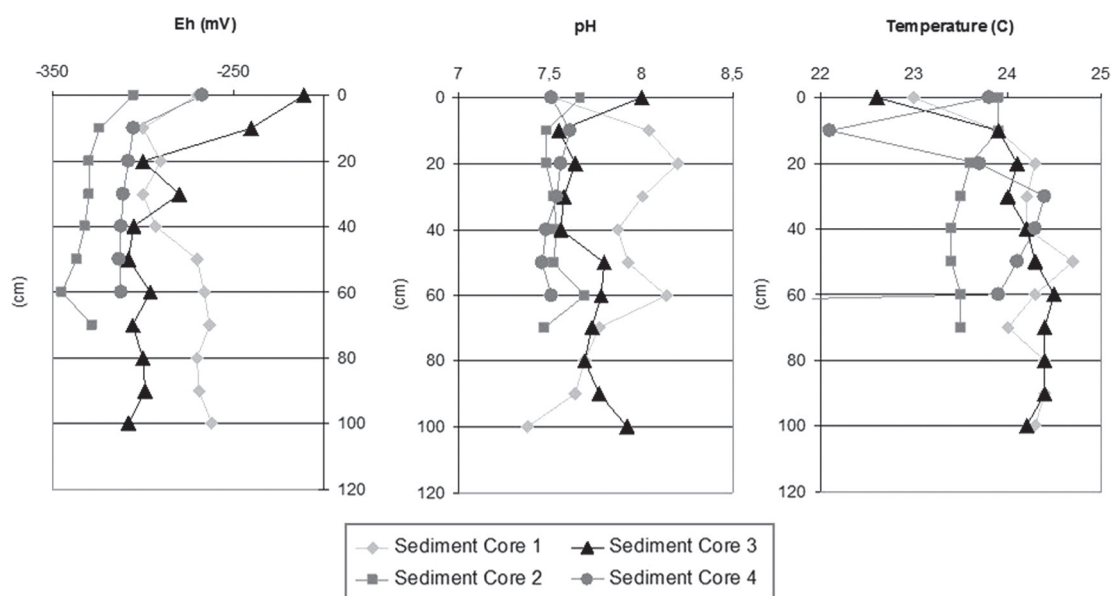
Figure 2 - Physico - Chemical parameters variation through sampling core.

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
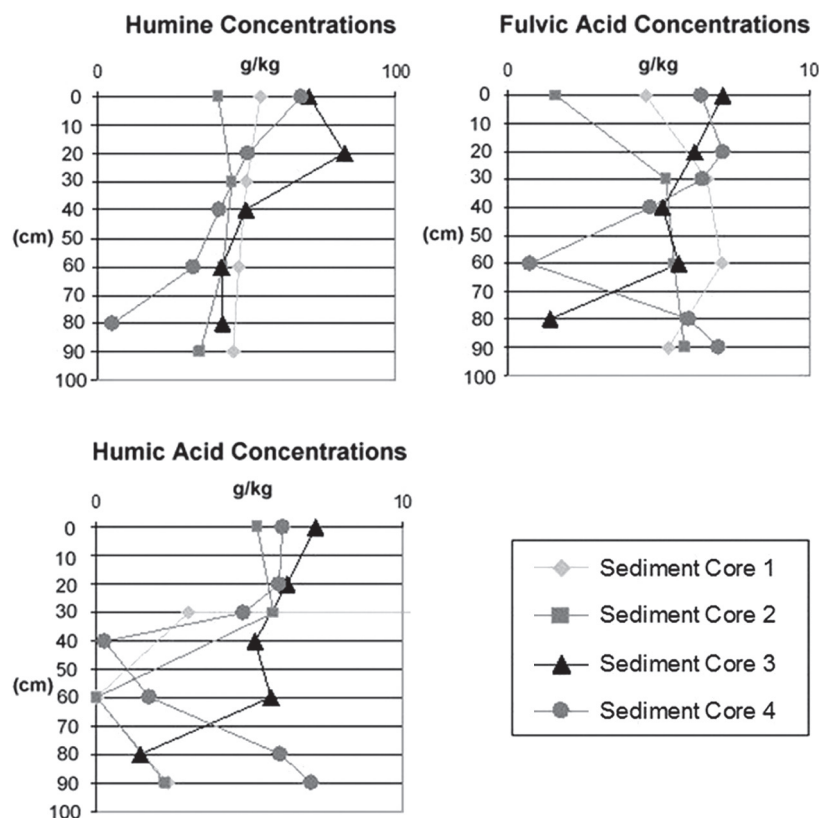
Humine Concentrations

Fulvic Acid Concentrations

Humic Acid Concentrations

Sediment Core 1
Sediment Core 2
Sediment Core 3
Sediment Core 4

Figure 3 - Humic Acids concentrations variations though 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
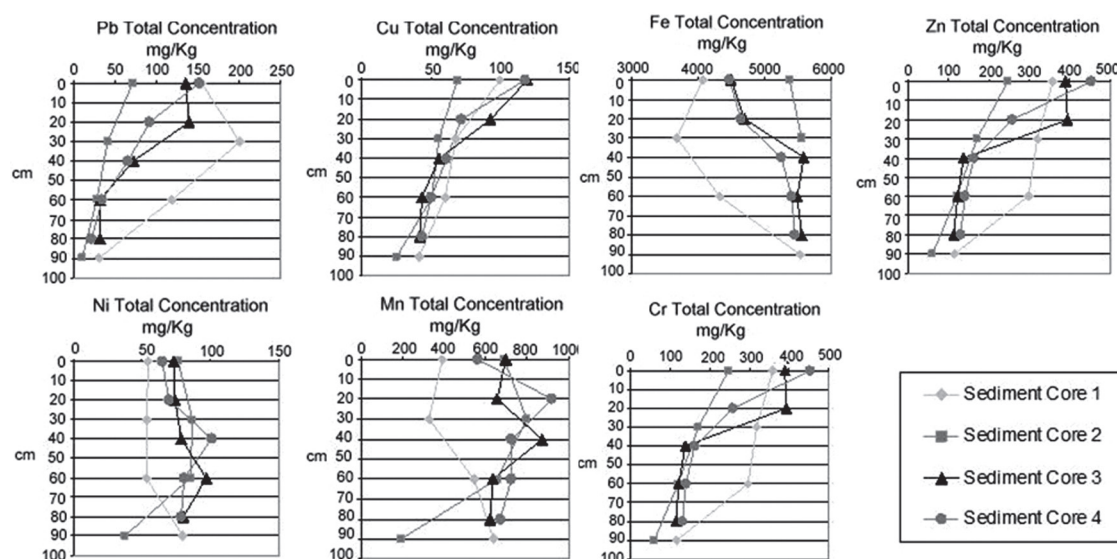
Figure 4 - Heavy metal total concentrations through sampling core.

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,
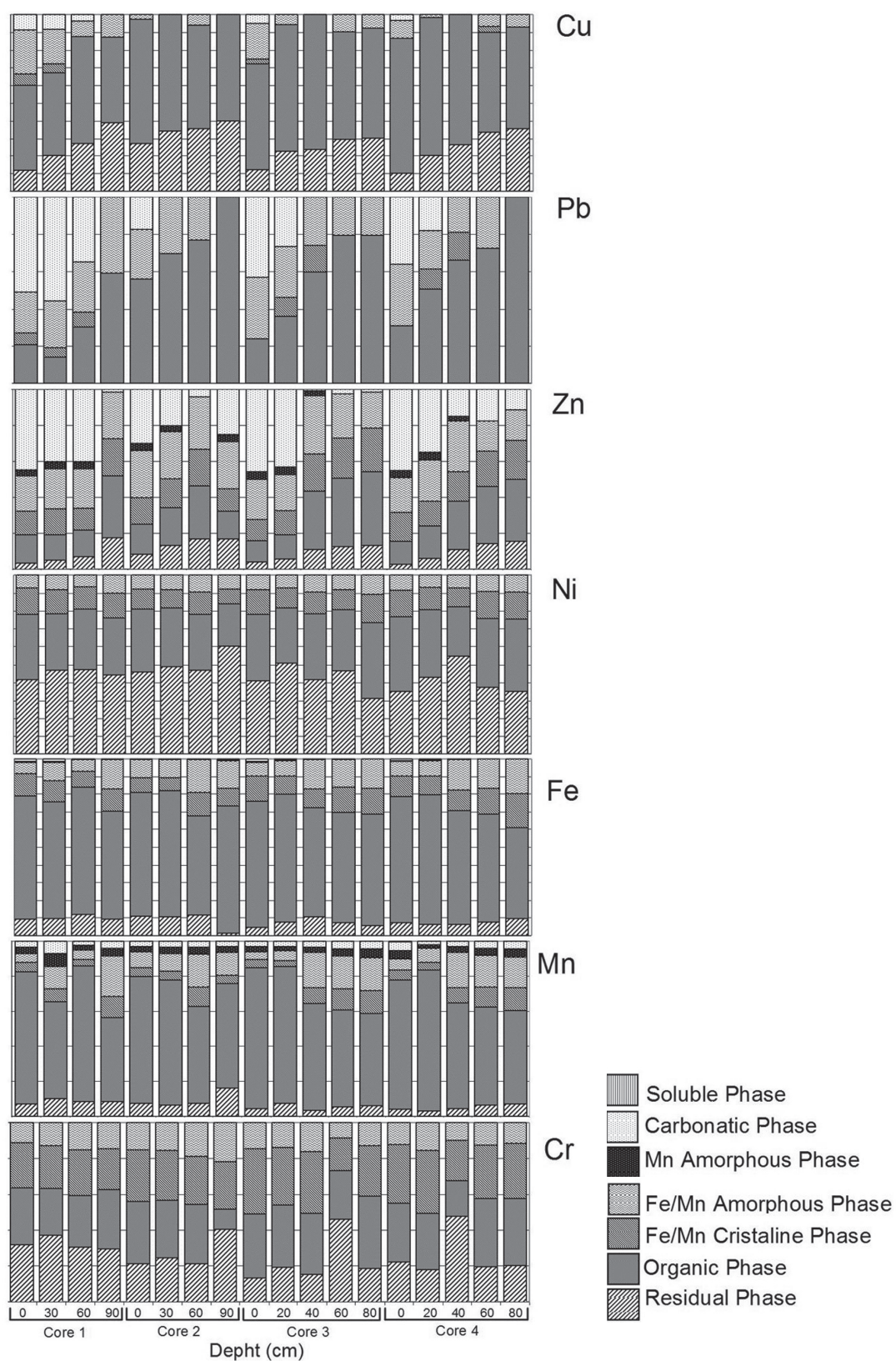
Figure 5 - Heavy metal fraccionament through sampling core.

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-hidroxides, 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 import 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.

ACKNOWLEDGMENTS

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.

REFERENCES

ALLARD B, HAKANSSON K AND KARLSSON S. 1987. The importance of sorption phenomena in relation to trace element speciation and mobility. In: Landner L (Ed), Speciation of Metals in Water, Sediment and Soil Systems. Lecture Notes in Earth Sciences Nº. 11. Springer, Berlin, p. 99-112.

ALLOWAY BJ. 1993. Heavy metals in soils. New York: Black Academic.

ANDERSSON S AND NILSSON SI. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. Oil Bio and Biochem 33: 1181-1191.

ANDREATA JV, MARCA AG, SOARES CL AND SILVA SANTOS R. 1997. Distribuição mensal dos peixes mais representativos da Lagoa Rodrigo de Freitas, Rio de Janeiro, Brasil. Ver Bras Zool 14: 121-134.

BENITES VM, MADARI B AND MACHADO PLOA. 2003. Extração e fracionamento quantitativo de substancias húmicas do solo: um procedimento simplificado de baixo custo. Comunicado técnico. EMBRAPA Solos. Rio de Janeiro.

BENTIVEGNA CS, ALFANO JE, BUGEL SM AND CZECHOWICZ K. 2004. Influence of Sediment Characteristics on Heavy Metal Toxicity in a Urban Mash. Urban Habitats 2: 1541-7115.

BERNER RA. 1981. A new geochemical classification of sedimentary environments. J Sedim Petrol 51: 359-369.

BROWN 1988. Structure and dynamics of basin forested wetlands in North America,In press. In: Lugo AE et al. (Eds), Forested wetlands. Elsevier.

BRYAN GW AND LANGSTON WJ. 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: A review. Environ Pollut 31: 89-131.

BURDON J. 2001. Are the traditional concepts of the structures of humic substances realistic? Soil Sci 166: 752-769.

BURTON ED, PHILLIPS IR AND HAWKER DW. 2004. Trace metals and nutrients in bottom sediments of the Southport Broadwater, Australia. Mar Pollut Bull 48: 378-402.

CAMPBELL JH AND EVANS RD. 1987. Inorganic and organic ligand binding of lead and cadmium and resultant implications for bioavailability. Sci Total Environ 62: 219-227.

CHAPMAN PM. 1990. The sediment quality triad approach to determining pollution-induced degradation. Sci Total Environ 97: 815-825.

CHARTIER M, MERCIER M AND BLAIS J. 2001. Partitioning of trace metals before and after biological removal of metals from sediments. Wat Res 35: 1435-1444.

COBELO-GARCIA A AND PREGO R. 2004. Chemical Speciation of Dissolved Copper, Lead and Zinc in a Ria Coastal System: the Role of Resuspended Sediments. Anal Chim Acta 524: 23-26.

COLEMAN DC, OADES JM AND UEHARA G. 1989. Dynamics of soil organic matter in tropical ecosystems. Honolulu: NifTAL Project, University of Hawaii at Manoa, USA, p. 173-200.

COSTA ACS. 2001. Determinação de cobre, alumínio e ferro em solos derivados do basalto através de extrações sequenciais. Maringa.

DABIN B. 1976. Methode d'extraction et de fractionnement des matieres organiques dans les sols tropicaux. Chah Orston Ser Pedol 4: 287-297.

DAVIES CA, TOMLINSON K AND STEPHENSON T. 1991. Heavy metals in River tees estuary sediments. Environ Technol 12: 961-972.

DE SOUZA MJ, NAIR BD AND CHANDRAMOHAN D. 2000. Phosphate solubilizing bacteria around Indian peninsula. Indian J Mar Sci 29: 48-51.

DZOMBAK DA, FISH W AND MOREL FMM. 1986. Metal-humate interactions: 1. Discrete ligand and continuous distribution models. Environ Sci Technol 20: 669-675.

EISMA D. 1986. Flocculation and de-flocculation of suspended matter in estuaries. Netherlands J Sea Res 20: 183-199.

ELLIS JB AND REVITT DM. 1982. Incidence of heavy metals in street surface sediments: Solubility and grain size studies. Wat Air Soil Pol 17: 87-100.

FORSTNER U AND WITTMANN GTW. 1983. Metal Pollution in Aquatic Environment. New York: Springer-Verlag.

GALAN E, GOMEZ-ARIZA JL, GONZALEZ I, FERNADEZ-CALIANI JC, MORALES E AND GRIALDEZ I. 2003. Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. Appl Geochem 18: 409-421.

GAO K, PEARCE J, JONES J AND TAYLOR C. 1999. Interaction between peat, humic acid and aqueous metal ions. Environ Geochem Health 21: 13-26.

GLUD RN AND MIDDELBOE M. 2004. Virus and bacteria dynamics of a coastal sediment: Implication for benthic carbon cycling. Limnol Oceanogr 49: 2073-2081.

GSELL TC, HOLBEN WE AND VENTULLO RM. 1997. Characterization of the sediment bacterial community in groundwater discharge zones of an alkaline fen: A seasonal study. Appl Environ Microbiol 63: 3111-3118.

GUO T, DELAUNE RD AND PATRICK WH. 1997. The influence of sediment redox chemistry on the chemically active forms of arsenic, cadmium, chromium and zinc in estuarine sediment. Environ Intl 23: 305-316.

HANSEN AM, LECKIE JO, MANDELLI EF AND ALTMANN RS. 1990. Study of copper association with dissolved organic matter in surface waters of three Mexican coastal lagoons. Environ Sci Technol 24: 683-688.

HANSON PJ, EVANS DW, COLBY DR AND ZDANOWICZ VS. 1983. Assessment of elemental contamination in estuarine and coastal environments based on geochemical and statistical modeling of sediments. Marine Environ Res 36: 237-266.

HILL PS. 1998. Controls on floc size in the coastal ocean. Oceanography 11: 13-18.

KIEKENS L. 1983. Behavior of heavy metals in soils. In: Berglund S, Davis RD and L'Hermite P (Eds), Utilization of sewage sludge on land: rates of application and long-term effects of metals. Dordrecht: D. Reidel Publishing.

KONONOVA MM. 1966. Soil organic matter. New York: Pergamon Press, 555 p.

LIN JG AND WANG KC. 1998. Characteristics of heavy metal adsorption of river bed sludge components. Toxicol Environ Chem 65: 41-56.

LOGAN EM, PULFORD IB, COOK T AND MACKENZIE AB. 1997. Complexation of Cu and Pb by peat and humic acid. Eur J Soil Sci 48: 685-696.

LOPEZ-SANCHEZ JF, RUBIO R, SAMITIER C AND RAURET G. 1996. Trace metal partitioning in marine sediments and sludges deposited off the coast of Barcelona (Spain). Water Res 30: 153-159.

LOVGREN L AND SJOBERG S. 1989. Equilibrium approaches to natural water systems: Complexation reactions of copper, cadmium. and mercury with dissolved organic surface coatings. Environ Sci Technol 16: 660-666.

LUOMA SN. 1983. Bioavailability of trace metals to aquatic organisms - a review. Sci Tot Environ 28: 1-23.

MCALISTER JJ, SMITH BJ, BAPTISTA NETO JA AND SIMPSON JK. 2005. Geochemical distribution and bioavailability of heavy metals and oxalate in street sediments from Rio de Janeiro, Brazil: a preliminary investigation. Environ Geoch Heal 27: 429-441.

MCALISTER JJ, SMITH BJ AND CURRAN JA. 2003. The use of sequential extraction to examine iron and trace metal mobilisation and the case hardening of building sandstone: a preliminary investigation. Microchem J 74: 5-18.

MCALISTER JJ, SMITH BJ AND TOROK A. 2008. Transition metals and water-soluble ions in deposits on a building and their potential catalysis of stone decay. Atm Environ 42: 7657-7668

MEYER J. 2002. The utility of the terms "bioavailability" and "bioavailable fraction" for metals. Mar Environ Res 53: 417-423.

MILLIGAN TG AND LORING DH. 1997. The effect of flocculation on the size distributions of bottom sediments in coastal inlets: Implications for contaminant transport. Wat Air Soil Poll 99: 33-42.

MORILLO J, USERO J AND GRACIA I. 2004. Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosph 76: 431-442.

NAIDU R, BOLAN NS AND ADRIANO DC. 2003. Bioavailability, toxicity and risk relationships in ecosystems: the path ahead. In: Bioavailability and its Potential Role in Risk Assessment. Science Publishers, New York, p. 331-339.

NGIAM L AND LIM P. 2001. Speciation patterns of heavy metals in tropical estuarine anoxic and oxidized sediments by different sequential extraction schemes. Sci Tot Environ 275(1-3): 53-61.

NIREL PM AND MOREL FMM. 1990. Pitfalls of sequential extraction. Wat Res 24: 1055-1056.

PARDO R, BARRADO E, PEREZ L AND VEJA M. 1990. Determination and speciation of heavy metals in sediments of the Pisuerga River. Wat Res 24: 373-379.

QUEVAUVILLER P, RAURET G, MUNTAU H, URE AM, RUBIO R, LOPEZ-SANCHEZ JF, FIEDLER HD AND GRIEPINK B. 1994. Evaluation of a sequential extraction procedure for the determination of extractable trace metals contents in sediments. Fres J Anal Chem 349: 808-814.

RAURET G, RUBIO R AND LOPEZ-SANCHEZ JF. 1989. Optimization of Tessier procedure for metal solid speciation in river sediments. Int J Environ Anal Chem 36: 69-83.

SAEKI K, OKAZAKI M AND MATSUMOTO S. 1993. The chemical phase changes in heavy metals with drying and oxidation of the lake sediments. Wat Res 27: 1243-1251.

SANSALONE J AND BUCHBERGER S. 1996. Characterization of metals and solids in urban highway snow and rainfall-runoff. Transp Res Rec 1523: 147-159.

SEMADS. 2001. Ambiente das Águas no Estado do Rio de Janeiro, p. 230. In: Weber W (Ed), Cooperação Técnica Brasil-Alemanha, Projeto PLANAGUA-SEMADS/GTZ.

SINGH AK, HASNAIN SI AND BANERJEE DK. 2004. Grain size and geochemical partitioning of heavy metals in sediments of the Damodar River - a tributary of the lower Ganga, India. Environ Geol 39(1): 90-98.

SPOSITO G. 1989. The chemistry of soils. Oxford Univ. Press, New York.

STUMM M AND MORGAN JJ. 1996. Aquatic chemistry. 3rd ed., John Wiley & Sons, New York.

SUTHERLAND RA, TACK FMG, TOLOSA CA AND VERLOO MG. 2000. Operational defined metal fractions in road deposited sediment. Honolulu, Hawaii. J Environ Qual 29: 1431-1439.

TAKÁCS M, ALBERTS JJ AND EGEBERG PK. 1999. Characterization of natural organic matter from eight Norwegian surface waters: proton and copper binding. Environ Int 25: 315-323.

TESSIER A, CAMPBELL PGC AND BISSON M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51: 844-850.

TESSIER A, CARIGNAN R, DUBREUIL B AND RAPIN F. 1989. Partitioning of zinc between the water column and the oxic sediments in lakes. Geochim Cosmochim Acta 53: 1511-1522.

TIPPING E, LOFTS S AND LAWLOR AJ. 1998. Modelling the chemical speciation of trace metals in the surface waters of the Humber System. Sci Tot Environ 211: 63-77.

TORRES JM. 1990. Laguna Rodrigo de Freitas. Revista Municipal de Engenharia. Prefeitura da Cidade do Rio de Janeiro. Rio de Janeiro 1: 31-63.

URE AM, QUEVAUVILLER PH, MUNTAU H AND GRIEPINK B. 1993. Speciation of heavy metals in solids and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. Intern J Environ Anal Chem 51: 135-151.

WALKLEY A AND BLACK IA. 1934. An examination of the Degtjareff method of determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci 37: 29-37.

WANG H, WANG CX, WANG ZJ AND CAO ZH. 2004. Fractionation of heavy metals in surface sediments of Taihu Lake, East China. Environ Geochem Health 26: 303-309.

WARREN LA AND HAACK EA. 2001. Biogeochemical controls on metal behaviour in freshwater environments. Earth-Science Rev 54: 261-320.

WARREN LA AND ZIMMERMAN AP. 1994. The influence of temperature and NaCl on cadmium, copper and zinc partitioning among suspended particulate and dissolved phases in an urban river. Water Res 28: 1921-1931.

XANTHOPOULOS C AND AUGUSTIN A. 1992. Input and characterization of sediments in urban sewer systems. Wat Sci Tech 25: 21-28.