Geochemical behavior of heavy metals in differents environments in Rodrigo de Freitas lagoon – RJ/Brazil

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ABSTRACT

The accelerated urbanisation without a planning, brought several environmental problems to Rio de Janeiro coastal zone, especially in areas such as Rodrigo de Freitas lagoon, which receives a great amount of untreated sewage every day. To assess the nature, potentially sources and extent of heavy metal pollution in the lagoon, sediments from the surrounding streets, from the entrance of the main canal that drains to the lagoon and from the bottom of the lagoon were collected and analysed by a modified selective extraction procedure in order to study the geochemical partitioning and bioavailability of Zn, Cu, Cr, Ni and Pb in these three compartments. The present study verified an increase in the Cu, Pb and Zn concentrations in the north of the Rodrigo de Freitas lagoon. Despite the different levels of oxidation between the sediments accumulated in the streets and in the bottom of the lagoon, the geochemical partitioning of the heavy metals did not show any pattern of variation for the metals, except for the element Cu. No concentrations were found in the soluble phase of samples collected in the surfacial sediments of the lagoon, suggesting no bioavailability of heavy metals.

Key words: heavy metals, Rodrigo de Freitas lagoon, sediments.

INTRODUCTION

Originated primarily in the continental crust, soil, sediments and urban dust constitute effective deposits of pollutants. The urban runoff sediments can be considered as a bigger influence factor on the human health in urban centers (Yongming et al. 2006). Although the great number of references regarding to the contamination of the urban sediments and dust, very little information on this subject is available referring to the developing countries (Banerjee 2003).

According to McAlister et al. (2005), urban runoff sediments accumulations throughout paved streets in urbanised areas represents important deposits of urban contaminated sediment, especially for heavy metals (Förstner and Wittmann 1983, McAlister et al. 2005), being able to reflect beyond the geologic conditions and the local environment quality.

In terms of toxicity and risk for the public health, heavy metals are frequently cited in studies dealing with deposited sediments in avenues of automotive transport (Olivero and Solano 1998). Heavy metals such as copper, lead and zinc are of particular interest in the studies

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on urban discharges due to their toxic character for the aquatic organisms and persistence in the environment (Hoffman et al. 1984, Borchardt and Sperling 1997, Walker et al. 1999, Brown and Peake 2006).

The main sources of contaminants for the streets also include the atmospheric dust, the degradation of automobiles parts and the fossils fuel burning (Sansalone and Glenn 2002, Pereira et al. 2007). Emissions of the motorized vehicles, drippings of the oil of the crankcase, degradation of the tires of vehicles and surfaces of roads are all diffuse sources of chemical contaminants in urban environments (Brown and Peake 2006). During the rainy periods, these contaminants are washed off the roofs, the traffic roads and other surfaces and, thus, can be carried by the collecting pluvial water canals for the adjacent water bodies. Mungur et al. 1995, and Shinya et al. 2000, suggest that the road runoff can contribute with up to 50% of solids in suspension, 16% of the total of hydrocarbons, and 35 to 75% of the total heavy metals received by the coastal water bodies.

The study of the contaminants in sediments involving concentration informations and species allow the tracking of potential sources (Walker et al. 1999, Gonzalez et al. 2000, McCready et al. 2000, Soclo et al. 2000).

Traditionally, the presence of heavy metals in the particulate matter is characterized in terms of total concentrations, although the environment significance depends, among others factors, on its specific partition and its particular affinities with the matrices present in the environment (Manno et al. 2006). The same authors suggested the necessity to understand the way in which the elements react to the main physicochemical variations in the environment, in order to determine their geochemical dynamic.

Considering the peculiar characteristic of drastic changes in the water physicochemical parameters, and because of the fine sediments accumulations that result from the low current energy and the great amount of load pollutants, mainly organic matter, and the aggressions of the urbanization processes, coastal environments have become, throughout history, extremly vulnerable (Benoit et al. 1999).

According to Benoit et al. (1999), estuarine ecosystems such as coastal lagoons are particularly environmentally complex due to their localization in the transitional zone, between the continent and the ocean, and their, main characteristic of semi-unclosed environments. Estuarine environments are characterized by high spatial fluctuations in the physicochemical parameters and by being constantly a target of anthropogenic impact, including the discharge of domestic and industrial sewage, which can modify their morphology and affect the quality of their water body. In this context, Rodrigo de Freitas coastal lagoon is located in a high urbanized area in the Rio de Janeiro city. Surrounded by several roads with a very intense daily automobiles traffic, this lagoon is influenced by several inputs of pollutants, including a high variety of heavy metals (D.D. Loureiro, unpublished data).

The aim of this work is to evaluate the levels of pollution in the Rodrigo de Freitas lagoon, and also to access the mains sources of its pollutants, throughout the analysis of the total concentrations and the partition of the heavy metals in order to understand the geochemical dynamics of heavy metals in several compartments of this ecosystem.

STUDY SITE

The Rodrigo de Freitas lagoon is located in the south region of Rio de Janeiro (22°57′02″S; 043°11′09″W) (Fig. 1). Its surface has an irregular polygon form, with an area of 2.5 km^2, a perimeter with about 7.5 km, and its bigger length reaches 3 km long (Barroso 1989). Its highest depths reach 11 m (Andreata et al. 1997). This lagoon is connected to the sea by a canal of the Jardim de Alah that separates the quarters of Ipanema and Leblon. The canal has a length of 835 m, and it is frequently blocked by sand deposits. The dynamics of the renewal of the lagoon waters is very complex. The draining basin is composed of the Macacos River, which is the main input of fresh water, and the Cabeça and Rainha Rivers (Andreata et al. 1997).

The lagoon is surrounded by a highly urbanised area, which is responsible for a huge input of pollutants loads, not only from its main tributaries rivers, but also from the pluvial water galleries. Previous works allowed to identify in this lagoon, places where the total metal concentrations had exceeded the background levels (D.D. Loureiro, unpublished data).
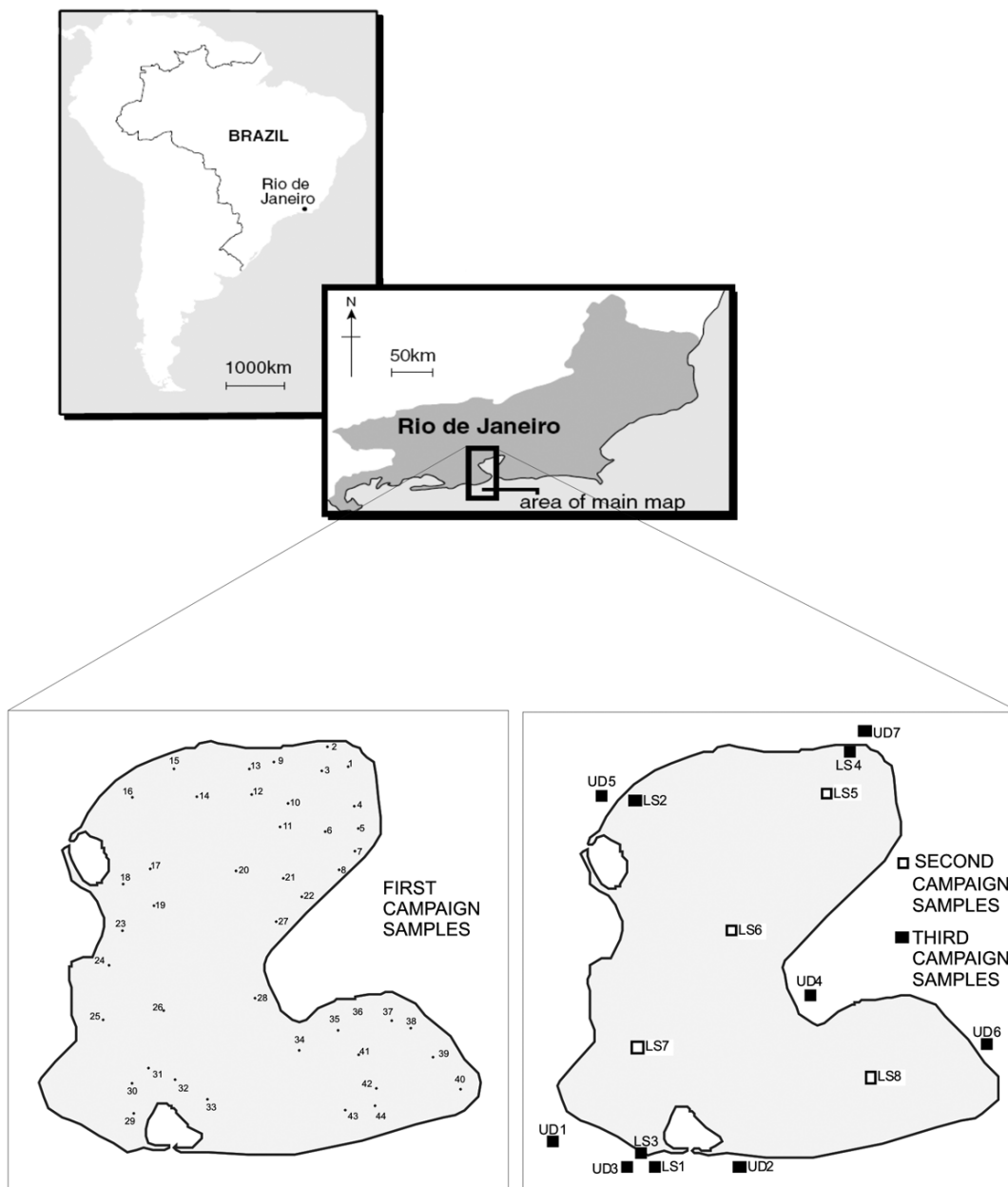
Fig. 1 – Localization of Rodrigo de Freitas lagoon and sampling stations.

On the other hand, from studies that have been carried out since the last three decades, it is possible to affirm that one of the factors that decreases the quality of this ecosystem is the stratification of water due to the restricted circulation and the water renewal (Rosman 1990). The deeper water layer soon becomes anaerobic and rich in sulfuric gas because of the oxidation of the organic matter in the bottom of the lagoon (Rosman 1990). Thus, one concludes that this environment presents favourable conditions for the accumulation of pollutants in its substratum.

MATERIALS AND METHODS

The present study used three approaches of sediments collection for the characterization of the heavy metal levels in the urban runoff sediments surrounding the lagoon and in its bottom:

The first approach consisted of the sampling of 44 botton sediments from the lagoon with a Van Veen grab sampler that covered the whole lagoon (Fig. 1). The second approach was the sampling of the botton sediments of four stations. The anoxic conditions of the samples in the second campaign were kept thought by the isolation of the sample in the subaqueous environment, freezing, opening under atmosphere of N_2 and liofilization in the lab.

The third approach aimed at the collection of the samples in the urban runoff sediments in the streets around the lagoon, where 7 samples were collected, and in the mouth of the main canals that drains to the lagoon, where 8 samples were collected (Fig. 1). In the second and in the third campaigns, the physical-chemical conditions of the aquatic environment was analysed through the measurement of the pH, Eh and temperature *in situ*. The pH analysed was carried out through a pHmeter Metrohm 744. The Eh was measured with a platinum electrode (Analion), model ROX 673, calibrated with its proper standards.

The selective extraction analysis used both shaking and heating techniques (McAlister et al. 2003), in which a prepared sample of 0,500 g was weighed into acid washed polyproplene tubes, and blanks were prepared by taking each extractant without the sample through all the preparation procedures prior to analysis. Water-soluble ions were extracted using a modified version of the Buurman et al. 1996 technique where a smaller sample weight was extracted with a lower volume of deionised water (2.5 ml), diluted to 10 ml and membrane filtered (0.2 μm) prior to analysis (McAlister et al. 2003). This extraction protocol was modified to include the organic phase, which was extracted using a 3:1 mixture of HNO_3 and HCl (Lefort aqua regia) to ensure a better oxidation of the organic matter. Acid digestion of the residual phase was carried out using a Perkin Elmer microwave digestion system. Analytical grade chemicals were used and all solutions were prepared using Grade A glassware and deionised water. Elemental analyses were carried out using a Perkin Elmer Model 3100 atomic absorption spectrometer. The detection limit for Cu, Pb, Zn, Cr and Ni was 0.05ppm; 0.1ppm; 0.01ppm; 0.05ppm and 0.04ppm, respectively.

RESULTS AND DISCUSSIONS

THE PHYSICAL-CHEMICAL PARAMETERS

According to Warren and Haack (2001), the combination between parameters such as potential redox and pH can affect the behaviour of metals, influencing their solubility. The Eh value recorded in the station LS4 was the lowest one, reaching –440mV and indicating the station LS4 as one of the most reduced stations. It was considered that this station is located closer to a pluvial source contaminated with organic loads, which can affect the physical-chemical parameters of the station water. In the other stations in the inner of the lagoon, the values ranged between –87 and –305mV, characterizing sufficiently reducing sediments at the time of the collection.

The pH has been pointed out as one of the most important physical-chemical parameters (Harter 1983, Basta and Tabatabai 1992a). Its variation can modify the load of surface of colloids, regulating, together with other attributes of the water, the magnitude of the adsorption of the metallic ions in the soil and sediments (Naidu et al. 1994). In low values of pH, the hydrated forms of the metallic ions are favoured, while in high pHs, a trend of the formation of a complex with hydroxiles and carbonates occur (Sposito 1989).

The recorded values of pH ranged between 7.51 and 8.38. The highest values were recorded in the stations LS1 and LS3. The average values found in the others stations was 7.56. The highest values were found near the canal that connected the lagoon with the ocean, which explains these values.

HEAVY METAL TOTAL CONCENTRATIONS

According to Yongming et al. (2006), the components and the respective concentrations found in the urban dust, soils and sediments are important factors to be evaluated in the analyses of the environmental quality, especially in big cities. In the special case of the urban runoff sediments, the interest in the concentrations of pollutants associated with this dust increased significantly in the last decades, mainly concerning the concentrations and distribution of lead (Jones and McDonald 1983, Von Schirnding and Fuggle 1996, Chatterjee and Banerjee 1999), copper and zinc, as well as the identifi-
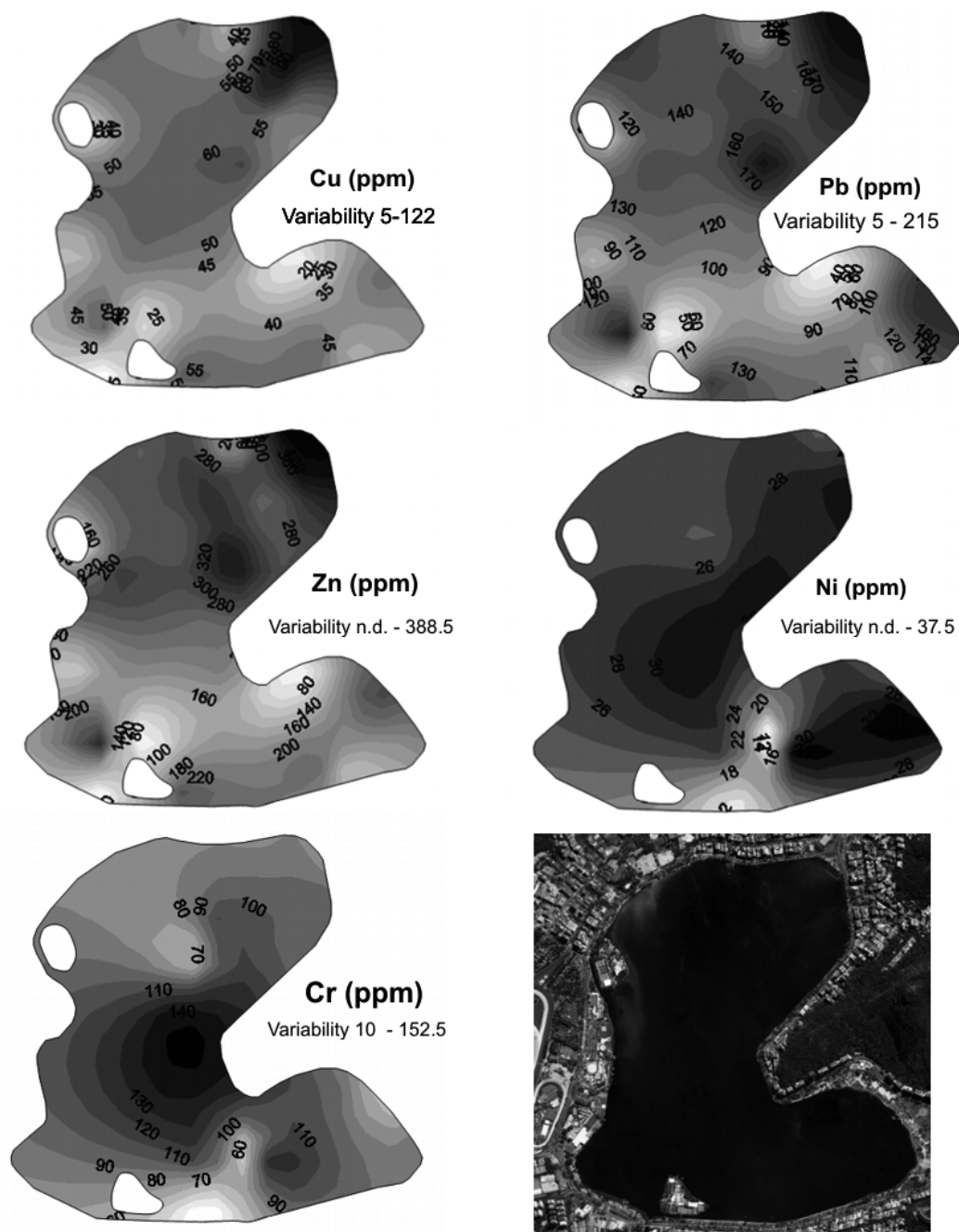
Fig. 2 – Heavy metal spatial variations during the first campaign.

cation of their sources (Fergunson and Kim 1991, Nagerotte and Day 1998). Urban soils, on the other hand, are not only deposits of pollution, but can also act as sources of pollution to the environment (Yongming et al. 2006).

The levels of the heavy metals concentrations found in the inner of the lagoon shows concentrations of Cu ranging from 5 to 122ppm, with an average of 48.7ppm. In order to obtain the spatial distribution of the heavy metals concentrations in the bottom sediments of the lagoon, the data were plotted in the located map (Fig. 2) in this map it is possible to observe an increase in the concentration of the Cu in the north of the lagoon. D.D. Loureiro, unpublished data, in a similar study in the same lagoon, recorded slightly lower con-

centrations of Cu, ranging around 100ppm. His method of extraction is based on the techniques described by Loring and Rantala (1991) and UNEP (1995). According to the methods of digestion, the decomposition of the sediment samples was induced under high temperatures and, when necessary, the pressure was used. The total digestion of his samples using HNO_3 and HCl (3:1) can explain the reason for the lower concentrations obtained in his study. Despite the higher aliquot of sediments used in his extraction (1 g) for his analyses, the method used in the present study had a more aggressive character of digestion. Benoit et al. (1999), used the same amount of sediment samples, 10ml a mixture of HNO_3 and HF (50:50); in samples of the Hudson Bay, New York, they found concentrations of total Cu ranging around 50ppm, which is lower if compared with the present study.

Sediment cores were collected in Jurujuba Sound, Niterói, a city near Rio de Janeiro, by Baptista Neto et al. (2000). Using the same method of extraction of the present work, they had determined similar concentrations of background 5ppm. In the same sediment cores, the authors found maximum concentrations after-urbanization of 100ppm, which is compatible with the results found in the present study.

The total concentrations of Cu in the street sediments of the urban runoff and in the sediments collected in the mouths of the rivers and in the Jardim de Alah canal were lower than the concentrations found in the sediments collected in the inner part of the Rodrigo de Freitas lagoon. In the sediments accumulated in the streets, the maximum concentrations recorded for Cu was 51ppm. The average values for Cu in the urban runoff sediments collected in the streets around Rodrigo de Freitas lagoon were lower than the majority of values found in the literature for other urban centers (Table I). McAlister et al. (2005) found higher values in the same city and in streets with intense traffic, including heavier types of transport such as buses and trucks.

The concentrations of Pb found in the present study ranged from 5 to 215ppm, with an average of 125.8ppm. The highest values were found either in the urban runoff sediments and in the bottom sediments of the lagoon. According to Alloway (1990a) and M.A.P. Pierangeli, unpublished data, the surfacial soil tend to accumulate Pb that came from atmospheric depositions or industrial and agricultural sources due to its low solubility and strong absorption to the sediment.

D.D. Loureiro, unpublished data once again found lower concentrations in the bottom sediments of the lagoon (about 100ppm). According to the study carried out by Baptista Neto et al. (1999), the concentrations of the regional background are of the order of 25ppm. The spatial distribution of the total concentrations of Pb in the Rodrigo de Freitas lagoon (Fig. 2) showed the same pattern of Cu, with an enrichment through the north of the lagoon. In the rivers mouth and in the canal that link the lagoon to the sea, the concentrations were lower, with maximum value reaching only 41ppm. After the partial or total prohibition of the tetraethyl, there was an addition in the gasoline in some countries and the concentration of the particulate Pb in the air of the urban areas decreased, but it did not solve the problem of the pollution by this metal. Other sources are responsible mainly for the atmospheric pollution, in the industrial zones, risking the health of the population (Cochran et al. 1998). In the case of the urban runoff sediments, as well as Cu, the concentration was lower than the average found in the literature (Table I). McAlister et al. (2005) recorded levels three times higher in the same area of this study. However, according to Pereira et al. (2007), the time of the sediment residence in the streets is very limited, with a low capacity of record. The comparison among different studies must take this characteristic into consideration. In terms of urban environment, Pb should be considered due to its negative effect for the human health (Vanz et al. 2003).

The pattern distribution of the total concentration of Zn was similar to Cu and Pb, with lower concentrations in the river mouth and in the Jardim de Alah canal. In these areas, the highest concentrations was 170.5ppm, and the highest concentration found in this study was in the inner bottom sediments of the lagoon, with 388.5ppm.

Zn showed the same distribution pattern of enrichment as Cu and Pb, indicating the same source of pollution in the north of the lagoon (Fig. 2). These results were higher than the values found by D.D. Loureiro, unpublished data and Benoit et al. (1999), who found values around 76.9 and 90ppm, respectively.

In the urban runoff sediments collected around

TABLE I
Average concentrations of heavy metals in urban dust around the world available in the literature.

Pb	Zn	Cu	Cr	Ni	Location	Author
127.52	305.71	32.78	44.91	66.07	Rio de Janeiro city, south zone, Brazil	Present work
368.88	1284.05	290.61	97.3	73.07	Rio de Janeiro city, south zone, Brazil	McAlister et al. 2005
230.52	421.46	94.98	167.28	—	Xi'na, China	Yongming et al. 2006
160	120	30	31	24	Residential area, Southeastern Michigan,US.	Murray et al. 2004
93	130	32	27	16	Commercial area, Southeastern, US.	
262	253	74	11	—	Naples urban region, Italy	Imperato et al. 2003

the lagoon, the average concentrations of Zn was 305.71ppm. This result is comparable with the ones of other urban areas, such as Naples, in Italy (Imperato et al. 2003) and in the urban regions of Michigan, USA (Murray et al. 2004) (Table I). McAlister et al. (2005) also found concentrations higher in the center of Rio de Janeiro, with an average reaching 1284.05ppm.

In Europe and in the USA, the studies about urban runoff sediments are highlighting mainly the dynamic of copper, lead and zinc (Charlesworth et al. 2003). There were a few studies about metals such as chromium and nickel (Yongming et al. 2006).

The concentrations of Cr recorded in this study show a higher average, in most of the samples, of the background found by Baptista Neto et al. (2000), which is 5ppm. Cr does not show a pattern of variations between the lagoon sediments and the urban runoff sediments, where the concentrations range from 10 to 152.5ppm, with an average of 83.9ppm (Fig. 3). The average concentrations of chromium in the urban runoff sediments of adjacent streets to the Rodrigo de Freitas lagoon were very similar to the average concentration observed in the literature (Table I). However, the concentrations of Ni showed a higher average, if compared with others studies (Table I). These ranged between n.d. and 37.5ppm, with an average of 25.9ppm in all the study area. On the other hand, the average concentrations of this element in the urban runoff sediments was 44.91ppm, which is lower than the one of the study carried out in Xi'na, China (Yongming et al.

2006). Baptista Neto et al. (2000) found concentrations levels around 5ppm in the same area of study, which can be considered a natural concentration.

HEAVY METAL SELECTIVE EXTRACTION

The selective extraction of Cu showed an extremely differentiated behaviour between the two first compartments (urban runoff sediments and the sediments collected in the mouths of the canals) and in the sediments collected in the interior of the lagoon. In the two first compartments, the reductive phase predominated, whereas in the latter, the oxidized fraction was predominant. The same behaviour was described by McAlister et al. (2005) in samples of urban runoff sediments accumulated in streets of high traffic conditions. According to Ross (1994), the adsorption of metals by organic substances is particularly important for Cu and Pb. Guilherme and Anderson (1998) suggested that, despite of the high degree of selectivity of the organic matter with Cu is caused by the formation of internal sphere complexes, also known as specific absorption, the preservation of the organic matter is directly linked with the levels of dissolved oxygen, it is expected that this phase has a greater importance in anoxic environments, such as the sediments of the Rodrigo de Freitas lagoon. Studies on this subject show an increase in the bioavailability of Cu during the aeration of anoxic sediments (Alastuey et al. 1999, Marseille et al. 2000), which suggests the great importance of the dissolved O_2 concentrations for the Cu speciation. In estuarine sediments
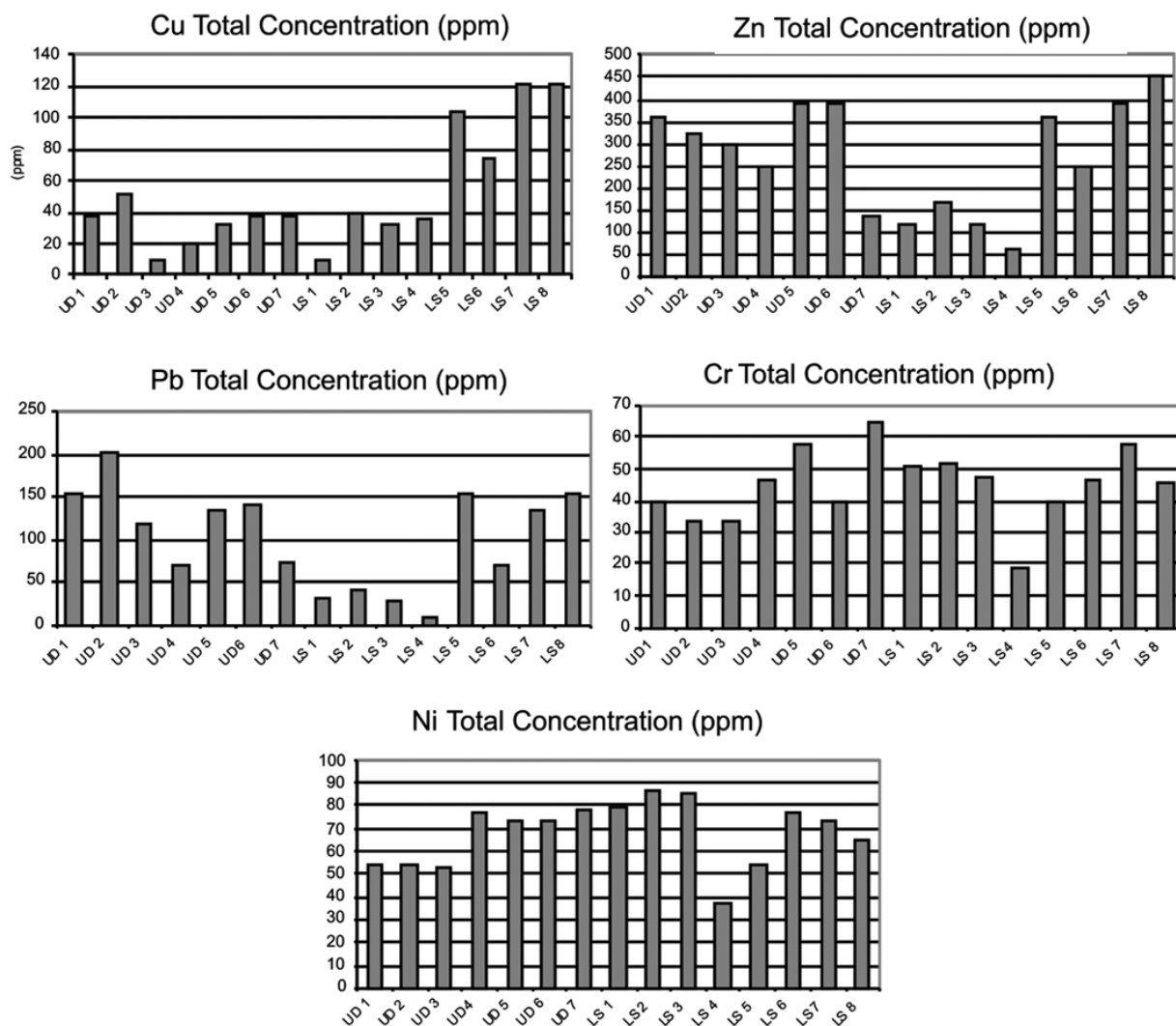
Fig. 3 – Heavy metal total concentration variation during the 2nd and 3rd campaigns.

from a tropical region, where the reductive and oxidable phases alternate, Ngiam and Lim (2001) recorded the same pattern of speciation. According to the same study, the levels of O_2 were determinative in the percentage of each phase.

The Cu residual phase was only recorded in the interior of the lagoon, probably due to its high concentration in this area. In the other stations, the concentrations of Cu were below the detection limit. Cu was not recorded in the water soluble phase.

Pb presented a differentiated pattern at the entrance of the rivers and in the other compartments. The organic phase showed that the highest percentage was found at the entrance of the rivers, reaching up to

100% in the station LS4. On the other hand, in the other stations the reductive phase was more important. In the urban runoff sediments accumulated in the streets of Rio de Janeiro, McAlister et al. (2005) recorded the same pattern of speciation, with the predominance of the reductive phase. The interchange between the organic and reductive phases was also verified by Ngiam and Lim (2001). Regarding the other phases, the carbonatic phase was extremely significant and predominated in some stations. In the stations located near the rivers entrances, however, the concentrations were below to the detention limit. Ngiam and Lim (2001) also commented on the great importance of the carbonatic phase for this metal. The residual

phase did not show concentrations above the detection limits of the method.

Zn also showed a different behaviour between the stations located in the rivers mouth and the other compartments. As well as Pb, the percentage of the carbonatic phase showed direct bonding with the total concentrations of Zn. Both metals presented higher affinity with this phase in the urban dust and in the lagoon bottom sediments. McLean and Bledsoe (1992) and Alloway (1990a) suggested that this pattern is due to the fact that Zn, wit a pH closer to 7.7, hydrolysate and is subsequently absorbed by clays, carbonates and oxides. McAlister et al. (2005) recorded the highest occurrence of the soluble phase in the water. In the present study, the soluble phase in the water was below to the detection limit, which can be attributed to this metal easy and quickly to adhere to many organic linked, mainly in the presence of electron donators such as nitrogen and surphur (G.A. Quináglia, unpublished data).

Cr and mainly Ni showed significant percentages of the residual phase, which can be the reason for few variation in the other phases. The same pattern was verified by McAlister et al. (2005). Morillo et al. (2004) recorded the highest percentage of the residual phase in the results of both metals. This result is similar to the one of the present study, suggesting the great linking of both metals with the sediment.

In the mobile phases, the organic phase predominated in the case of Ni. Alloway (1990a) suggests that, in aerobic conditions and pH lower than 9, the Ni complexation with hydroxide, carbonates, surphur and organic matrices and in reduced environments forms insoluble surphur. The oxidable phase interchanged with the reductive phase for Cr. The soluble and the carbonatic phases were below to the detected limit for both elements.

The pattern of the selective extraction for Ni and Cr did not show any differentiated pattern among the three compartments, despite the extremely differentiated environmental conditions (Fig. 4). On the other hand, the high percentage of the residual phase, mainly of Ni, can decrease the differences among the referring percentages to each phase. Benjamin and Leckie (1981) suggested that the heavy metal partition pattern is also influenced by the total concentration. According to

these authors, even the metals are absorbed by different degrees of affinity and it can occur the competition for the sites of the oxides absorption, mainly when the cations are in low concentrations, as in the case of the present study.

In a general way, the environmental differences among the compartments studied in this research showed the high influence on the partition of Cu and Pb. In these particular cases, the organic phase was more influent. However, in the case of Cr and Ni, it was not observed a differentiated pattern among the compartments, suggesting the highest stability of the composites formed with these metals. The great participation of the residual phase can also be responsible for the homogeneity in the dynamics of the partition of these metals (Fig. 4).

Heavy metals did not present concentrations above the detection limit, in the soluble phase in the water, suggesting that they were not bioavailable. However, the metals presented the highest percentage in the potentially mobile phase. Considering the dynamic character of the aquatic environments, the fluctuation of pH, organic matter concentrations and Eh in the sediments and in the interstitial water, resulting from the natural or anthropogenic processes such as dredging or bioturbation, can cause remobilization of these metals (Acevedo-Figueiroa et al. 2006). As these characteristics are subject to natural fluctuations that result from annual climatic variations, a seasonal study should be carried out in the area, in order to get a better understanding of the geochemical cycle in this ecosystem.

CONCLUSIONS

The Rodrigo de Freitas lagoon is considered one of the most polluted coastal lagoons in Rio de Janeiro State/ SE-Brazil. The presence of Cu, Pb, Zn, Cr and Ni in the bottom sediments of the lagoon was mostly due to anthropogenic sources, such as sanitary waste and urban dust. High concentrations of heavy metals in the urban runoff sediments suggested that this compartment can be considered an important sources of heavy metal to the lagoon, mainly Pb and Zn.

The highest concentrations of Cu in the bottom sediments of the lagoon, highlight the capacity of the sediments in estuarine environments to concentrate pollu-
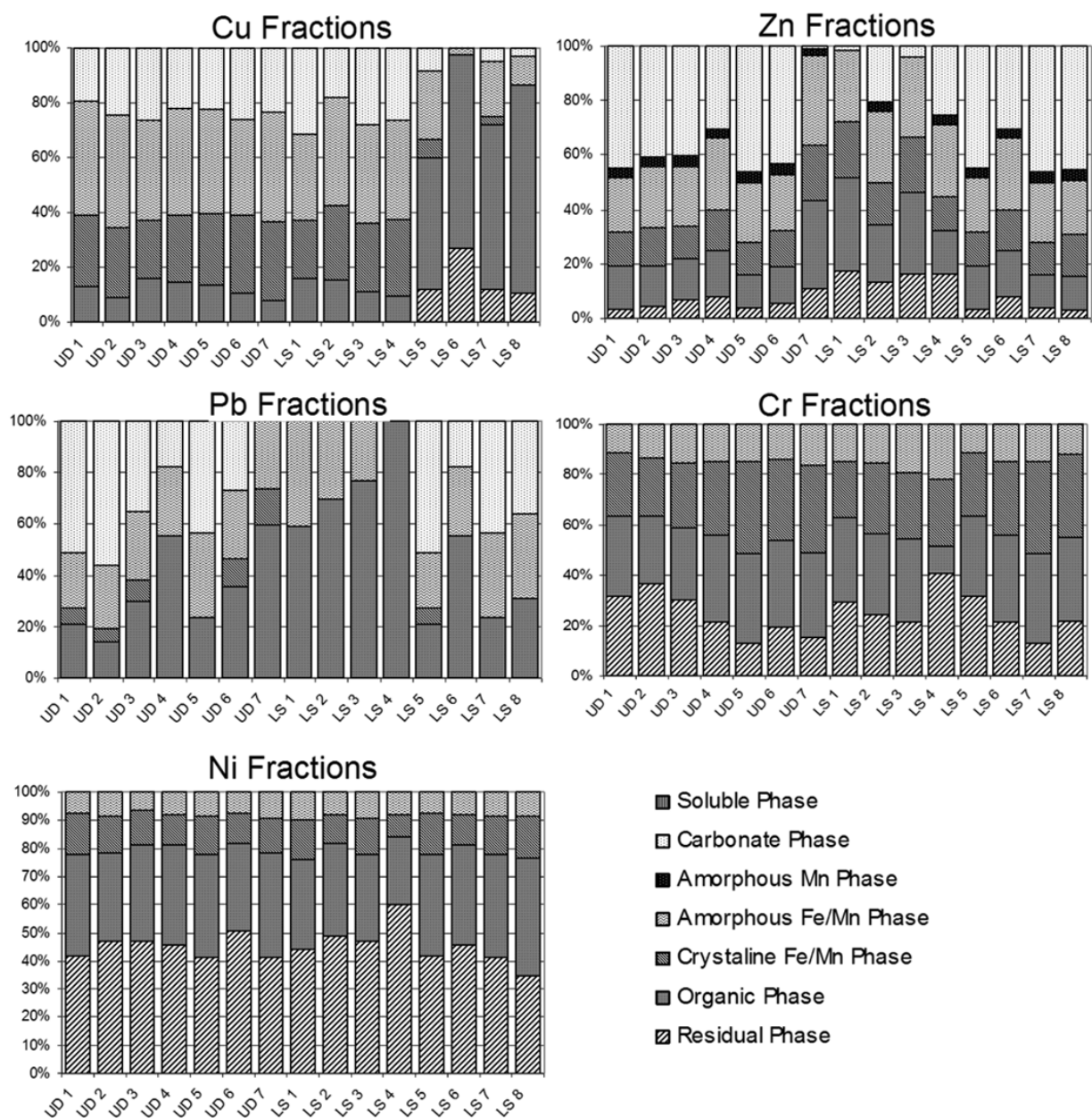
Fig. 4 – Heavy metal fraccionament during the 2nd and 3rd campaigns.

tants, mainly contaminants with high affinity with organic matter.

The low concentrations of Pb in the residual phases suggested that the anthropogenic sources predominate in the study area.

The analyses had not identified concentrations of heavy metals in the soluble phase, which suggests that the heavy metals are not bioavailable for the organisms.

On the others hand, the potentially bioavailable phases were present in all the heavy metals chemical partition, suggesting a potential remobilization in the case of physical-chemical fluctuations due to several processes, such as the opening of the Jardin de Alah canal, with the increase in the water exchange between the lagoon and the sea, or eventually the dredging of the bottom sediments of the lagoon. Studies involving bio-

indicators are necessary to evaluate the potential influence of heavy metals to living organisms.

RESUMO

A urbanização acelerada, sem planejamento, resultou em uma série de problemas à zona costeira do Rio de Janeiro, especialmente em áreas como a Lagoa Rodrigo de Freitas, a qual recebe uma grande descarga de esgoto não tratado todos os dias. No intuito de avaliar a natureza, as fontes potenciais e a extensão da poluição por metais pesados na lagoa, sedimentos das ruas do entorno, das entradas do principal canal de drenagem e de superfície de fundo foram coletados. As análises se deram através de um método modificado de extração sequencial, com o objetivo de estudar o fracionamento geoquímico e a biodisponibilidade de Zn, Cu, Cr, Ni e Pb, nestes três compartimentos. O presente estudo verificou um aumento nas concentrações de Cu, Pb, e Zn no setor norte da Lagoa Rodrigo de Freitas. Apesar dos diferentes níveis de oxidação entre os sedimentos acumulados nas avenidas e no sedimento de fundo da lagoa, o fracionamento geoquímico dos metais pesados não apresentou nenhum padrão de variação, com exceção do Cu. Não foram observadas concentrações na fase solúvel, das amostras coletadas nos sedimentos superficiais na lagoa, sugerindo a não biodisponibilidade dos metais pesados.

Palavras-chave: metais pesados, Lagoa Rodrigo de Freitas, sedimentos.

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