

Heavy metal inputs evolution to an urban hypertrophic coastal lagoon, Rodrigo De Freitas Lagoon, Rio De Janeiro, Brazil

Daniel Dias Loureiro · Marcos A. Fernandez ·
Friedrich W. Herms · Luiz D. Lacerda

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Abstract This work discusses the temporal variation of metal concentrations in a hypertrophic coastal lagoon located in the metropolitan area of Rio de Janeiro (Brazil). The lagoon watershed includes one of the mostly densely urbanized areas of the city but without industrial activities. Six sediment cores were collected in the lagoon between May and July 2003 and analyzed for the concentration of metals (Fe, Al, Mn, Zn, Pb, Cu, Cr, and Ni). Typical sedimentation rate was calculated as being $0.75 \text{ cm year}^{-1}$ and was uniform for at least the past 70 years. Therefore, the alterations in the dynamics of the lagoon caused by changes in its watershed were clearly indicated in sediment cores. The construction of an artificial canal to the sea and the increasing urbanization and soil use changes were the major factors affecting metal accumulation in the lagoon sediments. Metals typical of anthropogenic urban sources (Pb, Zn, and Cu) showed increasing loads following urbanization.

Keywords Metals · Pollution · Sediments · Urbanization · Tropical areas

Introduction

Coastal lagoons are common features along most coastlines. In a global, scale they occupy from tropical to polar environments (Fernandes 1996) about 13% of the world coastal areas ($332,000 \text{ km}^2$) with an average area of 78 km^2 and an average length around 10 km. The linking of coastal lagoons with the sea is made through channels or bars. Their quantity and size depend on the amount of water that flows for a given interval of time. Water volume of coastal lagoons is controlled by tidal range, number of daily tides, and freshwater discharge. Linking with the sea may also occur by underground waters, which are more significant in coastal lagoons whose channels are kept closed during long periods of time and/or in cases where the sand bar presents high porosity. Coastal lagoons are generally parallel to the coast, with small average depths of a few meters or even less. Depending on the freshwater input from the drainage basin and the water exchange with the adjacent sea, salinity of these environments can vary from freshwater to hypersaline (Kjerfve and Magill 1989).

Coastal lagoons are water bodies with restricted connections to the ocean and were

D. D. Loureiro (✉) · L. D. Lacerda
Universidade Federal Fluminense,
Niterói, Brazil
e-mail: danieldiasloureiro@vm.uff.br

M. A. Fernandez · F. W. Herms
Universidade do Estado do Rio de Janeiro,
Rio de Janeiro, Brazil

formed as a result of rising sea level during the Holocene/Pleistocene. The growing of sand barriers through marine processes partially or totally isolates the lagoons from the ocean. Therefore, they often have long water residence time, being ephemeral in geological timescale and their existence being mainly dependent on sea level fluctuations and human interference (Kjerfve and Magill 1989). They can also be characterized as areas of fast accumulation of fine-grained size sediments, rich in organic materials of autochthonous and allocthonous origin, because of low energy from tides, waves, and currents. These depositional environments intercept material transport at the land–sea interface and accumulate most of the fluvial derived sediments and associated chemical elements in bottom sediments. Along the Rio de Janeiro coast, for example, all rivers discharge into coastal lagoons prior to reaching the sea. For this reason, coastal lagoons are ideal places for studying the pollution history of coastal areas (Lacerda 1994; Ruiz-Fernandez et al. 2003).

Metals reach coastal lagoons from several sources, from fluvial and atmospheric deposition, sea water entrance, or percolating groundwater. In coastal lagoons situated in highly urban areas, runoff can be the main metal source (Lacerda and

Gonçalves 2001). Coastal lagoons are considered to function as traps, capturing metals from surface waters and preserving them in sediments, being one of the main reservoirs in the geochemical cycles of these elements at the land–sea interface (Yuan et al. 2004; Lacerda 1994). In the present study, we characterize and quantify the metal (Al, Fe, Mn, Cu, Pb, Zn, Cr, and Ni) loads to Rodrigo de Freitas Lagoon, a coastal lagoon located within the metropolitan area of Rio de Janeiro City, during the past century through the analysis of dated sediment cores.

Study area

Rodrigo de Freitas Lagoon is located between latitudes $22^{\circ}57'02''$ S and $22^{\circ}58'09''$ S and longitudes $043^{\circ}11'09''$ W and $043^{\circ}13'03''$ W and had its origin in the drowning of old fluvial basins generated by transgressive–regressive variations of sea level that occurred in the past 6,000 years along Rio de Janeiro State coast (Amador 1997). Total watershed of the Rodrigo de Freitas Lagoon has an area of 24 km². Urbanization of Rio de Janeiro city completely modified the morphology of the lagoon. Successive land reclamation

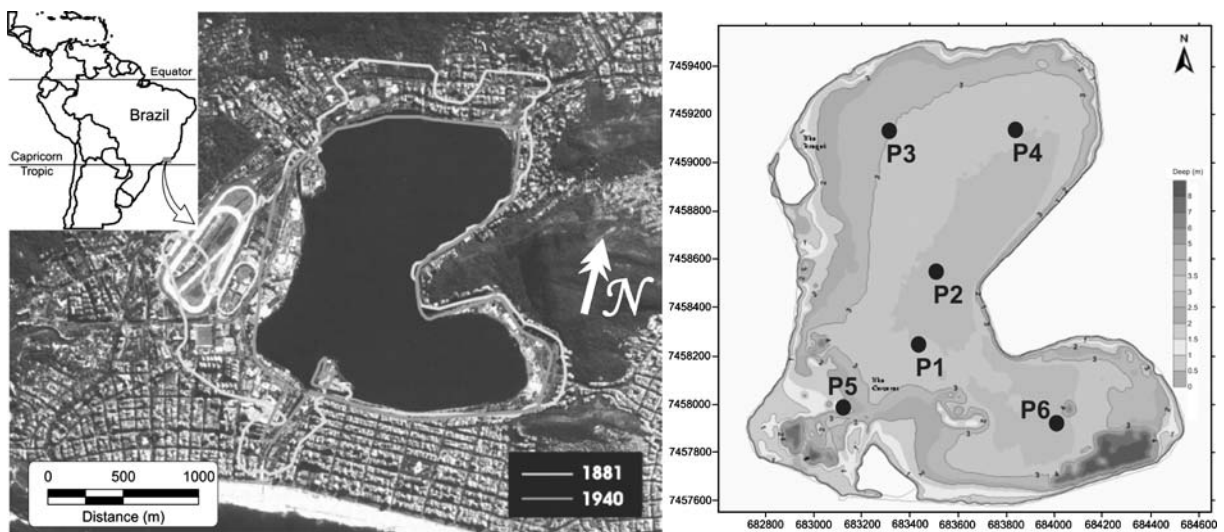


Fig. 1 Location of Rodrigo de Freitas Lagoon at the metropolitan area of Rio de Janeiro city. Modifications in the lagoon surface area due to land reclamation are shown

by lagoon margins traced for 1841 and 1940 (left). Present-day bathymetry and sediment core locations (Ambiental 2002) (right)

reduced surface area by about 1/3, to give place to new housing developments (Fig. 1).

Before 1921, the lagoon communicated with the sea through an unstable natural channel that remained obstructed by a sand bar except during a few days each year when rupture of the bar by flooding occurred, changing the water level by approximately 1.0 m. In 1921 the first stage of the construction of the Jardim de Alah Canal was concluded, with about 140 m in length and 10 m in width. Its final form was finished in 1942, measuring 835 m in length and width varying between 10 and 18 m and average depth of 0.70 m below mean sea level (Ambiental 2002).

After the canal construction, variations of the water level in the lagoon diminished significantly, being restricted to about 30 cm at each tidal cycle and also reflecting the effect of precipitation in the watershed (Rosman 1992). Simultaneously, the urban occupation of the lagoon drainage basin increased significantly after 1921, reaching a population of about 150,000 habitants in 2003.

Currently, the Rodrigo de Freitas Lagoon presents an area of about 2.26 km². The most recent bathymetric survey, carried out in December of 1999, showed mean depth of 3 to 4 m in almost all its extension, with deepest areas reaching 9 m at the southeast corner (close to station 6 in Fig. 1).

Although today lagoon waters are brackish, a smaller marine influence is currently evidenced when compared to that registered in the past. Two reasons can explain this: (1) the intense clogging of the canal by sand, causing a low efficiency in bringing salt water into the lagoon and (2) the greater input of fresh water derived from the intense urbanization of the area, eliminating infiltration points and natural vegetation areas facilitating rain water discharges directly into the lagoon through the pluvial water collecting system.

Materials and methods

Six sediment cores were collected between May and July of 2003, with recoveries ranging from 1.0 to 1.7 m of sediment. The corer presented 7.5 cm of diameter, and each core was sliced at 5 cm intervals. Sedimentation rate was determined by the

excess of ²¹⁰Pb method (Godoy et al. 1998; Smith 2001). Aliquots from slices of the best preserved core P1 were lyophilized and homogenized using an agate mortar. Three grams of sediments were taken for ²¹⁰Pb determination, at the Department of Chemistry of the Catholic University in Rio de Janeiro. From the results obtained in 15 samples along core P1, a model Constant Initial Concentration was used to determine the sedimentation rate (Robbins and Edgington 1975). Particular characteristics of the sedimentary record were then used to evaluate the relative dates in the other cores.

All sediment samples for metal analyses were sieved in duplicate, and only the silt and clay fraction (particle size < 63 μm) was used for analyses. Two geochemical fractions of heavy metals were analyzed in these samples: the fraction strongly bound to sediments, extracted by inverted *aqua-regia* (HNO₃/HCl, 3:1) and a weakly bound fraction, obtained by cold extraction with 0.1 N HCl.

Strongly bound metals were extracted from 1.0 g subsamples of dry sediment after digestion in Teflon bombs with 10 mL of the acid mixture and kept sealed in a digester block at 80°C for 12 h. After this period, temperature was raised to 190°C for 4 h with addition of 3 mL of concentrated HNO₃ and the final volume of the solution taken to 20 mL. This type of digestion does not remove metals incorporated in the crystalline lattice of minerals, as it is not expected that metals derived from anthropogenic activities can be incorporated into the mineral structure of sediments (Yuan et al. 2004; Forstner and Wittmann 1981; Tessier et al. 1979).

Weakly bound metals were extracted from 1.0 g subsamples of dry sediment by mixing in polypropylene tubes with 25 mL of 0.1 N HCl under agitation during 4 h at room temperature, and the final volume of the solution was 25 mL. Metals determined in this phase are considered bioavailable and the most critical phase in case of resuspension of the sediments (Fizszman et al. 1984).

The concentrations of Fe, Mn, Zn, Al, Pb, Cu, Cr, and Ni were determined by conventional flame atomic absorption spectrophotometry in a Perkin Elmer Analyst 300 equipment. The detection limits obtained were (1) for the strongly

bound fraction: 0.5 mg g⁻¹ for Al, 0.3 mg g⁻¹ for Fe, 12 µg g⁻¹ for Mn, 1.5 µg g⁻¹ for Cu, 1.4 µg g⁻¹ for Pb, 9.1 µg g⁻¹ for Zn, 0.3 µg g⁻¹ for Ni, and 1.6 µg g⁻¹ for Cr; (2) for the weakly bound fraction: 0.1 mg g⁻¹ for Al, 0.4 mg g⁻¹ for Fe, 3.2 µg g⁻¹ for Mn, 0.2 µg g⁻¹ for Cu, 0.9 µg g⁻¹ for Pb, 1.2 µg g⁻¹ for Zn, 0.4 µg g⁻¹ for Ni, and 0.3 µg g⁻¹ for Cr.

The fine fraction and organic matter content were determined by gravimetric methods. In core P1, complementary analyses were done for nutrients (NH₄⁺ and PO₄³⁻), salinity, and dissolved metals (Fe and Mn) in interstitial water. Identification of shell fragments, elementary composition of the organic matter (CHNS/O Perkin Elmer 2.400, Series II Autoanalyser), and total phosphorus content (APHA/AWWA/WPCF 1995) were also performed in this core.

Data were treated using programs XLSTAT-Pro 7.0[®] and STATISTICA 5.0[®]. Normality of data sets were tested using Lilliefors test, $p < 0.05$, and showed most of the data to present a nonparametric distribution. The significance of the observed differences in concentrations between surface layers and deeper layers in each core was tested using the Mann–Whitney test, $p < 0.05$. The Kruskal–Wallis test was used to verify the significance of distribution differences among the six cores for each metal, at the same significance level. After reduction of all variables, the whole data set was tested with principal components analysis, using the nonparametric Spearman coefficient.

Results

A comparison by Kruskal–Wallis test of each analyzed parameter in each sediment core showed no significant difference ($p > 0.05$) between the concentrations of Al, Mn, Zn, Fe, Cu, Pb, Cr, and grain size in the different cores suggesting a large uniformity of these parameters analyzed in Rodrigo de Freitas Lagoon sediments and allowing comparison of average values and behavior of these parameters. Concentrations of Ni, however, were significantly ($p < 0.05$) higher in cores 2 and 3 than in the other cores, but distribution was also similar among the six cores studied.

Sedimentation rate was estimated as 0.75 cm year⁻¹ in core 1, similar to those reported for other coastal lagoons of Rio de Janeiro State (Lacerda 1994). Therefore, we can consider that the first 60 cm layer was deposited after the construction of the canal in 1921. This is corroborated by changes in the deposition of some metals used as source tracers. After the canal construction, an intensive human occupation of the drainage basin occurred. When observing the behavior of all metals in the other sediment cores, a displacement of the layer corresponding to the canal construction is verified. This layer occurs in cores P2, P3, and P4 at similar depths to P1 (60, 70, and 65 cm, respectively). In cores 5 and 6, however, this layer occurred at 25 and 90 cm in the cores, respectively. The shallow depth verified for the canal construction layer in core P5 is probably a result of dredging operations occurring frequently in the area (Ambiental 2002).

Further statistical analysis of the results, however, showed significant differences ($p < 0.05$) in all the analyzed parameters, in all cores, between the sediments deposited above and below the corresponding layer of the construction of the Jardim de Alah Canal and the start of the fast urbanization of the lagoon basin.

In core P1, water content varied between 57% and 83%, with an average of $69 \pm 8\%$. Water content decreased with depth. Average bulk sediment density was 1.9 ± 0.7 g cm⁻³. Fine-grained sediments (<63 µm) dominated the entire cores with average concentration of $93 \pm 3\%$. Snail shells (*Littoridina* sp.), an indicator of brackish water conditions, were rarer below 60 cm, suggesting lower salinity before the construction of the artificial canal. Pore water salinity was higher (23.6) in the top of sediment core, whereas lowest values (9.1) were at 50–60 cm layer (Fig. 2). Organic matter content varied between 16% and 23% with relatively higher values in the top layers 0–20 cm and lower values below 60 cm. A richer organic layer (23%) was found in the 140 cm layer, suggesting an important environmental change in the lagoon history, but this observation is not detailed in the present study.

Dissolved phosphorus in interstitial waters varied between 14 and 160 µmol L⁻¹ (Fig. 2). Concentrations increased above the 60 cm layer,

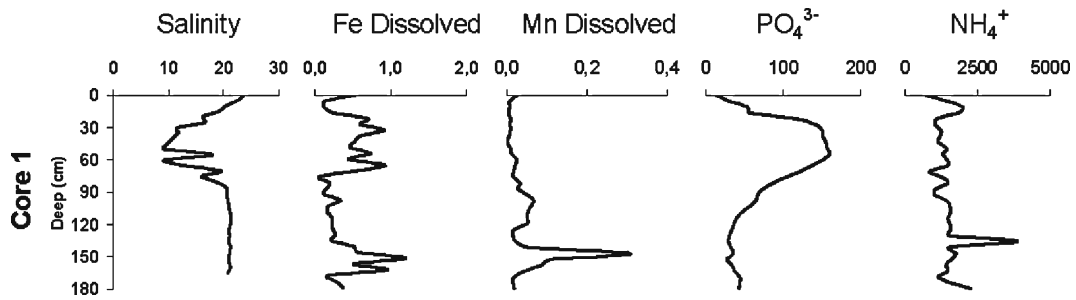


Fig. 2 Distributions of porewater compounds in core P1 (ammonia and phosphorus in $\mu\text{mol L}^{-1}$ and dissolved Mn and Fe in mg L^{-1})

suggesting increasing sewage inputs to the lagoon during the urbanization process. This observation is also supported by the change in the elemental composition of organic matter which changed from 354:25:1 (C/N/P), prior to the canal construction in 1921, to 244:16:1 in the top 20 cm. Dissolved Fe and Mn varied from 0.03 to 1.21 mg L^{-1} and from 0.01 to 0.31 mg L^{-1} , respectively. Dissolved Fe concentration showed higher values 60 cm layer at the top of the core (Fig. 2). A peak of dissolved Mn (0.31 mg L^{-1}) and Fe (1.21 mg L^{-1}) was observed near to 140 cm layer. This layer was deposited around 1800 A.D. and may be related to the existing agricultural activities at that period dominating the lagoon watershed.

Average total metal concentrations in the first 20 cm of each sediment core of Rodrigo de Freitas Lagoon, including a composite sample made of the first four sediment slices from the six cores and totaling 24 samples and where a relative homogeneity occurred, were $52 \pm 5 \text{ mg g}^{-1}$ for Al, $39 \pm 5 \text{ mg g}^{-1}$ for Fe, $376 \pm 80 \mu\text{g g}^{-1}$ for Mn, $105 \pm 6 \mu\text{g g}^{-1}$ for Cu, $107 \pm 18 \mu\text{g g}^{-1}$ for Pb, $341 \pm 38 \mu\text{g g}^{-1}$ for Zn, $21 \pm 8 \mu\text{g g}^{-1}$ for Ni, and $54 \pm 8 \mu\text{g g}^{-1}$ for Cr. Concentrations of Fe, Al, and Mn are lower, whereas those of Zn, Cu, Pb, and Ni are higher than the reported values for other coastal lagoons of Rio de Janeiro State, which are located mostly in rural areas (Fernandes 1996). Concentrations of these trace metals are in the upper range of values reported for lagoons located in industrialized (e.g., Ria de Aveiro Lagoon, Portugal (Monterroso et al. 2003), Indian lagoon, USA (Trocine and Trefry

1996), and Szczecin Lagoon, Poland (Glasby et al. 2004)) and urban areas (e.g., Chi-Ku Lagoon, Taiwan (Chen 2002), Venice Lagoon, Italy (Sfriso et al. 1995), Altata Lagoon, Mexico (Green-Ruiz and Paez-Osuna 2001), and San Rafael Lagoon, Chile (Ahumada and Rudolph 2004)).

The profiles of the strongly bound concentrations of Al and Fe (Fig. 3) show a clear reduction trend starting at the canal construction layer. Weakly bound concentrations of these two metals were not significantly affected. Averaging the results for the six cores, strongly bound concentrations of Al and Fe below this layer ranged from $744 \pm 166 \text{ mg g}^{-1}$ for Al, decreasing to $577 \pm 17 \text{ mg g}^{-1}$ at the top of the core. For Fe, strongly bound concentrations decreased from $533 \pm 8 \text{ mg g}^{-1}$ at the canal construction layer to $39 \pm 5 \text{ mg g}^{-1}$ at the top of the core. This suggests a reduction of their loads to the lagoon associated with decreasing soil surfaces available for leaching, since soils are the major source of these two elements to the lagoon. The lack of response of the weakly bound fractions of Al and Fe concentrations further supports this hypothesis.

The distribution of Mn also presented a sharp reduction in concentrations just after the construction of the canal (Fig. 3), since Mn is also enriched in the local watershed soils, where it is associated with Fe as oxy- and hydroxides (Lacerda and Marins 2006). Just above this layer, however, Mn concentrations increased, probably reflecting the more oxidizing conditions of the lagoon due to the opening of the canal, favoring Mn precipitation. Concentrations reached an average peak of $635 \pm 256 \mu\text{g g}^{-1}$ considering all the six cores analyzed.

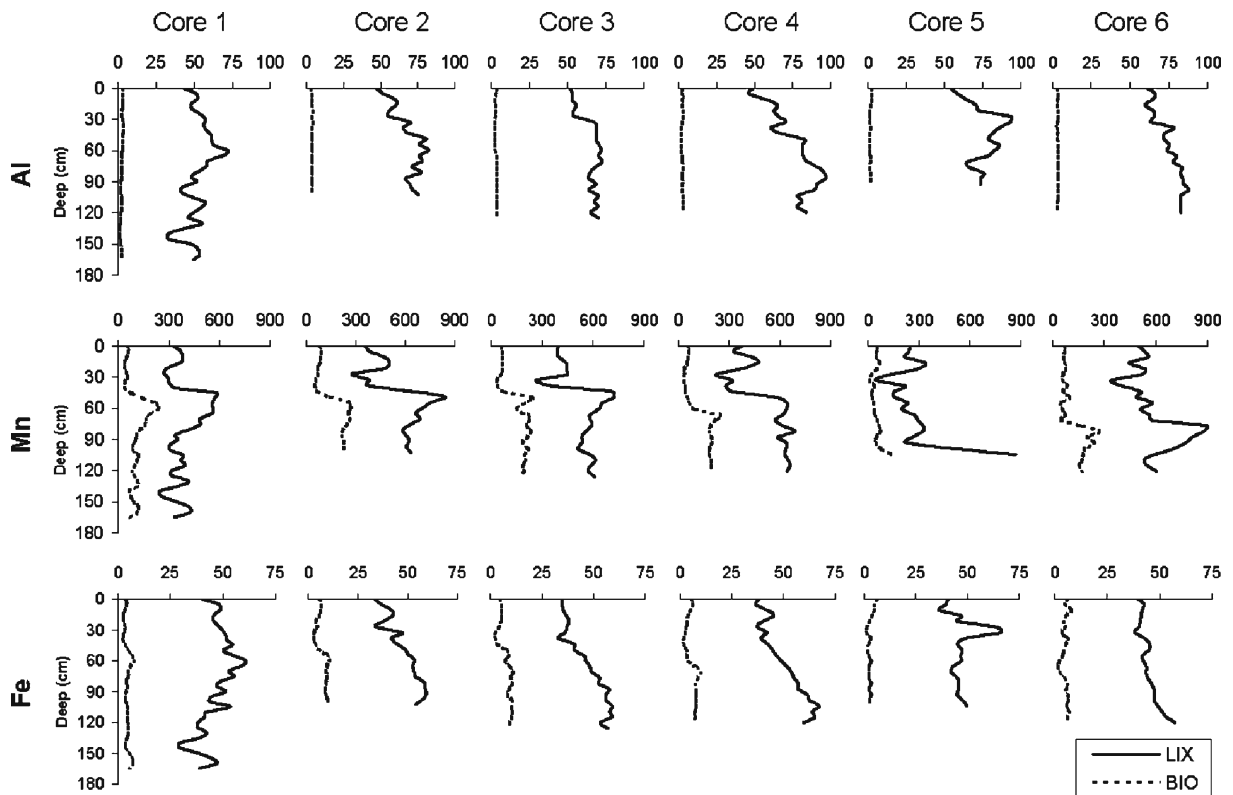


Fig. 3 Distributions of Al, Fe, and Mn concentrations in sediment cores from Rodrigo de Freitas Lagoon, Rio de Janeiro, SE Brazil (Al and Fe in mg g^{-1} d.w., Mn in $\mu\text{g g}^{-1}$, d.w.). *STR* strongly bound, *WEA* weakly bound

In more recent layers, with the clogging of the canal, Mn concentrations decreased again to the surface of the cores (average of $376 \pm 80 \mu\text{g g}^{-1}$ among the six cores), probably reflecting sub-oxic or even reducing conditions of the lagoon due to increasing eutrophication. These new environmental conditions probably resulted in an export of Mn from sediments to the water column, as indicated by the high porewater concentrations observed. The variability also observed in the weakly bound fraction of Mn concentrations in these sediments supports this assumption.

The distribution of Zn, Pb, and Cu (Fig. 4) also changed at the canal construction layer. Below this layer, these three metals presented relatively constant concentrations of $95 \pm 20 \mu\text{g g}^{-1}$ for Zn, $25 \pm \mu\text{g g}^{-1}$ for Pb, and $39 \pm 7 \mu\text{g g}^{-1}$ for Cu (averages of the six cores), both in the weakly and strongly bound fractions, probably reflecting the background values of these metals for the region. After the intensive human occupation verified

after the canal constructions, concentrations of Zn, Pb, and Cu increased steadily to their highest values at the surface of the sediment. The contribution of the weakly bound fraction is significant above the canal construction layer. In core P6, a second concentration peak of these metals occurs, and may be associated with Mn oxi-hydroxide coprecipitation suggested by Mn distribution in this core (Fig. 3) and probably associated with the opening of the canal.

These results suggest that, after the building of the canal, anthropogenic sources of Cu, Zn, and Pb dominated the flux of these metals to the lagoon. All three metals are ubiquitous components of urban runoff and urbanization in general and are transported both as particulate and dissolved forms, thus also affecting the weakly bound fraction of total metal concentrations (Grassi et al. 2005).

The concentrations of Cr and Ni (Fig. 4) showed a rapid reduction after the building of the

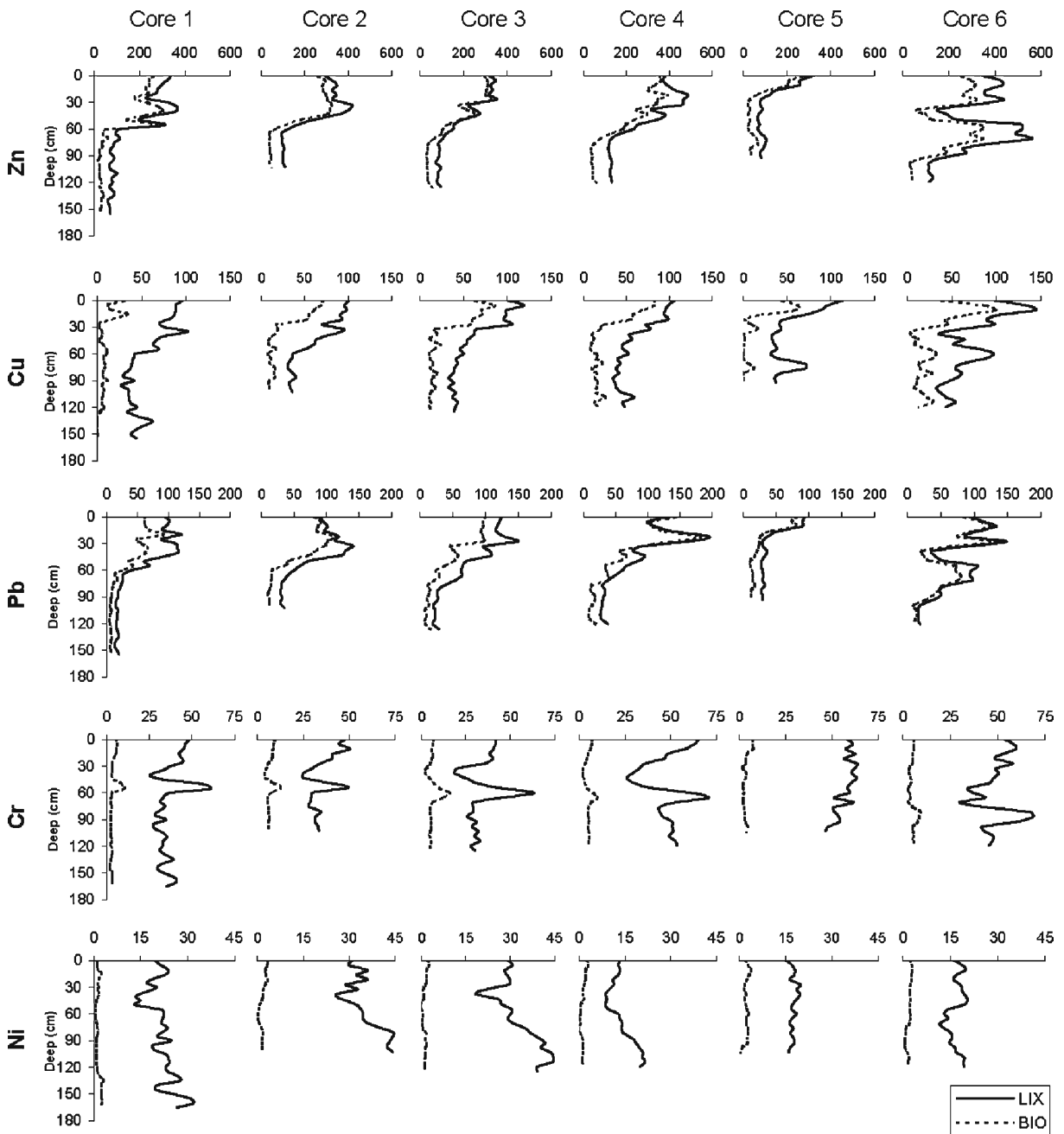


Fig. 4 Distributions of metals (Zn, Pb, Cu, Cr, and Ni) in sediment cores from Rodrigo de Freitas Lagoon, Rio de Janeiro, SE Brazil (all concentrations in $\mu\text{g g}^{-1}$, d.w.). *STR* strongly bound, *WEA* weakly bound

canal. Similarly to that observed for Al and Fe, these metals are enriched in local soils, and natural inputs are very significant (Lacerda and Marins 2006). However, they are also ubiquitously present in effluents of many anthropogenic

sources, and therefore concentrations started increasing with increasing urbanization, in a manner similar to the behavior verified for Mn. However, no significant effect was detected in the weakly bound fraction of these metals concentrations,

Table 1 Spearman correlation between the strongly bound fractions of metal concentrations analyzed

| | Al | Mn | Fe | Zn | Cu | Pb | Ni | Cr | Fine | O.M. |
|------|------|-------------|-------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Al | 1.00 | 0.42 | 0.55 | -0.15 | -0.38 | -0.26 | -0.15 | 0.30 | 0.04 | -0.45 |
| Mn | | 1.00 | 0.38 | 0.01 | -0.17 | -0.12 | 0.24 | -0.09 | 0.37 | 0.11 |
| Fe | | | 1.00 | -0.47 | -0.52 | -0.50 | 0.24 | 0.02 | 0.03 | -0.46 |
| Zn | | | | 1.00 | 0.81 | 0.89 | -0.34 | 0.05 | 0.28 | 0.63 |
| Cu | | | | | 1.00 | 0.83 | -0.19 | 0.23 | 0.02 | 0.71 |
| Pb | | | | | | 1.00 | -0.19 | 0.02 | 0.24 | 0.54 |
| Ni | | | | | | | 1.00 | -0.42 | 0.05 | -0.07 |
| Cr | | | | | | | | 1.00 | -0.28 | 0.09 |
| Fine | | | | | | | | | 1.00 | 0.16 |
| O.M. | | | | | | | | | | 1.00 |

Bold values = significant correlations at $p < 0.05$; $n = 144$ samples.

Fine fine fraction ($<63 \mu\text{m}$), *O.M.* organic matter content

suggesting low response to eventual changes in the physico-chemical conditions of the lagoon environment. Distribution of Cr in core P5 is rather odd and may reflect the rather altered nature of this core, probably as a result of dredging or sediment mobilization due to the proximity to the canal entrance.

The correlation matrix presented in Table 1 corroborates the discussion above. Two groups of metals can be easily characterized: (1) metals mostly of litogenic origin (Fe, Al, and Mn) with a reduction trend in concentrations toward the surface, after the building of the canal, possibly due to the reduction of erosion and leaching of soils in the drainage basin following urbanization and (2) metals of anthropogenic origin (Zn, Cu, and

Pb), showing highly significant positive correlation among them and with the organic matter content of sediments and negative correlations with Al, Fe, and Mn. The increasing concentrations are coincident with the beginning of the urban occupation with increasing input of sewage and surface runoff to the lagoon. A third group is represented by Cr and Ni, either showing correlations with the geogenic or the anthropogenic group, suggesting varying contributions of the different source groups.

Table 2 presents a comparison between weakly and strongly bound concentrations of all metals studied before (background values) and after the construction of the Jardim de Alah canal and the intensive human occupation and the

Table 2 Strongly and weakly bound metals concentrations in bottom sediments of Rodrigo de Freitas Lagoon, after and before the human activity (mean \pm standard deviation;

Al and Fe in mg g^{-1} , d.w., other metals in $\mu\text{g g}^{-1}$, d.w.; BCG—ground)

| Fraction | Age | Al | Fe | Mn | Cu | Pb | Zn | Cr | Ni |
|---|------------------------------------|-------------|---------------|---------------|---------------|---------------|----------------|---------------|---------------|
| Strongly bound | Before human activity ($n = 68$) | 66 ± 16 | 52 ± 9 | 515 ± 129 | 39 ± 7 | 25 ± 8 | 95 ± 20 | 36 ± 8 | 28 ± 10 |
| | After human activity ($n = 49$) | 65 ± 11 | 43 ± 5 | 489 ± 162 | 77 ± 24 | 96 ± 32 | 319 ± 100 | 44 ± 12 | 21 ± 8 |
| Weakly bound | Before human activity ($n = 68$) | 3 ± 1 | 7 ± 3 | 169 ± 54 | 10 ± 6 | 11 ± 6 | 36 ± 11 | 4 ± 1 | 1 ± 1 |
| | After human activity ($n = 49$) | 3 ± 1 | 5 ± 2 | 90 ± 68 | 31 ± 26 | 72 ± 33 | 248 ± 80 | 6 ± 3 | 2 ± 1 |
| Enrichment factor (Strongly bound fraction) | | – | 0.9 ± 0.1 | 1.0 ± 0.3 | 2.0 ± 0.6 | 3.9 ± 1.3 | 3.4 ± 1.1 | 1.3 ± 0.4 | 0.8 ± 0.3 |
| Enrichment factor (Weakly bound fraction) | | – | 0.6 ± 0.3 | 0.5 ± 0.4 | 2.7 ± 2.3 | 5.8 ± 2.7 | 6.23 ± 2.0 | 1.3 ± 0.6 | 1.3 ± 0.7 |

Background depths were different, depending on individual cores. In cores P1, P2, P3, and P4, background depths were below 60, 60, 70, and 65 cm, respectively, whereas in core P6, background depth was below 90 cm

respective enrichment factors. The corer P5 was excluded from this analysis due to the higher sand content and strong marine influence. Background depths were different depending on individual cores. In cores P1, P2, P3, and P4, background depths were below 60, 60, 70, and 65 cm, respectively, whereas in core P6 background depth was below 90 cm. Relating the background concentration values and the sediments deposited after human activities at the top of the cores makes possible the calculation of the enrichment factor. The metals' enrichment factors

were calculated using Al for data normalization (Table 2).

Metals (Al, Fe, Cr, and Ni) derived mostly from natural sources, in this case soil denudation, and presented higher concentrations in the strongly bound fraction prior to the building of the canal. For these metals, the weakly bound fraction contributes little to the total concentrations, less than 5% for Al and Ni and less than 10% for Cr and Fe, respectively. The weakly bound fraction of Cu, Pb, and Zn concentrations on the other hand significantly contributes to

Table 3 Principal components analyses of sediment core P1

| Variable | F1 | F2 | F3 | F4 |
|-------------------------------|-------|-------|-------|-------|
| Al (STR) | 0.134 | 0.550 | 0.059 | 0.107 |
| Al (WEA) | 0.730 | 0.140 | 0.004 | 0.004 |
| Mn (STR) | 0.008 | 0.520 | 0.264 | 0.001 |
| Mn (WEA) | 0.171 | 0.505 | 0.213 | 0.008 |
| Zn (STR) | 0.827 | 0.025 | 0.001 | 0.004 |
| Zn (WEA) | 0.864 | 0.003 | 0.021 | 0.009 |
| Cd (STR) | 0.398 | 0.000 | 0.151 | 0.103 |
| Cd (WEA) | 0.815 | 0.000 | 0.001 | 0.014 |
| Fe (STR) | 0.218 | 0.603 | 0.002 | 0.028 |
| Fe (WEA) | 0.169 | 0.254 | 0.461 | 0.009 |
| Cu (STR) | 0.715 | 0.160 | 0.031 | 0.000 |
| Cu (WEA) | 0.184 | 0.123 | 0.047 | 0.340 |
| Pb (STR) | 0.908 | 0.017 | 0.000 | 0.001 |
| Pb (WEA) | 0.910 | 0.006 | 0.003 | 0.003 |
| Cr (STR) | 0.321 | 0.000 | 0.327 | 0.091 |
| Cr (WEA) | 0.565 | 0.017 | 0.184 | 0.039 |
| Ni (STR) | 0.217 | 0.004 | 0.312 | 0.178 |
| Ni (WEA) | 0.003 | 0.488 | 0.040 | 0.000 |
| Fine fraction | 0.774 | 0.073 | 0.032 | 0.043 |
| Organic matter | 0.353 | 0.395 | 0.097 | 0.033 |
| Dissolved Mn | 0.572 | 0.017 | 0.008 | 0.009 |
| Dissolved Fe | 0.031 | 0.055 | 0.043 | 0.291 |
| P-Inorganic | 0.845 | 0.009 | 0.007 | 0.030 |
| P total | 0.834 | 0.045 | 0.003 | 0.003 |
| P-organic | 0.756 | 0.089 | 0.008 | 0.006 |
| C-inorganic | 0.224 | 0.504 | 0.005 | 0.015 |
| C total | 0.300 | 0.610 | 0.029 | 0.000 |
| C-organic | 0.286 | 0.613 | 0.023 | 0.000 |
| S total | 0.002 | 0.412 | 0.138 | 0.134 |
| N total | 0.520 | 0.215 | 0.001 | 0.003 |
| Salinity | 0.285 | 0.191 | 0.028 | 0.272 |
| Water percent | 0.892 | 0.000 | 0.003 | 0.001 |
| Density | 0.190 | 0.191 | 0.130 | 0.062 |
| Porosity | 0.787 | 0.035 | 0.034 | 0.038 |
| PO ₄ ³⁻ | 0.291 | 0.302 | 0.043 | 0.229 |
| NH ₄ ⁺ | 0.135 | 0.059 | 0.088 | 0.103 |
| <i>Littoridina</i> | 0.045 | 0.003 | 0.373 | 0.079 |
| Shell fragments | 0.564 | 0.036 | 0.043 | 0.020 |

STR strongly bound concentrations, WEA weakly bound concentrations

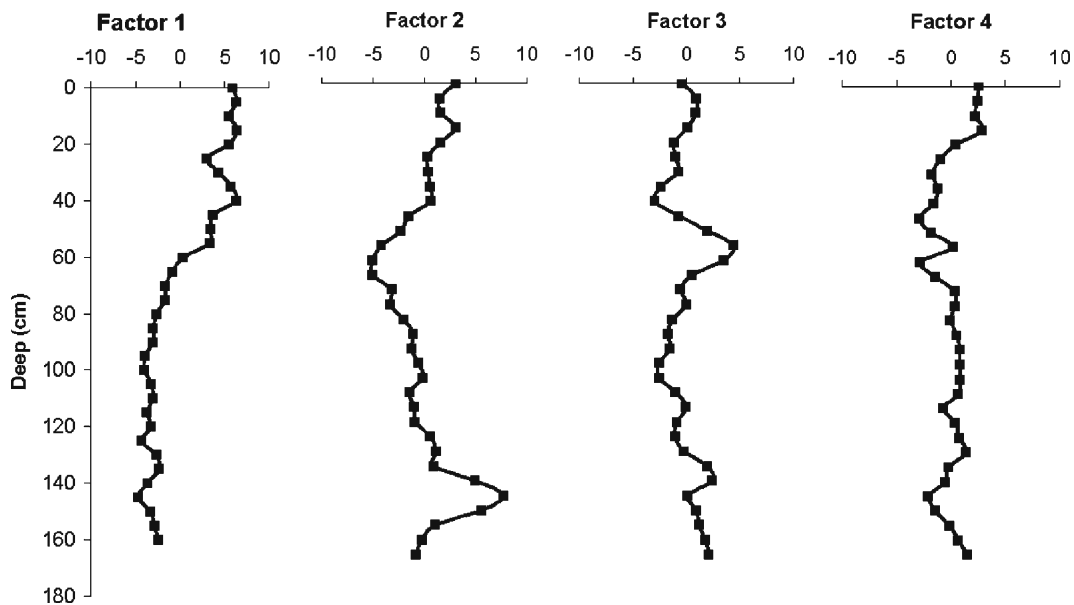


Fig. 5 Factor profiles of principal components analyses in sediment core P1

their total concentrations (Table 2), particularly after the building of the canal, following the urbanization of the watershed, when the contribution of the weakly bound fraction reached 28%, 43%, and 44% of the total concentrations of Cu, Pb, and Zn, respectively. Weakly and strongly bound concentrations of Mn decreased after the canal construction, suggesting changes in the redox equilibrium of sediments and export of Mn from sediments to the water column, as a result of increasing organic matter (sewage) input resulting from urbanization.

Enrichment factors reflect better the evolution of metal loads to the lagoon prior to and after the major changes occurring in the watershed. For Fe and Mn, enrichment factors were lower <1.0 after the construction of the canal to the surface of the core, implying a decrease of these metal loads from the watershed. Enrichment factors for Cu, Pb, and Zn were much higher than 1.0, suggesting large inputs from anthropogenic sources after urbanization. For Cr and Ni, enrichment factors were close to 1.0, implying that the decrease of natural loads from soil denudation was counterbalanced by anthropogenic inputs.

A principal component analysis (Table 3) was carried out through core P1, where the largest

amount of parameters was analyzed. The results show factor 1 (with 44% of data variance) to present a strong correlation with Pb and Zn, characterizing the anthropogenic impact in the area. Factor 2 (19%), with strong correlation with C, Al, Fe, and Mn, identifies an anomaly that occurred at 140 cm of depth, much before the anthropogenic activity in the region, which we have not evaluated in detail in this study. Factor 3 (8.6%), with strong correlation with weakly bound Fe concentrations, Cr and Ni, relates to the reduction of the lithogenic fraction input due to the construction of the canal. Finally, factor 4 (6.0%) relates to the influence of the composition of the interstitial water in the sediment, with strong correlation with weakly bound Cu, dissolved Fe, dissolved PO_4^{3-} , and salinity (Table 3, Fig. 5).

Conclusion

The results presented here show the influence of soil use change on the metal loads to Rodrigo de Freitas Lagoon. Building of an artificial canal and further urbanization of the watershed resulted in decreasing inputs of metals from natural sources (Fe and Al). On the other hand, urban runoff

increased the inputs of Pb, Zn, and Cu and, to a certain extent, of Mn, Cr, and Ni, to concentrations similar to areas receiving these metals from known anthropogenic point sources, showing very high enrichment factors and an increase in the proportion of weakly bound metals in sediments. This fraction is potentially mobilized to the water column. The relative shallowness typical of coastal lagoons and the high accumulation capacity of fine grained sediments may maximize the bioavailability of deposited metals present in sediments under weakly bound forms.

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