Marine Pollution Bulletin 146 (2019) 552–561

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

# Assessment of a coastal lagoon metal distribution through natural and anthropogenic processes (SE, Brazil)

Gaby Quintal F. Beraldi[a], Carlos Eduardo de Rezende[b], Marcelo Gomes de Almeida[b], Carla Carvalho[c], Luiz Drude de Lacerda[d], Roberto Nascimento de Farias[a], Marcella Vidal[c], Michael Douglas P. Souza[e], Mauricio Mussi Molisani[e,*]

[a] *Programa de Pós-Graduação em Ciências Ambientais e Conservação, Universidade Federal do Rio de Janeiro campus Macaé, Macaé, Brazil*
[b] *Laboratório de Ciências Ambientais, Universidade Estadual do Norte Fluminense Darcy Ribeiro, Campos dos Goytacazes, Brazil*
[c] *Programa de Pós-graduação em Geociências (Geoquímica), Universidade Federal Fluminense, Niterói, Brazil*
[d] *Instituto de Ciências do Mar, Universidade Federal do Ceará, Fortaleza, Brazil*
[e] *Instituto de Biodiversidade e Sustentabilidade, Universidade Federal do Rio de Janeiro, campus Macaé, Macaé, Brazil*

ARTICLE INFO

*Keywords:*
Domestic sewage
Contamination
Sedimentation rate
Mass-balance
Fish
Aquatic macrophyte

ABSTRACT

The present study intends to assess the metal pollution of a eutrophic coastal lagoon, analyzing the long-term and actual metal content in surface sediments, suspended particles, aquatic macrophyte and fish species, and the loads emitted from natural processes and anthropogenic sources, including the relative emission of domestic untreated sewage. Distribution indicated contamination of suspended particles with Cd and the predominance of Pb in the bioavailable form in surface sediments which may explain Cd and Pb contamination in fish. Domestic untreated sewage was an important source of Cu and due to the lagoon's management, this source may be increasing the metal content in the lagoon's surface sediments. Soil loss, atmospheric deposition and solid waste disposal also contributed to metal inputs to the lagoon. Extensive contamination has been prevented by the lagoon's management such as sandbar opening. Metal retention within the watershed soils reduce the effective metal transference and lagoon pollution.

## 1. Introduction

Metal contamination in coastal lagoons is always an important issue, since such lentic environments are hotspots for biodiversity and human activities, while, at the same time, they are also a sink for continental runoff, with possible long-term accumulation and consequent deleterious effects (Lacerda, 1994; Kjerfve, 1994; Esteves et al., 2008). The geological matrix, erosion and soil losses are the primary natural sources of metals to the lagoons, and, depending on metal binding to particles, water physicochemical conditions and potential solubility, metals can become available to food chains (Salomons and Forstner, 1984; Lacerda et al., 1992; Mendonza-Carranza et al., 2016). In fact, metal bioavailability from sedimentary compartment of the coastal zone, including tropical coastal ecosystems, is influenced by a wide range of physical, chemical, biological factors; from which the total concentration in sediments do not necessarily represents a potential risk to biota, as the entire metal bound onto particles may not be release from particles and be transfer to organism cells. Thus, to extract information about the metal availability and biological exposure from sediments, geochemical indexes or chemical extraction procedures has been applied, obviously with limitations (Chakraborty et al., 2014, 2019).

However, coastal lagoons are distributed throughout desirable human living areas and, consequently, anthropogenic activities have increased metal inputs to these ecosystems. Untreated domestic sewage seems one of the most frequent pollution sources in coastal lagoons. This effluent may be enriched with Zn, Cu, Cr, Pb and may increase the importance of this anthropogenic source to lagoon's metal budget when high sewage loads are discharged (Nriagu and Pacyna, 1988; Aguilar-Betancourt et al., 2016). In addition, metal pollution of coastal lagoons may be influenced by several features, such as shallow environments, exposure to winds and diurnal/semi diurnal tides as well as fluvial input that may lead to changes in the physical and chemical conditions of the water column, with possible effects on metal behavior (Kjerfve, 1994; Lacerda and Gonçalves, 2001; Caliman et al., 2010).

Some studies have evaluated metal distribution simultaneously in abiotic compartments and diverse biological groups (Radwan et al., 1990a, 1990b; Fernandes et al., 1994; Jara-Marini et al., 2009;

* Corresponding author.
*E-mail address:* mauriciomolisani@macae.ufrj.br (M.M. Molisani).

https://doi.org/10.1016/j.marpolbul.2019.07.007
Received 26 November 2018; Received in revised form 3 July 2019; Accepted 3 July 2019

Mendonza-Carranza et al., 2016), but none associated such metal distribution to the influence of natural processes and anthropogenic discharges, including the relative importance of untreated domestic sewage on lagoon's metal distribution. In developing countries, such as Brazil, untreated domestic sewage is still emitted into many coastal lagoons, surrounded by cities. In Brazil, spreading urbanization and socioeconomic development has occurred more intensively during the last 40–50 years, with extensive modification in land use and land cover, cities expansion and increased metal emissions from urban runoff, sewage, industries, animal husbandry, and soil loss among others (Knoppers et al., 1990; Fernandes et al., 1994; ., 2008; Molisani et al., 2013). In addition, urbanization imposes management practices of coastal lagoons, such as artificial sandbar openings that may also influence the chemical composition of the water body (Suzuki et al., 1998). In this context, this study aims to assess the metal pollution of a eutrophic coastal lagoon by means of information on the relative emissions from anthropogenic sources and natural processes, and the long-term and current metal distribution/accumulation in sediment, suspended particles, and different aquatic macrophytes and fish, under the hypothesis that domestic sewage influences metal distribution and bioavailability.

## 2. Material and methods

### 2.1. Study area

Imboassica Lagoon is a coastal environment located in southeastern Brazil, formed by ocean progression and transgression movements (Panosso et al., 1998). The drainage basin is small, 58 $km^2$, with a lagoon area of 3.26 $km^2$ and the Imboassica river as the main fluvial tributary. The lagoon has brackish waters with maximum water column depth of about 2.2. m. It is separate from the Atlantic Ocean by a sandbar which has one small channel connecting it to the open sea. Land use comprised forest (19%), pasture (43%), urbanization (12%) and *restinga* vegetation, exposed soil and others (26%) (Barreto, 2009). Since the late 80's, the lagoon's watershed has been urbanized due to offshore oil exploration activities. Petroleum exploration has brought an increasing population to this coastal region, which suffer intense unplanned occupation of its surrounding areas, leading to threats such as untreated domestic sewage discharges into the lagoon. Other activities installed throughout the lagoon watershed, mainly factories that manipulate metallic pipes for the offshore oil exploration activities are potential metal sources to the lagoon. As a result, many studies have investigated the eutrophic conditions induced by untreated sewage disposal and its overall effects in the Imboassica Lagoon (Esteves et al., 2008; Marotta et al., 2009).

### 2.2. Sampling and analytical methods

The importance of sewage and other anthropogenic sources (solid waste disposal, urban runoff, animal husbandry and agriculture) and natural processes (soil loss and atmospheric deposition) on metal emissions to the lagoon were evaluated by the emission factor model (Nriagu and Pacyna, 1988; USGS, 2011; Filho et al., 2015; Molisani et al., 2013). This approach estimates metal loads based on the watershed features, such as soil type and area, dry and wet atmospheric deposition, rainfall levels, population consumption and production, urbanization parameters, agriculture and animal husbandry production, as well as metal concentrations related to production/consumption parameters and natural processes. The data input includes the compilation of the range or mean values of parameters from the literature, but always adapted to local conditions when data are available to maximize the reliability of the emission factors.

Metal loads from atmospheric deposition are directly related to basin area and the concentration of the metals resulting from atmospheric deposition, adjusted by the retention rate of the element by the soil and were estimated according the Eq. (1):

$$L_{atm}^{M} = \rho_{rw} \cdot A_{ws} \cdot (1 - \alpha_{rs})/10^3 \tag{1}$$

where *LMatm* is the estimated metal load from atmospheric deposition (kg $yr^{-1}$), ρ*RW* is the deposition of each metal depending of concentrations in rainwater and the annual rainfall in the region (mg $m^2$ $yr^{-1}$), Aws is the basin area ($km^2$), α*rs* is the soil retention factor. Considering the level of preservation and incipient industrialization and urbanization n the study area, we have used average metal bulk atmospheric deposition from the proposed range of the literature from Brazilian coast for Cu: 0.28–3.5 mg $m^{-2}$ $yr^{-1}$; Zn: 0.9–9.3 mg $m^{-2}$ $yr^{-1}$; Pb: 2.7–15.0 mg $m^{-2}$ ano$^{-1}$; Cd: 0.4–5.0 mg $m^{-2}$ $yr^{-1}$ (Marins et al., 1996; Johnson and Lindberg, 1998; Tan and Wong, 2000; Mello, 2001; Silva-Filho et al., 1998, 2006) weighted by the basin area and annual rainfall (1200 mm) and corrected by the soil retention rates for each metal (Cu, Pb: 35%; Zn: 45%; Cd: 40%) (Malavolta and Dantas, 1980; Golley et al., 1978).

The metal emission from the physical and chemical denudation of soil type of the watershed were calculated according the Eq. (2):

$$L_s^M = \sum_{J=1}^{4} psj \cdot A_j \cdot L_s \cdot (1 - \alpha_{rs}) \tag{2}$$

where $L_s^M$ represents each metal load from soil loss to the river flow (kg $yr^{-1}$) as a function of ρ*sj* which is the concentration of each metal in a given soil, $A_j$ is the area corresponding to each type of soil in the basin area ($km^2$), Ls is the average soil loss from gentle tropical slopes and non-mechanized agriculture similar to the soils in the coastal areas of Brazil; α*rs* is the soil retention factor. When determining metal emissions from physical and chemical denudation of soils, we considered that agricultural and urban tropical soils under non-mechanized cultivation have an annual soil loss of 128 t $km^2$ $yr^{-1}$ (Greenland and Lal, 1977); soils types in the watershed (Latosol, Sand, Podsol/Latosol, Aluvial/Regosol) (Embrapa Solos, unpublished data) and the average metal concentration in soils from ranges for similar soils in Brazilian coastal areas with low declivity and industrial development: Zn: 21–126 μg $g^{-1}$; Cu: 9–25 μg $g^{-1}$; Pb: 0.8–53.0 μg $g^{-1}$; Cd: 0.7–2.0 μg $g^{-1}$ (Silva, 1996; Andrade and Mattiazzo, 2000; Ramalho et al., 2000; Ramalho and Sobrinho, 2001; Canellas et al., 2003; Fadigas et al., 2006).

Metal emission by domestic effluents have the assumption of no-treatment prior released into the lagoon. Metal loads from domestic effluents are directly proportional to the average concentrations of metals in wastewater (Zn: 0.12; Cu: 0.06; Pb: 0.02; Cd: 0.003, in mg $L^{-1}$) (Smith et al., 1997; Von Sperling, 1996; Houhou et al., 2009); the population in the watershed (10,000 inhabitants) (IBGE Cidades, 2014) and to the amount of water consumed per capita (125 l inhab$^{-1}$ day$^{-1}$ for rural inhabitants and 220 l inhab$^{-1}$ day$^{-1}$ for urban population (IBGE, 2012) and were calculated according to the Eq. (3):

$$L_{ww}^{M} = \sum_{i=1}^{2} \frac{(P_{ww} \cdot P_u i \cdot Q_u i \cdot \beta \cdot 365)}{10^9} + \sum_{i=1}^{2} \frac{(P_{ww} \cdot P_r i \cdot Q_r i \cdot \beta \cdot 365)}{10^9} \tag{3}$$

where $L_{WW}^{M}$ is the metal load from untreated domestic sewage of urban and rural areas of the watershed (kg $yr^{-1}$); $P_{ww}$ is the metal concentration in raw sewage (mg $L^{-1}$), $P_u$i and $P_r$i are the urban and rural population, respectively, in each municipality within the lagoon watershed; $Q_u$i and $Q_r$i are the urban and rural water consumption per capita, respectively; β is the water/sewage return rate.

In order to calculate the metal loads in urban runoff, we used the urbanization rate of watershed estimated at 12% of the basin area (Barreto, 2009), average annual rainfall (1200 mm) and the average metal concentrations in urban runoff (Davis et al., 2001; Sorme and Lagerkvist, 2002), as shown in Eq. (4). The study site lacks large urbanized areas and thus low level of soil impermeabilization.

$$L_{Urf}^{M} = \left(\frac{p_{Urf}.A_{Ui}}{10^6}\right) \tag{4}$$

where $L_{Urf}^{M}$ is the estimated metal load resulting from urban area runoff of the lagoon watershed; $p_{Urf}$ is the metal concentration obtained from urban runoff and annual rainfall; $A_{Ui}$ is the urban area within the basin ($km^2$).

Emissions from solid waste disposal are given as a function of population of the watershed, average waste per capita production of 0.45 kg inhab$^{-1}$ day$^{-1}$ (IPEA, 2012), and the average metal concentration of domestic solid wastes (Zn: 150; Cu: 45; Pb: 95; Cd: 9.5, all values in mg kg$^{-1}$) (Nriagu and Pacyna, 1988; Binner et al., 1996; Essakku et al., 2005). The estimates were corrected by metal soil retention (Golley et al., 1978) and the improper waste disposal, which in Brazil was estimated, on average, at 42% of total produced and properly disposed (ABRELPE, 2011), as described in Eq. (5):

$$L_{sw}^{M} = P_{sw}\cdot Pi\cdot G_{sw}i\cdot\delta_{sw}\cdot 365\cdot(1-\alpha_{rs})/10^9 \tag{5}$$

where $L_{sw}^{M}$ is the metal load from solid water disposal within the basin; $P_{sw}$ is the mean metal concentration in municipal solid waste; $P_i$ is the population within the lagoon watershed; $G_{sw}i$ is the per capita production of wastes; $\alpha_{rs}$ is the soil retention rate; $\delta_{sw}$ is the adequacy factor according to the type of the waste disposal.

The fertilizers and fungicides on crops are important responsible for the metal emission to water bodies from agriculture (Lima, 1994; Tundisi, 2006; Embrapa, 2013). Eq. (6) was used to calculate the emission estimates from this source.

$$L_{A}^{M} = \sum_{j=1}^{5}\left(\frac{P_{tj}\cdot A_{tij}}{10^3}\right) \tag{6}$$

where $L_{A}^{M}$ is the metal load from six most common crops cultivate in the watershed (banana, cassava, coconut, bean and sugar cane); Ptj is the metal applied as fertilized and fungicide (kg ha$^{-1}$) (Lima, 1994; Tundisi, 2006; Embrapa, 2013) and the loss percentage according to crop type (Silva et al., 2000; Golley et al., 1978); $A_{tij}$ is the cultivated area (ha yr$^{-1}$) of each crop (IBGE Cidades, 2014).

Livestock farming metal emissions were described in Eq. (7):

$$L_{LF}^{M} = \sum_{j=1}^{4} p_{tj}\cdot LF_{ij}\cdot(1-\alpha_{rs})/10^9 \tag{7}$$

where $L_{LF}^{M}$ is the metal load from animal manure in the region (cattle, chicken, pig, horse), $P_{tj}$ is the emission factor related to the annual quantity of manure produced per animal in the watershed (j) (10, 2.5, 1.0 and 0.18 kg animal$^{-1}$ day$^{-1}$, for cows, horses, pigs, and chicken, respectively) and the metal concentration in raw manure (mg kg$^{-1}$) (EMBRAPA, 2004); $LF_{ij}$ is the number of animals within the basin (i) (IBGE Cidades, 2014) and $\alpha_{rs}$ is the soil retention rate (Golley et al., 1978).

Surface sediment, suspended particles, and aquatic macrophytes were collected simultaneously from three sites in the lagoon, including the area under influence of the main river inputs (S1), during three events, covering the rainy and dry seasons between 2014 and 2015. (Fig. 1). Aquatic macrophyte species, floating *Eichornia crassipes* (Mart.) Solms and rooted and emergent *Typha domingensis* (Pers.) were collected from three stands and washed with lagoon water to remove attached particles. In the laboratory, leaves and roots were separated, and then they were washed again to remove particles and dried at 40 °C to a constant weight and ground in a fine powder in a laboratory mill. Fish species, the carnivorous *Hoplias malabarius* (Bloch) and omnivorous *Geophagus brasiliensis* (Quoy & Gaimard, 1824) were collected by gill nets placed in the middle of the lagoon ($n = 25$ and $n = 30$, respectively). Fish were measured and weighted in the laboratory, muscle and liver were separated and freeze-dried.

Suspended particles were obtained after filtration of surface water samples through 0.45 μm pore cellulose acetate membranes. Surface sediments were collected with a Teflon grabber. One sediment core was sampled and sliced at 1–2 cm intervals. In the laboratory, grain size was determined with a particle analyzer (Shimadzu SALD-310). C and N content in sediments (%) was determined with an Organic Elemental Flash 2000 analyzer (Thermo Scientific). Quantification was performed using analytical curves from Buffalo River standards (SRM 2704, National Institute Standards), with inter-replicate precision close to 95%. Accuracy was verified using the Standard OAS/isotope—Low Organic Soil (elemental microanalysis), with a 94% recovery. Stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) were also determined in sediments using a Thermo Quest-Finnigan Delta Plus isotope ratio mass spectrometer (Finnigan-MAT) interfaced to an Elemental Analyzer (Carlo Erba). Pee Dee Beleminite carbonate and atmospheric nitrogen were used as standard values and analytical precision was of ± 0.1‰ for $\delta^{13}C$ and ± 0.2‰ for $\delta^{15}N$.

The chronology of the core samples was determined through the sediment accumulation rates were determined by measuring the natural radioisotope $^{210}Pb$, which has a half-life of 22.3 years and yields accumulation rates for approximately the past 100 years, following Patchineelam and Smoak (1999). Sediments were oven dried (50 °C), disaggregated and homogenized before analyses and its water content was determined as the weight loss after drying. Before analysis, sediment sub-samples were sealed and stored for at least 21 days to allow the establishment of secular equilibrium between $^{226}Ra$ and its granddaughters. Sediment sub-samples were counted for at least 24 h to determine $^{226}Ra$ and $^{210}Pb$ activities by gamma ray spectrometry, using a Canberra HPGe (High Purity Germanium Detector) spectrometer with an efficiency of 40%, housed in a lead shield and coupled to a multichannel analyzer installed at the Laboratório de Radioisótopos Aplicados ao Meio Ambiente of Fluminense Federal University (LARAMAM). $^{214}Pb$ and $^{214}Bi$. $^{226}Ra$ activities were determined by a weighted average of two $^{214}Pb$ energies (295.2 and 351.9 keV) and a $^{214}Bi$ gamma peak at 609.3 keV, while $^{210}Pb$ activities were determined by the direct measurement of 46.5 keV gamma peak. Background energies were subtracted from the photo-peak areas and self-absorption corrections were also calculated.

Metal fluxes $T$ (mg m$^{-2}$ year$^{-1}$) were calculated according to Eq. (8):

$$T = \varpi\cdot p_s(1-\phi)\cdot C \tag{8}$$

where: ω is the sedimentation rates (cm yr$^{-1}$); ρs is the mean density of the solids (g.cm$^{-3}$); Ø is the porosity and C is the metal concentration of each sediment core layer (μg g$^{-1}$) (Berner, 1980). A mass-balance budget was constructed considering the surface metal fluxes (accumulation) of the lagoon's sediments in 2014, the emissions from natural processes and anthropogenic sources, also in 2014, and the difference between emission and fluxes (accumulation) to the lagoon representing the metal load retained in the watershed.

Metals in sediments (< 63 μm grain size particles) and suspended particles were obtained by a mixture $HNO_3$ (5 mL), HCl (2 mL) e HF (2 mL), digestion in microwave oven (Mars X-Press CEM) and analyses in ICP-AES (Varian Liberty Series II). The extracts were kept overnight at room temperature and digested in the microwave oven for 40 min (15 min/ramp and 25 min/hold) at 175 °C with potency of 1600 watts. After cooling (30 min), 9.0 mL of $H_3BO_3$ was added for HF neutralization and the samples were digested in microwaves oven for 25 min (15 min/ramp and 10 min/hold) at 175 °C. After cooling (30 min), the final extract was filtrated and the final volume (20 mL) calibrated with $HNO_3$ 0,5 N (adapted from EPA 3052). Metal concentrations were measured using triplicate and analytical blanks. The exchangeable metal (bioavailable) fraction of the surface sediments was determined after overnight 0.5 N $HNO_3$ leaching (Molisani et al., 1999). Accuracy was obtained by the analysis of reference estuarine sediments (NIST SRM 1646a) with total recoveries as follow: Cu: 93%; Zn: 93%; Pb: 96% and Cd: 105%. Aquatic macrophytes and fish were digested with $HNO_3$ according to a methodology adapted from Valitutto et al. (2006) and


**Fig. 1.** Map of the Imboassica coastal lagoon and the sampling sites (adapted from Google Earth).

Paez-Osuna et al. (1991), respectively, and expressed in dry weight.

Plant extraction accuracy was measured by the use of Apple Leaves certified reference material (NIST SRM 1515) with recoveries as follow: Cu: 93%; Zn: 82%; Pb: 93%. For fish, accuracy was obtained by the of Mussel Tissue certified reference material (NIST SRM 2976) with recoveries as follow: Cu: 87%; Zn: 87%; Pb: 89%; Cd: 97%. The bioconcentration factor (BCF) was calculated based on the ratio of metal concentrations in the organisms and in the suspended particles and surface sediments. Environmental and toxicological risk assessments were performed comparing metal concentrations in the organisms to values reported in the literature for pristine and contaminated areas and according to the Brazilian Health Regulatory Agency Guidelines (ANVISA, 1965; ANVISA, 2013).

The D'Agostino-Pearson normality test was applied to verify if the data presented Gaussian distribution. A one-way analysis of variance (ANOVA) followed by Dunnett's test (parametric) or Kruskal-Wallis followed by Dunn's test (nonparametric) was used for comparisons among different sampling sites, seasons and plant and fish species. Nonparametric correlation tests were performed according to the Gaussian test results to verify correlation among geochemistry sediment core parameters and fish biometry and metal concentrations. Differences among groups were considered statistically significant when $P < 0.05$. All analyses were carried out using the GraphPad Prism 5.0 (GraphPad software, USA).

## 3. Results

### 3.1. Relative metal emissions from untreated domestic sewage and other anthropogenic sources and natural processes

The trophic state is induced mainly by untreated domestic sewage which also contributes to the metal inputs to the lagoon. According to the emission factor calculations, metal loads from sewage were estimated for Zn: 93.6 $kg\,yr^{-1}$; Cu: 47.9 $kg\,yr^{-1}$; Pb: 16.7 $kg\,yr^{-1}$ and Cd: 2.2 $kg\,yr^{-1}$. When comparing these loads to those from other anthropogenic sources (agriculture, animal husbandry, urban runoff and solid waste disposal) and natural processes (soil losses and atmospheric deposition), untreated domestic sewage have shown a minor importance relative to the total metal inputs to the lagoon (Table 1). The higher relative contribution of untreated domestic sewage was for Cu (31% of total inputs). On the other hand, the lagoon receives important loads from atmospheric deposition (Cd, Zn), soil losses (Zn, Cu, Pb) and solid waste disposal (Pb, Zn, Cd) (Table 1).

### 3.2. Suspended particle and bottom sediment metal concentrations

Metals emitted from natural processes and anthropogenic sources contribute to the chemical composition of suspended particles and surface sediments. Abundances for suspended particles followed Zn > Cu > Pb > Cd, while surface sediments followed the accumulation order Zn > Pb > Cu > Cd. However, suspended particles

**Table 1**
Metal emission from natural processes and anthropogenic sources to the Imboassica Lagoon ($kg\,yr^{-1}$).

| | Cd | Zn | Cu | Pb |
|---|---|---|---|---|
| Soil losses | 4.0 | 270 | 90 | 100 |
| Atmospheric Deposition | 67 | 238 | 36 | 48 |
| Natural loads | 71 | 508 | 126 | 148 |
| °Agriculture | 0.005 | 0.10 | 1.3 | 0.001 |
| °Animal husbandry | 0.10 | 100 | 19 | 1.0 |
| °Sewage | 2.2 | 94 | 48 | 16.7 |
| °Urban runoff | 7.8 | 6.0 | 1.2 | 2.4 |
| °Solid waste disposal | 8.4 | 105 | 30 | 67 |
| Anthropogenic loads | 18 | 305 | 99 | 87 |
| Total loads | 89 | 813 | 225 | 235 |
| °Relative importance of anthropogenic sources (%) | 20 | 37 | 44 | 37 |
| °Relative importance of sewage (%) | 0.21 | 9.7 | 31 | 5.1 |

**Table 2**
Average ± standard deviation and range of total metal concentrations in suspended particles and surface sediments (μg g$^{-1}$) and labile metal concentrations (% total values) in surface sediments of the coastal lagoon (nd: below detection limit).

| | Zn | Cu | Pb | Cd |
|---|---|---|---|---|
| Suspended particles | 236 ± 145<br>28–446 | 81 ± 59<br>nd-152 | 12 ± 2<br>nd-14 | 8.0 ± 6.0<br>nd-15 |
| Sediment (total) | 45 ± 24<br>10–84 | 14 ± 2.0<br>11–17 | 21 ± 4.8<br>14–29 | 0.77 ± 0.70<br>0.23–2.2 |
| Sediment (labile %) | 34 ± 30<br>8.6–98 | 32 ± 16<br>8.8–60 | 60 ± 20<br>24–80 | 20 ± 14<br>nd-37 |

presented higher Zn, Cu, and Cd concentrations than surface sediments (Table 3). On average, metal bioavailability, here referred as the metal content extracted by 0.5 N $HNO_3$ leaching of surface sediments increased from Cd (20%), Cu (32%), Zn (34%) to Pb (60%) (Table 2). For suspended particles, Cd, Cu, and Zn presented higher concentrations during the rainy season while no differences were found for other metals ($P > 0.05$). Metals in surface sediments were not statistically different between the rainy and dry seasons ($P > 0.05$). Mostly, the lagoon exhibited higher metal concentrations in the area under the influence of the fluvial mouth, indicating river inputs as a controlling factor regarding metal concentrations, dispersion and bioavailability.

### 3.3. Aquatic macrophytes metal concentrations

Considering plant portions, higher metal concentrations were observed in roots compared to leaves for both species ($P < 0.05$) (Table 3), although floating *Eichornia crassipes* presented higher Cu concentrations in roots and Zn in leaves and roots than rooted *Typha domingensis* ($P < 0.05$). No statistical differences were found for the other evaluated metals ($P > 0.05$). Regarding the temporal analysis, metals were similar between seasons, while higher metal contents were determined in plants under the river influence, mainly Zn and Pb in *T. domingensis.*

### 3.4. Fish metal concentrations

Fish size ranged from 25 to 37 cm for *H. malabaricus* and from 15 to 23 cm for *G. brasiliensis* that indicate adult individuals. Liver displayed liver had statistically higher metal concentrations than muscle tissue, excepted for Pb that was similar in both organs in both species ($P > 0.05$) (Table 3). When comparing the fish species, statistically higher Zn values were found in *H. malabaricus;* while higher Pb and Cd concentrations were determined in *G. brasiliensis* liver. Values were similar for the other evaluated metals, values were similar ($P > 0.05$). In general, higher metal values were observed in the dry season, including Zn and Cu *(H. malabaricus),* while temporal variation for the other metals was not observed. Correlations among fish biometric data and metal concentrations were found only for *H. malabaricus*, with negative correlation between Zn and Cd and fish size ($r = -0.51$, $P = 0.01$; $r = -0.50$, $P = 0.01$) and weight ($r = -0.59$, $P < 0.003$; r = −0.59, $P < 0.003$) and positive correlations between Cd and fish biometric data ($r = 0.61$, $P < 0.02$; $r = 0.66$, $P < 0.01$), respectively.

### 3.5. Coastal lagoon metal distribution

The lagoon's metal distribution was analyzed by comparing the metal concentrations of suspended particles, surface sediments, and the average of metal concentrations in leaves from both aquatic macrophyte species and, at the same way, muscle for fish species (Fig. 2). The metal distribution of both producer and consumer organisms have shown similar abundance (plant: Zn > Cu > Pb > Cd; fish: Zn > Cu > Pb > Cd), and were partially consistent with the abiotic matrixes, such as surface sediments (Zn > Pb > Cu > Cd) and suspended particles (Zn > Cu > Pb > Cd). Suspended particles had higher metal concentrations of Cd, Zn, and Cu and were the main compartment of such metals in the lagoon, while Pb was observed mainly in bottom sediments. In general, aquatic macrophytes had higher metal concentrations than fish and their concentrations were smaller than values obtained for the sediments and particles. Based on the trophic chain interpretation, Zn and Cu concentrations in the aquatic macrophyte and fish species may reflect not only the Zn, Cu and Cd exchangeable concentrations in the bottom sediments, but also the higher total concentrations in the suspended particles, from which the exchangeable metal concentrations may gradually increase with increasing total metal loading found in the finer grain-size suspended particles. On the contrary, Pb in organisms may reflect the higher Pb exchangeable concentrations in the bottom sediments and in lesser intensity the smaller total concentrations in the suspended particles that, similarly, may gradually reduce the Pb exchangeable forms in the suspended particles.

**Table 3**
Mean ± standard deviation of metal concentrations (μg g$^{-1}$, dry matter) in plant portions and organs of fish species.

| | Zn | Cu | Pb | Cd |
|---|---|---|---|---|
| *T. dominguensis* | | | | |
| Leaf | 9.2 ± 3.0 | 2.1 ± 0.6 | 0.61 ± 1.0 | n.d - 0.05 |
| Root | 27 ± 17 | 5.2 ± 1.9 | 4.0 ± 2.2 | 0.40 ± 0.2 |
| *E. crassipes* | | | | |
| Leaf | 20 ± 8.4 | 3.9 ± 1.8 | 0.30 ± 0.1 | 0.10 ± 0.02 |
| Root | 51 ± 22 | 11 ± 3.5 | 5.7 ± 2.0 | 0.70 ± 0.2 |
| Uncontaminated freshwater plants [a] | 52 | 7.9 | 6.1 | 1.0 |
| Normal level in plant leaves [b] | 27–150 | 5–30 | 5–10 | 0.05–0.2 |
| Excess/Toxic level in plants [b] | 100–400 | 20–100 | 30–300 | 5–30 |
| *H. malabaricus* | | | | |
| Muscle | 13 ± 4.5 | 0.53 ± 0.13 | 0.19 ± 0.19 | 0.03 ± 0.02 |
| Liver | 211 ± 62 | 21 ± 12 | 0.15 ± 0.14 | 0.10 ± 0.06 |
| *G. brasiliensis* | | | | |
| Muscle | 15 ± 3.0 | 0.56 ± 0.22 | 0.25 ± 0.19 | 0.05 ± 0.03 |
| Liver | 63 ± 9.7 | 25 ± 18 | 0.32 ± 0.2 | 0.33 ± 0.1 |
| ANVISA | 50 [c] | 30 [c] | 0.3 [d] | 0.05 [d] |

(nd: below the detection limit, [a] Outridge and Noller, 1991; [b] Kabata-Pendias, 2010; [c] ANVISA, Brazilian Health Regulatory Agency Guidelines, 1965[c], ANVISA, 2013[d])

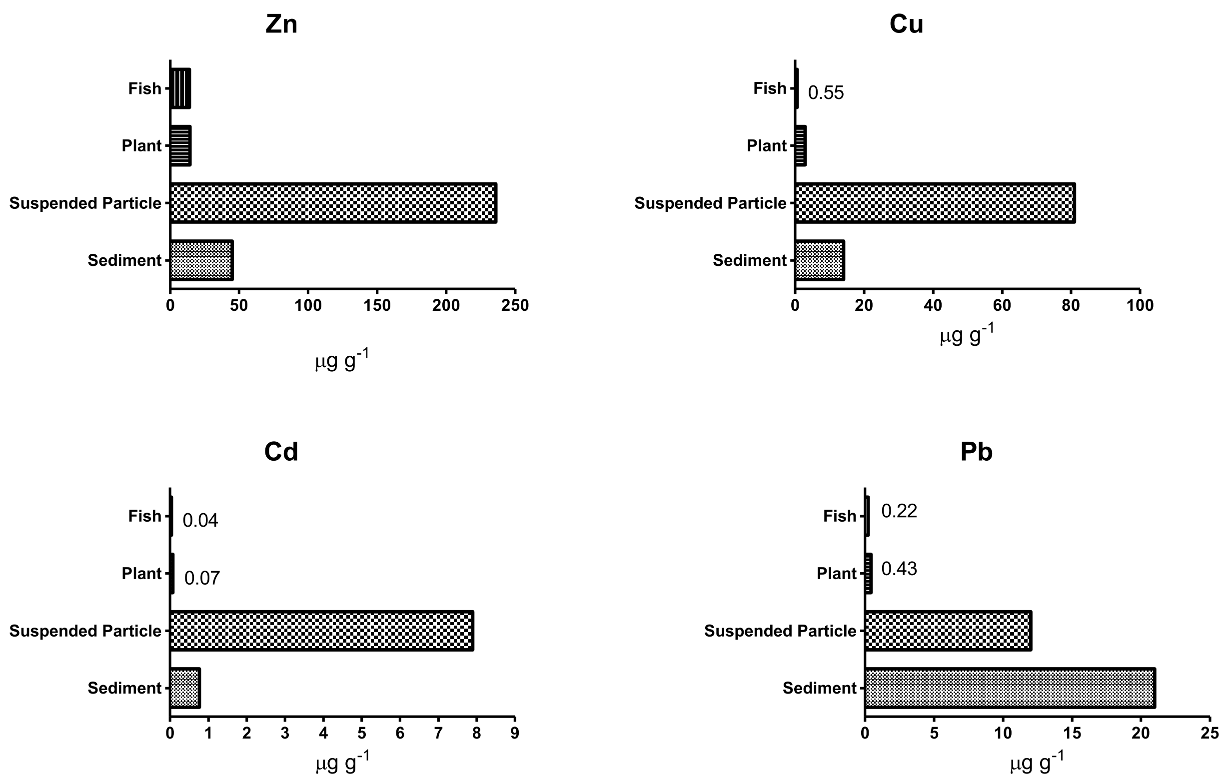


**Fig. 2.** Mean metal distribution in the surface sediments, suspended particles, aquatic macrophytes (leaves) and fish (muscle) at the Imboassica Lagoon.

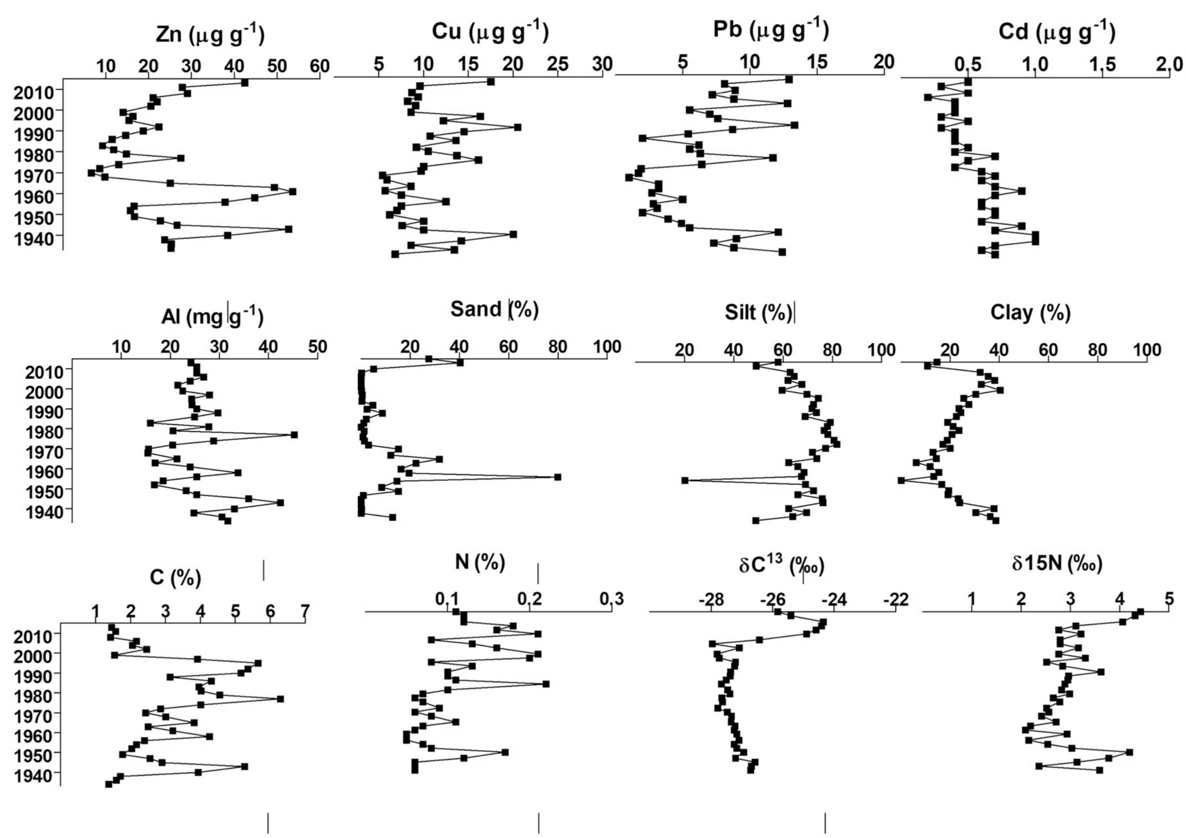


**Fig. 3.** Long-term geochemistry in sediments of the Imboassica Lagoon.

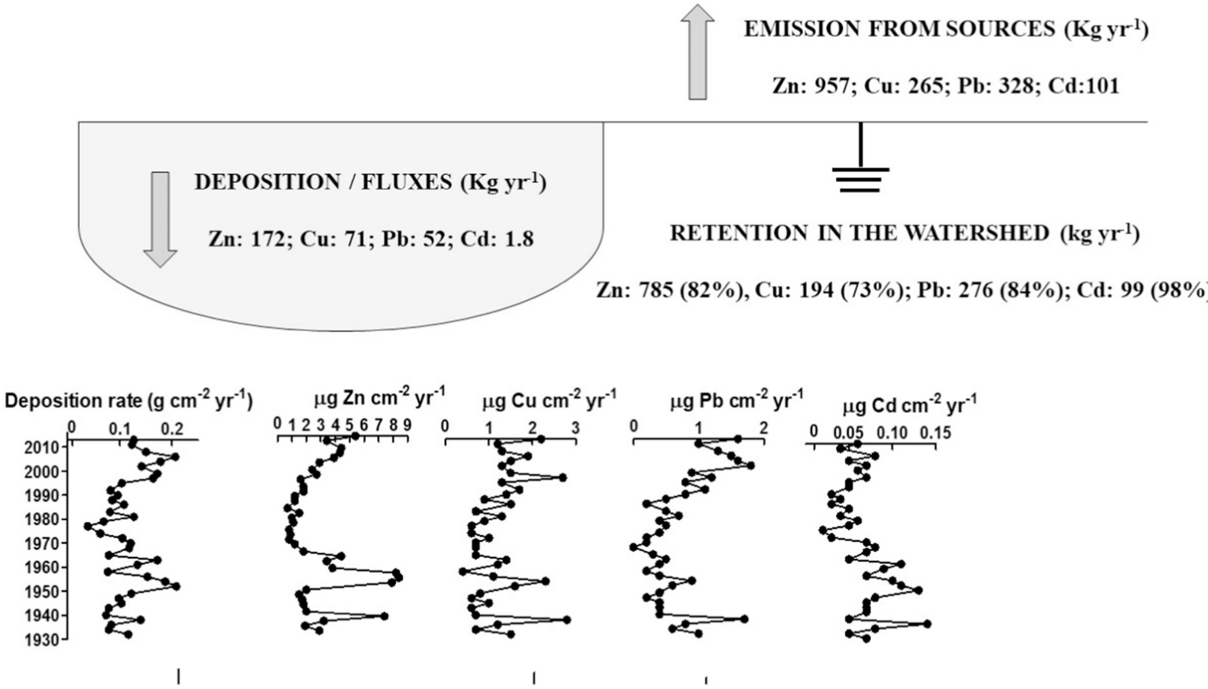


**Fig. 4.** Metal mass-balance budget and long-term deposition at the Imboassica lagoon.

### *3.6. Long-term metal distribution and fluxes in the coastal lagoon*

The long-term metal concentration and fluxes at Imboassica Lagoon were accessed through the sediment core that covered a period from 1934 to 2014 (Fig. 3). The mean sedimentation rate was of $0.45 \pm 0.07\ \mathrm{cm\,yr^{-1}}$ with a 35% variation during the evaluated time period (Fig. 4). On average, significantly higher sediment deposition rates have been occurring after 90's ($0.14\ \mathrm{g\,cm^{-2}\,yr^{-1}}$) compared to the period before intensive human occupation of the evaluated watershed ($0.10\ \mathrm{g\,cm^{-2}\,yr^{-1}}$) ($P = 0.02$). On average, the long-term grain size of the lagoon's sediments displayed a predominance of silt (68%), clay (23%) and sand (10%), with higher variability (coefficient of variation) found for sand (91%) compared to silt and clay (17 and 43%, respectively). In recent times, after urban occupation intensification, the C/N ratio became lower indicating an increase in N inputs, as demonstrated by the recent %N increases. During this period, $\delta^{15}N$ also increased from 2.1 to 4.4‰, as did $\delta^{13}C$ (from −27.9 to −25.9‰). The Spearman correlation test indicated a statistically negative correlation between the time period and Cd ($r = -0.80$, $P < 0.001$) and a positive correlation to %N ($r = 0.62$, $P < 0.001$). However, from the 90's, concentrations showed a clear increase in Zn and Pb intensified for all metals after 2010 (Fig. 3). Metals presented a statistically positive correlation to Al (Zn: $r = 0.45$, $P < 0.01$; Cu: $r = 0.55$, $P < 0.001$; Pb: $r = 0.58$, $P < 0.01$) indicating a similar geochemistry pathway (source, transport and fate), including soil erosion, runoff and river inputs. The exceptions were Cd and Cu, suggesting other emission sources or environmental processes controlling the input and behavior for these metals. A grain size effect on metal distribution was found only between clay and Pb ($r = 0.68$, $P < 0.001$). For organic matter, metals presented statistically significant correlations in sediments to %C (Cu: $r = 0.54$, $p < 0.001$) and %N (Cu: $r = 0.64$, $p < 0.0001$; Pb: $r = 0.66$, $p < 0.001$; Cd: $r = -0.55$, $p < 0.001$) suggesting organic matter as a geochemical support for metals, including not only sewage but also aquatic macrophytes and phytoplankton which have their biomass increased by nutrient enrichment from untreated domestic sewage.

Metal fluxes to the lagoon measured in the sediment core indicate statistically higher Cu ($P < 0.01$) and Pb ($P < 0.0001$) inputs of after the 90's when extensive human occupation of the watershed occurred (Fig. 4). For Zn and Cd, no statistically significant differences were observed for the evaluated period. When normalizing the fluxes to the whole lagoon area and comparing them to the metal loads emitted by natural processes and anthropogenic activities, most emitted metals were retained in the watershed, with only small loads reaching the lagoon. Cu displayed the highest lagoon inputs (Fig. 4).

## 4. Discussion

Imboassica Lagoon has a long history of eutrophication induced by untreated domestic sewage discharge from increasing amount of people living throughout the drainage basin since the 80's (Esteves et al., 2008). However, untreated domestic sewage represented a relatively minor metal contribution to the lagoon compared to other anthropogenic sources and natural processes, with higher contribution for Cu (31% of total emission). For other metals, such as Pb, Zn and Cd, solid waste disposal was more important regarding metal emissions to the lagoon than sewage. In addition, natural processes, such as atmospheric deposition and soil losses acted as important Cd, Zn and Cu sources to the lagoon. The relative importance of urbanization sources and natural processes to metal emission are typical for low to medium-intensity urbanized drainage basins, which is the case for most Brazilian coastal lagoons (Lacerda et al., 2008; Molisani et al., 2013).

To assess the pollution status of the lagoon, metal concentrations in surface sediments were compared to the area rock background. Rocks in the study area are composed by ortognaiss from the geological São Fidelis unit and Região dos Lagos complex. Concentrations ranged from 19 to $73\ \mu\mathrm{g\,g^{-1}}$ for Cu, 32 to $156\ \mu\mathrm{g\,g^{-1}}$ for Zn, and 8.6 to $24.4\ \mu\mathrm{g\,g^{-1}}$ for Pb (Mello, 1996; Almeida and Silva, 2012). The surface sediment concentrations indicate that Pb and Zn concentrations were within the background range, while Cu was lower than reference values. Such comparisons suggest that surface sediments did not reflect anthropogenic inputs, including sewage emissions, and thus indicate the absence of extensive contamination.

The non-contaminated status of surface sediments may be attributed to the fate of metal emissions and management practices. Most anthropogenic sources, including improper solid waste disposal, part of the untreated domestic sewage dumped into septic tanks and animal husbandry emitted metals to the watershed soils and, therefore, it is expected that such loads are not effectively transferred to the lagoon and its surface sediments, as demonstrated by the mass-balance budget (Fig. 4). In addition, the metal transfer from soils to the lagoon by river input are limited in view of the lagoon's small watershed area and the reduced and highly episodic fluxes from the 14 km-length Imboassica river, the main Imboassica Lagoon tributary. However, such episodic and rainfall-driven fluxes of metals from soils to the lagoon might explain the higher Cd, Cu and Zn concentrations in the suspended particles of the lagoon in the rainy season. On the other hand, part of the sewage discharge occurs directly into the lagoon and its importance to metal inputs may increase, as demonstrated by Cu, the less retained metal in the watershed (Fig. 4).

Another explanation for the non-contaminated status of surface sediments is concerns the artificial sandbar opening that affects many coastal lagoons (Suzuki et al., 1998). In this study area, disorganized urbanization of the lagoon's margin and periodic flooding of residences located at the lagoon shore in summer imposes management practices such as an artificial sandbar opening, which is capable of empty the lagoon, promoting the transference of metals to the ocean. However, after 2010, metal increases detected by the sediment core (Fig. 3) coincided with the decrease in the frequency of the sandbar opening, from 19 events before this period to 2 opening events after 2010 (Ecolagoas, unpublished data). In addition, this reduction in lagoon emptying frequency increased the accumulation of untreated domestic sewage and metal emissions from other sources, which may explain the recent (post 2010) increases in metal contents and in the fluxes into sediments, but not yet indicating extensive sediment contamination (Figs. 3 and 4).

However, the recent increase in sediment-bond metals and the wind-inducing resuspension which occurs in shallow coastal lagoons may lead to increased available of enriched particle binding metals in the water column (Lacerda and Gonçalves, 2001). At the Imboassica Lagoon, suspended particles exhibited higher Zn, Cu, and Cd concentrations when compared to bottom sediments (Table 2). Particulate Cd concentrations (maximum value of $15\,\mu g\,g^{-1}$) indicated contamination compared to the literature (Sigel et al., 2013). However, the small loads from sewage and solid waste management suggests the influence of other anthropogenic sources not inventoried by the emission factor model, such as companies located in the watershed that manipulate metallic structures for offshore oil exploration activities. This hypothesis is corroborated by the absence of correlation between Cd and other metals in the sediment core, and the inverse correlation with %N as an indicative of sewage inputs. Other metals detected in the suspended particles, such as Zn and Cu were also linked to the anthropogenic sources and the sewage discharge. Furthermore, Zn, Cu and Pb displayed higher labile (bioavailable) concentrations in the surface sediments, and when fine particles are resuspended, they disperse metals to the water column, with potential availability for biota uptake. In tropical coastal ecosystems, metals such as Cu, Cd and Pb were found to interact strongly with organic matter and other geochemical supports which increased bioavailability for organism (Chakraborty et al., 2012, 2015, 2019).

The recent increases of particle deposition rates and higher variation in sand content observed in the sediment core may indicate a long-term trend of lagoon's water column shallowing with consequent intensification of silt/clay resuspension, that, in turn may increase metal availability to pelagic organisms. Cd was affected by this lagoon processes as demonstrated by the long-term concentration reduction until 2014 displayed in the sediment core, and high concentrations in the suspended particles, which explained the fish Cd contamination.

The BCF calculated for plants and fish species and surface sediments and suspended particles at Imboassica Lagoon resulted in values lower than 1, indicating very low accumulation by organisms from the abiotic environments. The exception was Zn in *H. malabaricus* with a BCF = 2.5, albeit with a low accumulation. However, the Zn bioconcentration in the carnivorous species was also observed in fish from other lagoons, including those under the strong influence of domestic sewage and wastewater sources (Mendonza-Carranza et al., 2016).

The metal content in fish and aquatic macrophytes from Imboassica Lagoon was within the metal range of subgroups of aquatic organisms from pristine and uncontaminated environments (Quigg, 2008; Outridge and Noller, 1991). However, according to the Brazilian Health Regulatory Agency Guidelines (ANVISA, 1965; ANVISA, 2013), fish samples presented Cd and Pb concentrations above the proposed limits for food consumption, with omnivorous fish species presented a higher frequency of contaminated muscle tissue samples (Pb: 42% and Cd: 41%) than carnivorous species (Pb: 20% and Cd: 23%). Omnivorous fish contamination by Cd and Pb was related to the high Cd concentrations in suspended particles and to the Pb in surface sediments mainly in the bioavailable form. The emission factor indicated the involvement of solid waste disposal as a possible Pb source and atmospheric deposition as a pathway for Cd inputs. Molisani et al. (2015) described many possible Pb sources in the region, including banned persistent sources such as leaded gasoline used in motor vehicles that officially has been prohibited in Brazil since 1991, but remained in use until as recently as 2005 and possible explained Pb enrichment in sediments of the adjacent Macaé river basin. In addition, in the Imboassica Lagoon, such initial fish contamination status may also be related to the influence of other anthropogenic sources not calculated by the emission factors. On the other hand, untreated sewage showed little influence on Cd and Pb inputs (Table 2). Data from Aguilar-Betancourt et al. (2016) indicates evidences of a weak the relationship between metals in fish at the more polluted sites influenced by only untreated sewage in a coastal lagoon.

The importance of untreated domestic sewage as well as the other emission sources were evaluated by the long-term metal distribution in the sediment core, an indicative of lagoon conditions from 1934 to 2014 (Figs. 3 and 4). The recent increase in metal concentrations may be attributed to several factors including increased human occupation of the watershed and the decrease is related to the sand-bar opening frequencies. Apparently, the recent increase of $\delta^{15}N$ in the sediment core suggests the influence of untreated domestic sewage discharges by the increasing surrounding population. It is well-documented that $\delta^{15}N$ enrichment in sediments of aquatic environments with elevated untreated domestic sewage discharges, with $\delta^{15}N$ increases from 3‰ to 9‰ following the increased human population density (Vizzini and Mazzola, 2006; Wada, 2009; Zhe and Zhu, 2016), which corroborates to $\delta^{15}N$ increases at Imboassica Lagoon (2.5 to 4.5‰) that may also be related to the intensification of human occupation of the watershed. However, even with the recent increases of both metal concentration and fluxes in the lagoon, demonstrated by the sediment core, such distributions were in the same magnitude of past lagoon's conditions indicating that the influence of anthropogenic activities since the 90's and related management practices (sandbar opening and proper solid waste disposal) did not extensively altered the current lagoon conditions compared to the pre-urbanization period when mainly natural processes influenced metal distribution and fluxes.

## 5. Conclusion

Metal contamination of coastal lagoons is an important issue as demonstrated by the present study. Untreated domestic sewage induced eutrophication and was an important source of Cu to the lagoon and probably affecting distribution of other metals. However, the natural sources, such as soil loss and atmospheric deposition were the main metal emission sources to the lagoon. Total Cd enrichment in the suspended particles and the Pb bioavailable forms in the surface sediments indicated that such sedimentary compartments were an important fate of metals in the lagoon; at the same time, that were the metal pathway explaining the initial Cd and Pb fish contamination, mainly the omnivorous fish, that were also considered another fate of metals in the lagoon. Thus, the additional metal inputs to the lagoon from the anthropogenic sources associated to the measured total and bioavailable metal concentrations in the bottom and suspended particles may explained the Pb and Cd contamination in fish and the Cd enrichment in the suspended particles. However, extensive contamination was prevented by lagoon management, including sand-bar opening, reducing long-term metal accumulation. Furthermore, the retention of part of the discharged sewage and other anthropogenic and natural emissions within the watershed soil also reduced the effective metal transference to the lagoon and prevented extensive contamination.

## Acknowledgments

This work was support by Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ, E-26/110.544/2014), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq – PQ grant 311354/2016-5 to Carla Carvalho) and Comitê de Bacias Hidrográficas Macaé/Ostras. Beraldi GQF had a MS grant from Centro de Pesquisas Leopoldo Américo Miguez de Mello (CENPES) and Petróleo Brasileiro S.A. (PETROBRAS), while Souza MDP was undergraduate student from Programa de Educação Tutorial (PET) do Ministério de Educação.

## References

ABRELPE, 2011. Brazilian Association of Public Cleaning and Special Waste. Outlook of Solid Waste in Brazil. Available: http://www.abrelpe.org.br/panorama_apresentacao.cfm, Accessed date: 12 March 2016.
Aguilar-Betancourt, C.M., González-Sansón, G., Kidd, K.A., Munkittrick, K.R., Curry, L.A., Kosonoy-Aceves, D., Lucano-Ramírez, G., Ruiz-Ramírez, S., Flores-Ortega, J.R., 2016. Fishes as indicators of untreated sewage contamination in a Mexican coastal lagoon. Mar. Pollut. Bull. 113, 100–109.
Almeida, J., Silva, L.C., 2012. Geology and Mineral Resources of the Macaé SF.24-Y-A-I. State of Rio de Janeiro, CPRM, Belo Horizonte.
Andrade, C.A., Mattiazzo, M.E., 2000. Nitrate and heavy metals after application of biosolids in forest plantation of *Eucalyptus grandis*. Sci. Forest. 58, 59–72 (In Portuguese).
Anvisa Decree Law n° 55.781, of March 26, 1965. General Principles for the Establishment of Maximum Levels of Chemical Contaminants in Food and Maximum Limits of Tolerance for Inorganic Contaminants.
Anvisa RDC N° 42, 2013. August 29. Provide about the Technical Regulation MERCOSUL about the Maximum Limits of Inorganic Contaminants in Food.
Barreto, G., 2009. Mapeamento ambiental da bacia hidrográfica da Lagoa Imboassica: subsídio para construção do plano de bacias. Dissertation. Instituto Federal Fluminense, Brazil.
Berner, R.A., 1980. Early Diagenesis: A Theoretical Approach, First ed. Princeton University Press, New Jersey.
Binner, E., Lechner, P., Ziegler, C., Riehl-Herwirsch, Breitenau, G., 1996. Landfill - Water Balance, Emissions and a Look into the Landfill Body. Breitenau Landfill Co, Viena.
Caliman, A., Carneiro, L.S., Santangelo, J.M., Guariento, R.D., Pires, A.P.F., Suhett, A.L., Quesado, L.B., Scofield, V., Fonte, E.S., Lopes, P.M., Sanches, L.F., Azevedo, F.D., Marinho, C.C., Bozelli, R.L., Esteves, F.A., Farjalla, V.F., 2010. Temporal coherence among tropical coastal lagoons: a search for patterns and mechanisms. Braz. J. Biol. 70, 803–814.
Canellas, L.P., Velloso, A.X., Marciano, C.R., Ramalho, J.F.P., Rumjanek, V.M., Rezende, C.E., Santos, G.A., 2003. Chemical properties of cultivated Cambisol by sugar cane with straw preservation and long-term vinasse addition. R. Bras. Ci. Solo 27, 935–944 (In Portuguese).
Chakraborty, P., Babu, P.V., Sarma, V.V., 2012. A study of lead and cadmium speciation in some estuarine and coastal sediments. Chem. Geol. 294-295, 217–225.
Chakraborty, P., Ramteke, D., Chakraborty, S., Nath, B.N., 2014. Changes in metal contamination levels in estuarine sediments around India - an assessment. Mar. Pollut. Bull. 78, 15–25.
Chakraborty, P., Ramteke, D., Chakraborty, S., 2015. Geochemical partitioning of cu and Ni in mangrove sediments: relationships with their bioavailability. Mar. Pollut. Bull. 93, 194–201.
Chakraborty, S., Chakraborty, P., Sarkar, A., Kazip, A., Mascarenhas-Pereira, M.B.L., Nagender Nath, B., 2019. Distribution and geochemical fractionation of lead in the continental shelf sediments around India. Geol. J. 54, 1190–1204.
Cidades, I.B.G.E., 2012. Instituto Brasileiro de Geografia e Estatísticas. 1. http://www.ibge.gov.br/cidadesat/topwindow.htm?, Accessed date: November 2012.
Davis, A.P., Shokouhian, M., Shubei, M., 2001. Loading estimates of lead, copper, cadmium and zinc in urban runoff from specific sources. Chemosphere 44, 997–1009.
EMBRAPA, 2004. Brazilian Company for Agriculture and Livestock. Technologies for Waste Management in Animal Production: Manual of Good Practices/Coordinated by Paulo Armando Victoria de Oliveira. Embrapa Swine and Poultry, Concordia, pp. 109. 29cm. Available: http://www.cnpsa.embrapa.br/pnma/pdf_doc/doc_pnma.pdf, Accessed date: 23 March 2016.
EMBRAPA, 2013. Brazilian company for agriculture and livestock. Sugar-cane agroecology. http://www.cana.cnpm.embrapa.br/agroeco.html, Accessed date: 1 March 2016.
Essakku, S., Selvam, A., Joseph, K., Palanivelu, K., 2005. Assessment of heavy metal species in decomposed municipal solid waste. Chem. Speciat. Bioavail. 17, 95–102.
Esteves, F.A., Caliman, A., Santangelo, J.M., Guariento, R.D., Farjalla, V.F., Bozelli, R.L., 2008. Neotropical coastal lagoons: an appraisal of their biodiversity, functioning, threats and conservation management. Braz. J. Biol. 68, 967–981.
Fadigas, F.S., Sobrinho, N.M.B., Mazur, N., Anjos, L.H.C., Freixo, A.A., 2006. Proposition of reference values for heavy metal concentrations in soils. R. Bras. Eng. Agric. Amb. 10, 699–705 (In Portuguese).
Fernandes, H.M., Bidone, E.D., Veiga, L.H., Patchineelam, S.R., 1994. Heavy-metal pollution assessment in the coastal lagoons of Jacarepagua, Rio de Janeiro, Brazil. Environ. Pollut. 85, 259–264.
Filho, F.J.P., Marins, R.V., Lacerda, L.D., 2015. Natural and anthropogenic emissions of N and P to the Parnaíba River Delta in NE Brazil. Estuar. Coast. Shelf Sci. 166, 34–44.
Golley, F.B., Mc Guiness, J.T., Clements, R.G., Child, G.I., Duever, M.J., 1978. Mineral Cycling in a Humid Forest Ecosystem. EDUSP, São Paulo (In Portuguese).
Greenland, D.J., Lal, R., 1977. Soil Conservation and Management in the Humid Tropics. Wiley, Chischester.
Houhou, J., Lartiges, B.S., Montarges-Pelletier, E., Sieliechi, J., Ghanbaja, J., Kohler, A., 2009. Sources, nature, and fate of heavy metal-bearing particles in the sewer system. Sci. Total Environ. 407, 6052–6962.
IBGE Cidades Instituto Brasileiro de Geografia e Estatísticas. https://cidades.ibge.gov.br/, Accessed date: March 2014.
IPEA – Instituto de Pesquisa Economia Aplicada, 2012. Diagnostico dos resíduos sólidos urbanos. (Relatório Técnico).
Jara-Marini, M.E., Soto-Jimenez, M.F., Paez-Osuna, F., 2009. Trophic relationships and transference of cadmium, copper, lead and zinc in a subtropical coastal lagoon food web from SE gulf of California. Chemosphere 77, 1366–1373.
Johnson, D.W., Lindberg, S.E., 1998. Atmospheric Deposition and Forest Nutrient Cycling. Springer Verlag, Berlin.
Kabata-Pendias, A., 2010. Trace Elements in Soils and Plants. CRC Press, Boca Raton.
Kjerfve, B., 1994. Coastal Lagoon Processes. Oceanography Series Elsevier, pp. 60.
Knoppers, B.A., Lacerda, L.D., Patchineelam, S.R., 1990. Nutrients, heavy metals and organic micropollutants in a eutrophic Brazilian lagoon. Mar. Poll. Bul. 21, 381 384.
Lacerda, L.D., 1994. Biogeochemistry of heavy metals in coastal lagoons. In: Kjerfve, B. (Ed.), Coastal Lagoon Processes. Elsevier Oceanographic Series.
Lacerda, L.D., Gonçalves, G.O., 2001. Mercury distribution and speciation in waters of the coastal lagoons of Rio de Janeiro, SE Brazil. Mar. Chem. 76, 47–58.
Lacerda, L.D., Fernandez, M.A., Calazans, C.F., Tanizaki, K.F., 1992. Bioavailability of heavy metals in sediments of two coastal lagoons in Rio de Janeiro, Brazil. Hydrobiologia 228, 65–70.
Lacerda, L.D., Molisani, M.M., Sena, D., Maia, L.P., 2008. Estimating the importance of natural and anthropogenic sources on N and P emission to estuaries along the Ceará State Coast NE Brazil. Environ. Monit. Assess 141, 149–164.
Lima, J.S.L., 1994. Copper balances in cocoa agrarian ecosystems: effects of differential use of cupric fungicides. Agric. Ecosyst. Environ. 48, 19–25.
Malavolta, E., Dantas, J.P., 1980. Corn nutrition and fertilization. In: Paterniani, E. (Ed.), Corn Improvement and Production in Brazil, Second edition. Fundação Cargill, São Paulo (In Portuguese).
Marins, R.V., Silva-Filho, E.V., Lacerda, L.D., 1996. Atmospheric deposition of mercury over Sepetiba Bay, SE Brazil. J. Braz. Chem. Soc. 7, 177–180.
Marotta, H., Bento, L., Esteves, F.A., Enrich-Prast, A., 2009. Whole ecosystem evidence of eutrophication enhancement by wetland dredging in a shallow tropical lake. Estuar. Coast. 32, 654–660.
Mello, C.S.B., 1996. A Contribution of Geology and Geochemistry to the Environmental Assessment and Prognostic of Supply Water Quality of the Macaé River. Dissertation. Universidade Federal do Rio de Janeiro.
Mello, W.Z., 2001. Precipitation chemistry in the coast of the metropolitan region of Rio de Janeiro, Brazil. Environ. Pollut. 114, 235–242.
Mendonza-Carranza, M., Sepúlveda-Lozada, A., Dias-Ferreira, C., Geissen, V., 2016. Distribution and bioconcentration of heavy metals in a tropical aquatic food web: a case study of a tropical estuarine lagoon in SE Mexico. Environ. Pollut. 210, 155–165.
Molisani, M.M., Salomão, M.S.M.B., Ovalle, A.R.C., Rezende, C.E., Lacerda, L.D., Carvalho, C.E.V., 1999. Heavy metal in sediments of the lower Paraíba do Sul River. Bull. Environ. Contam. Toxicol. 63, 682–690.
Molisani, M.M., Esteves, F.A., Lacerda, L.D., Rezende, C.E., 2013. Natural and anthropogenic emission of nitrogen, phosphorous and metals to the Macaé river basin and the influence of offshore oil and gas exploration in Campos Basin quim. Nova 36, 27–33.
Molisani, M.M., Noronha Jr, F.R.C., Schultz, M.S., Rezende, C.E., Almeida, M.G., Silveira, C.S., 2015. Mismatch Between Sediment Metal Distribution and pollution Source gradient: A case study of a small-size drainage basin (Southeastern Brazil). Bull. Environ. Contam. Toxicol. 94, 770–776.
Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.
Outridge, P.M., Noller, B.N., 1991. Accumulation of toxic trace elements by freshwater vascular plants. Rev. Environ. Contam. Toxicol. 121, 2–63.
Paez-Osuna, F., Zazueta-Padilla, H., Izaguirre-Fierro, G., 1991. Trace metals in bivalves from Navachiste lagoon, Mexico. Mar. Pollut. Bull. 22, 305–307.
Panosso, R.F., Attayde, J.L., Dieter, M., 1998. Morphometry of Imboassica, Cabiúnas, Comprida and Carapebus lagoons: Implication for function and managment. In: Esteves, F.A. (Ed.), Ecology of Coastal Lagoons of the Jurubatiba Sandbank National Park and the Macaé Municipality, Brazil. Nupem/UFRJ, Rio de Janeiro, pp. 91–108.

Patchineelam, S.R., Smoak, J.M., 1999. Sediment accumulation rates along the inner eastern Brazilian continental shelf. Geo-Mar. Lett. 19, 196–201.
Quigg, A., 2008. Trace elements. In: Jorgensen, S.E., Fath, B.D. (Eds.), Ecological Stoichiometry. Encyclopedia of Ecology. vol. 5. Elsevier, Oxford, pp. 3564–3573.
Quoy, J.R., Gaimard, P., 1824. Zoologie. Poissons. Paris In: L. de Frecinet. Voyage autour de monde, entrepris par ordre du Roi, exécuté sur les corvettes de S M l'URANIE et la PHYSICIENNE, pendant les années 1817-1820, pp. 712.
Radwan, S., Kowalik, W., Kowalczyk, C., 1990a. Occurrence of heavy metals in water, phytoplankton and zooplankton of a mesotrophic lake in eastern Poland. Sci. Total Environ. 96, 115–120.
Radwan, S., Kowalik, W., Kornijow, C., 1990b. Accumulation of heavy metals in a lake ecosystem. Sci. Total Environ. 96, 121–129.
Ramalho, J.F.G.P., Sobrinho, N.M.B.A., 2001. Heavy metals in cultivated soils of sugar cane with the agroindustry residues. Florest. Amb. 8, 120–129 (In Portuguese).
Ramalho, J.F.G.P., Sobrinho, N.M.B.A., Velloso, A.C.X., 2000. Contamination of the Caetés watershed by heavy metals from the agro-chemistry use. Pesq. Agrop. Bra. 35, 1289–1303 (In Portuguese).
Salomons, W., Forstner, U., 1984. Metals in the Hydrocycle. Springer Verlag, Berlin.
Sigel, A., Sigel, H., Sigel, R.K.O., 2013. Cadmium: From Toxicity to Essentiality. Springer.
Silva, L.F., 1996. Tropical Soils: Pedological, Ecological and Management Aspects. Terra Brasilis Editora, São Paulo (In Portuguese).
Silva, E.C., Silva Filho, A.V., Almeida, M.A.R., 2000. Residual fertilization effects of potato on dry matter production and exploration of green corn. Ciênc. Agrotecnol. 24, 509–515.
Silva-Filho, E.V., Wasserman, J.C., Lacerda, L.D., 1998. History of metal inputs recorded on sediment cores from a remote environment. Cien. Cult. 50, 374–376.
Silva-Filho, E.V., Sella, S.M., Spinola, E.C., Santos, I.R., Machado, W., Lacerda, L.D., 2006. Mercury, zinc, manganese, and iron accumulation in leachate pond sediments from a refuse tip in southeastern Brazil. Microchem. J. 82, 196–200.
Smith, R.A., Alexander, R.B., Wolman, M.G., 1997. Regional interpretation of water monitoring data. Water Resour. Res. 33, 2781–2798.
Sorme, L., Lagerkvist, R., 2002. Sources of heavy metals in urban wastewater in Stockholm. Sci. Total Environ. 298, 131–145.
Suzuki, M.S., Ovalle, A.R.C., Pereira, E.A., 1998. Effects of sand bar openings on some limnological variables in a hypertrophic tropical coastal lagoon of Brazil. Hydrobiologia 368, 111–122.
Tan, P.A., Wong, A.Y.S., 2000. Soluble trace metals and major ionic species in the bulk deposition and atmosphere in Hong Kong. Wat. Air Soil Pollut. 122, 261–279.
Tundisi, J.G., 2006. Water in the XXI Century: Facing the Shortage. Rima, São Carlos (In Portuguese).
U.S. Geological Survey, 2011. SPARROW Surface Water-Quality Modeling. Available: http://water.usgs.gov/nawqa/sparrow/index.html, Accessed date: 6 July 2017.
Valitutto, R.S., Sella, S.M., Silva-Filho, E.V., Pereira, R.G., Miekeley, P., 2006. Accumulation of metals in macrophytes from water reservoirs of power supply plant, Rio de Janeiro state, Brazil. Wat. Air Soil Pollut. 178, 89–102.
Vizzini, S., Mazzola, A., 2006. The effects of anthropogenic organic matter inputs on stable carbon and nitrogen isotopes in organisms from different trophic levels in a southern Mediterranean coastal area. Sci. Total Environ. 368, 723–731.
von Sperling, M., 1996. Introduction of Water Quality and Sewage Treatment, Thirty edition. Departamento de Engenharia Hidráulica e Ambiental, UFMG, Belo Horizonte.
Wada, E., 2009. Stable $\delta^{15}N$ and $\delta^{13}C$ isotope ratios in aquatic ecosystems. Proc. Japan Acad. Ser. B 85, 98–107.
Zhe, S., Zhu, W., 2016. Analysis of isotope tracing of domestic sewage sources in Taihu Lake—a case study of Meiliang Bay and Gonghu Bay. Ecol. Indic. 66, 113–120.