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Artigo

Preliminary Study of Trace Metals by Environmental Quality Criteria in Sediments from a Mangrove Forest in *Saco do Mamanguá* (Ilha Grande Bay, Rio de Janeiro, Brazil)

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Estudo Preliminar de Metais Traço por Critérios de Qualidade Ambiental em Sedimentos de um Manguezal do Saco do Mamanguá (Baía da Ilha Grande, Rio de Janeiro, Brasil)

Resumo: As atividades urbanas e industriais são as principais fontes de poluição para as florestas de mangue. Sedimentos de manguezais podem atuar como reservatório para uma vasta gama de contaminantes, incluindo metais traço. O objetivo deste estudo foi investigar os teores de metais traço (Cu, Ni, Pb e Zn) em amostras de sedimentos de um ecossistema de manguezal presumivelmente não poluído no sul do estado do Rio de Janeiro, Brasil. Também foram feitas análises de pH, Eh, carbono orgânico, nitrogênio, fósforo e granulometria. De acordo de critérios internacionais de qualidade dos sedimentos, os resultados obtidos indicaram a colaboração de fontes antropogênicas, visto que alguns metais traço avaliados atingiram valores excessivos, o que pode afetar o equilíbrio do ecossistema estudado. De acordo com os resultados, a área não foi considerada livre de contaminação por metais traço. Apesar de não ter uma fonte antrópica significativa de metais traço em seu interior, a baía da Ilha Grande abriga um estaleiro, um terminal de petróleo e um porto comercial, bem como duas usinas termonucleares, os quais podem influenciar indiretamente a área de estudo.

Keywords: *Metais traço; contaminação; sedimentos; manguezais*.

Abstract

Urban and industrial activities are major sources of pollution to mangrove forests. Mangrove sediments can act as sink and reservoir for a wide range of contaminants, including heavy metals. The aim of this study was to investigate the contents of trace metals (Cu, Ni, Pb and Zn) in sediment samples from a potentially unpolluted mangrove ecosystem in the south of Rio de Janeiro state, Brazil. Determination of pH, Eh, organic carbon, nitrogen, phosphorus and particle size were also performed. In accordance to the international criteria of quality of sediment, the results indicate anthropogenic influence since some metals reached excessive values, which can affect the balance of the ecosystem studied. According to the results, the area cannot be considered a trace metal non-polluted area. Despite not having a significant source of metals inside the Bay nowadays, Ilha Grande Bay harbors a shipyard, an oil terminal, and a commercial port, as well as two thermonuclear power plants, all of which indirectly influence the study area.

Palavras-chave: *Trace metals; contamination; sediments; mangrove*.

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Preliminary Study of Trace Metals by Environmental Quality Criteria in Sediments from a Mangrove Forest in *Saco do Mamanguá* (Ilha Grande Bay, Rio de Janeiro, Brazil)

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1. Introduction

Mangrove forests exist where streams and rivers meet the sea and where tides and coastal currents mix. They are a rich source of commercial fishing and shellfish, and provide many recreational opportunities.[1] During recent decades, mangrove ecosystems have been disappearing worldwide at the rate of 1% to 2% per year, a rate greater than or equal to those of threatened ecosystems like coral reefs and tropical rainforests.[2,3,4] In Brazil, the area occupied by mangrove forests is estimated to be 13.000 km^2 from the far north (Oiapoque river – 04°20'N) to Laguna, Santa Catarina state, (28°30'S).[5]

The characterization of unpolluted or

slightly impacted areas is necessary for monitoring the environment, preventing impacts and implementing solutions where the remediation of environmental accidents is required. In this context, mangrove areas are important as they provide a barrier against pollutants and perform unique ecological roles, representing direct economic value.[6]

Since sediments are transported by rivers to other bodies of water or the sea, analyses of sediments are useful for tracking and managing the control of contaminant dispersal routes.[7] Most of the contaminants that enter aquatic systems accumulate in the bottom sediment. As such, sediments are the ultimate destination for all processes occurring in the air, water and soil, with the ability to accumulate low concentrations of the elements present in water.[8] Mangrove sediments are formed by suspended or deposited solids and they are a source of energy resources for biotic compartment and key components for assessing the ecological integrity of these environments.[9,10]

Due to their persistence, potential toxicity and bioavailability, trace metals represent a major threat to mangrove biodiversity and also to human health.[11] The anoxic conditions, the presence of fine particulate matter and high organic matter content (typical in the mangrove sediments) may help to reduce the potentially deleterious effects of contamination by trace elements (such as Cu, Ni, Pb, Zn, etc.).[12,13] This is due to the low availability of these elements for being accumulated within the sediments, and for the biota incorporation and remobilization.[14,15] However, the degradation of mangrove forests and the changes in environmental and physico-chemical conditions (pH, redox potential and microbial action, etc.) may remobilize the sediment trace elements, contaminating the water and leading to the bioaccumulation and the transfer in the trophic chain.[16,17,18,19]

In Brazil, the quality criteria for sediments to be dredged (National Council of the Environment-CONAMA Resolution 344/2004)[20] and for soils (CONAMA 420/2009)[21] exclude cover for marine sediments. Beyond this restriction, no criteria or guiding values have been established for the quality of marine sediments, although the marine domain is increasingly exploited and influenced by harbor activities, oil exploration, industrial activities and oil refining, which are potential sources of heavy metals.[22]

On the mainland of Brazil, between the cities of Rio de Janeiro and São Paulo, areas of high population density that have been widely impacted by anthropogenic activities, there is a mangrove located in *Saco do Mamanguá* harbor and part of Juatinga Ecological Reserve, which is a conservation area (APA Cairuçu), inside Ilha Grande Bay.[23] This mangrove is an example of a preserved area that is susceptible to environmental impacts.[24,25] About 2,000 people live in *Saco do Mamanguá*, but in the summer months it receives as many as 20,000 visitors. During this season, the increased volumes of sewage, garbage, boats and cars in adjacent areas can induce environmental impacts. These activities may lead to an accumulation of trace metals and other pollutants in mangrove sediments, resulting in rising toxic effects in individuals or populations in the medium and long term.[22]

The aim of this study was to obtain the contents of trace metals (Cu, Ni, Pb and Zn) in the sediments of a mangrove forest located at *Saco do Mamanguá* (Ilha Grande bay, Rio de Janeiro, Brazil). The determination of these pollutant levels will be useful for the local communities, management teams and government for registration and comparison with later data, and to give support to establish criteria and guiding values for the quality of marine sediments in Brazil. For this purpose, the samplings sites were also characterized for their physicochemical and granulometric properties.

2. Materials and methods

2.1. Study area and sampling procedure

The study area is located in a mangrove forest in Saco do Mamanguá, in the municipality of Parati, between latitude 23°17'S and 23°18'S and meridian 44°38'W, on the southern coast of Rio de Janeiro state (Figure 1a). Samples of surface sediments (0-10 cm depth) were collected at low tide in the fringe area (located in the intertidal zone) in March 2010, in one site (M; Figure 1b). In this site, samples were collected at five points in parallel to the shoreline (M1, M2, M3, M4 and M5) with a distance of approximately 10 m between them. Samples were collected with plastic spoons previously decontaminated with 1:1 nitric acid solution, packed in sealed polyethylene plastic bags and kept refrigerated until they reach the laboratory where they were frozen.

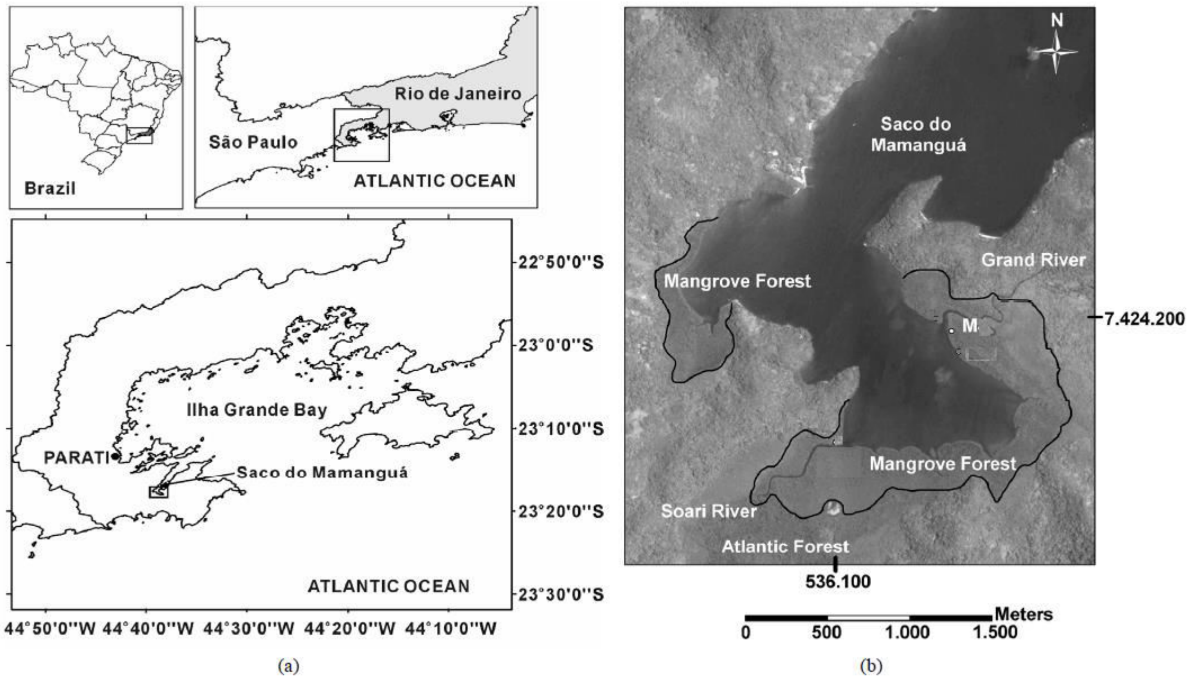

Figure 1. (a) Location map of the study area; (b) M, represents the site of the five sampling points in the Saco do Mamanguá mangrove forests

2.2. Reagents and materials

All glassware was washed with extran (5% v/v), with HNO_3 solution (50% v/v) and finally with deionized water. All solutions were prepared with "analytical grade" reagents (Merck or Sigma) and deionized water purified through the Milli-Q system (Millipore). The reference solutions to obtain the analytical curves for the determination of metals in sediment samples were prepared by serial dilution of stock solutions of 1000 mg dm^{-3} (Qhemis) of Pb, Cu, Ni and Zn in HNO_3 1.0 mol dm^{-3}.

2.3. Physicochemical characterization and particle size distribution of sediments

Sediment pH and temperature were determined *in situ* as described by Burton *et al.*[26] using a portable meter Q400AM (Quimis, Brazil), by directly inserting calibrated electrodes into the sediments at the sampling sites. The Eh (redox potential) of the sediment was measured in the same way using a combined platinum electrode with an Ag/AgCl/3 mol dm^{-1} KCl reference electrode. The measurements were corrected to the standard hydrogen electrode by calculating against the standard potential of the reference electrode.

In laboratory, the sediment analysis followed the methodology from Embrapa,[27] as summarized below: samples were dried (103-105°C), disaggregated and sieved through a 2 mm mesh. Organic carbon was measured by oxidizing the organic material with potassium dichromate in an externally heated acidic medium and titration with ferrous ammonium sulfate. The particle size distribution–thick sand (2.00–0.20 mm), fine sand (0.20–0.05 mm), silt (0.05–0.02 mm) and clay (<0.002 mm) – was determined by the densimeter method. Total nitrogen was determined by Kjeldahl steam distillation. Finally, the total phosphorus was determined by ICP-OES (Optima 3000 spectrometer from Perkin Elmer).[28]

2.4. Trace metals analysis

For the trace metals (Cu, Ni, Pb and Zn) analysis, the USEPA 3051A[29] protocol was used. This protocol is recommended for the United States Environmental Protection Agency (USEPA) to leach metals and has been widely applied in sediment, soil and sludge samples.[29,30] 0.50 g of sediment sample was weighed carefully into a Teflon digestion tube and 10 cm^3 of concentrated HNO_3 was added. Then the tubes were closed and the samples were heated in the microwave oven (Anton Paar - Multiwave 3000) under the following conditions: pressure 20 bar, power 1200 W; heating program: in the first step, the temperature was increased linearly from 25 to 175 °C in 5.3 h and in the second step, the temperature was held at 175°C for 4.3 h. Blank solutions and certified reference material NIST-8704 (Buffalo River Sediment) were prepared in the same way. After the digestions, the samples were filtered (Whatman n^o 42 filter), transferred to volumetric flasks and swollen to 50 cm^3 with deionizer water. Quantification of Cu, Ni, Pb and Zn was performed in triplicate by atomic absorption spectrophotometry using an AAS-240 (Varian) with air-acetylene flame and graphite tube atomizer.

3. Results and discussion

3.1. Physicochemical characterization and particle size distribution of sediments

The pH obtained (measured *in situ* at point M1) was 6.6. According to Salomons *et al.*,[31] mangrove sediments have wide variation in pH values due to such factors as the effect of products of decomposition of organic matter and hydrolysis tannins, which produce various types of acids, increasing either oxidizing or reducing conditions in mangrove sediments.[32,33]

Eh value obtained measured *in situ* at point M1 (-357 mV) suggests that the sediments in the region have reducing characteristics which favor the incorporation of trace elements by precipitation processes, mainly in the form of sulfides.[31] The high content of organic matter (132.7 ± 30.6 mg g^{-1}) favors the retention of trace elements by complexation processes with the humic acids.[34]

The results also indicates that the sediments in the five sampling points have high levels of total nitrogen (6.9 ± 1.4 mg g^{-1}) and total phosphorus (0.6 ± 0.06 mg g^{-1}). It is known that mangroves are naturally enriched with nutrients such as nitrogen and phosphorus, which may be present in organic and inorganic forms and integrate the environment through biogeochemical cycles.[35]

The granulometric analysis of the sediments (measured in point M1) shows that the fractions silt (388 g Kg^{-1}) and clay prevail (500 g Kg^{-1}) in the region. Teixeira[25] obtained similar results in his evaluation of sediments from several creeks in Ilha Grande bay and 23 specific points along Saco do Mamanguá, reporting that this latter harbor had the highest average clay content. Particles lower than 63 µm are the most important fraction for the analysis of contaminants, because their properties (e.g. large areas and high ion exchange capacity) make them effective cleaning agents for some contaminants that are discharged into aquatic systems.[10] According to Clark *et al.*,[36] the preferential distribution of mangrove forests in sheltered areas favors the deposition of fine particles by adsorption processes and heavy metals associated with these particles.

3.2. Trace metals analysis

The results obtained for the trace metals concentrations in the certified reference material NIST-8704 (Table 1) shows that there are no significant differences between the values obtained and certificates. The recovery rates were between 101 and 104%, within the recommended range of 75 to 125%.[29]

Table 1. Recovery ranges of trace metals in reference material NIST-8704

Trace-element	Obtained Value (mg Kg^{-1})*	Certified Value (mg Kg^{-1})	Recovery range (%)
Cu	85.4 ± 4.6	nc	na
Ni	43.2 ± 1.9	42.9±3.7	101
Pb	153.2 ± 5.6	150±17	102
Zn	424.3 ± 12.9	408±15	104

nc- non certified. na- not available. *mean ± standard deviation, n=3.

Brazilian environmental legislation still lacks quality criteria for sediment and also no *Background* data for the parameters determined in the sediments of the region under study. Thus, for purposes of comparison and for an approximation of the consequences of the trace metal levels in the sediments, we used the criteria established in the literature, represented by international environmental agencies, such as NOAA - *National Oceanic and Atmosferic and Administration* (USA).[37] These criteria are referenced as the threshold effect level (TEL-value below which adverse effects are rarely expected) and probable effect level (PEL-value above which adverse effects on biota are expected).

Results of trace metals analysis (Table 2) shows that *Saco do Mamanguá* cannot be considered a non-polluted area, according to the pollution levels determined by the NOAA.

Cu concentrations in all sampling points were below the TEL (34 mg kg^{-1}) (Figure 2A); Ni concentrations above TEL (18 mg kg^{-1}) and below PEL (36 mg kg^{-1}) (Figure 2B), were found in all sampling points; Pb concentrations above TEL (35 mg kg^{-1}) and below PEL (91.3 mg kg^{-1}) (Figure 2C), were found in M2, M3, M4 and M5 points. In all sampling points Zn concentrations obtained were below TEL level (123 mg kg^{-1} for Zn) (Figure 2D).

Despite not having significant sources of trace metals, Ilha Grande Bay harbors a shipyard, an oil terminal, and a commercial port, as well as two thermonuclear power plants, all of which indirectly influence the study area. Also, there is a considerable untreated waste outfall and Ilha Grande Bay presents a low water circulation, which contributes to the accumulation of metals in the inner bay.[38,39]

Table 2. Mean, minimum and maximum values and the total mean in mg kg^{-1} referring to each trace metal in all sampling sites (M1, M2, M3, M4 e M5) in mangrove sediments from *Saco do Mamanguá*

Trace metals		M1	M2	M3	M4	M5	Total mean
Cu	Mean	10.6	12.5	11.5	11.7	12.1	11.7
	Maximum	11.4	11.3	12.6	12.2	13.7	-
	Minimun	9.6	8.7	11.0	11.1	10.9	-
Ni	Mean	17.7	16.9	18.4	19.8	22.2	19.0
	Maximum	18.7	19.2	19.7	20.2	24.2	-
	Minimun	17.0	15.6	17.6	19.5	20.2	-
Pb	Mean	29.1	33.1	37.3	37.9	35.2	34.5
	Maximum	32.8	35.2	38.4	39.2	36.0	-
	Minimun	26.4	30.4	36.0	36.0	34.4	-
Zn	Mean	52.0	51.8	63.5	68.2	70.7	61.2
	Maximum	53.6	56.0	66.6	69.3	75.3	-
	Minimun	47.6	47.9	60.9	66.2	68.3	-

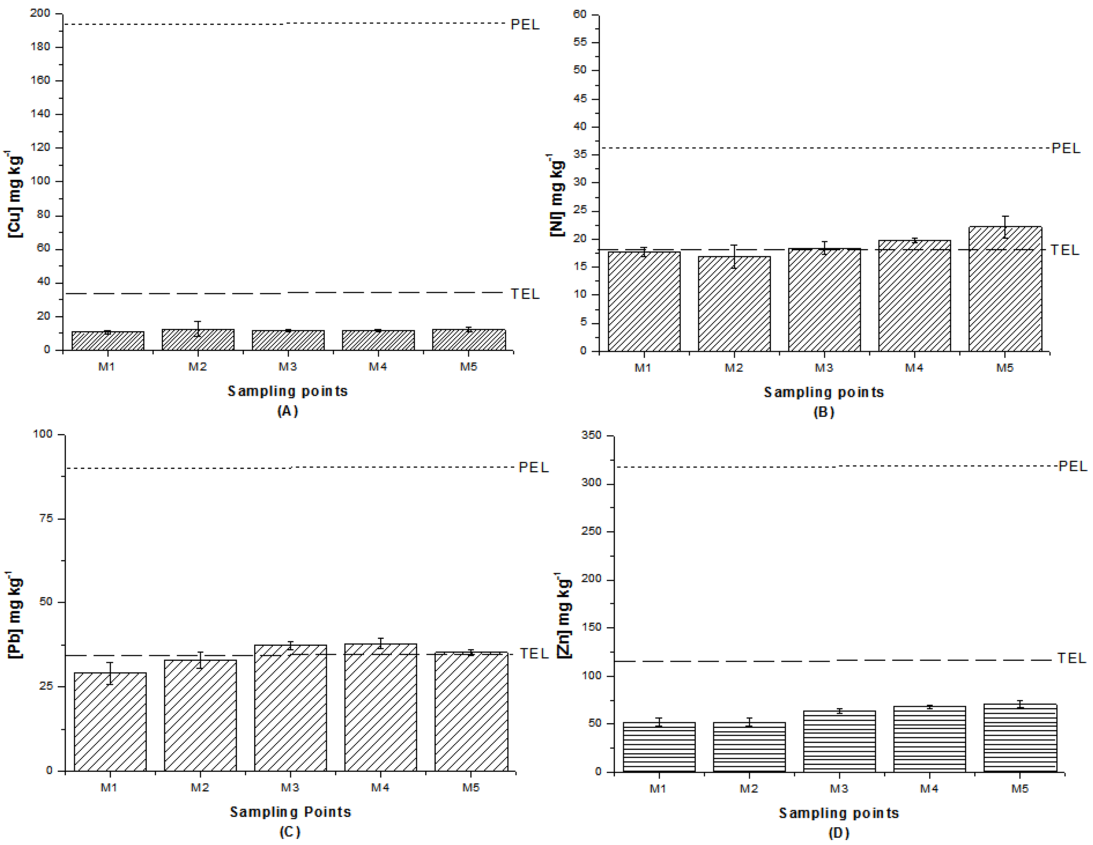

Figure 2. Spatial distribution of concentrations of trace metals in mangrove sediments from *Saco do Mamanguá* (mg kg^{-1}) and sediment quality values (NOAA)[37]: Cu (A), Ni (B), Pb (C) and Zn (D)

The high organic matter content, silt and clay dominant particle size and the low redox potential observed in the sediments, favors the adsorption and the complexation of these trace metals in the mangrove sediments of *Saco do Mamanguá*.[36,17] On the other hand, the contents of the trace metals, could be also related to a possible migration of these contaminants from the neighboring Sepetiba Bay, witch composes an estuarine system with Ilha Grande Bay.[40] Sepetiba Bay has been historically contaminated by trace elements from a large Zn smelting plant, which was closed in 1996, as well as from several other industries, mostly metallurgical plants.[41]

Compared to mangroves from other areas, the results found for *Saco do Mamanguá* presented higher values for Ni and Pb in *Itacurussá* mangrove, higher values for Ni in *Coroa Grande* mangrove and low values for all trace metals in *Guaratiba* mangrove, all located at Sepetiba Bay which is heavily impacted. The results presented low values when compared to Guanabara Bay, which is also heavily impacted (Table 3).

Table 3. Total mean comparison in mg kg^{-1} to results obtained by other works in mangrove sediments like: [a]Souza *et al*.;[42] [b]Coimbra;[43] [c]Velho *et al*.;[22] [d]Machado *et al*.,[44] and [e]Borges *et al.*[45]

Study area	Cu	Ni	Pb	Zn
Saco do Mamanguá	11.7	19.0	34.5	61.2
Guaratiba[a]	34.0	64.6	39.8	610.0
Itacurussa[a]	8.2	10.9	19.9	85.9
Coroa Grande[b]	23.6	13.0	-	436.0
Saco do Mamanguá[c]	66.8	16.2	17	-
Guanabara bay[d]	53	-	-	820
Guanabara bay[e]	65.3	-	35.3	-

Velho *et al.*,[22] has also found Cu concentrations (Table 3) above TEL (34 mg kg^{-1}), corroborating the statements that *Saco do Mamanguá* cannot be considered a non-polluted area according to the pollution levels determined by the international rules (NOAA - *National Oceanic and Atmosferic and Administration* -USA).[37]

4. Conclusions

This study shows that the evaluated sediments of the mangrove forest from *Saco do Mamanguá*, reached concentration levels for some trace metals that can affect the balance of the ecosystem, according to the international classification criteria of sediments from NOAA.

These results indicates a non-polluted area, suggesting regular monitoring of trace metals in the sediments should be undertaken, due to the rapid growth of economic and tourism activities in the surrounding regions of *Saco do Mamanguá.*

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