ACUMULACIÓN DE METALES PESADOS EN SEDIMENTOS DEL DELTA DEL RÍO PARNAÍBA

ACCUMULATION OF HEAVY METALS IN SEDIMENTS OF THE PARNAÍBA RIVER DELTA

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Abstract

This study was carried out to assess the impacts of heavy metals coming into the Parnaíba River Delta in the Brazilian Northeastern region. The sediment concentrations of different heavy metals, such as Pb, Ni, Cr, Cd, Zn, Cu, Fe, Al and Mn, were measured by flame spectrometry. The sediments were collected from 19 sites distributed along 5 estuarine channels. The average concentrations found for Cu and Zn are compatible with the TEL (Threshold Effect Level). However, Cd concentrations were above the PEL (Probable Effect Level) values, while Ni and Cr showed intermediate mean concentrations. There are no established concentration limits for Mn, Al and Fe. These are the first metal biogeochemistry findings in the area and will contribute to the decision-making of environmental authorities, aiming to control the emissions of metallic pollutants in this important area of the Brazilian coast.

Key words: *Enrichment factor, Geoaccumulation index, Pollution, Biogeochemistry.*

Introduction

The inadequate disposal of waste containing heavy metals in the most varied natural environments has caused great ecological concern, especially in those environments with a greater interaction with man. Such disposal may increase the natural concentrations of these metals in the soil, reaching the threshold above which there is a greater probability of effects on the biota. Among the main mechanisms for the contamination of aquatic systems, we can mention, among others, the discharge of domestic or industrial effluents and the leaching of pesticides in agricultural areas. These activities, therefore, have a greater potential to affect the quality of the ecosystem. This is a very important environmental issue, since metals are transported by rivers and ultimately reach the marine environment, where they accumulate in sediments or bioaccumulate, thus damaging the local ecosystem. Studies in watersheds and coastal areas of the Brazilian NE region have shown that anthropogenic emissions of some trace metals exceed natural emissions by an order of magnitude, while these additional loads can alter the quality of estuarine waters (De Paula Filho et al., 2015). In this context, the Parnaíba River Delta has a unique ecological importance for the conservation of wild animals and fisheries in the semi-arid Atlantic coast of NE Brazil. In this region, the preservation and sound management of water resources are essential to adequately support the local human population and the maintenance of its economic activities. Thus, this study was aimed to determine the concentrations of heavy metals (Cu, Cd, Pb, Cr, Mn, Ni, Zn, Al and Fe) in surface sediments in the mangrove areas of the Parnaíba River delta.

Materials and methods

The Environmental Preservation Area of the Parnaíba River Delta is the only open ocean delta in the Americas. It is formed by more than 75 islands and is geolocated between the 2°37' and 3°05' southern latitude parallels and between the 41°08' and 42°30' western meridians (MMA, 2006). The deltaic system of the Parnaíba River is a complex and important ecosystem because of its marine-fluvial dynamics and for harboring important plant and animal communities. It is characterized by extensive fluvial-marine plains intersected by channel-forming islands formed by the accumulation of terrigenous materials. Extensive mangrove areas developed under the influence of these environments, representing an important area of deposition of materials of continental origin. The sampling campaign was conducted in April 2017 on sites located in mangrove areas along the estuarine channels. All in all, surface sediments were sampled from 19 sampling points (Figure 1). The sediments were collected using a plastic shovel and were then stored in plastic bags.

Figure 1. Location map highlighting the sampling points along the Parnaíba River Delta.

The samples were oven-dried at 80°C and the clods that formed in the drying stage were pulverized. Acid extracts were obtained from the leaching of about 1.0000 g of the 63 µm fraction in 30.0 ml of a 50% aqua regia solution ($3HCl.HNO_3$). The procedure was performed in a closed system heated to 80ºC for 2 hours (Aguiar et al., 2007). The obtained extracts were tested by flame atomic absorption spectrophotometry (FAAS) using a VARIAN SpectraA 50b spectrophotometer at the Analytical Lab of the Federal University of Cariri. The validation of this method was performed by testing a Standard Reference Material sample - NIST 1646a (US National Institute of Standards and Technology). Recovery rates for the metals were 96% for Zn, 94% for Cu, 91% for Cd, 89% for Pb, 92% for Ni, 89% for Cr, 92% for Mn, 85% for Al and 101% for Fe. Standard curves were constructed using standard solutions with known concentrations in order to calculate the concentrations of the samples. All samples were tested in duplicate. The results were compared to the sediment quality criteria for the presence of heavy metals as described in CONAMA Resolution No. 454 (CONAMA, 2012). Although this regulation refers to the bulk fraction (<2 mm), we used the fine fraction (<63 µm) as it has a higher capacity to concentrate contaminants and is the one usually used in environmental studies. Excess amounts of toxic metals in the environment can cause pollution problems in coastal areas. The metal enrichment factor (EF) and the geoaccumulation index (Igeo) have been widely used to assess metal pollution of environmental concern in the sediments. Iron was used as a normalizing element. Metal EF values are divided into five categories based on the degree of enrichment, i.e. EF<1 No enrichment; 1-3: minimal enrichment; 3–5: moderate enrichment; 5–10: significant enrichment; 10–25: severe enrichment; 25-50: very severe enrichment; and >50: extreme enrichment (Taylor, 1964). The Igeo classes and scales are divided as follows: Class 0: <0, suggesting an unpolluted environment: Class 1: 0 -1 (unpolluted to moderately polluted); Class 2: 1 – 2 (moderately polluted); Class 3: 2–3 (moderately to strongly polluted); Class 4: 3–4 (strongly polluted); Class 5: 4–5 (strongly to extremely polluted); and Class 6: >5 (Extremely polluted) (Müller, 1969).

Results

Among the 19 monitored sites, P9 was the sampling point that presented the highest concentrations of Cu, Cr and Mn. P13 presented the highest concentration of Cd, while P10 presented the highest concentrations of Ni and Zn. The highest values for Al and Fe were obtained in P11 and P7, respectively (Figure 2).

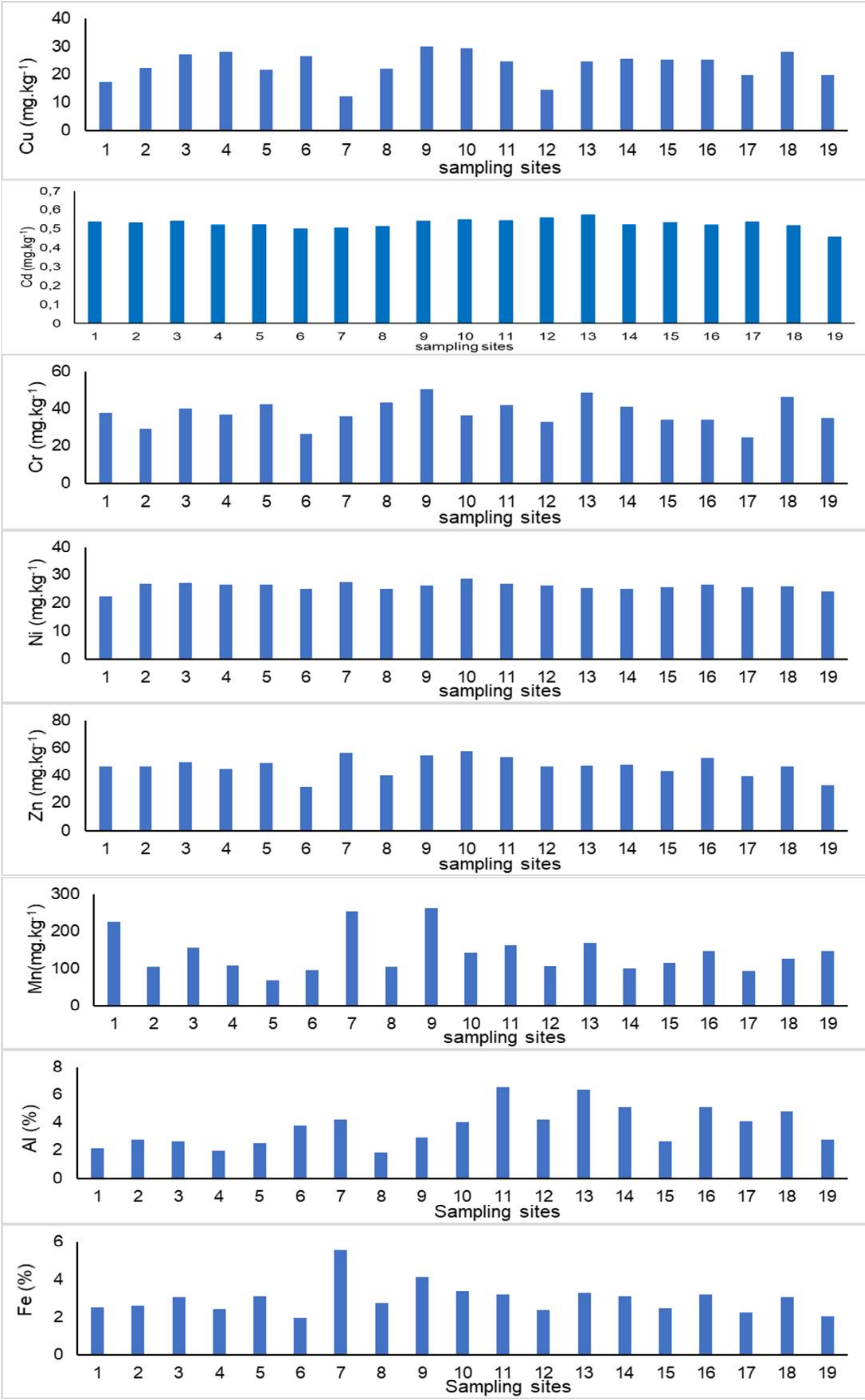

Figure 2. Spatial distribution of heavy metal concentrations in surface sediments of the Parnaíba Delta.

Table 1 shows the descriptive statistics of metal concentrations. The values were compared to the TEL and PEL limits provided under CONAMA Resolution No. 454 (CONAMA, 2012). The Cu, Cd, Cr, and Zn concentration ranges were lower than Level 1 (TEL). Below those values a low probability of adverse effects to the biota are expected to occur. On the other hand, the range of Pb and Ni concentrations were below Level 2 (PEL), which corresponds to a threshold above which a probable adverse effect on the biota is to be expected. However, the concentrations at all sampling sites exceeded the TEL values in the form of intermediate values. Mn, Al and Fe are not considered in the legislation, yet their concentrations are strongly related to the predominance of Oxisol soils, which are present in the watershed of the Parnaíba River. These soils are characterized by an advanced state of weathering, with an accumulation of insoluble iron and aluminum oxides, being the most frequent goethite ($\alpha FeOOH$), hematite ($\alpha Fe_2 0_3$) and gibbsite ($\gamma Al(OH)_3$).

Table 1. Descriptive statistics and limit values for trace metal concentrations in surface sediments

Metal	**Range**	Average	Q. 25%	Q. 75%	**EF**	**Igeo**	**TEL**	**PEL**
Cu	12.1 – 29.8	21.4	19.9	27.1	0.7 – 3.0	0.3 – 1.5	34	270
Cd	0.46 – 0.57	0.53	0.52	0.54	0.24 – 0.54	-1.0 – - 0.7	1.2	9.6
Pb	57.8 – 99.5	80.9	68.5	99.9	4.1 – 10.8	2.7 -3.5	46.7	218
Cr	24.9 – 50.5	35.6	34.0	42.2	0.5 – 1.2	-0.1 - 0.8	81	370
Mn	67.1 – 262.1	138.3	103.6	161.9	0.04 – 0.2	-3.8 – -1.2	-	-
Ni	22.4 – 28.7	25.9	25.2	26.8	0.1 - 0.3	-2.2 – -1.8	20.9	51.6
Zn	31.7 – 57.6	45.7	43.0	49.6	1.1 – 1.9	0.7 – 1.5	150	410
Al	2.2 – 6.5	4.0	2.6	4.8	-	-	-	-
Fe	1.9 – 5.6	2.9	2.4	3.2	-	-	-	-

The Igeo values indicate that the sediments can be classified as non-polluted to moderately polluted for Cr, Cd, Mn and Ni. The moderately polluted soils owe such classification predominantly to Cu and Zn. Moderately to severely polluted soils were classified as such due to their Pb content.

Conclusions

In general, the results show that the sediments of the Parnaíba Delta present low concentrations of metals when compared with reference values. In general, most sampling sites showed concentrations below the threshold effect level (TEL), below which adverse biological effects are expected to occur. Still, the geochemical indices show that, at certain sampling sites, there is a moderate to severe degree of pollution.

References

Aguiar, J.E., Marins, R.V., Almeida, M. D., 2007. Comparison of marine sediment digestion methodologies for the characterization of trace-metal geochemistry on the northeast Brazilian continental shelf. Geochimica Brasiliensis, v. (21), n. 3, p.304-323.

Conselho Nacional de Meio Ambiente - CONAMA. Resolução nº 454. Estabelece as diretrizes gerais e os procedimentos referenciais para o gerenciamento do material a ser dragado em águas sob jurisdição nacional - Publicação DOU, de 08/11/2012, Seção 1, pág. 66.

De Paula Filho, F. J., Marins, R. V., De Lacerda, L. D., Aguiar, J. E., & Peres, T. F., 2015. Background values for evaluation of heavy metal contamination in sediments in the Parnaíba River Delta estuary, NE/Brazil. Marine Pollution Bulletin, 91(2), 424–428.

Ministério do Meio Ambiente – MMA., 2006. Secretaria de Recursos Hídricos. Caderno da Região Hidrográfica do Parnaíba. Brasília: 2005.

Müller, G., 1969. Index of geo-accumulation in sediments of the Rhine River. Geojournal, 2:108–118.

Taylor, S.R., 1964. Abundance of chemical elements in the continental crust: a new table. Geochimica et Cosmochimica Acta. 8(1):1273–1285.