Artigo

Distribution and Fractionation of Metals in Mangrove Sediment from the Tibiri River Estuary on Maranhão Island

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Distribuição e Fracionamento de Metais em Sedimentos de Manguezais do Estuário do Rio Tibiri na Ilha do Maranhão

Resumo: Diretrizes de qualidade de sedimentos e o protocolo de extração química sequencial da Comissão Europeia foram aplicados para a avaliação de Cd, Cr, Cu, Ni, Pb e Zn em sedimentos de manguezais do Rio Tibiri na Ilha do Maranhão. As concentrações dos metais foram determinadas usando a espectrometria de emissão óptica com plasma indutivamente acoplado (ICP OES). Os resultados demonstraram que os níveis de metal estavam abaixo do TEL (*threshold effect level*) e ERL (*effect range low*), faixas associadas à efeitos biológicos adversos ocasionais para a vida aquática. A mobilidade dos metais na ordem decrescente foi: Ni (24%) > Zn (20,6%) > Cu (14,5%) > Pb (1,9%). Exceto para Ni e Zn, outros metais não foram encontrados na fração trocável/ácido solúvel (F1). Os metais Ni, Zn e Cu estavam presentes na fração redutível (F2). A maior porcentagem de metal estava associada à fração oxidável (F3) e fração residual (F4). Neste último, a porcentagem de metal variou 76-100%, o que sugere um impacto inexpressivo de atividades antropogênicas.

Palavras-chave: Protocolo BCR; estuário; manguezal.

Abstract

Sediment quality guidelines and the sequential chemical extraction protocol of the European Commission were applied for the assessment of Cd, Cr, Cu, Ni, Pb and Zn in mangrove sediments from the Tibiri River on Maranhão Island. Metals concentrations were determined using the inductively coupled plasma optical emission spectrometry (ICP OES) technique. The results demonstrated that metal levels were below TEL (Threshold effect level) and ERL (effect range low), range associated with occasional adverse biological effects for the aquatic life. Metal mobility in decreasing order was: Ni (24%) > Zn (20.6%) > Cu (14.5%) > Pb (1.9%). Except by Ni and Zn, other metals were not found in the exchangeable/acid-soluble fraction (F1). Only Ni, Zn and Cu were present in the reducible fraction (F2). The major metal percentage was associated to oxidizable fraction (F3) and residual fraction (F4). In the latter, metal percentage ranged from 76 to 100%, which suggests an inexpressive impact of anthropogenic activities.

Keywords: BCR protocol; estuary; mangrove.

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1. Introduction

Natural processes are responsible for dissemination of metals from primary rocks through the different environmental compartments, such as soil, atmosphere, groundwater, surface waters and sediment. The environmental importance of studying metals is related to their potential toxicity, even though some of them are essential for life, such as Zn, Cr and Cu.[1, 2] Sediment is formed by continuous deposition of autochthonous particles, produced in water columns, and allochthonous particles from drainage basins. In consequence, sediment can suffer expressive metal accumulation due to presence of iron and manganese oxides, clays or organic matter among other constituents. Occasionally, in function of physical and chemical changing of environments, metals can be released into porewater and reach aquatic biota,[3] where they may even suffer bioaccumulation and biomagnification, as is the case of Hg. When the ecosystem is an estuary, an intermediate region between terrestrial and marine environment marked by daily tidal flooding, specific biomes, such as mangrove forests, may appear.[4] In the case of mangroves, they are known for the high organic matter content. In this situation, mangrove sediment is favorable to reducing conditions, where metals can be immobilized in the form of sulphides or complexed with organic matter.

Different conceptual models are used to assess the environmental risk of metals, e.g., the threshold effect level (TEL) and probable effect level (PEL) of the Canadian Environment;[5-7] sulfides volatile acids, SAV (Jonge et al., 2012)[8] and sequential extractions as Tessier et al. (1979)[9] methods and BCR protocol (Community Bureau of Reference, now Standards, Measurement and Testing Programme).[3, 10-12] TEL/PEL are concepts that establish limits (threshold) based on a toxicological curve of a given element or substance. TEL refers to the concentration below which effects on the aquatic life are rarely observed and PEL is the limit above which adverse effects are frequently observed. The concentration of metals for using the above criteria is done by digestion with acids, strong enough to remove metals considered bioavailable (Hübner et al., 2009).[6] The simple determination of metal concentration in sediment is not enough assess the mobility and further bioavailability and toxicity. Therefore, sequential chemical extractions are intended to convert metals bonded in the solid phase of sediments into soluble forms by specific extraction solutions, which progressively release the metals more strongly linked to the sediment matrix. Accordingly, fractions can be associated with the bioavailability of metals, what is associated with risk for aquatic life.[8, 13]

This work is based on the protocol established by the BCR to evaluate the three geochemical fractions of sediments (exchangeable/acid-soluble, reducible and oxidizable fractions) of trace metals (Cd, Cr, Cu, Ni, Pb and Zn) in mangrove sediments.[14] They were collected from the Tibiri River Estuary on Maranhão Island, located in the Amazon region. In addition, this work assesses the risks of trace metals using the TEL/PEL and ERL/ERM guide values for protection of the aquatic life. Both protocols, the BCR and sediment quality guide, aim to assess whether ecosystems are impacted by trace metal.

2. Materials and methods

2.1. Area of Study

The Figure 1 shows the drainage basin of the Tibiri River Estuary, which has an area of 140 km^2 and a perimeter of 52.88 km (adapted from authors Alcântara, 2004[15] and Pereira et al., 2007[16]). It is located in the southwest of Maranhão Island. The river flows into São José Bay and suffers expressive intrusion of saline waters from the Atlantic Ocean, where the mean tidal range reaches six meters.[17] The Tibiri River has important

mangrove vegetation.[17-19] The predominant species in the area are: *Rhizophora mangle, Avicennia germinans, Laguncularia racemosa* and *Avicennia schaveriana*.[20] Mangrove areas are nursery and breeding grounds for several commercially important species of marine fauna. These areas are rich in shellfish, such as crustaceans, as well as in activities of commercial fishing and subsistence.[20] The State of Maranhão has most of the Brazilian mangrove forest. Several environmental impacts due to urbanization have been pointed out in this basin, such as raw sewage disposal, deforestation, extraction of clay,

presence of a municipal industrial district and a municipal landfill. In the Tibiri River Estuary, activities such as shrimp fishing, irrigation of horticulture and source of recreation on weekends are yet common.[18, 20] Sabino stream tributary stands out due to the presence of the municipal landfill of the city of São Luis in its basin, which represents a high risk of contamination of soil, groundwater, atmosphere and superficial waters,[19] especially due to its precarious structure.
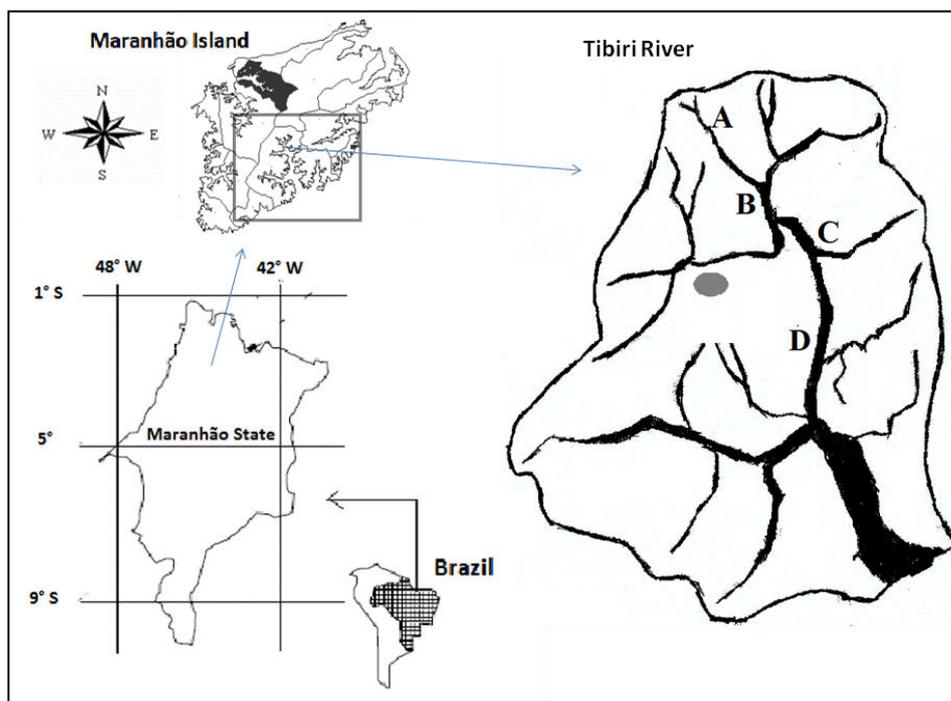
Figure 1. Sampling sites in the Tibiri River: A (Nascente), B (Afluente), C (Ribeira), D (Taçajoaba). Ellipse corresponds to municipal landfill

2.2. Sampling

The surface sediment samples were collected along the bed of the river (Fig. 1). The first site (letter *A* in Fig. 1) corresponds to an area near the source of the river (Nascente). The second sampling site (letter *B* in Fig. 1) corresponds to an intermediate location where the Tibiri River has already received water discharge from its small

tributaries (Afluente). The third site (C) corresponds to a place where the Tibiri River receives water from Sabino stream (Ribeira). The last site (D) corresponds to an area located after Sabino stream confluence (Tajaçoaba). The sediment samples were collected from surface sediment in November 2011. The collection was performed using a stainless steel Van Veen dredge type, specific for sediments. At the time of sampling, the sediments were submerged. Subsequently,

the samples were stored in plastic bags properly identified and packed in thermal boxes with ice. After being packed in plastic bags and refrigerated, the samples were sent to the laboratory. Drying process was initiated on the same day. Sediment samples were dried at 40 º C during 72 h, and homogenized to a fine powder in a porcelain mortar. Subsequently, they were sieved in a 63 µm sieve (this fraction, formed by silt and clay, is the most important for the study of metal contamination). They were stored in a plastic bag for future analysis.[13]

2.3. Analysis of Sediment

The determination of exchangeable cations and exchangeable acidity followed the methodology described by Cotta (2006).[21] The sum of both constituted the effective cation exchange capacity (CEC). The organic matter determination was made using the gravimetric method. The pipette method was used for particle size analysis.[22] All material was weighed on an analytical balance accurate to 0.1 mg**.**

2.4. Metal Analyses and Quality Control

All glassware was decontaminated in a 30% HNO_3 bath for 72 hours and subsequently washed with Milli-Q ultrapure water (conductivity 0.056 µS/cm,25°C). All reagents were of analytical grade or Suprapur quality (Merck®) and metal analytical standard were SpecSol® mark with certificates of origin. Metals analysis was performed by inductively coupled plasma optical emission spectrometry (ICP OES) Varian 720ES of UEMA (State University of Maranhão). The lines used were Cd (λ = 214.4 nm), Cr (λ = 283.5 nm), Cu (λ = 324.7 nm), Ni (λ = 231.6 nm), Cu (λ = 324.7 nm), Pb (λ = 220.3 nm), and Zn (λ = 213.8 nm). The extraction steps in each batch were accompanied by a blank (all reagents except the sediments). The precision of extraction was evaluated by triplicate measurements for each extraction step, including all sediment samples. Certificate reference material (BCR 701) was used to validate the extraction steps. This material is supplied by Institute for Reference Materials and Measurements from European Commission. Extractable mass fractions based on dry mass are presented for six metals (Cd, Cr, Cu, Ni, Pb and Zn).

2.5. Extraction Procedure

The extraction procedure applied in this study followed the protocol adopted by the Standards, Measurements and Testing Programme (SMT-BCR) of the European Commission (Table 1).[23-25] To evaluate the toxicity of sediments used in this study, the total metal concentration in sediments (without sieving) was determined through digestion with *aqua-regia* (HCl/HNO_3; 3:1).[25] These values are considered pseudo total concentration. It must be clear that procedure does not represent the total metal concentration in the sample, because that metal in mineral lattice is not released. In this text "pseudo total concentration" will called only "metal concentration".

Table 1. Sequential chemical extraction of trace metals in sediment by BCR protocol

Fraction	Description	Reagents	Vol (mL)	T (ºC)	Extraction time
F1 (Exchangeable/acid-soluble)	Exchangeable cations and carbonates	0.11 mol L^{-1} CH$_3$COOH	40	22±5	Mechanical stirring for 16 h (end-over-end)
F2 (Reducible)	- oxides and hydroxides of iron and manganese	0.5 mol L^{-1} de NH$_2$OH.HCl; acidified with HNO$_3$ 2 mol L^{-1} until pH =2	40	22±5	Mechanical stirring for 16 h (end-over-end)
F3 (Oxidizable)	Organic matter and sulphides	8.8 mol L^{-1} H$_2$O$_2$;	10	22±5	Digestion 1 h stirring
				85±5	Digestion 1 h
			10	85±5	Digestion 1 h
		1 mol L^{-1} de CH$_3$COONH$_4$ (pH 2);	50	22±5	Digestion 1 h stirring occasionally
F4 (Residual)	Silicate materials	*Aqua-regia* HCl/HNO$_3$ (3:1)	10	22±5	16 h rest
				85±5	Heating 2 h with occasional agitation

3. Results and Discussion

3.1. Quality Assurance

The Pearson coefficients for the standard curves were greater than r^2 = 0.998. The calibration ranged from 0.01 to 10 mg L^{-1}. The values of the relative standard deviation ranged from 4.4 to 12%, which can be considered reasonable for this concentration range. Table 2 shows that the recovery rates for certificate reference material (BCR 701) ranged from 87 to 120%.

Table 2. Analysis results of standard reference material BCR-701 (mean ± standard deviation, n = 3). Concentration in mg kg^{-1}

Metal		Cd	Cr	Cu	Ni	Pb	Zn
Sequential extraction							
Step 1	Analyzed	9.5 ± 0.8	1.96 ± 0.08	46.8 ± 1.9	13.7 ± 0.7	3.82 ± 0.22	225 ± 11
	Certified	7.3 ± 0.4	2.26 ± 0.16	49.3 ± 1.7	15.4 ± 0.9	3.18 ± 0.21	205 ± 6
Step 2	Analyzed	4.03 ± 0.21	47.1 ± 2.8	154 ± 10	24.7 ± 2.2	142 ± 17	98 ± 6
	Certified	3.77 ± 0.28	45.7 ± 2.0	124 ± 3	26.6 ± 1.3	126 ± 3	114 ± 5
Step 3	Analyzed	0.26 ± 0.02	159± 15	6 4 ± 3	19.1 ± 1.2	8.2 ± 0.9	43 ± 3
	Certified	0.27 ± 0.06	143 ± 7	55 ± 4	15.3 ± 0.9	9.3 ± 2.0	46 ± 4

3.2. Metal Concentration

The profile of the total metal concentration in the sediment along the sampling sites (Nascente, Afluente, Ribeira and Tajaçoaba) is shown in Table 3 with respective standard deviations. These results were obtained with digestion of the dry sediment (without sieving) using *aqua-regia* and they are important to compare metal concentration with guide parameters (TEL/PEL). This procedure is known as pseudo total concentration due to metal in mineral lattice not being measured.[7]

Table 3 shows that Cd was not detected in sediments studied in this work (below detection limit). This can be explained by considering the low background value of this metal. It is worth mentioning that Cd mean shale was 0.25 mg kg^{-1}, which was the lowest background value of metals studied in this work. The highest concentrations observed belonged to Zn, especially in Tajoçoaba sediment (38 mg kg^{-1}), but yet it was lesser than TEL for marine sediment (124 mg kg^{-1}). Regarding Pb, concentration reached a maximum value of 14.5 mg kg^{-1} in Tajaçoaba

sediment and does not represent risk for aquatic life, considering that TEL is 30.2 and PEL is 112 mg kg^{-1}. Another toxic metal, i.e., Ni, presented low concentration, ranging from 6.3 up to 12.4 mg kg^{-1}. These values were below sediment quality guide, TEL = 15.9 mg kg^{-1}. Concentrations of Cr in sediments from the Tibiri River (5.7 to 13 mg kg^{-1}) were below TEL (52.3 mg kg^{-1}), as prescribed to marine environments. Cu concentrations ranged from 11.7 to 16.2 mg kg^{-1}. These values were also below TEL value, i.e., 18.7 mg kg^{-1}.

Another criterion to assess metal toxicity was developed by Long *et al.* (1995)[26] and it is similar to Canadian TEL/PEL. This criterion has also two thresholds: ERL (effect range low), concentration below which effects on the aquatic life are rarely observed; and ERM (effect range medium), concentration above which effects on the aquatic life are probably observed. Both criteria were developed for sediment from marine and estuarine regions. ERL/ERM criteria have concentration limits higher than TEL/PEL. For example, while Pb has TEL of 30.2 mg kg^{-1}, ERL is 46.7 mg kg^{-1}; in turn, PEL is 112 mg kg^{-1} while ERM is 218 mg kg^{-1}.

Table 3. Total metal concentration in sediment samples from the Tibiri River

Site	Nascente	Afluente	Ribeira	Tajaçoaba
Metal Concentration / mg kg^{-1}				
Cd	nd*	nd	nd	nd
Cr	11.1 ± 0.33	5.76 ± 0.45	12.2 ± 1.47	13.3 ± 0.40
Cu	16.2 ± 1.02	16.0 ± 0.57	15.1 ± 048	11.7 ± 0.58
Ni	9.72 ± 0.95	12.4± 1.24	6.27 ± 0.14	8.05 ± 0.41
Pb	9.40 ± 0.68	8.22 ± 0.72	9.59 ± 0.38	14.5 ± 0.42
Zn	19.5 ± 0.97	35.8 ± 0.35	22.1 ± 0.44	38 ± 4.1

nd : not detectable

Table 4 shows the comparison of the Tibiri River with other aquatic systems with anthropogenic activities. Particularly compared to sediment from Bacanga River on the same island, marked by high human presence, the Tibiri River presented smaller metal concentrations. For example, sediment from the Bacanga River showed Cr values ranging from 24 to 90 mg kg^{-1}, while the Tibiri River showed values from 5.7 to 13 mg kg^{-1}. Metal levels in the Tibiri River are more similar to background values prescribed by National Oceanic and Atmospheric Administration NOAA (2012).[27]

Table 4. Total concentration of metals in different aquatic systems

	Pb	Cu	Ni	Zn	Cd	Cr
1. Guanabara Bay [30]	43	55	5.3	235	0.9	-
2. Todos os Santos Bay [31]	1-25	0.8–10	1- 19	4-37	-	-
3. Santos-São Vicente Estuary [5]	2-204	-	1.3-44	6-284	< 1.49	< 111
4. Poxim River [13]	4,8–27	4.3-52.5	2.6 - 26	6,6 - 127	-	5.3-27.3
5. Background (NOAA)[27]	4–17	10 – 25	9.9	7–38	0.1– 0.3	7-13
6. Bacanga River [32]	25-94	< 10	0.2 -10	27-125	0.1- 0.57	27- 90
7. Tibiri River	8.2–14.2	11– 6	6.3-12.4	22 -60	-	5.8– 13.3

Major factors control the stock of metals in sediment such as particle size, pH, organic matter and cation exchange capacity (CEC). Therefore, knowledge about them in sediments is fundamental. These properties are shown in Table 5. pH values remained slightly alkaline (7.9) in sediment samples. According to Middelburg et al. (1996),[28] mangrove sediments have pH values ranging from 3.5 to 8.5 due to their limited buffer capacity. Organic matter degradation, as consequence of anaerobic respiration by sediment bacteria, has two functions: it is important for keeping the redox potential in mangrove sediments low and it also produces organic acids responsible for pH decreasing.

Sulphides oxidation has important role in pH decline,[29] according to the following reaction: $FeS_2 + 3.75\ O_2 + 2.5\ H_2O = FeOOH + 2\ H_2SO_4$ and $H_2S + 2O_2 = H_2SO_4$. On the other hand, as observed in this study, the slightly alkaline values of pH found in Tibiri sediments are favorable to metal adsorption and metal precipitation as carbonate due to the absence of proton competition. Adsorption capacity was measured through CEC whose values ranged from 28.4 to 36.8 $cmol_c\ kg^{-1}$. This capacity is associated to the presence of silt/clay (mean of 32.4 %), organic matter (mean 16.5%), and iron and manganese oxides, which represent important substrates for metal adsorption. Among these substrates, organic matter has the highest CEC (150 to 400 $cmol_c\ kg^{-1}$). Spermann correlation coefficient was not expressive among the parameters above mentioned.

Table 5. Chemical and physical characteristics of sediments from the Tibiri River, Maranhão Island.

	NASCENTE	AFLUENTE	RIBEIRA	TAJAÇOABA
Silt / %	59	64	61	60
Clay / %	40	36	38	40
CEC[a] / $cmol_c\ kg^{-1}$	28.4	32.8	36.8	31.6
OM[b] / %	16.3	20	14.6	15.3
pH	7.9	7.9	7.8	7.8

[a] Cation exchange capacity; [b] Organic Matter

3.4. Metal Fractionation

Figure 2 shows metal fractionation in sediments. Metals were absent in exchangeable/acid-soluble fraction (F1) (Fig. 2A to 2E), except for Ni in Nascente, in spite of the sediment samples have had expressive CEC and alkaline conditions to form carbonates. In turn, metals in reducible fraction (F2) were more expressive for Zn in Nascente, Afluente and Ribeira. In this fraction, the decreasing order was: Zn (6.8%) > Ni (2.2%) > Pb (1.9%). Zn is extremely toxic to microscopic aquatic organism; however, it is also an essential element for aquatic and terrestrial living organism. Soluble species of Zn are readily available for biota assimilation. Therefore, Zn species associated to sediment and particles are very important for performing environmental assessment.

Reducible fraction (F2) is formed by Fe-Mn oxides and oxihydroxides (e.g., goethite and pyrolusite) which occludes metals by coprecipitation during oxide formation and isomorphic substitution.[4, 29] Possible explanation for the inexpressive reducible fraction (F2) is the prevalence of low redox potential due to high organic matter content in mangrove sediment. Generally, F1 and F2 fractions are smaller than F3 and F4 fractions in environment (Figure 2).

Metal in the oxidizable fraction (F3) had the following decreasing order (Fig. 2): Cu (14.5%) > Ni (14.3%) > Zn (13.8%). Cr and Pb showed no detectable presence in oxidizable fraction (F3) (Fig. 2B and 2C). Zn and Ni appeared in the oxidizable fraction (F3) (Fig. 2D and 2E), but not in all sites. In all sampling sites, Cu concentration was distributed between oxidizable fraction (F3) and residual fractions (F4). This significant Cu association with organic matter occurs due to the high affinity of this metal with this substrate and its ability to form complexes with humic substances present in sediments.[33, 34] In this work, after Cu, Ni showed larger percentage concentration (13.3%) in oxidizable fraction

(F3). Marchand et al. (2011)[4] studying metal behavior in mangrove from New Caledonia Island observed that Ni was present as component of sulfides and organic matter. Metal participation in oxidizable fraction (F3) corroborates the fact that in mangrove sediment both the high presence of organic matter (mean 16.5%) and anoxic conditions are favorable to the accumulation of metals.[4] It should be observed that mangroves are tidal ecosystems, whose chemical properties such as salinity and oxygen concentration suffer great variation affecting chemical reactions in the surface sediment. For example, oxic/anoxic conditions affect redox equilibrium such as S_2^-/SO_4^{2-} and Fe^{2+}/Fe^{3+}. Redox potential is also influenced by depth and vegetal zones. It is worth noticing that present work does not include this seasonal study.

Another important aspect of metal fractionation is the presence of Cr only in the residual fraction (F4). Two species of Cr are found in environmental as Cr^{6+} and Cr^{3+}; the first is soluble and highly toxic while the latter is low soluble and important to living organisms. Organic matter, sulphides and Fe^{2+} are able to reduce Cr^{6+} to Cr^{3+}, minimizing mobility and environmental risk. Manganese oxide is known for its capacity to oxidize Cr^{3+}, increasing environmental risk. In this work, Cr showed no mobility, belonging to residual fraction (F4), which means that it does not have capacity to be available in pore water and consequently reach aquatic biota. Mobility absence also occurred with Pb, except for Tajaçoaba, where there was a small reducible fraction (F2), Pb (1.9%). The most important Pb species in natural environment is Pb^{2+}, which forms oxides and hydroxides. Low solubility compounds are formed with Cl-, CO_3^{2-}, SO_4^{2-} and PO_3^{2-} and organic ligands such as humic and fulvics acids. Insoluble lead carbonate formation is more favorable with pH above 6. In spite of the fact that these compounds are common in environment, in this work, almost total Pb belonged to residual fraction (F4), indicating inexpressive Pb contamination.

In unpolluted sediments, trace metals exist mainly associated to mineral lattice from lithogenic origins. In turn, polluted sediments will have more trace metals in the three first fractions, which are vulnerable to environmental changes, i. e.: a) metal in exchangeable/acid-soluble fraction (F1) represents the amount of elements that would be released to pore water if pH diminishes, since more acid conditions lead to metallic carbonates dissolution and competition by sorption sites; b) in reducible fraction (F2), lower redox potential would release metal from Fe-Mn oxides by Fe and Mn reduction; c) in opposite direction, increase of redox potential would oxide organic matter and sulphide, releasing metal from oxidizable fraction (F3). Since the first three fraction has potential capacity to release metal to the environment, metal mobility can be calculated by dividing the most labile fractions (F1 + F2 + F3) by the sum of all fractions (F1 + F2 + F3 + F4), expressed as a percentage.[35-39]

According to Figure 3, Pb only showed mobility in Tajaçoaba (7.7%), Ni had expressive mobility in Nascente and Afluente. Afluente stood out due to the high value of Ni (65.9%). Zn and Cu were the only metals to have mobility in all sites. Using mean values of mobility, it can be observed that the order of metal decreasing mobility was: Ni (24%) > Zn (20.6%) > Cu (14.5%) > Pb (1.9%) > Cr, Cd (< detection limit). The results reveal that the most part of metals in the mangrove sediment belonged to residual fraction (F4) and metal from human activities were inexpressive.
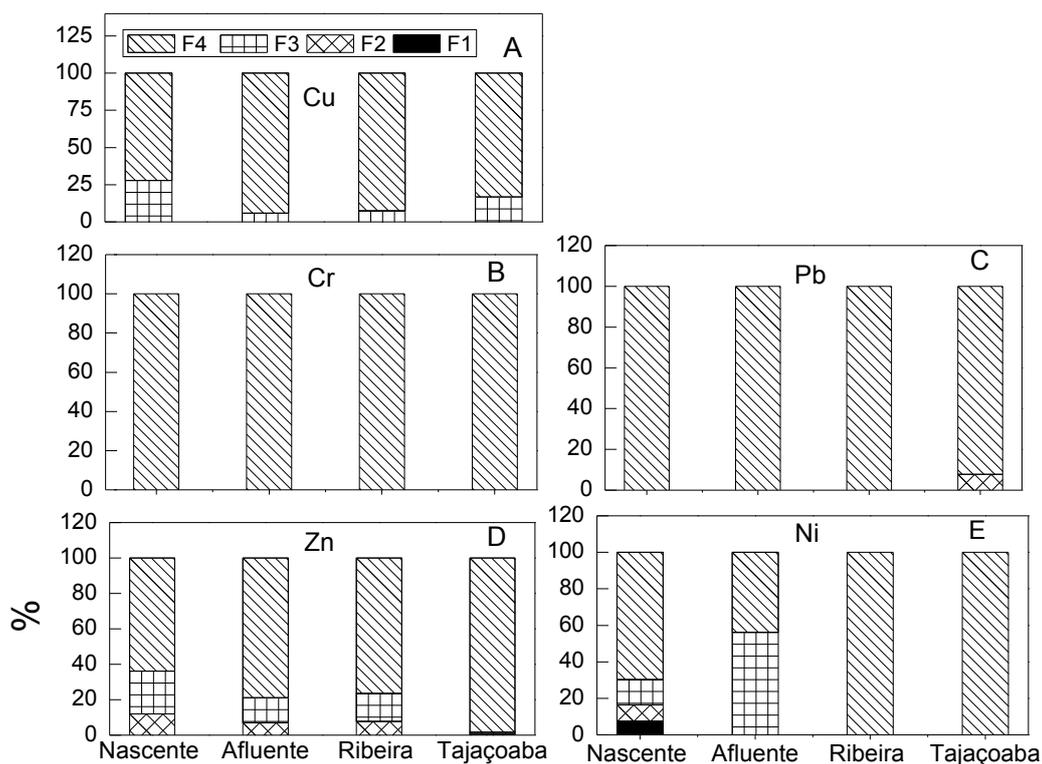
Figure 2. Metal fractionation in sediments from the Tibiri River Estuary, Maranhão Island
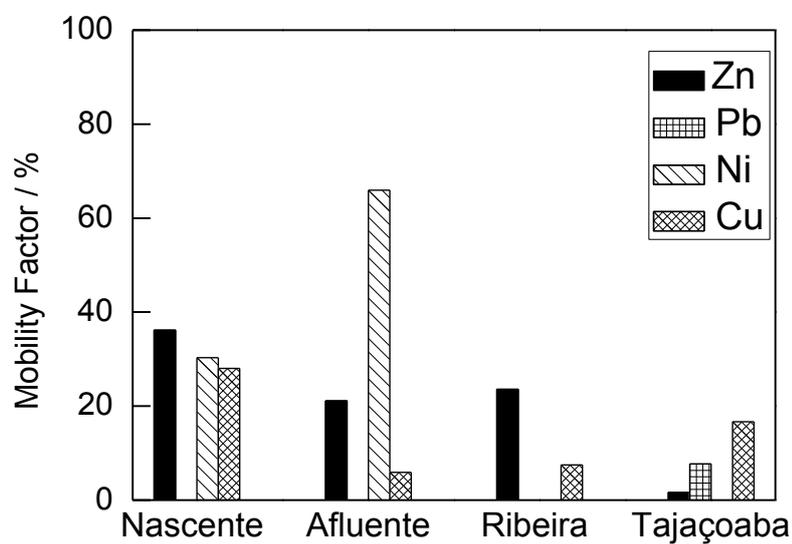
Figure 3. Metal mobility considering the three first fractions (exchangeable/acid-soluble, reducible and oxidizable) in mangrove sediment from the Tibiri River, Maranhão Island

4. Conclusion

Cd, Cr, Cu, Ni, Pb and Zn remained at levels compatible with NOAA.[27] They had concentrations whose values were below the threshold associated with occasional adverse effects to aquatic life according to TEL/PEL and ERL/ERM criteria. The order of mobility (considering the sum of the first three most mobile fractions) was: Ni (24%) > Zn (20.6%) > Cu (14.5%) > Pb (1.9%) > Cd, Cr (no detectable). Among the most mobile fractions, oxidizable fraction (F3) was the most expressive showing the following order: Cu (14.5%) > Ni (14.3%) > Zn (13.8%). Major metal concentrations were found in residual fraction (F4), with an average ranging from 76 to 100%, what suggests an inexpressive impact of anthropogenic activities.

Acknowledgments

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