Revista Virtual de Química

ISSN 1984-6835

Artigo

# The Role of Metals and their Fractions in the Bacanga River Estuary: an Example of the Anthropogenic Interference in a Tropical Ecosystem

**da Silva, G. S.;* Corrêa, L. B.; Marques, A. L. B.; Marques, E. P.; Nunes, M. L. F.; Sousa, E. R.; Silva, G. S.**

*Rev. Virtual Quim.*, **2015**, *7* (4), 1130-1144. Data de publicação na Web: 15 de março de 2015

http://www.uff.br/rvq

## O Papel dos Metais e suas Frações no Estuário do Rio Bacanga: um Exemplo da Interferência Antropogênica em um Ecossistema Tropical

**Resumo**: O Rio Bacanga localizado na cidade de São Luís, estado do Maranhão-Brasil, é um estuário cuja hidrologia foi drasticamente alterada pela construção de uma barragem e pela ocupação humana. Para avaliar o papel dos metais traço (Cu, Cd, Cr, Pb, Ni e Zn) na qualidade dos sedimentos foi determinada a concentração total desses metais por espectrometria de emissão atômica por plasma indutivamente acoplado (ICP OES). As características físicas e químicas foram analisadas pelos métodos clássicos. As frações geoquímicas dos metais no sedimento foram determinadas aplicando-se a extração química sequencial, segundo protocolo da Comunidade Europeia. Os resultados foram analisados estatisticamente pelo uso da análise dos componentes principais e análise hierárquica. As concentrações dos metais demonstram que Pb e Cr apresentam risco à vida aquática segundo critérios desenvolvidos pela agência ambiental canadense. Outros metais estão abaixo desse limiar e raramente oferecem risco para a vida aquática, embora estejam em níveis superiores às condições normais naturais. A labilidade parcial dos metais apresentou a seguinte ordem: Zn (63,4%) > Cu (53,5%) > Cd (50,7%) > Pb (47,0%) > Ni (40,8%) > Cr (35,0%), tornando-se um fator que minimiza o risco ambiental. Os resultados desse trabalho indicam que os sedimentos estão contaminados por metais traço e apresentam risco à vida aquática (Pb e Cr), o que demanda ações imediatas de minimização/eliminação das fontes de poluição.

***Palavras-chave:*** Extração química sequencial; sedimento; manguezal.

## Abstract

The Bacanga River in the city of São Luís, Maranhão state, Brazil, is an estuary whose hydrology was drastically altered by the construction of a dam and human occupation. To evaluate the role of trace metals (Cu, Cd, Cr, Pb, Ni and Zn) in sediment quality was determined the total concentration of these metals by atomic emission spectrometry by inductively coupled plasma (ICP OES). The physical and chemical characteristics were analyzed by classical methods. The geochemical fractions of metals in the sediment were determined by applying the sequential chemical extraction, according to the European Community's protocol. The results were statistically analyzed using analysis of the principal components and hierarchical analysis. The metal concentrations show that Pb and Cr present risk to aquatic life in accordance with criteria developed by the Canadian Environmental Agency. Other metals are below this threshold and rarely offer risk to aquatic life, although they are at higher levels to natural although they are at higher levels than natural conditions. Partial lability of metals followed the sequence: Zn (63.4%)> Cu (53.5%)> Cd (50.7%)> Pb (47.0%)> Ni (40.8%)> Cr (35.0%), becoming a factor that minimizes environmental risk. The results of this work indicate that the sediments are contaminated with trace metals and present a risk to aquatic life (Pb and Cr), which requires immediate action to minimize/eliminate pollution sources.

***Keywords:*** Sequential chemical extraction; sediment; mangrove.

* Federal Institute of Education Science and Technology of Maranhão, Department of Chemistry, Monte Castelo Campus, Av. Getúlio Vargas nº 04, Zip Code 65030-005, São Luís-MA, Brazil.

gilmarsilverio@gmail.com

**DOI: 10.5935/1984-6835.20150063**

Volume 7, Número 4

Julho-Agosto 2015

Revista Virtual de Química
ISSN 1984-6835

# The Role of Metals and its Fractions in the Bacanga River Estuary: an Example of the Anthropogenic Interference in a Tropical Ecosystem

**Gilmar S. da Silva,[a,*] Luciana B. Côrrea,[b] Aldalea L. B. Marques,[b] Edmar P. Marques,[b] Maria de L. F. Nunes,[b] Eliane R. de Sousa,[c] Gilberto S. da Silva[d]**

[a] Federal Institute of Education, Science and Technology of Maranhão, Department of Chemisty, Monte Castelo Campus, Getúlio Vargas Avenue, nº 04, Zip Code 65030-005, São Luís, MA, Brazil.
[b] Universidade Federal do Maranhão, Campus Bacanga, Departamento de Química, Av. Portugueses, s/n, Bacanga, CEP 65080-040, São Luís, MA, Brasil.
[c] Federal Institute of Education Science and Technology of Maranhão, Maracanã Campus, Av. dos Curiós, S/N, Vila Esperança, São Luís-MA Zip Code 65095-460.
[d] Instituto Federal de Educação, Ciência e Tecnologia Goiano, Campus Morrinhos BR 153 Highway, Zip Code 75650-000, Morrinhos, GO, Brazil.

* gilmarsilverio@gmail.com

*Recebido em 1 de julho de 2014. Aceito para publicação em 3 de março de 2015*



## 1. Introduction

Although metals such as Pb, Cd and Hg have no essential function for life, together with metals like Cr, Cu, Zn, and Ni, they form a set of elements which, at high concentrations, may cause risks to the equilibrium of ecosystems.[1-3] One of the important characteristics of these pollutants, different from organics, is that they cannot be destroyed. Moreover, as well as organic pollutants, they may even suffer bioaccumulation. At the same time, Hg has also an important characteristic of suffering biomagnification. The sources of these pollutants can be natural, resulting from weathering or anthropogenic activities, such as paints, batteries, leather and agricultural fertilizers. In addition, anthropogenic sources may be non-diffuse – as urban industrial effluents – or diffuse, originating from urban or agricultural drainage. In aquatic systems, metals can be deposited in the sediment and reach concentrations high enough to become a risk for aquatic life. This risk is directly related to the bioavailability of metals that can reach the benthic population, among others.[4] Different conceptual models are used to assess the environmental risks caused by metals, e.g., the threshold effect level (TEL) and probable effect level (PEL) of Canadian Environment;[5,6] acids volatile sulfides;[7] sequential extractions as Tessier et al.[8] methods and the BCR protocol (Community Bureau of Reference, now Standards, Measurement and Testing Program).[9-12] 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, which are strong enough to remove metals considered bioavailable.[6] Sequential chemical extractions are intended to convert metals bonded in the solid phase of sediments into soluble forms by specific extraction solutions,[3,13] which progressively release the metals more strongly linked to the sediment matrix.

This work uses the protocol established by the BCR in order to evaluate the three geochemical fractions of sediments (exchangeable/acid soluble, reducible and oxidizable) of trace metals (Cd, Cr, Cu, Ni, Pb and Zn) in sediments from the Bacanga River on Maranhão Island.[14] In addition, this work assesses the risks caused by trace metals using the sediment quality guidelines for protection of the aquatic life. For the best knowledge of the authors, especifically to Bacanga estuary, there is not metal assessment of metal in sediment. Then, this work collaborates to evaluate the environmental conditions of this ecosystem.

## 2. Materials e methods

### 2.1. Area of study

The Bacanga River Estuary is located in the São Luís city, Maranhão State-Brazil, and has an area of 105.9 km$^2$ and the main river bed has a length of 23.84 km (Figure 1).[15,16] Part of the Bacanga River basin is inside the Bacanga State Park with an area of 3,075 hectares. This river had its hydrology greatly altered by the construction of the Bacanga Dam in the 1960 and 1970 decades. Several environmental impacts caused by urbanization have been pointed out in this basin, such as grounding of mangroves, garbage and raw sewage disposal, deforestation and extraction of clay and stones.[17] Large areas around the Bacanga River were excluded from the park, such as the Bacanga Dam, and they were replaced by large urban concentrations, responsible for large quantities of untreated sewage. The Bacanga River flows into São Marcos Bay and suffers, periodically, intrusion of saline waters from the Atlantic Ocean.

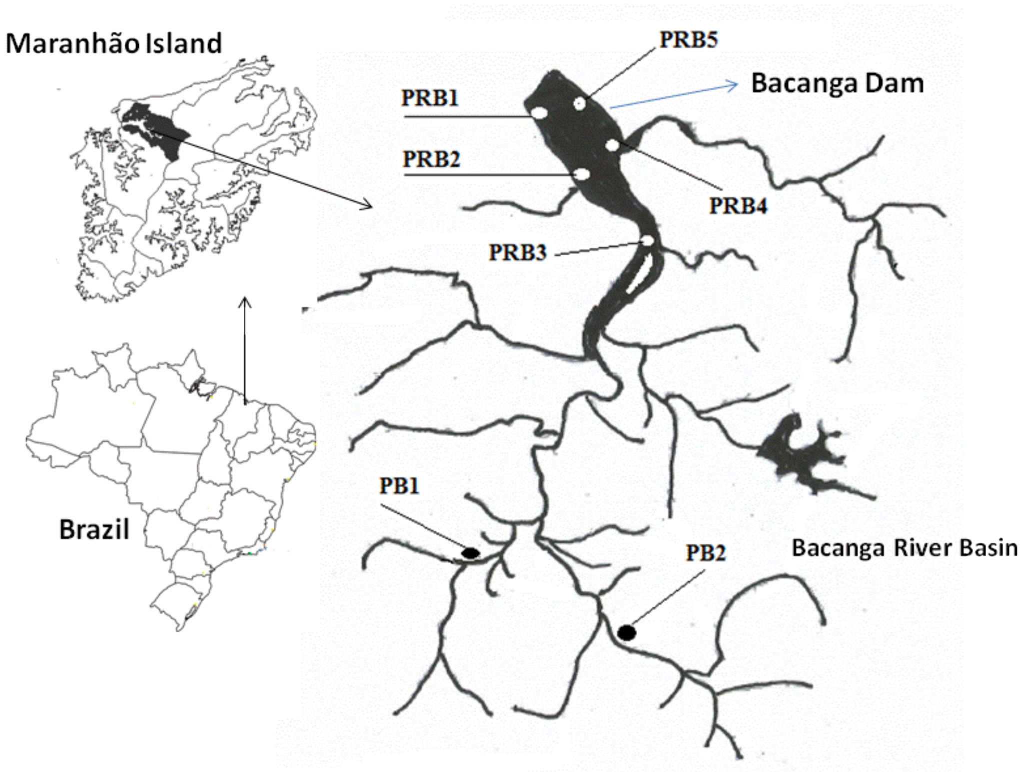


**Figure 1.** Sampling sediments sites: Bacanga River Estuary sites: tributaries (PB1, PB2) and Dam (PRB1 to PRB5). Adapted from Bezerra[15] and Alcântara[16]

### 2.2. Sediment Sampling

Sediment samples were collected along the Bacanga riverbed (Figure 1). The sampling sites in the tributaries near the sources of the Bacanga River were PB1 (2°36'24.58.5"S; 44°18'02.328"N) and PB2 (2°35"S; 44°17'45"N). Neither salty water from São Marcos Bay nor mangrove forests were found in these sites. In Bacanga Dam, samples were collected at five sites: PRB1(2°33'01.59"S; 44°18'09.26"N), PRB2 (2°33'24.88"S; 44°17'50.28"N), PRB3 (2°34'07.94"S; 44°17'08.49"N), PRB4 (2°33'11.80"S; 44°17'32,72"N) and to PRB5 (2°32'49.33"S; 44°17'54.95"N). Each site corresponds to four mixed subsamples collected at a distance of twenty meters from each. These locations are affected by saline waters from São Marcos Bay. The dates of sampling at PB1 and PB2 sites were 09/09/2010 and 29/10/2010 in Bacanga Dam (PRB1 to PRB5). The collection was held in the morning and with the sunny weather. The sediment samples were collected from surface sediment. The collection was performed using a stainless steel Van Veen dredge type, specific for sediments. Subsequently, the samples were stored in plastic bags properly identified and packed in thermal boxes with ice. One sample was collected at each site totalizing seven sediment samples. After being packed in plastic bags and refrigerated, the samples were sent to the laboratory. Sediment samples were dried at 40 $^0$C during 72 h (until constant mass). 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) and stored.

### 2.3. Analysis of sediment

The determination of exchangeable cations and exchangeable acidity followed the methodology described by Cotta.[18] The sum of both constituted the total cation exchange capacity (CEC). The determination of organic matter was performed by using the gravimetric method.[19] Sulphate concentration and pH analysis followed the method proposed by Silva.[19] The granulometric analysis in sediment is the process aimed at defining, for certain pre-established ranges of grain size, the weight that each fraction has on the total mass of the sample under analysis. Particle size analysis was performed following the technical standard NBR 7181.[20] We used the method of sieving (coarse) and pipetting of the fraction <0.062 mm.

### 2.4. Extraction procedure

Table 1 shows the extraction procedure applied in this study following the protocol adopted by The Standards, Measurements and Testing Program (formerly BCR, Community Bureau of Reference) of the European Commission.[21,22] A residual fraction was added in the BCR three-stage protocol. In order to evaluate the toxicity of sediments used in this study, the metal concentration in sediments was determined through digestion with *aqua regia*, $HCl/HNO_3$ (3:1).[21] These values are called pseudo total concentration in this text. 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.

**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/acid soluble cations and carbonates | 0.11 mol $L^{-1}$ $CH_3COOH$ | 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 $NH_2OH.HCl$; 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 $L^{-1}$ $H_2O_2$; | 10 | 22 ± 5 | Digestion for 1 h - stirring |
| | | | | 85 ± 5 | Digestion for 1 h |
| | | | 10 | 85 ± 5 | Digestion for 1 h |
| | | 1 mol $L^{-1}$ de $CH_3COONH_4$ (pH 2); | 50 | 22 ± 5 | Digestion for 1 h stirring - occasionally |
| F4 (Residual) | Silicate materials and oxides | *Aqua regia* $HCl/HNO_3$ (3:1) | 10 | 22 ± 5 | 16 h rest |
| | | | | 85 ± 5 | Heating for 2 h with occasional agitation |

### 2.5. 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. All reagents were of analytical grade (Merck®) and metal analytical standard were SpecSol® brand with certificates of origin. Metals analysis was performed by inductively coupled plasma optical emission spectrometry (ICP OES) Varian 720ES of UEMA (Universidade Estadual do Maranhão). The lines used were Cd ($\lambda$ = 214.4 nm), Cr ($\lambda$ = 283.5 nm), Cu ($\lambda$ = 324.7 nm), Ni ($\lambda$ = 231.6 nm), Cu ($\lambda$ = 324.7 nm), Pb ($\lambda$ = 220.3 nm), and Zn ($\lambda$ = 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. The correlation coefficients for the standard curves were higher than $r^2$ = 0.998 and 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.

### 2.6. Validation of the fractionation protocol

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). Table 2 shows that the recovery rates for BCR 701 ranged from 87 to 125 %.

**Table 2.** Results of analysis of standard reference material BCR-701 (mean ± standard deviation, n = 3)

| | | Cd (mg kg$^{-1}$) | Cr (mg kg$^{-1}$) | Cu (mg kg$^{-1}$) | Ni (mg kg$^{-1}$) | Pb (mg kg$^{-1}$) | Zn (mg kg$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 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 ± 10.9 |
| | Certified | 7.3 ± 0.4 | 2.26 ± 0.16 | 49.3 ± 1.7 | 15.4 ± 0.9 | 3.18 ± 0.21 | 205 ± 6 |
| | % Recovery | 103.7 | 86.7 | 94.9 | 88.9 | 120.1 | 109.8 |
| Step 2 | Analyzed | 4.03 ± 0.21 | 47.1 ± 2.8 | 153.8 ± 10 | 24.7 ± 2.2 | 142 ± 17 | 98.0 ± 6.01 |
| | Certified | 3.77 ± 0.28 | 45.7 ± 2.0 | 124 ± 3 | 26.6 ± 1.3 | 126 ± 3 | 114 ± 5 |
| | % Recovery | 106.9 | 103.1 | 124.0 | 92.9 | 112.7 | 85.9 |
| Step 3 | Analyzed | 0.26 ± 0.02 | 159± 14.6 | 6 3.5 ± 3.25 | 19.1 ± 1.15 | 8.23 ± 0.87 | 43.0 ± 3.35 |
| | Certified | 0.27 ± 0.06 | 143 ± 7 | 55 ± 4 | 15.3 ± 0.9 | 9.3 ± 2.0 | 46 ± 4 |
| | % Recovery | 96.3 | 111.2 | 115.5 | 124.8 | 88.5 | 93.5 |

The cluster analysis (HA) using BioEstat® 5.0 software was used to find the similarities among the sediment samples considering their metal concentrations and physical and chemical properties. It was also applied the principal component analysis (PCA) using Unscrambler® software in order to assess the contribution of geochemical fractions (F1, F2, F3 e F4) to sediments samples grouping.

## 3. Results and Discussion

### 3.1. Metal Concentration

The pseudo total concentration of metals in sediment along the sampling sites is showed in Table 3. Among the sediment samples Cd, Cu and Ni presented the lowest concentrations. Comparatively, Cr, Zn and Pb stood out because they had the highest concentrations. Sediments from PB1 and PB2 showed the lowest metal concentrations, while sediments from Bacanga Dam (PRB1 to PRB5) showed the highest values.

**Table 3**. Total metal concentration (mg $kg^{-1}$ ) in marine sediments samples from Bacanga River

| | | Metals | | | | | |
|---|---|---|---|---|---|---|---|
| | | Cd | ***Cr***[a] | Cu | Ni | ***Pb***[a] | Zn |
| Sites | PB1 | 0.122 ± 0.01 | 32.8 ± 4.82 | 1.66 ± 0.32 | < dl* | **35.0 ± 2.68** | 13.65 ± 1.21 |
| | PB2 | 0.274 ± 0.08 | 27.1 ± 1.19 | 2.33 ± 0.06 | 0.226 ± 0.05 | 25.4 ± 1.27 | 15.14 ± 0.33 |
| | PRB1 | 0.287 ± 0.02 | 45.46 ± 4.35 | 9.782 ± 0.13 | 4.547 ± 0.11 | **58.14 ± 1.84** | 44.98 ± 6.74 |
| | PRB2 | 0.522 ± 0.02 | **56.49 ± 1.13** | 11.77 ± 0.60 | 6.723 ± 0.42 | **70.60 ± 0.84** | 61.6 ± 2.53 |
| | PRB3 | 0.366 ± 0.04 | **71.77 ± 2.96** | 9.711 ± 0.21 | 6.512 ± 0.48 | **78.85 ± 4.82** | 67.02 ± 6.7 |
| | PRB4 | 0.571 ± 0.06 | **90.45 ± 2.82** | 13.82 ± 0.71 | 10.31 ± 0.22 | **94.80 ± 1.06** | 94.49 ± 2.83 |
| | PRB5 | 0.241 ± 0.01 | **61.18 ± 2.53** | 13.15 ±1.31 | 7.432 ± 0.85 | **75.38 ± 11.3** | 53.57 ± 3.21 |
| Criterion | TEL | 0.68 | 52.3 | 18.7 | 15.9 | 30.2 | 124 |
| | PEL | 4.21 | 160 | 108 | 42.8 | 112 | 271 |
| | ERL | 1.2 | 81 | 34 | 20.9 | 46.7 | 150 |
| | ERM | 9.6 | 370 | 270 | 51.6 | 218 | 410 |

*[a] Bold numbers represent values above TEL; * dl: detection limit; TEL: threshold effect level; PEL: probable effect level; ERL: effects range low; ERM: effects range median.*

Cr, Pb and Zn from the Bacanga River estuary presented concentrations higher than background values prescribed by the National Oceanic and Atmospheric Administration (in mg $kg^{-1}$: Cd:0.1-0.3; Cr: Pb: 7-13; Cu: 10-25; Ni: 9.9 and Zn: 4-17)[23] except for Zn in the tributaries (PB1 and PB2). Other metals remained at levels compatible with NOAA. TEL/PEL criteria were used to assess the health risk for aquatic life.[6,24] Table 3 shows pseudo total concentrations of Cr in sediments from Bacanga Dam, PRB2=56.49 mg $kg^{-1}$ to PRB5 = 61.18 mg $kg^{-1}$, with values above TEL (52.3 mg $kg^{-1}$) and below PEL (160 mg $kg^{-1}$) as prescribed to marine environments. Within this range, occasionally adverse effects for aquatic life can be observed. The same argument can be used regarding Pb, whose concentrations in the Bacanga Dam (PRB1 to PRB5) also fell into the transition range between TEL (30.2 mg $kg^{-1}$) and PEL (112 mg $kg^{-1}$). Metal concentrations in other sites remained below TEL values.

Quality guidelines are used to estimate risk for aquatic life. These values serve as the initial screening for quality sediment assessment. Another criterion to assess metal toxicity was developed by Long et al.[25] and it is similar to that of Canadian (TEL/PEL) used above. These criteria have 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 (see Table 3). These criteria have higher concentration limits than TEL/PEL. For example, TEL value for Pb is 30.2 mg $kg^{-1}$ as ERL is 46.7 mg $kg^{-1}$; in turn, PEL is 112 mg $kg^{-1}$ as ERM is 218 mg $kg^{-1}$. Using ERL/ERM criteria for pseudo total concentrations (Table 3), both Cr and Pb remained between ERL and ERM, within a range whose effects on the aquatic life are occasionally observed. This condition is similar to previous conclusion, but in this case, more distant than the higher limit (ERM). Therefore, using ERL/ERM, the risk for aquatic life becomes lower. Both methodologies (TEL/PEL and ERM/ERL) were chosen because they were adopted by the Brazilian Environmental National Council (CONAMA) through Resolution nº 454,[26] whose content treats about sediment quality guidelines for the protection of aquatic life. Although chemical quality guidelines are important to sediment assessment for aquatic life, it should be mentioned that additional protocols are necessary to reach more secure conclusion, such as biological essays.

High concentrations of Cr and Pb in sediments of the Bacanga Dam (PRB1 to PRB5) indicates that sediment have accumulated metals. The pollution source is, probably, untreated sewage, since the human occupation has increased greatly after dam construction. Around a quarter of the population of São Luis lives in its drainage basin. These values are higher than those found in Rio Tibiri,[27] also located in the Maranhão Island, but in much more preserved situation.

### 3.2. Sediment Properties

Physical and chemical properties are important to understand metal behavior in sediments. In this direction, Table 4 shows environmental parameters of sediment samples. It can be observed that lotic sediments (PB1 and PB2) had expressive presence of sand, 51.9 and 75.8 %, respectively, as Bacanga Dam had high silt fraction. All sediments were characterized by negligible presence of clay which reached a maximum of 6.4% in PB1.

**Table 4**. Chemical and physical characteristics of sediment from the Bacanga River Estuary

| | PB1 | PB2 | PRB1 | PRB2 | PRB3 | PRB4 | PRB5 |
|---|---|---|---|---|---|---|---|
| pH | 4.86 | 4.35 | 7.63 | 7.80 | 7.44 | 6.82 | 7.71 |
| O.M (%) | 11.80 | 12.27 | 9.47 | 14.60 | 14.30 | 14.07 | 13.83 |
| $SO_4^{2-}$ (mg kg$^{-1}$) | 41.8 | 72.8 | 2917.5 | 3634.6 | 3704.2 | 4063.0 | 1231.0 |
| Silt (%) | 41.7 | 18.9 | 99.2 | 99.2 | 97.6 | 99.2 | 99.5 |
| clay (%) | 6.4 | 5.3 | 0.2 | 0.1 | 0.5 | 0.2 | < dl* |
| Sand (%) | 51.9 | 75.8 | 0.6 | 0.7 | 1.9 | 0.6 | 0.5 |
| CEC (cmol$_c$ kg$^{-1}$) | 8.2 | 7.8 | 18.6 | 20.1 | 18.1 | 19.3 | 16.4 |
| C:N | 17.98 | 16.89 | 16.05 | 17.64 | 22.52 | 19.15 | 18.16 |

**dl: detection limit*

In turn, $SO_4^{2-}$ showed expressive concentrations in Bacanga Dam sediments, reaching 4.06 mg kg$^{-1}$ in PRB4. These high values are observed due to estuarine characteristics of the sediments, i.e., ocean waters are important source of $SO_4^{2-}$. In addition, pH of sediments from Bacanga Dam (7.48) were more alkaline than the tributaries PB1 (4.86) and PB2 (4.35), corroborating the estuarine characteristics of these sediments. The CEC had the lowest values in PB1 (8.2 cmolc kg$^{-1}$) and PB2 (7.8 cmolc kg$^{-1}$). In Bacanga Dam, these values reached 20.1 cmol$_c$ kg$^{-1}$ in PRB2.

In this work, organic matter percentage ranged from 9.47 to 14.60%. In turn, C:N ranged from 16 to 22, suggesting the predominance of organic matter from continental origin (C:N about 20 or higher). Organic matter content in aquatic body depends of water productivity, microbiological degradation and terrestrial diffuse sources. Depending of sources, different C:N ratios will be observed. Organic matter from ocean phytoplankton has C:N ratio between 5 and 6.[28] Similar values were found in rivers with expressive anthropogenic presence.[29]

In sediments, anaerobic microbiological organic degradation is responsible for production of organic acids that decrease pH. In presence of the oxygen, another process responsible for acidification of sediment is sulphides oxidation that converts compounds like pyrite ($FeS_2$) to acid ($H_2SO_4$). Acid conditions lead to the increase of metal mobility in soil and sediment,[30] due to proton competition by a negative adsorption site. On the other hand, as observed in sediment samples from Bacanga Dam, pH is alkaline due to ocean waters presence, conditions more favorable to metal adsorption and precipitation as carbonate ($CO_3^{2-}$).

### 3.3. Metal Fractionation

Considering now the distribution of metals in different fractions, the BCR protocol offers an indication of their mobility and subsequent availability, which are associated to increased risk for aquatic life.[31] Figure 2 shows the distribution profile of geochemical fractions of metals in sediments. Presence of metal in exchangeable/acid soluble fraction (F1), characterized by the presence of adsorption processes and carbonates, was more expressive for Zn and Pb. Using mean values, metal percentage in the exchangeable/acid soluble fraction (F1) followed the decreasing order: Pb (13.5%) > Zn (11.6%) > Cd (6.4%) > Cu (0.17%) > Cr (0.12%) > Ni (< detection limit). Cu, Ni and Cr had no expressive exchangeable/acid soluble fraction (F1) participation. In the next fraction, reducible fraction (F2), metal percentage followed the decreasing order: Zn (38.0%) > Cd (35.2%) > Pb (22.9%) > Cr (14.0%) > Ni (10.6%) > Cu (4.4%). In turn, oxidizable fraction (F3) metal percentage showed the following decreasing order: Cu (48.9%) > Cr (20.3%) > Ni (15.9%) > Pb (14.3%) > Zn (12.8 %) > Cd (4.8%).

Finally, in residual fraction (F4), metal presence was significant in all sampling sites and for all metals: Cr (65.0%) > Ni (59.2%) > Pb (53.0%) > Cd (49.3%) > Cu (46.5%) > Zn (36.6%). Zn and Pb were the only metals distributed between four fractions in all sediments analyzed. Mean value of percentage of each fraction in metal distribution follows this decreasing order: F4 (51.7%) > F2 (21.1%) > F3 (19.5%) > F1 (5.3%).

The reducible fraction (F2), formed by Fe-Mn oxides (e.g., goethite and pyrolusite), have important characteristics for retaining trace metals through high CEC, co-precipitation and isomorphic substitution. However, reductive conditions found in the estuarine sediments are not favorable to oxides formation. In this work, Zn (38%) and Cd (35.2%) were metals that showed the greatest affinity to Fe-Mn oxides. In turn, Pb represents only 22.9%. The most important species of Pb in the natural environment is $Pb^{2+}$, which forms oxides and hydroxides. Low solubility Pb 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 the reducible fraction (F2), $Fe^{3+}$ from iron oxide can be substituted by $Cr^{3+}$, $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ via isomorphous substitution.[32]

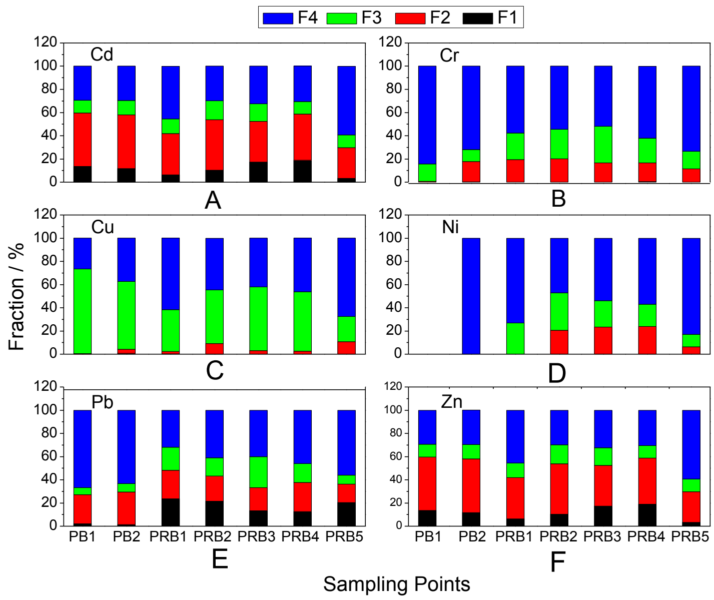


**Figure 2**. Metal fractions (%) in sediments from the Bacanga River Estuary

In the oxidazible fraction (F3), Cu was the most associated metal with ratios of up to 72.8%. This significant association occurs due to the high affinity of this metal to organic matter and its ability to form complexes with humic substances present in sediments.[33] The organic matter of aquatic systems is largely formed by humic and fulvic substances, in which functional groups such as hydroxyls and carboxyl are responsible for metal complexation. Besides Cu, in this fraction, the Cr deserves attention. The presence of organic matter as well as sulphides and $Fe^{2+}$ are able to reduce $Cr^{6+}$ to $Cr^{3+}$, minimizing mobility and environmental risk. As $Cr^{6+}$ is soluble and highly toxic, $Cr^{3+}$ is low soluble and important to living organisms.

In order to assess risk for aquatic life, it is necessary to consider physical and chemical changes in sediment able to increase the metal mobility. Natural or anthropogenic changes in sediments such as in ionic strength can release exchangeable/acid soluble metals, while a reduction of pH can release metals bonded to carbonates. In turn, a decrease of the $E_h$ can act on Mn and Fe oxides, making metals of reducible fraction available. On the other hand, an increase in the $E_h$ can release metals bonded to sulphides.[10,34-37]

These modifications in the environmental conditions involve the first three fractions that have potential *capacity of releasing* metal to the environment, which can calculated by dividing these most labile fractions (F1 + F2 + F3) by the sum of all fractions (F1 + F2 + F3 + F4), expressed as a percentage as showed in Figure 3.

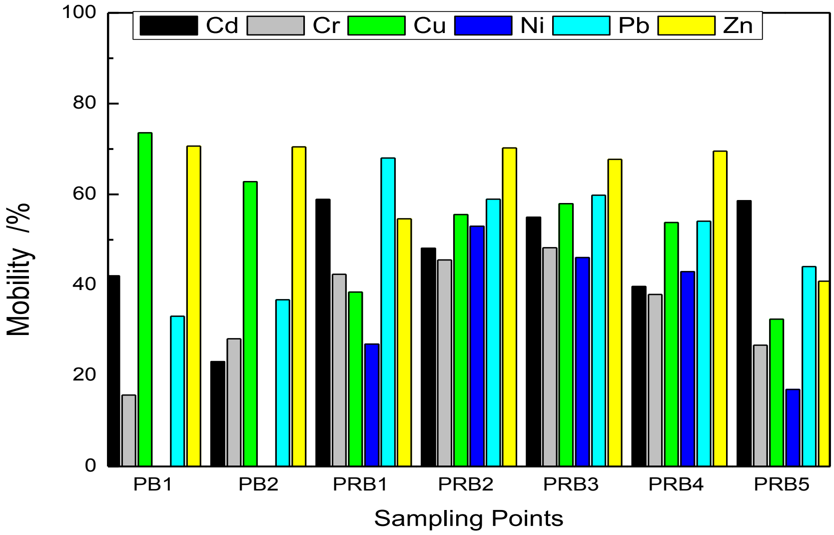


**Figure 3**. Mobility considering the first three fractions (exchangeable/acid soluble and carbonates, reducible and oxidizable)

Figure 3 shows that the mobility of Cr was below 30% in PB1 and PB2, and that reached the maximum value in the Bacanga Dam, i.e., 48% in PRB3. In turn, Pb mobility values ranging around 37% in the first two sites mentioned above and achieved significant increases in lentic environment (PRB1 to PRB5), reaching a maximum peak of 70% (PRB1). Using the mean mobility value of each fraction, it can be observed that mobility shows the following decreasing order: Zn (63.4%) > Cu (53.5%) > Cd (50.7%) > Pb (47.0%) > Ni (40.8%) > Cr (35.0%).

Polluted sediment will have more trace metals in three first fractions. These results are similar in magnitude to that found by Passos et al.[38] in metal fractionation in sediments of the Sergipe River, northeast of Brazil. Although Zn and Cu do not offer risk for aquatic life health, they have the highest mobility. In large part, the sampling sites of the Bacanga Dam (PRB1, PRB2, PRB3 and PRB4) showed similar behavior among them, with a metal mobility of about 50 %.

### 3.4. Statistical analysis

Applying cluster analysis in a matrix formed by parameters from Tables 3 and 4, it's possible to separated the sampling sites in two groups (Figure 4): a) first group formed by PB1 and PB2, where prevails of high sand content, acid condition, low concentrations of organic matter and sulphate; and a second group, formed by lentic system (PRB1 to PRB5) where stands out silt, sulphate and pH more alkaline. The former group presents worse conditions to metal immobilization than latter. Although sediments from Bacanga Dam have more conditions such as silt fraction, organic matter and alkaline pH, exchangeable/acid soluble fraction (F1) was not so expressive. Generally, F1 fraction is smaller than other fractions in the environment.

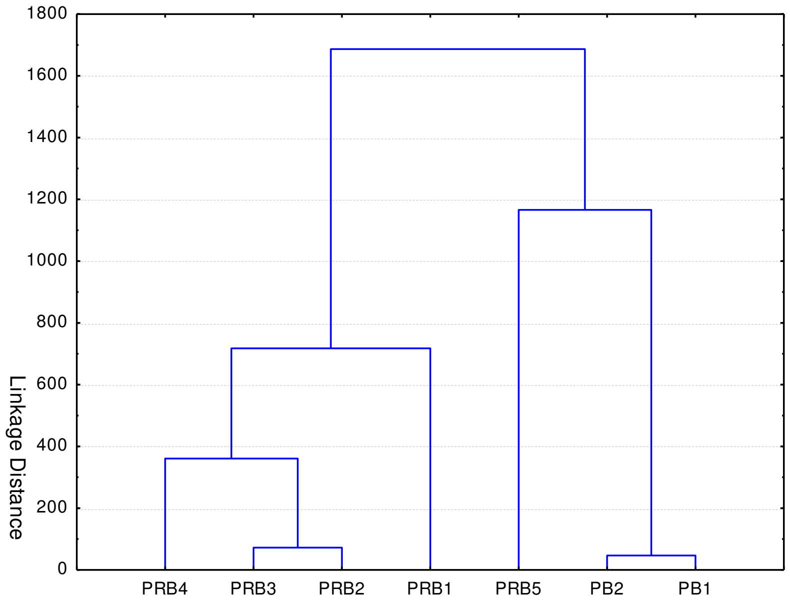


**Figure 4**. Cluster analysis of sediments from the Bacanga River

The PCA applied in a matrix formed by sampling points (PB1, PB2 and PRB1 to PRB5) and metal percentage of each fraction (data from Figure 2) is demonstrated in Figure 5A. In the score graphic, sampling points were separated among them. Three different regions can be observed: first, formed by PB1; second, formed by PB2 and third, formed by Bacanga Dam sampling points (PRB1 to PRB5). PC1 was responsible by 52% of explained variance as PC2 by 26%.

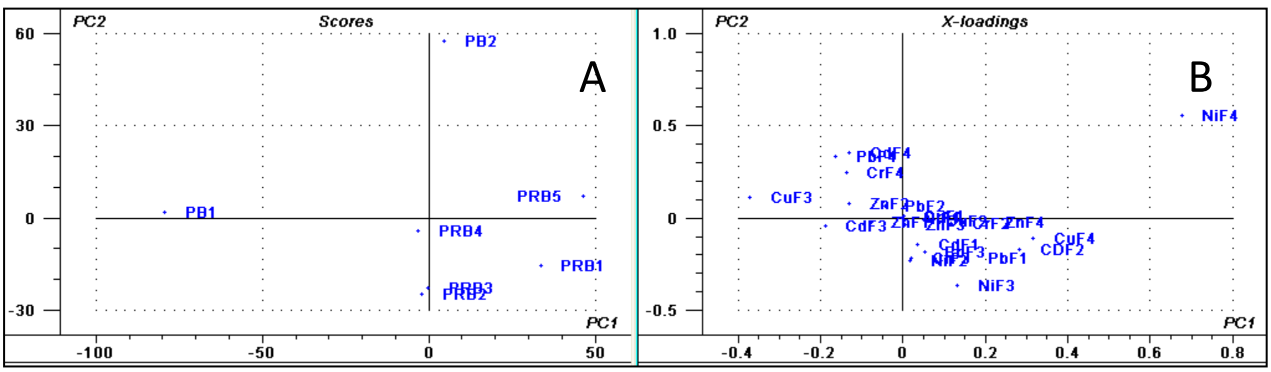


**Figure 5**. Principal component analysis of metal fractions in sediments from the Rio Bacanga

The loading graph (Figure 5B) indicates the weight of each variable to PC1 and PC2. It is possible to observe that residual fraction (F4) of Pb, Cr, Ni and Cd had great influence of PB1 and PB2 separation. The most labile fractions (F1, F2 and F3) had higher influence to PRB1 to PRB5 separation. These results corroborate that metal mobility (represented by sum of F1, F2 and F3) in sediments is associated to anthropogenic origin, since sampling points from Bacanga Dam have received a lot of untreated domestic sewage for almost four decades.

## 4. Conclusion

Cr, Pb and Zn in the Bacanga River Estuary presented concentrations higher than background values prescribed by NOAA (2012) in Bacanga Dam. Cu, Ni and Cd remained at levels compatible with NOAA. Pb and Cr had concentrations whose values were associated with occasional adverse effects to aquatic life according to TEL/PEL and ERL/ERM criteria. Metal mobility can be organized in the following order: Zn (63.4%) > Cu (53.5%) > Cd (50.7%) > Pb (47.0%) > Ni (40.8%) > Cr (35.0%). Mobility showed mean value of 48.4%, indicating that about half of metal concentration had potential to be released into interstitial waters. Cluster analysis revealed that sediment samples of the PB1 and PB2 have similarity and they are different from sediments from Bacanga Dam. These results corroborate the fact the latter sediments are amended with the human intervention. In turn, principal component analysis demonstrated that most mobile fractions (F1,F 2 And F3) are more expressive to Bacanga Dam sediments, justly because metals from anthropogenic activities belong to these fractions. These results pointed out that Bacanga Dam has been impacted by metal and governmental actions are fundamental to reverse actual scenery.

## Acknowledgments

The authors thank the Foundation of Research and Scientific and Technological Development of Maranhão (FAPEMA) for their financial support; the Federal Institute of Education Science and Technology of Maranhão (IFMA - Monte Castelo Campus); and to the Research Laboratory of Analytical Chemistry of the Federal University of Maranhão (LPQA).

**References**

[1] Rifkin, E.; Gwinn, P.; Bouwer, E. Chromium and Sediment Toxicity. *Environmental Science and Technology* **2004**, *15*, 267A. [CrossRef]

[2] Saraiva, V. K.; Nascimento, M. R. L.; Palmieri, H. E. L.; Jacomino, V. M. F. Avaliação da qualidade de sedimentos - estudo de caso: Sub-Bacia do Ribeirão Espírito Santo, afluente do Rio São Francisco. *Química Nova* **2009**, *32*, 1995. [CrossRef]

[3] Oyeyiola A. O.; Olayinka; K. O., Alo B. I. Comparison of three sequential extraction protocols for the fractionation of potentially toxic metals in coastal sediments *Environmental Monitoring and Assessment* **2011**, *172*, 319. [CrossRef] [PubMed]

[4] Di Toro, D. M.; McGrath, J. A.; Hansen, D. J.; Berry, W. J.; Paquin, P. R.; Mathew, R.; Wu, K. B.; Santore, R. C. Toxicity of cadmium in sediments: The role of acid volatile sulfide**.** *Environmental Monitoring and Assessment* **2005**, *24*, 2410. [CrossRef]

[5] Hortellani, M. A.; Sarkis, J. E.S.; Abessa, D. M. S; Sousa E. C. P. M. Avaliação da contaminação por elementos metálicos dos sedimentos do Estuário Santos – São Vicente. *Química Nova* **2008**, *31*, 10. [CrossRef]

[6] Hübner, R.; Astin, K. B.; Herbert, R. J. H. Comparison of sediment quality guidelines (SQGs) for the assessment of metal contamination in marine and estuarine environments. *Journal of Environmental Monitoring* **2009**, *11*, 713. [CrossRef] [PubMed]

[7] Jonge, M.; Teuchies, J.; Meire, P.; Blust R.; Bervoets, L. The impact of increased oxygen conditions on metal-contaminated sediments part II: Effects on metal accumulation and toxicity in aquatic invertebrates. *Water Research* **2012**, *46*, 3387. [CrossRef]

[8] Tessier, A.; Campbell, P. G. C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* **1979**, *51*, 844. [CrossRef]

[9] Ure, A.M.; Quevauviller, P.; Muntau, H.; Griepink, B. Speciation of Heavy Metals in Soils and Sediments. An Account of the Improvement and Harmonization of

Extraction Techniques Undertaken Under the Auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry* **1993**, *51*, 135 [CrossRef]

[10] Filgueiras, A. V.; Lavilla, I.; Bendicho, C. Chemical sequential extraction for metal partitioning in environmental solid samples. *Journal of Environmental Monitoring* **2002**, *4*, 823. [CrossRef] [PubMed]

[11] Bacon, J. R.; Davidson, C. M. Is there a future for sequential chemical extraction? *Analyst* **2008**, *133*, 25. [CrossRef] [PubMed]

[12] Rocco, M.; Rubio, M. A. Reinterpretation of the first step of the sequential extraction proposed by the SMT. *Journal of the Chilean Chemical Society* **2009**, *54*, 323. [CrossRef]

[13] Pueyo, M.; Rauret, G.; Lück D.; Yli-Halla, M.; Muntau, H.; Quevauviller, P.; López-Sánchez, J. F. Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. *Journal of Environmental Monitoring* **2001**, *3*, 243. [CrossRef] [PubMed]

[14] Rao, C. R. M.; Sahuquillo, A.; Sanchez, J. F. L. A Review of the Different Methods Applied in Environmental Geochemistry For Single and Sequential Extraction of Trace Elements in Soils and Related Materials. *Water, Air and Soil Pollution* **2008**, *189*, 291. [CrossRef]

[15] Bezerra, J. F. R.; *Dissertação de Mestrado,* Universidade Federal de Rio Janeiro, 2011.

[16] Alcântara, E. H. *Caminhos de Geografia* **2004**, *8*, 158. [Link]

[17] Pereira, E. D.; Zaine, J. E. Mapa geológico-geotécnico do Bacanga - São Luis (MA). *Geociências* **2007**, *26*, 45. [Link]

[18] Cotta, J. A. O.; Rezende, M. O. O.; Piovani, M. R. Avaliação do teor de metais em sedimento do rio Betari no Parque Estadual Turístico do Alto Ribeira - PETAR, São Paulo, Brasil. *Química Nova* **2006**, *29*, 40. [CrossRef]

[19] Silva, F. C. (1999) Manual de Análises químicas de Solos, Plantas e Fertilizantes. EMBRAPA, Brazil.

[20] Associação Brasileira de Normas Técnicas, ABNT; NBR 7181. Análise granulométrica de solos/método de ensaio, ABNT: Rio de Janeiro, 1982.

[21] Rauret, G.; López-Sánchez, J. F.; Sahuquillo, A.; Rubio, R.; Davidson, C.; Ure, A.; Quevauviller, P. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring* **1999**, *1*, 57. [CrossRef] [PubMed]

[22] Pereira, J. C.; Guimarães-Silva, A. K.; Nalini Junior, H. A.; Pacheco-Silva, E.; Lena, J. C. Distribuição, fracionamento e mobilidade de elementos traço em sedimentos superficiais. *Quimica Nova* **2007**, *30*, 1249. [CrossRef]

[23] The National Oceanic and Atmospheric Administration (NOAA). Available in: <http://response.restoration.noaa.gov/environmental-restoration/environmental-assessment-tools/squirt-cards.html>. Accessed: 20 November 2013.

[24] Canadian Council of Ministers of the Environment (CCME). Available in: <http://ceqg-rcqe.ccme.ca>. Accessed: 8 October 2013.

[25] Long, E. R.; MacDonald, D. D. Recommended Uses of Empirically Derived, Sediment Quality Guidelines for Marine and Estuarine Ecosystems. *Human and Ecological Risk Assessment: An International Journal* **1998**, *4*, 1019. [CrossRef]

[26] Conselho Nacional do Meio Ambiente (CONAMA), Resolução nº 454, de 01 de Novembro de 2012. Available in: <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=693>. Accessed: 12 January 2015.

[27] da Silva, G. S.; do Nascimento, A. S.; de Sousa, E. R.; Marques, E. P.; Marques, A. L. B.; Corrêa, L. B.; Silva, G. S. Distribution and Fractionation of Metals in Mangrove Sediment from the Tibiri River Estuary on Maranhão Island. *Revista Virtual de Química*, **2014**, *6*, 323. [CrossRef]

[28] Pahlow, M.; Riebesell, U. Temporal Trends in Deep Ocean Redfield Ratios, *Science* **2000**, *287*, 831. [CrossRef]

[29] Froehner, S; Martins, R. F. Avaliação da composição química de sedimentos do Rio

Barigüi na região metropolitana de Curitiba. *Química Nova* **2008**, *31*, 2020. [CrossRef]
[30] Chen, K.; Jiao, J. J. Metal concentrations and mobility in marine sediment and groundwater in coastal reclamation areas: A case study in Shenzhen, China, *Environmental Pollution* **2008**, *151*, 576. [CrossRef]
[31] Templeton, D. M.; Ariese, F.; Cornelis, R.; Danielsson, L-G.; Muntau, H.; van Leeuwen, H. P.; Lobinski, R. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000). *Pure & Applied Chemistry* **2000**, *72*, 1453. [CrossRef]
[32] Sparks, L. D. Environmental Soil Chemistry. 2nd ed. Academic Press. San Diego, 2003, 352 pp.
[33] Wasserman, J. C.; Wasserman, A. A. Em *Comportamento de metais em sedimentos*; Neto J. A. B.; Wallner- Kersanach M.; Patchineelam S. M., eds.; Poluição Marinha, 1a. ed., Interciência: Rio de Janeiro, 2008, v.1.
[34] Kabala, C.; Singh, B. R. Fractionation and Mobility of Copper, Lead, and Zinc in Soil Profiles in the Vicinity of a Copper Smelter. *Journal of Environmental Quality* **2001**, *30*, 485. [CrossRef] [PubMed]
[35] Chrastný, V.; Komárek, M.; Tlustos, P.; Svehla, J. Effects of Flooding on Lead and Cadmium Speciation in Sediments from a Drinking Water Reservoir. *Environmental Monitoring and Assessment* **2006**, *118*, 113. [CrossRef] [PubMed]
[36] Venugopal, T.; Giridharan, L.; Jayaprakash, M. Characterization and risk assessment studies of bed sediments of River Adyar-An application of speciation study. *International Journal of Environmental Research* **2009**, *3*, 581. [CrossRef]
[37] da Silva, I. S.; Abate, G.; Lichtig, J.; Masini, J. C. Heavy metal distribution in recent sediments of Tietê-Pinheiros e river system in Sao Paulo state, Brazil. *Applied Geochemistry*, **2002**, *17*, 105. [CrossRef]
[38] Passos, E. A.; Alves J. P. H.; Garcia C. A. B.; Costa, A. C. S. Metal fractionation in sediments of the Sergipe River, northeast, Brazil. *Journal Brazilian Chemical Society* **2011**, *22*, 828. [CrossRef]