

# Transport of cadmium and zinc from Sepetiba bay to Cabuçu-Piraquê river estuary (Brazil)

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**Abstract:** Cabuçu-Piraquê River, a tributary of Sepetiba Bay (Rio de Janeiro State, Brazil), has a history of pollution for decades, but without a systematic study of origin and fate of trace elements such as cadmium and zinc, in its environmental compartments. The bioaccumulation of these elements can cause serious damage to the biota of mangroves in its estuary, and to human consumers of local fisheries. In this study, it was evaluated the current state of contamination of water and sediment from that river, as well as the occurrence of accumulation of these metals in the estuary's sediment fraction brought by the bay waters during high tides. Concentrations of cadmium and zinc above those considered safe by Brazilian law were found both in the fine fraction ( $< 63 \mu\text{m}$ ) of sediment, averages of 4.4 and 1232 mg/kg, respectively, and at high tide waters, 0.08 and 0.24 mg/L, respectively. Both metals were found only in the most bioavailable operational fractions of waters, while sediment average values of 96 % were found for Cd, and 98 % for Zn at same most bioavailable fractions. From the concentrations of these metals in water from the saline wedge generated by the bay, it was possible to infer such an influx into the estuary from the material present in the bay waters, and this transport process may be shipping a major contributor to contamination of the local mangroves.

**Keywords:** Heavy Metal, Sediment, Water, Bioavailable Fractions, Trace Metal Extraction, Contamination, Rio de Janeiro

## 1. Introduction

Although the metallic elements can undergo various chemical reactions and transfers between different media, fundamentally their chemical species are persistent and can remain indefinitely in the environment. However, the chemical form of a metallic element is probably the most important factor and that generates a significant impact on their behavior and environmental effects [1].

In river waters, trace elements are found both in the dissolved and in suspension fractions, in quantities that vary significantly from one element to another. The ratio of an element between the fractions depends on their solubility and concentration of other chemical species, of the physical, chemical and biological conditions of the water body, as well

as the total concentration of particulate matter in suspension. Thus, to assess the load and transport behavior of these elements in rivers, both fractions should be analyzed.

The typical analytical concentration of total metallic element in water (the total fraction) is the sum of the concentrations of free ion and its soluble complexes (the dissolved fraction) with concentrations of chemical species that are associated with the suspended solids (the suspension fraction), whether organic (organic matter) or mineral. However, the fate of more than 99% of the chemical species that reach the aquatic environments is to be incorporated into the background sediments [2].

Estuaries are the linkage between coastal marine systems and rivers, carrying several compounds, including trace elements of natural and/or anthropogenic origin. Several

metallic elements are presented as important contaminants and are widely studied because of the environmental associated risks, their persistence in the environment and to its biogeochemistry recycling. Many trace elements (such as iron, copper and zinc) are micronutrients that are essential to the growth of many organisms, but in high concentrations, such elements can become toxic. Already other metallic elements, such as cadmium and lead, not show physiological functions, and are highly toxic in very small amounts [3]. Therefore, the quantification of trace elements in environments such as estuaries, considered a nursery of coastal life, takes on a crucial importance for the assessment of possible risks to these ecosystems.

The input of trace elements in estuaries occurs mainly by the discharge from river water containing such elements dissolved and/or associated with suspended matter, and by atmospheric deposition. Several parameters, such as salinity, temperature, pH, suspended particulate material (SPM) and concentration of dissolved oxygen, are of the utmost importance to the transport processes and mixture of these elements in estuarine systems [4].

Processes of adsorption, flocculation and sedimentation may deposit such elements in sedimentary fraction, from its association to suspended solids present in the water, and, usually, the sediment becomes your final destination. However, resuspension of sediments can re-engage these elements to the water column through changes of hydrogeochemical variables associated to tidal variations. Thus, the quantification of trace elements in sediments makes it possible to determine the level of contamination present in water and benthic organisms [4].

Mangroves are ecosystems that occur in tidal areas, generated in regions of mixture of freshwaters and saline waters such as estuaries, bays and coastal lagoons. These systems act as links between the marine and terrestrial environments and its occurrence is closely linked to the swampy soils formed by fine-grained sediment deposition in the back bays and estuaries subject to influence of brackish water. These areas provide a unique environment for a variety of species of wild fauna and flora, and are related to a leading role in the export of carbon and nutrients to the coastal zone and oceans [5].

The numerous relationships between the occurrence, bioavailability, effects and fate of anthropogenic origin substances in mangrove ecosystems, have been described in several recent reviews [4,6,7]. High concentrations of contaminants were found in these ecosystems, in its various compartments (water, sediment and biota), and in coastal areas dominated by drainage basins densely occupied by urban and rural populations. In addition, the mangroves may have an important role in contaminant cycling in tropical marine systems.

Although the mangroves are clearly recognized as important ecosystems, still remain several gaps in the understanding of its ecotoxicology, including the interactions between contaminants and abiotic components of the mangroves (such as sediment) in the prediction of

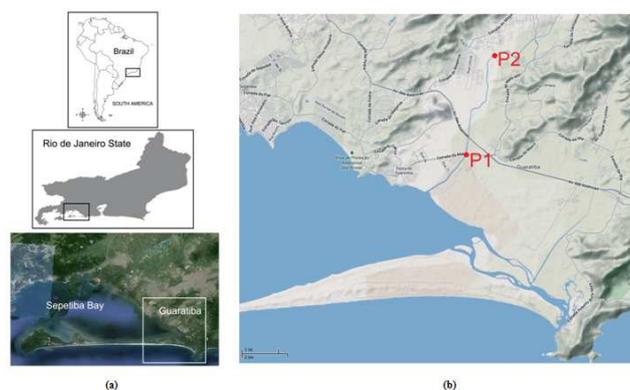
contaminant bioavailability, and in the quantification of these flows in the mangrove systems interfaces in order to characterize such systems as fate or source of these contaminants.

## 2. Study Area

### 2.1. Sepetiba Bay

Sepetiba Bay (Fig. 1a) is a semi-enclosed waterbody located at west of Rio de Janeiro City, and is an example of aquatic environment that has undergone a huge impact by human settlement and industrial activities developed in their watershed. About 400 companies with polluting potential, including various metallurgical, petrochemical industry and foundry, which emit pollutants into the air, soil and water, settled in the region during the end of the 20th century [8]. In addition, it receives a large volume of water through the transposition into Guandu River (one of their main tributaries) of an adjacent basin, the Paraíba do Sul River system, a highly industrialized region. It has a surface area of about 520 km<sup>2</sup>, an average depth of 7.7 m, a mixed semi-diurnal tidal regime (with two high tides each day with different heights, and two low tides also of different heights), its waters vary from brackish to saline (its salinity generally is between 34 and 20 ‰), and their sediments are composed of sandy banks, silt and clay soils, the latter two covering about 70% of the area of distribution of the sediments, with a sedimentation rate of the bay being estimated between 0.30 to 1.0 cm/year [9].

A review of anthropogenic impacts on the Sepetiba Bay area [8] indicated the existence of a severe contamination of this region by zinc and cadmium, its main contaminants; in addition to these, lead, mercury and other elements also performed in significant concentrations. The concentrations at sediment leave to 37300 mg/kg to zinc and 396 mg/kg to cadmium, with these high concentrations apparently associated with the beginning of operations, in the late 1950's, to the bankrupt Ingá Industrial and Mercantile Company, a metallurgical company that processed zinc ore, located on the shores of the bay.



**Figure 1.** Map showing the location of Sepetiba Bay and Guaratiba (a) and the sampling locations in the Cabuçu-Piraquê River (b); P1 indicates the sampling site near the river's base level, and P2 the site in the river's middle course (adapted from [10])

It is estimated that this company has downloaded about 24 ton/year of Cd, and 3660 ton/year of Zn to the Sepetiba Bay until its closing, at 1997, suggesting that this has been the main source of contamination of the water body and its basin. Such data comes to against presented by [11] that showed that the flow of Cd and Zn from the Guandu River to the bay in the last 50 years has increased by more than an order of magnitude (Cd:  $1.6 \times 10^{-3}$  to  $2.2 \times 10^{-2}$  g/m<sup>2</sup>year; Zn: 0.26 to 4.27 g/m<sup>2</sup>year), having been estimated that the stock of excess metallic element in the sediment column is of 0.85 g/m<sup>2</sup> to Cd, and of 144 g/m<sup>2</sup> to Zn.

It was suggested [12] that frequent resuspension episodes and the long distances covered by SPM enriched in trace elements promote the remobilization and the dispersion of these elements in the bay, and that such facts, associated with large dimensions of this body of water and its advective currents, allow large displacements of particles before its deposition. On the other hand, the episodes of resuspension is said to be very important in the process of redistribution of sediments, in addition to being responsible for the release of particles linked to trace elements.

Some works [13,14] demonstrated that various trace elements (Pb, Cd, Zn, Cu, Cr and Hg) are accumulated in the northeast and east margins of bay, where there is a high sediment resuspension combined with a high production and accumulation of organic matter, which contribute to the process of adsorption of metallic elements in the sediment. The intensity of the sediment transport along the eastern shore of the bay is connected with the clockwise pattern of movement of waters [15], and contributes to the observed concentration gradient in sediments.

## 2.2. Cabuçu-Piraquê River

The Cabuçu-Piraquê River is located at east-southeast portion of the Sepetiba Bay, and composes, along with the Portinho and Piração Rivers, the river basins in this region (Fig. 1b). It covers a total of 23 km until it enters in Sepetiba Bay, presenting a good quality of its waters, near its headwaters (where human occupation is thin), but when crossing urban areas, its quality is compromised [16,17]. The flow and water quality of this river vary in time and according to the seasons, depending on the precipitation conditions and on point and nonpoint pollution sources. It also suffers influence of saline wedge intrusion, the process that occurs when the flow of fresh water, which is injected in the estuary by the river, tends to launch itself in the bay about draining a lower layer of salt water that moves preferentially from the bay to the land [9].

Contamination by trace elements, especially zinc and cadmium, is a major risk factor to the different Sepetiba Bay's environmental compartments (water, biota and mangrove forest [18-26]). Many studies have already been carried out in order to search for information on this subject, and of its impacts, with regard to Sepetiba Bay [13,27,28] and its larger tributaries [29]. However, little is known about the influence of the tides of the bay on the contamination of smaller rivers, especially those located on its east-southeast

portion, where sediments and suspended solids from the bay are washed down [17,30,31]. Due to the minor depths in this region (the innermost of the bay and where Cabuçu-Piraquê River flows), there is a progressive loss in movement, which favors a greater retention of the saline wedge in rivers and, with it, a likely transposition of suspended solids containing trace elements from the bay to the estuarine region of these water bodies [9].

As already pointed out, numerous works were published widely on topics related to the region of Sepetiba Bay, as well as upon the waters, sediments and the relationship between pollutants and the biota of the Guandu River basin, with only one recent study paper [30] and two older studies (a Master degree dissertation [31] and a diagnostic report [17] of the basin water of Sepetiba Bay) regarding the quality of the Cabuçu-Piraquê River waters. Thus, the data presented in this paper update those related to this region, so far, little studied.

This study aimed to establish the possible contamination by cadmium and zinc of the Cabuçu-Piraquê River's water and sediment at its estuary region, investigating a possible transport of those elements from the Sepetiba Bay to its tributary's bed, through the invasion of the waters of the bay along the river (saline wedge).

## 3. Materials and Methods

### 3.1. Sampling Locations

Samples were obtained for analysis of levels of dissolved compounds and those compounds present in particulate matter in surface water samples and superficial sediments of two representative regions of the Cabuçu-Piraquê River (Fig. 1b). At the region near its mouth (P1; 22° 59' 36" S, 43° 36' 24" W) were investigated the influence of the saline wedge on deposition of suspended solids contaminated with trace elements in the river bed (from possible transportation of sediments and/or suspended solids), and dissolved material from the bay to that region. At the central region of the watercourse (P2; 22° 57' 15" S, 43° 35' 41" W), above the reach of the saline wedge, and after its passage by regions impacted by anthropogenic activities (Fig. 2), it was studied the contribution of anthropogenic sources on water contamination by trace elements in water.

### 3.2. Sampling Procedures

The data presented here result from two sampling campaigns held in December 2011 and February 2012. In estuarine region were made two collections in a same day: one at low tide, representative of the stream waters' quality with the least possible influence of brackish waters of the bay, and another on the high tide, to investigate the possible influence of the saline wedge on the object of study (Fig. 3). Such samplings were made in spring tides, which are characterized by the strengthening between lunar and solar tides, noted in the new moon and full moon, when it produce the greatest high tides and the smaller low tides.



Figure 2. Partial view of sampling region in the middle course of the river.



Figure 3. General appearance of sampling region near the river's mouth, at low tide (a) and at high tide (b).

At the sampling region near the river's mouth the surface water samples were collected in the middle of the water body with the aid of a 3.5 L PVC Van Dorn water sampler (Husky Duck). Already in section located in the central region of the watercourse, with depth less than 40 cm, the collections were made with the aid of a plastic bucket; all the collections were made off of bridges.

A van Veen stainless steel dredger (3 L, Husky Duck) was used to collect the sample surface sediment at the site near the river's mouth. This sediment portion sits at the top of the sedimentary column or in the sediment/water interface and presents sedimentological, geochemical, physical and biological characteristics determined by present time environmental processes. The dredger was carefully opened on a large and clean tray, after that it was collected a fraction of surface sediment, up to 5 cm deep. About 250 g of sample were collected in plastic pots previously cleaned and free from contamination, to perform metallic elements and organic matter analyses. All samples were keeping refrigerated until analysis.

Water samples collected were stored in separate vials: a portion filtered on-site was take for analysis of cations and anions by ion chromatography; the other portions of raw water were taken for metallic elements analysis (total and dissolved) by flame atomic absorption spectrometry (FAAS), for suspended solids analysis, and for organic matter analysis. The samples that would pass by the processes of metallic elements extraction were acidified with 2 mL of  $\text{HNO}_3$  1:1 (V/V) solution. For the analysis by ion chromatography, aliquots of the raw water collected were filtered to polypropylene tubes using a syringe and a pair of filter systems (Sartorius Biotec) containing Millipore membrane filters (AAWP02500 and GSWP02500).

Fine sediment samples were obtained in the laboratory from the raw sediment's wet screening with ultrapure water,

using a nylon mesh particle size sieve with opening of 63  $\mu\text{m}$  (Bertel), and subsequent drying of thin sediment in an oven at 60  $^\circ\text{C}$ , followed by grinding in mortar and stocking in polypropylene vials, refrigerated.

### 3.3. Reagents and Materials

The following cleaning procedures were used in all laboratory glassware: washing with 5% (V/V) Extran® solution (Merck), 10% (V/V)  $\text{HNO}_3$  solution, and finally with deionized water. All solutions were prepared with ultrapure grade reagents (Sigma-Aldrich):  $\text{HNO}_3$  puriss. p.a., 65 % (m/m),  $\text{Hg} \leq 0,000\ 000\ 5\%$ ;  $\text{HCl}$  puriss. p.a., 37 % (m/m), ACS, ISO and Ph.Eur. reagent grade; and deionized water purified by a Milli-Q® system (Millipore; type I ultrapure water, with resistivity of 18,2  $\text{M}\Omega\ \text{cm}$  at 25  $^\circ\text{C}$ ). The response curves of metallic elements at samples were determined from reference solutions prepared by sequential dilutions of 1000 mg/L reference solutions (Qhemis) of Zn and Cd at 1.0 mol/L  $\text{HNO}_3$ .

### 3.4. Characterization of Samples and Sampling area

In the sampling campaigns measurements of physical and chemical parameters of water were carried out (pH, conductivity, temperature, salinity, total dissolved solids, dissolved oxygen and oxidation-reduction potential) by means of a portable digital multiparameter meter (Hanna HI9828). Were also collected environmental parameters (wind speed and direction, temperature and relative humidity) through a multifunctional digital anemometer (Speedtech WindMate 300), the superficial stream level and the depth of the collection (with a C507M-20M Starrett gaging tape), the flow of water (estimated from measurement of the stream width, from different depths throughout its cross section, and the flow velocity by means of floating devices) [32], and meteorological data.

### 3.5. Trace Elements Extractions

The fraction corresponding to dissolved metallic elements was obtained from the method 3030B of Standard Methods for the Examination of Water & Wastewater from the American Public Health Association (APHA) [33], where vacuum filtration of raw water samples (not acidified) was held within a period of up to 24 h after collection, in the lab, using a microfiltration apparatus (Millipore XX1504700 kit type, glass, 47 mm), through a membrane filter with an average diameter of 0.45  $\mu\text{m}$  pore (Millipore HAWP04700). The filtered samples were preserved with  $\text{HNO}_3$  solution 1:1 (V/V), and stored under refrigeration until their analysis.

For dissolution of trace elements present in the samples and their subsequent determination were adopted three methods presented by Standard Methods for the Examination of Water & Wastewater [33], where acid mineralization is used without the presence of hydrofluoric acid. This last acid acts on the residual fraction, where the metal elements are bonded to silicates and that contains primarily trace elements retained in the crystal structure of

minerals, which makes them likely to be released into solution, under natural conditions, in a reasonable period of time [34]. This fraction (residual), by presenting such characteristics, is not bioavailable, and therefore is not part of the scope of this work.

The methods chosen were, in ascending order of strength of extraction: acid-extractable metals procedure (3030C method), recoverable metals by HNO<sub>3</sub>-HCl procedure (method 3030F.3b) and total metals dissolved by HNO<sub>3</sub>-HCl procedure (3030F.3a method) [33]. All trials were performed in duplicate.

The Standard Methods' 3030C procedure considers like "acid-extractable metals" those that are weakly adsorbed on particulate matter and obtained in solution after the treatment of a non-filtered sample with hot dilute mineral acid [33]. At this paper this fraction was named as exchangeable fraction (see section 4.2). In this procedure a sample portion (40.0 mL of raw water (unfiltered) preserved with acid, or about 200 mg of sifted and dried fine sediment mixed with this same volume of ultrapure water) was transferred to a beaker of 100 mL, to which were added 4.0 mL of 1:1 (*V/V*) HCl solution. The mixture was heated to 95 °C for 15 min in a heating block (Tecnal TE015), after it was cooled and transferred to a polypropylene vial (Environmental Express SC475), and made up to 50.00 mL using ultrapure water. The solution was then filtered in the bottle with the aid of a filtration system FilterMate™ with an average diameter of 2 µm pore (Environmental Express SC0401), and finally stocked, under refrigeration, until analysis.

The extraction of the "recoverable metals" fraction, which is associated with metallic elements soluble in acids (in the form of carbonates; see section 4.2), is a procedure performed with adaptations from the method 3005A from the United States Environmental Protection Agency's (US EPA) [35], in which is based on the APHA's 3030F.3b method [33]. A portion of the sample (similar to that used in the previous process, but with a volume of 50.00 mL) was transferred to a beaker with 1.0 mL of 1:1 (*V/V*) HNO<sub>3</sub> solution and 5.0 mL of 1:1 (*V/V*) HCl solution. The beaker was covered with a polypropylene ribbed watch glass (Environmental Express SC505), and carefully heated in a heating block at a temperature of 95 °C to reduce volume (without boiling) about 15 mL. It was used a beaker with deionized water and a digital thermometer (Minipa MV362) in one of the heater block wells to control the temperature of the water so that it does not exceed 95 °C [36,37]. After cooling, the solution passed through the final process presented in the previous paragraph, before being stocked refrigerated until analysis.

In this work, the APHA's "total metals fraction" is renamed to pseudototal fraction of metallic elements: the concentration of metallic elements present in solution after the treatment of a non-filtered sample with hot concentrated mineral acid, which includes all dissolved and particulate metallic elements, bounded to organic or inorganic matrices [33]. Thus, the difference between the concentrations

obtained in this procedure and the extraction procedures (fractions) presented before, it can be associated with oxidizable compound (sulfides and organic matter; see section 4.2). Here we use the nomenclature "pseudototal fraction" not to confuse it with the term "total metals", which is associated with the total concentration of metallic elements in the sample, including those extracted from silicates by using HF [38].

The extraction of pseudototal fraction of metallic elements is based on the 3030F.3a method of APHA [33] and used a portion of 50.0 mL of the sample (water or resuspended sediment), to which were added 1.5 mL of concentrated HNO<sub>3</sub> in a beaker, covered with a polypropylene ribbed watch glass, and carefully heated to a temperature of 95 °C in a heating block to evaporate the volume to less than 5 mL, without boiling. The mixture was cooled, the walls of the beaker and the watch glass were rinsed with minimal ultrapure water, then were added 2.5 mL of concentrated HNO<sub>3</sub>, covered the beaker with a glass smooth watch glass, and warmed up the set in the block heater in order to obtain a mild reflux. The heating was kept (with the addition of more acid, if necessary) until the extraction is completed, which was evidenced by the light color to the solution with the metallic elements extracted were present. Once more time the mixture was cooled, then were added 5.0 mL of 1:1 (*V/V*) HCl solution and 7.5 mL of ultrapure water to the mixture, that was warmed up for another 15 min in the block heater. The solution was cooled and the walls of the beaker and the watch glass were rinsed with small portions of ultrapure water. Again, the material was quantitatively transferred to a polypropylene vial, where the solution was filtered and stored, as in the preceding procedures.

At this work were used the following relationship for calculation of concentrations: the concentration of trace element in a given fraction is equal to the concentration obtained on the analytical procedure for the respective extraction method subtracted from those found for methods with lower extraction strengths. So, for example, the concentration of zinc present only in pseudototal fraction of a given sample was calculated from the concentrations found in the FAAS analysis for this extraction method minus the values founded for this trace element for recoverable, exchangeable and dissolved fractions (this last only applicable to water samples).

### 3.6. Analytical Procedures

Samples of metallic elements were analyzed by FAAS (methods 3111 from APHA [33] and 7000B from US EPA [39]) at a Varian AA240 atomic absorption spectrometer, with an air/acetylene flame and a aspiration rate of 6 mL/min. Determinations were performed in triplicate with deuterium arc correction and with the following wavelengths: 228.8 nm for cadmium, and 213.9 nm for zinc. Application of standard addition method, to check possible matrix interference, demonstrated that there was no need to use it for examination of the samples. In some cases

(sediment samples) it was necessary to dilute the samples for the determination of Zn, for they are at concentrations greater than those used in the response curve.

Determinations of chloride, fluoride, phosphate and sulfate anions, and ammonium, sodium, potassium, calcium and magnesium cations in water were performed in triplicate at a Dionex ICS-3000 Dual ion chromatograph, based on 4110B method of APHA [33] and on supplier recommendations [40], with the following parameters: eluent to anions, carbonate:bicarbonate; eluent to cations, methanesulfonic acid; analytical and guard columns to anions, Dionex IonPac® AS23 2 x 250 mm, and AG23 2 x 50 mm, and for cations, CS16 3 x 250 mm, and CG16 3 x 50 mm; detection of anions and cations by suppressed conductivity. The samples were diluted before they are injected (1:1250 (V/V) for those collected during high tide, and 1:25 (V/V) for the other samples), and dealt with through passage by Dionex cartridge OnGuard® II RP (1 mL, preconditioned with methanol p.a. (Sigma-Aldrich), followed by ultrapure water) for removal of nonpolar species, to avoid damages to columns and detectors.

To assess the amount of suspended solids present, it was used the 2540D method of APHA [33]: a volume of water sample (well homogenized) was filtered on a glass fiber filter without binder (Millipore AP40), and the residue retained on the filter was dried until constant mass, at a temperature between 103 and 105°C. Due to the importance of organic matter present in sediments on the retention/sorption of various dissolved and particulated species [7] (like metallic elements), this parameter was indirectly evaluated, both in fine sediment samples, as in the suspended solids retained in the glass fiber filter mentioned, through methodology for measurement of volatile loss at 550°C, the 2540G method of APHA [33].

## 4. Results and Discussion

### 4.1. Characterization of Samples and Sampling Area

Brazilian law establishes criteria for the assessment of water quality by means of Resolution 357/2005 from the National Environmental Council (CONAMA) [41], which rules on the classification and environmental guidelines for outlining of surface water bodies. The freshwaters (those with salinity less than or equal to 0.5 ‰), brackish waters (with salinity between 0.5 and 30 ‰) and salt waters (salinity greater than or equal to 30 ‰) are classified according to the quality required for their greater uses.

For the purpose of analysis of results of this work were employed following water quality standards (WQS): Class 1 brackish waters and Class 2 freshwaters, both intended for human consumption supply, primary contact recreation (swimming etc.), protection of aquatic communities, and for aquaculture and fishing activities.

Such a choice comes from following facts: between the median portion and the mouth of this watercourse there are an environmental reserve (Biological and Archaeological Reserve of Guaratiba), an extensive area for livestock (Mato Alto Farm, in Guaratiba), in addition to the establishment of families to their shores who practice small-scale fishing in nearby areas of mangrove and the cultivation of vegetables and other crops [17].

Table 1 shows the results of flow measurements carried out, and it can be observed that the volume of water of the bay that rises the river at maximum level of high tide is more than three times that dumped by the river itself during low tide. The data of salinity, conductivity and concentrations of sodium and chloride ions examined at the mouth during periods of low and high tides show that the waters dumped by the river on these occasions are brackish waters.

Table 1. Characterization of river waters (mean ± standard deviation (SD), n = 4)<sup>a</sup>

Parameter	Mouth (high tide)	Mouth (low tide)	WQS brackish <sup>b</sup>	Middle course	WQS freshwater <sup>c</sup>
Volumetric flow rate / m <sup>3</sup> /s	22 ± 10	6.8 ± 3.8	—	1.15 ± 0.77	—
Salinity / ‰	20.7 ± 5.5	0.89 ± 0.33	0.5-30	0.23 ± 0.05	≤ 0.5
Conductivity / mS/cm	33.1 ± 8.1	1.77 ± 0.62	—	0.48 ± 0.10	—
pH	7.09 ± 0.05	6.99 ± 0.11	6.5-8.5	6.96 ± 0.11	6.0-9.0
Dissolved oxygen (DO) / mg/L	<b>3.1 ± 1.5</b>	<b>0.69 ± 0.59</b>	≥ 5	<b>0.67 ± 0.24</b>	≥ 5
Total dissolved solids (TDS) / mg/L	16600 ± 400	0.89 ± 0.31	—	0.24 ± 0.05	500
Suspended solids / mg/L	28.7 ± 2.1	83.3 ± 6.4	—	41.0 ± 2.6	—
Oxidation-reduction potential / mV	5 ± 57	133 ± 36	—	92 ± 10	—
Sodium / mg/L	3849 ± 20	223.87 ± 0.74	—	35.82 ± 0.08	—
Ammonium / mg/L	ND	<b>13.6 ± 2.0</b>	0.40 <sup>d</sup>	<b>13.44 ± 0.16</b>	3.7 <sup>d</sup>
Chloride / mg/L	9317 ± 35	473.6 ± 3.6	—	42.27 ± 0.51	250
Phosphate / mg/L	ND	<b>3.82 ± 0.15</b>	0.124 <sup>e</sup>	<b>3.50 ± 0.11</b>	0.1 <sup>e</sup>

<sup>a</sup> Except for volumetric flow rate, salinity, conductivity, pH, DO and TDS (n = 2). <sup>b</sup> Brackish water class 1 Quality Standards. <sup>c</sup> Freshwater class 2 Quality Standards. <sup>d</sup> Total ammoniacal nitrogen, for pH < 7.5. <sup>e</sup> Total phosphorus (lotic ecosystems). Values in italic bold present out of WQS according to [41]. ND: not detected.

Important factors, from an environmental point of view, are the values of concentration of dissolved oxygen, always below the minimum considered suitable by the Brazilian legislation (CONAMA Resolution 357/2005) [41] and high values for ammonium and phosphate, for both classes of waters (except at high tides). Such concentrations suggest

that this river is highly impacted by anthropogenic pollution [42], corroborated by observation of large quantities of floating materials and solid waste at its surface, as well as nasty odor and aspect of the water, in collections held. Sediment collected at the river mouth presented a mean concentration of volatile matter (associated with the

presence of organic matter) equal to  $156.1 \pm 2.7$  g/kg, larger than of organic matter in sediment of mangrove located next to the mouth of this river (107.1 g/kg) [21].

Analyses of the sediment particle size composition of nearby regions demonstrate that it has a high content of silt/clay fractions (> 85%) and negative oxidation-reduction potential (ORP) values [21,27]. Negative ORP values were also found in water collected near the streambed of Cabuçu-Piraquê River's mouth at high tides (Table 1), which features anoxic conditions that can lead to reduction of sulfate. This set of characteristics favors the adsorption and complexation of trace elements in sediments in this region [7].

#### 4.2. Trace Elements Analysis

In Brazil, there is no legislation that set criteria for the assessment of sediment quality [21], only a norm for the classification and regulation of the disposal of material to be dredged (CONAMA Resolution 454/2012) [43]. This resolution lays down the general guidelines and the minimum procedures for dredged sediment assessment in Brazilian waters and defines the quality criteria for trace elements and other contaminants in sediments based on international experience [44,45]. To do so, it establishes three tracks for classification of sediment separated by two levels: Level 1 (L1), which indicates the threshold value below which there is low probability of adverse effects to biota, and Level 2 (L2), the threshold value above which adverse effects on the biota are expected. Table 2 presents these levels for trace elements studied.

**Table 2.** Sediment classification levels (at mg/kg) of brackish waters [43]

Trace element	Level 1 <sup>a</sup>	Level 2 <sup>b</sup>
Cadmium	1.2	7.2
Zinc	150	410

<sup>a</sup> Threshold value below which there's low probability of adverse effects to biota. <sup>b</sup> Threshold value above which adverse effects on the biota are expected.

An analysis of the sums of concentrations of trace elements obtained from the various operational fractions ( $\Sigma_{total}$ , dry mass) in fine sediment (< 63  $\mu$ m) of the estuary showed that the value found for zinc,  $1232 \pm 63$  mg/kg, was three times above the level 2 of CONAMA Resolution 454/2012 (Fig. 4a) [43]; for cadmium, the value found,  $4.4 \pm 1.5$  mg/kg, is between the two levels of the same resolution (Fig. 4b). Thus, the surface layer of sediment presents a worrying level of contamination with these metallic elements.

Since there is not necessarily a direct relationship between the total concentration of certain trace element in sediment and its availability, the partition between specific fractions of this matrix must be evaluated, in order to seek to determine the mobility and the ecotoxicity of this element in the various environmental compartments involved (sediment and water) [4].

For a more accurate assessment of the bioavailability of a trace element, it uses a set of extraction methods based on

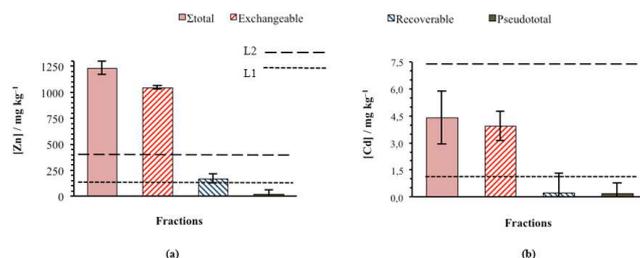
the increase in strength of the extractor, whose answer is inversely proportional to the mobility of the metallic element extracted. Next, it presents a way of qualifying the fractions obtained from a sample from operational definitions, in ascending order of strength of extractor [46]:

- Water-soluble fraction includes ions, ions complexed with dissolved organic matter, and other constituents; it contains trace elements of greater mobility and the most bioavailable.
- Exchangeable fraction includes metallic elements weakly adsorbed on solid surface, and those who can be released by ion-exchange processes. Changes in ionic composition or a decrease at pH can lead a metal element remobilization from this fraction.
- Acid-soluble fraction contains the metal ions precipitated by carbonate ions; it is weakly linked to solid and subject to change with environmental conditions and, along with exchangeable fraction, is considered readily and potentially bioavailable.
- Reducible fraction is composed of manganese and iron oxides-hydroxides of trace elements, which are extracted together, and are present in large proportion in sediments, where they are unstable under anoxic conditions, and where benthic organisms attack them.
- Oxidizable fraction, which includes trace elements bound to sulfides or associated with organic material (living organisms, debris or mineral particles coatings) through complexation or bioaccumulation, is not considered very mobile or available, once believed to be associated with stable humic substances, which slowly releases small amounts of metallic elements.

In this work, the extraction methods of trace elements described earlier (see section 3.5) present the following equivalence with the definitions above: the treatment for "acid-extractable metals" (3030C method) is associated with the exchangeable fraction; the dissolution of "recoverable metals" by HNO<sub>3</sub>-HCl (method 3030F.3b), to the acid-soluble fraction; and the "total metals" dissolved by HNO<sub>3</sub>-HCl (3030F.3a method), to the oxidizable fraction.

Relatively to trace elements concentrations in this studied sediment (Fig. 4), worrying is the fact that both are almost entirely in exchangeable fraction, i.e., the more labile and, therefore, that becomes bioavailable more easily to animals that assimilate such elements directly from water and sediment particles (whether by filtering, feeding etc.) of beds of estuaries [47], like crabs, which are a income source for local fishermen.

The results obtained for both metallic elements in estuarine region of this river are higher than found in other studies conducted in the early 1990 [17,31], whose averages fluctuated between 125 and 422 mg/kg to zinc, and between 1.2 and 3.1 mg/kg to cadmium. However, recent work in regions of the bay near the Cabuçu-Piraquê River's mouth point values closest to those presented here: on the order of 600 mg/kg for zinc [21,27], and between 3 and 6 mg/kg for cadmium [27,48].



**Figure 4.** Concentrations of operational fractions of zinc (a) and cadmium (b) at fine sediment fraction. L1, threshold value below which there is low probability of adverse effects to biota; L2, threshold value above which adverse effects on the biota are expected [43]; Mean  $\pm$  SD,  $n = 4$ .

Wasserman et al. [49] recorded that some studies, when assessing the bioavailability of trace elements in sediments of Sepetiba Bay through sequential extraction (phases equivalent to exchangeable and recoverable fractions used in this work), demonstrated that the amount of bioavailable cadmium is 70 %, and for zinc, bioavailable concentrations are 50 % – both smaller than those obtained in this study.

The allowable limits of cadmium and zinc in water established for the quality standards of both classes of waters used here are presented in Table 3.

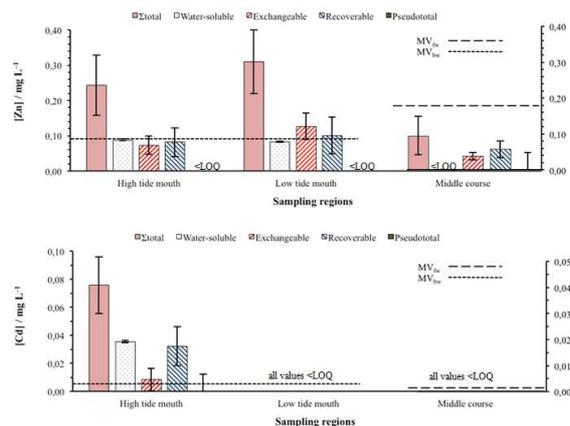
**Table 3.** Water quality standards (in mg/L), according CONAMA [41]

Trace element	MV <sub>fw</sub> <sup>a</sup>	MV <sub>bw</sub> <sup>b</sup>
Cadmium (total)	0.001	0.005
Zinc (total)	0.18	0.09

<sup>a</sup> Maximum allowable value for class 2 freshwaters. <sup>b</sup> Maximum allowable value for class 1 brackish water.

The  $\Sigma$ total values for zinc in waters of Cabuçu-Piraquê River (Fig. 5) in the period of high tide and low tide ( $0.24 \pm 0.09$  and  $0.31 \pm 0.09$  mg/L, respectively) are 2.7 to 3.4 times above the maximum allowed by Brazilian legislation [41], although values close to half this limit ( $0.10 \pm 0.05$  mg/L) have been observed in waters from the own river (middle course of the river, Fig. 5). In the sample that represents the maximum input of waters of the bay (high tides), 64 % of zinc are linked to the material in suspension (difference between  $\Sigma$ total and dissolved fraction), and all of it is found in the most bioavailable fractions of water (dissolved, exchangeable and recoverable). At freshwaters (middle course of the river), as the results for the dissolved fraction of the sample collected at this point were below the limit of quantitation of the method for zinc (0.014 mg/L), can be deduced that all this trace element is associated to the suspended matter.

The results of samples collected at mouth are consistent with those observed in water from the river itself in the region next to the above site, of  $0.30 \pm 0.02$  mg/L [30], as well as with those of the Sepetiba Bay near the study area of this work [48], where the average was  $0.34 \pm 0.07$  mg/L.



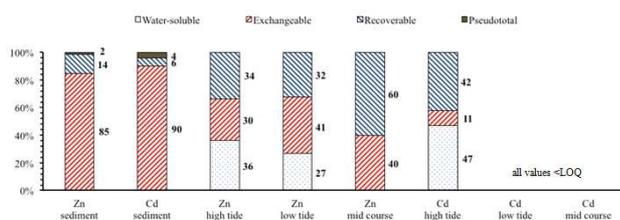
**Figure 5.** Concentrations of operational fractions of zinc (upper panel) and cadmium (lower panel) in water samples in different sampling regions and stages of tide (MV<sub>fw</sub> and MV<sub>bw</sub>, maximum allowable values for class 2 freshwaters and class 1 brackish waters, respectively [40]; mean  $\pm$  SD,  $n = 4$ ; <LOQ, smaller than the limit of quantitation of the method)

The average result obtained for the  $\Sigma$ total of cadmium in high tide waters (Fig. 5),  $0.08 \pm 0.02$  mg/L, is 16 times above the maximum allowable limit.

All other samples (mouth at low tide and middle course of the river) showed concentrations below the limit of quantification of the method (0.010 mg/L). Such results suggest that cadmium found in the surface sediment of the estuarine region of this river (Fig. 4) is from an exclusively transposition of this trace element from the waters of the bay, through the transport associated with the particulate matter and dissolved fraction of these waters.

Unlike the zinc, values found in the sample collected on the high tide (mouth) for cadmium are much larger than those found by a work performed in the period from 1990 to 1996, in a river location rather close to that used in this work [17], which was average  $0.003 \pm 0.009$  mg/L, and with the average obtained in Sepetiba Bay near the study area of this work [48], of  $0.0011 \pm 0.0003$  mg/L.

When a comparison between the percentages of the operationally defined fractions used in this work is made (Fig. 6), it can be observed that in samples of water from all locations and stages of tide the presence of trace elements surveyed is completely into more available fractions. For sediments, these values represent almost all: 98 % for zinc, and 96 % for cadmium. One can also notice a similarity in the distribution of fractions of both trace elements in sediment, which suggests a similar behavior of those metals to their compartmentalization. In addition, the results obtained in relation to fractions of Zn and Cd during the high tides present a profile very similar to each other and quite different from that observed for Zn in the middle course of the river, relatively to their distribution between the fractions analyzed. This suggests a possible importance of features found in the brackish waters of the bay (compared to the freshwaters of the middle course of the river) for the distribution of these trace elements in the various operational fractions studied.



**Figure 6.** Percentage relationships between operating fractions of trace elements in sediment and water samples at different sampling regions and tide stages (<LOQ, smaller than the limit of quantitation of the method)

Finally, one cannot rule out the possibility that contamination of these freshwater beds, with their estuarine regions characterized by the presence of extensive mangroves with diurnal phases of brackish water, can generate a transfer of such contaminants to the biota that resides there. Furthermore, it is possible to extend the results presented here, mainly, to the other rivers of this region (Covanca, Piracão and Portinho) and, perhaps to a lesser extent, to the hydrographic regions further west (in the regions of Itaguaí and Mangaratiba), as well as for the extensive flood areas of mangrove in this region, which suggests a probable contamination of local fauna and flora, impacting negatively on extractive production due to, for example, fishing for crabs by the community of fishermen who settled there, and thus causing a high risk of contamination of human beings.

## 5. Conclusions

The results obtained in this study indicated a strong environmental impact on the water quality of the Cabuçu-Piraquê River estuary: zinc, cadmium, ammonium and phosphate ions concentrations far above those established for both classes of water (freshwater and brackish), besides the dissolved oxygen concentrations below the water quality standard [41].

The sediments of this region showed concentrations of Zn and Cd in levels of concern. The zinc average concentration was over three times the threshold above which there is higher probability of adverse effects to biota. In the case of cadmium, despite the average concentration was below the limit indicator that could cause damage to biota, was greater than that deemed safe for aquatic life of brackish waters [43].

The waters of Sepetiba Bay, despite contributing to the increase in dissolved oxygen concentration in waters of the estuarine region of this river, also acts as a carrier of trace elements from the bay to this region, both in dissolved form, as also in the fraction attached to suspended particles.

The results presented here suggest the existence of a transport of zinc and cadmium from the waters of Sepetiba Bay to the sediment of Cabuçu-Piraquê River by transposition of particulate matter containing high concentrations of trace elements found in the first, and the subsequent deposition of solid material in the second, through the saline wedge intrusion associated with the high

tides observed in estuarine region. This fact is justified, because the total concentrations ( $\Sigma_{total}$ ) found in the waters of this region during the high tides periods, both for zinc, and, especially, for cadmium, are far superior to those observed in the waters of the central region of the course of this river (Fig. 5).

Also it should highlight the importance of data presented here from the point of view of the update of the data pertaining to this region, yet little studied.

A continuation of this study, by analyzing data from winter season and comparing these with summer's data, is necessary to correlate the influence of natural processes (tides and seasonal aspects) on variations of trace elements values and the translocation of these contaminants from the Sepetiba Bay to streambed and waters of the region studied at this work.

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