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Potentially mobile of heavy metals on the surface sediments in tropical hyper-saline and positive estuaries

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ABSTRACT

Estuarine sediments represent important pools of trace metals, released from both anthropogenic and natural sources. Fluctuations in the water column physicochemical conditions, on the other hand, may transfer metals from solid to liquid compartment and resulting in contamination of the surrounding environment. The present research was carried out to evaluate the weakly bounded heavy metal levels in tropical hyper-saline and positive estuaries, in order to quantify its potentially availability. The monitoring includes five metals (Cd, Cr, Cu, Pb, Zn) and cover nine estuaries in Rio Grande do Norte state/Brazil, including four hypersaline and five true estuaries. 50 surface sediment samples were collected in each estuary. At the same time, organic matter concentrations were evaluated in order to help explaining possible local variations in heavy metal levels. Organic matter results (0.7% – 7.3%) suggest the positive Potengi estuary as the most critical environmental quality situation. On the other hand, according to heavy metals levels, both Conchas and Potengi estuaries registered the higher concentrations of Cr. The highest concentrations were observed in the hyper-saline estuaries, with the exception of the Zn. The present study revealed that the watershed occupation has significantly influenced the heavy metal concentrations in the estuaries.

Key words: weakly bounded heavy metal, hyper-saline waters, positive estuaries, surface sediment.

INTRODUCTION

Available contaminant in water-bodies can result in negative impacts to marine environment, which above critic concentrations can impact biota communities (Singh et al. 2011) and dietary restrictions on seafood production (Hosseini et al. 2013). Regardless of the source, contaminants such as heavy metals are immediately scavenged by floating particles in the water column and are concentrated in hydrodynamically calm water basins where fine sediments accumulate. Thus,

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sheltered estuaries tend to be particularly sensible to contaminated loads (Vaalgamaa 2004).

Heavy metals are one of the most usual pollutants in water ecosystems and may have its sources from natural and anthropogenic origins, such as industrial, agricultural and domestic loads (Hang et al. 2009, Ramos e Silva et al. 2006, Davutluoglu et al. 2011). When released in aquatic environment, these metals tend to accumulate in the sub aquatic bottoms, where sediments have high deposition capacity and further potential to liberate these contaminants (Salomons and Stigliani 1995, Passos et al. 2011). This return into the overlying water column layer may be resulted from variations in water physicochemical features such as pH, redox potential and oxygen concentrations (Förstner and Kersten 1989, Davutluoglu et al. 2011). Nevertheless, the bottom particles act as sinks of metals, representing a record of the pollution chronology of the environment (Hang et al. 2009, Davutluoglu et al. 2011).

Total concentrations of heavy metal study in sediments is not considered an effective indicator when the goal is the evaluation between natural and anthropogenic sources (Relic et al. 2010, Passos et al. 2011, Okoro et al. 2012) and its potential availability (Zhong et al. 2011). Therefore, recent researches have applied partial extraction approaches to analyze the specific chemical forms with sedimentary phases and metal sources (Hang et al. 2009, Davutluoglu et al. 2011).

Surveys on heavy metal contamination, especially in coastal areas, have improved over the last decades around the world. In recent time, the use of innovative artificial mussel (AM) technology has been used to monitor heavy metals in the Oceans, coastal areas, estuaries, rivers in different countries in the world (Kibria et al. 2012, 2016). However, in tropical and subtropical regions such as Brazil and other South American countries, only limited information about this matter is available, mainly in estuarine areas where, added to natural inputs, concomitant anthropogenic activities such as port activities, together with industrial, agricultural and residential activities around the water body can provide pollutants, especially heavy metals, to the environment.

The evaluation of heavy metal contaminants in semi-enclosed water bodies like estuaries is a complex process influenced by physical and chemical variables.

Nowadays the coastal environments of the northeast shore of Rio Grande do Norte state are passing through a strong anthropogenic stress, such as: mainly oil exploration, salt production and marine shrimp culture expansion (Costa et al. 2015). Particularly, shrimp farming affects the environment primarily through the discharge of harmful effluents (fertilizers and other chemicals) and mangrove deforestation (Ramos Silva et al. 2010).

The main objective of the present study are to understand the distribution of the potentially available heavy metals in estuarine sediments in tropical hyper-saline and positive estuaries.

MATERIALS AND METHODS

Nine estuaries in Rio Grande do Norte (RN), Northeastern Brazil, were studied. Four of these, Apodi, Guamaré, Galinhos and Conchas (Figure 1), are classified as hyper-saline estuaries, that is, estuaries that experience low inflow at times, and are located in a more arid region of Northern RN. The other five systems, Ceará-Mirim, Potengi and Nísia-Floresta, Papeba and Guaraíra estuaries (Figure 2), are positive estuaries located in the eastern region of the state, where most domestic effluents are released (Ramos e Silva et al. 2006).

Fifty surface sediment samples were collected with a Van Veen grab in each estuary, totalizing 450 samples. The material collected was stored in plastic bags, cooled to 4°C and sent to the laboratory, where the fraction with particle size

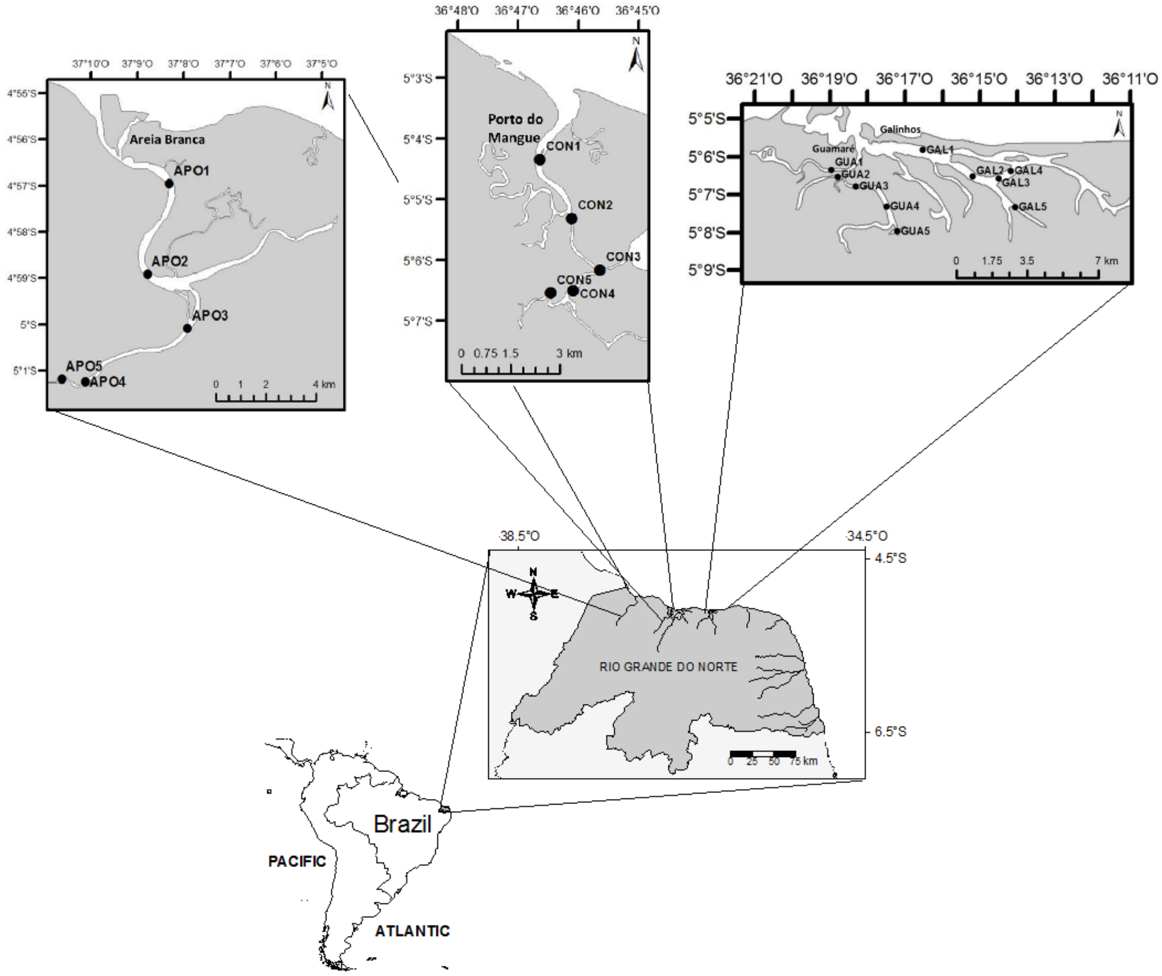

Figure 1 - Study Area (APO – Apodi sampling station / CON – Conchas sampling station / GUA - Guamaré sampling station / GAL – Galinhos sampling stations).

<1mm was separated by sieving. To evaluate the potentially mobile metals, cold acid extraction procedures were used, in order to simulate the natural mobilization processes of these more “labile” elements of the sediments (Bevilacqua et al. 2009). The extraction procedure with 0.5mol/L diluted hydrochloric acid (HCl) was applied (Sutherland and Tack 2008, Bevilacqua et al. 2009, Li et al. 2009). The procedure is based on the extraction of 0.5 g of sample with 10 mL of a solution of 0.5 mol/L HCl under continuous stirring at 200 rpm for 1 h at 20°C. The suspended material obtained was filtered through cellulose ester filter of 0.20 mm porosity prior to quantification of Cu, Cr, Ni, Pb, and Zn, certified for the reference material BCR-701. The quantification of metallic cations in solution was performed in an ICP-OES at the Agricultural School of Jundiaí, in Federal University of Rio Grande do Norte.

At the same time, organic matter concentrations were evaluated in order to explain possible local variations in heavy metal levels.Organic matter content in the sediments was determined by the calcination technique according to Byers et al. (1978).

Obtaining the volume and the area of the channels of the Potengi, Nísia-Floresta, Papeba and Guarairas estuaries took into account the

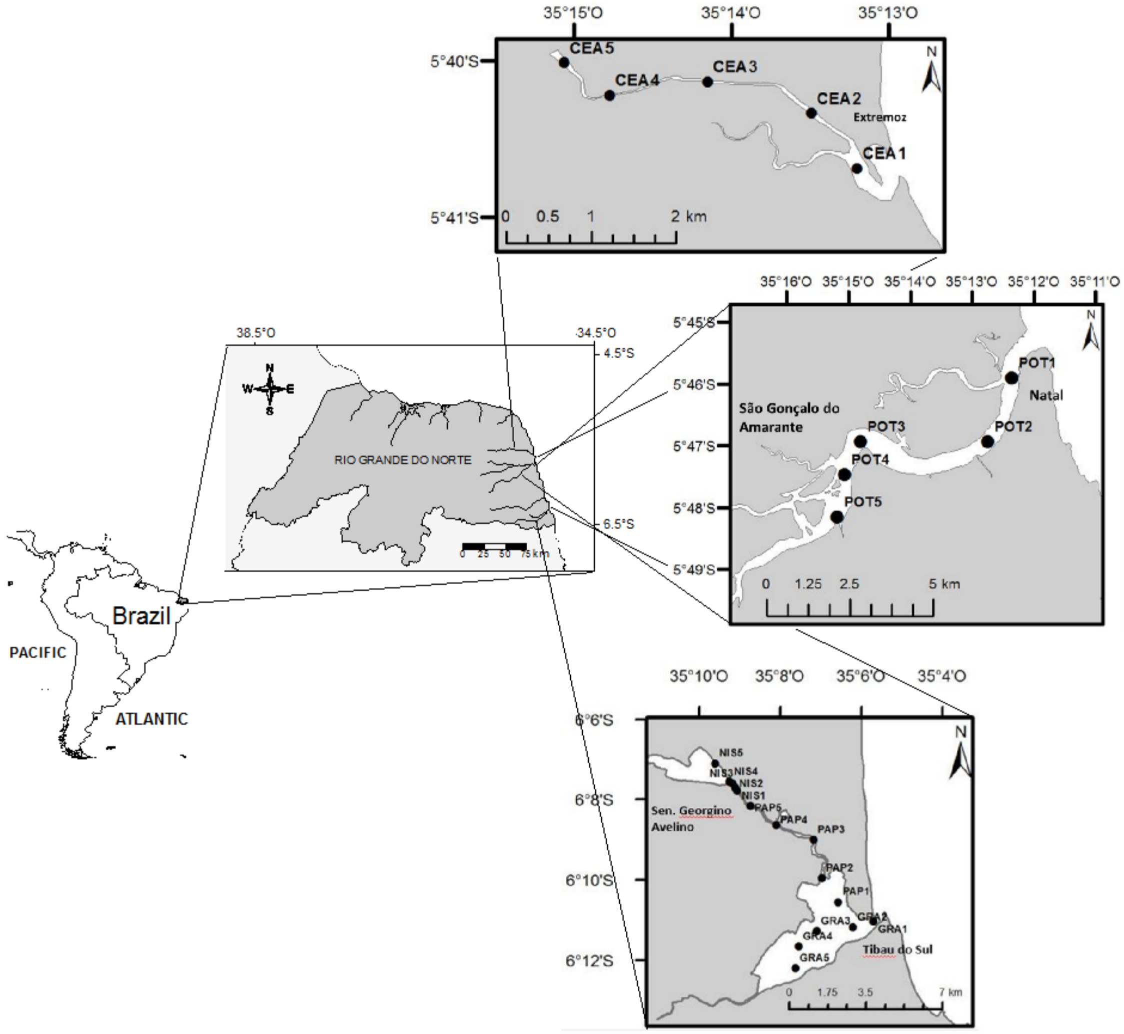

Figure 2 - Study area (CEA - Ceara Mirim sampling stations / POT - Potengi sampling stations / NIS – Nísia-Floresta sampling stations / PAP – Papeba sampling stations / GRA – Guaraíra sampling stations.

bathymetric data regarding field surveys using an eco-sound. The depths were corrected according to the tide variation, obtaining the pairs of coordinates and the depths of each point (*x, y, z*). For this, the Surfer v.7.0 program (continuous surface modeling) was used, where the margins of each estuary were digitized to delimit the channels. The isotropic method of kriging was used for the calculation of volume and area.

The areas and volumes of the Apodi, Conchas, Guamaré, Galinhos, and Ceará-Mirim estuaries were obtained from the sum of the sampling areas (Figures 1 and 2), digitized on the official topographical charts and multiplied by the depth obtained in Field at the moment of sample collection in quadrature cycles. That is, with little variation of depth. This was intended to have a better approximation of the volume.

The areas and volumes allowed to obtain the dilution capacity of each estuary (Table II).

The Kruskal-Wallis variance test was performed to identify statistically significant differences ($p<0.05$) between negative and positive estuaries, based on heavy metal and organic matter concentrations. Lastly, correlations between the analyzed parameters were made by applying

Spearman's test. The probability of 0.05 or less was considered significant.

RESULTS AND DISCUSSION

Extraction of metals with 0.5 M HCl is effective in the dissolution of complex formation, adsorbed and precipitated metals in the sediment without attacking the silicate. Agemian and Chau (1976) observed that the average amount of silicon extracted with the 0.5 M HCl method corresponds to 1% of the total concentration. Moalla (1997) compared the extraction technique with 0.5M HCl with other more conventional techniques using ammonium oxalate and royal water and confirmed that the former is a reliable, fast, harmless, simple and inexpensive method for measuring concentrations of potentially available or anthropogenic metals in aquatic sediments.

According to Sindern et al. (2007), human presence can be verified by heavy metal levels exceeding the range of background concentrations. The hyper-saline Apodi and Conchas estuaries had the highest concentrations for Cr, Cu, Cd and Pb, respectively (3.2 µg/g, 5.1 µg/g, 0.5 µg/g; 21.4 µg/g). On the other hand, positive Nísia-Floresta estuary had the highest concentration for Zn (7.6 µg/g). The reason for the observed geographical variation in the availabilities of the metals is most probably the input of these metals in dissolved and/or particulate form through anthropogenic activities (Ramos e Silva et al. 2003). The nine estuaries systems are under different human activities, such as: agriculture, shrimp farm, domestic sewage, husbandry and soil drilling activities (Ramos e Silva et al. 2003, Lacerda et al. 2006). These activities are potential sources of metals (Cr, Cu, Cd, Pb and Zn) to the estuaries. Added to these the hyper-saline estuaries are under high mean evaporation of approximately 2,600 mm/yr (Ramos e Silva et al. 2006). Among the hyper-saline estuaries, Guamaré showed the lowest concentrations for all metals (Table I). This scenario may be explained by its high dilution capacity (area to volume ratio = 0.42 m^2 / m^3; Table II). On the other hand, the high concentrations of Zn in Nízia-Floresta positive estuary can be explained by its lower dilution capacity (area to volume ratio = 0.95 m^2 / m^3; Table II, besides the anthropogenic activities already mentioned. Our ratio values between area and volume (m^2 / m^3) to Apodi, Guamaré, Ceará-Mirin and Guaraíra estuaries are an order of magnitude below the values recorded by Lacerda et al. (2006). These authors considered the entire basin area to discuss the dilution of loads within the channel of each estuary.

As mentioned above Conchas estuary revealed higher potentially mobile Cr levels among all studied estuaries (Table I). It is well known that possible sources of Cr include leather manufacturing (Földi et al. 2013, Kumar et al. 2014), being the tanning method the most utilized for a century (Mutlu et al. 2014). So, Testa et al. (2004) confirmed the leather tanning is a significant activity present in the Piranhas-Açu watershed.

Nowadays, the estuarine region of Galinhos presents soil occupation problems with irregular open dumps zones installed (Diniz et al. 2015). Additionally, the area represents its mangrove ecosystem impacted with the growing of shrimp farms. Lastly, the local marine tourism represents an important activity, with potential environmental impacts (Diniz et al. 2015).

The Ceará-Mirim estuarine area and the Papeba and Guaraíra estuaries registered the smaller concentrations of all the analyzed metals (Table I). The coastal region of Ceará-Mirim presents some environmental protection areas. Nevertheless, no heavy metal enrichment pattern was registered. Cr, Cd and Pb presented minimum concentrations in the Nísia-Floresta estuary, however Cu and Zn showed the higher concentration of all estuaries studied. These three positive estuaries are inserted in an environmental protection area.

TABLE I

Metal concentrations in the estuaries of Rio Grande do Norte and reference data in sediments of different systems around the world (average values in μg/g).

Estuaries	Method	Sediment fraction	Cr	Cu	Cd	Pb	Zn	References
Apodi estuary	0.5M HCl extraction	<1 mm	3.2	2.3	0.5	21.4	5.4	This study
Conchas estuary	0.5M HCl extraction	<1 mm	7.0	5.1	<0.4	17.1	6.0	This study
Guamaré estuary	0.5M HCl extraction	<1 mm	3.2	0.5	<0.4	6.4	1.6	This study
Galinhos estuary	0.5M HCl extraction	<1 mm	3.8	1.2	<0.4	18.6	4.1	This study
Ceará-Mirim estuary	0.5M HCl extraction	<1 mm	<0.4	<0.4	<0.4	<0.4	0.1	This study
Potengi estuary	0.5M HCl extraction	<1 mm	4.8	3.2	<0.4	9.5	6.9	This study
Nísia-Floresta estuary	0.5M HCl extraction	<1 mm	<0.4	5.1	<0.4	<0.4	7.6	This study
Papeba estuary	0.5M HCl extraction	<1 mm	<0.4	<0.4	<0.4	<0.4	1.1	This study
Guaraíra estuary	0.5M HCl extraction	<1 mm	<0.4	<0.4	<0.4	<0.4	<0.4	This study
Sinos estuary, Brazil	0.5M HCl extraction	<63 μm	20.7	45.4	-	12.7	83.9	Schneider et al. 2014
Lake Karla, Greece	0.5M HCl extraction	<63 μm	298.3	38.2	-	34.3	2.2	Skordas et al. 2015
Laurel Creek, Canada	0.5M HCl extraction	<63 μm	8.6	48.6	2.2	58.5	-	Kominar 2002
Manoa watershed, USA	0.5M HCl extraction	<125 μm	-	52.0	-	41.0	142	Sutherland 2002
Suape Harbor, Brazil	0.1M HCl extraction	<53 μm	1.82	5.1	0.4	3.6	13.7	Téodulo et al. 2003
Poxim estuary, Brazil	BCR Sequencial extraction	-	3.5	5.7	0.2	9.0	12.4	Passos et al. 2010
Mahanadi River basin, India	Sequencial extraction (Tessier)	<88 μm	3.1	4.0	1.4	7.9	20.0	Sundaray et al. 2011
Pearl estuary, China	Simultaneous extraction	-	-	16.7	4.1	32.5	52.6	Fang et al. 2005

TABLE II
Major environmental characteristics of the nine estuaries studied along the coast of Rio Grande do Norte, NE Brazil.

Classification/ Estuary	Lower basin area (km^2)	Estuarine volume (10^3 m^3)	Area to volume ratio (m^2/m^3)
Hyper-Saline			
Apodi	3.90	17,489.01	0.22
Conchas	2.04	5,022.56	0.41
Guamaré	3.36	8,037.77	0.42
Galinhos	10.00	53,367.32	0.19
Positive			
Ceará-Mirim	0.73	1,095.00	0.66
Potengi	18.14	35,151.96	0.52
Nísia-Floresta	3.55	3,750.00	0.95
Papeba	1.19	950.00	1.25
Guaraíra	12.29	13,294.13	1.01

The Kruskal-Wallis (1952) statistic test applied to the estuaries comparison suggested a significant difference between the positive and hyper-saline classified estuaries. The positive Papeba, Guaraíra and Nísia-Floresta estuaries also presented difference when compared to the hyper-saline estuaries. In a general way, the higher heavy metal concentrations were found in the hyper-saline estuaries. These results can be a response of the higher pollutants loads to these areas. On the other hand, the hydrodynamic conditions can lead to the biggest potential for pollutants to accumulate. According to Largier et al. (1997), hyper-saline estuaries are usually characterized by weak tide dispersion capacity, resulting in longer water resident time along the estuarine bed. So, as a result, these ecosystems tend to accumulate contaminants rather than export them to neighbor systems (Blake et al. 2004). Another typical feature of these areas are the high evaporation rates, contributing to the concentration of solutes in the water column, inducing to coagulation and finally precipitation of insoluble authigenic minerals in surface sediment (Shumilin et al. 2002).

In the hypersaline environments precipitation dynamic, Soto-Jiménez and Páez-Osuna (2008) suggested that metals highly associated with sediment matrixes like organic matter, carbonates or oxides, represents an important fraction. According to Sindern et al. (2007), the predominantly fine grain sized sediments and high levels of organic matter turned the studied area a potential deposit for pollutants. However, it is not possible to observe in the present study, any significant correlation between organic matter and metals concentrations ($r < 0.35$; $p < 0.05$). The low levels of organic matter did not influence the local heavy metal concentration. Results suggest that the heavy metal concentrations present in the studied area may be linked with another sediment matrix.

Although concentrations of some metals are higher in most hyper-saline estuaries (except for Zn), these concentrations are below the natural background concentrations of metals in sediment (Table III). The shale is a sedimentary rock formed by silty-clay particles, being one of the most common sedimentary rocks on the planet. It is a rock that breaks easily and separates into thin layers along well developed planes very close to each other (Lutgens and Tarbuck 1989). It is well known that heavy metal concentrations is not homogeneously among the various particle fractions of sediment, were the finer fractions (< 8 μm) retain the higher metal concentrations in relation to bulk sediments. Thus, it is necessary to consider that the extraction of metals in this study was done in the fraction less than 1 mm (composed of the primary mineral quartz), which is a poor adsorbent for metals. This fraction can be up to 4 times less than the concentration of metals present in the fraction smaller than 8 μm. In this way, we can consider worrying the concentrations potentially available in these estuaries, resulting from the anthropic activities.

The relatively low concentrations of the environment didn't exceed the values obtained

TABLE III
Concentration in µg/g of some metals in continental crust, shale and coastal sediments.

Metal	Continental Crust[1]	Shale[2]	Coastal Sediments (*background*)[3]	Coastal Sediments (“high” concentration)[4]
Cd	0.1	0.3	0.1-0.6	0.54
Cr	126	90	50-100	125
Cu	25	45	10-50	42
Pb	14.8	20	5-30	45
Zn	65	95	1.2->100	135

[1]Wedepohl (1995); [2]Mason and Moore (1982); [3]NAVFAC (2000); [4]Daskalakis and O’Connor (1995): The “high” concentration of the elements in sediments was defined as the geometric mean of the concentrations plus a standard deviation of the mean of the National Status and Trends.

in the other locations (Table I), with Pb and Cr concentrations similar to the Poxin and Mahanadi estuaries. The differences between the present study and the referenced literature can be explained taking into account the influence of fine grain size on the dynamics of accumulation of heavy metals (Maslennikova et al. 2012).

The Potengi estuary presented some of the higher heavy metals levels in the whole research. According to Souza and Ramos e Silva (2011) and Ramos e Silva et al. (2003, 2006), during the last decades, the Potengi estuary passed through intensive ecosystem degradation. The expansion of the cities of Natal, São Gonçalo do Amarante and Macaíba increased the loading from industrial and domestic wastewater into the estuary. Ramos e Silva et al. (2001) registered that concentrations in *Crassostrea rhizophorae* from the Potengi can be interpreted to be high on a global scale for Zn and Cu, indicating atypically raised bioavailabilities. Emerenciano et al. (2009) studied heavy metals concentrations in the *Anomalocardia brasiliana* mussels living in the same area. The authors also found critical high concentrations of Cr, Zn and Pb. Silva et al. (2001) explained the high levels of heavy metal load as the result of dredging, fertilizers and pesticides use in agriculture and other anthropogenic activities, as well as domestic and industrial discharges that reach the Potengi river through the Baldo channel. Meantime, Medeiros (2009) connected the higher heavy metals concentrations to the fine grain size sediment and the organic matter available in the area.

Lastly, the low Cd levels reached in all of the sampling sites of the present study agreed with the result obtained by Téodulo et al. (2003) and Passos (2010) in the sediment of Suape and Poxim estuaries, both of them in the Northeast region of Brazil. Still, according to Passos (2010), Cd is present only in the residual phase, inaccessible to the approach used in the present work. On the other hand, Sindern et al. (2007) concluded that in the Potengi estuary, close to wastewater outlets, a characteristic anthropogenic heavy metal signature is clear in enhanced Cd concentrations relative to reference elements such as Al and Fe. The same pattern occurred for other metals.

CONCLUSIONS

Nine estuaries of Rio Grande do Norte coast were evaluated for potentially mobile heavy metals concentrations, through the application of diluted hydrochloric acid (HCl). The potential heavy metal bioavailability results followed the descending order Pb<Zn<Cr<Cu<Cd. None of the values exceeded the safe limits proposed by the available literature. On the other hand, some authors suggested that the tissues of some benthic organisms of Potengi river already contain levels above the secure concentrations, reinforcing the

importance of the heavy metal bioavailability evaluation in the area.

The negative estuaries showed to be significantly more contaminated then the positive. Nevertheless, the obtained data did not permit the elucidation of the reasons for these differences. Thus, results obtained in the present research represent one more step in the heavy metal accumulation comprehension in the study site. Notwithstanding, more and different approaches must be applied for better understanding of the heavy metal cycling in the Rio Grande do Norte estuarine sites.

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