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SPATIO-TEMPORAL VARIATION OF METAL CONCENTRATIONS IN ESTUARINE ZONES OF THE TODOS OS SANTOS BAY, BAHIA, BRAZIL

VARIAÇÃO ESPAÇO-TEMPORAL DAS CONCENTRAÇÕES DE METAIS EM ZONAS ESTUARINAS DA BAÍA DE TODOS OS SANTOS, BAHIA, BRASIL

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ABSTRACT - The knowledge of metal behavior in the aquatic environment is important for understanding its effects in estuarine zones and mangrove areas. These important and precious ecosystems are affected by many different factors that may vary temporally and spatially. The present study investigated the spatial and temporal variation of physicochemical parameters (pH, dissolved oxygen, temperature, salinity, etc.) and metal concentrations (Zn, Fe, Ni, Cu) at three different locations along the Todos os Santos Bay, North East Brazil, by analyzing surface water, sediment and mangrove oysters (*Cassostrea rhizophorae* (Guildin, 1828)). Metal concentrations in surface waters and sediments differed between the three sampling times (March and August 2014; January 2015) and locations and were affected by fluctuating physicochemical parameters, which in this way also affected the metal bioconcentration in the oysters. The pH of the surface waters, for example, increased from the 1st to the 3rd sampling time while the concentrations of Zn and Fe decreased during the same period. The sediment concentrations of Zn and Fe were strongly correlated with organic matter content. These results suggests that seasonality as well as the different water and sediment properties along the bay directly affect metal concentration and bioavailability in the environment.

Keywords: metal behavior; physicochemical parameters; seasonality; variation.

RESUMO - O conhecimento do comportamento de metais no meio aquático é importante para a compreensão dos seus efeitos em zonas estuarinas e nas áreas de manguezais. Esses importantes e preciosos ecossistemas são afetados por muitos diferentes fatores que podem variar temporalmente e espacialmente. O presente estudo investigou a variação espacial e temporal de parâmetros fisicoquímicos (pH, oxigênio dissolvido, temperatura, salinidade, etc.) e as concentrações de metais (Zn, Fe, Ni, Cu) em três locais diferentes ao longo da Baía de Todos os Santos, Nordeste Brasil, analisando as águas superficiais, os sedimentos e as ostras de manguezal (*Cassostrea rhizophorae* (Guildin, 1828)). As concentrações de metais em águas superficiais e sedimentos diferiram entre os três tempos e locais de amostragem (março e agosto de 2014, janeiro de 2015) e foram afetados por parâmetros fisicoquímicos flutuantes, o que também afetou a bioconcentração de metal nas ostras. O pH das águas superficiais, por exemplo, aumentou do 1º ao 3º tempo de amostragem, enquanto as concentrações de Zn e Fe diminuíram durante o mesmo período. As concentrações de sedimentos de Zn e Fe foram fortemente correlacionadas com o teor de matéria orgânica. Esses resultados sugerem que a sazonalidade, bem como as diferentes propriedades de água e sedimentos ao longo da baía, afetam diretamente a concentração e a biodisponibilidade do metal no meio ambiente.

Palavras-chave: comportamento do metal; parâmetros fisicoquímicos; sazonalidade; variação.

INTRODUCTION

Estuarine environments and its mangrove forests have large ecological importance by serving as habitat for many species (Campana et al., 2005; Onofre et al., 2007). Due their natural conditions, these ecosystems are very special, but also very sensitive to disturbances like pollution (Nizoli & Luiz-Silva, 2009; Strady et al., 2011).

Because of human activities, the levels of metals in the environment have increased. This also concerns marine environments, so metals may also cause a potential threat to mangrove ecosystems (Nizoli & Luiz-Silva, 2009; Strady et al., 2011). Metals may have direct effects on organisms living in mangrove areas, such as reducing their growth and reproduction and in this way potentially affecting population growth and eventually biodiversity. When metals accumulate in organisms, they may end up in the food chain and cause indirect effects. In this way, they may even pose a risk for human health.

Mollusks are sedentary animals that have the potential to accumulate high levels of metals in their tissues. They also are an important food source for humans. For these reasons, they have been considered important organisms for measuring and monitoring available metal concentrations, also in mangrove ecosystems (Silva et al., 2006; Strady et al., 2011; Ruelas-Inzunza & Paez-Osuna, 2000; Harding, 2007).

The Todos os Santos Bay, in Salvador, located in the Rencôncavo Baiano region, North East of Brazil, is a unique area that has many ecosystems with a high fauna and flora biodiversity. The Bay also is used for industrial activities, which on one hand brings economic value for society, but on the other hand has led to possible exposure with metals and deterioration of the environment. The dissolved or available levels of metals in aquatic ecosystems are influenced by many different factors, such as pH, redox conditions, organic matter, mineral particles and salinity (Du Laing et al., 2008; Reitermajer et al., 2011). These factors may vary during the year, mainly because of the difference in rainfall intensity between seasons. Therefore, seasonal patterns may have important impacts on metal availability due to their influence on the physicochemical parameters of the surface water (Nizoli & Luiz-Silva, 2009). The Todos os Santos Bay is unique because it consists of a range of different habitats with different characteristics. This spatial variation in characteristics, together with the temporal variation, may however, also lead to large differences in metal availability and consequent metal risks (Queiroz & Celino, 2008). It therefore is essential to evaluate metal concentrations in water, sediment and biota and combine this with knowledge about the geochemistry of the system to assess the quality of the mangrove areas in the bay (Cundy et al., 2005).

The aim of this study is determining the spatial and temporal exposure to metals of three different mangrove areas in the Todos os Santos Bay. This involved analyzing metal concentrations in surface water and sediment. Metal bioavailability was estimated by measuring concentrations in soft tissues of the oyster *Crassostrea rhizophorae* (Guildin, 1828), popularly known as mangrove oyster. This species is widely distributed along the entire Todos os Santos Bay. It is a sessile filter-feeder of reasonable size and sedentary, which can easily be sampled. Water, sediment and oysters were sampled during three different seasons of the year. All samples were analyzed for Zn, Fe, Ni and Cu concentrations. By analyzing also physicochemical parameters in water and sediment, speciation calculations could be made to estimate possible fluctuations in available metal concentrations at different points in the bay.

MATERIALS AND METHODS

This study was carried out in the Todos os Santos Bay (32º 02' 30" - 38º 37' 30"W and 13º 07' 30" - 12º 37' 30"S) in Brazil, in three different estuarine zones near the (A) Maragojipe, (B) Jaguaripe and (C) São Paulo Rivers (Figure 1). The Todos os Santos Bay is the biggest and most important navigable bay of the Brazilian coast, with a surface area of about 1.200 km² and a coast length of 462 km.

These estuarine zones, near the Maragojipe, Jaguaripe and São Paulo Rivers, where a magnificent mangrove system develops, have a fundamental importance to the local food chain and also to the livelihood of many of the inhabitants of the region. Even though they belong to the same bay, the spatial variation makes these areas having different characteristics. These estuarine ecosystems have been affected by many human activities, such as contamination by chemical industries, which have contributed to their deterioration (Carvalho, 2007).

Geologically, the Todos os Santos Bay is included in the sedimentary basin of the Reconcavo Baiano. The climate is tropical-humid and presents a remarkable seasonal cycle (Figure 2). Rainfall in this region is around 300 mm month^{-1} between April and June, characterizing the wettest period. Between January and March, the rain is less intense and well distributed with a precipitation of around 125 mm month^{-1}. Average annual temperature is about 25 ºC (Kirimure, 2013).

The economic activities in this region are considered as industrial, and cases of oil spill have been reported, as well as emissions of industrial and domestic effluents from municipalities around the region (Jesus, 2011; Milazzo et al., 2014).

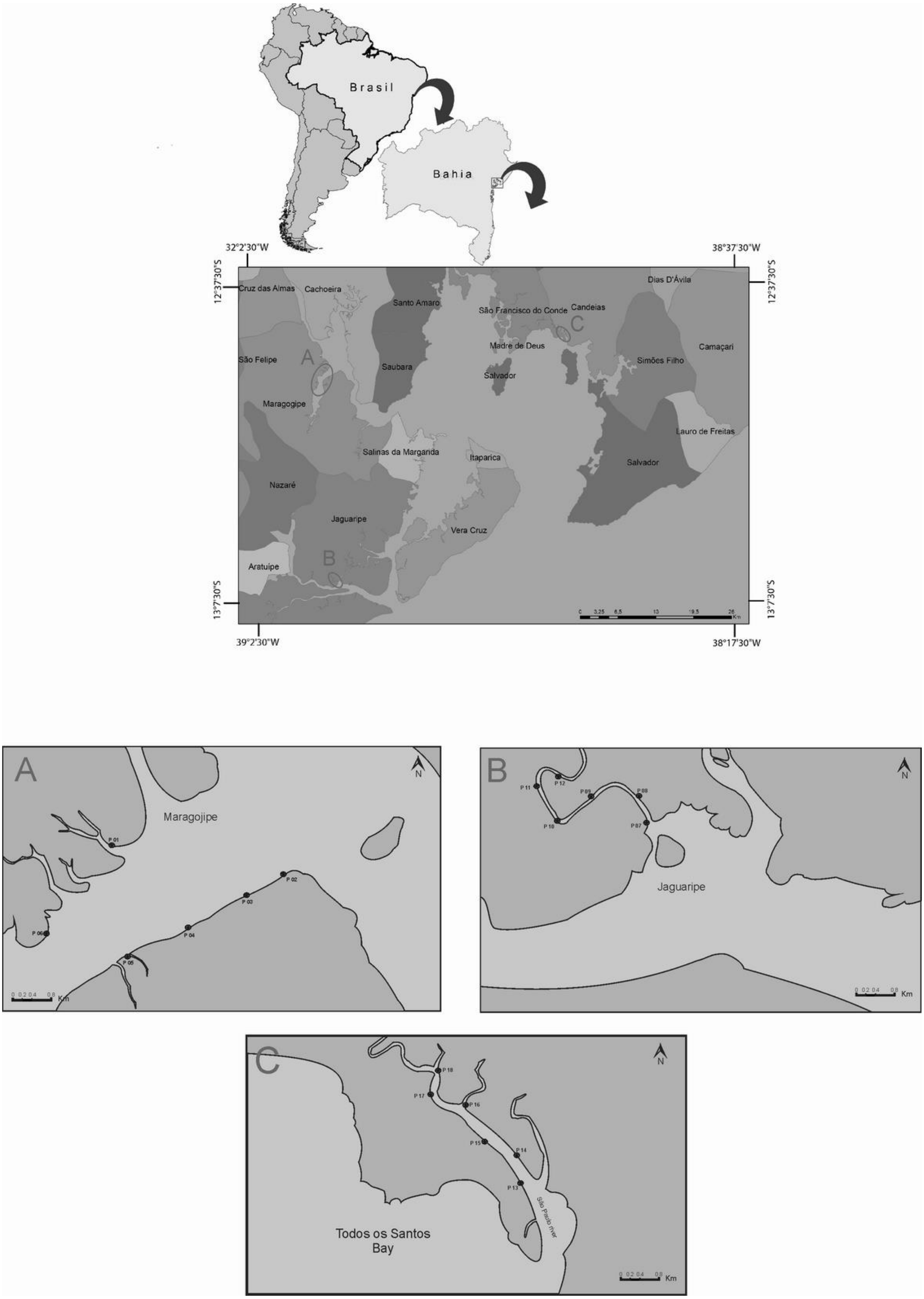

Figure 1 - Location of the sampling sites used for this study. Insert shows a map of the Bahia region in Brazil with the Todos os Santos Bay. The detailed overview of the Todos os Santos Bay area shows the sampling sites near the Maragojipe (A), Jaguaripe (B) and São Paulo (C) Rivers.

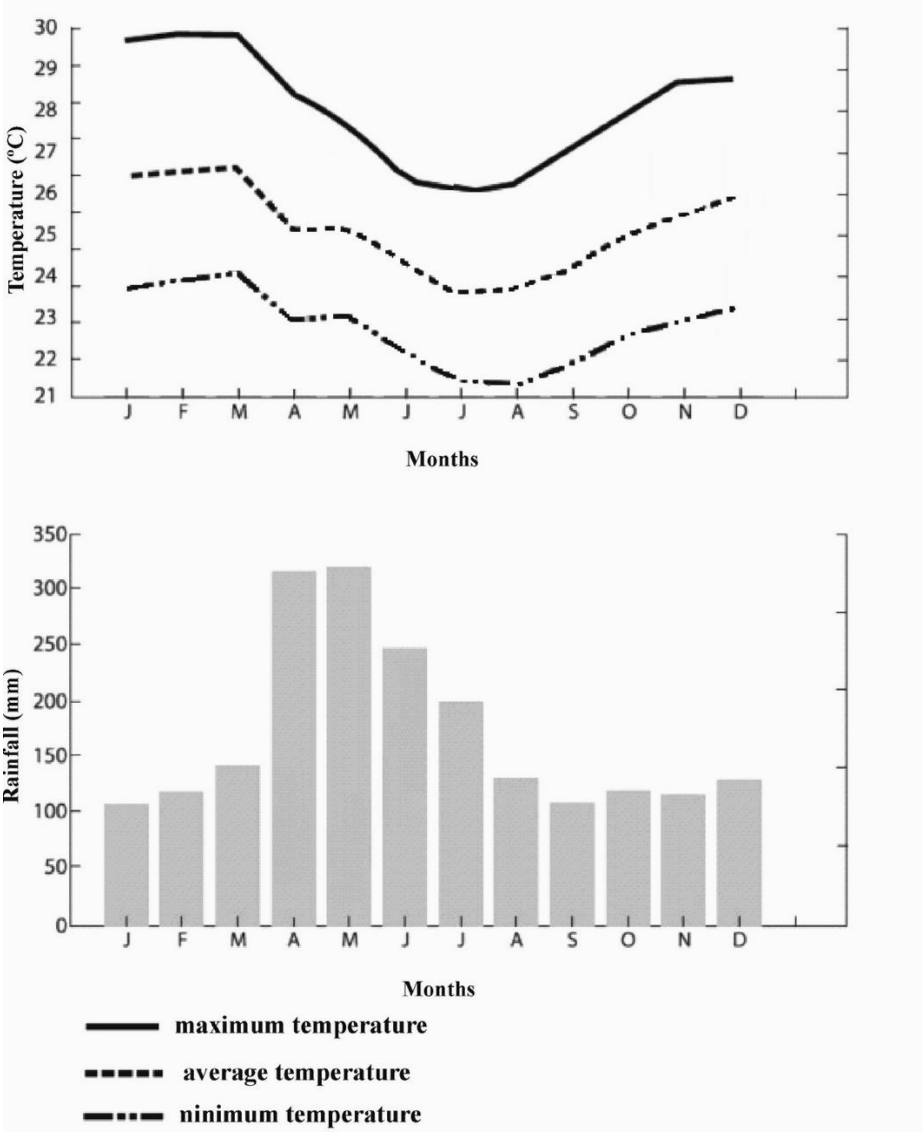

Figure 2 - Average seasonal variation of temperature and rainfall in the study area registered by the Ondina Weather Station for the period of 1961-2009 (INMET, 2015). This station, located in Salvador-Bahia, is the closest weather station of the Todos os Santos Bay.

Sampling

The sampling was carried out in three periods, March 2014, January 2015 (dry season) and August 2014 (rainy season).

Sampling always was done during the low tide, taking into account the tidal period, for more details see Table 1.

Sediment, surface water and mollusk samples were collected from 18 points (6 in each estuary), with a spatial distance of approximately 200 m between each sampling point. This distance is sufficient to consider sampling points as true replicates, since the organisms collected for the study are sessile. The sampling points were randomly chosen across each sampling location, in order to avoid any bias in the results.

Table 1 - Location, dates, time and tide height (m) of the samplings of the three locations in the Todos os Santos Bay, Bahia, Brazil, using Madre de Deus Port tide as a reference.

Location	Date			Hour			Tide height (m)		
Season	1st (2014)	2nd (2014)	3rd (2015)	1st (2014)	2nd (2014)	3rd (2015)	1st (2014)	2nd (2014)	3rd (2015)
Maragojipe River	18/03	26/08	07/01	10:51 a.m.	10:02 a.m.	11:09 a.m.	0.2	0.2	0.4
Jaguaripe River	20/03	27/08	08/01	10:51 a.m.	10:54 a.m.	11:47 a.m.	0.3	0.3	0.5
São Paulo River	21/03	29/08	09/01	12:19 a.m.	11:49 a.m.	12:13 p.m.	0.4	0.4	0.6

Water Collection and Preparation for Analysis

Surface water samples (500 mL) were taken at a depth of 0 - 20 cm using polyethylene bottles, and kept in coolers at a temperature of approximately 4^o C until arrival at the laboratory. In the laboratory, the water samples were acidified with 0.5 mL of HNO_3 (ACS ISO MERCK, 65%, for analysis), corresponding with a standard of 0.1% relative to the total volume of each sample (Carvalho, 2007). The water samples were analyzed for metals according to ASTM (1992). Physicochemical parameters (pH, Eh, temperature and salinity) were monitored at each sampling point. For pH, Eh and temperature measurements, a pH-meter/mV Handylab1 Schott Glaswerke Mainz was used. For salinity measurements, a portable refractometer Atogo S/Mill-E was used, and for dissolved oxygen determination a multiparameter water/ Manta 2.

For metal analyses, the water samples were filtered over a 0.45 µm cellulose acetate membrane. After filtration, 100 mL were transferred to a beaker, and 10 mL of HNO_3 (ACS ISO MERCK, 65%, for analysis) was added. The beakers were placed on a hot plate, until the volume was reduced to approximately 20 mL. After cooling, the fraction was diluted to 25 mL and stored in a volumetric flask for metal determination.

Sediment Collection and Preparation for Analysis

For the sediments, approximately 300 g were sampled from the top 0 - 15 cm layer, and stored in polyethylene packages with a sufficient amount of water from the sampling site to preserve their characteristics. The samples were placed in coolers with ice to maintain a temperature of 4 ^oC, according to Jesus et al. (2003). The cores were taken to the laboratory, and analyzed for metals, particle size distribution (classified as sand, silt and clay), and organic matter content.

To digest sediment samples, the microwave oven partial extraction technique was used, according to the D 5258-92 methodology from Standard Practice for Acid-Extraction of Elements from Sediments Using Closed Vessel Microwave Heating (ASTM, 1992), adapted to the manual of the No. 11 equipment (Provecto DGT 100 plus Microwave Manual of the Institute of Geoscience of the Federal University of Bahia. The method consisted of weighing 1.0 g dry sediment samples in beakers and adding 10 mL of HNO_3 (ACS ISO MERCK, 65%, for analysis). After 30 minutes, 10 mL of H_20 ultrapure was added for digestion in a Microwave Oven. The digested samples were passed through a quantitative filter (0.80 µm), diluted to 50 mL with deionized water and stored in plastic 100 mL bottles for metal analysis.

Mollusk Collection and Preparation for Analysis

The mollusks were sampled at the same sampling points as the sediment and water. A total of 16 specimen of *C. rhizophorae* were gathered at each sampling point, through active visual search. The specimens were maintained in polyethylene bags, transported and kept in coolers with ice. From each sampling point, twelve individuals were randomly selected for metal analysis. The body size of each individual was measured. Length and width were obtained based on the distance between posterior and anterior axle. The individual mollusks were weighted with the shell and the tissue. Subsequently, the tissue was removed and the shell was weighted again to obtain the weight of the tissue. Then the animal tissue was freeze-dried.

For the analysis of metals, 0.5 g of freeze-dried crushed tissue was digested in 5 mL of HNO_3 (ACS ISO MERCK, 65%, for analysis) and 3 mL of concentrated hydrogen peroxide (H_2O_2) according to the methodology adapted from the manual of equipment No. 24, Provecto DGT 100 plus Microwave Manual of the Institute of Geoscience institute of the Federal University of Bahia. The digested samples were diluted to 25 mL with deionized water and stored in 30 mL plastic flasks for metal analysis.

Metal Analysis

Metal analysis in digests from different matrices was performed at the Laboratory of Petroleum Studies (LEPETRO), at the Center of Environment Studies (NEA) located at the Institute of Geoscience of the Federal University of Bahia (UFBA), at the Department of Ecological Science, Faculty of Science, of the Vrije Universiteit, Amsterdam and at the Chemical Biological Soil Laboratory of Wageningen University, The Netherlands. The concentrations of metals in sediment and mollusks were determined by flame atomic absorption spectrophotometry (AAS; Perkin Elmer Analyst 100) after digestion; metals in surface water were measured directly by inductively coupled plasma-mass spectrometry (ICP-MS NEXION 300D).

Quality control of the analysis was carried out using duplicates (20% of total samples) and triplicates (10% of total samples), while maintaining acceptable accuracy and precision in the analysis by the estimated experimental error, in addition to blank samples for each matrix. The certified reference materials SLEW-3 (Estuarine water; National Research Council of Canada), SEDIMENT ISE 989 (River clay Wageningen) and DOLT-4 (dogfish; LGC Standards) were used for quality control and the certified values for Zn, Fe, Ni and Cu, are shown in the Table 2. One sample of reference material was measured for each batch of 9 samples for each matrix, and the metal concentrations were always within 83-122% of the certified values.

Table 2 - Metal concentrations reported for certified reference materials (average (±SD)) and values found upon quality control (min., max., average (±SD; n=2)) in this study for Water (SLEW-3), Sediment (ISE 989) and biota (DOLT-4).

	SLEW-3* ($\mu g\ L^{-1}$)	**Sediment ISE 989** ($mg\ kg^{-1}$)**	**DOLT-4*** ($mg\ kg^{-1}$)**	**Water values found ($\mu g\ L^{-1}$)**	**Sediment values found ($mg\ kg^{-1}$)**	**Oysters values found ($mg\ kg^{-1}$)**	**Recovery (%) of elements from reference material**		
							Water	**Sediment**	**DOLT**
Zn	0.20 (±0.03)	1060 (±43)	116 (±6)	0.21 0.23 0.22 (±0.01)	1052 1072 1062 (±13.6)	138 147 142,5 (±7)	110	100	122
Fe	0.56 (±0.05)	40100 (±1180)	1833 (±75)	0.55 0.59 0.57 (±0.02)	33498 35345 34421,5 (±1305)	1505 1522 1513,5 (±12.6)	109	83	83
Ni	1.23 (±0.07)	62.2 (±3.2)	0.97 (±0.11)	1.19 1.20 1.19 (±0.01)	56.3 59.2 57.7 (±2.08)	0.99 0.99 0.99 (±0.00)	97	92	83
Cu	1.55 (±0.12)	157 (±5.2)	31.2 (±1.1)	1.57 1.60 1.58 (±0.02)	144 145 144,5 (±0.32)	37.6 39.0 38.3 (±0.97)	101	92	122

* Estuarine Water; National Research Council of Canada
** River Clay Wageningen
*** Dogfish liver; LGC Standards

Data Analysis

The data were analyzed using STATISTICA 7 to observe summary statistics and trends of metal behavior and physicochemical parameters. Microsoft Office Excel 2007 as well as STATISTICA 7 were used to correlate metal concentrations with physicochemical parameters. In addition, chemical speciation of metals and some cations was estimated using Visual MINTEQ (Gustafsson, 2016). Input parameters included pH, DOC (Dissolved Organic Carbon) and concentrations of Ca^{2+}, Cl^{-}, H^{+}, K^{+}, Mg^{2+} and SO_4^{2-}. Metal concentrations in the mollusks were related to metal concentrations and free metal ion activities in the water and metal concentrations in the sediment samples.

RESULTS

The physicochemical parameters measured in surface waters and sediments from the Maragojipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons, are summarized in Table 3.

In the surface waters, the pH increased with time for all rivers, except for the São Paulo River which had the highest pH (7.29) during the second season. The pH of the sediments showed the same increasing trend with time, however, during the last sampling season sediment pH in the Maragojipe River was lower than in the second season.

The Eh values showed a quite similar behavior for both surface waters and sediments. In the Maragojipe River, the Eh values were negative in all seasons. In the São Paulo River, Eh of surface water was negative at the first and second sampling. For the sediments the Eh values in general were negative during the first and last season and positive in the second season.

During the second sampling (rainy season), temperatures were lower than at the first and third sampling (dry season). In the sediments, the same trend was noticed for Jaguaripe and São Paulo Rivers while in the Maragojipe River temperature increased from the first to the third sampling.

Dissolved oxygen concentrations showed the same trends in Maragojipe and São Paulo Rivers with the highest values recorded during the first (6.9 and 3.6 mg L^{-1}) and third (7.7 and 3.6 mg L^{-}

^{1}) season. In the Jaguaripe River the highest mean dissolved oxygen concentration was measured during the third season (9.3 mg L^{-1}), while it was similar during the first and second season (3.8 mg L^{-1}).

The conductivity of the surface water showed a different trend for the different Rivers. In the Maragojipe River conductivity was highest during the second season (44.7 ms cm^{-1}), while in the São Paulo River it was lowest (49.9 ms cm^{-1}) during the second season. In the Jaguaripe River conductivity increased from the first to the third sampling. The conductivity of the sediment of the Jaguaripe and São Paulo Rivers was also lowest during the rainy season, while it was highest for the Maragojipe River sediments (49.5 ms cm^{-1}) during the rainy season.

Salinity of the São Paulo River was highest (34.6 and 33.1) during the first and third season, respectively, while in the Maragojipe River the highest value (28.6) was recorded during the second season. In the Jaguaripe River, salinity increased from the first to the third season, from 14.3 to 23.0.

Table 3 Physicochemical parameters of surface waters and sediments in the Maragojipe, Jaguaripe and São Paulo Rivers, Brazil, sampled in three different seasons (1st: March 2014; 2nd: August 2014; 3rd: January 2015. The values shown are mean ± standard deviation (n = 6).

Variables	**River / Season**	**Mean ± St.dev.**		
		1st	**2nd**	**3rd**
pH (water)	Maragojipe	6.75 ± 0.29	7.59 ± 0.13	7.70 ± 0.43
	Jaguaripe	5.44 ± 0.26	6.81 ± 0.19	7.25 ± 0.09
	São Paulo	5.91 ± 0.25	7.29 ± 0.16	7.05 ± 0.42
Eh (mV) (Water)	Maragojipe	-7.8 ± 17.9	-30.1 ± 8.0	-25.1 ± 27.3
	Jaguaripe	3.8 ± 16.7	16.0 ± 11.8	2.6 ± 5.9
	São Paulo	-22.8 ± 14.9	-12.3 ± 9.9	16.0 ± 25.4
Temp. (ºC) (Water)	Maragojipe	29.2 ± 0.5	26.1 ± 1.1	30.7 ± 1.3
	Jaguaripe	28.4 ± 0.9	24.4 ± 0.3	27.6 ± 0.2
	São Paulo	29.7 ± 0.6	25.5 ± 0.6	27.3 ± 0.4
Salinity (water)	Maragojipe	22.3 ± 4.1	28.6 ± 2.1	22.0 ± 1.4
	Jaguaripe	14.3 ± 2.8	16.0 ± 3.5	23.0 ± 2.0
	São Paulo	34.6 ± 3.8	32.1 ± 0.9	33.1 ± 3.6
D.O. (mg L^{-1}) (water)	Maragojipe	6.9 ± 1.0	5.9 ± 1.2	7.7 ± 0.9
	Jaguaripe	3.8 ± 0.4	3.8 ± 0.3	9.3 ± 1.1
	São Paulo	3.6 ± 0.3	3.1 ± 0.4	3.6 ± 1.4
Cond. (ms cm^{-1}) (water)	Maragojipe	35.8 ± 6.0	44.7 ± 2.3	35.4 ± 1.9
	Jaguaripe	24.0 ± 4.2	26.5 ± 5.3	36.5 ± 2.7
	São Paulo	52.7 ± 4.6	49.9 ± 1.4	50.6 ± 4.7
pH (sed)	Maragojipe	6.81 ± 0.13	7.10 ± 0.36	6.80 ± 0.18
	Jaguaripe	6.71 ± 0.37	6.99 ± 0.20	7.21 ± 0.14
	São Paulo	6.85 ± 0.21	7.06 ± 0.23	7.23 ± 0.18
Eh (mV) (sed)	Maragojipe	-5.6 ± 7.1	-5.6 ± 21.2	13.6 ± 10.5
	Jaguaripe	-4.6 ± 10.9	4.1 ± 12.5	-1.5 ± 7.4
	São Paulo	-5.0 ± 14.0	0.0 ± 13.3	-3.1 ± 10.7
Temp. (ºC) (sed)	Maragojipe	27.5 ± 1.3	28.4 ± 2.6	30.7 ± 2.0
	Jaguaripe	27.6 ± 1.3	25.5 ± 0.7	29.5 ± 2.4
	São Paulo	28.6 ± 0.6	26.9 ± 1.5	28.9 ± 1.1
Cond. (ms cm^{-1}) (sed)	Maragojipe	42.4 ± 3.7	49.5 ± 3.8	44.6 ± 3.6
	Jaguaripe	40.1 ± 3.4	31.3 ± 3.7	41.1 ± 3.9
	São Paulo	55.3 ± 2.0	51.4 ± 2.2	56.5 ± 1.8

Table 4 shows the particle size distribution (sand, silt, clay) and organic matter content of the sediment for each river in the three different sampling seasons. Organic matter content showed the same trend in all three rivers, being much lower in the rainy season (2nd sampling) than in the dry seasons. Overall, the Sao Paulo River sediment had the lowest organic matter content.

Particle size distribution also showed some variation between seasons and rivers. Clay content, for instance, showed the same trend in the Maragojipe and São Paulo Rivers, increasing with time from 26.6 to 47.3% in the Maragojipe River and from 17.1 to 30.5% in the São Paulo River. In the Jaguaripe River sediment clay content was highest (23.0 and 24.5%) during the first and third season and lowest (18.4%) during the second season.

Metal concentrations measured in surface water, sediment and oysters from the Maragojipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons, are plotted in Figures 3, 4 and 5.

Table 4 - Particle size distribution (silt, clay and sand) and organic matter contents (O.M.) (in %) of sediments in the Maragojipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons: March 2014 (1st), August 2014 (2nd) and January 2015 (3rd).

Variable	**River** / **Season**	**Sediments**		
		1st	**2nd**	**3rd**
Silt	Maragojipe	24.8	35.5	36.2
	Jaguaripe	28.2	29.0	34.0
	São Paulo	29.9	27.2	28.3
Clay	Maragojipe	26.6	41.1	47.3
	Jaguaripe	23.0	18.4	24.5
	São Paulo	17.1	29.4	30.5
Sand	Maragojipe	48.4	23.2	16.3
	Jaguaripe	48.7	52.5	41.4
	São Paulo	52.8	43.3	41.0
O.M.	Maragojipe	10.3	6.1	13.2
	Jaguaripe	10.2	8.2	12.5
	São Paulo	9.7	5.6	9.6

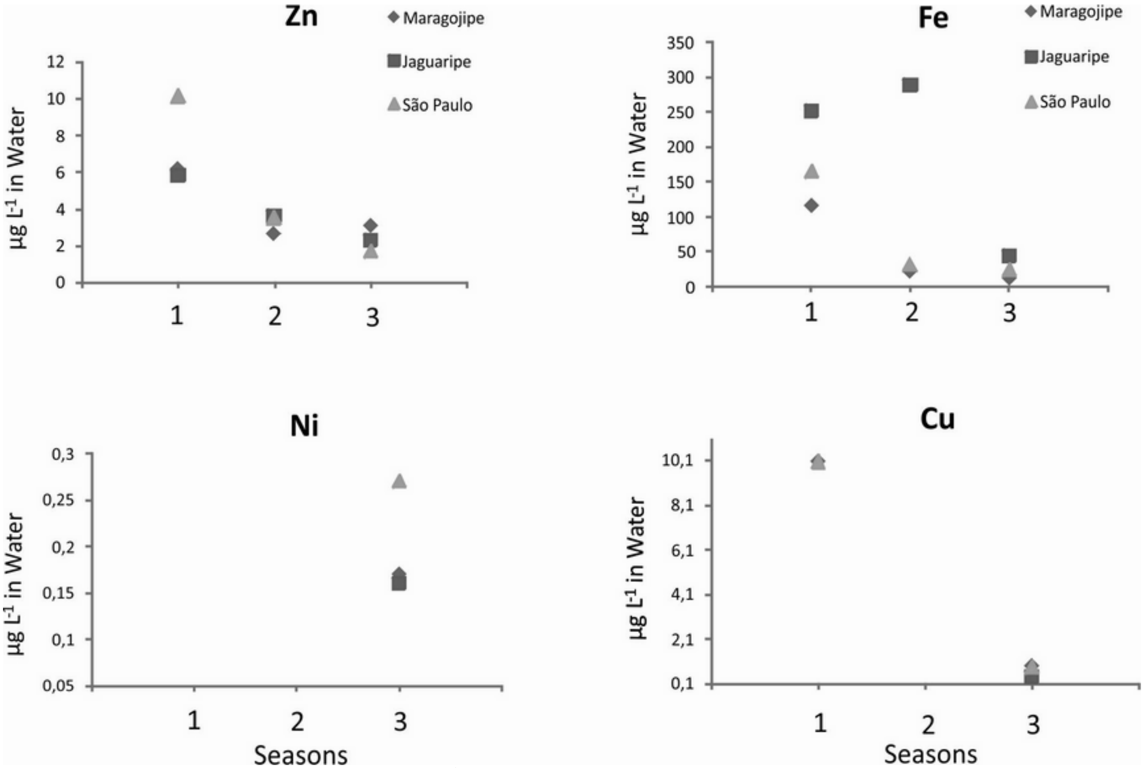

Figure 3 - Average metal concentrations (µg L^{-1}) in surface water of the Maragojipe, Jaguaripe and São Paulo Rivers sampled in three different seasons: 1st: March 2014; 2nd: August 2014; 3rd: January 2015.

Cu levels showed almost the same trends in all matrices, with lower concentrations in the second season compared to the first and third one. Only exception was the Jaguaripe River, where copper concentration in the water was higher in the second season than in the first one.

The Zn levels in sediments and oysters of the Jaguaripe and São Paulo Rivers showed exactly the same trend, being higher in the first and third season. Ni concentrations showed quite different trends in time and between locations. In surface waters, the Ni concentration stayed below the detection limit for the first and second season and ranged from 0.16 to 0.27 µg L^{-1} in the third season in the Jaguaripe and São Paulo Rivers (Figure 3).

The Ni concentrations in sediments were highest in the third season with 12.1, 17.4 and 23.9 mg kg^{-1} in Jaguaripe, São Paulo and Maragojipe Rivers, respectively (Figure 4). In oysters, the concentrations of Ni showed quite some variation between seasons and rivers, but all ranged between 0.20 and 0.95 mg kg^{-1} dry weight (Figure 5)

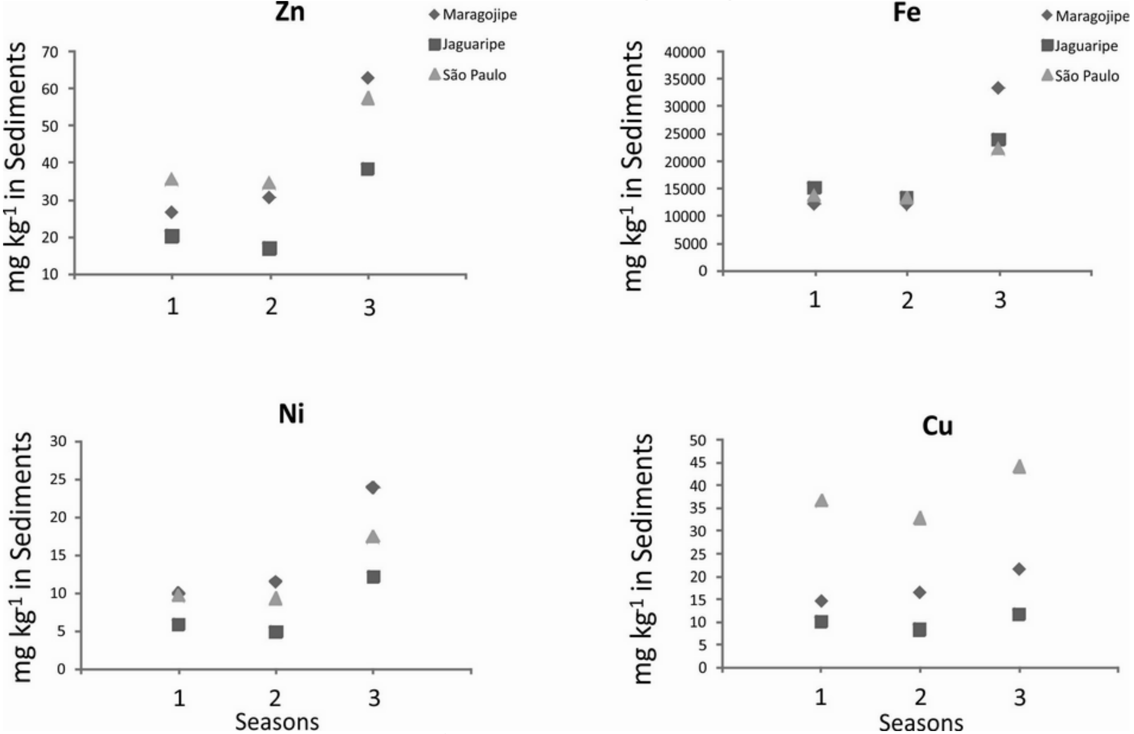

Figure 4 - Average metal concentrations (mg kg^{-1} dry weight) in sediments from the Maragojipe, Jaguaripe and São Paulo Rivers, sampled in three different seasons: 1st: March 2014; 2nd: August 2014; 3rd: January 2015.

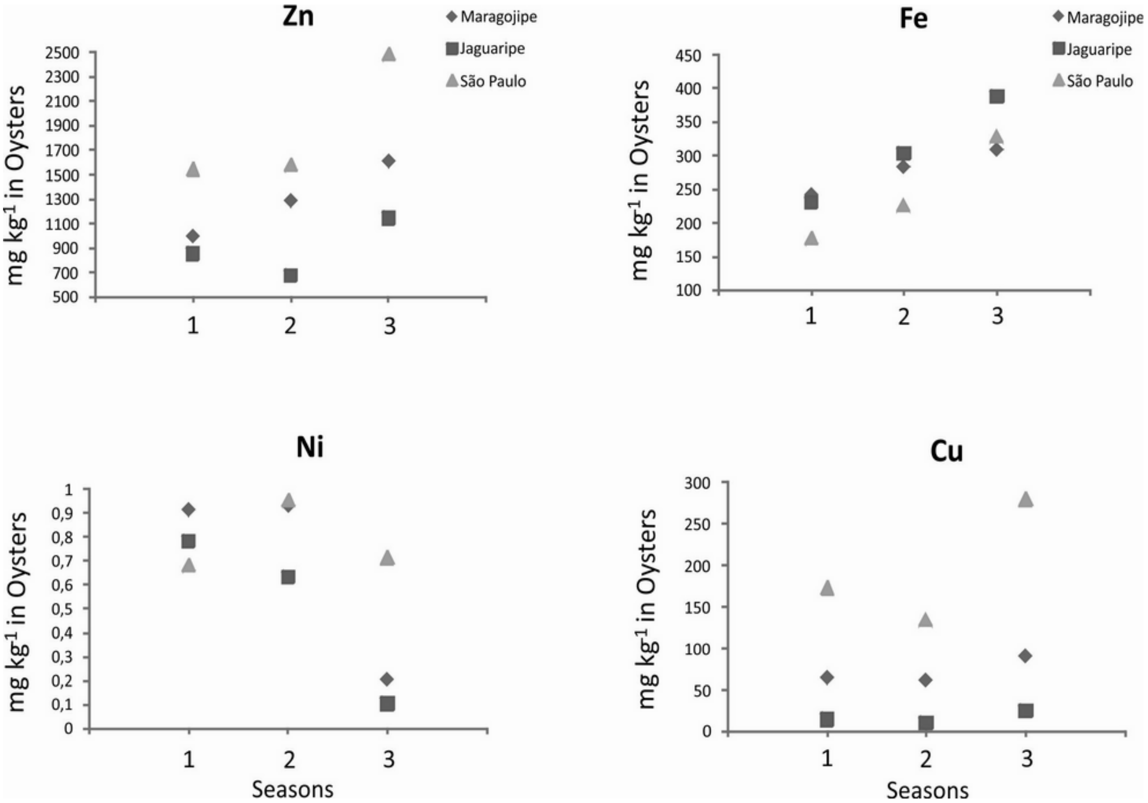

Figure 5 - Average metal concentrations (mg kg^{-1} dry weight) in oysters (*Crassostrea rhizophorae*) collected from the Maragojipe, Jaguaripe and São Paulo Rivers in three different seasons: 1st: March 2014; 2nd: August 2014; 3rd: January 2015.

Speciation calculations were made to check possible fluctuations in available metal concentrations in surface waters at different points in the bay.

The results showed that the waters with the highest metal concentrations also had the highest free ion activities (1st season). The only exception was Zn in the São Paulo River where the highest free ion activity was found during the second season (Table 5). Metal speciation also showed some trends with the pH and ion activities of the water. The free metal ion activity generally decreased with increasing pH for all rivers studied.

Table 5 - Results of the metal speciation analysis in the surface waters. Data shows the pH values and free ion activities of Cu^{2+}, Fe^{2+} and Zn^{2+} (mol L^{-1}) in the Maragojipe, Jaguaripe and São Paulo Rivers in three different seasons (1st: March 2014; 2nd: August 2014; 3rd: January 2015).

			Ions		
Rivers	**Season**	**pH**	**Cu^{2+}**	**Fe^{2+}**	**Zn^{2+}**
Maragojipe	1st	7.59 ± 0.13	$3,67x10^{-11}$	$2,30x10^{-8}$	$7,75x10^{-9}$
	3rd	7.70 ± 0.43	$1,91x10^{-12}$	$1,89x10^{-9}$	$9,15x10^{-9}$
Jaguaripe	1st	5.44 ± 0.26	$4,91x10^{-11}$	$1,38x10^{-6}$	$2,46x10^{-8}$
	2nd	6.81 ± 0.19	$7,90x10^{-12}$	$1,87x10^{-6}$	$1,97x10^{-8}$
	3rd	7.25 ± 0.09	$2,67x10^{-12}$	$1,13x10^{-7}$	$7,32x10^{-9}$
São Paulo	1st	5.91 ± 0.25	$1,16x10^{-9}$	$6,56x10^{-7}$	$2,48x10^{-8}$
	2nd	7.29 ± 0.16	$1,13x10^{-12}$	$6,97x10^{-8}$	$3,98x10^{-8}$
	3rd	7.05 ± 0.42	$1,94x10^{-11}$	$3,34x10^{-8}$	$4,31x10^{-9}$

DISCUSSION

The physicochemical parameters and the metal concentrations in water, sediment and mollusks at the three sampling locations showed different spatial and temporal trends during the sampling period of this study. The temperature of water and sediment is the first to change in response to the input of water and to air temperature, which normally decreases when the rainy season starts. But many other parameters also showed different patterns during the different seasons. In some cases, these fluctuations were not expected, indicating that probably some other factors were affecting the physicochemical properties of the water and sediment of the sampling sites.

In the present study, temperature of the surface water at all locations decreased during the rainy season. In August, the land breezes, precipitation and fresh water influx together were responsible for the lower water temperatures compared with the dry season. The intensity of solar radiation and evaporation also influence surface water temperature, which, as a consequence, was higher during the dry season (1st and 3rd sampling).

The pH of the surface water varied from 5.44 to 7.70 between rivers, ranging from acid to alkaline. The highest pH values were recorded in the Maragojipe River, which might be attributed to that region receiving more effluent discharge (mainly domestic ones) which may make the water more alkaline (Dublin-Green, 1990). Comparing the Jaguaripe and São Paulo Rivers, the latter one had the highest pH during the 1st and 2nd sampling (Table 3). This probably is explained from sea water penetration which may lead to an increase of the pH of estuarine waters (Anitha & Sugirtha, 2013). With values ranging between 7.40 and 8.50 for sea waters, pH showed the influence of the ocean, which was different depending on the location and sampling time. São Paulo River is closer to the ocean which can explain the highest pH values.

The pH fluctuation of surface water generally is attributed to factors like dilution of seawater by freshwater influx leading to salinity reduction, temperature and decomposition of organic matter (Gadhia et al., 2012). The variation in water pH between seasons and locations can easily be explained by the different characteristics of each location. The studied rivers are at a different distance from the ocean and differ in the input of effluent discharge.

Metal concentrations in the surface waters can be affected by pH. Water pH will affect the solubility of metal ions in the environment and their binding to solid or dissolved phases like sediment or dissolved organic carbon (Niyogi & Wood, 2004). This means that pH also may control the availability of these metals for uptake by organisms (Dixit et al., 2013).

The zinc and iron concentrations in the surface waters generally decreased with increasing pH (Figure 6). The concentrations of these elements decreased when the pH values increased from the 1st to the 3rd sampling. Only exceptions were Zn concentrations in the Maragojipe River at the 3rd sampling and Fe concentrations in the Jaguaripe River at the 2nd sampling.

Eh values of the surface waters ranged from -30.1 to 16.7 mV in the different rivers and at different sampling times. Most of the time redox potential was negative, which is normal for estuarine environments and mangrove areas with their high organic matter content. In such environments, oxygen is rapidly consumed by microorganisms giving this ecosystem a reductive feature (Queiroz & Celino, 2008). The variation in Eh values might be related with the tide and sampling time among the rivers. Also in the sediments redox potential mostly was negative. The variation in Eh values can be associated with the location of sampling since for each location the microbial activity may be different.

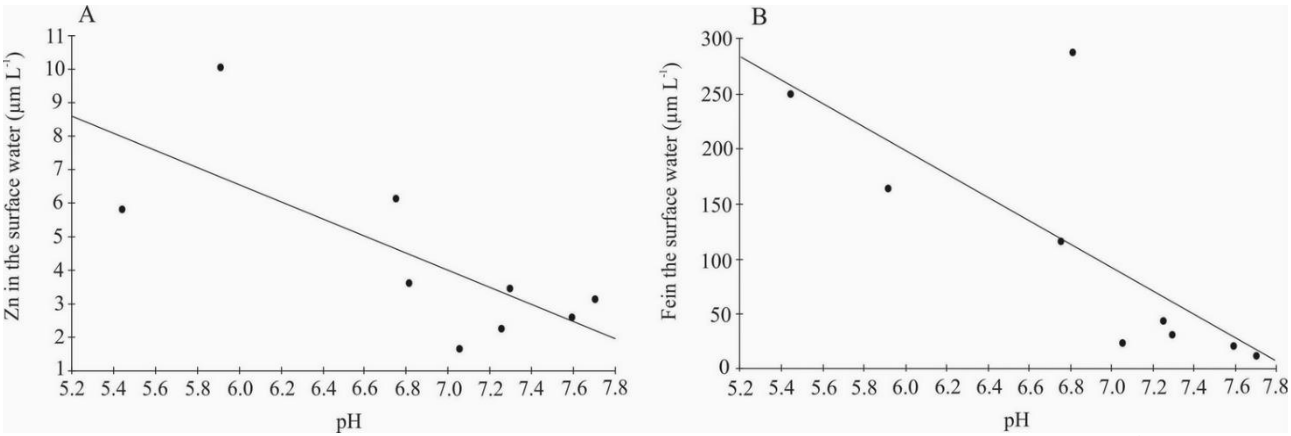

Figure 6 - Relationship between average concentrations of Zn (A) and Fe (B) in the surface water (μg L^{-1}) and average pH of Maragojipe, Jaguaripe and São Paulo Rivers sampled in three different seasons (March 2014; August 2014; January 2015).

Dissolved oxygen (D.O.) levels showed the same pattern for all locations studied, being lower during the rainy season (Table 3). Theoretically, the D.O. level is mostly affected by the temperature and salinity of the water (Palpandi, 2011). In this study, the D.O. level followed the same trend as temperature: when the temperature decreased, the D.O. level also decreased. The opposite was shown by Anita & Surgitha (2013). The salinity also affects the water's capacity to dissolve oxygen, but in an opposite manner: with increasing salinity, D.O. level will decrease (Abowei, 2010). In this study, this trend was only seen in the Maragojipe River (Table 3).

D.O. is an important indicator of water quality as it influences many biological and chemical processes. In general, a D.O. level of 4-5 mg L^{-1} is indicative of good quality, while a D.O. lower than 2 mg L^{-1} is the lowest level for life and defined as hypoxic conditions (NOAA, 2012; Sato et al., 2016). In this study, for all locations the D.O. values ranged between 3.1 and 9.3 mg L^{-1}, so it may be qualified as good according to the international guidelines. However, according to Brazilian legislation (CONAMA, 2005), the D.O. values shouldn't be below 5.0 mg L^{-1}. The D.O. values for São Paulo River for all seasons and Jaguaripe River for the 1st and 2nd samplings were below the latter limit. The low D.O. levels in these locations may cause reduction of some organisms like fishes and the deoxygenation can increase the population of anaerobic microorganisms, specially bacteria. This can induce reproductive failure and death of fishes, in this way causing changes in the local environment, changing abundance and diversity of species (Abowei, 2010). This situation might be triggered by the effects of nutrient pollution since there is no suitable sewage treatment in these locations.

The salinity of the surface waters showed no clear trend. This parameter is always associated with the flood and ebb tides, evaporation rates, rainfall, river discharge and dilution in the estuary (Dublin-Green, 1990; Dixit et al., 2013). Theoretically, salinity should have been lower during the rainy season (2nd sampling period), when the rainfall was higher leading to a higher dilution by the higher input of river discharge.

Only in the São Paulo River salinity level followed this trend. The São Paulo River had the highest salinity (32.1-34.6) which is easily explained from its location closer to the sea compared to the other two rivers. Similar results were reported by Milazzo et al. (2014). However, in the Jaguaripe River salinity increased from the first to the third sampling and for the Maragojipe River the opposite trend was seen, with highest salinity during the rainy season.

Because no tide information was available for the sampling sites, the present study used the Madre de Deus port tide as a reference. This is a harbor about 30, 45 and 10 km away from the sampling locations in the Maragojpe, Jaguaripe and São Paulo Rivers, respectively. It was used to estimate the time of the low tide, so to determine the appropriate time to sample the field. The use of a reference so far away from the sampling points may have caused small errors in assessing the correct time of the low and high tide of the sea. In the Maragojipe River during the second sampling period (rainy season), due to practical problems, the sampling was carried out at the middle tide, which means that there was a higher influence of the sea water.

In the Jaguaripe River the sampling during the 1st season was carried out after and during a rainy day. Also events like rain (before sampling) in the dry season and/or the influence of sea water with flood and ebb tide effects during the sampling may have contributed to the different patterns of the salinity in the Maragojipe and Jaguaripe Rivers. These factors may have contributed to the deviating patterns in salinity of the water.

The conductivity of the surface water showed opposite trends in the Maragojipe (with the highest value during the rainy season) and São Paulo Rivers (lowest value in the rainy season), while in the Jaguaripe River it increased from the first to the third sampling period. The conductivity is directly related to the concentration of ions in the water and it can be a good indicator of the presence of some contaminants (Nazir et al., 2015).

However, the metal concentrations showed quite different patterns compared with the conductivity, which confirms that many others parameters influenced the metal concentrations in the surface waters.

The highest conductivity in the São Paulo River compared with the other rivers confirms its location closer to the sea (Cox et al., 1967; Mantyla, 1980). As expected, the conductivity showed the same patterns as the salinity (Table 3).

The metal concentrations in the surface waters did not show a clear pattern. For Zn, for example, there were two trends. The Maragojipe River had the highest concentrations (6.1 and 3.1 µg L^{-1}) during 1st and 3rd season, respectively, while in the Jaguaripe and São Paulo Rivers, Zn concentrations decreased from the 1st (5.8 and 10.1 µg L^{-1}) to the 3rd (2.3 and 1.6 µg L^{-1}) season. Related to the Brazilian legislation (CONAMA, 2005), these concentrations are well below the maximum limit of 90 µg L^{-1} for brackish (Maragojope and Jaguaripe Rivers) and saline (São Paulo River) waters (Table 6).

Also for the iron concentrations in the water two different trends were observed. In the Jaguaripe River, Fe concentration increased from 250 µg L^{-1} to 288 µg L^{-1} in the 1st and 2nd season, respectively and decreased to 44 µg L^{-1} in the 3rd season.

In the Maragojipe and São Paulo Rivers the concentrations of iron decreased from 116 and 165 µg L^{-1} in the 1st season to 12 and 23 µg L^{-1} in the 3rd season, respectively. For all rivers, Fe concentrations were below the maximum limit (300 µg L^{-1}) established by CONAMA (2005) for both brackish and saline waters (Table 6). For the other metals analyzed, Ni and Cu, no real pattern was observed because most concentrations were below the detection limits.

Table 6 - Maximum acceptable metal concentrations in surface water (µg L^{-1}), sediment (mg kg^{-1}) and mollusks (mg kg^{-1}) established by national and international institutions.

Institutions		Metals/Values			
		Zn	Fe	Ni	Cu
CONAMA (2005)	Water	90	300	25	5
CONAMA (2009)	Sediment	300	**	30	60
NIST	mollusks	1424 ± 46	205 ± 6.8	1.04 ± 0.09	71.6 ± 1.6

CONAMA: Brazilian National Environment Council. NIST: National Institute of Standards and Technology, USA.
** No value available.

Even though metal concentrations were below the levels established by the Brazilian legislation, it is known from the literature that the total metal content is not a reliable indicator of risk. A better indicator of the bioavailability and possible environmental risk of metals is the free ion activity (Temminghoff et al., 2000). In this study, the free ion activities were higher when the metal concentrations were also higher, except for Zn in the São Paulo River (Table 5). The metal free ion activities showed a negative relation with pH for all rivers studied (Table 5). An increase in pH may increase the sorption of the metals, reducing free ion activity in the water column (Lee & Saunders, 2003), and in this way also reducing metal availability for uptake by organisms. Along the seasons studied, the availability of Zn and Fe generally decreased when the pH increased. But metal uptake by biota also depends on the nature of the organism and its metabolism, size, mass, etc. In addition, organisms like mollusks may not only interact with metals in the water but may also be exposed to metals in the sediment.

For all metals studied in the sediment (Zn, Fe, Ni and Cu) the trend was the same for Jaguaripe and São Paulo Rivers with the lowest values being recorded during the 2nd sampling period (rainy season). The same pattern was noticed for organic matter content, which also showed the lowest values during the rainy season.

These results might be connected since organic matter has a high affinity for binding metals (Lin & Chen, 1998; Marchand et al., 2011).

The metal concentrations in the sediment also strongly correlated with clay content (Figure 7), which can be explained from the surface chemical properties that favour binding of cations (Finzgar et al., 2007). This was obvious for the Maragojipe River, where metal concentrations and clay contents increased from the 1st to the 3rd sampling, the only exception was the iron concentration, which was slightly lower in the 2nd sampling compared with the 1st one and increased in the 3rd season.

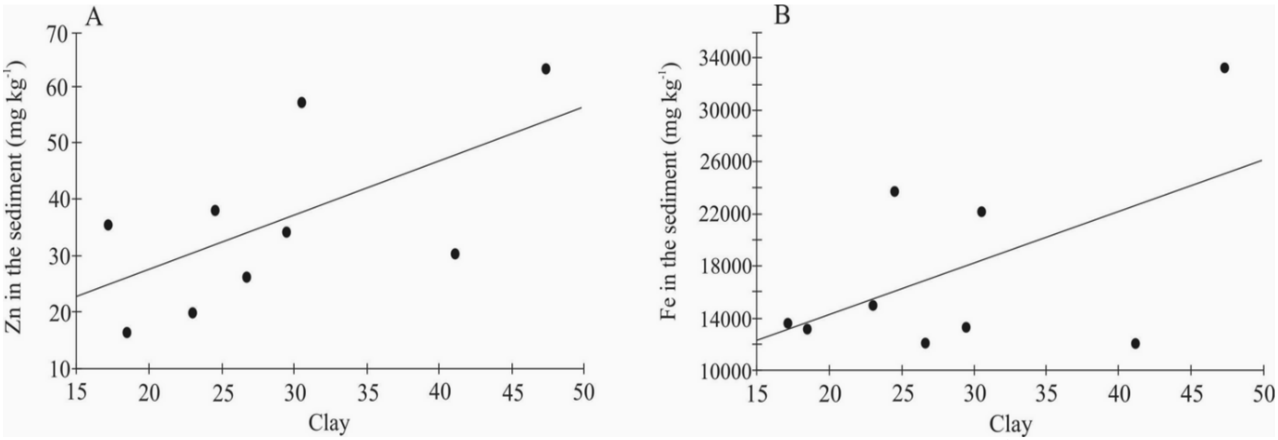

Figure 7 - Relationship between Zn (A) and Fe (B) concentrations in the sediment ($mg\ kg^{-1}$) and clay content of the Maragojipe, Jaguaripe and São Paulo Rivers sampled in three different seasons (March 2014; August 2014; January 2015).

The metal concentrations in the studied sediments were negatively correlated with pH (for more details see Figure 8). In all cases the metal concentrations in the sediment decreased when pH increased from 6.71 to 7.06, which represent two of the three sampling times. Metal concentrations in the sediment, however, increased when pH increased from 7.10 to 7.23, except for Fe in the Maragojipe River. In general, pH is an important parameter to explain ion binding processes in soils and sediments (Niyogi & Wood, 2004). At decreasing pH, the higher competition of protons may cause a reduced metal binding to sediments. This explains the first finding. The second finding, however, indicates that one parameter (pH) by itself cannot fully explain the total metal concentrations in sediments. Rather a set of parameters will be involved.

The sediment metal concentrations were compared with the limit values established by CONAMA (2009) (Table 6). This legislation doesn't bring limits for iron, as it is an element which by nature is highly abundant in soils and sediments. For the other metals studied (Zn, Ni and Cu), the values found were below the limits established as prevention values, 300 $mg\ kg^{-1}$ for Zn, 30 $mg\ kg^{-1}$ for Ni and 60 $mg\ kg^{-1}$ for Cu. The total concentration however, is not the best indicator of the risk of metals to the environment

(Shivakumar et al., 2012). Even though the total metal concentrations were below the limits established by Brazilian legislation, a study on their bioavailability should be done to check the actual exposure risk.

Internal metal concentrations, which reflect the actual exposure of organisms in a specific area, allow for a more trustful assessment of the actual risks to the environment than do reference values or effect levels reported in the literature. In this study, metal concentrations in oysters (*C. rhizophorae*) fluctuated in time, with a seasonal pattern being observed for Cu, while for Fe tissue concentrations increased with time. The variation in metal concentrations in the oysters was larger than the fluctuations observed in sediment and surface water concentrations at the same sampling sites.

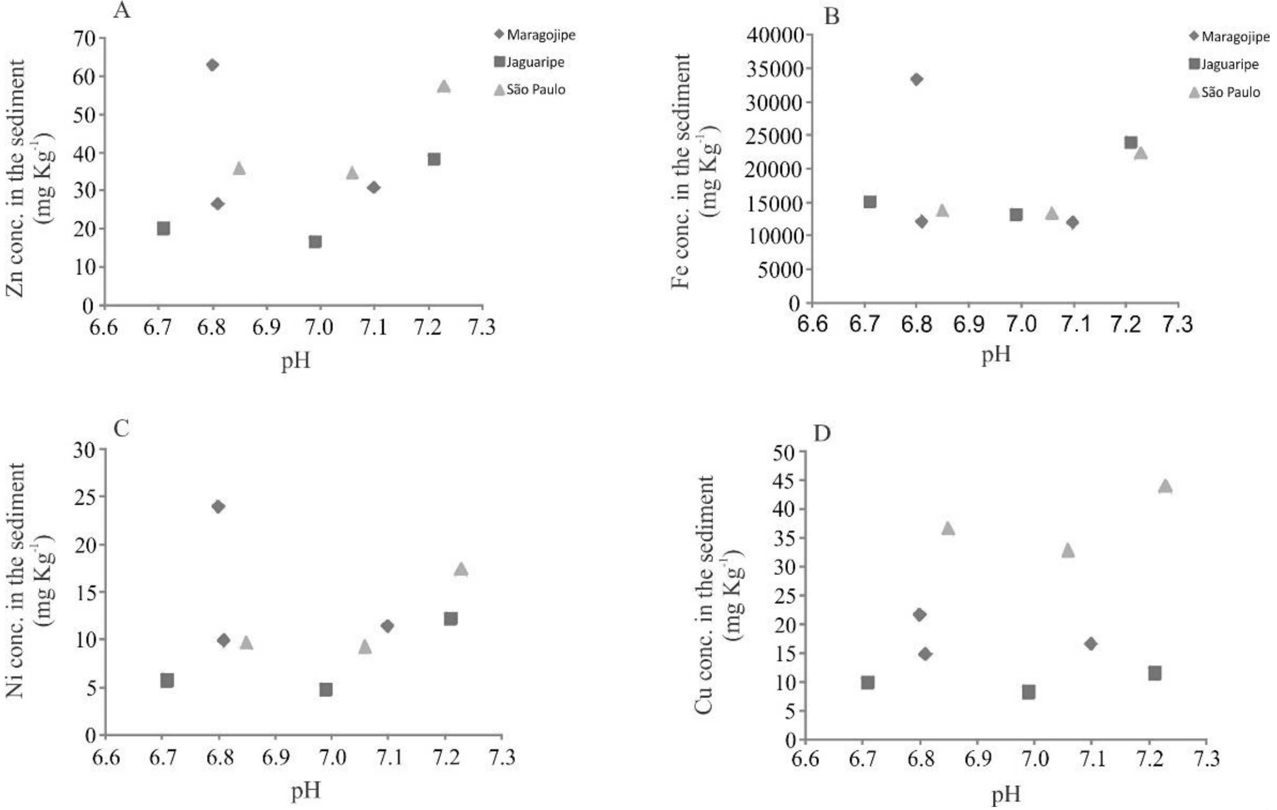

Figure 8 - Relationship between average concentrations of Zn (A), Fe (B), Ni (C) and Cu (D) in the sediment (mg kg^{-1}) and average pH of Maragojipe, Jaguaripe and São Paulo Rivers sampled in three different seasons (March 2014; August 2014; January 2015).

Iron concentrations in *C. rhizophorae* were higher during the 3rd season for all rivers and quite high in comparison with other studies in the São Paulo River, which reported a concentration of 272 mg kg^{-1} (Milazzo et al., 2014). The copper concentrations showed the same pattern for all rivers, with the highest values (63.9 and 89.6 mg kg^{-1} in the Maragojipe River, 14.0 and 23.8 mg kg^{-1} in the Jaguaripe River and 172 and 279 mg kg^{-1} in the São Paulo River) during the 1st and 3rd season, respectively. For the Ni and Zn no defined pattern was observed, but in some cases we could identify some trends. Nickel concentrations in oysters from the Maragojipe and São Paulo Rivers were higher during the 2nd season (0.98 and 1.0 mg kg^{-1}, respectively), whereas in the Jaguaripe River the concentrations decreased from the 1st (0.8 mg kg^{-1}) to the 3rd (0.09 mg kg^{-1}) season. Zinc concentrations in *C. rhizophorae* didn't show a clear pattern. In the Maragojipe River the levels increased from the 1st to the 3rd season (ranging from 996 to 1603 mg kg^{-1}), in the Jaguaripe River the values were higher during the 1st and 3rd season (849 and 1140 mg kg^{-1}, respectively), and in the São Paulo River the highest value was found in the 3rd season (2478 mg kg^{-1}) (Fig. 5). Zinc, being an essential element, can be regulated to fairly constant concentrations by organisms as long as sediment concentrations are below the toxic limit (Chu et al., 1990; Van Gestel et al., 2009).

In Brazil, there is no legislation with guidelines or maximum limits for metal concentration in mollusks. For this reason, a comparison was made with the Certified Reference Materials developed by the National Institute of Standards and Technology (NIST), USA (Table 6). The Ni concentrations in oysters were below the limits, in all rivers during all seasons. For copper the levels were above the limits in the São Paulo River during all seasons and in the 3rd season in the Maragojipe River. Zn concentration was below the limits in the Jaguaripe (all seasons) and Maragojipe (1st and 2nd seasons) Rivers, and for Fe only the concentrations in the São Paulo River during the 1st season were below the limit.

Although in some cases the metal concentrations in oysters were above the limits, it is important to note that these elements are essential for organisms, with important functions in metabolism. This means that the levels found not necessarily are dangerous.

Speciation calculation can help to understand the possible risks of metals to organisms in the environment. In the present study, a competition effect of H^+ in surface waters and the Zn and Fe uptake in *C. rhizophorae* was found. The metal concentrations in the oysters significantly decreased when the free ion activity in the water increased (Figure 9). This indicated that H^+ activity in the surface waters inhibited the uptake of Zn and Fe by *C. rhizophorae*. This is in agreement with the hypothesis that metal ions and other cations compete for binding on the biotic ligands on biological surfaces (He et al., 2014). Probably other cations should have different effects on metal uptake by the oysters since different metal ions generally have different paths to enter organisms by, for example, employing ion channels or carriers involved in the uptake of different cations (Bridges & Zalups, 2005). In this way, effects of cations like Ca^{2+}, Mg^{2+}, and K^+ may also affect metal uptake. In addition, there also may have been uptake of metals from sediment by the oysters, further complicating the situation. The mechanisms of the interaction of different cations and the contribution of water and sediment to metal bioaccumulation in oysters should be studied further.

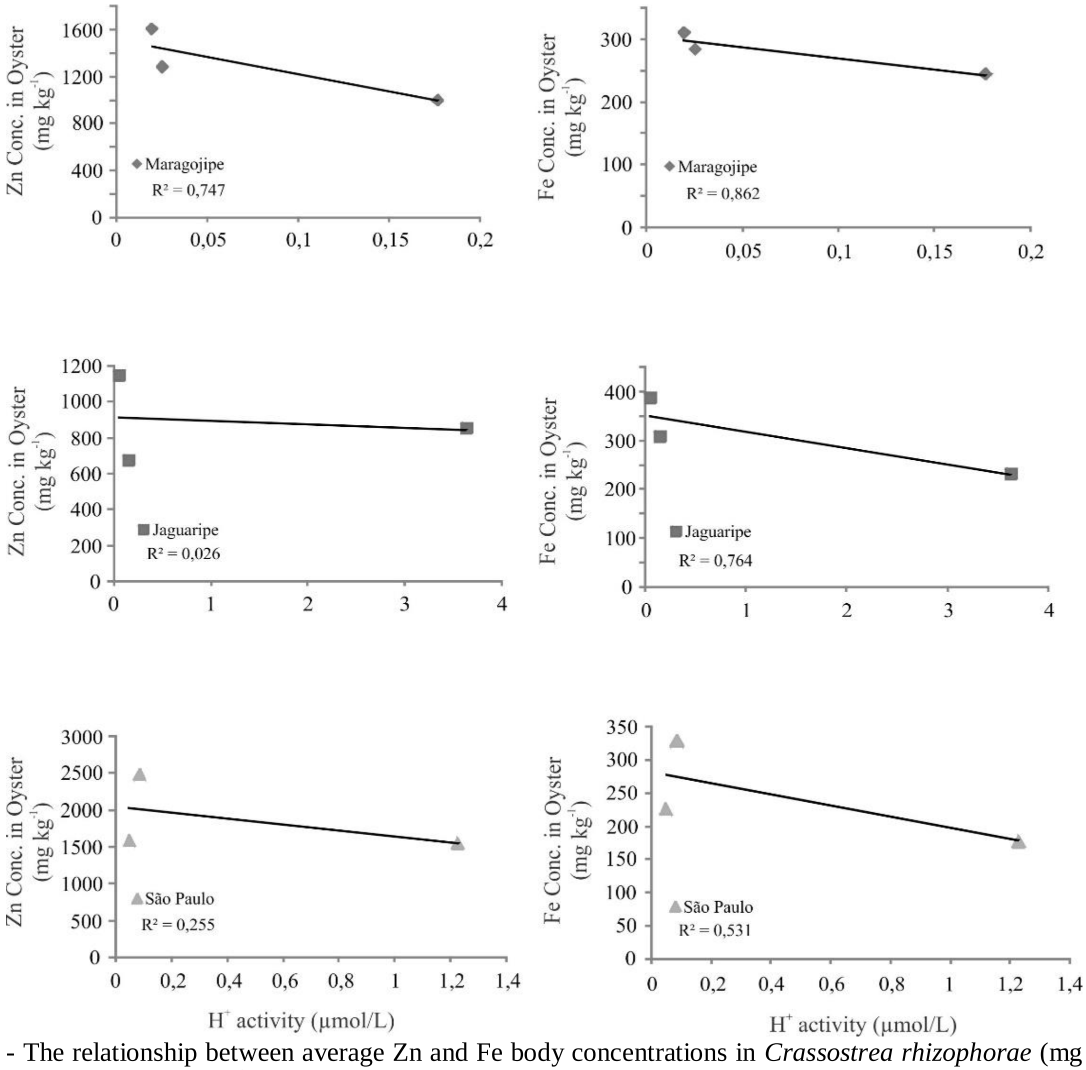

Figure 9 - The relationship between average Zn and Fe body concentrations in *Crassostrea rhizophorae* (mg kg^{-1}) and the free H^+ ion activity (µmol L^{-1}) in surface waters from the Maragojipe, Jaguaripe and São Paulo Rivers in three different seasons (March 2014; August 2014; January 2015).

CONCLUSION

The physicochemical parameters and the metal concentrations of surface waters, sediments and the internal metal concentrations in the oyster *C. rhizophorae* along the Todos os Santos bay exhibit spatial and temporal variations. These variations are related with the different characteristics of each sampling location as well as the meteorological conditions, which change the input of rain and the penetration of seawater into the rivers. In the Maragojipe River domestic sewage may have contributed to the high water pH, indicating that not only natural but also anthropogenic factors are responsible for the conditions of the estuarine zones.

Seasonal studies are important in determining the effects of physicochemical parameters on metal concentrations in water, sediment and biota, since they are directly influenced by factors like pH, Eh, conductivity, etc. These physicochemical parameters are governed by sea water intrusion, river water flow and urban sewage and this situation does influence the metal concentrations in water, sediment and organisms in the studied rivers.

Metal concentrations in the sediment and water of the sampling sites along the Todos os Santos bay generally were below limits established by the Brazilian regulations. Concentrations in the oysters however, did exceed the limits in a few cases but this does not mean that levels found are dangerous as some elements are essential to the organisms. Further research is needed to obtain more detailed information on metal speciation in these estuarine environments and to investigate their actual risk to organisms. This may support a proper risk assessment of metal pollution in the Todos os Santos Bay.

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REFERENCES

ABOWEI, J.F.N. Salinity, dissolved oxygen, pH and surface water temperature conditions in Nkoro River, Niger Delta, Nigeria. **Advanced Journal of Food Science and Technology, v.** 2, n. 1, p. 36-40, 2010.

ANITHA, G. & SURGITHA, P.K. Seasonal variations in physico-chemical parameters of Thengapattanam estuary, South west coastal zone, Tamilnadu, India. **International Journal of Environmental Sciences**, v. 3, n. 4, p. 1253-1261, 2013. doi:10.6088/ijes.2013030400004

ASTM. **D3974–1981 Standard practice for extraction of trace elements from sediments. American Society for Testing and Materials.** West Conshohocken, PA, 4 p., 1992.

BRIDGES, C.C. & ZALUPS, R.K. Molecular and ionic mimicry and the transport of toxic metals. **Toxicology and Applied Pharmacology, v.** 204, p. 274-308, 2005. doi: 10.1016/j.taap.2004.09.007.

CAMPANA, O.; RODRÍGUEZ, A.; BLASCO, J. Bioavailability of heavy metals in the Guadalete River Estuary (SW Iberian Peninsula). **Ciencias Marinas**, v. 31, n. 1B, p. 135–147, 2005. doi: http://dx.doi.org/10.7773/cm.v31i12.100

CARVALHO, L.V.M. DE. **Estudo da qualidade da água superficial em zona estuarina do rio São Paulo – Região de Candeias – BA.** Salvador, 2007. 129 p. Dissertação (Mestrado em Geoquímica) - Instituto de Geociências, Universidade Federal da Bahia.

CHU, K.H.; CHEUNG, W.M.; LAU, S.K. Trace metals in bivalves and sediments from Tolo Harbour, Hong Kong. **Environmental International**, v. 16, n. 1, p. 31-36, 1990. doi: http://dx.doi.org/10.1016/0160-4120(90)90202-H

CONAMA. **Resolution No. 357 of the Brazilian National Environment Council**, DOU NO. 53, 27 p., 2005.

CONAMA. **Resolution No. 420 of the Brazilian National Environment Council**, DOU NO. 249, 20 p., 2009.

COX, R.A.; CULKIN, F.; RILEY, J.P. The electrical conductivity/chlorinity relationship in natural sea water. **Deep Sea Research and Oceanographic Abstracts**, v. 14, n. 2, p. 203-220, 1967. doi:10.1016/0011-7471(67)90006-X

CUNDY, A.B.; HOPKINSON, L.; LATIFE, R.; SPENCER, K.; TAYLOR, J.A.; OUDDANE, B.; HEPPELL, C.M.; CAREY, P.J.; CHARMAN, R.; SHELL, D.; ULLYOTT, S. Heavy metal distribution and accumulation in two *Spartia sp.*-dominated macrotidal salt marshes from the Seine estuary (France) and the Medway estuary (UK). **Applied Geochemistry**, v. 20, n. 6, p. 1195–1208, 2005. doi: http://dx.doi.org/10.1016 /j.apgeochem.2005.01.010

DIXIT, P.R.; KAR, B.; CHATTOPADHYAY, P.; PANDA, C.R. Seasonal variations of the physicochemical properties of water samples in Mahanadi Estuary, East Coast of India. **Journal of Environmental Protection**, v. 4, p. 843-848, 2013. doi: http://dx.doi.org/10.4236/jep.2013.48098

DU LAING, G.; DE VOS, R.; VANDECASTEELE, B.; LESAGE, E.; TACK, F.M.G.; VERLOO, M.G. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. **Estuarine, Coastal and Shelf Science**, v. 77, p. 589–602, 2008. doi:10.1016/j.ecss.2007.10.017

DUBLIN-GREEN, C.O. Seasonal variations in some physico-chemical parameters of the Bonny Estuary. Niger Delta. **Nigerian Institute for Oceanography and Marine Research Lagos**, v. 59, p. 3-25, 1990. doi http://hdl.handle.net/1834/2408

FINZGAR, N.; TLUSTOS, P.; LESTAN, D. Relationship of soil properties to fractionation, bioavailability and mobility of lead and zinc in soil. **Plant soil and environment, v.** 53, n. 5, p. 225-238, 2007.

GADHIA, M.; SURANA, R.; ANSARI, E. Seasonal variations in physico-chemical characteristics of Tapi Estuary in Hazira Industrial area. **Our Nature**, v. 10, p. 249-257, 2012. doi: http://dx.doi.org/10.3126/on.v10i1.7811

GUSTAFSSON, J.P. A Windows version of MINTEQA2 version 4.03, MINTEQA2 by the US Environmental Protection Agency. Visual MINTEQ version 3.1, 2016.

HARDING, J.M. Comparison of growth rates between diploid deby eastern oysters (*Crassostrea virginica*, gmelin 1791), triploid eastern oysters, and triploid suminoe oysters (*C. ariakensis*, Fugita, 1913). **Journal of Shellfish Research**, v. 26, n. 4, p. 961–972, 2007. doi: http://dx.doi.org/10.2983/0730-8000(2007)26[961:COGRBD]2.0.CO;2

HE, E.; QIU, H.; VAN GESTEL, C.A.M. Modelling uptake and toxicity of nickel in solution to *Enchytraeus crypticus* with biotic ligand model theory. **Environmental Pollution**, v. 188, p. 17-26, 2014. doi: http://dx.doi.org/10.1016/j.envpol.2014.01.013

INMET. **Weather national institute**. Available in: http://www.inmet.gov.br/portal/index.php?r=clima/mesTempo . Last accessed on: 16th March 2016.

JESUS, H.C.; FERNANDES, L.F.L.; ZANDONADE, E.; ANJOS JR, E.E.; GONÇALVES, R.F.; MARQUES, F.C.; REIS, L.A.; ROMANO, C.T.; TEIXEIRA, R.D.; SANTOS SAD, C.M. **Avaliação da contaminação por metais pesados em caranguejos e sedimentos de áreas de manguezal do sistema estuarino de Vitória - ES.** Technical Report – Project Facitec/PMV-ES, contract number 4985717/2001, 40 p., 2003.

JESUS, R.S. DE. **Metais traço em sedimentos e no molusco bivalve *Anomalocardia brasiliana* (Gmelin, 1791), municípios de madre de deus e de Saubara, Bahia.** Salvador, 2011. 101 p. Dissertação (Mestrado em Geoquímica) - Instituto de Geociências, Universidade Federal da Bahia.

KIRIMURÊ INSTITUTE. **Baía de Todos os Santos**. Available in: < http://www.btsinstitutokirimure.ufba.br/?p=4>. Last accessed: 6th June 2013.

LEE, M.-K. & SAUNDERS, J.A. Effects of pH on metals precipitation and sorption: Field bioremediation and geochemical modeling approaches. **Vadose Zone journal**, v. 2, p. 177-185, 2003. doi: 10.2113/2.2.177

LIN, J.-G. & CHEN, S.-Y. The relationship between adsorption of heavy metal and organic matter in river sediments. **Environment International**, v. 24, n. 3, p. 345-352, 1998. doi:10.1016/S0160-4120(98)00012-9

MANTYLA, A.W. Electrical conductivity comparisons of standard seawater batches P29 to P84. Deep Sea Research Part A. **Oceanographic Research Papers**, v. 27, p. 837-846, 1980. doi:10.1016/0198-0149(80)90047-3

MARCHAND, C.; ALLENBACH, M.; LALLIER-VERGÈS, E. Relationships between heavy metals distribution and organic matter cycling in mangrove sediments (Conception Bay, New Caledonia). **Geoderma**, v. 160, p. 444-456, 2011. doi:10.1016/j.geoderma.2010.10.015

MILAZZO, A.D.D.; SILVA, A.C.M.; OLIVEIRA, D.A.F. DE.; CRUZ, M.J.M. The influence of seasonality (dry and rainy) on the bioavailability and bioconcentration of metals in an estuarine zone. **Estuarine, Coastal and Shelf Science,** v. 149, p. 143-150, 2014. doi: http://dx.doi.org/10.1016/j.ecss.2014.08.013

NAZIR, R.; KHAN, M.; MASAB, M.; REHMAN, H.U.; RAUF, N.U.; SHAHAB, S.; AMEER, N.; SAJED, M.; ULLAH, M.; RAFEEQ, M.; SHAHEEN, Z. Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat. **Journal of Pharmaceutical Sciences and Research**, v. 7, n. 3, p. 89-97, 2015.

NIST. **National Institute of Standards & Technology, Certificate of Analysis, Standard Reference Material SRM 1566b**. United States of America, 9 p., 2016.

NIYOGI, S. & WOOD, C.M. Biotic ligand model, a flexible tool of developing site-specific water quality guidelines for metals. **Environmental Science & Technology**, v. 38, n. 23, p. 6177-6192, 2004. doi: 10.1021/es0496524

NIZOLI, E.C. & LUIZ-SILVA, W. O papel dos sulfetos volatilizados por acidificação no controle do potencial de biodisponibilidade de metais em sedimentos contaminados de um estuário tropical, no sudeste do Brasil. **Química Nova, v.** 32, n. 2, p. 365–372, 2009. doi: http://dx.doi.org/10.1590/S0100-40422009000200018

NOAA. **Dissolved oxygen - NOAA's National Oceanic Service. National Oceanic and Atmospheric Administration.** Available in: http://oceanservice.noaa.gov/education/tutorial_estuaries/media/supp_est10d_dis.html. Last accessed: 19th January 2016.

ONOFRE, C.R.E.; CELINO, J.J.; NANO, R.M.W.; QUEIROZ, A.F. DE S. Biodisponibilidade de metais traços nos sedimentos de manguezais da porção norte da Baía de Todos os Santos, Bahia, Brasil. **Revista de Biologia e Ciências da Terra**, v. 7, n. 2, p. 65–82, 2007.

PALPANDI, C. Hydrobiological parameters, population density and distribution pattern in the gastropod *Nerita (dostia) crepidularia* Lamark, 1822, from mangroves of Vellar estuary, Southeast India. **International Journal of Biodiversity and Conservation**, v. 3, n. 4, p. 121-130, 2011.

QUEIROZ, A.F. DE S. & CELINO, J.J. 2008. **Manguezais e ecossistemas estuarinos da Baía de Todos os Santos**. In: Queiroz, Antônio Fernando de Souza; Celino, Joil José. Avaliação de Ambientes na Baía de Todos os Santos: Aspectos geoquímicos, geofísicos e biológicos. ed. Gisele Mara Hadlich. Salvador, UFBA Publications, 39-58 p., 2008.

REITERMAJER, D.; CELINO, J.J.; QUEIROZ, A.F. DE S. Heavy metal distribution in the sediment profiles of the Sauípe River Estuary, north seashore of the Bahia State, Brazil. **Microchemical Journal, v.** 99, p. 400–405, 2011. doi: http://dx.doi.org/10.1016/j.microc.2011.06.015

RUELAS-INZUNZA, J.R. & PÁEZ-OSUNA, F. Comparative bioavailability of trace metals using three filter-feeder organisms in a subtropical coastal environment (Southeast Gulf of California). **Environmental Pollution**, v. 107, n. 3, p. 437–444, 2000. doi: http://dx.doi.org/10.1016/S0269-7491(99)00157-8

SATO, M.; HORNE, J.K.; PARKER-STETTER, S.L.; ESSINGTON, T.E.; KEISTER, J.E.; MORIARTY, P.E.; LI, L.; NEWTON, J. Impacts of moderate hypoxia on fish and zooplankton prey distributions in a coastal fjord. **Marine Ecology Progress Series**, v. 560, p. 57-72, 2016. doi: 10.3354/meps11910.

SHIVAKUMAR, D.; SRIKANTASWAMY, S.; SREENIVASA, S.; KIRAN, B.M. Speciation and geochemical behavior of heavy metals in industrial area soil of Mysore City, India. **Journal of Environmental Protection**, v. 3, p. 1384-1392, 2012. doi: http://dx.doi.org/10.4236/jep.2012.310157

SILVA, C.A.E.; SMITH, B.D.; RAINBOW, P.S. Comparative biomonitors of coastal trace metal contamination in tropical South America (N. Brazil). **Marine Environmental Research**, v. 61, p. 439–455, 2006. doi: http://dx.doi.org/10.1016/j.marenvres.2006.02.001

STRADY, E.; SCHÄFER, J.; BAUDRIMONT, M.; BLNC, G. Tracing cadmium contamination kinetics and pathways in oysters (*Crassostera gigas)* by multiple stable Cd isotope spike experiments. **Ecotoxicology and Environmental Safety,** v. 74, n. 4, p. 600–606, 2011. doi: http://dx.doi.org/10.1016/j.ecoenv.2010.10.020

TEMMINGHOFF, E.J.M.; PLETTE, A.C.C.; VAN ECK, R.; VAN RIEMSDIJK, W. Determination of the chemical speciation of trace metal in aqueous systems by the Wageningen Donnan Membrane Technique. **Analytica Chimica Acta**, v. 417, n. 2, p. 149-157, 2000. doi: http://dx.doi.org/10.1016/S0003-2670(00)00935-1

VAN GESTEL, C.A.M.; KOOLHAAS, J.E.; HAMERS, T.; VAN HOPPE, M.; VAN ROOVERT, M.; KORSMAN, C.; REINECKE, S.A. Effects of metal pollution on earthworm communities in a contaminated floodplain area: Linking biomarker, community and functional responses. **Environmental Pollution**, v. 157, n. 3, p. 895-903, 2009. doi: http://dx.doi.org/10.1016/j.envpol.2008.11.002

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