Pollutants potential mobilization in Santos bay/Brazil: subsidies for the environmental management of a highly anthropized estuary

Potencial de mobilização de poluentes na baía de Santos/Brasil: subsídios para a gestão ambiental de um estuário altamente antropizado

Adriana Azevedo Netto
MBA in People Management
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: adriana.projetosuff@gmail.com

Leonardo da Silva Lima
PhD student in Ocean and Earth Dynamics
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: leodslima@gmail.com

Khauê Silva Vieira
PhD in Ocean and Earth Dynamics
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: kvieira87@gmail.com

Jessica de Freitas Delgado
Master in Ocean and Earth Dynamics
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: jessiicafdelgado@gmail.com

Patricia Farias de Souza
Master's degree from the Graduate Program in Ocean and Earth Dynamics
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: patricia.projetosuff@gmail.com

Thulio Righetti Correa
Master's degree from the Graduate Program in Ocean and Earth Dynamics
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: thuliorigheti@hotmail.com

José Antônio Baptista Neto
PhD in Marine Geology
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: jabneto@id.uff.br

Christine C. Gaylarde
PhD in Biotechnology
Institution: Department of Microbiology and Plant Biology, Oklahoma University
Address: 770 Van Vleet Oval, Norman, OK, 73019, USA
E-mail: cgaylarde@googlemail.com

Estefan Monteiro da Fonseca
PhD in Marine Geology
Institution: Universidade Federal Fluminense (UFF)
Address: Av. Gal. Milton Tavares de Souza, S/Nº, Boa Viagem, Niterói – RJ,
CEP: 24210-346
E-mail: oceano25@hotmail.com

ABSTRACT
Understanding the dynamics and spatial variation of subaquatic sediment contamination in the Santos Estuarine System has been of interest to the scientific community and environmental managers; the hazardous contaminant compounds, either individually or synergistically, can affect the health of the local community. In the present study, water column salinity and sediment geochemical properties (calcium and organic matter content, grain size) of the Santos Estuarine System were correlated with heavy metal concentrations (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and Fe) in order to elucidate the relationship between the toxic elements and the dynamics of water mixing. To assess the potential relationships, Spearman's correlation test and Principal Component Analysis (PCA) between were applied. The heavy metal concentrations were also evaluated by calculating Contamination Factor, Geoaccumulation index and Enrichment Factor. Results revealed extremely heterogeneous particle sizes within the sampling stations. Most of the heavy metal concentrations were not at critical levels. The only exception was arsenic, which reached levels above the threshold effect. The statistical analysis allowed the influence of organic matter and grain size on the dynamics of heavy metal accumulation to be demonstrated. The values between these binding matrices and metals were mostly significant. Bottom water salinity, on the other hand, showed no apparent influence on the distribution of metals. However, the various pollution indices used were contradictory, with certain cases presenting critical results. The Geoaccumulation Index presented the Mn as highly polluting at all sampling stations and classified the environment as moderately polluted by Zn. The same pollution pattern was not found by the other contamination indexes.

RESUMO

A compreensão da dinâmica e da variação espacial da contaminação dos sedimentos subaquáticos no Sistema Estuarino de Santos tem sido de interesse da comunidade científica e dos gestores ambientais; os compostos contaminantes perigosos, seja individualmente ou sinergicamente, podem afetar a saúde da comunidade local. No presente estudo, a salinidade da coluna de água e as propriedades geoquímicas do sedimento (teor de cálcio e matéria orgânica, tamanho dos grãos) do Sistema Estuarino de Santos foram correlacionadas com concentrações de metais pesados (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn e Fe) a fim de elucidar a relação entre os elementos tóxicos e a dinâmica da mistura da água. Para avaliar as relações potenciais, foram aplicados o teste de correlação de Spearman e a Análise de Componentes Principais (PCA) entre eles. As concentrações de metais pesados também foram avaliadas através do cálculo do Fator de Contaminação, índice de Geoacumulação e Fator de Enriquecimento. Os resultados revelaram tamanhos de partículas extremamente heterogêneos dentro das estações de amostragem. A maioria das concentrações de metais pesados não estavam em níveis críticos. A única exceção foi o arsênico, que atingiu níveis acima do efeito limiar. A análise estatística permitiu demonstrar a influência da matéria orgânica e do tamanho do grão na dinâmica do acúmulo de metais pesados. Os valores entre essas matrizes de ligação e os metais eram em sua maioria significativos. A salinidade da água de fundo, por outro lado, não mostrou influência aparente na distribuição dos metais. Entretanto, os vários índices de poluição utilizados eram contraditórios, com certos casos apresentando resultados críticos. O Índice de Geoacumulação apresentou o Mn como altamente poluente em todas as estações de amostragem e classificou o meio ambiente como moderadamente poluído por Zn. O mesmo padrão de poluição não foi encontrado pelos outros índices de contaminação.

Palavras-chave: poluição, estuário, metais pesados, sedimento.

1 INTRODUCTION

Estuarine areas are considered gradational environments, resulting from the mixture of fluvial fresh and marine salt water. Riverine freshwater influx carries nutrients into these ecosystems, providing the substances necessary to maintain productivity and the special estuarine habitats of estuarine (Nixon et al. 2010). As a result, these ecosystems are able to support ecologically and economically important animal populations (Wallner-Kersanach et al. 2016).

Chemical elements and compounds proceeding from fluvial drainage tend to be transported and transformed during their way along the estuarine water course (Regnier et al., 2013). The innermost estuarine areas receive a wide range of different chemical materials from the drainage basin. These compounds go through many chemical transformations under a pronounced aquatic physical-chemical gradient resulted from

water mixing (Mosley and Peter, 2019). Advective and diffusive fluxes, solubilization/precipitation changes and biological assimilation are some components of these transforming processes (Pritchard and Schubel, 1981). Additionally, the physical-chemical transformations of water and molecular interactions are strongly impacted by salinity, resulting, for example, in organic matter mineralization (Telesh et al., 2010; Cloern et al., 2017).

Ionic concentrations in the water column play a fundamental role in the chemical processes within the salinity gradient. One of the most frequent ways to calculate the ionic balance in estuarine environments is through the correlation of the levels of the chemical species of interest as a function of salinity. This allows the understanding of transformation spots across the mixing zones, (Brandini et al., 2016).

The permanence of potential contaminants in subaquatic sediments results from complex physical and chemical mechanisms of absorption. Permanency is influenced by sediment characteristics such as composition, structure and properties, as well as by the properties of the contaminant compounds (Ghrefat and Yusuf, 2006). In other words, accumulation on the estuarine subaquatic bottom results from the transformation into the solid phase, through the mechanisms of ion exchange and complexation with organic acids, and adsorption reactions with sediment matrices like clay and other minerals, iron and manganese hydroxides (Sounthararajah et al., 2015).

Sediments are important momentaneous deposits for various pollutants in the estuarine environment, including heavy metals. After they accumulate in the sediments, their potentially mobilizable fraction can be released into the water bodies and, consequently, taken up by living organisms, depending on the speciation of the metals and other factors such as organic matter (Shaheen and Rinklebe, 2014; Rinklebe and Shaheen2014).

During the last decades, the coastal region of Santos (SE Brazil) has suffered the release of considerable domestic wastes and industrial effluents into the estuarine waters. These impacts are accelerating the contamination by toxic compounds such as metals and hydrocarbons. This region is considered to be one of the major examples of coastal degradation in Brazil for inorganic contamination (Casarini, 2010). The present work aimed to evaluate the potentially removable heavy metal fraction (PRF) in sediments of the Santos Estuarine System (SES) and the estuarine physical-chemical gradient, in order to evaluate the contaminant distribution dynamics and its relationship with the environment.

2 STUDY SITE

The Santos Estuarine System (SES) (Figure 1) consists of a coastal area subjected to a variety of potential contamination sources, being occupied by a complex industrial park, intensely populated and also with agricultural and livestock activities. The main sources of pollution have been concentrated in Cubatão industrial park, located in the Santos watershed basin. Currently, the region is influenced by irregular depositions of industrial solid waste, by port activities, sewage treatment stations, submarine outfall and clandestine discharges of domestic sewage and sanitary landfills. The system also has spots where potentially contaminated sediments from river dredging activities are discharged (Figure 1). The Port of Santos complex is the largest port in Latin America, with several terminals for product shipments.

On the other hand, the region is the main tourist coastal area of São Paulo State; its metropolitan region comprises nine municipalities, with Santos and São Vicente being the most intensely populated (Muto et al., 2014). The most visited beaches in the cities of São Vicente and Santos are important tourism spots during the summer (Braga et al., 2000). In addition, marine and estuarine fisheries are important economic activities in the area. Santos Bay has been intensely studied because of its economic, ecological and potentially polluting importance (Hortellani et al., 2008).

3 MATERIALS AND METHODS

Sampling was carried out in September of 2019. The sampling area (Figure 1) consisted of 20 stations characterizing the three main contributing rivers (Paçaguera, Perequê and Cubatão) and the Santos canal. Salinity was evaluated with a multiparameter Horiba U10 probe (Figure 1). Physico-chemical measurements were made at surface and bottom water depth, during the ebb and flow tides.

Figure 1. Santos estuarine complex and sampling stations
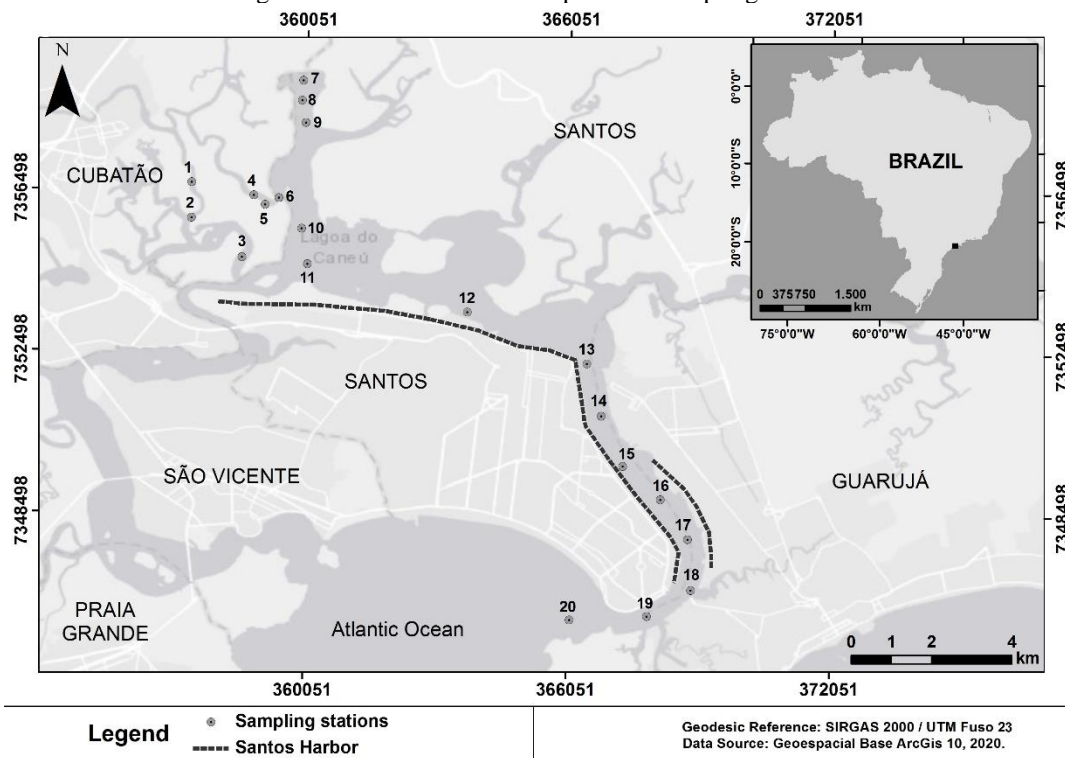
Data from past monitoring were also used to increase the accuracy of the physical analysis of the waters. Two other data groups were used, corresponding to January and March in the same locations. The averages of the 3 data groups were compared with the heavy metal concentrations and other geochemical parameters.

Sediment samples were collected at each site using a Van Veen grab. They were properly stored in cool-boxes for transport to the laboratory, where they were frozen (~-20ºC) until analysis. Sediment grain size, Total Organic Carbon (TOC) levels, Total Phosphorus content, Calcium content and Metals (As, Cd, Cr, Cu, Mn, Ni, Pb, Zn and Fe) and As were determined. First, inorganic carbon was removed by using 2N HCl with heating at 60ºC. TOC levels were evaluated using a Perkin Elmer Series II CHNS/O analyzer, Model 2400. Total Phosphorus concentrations were obtained by ignition at 550 °C for 12 hours followed by acidification of residual material with 1.0 M HCl with mixing.

Samples for heavy metal analysis were stored in pre acidified plastic containers and transferred to the laboratory for analysis. They were first sifted for grain size evaluation. Then, the fine material (below 0.063mm) was evaluated for heavy metals. The heavy metals digestion approach followed USEPA Method 3050B (USEPA, 1992). First, concentrated HNO_3 and concentrated $H_2O:HCl$ were used with heating in a microwave.

After cooling, the samples were centrifuged and diluted. Heavy metals (Pb, Cu, Co, Cr, Ni, Zn, Ca, Mn and Fe) were evaluated by Inductively Coupled Plasma-Atomic Emission Spectrometry, and Cd and As were analyzed by Inductively Coupled Plasma-Mass Spectrometry. A certified reference material was analyzed (CRM NIST 2782), and sample replicates were inserted in the analysis. The recovery rates for the heavy metals in the CRM NIST 2782 standard were higher than 82%. Mean recoveries were as follows: Pb, 92.0%; Cu, 95%; Co, 85%; Cd, 82%, As, 78%, Cr, 89.0%; Ni, 85%; Zn, 84%; Ca, 87%, Mn, 85% and Fe, 92%. The detection limits of the method are respectively: Pb, 0.4mg/Kg; Cu, 0.1mg.Kg^{-1}; Co, 0.02mg.Kg^{-1}; Cd, 0.1mg. Kg^{-1}; As, 1mg.Kg^{-1}; Cr, 0.1mg.Kg^{-1}; Ni, 0.4mg.Kg^{-1}, Zn, 0.4mg.Kg^{-1}; Ca, 0.006mg/Kg^{-1}; Mn, 0.1mg/Kg-1 and Fe; 0.1mg/Kg-1.

To evaluate the potential ecotoxicological impacts of the sediments, three sets of Sediment Quality Guidelines developed for marine and estuarine ecosystems (Persaud et al. 1993, CCME, 2002; MacDonald et al. 2000; NOAA, 2012) were applied: (a) the effect range—low (ERL)/ effect range—median (ERM); (b) the threshold effect level (TEL)/probable effect level (PEL) values; and (c) the Guidelines for Metals in sediments (LEL/SEL) for metals not included in the other indexes (Mn) (Figures 6 and 7). The residual metal phase from other references was used for comparison with the results obtained (Table 5).

The normal distribution of the data was tested with the Shapiro-Wilk test. Spearman's correlation was used to evaluate the relationship between heavy metals and the environmental parameters. Principal component analysis (PCA) was used to evaluate any synergy between all the parameters. Multivariate analysis was carried out using the software Past v.3.

The evaluation of sediment metal enrichment was carried out using the contamination factor (*CF*), which is considered to be a simple and effective approach in monitoring the heavy metal pollution (Hakanson et al., 1980). CF was calculated through the following equation:

$$CFi = Ci/Bi$$

Where C_i and B_i represent the analyzed levels and the background value of the metallic element *i*, respectively, based on Turekian and Wedepohl (1961) values. The CF establishes four levels of sediment quality as shown in Table 1 (Hakanson, 1980).

Table 1. Contamination Factor classes (*CF*) and potential ecological risk.

CF	Contamination Degree
CF$_i$ < 1	Low
1 ≤ CF$_i$ < 3	Moderate
3 ≤ CF$_i$ < 6	Considerable
CF$_i$ ≥ 6	Very high

The second contamination index used in the present study, is the Geoaccumulation Index (*I$_{geo}$*), which was developed by Muller (1969) based on the evaluation of pollution by comparing the current levels of metal concentrations and the natural soil levels. This index is reached by the following equation:

$$Igeo = log2[\frac{Cn}{1.5Bn}]$$

Where:

C$_n$ = Analyzed levels of the element in the studied area, and;

B$_n$ = Geochemical background value.

The values suggested by Rudnick and Gao (2003) were used for the Geochemical background value. The constant 1.5 is applied to minimize the effect of potential fluctuation in the background values that may be linked to diagenetic variations in the soil or sediments. The classes established for I$_{geo}$ are given (Muller, 1969 *apud* Fonseca et al., 2014) (Table 2):

Table 2. Geoaccumulation Index (*I$_{geo}$*) classification according to Muller (1969)

Geoaccumulation Index (*I$_{geo}$*)	Classification
< 0	practically unpolluted
0 <I$_{geo}$< 1	unpolluted to moderated polluted
1 <I$_{geo}$< 2	moderately polluted
2<I$_{geo}$< 3	moderately to strongly polluted
3<I$_{geo}$<4	strongly polluted
4<I$_{geo}$<5	strongly to extremely polluted
> 5	extremely polluted

In this study, we calculated the I$_{geo}$ index using grain fraction < 0.063 mm according to González-Macías et al. (2006).

The enrichment factor (EF) was used to evaluate the level of pollutants and the potential anthropogenic impact in sediments of Santos Estuarine System. To verify anomalous metal levels and to access metal abundance, geochemical normalization of the

trace metal data to a conservative element (Fe) was used. According to Ergin et al (1991), the metal enrichment factor (EF) is defined as follows:

$$Enrichment\ Factor\ (EF)\ =\ \frac{C(sample)/Fe(sample)}{C(crust/Fe(crust)}$$

Where:

$C_{(sample)}$ = trace element concentration in the sample;

$C_{(crust)}$ = trace element concentration in the continental crust;

$Fe_{(sample)}$ = Fe content in the sample;

$Fe_{(crust)}$ = Fe content in the continental crust (Taylor and McLennan, 1998).

The background concentrations of metals for the EF calculation were taken from the average shale (Turekian and Wedepohl, 1961) to quantify the extent and degree of metal pollution (Table 3). EF values were interpreted as the levels of trace metal pollution as suggested by Birch and Olmos (2008) where:

Table 3. Enrichment Factors (EF) interpretation (Birch and Olmos ,2008)

Enrichment Factor	Classification
< 1	no enrichment
< 3,	is minor
3 – 5	is moderate
5 – 10	is moderately severe
10 – 25	is severe
25 – 50	is very severe
> 50	is extremely severe

4 RESULTS AND DISCUSSION

The impact of salinity on metal transference dynamics has been studied in detail in estuaries (Van Eck, 1999; Gerringa et al., 2001; Du Laing et al., 2008; Acosta et al., 2011; Wang et al., 2016). However, there is little information on the equivalent impact in subaquatic sediments. The salinity gradient is one of the main properties of any estuarine environment (Telesh and Khlebovich, 2010). Most of the time, the salinity decreases from the ocean toward the interior of the estuary due to freshwater dispersion. With respect to heavy metal mobility, the increase of salinity is proportional to the levels of enhancement of the major cation levels (e.g., Na, K, Ca, Mg). These, in turn, compete for the sorption sites with metallic elements, improving the mobility of trace metals (Zhang et al., 2014). In the present study the salinity increases seaward, being significantly minor in the river Cubatão (Figure 2), where the riverine flux seems to be more intense. Garcia et al. (2014)

confirmed this fact. The authors obtained low results, similar to the present study. Saline stratification in the water column, on the other hand, was clear at all sampling stations, suggesting the influence of seawater along the whole SES.

Figure 2. Salinity variation along the Santos Estuarine System
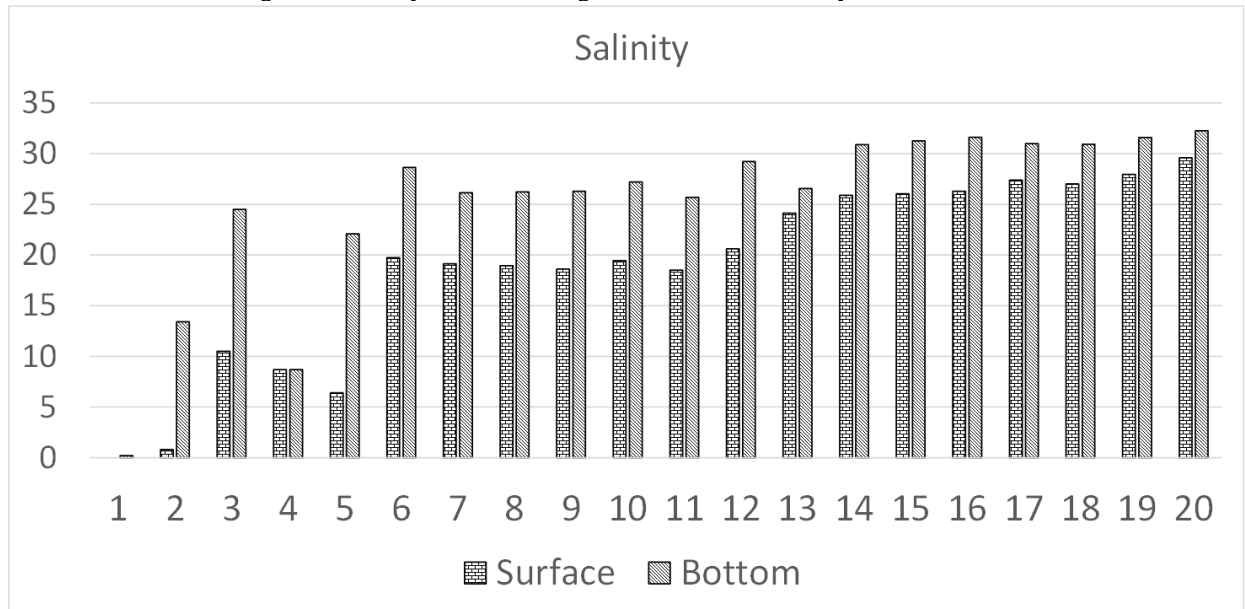
The accumulation and distribution of trace elements is greatly influenced by the physical and chemical characteristics of the sediment such as grain size (particularly fine fraction content) (Maslennikova et al., 2012), the organic carbon content (Zhang et al., 2014), carbonates and other parameters (Zhang et al., 2014; Rzetala et al., 2019). These peculiarities influence sorption/precipitation patterns, also determining bioavailability and potential toxicity (Du Laing et al., 2008). Particle texture of estuarine sediments, in its turn, are determined by many environmental parameters, including source area composition, climatology, water flux intensity and redox conditions in the depositional ecosystem (Dickhudt et al. 2011). Many studies focus on grain size distribution to determine sources and hydrodynamic patterns of subaquatic sediments (Carranza-Edwards et al. 2005; Senapathi et al., 2014; Venkatramanan et al., 2014; Wang et al., 2020). Grain size variation is a function of the availability of different particles and the forces involved in the physical distribution dynamics in the area where the particles were deposited (Mansour et al., 2013). The results obtained in the present study are presented in Figure 3.

Figure 3. Grain Size percentages
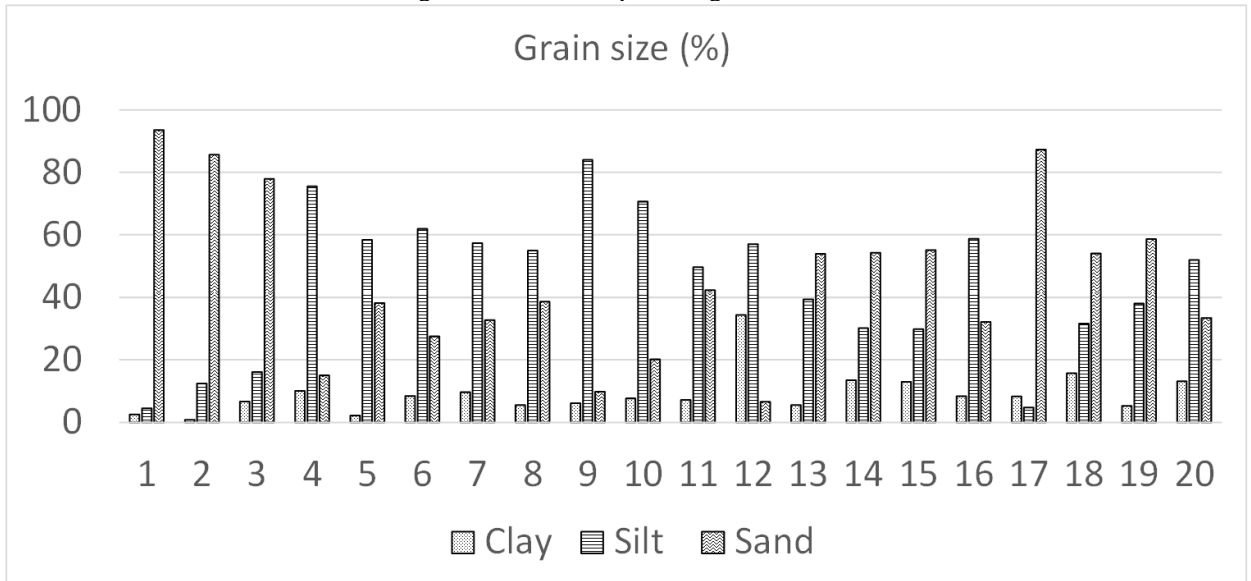
The surface sediment grain sizes vary throughout the estuarine system from very fine silt to very coarse sand. The values in the interior sampling stations showed coarse grains, suggesting a more intense hydrodynamics, mainly in the Cubatão and Perequê rivers (Sampling stations 1, 2, 3 and 4). The same rivers were studied by Borrely et al. (2018), who confirmed the local coarser grain size. The change of mean grain size may reflect different erosions and accretions, as well as the influence of shell fragments (El Nemr et al., 2013). In the present study, however, the results suggest higher river flux intensity; the low concentrations of calcium in this area may inhibit the existence of biogenic material (Figure 4). The statistical analysis confirmed this statement, since Ca concentrations did not show an inverse correlation with the fine particle size fraction (Table 6).

Figure 4. Calcium levels
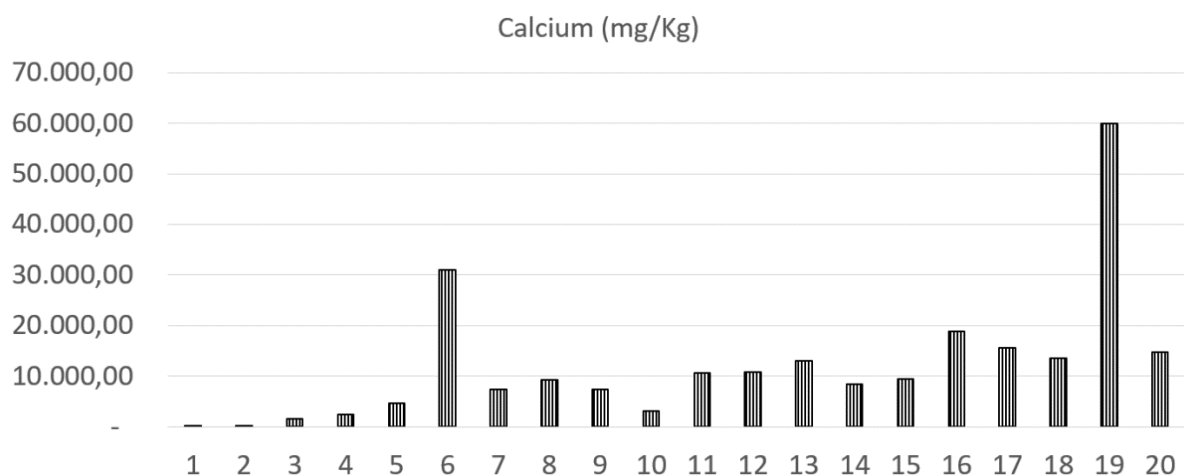
Although various studies have focused on the dynamics of organic matter in estuaries, this is still a subject of debate (Krishna et al., 2013). Estuarine organic matter accumulations present both continental and marine origins. Their composition can vary drastically depending on the sources and fate (Graham et al., 2001; Lamb et al., 2006). The input of anthropogenic discharges can also contribute significantly to the organic matter concentrations in intertidal sediments (Rumolo et al., 2011; Pradhan et al., 2014). Deposition of these matrices follows the same rules as fine particles, with both tending to accumulate in low current zones (Dalia et al., 2014). Total organic carbon levels determined in the study range between 6.2mg/Kg at the River Cubatão and 50.5mg/Kg in Santos canal mouth (Figure 5). The low values recorded at some sampling stations may indicate that the oxidizing conditions are dominant as a result of the strong currents and low sedimentation rates (El Nemr et al., 2013). The results obtained in the present study were of the same scale as those in other areas along the Brazilian coast (Table 4).

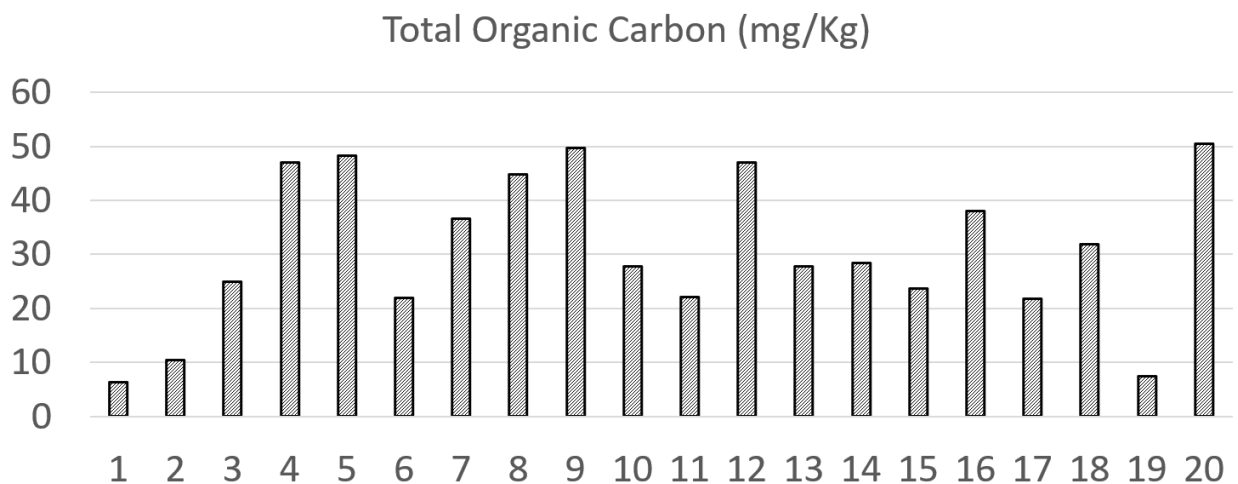Figure 5. Total Organic Carbon percentages

Total Organic Carbon (mg/Kg)

Table 4. Total Organic Carbon sediment content along the Brazilian coast

Author	Study Site	Total Organic Carbon Content (%)
Present Study	Santos Bay, Brazil	0.62 – 5.05
Delgado et al., 2020	Harbor area São Marco Bay, Brazil	0.54–0.91
Ribeiro et al., 2008	Guanabara Bay, Brazil	0.82–10.60
Martins et al., 2018	NE Sector of Guanabara Bay, Brazil	1.0–6.1
Vilela et al., 2003	Guanabara Bay, Brazil	0.05–6.13
Rodrigues et al., 2017	Sepetiba Bay, Brazil	0.06–4.79
Costa et al., 2011	Todos os Santos Bay, Brazil	0.95–2.7
Venturini et al., 2004	Todos os Santos Bay, Brazil	0.12–3.5
Burone et al., 2003	Ubatuba Bay, Brazil	0.10–2.86
Alexandre et al., 2006	Babitonga Bay, Brazil	0.67–4.64

Over the last decades, global environments have become intensively impacted by high anthropogenic nutrient inputs, especially phosphorus (P) (Childers et al., 2011; Lu and Tian, 2017), mainly due to artificial enrichment for agriculture. Even the most positive future scenarios indicate an overall increased use of fertilizers worldwide (Van Vuuren et al., 2010). Yan et al. (2016) highlighted the fact that P seems to accumulate faster than N in aquatic systems, which means that even reduced P loads can still increase the P background within systems. The results of phosphorus measurements in the present study are presented in Figure 6. The total Phosphorus content ranged from 142.9mg/Kg at sampling station 2 to 2632.5mg/Kg at sampling station 8.

Figure 6. Total Phosphorus content
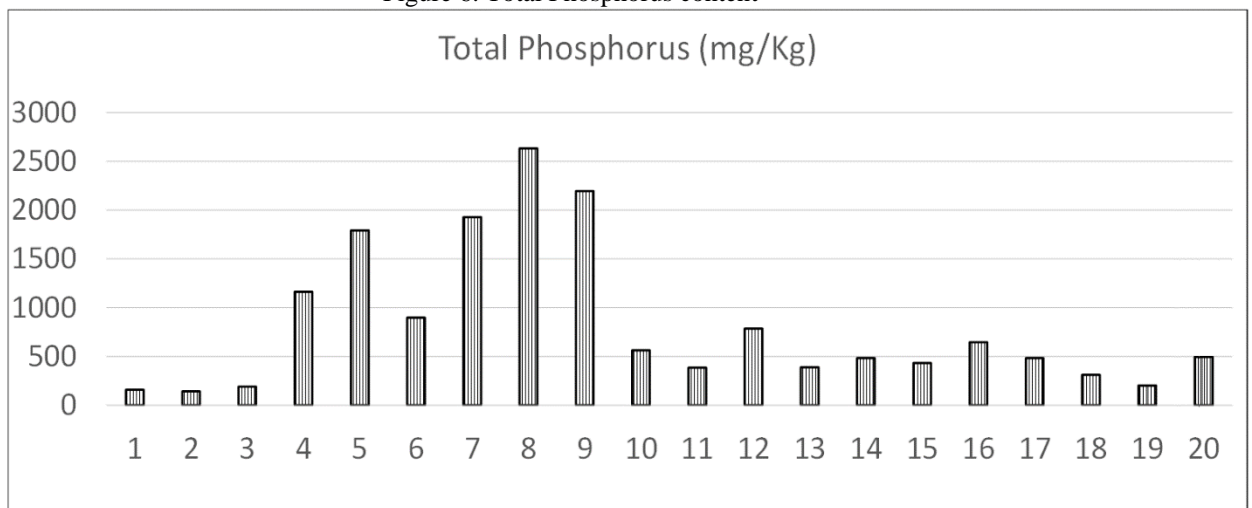
Spatial variability of metals in sediments can provide some clues about human activities and their impacts on the environment and allows us to assess the risks linked with discharge of human residues (Luo et al., 2010). The levels of the heavy metals detected in the surface sediments of the Santos Estuarine System are presented in Table 5.

Normally, most of the iron in the environment is associated with the carbonate fraction, probably sorbed on the surface of the particles or, more probably, substituting Ca in the mineral crystals (De Baar and De Jong, 2000). Wang et al. (2019) showed the influence of organic matter in scavenging this metal. In the present study, iron was detected in an amount that fluctuated between 6034.80 and 28039.30mg/Kg (Figure 7; Table 5). According to the statistical analysis, there is no direct relation between iron and the carbonate fraction in the studied area. Nevertheless, the influence of organic matter was proven by the high correlation in the Spearman test (Table 6).

Manganese, part of the composition of all living organisms, is an essential element necessary for some enzymatic processes (Sivaperumal et al., 2007). High levels of exposure, however, can cause disease (ATSDR, 2000). The manganese concentrations in sediments of the studied stations ranged between 63.064 mg/Kg at the estuarine Cubatão sampling station and 879.567mg/Kg at the outermost sampling station in Santos Bay (Table 5). The concentrations of Mn in some sediment samples were above the lowest effect level (LEL) (Persaud et al., 1993) (Figure 7). The highest values were obtained at the most external spots in Santos bay and may be associated with port activities. Other authors confirmed anomalous Mn values in environments potentially impacted by ports (Jahan and Strezov, 2019). Mn concentrations were shown to be closely linked to both salinity and the geochemical characteristics of the sediment (organic matter content and fine grain size) (Table 6). Zhao et al. (2013), on the other hand, suggested the chemical content of the sediment of Yangtze Estuary as the only influencer of Mn geochemistry. In the same way, Beck et al. (2010) highlighted the importance of organic matter in the Mn sediment retention process.

Zinc is of basic importance in the generation of enzymes and proteins (Vallee, 1978), having detoxifying effects on both cadmium and lead (Calabrese et al., 1985). Additionally, this element is widely present in the environment (Irwin et al., 1997). However, it is repeatedly recorded in industrial and mining disposal waste (Cameron, 1992; Mulligan et al., 2001). In the present study, the concentrations of zinc showed values between 11.2 and 181.6mg/Kg. The average concentration of Zn in the present study was lower than the effect range medium (ERM), the effect range low (ERL), threshold effect level (TEL) and probable effect level (PEL) (NOAA, 2012; CCME, 2002, Mac Donald et al., 2000; Persaud et al., 1993). Only sampling station 7 presented a higher concentration (Figure 7), which may be related to the proximity of the source of this metal. With regard to statistical analysis, once again both the content of organic matter and the percentage of fines were directly related to the levels of metals found in the samples (Table 6).

Table 5. Potentially Remobilizable Fraction results available in the literature

	As (mg/Kg)	Cd (mg/Kg)	Cr (mg/Kg)	Cu (mg/Kg)	Mn (mg/Kg)	Ni (mg/Kg)	Pb (mg/Kg)	Zn (mg/Kg)	Fe (mg/Kg)	Co (mg/Kg)
Present Study min-max (mean)	2.23 - 14.30 (9.07)	N.D. - 0.63 (0.14)	5.15 - 30.06 (20.52)	2.60 - 21.30 (11.14)	63.06 - 879.56 (360.00)	2.00 - 13.60 (8.39)	3.16 - 37.53 (15.55)	11.20 - 181.60 (58.40)	6034.80 - 28039.30 (17188.43)	1.92 - 7.56 (4.85)
Guanabara Bay, Brazil[1]	-	-	86.6 – 234.6	45.3 - 123	301.6 - 821	28.2 – 44.2	51.7 – 101.8	200.8 – 424.9	25451.0 – 45379.0	-
Rodrigo de Freitas Lagoon, Brazil[2]	-	-	7.0 – 40.0	9.5 – 51.0	26.0 – 224.5	8.5 – 29.0	N.D. – 45.0	27.0 – 438.0	3050.0 – 24415.0	-
Lagos Lagoon, Nigeria[3]	-	18.51	33.55	-	-	14.3	44.3	137.85	-	-
Pearl River Estuary, China[4]	-	-	-	16,92	-	9.54	-	48.91	-	7.96
Hugli River Estuary, India[5]	22.16	9.74	210.0	212.5	339.9	56.4	121.5	345.4	8232.8	7.14
Al Shabab Lagoon, Saudi Arabia[6]	-	59.6	-	74.6	-	-	67,2	64,5	-	-
Bestari Jaya, Malaysia[7]	0.10 – 0.22	-	12.53 – 31.97	3.7 – 14.29	-	-	11.81 – 15,0	17.59 – 62.80	-	-
Kolkata wetlands, India[8]	-	-	65.98	13.69	77,58	7.8	14.14	59.26	4031.41	-

1 – Fonseca E.M. et al. (2009); 2 - Fonseca E.M. et al. (2014); 3 - Ladigbolu et al. (2014); 4 – Li et al. (2000); 5 – Sarkar et al. (2014); 6 – Turki A.J. (2007); 7 – Ashraf et al. (2012); 8 – Kumar et al., 2011

Table 6. Correlation of Spearman Classification (R) between metals, fine grains and geochemical variables. Significant correlations for p <0.05 were marked.

	Fe	Cu	Ni	Zn	Ca	Cd	Pb	Cr	Mn	Co	As	FGS	BWS	SWS	TOC	P
Fe																
Cu	**0,70**															
Ni	**0,91**	**0,76**														
Zn	**0,92**	**0,83**	**0,92**													
Ca	-0,07	-0,29	-0,29	-0,29												
Cd	**0,67**	**0,77**	**0,73**	**0,79**	**-0,55**											
Pb	**0,91**	**0,70**	**0,75**	**0,89**	0,10	**0,55**										
Cr	**0,98**	**0,75**	**0,93**	**0,93**	-0,12	**0,65**	**0,89**									
Mn	**0,48**	0,17	0,24	0,37	**0,53**	-0,01	**0,69**	0,44								
Co	**0,83**	**0,61**	**0,92**	**0,78**	-0,14	**0,48**	**0,68**	**0,87**	0,35							
As	**0,90**	**0,59**	**0,76**	**0,80**	0,17	0,43	**0,94**	**0,88**	**0,71**	**0,76**						
FGS	**0,80**	**0,55**	**0,75**	**0,68**	0,12	**0,45**	**0,67**	**0,77**	**0,50**	**0,77**	**0,72**					
BWS	-0,09	-0,15	-0,30	-0,13	**0,75**	**-0,45**	0,22	-0,10	**0,62**	-0,23	0,20	-0,01				
SWS	-0,06	-0,11	-0,28	-0,12	**0,81**	-0,41	0,26	-0,08	**0,56**	-0,20	0,24	-0,04	**0,92**			
TOC	**0,85**	**0,70**	**0,80**	**0,83**	-0,03	**0,52**	**0,87**	**0,88**	**0,56**	**0,76**	**0,88**	**0,71**	0,15	0,13		
P	**0,88**	**0,60**	**0,75**	**0,76**	0,08	**0,66**	**0,78**	**0,83**	0,42	**0,63**	**0,75**	**0,76**	-0,02	0,02	**0,71**	

FGS -Fine Grain Size
*BWS - Bottom Water Salinity*
SWS - Surface Water Salinity
TOC - Total Organic Carbon

As with Zn, Co has an essential role for living organisms (Underwood, 1977). In estuaries, sediment may release Co to the dissolved water compartment due to desorption of metals promoted by salinity fluctuations (Kraepiel et al., 1997). An increasing number of studies have demonstrated that Co sediment flux dynamics and sewage inputs can also affect Co distributions during estuarine mixing (Martino et al., 2002; Tovar-Sánchez et al., 2004; Audry et al., 2006; Santos-Echeandia et al., 2009). It has also been suggested that resuspension of metal-enriched sediment may be a significant source for Co during estuarine mixing (Chiffoleau et al., 1994; Martino et al., 2002). Thus, the potential for the desorption of Co is not entirely attributable to riverine suspended particulate matter. Sediments sampled in Santos bay recorded low Co concentrations, varying between 1.48 and 7.56mg/Kg (Figure 7). With respect to the Co variation dynamics, statistical analysis suggested a direct relation between this metal and sediment features like fine grain size percentages and organic matter levels. Salinity variation, on the other hand, showed no relation (Table 6).

Above 90% of the arsenic in aquatic ecosystems can remain in pools and sediment. It can be released in several ways, to the atmosphere, in liquid effluent discharges, as land surface runoff, and as leachates from various urban, industrial, and agricultural processes. According to Karageorgis et al. (2002), As accumulation can be higher in coastal semi-enclosed water bodies, where exchange of water with the adjacent sea is restricted. In the present study, As concentrations varied between 2.22 and 14.29mg/Kg. In most sampling stations, As presented concentrations higher than the effect range low (ERL) and the threshold effect level (TEL) (NOAA, 2012; CCME, 2002) (Figure 8). Despite the rare studies on this metal that use the same extraction methodology, it appears that the values obtained here are environmentally significant. The statistical results reinforce the importance of organic matter and fine-grained particles in As distribution in the SES (Table 6).

Figure 7. Heavy metals concentrations (Zn, Fe, Co and Mn)
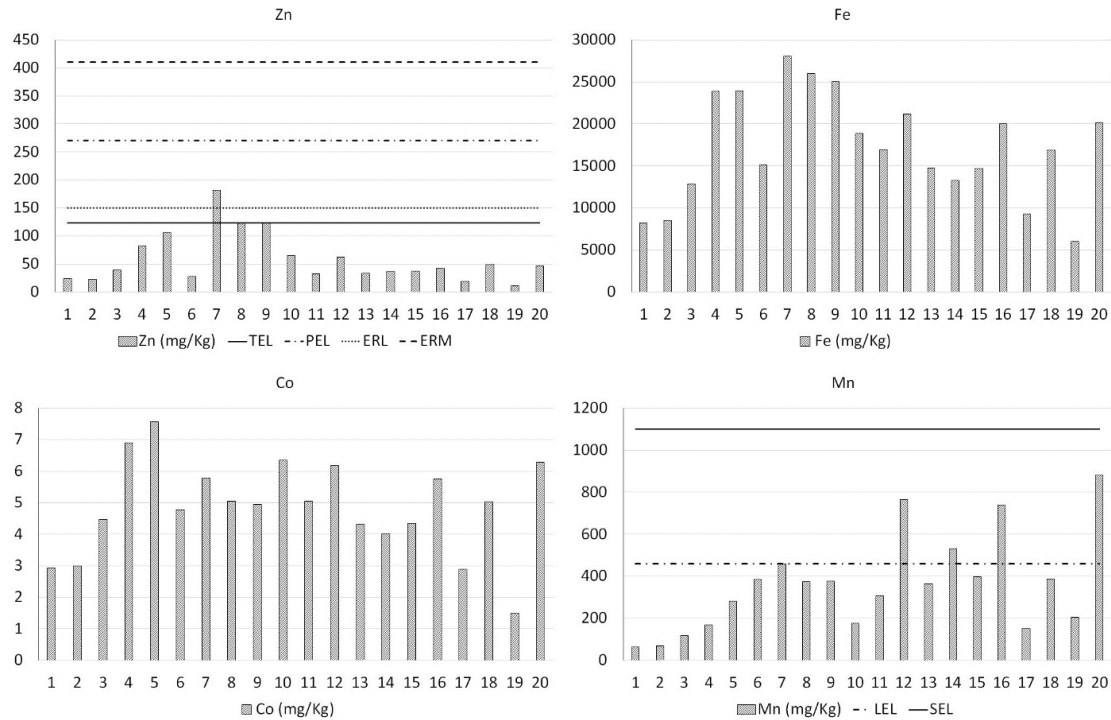
Copper is necessary to living organisms; it participates in the production of hemoglobin (Liu et al., 2017) and is a fundamental constituent of several enzymes (Underwood, 1977). However, high assimilation rates of Cu can result in adverse health problems (Gorell et al., 1997). In the present study, Cu levels varied from 2.6 and 21.3mg/Kg (Figure 8). The levels of Cu at all sampling spots were below the ERL, which means that biological effects are not likely. They were also lower than the threshold effect level (TEL) (CCME, 2002) and probable effect level (PEL)(CCME, 2002) (Figure 8). Comparing values available in the literature, the present study gave values below those in Guanabara Bay and the Rodrigo de Freitas Lagoon, both environments located in Brazil (Table 5). Even so, the values were significant in relation to other areas around the world. Once again, factors such as particle size and organic matter content were found to be decisive in the distribution of Cu in Santos bay (Table 6)

Figure 8. Heavy metal concentrations
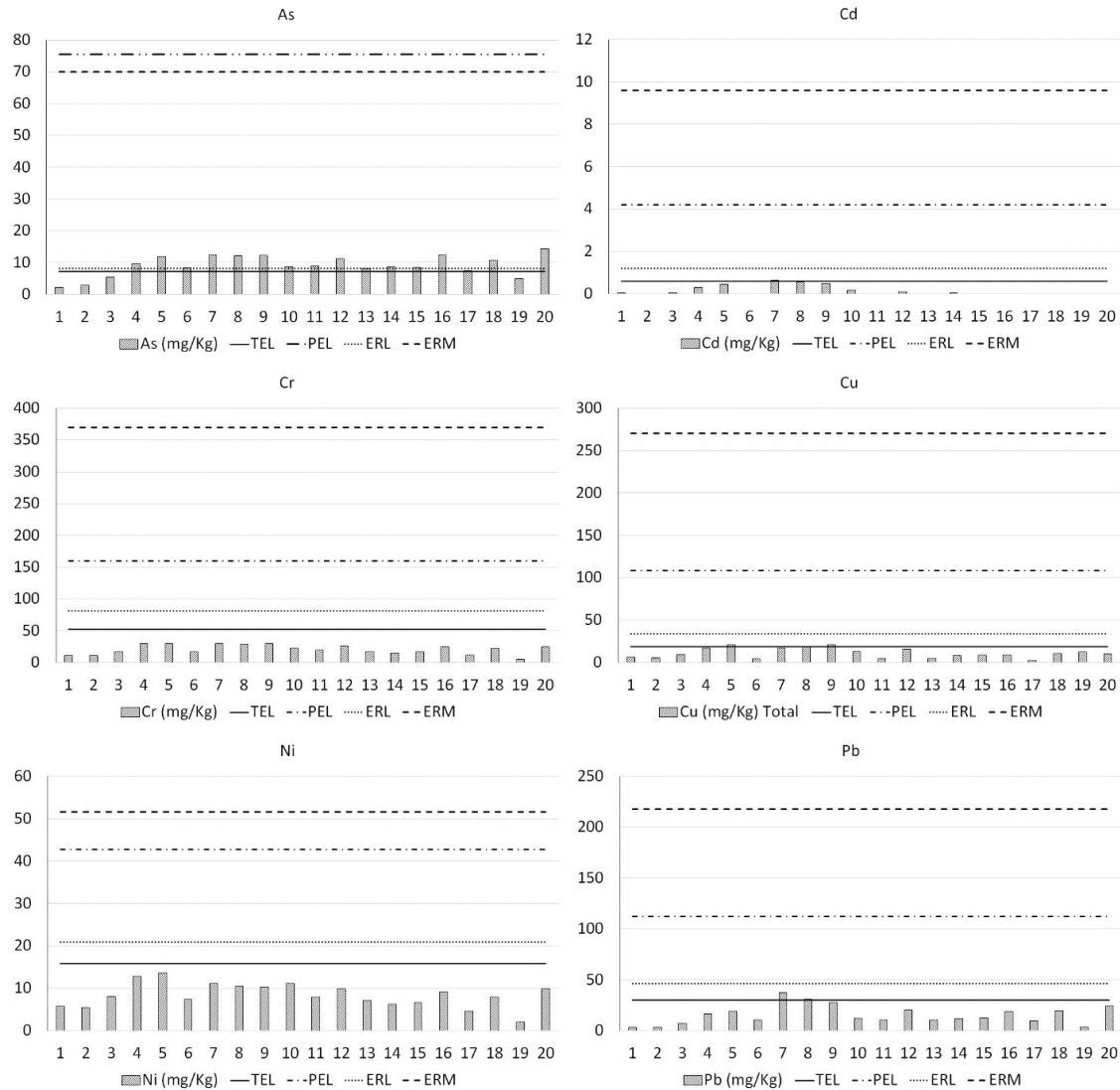
In contrast to the other metals in the present study, cadmium, lead, nickel and chromium are classified as toxic (EC, 2001; USFDA, 1993). The role of Cd in batteries, pigments, plating, and stabilizer industries reinforces the increasing dependency on Cd which are potential causes for its environmental impact (Lin et al., 2013). In the present study, the Cd concentrations were low. The levels in sediments may be attributed to the terrestrial source. Concentrations of this metal in all samples were below the ERL, suggesting that biological impacts would be rarely expected. They are also lower than the threshold effect level (TEL) and probable effect level (PEL) (CCME, 2002) (Figure 8). Although low when compared to other metals, Cd concentrations were influenced by the same factors. According to Laing et al. (2008), salinity enhances Cd mobility. In the present study, on the other hand, this was not apparently the case, since the correlation between both parameters was negative (Table 6).

Nowadays, chromium is produced by and used in industrial processes, including chrome plating, leather pigmentation and wood preserving (Lin et al., 2013). In natural environments, most of the chromium in surface waters may originate from rock degradation (ATSDR, 2000). According to Corbi et al. (2011), the natural concentrations in soils vary around $40mg.Kg^{-1}$ and no negative impacts are produced under 75 $mg.kg^{-1}$. Leslie et al. (1999) suggested that higher chromium levels have a negative influence on aquatic organisms, decreasing diversity or even having sublethal effects on community members. In the current study, chromium was recorded in all the samples and ranged between 5.14 and 30.06mg/Kg, all below the ERL. The values obtained in the present study were relatively low in relation to values available in the literature (Table 5; Figure 8).

The natural source of lead is mainly rock degradation. However, Pb can accumulate through traffic exhaust fumes, lead–zinc smelting industries, dumps and other sites receiving industrial and household residues (Cameron, 1992). The Pb concentrations in the studied stations range between 3.61 and 37.53mg/Kg. Lead levels in all samples were below the ERL value, which means that biological effects would be rarely observed. The levels are also lower than the ERM, TEL and PEL (Figure 8). Like other metals, Pb distribution was directly related to particle size and organic matter content (Table 6). The literature confirms that adsorption on organic matter and clay minerals are processes that significantly remove lead from the water column and transfer it to the sediment (Irwin et al. 1997).

The fundamental role of nickel as a component of enzymes (urease and hydrogenase) in most vegetables and some microorganisms is well known. On the other hand, nickel has a carcinogenic potential and overexposure to it can cause heart and liver diseases (Homady et al., 2002). The nickel levels in the current samples showed wide variation, the highest being detected in the estuarine area and the lowest at the mouth of the Santos canal. Proximity to port activity may be the cause of its high levels in the Santos channel. Nickel concentrations in all samples were below the ERL values as well as other indices (Figure 5).

Figure 9: Principal component analysis (PCA) of all metallic elements and geochemical parameters
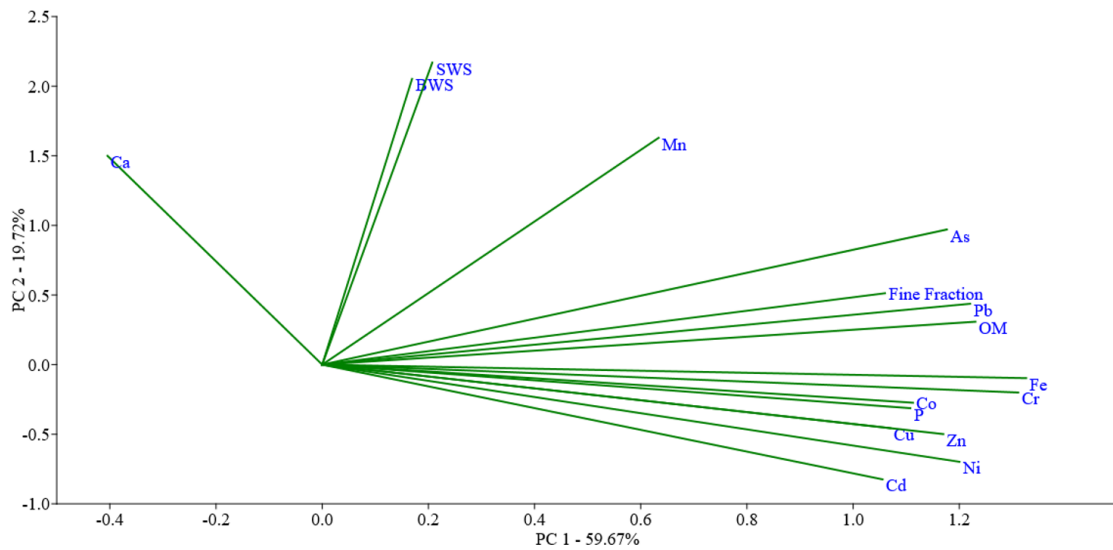
The PCA evaluation (Figure 9) showed a total variance of 70.39%, with 59.67% related to main component 1 and 19.72% to component 2 (the vertical axis). The interaction among metals and the sediment fine fraction and the organic content in the sediment was confirmed, and this explains more than half of the variation in the data set.

Contamination indices are globally used as a powerful approach for the understanding of pollution levels. They can have a fundamental importance in the assessment of sediment quality and the prediction of future ecosystem sustainability (Kowalska et al., 2018). To understand the current status of the environment and the heavy metal contamination with respect to the natural environment in the Santos Estuarine System, Contamination Factor (CF) (Figure 10), Geoaccumulation index (I_{geo}) (Figure 11) and Enrichment Factor (EF) (Figure 12) were applied in this study.

According to the CF, collection stations 5, 7, 8 and 9 presented moderate levels of Cd (Figure 10). The other metals presented low levels of contamination at all points along the estuarine system.

Figure 10. Contaminant Factors recorded in the present study

Contamination Factor (CF)
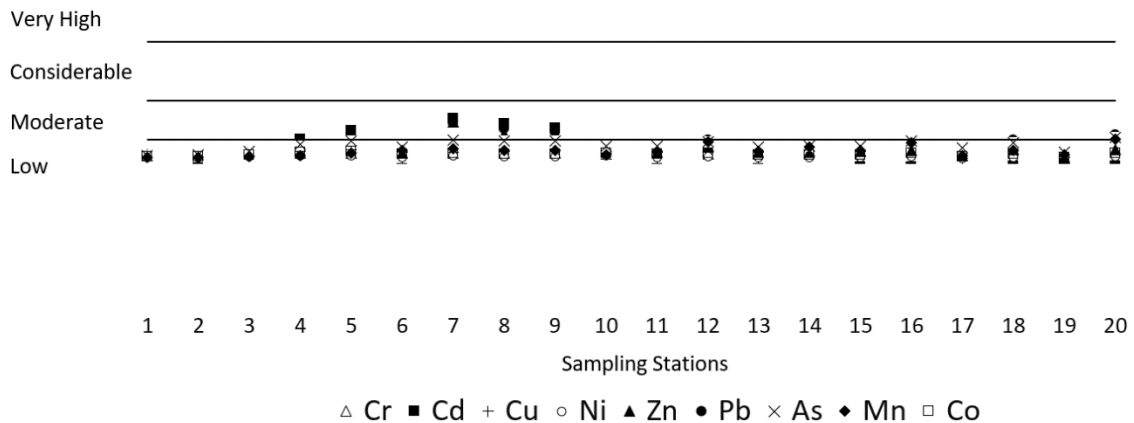
Regarding the Geoaccumulation Index (I_{geo}), Mn was classified as highly polluting at all sampling stations (Figure 11). Zn could be classified as moderately polluting, mainly in the innermost points of the bay. The other metals were classified as "practically non-polluting" or "non-polluting".

Figure 11. Geochemical Indices recorded in the present study

Geochemical Index (I_{geo})
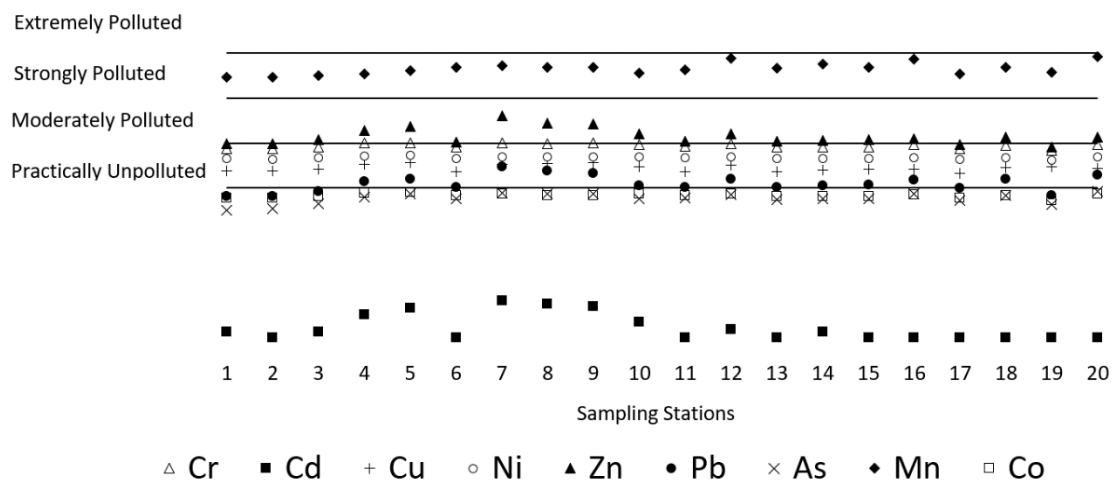
Finally, according to the Enrichment Factor (Figure 12), Cd once again stood out as moderately enriched in the innermost points of the bay. This was followed by As and Pb, both classified as less enriched.

Figure 12. Enrichment Factors recorded in the present study

Enrichment Factor (EF)

△ Cr ■ Cd + Cu ○ Ni ▲ Zn ● Pb × As ◆ Mn □ Co
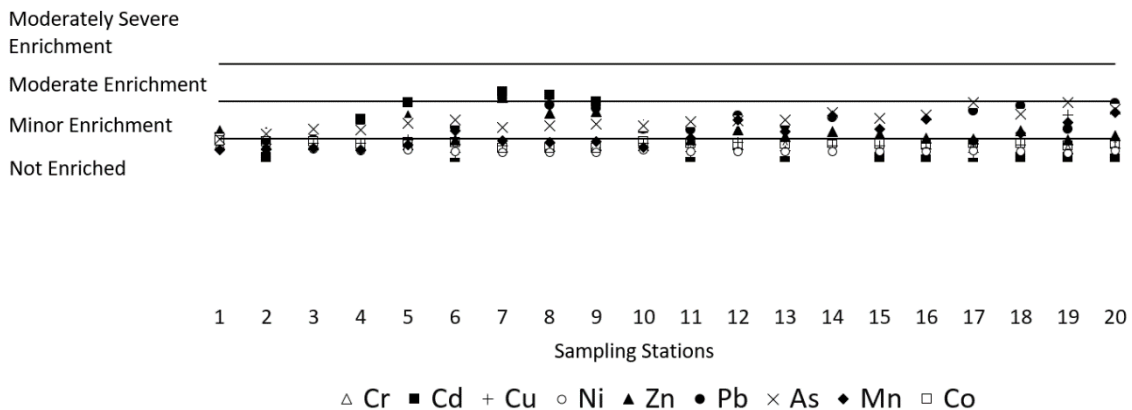
5 CONCLUSIONS

The present study indicated an extremely heterogeneous particle size among the sampling stations, varying mainly between silt and sand. Most of the heavy metal levels did not present critical values. The only exception was arsenic, which reached levels higher than the TEL. The statistical analysis clearly shows the influence of organic matter and granulometry on the dynamics of heavy metal deposition. The values between these binding matrices and metals were mostly significant. The same result was obtained in the PCA evaluation. Bottom water salinity, on the other hand, had no apparent influence on the distribution of metals. Finally, the various pollution indices applied were contradictory, with particular cases presenting critical results. The Geoaccumulation Index presented the Mn as highly polluting at all sampling stations and classified the environment as moderately polluted by Zn. The same pollution pattern was not found by the other contamination indexes.

ACKNOWLEDGMENTS

REFERENCES

Acosta, J., Jansen, B., Kalbitz, K., Faz, A. and Martínez-Martínez, S. 2011. Salinity increases mobility of heavy metals in soils. *Chemosphere*, **85**, 1318-24.

Alexander, C.S. 1972. Cobalt-beer cardiomyopathy. A clinical and pathologic study of twenty-eight cases. *American Journal of Preventive Medicine*, **53**, 395-417.

Alexandre, M.R., Huang, Y. and Madureira, L. A. S. 2006. Avaliação De Compostos Orgânicos Em Sedimentos Superficiais Da Baía De Babitonga, Santa Catarina, Brasil. *Geochimica Brasiliensis*, **20(2)**, 208-218.

Ashraf, M. A., Maah, M. J. and Yusoff, I. 2012. Speciation of heavy metals in the sediments of former tin mining catchment. *Iranian Journal of Science and Technology*, **2**, 163-180

ATSDR. 2000. Toxicological Profile for Manganese. September. www.atsdr.cdc.gov/toxprofiles/tp151.html

Audry, S., Blanc, G., Schäfer, J., Chaillou, G. and Robert, S. 2006. Early diagenesis of trace metals (Cd, Cu, Co, Ni, U, Mo, and V) in the freshwater reaches of a macrotidal estuary. *Geochimica et Cosmochimica Acta*, **70**, 2264-2282.

Beck, A., Cochran, J. and Sañudo-Wilhelmy, S. 2010. The distribution and speciation of dissolved trace metals in a shallow subterranean estuary, *Marine Chemistry*, **121**, 145-156.

Beltagy, A. I. (1984). Elemental geochemistry of some recent marine sediments from north Red Sea. *Bulletin of the Institute of Oceanography and Fisheries*, **10**, 1-12.

Borrely, S.I., Garcia, V.S.G., Borrely, T. and Fávaro D.I.T. 2018. Metals, trace elements and ecotoxicity in sediments of the Cubatão River, Brazil. *Ecotoxicology and Environmental Contamination*, **13**, 49-61.

Braga, E.S., Bonetti, C.V.D.H., Burone, L. and Bonetti Filho, J. 2000. Eutrophication and bacterial pollution caused by industrial and domestic wastes at the Baixada Santista Estuarine System-Brazil. *Marine Pollution Bulletin*, **40(2)**,165-173.

Brandini, N., Rodrigues, A.P. de C., Abreu, I. M., Cotovicz Junior, L.C., Knoppers B. A. and Machado, W. (2016). Nutrient behavior in a highly-eutrophicated tropical estuarine system. *Acta Limnologica Brasiliensia*, **28**, 3.

Burone, L., Muniz, P., Pires-Vanin, A.M.S and Rodrigues M. 2003. Spatial distribution of organic matter in the surface sediments of Ubatuba Bay (Southeastern – Brazil). *Anais da Academia Brasileira de Ciências*, **75(1)**, 77-90.

Calabrese, E.J., Canada, A.T., and Sacco, C. 1985. Trace elements and public health. *Annual Review of Public Health*, **6,** 131- 146.

Cameron, R. E. 1992. Guide to site and soil description for hazardous waste site characterization, vol 1: metals. Washington, DC: *Environmental Protection Agency* EPA/600/4-91/029

Carranza-Edwards, A., Rosales-Hoz, L., Urrutia-Fucugauchi, J., Sandoval Fortanel, A., Morales de la Garza, E. and Lozano Santa Cruz, R. 2005. Geochemical distribution pattern of sediments in an active continental shelf in Southern Mexico. *Continental Shelf Research,* **25,** 521–537.

Casarini, L.M., Henriques, M.B., Graça-Lopes, R. and Souza, M.R. de. 2010. Chemical and bacteriological evaluation of the water and mussels from Santos bay, São Paulo, Brazil. Revista do Instituto Adolfo Lutz, **69**, 297-303.

CCME (Canadian Council of Ministers of the Environment). 2002. Canadian sediment quality guidelines for the protection of aquatic life: Summary tables, Updated. In: Canadian Environmental Quality Guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg

Chiffoleau, J.F., Cossa, D., Auger, D. and Truquet, I. 1994. Trace metal distribution, partition and fluxes in the Seine estuary (France) in low discharge regime. Marine Chemistry, **47**,145-158.

Childers, D.L., Corman, J., Edwards, M. and Elser, J.J. 2011. Sustainability challenges of phosphorus and food: solutions from closing the human phosphorus cycle. Bioscience, **61**, 117-124.

Cloern, J.E., Jassby, A.D., Schraga, T.S., Nejad, E. and Martin, C. 2017. Ecosystem variability along the estuarine salinity gradient: Examples from long-term study of San Francisco Bay. Limnology and Oceanography, **62**, 272–291.

Corbi, J.J., Santos, F.A., Zerlin, R., Santos, A., Froehlich, Claudio G., and Trivinho-Strixino, S. 2011. Assessment of chromium contamination in the Monte Alegre stream: a case study. Brazilian Archives of Biology and Technology, **54(3)**, 613-620.

Costa, A.B., Novotny, E.H., Bloise, A.C., Azevedo, E.R., Bonagamba, T.J., Zucchi, M.R., Santos, V.L.C.S. and Azevedo, A.E.G. 2011. Characterization of organic matter in sediment cores of the Todos os Santos Bay, Bahia, Brazil, by elemental analysis and 13C NMR. Marine Pollution Bulletin, **62,** 1883–1890.

Dalia, M.S. Salem, A., Abou-Elmagd, F., Morsy, M., El Nemr, A., El-Sikaily, A. and Khaled, A. 2014. The monitoring and risk assessment of aliphatic and aromatic hydrocarbons in sediments of the Red Sea, Egypt. Egyptian Journal of Aquatic Research, **71**.

Dancey, C., Reidy, J. 2006. Estatística Sem Matemática para Psicologia: Usando SPSS para Windows. Porto Alegre, Artmed.

De Baar, H.J.W, de and De Jong, Jeroen. 2001. Distributions, sources and sinks of iron in seawater. The biogeochemistry of iron in seawater. Edition: IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, V. 7 Chapter: Distributions, sources and sinks of iron in seawater. John Wiley & Sons Ltd., Chichester, UK. Editors: D. Turner, K. Hunter

Delgado, J. de F., Lima, L. da S., Britto, E. B. C. C., Almeida, M. P., Vieira, K. S., Amorim, R. M., Baptista Neto, J. A. and Fonseca, E. M. 2020. Evaluation of Metal

Pollution in Sediments and Water of Sao Marco Harbor (Maranhão, Brazil). Oceanography & Fisheries Open Access Journal. **12**, 3.

Dickhudt, P.J., Friedrichs, C.T. and Sanford, L.P. 2011. Mud matrix solids fraction and bed erodibility in the York River estuary, USA, and other muddy environments. Continental Shelf Research, **31**, 3–13.

Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F.M.G. and Verloo, M.G. 2008. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. Estuarine and Coastal Marine Science, **77**, 589-602.

E.C. (2001). Commission Regulation No. 466/2001, 08.03. 2001. Official Journal of European Communities, 1.77/1.

El Nemr, A., El-Sadaawy, M.M., Khaled, A. and Draz, S.O. 2013. Aliphatic and polycyclic aromatic hydrocarbons in the surface sediments of the Mediterranean: assessment and source recognition of petroleum hydrocarbons. Environmental Monitoring and Assessment, **185**, 4571– 4589.

Fonseca, E. M. da, Baptista Neto, J. A., McAllister, J. J., Smith, B. J. and Crapez, M. 2014. Bioavailability Of Pollutants In Bacterial Communities of Rodrigo De Freitas Lagoon – Rio De Janeiro, Brazil. Brazilian Journal of Microbiology, **45**, 953-962.

Fonseca, E.M., Baptista Neto, J.A., Pereira, M.P.S., Silva, C.G. and Arantes Junior, J.D. 2014. Study of pollutant distribution in the Guaxindiba Estuarine System; SE Brazil. Marine Pollution Bulletin, **82**, 45-54.

Fonseca, E.M., Baptista Neto, J.A., Crapez, M.C., McAllister, J.J., Fernandez, M.A. and Bispo M.G. 2009. Bioavailability of Heavy Metals in Guanabara Bay, Rio de Janeiro (Brazil). Journal of Coastal Research, **56**, 802-806.

Ghrefat, H.A. and Yusuf, N. 2006. Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. Chemosphere, **65(11)**, 2114–2121.

González-Macías, C., Schifter, I., Liuch-Cota, D. Mendez, L.C and Hernández-Vázquez, S. 2006. Distribution, Enrichment and Accumulation of Heavy Metals in Coastal Sediments of Salina Cruz Bay, México. Environmental Monitoring and Assessment, **30**, 118-211.

Gorell, M., Johnson, C.C., Rybicki, B.A., Peterson, E.L., Kortsha, G.X. and Brown, G.G. 1997. Occupational exposures to metals as risk factors for Parkinson's disease. Neurology, **48**, 650-658

Graham, M., Eaves, M., Farmer, J., Dobson, J. and Fallick, A.A. 2001. study of carbon and nitrogen stable isotope and elemental ratios as potential indicators of source and fate of organic matter in sediments of the Forth Estuary, Scotland. Estuarine and Coastal Marine Science, **52**, 375-380.

Hakanson, L. 1980. An ecological risk index for aquatic pollution control: A sediment ecological approach. Water Research, **14**, 975–1001.

Homady, M., Hussein, H., Jiries, A., Mahasneh, A., Al-Nasir, F., Khleifat, K. 2002. Survey of some heavy metals in sediments from vehicular service stations in Jordan and their effects on social aggression in prepubertal male mice. Environmental Research, **89**, 43–49.

Hortellani, M. A., Sarkis, J.E.S., Abessa, D.M.S. and Sousa, E.C.P.M. 2008. Avaliação da contaminação por elementos metálicos dos sedimentos do estuário Santos – São Vicente. Química Nova, 31(1), 10-19.

Irwin, R.J., Mouwerik, M.V., Stevens, L., Seese, M.D. and Basham, W. 1997. Environmental contaminants encyclopedia: zinc entry. National Park Service, Water Resources Division, Fort Collins, CO. Available from: ,http://www.Nature.nps.gov/hazardssafety/toxic/zinc.pdf

Jahan, S. and Strezov, V. 2019. Assessment of trace elements pollution in the sea ports of New South Wales (NSW), Australia using oysters as bioindicators. Scientific Reports, 9, 1416.

Jiao, Z, Li, H., Song, M. and Lin, W. 2018. Ecological risk assessment of heavy metals in water and sediment of the Pearl River Estuary, China. IOP Conference Series: Materials Science and Engineering, 394.

Kowalska, J.B., Mazurek, R., Gasiorek, M. and Zaleski, T. 2018. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination – A review. Environmental Geochemistry and Health, **40**, 2395–2420.

Kraepiel, A.M.L., Chiffoleau, J.-F., Martin, J.-M., Morel, F.M.M. 1997. Geochemistry of trace metals in the Gironde estuary. Geochimica et Cosmochimica Acta, **61**, 1421-1436.

Krishna, M., Naidu, S., Subbaiah, C.V., Sarma, V. and Reddy N. 2013. Distribution and sources of organic matter in surface sediments of the eastern continental margin of India. Journal of Geophysical Research: Biogeosciences, **118**, 1484-1494.

Kumar, B., Shah, R. and Mukherjee D. 2011. Geochemical distribution of heavy metals in sediments from sewage fed fish ponds from Kolkata Wetlands, India. Chemical Speciation and Bioavailability. **23(1)**, 24-32.

Ladigbolu, I.A., Appia, J., Balogun, K.J. and Adedeji, A.K. 2014. Geochemical fractionation of Heavy metals in the sediment at the point of discharge of Iyalaro stream into Lagos Lagoon. Journal of Environmental Science, Toxicology and Food Technology, **8**, 8.

Laing, G., De Vos D., R., Vandecasteele, B., Lesage, E., Tack, F.M.G. and Verloo, M.G. 2008. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. Estuarine and Coastal Marine Science, **77**, 589-602.

Lamb, A.L., Wilson, G.P. and Leng, M.J. 2006. A review of coastal palaeoclimate and relative sea-level reconstructions using δ13C and C/N ratios in organic material. Earth-Science Reviews, **75**, 29–57.

Li, X., Shen, Z., Wai, O.W.H. and Li, Y., 2000. Chemical partitioning of heavy metal contaminants in sediments of the Pearl River Estuary. Chemical Speciation and Bioavailability, **12**.

Liu, Y., Wang, Y., Yan, M. and Huang, J., 2017. Selective Removal of Hemoglobin from Blood Using Hierarchical Copper Shells Anchored to Magnetic Nanoparticles. BioMed Research International.

Long, E.R. and MacDonald, D.D. 1998. Recommended uses of empirically derived sediment quality guidelines for marine and estuarine ecosystems. Human and Ecological Risk Assessment: An International Journal, **4**, 1019–1039

Lu, C., and Tian, H. 2017. Global nitrogen and phosphorus fertilizer use for agriculture production in the past half century: shifted hot spots and nutrient imbalance. Earth System Science Data, **9**, 181–192.

Luo, W., Lu, Y., Wang, T., Hu, W., Jiao, W., Naile, J. E., Khim, J. S. and Giesy J. P. 2010. Ecological risk assessment of arsenic and metals in sediments of coastal areas of northern Bohai and Yellow Seas, China. AMBIO, **39**, 367–375.

MacDonald, D.D., Ingersoll, C.G. and Berger. T.A. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology, **39**, 20-31.

Mansour, A., Askalany, M., Madkour, H. and Assran, B. 2013. Assessment and comparison of heavy-metal concentrations in marine sediments in view of tourism activities in Hurghada area, northern Red Sea, Egypt. Egyptian Journal of Aquatic Research, **39**, 91–103.

Martino, M., Turner, A., Nimmo, M. and Millward, G.E. 2002. Resuspension, reactivity and recycling of trace metals in the Mersey Estuary, UK. Marine Chemistry, **77**, 171-186.

Martins, M.V.A., Rodrigues, R, Pereira. E, Miranda, P., Laut, L., Belart, P., Villena, H.H., Geraldes, M.C., Sousa, S.H.M.E., Duleba, W. and Bergamashi, S. 2018. Organic Pollution in the NE Sector of Guanabara Bay (SE, Brazil). Journal of Sedimentary Environments, **3(3)**, 138-154.

Maslennikova, S., Larina, N. and Larin, S., 2012. The effect of sediment grain size on heavy metal content. Lakes Reservoirs and Ponds. **6,** 43-54.

Mosley L. M. and Liss P. S., 2019. Particle aggregation, pH changes and metal behaviour during estuarine mixing: review and integration. Marine and Freshwater Research, **71**, 300-310.

Mulligan, C. N., Yong, R. N., and Gibbs, B. F. 1999. On the use of biosurfactants for the removal of heavy metals from oil contaminated soil. Environmental Progress, **18(1)**, 50–54.

Muto, E.Y., Corbisier T. N., Coelho L. I., Arantes, L. P. L., Chalom, A. and Soares, L. S. H. 2014. Trophic Groups of Demersal Fish of Santos Bay and Adjacent Continental Shelf, São Paulo State, Brazil: Temporal and Spatial Comparisons. Brazilian Journal of Oceanography, **62(2)**, 89-102.

Nixon, S. W., Oviatt, C. A., Frithsen, J. and Sullivan, B. 2010. Nutrients and the productivity of estuarine and coastal marine ecosystems. J. of the Limnological Society of Southern Africa, **12(1-2)**, 1986.

NOAA (2012). Screening Quick Reference Tables. National Oceanic and Atmospheric Administration. Available from:<http://archive.orr.noaa.gov/book_shelf/122_NEW-SQuiRTs.pdf>

Persaud, D., Jaagumagi, R. and Hayton, A. 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario. Water Resources Branch, Ontario Ministry of the Environment, Toronto, 27 pp.

Pradhan, U., Wu, Y., Shirodkar, P., Zhang, J. and Zhangm, G., 2014. Sources and distribution of organic matter in thirty-five tropical estuaries along the west coast of India-a preliminary assessment. Estuarine Coastal and Shelf Science, **151**, 21-33.

Pritchard, D.W. and Schubel, J.R. 1981. Physical and geological processes controlling nutrient levels in estuaries. In B.J. NEIL-SON and L.E. CRONIN, eds. Estuaries and nutrients. New York: Human Press, 1981, 47-69.

Regnier, P., Arndt, S., Goossens, N., Volta, C., Laruelle, G. G., Lauerwald, R. and Hartmann, J. 2013. Modelling Estuarine Biogeochemical Dynamics: From the Local to the Global Scale. Aquatic Geochemistry, **19**, 591–626.

Ribeiro, L.G.L., Carreira, R.S. and Wagener, A.L.R., 2008. Conteúdo e distribuição de carbono negro em sedimentos do litoral brasileiro (Baía de Guanabara). Journal of the Brazilian Chemical Society, **19(7)**, 1277-1283.

Rinklebe, J. and Shaheen, S.M. 2014. Assessing the mobilization of cadmium, lead, and nickel using a seven-step sequential extraction technique in contaminated floodplain soil profiles along the Central Elbe river, Germany. Water Air Soil Pollution. 225: 2039.

Rodrigues, C.A.L., Ribeiro, R.P., Santos, N.B. and Almeida, Z.S. 2016. Patterns of mollusc distribution in mangroves from the São Marcos Bay, coast of Maranhão State, Brazil. Acta Amazonica. **46(4)**, 391-400.

Rudnick, R. and Gao, S. 2003. Composition of the continental crust. Treatise on Geochemistry, **3**,1–64.

Rumolo, P., Barra, M., Gherardi, S., Marsella, E. and Sprovieri, M. 2011. Stable isotopes and C/N ratios in marine sediments as a tool for discriminating anthropogenic impact. *J. of Environ. Monit.*13: 3399-3408.

Rzetala, M., Babicheva, V. A. and Rzetala, M. A. 2019. Composition and physico-chemical properties of bottom sediments in the southern part of the Bratsk Reservoir (Russia). Scientific Reports, **9**, 12790.

Santos-Echeandia, J., Prego, R., Cobelo-García, A. and Millward, G.E. 2009. Porewater geochemistry in a Galician Ria (NW Iberian Peninsula): implications for benthic fluxes of dissolved trace elements (Co, Cu, Ni, Pb, V, Zn). Marine Chemistry, **117**, 77-87.

Sarkar, S.K., Favas, P.J.C., Rakshit, D. and Satpathy, K.K. 2013. Geochemical Speciation and Risk Assessment of Heavy Metals in Soils and Sediments. Environmental Risk Assessment of Soil Contamination.

Shaheen, S.M. and Rinklebe, J. 2014. Geochemical fractions of chromium, copper, and zinc and their vertical distribution in floodplain soil profiles along the Central Elbe. Geoderma, **228**, 152–159

Sivaperumal, P., Sankar, T., Viswanathan V. and Nair, P.G. 2007. Heavy metal concentrations in fish, shellfish and fish products from internal markets of India vis-a-vis international standards. Food Chemistry, **102**, 612–620

Sounthararajah, D.P., Loganathan, P., Kandasamy, J. and Vigneswaran, S. 2015. Effects of Humic Acid and Suspended Solids on the Removal of Heavy Metals from Water by Adsorption onto Granular Activated Carbon. International Journal of Environment Research and Public Health, **12(9)**, 10475-10489.

Szefer, P., Glasby, G.P., Kusak, A., K., Szefera, H., Jankowska, Wolowiczc, M. and Alid A.A. 1998. Evaluation of the anthropogenic influx of metallic pollutants into puck bay, southern baltic. Applied Geochemistry, **13(3)**, 293–304.

Taylor, S.R. and McLennan, S.M. 1995. The geochemical evolution of the continental crust. Reviews of Geophysics, **33(2)**, 241–265.

Telesh, I. and Khlebovich, V. 2010. Principal processes within the estuarine salinity gradient: A review. Marine Pollution Bulletin, **61,** 149-55.

Tovar-Sánchez, A., Sañudo-Wilhelmy, S.A. and Flegal, R.A. 2004. Temporal and spatial variations in the biogeochemical cycling of cobalt in two urban estuaries: Hudson River Estuary and San Francisco Bay. Estuarine and Coastal Marine Science, **60,** 717 - 728.

Turki, A.J. (2007). Metal Speciation (Cd, Cu, Pb and Zn) in Sediments from Al Shabab Lagoon, Jeddah, Saudi Arabia. Bulletin of Marine Science, **18,** 191-210.

Underwood, E.J. 1977. Trace elements in human an animal nutrition. 4.ed. New York: Academic Press. 545p.

USFDA (1993). Food and drug administration. Guidance document for arsenic, chromium, nickel in shellfish. Washington, DC: DHHS/PHS/FDA/CFSAN/Office of Sea Food.

Van Vuuren, D. P., Bouwman, A. F. and Beusen, A. H. W. 2010. Phosphorus demand for the 1970-2100 period: a scenario analysis of resource depletion. Global Environmental Change, **20**, 428–439.

Venkatramanan, S., Yong, S.C., Thirunavukkarasu R., Namsik P. 2014. Grain Size Trend and Hydrodynamic Condition of Tirumalairajan River Estuary, East Coast of India. Oceanology, **54**, 532-540.

Venturini, N., Tommasi, L.R., Bícego, M.C. and Martins, C.C. 2004. Characterization of the Benthic Environment of a Coastal area Adjacent to an Oil Refinery, Todos os Santos Bay (NE-Brazil). Estuarine and Coastal Marine Science, **52(2),** 123-134.

Vilela, C.G., Sanjinés, A.E.S., Ghiselli, J.R. R.O., Mendonça Filho, J.G., Baptista Neto, J. A. and Barbosa, C.F. (2003). Search for Bioindicators of Pollution in the Guanabara Bay: Integrations of Ecologic Patterns. Anuário do Instituto de Geociências – UFRJ*,* **26**, 25-35.

Wallner-Kersanacha, M., Mirlean, N., Baumgarten, M. da G. Z., Costa, L. D. F. and Baisch P. 2016. Temporal evolution of the contamination in the southern area of the Patos Lagoon estuary, RS, Brazil. Journal of Integrated Coastal Zone Management, **16**, 3.

Wang, C., Chen, M., Qi, H., Intasen, W. and Kanchanapant, A. 2020. Grain-Size Distribution of Surface Sediments in the Chanthaburi Coast, Thailand and Implications for the Sedimentary Dynamic Environment. Marine Science and Engineering, **242**.

Wang, Y., Liu, R., Zhang, Y., Cui, X., Tang, A. and Zhang, L. 2016. Transport of heavy metals in the Huanghe River estuary, China. *Environ. Earth Sci*. **75**.

Yan, Z., Han, W., Penuelas, J., Sardans, J., Elser, J., Reich, P. and Fang, J. 2016. Phosphorus accumulates faster than nitrogen globally in freshwater ecosystems under anthropogenic impacts. Ecology Letters, 19.

Yung-Chang, L., Chang-Chien, G.-P., Chiang, P.-C., Chen, W.-H. and Lin, Y.-C. 2013. Multivariate analysis of heavy metal contaminations in seawater and sediments from a heavily industrialized harbor in Southern Taiwan. Marine Pollution Bulletin, **76(1–2)**, 266-275.

Zhang, C., Yu, Z., Zeng, G., Jiang, M., Yang, Z., Cui, F., Zhu, M., Shen L.and Hu, L. 2014. Effects of sediment geochemical properties on heavy metal bioavailability, Environment International, **73**, 270-281.

Zhao, S., Feng, C., Wang, D., Liu, Y. and Z. Shen. 2013. Salinity increases the mobility of Cd, Cu, Mn, and Pb in the sediments of Yangtze Estuary: Relative role of sediments' properties and metal speciation, Chemosphere, **91(7)**, 977-984.