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Evaluation of Metal Pollution in Sediments and Water of Sao Marco Harbor (Maranhão, Brazil)

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Abstract

The assessment of pollution in poor regions remains a challenge for developing countries. Difficult access to and low availability of logistical conditions result in a lack of information on environmental quality in these regions. To provide information on heavy metals concentrations in water and sediments, samples were collected in seven sampling stations in São Marco Bay's harbor area, seasonally, from August 2017 to September 2018. Water samples were evaluated for temperature, turbidity, salinity, Eh, oxygen content, pH, phosphorus, total organic carbons, and heavy metals. In sediment samples, heavy metals' potentially mobilizable fractions were evaluated. In parallel, grain size, organic matter and redox potential were also analyzed. The average values of water and its physicochemical parameters revealed an unstratified environment with a great influence of ocean waters. High concentrations of metals were recorded in the water of sediment contamination. The present study suggested the high hydrodynamics and resulting coarser grain size accumulation as the cause for the relatively balanced environment conditions.

Kewords: Contaminants; Physicochemical parameters; Seasonal variation

Introduction

Anthropogenic contaminants discharged into aquatic environments can cause negative impacts to marine biota, especially in urbanized, industrialized or harbor sites [1]. As a result of the low hydrodynamics and inherent protection against waves and strong currents, estuarine areas tend to concentrate contaminants. This is the same reason why pollutant levels are generally higher in estuaries than in the open sea. Many harmful pollutants found in trace levels in water may accumulate to elevated concentrations in sediments. Thus, sediments act both as reservoirs and sources of contaminants to the water column and tend to integrate contaminant concentrations over time [2]. Regardless of the source, contaminants such as heavy metals are potentially adsorbed to fine-grained and organic rich sediments [3,4]. These contaminants tend to deposit in hydrodynamically quiet areas like estuaries and bays [5], where the low circulation allows stabilization of finer particle fractions and maintenance of subtoxic patterns, which in turn allows the retention of organic matter.

Potentially toxic metals may occur mainly due to industrial and agricultural wastes [6-8]. Some metals are essential for living organisms, such as Cu and Zn [9]. However, some are toxic to living organisms [10]. Lead, Arsenic, Mercury, and Cadmium, for example, are considered some highly toxic metals whose widespread use has caused extensive environmental contamination and health problems in many parts of the world [11]. Heavy metals are regarded as especially dangerous contaminants because of their environmental persistence, toxicity, and ability to be incorporated into food chains [12]. The strongest toxic properties are characteristic of inorganic metals compounds, which are easily soluble [13]. Some heavy metals dissolve immediately and tend to accumulate in aquatic organisms [14].

After entering the aquatic environment, heavy metals tend to be sequestered at the bottom [15]. They tend to be adsorbed into inorganic and organic particulates and finally incorporated into sediment compartments, generating elevated levels of heavy metals in bottom sediments [16]. On the other hand, heavy metals

are not necessarily stored in sediments permanently. Some of the sediment-bound metals may remobilize and be released back into the water through a variation of environmental conditions [17]. The distribution processes of the metals entering natural waters are controlled by a dynamic set of physicochemical interactions, and their solubility is controlled mainly by hydrogen ionic potential (pH), type of metal species, organic matter content, the oxidation state of mineral components and the redox environment of the aquatic system [18,19].

The Brazilian coastline presents a great diversity of geomorphological features [20], with many bays and estuaries, where different economic activities with great polluting potential exist. Port terminals and harbor areas have great importance in the economy around the globe. However, their operation has been very impactful on marine and coastal ecosystems [21]. Despite being a consequence of port operation, aquatic pollution represents a problem in port management, especially about potentially toxic metals. The aim of this study is to evaluate the metal concentrations in water and sediment samples collected in São Marco Bay harbor area.

Study Site

The northern coast of Brazil is characterized as an extremely irregular shoreline [22], formed by many estuaries extending from São Marcos Bay, in Maranhão State, up to the extreme north of Amapá State [23]. São Marcos bay is an active estuary, spread approximately 100km in length, with the hydrographic basin composed of Grajaú, Mearim, and Pindaré rivers (Figure 1). The climate is formed by two main seasons: a rainy and a dry season [24] (Figure 2). The hydrodynamic regime is characterized by a semidiurnal macrotide with current velocities higher than 1.1 ms^{-1} (maximum tidal currents of 2.42 ms^{-1}) [25]. The bay is surrounded by a wide mangrove environment [26]. The entrance of the bay presents a width of ~55 km, which narrows to 1.5 km at the intersection of Pindaré and Mearim rivers.

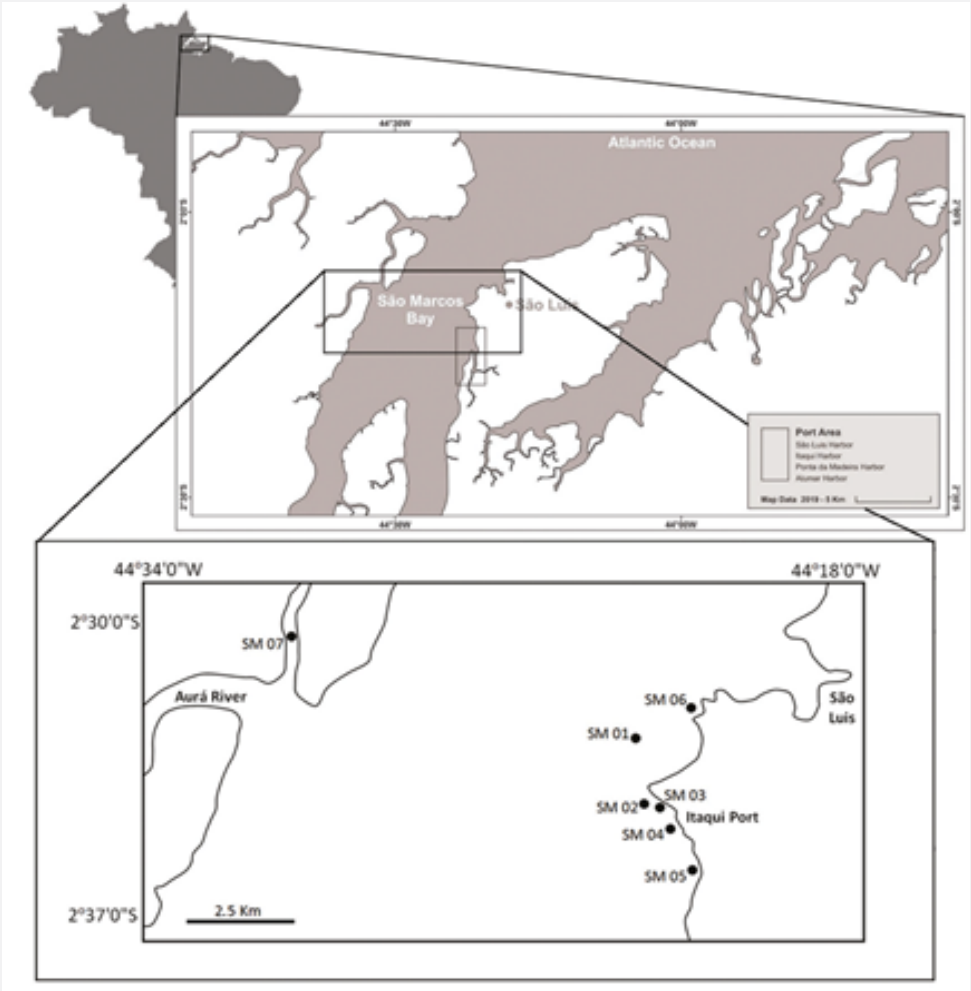

Figure 1: Study Site.

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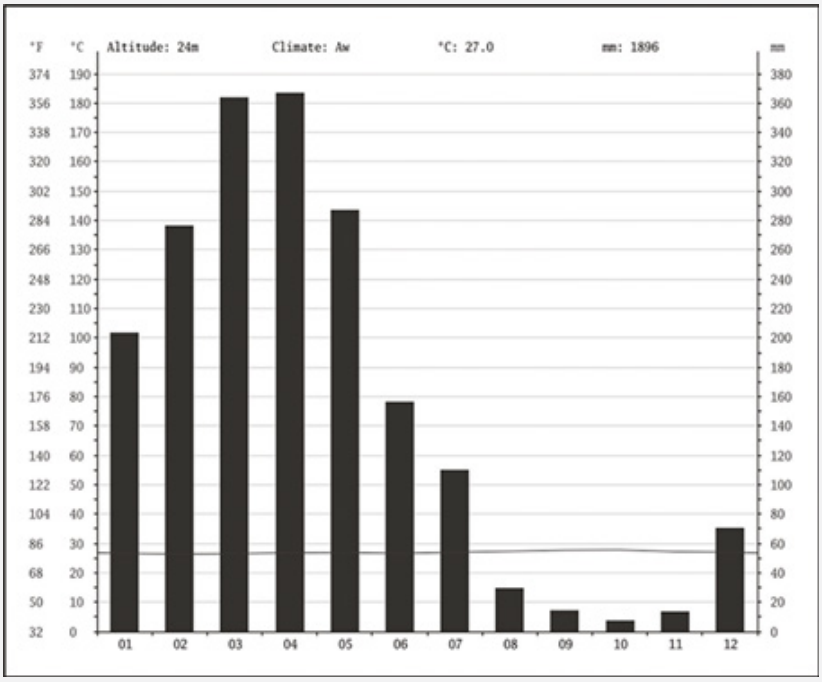

Figure 2: Typical pluviogram of the city of Sao Luiz (Source: Climate-data.org).

The bay contains a central channel with depth measuring up to 90 m, which works as a waterway for the second-most important port complex of Latin America, which includes São Luís harbor, Itaqui harbor, Ponta da Madeira port terminal and Alumar port terminal [27]. Ponta da Madeira terminal passed through an expansion to increase its export capacity to 235 million tons per year of iron mineral, becoming the port with the largest volume of cargo in Brazil. In addition to ore export, the region has steel and aluminum mills, such facilities representing the major economic activity of the region [25]. Finally, São Marcos Bay represents an important fishing spot. In the last few decades, chemical pollution of that environment due to sewage discharge, the nutrient runoff from pesticides, and industrial waste have impacted the region. Combined with the unsustainable use of resources, this has had an increasing threat to the health of aquatic organisms [28].

Materials and Methods

Four seasonal field campaigns were carried out, during ebb tide, from August/2017 to September/2018, when seven sampling stations were established and marked using global positioning system coordinates.

Physicochemical parameters (temperature, pH, dissolved oxygen levels (DO), salinity and redox potential) were analyzed *in situ*, using a multi parameter probe (Horiba U-51). Surface water samples were obtained with a 5L Van Dorn bottle. Water was analyzed for Total Organic Carbon (TOC), Phosphate, and Metals (Pb, Cu, Cr, Cd, Ni, Zn, and Hg) and As. Water samples were filtered through 0.45 µm cellulose acetate membrane filters using a vacuum filtration, preserved in plastic bottles (Polypropylene bottles) and maintained in cooler boxes until laboratory analysis.

For heavy metals analysis, the sampling bottles were pre-conditioned with 5% nitric acid and later rinsed thoroughly with distilled de-ionized water. At each sampling site, the polyethylene sampling bottles were rinsed at least three times before sampling was done. About 0.5 L of the water samples were taken at each sampling site. Samples were acidified with 10% HNO_3, placed in an ice bath and brought to the laboratory. Sediment samples were collected at each site using a Van Veen grab to determine the sediment grain size, TOC, Phosphate and Metals (Pb, Cu, Cr, Cd, Ni, Zn, and Hg) and As. After sampling, sediment samples were properly stored in a cooler box.

Water Analysis

Total Organic Carbon was determined using a dry combustion method with a Perkin Elmer 2400 CHN (carbon, hydrogen, and nitrogen) analyzer (series II). The instrument was calibrated using standard solutions of potassium hydrogen phthalate, diluted to different concentrations according to the estimated TOC content of the samples. The value obtained for each sample was the average of at least three satisfactory injections in terms of the coefficient of variation (≤ 2%). Total phosphorus concentrations were obtained by persulfate oxidation [29]. The concentrations of heavy metals (Pb, Cu, Cr, Zn, and Ni) and as were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Thermo Fisher scientific X series 2). Cd and Hg were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Thermo Fisher scientific X series 2).

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Sediment Analysis

The sediment grain size was measured by wet sieving and pipette analysis as described by Hsieh (1995). The samples were transferred to the laboratory and frozen (~-20°C) until analysis. Freeze-dried sediment samples were first heated at a relatively low temperature (60°C), after 2-3 treatments with 2 N HCl to remove inorganic carbon. TOC concentrations were determined using a PerkinElmer Series II CHNS/O analyzer, Model 2400. Total Phosphate was obtained after the sample ignition at 550 °C for 12 hours. Ashes were digested by HCl 1.0 M under stirring.

Heavy metal samples were placed into acid-washed plastic bags and transported to the laboratory where they were wet-sieved, and fractions < 0.063 mm analyzed for geochemical parameters. The digestion method to extract heavy metals was based on the USEPA Method 3051A [30,31]. 0.5-g dry weight (dw) were digested with 10 mL of HNO_3 in a Microwave Sample Preparation System (Model 1000, CEM Corp, Matthews, NC). Acidified sediment extracts were filtered through a Whatman 41 filter paper, diluted to 50 mL with distilled deionized water (ddw), and stored in 60 mL polypropylene Nalgene bottles. Digestion for Hg determination was based on the USEPA Method 7471 A [30].

Briefly, about 1 g dw equivalent of each sample was digested with 5 mL H2SO4 and 2.5 mL HNO3. Samples were placed in a water bath at a temperature of 95 °C for two minutes. When samples achieved room temperature, 25 mL of ddw and 40 mL of 5 % w/v $KMnO_4$ were added. Samples were placed back in the water bath for one hour. Digested samples were diluted to 100 mL with ddw and discolored with 10 mL of a sodium chloride-hydroxylamine sulfate solution. The heavy metals (Pb, Cu, As, Cr, Ni, Zn and Ni) concentrations of the solutions were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima, 2000DV), and Cd and Hg were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Thermo Fisher Scientific X series 2)

For quality control, reagent blanks, standard reference materials (GBW07333), and sample replicates were inserted in the analysis. All reagents were ultrapure and glassware/plastic ware/filters cleaned according to the method of Harrison and Laxen (1980). The result showed that there was no sign of contamination in the analysis and all the relative standard deviations of the replicate samples were < 10 %. The recovery rates for the heavy metals in the GBW07333 standard were higher than 82%. Mean recoveries were as follows: Pb, 92.0 %; Cu, 95 %; Cd, 82 %, As, 78 %, Cr, 89.0 %; Ni, 85 %; Zn, 84 % and Hg, 92 %. The detection limits of the method are respectively: As, 1 mg Kg^{-1}; Cd, 0.1 mg Kg^{-1}; Pb, 0.4 mg Kg^{-1}; Cu, 0.1 mg Kg^{-1}; Cr, 0.1 mg Kg^{-1}; Hg, 0.02 mg Kg^{-1}; Ni, 0.4 mg Kg^{-1} and Zn, 0.4mg Kg^{-1}.

The sediment properties and total metal concentrations from different sampling stations were compared using multivariate analysis of variance (ANOVA) and Tukey test followed by a Pearson significant correlation test. Normality of the data was tested with the Shapiro-Wilk test prior to analysis. Finally, the assessment of sediment elements enrichment was carried out through the calculation of the geo accumulation index (*Igeo*). Igeo was originally used in bottom sediments by Muller [32] enabling the contamination assessment by comparing the current levels of metal concentrations and the original preindustrial concentrations in the soils. This index is computed by the following equation:

$$Igeo = \log 2[\frac{Cn}{1.5Bn}]$$

where:

Cn = Measured concentration of the element in the tested sediment

Bn = Geochemical background value of the element in fossil argillaceous sediment.

The present work considered the values reached by Rudnick & Gao [33]. The constant 1.5 is introduced to minimize the effect of possible variations in the background values that may be attributed to lithologic variations in the sediments. The following interpretation for the Igeo is given [32,34]: Igeo< 0 = practically unpolluted; 0 <Igeo< 1 = unpolluted to moderated polluted; 1 <Igeo< 2 = moderately polluted, 2<Igeo< 3 =moderately to strongly polluted; 3<Igeo<4 = strongly polluted; 4<Igeo<5 = strongly to extremely polluted; and Igeo> 5 = extremely polluted. In this study, we used the Igeo index using grain fraction < 0.063mm according to González-Macías et al [25].

Results and Discussion

Water

The physicochemical conditions of surface and bottom water in the São Marco Bay were recorded from August/2017 to September/2018, showing temperature variation ranging from 24.9 to 29.6°C and the highest and the lowest values were recorded in February (rainy season). In general, in the present study, temperatures at the bottom and surface appeared to be similar, suggesting a negligible thermal stratification in the water column (Figure 3). The ANOVA test did not confirm the water column thermal stratification to be significant ($p > 0.05$).

On the other hand, temperature can promote direct impacts on fauna and flora physiological processes involving oxygen consumption/production balance. Also, temperature can stimulate planktonic and benthic respiration rates [35]. It is assumed that primary production is also enhanced in the summer in many temperate estuarine zones [36], while an accumulation of phytoplankton biomass can result in bottom-water oxygen depletion [37]. Temperatures recorded in the August campaign were significantly lower than in the other campaigns (ANOVA: $p < 0.05$). Rodrigues et al. [38] recorded similar thermal patterns during two years of monitoring in areas adjacent to the present study site.

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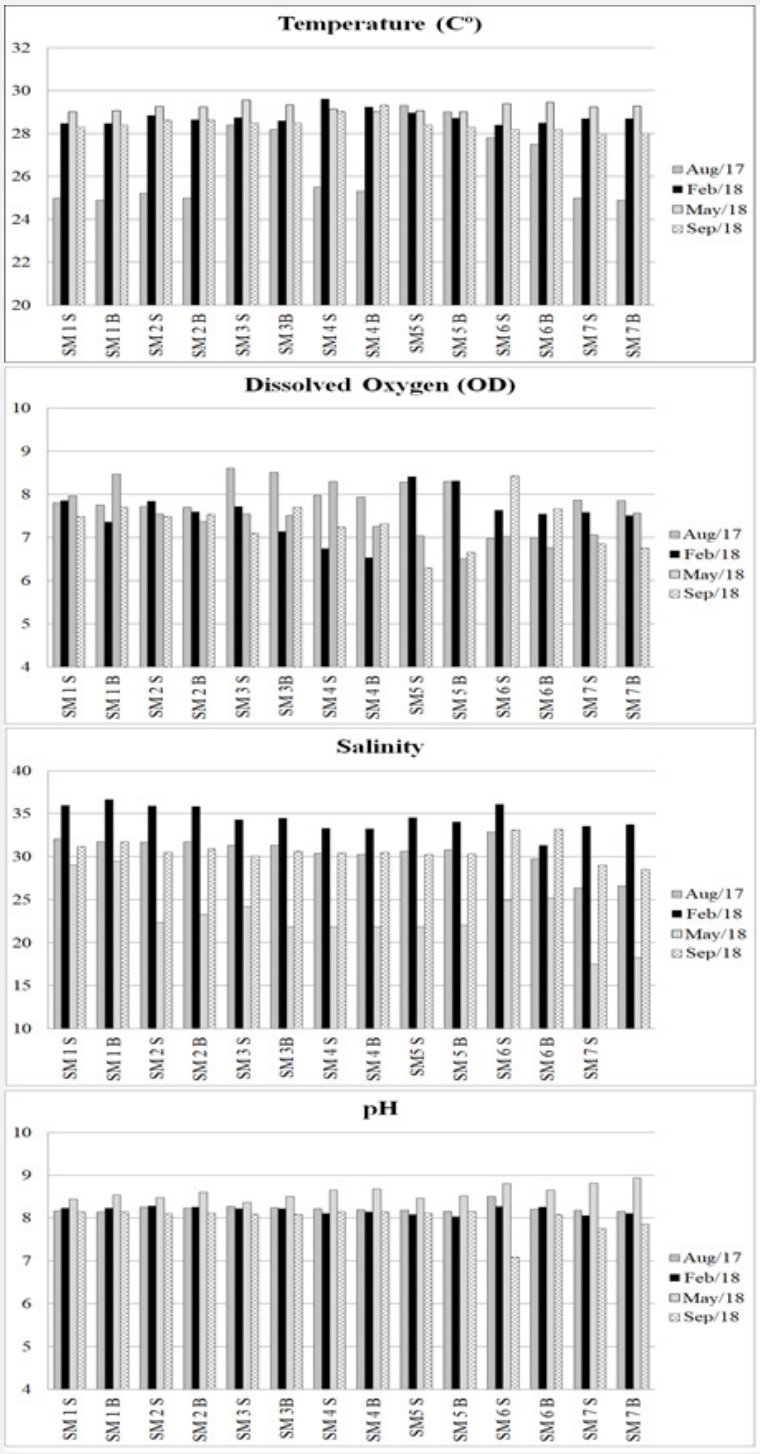

Figure 3: Water column physicochemical results.

The anthropogenic acidification of estuarine water can cause several negative impacts on primary and secondary producers. Additionally, because of the high levels of some ions, like bicarbonate and calcium, seawater presents significant buffering capacity against pH changes [31]. In the open ocean, seawater typically varies between 7.8 to 8.4. In coastal areas such estuaries, on the other hand, pHs can reach considerably lower values (7 into strongly acidic conditions). In the present study, the recorded

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pH values showed to be predominantly basic, suggesting the influence of the open sea carbonate system [39], varying between 7.09 in September to 8.94 in May (Figure 3).

According to the ANOVA test, no significant statistical variation was found between sampling depths ($p>0.05$), suggesting the predominance of seawater influence. González-Gorbeña et al. [25] confirmed the significant power of tidal currents in the study site, suggesting tides as the most important local energy component. This feature may interfere considerably with the quality of the water, promoting turbulent mixing and not allowing the stratification of the water column. Estuaries tends to exhibit significant spatial and temporal variation in dissolved oxygen levels across the ecosystem [37]. Within this context, high oxygen consumption rates can be due to direct organic discharges from the watershed or can be caused by phytoplankton blooms (autochthonous organic matter production) fed by inorganic nutrient loadings [40].

Additionally, it is now discussed that global warming may also result in changes in the dissolved oxygen content of coastal and estuarine waters [41]. The present study recorded levels of dissolved oxygen varying between 6.3 to 8.6 mg L^{-1}, suggesting a relative intense oxygenation of the environment, because of the influence of the oceanic water into the system (Figure 3). Rodrigues et al. [38] reported mean levels of oxygen in the two mangroves in the vicinity of the study area, varying around 4 mg L^{-1}, confirming the good oxygenation of the area, even in the mangrove areas. Cavalcanti et al. [42], on the other hand, recorded dissolved oxygen varying between 3.08 mg L^{-1} to 6.5 mg L^{-1}, highlighting a seasonal pattern with significant differences between the rainy and the dry seasons, with higher values observed in the dry season and ebb tide.

The relatively high levels of oxygen can be attributed to the peculiar characteristics of São Marco Bay, since this bay is dominated by a macro tide regime where wind force also develops continuous vertical mixing of the water column, allowing the translocation of oxygen- saturated water and preventing proximate coastal water bodies from eutrophication since macrotidal currents decrease the response of primary production to enhanced nutrient inputs [43]. Salinity plays a crucial role and defines structural and functional dynamics of aquatic biota in estuarine environment [44]. As a result of the mixing of oceanic and continental waters, estuaries tend to have large salinity variations, both vertically and spatially [44].

Mainly, because of the estuarine mixture, heavy metals in different forms are influenced by various processes whose flocculation is one of these reactions [45], transferring heavy metals from soluble forms to particulate fraction. Our results varied between 17.5 in May and 36.6 in February, suggesting the alternation between continental and oceanic water presence (Figure 3). Salinity may vary daily with tidal cycles, or episodically due to rain events. ANOVA statistical analysis, on the other hand, did not show any significant variation between sampling stations or depths ($p>0.05$). Seasonal evaluation, on the other hand, showed significant differences for all the physical chemical parameters among different campaigns, suggesting an important climatological influence in the estuarine water dynamics ($p<0.05$).

According to Middelburg and Soetaert [46], in the water-sediment interface, the stratification of biogeochemical processes corresponds to a vertical distribution of the electron-acceptor. The same authors argue that the processes that govern the fate of these substances in the sediment result from the complex interactions with the biogeochemical cycles of major redox and biogenic elements such as C, N, O, P and Si. So, in the present study, water oxidation–reduction potential varied between 124.8 and 239.2 (Figure 4), confirming an oxidant environment. In the sediment, on the other hand, results presented only negative values (between -90 and -155) suggesting a hypoxic environment. The sediment data can be explained because of the limited oxygen percolation horizon in sediments, varying between 1 mm (in fine muddy grain size) to a few cm (in coarser sandy sediments) [47]. Additionally, the organic matter is degraded by heterotrophic bacteria or respired and mineralized [48] stimulating the oxygen depletion rates [49], resulting in hypoxic or anoxic conditions and negative redox patterns.

The total phosphorus concentrations, varied between 0.07 and 26.40 mg L^{-1}, presenting values higher than environments such as Guanabara Bay [50]. The concentrations of heavy metals in the water samples are shown in Figure 5. Hg, Ni, As, Pb, and Cd were below the detection limits, suggesting no anthropogenic source for these metals in the studied area. Concentration of Cu and Cr ranged between n.d. (not detected) – 3.95 mg L-1 and 0.35 – 1.36mg 268 L^{-1} respectively (Figure 5 and Table 1). Zn had its highest concentration of 3.36 mg L^{-1} in August and its lowest concentration of 0.03 mg L^{-1} in February. Such results showed a significant difference among seasons, suggesting the solubilization of water heavy metals during rainy season and highlighting the local climatology as an important variable in the geochemical dynamics of the estuarine water. Carvalho et al. [51] determined the concentrations of Cu, Zn, Pb, and Cd in the mussel *Mytella falcata* from the Bacanga River estuary, located in the same bay. These authors suggested that Zn presented slightly higher values than the maximum ones established by the Brazilian government, reinforcing the idea of the bioavailability of this metal.

Sediment

In the present study, the total organic carbon levels in the sediment varied between 0.54 and 0.91 % (Table 2). Other studies developed in the Brazilian coast showed very similar levels [52,53]. The highest polluted areas in Brazil such as Guanabara Bay and Sepetiba Bay, on the other hand, present higher values (Table 2). Previous studies on sediment and water contamination in the studied area showed significantly higher levels of mercury and chrome, which confirms that São Marcos Bay is a site with

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high exposure risks for some contaminants [28]. The present study did not show the same pattern, where the concentration of Hg was below the detection limits of the method, probably because the samples were not collected in the same place, where sedimentological characteristics may differ.

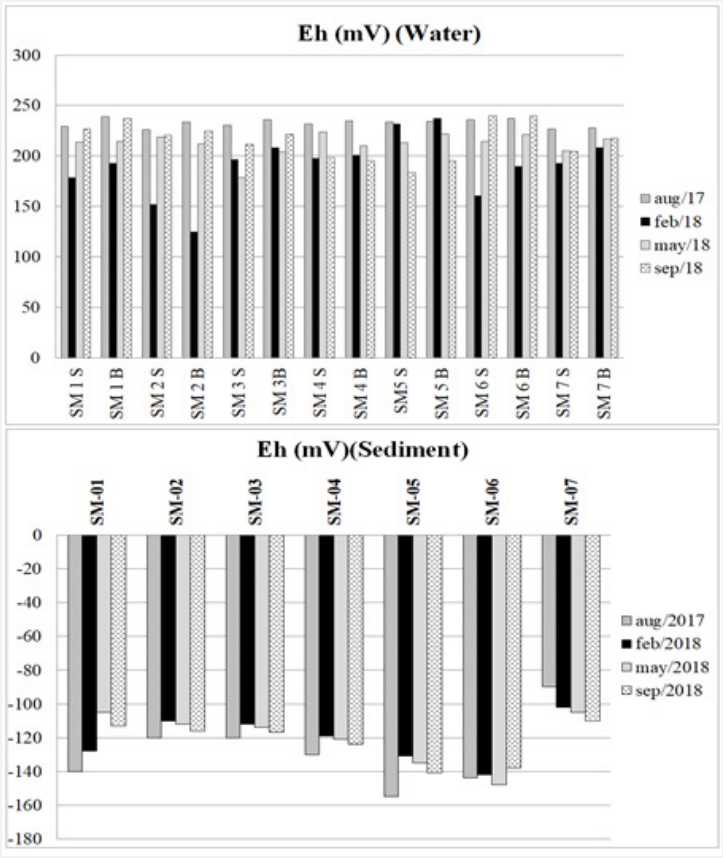

Figure 4: Eh Results.

Table 1. Water analysis results.

		Total Phosphorus (mg L^{-1})				Copper (mg L^{-1})				Chrome (mg L^{-1})				Zinc (mg L^{-1})			
	Date	Aug-2017	Feb-2018	May-2018	Sep-2018	Aug-2017	Feb-2018	May-2018	Sep-2018	Aug-2017	Feb-2018	May-2018	Sep-2018	Aug-2017	Feb-2018	May-2018	Sep-2018
SM-01	Surface Water	20.3	22.5	21.5	1.5	3.03	0.83	0.88	0.91	1.13	0.57	0.5	0.62	2.71	1.44	1.39	1.5
	Bottom Water	26.4	15.85	14.9	2.01	3.95	0.95	0.75	0.99	1.36	0.7	0.66	0.73	3.36	1.9	1.85	2.01
SM-02	Surface Water	18.7	25	19.15	0.07	2.84	0.4	2.12	0.46	0.95	0.81	0.77	0.86	2.58	0.03	0.58	0.07
	Bottom Water	25.2	17.25	14.1	0.13	3.73	2.94	0.34	2.99	1.19	0.96	0.92	1	3.24	0.08	0.58	0.13
SM-03	Surface Water	18.1	25.3	20.3	2.05	2.78	1.77	1.73	1.65	0.9	0.85	0.82	0.75	2.52	2.2	1.8	2.05
	Bottom Water	24.8	19.2	14.9	2.9	3.67	2.57	2.29	2.44	1.12	1	0.93	0.9	3.17	3	2.76	2.9

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SM-04	Surface Water	19.3	21.3	20.05	1.52	2.91	1.62	1.54	1.69	1.02	0.6	0.54	0.65	2.62	1.44	1.35	1.52
	Bottom Water	25.6	13	10.5	1.8	3.77	1.63	0.58	1.74	1.24	0.73	0.69	0.77	3.28	1.7	1.61	1.8
SM-05	Surface Water	19.75	20.45	18.9	1.6	2.95	1.63	1.58	1.7	1.07	0.7	0.67	0.8	2.67	1.55	1.5	1.6
	Bottom Water	25.9	24	15.3	1.99	3.82	2.28	2.09	2.35	1.29	0.86	0.83	0.94	3.31	1.9	1.83	1.99
SM-06	Surface Water	17.45	18.3	18.2	1.54	2.72	1.22	1.15	1.4	0.81	0.54	0.49	0.62	2.44	1.46	1.36	1.54
	Bottom Water	24.1	14.55	12.7	1.8	3.62	2.33	2.02	2.45	1.06	0.7	0.66	0.76	3.11	1.71	1.65	1.8
SM-07	Surface	19.8	15.95	14.9	1.21	2.97	1.08	0.96	1.2	1.08	0.39	0.35	0.6	2.65	0.99	0.92	1.21
	Bottom	25.9	12.3	9.3	1.36	3.83	0.2	0	0.4	1.31	0.47	0.44	0.69	3.33	1.1	0.97	1.36

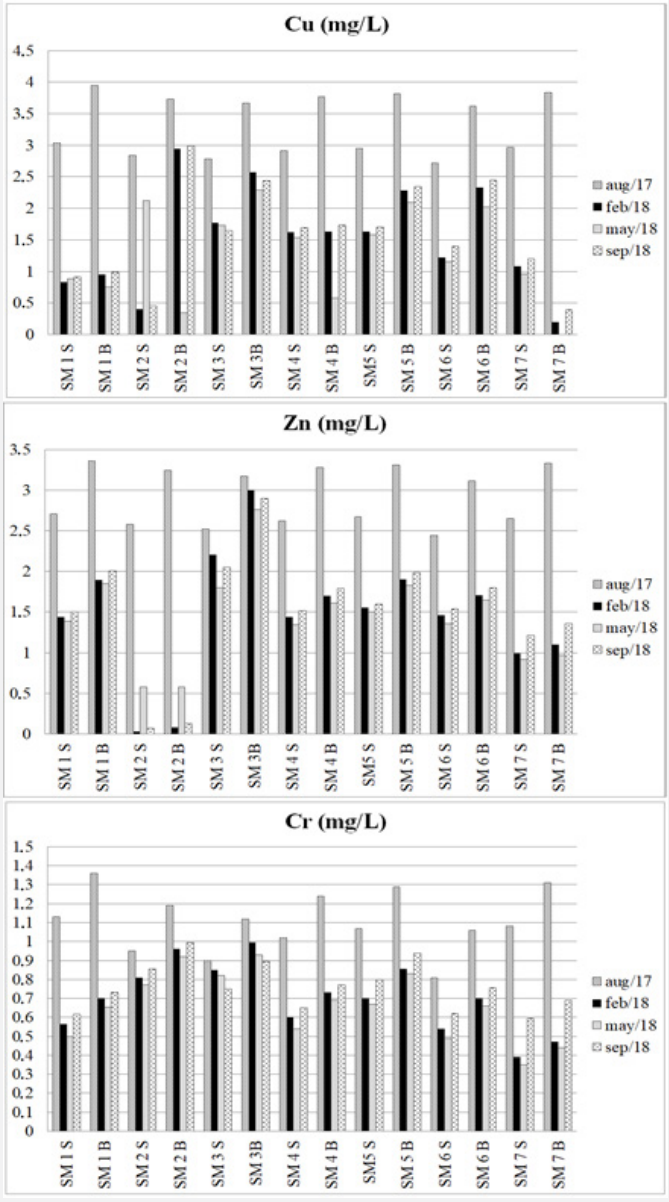

Figure 5: Seasonal variation of Heavy Metals levels in water.

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Table 2: Total Organic Carbon sediment content along Brazilian coast.

Author	Study Site	Total Organic Carbon Content (%)
Present Study	Harbor area São Marco Bay	0.54–0.91
Ribeiro et al., 2008	Guanabara Bay	0.82–10.60
Martins et al., 2018	NE Sector of Guanabara Bay	1.0–6.1
Vilela et al., 2003	Guanabara Bay	0.05–6.13
Rodrigues et al., 2017	Sepetiba Bay	0.06–4.79
Costa et al., 2011	Todos os Santos Bay	0.95–2.7
Venturini et al., 2004	Todos os Santos Bay	0.12–3.5
Perina et al., 2018	São Vicente Estuarine System	0.8–8.6
Burone et al., 2003	Ubatuba Bay	0.10–2.86
Alexandre et al., 2006	Babitonga Bay	0.67–4.64

Many researchers suggested the direct relationship between levels of pollutants and the availability of fine sediments [54-56]. This process is explained adsorption, co-precipitation, and complexing reactions of metals on particle surfaces [57]. In the present study, results exposed the dominance of fine sand (Figure 6), suggesting the influence of macrotidal currents typical in São Marco Bay [42] on preventing mud accumulation. Furthermore, according to Manning et al. [58] tidal currents are very important for sediment distribution in tide-dominated ecosystems. Low levels of organic matter were recorded (between 0.54 and 0.91 %), confirming that low organic matter concentration results for sediments with coarser grain size particles [59-61]. Additionally, a Spearman test revealed no significant correlation between grain size and organic carbon content.

Heavy metals levels showed relatively low concentrations in sediments (Table 3). The concentrations of Hg and Cd in the sediment showed values below the method detection limit. The concentration of Pb, on the other hand, ranged from 0.49 mg Kg^{-1} in February to 1.63 mg Kg^{-1} in May. A lower concentration of Pb was recorded in the sampling stations SM-01 and SM-02. Surface sediments concentration of Cu ranged from 1.38 mg Kg^{-1} in February to 1.95 mg Kg^{-1} in February. For the sediment's Zn concentration, the values ranged from 2.17mg Kg^{-1} in May to3.92 mg Kg^{-1} in October. Seasonal data show that during the study period the sediments' Zn content was lower in rainy season (152.76 ± 46.44 mg Kg^{-1}) compared to the values of dry (198.70 ± 86.09 mg Kg^{-1}) and rainy (211.27 ± 98.46 mg Kg^{-1}) seasons. Cr and Ni varied between 1.65–3.56 mg Kg^{-1} and 1.38–1.92 mg Kg^{-1} respectively. Finally, as concentrations varied between, 1.12 and 1.84 mg Kg^{-1}.

Table 3: Sediment analysis results.

Parameter	Date	SM-01	SM-02	SM-03	SM-04	SM-05	SM-06	SM-07
Nitrogen (mg Kg^{-1})	August/2017	47	54	49.6	61.2	63.4	54.8	69.8
	February/2018	44	63	43.5	58.3	59.7	56.5	71.2
	May/2018	62	58	54.1	63.1	64.12	48.4	74.2
	September/2018	74	62	73.2	58.72	81.12	62.13	69.42
Phosphorus (mg Kg^{-1})	August/2017	408	400	412	419	402	424	432
	February/2018	398	401	392	388	389	412	445
	May/2018	411	399	404	414	396	427	418
	September/2018	395	405	419	403	417	414	406
TOC (%)	August/2017	0.67	0.62	0.7	0.73	0.65	0.76	0.79
	February/2018	0.59	0.58	0.64	0.6	0.61	0.78	0.81
	May/2018	0.72	0.64	0.72	0.54	0.72	0.84	0.67
	September/2018	0.84	0.76	0.83	0.65	0.83	0.91	0.79

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Copper (mg Kg^{-1})	August/2017	0.57	0.64	1.563	1.611	1.604	1.592	1.624
	February/2018	0.49	0.68	1.549	1.596	1.598	1.588	1.598
	May/2018	0.63	0.49	1.623	1.614	1.631	1.496	1.477
	September/2018	0.59	0.52	1.458	1.712	1.582	1.532	1.511
Chrome (mg Kg^{-1})	August/2017	2.239	2.414	3.32	3.46	3.55	3.41	3.56
	February/2018	2.114	2.112	3.26	3.39	3.38	3.35	3.48
	May/2018	1.802	2.063	3.12	3.56	3.19	3.42	3.27
	September/2018	1.651	1.894	2.97	2.92	3.03	3.28	3.19
Nickel (mg Kg^{-1})	August/2017	1.66	1.75	1.68	1.72	1.79	1.73	1.79
	February/2018	1.54	1.52	1.55	1.64	1.72	1.69	1.67
	May/2018	1.63	1.39	1.38	1.75	1.84	1.6	1.67
	September/2018	1.47	1.77	1.49	1.84	1.92	1.57	1.72
Zinc (mg Kg^{-1})	August/2017	2.62	2.73	3.6	3.8	3.8	3.55	3.92
	February/2018	2.39	2.48	3.3	3.6	3.6	3.48	3.85
	May/2018	2.24	2.17	2.98	3.23	3.2	3.33	3.72
	September/2018	2.41	2.29	3.09	3.02	3.11	3.44	3.54
Arsenic (mg Kg^{-1})	August/2017	2.62	2.73	3.6	3.8	3.8	3.55	3.92
	February/2018	2.39	2.48	3.3	3.6	3.6	3.48	3.85
	May/2018	2.24	2.17	2.98	3.23	3.2	3.33	3.72
	September/2018	2.41	2.29	3.09	3.02	3.11	3.44	3.54

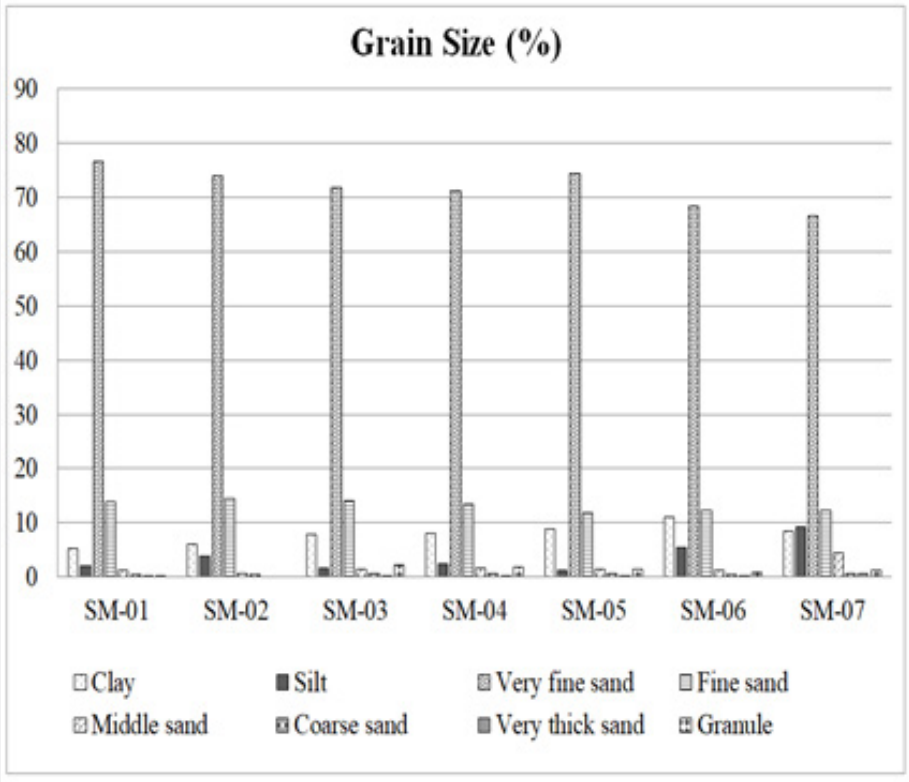

Figure 6: Grain size results.

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In the present study, Canadian sediment quality guidelines (Threshold Effect Level - TEL and Probable Effect Level - PEL) [51] and the average concentrations of heavy metal in UCC are used to compare with heavy metals concentrations in surface sediments [62] (Table 4). Although they were developed for freshwater environments, the limits suggested by MacDonald et al. [51] can be considered conservative, as the precipitates formed in the sea water have extremely low solubilities at surface water pHs (8.1-8.3) [63], as recorded in the present study. Heavy metals concentrations in sediments recorded in the present study suggest no risk to the local biotic community [64-70].

Concerning the statistical treatment (ANOVA), no significant differences were found among surveys. The significant correlation between heavy metals suggested the same onshore origin or similar responses in relation to environmental parameters [71-78] (Table 5). The heavy metal concentrations presented relatively low levels in the sediments. All the Igeo results confirmed the sediment from harbor site as "unpolluted to moderated polluted" for all the studied metals since the index remained between 0.59 and 0.76 [78-85] (Table 6).

Table 4: Concentrations of heavy metals in sediment in estuaries in Brazil , global average, TEL and PEL.

Local:	Pb (mg Kg^{-1}) Min-Max		As (mg Kg^{-1}) Min-Max		Cd (mg Kg^{-1}) Min-Max		Zn (mg Kg^{-1}) Min-Max		Cr (mg Kg^{-1}1) Min-Max		Cu (mg Kg^{-1}) Min-Max		Ni (mg Kg^{-1}) Min-Max	
São Marcos Bay (present study)	0.49	1.71	1.12	1.84	<0.15		2.17	3.92	1.651	3.56	1.38	1.95	1.38	1.92
Ribeira Bay[a]	0.02	0.14	-		<0.002		-0.26	164	-		0.03	0.23	<0.05	0.36
Todos os Santos Bay[b]	0.16	107	-		0.003	5.56	0.44	332	-		0.1	429	-	
Sepetiba Bay[c]	6.5	85.7	-		0.5	8.7	18.1	795	23.9		2.1	166	-	
Guanabara Bay[d]	3.6	110	-		0.02	2.6	78	707	3.5		2.4	300	-	
Gobal averag[ee](Soil)	19		1.4		0.03		95		75.6		33		52	
TEL[f]	35		5.9		0.6		123		37.3		0.6		18	
PEL[f]	91.3		17		3.5		315		90		3.5		35.9	

Chiappettaet et al. 2016[a]; CRA 2004[b]; Lacerdaet et al. 1987 and Marinset al. 1998[c]; Fonseca et al. 2013[d]; Wedepohl 1995[e]; MacDonald et al 2000[f].

Table 5: Pearson Test Results.

	Temp	pH	Turbidity	Dissolved Oxygen	Salinity	Condutibility	Eh	Cu	Cr	P	Fe	Mn	Zn
Temp	1												
pH	0.25	1											
Turbidity	0.22	0.07	1										
Dissolved Oxygen	-0.19	-0.14	-0.35	1									
Salinity	-0.18	-0.62	-0.28	0.21	1								
Condutivity	-0.2	**-0.56***	-0.33	0.17	**0.93***	1							
Eh	-0.35	-0.1	-0.04	0.28	-0.19	-0.22	1						
Cu	**-0.58***	-0.16	-0.25	0.22	0.15	0.24	0.36	1					
Cr	**-0.62***	-0.18	-0.13	0.24	0.16	0.21	0.32	**0.83***	1				
P	-0.28	0.28	**-0.55***	0.38	0.05	0.17	0.02	0.42	0.36	1			
Fe	-0.45	-0.08	-0.27	0.07	-0.01	0.05	0.36	**0.70***	**0.68***	0.37	1		
Mn	**-0.64***	-0.12	-0.23	0.3	0.16	0.19	0.44	**0.84***	**0.90***	0.45	**0.77***	1	
Zn	**-0.56***	-0.11	-0.25	0.22	0.1	0.12	**0.51**	**0.71***	**0.64***	0.39	**0.77***	**0.88***	1

Bold* = significant correlation ($p<0.05$)

Table 6: Annual average of Geo accumulation Index (I_{geo}) results.

	Zn	Cu	Ni	Cr	Pb	As
SM 1	0.62	0.63	0.62	0.62	0.63	0.72
SM 2	0.62	0.64	0.62	0.62	0.63	0.74

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SM 3	0.59	0.64	0.62	0.63	0.69	0.75
SM 4	0.64	0.64	0.62	0.64	0.7	0.76
SM 5	0.64	0.64	0.62	0.64	0.7	0.76
SM 6	0.64	0.64	0.62	0.62	0.69	0.75
SM 7	0.63	0.64	0.61	0.64	0.69	0.76

Conclusion

The region was characterized by high hydrodynamics, with an important influence of oceanic waters, which promotes oxygenation and high pH, and prevents water column stratification. São Marco estuarine waters presented strong physicochemical variations during the study, suggesting a significant climatological influence on the water chemistry. Despite the low concentrations of heavy metals in the sediment, high levels of metals were observed in the water. This aspect was confirmed by the sandy grain size found in the sediment samples collected and the low organic carbon concentrations, highlighting the importance of the currents that added to the proximity of the sampling stations to the open sea, the minor industrial and urban concentration in the study site as the main factors controlling the quality of the environmental conditions.

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