Environ Monit Assess (2019) 191: 552
https://doi.org/10.1007/s10661-019-7626-6

Carbon influence on metal distribution in sediment of Amazonian macrotidal estuaries of northeastern Brazil

Thays Thayanne Luz Santos · **Rozane Valente Marins** · **Francisco José da Silva Dias**

Received: 19 March 2019 / Accepted: 1 July 2019 / Published online: 9 August 2019

Abstract The present work aims to observe the spatial distribution of metals associated with carbon forms (fraction < 2 mm) in surface sediments of two macrotidal estuaries, São Marcos Bay and Anil River Estuary, which are located within the transition region between the Amazonian and the semi-arid northeast regions. Grain size, metal content (Al, Fe, Mn, Cu, Pb, Cr, Zn, and Ni), organic matter, and calcium carbonate content were determined. Grain size analyses showed the predominance of the sand-sized fraction < 2 mm due to the local hydrodynamic conditions. Anil River Estuary sediments exhibited high organic matter content due to both the mangrove outwelling and domestic sewage discharge. They also presented high calcium carbonate content as a result of abundant remnants of gastropod shells. Organic matter acted as the primary geochemical carrier for most metals in both estuaries, while calcium carbonate acted as the secondary carrier. Enrichment factors indicated Mn sediment contamination in São Marcos Bay and Fe, Pb, and Zn contamination in the Anil River Estuary. These results also suggest that São Marcos Bay is influenced by harbor activities, mostly ore shipment, whereas Anil River Estuary sediments are enriched in these metals as a result of domestic and hospital effluents reaching the urbanized drainage basin.

Keywords Geochemistry · Urbanization · Harbor activities · São Marcos Bay · Anil Estuary

T. T. L. Santos (✉)
Department of Oceanography and Limnology, Federal University of Maranhão, Av. dos Portugueses, 1966, Vila Bacanga, São Luís, MA 65080-805, Brazil
e-mail: thays_luzsantos@hotmail.com

T. T. L. Santos · R. V. Marins
Marine Science Institute/LABOMAR, Federal University of Ceará, Av. da Abolição, 3207, Meireles, Fortaleza, CE 60165-081, Brazil

R. V. Marins
e-mail: rmarins@ufc.br

F. J. da Silva Dias
Marine Science Institute/ICMar, Federal University of Maranhão, Av. dos Portugueses, 1966, Vila Bacanga, São Luís, MA 65080-805, Brazil
e-mail: geofranzedias@gmail.com

Introduction

Estuarine sediments are recognized as the largest repository of metals in aquatic environments, which may remain stored for long periods. Metals derived from natural enrichment processes and anthropogenic contamination are present in all depositional sequences of fluvial, estuarine, and continental sediments integrating these processes over the years, thus manifesting the increase of the anthropogenic activities over natural sources, mostly in coastal regions. In numerous studies, the distribution of metal contaminants in sediments is used as a reliable tool in the assessment of environmental pollution, as this approach allows for the determination of possible sources of pollution to the estuary (Meng et al. 2008; Marques et al. 2011).

The increase of metal content in estuarine sediment depends upon the deposition processes, which mostly occurs due to the increase of pH and organic matter content (Du Laing et al. 2008). Salinity and grain size can also affect these processes (Regnier and Wollast 1993; Nilin et al. 2013). Sedimentary carbon can be found in organic and inorganic forms, such as organic matter and calcium carbonate. Organic matter in estuarine sediments can originate from riverine particulate carbon (POC) and dissolved organic carbon (DOC), which flocculates or precipitates, resulting in particulate organic carbon and subsequent settlement onto the sediments (Biati et al. 2010). Mangroves in most tropical estuaries are a significant autochthonous source of organic matter to sediments. Calcium carbonate in tropical estuaries is mostly originated from the continental shelf and calcareous shell material from organisms. Whereas metal complexing with organic matter may vary from weakly to strongly bound, association with carbonates is generally a weak binding event that is susceptible to changes in temperature and pH (Costa et al. 2015; Nayak 2015). Therefore, mobility and bioavailability of metals in the estuarine environment strongly depends on metal binding to carbon substrates present in sediments.

The present study investigates metal-carbon associations in a region located between the Amazonian climate, with high river discharge of organic matter (Medeiros et al. 2015; Gonsior et al. 2016), and the semi-arid region, which is characterized by a carbonate domain in the continental shelf (Aguiar et al. 2007, 2014). These carbon forms can act as significant geochemical carriers of trace metals in the estuarine environment. Therefore, this work aims to identify how the carbon forms influence the geographical distribution of trace metals in two macrotidal estuaries from this region and if the presence of trace metals in the environment alters the sediment quality of the region based on the geochemical index.

Materials and methods

Environmental setting

São Marcos Bay and Anil River Estuary, located in the Maranhão coastal zone of Brazil (Fig. 1), are located in a transition region between the humid climate of the Amazon region and the semi-arid northeast and are governed by semidiurnal tides with macrotidal variation (7 m). Temperatures range from 26 to 28 °C, and annual precipitation exceeds 1,900 mm, which primarily occurs from January to June (El-Robrini et al. 2006; Costa et al. 2016). The region harbors the largest area of mangroves in Brazil, which covers an area of approximately 5,415 km^2 (Rodrigues et al. 2016).

São Marcos Bay receives water contribution mostly from the Mearim River drainage basin, with river discharge of 45.2 $m^3\ s^{-1}$ (González-Gorbeña et al. 2015). This region has a well-defined central channel that has depths of up to 97 m. The channel is used as a navigable waterway for the main harbor facilities. The harbor complex of São Luís consists of Itaqui and Alumar harbors, which have numerous small terminals for private companies and a 1,936-m-long wharf; the terminal depths vary between 9.5 and 19 m, depending on the tide, thus providing maneuverability to deep draft vessels (Diniz et al. 2014). São Marcos Bay exports millions of tons per year of iron ore and pellets, manganese, ferroalloys, and fertilizers, making it the harbor with the largest volume of cargo in Brazil. In addition to the ore shipments, the region has steel and aluminum mills, which represent the main economic driving force of the region (González-Gorbeña et al. 2015). The total human population of the basin represents 31.53% of the state total, with 2.1 million inhabitants.

The Anil River Estuary is mostly urbanized (65.2% of the total sub-basin area) and has a population of 250 thousand inhabitants, which represents 0.024% of the total inhabitants of the São Luís metropolitan area. Traditional fisheries and crab hunting in the mangroves are still important activities for the local population. However, increasing urbanization, including stilt house construction, mangrove deforestation and conversion, and domestic and hospital sewage discharge, that can change the environmental equilibrium and pollute the aquatic system have been observed.

Sampling and analytical procedures

Sample collections were carried out through two campaigns in São Marcos Bay (SMB), which occurred in August and December 2016, and two campaigns were performed in the Anil River Estuary (ARE), which

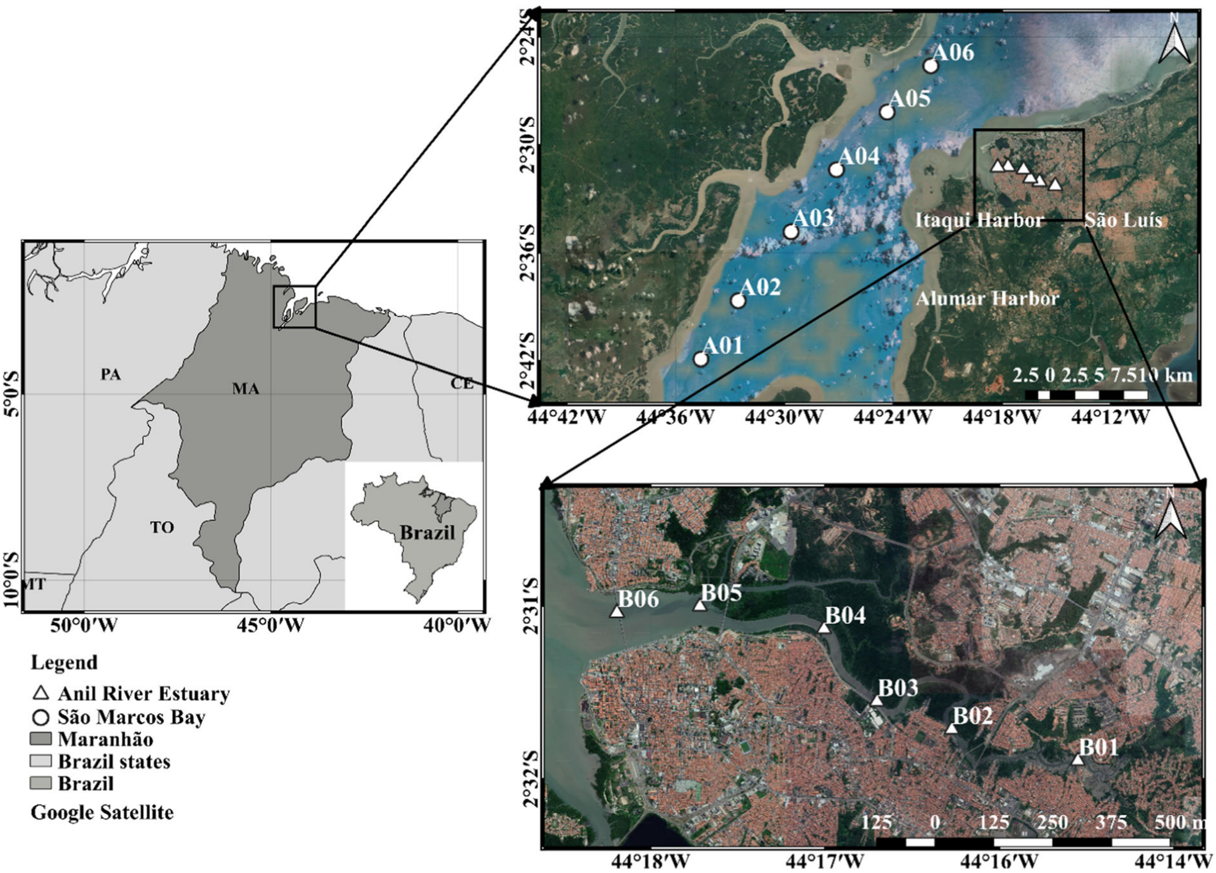

Fig. 1 Location map of 12 sampling sites in São Marcos Bay (SMB) (A01-A06) and in the Anil River Estuary (ARE) (B01-B06), in the coastal zone of Maranhão, Brazil

occurred in October and December 2016. During the four campaigns, duplicate sediment samples were collected from six points within reach of the areas. Surface sediment samples were collected using a Gibbs dredge. Two launches were made at each site, totaling 48 sediment samples. All samples were stored, refrigerated, and sent to the laboratory for analytical determinations. Sediment samples were oven-dried at 60 °C and sieved to obtain the sediment fraction < 2 mm. The grain sizes were classified according to Folk and Ward (1957). Total organic matter (OM) was determined following the loss-on-ignition method of Jolivet et al. (1998), and calcium carbonate ($CaCO_3$) content was determined according to Loring and Rantala (1992).

Metals were extracted from the < 2.0 mm grain size fraction with 50% aqua regia ($HCl:HNO_3$, 3:1) in a microwave oven, following the methodology described in Aguiar et al. (2007). All of the analyses were performed in duplicate ($n = 2$). Metal contents (Al, Fe, Mn, Cu, Pb, Cr, Zn, and Ni) were measured by a flame atomic absorption spectrometer (FAAS) (Shimadzu AA 6200). The equipment was previously calibrated with respective standard metal solutions. The precision and accuracy of the methodology was tested with Estuarine Sediment Reference Material NIST-1646a (National Institute of Standards & Technology). The recovery values of the extraction method for all metals were 48% for Al, 72% for Fe, 57% for Mn, 84% for Cu, 65% for Pb, 52% for Cr, 71% for Zn, and 71% for Ni. The detection limits (DLs) of the equipment were calculated for each metal by multiplying the estimated standard deviation between the axes (x, y) of the calibration curve by a factor of 3 then dividing by the sensitivity of the linear regression obtained from the calibration curve (Miller and Miller 2010).

To determine anomalous metal contents in sediments and potentially indicate anomalies from anthropogenic sources, enrichment factors (EFs) were used. The EF was determined by the following equation: $([Metal_{(i)}]/Al_{(i)})/([Metal_{(background)}]/Al_{(background)})$. Aluminum was used as a normalizer due to the correlation with fine fraction, low reactivity, and the nonexistence of a known metal background for the Maranhão coast. $Metal_{(i)}$ and $Al_{(i)}$ were the values of each sampling site. The $Metal_{(background)}$ and $Al_{(background)}$ values were considered the average content from all sampling sites. EF values were used to classify the sediment contamination as follows: no enrichment (EF < 1), minor enrichment (EF 1 < 3), moderate enrichment (EF 3 < 5), moderately severe enrichment (EF 5 < 10), severe enrichment (EF 10 < 25), very severe enrichment (EF 25 < 50), and extremely severe enrichment (EF > 50) (Aprile and Bouvy 2008; Taylor 1964). Metal content data were represented in isosurface plots through the open software package Ocean Data View (Schlitzer 2018). Student's *t* test with confidence interval of 95% ($p < 0.05$) was applied to compare the variables measured in different sample campaigns and between the estuaries (Duquesne et al. 2006). Spearman's rank-order correlation was used to observe the relationship among grain size, carbon forms, and trace metals ($p < 0.05$) for each environment between campaigns. Multivariate cluster analysis with Ward's method of applying the squared Euclidean distance was used to determine the similarity of measured variables along the estuaries between the campaigns.

Results

Particle size (grain size) analyses revealed the predominance of the fine sand fraction (< 2 mm) in the sediments, composing 92.44 to 99.58% of the total content. The fine-grained fraction < 63 μm (silt and clay) varied from 0.81 to 2.22% in both estuaries. The sediment grain size increased downstream in SMB and upstream in ARE, with no significant variation observed between the campaigns ($p > 0.05$). Most probably, the sediment grain variability reflects the hydrodynamics of the rivers. Sediments in the other sites in SMB were classified as medium sand. In ARE, B01, B02, and B03 sites presented medium sand classification, while B04 and B05 sites included fine sand in all campaigns. The B06 site ranged from very fine to fine sand from one campaign to another.

In general, the sediment samples from ARE were more enriched in OM and $CaCO_3$ contents than those of SMB. OM content in SMB ranged from 0.61 to 3.62%, with no significant variation between the campaigns ($p > 0.05$). The highest OM values were found in the A02 site for both campaigns. The values of OM in ARE varied between 0.93 and 16.53% (Fig. 2a, b). The OM levels decrease downstream, and there was also a drastic reduction of OM contents from the 1st to the 2nd campaign ($p < 0.05$), with maximum values observed in points B04 and B05 (near the mouth). The values of the $CaCO_3$ content varied from 1.02 to 1.74% in SMB and 0.60 to 7.57% in ARE, and both estuaries presented no significant variation ($p > 0.05$) in carbonate contents between the campaigns (Fig. 2c, d).

The metal content varied both between the estuaries and the campaigns, with average and range of 1.31% (0.08–7.37%) for Al, 1.07% (0.23–3.29%) for Fe, 263.44 μg g^{-1} (12.48–960.36 μg g^{-1}) for Mn, 4.69 μg g^{-1} (0.32–18.53 μg g^{-1}) for Cu, 6.33 μg g^{-1} (1.37–43.27 μg g^{-1}) for Pb, 10.33 μg g^{-1} (1.08–43.27 μg g^{-1}) for Cr, 19.06 μg g^{-1} (3.00–77.14 μg g^{-1}) for Zn, and 6.08 μg g^{-1} (0.60–33.32 μg g^{-1}) for Ni. Metal contents were higher in ARE than SMB when compared with the values of the metal analyzed for both campaigns.

In SMB, it was observed that site A02 presented the highest metal content compared to the other sites for both campaigns (Fig. 3). Mean metal contents followed the order of Al > Fe > Mn > Zn > Pb > Cr > Ni > Cu in both campaigns in SMB, and the *t* test indicated no significant variation for all metals between the two campaigns ($p > 0.05$).

Metal contents in ARE exhibited a decreasing spatial distribution downstream in both campaigns, with the highest values occurring from B01 to B04 sites (Fig. 4). ARE exhibited the order of Al > Fe > Mn > Zn > Pb > Cr > Ni > Cu during the 1st campaign and Fe > Al > Mn > Zn > Cr > Ni > Cu > Pb for the 2nd campaign. A change in the sediment composition was shown between these campaigns. The *t* test showed significant variation between the campaigns for Al, Mn, Cr, Zn, and Pb only ($p < 0.05$).

Enrichment factors in SMB showed only anomalies for Fe, Mn, Pb, and Zn in this estuary (Fig. 5a). Mn had the highest EF obtained during both campaigns in the entire estuary and showed moderately severe

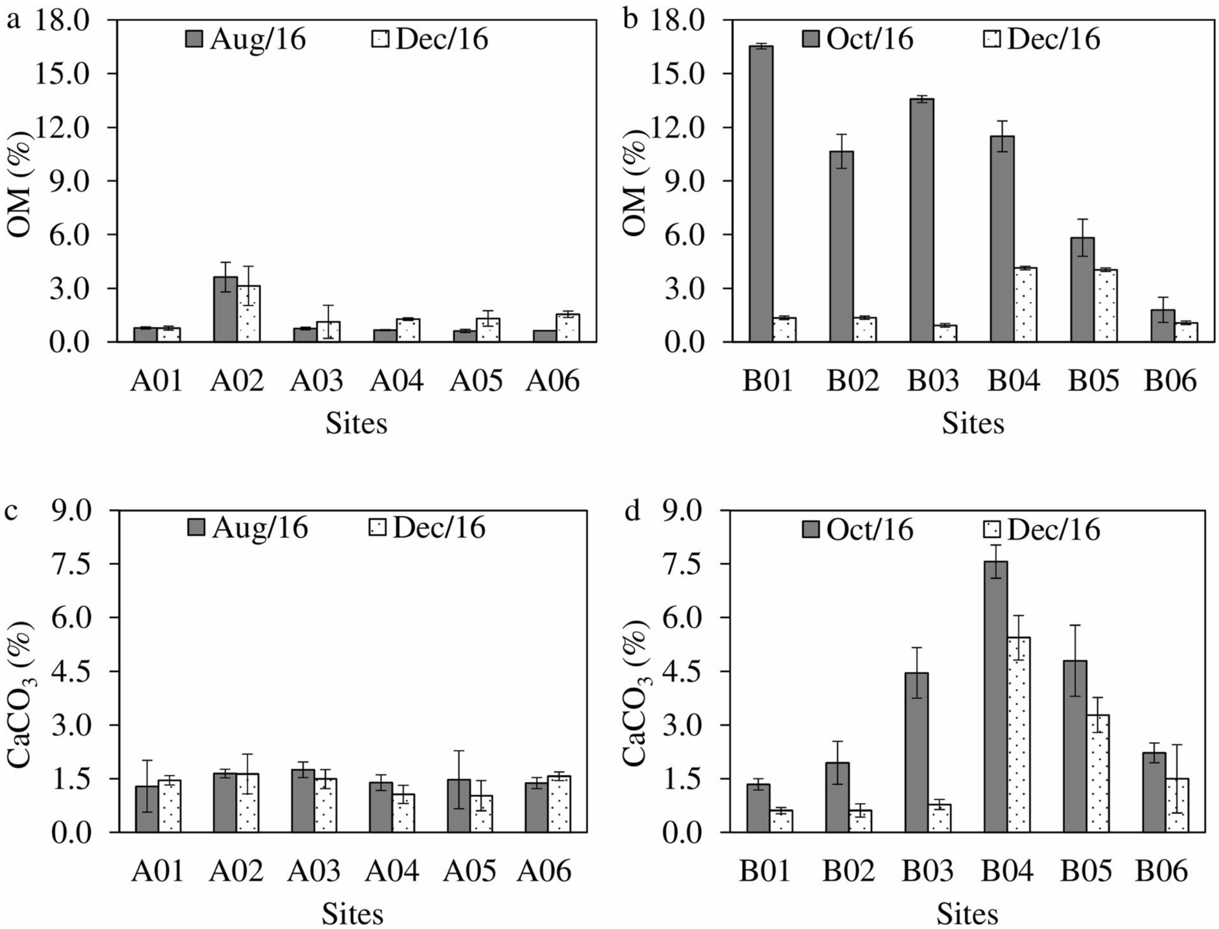

Fig. 2 Spatial and temporal distribution of the organic matter contents—OM (%) and calcium carbonate—$CaCO_3$ (%) of the sediments of collection points along **a** and **c** São Marcos Bay (SMB) (A01-A06) and **b** and **d** Anil River Estuary (ARE) (B01-B06) during the dry season

enrichment (EF 5 < 10). Fe, Pb, and Zn showed increasing EFs from the 1st to the 2nd campaign and demonstrated minor enrichment (EF 1 < 3). EFs in ARE were higher in the B01 to B04 sites during the 1st campaign but decreased over the 2nd campaign (Fig. 5b). EF anomalies in ARE were found for all metals. Fe, Pb, and Zn showed the highest EFs and presented moderately severe enrichment (EF 3 < 5) during the 1st campaign. Al, Cu, and Ni showed moderate enrichment (EF 3 < 5), while Mn and Cr demonstrated minor enrichment (EF 1 < 3).

Correlation analysis (n = 24, p < 0.05) in SMB showed a positive correlation among OM with Al, Pb, Ni, and Zn, while $CaCO_3$ was positively correlated with Pb and Cu. The ARE presented positive correlation among the OM with all trace metals, and $CaCO_3$ with Mn, Ni, and fine-grained fraction. In both environments, $CaCO_3$ was negatively correlated with the sand fraction (Table 1). The cluster analysis resulted in dendrograms for each estuary for the different carbon fractions studied. The dendrograms for SMB exhibited two similar groups for both campaigns. In the 1st campaign (Fig. 6a), the first group showed that $CaCO_3$ was the main geochemical carrier of Mn, Fe, and Zn in sediments and probably of the other metals, as they were from the same origin. The second group exhibited OM as the main geochemical carrier of Al and Cu. For the 2nd campaign, the dendrogram presented a change in sediment composition, showing that Pb was statistically correlated with $CaCO_3$ (Fig. 6b).

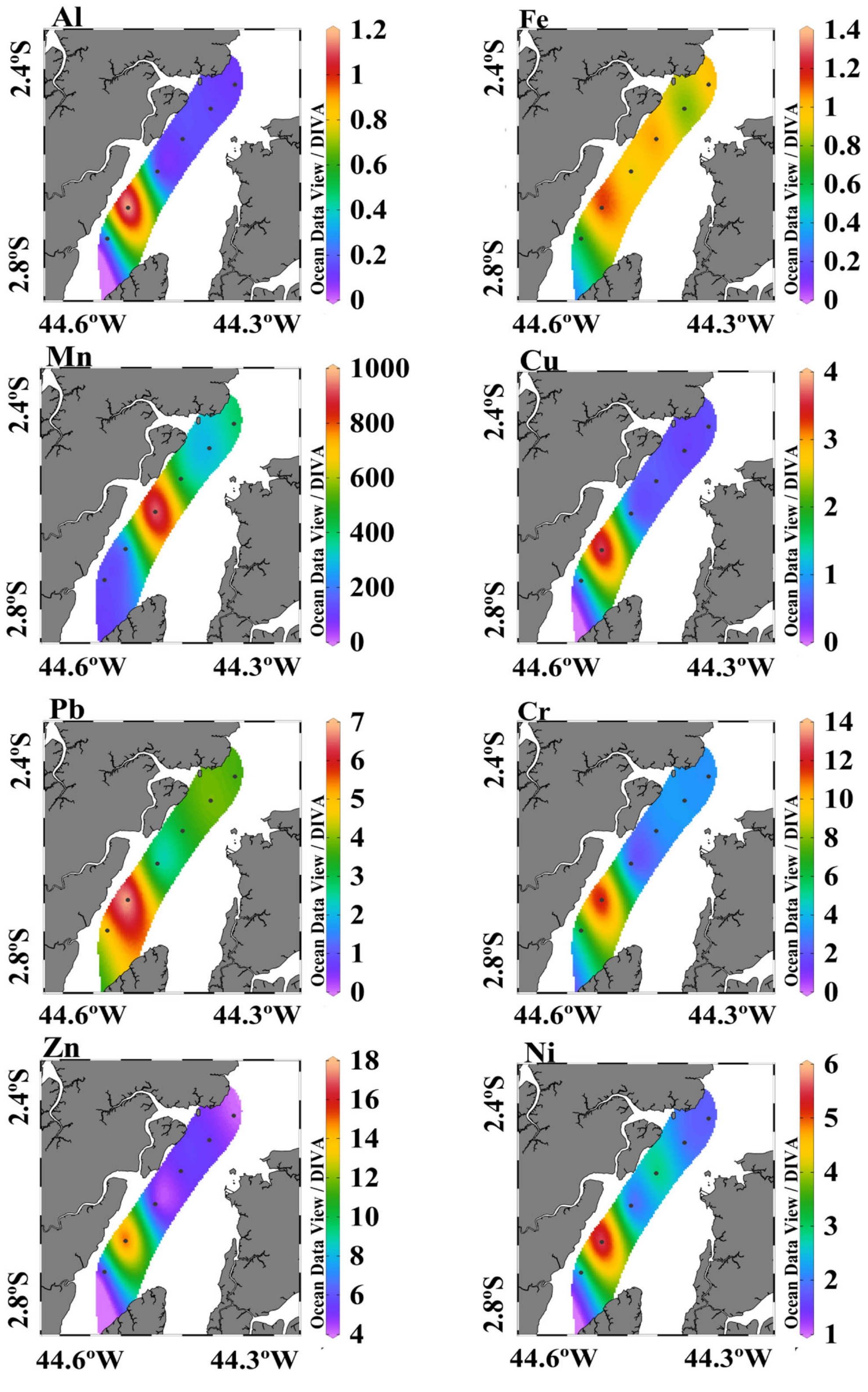

Fig. 3 *Metal concentrations in surface sediments of São Marcos Bay (SMB) between* **a** *August and* **b** *December of 2016*

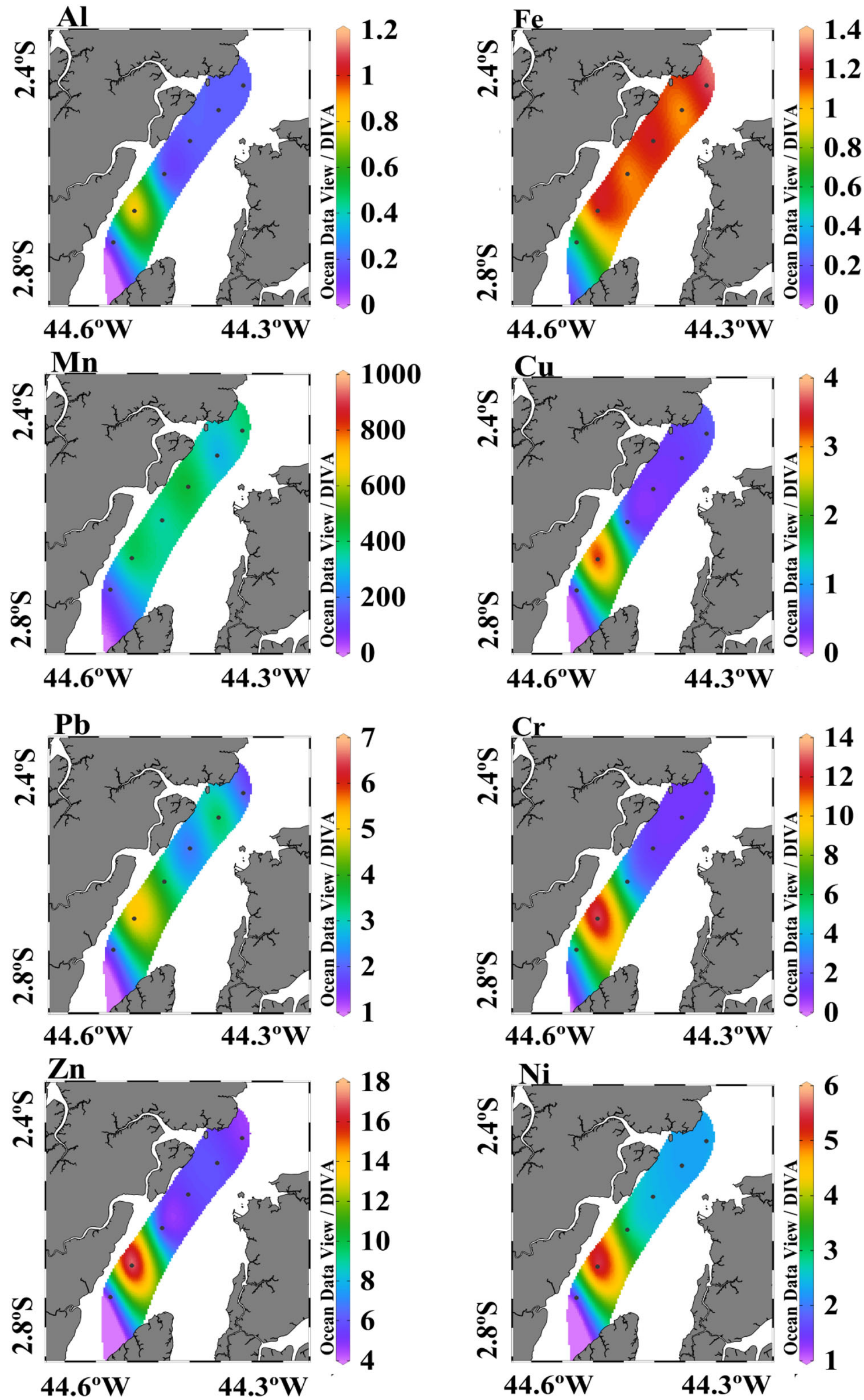

Fig. 3 (continued)

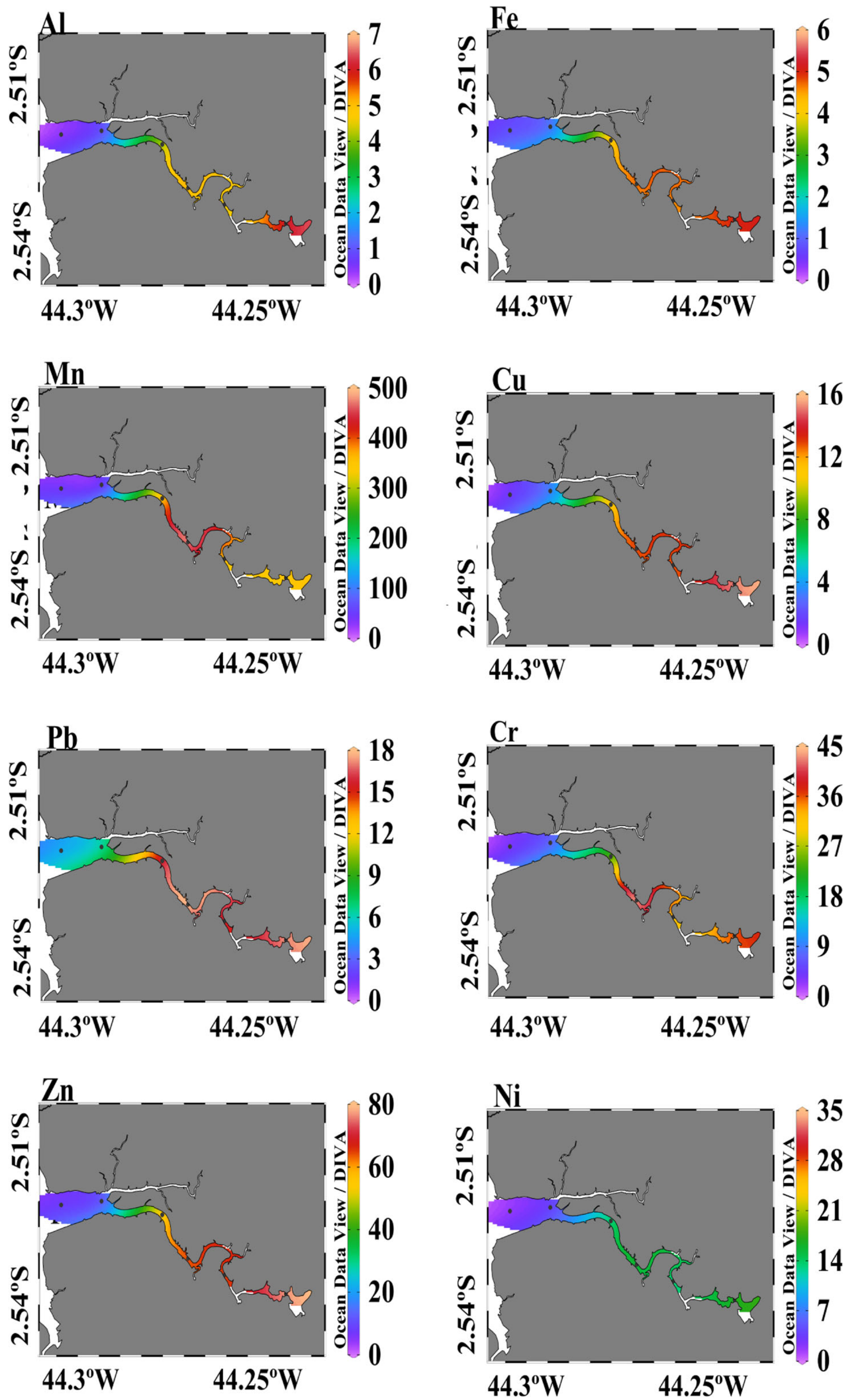

Fig. 4. Metal concentrations in surface sediments of Anil River Estuary between **a** October and **b** December of 2016

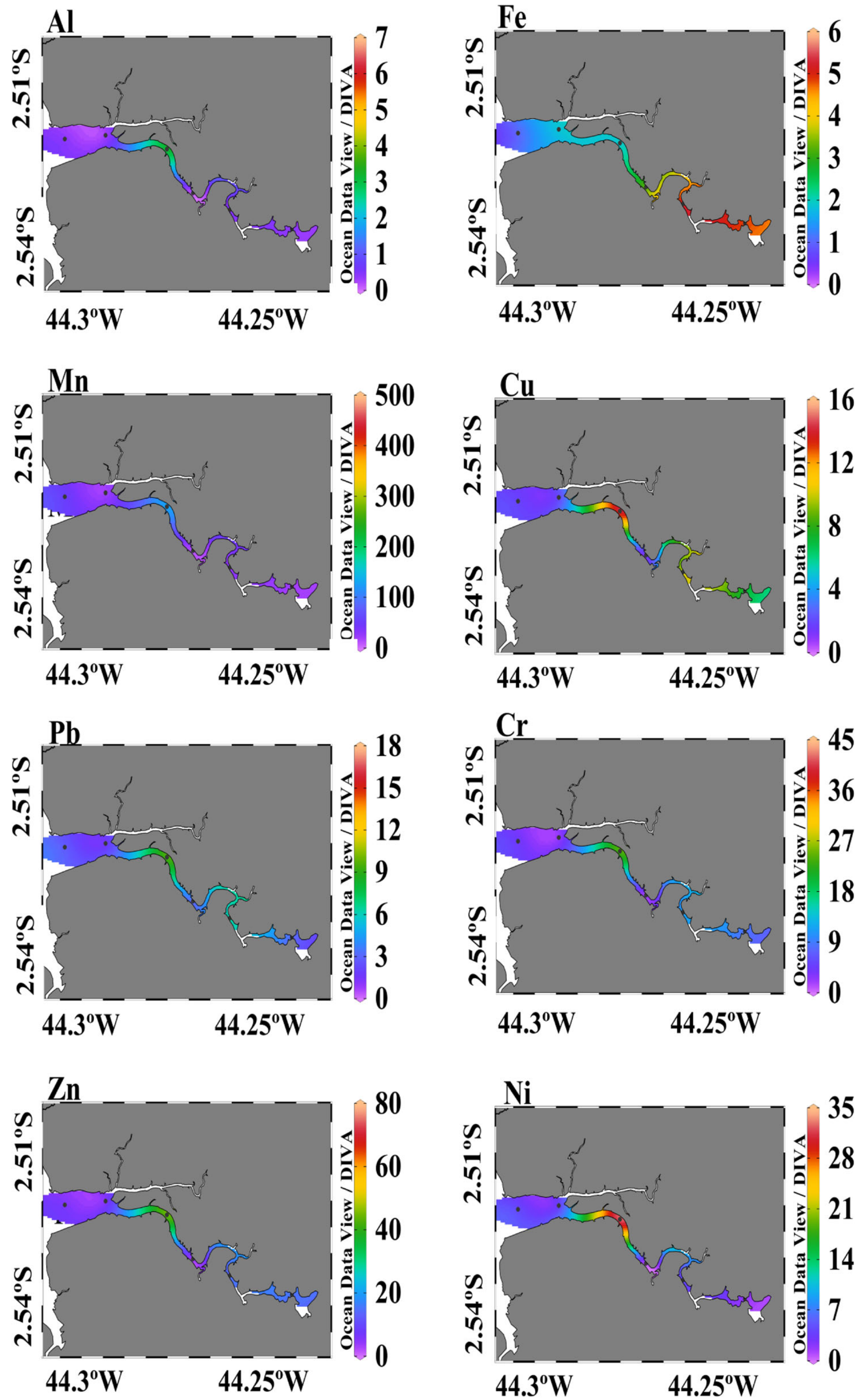

Fig. 4 (continued)

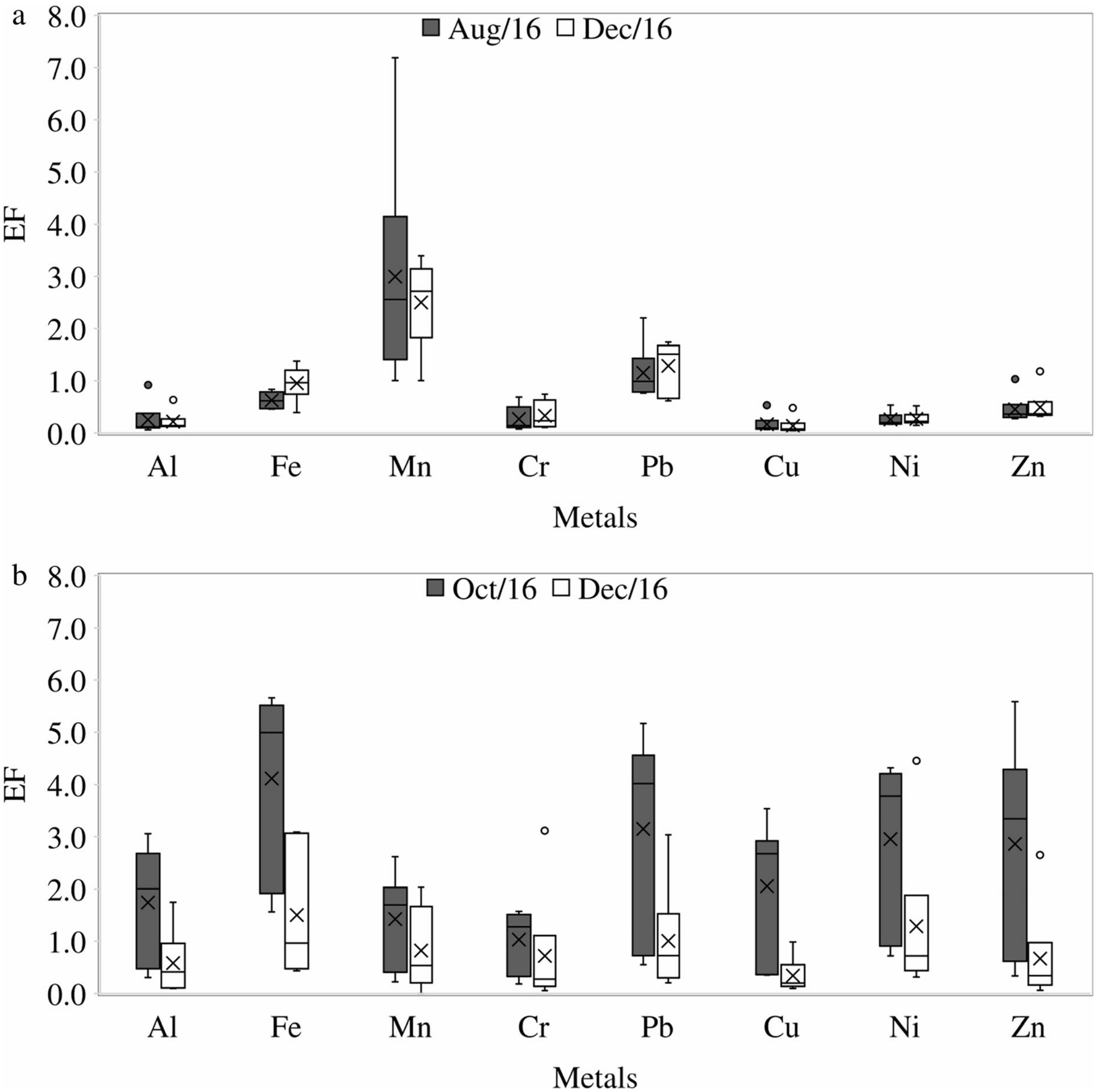

Fig. 5. Enrichment factors (EF) for metal concentrations in sample sites between the two campaigns in **a** São Marcos Bay and **b** Anil River Estuary for the fraction < 2 mm

Statistical analyses for ARE also exhibited two groups. During the 1st campaign (Fig. 6c), $CaCO_3$ was not a significant geochemical carrier of the evaluated metals, since it did not maintain a significant correlation with any of the metals. In the second group, it was observed that OM was the main geochemical carrier of Al and Cu, whereas a secondary influence was shown by both $CaCO_3$ and OM. However, in the 2nd campaign (Fig. 6d), the dendrogram indicates that Mn, Fe, Al, Ni, Zn, and Cr have higher correlation with $CaCO_3$. The Zn and Cr positions in the dendrogram suggest a different origin from other metals of this group. Pb and Cu did not correlate with the $CaCO_3$, and their positions in the dendrogram suggest a similar origin.

Discussion

In SMB, the predominance of fine and very fine sand covering the entire studied areas results from

Table 1 Spearman's rank-order correlation for sediment data in sample sites of São Marcos Bay and Anil River Estuary during the dry season (n = 24; p < 0.05)

	Sand	Fine	OM	$CaCO_3$	Al	Fe	Mn	Cr	Pb	Cu	Ni	Zn
São Marcos Bay												
Sand	1.00											
Fine	− 0.80	1.00										
OM	–	–	1.00									
$CaCO_3$	− 0.44	–	–	1.00								
Al	–	–	0.77	–	1.00							
Fe	–	− 0.64	–	–	–	1.00						
Mn	–	− 0.46	–	–	–	0.48	1.00					
Cr	–	0.68	–	–	0.60	–	− 0.56	1.00				
Pb	–	–	0.52	0.47	–	0.59	–	–	1.00			
Cu	− 0.68	0.79	–	0.52	0.44	–	–	0.60	–	1.00		
Ni	–	–	0.43	–	0.56	0.66	–	–	0.61	–	1.00	
Zn	–	–	0.48	–	0.72	–	–	0.64	0.42	–	0.64	1.00
Anil River Estuary												
Sand	1.00											
Fine	− 0.88	1.00										
OM	− 0.61	0.63	1.00									
$CaCO_3$	− 0.75	0.82	–	1.00								
Al	− 0.72	0.77	0.80	–	1.00							
Fe	− 0.72	0.74	0.62	–	0.91	1.00						
Mn	− 0.72	0.87	0.74	0.50	0.89	0.83	1.00					
Cr	− 0.70	0.71	0.71	–	0.95	0.95	0.86	1.00				
Pb	− 0.76	0.76	0.76	–	0.95	0.91	0.88	0.96	1.00			
Cu	− 0.54	–	0.50	–	0.80	0.88	0.55	0.84	0.76	1.00		
Ni	− 0.62	0.82	0.60	0.59	0.79	0.81	0.84	0.75	0.71	0.66	1.00	
Zn	− 0.66	0.69	0.77	–	0.95	0.92	0.83	0.96	0.94	0.82	0.74	1.00

No significant correlations are represented by (–). Values of trace metal are in micrograms per gram, except sand, fine-grained, OM, $CaCO_3$, Al, and Fe (%)

aeolian sands transported from dunes surrounding the embayment (Samaritano et al. 2013). Great amounts of suspended material are brought in by rivers, as well as by increasing harbor activities, which requires frequent dredging of navigation canals (Bandeira et al. 2005; Amaral and Alfredini 2010). However, fine materials are easily resuspended by the high-speed currents (1.10 to 2.63 m s^{-1}) and exported out of the estuary to the continental shelf (Bandeira et al. 2005). The exception was the OM-rich sediments in the SMB A02 site, an exceptional low-energy zone, where fine materials can be deposited, and the organic matter can be enriched. The grain size distributions found in this present study are in general agreement with previous studies (Nelson and Lamothe 1993; Amaral and Alfredini 2010).

At ARE, in particular at its weaker hydrodynamic higher reaches, sediments showed much higher OM contents than at the SMB stations. The mangrove forests of the region may be one significant source of OM to the sediment. Additionally, ARE suffered more degradation by urban growth than did SMB. Field observation reveals that domestic sewage discharge is an important source of OM for this estuary. According to the Brazilian Institute of Geography and Statistics 2008 census, Maranhão presented 93.55% of inadequate sewage disposal throughout the state. The drastic reduction of OM

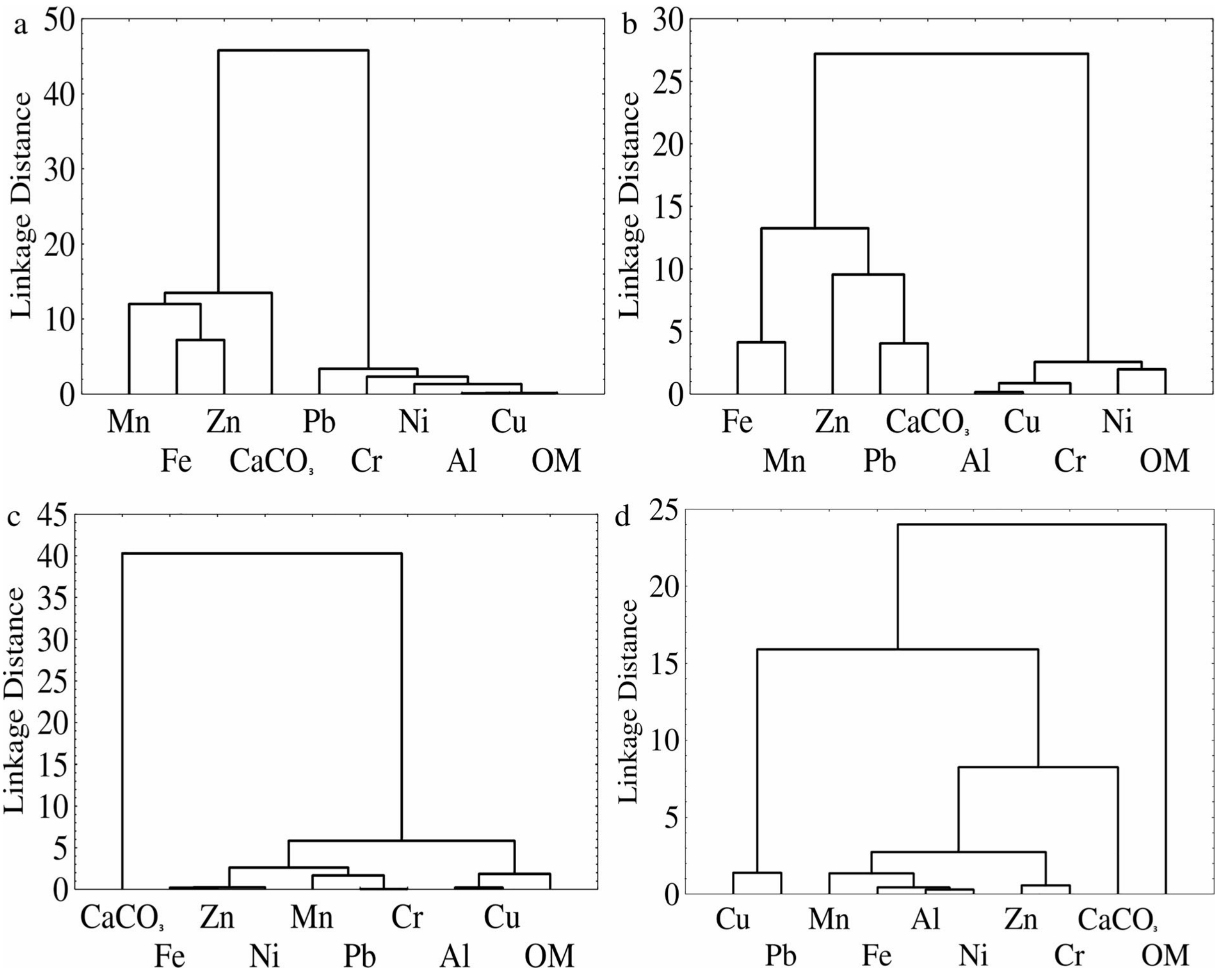

Fig. 6 Cluster analysis for sediment data in sample sites of < 2-mm fraction in **a** and **b** São Marcos Bay (SMB), and **c** and **d** Anil River Estuary (ERA) during the dry season

in sediments downstream of ARE is related to the change in hydrodynamics and the depositional processes when approaching SMB.

The carbonates present in sediment derived from allochthonous sources at the continental shelf and from autochthonous bioclastic materials. $CaCO_3$ content was similar throughout the SMB estuarine channel due to marine influence in the environment dominated by macrotides, which occurs because the riverine influence is restricted to the southern region of the estuary and is almost 80 km away from the sea (González-Gorbeña et al. 2015). Meanwhile, the highest $CaCO_3$ value at the B04 site in ARE was due to the large number of remnants of gastropods in the sediment, as observed in the field.

The highest metal contents were also found in the A02 site (SMB), the same low-energy zone of the estuary, and suggest a larger binding capacity in these relatively finer and organic-rich sediments. Decreased contents of metals downstream of the estuary suggest a predominant origin in the fluvial discharges that are diluted by seawater along the estuaries. Anomalous values for Al may result from the natural source of sedimentary deposits of bauxite existing in regional drainage basins, in addition to the harbor activity contribution with bauxite exportation (Aguiar et al. 2007; Bandeira 2013). The main Fe sources for the study areas are lithogenic, as the region presents a sedimentary basin within the iron-rich Barreiras Formation, which is composed of coarse- to medium-grained ferruginous sandstone blocks (De Sousa 2000). This source, in association with oxic environmental conditions, favors the precipitation of Fe–Mn oxyhydroxides.

Mn presented anomalous values in SMB, mainly as oxyhydroxide depositions, which occurs when well-oxidized marine waters penetrate the estuarine environment, as shown for other tropical estuaries in Brazil (Lacerda et al. 1999; Amorim et al. 2007). In addition to natural Mn source, anomalous values are probably linked to harbor activities involving manganese ore shipment rather than the binding capacity of SMB sediments, as observed by the negative correlation with fine-grained fraction. Higher Mn contents in sediments from ARE result from the association with clay-sized particles and the abundant organic matter in this estuary relative to SMB, as observed in other studies in organic-rich estuarine sediments (Nayak 2015; Williams and Block 2015). The anomalous values for Cr in SMB and ARE indicated lithogenic sources that were deposited in sites more upstream and diluted downstream of each estuary; these values were also similar to observed results in other tropical estuaries in Brazil (Amorim et al. 2007).

Sediment contamination for Cu in ARE indicated potential anthropogenic sources, mainly from domestic sewage discharge landward of the estuary (Nelson and Lamothe 1993; Costa et al. 2015). According to Williams and Block (2015), Cu can also be released from antifouling paint used in boats and from the influx of fungicide used in agriculture in the drainage basins. Pb and Cr may originate from the disposal of urban solid waste in inappropriate places, such as piles. However, at SMB, harbor activity has the potential to cause Pb and Cr contamination due to erosion of ship hulls and harbor equipment. Deposition of atmospheric dust from fossil fuel combustion and hospital sewage were possible sources of Pb, which possibly contribute to the contamination observed in ARE (Meng et al. 2008; De Oliveira and Marins 2011; Costa et al. 2015; Laffite et al. 2016). Values from the present study were lower, however, than those found in the highly historically polluted Guanabara Bay (Brazil), which has metal contents as high as 40 to 58 μg g^{-1} for Pb and 40 to 79 μg g^{-1} for Cu (Faria and Sanchez 2001).

The enrichment factor for Ni indicated sediment contamination only in ARE, which may be attributed to domestic sewage discharge that was diluted from upstream to downstream of the estuary. Agricultural activities, fossil fuel combustion, and domestic sewage discharge are also likely sources of Zn for estuarine environments (De Oliveira and Marins 2011; Budiyanto and Lestari 2014; de Melo et al. 2015). Similar to Cr and Pb, Ni and Zn are metals which are also present in hospital effluents and which were observed being dumped during the campaigns, so this particular source cannot be ruled out (Baptista Neto et al. 2013; Amouei et al. 2015; Laffite et al. 2016). However, Zn also presented contents lower than those exhibited in São Vicente Estuary and Guanabara Bay (Brazil), two of the most contaminated areas of the Brazilian coast, with values of 22 to 79 μg g^{-1} and 194 to 204 μg g^{-1} (Faria and Sanchez 2001; Amorim et al. 2007).

The low metal contents found in SMB, with the exception of Mn, suggest a low probability of adverse effects for the local aquatic biota (de Paula Filho et al. 2015), while the adverse effects of urbanization without control in the ARE already suggest possible adverse effects on the local biota. When the bioavailable metal is absorbed by the organism, it can be transferred all along the food chain, reaching the top of organisms such as humans, as observed metal bioaccumulation in tissues of estuarine catfish species by Azevedo et al. (2012). In another tropical estuary, Nilin et al. (2013) detected cell destruction, delayed development, and the absence of zygote after a toxicity test in species of *Lytechinus variegatus* due to metal enrichment on sediment.

Statistical analysis in SMB indicated different origins and carriers for the metals analyzed. The correlations among the Mn, Fe, and Zn suggested that the $CaCO_3$ was the major geochemical carrier during the 1st campaign. The Mn–Fe–Zn association substrates in SMB sediments may also indicate co-precipitation in the environment, with Fe–Mn oxyhydroxides serving as the major process in the accumulation of these metals as sediments in the SMB, as observed by the positive correlation. The Zn adsorption onto these oxides demonstrates higher stability constants than onto carbonates (Li et al. 2001). $CaCO_3$, in general, plays a minor role in binding trace metals, except for Mn, in sediments. This association may lead to the precipitation of rhodochrosite ($MnCO_3$) from calcite during the co-precipitation of a calcite–manganese phase without Mn co-precipitating with Fe (Ho et al. 2010; Williams and Block 2015).

The second group of metals, including Pb, Cr, Ni, Al, and Cu, had similar sources for the estuary and were preferentially associated with OM during the 1st campaign, as indicated by the positive values in the Spearman's correlation table. As mentioned previously, the Al originated from a lithogenic source and was associated with OM and the other trace metals to form secondary minerals. The association of secondary minerals such as clays with organic OM is common in several sedimentary environments (Fernandes et al.

2016). Du Laing et al. (2008) and Costa et al. (2015) reported this strong association of Cu with OM in estuarine sediments.

During the 2nd campaign in SMB, it was observed that Pb associations differed from lithogenic sources and were associated with $CaCO_3$. Pb tended to bind with the coarser sediment fraction (Budiyanto and Lestari 2014). Thus, it was concluded that the predominant source of Pb was anthropogenic. The different chemical association forms of Pb can affect the solubility and mobility of the metal from sediments (Li et al. 2001).

ARE sediments showed Fe, Zn, Ni, Mn, Pb, and Cr to be strongly associated, indicating the same lithogenic source during the 1st campaign, as the positive correlations showed in the Spearman's correlation table. The second group also indicates the association of Al minerals with OM and Cu. All of these metals and OM were associated with $CaCO_3$ in these sediments. Similar to the observed SMB sediments, ARE sediments also exhibited an association with Fe and Zn, as well as with Al, Cu, and OM. These relations indicate that similar geochemical processes occur during the sampling period (dry season) along this region. Metals may be coprecipitated in the environment in the form of Fe–Mn oxyhydroxides and aluminosilicates, which have strong affinity with OM (De Oliveira and Marins 2011). In the 2nd campaign, OM remains the main geochemical carrier, followed by $CaCO_3$ that is evidenced by the positive Spearman's correlation among all trace metals with OM. Cu and Pb shift from the $CaCO_3$ group, indicating a greater association of these metals with OM. Costa et al. (2014) and Williams and Block (2015) also found correlations among Cu, Pb, and OM in previous studies in other tropical estuaries with intense urbanization. A significant proportion of metal contents is probably derived from domestic and urban effluents caused by population growth, as found by Costa et al. (2014) in another tropical tidal Brazilian estuary that results in sediment quality degradation.

Conclusion

The present study indicates that metal contents in sediments varied significantly between the estuaries, with the highest values being found in the Anil River Estuary. Notwithstanding the large diluting capacity of this waterway, it is possible to observe the anthropogenic influence from domestic and hospital effluents, as well as ore shipment that occurs around the watershed. In general, organic matter acts as the predominant geochemical carrier for most metals throughout the environments, while carbonates perform as secondary carriers. The association of metals with the studied carbon forms (organic matter and calcium carbonate) in the sediment can cause the release of different metal species with high availability, under certain environmental conditions, which can be incorporated by the biota over the food chain and cause toxic effects in these ecological and economic important macrotidal estuaries of the Amazonian region.

Acknowledgement The authors would like to thank Dr. S.A. Eschrique (Federal University of Maranhão) and all of the members of the Coastal Biogeochemistry Laboratory (Federal University of Ceará/LABOMAR) for technical support in the field and laboratory work during this research. We are extremely grateful to Prof. Dr. Luiz Drude de Lacerda for valuable comments and suggestions.

Funding information This study received financial support from the Fundação de Amparo à Pesquisa e ao Desenvolvimento Científico e Tecnológico do Maranhão, Brazil (FAPEMA).

References

Aguiar, J. E., Marins, R. V., & Almeida, M. D. (2007). Comparação de metodologias de digestão de sedimentos marinhos para caracterização da geoquímica de metais-traço na plataforma continental nordeste oriental brasileira. *Geochimica Brasiliensis, 21*(3), 304–323. https://doi.org/10.21715/gb.v21i3.274.

Aguiar, J. E., de Lacerda, L. D., Miguens, F. C., & Marins, R. V. (2014). The geostatistics of the metal concentrations in sediments from the eastern Brazilian continental shelf in areas of gas and oil production. *Journal of South American Earth Sciences, 51*, 91–104. https://doi.org/10.1016/j.jsames.2013.12.005.

Amaral, R., & Alfredini, P. (2010). Modelação Hidrossedimentológica no Canal de Acesso do Complexo Portuário do Maranhão. *Revista Brasileira de Recursos Hídricos, 15*(2), 5–14. https://doi.org/10.21168/rbrh.v15n2.p5-14.

Amorim, E. P., Fávaro, D. I. T., Berbel, G. B. B., & Braga, E. S. (2007). Metal and trace element assessment of estuary sediments from Santos, Brazil, by neutron activation and atomic absorption techniques. *International Nuclear Atlantic Conference*. Santos.

Amouei, A., Asgharnia, H., Fallah, H., Faraji, H., Barari, R., & Naghipour, D. (2015). Characteristics of effluent wastewater in hospitals of Babol University of Medical Sciences, Babol, Iran. *Health Scope, 4*(2), 4. https://doi.org/10.17795/jhealthscope-23222.

Aprile, F. M., & Bouvy, M. (2008). Distribution and enrichment of heavy metals in sediments at the Tapacurá River Basin, North Eastern Brazil. *Brazilian Journal of Aquatic Science and Technology, 12*(1), 1–8. https://doi.org/10.14210/bjast.v12n1.p1-8.

Azevedo, J. D. S., Hortellani, M. A., Eduardo, J., & Sarkis, D. S. (2012). Accumulation and distribution of metals in the tissues of two catfish species from Cananéia and Santos-São Vicente Estuaries. *Brazilian Journal of Oceanography, 60*(4), 463–472. https://doi.org/10.1590/S1679-87592012000400005.

Bandeira, I. C. N. (2013). *Geodiversidade do Estado do Maranhão* (1st ed.). Teresina, Brasil: CPRM Serviço Geológico do Brasil.

Bandeira, J. V., Salim, L. H., & Aun, P. E. (2005). *The use of nuclear techniques for the quantification of sediment transport and bulk density of deposits – application to dredging and dumping operations optimisation and environmental impact studies*. Santos, Brazil: International Nuclear Atlantic Conference.

Baptista Neto, J. A., Peixoto, T. C. S., Smith, B. J., Mcalister, J. J., Patchineelam, S. M., Patchineelam, S. R., & Fonseca, E. M. (2013). Geochronology and heavy metal flux to Guanabara Bay, Rio de Janeiro state: a preliminary study. *Anais da Academia Brasileira de Ciências, 85*(4), 1317–1327. https://doi.org/10.1590/0001-3765201394612.

Biati, A., Karbassi, A. R., Hassani, A. H., Monavari, S. M., & Moattar, F. (2010). Role of metal species in flocculation rate during estuarine mixing. *International Journal of Environmental Science & Technology, 7*(2), 327–336. https://doi.org/10.1007/BF03326142.

Budiyanto, F., & Lestari, L. (2014). Distribution of metals in Cisanggarung estuary sediment, West Java, Indonesia. *Marine Research in Indonesia, 39*(1), 23–30. https://doi.org/10.14203/mri.v39i1.90.

Costa, E. S., Grilo, C. F., Wolff, G. A., Thompson, A., Figueira, R. C. L., & Neto, R. R. (2014). Evaluation of metals and hydrocarbons in sediments from a tropical tidal flat estuary of Southern Brazil. *Marine Pollution Bulletin, 92*(1–2), 259–268. https://doi.org/10.1016/j.marpolul.2014.11.028.

Costa, A. d. S., Santos, N. A., & Braga, C. C. (2016). Rainfall diagnosis in different time scales in Maranhão using the wavelet transform. *Journal of Hyperspectral Remote Sensing, 6*(2006), 295–304. https://doi.org/10.5935/2237-2202.20160029.

De Melo, G. V., Neto, J. A. B., Malm, O., Fernandez, M. A. d. S., & Patchineelam, S. M. (2015). Composition and behaviour of heavy metals in suspended sediments in a tropical estuarine system. *Environmental Earth Sciences, 73*(3), 1331–1344. https://doi.org/10.1007/s12665-014-3491-3.

De Paula Filho, F. J., Marins, R. V., de Lacerda, L. D., Aguiar, J. E., & Peres, T. F. (2015). Background values for evaluation of heavy metal contamination in sediments in the Parnaíba River Delta estuary, NE/Brazil. *Marine Pollution Bulletin, 91*(2), 424–428. https://doi.org/10.1016/j.marpolbul.2014.08.022.

De Sousa, S. B. (2000). Sistema Aquífero da Ilha do Maranhão (MA). In *Anais do 1st Joint World Congress on Groundwater* (pp. 1–17). Fortaleza.

Diniz, L. G. R., Jesus, M. S., Dominguez, L. A. E., Fillmann, G., Vieira, E. M., & Franco, T. C. R. S. (2014). First Appraisal of water contamination by antifouling booster biocide of 3rd Generation at Itaqui Harbor (São Luiz - Maranhão – Brazil). *Journal of the Brazilian Chemical Society, 25*(2), 380–388. https://doi.org/10.5935/0103-5053.20130289.

Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F. M. G., & Verloo, M. G. (2008). Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. *Estuarine, Coastal and Shelf Science, 77*(4), 589–602. https://doi.org/10.1016/j.ecss.2007.10.017.

Duquesne, S., Newton, L. C., Giusti, L., Marriott, S. B., Stark, H. J., & Bird, D. J. (2006). Evidence for declining levels of heavy-metals in the Severn Estuary and Bristol Channel, U.K. and their spatial distribution in sediments. *Environmental Pollution, 143*(2), 187–196. https://doi.org/10.1016/j.envpol.2005.12.002.

El-Robrini, M., Valter Marques, J., Silva, M. A. M. A. da, Robrini, M. H. S. E., Feitosa, A. C., Tarouco, J. E. F., et al. (2006). Maranhão. In D. Muehe (Ed.), *Erosão e Progradação do Litoral Brasileiro.* (pp. 87–130). Brasília. doi:https://doi.org/10.13140/RG.2.1.1916.8723

Faria, M. d. M., & Sanchez, B. A. (2001). Geochemistry and mineralogy of recent sediments of Guanabara Bay (NE sector) and its major rivers - Rio de Janeiro State - Brazil. *Anais da Academia Brasileira de Ciências, 73*(1), 120–133. https://doi.org/10.1590/S0001-37652001000100010.

Fernandes, A. M., Hissler, C., da Conceição, F. T., Spatti Junior, E. P., & Mortatti, J. (2016). Combined analysis of trace elements and isotopic composition of particulate organic matter in suspended sediment to assess their origin and flux in a tropical disturbed watershed. *Environmental Pollution, 218*, 844–854. https://doi.org/10.1016/j.envpol.2016.08.008.

Folk, R. L., & Ward, W. C. (1957). Brazos River bar: a study in the significance of grain size parameters. *Journal of Sedimentary Petrology, 27*(1), 3–26. https://doi.org/10.1306/74D70646-2B21-11D7-8648000102C1865D.

Gonsior, M., Valle, J., Schmitt-Kopplin, P., Hertkorn, N., Bastviken, D., Luek, J., Harir, M., Bastos, W., & Enrich-Prast, A. (2016). Chemodiversity of dissolved organic matter in the Amazon Basin. *Biogeosciences, 13*(14), 4279–4290. https://doi.org/10.5194/bg-13-4279-2016.

González-Gorbeña, E., Rosman, P. C. C., & Qassim, R. Y. (2015). Assessment of the tidal current energy resource in São Marcos Bay, Brazil. *Journal of Ocean Engineering and Marine Energy, 1*(4), 421–433. https://doi.org/10.1007/s40722-015-0031-5.

Ho, H. H., Swennen, R., & Van Damme, A. (2010). Distribution and contamination status of heavy metals in estuarine sediments near Cua Ong harbor, Ha Long Bay Vietnam. *Geologica Belgica, 13*(1–2), 37–47 https://popups.uliege.be:443/1374-8505/index.php?id=2844.

Jolivet, C., Arrouays, D., & Bernoux, M. (1998). Comparison between analytical methods for organic carbon and organic matter determination in sandy spodosols of France. *Communications in Soil Science and Plant Analysis, 29*(15–16), 2227–2233. https://doi.org/10.1080/00103629809370106.

Lacerda, L. D., Ribeiro, J., & Gueiros, B. B. (1999). Manganese dynamics in a mangrove mud flat tidal creek in SE Brazil. *Mangroves and Salt Marshes, 3*(2), 105–115. https://doi.org/10.1023/A:1009992418964.

Laffite, A., Kilunga, P. I., Kayembe, J. M., Devarajan, N., Mulaji, C. K., Giuliani, G., Slaveykova, V. I., & Poté, J. (2016).

Hospital effluents are one of several sources of metal, antibiotic resistance genes, and bacterial markers disseminated in sub-Saharan urban rivers. *Frontiers in Microbiology, 7*(JUL), 1–14. https://doi.org/10.3389/fmicb.2016.01128.

Li, X., Shen, Z., Wai, O. W. H., & Li, Y.-S. (2001). Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. *Marine Pollution Bulletin, 42*(3), 215–223. https://doi.org/10.1016/S0025-326X(00)00145-4.

Loring, D. H., & Rantala, R. T. T. (1992). Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Reviews, 32*(4), 235–283. https://doi.org/10.1016/0012-8252(92)90001-A.

Marques, J. S. J., Rangel, T. P., Brito, F. P., Almeida, M. G., Salomão, M. S. M. B., Gobo, A. A. R., Souza-Santos, L. P., Araújo-Castro, C. M. V., Costa, M. F., & Rezende, C. E. (2011). Geoquímica de Metais em Sedimentos da Zona Estuarina do Complexo Industrial Porto de Suape, PE - Brasil. *Revista da Gestão Costeira Integrada, 11*(4), 379–387. https://doi.org/10.5894/rgci183.

Medeiros, P., Seidel, M., Ward, N. D., Carpenter, E., Gomes, H., Niggemann, J., et al. (2015). Fate of the Amazon River dissolved organic matter in the tropical Atlantic Ocean. *Global Biogeochemical Cycles, 29*, 677–690. https://doi.org/10.1002/2015GB005115.

Meng, W., Qin, Y., Zheng, B., & Zhang, L. (2008). Heavy metal pollution in Tianjin Bohai Bay, China. *Journal of Environmental Sciences, 20*, 814–819. https://doi.org/10.1016/S1001-0742(08)62131-2.

Miller, J. N., & Miller, J. C. (2010). *Statistics and Chemometrics for Analytical Chemistry (Sixth., Vol. 46)*. Harlow: Pearson Education Limited. https://doi.org/10.1198/tech.2004.s248.

Nayak, G. N. (2015). Bioavailability of metals in estuarine sediments and their possible impacts on the environment. *Environmental and Social Sciences, 2*(1), 1–4.

Nelson, C. H., & Lamothe, P. J. (1993). Heavy metal anomalies in the Tinto and Odiel River and Estuary System , Spain. *Estuaries, 16*(3), 496–511. https://doi.org/10.2307/1352597.

Nilin, J., Moreira, L. B., Aguiar, J. E., Marins, R., Denis, M. d. S. A., Tito, M. d. C. L., & Costa-Lotufo, L. V. (2013). Sediment quality assessment in a tropical estuary: The case of Ceará River, Northeastern Brazil. *Marine Environmental Research, 91*, 89–96. https://doi.org/10.1016/j.marenvres.2013.02.009.

De Oliveira, R. C. B., & Marins, R. V. (2011). Dinâmica de metais-traço em solo e ambiente sedimentar estuarino como um fator determinante no aporte desses contaminantes para o ambiente aquático: Revisão. *Revista Virtual de Química, 3*(2), 88–102. https://doi.org/10.5935/1984-6835.20110014.

Regnier, P., & Wollast, R. (1993). Distribution of trace-metals in suspended matter of the Scheldt Estuary. *Marine Chemistry, 43*(1–4), 3–19. https://doi.org/10.1016/0304-4203(93)90212-7.

Rodrigues, C. A. L., Ribeiro, R. P., Santos, N. B., & 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. doi:10.1590/1809-4392201600493Samaritano, L., Chagas, F. M., Bernardino, J. C. M., Siegle, E., Tessler, M. G., Uemura, S., & 1. (2013). *Hydrodynamic modeling over a sand wave field at São Marcos*. *Marine and River Dune Dynamics*. Bruges, Belgium: Marine and River Dune Dynamics.

Samaritano, L., Chagas, F. M., Bernardino, J. C. M., Siegle, E., Tessler, M. G., & Uemura, S. (2013). *Hydrodynamic modeling over a sand wave field at São Marcos. Marine and River Dune Dynamics*. Bruges: Marine and River Dune Dynamics.

Schlitzer, R. (2018). *Ocean Data View*. Bremerhaven: Alfred Wegener Institute. odv.awi.de.

Taylor, S. R. (1964). Abundances of chemical elements in the continental crust: a new table. *Geochimica et Cosmochimica Acta, 28*(28), 1273–1285. https://doi.org/10.1016/0016-7037(64)90129-2.

Williams, N., & Block, K. A. (2015). Spatial and vertical distribution of metals in sediment cores from Río Espíritu Santo estuary, Puerto Rico, United States. *Marine Pollution Bulletin, 100*(1), 445–452. https://doi.org/10.1016/j.marpolbul.2015.08.007.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.