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THEMATIC ISSUE

Assessment of heavy metals in sediments of the Parnaíba River Delta in the semi-arid coast of Brazil

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Abstract

Studies related to heavy metal concentrations in coastal sediments are important to monitor and assess environmental health of estuarine ecosystems. Twenty-eight samples from Parnaíba River Delta, the largest open-ocean delta in the Americas, northeastern of Brazil were tested for heavy metals concentrations (Cd, Cr, Cu, Mn, Ni, Pb, Zn, Al and Fe), grain-size and easily oxidizable carbon. The relations of the heavy metals with sediment composition were evaluated using a multivariate statistical analysis. Sediment pollution assessment was carried out by enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (CF) and potential ecological risk index (PERI). The average concentrations were 0.50 ± 0.09 mg Cd kg^{-1}, 6.95 ± 2.13 mg Pb kg^{-1}, 19.02 ± 8.75 mg Cu kg^{-1}, 23.20 ± 5.04 mg Ni kg^{-1}, 33.52 ± 6.82 mg Cr kg^{-1}, 43.99 ± 7.47 mg Zn kg^{-1}, 165.73 ± 86.71 mg Mn kg^{-1}, $2.93 \pm 0.89\%$ to Fe and $3.78 \pm 1.17\%$ to Al. The results indicate lower concentrations of heavy metals relative to limit concentrations defined by the Brazilian regulatory framework. The multivariate analysis reflected the binding of heavy metals to clay minerals and organic carbon. The different geochemical indices indicated sediments minimally enriched by metals and a low potential ecological risk level. Our assessment confirms the pristine conditions of Parnaíba Delta protected area to heavy metal contamination, except Igaraçú channel near Parnaíba city.

Keywords Heavy metals · Enrichment factor · Geoaccumulation index · Pollution · Potential ecological risk index

Introduction

Estuarine sediments are significant deposits of heavy metals of natural and anthropic origin. In recent decades, researchers have demonstrated that pollution of estuarine and marine environments by heavy metals is a serious environmental problem (Rios et al. 2016; De Paula Filho et al. 2015a; Moreira et al. 2019, 2020; Lacerda et al. 2020). Following this trend, studies on pollution caused by heavy metals are increasingly recurrent in developing countries (Liu et al. 2011; Mendonza-Carranza et al. 2016; Sharifinia et al. 2018; Beraldi et al. 2019; Chakraborty et al. 2019). Besides, environmental monitoring, mainly in protection areas, is necessary for the maintenance of the ecological functions and services. Information on this topic is still limited in tropical estuaries in regions with incipient industrialization, such as on the Northeast coast of Brazil (Lacerda et al. 2008; Paula et al. 2010; De Paula Filho et al. 2015a).

The primary natural sources of metals for the estuaries are the geological matrix, erosion and the natural loss of soil in the drainage basins. On the other hand, the anthropic influence on the variation of transport and deposition of metals at the continent–ocean interface has increased significantly in several coastal basins on a global scale (Liu et al. 2011; Aguiar et al. 2014; Beraldi et al.

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2019). The main anthropogenic drivers of the contamination of aquatic systems include the discharge of domestic and industrial effluents and the leaching of pesticides in agricultural areas (Lacerda et al. 2008; Paula et al. 2010; De Paula Filho et al. 2015b; Beraldi et al. 2019). The inadequate disposal of wastes and effluents containing heavy metals in the most varied natural environments has caused great ecological concern (Rios et al. 2016; Buzzi and Marcovecchio 2018; Moreira et al. 2019, 2020). Such disposal may increase the concentrations of these metals in the sediment, reaching the threshold above which there is a greater probability of effects on the biota and this process depends on metal binding to particles, water physicochemical conditions and metals' potential solubility to turn these contaminants become available to food chains (Jara-Marini et al. 2009; Mendonza-Carranza et al. 2016; Liu et al. 2011; Devanesan et al. 2017; Moreira et al. 2019, 2020).

Estuarine sediments act as a sink for different chemical species such as nutrients, pesticides and heavy metals, as they absorb these contaminants in suspended matter precipitating them as bulk sediment. Then, heavy metals are aggregated to fine-grained particles (silt and clay), organic matter, iron and manganese oxi-hydroxydes that find conditions in the estuaries for flocculation and eventually move into the depositional areas. In addition, metals in silt and clay fractions are more easily available to biological organisms than those in the bulk sediments (Oliveira and Marins 2011). Therefore, based on the determination of the metal concentrations and their spatial distribution, these characteristics allow us to infer on the potential health of coastal ecosystems. For this purpose, geoenvironmental criteria or pollution indices are used in assessing the quality of sediments, such as the enrichment factor (EF), the geoaccumulation index (Igeo) and the potential ecological risk index (PERI) (Devanesan et al. 2017; Sharifinia et al. 2018; El-Kady et al. 2019). These tools allow the assessment of heavy metals' anomalies in estuarine and the characterization of major sources. In this way, they provide an objective support to decision-making by the public authorities for the proper use of natural resources in order to establish prevention and/or restoration programs (De Paula Filho et al. 2015a, b).

Estimated loads measured in coastal areas of the Brazilian NE region have shown that anthropogenic emissions of some heavy metals exceed natural emissions by an order of magnitude and these additional loads can alter the quality of estuarine waters (Paula et al. 2010; De Paula Filho et al. 2014). In this context, the Parnaíba River Delta estuary (PRD) has a unique ecological importance for the conservation of wild animals and fisheries in the semi-arid Atlantic coast of NE Brazil and the area integrate an environmental protection zone (Federal Decision 28th August 1996; MMA 2006). In this region, the preservation and sound management of water resources are essential to adequately support the local human population, include traditional habitants and the maintenance of their economic activities.

A previous study has established regional background levels and upper thresholds (geochemical baselines) for Zn, Cu, Pb, Cr, Mn and Fe in the sedimentary environment of the PRD (De Paula Filho et al. 2015a). In the current study, we assessed the levels and spatial distribution of a suite of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn, Al and Fe) in surface sediments collected from five estuarine channels in the Parnaíba River Delta. Our investigations aimed to (i) determine the concentration of heavy metals in surface sediments, (ii) assess the spatial extent and distribution patterns of heavy metals contamination and (iii) evaluate the heavy metal contamination of the sediments using the geochemical indices and potential ecological risk indices.

Materials and methods

Study area

The Parnaíba River Delta is a tropical estuary located in the Brazilian semi-arid coast (≈ 2° 37′ S–3° 05′ S and 41° 08′ W–42° 30′ W), between the states of Ceará, Piaui and Maranhão (Fig. 1). The delta is the final portion of the Parnaíba River basin (344,112 km^2) which is characterized by an incipient urban and industrial development. The basin supports 4.8 million people, 279 municipalities and three different biomes (Cerrado, Caatinga and Costeiro). Until reaching the Atlantic Ocean, the Parnaíba River runs along 1400 km, receiving inputs from twelve main tributaries, some of them are intermittent rivers. The upper river has a hydroelectric power plant, dams and marginal lakes distributed along its course (De Paula Filho et al. 2015b). Upon its arrival in the coastal zone, it forms a wide and branching delta that extends over 2750 km^2 and is formed by more than 70 islands, being the only open-ocean delta in the Americas (Farias et al. 2015).

This deltaic system is a complex and important ecosystem because of its marine-fluvial dynamics and for harboring important plant and animal communities. It is characterized by extensive fluvial-marine plains intersected by channel-forming islands formed by the accumulation of terrigenous materials. The main estuarine channels are the Igaraçú River (Ig), which crosses the main urban area of the lower region of the river (Parnaíba city), and the Parnaíba River (P), the main river drainage receiving contributions from the entire hydrographic basin. The other three major channels flow into bays called Cajú (Cb), Melancieiras (Mb) and Tutóia (Tb).

The Delta is embedded in the morphological unit known as the "Late Tertiary Barreiras Formation", comprised of unconsolidated iron-rich alluvial sediments encompassing

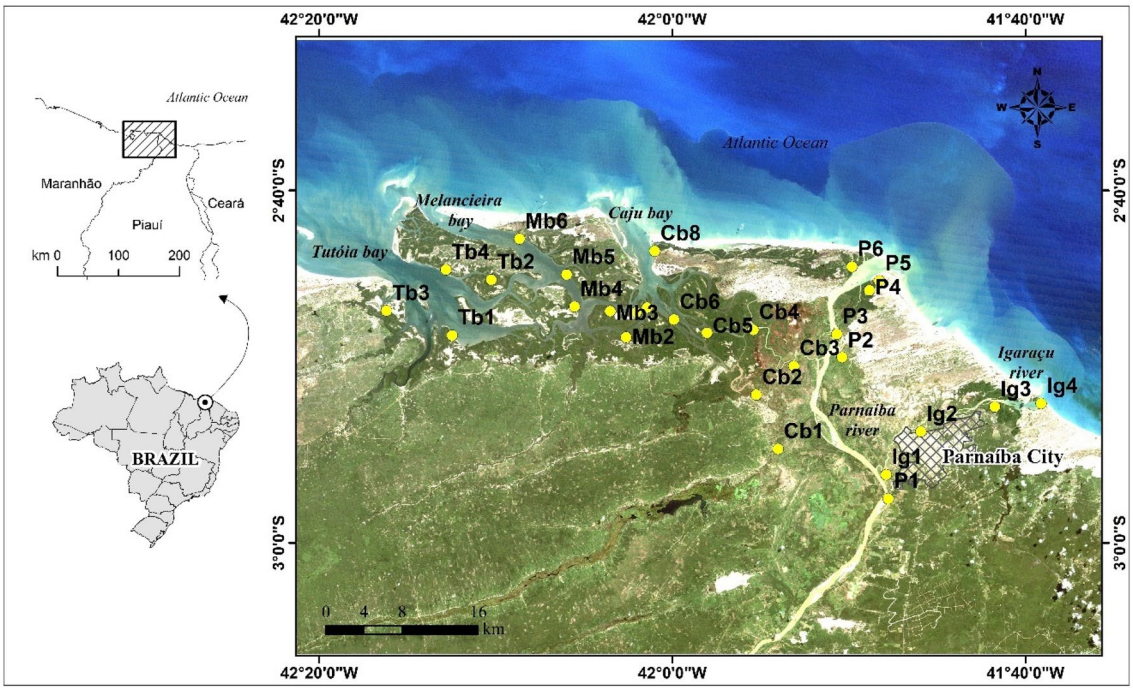

Fig. 1 Location map highlighting the sampling sites along the five estuarine channels in the Parnaíba River Delta: Igaraçú river (Ig), Parnaíba river (P), Caju bay (Cb), Melancieiras bay (Mb) and Tutóia bay (Tb)

the entire Brazilian eastern and northeastern shoreline. Extensive mangrove areas developed under the influence of these environments, representing an important area of deposition of materials of continental origin (MMA 2006). It is characterized by being a shallow estuary, where its different estuarine channels are on average approximately 4.0 m deep, being subject to a mesotidal regime and variable salinity (Sabadini-Santos et al. 2009; Dias et al. 2016).

The Delta has few point sources of contaminants and, therefore, diffuse pollution sources prevail, which are typically difficult to control and monitor (De Paula Filho et al. 2014, 2015a, b). Parnaíba city has a population of approximately 150,000 and is located on the western boundary of the environmental protection area. The major environmental impacts are the release of domestic effluents, deforestation and erosion. In this regard, the negative effects of the release of domestic and industrial effluents into the water system should not be ignored (De Paula Filho et al. 2014, 2015a, b).

Sample collection and laboratory analysis

The sampling campaign was conducted in April 2017, at the end of the rainy season, on sites located in muddy deposition areas along the five estuarine channels. Surface sediments were sampled from 28 sites under spring tide (Fig. 1). Sample site locations were positioned by GPS (Garmin II) and plotted with the Surfer Version 8.00 software (Golden Software, Inc., USA). Surface sediments (0–5 cm) were collected in duplicate in the tidal zone using a plastic shovel and stored in polyethylene bags at 4 °C until analysis.

The samples were oven-dried at 60 °C and the clods that formed in the drying stage were pulverized, using an agate mortar. The controlled temperature avoids the modification of the clay–mineral structure and the excessive hardening of the sediment (Aguiar et al. 2007; Sharifinia et al. 2018). Samples were stored in a desiccator until analysis. Part of the sample was taken for analysis of the granulometric composition. Once dried, the particle size distribution was measured by the wet sieving method to separate the total muddy fraction (< 63 µm) (silt + clay) from the sand and gravel fractions (McCave and Syvitski 1991). To present the results, the logarithmic scale Φ (phi = $\log_2$ diameter mm) was adopted (Krumbein 1934).

The readily oxidizable organic carbon (OC) content was determined with the Walkey–Black titration method modified by heating of the sample during sample digestion. Cleaning procedures were performed to minimize overestimation of OC caused by the presence of interfering ions (e.g. Fe^{2+} and Cl^{-}). For example, the chloride oxidation can be prevented by using Ag_2SO_4 in the digestion mixture (Nelson and Sommers 1982; Loring and Rantala 1992).

Acid extracts were obtained from the leaching of about 1.0000 g of the fine fraction (< 63 µm) in 30.0 ml of a 50% aqua regia solution ($3HCl.HNO_3$). The procedure was

performed in a closed system heated to 80 °C for 2 h (Aguiar et al. 2007). The obtained extracts were analyzed by flame atomic absorption spectrophotometry (FAAS) using a VARIAN SpectraA 50b spectrophotometer according to recommendations of the manufacturer's handbook.

Quality assurance and quality control

All determinations were conducted in accordance with strict quality control. The quality assurance/quality control procedures involved the use of standard reagents and the analysis of certified reference sediment (Table 1). The precision of analysis for heavy metals was validated through Standard Reference Material sample—NIST 1646a (US National Institute of Standards and Technology). Standard curves were constructed using standard solutions with known concentrations in order to calculate the concentrations of the samples. All samples were tested in duplicate.

Data source and processing

The Microsoft Excel® software was used for the pre-treatment of data. Data normality was tested using the Shapiro–Wilk test. When necessary, data were log-transformed to satisfy the parametric assumptions. Data in the figures were not transformed. The association between pairs of variables was assessed using the Pearson correlation coefficient ($p < 0.05$) for the better understanding of relationships between the heavy metal's concentration with OC and sediment particle size. Spatial variations in the environmental variables were studied using a one-way analysis of variance (ANOVA).

Multivariate statistical approaches, including Hierarchical Cluster Analysis (HCA) by Ward's method and the Principal Component Analysis (PCA), were performed to adjust the index parameters. The cluster analysis based on Euclidian distances was used to compare and establish relationships between sampling sites. The data matrix was applied to the principal component analysis (PCA) to visualize potential pollution sources. Varimax rotation with Kaiser normalization was chosen in PCA to maximize factor variance and to simplify the columns of the factor matrix.

All statistical tests were done with the Statistica 8.0 software (StatSoft, Inc. 1984–2007). The spatial distribution of heavy metal concentrations in PRD was performed from the data geoprocessing in the ArcMap ArcGis 9.0 package. For that, the quantitative values of metals were grouped into classes in a frequency diagram of univariate analysis in ArcMap (North 2009).

Heavy metal pollution indices and ecological risk assessment

Several different indices were used to evaluate the metal enrichment, degree of pollution and potential ecological risk in the sediments. Table 2 shows the equations, descriptions and ranges of the metal pollution factors and indices. We used the Enrichment Factor (EF) (Eq. 1) and the geoaccumulation Index (Igeo) (Eq. 2) for the quantitative measurement of sediment contamination by Cu, Cd, Cr, Pb, Ni and Zn. Iron was used as a normalizing element (De Paula Filho et al. 2015a; Sharifinia et al. 2018).

Globally, the identification of the toxicological risk associated with heavy metals in sediments has been carried out through pollution indices (Hakanson 1980; Liu et al. 2015; Ismail et al. 2016; Chen et al. 2018; Sharifinia et al. 2018). The contamination factor (CF_j^i) represents the potential hazard of heavy metal contamination by indicating the toxicity of each element relative to the background value (Eq. 3). The CD_J represents the total contamination factor and was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity and the response of the

Table 1 Quality Assurance/Quality Control procedures used in the chemical testing, including the concentrations in the reference samples

Heavy metal	Certified values[a] (mg kg^{-1})	Detection limits (mg kg^{-1})	Observed concentration (mg kg^{-1})	Recovery (%)
Al[b]	2.297 ± 0.018	0.31	1.95 ± 0.03	85
Cd	0.148 ± 0.007	0.03	0.14 ± 0.01	95
Cr	40.9 ± 1.9	0.10	36.40 ± 2.50	89
Cu	10.01 ± 0.34	0.08	9.41 ± 0.25	94
Fe[b]	2.008 ± 0.039	0.12	1.98 ± 0.06	99
Mn	234.5 ± 2.8	0.10	215.70 ± 4.90	92
Ni[c]	23	0.03	21.20 ± 1.10	92
Pb	11.7 ± 1.2	0.10	10.40 ± 0.90	89
Zn	48.9 ± 1.6	0.26	46.90 ± 2.70	96

[a]Standard Reference Material® 1646[a]. Estuarine Sediment

[b]Mass percentage (%)

[c]Noncertified Value

Table 2 Pollution metal indices: equations, descriptions and contamination ranges

Equation	Description	Ranges	References
(1) $EF = \frac{[(C^i)_s/(Fe)_s]}{[(C^i)_b/(Fe)_b]}$	EF: Enrichment factor $(C^i)_s$ and $(C^i)_b$, metal concentration in samples and metal background[a] $(Fe)_s$ and $(Fe)_b$, concentration and background concentration of the reference element Fe[a]	EF < 1: No enrichment 1–3: minimal enrichment 3–5: moderate enrichment 5–10: significant enrichment 10–25: severe enrichment 25–50: very severe enrichment > 50: extreme enrichment	Taylor (1964)
(2) $I_{geo} = \log_2\left[\frac{(C^i)_s}{1.5\times(C^i)_b}\right]$	I_{geo}: Geoaccumulation index A factor of 1.5 was used to minimize the effect of possible variations in the background values	C1: 0–1 unpolluted to moderately polluted C2: 1–2 moderately polluted C3: 2–3 moderately to strongly polluted C4: 3–4 strongly polluted C5: 4–5 strongly to extremely polluted C6: > 5 Extremely polluted	Müller (1969)
(3) $CF^i_j = \frac{(C^i)_s}{(C^i)_b}$	CF^i_j: is the contamination factor of single heavy metal (i) at sampling site (j) $(C^i)_b$: heavy metal background (mg kg^{-1})[a]: (Cd = 0.8, Cr = 20, Cu = 9.9, Fe = 1.8, Pb = 8.1, Ni = 17, Zn = 18.6)	CF < 1: low contamination 1 ≤ CF < 3: moderate contamination 3 ≤ CF < 6: considerable contamination CF > 6: very high contamination	Hakanson (1980)
(4) $CD_J = \sum_{i=1}^{n} CF^i_j$	CD_J: total contaminant factor of heavy metal at sampling site (j)	CD < 6: low degree of contamination 6 ≤ CD < 12: moderate degree of contamination 12 ≤ CD < 24: considerable degree of contamination CD > 24: high degree of contamination	Hakanson (1980)
(5) $E^i_j = T_C \times CF^i_j$	E^i_j is the index of a single potential ecological risk of heavy metal (i) at sampling site (j) T_C: Is the toxic response coefficient of heavy metal i (Zn = 1, Cr = 2, Ni = Pb = Cu = 5, Cd = 30)	E^i_j < 40: low ecological risk 40 < E^i_j < 80: moderate ecological risk 80 < E^i_j < 160: strong ecological risk 160 < E^i_j < 320: Quite strong ecological risk E^i_j > 320: Extremely strong ecological risk	Hakanson (1980)
(6) $PERI_j = \sum_{i=1}^{n} E^i_j$	$PERI_j$ is the index of comprehensive potential ecological risk at sampling site j	$PERI_j$ < 70: low potential ecological risk 70 < $PERI_j$ < 140: moderate ecological risk 140 < $PERI_j$ < 280: strong ecological risk 280 < $PERI_j$ < 560: Quite strong ecological risk $PERI_j$ > 560: Extremely strong ecological risk	Chen et al. (2018)

[a]Background values for Cr, Cu, Fe, Pb and Zn (De Paula Filho et al. 2015a). For Cd and Ni (Fadigas et al. 2006)

environment (Eq. 4). The E^i_j is the monomial potential ecological risk factor concerning the toxic response factor (T_C), representing the potential hazard of heavy metal contamination by indicating the toxicity of a particular heavy metal and the environmental sensitivity to contamination (Eq. 5). The global potential ecological risk index ($PERI_j$) was applied in order to classify the estuarine sampling sites as to their susceptibility to a potential ecological risk at each site (Eq. 6).

Heavy metal concentration results were compared to the sediment quality guideline (SQG) for heavy metals as described in the Brazilian Environmental Council Resolutions (BRASIL 2012). The regulation establishes guiding values for metals in fresh and estuarine sediments. Despite the sediment quality standards (SQSs) adopted in Brazil, refer to the bulk fraction (< 2 mm), in this study the concentrations of heavy metals were determined in the fine fraction of the sediments (< 63 µm). This fraction is recognized for concentrating contaminants considering that heavy metals are mainly linked to silt and clay and normally used in studies on heavy metal contamination (De Paula Filho et al. 2015a; Devanesan et al. 2017; Sharifinia et al. 2018). Another important factor is the ability to transport contaminants, since this grain size is associated with matter suspended in water (Pereira et al. 2010; Dias et al. 2016).

Two levels are established, a threshold below which there is a lower likelihood of adverse effects to the biota (Level 1 or TEL—Threshold Effect Level), and a second threshold above which there is a greater likelihood of adverse effects to the biota (Level 2 or PEL—Probable Effect Level), which do not apply to Mn, Al and Fe. Between the TEL and PEL possible adverse effects occasionally occur. The TEL—PEL sediment quality guidelines or environmental assessment criteria were used to check if metal concentrations in sediments may occasionally be associated with adverse

biological effects. These toxicity criteria are based on the compilation of matching biological and chemical data from numerous modeling, laboratory, and field measurement in marine and estuarine sediments (Long and Morgan 1990; CCME 2001; BRASIL 2012).

Results and discussion

Particle size distribution and organic carbon

The sediments in the mud area from the five channels of the Parnaíba River Delta mainly consist of sandy and fine-grained (< 63 µm) fractions (Table 3). The spatial distribution of the fine fraction contents is shown in Fig. 2a. The representativeness ranges for each fraction varied between 0.30 and 7.30%, with an average of 1.53 ± 1.61% for coarse sand, 69.70–92.60%, with an average of 84.51 ± 5.26% for sand, and 7.10–28.90%, with an average of 14.28 ± 4.47% for fine-grained sediment. The results showed a predominance of the sandy fraction from very fine to medium (1−4 Φ) following an upward trend according to the estuarine gradient. An increase in the size of the sedimentary particle towards the mouth of the main channels of the delta was observed, ranging from very fine sand (3−4 Φ) to medium sand (1−2 Φ). The mud or fine fraction (> 4 Φ) showed higher values in deposition areas more internal to the delta. The sediments in PRD present concentrations of the fine fraction below that reported for the São Francisco River estuary, whose values varied between 22 and 99% (Sabadini-Santos et al. 2009). Mud sediments were lower at the inner portion of the Tutóia bay and at the seaward end of the channel, all exposed to the interaction between river flow and mesotidal action (Dias et al. 2016). Part of the fine sediment is exported to the inshore sector of the continental shelf adjacent to the delta (Nascimento et al. 2010).

The OC distributes quite evenly in the mud area of the PRD, varying from 6.90 to 10.10%, with an average of 8.53 ± 0.71%. Despite the relative stability in its concentration in the superficial sediments, a greater retention of OC was observed in the innermost areas of the estuary. This trend accompanies the distribution behavior of fine sediments. The highest concentrations of OC occurred in more internal sampling sites in the estuary. Figure 2b shows the spatial behavior of organic carbon in the surface sediments of the delta. In the supplementary material, Table S1 details the concentrations of the different granulometric fractions determined in the 28 sampling sites.

Heavy metal concentrations

The concentration results for Cd, Cr, Cu, Mn, Ni, Pb, Zn, Al and Fe in the surface sediments of the twenty-eight sampling sites of the PRD are shown in Table 3. Considering the average values, the total heavy metal concentrations followed the following ranking: Al > Fe > Mn > Zn > Cr > Ni > Cu > Pb > Cd. In the supplementary material, Table S2 shows the concentrations of heavy metals in the 28 sampling sites.

The results were compared to the world average of metal concentrations of the shale (Turekian and Wedepohl 1961). Only Cd showed an average concentration higher than that reported for shales (0.3 mg kg^{-1}). Cadmium concentrations lower than the earth's crust were verified at the sampling sites Tb1 (0.22 mg kg^{-1}) and Tb4 (0.28 mg kg^{-1}). Several studies have reported that the world average metal concentrations in the shale are too high to represent background levels in different sedimentary basins (Marins et al. 2004; Santos-Francés et al. 2017; Li et al. 2019). One of the solutions proposed since the beginning of heavy metal evaluations is to define background limits through the local or regional evaluation of the existing contents in sediments deposited in sedimentary basins in pre-industrial eras (Sabadini-Santos et al. 2009; De Paula Filho et al. 2015a; Santos-Francés et al. 2017; Li et al. 2019). In the present study, higher average values than those of the regional background were observed for Cu, Cr, Ni, Zn and Fe. Metal load estimates for the Parnaíba River Delta indicated that the emissions of Zn and Cu by anthropic sources exceed natural emissions of those metals (De Paula Filho et al. 2014). On the other hand, a review of local background values can be considered in view of a more comprehensive study in time and space (Marins et al. 2004; De Paula Filho et al. 2015a).

The concentration averages in the PRD sediments were within or below the concentration ranges reported in related studies carried out in other coastal areas in the world (Sabadini-Santos et al. 2009; Marcovecchio and Ferrer 2005; Zhang et al. 2007; Neşer et al. 2012). In general, the PRD heavy metal concentration levels are in the same order of magnitude and range as the sediments of the São Francisco River estuary, also located in Northeast Brazil (Sabadini-Santos et al. 2009), and in Bahia Blanca in Argentina (Marcovecchio and Ferrer 2005; Buzzi and Marcovecchio 2018). However, in the regional comparison, the upper limits of the Cr, Cu and Fe ranges observed in this study exceeded those reported for the Bahia Blanca estuary. As an exception, the average Cd value in the PRD sediments was 50 times higher than the upper limit reported by Buzzi and Marcovecchio (2018). In this specific case, the authors indicated the strong biological influence of metal retention in indigenous mussel tissues (*Brachidontes rodriguezii*) reducing Cd concentrations in the evaluated sediments. Also, the Cd bands in the PRD sediments were up to an order of magnitude higher than that reported for Zhelin Bay in Guangdong, China (Wang et al. 2013). The other metals showed similarities in their low concentration levels, except for Pb whose upper limit in the PRD was about 10 times lower than the one reported for

Table 3 Textural and chemical data for superficial sediments of samples collected at the Igaraçú river (Ig), Parnaíba river (P), Caju bay (Cb), Melancieiras bay (Mb) and Tutóia bay (Tb). Heavy metals concentrations expressed in mg kg^{-1}, except Al and Fe (%). Grain size particles and organic carbon (%)

	Coarse sand[a]	Sand[b]	<63μm[c]	OC	Cd	Pb	Cu	Ni	Cr	Zn	Mn	Fe	Al
Range	0.30–7.30	69.70–92.60	7.10–28.90	6.90–10.10	0.22–0.62	3.60–10.00	1.80–47.20	6.92–29.01	20.08–46.59	30.58–57.60	67.06–398.30	1.50–5.55	1.80–6.49
Mean ± σ	1.53 ± 1.61	84.51 ± 5.26	14.28 ± 4.47	8.53 ± 0.71	0.50 ± 0.09	6.95 ± 2.13	19.02 ± 8.75	23.20 ± 5.04	33.52 ± 6.82	43.99 ± 7.47	165.73 ± 86.71	2.93 ± 0.89	3.78 ± 1.17
CV (%)	105	6.2	31	8.3	19	31	46	22	20	17	52	31	31
Earth's crust[d]	–	–	–	–	0.3	20	45	68	90	95	850	4.7	8.0
Regional background[e]	–	–	–	–	0.8[f]	8.1	9.9	17 [f]	20	18.6	829	1.8	–
São Francisco estuary, Brazil[g]	–	–	–	–	–	4–16	1–26	2–27	10–82	1–57	187–257	0.4–4.3	–
Bahía Blanca, Argentina	–	–	–	–	0.15–2.23[h] n.d–0.01[i]	8.53–19.82[h] 4.11–8.50[i]	5.88–18.10[h] 15.36–38.83[i]	6.30–10.03[i]	3.56–9.21[h] 7.45–20.25[i]	25.73–60.21[h] 25.88–57.29[i]	–	1.23–2.10[h]	–
Zhelin Bay, China[j]	–	–	–	–	0.01–0.10	17.3–104	5.40–36.4	3.90–15.3	8.21–27.2	29.6–91.6	252–1690	1.4–3.5	–
Aliağa Bay, Turkey[k]	–	–	–	1.7–6.4	0.42–3.94	91.3–751	49.7–703	95–240	81.1–264	180–685	587–1192	3.62–5.46	1.52–3.97
TEL – PEL[l]	–	–	–	–	0.6–3.5* 1.2–7.2**	35–91.3* 46.7–218**	35.7–197* 34–270**	18–35.9* 20.9–51.6**	37.3–90* 81–370**	123–315* 150–410**	–	–	–

[a]Sand—coarse to very coarse (−1 to 1 Φ); [b]Sand (1 to 4 Φ); [c]mud or fine fraction (>4 Φ); [d]Turekian and Wedepohl, (1961); [e]De Paula Filho et al. (2015a); [f]Fadigas et al. (2006); [g]Sabadini-Santos et al. (2009); [h]Marcovecchio and Ferrer (2005); [i]Buzzi and Marcovecchio (2018); [j]Wang et al. (2013); [k]Neşer et al. (2012); [l]BRASIL (2012):*For freshwater environments, **For marine and estuarine environments

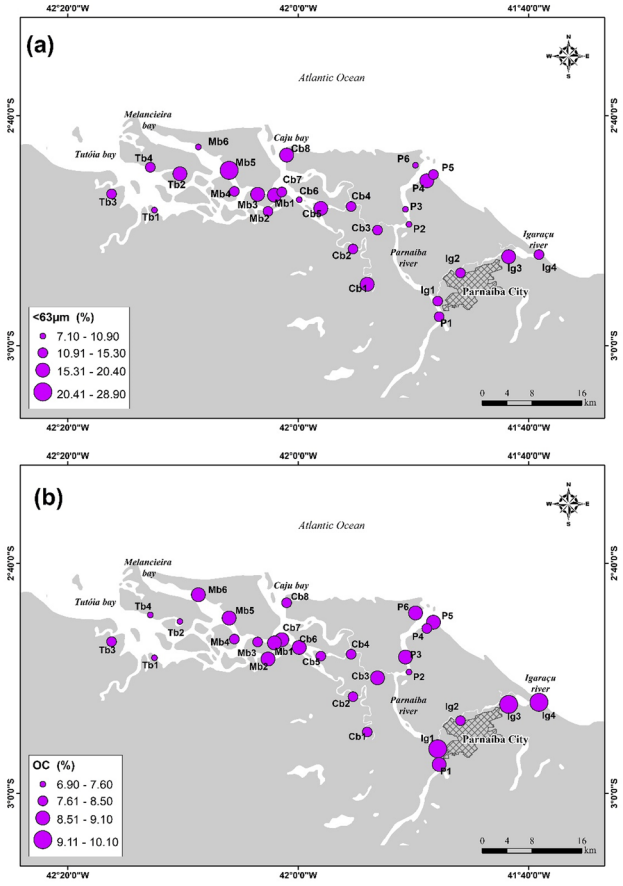

Fig. 2 Spatial distribution of the fine fraction (< 63 μm) an OC (%) contents in sampling sites along the Parnaíba River Delta (The diameter of the purple circumference is proportional to the fine fraction and OC concentration level at each sampling site)

Zhelin Bay. Highly impacted systems such Aliağa bay in the coast of Turkey presented sedimentary metal contents several orders of magnitude higher than those found in the PRD (Neşer et al. 2012). For example, the concentrations of Cu, Zn and Pb in PRD were, respectively, 15, 69 and 75 times lower than the quantified concentration limit in Aliağa bay.

Considering the threshold values provided for the reference guideline for metals in sedimentary environments (BRASIL 2012), the concentration ranges of Cd, Cr, Pb and Zn were lower than the TEL (Level 1) limits. On the other hand, the values of the upper limit for Cu and Ni were significantly lower than the PEL. For Cu and Ni, although the upper limit found in the sediments has exceeded the TEL value, these were up to two times lower than the PEL (Level 2). In 61% of the sampling sites, copper concentrations exceeded TEL, mainly in areas of greater sediment deposition in the Parnaíba River and in the Cajú and Melancieira bays. Thus, concentrations between the TEL and PEL indicated the possible effect range within which adverse effects occasionally occur (BRASIL 2012). On the other hand, this approach has limitations due to the overestimation of heavy metal concentrations since they refer only to the fine-grained fraction.

Mn, Al and Fe concentrations are strongly related to the predominance of Oxisols in the Parnaíba River basin. These soils are characterized by an advanced weathering state, with an accumulation of insoluble iron and aluminum oxides, the most frequent being goethite (αFeOOH), hematite (αFe_2O_3) and gibbsite ($\gamma Al(OH)_3$) (De Paula Filho et al. 2015a; Santos et al. 2018). These minerals are involved in various soil phenomena, such as in adsorption of anions, cations and organic compounds. Fe and Al oxides are important tropical soil and sediment minerals, responsible for the low mobility and bioavailability of heavy metals. The metal ions can be eletrostatically adsorbed or specifically, through covalent or partly covalent bindings to oxygen atoms from the mineral structure (Mellis et al. 2004).

Heavy metal spatial distribution

Although the concentrations of most studied metals are below the TEL range in most sampling sites, the study of their spatial distribution may elucidate further details about areas of preferential deposition within the Delta. Figure 3 shows the distribution maps for Cd(a), Pb(b), Cu(c), Ni (d), Cr(e), Zn(f), Mn(g), Fe(h) and Al(i) in the five estuarine channels of the PRD.

The data available in Tables S1 and S2, and the distribution maps (Fig. 3), show the distinction in the preferred areas for accumulation of heavy metals in the different estuarine channels. For example, in the channels with the greatest influence of river flows, P and Ig, or subject to greater intensity of coastal forces (e.g. wind shear, tidal waves and currents) as in Tb, there was a greater tendency in accumulate metals in places further downstream (P5, P6 and Ig4), following the river-marine gradient. On the other hand, in the Melancieiras and Cajú bays, there was a greater tendency for metals to accumulate in more internal sampling sites (C3, C4, M2 and M4), except for Aluminum. Especially for Cb and Mb, the hydrodynamic processes are apparently dominated by the tide. In this condition, elongated sandy bars and wide sandy tidal plains develop according to the direction of the marine currents, forming a channel of low sinuosity followed by an area of tight meanders and, finally, an interior area dominated by fluvial processes (Fig. 1). The energy of the tidal currents exceeds and dissipates the energy of the waves at the mouth, contributing to a greater estuary deposition (Schettini et al. 2016). This is corroborated by the distribution map of Iron. This metal is strongly associated with local lithology (De Paula Filho et al. 2015b).

The delta is integrated by a set of ecosystems embedded in pre-coastal boards of the Quaternary Formation (the Barreiras Formation). In this geomorphological units, the

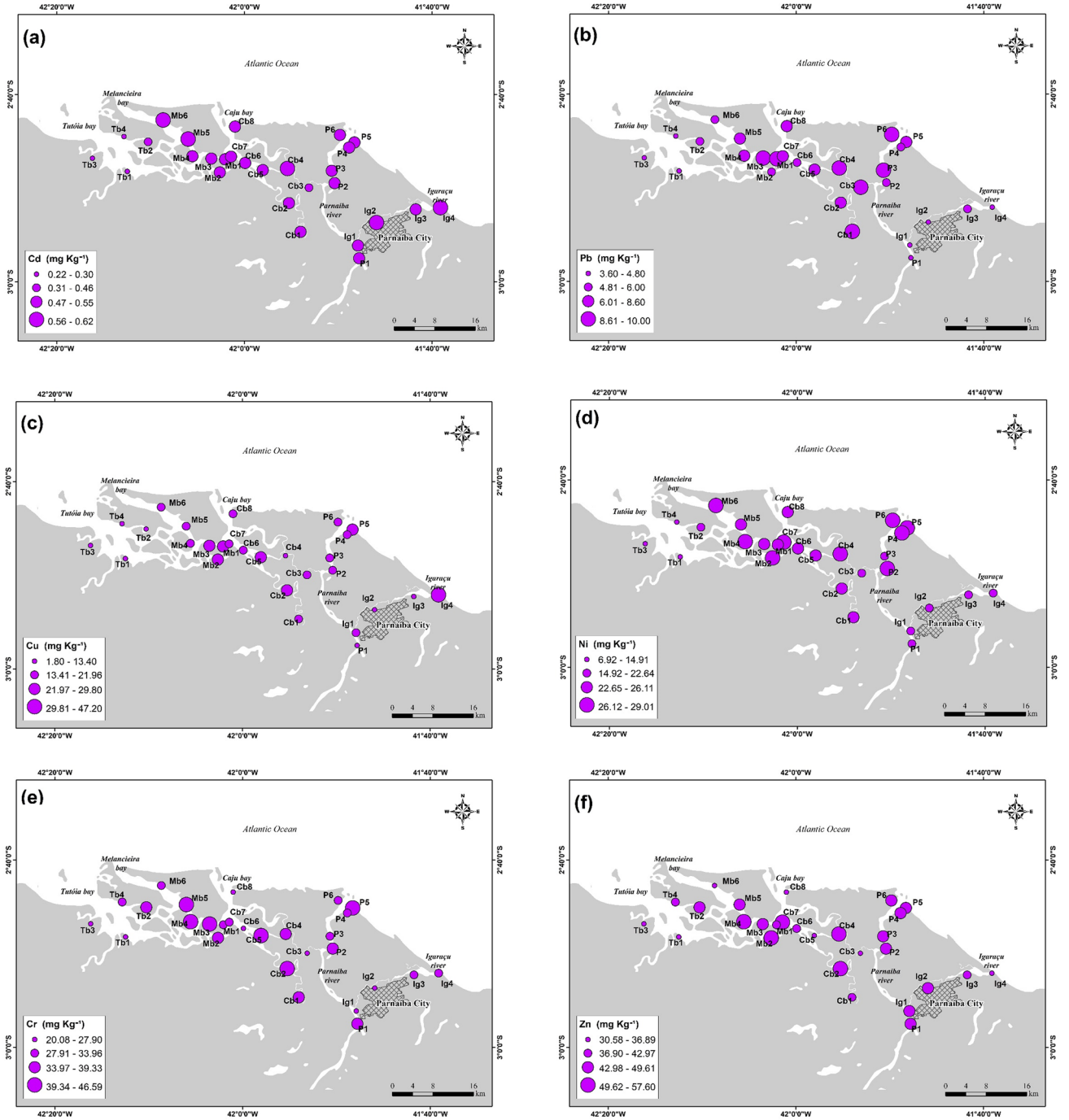

Fig. 3 Spatial distribution patterns of heavy metals in surface sediments of the Parnaíba River Delta (The diameter of the purple circumference is proportional to the metal concentration level at each sampling site)

characteristic soils are Oxisols, which provide loads of clay minerals to the estuarine zone. Clay minerals (kaolinite, iron oxides and aluminum oxides) have a strong ability to associate with heavy elements (micronutrients) such as copper and zinc. This also corroborate the tendency of chromium accumulation in sampling sites P2, P5, Cb2, Cb5 and Mb3–Mb5, of copper in Ig4, P5, Cb2, Cb5 and Mb1−Mb3, of nickel in P2, P4−P6, Cb4, Cb7, Mb2, Mb4 and Mb6, of lead in P3, P6, Cb1, Cb3, Cb4, Mb1 and Mb3 and of zinc in Cb2, Cb4, Cb7, Mb2 and Mb4.

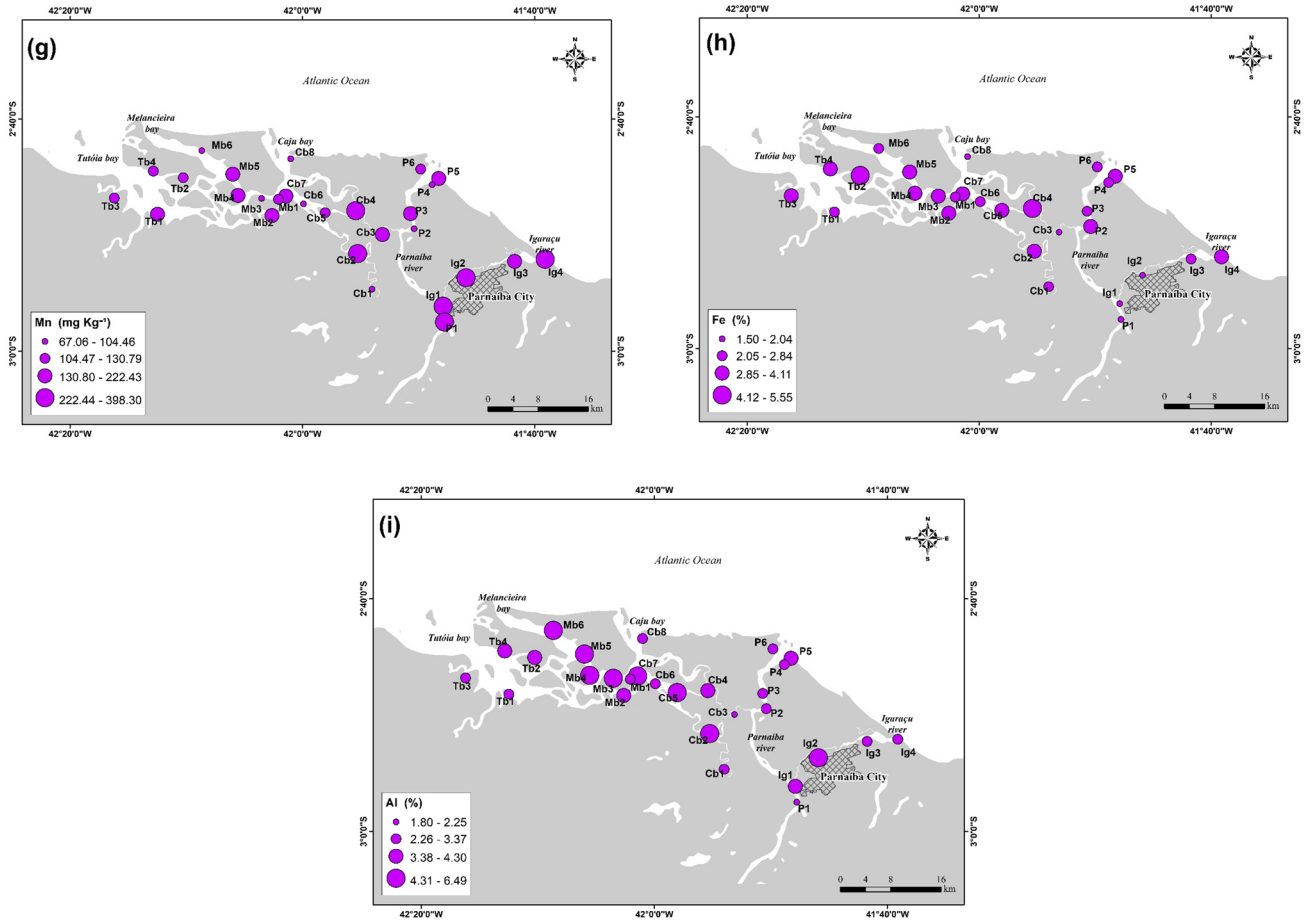

Fig. 3 (continued)

Statistical analysis

Geostatistical techniques were used to evaluate the differences in the geochemistry of metals in the estuarine sediments (Aguiar et al. 2014). The Shapiro–Wilk normality tests ($n = 28$, $p < 0.05$) demonstrated a normal distribution for Cu, Cr, Zn, Al and Fe. The logarithm-transformed data were applied to eliminate the influence of different units of variance and give each variable an equal weight. The analysis of the coefficients of variance (CV) showed that the concentrations of metals in the samples reflect their spatial distribution in the PRD (Table 3). Four categories were extracted from the statistical testing: (i) low distribution variability (CV < 20%) for OC, Sand, Zn, Cd and Cr; (ii) moderate variability (20% ≤ CV < 50%) for the fine-grained fraction (< 63 µm), Cu, Ni, Pb, Al and Fe; (iii) high variability (50% ≤ CV < 100%) for Mn; and (iv) very high variability for coarse sand (CV ≥ 100%) (Karim et al. 2014).

The Pearson correlation test showed positive interelemental correlations for Cu–Cr ($r = 0.53$, $p < 0.01$), Cu–Cd ($r = 0.50$, $p < 0.01$), Cu–Ni ($r = 0.46$, $p < 0.05$), Cu–Fe ($r = 0.41$, $p < 0.05$), Cd–Ni ($r = 0.78$, $p < 0.01$), Cd–OC ($r = 0.60$, $p < 0.01$), Cd–Pb ($r = 0.46$, $p < 0.05$), Cd–Zn ($r = 0.43$, $p < 0.05$), Cd–Cr ($r = 0.41$, $p < 0.05$), Cr–Ni ($r = 0.58$, $p < 0.01$), Cr–Pb ($r = 0.49$, $p < 0.01$), Pb–Ni ($r = 0.63$, $p < 0.01$), Pb–Zn ($r = 0.59$, $p < 0.01$), Pb–Fe ($r = 0.39$, $p < 0.05$), Ni–Zn ($r = 0.59$, $p < 0.05$) and Zn–Fe ($r = 0.42$, $p < 0.05$).

The availability of metals can be negatively or positively affected by organic carbon as a result of the formation of chelates or metal complexes (Mellis et al. 2004). The positive correlation between OC and Cd may mean a greater metal retention by biogenic fractions of the sediment. The bioavailability of metals is affected differently, depending on the matrix to which it is associated, whether geogenic or biogenic (Buzzi and Marcovecchio 2018).

One of the important factors that control the adsorption and retention of metals in the sediment is the size of the particles, with the recognition that most heavy metals are linked to the fine fraction (< 63 µm) of the sediment, mainly due to the high surface area (Zhang et al. 2007; Sabadini-Santos et al. 2009). Sediments with smaller

grain sizes, higher levels of OC, Fe and Mn have a greater capacity to adsorb heavy metals (He et al. 2016). Confirming this premise, the positive correlation between all metals and the silt + clay fraction demonstrates a possible common geogenic-lithogenic origin.

The results obtained from the Pearson's correlation test point to a greater association of heavy metals with lithogenic sources. The predominantly mineral origin of the metal concentrations in the PRD sediments is confirmed by the analysis of variance (ANOVA). When analyzing the variables for the different estuarine channels (Ig, P, Cb, Mb and Tb), the ANOVA test, based on available samples only, demonstrated that there was no statistically significant difference among them ($p < 0.01$) regarding the concentrations of metals. This result reflects the low to moderate metals concentration variability (CV%) in the sediments of the different estuarine channels, which may point to a common lithogenic origin of the heavy metals evaluated in this study. However, the relatively small numbers of samples from sampled channels may also contributed to this lack of significant differences.

The Hierarchical Cluster Analysis (HCA) was applied to the surface sediment dataset to group the similar analyzed variables (Fig. 4a). The variables were then grouped into two distinct groups. In both clusters it is possible to see the association between metals and their lithogenic origin. Cluster 1 shows the association between the major elements in clay minerals (Al and Fe) and Mn, Cr and Zn. Cluster 2 includes Cu, Cd, Ni, Pb and OC, which are associated with the fine sediment fraction (< 63 µm). On the other hand, anthropic factors can also contribute to the associations evidenced by HCA. The carrying of pedological material from adjacent agricultural areas containing metal–organic residues may, in part, explain this association (Carvalho et al. 2002).

The PCA were performed to compare the compositional pattern between the sediment samples and the factors influencing each one (Fig. 4b). Three principal components (PCs) with eigenvalues > 1 were extracted from the element concentrations, which explained 64% of the total variance in the sediment quality dataset. The first PC_1, which accounted for 34% of the total variance, was correlated (loading > 0.70) with OC (0.77) and Cd (0.89). The second PC_2, which accounted for 17% of total variance, had strong positive loadings on Al (0.70), Cr (0.72) and Zn (0.83). On the same PC, iron expressed moderate to high loading (0.62). PC_3 explains 13% of the observed variance and had a strong negative loading on Mn (− 0.85). The results obtained from the multivariate analysis of the data reflect the binding of heavy metals to clay minerals and organic matter and, as such, their distribution patterns are controlled by the fine fraction (< 63 µm). Since Al and Fe represent the terrigenous siliciclastic materials and are not influenced by urban activities in the study area, this factor can be considered to reflect the natural origin of major elements and heavy metals from weathering and erosion. However, contributions from runoff of the agriculture soils around the PRD should not be disregarded.

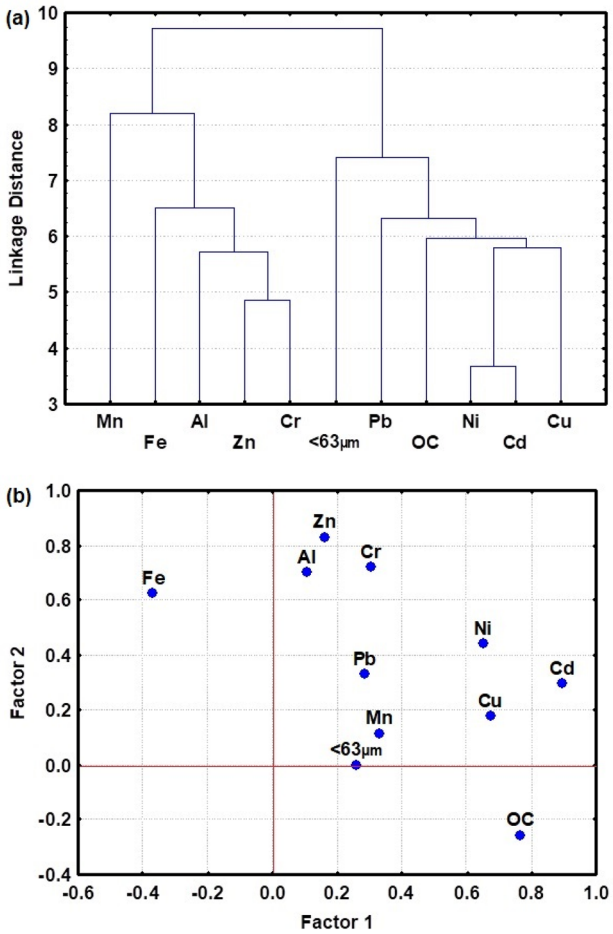

Fig. 4 **a** Dendrogram showing the clustering of the analyzed variables and **b** Loading plots obtained for the dataset

Heavy metal enrichment and geoaccumulation index

The calculation of the enrichment factor according to Eq. (1) showed that the sediments are not enriched in 78.5% of the sampling sites, minimally enriched in 21% of the cases and moderately enriched by metals in only 0.5% of the sampling sites. Considering the average EF value for the different sampling sites, the following ranking could be established: $EF_{Cd} < EF_{Pb} < EF_{Ni} < EF_{Cr} < EF_{Cu} < EF_{Zn}$. Enrichment factor and geoaccumulation indices for heavy metals at the PRD are summarized in Fig. 5, where standard error (SE) accounts for spatial variability. Figure 5a presents a graph with the mean values for the enrichment factor (EF) determined for each of the five estuarine channels (Ig, P, Cb, Mb and Tb).

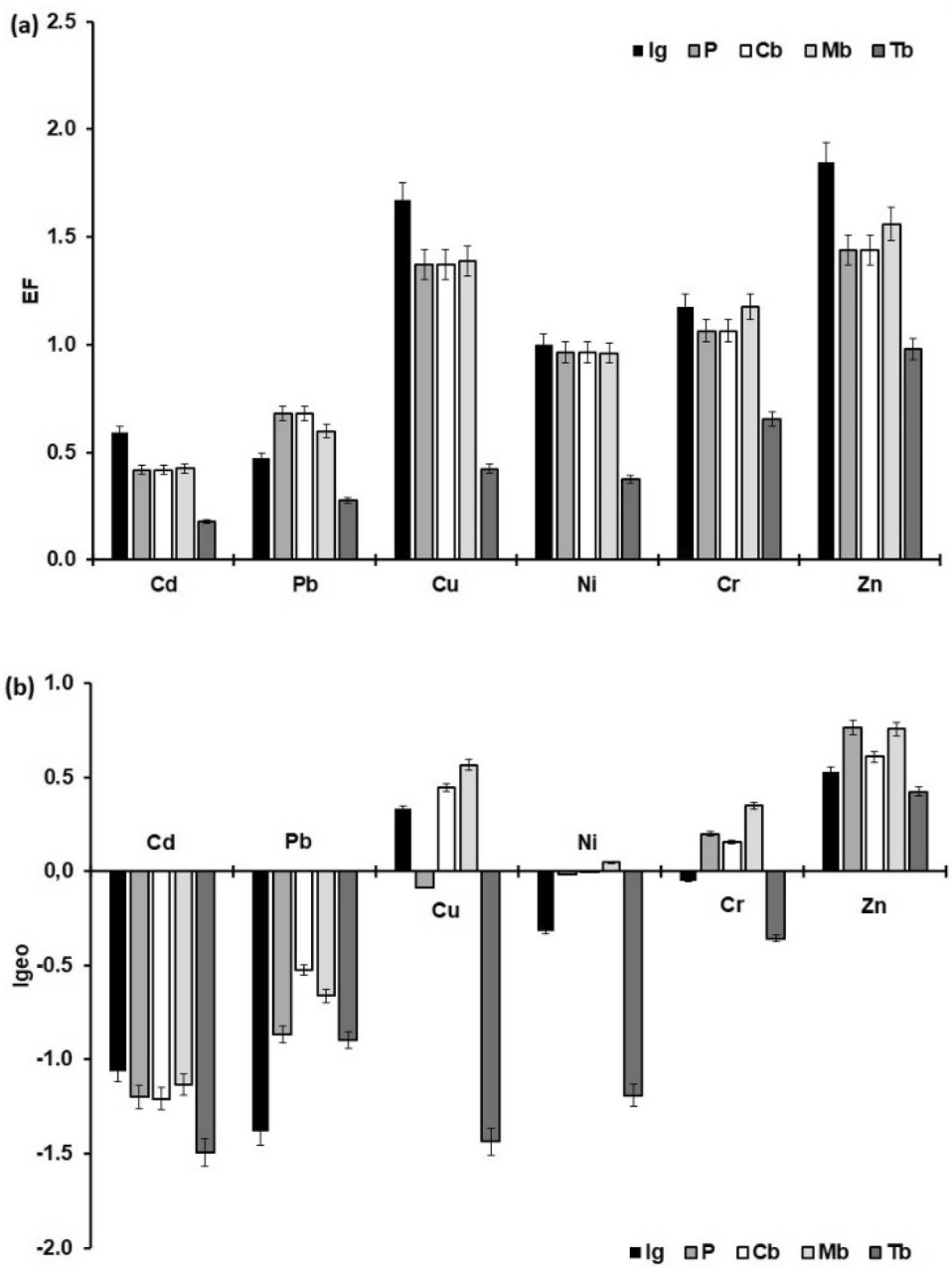

Fig. 5 **a** Enrichment factor (EF) and **b** Geoaccumulation index (Igeo) for metals in the surface sediments of the Parnaíba River Delta (mean value ± SE)

In this approach, Tutóia Bay presented EF values < 1 for all evaluated metals and, therefore, its sediments are classified as not enriched. The same is true for all other estuarine channels in relation to Cd and Pb. The results show higher values of sediment enrichment for Cr, Cu and Zn, although they are classified as minimally enriched. The Ig channel presented greater enrichment levels for most metals, which was probably related to the anthropic influence of Parnaíba city, the main regional urban center. Sharifinia et al. (2018) found similar behavior by Igeo in estuarine sediments close to industrial areas and receiving municipal effluents of Khamir City. De Paula Filho et al. (2014) estimated the metal loads from different natural and anthropogenic sources to the PRD. The effects of loads of metallic contaminants from urban runoff, sewage discharge and port activities can have an impact on the greater enrichment of the sediments of the Ig estuarine channel. In only one sampling site (P1) the EF reached values showing a moderate enrichment (EF = 3.12).

The Igeo results, according to Eq. (2), presented predominantly negative values. Figure 5b shows the behavior of the indicator considering each metal and the average value by estuary sector. According to the average values, the increasing order of geoaccumulation of metals was $Igeo_{Cd} < Igeo_{Pb} < Igeo_{Ni} < Igeo_{Cu} < Igeo_{Cr} < Igeo_{Zn}$.This behavior further

confirms the trend observed for the enrichment factor. In the estuarine channels there was a predominance of negative Igeo values for Cd and Pb. All sampling sites had an Igeo < 1 (Class 1), demonstrating that the sediments are not polluted by metals. Only the Ig4 site (Igeo = 1.67) was classified as Class 2 (moderately polluted) for Cu. These results are partly explained by the low regional background values considered in this study (Table 3). In the supplementary material, Table S3 presents the values of the enrichment factors and geoaccumulation index for each heavy metal in each sampling site of the Parnaíba River Delta.

Assessment of the heavy metal ecological risk

From the Cd, Cr, Cu, Pb, Ni and Zn concentration data in the PRD surface sediments it was possible to evaluate the susceptibility of the estuarine system with regard to heavy metal contamination. Table 4 presents the contamination factors (CF_j^i) and monomial potential ecological risk (E_j^i) obtained according to Eqs. (3) and (5) (Table 2). The obtained factors were then compared to those obtained in related studies carried out in coastal environments in other regions of the world. About 30% of the obtained results had a low contamination factor ($CF_j^i < 1$), according to the following ranking: $CF_{Cd} < CF_{Pb} < CF_{Ni} < CF_{Cr} < CF_{Cu} < CF_{Zn}$. Cd showed low contamination levels in all sampling sites. These results confirm the low enrichment of sediments by metals (Fig. 4). In the estuarine channels of the Igaraçú river (Ig) and Tutóia Bay (Tb) the CF_j^i confirmed a low lead contamination. Among all estuarine channels evaluated, Tb showed the lowest contamination factors, except for Zn. In 69% of the results, there was a predominance of moderate contamination conditions ($1 \leq CF_j^i < 3$). However, the lower limit of the classification range for considerable contamination was reached in Cb2 for copper, and in Cb4 and Mb2 for zinc. In these locations the concentrations of these metals exceeded by three times the local background values (De Paula Filho et al. 2015a). However, the need to review the local geochemical base values should be weighed, considering that the only study carried out in this area covered only sediments from the Parnaíba and Igaraçú channels.

According to Table 4, the Cd and Pb contamination factor ranges were lower than those reported for estuaries located in Iran coast of the Persian Gulf and Gulf of Oman (Sharifinia et al. 2018). However, the lower limit of Zn exceeds the upper limit of the range observed for metal in the subtropical estuaries evaluated in the same region. For copper, overlap occurs in the contamination factor ranges. Devanesan et al (2017) determined CF values between low and moderate for Al, Ni, Cr, Mn, Fe and highly contaminated for Pb in the sediments of the Tamilnadu coast, India. These different estuarine areas have similarities in terms of the presence of

Table 4 Contamination factors and potential ecological risk for each heavy metal in surface sediments of the Igaraçú river (Ig1–Ig4), Parnaíba river (P1–P6), Caju Bay (Cb1–Cb8), Melancieiras Bay (Mb1–Mb6) and Tutóia Bay (Tb1–Tb4), in the Parnaíba River Delta

Site	CF_j^i						E_j^i					
	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
Range	0.28–0.78	1.00–2.33	0.18–4.77	0.41–1.71	0.44–1.23	1.64–3.10	8.25–23.25	2.01–4.66	0.91–23.84	0.41–1.71	2.22–6.17	1.64–3.10
Mean ± σ	0.63 ± 0.12	1.68 ± 0.34	1.92 ± 0.90	1.36 ± 0.30	0.89 ± 0.26	2.36 ± 0.40	19.04 ± 3.32	3.36 ± 0.65	9.72 ± 4.15	1.37 ± 0.28	4.30 ± 1.27	2.37 ± 0.38
Khamir Estuary[a]	15.37–17.65	–	0.42–0.61	–	3.02–4.56	0.38–0.49	–	–	–	–	–	–
Tiyab Estuary[a]	10.39–13.07	–	0.34–0.46	–	2.92–3.74	0.34–0.41	–	–	–	–	–	–
Jagin Estuary[a]	3.90–4.53	–	0.18–0.21	–	1.92–2.16	0.22–0.26	–	–	–	–	–	–
Coast of Tamilnadu[b]	–	1.24–10.52	–	0.42–0.74	0.46–7.88	0.49–1.43	–	2.49–21.04	–	2.10–3.69	2.30–39.38	0.49–1.43
Gorgan Bay[c]	–	–	–	–	–	–	–	1.1–2.7	4–11	4.4–6.6	4.2–8.3	0.5–1.2

[a]Sharifinia et al. (2018)
[b]Devanesan et al. (2017)
[c]Gholizadeh and Patimar (2018)

mangrove forests and extensive muddy areas with high salinity in their waters. However, the different estuaries in Table 4 have significant differences in terms of anthropic stress levels. Although PRD is a pristine area subject to restrictions on human use and occupation, the CF results obtained for some metals may surpass areas subject to more significant anthropic interventions.

Table 4 also presents the individual behavior of the potential ecological risk for each type of heavy metal. The ranking obtained from the average values per metal followed this increasing order: $E_{Ni} < E_{Zn} < E_{Cr} < E_{Pb} < E_{Cu} < E_{Cd}$. All sites presented a low ecological risk ($E_j^i < 40$) for the evaluated metals. In the Igaraçú river (Ig4), the highest ecological risk indices were recorded for Cd and Cu (23.25 and 23.84, respectively). The Cb1 site presented a higher ecological risk for Pb (6.17), while Cb2 for Cr (4.66). The highest ecological risk values for Ni (1.71) and Zn (3.10) were obtained in Mb2. In general, Tutóia Bay presented the lowest E_j^i values for sediments among the different PRD estuarine channels, confirming the observations made for the enrichment factor and geoaccumulation index. Similarly, the results of E_j^i values in the Tamilnadu for Cr, Ni, Zn and Pb were less than 40, indicating that sediments are low potential ecological risk (Devanesan et al. 2017). In the Gorgan Bay, southeast end of the Caspian Sea, the results of the ecological risk of individual metals for Cr, Cu, Ni, Pb and Zn reveled that metals had a low ecological risk at all stations (Gholizadeh and Patimar 2018). However, in general the values were higher than those observed for PRD.

Both indices showed that the sediments do not present a degree of danger to the local biota in PRD. However, Pb, Cu and Cd present different ecological risks in some specific areas reflecting primarily the characterization of potential anthropogenic sources of these metals since it occurs in areas near Parnaíba city and neighbors, where there are tourism and fishery small harbors. In the supplementary material, Table S4 presents the values of the contamination factors and potential ecological risk for each heavy metal in each sampling station of the Parnaíba River Delta.

In estuarine ecosystems, the exposure of organisms to the ecotoxicological effects of metals depends on the biogeochemical circulation and the specific ecotoxicity of each metal. When exceeding the concentration limits, adverse biological effects can occur (Jara-Marini et al. 2009; Liu et al. 2015; Buzzi and Marcovecchio 2018). Thus, the contamination degree (CD) and the potential ecological risk index (PERI) were determined for each sampling site according to Eqs. (4) and (6) (Table 2). The results are presented through box-plot graphs considering each estuarine channel, as shown in Fig. 6.

The contamination degree (CD) ranged from 4.66 to 11.55, with an average of 8.72 ± 1.72. In terms of CD

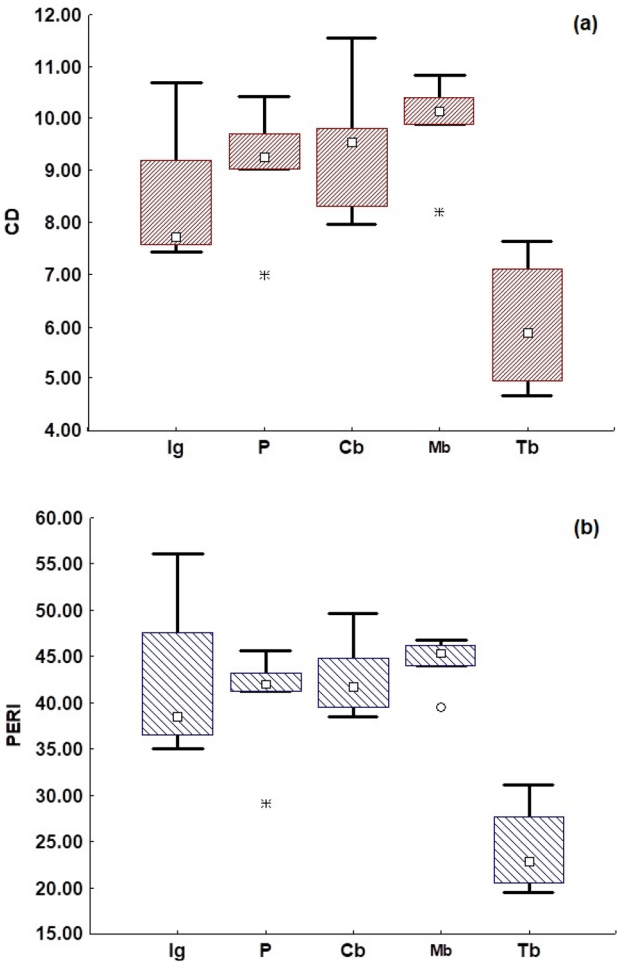

Fig. 6 **a** Total contamination degree (CD) and **b** potential ecological risk level (PERI) of heavy metals in the surface sediments of the main estuarine channels of the Parnaíba River Delta. (open square) Median, (open rectangle) 50% of the concentration data, whiskers or horizontal bars represent the 25−75% quartiles, (open circle) Outliers (⁜) Extremes

average, the sediments of the Parnaíba River Delta can be classified as having a moderate degree of contamination ($6 \leq CD < 12$). Only the sediments of sampling sites Tb1 and Tb3 had a $CD < 6$, which showed a low degree of contamination. PERI ranged from 19.52 to 56.01 with an average of 39.84 ± 8.30, values that classify the PRD sediments as having low potential ecological risk. As shown in Fig. 6, there is an upward trend in the CD and PERI values according the following order: $CD_{Tb}/PERI_{Tb} < CD_{Ig}/PERI_{Ig} < CD_P/PERI_P < CD_{Cb}/PERI_{Cb} < CD_{Mb}/PERI_{Mb}$.

In the estuaries of the Persian Gulf and Gulf of Oman the results of the contamination degree ranged from 6.23 to 23.29 and the potential ecological risk index varied between 127.93 and 556.02, values that are higher than those verified in PRD (Table 4). On average, the results of CD and PERI in the PRD sediments were about 2–8 times lower than those

reported for estuaries of the coast of Iran (Sharifinia et al. 2018). The CD results for metals in the coast of Tamilnadu, India were higher than those of PRD, ranging from moderate (Cd) to high degree of contamination (Cr, Mn, Ni, Zn and Fe) of sediments (Devanesan et al. 2017). But the *PERI* values of Cr and Pb show the moderate to strong potential ecological risk.

The results of the different factors and indices used in the study reinforce the classification of Tutóia Bay as an uncontaminated area with a low potential for ecological risk for the evaluated metals. Geographically located at the western end of the Environmental Protection Area of the Parnaíba Delta, Tutóia Bay is less influenced by the river inputs of the Parnaíba River. Its hydrodynamic circulation is strongly affected by the action of the tides and winds, which combined promote intense transport of materials launched to the adjacent platform (Pereira et al. 2010). In this sector of the delta we obtained the lowest average levels of organic carbon (7.5%) and fine fraction (< 63 µm). Consequently, the sediment retention capacity is reduced since OC and the clay minerals present in the fine fraction have a high geochemical activity in adsorbing different contaminating chemical species. On the other hand, the Cb and Mb channels represent areas with strong material retention. The morphodynamical characteristics are affected by the mesotidal regime active in the region, which formed dozens of internal islands (Schettini et al. 2016). In this region of the estuary, the fine fraction of the sediments reached up to 29% in mass, with an average of 16%, reflecting a greater metal retention. This is corroborated by the metal distribution data showed in Fig. 3 and by the higher CD and PERI values.

Conclusions

Different useful tools, methods, guidelines and indices have been employed for evaluation of sediment contamination in the Parnaíba River Delta. The ranking of the different metals in the estuarine channels using different contamination criteria showed adequate for the environmental assessment of the area.

Several factors explain the low concentrations of metals, such as the low intensity of anthropogenic activities near the PRD, the high hydrodynamics and the sediment texture, as sandy sediments tend to retain less contaminants than finer ones. Thus, sediments from the Tutóia Bay channel appeared to present a low contaminant accumulation capacity. Nevertheless, some attention should be given to the Igaraçú river and the potential anthropogenic sources of Pb, Cu and Cd, as its sediments presented higher percentages of fine sediments and organic matter, and thus this region may become more vulnerable to urban contamination from Parnaíba city.

Finally, the PRD presents pristine conditions, as it could be expected due to its isolation and the restrictions to human presence that were imposed in recent history. Concentrations of heavy metals in sediments from the PRD may be the regional background values, except Igaraçú area, and should be considered the baseline for future monitoring programs on the environmental quality of the NE coast of Brazil. These baseline values are of special interest, considering the protected status of this area.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s12665-021-09456-2.

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Author contributions FJDePF: investigation, validation, writing—original draft. conceptualization, funding acquisition, resources, writing—review and editing, formal analysis, project administration. RVM: conceptualization, funding acquisition, supervision, resources, formal analysis, writing—review and editing, project administration. DVS: investigation, validation. RFPJ: investigation, validation. JMCM: methodology, investigation, validation. Writing—review and editing. FGCG: methodology, formal analysis, validation. AG: writing—review and editing, investigation, resources. RNPT: methodology, investigation, validation.

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Aguiar JE, Marins RV, Almeida MD (2007) Comparison of marine sediment digestion methodologies for the characterization of trace-metal geochemistry on the northeast Brazilian continental shelf. Geochim Bras 21(3):304–323

Aguiar JE, Lacerda LD, Miguens FC, Marins RV (2014) The geostatistics of the metal concentrations in sediments from the eastern Brazilian continental shelf in areas of gas and oil production. J S Am Earth Sci 51:91–104. https://doi.org/10.1016/j.jsames.2013.12.005

Beraldi GQF, Rezende CE, Almeida MG, Carla C, Lacerda LD, Farias RN, Vidal M, Souza MDP, Molisani MM (2019) Assessment of a coastal lagoon metal distribution through natural and anthropogenic processes (SE, Brazil). Mar Pollut Bull 146:552–561. https://doi.org/10.1016/j.marpolbul.2019.07.007

BRASIL (2012) Brazilian National Council of the Environment—CONAMA. Resolution no. 454. Publication DOU, of 11/08/2012, Section 1, p. 66. http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=693. Accessed 20 Dec 2019

Buzzi NS, Marcovecchio JE (2018) Heavy metal concentrations in sediments and in mussels from Argentinean coastal environments.

S Am Environ Earth Sci 77:321. https://doi.org/10.1007/s12665-018-7496-1

Carvalho CEV, Salomão MSMB, Molisani MM, Rezende CE, Lacerda LD (2002) Contribution of a medium-size tropical river to the particulate heavy-metal load for the South Atlantic Ocean. Sci Total Environ 284:85–93. https://doi.org/10.1016/S0048-9697(01)00869-5

CCME—Canadian Council of Ministers of the Environment (2001) Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Introduction, updated in Canadian Environmental Quality Guidelines. 1999. Winnipeg, Manitoba. https://www.pla.co.uk/Environment/Canadian-Sediment-Quality-Guidelines-for-the-Protection-of-Aquatic-Life. Accessed 20 Dec 2019

Chakraborty S, Chakraborty P, Sarkar A, Kazip A, Mascarenhas-Pereira MBL, Nagender Nath B (2019) Distribution and geochemical fractionation of lead in the continental shelf sediments around India. Geol J 54:1190–1204. https://doi.org/10.1002/gj.3218

Chen Y, Jiang X, Wang Y, Zhuang D (2018) Spatial characteristics of heavy metal pollution and the potential ecological risk of a typical mining area: a case study in China. Process Saf Environ 113:204–219. https://doi.org/10.1016/j.psep.2017.10.008

De Paula Filho FJ, Marins RV, Aguiar JE, Peres TF, Lacerda LD (2014) Emisiones naturales y antrópicas de Zn, Cu, Pb, Cr, Cd y Hg al Delta del Río Parnaíba/NE/Brasil. In: Marcovecchio, Botté, Freije (eds) Procesos Geoquímicos de la Superficie en América Latina. Sociedad Iberoamericana de Física y Química Ambiental, Sección 2 – Capítulo 13. Salamanca, España, pp 179–202. https://www.sifyqa.org.es/libro_pqsi.pdf. Accessed 10 Dec 2019

De Paula Filho FJ, Marins RV, Lacerda LD, Aguiar JE, Peres TF (2015a) Background values for evaluation of heavy metal contamination in sediments in the Parnaíba River Delta estuary. NE/Brazil Mar Pollut Bull 91(2):424–428. https://doi.org/10.1016/j.marpolbul.2014.08.022

De Paula Filho FJ, Marins RV, Lacerda LD (2015b) Natural and anthropogenic emissions of N and P to the Parnaíba River Delta in NE Brazil. Estuar Coast Shelf Sci. 166:34–44. https://doi.org/10.1016/j.ecss.2015.03.020

Federal Decision 28th August (1996) Brazilian Federal Government. http://www.planalto.gov.br/ccivil_03/DNN/Anterior%20a%202000/1996/Dnn4368.htm Accessed 01 Nov 2020

Devanesan E, Suresh Gandhi M, Selvapandiyan M, Senthilkumar G, Ravisankar R (2017) Heavy metal and potential ecological risk assessment in sedimentscollected from Poombuhar to Karaikal Coast of Tamilnadu using Energy dispersive X-ray fluorescence (EDXRF) technique. Beni-Suef Univ J Basic Appl Sci 6:285–292. https://doi.org/10.1016/j.bjbas.2017.04.011

Dias FJS, Castro BM, Lacerda LD, Miranda LB, Marins RV (2016) Physical characteristics and discharges of suspended particulate matter at the continent-ocean interface in an estuary located in a semiarid region in northeastern Brazil. Estuar Coast Shelf Sci 180:258–274. https://doi.org/10.1016/j.ecss.2016.08.006

El-Kady AA, Wade TL, Sweet ST, Klein AG (2019) Spatial distribution and ecological risk assessment of trace metals in surface sediments of Lake Qaroun. Egypt Environ Monit Assess 191:413. https://doi.org/10.1007/s10661-019-7548-3

Fadigas FS, Sobrinho NMBA, Mazur N, Anjos LHC, Freixo AA (2006) Proposition of reference values for natural concentration of heavy metals in Brazilian soils. Rev Bras Eng Agric Ambient 10(3):699–705. https://doi.org/10.1590/S1415-43662006000300024

Farias ACS, Filho AAF, Ivo CTC, Fernande CAF, Cunha FEA (2015) Productive chain of fishing in the interior of the Parnaíba Delta and adjacent marine area. RDS, Fortaleza, p 240

Gholizadeh M, Patimar R (2018) Ecological risk assessment of heavy metals in surface sediments from the Gorgan Bay. Caspian Sea Mar Pollut Bull 137:662–667. https://doi.org/10.1016/j.marpolbul.2018.11.009

Hakanson L (1980) An ecological risk index for aquatic pollution control: a sedimentological approach. Water Res 14(8):975–1001. https://doi.org/10.1016/0043-1354(80)90143-8

He D, Shi X, Wu D (2016) Particle-size distribution characteristics and pollution of heavy metals in the surface sediments of Kuitun River in Xinjiang. China Environ Earth Sci 75:104. https://doi.org/10.1007/s12665-015-4882-9

Ismail A, Toriman ME, Juahir H, Zain SM, Habir NL, Retnam A, Kamaruddin MK, Umar R, Azid A (2016) Spatial assessment and source identification of heavy metals pollution in surface water using several chemometric techniques. Mar Pollut Bull 106(1–2):292–300. https://doi.org/10.1016/j.marpolbul.2015.10.019

Jara-Marini ME, Soto-Jimenez MF, Paez-Osuna F (2009) Trophic relationships and transference of cadmium, copper, lead and zinc in a subtropical coastal lagoon food web from SE gulf of California. Chemosphere 77:1366–1373. https://doi.org/10.1016/j.chemosphere.2009.09.025

Karim Z, Qureshi BA, Mumtaz M, Qureshi S (2014) Heavy metal content in urban soils as an indicator of anthropogenic and natural influences on landscape of Karachi—a multivariate spatiotemporal analysis. Ecol Indic 42:20–23. https://doi.org/10.1016/j.ecolind.2013.07.020

Krumbein WC (1934) Size Frequency distribution of sediments. J Sediment Petrol 4(2):65–77. https://doi.org/10.1306/D4268EB9-2B26-11D7-8648000102C1865D

Lacerda LD, Molisani MM, Sena D, Maia LP (2008) Estimating the importance of natural and anthropogenic sources on N and P emission to estuaries along the Ceará State Coast NE Brazil. Environ Monit Assess 141:149–164. https://doi.org/10.1007/s10661-007-9884-y

Lacerda LD, Marins RV, Dias FJS (2020) An Arctic Paradox: response of Fluvial Hg inputs and bioavailability to global climate change in an extreme coastal environment. Environ Front Earth Sci 8:93. https://doi.org/10.3389/feart.2020.00093

Li Z, Deblon J, Zu Y, Colinet G, Li B, He Y (2019) Geochemical baseline values determination and evaluation of heavy metal contamination in soils of Lanping Mining Valley (Yunnan Province, China). Int J Environ Res Public Health 16(23):4686. https://doi.org/10.3390/ijerph16234686

Liu S, Shi X, Liu Y, Zhu Z, Yang G, Zhu A, Gao J (2011) Concentration distribution and assessment of heavy metals in sediments of mud area from inner continental shelf of the East China Sea. Environ Earth Sci 64:567–579. https://doi.org/10.1007/s12665-011-0941-z

Liu X, Huang D, Zhu Y, Chang T, Liu Q, Huang L, Zhao W, Lin K, Liu L (2015) Bioassessment of marine sediment quality using meiofaunal assemblages in a semi-enclosed bay. Mar Pollut Bull 100:92–101. https://doi.org/10.1016/j.marpolbul.2015.09.024

Long ER, Morgan LG (1990) The potential for biological effects of sediments-sorbed contaminants tested in the National Status and Trends Program. Seattle: NOAA Tech Memo NOS OMA 52. U.S. National Oceanic and Atmospheric Administration. 175 pp + appendices. http://udspace.udel.edu/handle/19716/1562. Accessed 20 December 2019

Loring DH, Rantala RTT (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci Rev 32(4):235–283. https://doi.org/10.1016/0012-8252(92)90001-A

Marcovecchio J, Ferrer L (2005) Distribution and geochemical partitioning of heavy metals in sediments of the Bahía Blanca estuary. Argentina J Coast Res 21(4):826–834. https://doi.org/10.2112/014-NIS.1

Marins RV, Paula Filho FJ, Maia SRR, Lacerda LD, Marques WS (2004) Total mercury distribution as a proxy of urban and

industrial pollution along the Brazilian coast. Quim Nova 27:763–770. https://doi.org/10.1590/S0100-40422004000500016

McCave I, Syvitski J (1991) Principles and methods of geological particle size analysis. In: Syvitski JPM (ed) Principles, methods and application of particle size analysis. Cambridge University Press, Cambridge, pp 1–21. https://doi.org/10.1017/CBO9780511626142

Mellis EV, Cruz MCP, Casagrande JC (2004) Nickel adsorption by soils in relation to pH, organic matter, and iron oxides. Sci Agric 61(2):190–195. https://doi.org/10.1590/S0103-90162004000200011

Mendonza-Carranza M, Sepúlveda-Lozada A, Dias-Ferreira C, Geissen V (2016) Distribution and bioconcentration of heavy metals in a tropical aquatic food web: a case study of a tropical estuarine lagoon in SE Mexico. Environ Pollut 210:155–165. https://doi.org/10.1016/j.envpol.2015.12.014

Schettini CAF, Miranda JB, Valle-Levinson A, Truccolo EC, Domingues EC (2016) The circulation of the lower Capibaribe Estuary (Brazil) and its implications for the transport of scalars. Braz J Oceanogr 64(3):263–276. https://doi.org/10.1590/S1679-87592016119106403

MMA (2006) Ministério do Meio Ambiente. Secretaria de Recursos Hídricos. Caderno da Região Hidrográfica do Parnaíba. Brasília: 2005. http://pnrh.cnrh-srh.gov.br. Accessed 13 Dec 2019

Moreira LB, Saes RVST, Peres TF, Taniguchi S, Bicego MC, Marins RV, Abessa DMS (2019) Toxicity of sediments and dredged material from a semi-arid coastal system to marine invertebrates. Ecotox Environ Safe 14(1):79–89. https://doi.org/10.5132/eec.2019.01.10

Moreira LB, Sasaki ST, Taniguchi S, Peres TF, Figueira RCL, Bícego MC, Marins RV, Costa-Lotufo LV, Abessa DMS (2020) Biomarkers responses of the clam Anomalocardia flexuosa in sediment toxicity bioassays using dredged materials from a semi-arid coastal system. Heliyon 6(5):e04030. https://doi.org/10.1016/j.heliyon.2020.e04030

Müller G (1969) Index of geo-accumulation in sediments of the Rhine River. Geo J 2:108–118

Nascimento FS, Freire GSS, Miola B (2010) Geochemistry of marine sediments of the Brazilian Northeastern continental shelf. Braz J Oceanogr 58(spe2):01–11. https://doi.org/10.1590/S1679-87592010000600002

Nelson DW, Sommers LE (1982) Total carbon, organic carbon, and organic matter. In: Page AL, Miller RM, Keeney DR (eds) Methods of soil analysis: part 2 ed., Chemical and microbiological properties, second ed. Agronomy Series 9. American Society of Agronomy, Madison, pp 539–579

Neşer G, Kontas A, Ünsalan D, Uluturhan E, Altay O, Darılmaz E, Küçüksezgin F, Tekoğul N, Yercan F (2012) Heavy metals contamination levels at the Coast of Aliağa (Turkey) ship recycling zone. Mar Pollut Bull 64:882–887. https://doi.org/10.1016/j.marpolbul.2012.02.006

North MA (2009) A method for implementing a statistically significant number of data classes in the Jenks algorithm. In: Fuzzy Systems and Knowledge Discovery, 2009. FSKD'09. Sixth International Conference on, IEEE, pp. 35–38. https://doi.org/10.1016/10.1109/FSKD.2009.319

Oliveira RCB, Marins RV (2011) Trace metals dynamics in soil and estuarine sediment as a major factor controlling contaminants contribution to the aquatic environment: review. Rev Virtual Quim 3(2):88–102. https://doi.org/10.5935/1984-6835.20110014

Paula FCF, Lacerda LD, Marins RV, Aguiar JE, Ovalle ARC, Falcao Filho CAT (2010) Natural and anthropogenic emissions of metals and nutrients to the lower contas river basin, Bahia state. Brazil. Quím Nova. 33(1):70e75. https://doi.org/10.1590/S0100-40422010000100014

Pereira MD, Siegle E, Miranda LD, Schettini CAF (2010) Seasonal hydrodynamic and suspended particulate matter transport in a tidally dominated estuary: Caravelas Estuary, Bahia. Brazil Rev Bras Geof 28(3):427–444. https://doi.org/10.1590/S0102-261X2010000300008

Rios JHL, Marins RV, Oliveira KF, Lacerda LD (2016) Long-Term (2002–2015) Changes in Mercury Contamination in NE Brazil Depicted by the Mangrove Oyster Crassostraea rhizophorae (Guilding, 1828). Bull Environ Contam Toxicol 97:474–479. https://doi.org/10.1007/s00128-016-1855-y

Sabadini-Santos E, Knoppers BA, Oliveira EP, Leipe T, Santelli RE (2009) Regional geochemical baselines for sedimentary metals of the tropical São Francisco estuary. NE-Brazil Mar Pollut Bull 58:601–634. https://doi.org/10.1016/j.marpolbul.2009.01.011

Santos HG, Jacomine PKT, Anjos LHC, Oliveira, VA, Lumbreras JF, Coelho MR, Almeida JA, Araujo Filho JC, Oliveira JB, Cunha TJF (2018) Sistema brasileiro de classificação de solos. Brasília, DF. https://www.infoteca.cnptia.embrapa.br/infoteca/bitstream/doc/1094003/2/SiBCS2018ISBN9788570358004.pdf. Acessed 10 November 2019

Santos-Francés F, Martínez-Graña A, Rojo PA, Sánchez AG (2017) Geochemical background and baseline values determination and spatial distribution of heavy metal pollution in soils of the Andes mountain range (Cajamarca-Huancavelica, Peru). Int J Environ Res Public Health 14(8):859. https://doi.org/10.3390/ijerph14080859

Sharifinia M, Taherizadeh M, Namin JI, Kamrani E (2018) Ecological risk assessment of trace metals in the surface sediments of the Persian Gulf and Gulf of Oman: Evidence from subtropical estuaries of the Iranian coastal waters. Chemosphere 191:485–493. https://doi.org/10.1016/j.chemosphere.2017.10.077

Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. Geochim Cosmochim Acta 8(1):1273–1285. https://doi.org/10.1016/0016-7037(64)90129-2

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the Earth's crust. Geol Soc Am Bull 72:175–192. https://doi.org/10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2

Wang S-L, Xu X-R, Sun Y-X, Liu J-L, Li H-B (2013) Heavy metal pollution in coastal areas of South China: a review. Mar Pollut Bull 76:7–15. https://doi.org/10.1016/j.marpolbul.2013.08.025

Zhang W, Yu L, Lu M, Hutchinson SM, Feng H (2007) Magnetic approach to normalizing heavy metal concentrations for particle size effects in intertidal sediments in the Yangtze Estuary. China Environ Pollut 147:238–244. https://doi.org/10.1016/j.envpol.2006.08.003