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Review on metal contamination in equatorial estuaries in the Brazilian Northeast

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The present study provides an overview and assessment of the metals and trace metals registered in water, sediment, and biota in estuaries of the Equatorial Zone of the Brazilian Northeast (EZBN). The study aims to compare the degree of contamination and highlight necessary complementary research. The EZBN is characterized by the transition between the humid and hot Amazonian climate and the hot and dry semiarid climate. The spatial distribution identified enrichment for Cu, Pb, Zn, Hg, and Fe in the sediment, and sequential extraction of metals suggested low to medium mobility of metals along the environments. The Parnaíba River Delta, Curimataú, and the Anil and Bacanga estuaries were the environments with the lowest sediment quality for Pb, Zn, Cu, and Fe, identified by the geoaccumulation index (Igeo). The deposits in these estuaries were related to anthropogenic contributions from domestic sewage and inadequate disposal of wastewater from shrimp farms. However, more studies to determine the natural background levels based on sediment cores and metal speciation are necessary to better differentiate between natural and anthropic sources. Oysters, carnivorous fishes, and crustaceans had the best feedback as biomonitors for Cu, Pb, Zn, and Hg, but the application of biomonitoring needs to be expanded and maintained so that the potential for environmental degradation, which can have significant consequences both for the ecosystem and for human health, can be closely monitored in the EZBN estuaries.

KEYWORDS

sediments, sequential extraction, estuarine waters, biomonitor, Igeo accumulation index

1 Introduction

An estuary is a good example of a coupled system that can balance physical, chemical, and biotic components, and that consists of several subsystems intertwined and influenced by the seawater flow. Estuaries provide goods and services that are economically and ecologically indispensable as well as support the establishment of economic activities. However, to fully characterize environmental impacts in estuaries, activities located at the drainage basin upstream of the estuary need to be considered because their magnitude and changing nature can impact the support capacity of estuarine ecosystems (Santana et al., 2015). Local and upper drainage basin discharges from anthropogenic activities deposit many substances in estuaries, including trace metals. Most trace metal contamination causes serious environmental problems globally because of their toxicity, non-biodegradable properties, and accumulation and biomagnification in the food chain (Barletta et al., 2019). When contaminants enter estuaries, they can adsorb onto suspended particles,

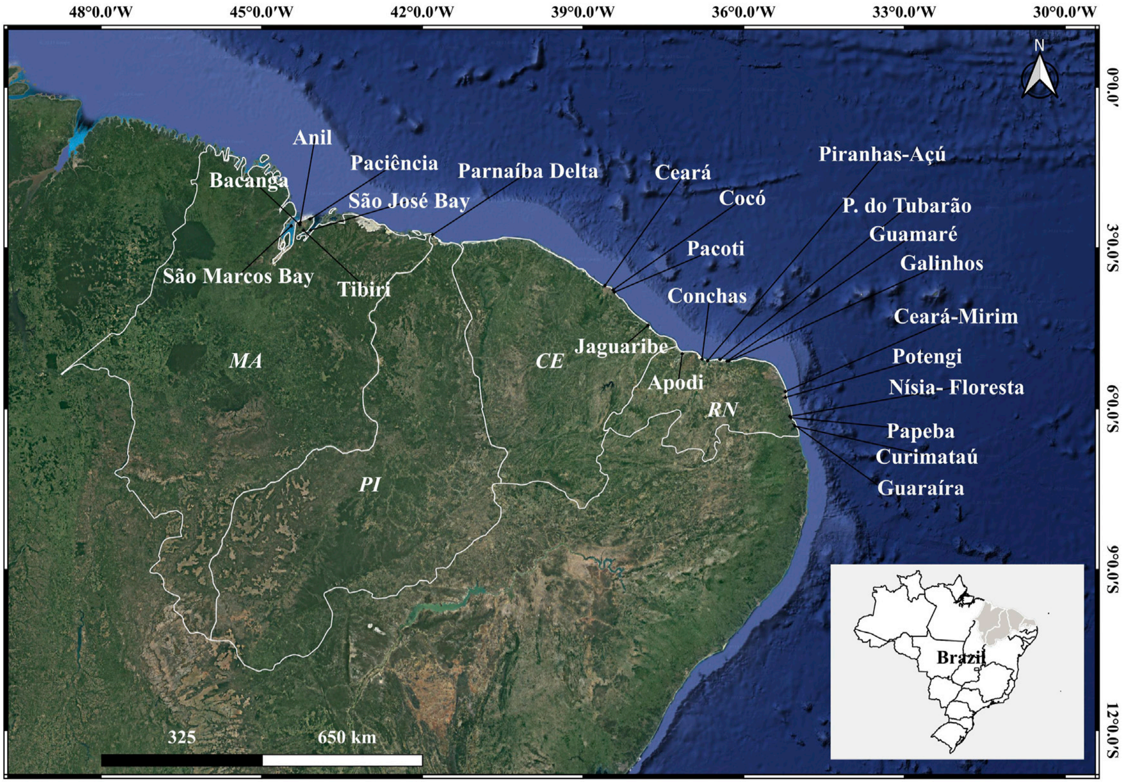

FIGURE 1
Location map of the 23 estuaries evaluated in the Equatorial Zone of the Brazilian Northeast (EZBN).

form complexes, and settle on surface sediments, where they reach contents high enough to become a risk to aquatic life (Buruaem et al., 2012; Silva et al., 2015).

There are few studies dealing with trace metal contamination in the Equatorial Zone of the Brazilian Northeast (EZBN) that characterize and quantify major sources, the spatial and temporal variability of trace metals in compartments of the estuarine environment, and the eventual risk to the biota. The present article will focus on the EZBN including the states of Maranhão (MA), Piauí (PI), Ceará (CE) and the Rio Grande do Norte (RN). This region includes more than 88 cities, totaling approximately 7.9 million inhabitants, with 85.1% of the population in urban regions and 14.9% in rural areas (IBGE, 2020).

The objective of the present study is to provide an overview of metals (Al, Fe, Mn, As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, and Zn) of environmental interest and the biogeochemical processes influencing their fate in water, sediment, and biota as a biomonitor, as reported previously in published research, including monographs, dissertations, thesis, scientific articles, and information from regional environmental protection agencies, in estuarine environments of the EZBN. This review identifies metal contaminations, highlights future complementary studies, and suggests necessary complementary research. The data collected are from 23 estuaries situated near the major coastal cities in the EZBN, that presents different socio-economic activities.

2 Environmental setting

The EZBN comprises the region located between 1°5′S and 46°1′W to 6°30S and 34°58′W (Figure 1). It is characterized by the transition from the humid and hot Amazonian climate to the hot and dry semiarid climate, with average annual temperatures ranging from 18.4oC to 34.9°C, considering all the EZBN and data from 1981 to 2010 (MMA, 2006; INMET, 2019). Precipitation in this region is influenced by the migration of the Intertropical Convergence Zone (ITCZ), El Niño, La Niña, and by the action of the trade winds from the Atlantic Ocean, which define the seasonal rainy and dry periods (Polzin and Hastenrath, 2014). The Amazonian region is very well-defined, with high precipitation from January to June and low precipitation from July to December, while the semiarid region shows a short rainy season from February to May and a longer dry season from June to January. There is a west-east decrease in the average accumulated rainfall along the coast with the state of MA exhibiting an average accumulated rainfall of 1,599 mm (1,177 to 2,200 mm), the state of PI 1,007 mm (635–1,423 mm), the state of CE 969 mm (599–1,669 mm), and the state of RN 904 mm (518–1,721 mm) between 1981 to 2010 (FUNCEME, 2019; INMET, 2020). Carvalho et al. (2020) detected a reduction in the number of rainy days in Northeastern Brazil in the past 30 years. For example, in Fortaleza, the capital of the state of Ceará, an annual decrease of 19 days of rain has been recorded during this period. In addition, the change in the rainfall distribution has an impact on the occurrence of extreme events, such as drought and floods, in the EZBN, which has witnessed an increase both in frequency and extension of extreme events (Lacerda et al., 2020).

The semidiurnal tidal regime is characteristic of the coastal environments of the EZBN with amplitudes varying from macro tidal, as observed in the coast of MA (0.2–7.3 m), to mesotidal regimes found in PI (0.5–4.0 m), CE (0.6–3.5 m) and RN (0.1–3.9 m) (CHN, 2019). Tidal variation along the EZBN can influence the morphology and hydrodynamics of the coast, as well as the dispersion of sediments and contaminants (Landim et al., 2005; Aquino da Silva et al., 2019). The coastline has 1,689 km in extension, composed of complex ecosystems such as sandy beaches, mangroves, estuaries, bays, and one of the largest open-sea deltas of the Americas and the third largest in the world, the Parnaiba River Delta, which suffers periodical seawater intrusion (Paula Filho et al., 2015; Souza Silva et al., 2015). The state of Maranhão harbors the largest continuous range of protected mangroves in the world with three dominant mangrove genera: *Rhizophora, Laguncularia*, and *Avicennia.* Mangroves in the EZBN cover a total area of approximately 544,100 ha, representing 38.9% of Brazilian mangroves, and serve as the greatest natural source of organic matter (OM) for the aquatic system (ICMBio, 2018; Mounier et al., 2018).

The geology comprises several lithostratigraphic units, and the diabase dikes and sedimentary basins of the MA coastline belong to the Pre-Cambrian to the Cenozoic, with Codó, Grajaú, Itapecuru, Pirabas, and Barreira's formations (El-Robrini et al., 2006). The state of Ceará has geological characteristics from the Pleistocene to the Holocene, compounded by the Barreiras, Camocim, and Serra Grande formations (Morais et al., 2006). The geology of the state of RN consists of sedimentary rocks of the Cretaceous age, which are covered by rocks of the Barreiras Formation and Quaternary sediments (Vital et al., 2006). The driest region of the EZBN has scarce water resources and marked climatic seasonality, resulting in the presence of 235 medium to large artificial reservoirs with storage capacities varying from 571 to 18.738 hm^3; 66% of the total number of reservoirs in the EZBN are located in the state of CE (IBGE, 2020). Besides the benefits of water supply or for the generation of electric energy, these dams decrease the water and material discharge from the continent to coastal environments, altering estuarine ecosystems (Marins et al., 2003; Dias et al., 2013; Diasda et al., 2016).

3 Major anthropogenic sources of trace metals in the EZBN

Most trace metals derive from igneous rocks, simply based on the relative fraction of igneous rocks in comparison with sedimentary and metamorphic rocks in the Earth's crust. However, the EBZN shows a predominance of sedimentary and metamorphic rocks in the continent and consequently, the continental shelf differs from other Brazilian regions where igneous rocks predominate (Aguiar et al., 2014). Resuspension of soil particles by winds, salt spray, forest fires, and soil and surface runoff are among the drivers that can contribute to the natural emissions of trace metals to watersheds of rivers and potentially affect metal content in the coastal ecosystems (Marins et al., 2004; Bianchi, 2007).

The contamination process began with anthropic activities that expanded significantly as urbanization and industry increased, and the consequent rise of energy and raw materials consumption, frequently associated with deforestation and conversion of natural areas into urban regions, remobilizing soils (Oliveira and Marins, 2011).

According to Soares et al. (2021), the Brazilian semi-arid coast is one of the most densely populated areas globally. For this reason, there are many activities, such as industries, agriculture, mining operations, and aquaculture, located in coastal and adjacent areas to supply the population's needs (Pinheiro et al., 2008; Lacerda et al., 2011; Soares, 2011). Only approximately 46% of northeastern households have a domestic sewage collection network, with the states of PI and MA having the lowest percentages, 4.5% and 6.5%, respectively (IBGE, 2020). The discharge of domestic sewage and solid wastes *in natura* carries several pollutants into water bodies. Other main economic activities in the area are civil construction and industrial utilities, including pulp and paper industry, food, leather and footwear, oil and natural gas extraction, metallurgy, and the production of oil and biofuels (CNI, 2019).

Harbor activities have great economic importance in the exportation of iron ore and pellets, manganese, ferroalloys, fertilizers, oil and byproducts, wheat, and salt. Major harbors in the EZBN are Itaqui (MA), Fortaleza and Pecém (CE), and Natal and the Terminal Salineiro de Areia Branca (RN) (Lima, 1999; González-Gorbena et al., 2015). According to the National Socioeconomic Development Bank of Brazil (BNDES), the coasts of the states of CE and RN do not have many natural conditions for the implementation of new harbors due to sheltered areas and bays or estuaries with deep waters. Therefore, the Itaqui harbor (MA) is the only one located in a deep, sheltered area in São Marcos Bay (MA), and the other harbors are positioned in the open sea or offshore to receive large cargo ships, while the small estuaries allow docking of smaller fishing and tourism boats (Lima, 1999). This activity is a potential source of trace metals due to accidents with the spillage products during the loading and unloading into aquatic systems. For example, 92% of the cargo handled in the Itaqui harbor, which is the second largest in terms of tons handled in the country, corresponds to bulk ore. Harbor operation, in particular dredging to increase the depth of the navigation channels, can resuspend deposited metals from the bottom, increasing their bioavailability, as demonstrated in the Mucuripe Harbor, CE state (Maia, 2004; Lacerda et al., 2019; Moreira et al., 2021).

Another potential source of trace metals is shrimp farming, with 98.8% of the total 41 tons of shrimp produced in 2017 having come from the Brazilian northeastern. The states evaluated in the present study were responsible for the production of around 30 tons of shrimp, representing 74.6% of the entire northeastern region, with the state of RN being the largest producer (IBGE, 2020). Shrimp farming showed significant Hg and Cu emissions to the environment, as detected by bioindicators, sediment, and water analyses. Mercury is mostly derived from fish meal present in aquafeeds, whereas Cu comes mostly from the use of algaecides during pond cleaning. Emission factors for Hg (0.03–0.04 $kg.km^{-2}.yr^{-1}$) and Cu (38.6–59.8 $kg.km^{-2}.yr^{-1}$) are among the highest from anthropogenic sources (Lacerda et al., 2006; 2011; Lacerda and Marins, 2006; Torres, 2009; Costa et al., 2013; Paula Filho et al., 2014; Rios et al., 2016; Moura and Lacerda, 2018).

According to Costa et al. (2015), Baptista Neto et al. (2013), and Duquesne et al. (2006), the disposal of domestic sewage and urban solid wastes, such as batteries, in unsuitable places, are important sources of Hg, Zn, Pb, Ni, Cu, and Cr, and these are the major trace metal sources to estuaries bordering metropolitan areas along the EBZN.

Industrial discharges have commonly caused contamination by As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in nearshore sediments, river channels, and coastal zones (Li et al., 2013; Souza and Silva, 2016), but the low industrialized nature of the EBZN decreases the relative importance of these sources. The emission factor determined by Vaisman and Lacerda (2003) also suggests coal burning as a significant source of As and Hg. Boats may also contribute to the trace metal inputs since some of these elements (Zn, Cd, Cu, and Pb) are contained in fossil fuel residues and have a significant correlation with the petroleum markers (Yunus and Chuan, 2009; Costa et al., 2015). Unfortunately, notwithstanding the high intensity of fisheries and recreational boat activities along the EBZN, and the evidence of biological impacts of pollutants from naval-related activities, with the exception of studies on TBT (Castro et al., 2000; 2008; Braga et al., 2006), no study, to our knowledge, has addressed the significance of this source of trace metals to the EBZN.

Emission factors of trace metals estimated to the Parnaíba River Delta (MA-PI-CE) identified significant anthropogenic contributions for Zn and Cu (117 and 71 t $year^{-1}$, respectively) derived from urban runoff and inadequate disposal of urban solid waste, while the other metals showed erosion and leaching of soils as a dominant natural source to the environment, with 65.6 t of Pb $year^{-1}$, 42.4 t of Cr $year^{-1}$, 7.4 t of Cd $year^{-1}$, and 0.6 t of Hg $year^{-1}$ (Paula Filho et al., 2014).

4 Metals and trace metals in estuarine sediments of the EZBN

Sediments act as a reservoir of metals that can account for more than 99% of trace metals that enter rivers (Huang et al., 2012), integrating the impact of the different sources to the adjacent drainage basin to the estuaries, and through relatively long periods. Most studies on trace metal concentrations in sediments were quantified in the fine grain size fraction (<63 μm) due to trace metals' preferential association with fine materials such as clays, silt, and particulate organic matter (POC), which are their major geochemical carriers in aquatic ecosystems (Marins et al., 2004; Nilin, 2008; Oliveira, 2012; Nascimento, 2013; Silva et al., 2015; Rios, 2018). Nevertheless, in estuaries with high hydrodynamic conditions, the analytical determinations were frequently performed in larger grain size fractions (<2 and <1 mm) of the sediment (Garlipp, 2006; Peres, 2012; Santos et al., 2019). Table 1 presents the average contents of metals and trace metals in sediments of different estuaries of the EZBN, as reported in the literature in the past 2 decades.

Sediments of São Marcos Bay (MA) showed higher concentrations during the dry season for Cu, Zn, Al, and Mn, while Fe was higher during the rainy season (Sousa, 2009). The author concluded that Al, Fe, and Mn were above the concentration limit allowed by the applicable Brazilian legislation (CONAMA 344/04, 2004) and also suggested a great availability of these elements. Santos et al. (2019) also found anomalous values for Mn in the same region, indicating the influence of ore shipment. Anil River and São José estuaries (MA), both located in the Maranhão Gulf, showed anomalous values, especially for Pb, resulting mainly from domestic and hospital sewage to the Anil River, while in the São José estuary, Pb was mostly derived from the lithogenic source with small anthropogenic contribution (Azevedo, 2019; Santos et al., 2019).

Paula Filho et al. (2015) established background values for trace metals in sediment cores in the largest open sea delta of the Americas, the Parnaíba River Delta (PI). Most of the metals were below two threshold levels established by sediment quality guidelines: the Probable Effect Level (PEL), in which there is a greater likelihood of adverse effects on the biota, and the Threshold Effect Level (TEL), in which there is a lower likelihood of adverse effects on the biota. However, in a more recent study in the Parnaíba River Delta, an anthropogenic influence was observed in surface sediments, classifying them as moderately to severely polluted by Cu, Zn, and Pb (Paula Filho et al., 2019). Analytical microscopy (SEM/EDS) identified pyrites in sediments from the continental shelf of the state of PI, near the Parnaíba River Delta. These pyrites were wrapped in a clay matrix and observed in a raspberry-shaped format, which is commonly found in organic-enriched marine and estuarine sediments (Aguiar, 2014). These studies collected sediment in different stations along the continental shelf, which evidences the large variability of the complex deltaic ecosystem with mangrove forest, dunes and bays under anthropogenic activities that influence contaminant inputs.

Estuaries in the state of CE have been the subject of more trace metal contamination studies than the other states listed here. In the metropolitan region of Fortaleza city (MRF), the Pacoti River, one of the most pristine in the metropolitan region, was initially not impacted by Zn, Cu, and Hg contents in estuarine sediments (Aguiar, 2005; Vaisman et al., 2005). However, this has changed in more recent years, with an evident accumulation of Fe, Cu, Pb, Zn, and Hg (Rios et al., 2016; Souza and Silva, 2016) due to intensive metal load in the misuse of water resources, whether by tourist activities and deforestation in the region previously covered by dunes and mangroves. Also in the MRF, the urbanized Cocó River exhibited Hg concentrations in bottom sediments about 112 times higher upstream than downstream of the estuarine mixing zone (Vaisman et al., 2005; Almeida, 2015). The highest values were related to urbanization and to the proximity of a decommissioned landfill that continues to be a significant point source of toxic substances to the river. In the Ceará River, also in the urban region, Cu and Hg contents in the sediment were associated with non-lithogenic sources (Aguiar, 2005; Vaisman et al., 2005). In addition, Nilin (2012) and Nilin et al. (2013) performed studies to assess the human influence on the sediment quality of these rivers. They identified high Zn and Cu accumulation near the river mouth, with Zn concentrations one order of magnitude higher than in upstream stations, and the estuary was considered moderately contaminated by Hg compared to other Brazilian coastal regions.

One of the first assessment studies in sediment cores in the Jaguaribe River, the largest basin under a semiarid climate, determined 15 ng g^{-1} of Hg as the regional background concentration for the Brazilian Northeastern Equatorial Coast

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TABLE 1 Metal contents in the sediment of different estuaries in the Equatorial Zone of the Brazilian Northeast [values in µg g^{-1}, except Al and Fe (%) and Hg (ng g^{-1})]. <DL is below the detection limit.

References	Environment	Fraction	Al	Fe	Mn	As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Sousa (2009)	São Marcos Bay (MA)	<63 µm	0.3	0.2	190.8	—	—	5.8	—	—	8.7	—	<DL	<DL	19.7
Nascimento (2013)	Tibiri (MA)	<63 µm	—	—	—	—	—	<DL	—	10.6	14.8	—	9.1	10.4	28.9
Carvalho et al. (2014)	Paciência (MA)	<63 µm	—	—	—	—	—	<DL	—	5.7	<DL		<DL	24.3	4.4
Silva et al. (2015)	Bacanga (MA)	<63 µm	—	—	—	—	—	0.3	—	55.0	8.9	—	6.0	62.6	50.1
Santos et al. (2019)	São Marcos Bay(MA)	<2 mm	0.3	1.0	365.0	—	—	—	—	4.7	1.1	—	2.8	3.6	7.1
	Anil (MA)	<2 mm	2.2	2.0	159.7	—	—	—	—	16.7	7.8	—	9.5	8.7	31.0
Azevedo (2019)	Arraial/São José (MA)	<63 µm	2.3	1.3	166.3	—	—	—	—	24.6	4.8	—	8.2	23.9	22.7
Paula Filho et al. (2015)	Parnaíba River Delta (PI)	<63 µm	—	1.4	633.0	—	—	—	—	18.0	6.8	—	—	5.9	13.4
Paula Filho et al. (2019)	Parnaíba River Delta (PI)	<63 µm	4.0	2.9	138.3	—	—	0.5	—	35.6	21.4	—	25.9	80.9	45.7
Marins et al. (2004)	Jaguaribe (CE)	<63 µm	—	—	—	—	—	—	—	—	—	19.0	—	—	—
	Ceará (CE)	<63 µm	—	—	—	—	—	—	—	—	—	45.0	—	—	—
Aguiar (2005)	Pacoti (CE)	<63 µm	1.3	1.5	—	—	—	—	—	—	1.3	—	—	—	3.5
	Ceará (CE)	<63 µm	1.4	1.3	—	—	—	—	—	—	4.6	—	—	—	5.2
Torres (2009)	Jaguaribe (CE)	Total	—	—	—	—	—	—	—	—	10.6	—	—	9.5	—
	Pacoti (CE)	Total	—	—	—	—	—	—	—	—	6.9	—	—	10.2	—
Oliveira (2012)	Jaguaribe (CE)	<63 µm	1.6	1.6		—	—	—	—	24.5	7.8	—	11.4	8.3	22.5
Peres (2012)	Jaguaribe (CE)	<2 mm	1.9	3.0	470.0	—	—	—	—	—	9.6	—	—	11.8	42.1
Nilin (2012)	Ceará (CE)	<63 µm	—	—	—	—	—	—	—	—	—	5.7	—	—	—
Nilin et al. (2013)	Ceará (CE)	<63 µm	0.9	1.2	—	—	—	—	—	28.1	8.8	—	—	14.2	60.2
Almeida (2015)	Cocó (CE)	<63 µm	—	—	—	—	—	—	—	—	—	86.5	—	—	—
Souza and Silva (2016)	Pacoti (CE)	Total	—	0.5	—	—	—	—	—	—	1.3	—	—	2.3	2.6
Rios (2018)	Jaguaribe (CE)	<63 µm	3.3	—	—	—	841.6	-	—	—	13.5	—	—	—	50.9
Lacerda et al. (2004)	Curimataú (RN)	<63 µm	—	—	—	—	—	0.4	—	—	0.7	—	—	7.6	17.0
	Jaguaribe (CE)	<63 µm	—	—	—	—	—	0.4	—	—	9.1	—	—	3.2	27.5
	Piranhas-Açú (RN)	<63 µm	—	—	—	—	—	0.3	—	—	15.3	—	—	6.7	31.1
Garlipp (2006)	Curimataú (RN)	<1 mm	2.4	13.2	30.0	—	62.2	—	—	6.6	64.4	—	15.7	87.7	—
Correa (2008)	Potengi (RN)	<63 µm	2.0	2.9	—	4.0	103.9	0.1	11.9	86.1	26.6	0.1	34.8	15.0	69.7

(Continued on following page)

TABLE 1 **(*Continued*) Metal contents in the sediment of different estuaries in the Equatorial Zone of the Brazilian Northeast [values in µg g^{-1}, except Al and Fe (%) and Hg (ng g^{-1})]. <DL is below the detection limit.**

References	Environment	Fraction	Al	Fe	Mn	As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Silva et al. (2017)	Apodi (RN)	<1 mm	—	—	—	—	—	0.5	—	3.2	2.3	—	—	21.4	5.4
	Conchas (RN)	<1 mm	—	—	—	—	—	<DL	—	7.0	5.1	—	—	17.1	6.0
	Guamaré (RN)	<1 mm	—	—	—	—	—	<DL	—	3.2	0.5	—	—	6.4	1.6
	Galinhos (RN)	<1 mm	—	—	—	—	—	<DL	—	3.8	1.2	—	—	18.6	4.1
	Ceará-Mirim (RN)	<1 mm	—	—	—	—	—	<DL	—	<DL	<DL	—	—	<DL	0.1
	Potengi (RN)	<1 mm	—	—	—	—	—	<DL	—	4.8	3.2	—	—	9.5	6.9
	Nísia- Floresta (RN)	<1 mm	—	—	—	—	—	<DL	—	<DL	5.1	—	—	<DL	7.6
	Papeba (RN)	<1 mm	—	—	—	—	—	<DL	—	<DL	<DL	—	—	<DL	1.1
	Guaraíra (RN)	<1 mm	—	—	—	—	—	<DL	—	<DL	<DL	—	—	<DL	<DL
Cantinho (2017)	Ponta do Tubarão (RN)	Total	—	—	—	—	—	0.4	—	0.4	1.3	3.8	1.3	—	3.4

(Marins et al., 2004). The authors also suggested the use of Hg as a proxy to indicate anthropogenic pollution for the region in reason of its absence in the local geology. Lacerda et al. (2004) compared Cu, Zn, Cd, and Pb contents in the Jaguaribe River with two other estuaries located on the coast of the state of RN: the Piranhas-Açú and Curimataú Rivers. Cd and Pb values were similar in the three rivers, whereas Zn and Cu were lower in the Curimataú and higher in the Piranhas-Açú. The authors suggest that Cd and Pb inputs were heavily driven by natural processes, such as soil denudation, while Cu and Zn emissions were due to agriculture and inadequate disposal of wastewater and solid waste. Peres (2012) found in a sediment core from the Jaguaribe River estuary that OM, Fe, and Mn acted as the main geochemical carriers of Cu and Zn, due to the suboxic conditions that favor the formation of Fe-Mn oxy-hydroxide or pyritization (FeS_2), common in this environment.

Metal (Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) accumulation in superficial sediment and cores analyzed in the Curimataú River (RN) indicated lower concentrations compared to other estuaries, except for Mn and Cu, which showed enrichment in some stations (Garlipp, 2006). When compared to Lacerda et al. (2004), it is possible to observe the intensification of Pb and Cu inputs, with values one and two orders of magnitude higher, respectively. The observed high concentrations can result from trace metal contamination by the increase of effluent discharges from shrimp farming to rivers.

The evaporation in some estuaries in the state of RN exceeds the freshwater input, making the upstream of the river become a source of dense water, saltier than seawater. This condition characterizes the environment as negative hyper-saline estuaries, as in the Apodi and Conchas Rivers. These environments showed significantly higher contamination by Cr, Cu, Cd, and Pb than the positive Potengi estuary, also in RN state, at least for Cr (Silva et al., 2017), which exhibits salinity increases seaward. The authors also indicated anthropogenic influence on a load of trace metals in addition to the hydrodynamic conditions characterized by weak tide dispersion capacity, which increases the water resident time along the estuary. The high content of Pb and Zn was also identified in Ponta do Tubarão estuary (RN), which featured the highest metal concentrations detected near the urban area and anchoring boats, but still below the limit established by Brazilian legislation (Cantinho, 2017).

The results indicated higher levels of Zn, Cu, and Pb for at least one estuary of each state. Anomalous values for Fe were also identified in estuaries in the states of MA and CE, as well as high content of Mn in aquatic systems in the states of MA and RN. Estuaries in the CE state also showed a significant amount of Hg in their sediments, but this metal was not analyzed in the other EZBN regions. The similar Zn, Cu, and Pb contaminations among the estuaries along the EZBN may result initially from the regional and local geological characteristics associated with the Barreiras Formation (Morais, 1977; El-Robrini et al., 2006; Vital et al., 2006) and the intense increase of anthropogenic activities developed on the discharge basins, which aggravates the enrichment of metals in the coastal zone.

Xavier et al. (2017) identified that even the Capibaribe estuary, in a metropole of another Northeast state of Brazil out of the EZBN, showed good environment quality for the sediment related to Mn, Fe, Cu, Zn, Pb, and other trace metal concentrations. However, Fe,

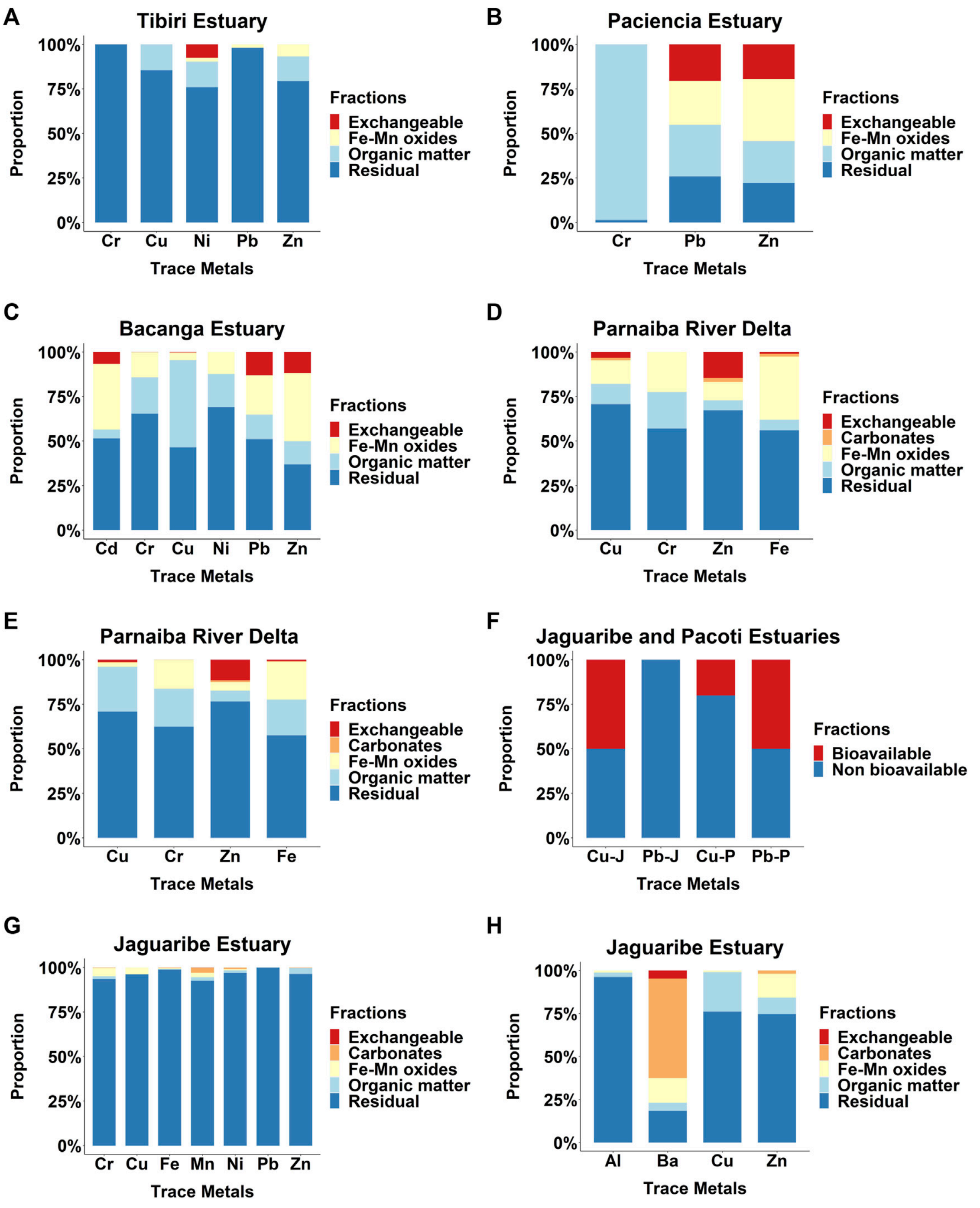

FIGURE 2
Trace metal sequential extractions (%) in estuarine sediments in the Equatorial Zone of the Brazilian Northeast. Data sources from **(A)** Nascimento (2013), **(B)** Carvalho (2014), **(C)** Silva et al. (2015), **(D,E)** Present study, **(F)** Torres (2009), **(G)** Oliveira (2012), and **(H)** Rios (2018).

Mn, Pb, and other concentrations in sediments were higher than those found in most estuaries of the EZNB. The authors affirm that the Barreiras Formation was the main source that increased metals in the environment, whereas anthropic influence was unlikely due to the low values of local sediment quality indices.

In fact, the measurement of total metals and trace metals in sediment are not satisfactory to assess the mobility and availability in the estuarine ecosystems (Passos et al., 2011; Pejman et al., 2017). However, the use of sequential extractions furnishes detailed information about metals' origin, mode of occurrence, availability, mobility, and transport (Tessier et al., 1979). Tessier et al. (1979) determined trace metals in five sediment fractions: the exchangeable fraction, which includes the metal bounded with cations that can be exchanged by ions present in water, the fraction bound to carbonates that can be mobilized by changes in pH, the reducible fraction bound to Fe-Mn oxides and released

TABLE 2 Metal contents in the water of different estuaries in the Equatorial Zone of the Brazilian Northeast. D is dissolved, P is particulate, and T is the total fraction.

References	Environment	Fraction	Unit	Al	Fe	Mn	Cd	Co	Cu	Hg	Ni	Pb	Zn
Furtado (2007)	São Marcos Bay (MA)	D	mg L^{-1}	—	3.3–7.2	—	—	0.006–0.02	0.02–0.05	—	0.05–0.09	0.009–0.09	—
Sousa (2009)	São Marcos Bay (MA)	D		6.2–36.3	0.7–6.8	<DL- 0.06	<DL-0.0007	—	0.00007–0.002	—	< DL	0.009–0.02	0.005–0.7
Dias (2007)	Jaguaribe (CE)	P	mg g^{-1}	0.002	—	—	—	—	0.01	—	—	—	6.2
Dias et al. (2009)	Jaguaribe (CE)	P	mg g^{-1}	<DL-47.3	20–29	0.5–15.5	—	—	0.005–0.01	—	—	<DL-0.007	<DL-4.4
Torres (2009)	Jaguaribe (CE)	P	mg g^{-1}	26.4–46.7	—	—	—	—	0.01–0.03	—	—	<DL	—
Costa (2009)	Jaguaribe (CE)	D	ng L^{-1}	—	—	—	—	—	—	1.1–23.5	—	—	—
		P	ng L^{-1}	—	—	—	—	—	—	3.2–15.0	—	—	—
		T	ng L^{-1}	—	—	—	—	—	—	6.3–32.1	—	—	—
Soares (2011)	Jaguaribe (CE)	P	ng L^{-1}	—	—	—	—	—	—	0.1–3.8	—	—	—
		D	ng L^{-1}	—	—	—	—	—	—	0.1–11.9	—	—	—

under anoxic conditions (i.e., low Eh), the oxidizable fraction bound to OM and sulfides that are solubilized under oxidizing conditions, and the residual fraction, which holds trace metals within the crystal lattice of minerals that are not expected to mobilize easily in solution.

Unfortunately, for the region, there are few studies based on the sequential extraction mentioned above (Figure 2). In the MA state, Nascimento (2013), Carvalho (2014), and Silva et al. (2015) extracted metals present in the exchangeable (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions from estuarine sediments (Figures 2A–C). The authors identified the dominance of all trace metals bound to the residual fraction, except for Cr, Pb, and Zn in the Paciência River estuary and Cu in the Bacanga River estuary, which were mostly associated with the oxidizable fraction. These results indicate the predominance of trace metals in non-labile fractions, except for Cr, Pb, Cu, and Zn, which can be mobilized from the sediment to the water column with the change of physicochemical conditions, mainly in the Paciência and Bacanga river estuaries, where some of these metals are often associated to oxidizable fraction, meaning that geochemistry of these elements can be controlled by OM.

The present study provides data about trace metal sequential extractions (Cu, Cr, Zn, and Fe) in surface sediments in two stations from the Parnaíba River Delta, sampled in 2019. The results identified the dominance of the residual fraction (circa 50%–75%) for all metals evaluated (Figures 2D, E). However, Zn was significantly associated with exchangeable fractions, whereas Fe was bounded to the reducible fraction (circa 60%) in both stations. Cu and Cr showed a large spatial geochemical variability in the sediments binding to different reducible and oxidizable fractions. The association of trace metal to labile fractions indicates the occurrence of elements from secondary sources that are adsorbed, complexed, and settled distinctly to the bottom by the influence of local hydrodynamics. Zn exhibited medium mobility by the association to the exchangeable fractions, corroborating with a previous study that suggested that untreated domestic effluent and livestock activities from the main regional urban center of Parnaíba city were the main source of this element to the environment (Paula Filho et al., 2015).

Other studies developed in the Jaguaribe River (CE) applied sequential procedures to determine metals (Figures 2G, H) in the five sediment fractions (Oliveira, 2012; Rios, 2018). Sequential extraction to determine the potentially bioavailable (F1 + F2 + F3 + F4 fractions) and non-available trace metals (F5) in the Jaguaribe and Pacoti rivers (Figure 2F) found Cu predominated associated with the non-available fraction, while Pb was available in sediment samples from the Pacoti River (Torres, 2009).

The different extractions, sediment fractions, and sampling points along the Jaguaribe estuary, the most studied in the EZBN relative to sequential extraction of metals, showed that these methodological differences produced different results, but they showed that 50%–100% of metal (Cu, Zn, Cr, Pb, Ni, Fe, Mn, and Al) concentrations were bounded to the residual fraction, suggesting a small contribution from local anthropogenic sources in the estuarine region, although aquaculture effluents and urban discharges have been found to influence the trophic state of the region (Marins et al., 2011; Marins et al., 2021). A different geochemical partitioning was observed for Ba, which is bounded to carbonates and is related to pH increase.

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TABLE 3 Trace metal in organisms (wet weight) of different estuaries in the Equatorial Zone of the Brazilian Northeast (values in μg g^{-1}). (a) Indicates the maximum values of trace metals in fish set by ANVISA RDC n°42/13 (Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013) and (b) indicates the trace metal range allowed in food in general by ANVISA n° 685/98 (Brasil, 1998).

References	Estuary	Group	Scientific name	Al	Fe	Mn	Ba	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn
Brazilian Legislation		Fish- shellfish	—	—	—	—	—	0.05–2.0	—	0.1–10	0.5–1.0	—	0.3–1.5	—	—
Carvalho et al. (2000)	Bacanga (MA)	Oyster	*Mytella falcata*	—	—	—	—	<DL	—	1,240.0	—	—	<DL	—	11,274
Sousa (2009)	São Marcos Bay (MA)	Fish	*Arius proops*	3.3	2.2	<DL	—	<DL	—	<DL	—	<DL	<DL	—	6.0
			Arius rugispinis	1.3	4.1	0.2	—	<DL	—	0.3	—	<DL	<DL	—	43.2
			Hexanematicht hys herzbergii	0.5	2.4	0.2	—	<DL	—	0.1	—	<DL	<DL	—	29.3
			Bagre marinus	3.3	5.0	0.4	—	<DL	—	0.3	—	<DL	<DL	—	38.8
			Lophiosilurus alexandri	2.0	4.5	0.9	—	<DL	—	0.3	—	<DL	<DL	—	6.2
			Geniatremus luteus	0.5	3.4	0.4	—	<DL	—	0.2	—	<DL	<DL	—	9.1
			Micropogonias furnieri	0.3	1.5	0.4	—	<DL	—	0.1	—	<DL	<DL	—	5.7
Vaisman, Marins and Lacerda (2006)	Ceará (CE)	Oyster	*Crassostraea rhizophorae*	—	—	—	—	—	—	—	30.8	—	—	—	—
	Cocó (CE)			—	—	—	—	—	—	—	16.8	—	—	—	—
	Pacoti (CE)			—	—	—	—	—	—	—	9.0	—	—	—	—
	Jaguaribe (CE)			—	—	—	—	—	—	—	10.4	—	—	—	—
Torres (2009)	Jaguaribe (CE)	Crustacean	*Callinectes sapidus*	—	—	—	—	—	—	—	—	—	<LD	—	—
			Litopenaeus schimitti	—	—	—	—	—	—	4.2	—	—	<LD	—	—
		Oyster	*Crassostrea rhizophorae*	—	—	—	—	—	—	1.5	—	—	<LD	—	—
		Seaweed	*Ulva lactuca*	—	—	—	—	—	—	0.3	—	—	<DL	—	—
	Pacoti (CE)	Oyster	*Crassostrea rhizophorae*	—	—	—	—	—	—	1.5	—	—	0.4	—	—
			Mytella falcata	—	—	—	—	—	—	3.1	—	—	<DL	—	—
			Anomalocardia brasiliana	—	—	—	—	—	—	1.7	—	—	1.3	—	—
Costa (2009)	Jaguaribe (CE)	Fish	*Sphoeroides testudineus*	—	—	—	—	—	—	—	9.9	—	—	—	—
			Cathorops spixii	—	—	—	—	—	—	—	31.8	—	—	—	—
Lopes (2012)	Jaguaribe (CE)	Fish	*Cichla sp*	—	—	—	—	—	—	—	28.8	—	—	—	—
			Serrasalmus rhombeus	—	—	—	—	—	—	—	40.9	—	—	—	—
			Centropomus parallelus	—	—	—	—	—	—	—	25.4	—	—	—	—
			Menticirrhus americanus	—	—	—	—	—	—	—	7.6	—	—	—	—

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TABLE 3 (*Continued*) Trace metal in organisms (wet weight) of different estuaries in the Equatorial Zone of the Brazilian Northeast (values in µg g^{-1}). (a) Indicates the maximum values of trace metals in fish set by ANVISA RDC n°42/13 (Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013) and (b) indicates the trace metal range allowed in food in general by ANVISA n° 685/98 (Brasil, 1998).

References	Estuary	Group	Scientific name	Al	Fe	Mn	Ba	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn
			Cathorops spixii	—	—	—	—	—	—	—	17.0	—	—	—	—
			Plagioscion squamosissimus	—	—	—	—	—	—	—	44.5	—	—	—	—
			Prochilodus sp	—	—	—	—	—	—	—	7.9	—	—	—	—
			Leporinus friderici	—	—	—	—	—	—	—	26.6	—	—	—	—
			Oreochromis niloticus	—	—	—	—	—	—	—	10.3	—	—	—	—
Almeida (2015)	Cocó (CE)	Fish	*Oreochromis niloticus*	—	—	—	—	—	—	—	2.1	—	—	—	—
			Hypostamus pusarum	—	—	—	—	—	—	—	3.4	—	—	—	—
			Pseudancistrus papariae	—	—	—	—	—	—	—	14.3	—	—	—	—
			Prochilodus brevis	—	—	—	—	—	—	—	8.4	—	—	—	—
Rios et al. (2016)	Ceará (CE)	Oyster	*Crassostraea rhizophorae*	—	—	—	—	—	—	—	18.6	—	—	—	—
	Jaguaribe (CE)			—	—	—	—	—	—	—	15.0	—	—	—	—
	Pacoti (CE)			—	—	—	—	—	—	—	10.4	—	—	—	—
	Cocó (CE)			—	—	—	—	—	—	—	12.2	—	—	—	—
Soares (2017)	Jaguaribe (CE)	Oyster	*Crassostrea rhizophorae*	—	—	—	—	—	—	9.6	7.7	—	—	—	—
Moura and Lacerda (2018)	Jaguaribe (CE)	Fish	*Cathorops spixii*	—	—	—	—	—	—	—	10.0	—	—	—	—
			Centropomus parallelus	—	—	—	—	—	—	—	7.8	—	—	—	—
			Elops saurus	—	—	—	—	—	—	—	21.8	—	—	—	—
			Eugerres brasilianus	—	—	—	—	—	—	—	7.6	—	—	—	—
			Gobionellus oceanicus	—	—	—	—	—	—	—	2.8	—	—	—	—
			Lutjanus jocu	—	—	—	—	—	—	—	16.8	—	—	—	—
			Lutjanus synagris	—	—	—	—	—	—	—	12.2	—	—	—	—
			Menticirrhus americanus	—	—	—	—	—	—	—	20.8	—	—	—	—
			Mugil curema	—	—	—	—	—	—	—	4.2	—	—	—	—
		Crustacean	*Callinectes bocourti*	-	-	-	-	-	-	-	40.2	—	—	—	—
			Callinectes danae	—	—	—	—	—	—	—	13.8	—	—	—	—
			Callinectes exasperatus	—	—	—	—	—	—	—	4.6	—	—	—	—

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TABLE 3 (*Continued*) Trace metal in organisms (wet weight) of different estuaries in the Equatorial Zone of the Brazilian Northeast (values in µg g^{-1}). (a) Indicates the maximum values of trace metals in fish set by ANVISA RDC n°42/13 (Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013) and (b) indicates the trace metal range allowed in food in general by ANVISA n° 685/98 (Brasil, 1998).

References	Estuary	Group	Scientific name	Al	Fe	Mn	Ba	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn
			Callinectes larvatus	—	—	—	—	—	—	—	20.8	—	—	—	—
			Litopenaeus vannamei	—	—	—	—	—	—	—	2.8	—	—	—	—
		Oyster	*Anomalocardia brasiliana*	—	—	—	—	—	—	—	10.2	—	—	—	—
			Mytella charruana	—	—	—	—	—	—	—	10.4	—	—	—	—
		Gastropod	*Pugilina morio*	—	—	—	—	—	—	—	9.8	—	—	—	—
Silva et al. (2001)	Potengi (RN)	Oyster	*Crassostrea rhizophorae*	—	100.0	5.9	—	0.3	0.5	19.8	—	0.3	0.7	—	487.0
Carvalho et al. (2002)	Potengi (RN)	Oyster	*Tagelus plebeius*	—	—	—	0.7	<DL	0.9	0.9	—	3.0	4.2	23.8	149.0

The few studies about sequential extractions in estuaries of the EZBN suggest low to medium mobility of these metals in the environment related to the prevailing percentage in residual fractions. Although, it is notable that the associations among trace metals with Fe-Mn oxides (reducible fraction), OM, and carbonates can act as important geochemical carriers of metals along these environments. Therefore, investigation on the quantification and qualification of geochemical carriers present in the EZBN could be relevant to the comprehension of many mobilization and transport processes and the fate of contaminants along the region, as observed by the complexation of Cu-OM in the Pacoti River (Mounier et al., 2018). In addition, no study has evaluated if the estuaries in the EZBN can function as a source or sinks of contaminants to adjacent marine environments, and if the eventual mobility verified in certain estuaries is related to concentrations and distribution of these metals on the adjacent continental shelf.

5 Trace metals in estuarine waters of the EZBN

Most trace metals that enter the estuarine ecosystems are influenced by local hydrodynamic, physical, and chemical parameters, such as temperature, pH, salinity, and dissolved oxygen, usually resulting in a non-conservative behavior along the estuary (Machado et al., 2016; Wang et al., 2017; Mori et al., 2019; Mosley and Liss, 2019). The comprehension of geochemical processes that influence the partitioning of trace metals among colloidal, dissolved, and particulate fractions indicates the possible fate and transport of these contaminants in the environment (Robert et al., 2004; Machado Júnior and Macedo, 2016). Suspended particulate matter (particles with a size smaller than 63 µm) has a high capacity to carry trace metals due to the increase in specific surface area (Yao et al., 2015). Metals in particulate fractions can be associated with Fe-Mn hydroxides, carbonates, OM, silt, and clay minerals (Du Laing et al., 2009). These metal-particle associations can suffer precipitation, dissolution, complexation, absorption, and dissociation processes in the estuary. The coefficient evaluation of metal-organic complexation (<0.45 µm) and metals in colloidal forms (<0.025 µm) play a major role in metal bioavailability and the hazard posed by them (Simpson et al., 2014). Quantification of trace metals in estuarine water is scarce in the EZBN due to the necessity of methods and equipment with a low detection limit and high sensibility and selectivity, which can determine the very low concentrations of these elements found naturally in natural waters (less than 1 ppb). Available published data from the EZBN are presented in Table 2.

There is a great lack of data on metal concentration in the waters of the EZBN as demonstrated in Table 2. São Marcos Bay (MA) and the Jaguaribe River Estuary (CE) were the only environments where trace metals were determined in the water. São Marcos Bay is composed of diverse estuaries that discharge on it, with an important harbor complex with a large movement of ore and grains, which influences trace metal contamination in the region. Dissolved Cu and Ni concentrations were reported above the maximum allowed by Brazilian legislation (CONAMA n° 357,

TABLE 4 A summary of environmental conditions and the major drivers of metal contamination in estuaries of the Equatorial Zone of the Brazilian Northeast.

Hydrographic basin	Estuaries	Igeo classes	Biomonitor	Major driver	Driver tendence (2013–2035)	Responses
Piranha-Açú	**Conchas**	Pb = uncontaminated to moderately contaminated; No speciation data	No data	Natural sources, agriculture effluents and solid waste	Slow urbanization of 0.9% per year	Monitoring
	Piranhas-Açú	Cu and Zn = uncontaminated to moderately contaminated; No speciation data				
Ceará-Mirim	**Ceará-Mirim**	Zn = uncontaminated; No speciation data	No data	Natural sources, and aquaculture effluents	Fast urbanization of 1.1% per year	Monitoring
Trairi	**Nísia-Floresta**	Cu and Zn = uncontaminated; No speciation data	No data	Agriculture, aquaculture, domestic sewage	Fast urbanization of 1.5% per year	Monitoring
Northern coastline of RN	**Galinhos**	Pb = uncontaminated to moderately contaminated; No speciation data	No data	Natural sources, and aquaculture effluents	Slow urbanization of 0.9% per year	Monitoring
	Guamaré	All metal = uncontaminated; No speciation data				
	Ponta do Tubarão	All metal = uncontaminated; No speciation data				
Apodi	**Apodi**	Cr, Cu and Zn = uncontaminated; Pb = moderately contaminated; No speciation data	No data	Domestic sewage, and aquaculture effluents	Fast urbanization of 1.7% per year	Confirm Pb speciation; Monitoring and reduce the emissions; Biota monitoring
Itapecuru and Munim	**São José Bay**	Zn = uncontaminated to moderately contaminated; Pb = moderately contaminated; No speciation data	No data	Natural sources, and domestic sewage	Fast urbanization of 1.0% per year	Confirm Pb speciations; Monitoring
Mearim	**São Marcos Bay**	Cr and Zn = uncontaminated to moderately contaminated; Pb = moderately contaminated; No speciation data	High Zn value in fish; Cu below than permitted by law in fish	Harbor activities, deforestation, decommissioned landfill, industrial and domestic sewage	Fast urbanization of 1.0% per year	Confirm Pb speciations; Monitoring and reduce the emissions; Biota monitoring; Advisories on biota contamination by metals.
Jaguaribe	**Jaguaribe**	Fe, Cu and Pb = uncontaminated to moderately contaminated; Zn = moderately contaminated; Cu with 50% bioavailable and Ba with 62% in labile fractions with exchangeable and carbonates	Cu in oyster near to the maximum permitted by law	Domestic sewage, aquaculture, and deforestation	Fast urbanization of 1.2% per year	Monitoring and reduce the emissions; Biota monitoring; Advisories on biota contamination by metals.
Metropolitan basin of Fortaleza	**Ceará**	Cr and Pb = uncontaminated to moderately contaminated; Hg and Zn = moderately contaminated; No speciation data	Hg in oyster below than permitted by law	Harbor activities, tourism, deforestation, decommissioned landfill and domesticsewage	Fast urbanization of 1.1% per year	Confirm Hg, Pb,Cu, and Zn speciations; Monitoring and reduce the emissions; Biota monitoring
	Cocó	Hg = moderately contaminated; No speciation data	Hg in oyster and fishes below than permitted by law			
	Pacoti	Pb = uncontaminated to moderately contaminated; Cu with 20% and Pb with 50% bioavailable	Pb in oyster near to the maximum permitted by law			

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TABLE 4 (*Continued*) A summary of environmental conditions and the major drivers of metal contamination in estuaries of the Equatorial Zone of the Brazilian Northeast.

Hydrographic basin	Estuaries	Igeo classes	Biomonitor	Major driver	Driver tendence (2013–2035)	Responses
Potengi	**Potengi**	Hg = uncontaminated; Fe and Pb = uncontaminated to moderately contaminated; Cr, Cu and Zn = moderately contaminated; No speciation data	Cu and Pb in oyster higher than permitted by law; High Zn value in oysters	Domestic sewage, industrial and aquaculture effluents	Slow urbanization of 0.8% per year	Confirm Cr, Cu and Zn speciations; Emissions reductions; Biota monitoring; Advisories on biota contamination by metals
Maranhão Island	**Anil**	Fe, Cr and Cu = uncontaminated to moderately contaminated; Pb = moderately contaminated; Zn = moderately to heavily contaminated; No speciation data	No data	Harbor activities, domestic, hospital and industrial sewage	Slow urbanization of 0.8% per year	Confirm metals speciations; Monitoring and reduce the emissions; Biota monitoring; Advisories on biota contamination by metals
	Bacanga	Cr = moderately contaminated; Pb = moderately to heavily contaminated; Pb and Zn circa of 13 and 11% exchangeable	High Zn value in oyster			
	Paciência	Pb = moderately contaminated; Pb and Zn circa of 20% exchangeable	No data			
	Tibiri	Cu, Pb and Zn = uncontaminated to moderately contaminated; Cr, Cu and Zn residual fraction and Ni circa of 10% exchangeable	No data			
Parnaíba	**Parnaíba River Delta**	Fe and Cr = uncontaminated to moderately contaminated; Cu and Zn = moderately contaminated; Pb = heavily contaminated; Zn circa of 16% in labile fractions with exchangeable and carbonates	No data	Natural sources, domestic sewage and livestock activities	Fast urbanization of 1.1% per year	Confirm Pb speciation; Cu, Pb and Zn biota monitoring; Monitoring and reduce the emissions
Southern coastline of RN	**Curimataú**	Fe and Cu = moderately to heavily contaminated; Pb = heavily contaminated; No speciation data	No data	Domestic sewage, and shrimp farming effluents	Slow urbanization of 0.9% per year	Confirm Cu and Pb speciations; Monitoring and reduce the emissions; Biota monitoring
	Papeba	Zn = uncontaminated; No speciation data				

2005), while dissolved Al and Fe concentrations increased in the dry and rainy seasons, respectively (Furtado, 2007; Sousa, 2009), since their concentrations' variability in the water columns is related to aluminosilicates and oxyhydroxide of Fe and Mn coming from weathering in the drainage basin. These elements are associated with finer particles (related to grain size), and their concentrations should not be altered by anthropogenic sources (Barbieri, 2016). In addition to the natural sources, the variability of Al and Fe concentrations may result from bauxite mining, as in the Mearim river basin, and from ore and grain cargo ships in the city of São Luís, adjacent to São Marcos Bay (Bandeira, 2013). High values of Al and Fe in the water corroborate with values observed in the sediment compartment, as discussed previously for São Marcos Bay.

The Jaguaribe River Estuary is a negative estuary with strong shrimp farming activity in CE state. Some studies evidenced the lithogenic source for particulate Fe, Al, and Mn with the highest values upstream of the estuary, while Zn and Pb showed diffuse and point sources with enrichment near urban zones, major agriculture activities, and along the navigation routes of large fishing boats (Dias, 2007; Dias et al., 2009). Particulate Cu had an interesting variation; the first studies reported that Cu origin was mostly from lithogenic sources but increased up to an order of magnitude in

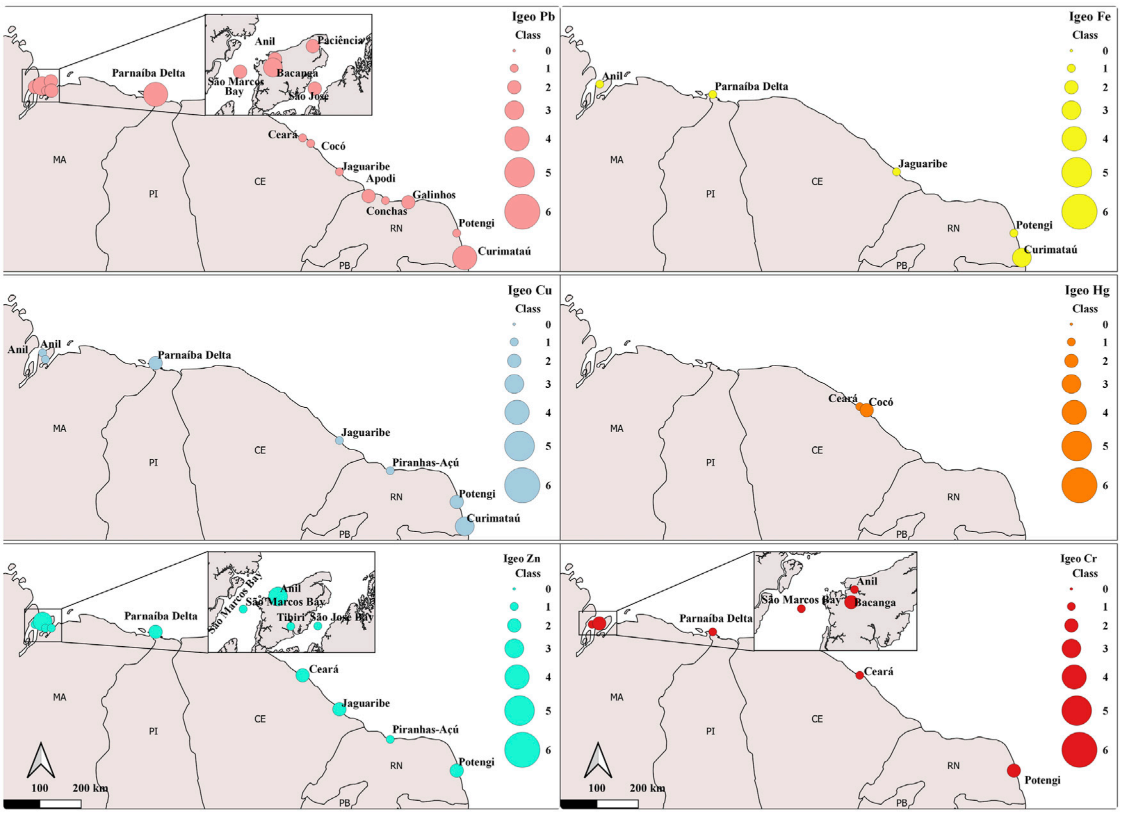

FIGURE 3
Geoaccumulation Index for Pb, Fe, Cu, Hg, Zn, and Cr in estuarine sediments along the Equatorial Zone of the Brazilian Northeast.

different locations of the estuary over time (Dias, 2007; Torres, 2009). This recent increase was associated with the increasing extension of shrimp aquaculture farms along the estuary, and the authors observed higher values near the releasing point of shrimp pond effluents. An increase in the available fraction of metals in bottom sediments affected by shrimp farm effluents has also been reported (Costa et al., 2013).

Both environments in MA and CE states present high concentrations of Cu, which may derive from the desorption of the particulate phase under salinity variation with tidal flooding, increasing the dissolved Cu fraction. Bottom sediments can be another source for Cu in the water column because even though Cu is dominantly bound to a residual fraction in the estuaries of the EZBN, the element was also found associated with an oxidizable fraction of OM and sulfides that are solubilized under oxidizing conditions in the environment, as observed in bottom sediments. Copper in estuarine environments can be found commonly complexed with dissolved and colloidal organic matter as metal-OM complex as observed in the Cocó and Pacoti river estuaries in the state of CE (Mounier et al., 2018). These complexes occur due to the attraction of the positive charge of dissolved metals to the negatively charged OM, which is bound to functional groups.

In the Jaguaribe estuary, in the CE state, Hg in particulate and dissolved forms showed a predominant positive correlation with continental geochemical tracers (Si, Ba, and suspended particulate matter), but the dissolved fraction showed some enrichment near the releasing point of the shrimp farms effluents (78.3% of the total Hg content in waters) in comparison to particulate Hg (Costa, 2009; Soares, 2011). Estuarine regions can present Hg in the most toxic species, such as methylmercury ($MeHg^{+}$), during hypoxic conditions and associated with organic particulates (Horvat, 1997). The semiarid estuaries of the EZBN present low natural continental runoff made lower due to anthropogenic influence in association with global climate change. These factors could increase the residence time of the fluvial waters entering the estuaries, in their middle section, resulting in increasing reactivity and bioavailability of metal forms. This biogeochemical estuarine process has been observed to control Hg dynamics in these semiarid estuaries (Lacerda et al., 2012; 2020).

There is no study focusing on the distribution coefficient (Kd) between dissolved and particulate fractions of trace metals in the water column of the EZBN that measured and compared metal retention capacity. High values of Kd indicate that the metal is retained by the solid phase (particulate) through adsorption reactions, whereas low values indicate that an important proportion remains soluble (dissolved) (Yang and Wang, 2017). This parameter has valuable information to allow the evaluation of metal-related pollution in a water body and the identification of sites where waste management decisions need to be remediated.

Comparing the range of dissolved trace metals to other Brazilian tropical estuaries under anthropogenic pressure, such as Tapacurá River (Pernambuco), Rio Una (Bahia), Sepetiba Bay (Rio de Janeiro), and Lagoa dos Patos (Rio Grande do Sul), and the Brazilian legislation (CONAMA nº 357, 2005 we can recognize high values for most metals found in estuaries of the EZBN, except dissolved Cd and Mn, which were 7.1 and 1.6 times lower than CONAMA values for brackish water, respectively (CONAMA nº 357, 2005; Molisani et al., 2007; Aprile and Bouvy, 2010; Barbosa et al., 2012; Jesus and Cruz, 2019). Tapacurá River and Rio Una identified enrichment of dissolved Cu, Zn, and Cd as a result of surrounding anthropic activities such as domestic sewage and agriculture runoff (Aprile and Bouvy, 2010; Jesus and Cruz, 2019). These elements are probably available to aquatic organisms and cause harm due to high metal toxicity. The concentrations of dissolved Hg from lithogenic sources in Sepetiba Bay (Molisani et al., 2007) are 11 times lower than the concentration found in the Jaguaribe estuary. However, there are no significant sources of Hg in the Jaguaribe estuary, but there are seasonal geochemical processes that increase the Hg mobility and solubility in the EZBN (Lacerda et al., 2012; 2020). The effects of these processes were not evaluated for other metals rather than Hg.

The frequent sediment dredging in harbor areas decreases the concentration of dissolved Pb, Cu and Zn by the dilution and dispersion of the metals accumulated in the environment over time, in the harbor zone in Lagoa dos Patos, located at the southern end of the Brazilian coast. However, it was not observed for Cd due to the abundance of chloride ions from seawater intrusion that forms soluble complexes in the water column with Cd from domestic effluent and fertilizer industries (Barbosa et al., 2012). However, the value of dissolved Cd in Sao Marcos Bay, also with an important harbor, Itaqui Harbor, was five times lower than in Lagoa dos Patos.

The particulate Zn in the EZBN estuaries was the only element with high concentrations in comparison to other Brazilian tropical estuaries, such as Rio Una (Bahia) and Paraíba do Sul (Rio de Janeiro) (Carvalho et al., 2002; Gonçalves and Carvalho, 2006; Jesus and Cruz, 2019). The Jaguaribe estuary showed particulate Cu and Pb concentrations two and five times lower, respectively, than Rio Una, while particulate Al and Fe were three times lower than concentrations observed in the Paraíba do Sul. In general, the concentration of trace metals in the dissolved fraction of the EZBN estuaries was higher than the particulate fraction when compared to other tropical urban estuaries. It points to the high desorption of trace metals from the solid to liquid phase in the water column of the EZBN estuaries resulting from changes in physicochemical conditions associated with saline intrusions in the flood tide. There is, therefore, a need for more studies on the distribution coefficient in environmental compartments and how it may impact local aquatic biota, especially those of commercial value for human consumption.

6 Organisms of the EZBN as biomonitors

Metals can be classified as essential (Fe, Mn, Zn, Cr, and Cu) depending on their concentrations or toxicity (Hg) to organisms, but when present in the environment in high concentrations, most of them can cause the death of organisms (Abessa et al., 2005). For this reason, some biomonitors, living organisms that accumulate trace metals in their tissues, are utilized to monitor the process of bioaccumulation of bioavailable contaminants present in riverine, estuarine, or coastal ecosystems through time (Rainbow and Phillips, 1993). In addition, biomagnification can be a serious problem due to the contaminant transfer along the food chain, especially if the concentrations reach toxic levels in top organisms, such as humans.

As observed in the few studies about the water compartment of the EZBN estuaries there is potential mobility of trace metals from the particulate to the dissolved fraction, due to the change of physicochemical conditions, which suggests the presence of available trace metals species contaminate the aquatic organisms. Therefore, the National Sanitary Surveillance Agency-ANVISA (Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013) developed the Resolution RDC n° 42/13 derived from the Ordinance n° 685/98, which determined the maximum levels of chemical contaminants in food that may constitute a risk to human health (Table 3). Considering this legislation, the present study examined the trace metal contents in the wet weight of the organisms to better comparison. When concentrations reported in a given study were in dry weight, they were converted to wet weight, using the percentage of water reported for a given organism, or considering 80% humidity when humidity data were not available (Kütter et al., 2021).

Aquatic organisms in the state of MA, such as oysters (*Mytella falcata)* and fishes (*Arius props, Arius rugispinis, Hexanematicht hys herzbergii, Bagre marinus, Lophiosilurus alexandri, Geniatremus luteus*, and *Micropogonias furnier)* exhibited concentrations for Cd, Cu, and Pb below to the level set by ANVISA n° 42/13 (Carvalho et al., 2000; Sousa, 2009; Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013), but Zn in oysters was identified with contents one or two orders of magnitude above the contents compared to the oyster from the other environments (Table 3). This result corroborates the lability of Zn identified in the MA sediments discussed in the previous section. The assimilation of Zn in the oyster muscles may result from the resuspension of this element from the sediment to the water column that uses the suspended material contaminated with Zn in their filter-feeding diet.

Trace metal accumulation was also identified in another oyster in estuaries from the state of CE. The mangrove oyster (*Crassostrea rhizophorae)* usually acts as a consistent Hg regional biomonitor, reflecting the degree of anthropogenic impact on estuary systems. In the Metropolitan basin of Fortaleza (CE), this organism showed a greater bioaccumulation of Hg in the estuary of the urban Ceará River than in other estuaries. However, it does not present a significant correlation with the size and sediment contents, which vary due to the influence of the hydrodynamics on this estuarine compartment (Vaisman et al., 2005; Rios et al., 2016). Notwithstanding, Almeida (2015) identified higher Hg in detritivores fish species (*Pseudancistrus papariae* and *Prochilodus brevis*) than in omnivores species (*Oreochromis niloticus* and *Hypostamus pusarum*) at the Cocó Estuary, something the author associated to the largest size observed in the first group. Organisms present in the Jaguaribe Estuary showed Hg biomagnification, most in genera of carnivorous fish (*Sphoeroides testudineus, Cathorops spixii, Elops saurus, Menticirrhus americanus,* and *Plagioscion squamosissimu)* and in carnivorous crustaceans (*Callinectes bocourti, Callinectes Larvatus,* and *Callinectes Danae*) (Costa, 2009; Torres, 2009; Lopes, 2012; Costa and Lacerda, 2014; Moura and Lacerda, 2018). These contents were correlated to biological factors, such as weight, size, feeding habits, and trophic level. As mentioned previously, in the water and sediment sections, Hg was dominantly from the input from shrimp farming effluents, but despite the biomagnification process, its contents do not present a risk for human health as values were in the range accepted by ANVISA n° 42/13 (Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013). In addition, Pb contents in oysters from the Pacoti estuary were observed near the maximum value permitted by the legislation (Torres, 2009).

Torres (2009) identified low values of Cu in oysters (*C. rhizophorae*) and cockles (*Anomalocardia brasiliana*) in the Jaguaribe River estuary, but the contents of Cu in the crustacean's exoskeleton (*Callinectes sapidus*) were up to twice higher than obtained in their muscles. This variation demonstrates that crustaceans may be subject to anomalous Cu levels exceeding their physiological needs, thus resulting in the export of Cu to the carapace prior to ecdysis, as a detoxification process. A few years later, Cu contents in the muscles of oysters (*C. rhizophorae*) exhibited values closer to the limit for food in general allowed by ANVISA n° 685/98 (Soares, 2017). It was also notable that the study by Torres (2009) found that the increased Cu concentrations in the water column were associated with the high content in the sediment, typical also to almost all the EZBN estuaries, as noticed in the previous sections. Cu is associated with OM as identified in the sediment partition and is easily available to filter-feeding organisms.

A study developed in the Potengi Estuary (RN) reported bioaccumulation of Fe, Zn, Cu, Cr, Pb, Cd, Ni, and Ag in oysters (*C. rhizophorae)*, as a consequence of discharges of sewage and industrial effluents (Silva et al., 2001) where Cu and Pb were higher than those allowed by ANVISA n° 685/98 and ANVISA RDC n° 42/13 (Brasil, 1998; Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013). Besides, there is no limit value for Zn determined by Brazilian legislation; however, Zn concentrations were an order magnitude higher than observed in São Marcos Bay.

It is remarkable that oysters and carnivorous fish and crustaceans had the best feedback as biomonitors of trace metals, especially for Hg, Cu, Zn, and Pb, in the estuaries of the EZBN. Oysters are widely used as biomonitors due to their filter-feeding and sedentary habits, which incorporate the bioavailable trace metals species from the environment (Rainbow and Phillips, 1993; Góngora-Gómez et al., 2017; Lu et al., 2017). The bioaccumulation of Hg, Cu, Zn, and Pb in the organisms of oysters may result from element availability in the water column of EZBN estuaries, as mentioned previously. Carnivorous fishes are affected by feeding habits and high trophic levels (Bisi et al., 2012). These species are highly consumed by the local population, and although most values were below the legal limit, the constant consumption of these organisms throughout someone's life can lead to toxicity and deleterious effects.

The accumulation occurs when the rate of metal uptake into the body exceeds the combined rate of excretion and detoxification of the metabolically available metal. As a consequence, some aquatic organisms can present changes in the metabolic regulatory processes in the biological system, at molecular, cellular, or physiological levels (NRC, 1987; Rainbow, 2002). Geochemical partitioning showed medium mobility to Pb, Cu, and Zn in sediments and efficient desorption of Pb, Cu, Zn, and Hg from particulate to dissolved fraction in the water column in the EZBN estuaries (Torres, 2009; Carvalho, 2014; Silva et al., 2015; Rios, 2018). These trace metals' mobility reflects on the bioaccumulation and biomagnification in oysters, carnivorous fish, and crustaceans, especially for Pb, Cu, Zn, and Hg. This process may occur due to environmental availability, in which the metal interacts with other environmental matrices that influence their fate and transport processes (Drexler et al., 2003). For example, dissolved Cu can be available for interaction with the gills of an invertebrate, binding to dissolved OM, whereas Cu bound to sulfide in sediments is not (Drexler et al., 2003). Therefore, the monitoring and assessment of aquatic biota with trace metal bioaccumulation and biomagnification is helpful to examine the environmental quality. However, to better understand the processes that act on the reactivity of metals to promote incorporation by biota, it is necessary to expand the collection of data on the metals partition in the EZBN estuarine waters.

7 Assessment of the environmental quality of the EZBN's estuaries

Currently, trace metal studies utilize the sediment quality index as an important tool to evaluate and classify the contamination degree of sediments. It indicates anomalous values in the region originated from natural and/or anthropogenic sources and allows for the comparison of different sedimentary matrices. The most common indexes are the Enrichment Factor (EF) and Geoaccumulation Index (Igeo) (Marins et al., 2004; Buruaem et al., 2012; Nilin et al., 2013; Paula Filho et al., 2015; Barbieri, 2016; Santos et al., 2019). In the present study, Igeo was applied to the metal's contents (Figure 3). This index was proposed by Müller (1986) to measure the level of sediment contamination by environmentally relevant inorganic contaminants. It is determined by the following equation Igeo = $\log_2(Cn/1.5^*Bn)$, in which Cn is the content of the element in the clay fraction of the sediment, 1.5 is a factor to include the natural fluctuations and even in low anthropogenic inputs, and Bn is the geochemical background value of the element. The Igeo classes and scales range in six degrees of contamination: Class 0: <0 suggests an uncontaminated environment and Class 6: >5 indicates very heavily contaminated sediment.

There are only a few elements with regional background values determined in two estuaries of the EZBN, as mentioned previously. Therefore, these values will be considered representative for all the regions to evaluate the sediment contamination due to the similarity observed in the spatial distribution of metals along with the sediments of the EZBN. The background values utilized were 1.4% for Fe, 633 $\mu g.g^{-1}$ for Mn, 18 $\mu g.g^{-1}$ for Cr, 6.8 $\mu g.g^{-1}$ for Cu, 15 $ng.g^{-1}$ for Hg, 5.9 $\mu g.g^{-1}$ for Pb, and 13.4 $\mu g.g^{-1}$ for Zn (Marins et al., 2004; Paula Filho et al., 2015). The maximum metal concentrations of each estuary were used to determine the index, because some of the studies showed only the minimum and maximum range, and others just the average values.

In Supplementary Material—Supplementary Table S1, Pb and Zn showed Igeo values higher than moderately contaminated (Class 2) in 53% and 25% of the EZBN estuaries, respectively. While for Mn all estuaries were considered uncontaminated. Pb was classified as moderately contaminated (Class 2) in the Anil, São Marcos, São José, Paciencia River, Apodi, and Galinhos estuaries. The Bacanga estuary was indicated as moderately to heavily contaminated (Class 3), while the Parnaíba River Delta and Curimataú estuary were found heavily contaminated for this element (Class 4). Pb is a toxic metal to aquatic biota and humans (Jesus and Cruz, 2019; Kütter et al., 2021), but the main source of Pb for the region is mainly from natural contribution, urban runoff, inadequate disposal of solid waste, and Pb present in aerosols resulting from the burning of fossil fuels. Pb can be correlated with suspended particulate material, which may favor the co-precipitation of Pb with Fe–Mn oxyhydroxides and $PbCO_3$ in an environment with pH > 6 (Nascimento, 2013; Paula Filho et al., 2014; Azevedo, 2019; Santos et al., 2019), explaining the large spatial distribution of Pb in these estuarine sediments. The anomalous concentrations of Pb reflect its bioaccumulation in oysters with values higher than the limits allowed by the Brazilian legislation ANVISA RDC n° 42/13 (Ministério da Saúde. Agência Nacional de Vigilância Sanitária, 2013).

The Parnaíba River Delta, Ceará, Jaguaribe, and Potengi estuaries were classified as moderately contaminated for Zn (Class 2), while the Anil estuary was considered moderately to heavily contaminated (Class 3). This element is an essential element that participates in the metabolism of proteins, nucleic acids, carbohydrates, and lipids in organisms (Kütter et al., 2021). These high values of Zn in sediments are mostly from lithogenic sources with anthropogenic enrichment from urban runoff and inadequate disposal of solid waste observed in the Parnaíba River Delta (Paula Filho et al., 2014), as identified by the sediment partitioning of Zn associated mainly to residual fraction and secondly to Fe-Mn oxides (Oliveira, 2012; Silva et al., 2015; Rios, 2018). Therefore, Zn from anthropogenic activities that are found bound to the reducible forms in the sediments may be available as soluble species under anoxic conditions (Tessier et al., 1979). As previously mentioned, Zn was also found desorbed in the water column and led to bioaccumulation in oysters of the EZBN estuaries.

Sediments of the Parnaíba River Delta and Potengi estuary were classified as moderately contaminated for Cu (Class 2), and the Curimataú estuary was classified as moderately to heavily contaminated (Class 3). The presence of Cu in high concentrations in water and sediments facilitate bioaccumulation and biomagnification in aquatic organisms (oyster and crustaceans) as observed in the EZBN estuaries. The main sources of Cu observed for the region were natural processes of soil denudation, electroplating, iron smelting, mining, agriculture, and inadequate disposal of wastewater and solid waste (Correa, 2008; Torres, 2009; Paula Filho et al., 2014).

The Curimataú estuary was considered moderately to heavily contaminated by Fe (Class 3). Iron is necessary to the circulatory system of organisms and it is commonly found in high concentrations in soils and sediments in the Earth's crust (Salomons and Förstner, 1984). The presence of Fe in the sediments may be related to the lithogenic source from the Barreiras Formation, which is rich in Fe, Mn, Co, and Cu (Xavier et al., 2017). Igeo for Cr classified Bacanga and Potengi estuaries as moderately contaminated (Class 2). The presence of Cr is related to emissions from agriculture, untreated sewage, and fossil fuels from anchoring boats. Cr is an essential metal to fish metabolism and algal photosynthesis but can be highly toxic when present as soluble species as a result of pH variation (Jesus and Cruz, 2019).

The Ceará and Cocó estuaries, in the state of CE, were the only environments that were uncontaminated and moderately contaminated by Hg, presenting class 1 among all the EZBN estuaries evaluated. Hg is a non-essential metal that is bioaccumulated in oysters and possibly biomagnified in detritivores and omnivores fishes (Vaisman et al., 2005; Almeida, 2015; Rios et al., 2016). Stronger seawater intrusion facilitates the mobilization of Hg from the sediment to the water column and Hg methylation increases its bioavailability (Marins et al., 2004; Dias et al., 2009; Lacerda et al., 2012). This element was found bioaccumulated in oysters and biomagnified in carnivorous fishes and crustaceans in estuaries of the EZBN (Vaisman et al., 2005; Costa, 2009; Torres, 2009; Lopes, 2012; Costa and Lacerda, 2014; Rios et al., 2016; Moura and Lacerda, 2018).

Table 4 shows an overview of the environmental conditions considering the metal contamination, lability indicated by sequential extractions, influence on the aquatic biota, and other major drivers. The estuaries were grouped into 13 hydrographic units according to the National Water Resources Plan (PNRH) to determine the urban population by municipalities (ANA, 2006; ANA, 2017). The annual urbanization rate through population growth, between 2013 and 2035, was estimated according to the United Nations guideline (2018) to estimate the growth of the main anthropogenic factors of contamination by residual metals. Rate urbanization with values below 1% present slow growth, and above 1% demonstrate fast growth. The Anil, Tibiri, Paciência, and Bacanga estuaries are located in the Maranhão Island basin. Ceará, Cocó, and Pacoti estuaries belong to the Metropolitan basin of Fortaleza. Conchas and Piranha-Açu belong to the Piranha-Açu basin. Galinhos, Guamaré, and Ponta do Tubarão estuaries compose the Northern coastline with a diffuse flow of the RN basin, while Papeba and Curimataú estuaries are located in the southern coastline with a diffuse flow of the RN basin. The other environments represent their own hydrographic unit.

The Piranha-Açu, Ceará-Mirim, Nísia-Floresta, and the northern coastline of the RN basin have been found to exhibit low trace metal contamination with uncontaminated to moderately contaminated levels. However, there is no available data about metal speciation and the potential influence of these trace metals on the local biota. The Igeo results suggest trace metal contents are from natural sources, but it should be noted that the margins of these estuaries are home to many aquaculture farms and urban centers. While the rate of urbanization in the estuaries from the northern coastline of the RN and Piranha-Açú basins is slow, with an increase of 0.9% per year between 2013 and 2035, the other basins are experiencing fast growth, with an increase of more than 1% per year.

This indicates that anthropogenic activities in Ceará-Mirim and Nísia-Floresta will increase, leading to a potential rise of metal loads to these environments. While the trace metal contents are not a significant concern, it is essential to monitor the aquatic organisms and the other compartments of these estuaries to evaluate the possible increase of contamination. The monitoring will help to detect any potential risks to the ecological health of these estuaries and help the development of effective management strategies to protect these ecosystems.

The Apodi, São José Bay, and São Marcos Bay environments have been classified as uncontaminated or uncontaminated to moderately contaminated for Cr, Cu, and Zn, while surface sediments are commonly found to be moderately contaminated for Pb. Among these three environments, only São Marcos Bay has reported high concentrations of Zn in fish, and Pb values were not detectable. Its main drivers of metal contamination are natural sources and domestic sewage. Additionally, São Marcos Bay has intense harbor activities for ore loading, while the Apodi estuary has diverse aquaculture farms on its margins. All basins experience fast growth at a rate of more than 1% per year, suggesting a potential rise of trace metal sources. Therefore, it is crucial to identify the lability of Pb through sequential extractions and monitor and reduce its emissions. Developing biota monitoring is also essential to provide information on the bioaccumulation and biomagnification of metals through the food chain, which is necessary for understanding the potential risks to human health.

The Jaguaribe basin and Metropolitan basin of Fortaleza have been commonly classified as uncontaminated to moderately contaminated for Pb, while Zn and Hg have been identified as the trace metals of most concern, with moderate contamination levels. Although the Jaguaribe estuary is classified as uncontaminated to moderately contaminated for Cu, approximately 50% of Cu in the surface sediments is bioavailable. This bioavailability has a significant impact on the bioaccumulation of Cu in oysters, with concentrations nearing the maximum limit allowed by law. The presence of Ba is also a concern due to its lability, circa 62% in the sediment bounded to exchangeable and carbonates fractions.

Besides the values of Hg in the Ceará and Cocó estuaries, the oysters and fishes did not accumulate this element in their tissues. The Pacoti estuary is classified as uncontaminated to moderately contaminated for Pb, with approximately 50% of the Pb in the surface sediments being bioavailable. This high bioavailability has a notable impact on the oyster population, as they are absorbing the Pb and reaching concentrations close to the maximum limit allowed by law. All basins estimate fast growth at a rate of more than 1% per year, suggesting a potential expansion of trace metal loadings. So, it is important to develop strategies to monitor and reduce the emissions from domestic sewage, aquaculture, and harbor activities because the biota is showing evidence of environmental degradation due to the potential availability of metals. This condition can have significant consequences for both the ecosystem and human health, as oysters are a common food source for many people in the region.

Sediment from the Potengi estuary was classified as moderately contaminated for Cr, Cu, and Zn, but there were no speciation data to estimate the lability of these elements. However, oysters were showing evidence of the availability of Cu and Pb with concentrations higher than what is permitted by Brazilian law. Additionally, while there is no specific legislation on the permitted amount of Zn for seafood consumption, the values of Zn observed in oysters were an order of magnitude greater than those found in oysters from São Marcos Bay. A total of 90% of the population of the Potengi Basin was already living in urban areas in 2013, however, the basin has had a slow rate of urbanization, at 0.8% per year between 2013 to 2035, suggesting stabilization of trace metal emissions that can be considered high. So, it is necessary to warn the population about aquatic organisms that are not appropriate for consumption, conduct more studies to confirm metal speciation for Cu and Pb, and increase monitoring of the local biota, as well as develop strategies to reduce the trace metal emissions from domestic sewage and industrial and aquaculture effluents.

Nevertheless, the environments with the highest concerned contamination in sediment conditions are located in the Maranhão Island basin, the Southern coastline of the RN basin, and the Parnaíba River Delta. The estuaries in Maranhão Island demonstrated moderate contamination and were moderately contaminated to heavily contaminated for Pb, except the Tibiri estuary, which was uncontaminated to moderately contaminated. Some lability of trace metals (Pb, Zn, and Ni) was observed in the sediment of these estuaries, except in the Anil estuary, which did not feature in any of the studies. The Bacanga estuary was the only environment with some data about trace metal bioavailability. The oysters presented Zn in an order of magnitude higher than oysters found in the Potengi estuary. Besides the slow rate of urbanization, 0.8% from 2013 to 2035, Maranhão Island presented more than 80% of the urban population in its area in 2013. Therefore, the metal loads from harbor activities and from domestic, hospital, and industrial sewage must be controlled, and monitoring of the biota quality consumed by the population should begin.

The Curimataú estuary, located on the southern coastline of the state of RN, and the Parnaíba River Delta have shown significant levels of metal contamination. The Curimataú estuary was found to be moderately to heavily contaminated with Fe and Cu, and heavily contaminated with Pb. The presence of Fe in the sediment may be attributed to a lithogenic source from the Barreiras Formation, while Cu and Pb are the result of effluent discharges from shrimp farming and domestic sewage. The Parnaíba River Delta is designated as an Environmental Protection Area, but sediment from the area also shows metal enrichment similar to that of the Curimataú estuary for Pb. Unfortunately, there have been no studies conducted on Pb speciation or contamination in organisms in both environments. However, Zn was found to be present in labile fractions, with 16% bound to exchangeable carbonates in the Parnaíba River Delta. The urbanization rate is estimated to increase moderately from 2013 to 2035 for the protected area and it is expected to remain low for the estuaries in the southern coastline of the state of RN. Therefore, it is strongly recommended that metal speciation is conducted as well as monitoring and reducing metal emissions in these areas.

In general, most of the environments present a lack of information about metal speciation in sediments that exhibited an enrichment of contaminations, as well as there were little data about the biomonitoring of the local organisms. The major drivers of contamination include natural sources, agriculture and aquaculture effluents, domestic and industrial sewage, harbor activities, deforestation, and landfill. Most of the estuaries present an increase of urbanization at a rate of more than 1% per year, suggesting a potential rise of trace metal loadings and anthropogenic contaminations. So, the main responses to these contaminations include identifying and reducing emissions, monitoring the biotic and abiotic compartments, and public warnings on biota contamination by metals that can be a risk to human health. Sediment from the Curimataú estuary, the Parnaíba River Delta, and the Anil and Bacanga estuaries presented the highest metal contaminations for Pb, Zn, Cu, and Fe.

Compared to other urban estuaries located in tropical zones, the EZBN estuaries exhibited Igeo values for Hg, Cu, and Zn below those observed in the Vembanad estuary in India, which is deemed extremely contaminated (Class 6) (Sruthi et al., 2018). However, the Parnaíba River Delta and the Curimataú estuary showed a similar classification for Pb as the Bumbu River and Kokolo

Canal in the Democratic Republic of the Congo, which are considered heavily contaminated (Class 4). The Anil estuary received a similar classification of moderate to heavily contaminated (Class 3) for Zn as the Pearl River Estuary (China) (Kayembe et al., 2018; Chai et al., 2019). In addition, the Igeo value of Pb, Cu, and Zn in the Saigon River Estuary in Vietnam and the Capibaribe Estuary in Brazil exhibited a classification below that observed in the EZBN estuarine sediments, with uncontaminated to moderately contaminated (Class 1) and moderately contaminated (Class 2), respectively (Xavier et al., 2017; Noncent et al., 2020). These comparisons show the similarity of trace metal enrichment in the EZBN estuaries and other tropical estuaries under anthropogenic pressures.

Igeo results have a limitation that needs to be taken into consideration since the reviewed estuaries present some different geological aspects that may affect metal concentrations (El-Robrini et al., 2006; Morais et al., 2006; Vital et al., 2006). Therefore, it is necessary to conduct more studies to determine the natural background levels based on sediment cores and better differentiate between natural and anthropic sources through the Igeo index. Sequential extractions of metals in sediment, and distribution coefficients between the soluble phase (dissolved) and solid phase (particulate and sediment) are necessary to evaluate the mobility of these elements in the environments and their potential for biota intoxication. On the other hand, these assessments accompanied by biomonitoring include all the properties of the estuarine systems and can qualify these systems. However, this review has provided a snapshot of metal contamination in the EZBN, which may help the development of new investments in environmental research in the region as well as assist authorities in their decision-making processes to diminish trace metal inputs from anthropogenic sources, thus reducing the bioaccumulation and biomagnification of metals and reducing risks to human health.

8 Final considerations

Trace metals in the Equatorial Zone of the Brazilian Northeast were more intensively studied in the state of CE, which was distinct from the other three states. Most of the environments showed some anthropogenic enrichment of trace metals (Cu, Pb, Zn, and Hg) either from shrimp farming effluents or domestic and industrial discharges, all of which can alter the environmental quality of the estuaries. Sequential extractions in the sediment suggested low to medium mobility of metals, and that Fe-Mn oxides, OM, and carbonates can act as geochemical carriers of trace metals along the estuarine gradient. These results pointed to the importance of monitoring the main anthropogenic activities in the region, such as shrimp farming effluents and domestic and industrial discharges.

However, compared with studies in other Brazilian estuaries, metals data in EZBN sediments, such as Sr, V, and Mg, are still scarce. The observed metal concentration in water for Cu, Pb, Zn, Hg, and Fe varies over two orders of magnitude in the same large-scale geological province, highlighting the influence of the anthropogenic uses of drainage basins.

Most of the organisms presented trace metal values below the maximum limit established by the Brazilian legislation, but, remarkably, oysters, carnivorous fishes, and crustaceans were the most dependable biomonitors of Cu, Pb, Zn, and Hg, in agreement with the sediment contamination degree evidenced by Igeo. Igeo exhibited anomalous values in the Curimataú estuary, Parnaíba River Delta, and the Anil and Bacanga estuaries for Pb, Zn, Cu, and Fe with a classification of moderately to heavily contaminated and heavily contaminated. Anomalous values may be related to lithogenic sources, domestic sewage, and inadequate disposal of wastewater from aquaculture and solid waste. In addition, more studies to determine the natural background levels, based on cores sampled in different estuaries, and metal speciation are necessary to better differentiate between natural and anthropic sources.

Author contributions

TS was responsible for the analyses of metals from the Parnaíba River Delta and part of São Marcos Bay, for the supervision of LA, literature review, preparation of graphs and tables, and writing of the manuscript. RM was responsible for guidance of practical work and preparation of the article, writing of the manuscript, and funding. LA made the sequential analyses of metals in the sediments and discussion of results from the Parnaíba River Delta mentioned in the manuscript. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2023.1142649/full#supplementary-material

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