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GEOCHEMISTRY OF TRACE METALS AND ORGANIC MATTER IN EQUATORIAL ESTUARIES OF NORTHEASTERN BRAZIL

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Geochemistry of Trace Metals and Organic Matter in Equatorial Estuaries of Northeastern Brazil

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THAYS THAYANNE LUZ SANTOS

GEOCHEMISTRY OF TRACE METALS AND ORGANIC MATTER IN EQUATORIAL
ESTUARIES OF NORTHEASTERN BRAZIL

Thesis presented in cotutele regime to the Postgraduate Program in Tropical Marine Sciences at the Federal University of Ceará and the École de Doctorale Mer et Science at the Université de Toulon as partial requirement to obtain the title of Doctor in *Ciências Marinhas Tropicais* and Doctor in *Sciences de l'Univers*.

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FORTALEZA
2022

THAYS THAYANNE LUZ SANTOS

GEOQUÍMICA DE METAIS TRAÇOS E MATÉRIA ORGÂNICA EM ESTUÁRIOS
EQUATORIAIS DO NORDESTE DO BRASIL

Tese apresentada em regime de cotutela ao Programa de Pós-Graduação em Ciências Marinhas Tropicais da Universidade Federal do Ceará e na *École de Doctorale Mer et Science* da *Université de Toulon* como requisito parcial à obtenção do título de Doutora em Ciências Marinhas Tropicais e Doutora em *Sciences de l'Univers*.
Área de concentração: Utilização e Manejo de Ecossistemas Marinhos e Estuarinos.

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To God.
To my Family José, Joana, Thallyta and Kalel.
As also to my dear friends.

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"It is a curious situation that the sea, from which life first arose, should now be threatened by the activities of one form of that life. But the sea, though changed in a sinister way, will continue to exist: the threat is rather to life itself"

Rachel Carson, Marine Biologist.

ABSTRACT

The Parnaíba River Delta (PRD) is a coastal Environmental Protection Area (APA) located in the Equatorial Zone of Northeast Brazil (EZNB), composed of estuaries, islands, bays and dunes. The APA is located in the third-largest mangrove forest in the world and can provide a large amount of organic matter (OM) to the environment. The review of the literature provided the trace metal fate in the EZNB's estuaries that showed enrichment of trace metals in PRD sediments, originating from natural processes and from anthropogenic sources, similar to heavily urbanized coastal environments of the region, and the OM is one of the three main geochemical carrier of metals observed in the region. Therefore, the present work hypothesizes that trace metals from natural and non-natural sources can be controlled by dissolved organic matter (DOM) from the mangrove forest, which act as a geochemical carrier that regulates the partition, mobility and possible toxicity to the biota under the geochemical and hydrodynamic conditions of the equatorial estuary of the PRD. Sampling campaign was performed in December 2019 to collect subsurface water to obtain the dissolved and particulate fractions. The fractions were collected at thirteen stations along an extension of approximately 76 km from the main channel of the Parnaíba River to the Tutóia Bay. In parallel, water samples were also taken at six stations along a salinity gradient (0-36) for the ultrafiltration procedure, totaling 42 subsamples. In the dissolved fractions, trace metals, dissolved organic carbon (DOC), UV-Visible absorption spectrophotometry, composition of OM by fluorescence, and complexation capacity of OM with copper were determined. Suspended particulate matter (SPM) and the trace metal content in the SPM were determined in the particulate fraction. All analyzes were performed in duplicates. The results of environmental quality index indicated anomalies for the Zn in the particulate fraction suggesting possible anthropogenic enrichment through domestic effluents and agricultural activities. The trace metals in the particulate fraction showed desorption increase to the dissolved fraction with salinity rise, as observed mainly for Ba and Zn. This behavior was evident with the distribution coefficient that indicated potential mobility for Ba, Zn and Cu. Fluorescence confirmed the contribution of mangroves in the composition of DOM. The DOM showed a composition of humic substances of terrestrial origin (degradation of mangrove plant material) and of primary productivity (peaks A+C), as well as of marine origin (peak M) of microbial oxidation and phytoplankton degradation. Autochthonous DOM is more labile with lower molecular weight and low aromaticity, while allochthonous DOM has structures with high molecular weight, aromaticity and they are more

refractory. The complexation capacity showed a strong interaction of DOM with Cu in the stations of the Mangrove Channel, suggesting a tendency of lower availability of metal in the water, and the low values found in the waters of the Main River and the Bay area. Fluorescence decomposition of ultrafiltration subsamples identified protein-like components, in addition to the humic substances identified previously. Therefore, the present study characterized the importance of MOD of high molecular weight, aromatic and refractory mangroves in the control trace metal partitioning in the equatorial estuarine system, as this case study of DRP.

Keywords: Contamination. Delta. Mangrove. Parnaíba River.

RESUMO

O Delta do Rio Parnaíba (DRP) é uma Área de Proteção Ambiental (APA) costeira localizada na Zona Equatorial do Nordeste Brasileiro (ZENB), composto por estuários, ilhas, baías e dunas. A APA está localizada na terceira maior floresta de mangue do mundo podendo fornecer grande quantidade de matéria orgânica (MO) ao meio ambiente. Revisão realizada nos estuários do ZENB mostrou enriquecimento de metais-traço em sedimentos do DRP, originados de processos naturais e de fontes antropogênicas, semelhantes a ambientes costeiros fortemente urbanizados da região e a matéria orgânica é um dos três principais carreadores geoquímicos de metais observados na região. Portanto, o presente trabalho tem como hipótese que os metais-traço de fontes naturais e não naturais podem ser controlados pela matéria orgânica dissolvida (MOD) oriundas da floresta de mangue, que agem como carreador geoquímico que regulam a partição, mobilidade e possível toxicidade para a biota sob a condições geoquímicas e hidrodinâmicas do estuário equatorial DRP. Campanha amostral foi realizada em dezembro de 2019 para coleta de água subsuperficial para obtenção das frações dissolvida e particulada. As frações foram coletadas em treze estações a longo de uma extensão de aproximadamente de 76 km do canal principal do Rio Parnaíba à Baía de Tutoia. Paralelamente, também foram feitas amostragem de água em seis estações ao longo de um gradiente de salinidade (0-36), para o procedimento de ultrafiltração, totalizando 42 subamostras. Nas frações dissolvidas foram determinadas metais-traço, carbono orgânico dissolvido (COD), espectrofotometria no UV-Visível, composição da MO por fluorescência e complexação da MO com cobre. Na fração particulada foram determinadas o material particulado em suspensão (MPS) e o teor de metais-traço no MPS. Todas as análises foram feitas em duplicatas. Os resultados do índice de qualidade ambiental de metais-traço indicaram anomalias para o conteúdo de Zn na fração particulada que sugerem possíveis enriquecimento antropogênicos através de efluente domésticos e atividades agrícolas. Os metais-traço contidos na fração particulada demonstraram aumento da dessorção para a fração dissolvida com o aumento da salinidade, observadas principalmente para Ba e Zn. Esse comportamento ficou evidente com o coeficiente de distribuição que indicou potencial mobilidade para Ba, Zn e Cu. A fluorescência confirmou a contribuição dos manguezais na composição de MOD. A MOD apresentou composição de substâncias húmicas de origem terrestres (degradação do material vegetal dos manguezais) e da produtividade primária (*peaks* A+C), assim como de origem marinha (*peak* M) da oxidação microbiana e degradação do fitoplâncton. A MOD autóctone é mais lábil com menor peso

molecular e baixa aromaticidade, enquanto a MOD alóctone apresenta estruturas com alto peso molecular, aromaticidade e mais refratária. A capacidade de complexação mostrou forte interação da MOD com Cu nas estações do Canal de Mangue sugerindo tendência de menor disponibilidade de metal na coluna d'água, e os baixos valores encontrados nas águas do canal principal do rio e das baías. A decomposição da fluorescência das subamostras da ultrafiltração identificaram componentes de tipo proteína, além das substâncias húmicas identificadas anteriormente. Portanto, o presente estudo caracterizou a importância de MOD dos manguezais de alto peso molecular, aromaticidade e refratária no controle da partição de metais-traço no sistema estuarino equatorial, como nesse estudo de caso no DRP.

RÉSUMÉ

Le Delta du Fleuve Parnaíba (DFP) est une zone côtière de protection de l'environnement (APA) située dans la zone équatoriale du nord-est du Brésil (ZENB), composée d'estuaires, d'îles, de baies et de dunes. L'APA est située dans la troisième plus grande forêt de mangroves au monde et peut fournir une grande quantité de matière organique (MO) à l'environnement. Un examen effectué pour les estuaires de le ZENB a montré un enrichissement en métaux traces dans les sédiments du DFP, provenant de processus naturels et de sources anthropiques, similaire aux environnements côtiers fortement urbanisés de la région, et la matière organique est l'un des trois principaux transporteurs géochimiques de métaux observés dans la région. Par conséquent, le présent travail émet l'hypothèse que les métaux traces provenant de sources naturelles et non naturelles peuvent être contrôlés par la matière organique dissoute (MOD) de la forêt de mangrove, qui agit comme un transporteur géochimique qui régule la répartition, la mobilité et la toxicité éventuelle pour le biote sous les conditions géochimiques et hydrodynamiques de l'estuaire équatorial du DFP. Une campagne d'échantillonnage a été réalisée en décembre 2019 pour collecter l'eau souterraine afin d'obtenir les fractions dissoutes et particulaires. Des fractions ont été recueillies à treize stations le long d'une extension d'environ 76 km du chenal principal de la rivière Parnaíba à la baie de Tutoia. En parallèle, des échantillons d'eau ont également été prélevés à six stations le long d'un gradient de salinité (0-36) pour la procédure d'ultrafiltration, totalisant 42 sous-échantillons. Dans les fractions dissoutes, les métaux traces, le carbone organique dissous (COD), la spectrophotométrie d'absorption UV-Visible, la composition de la MO par fluorescence et la capacité de complexation de la MO avec le cuivre ont été déterminés. Les matières particulaires en suspension (MPS) et la teneur en métaux traces dans les MPS ont été déterminées dans la fraction particulaire. Toutes les analyses ont été réalisées en double. Les résultats de l'indice de qualité environnementale des métaux traces ont indiqué des anomalies pour la teneur en Zn dans la fraction particulaire qui suggèrent un possible enrichissement anthropique par les effluents domestiques et les activités agricoles. Les métaux traces dans la fraction particulaire ont montré une augmentation de la désorption vers la fraction dissoute avec l'augmentation de la salinité, comme observé principalement pour Ba et Zn. Ce comportement était évident avec le coefficient de distribution qui indiquait une mobilité potentielle pour Ba, Zn et Cu. La fluorescence a confirmé la contribution des mangroves dans la composition des MOD. La MOD a présenté une composition de substances humiques d'origine terrestre (dégradation du matériel végétal des mangroves) et de productivité

primaire (*peaks* A+C), ainsi que d'origine marine (*peaks* M) d'oxydation microbienne et de dégradation du phytoplancton. La MOD autochtone est plus labile avec un poids moléculaire plus faible et une faible aromaticité, tandis que la MOD allochtone a des structures de poids moléculaire élevé, d'aromaticité et elles sont plus réfractaires. La capacité de complexation a montré une forte interaction de la MOD avec le Cu dans les stations du Mangrove Channel, suggérant une tendance à une plus faible disponibilité du métal dans la colonne d'eau, et les faibles valeurs trouvées dans les eaux du Main River et les Bays. La décomposition par fluorescence des sous-échantillons d'ultrafiltration a identifié des composants de type protéine, en plus des substances humiques identifiées précédemment. Par conséquent, la présente étude a caractérisé l'importance de la MOD des mangroves de haut poids moléculaire, aromatiques et réfractaires dans le contrôle de la partition des métaux traces dans le système estuarien équatorial, comme cette étude de cas de DFP.

Mots-clés: Contamination. Delta. Mangrove. Fleuve Parnaíba.

FIGURE LIST

TABLE LIST

SUMMARY

1. INTRODUTION

The coastal zone comprises complex ecosystems that contain bays, estuaries, mangroves, salt marshes, wetlands, beaches and dune habitats that thrive under to high concentrations of energy (e.g. sunlight, winds and waves), sediments and nutrients that stimulate both high biological productivity and a diversity of habitats and species (CROSSLAND et al., 2005). Due to convenient traffic conditions and abundant natural resources, estuarine areas often have high population densities and intense economic activity (YAO et al., 2016). Hence, estuaries are often highly affected by anthropogenic activities in theirs drainage basin that are increasing substantially the loadings of anthropogenic contaminations such as metal pollutants in coastal environments (MOLISANI et al., 2007; NABELKOVA, 2013).

Trace metals are very common from metal mining and processing, as well as from many other industrial, municipal and agricultural activities (APRILE; BOUVY, 2010). These elements are a great concern due to being persistent pollutants under natural conditions of estuarine environments, and to their long-term accumulation that can cause toxic effects on biota and pose a risk to human health through the consumption of commercial aquatic organisms (WANG; WANG, 2016; YAO et al., 2016).

The role of an estuarine system in the speciation and exportation of metals to coastal zones depends upon several intrinsic characteristics of each estuary (GONÇALVES; CARVALHO, 2006). Biogeochemical processes and physicochemical parameters such as pH, redox potential, and salinity have important controlling factors on contaminant partitioning and fate along the estuarine environment, such as the salinity influence on the conservative or non-conservative behaviors (KRULL et al., 2014; SEDEÑO-DÍAZ et al., 2019; YAO et al., 2016). Thus, it is important to consider specific salinity zones when assessing pollution-induced degradation in estuarine systems (KRULL et al., 2014).

During estuarine mixing great amount of the dissolved metals from river discharge tends to adsorb on the solid particulate matter phase due to flocculation processes induced by the pH and salinity changes, and deposit in the bottom (SAMANI et al., 2015) (Figure 1). It indicates that the settling process affects the suspended particle composition and concentration of dissolved metal in the water column (APRILE; BOUVY, 2010). Suspended particulate matter and sediment are represented by a wide combination of inorganic material (i.e. clay minerals; Fe and Mn oxi-hydroxides) and organic matter (detritus or alive) that can be classified by the predominant chemical (siliceous, calcareous) and mineralogical composition (GONÇALVES;

CARVALHO, 2006; LORING; RANTALA, 1992). Accumulated metal in the sediment can be released into the water column by the exposure of anoxic sediment to oxidant water increasing metal mobility over the environment (GABRIEL et al., 2020; MONTE et al., 2015). Therefore, it is important to assess metals on the different fractions to determine their degree of mobility, availability, transport and persistence in the environment as contaminant (YAO et al., 2016).

Figure 1 Geochemical factors controlling the concentration of trace metal along estuary environment. Figure adapted from Jokinen et al. (2020) and Bianchi (2007). M- represent trace metals. Elaborated by the author.
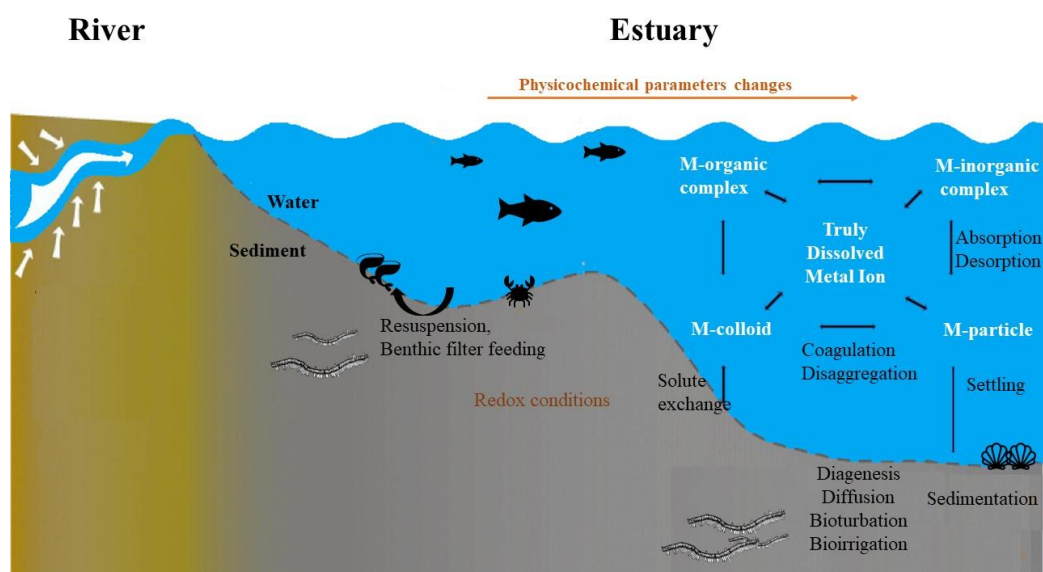
As mentioned previously, the solid phase is composed of organic and inorganic material, such as clay minerals, Fe and Mn oxi-hydroxides, carbonates (CO_3^{2-}), sulfides (S_2^-) and organic matter that can act as geochemical carriers along with the ecosystem (BURUAEM et al., 2012). Among these carriers, the interaction of organic matter (humic and fulvic substances) with the metal ions present a marked effect on the speciation and toxicity to the biota (BEZERRA; TAKIYAMA; BEZERRA, 2009).

Organic matter (OM) is a highly complex and heterogeneous mixture of organic molecules resulting from natural decomposition and transformation of e.g. algal, plant, and microbial material, that vary in their reactivity and ecological role (FELLMAN; HOOD; SPENCER, 2010; VAN ZOMEREN, 2008). Due to its abundance at the earth's surface, the production and decomposition of OM play an important role in the global carbon cycling (which C represents 58% of OM mass). Principal OM sources in the estuarine environment can be from

allochthonous and autochthonous materials (CONSTANTINO et al., 2020). Allochthonous sources are humic substances from terrigenous materials such as eroded soils and/or sediment, vegetation and animal detritus carried out by the river discharges until the estuary. Autochthonous sources are more results from biological processes, such as autotrophic productivity, zooplankton feeding, and bacterial decomposition in the water column (BEZERRA; TAKIYAMA; BEZERRA, 2009; CANUEL; HARDISON, 2016). There are also DOM from anthropogenic sources that are defined as any organic compound originated from organic synthesis, biotechnological production, or human excretion carried by urban rivers (HARJUNG et al., 2020; KELSO; BAKER, 2020). The intense anthropogenic OM input may cause eutrophication in coastal ecosystems with consequent algal blooms, oxygen consumption and oxygen depletion in the estuarine compartments leading frequently to the mortality of the biota (MARTINS *et al.*, 2018). These anthropogenic inputs of OM in the aquatic systems can exceed natural contributions, mainly in places where there is high population density with agricultural, aerial dispersal, industrial and urban runoff.

Operatively, the OM found in the aquatic systems are present as particulate (POM; > 0.45μm glass fiber filter) dissolved (DOM; <0.45μm glass fiber filter) (Figure 2). Particulate organic carbon (POC) and dissolved organic carbon (DOC) are about 50% of POM and DOM, respectively (MILLERO, 2013). Coastal environments present concentrations of DOM and POM varies from 60-120 μM and 4-83 μM, respectively, while estuarine system presents concentration of 8-833 μM for DOM and POM. These environments present more concentration of OM than the surface seawaters (DOM range of 75–150 μM and POM range of 1–17 μM) due to the high productivity and wide OM source in these regions (MILLERO, 2013).

The POM distribution in the water is governed primarily by the dynamics of suspended particles, which its degradation provides energy and nutrients utilized by microorganisms and plants (MIDDELBURG; HERMAN, 2007; SAVOYE et al., 2012). DOM is the largest reduced carbon pool and play important role in a variety of biogeochemical processes and ecosystem functioning (YI et al., 2014), and it represents the most important component of the global carbon cycle. DOM is often characterized operationally as labile, semi-labile, or refractory based on biological or photochemical reactivity (TIMKO; GONSIOR; COOPER, 2015). One can considers also that DOM could be divided into the pools of colloids and 'truly dissolved'. Colloids are dynamic complexes in a size range between 1 nm and 0.2 μm (STOLPE et al., 2010). The truly dissolved is the smallest size fraction with <1 kDa weight

cut off consisted mainly of hydrolyzed ions that are typically considered as bioavailable (BROCKMEYER; SPITZY, 2013; LINDFORS et al., 2020).

Figure 2 Organic matter partition in the natural waters. Adapted from Verdugo et al. (2004). Elaborated by the author.
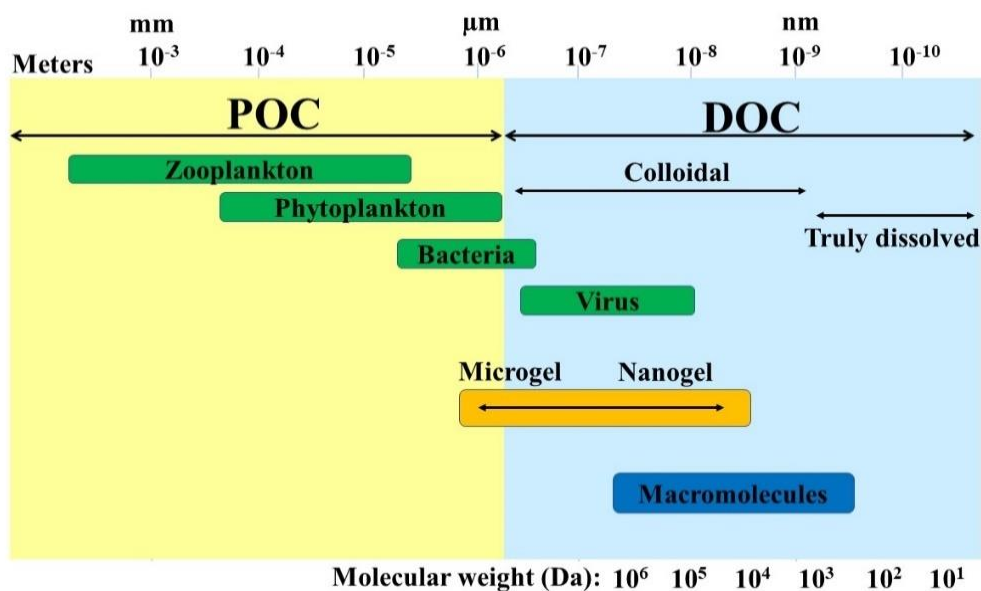
There are many techniques used to fractionate of DOM and trace metals into different size and molecular weight fractions, such as reverse osmosis coupled with electrodialysis (THIBAULT et al., 2019), XAD® resins (PENRU et al., 2013) and cross-flow ultrafiltration (YI et al., 2014). The cross-flow ultrafiltration (UF) methods are applicable to a wide range of different elements and present advantages when compared with conventional UF using closed stirred cells for the assessment of complexation parameters: it is fast with "open" samples, it is simple to scale-up, it has in situ capability, and its presents reduction of membrane clogging and fouling due to tangential flow (ROMÃO et al., 2003).

To characterize OM in coastal ecosystems, scientists utilize advanced methodologies to provide useful information about the source, composition, and function of OM in natural compartments, which the most acceptable techniques currently used are the spectroscopic methods: such as Ultraviolet-visible (UV-Vis) absorbance and fluorescence spectrometry (ABAKER et al., 2018; LOUIS et al., 2015; SANYAL et al., 2020). Absorbance is the capacity of a substance to absorb light (photons) of a specified wavelength (HU; MULLER-KARGER; ZEPP, 2002). The fraction of DOM that absorbs UV-Vis is referred as

chromophores or colored dissolved organic matter (CDOM) (HELMS et al., 2008) that can work as a simple indicator of organic compound in water. Due to difference of the molecular structures of humic substances the UV-vis technique can give intense absorbances in distinct wavelengths. The fluorescence phenomena typically occur in aromatic molecules present in OM, that absorb (chromophores) and re-emit light referred to as fluorescent chemical substances (fluorophores) (FELLMAN; HOOD; SPENCER, 2010) called Fluorescence Dissolved Organic Matter (FDOM).

There are three different fluorescence measurement techniques including (I) emissions scan at fixed excitation wavelengths (2D-fluorescence), (II) synchronous scan at a constant offset wavelength between excitation and emission wavelengths (2D-fluorescence), and (III) excitation-emission matrix (EEM) which fluorescence intensity was presented as a function of excitation wavelength on one axis and emission wavelength on the other (3D-fluorescence) (COBLE, 1996). The last one is the state-of-the-art technique used with plots the EEM into 3D "map' of optical space allowing the visualization of a mixture of fluorophores in a given sample (HUDSON; BAKER; REYNOLDS, 2007). The combination between 3D-EEMs and the multivariate modeling technique parallel factor analysis (PARAFAC) is very well applied to OM characterization that decomposition results are a combination of excitation and emission wavelengths (Ex_{max}/Em_{max}) and produce spectra with maximum fluorescence of the unknown fluorophores in the samples (MURPHY et al., 2013). Coble (1996) analyzed large amounts of samples from freshwater and marine environments and proposed nomenclature for each Ex_{max}/Em_{max} peak of the major organic molecules. Humic-like are represented as peak A and C (vascular plant sources, aromatic in nature and highly conjugated), marine humic-like as peak M, protein-likes (tyrosine and tryptophan-like) are defined as peak B and T. The Table 1 present the fluorescence maxima of each component summarized in coastal environments around the world.

DOM has an effective complexing capacity to form strong metal-ligand complexes that are kinetically non-labile. This process can make a large contribution to trace metal life cycles along with the groundwater, freshwater and seawater environments (HUDSON; BAKER; REYNOLDS, 2007; LAGLERA; BATTAGLIA; VAN DEN BERG, 2007; MOUNIER et al., 2018). The metal-OM interaction is influenced by inherent variables such as surface charge, chemical structure and functional properties of the humic substances (BEZERRA; TAKIYAMA; BEZERRA, 2009; CONSTANTINO et al., 2020) but also external parameter like ionic strength and pH (MOSLEY; LISS, 2019). Binding the free-ion forms of a trace metal by strong ligands

may reduce the exposure and toxicity, or enhance uptake of the complex for nutritional purposes (SANDER et al., 2011). The equilibrium constant between labile and non-labile trace metals species indicate reactions that regulate the partitioning that occur rapidly relative to advective transport along the environment compartments (BECK; COCHRAN; SAÑUDO-WILHELMY, 2010). Therefore, studies of the complexation properties of OM with trace metals in different fractions are vital in order to better understand, the speciation and transport of metallic pollutants (COSTA, *et al.*, 2011) bioavailability and the hazard to the estuarine environment.

Table 1 Major fluorescent components identified for coastal environments around the world. Elaborated by the author.

Reference	Components λex (nm)	λem (nm)	Type/Nature	Environment
Coble, 1996	260	380-460	Humic-like	Atlantic and Pacific Oceans
	275	310	Tyrosine-like	
	350	420-480	Humic-like	
	312	380-420	Marine humic-like	
	275	340	Tryptophan-like	
Chen et al. 2003	<250	<350	Tyrosine	Standard Suwannee River fulvic acid (United States)
	250-280	<380	Soluble microbial by product-like	
	>280	>380	Humic acid-like organics	
	<250	>350	Fulvic acid-like	
Chen et al. 2013	280	330	Tryptophan-like, protein-like	Yangtze River (China)
	305	385	Marine humic-like	
	350	450	Humic like	
Timko et al. 2015	< 250	418	Humic-like	Suwannee River Natural Organic Matter (United States)
	300	418	Marine humic-like	
	< 250	454	Humic-like	
	272	504	Humic-like	
Ferretto et al. 2016	250	394	Humic-like (inland)	Rhône River delta and Fos-Marseille marine area (French Mediterranean Sea)
	230	340	Tryptophan-like	
	250	454	Humic-like	
	<220	<300	Tyrosine-like (marine)	
	230	342	Tryptophan-like	
	245	450	Humic-like	
Lee et al. 2020	322	405	Humic-like	Masan Bay (Republic of Korea)
	386	450	Humic-like	
	280	330	Protein-like	
Constantino et al. 2020	300	421	Humic like	Rio Negro and Carú River (Brazil)
	300	426	Humic like	
	310	420	Humic like	

Trace metal complexation with DOM has been previously measured through polarography and voltammetry methods (BEZERRA; TAKIYAMA; BEZERRA, 2009; LOUIS et al., 2015), ion-selective electrode (ISE) (ROMÃO et al., 2003), and fluorescence quenching (COSTA et al., 2011; MERDY et al., 2012). This last technique is prefferentially applied due to being easy to use and sensitive to low OM concentrations, and thus suitable for use on samples under natural conditions (SODRÉ; GRASSI, 2007). Fluorescence quenching refers to any process that decreases the fluorescence intensity when the excited-state fluorophore is deactivated upon contact with some other molecule in solution, which is called the quencher (LAKOWICZ, 2006). Trace metals are good examples of quenchers (NOUHI *et al.*, 2018; SANTOS *et al.*, 2020).

2.   STUDY AREA: PARNAÍBA RIVER DELTA

Parnaíba River Delta (PRD) is the largest open sea delta on the South and North American continents, with an area of about 2,750 km² that expands under natural conditions (GUZZI, 2012; PORTELA et al., 2020; SALGADO; SANTOS; PAISANI, 2019). It is located between the coordinates 2°21'S - 11°06'S of latitude and 47°21'W - 39°44'W of longitude along the climate transition of humid Amazonian and the dry semi-arid in the Equatorial Zone of Brazil Northeast (FIGUEIREDO, 2004; VEIGA JÚNIOR, 2000). Istorical average annual temperatures vary between 23 to 32 ºC along the year (INMET, 2020). Precipitation distribution is characterized by two establish seasons: rainy season from January to June, with maximum monthly precipitation of 268 mm; and the dry season during July to December, with monthly maximum precipitation of 38.5 mm (Figure 3). The Intertropical Convergence Zone (ITCZ) is the main associated system to precipitation, followed by the El Nino, and the South Atlantic anticyclone (ABREU; MUTTI; LIMA, 2019; INMET, 2019).

Figure 3 Historical Mean Annual Rainfall (mm) in the Parnaíba River Delta, Brazil.
Source: Elaborated by the author from BDMEP – INMET (2021)
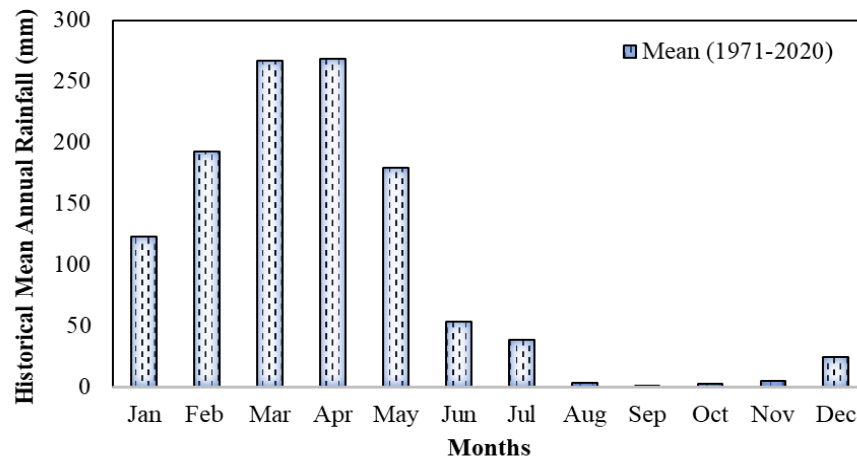
The Parnaíba River rises in the Chapada das Mangabeiras and divides Maranhão from Piauí states, with 1400 km of extension and 774 m³ s^{-1} of river discharge in the closest station to the coast (ANA, 2017, 2020). The river flow cross different biomes, such as the Cerrado in the Alto Parnaíba, Caatinga in Médio and Baixo Parnaíba, and coastal region in Baixo Parnaíba, making differentiated the hydrological characteristics of each of these region different (MMA, 2006a). The south boundary of the basin, there is the Serra da Tabatinga, which separates it from the São Francisco River Basin. In the southwest, it borders of Tocantins Basin. Over the east side, there is Serra Grande between the border Piauí-Ceará, and Chapada do Araripe along the border of Piauí-Pernambuco (ABREU; MUTTI; LIMA, 2019). The river is navigable in practically all its extension, and flows into five bays in the delta: Baía de Tutóia, Melancieira, Cajú, Canárias e Igaraçu (Figure 4)(GUZZI, 2012). Local hydrodynamic of the delta is featured by meso-tidal with amplitudes range from 0.2 to 4.0 m under semidiurnal regime (CHN, 2019). North-Northeast (NNE) was the principal current direction which the maximum velocities reached 0.52 m s^{-1}, with the mean of 0.19m s^{-1} (Silva et al., 2015).

Due to its socio-environmental importance, an Environmental Protection Area (APA) was created, with an area of 313,800 ha that covers 10 cities over MA, PI and CE states (BRASIL, 1996; IBGE, 2020). After in 2000, inside of the APA was inserted the Parnaíba River Delta Marine Extractive Reserve (27.021 ha) to guarantee self-sustainable exploitation and the

Figure 4 Hydrographic Basin and Environmental Protection Area of the Parnaíba River Delta. Elaborated by the author.
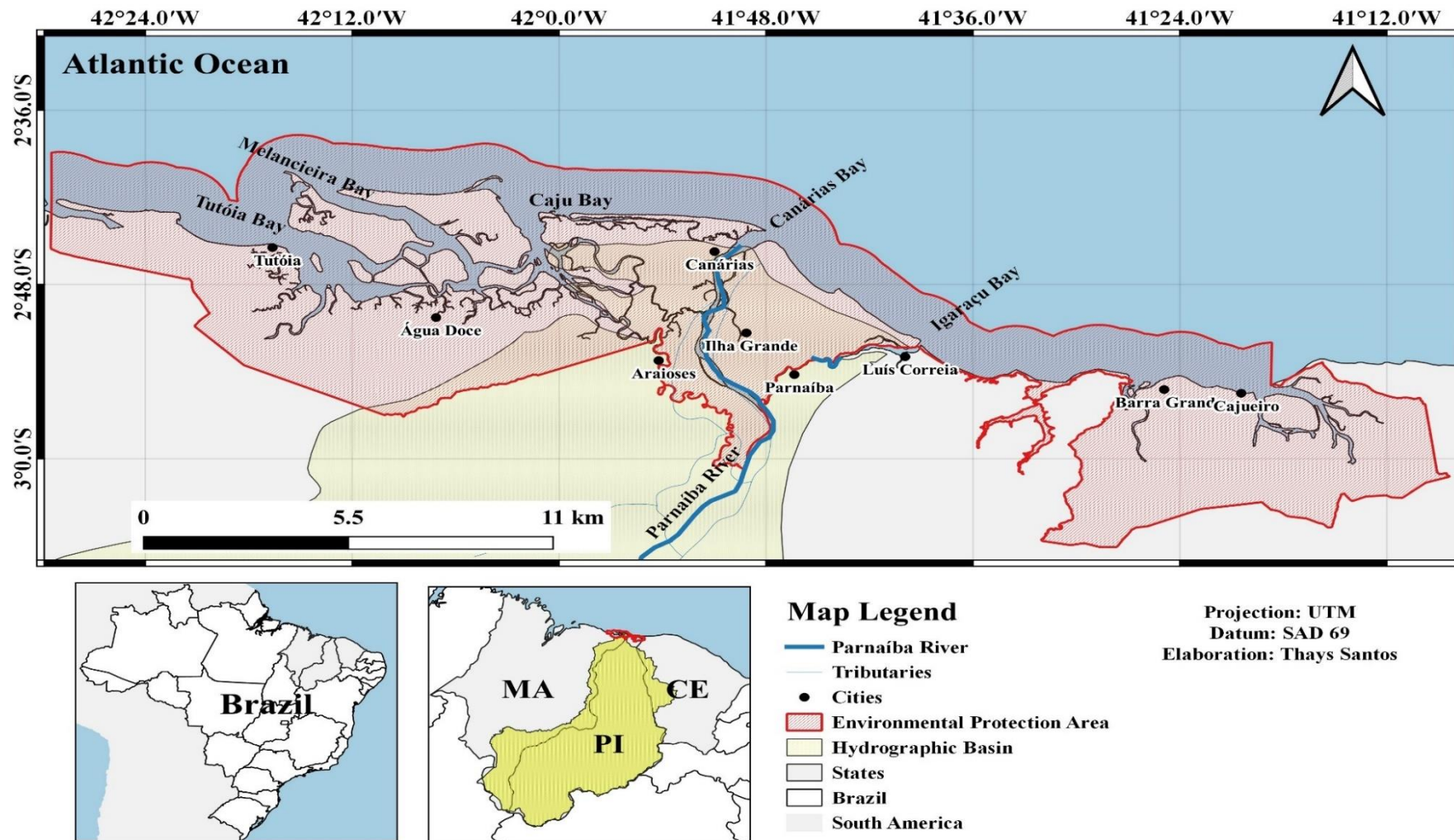
conservation of renewable natural resources traditionally used by the extractive population in the area (BRASIL, 2000).

Most part of the Parnaíba river is located in the Parnaíba basin and the delta is on the Barreirinhas basin (CAPUTO; IANNUZ; FONSECA, 2005). The sedimentary record is 3,500 m thick made of siliciclastic and chemical rocks mainly of Paleozoic age, but it also includes Jurassic to Cretaceous volcanic rocks (MENDONÇA BARBOSA; NOGUEIRA; DOMINGOS, 2015). According to Codevasf (2016) the river banks of the Parnaíba are alluviums with a high salt content, while in the small rivers that flow to the northeast, Solonchak and Hydromorphic Soils occur. They are generally coarse-textured soils, with the exception of Oxisols and Plinthosols, which have higher clay content and high drainage rates.

The hydrographic basin of the Parnaiba River has multiple uses as the generation of electric energy (Boa Esperança dam), irrigation (coastal boards and Plateaus de Guadalupe) and human supply (ANA, 2020).The total human population estimated on the APA is 362.449 inhabitants, which only 1.30 - 23.50% of the domiciles has adequate sanitation (IBGE, 2020).

River mouth separates the delta coastline in two different sectors, the east part is composed by active coastal dunes that covers mangrove forests, and the west part is characterized by tidal channels associated with estuarine-lagoonal conditions (AQUINO DA SILVA *et al.*, 2019; SZCZYGIELSKI *et al.*, 2014). The delta present five distinct vegetation types: psammophile pioneer vegetation, dune subevergreen vegetation, mangrove evergreen vegetation, floodplain vegetation and vegetation associated with carnaubals (PORTELA et al., 2020). The delta is included in the third largest mangrove forest in the world, with 7 % of the world total (FAO, 2020). The main mangrove plant genera in this region are *Rhizophora, Laguncularia* and *Avicennia* that can reach 40 and 45 m in height (Figure 5) (GUZZI, 2012).

Figure 5 Mangrove floret in Parnaíba River Delta, Brazilian Northeast. Source: Author.

The regional economy is based on agriculture, farming, fishing, vegetal extractions and tourism. According to MMA (2001), agriculture is developed by micro-producers who make subsistence crops predominantly of cassava, maize, beans, rice, cultivated in small areas. Subsistence farming practiced on small properties and extensive livestock raising predominantly with cattle and secondarily goats and sheep. Artisanal and industrial fishing of fish, lobsters, crabs and other organisms of commercial value. But currently the main economic activity is the extraction and processing of carnauba wax, babassu oil, coconut fat, jaborandi leaf, cashew nut, milk, cotton and leather, which have significantly contributed to economic growth. There are several tourism agencies that make a tourist route to visit the islands in the region, which has great ecotourism, scientific and cultural touristic potential (MACHADO JÚNIOR; MACEDO, 2016).

3.   HYPOTHESIS AND OBJECTIVES

The Parnaíba River Delta mangrove provides great amount of organic matter to the environment. Notwithstanding the creation of an Environmental Protection Area in this ecosystem, it was identified anomalous values for trace metals (Pb, Cu and Zn) in the sediment in previous studies (PAULA FILHO *et al.*, 2019), as a result of erosion and leaching of soils, and additional inputs from anthropogenic activities derived from urban runoff and inadequate disposal of solid waste (PAULA FILHO *et al.*, 2014). Trace metals and the role of organic

matter in this estuary have rarely been studied. And the pathways of organic matter and trace metals in the tidal estuaries are difficult to delimit due to intensive physical mixing and biological processing with both impact its distribution. Therefore, the hypothesis is the fate of trace metals from natural and non-natural sources may be controlled by organic matter from PRD's mangrove forest, that acts as the main geochemical carrier regulating metal partitioning, transport and mobility. Furthermore, the salinity from seawater, that are distinct along the PRD's zones (AQUINO DA SILVA *et al.*, 2015), influence in the spatial distribution and partition of trace metals and in the quality of dissolved organic matter of this equatorial tidal estuary located between the Amazon and semi-arid climate conditions.

3.1 GENERAL OBJECTIVE

The present research work aims to understand the geochemical processes that correlate the composition and sources of the organic matter with the trace metal distributions and partitioning in the estuarine waters in Parnaíba River Delta (PRD) located in the Brazilian Equatorial Northeast, in a transition region between Amazon and semi-arid climate.

3.2 SPECIFICS OBJECTIVES

a Review the trace metal distribution and sources, and to comprehend the interaction among the environmental compartments (sediment, water and biota) of estuaries located in the Equatorial Brazilian Northeast;

b Determinate spatial distribution of trace metals and organic matter in the water column along the PRD, including bays, mangrove channels, major river channel and areas close to dune fields;

c Determinate the geochemical partitioning of trace metals in water by applying the coefficient of distribution;

d Assess the environmental quality of trace metals in the water column by applying the geochemical index of sediment quality;

e Characterize the source and quantify the organic matter in the water column;

f Characterize the dissolved organic matter in different size fractions along a salinity gradient;

g   Identify the interaction and size distribution of organic matter with trace metal by the measurement of complexation capacity of dissolved organic matter with dissolved copper.

4.   RESEARCH STRATEGIES

The results were organized in scientific articles and an additional chapter to reach the specific objectives described in section 3. The first article in section 5.1 entitled "A Review on Trace Metals Fate in Equatorial Estuaries in The Brazilian Northeast" describes the results determined by the specific objective "a".

A sampling campaign in December 2019 was carried on in the Parnaíba River Delta to collect subsurface water to obtain the dissolved and particulate fractions, and to measure physicochemical parameters *in situ* along with thirteen stations. The second article contains the results of trace metals to grant the specific objectives b, c and d, in section 5.2 titled "Trace Metals Partitioning in Parnaíba Delta Waters, Brazil Equatorial Coast". The third article, in section 5.3 entitled "Dissolved Organic Matter Complexation Capacity and Signatures of Chromophoric Dissolved Organic Matter (CDOM) in Parnaíba River Delta, Brazil Northeast" contribute to the specific objective e and g. Section 5,4 named "Evaluation of Size And Composition of Dissolved Organic Matter of Estuarine Waters of Parnaíba Delta" provides the results of ultrafiltration procedures to answer the specific objectives proposed in e and f.

5.   RESULTS E DISCUSSION

5.1 A REVIEW ON TRACE METALS FATE IN EQUATORIAL ESTUARIES IN THE BRAZILIAN NORTHEAST

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Abstract

The present study provides an overview and assessment of trace metals in water, sediment, and biota registered in estuaries of the Equatorial Zone of the Brazilian Northeast (EZBN) to compare the grade of contamination and point out 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 a medium mobility from solid to liquid phase along with the environments. Curimataú estuary and Parnaíba River Delta were the environments with the lowest sediment quality, identified by Igeo for Pb, Zn, Cu and Fe, related to the enrichment of anthropogenic contributions from the agriculture, inadequate disposal of wastewater, solid waste and burning of fossil fuels. Oysters, carnivorous fishes and crustaceans had the best feedback as a biomonitor for Cu, Pb, Zn and Hg. However, more studies to determine the natural background levels based on sediment cores are necessary to better differentiate from natural to anthropic sources. Other essential information is the determination of the main geochemical carriers (e.g., organic matter, $CaCO_3$, Al and Fe) to comprehend the mobility and reactivity of trace metals in coastal zone. Partitioning of trace metals (dissolved, colloidal and particulate phases), distribution coefficients and possible incorporation in the organisms will also turn more integrated studies to EZBN.

Keywords: Sediments; Estuarine Waters; Biota; Contamination. Igeo.

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, that favor the occupation and the establishment of economic activities, however characterize the impacts of the drainage basin upstream that affect the estuaries is important because if they are constant, or they are growing, the support capacity of the ecosystem can be surpass (SANTANA; LOTUFO; ABESSA, 2015). Local and upper drainage basin discharges marked by anthropogenic activities enrich estuaries including trace metal contents. Most of the trace contamination causes serious environmental problems worldwide because of their toxicity, non-biodegradable properties, and accumulation and biomagnification in the food chain (BARLETTA; LIMA; COSTA, 2019). When contaminants enter estuaries, they can adsorb onto suspended particles, form complexes, settle on surface sediment that reach contents high enough to become a risk for 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), such as major sources, the spatial and temporal variability in compartments of the estuarine environment and the substantial risk for the biota. The present article will focus on this region between Maranhão (MA), Piauí (PI), Ceará (CE) and the Rio Grande do Norte (RN) states, includes more than 88 cities, totaling about 7.9 million inhabitants, with 85.1% in urban regions and 14.9% in rural areas (IBGE, 2020). The major sources, the spatial and temporal variability in compartments of the estuarine environment and the substantial risk for the biota and the environment are still little knowns.

The objective is to provide an overview of trace 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, reported previously in published research, including monographies, dissertations, thesis, scientific articles, and information from regional environmental protection agencies, in estuarine environments of the EZBN, to identify possible trace metal contaminations and identify lack of data for future complementary research and suggests necessary complementary research. The data collected are from estuaries located close to the largest coastal cities in the region that presents different socio-economic uses. The investigated estuaries were the Anil, Bacanga, Paciência, Tibiri and São

Marcos and São José bays located in Maranhão state (MA), Parnaíba Delta in Piauí state (PI), Ceará, Cocó, Jaguaribe and Pacoti situated in Ceará state (CE) and Curimataú, Apodi, Ceará-Mirim, Conchas, Galinhos, Guamaré, Nísia Floresta, Papeba, Piranhas-Açú and Potengi estuaries in Rio Grande do Norte state (RN).

Environmental Setting

The Equatorial Zone of the Brazilian Northeast (EZBN) comprises the region roughly between 1°5' S and 46°1'W to 6°30'S and 34°58'W (Figure 6). It is characterized by the transition from the humid and hot Amazonian climate to the hot and dry semiarid climate, with average annual temperatures from 1981 to 2010, ranging from 18.4 to 34.90ºC all along the EZBN (INMET, 2019; MMA, 2006b). Precipitation in this region is influenced by the migration of the Intertropical Convergence Zone (ITCZ), El Niño e La Niña and by the action of the trade winds in the Atlantic Ocean, which define the seasonal rainy and dry periods (POLZIN; HASTENRATH, 2014). The Amazonian region is very well defined, with high precipitation from January to June and low from July to December, while the semiarid region shows a short rainy season from February to May a longer dry season from June to January. There is a west-east decrease of the average accumulated rainfall along this coast, with MA state exhibiting 1,599 mm (1,177 to 2,200 mm), PI state 1,007 mm (635 to 1,423 mm), CE state 969 mm (599 to 1,669 mm), and RN state 904 mm (518 to 1,721 mm), between 1981 to 2010 (FUNCEME, 2019; INMET, 2020). Carvalho et al. (2020) detected a reduction in the number of rainy days on the Northeastern, as in Fortaleza (CE) that decreased 19 days of rain, in the past 30 years. The change of the rainfall distribution has an impact on the occurrence of extreme events, such as drought and floods in the EZBN.

The semidiurnal tidal regime is characteristic of the coastal environments of the EZBN with amplitudes variation from macrotidal, as observed in the MA coast (0.2 to 7.3 m), to mesotidal regimes found in PI (0.5 to 4.0 m), CE (0.6 to 3.5 m) and RN (0.1 to 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 (AQUINO DA SILVA *et al.*, 2019; LANDIM *et al.*, 2005). The coastline has 1,689 km in extension, composed of complex ecosystems such as sandy beaches, mangroves, estuaries, bays and, one the largest open-sea delta of the Americas and third largest in the world, the Parnaiba River Delta, which suffers periodical seawater intrusion

(Paula Filho et al., 2015; Silva et al., 2015). MA state is placed in 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 about 544,100 ha, representing 38.9% of the entire Brazilian mangroves, serving as the greatest natural source of organic matter for the aquatic system (ICMBIO, 2018; MOUNIER et al., 2018).

The geology comprises several lithostratigraphic units, 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). Ceará has geological characteristics from the Pleistocene to the Holocene, compounded by the Barreiras, Camocim and Serra Grande's formations (MORAIS et al., 2006). RN geology 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 a scarcity of water resources and marked climatic seasonality, these states have 235 reservoirs with capacity varied from 571,13 to 18.737,57 hm³ constructed along with the water bodies, with 66% of the total in CE state (ANA, 2021). Besides the benefits of water supply or for the generation of electric energy, in the Boa Esperança Hydroelectric Power Station (PI), these dams decrease the water and material discharge from the continent to coastal environments, altering the estuarine ecosystem (DIAS et al., 2016; DIAS; MARINS; MAIA, 2013; MARINS et al., 2003).

Figure 6 Equatorial Zone of the Brazilian Northeast (EZBN).

Major Anthropogenic Sources of Trace Metals at 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 vectors that can contribute to the natural emissions of trace metals to watersheds of rivers and potentially affecting metal content in the coastal ecosystems (BIANCHI, 2007; MARINS et al., 2004).

The contamination process began with anthropic activities that expand significantly with urbanization increase, industry emergence and the consequent rise of energy and raw materials consumption (OLIVEIRA; MARINS, 2011). According to Soares et al. (2021), the Brazilian semi-arid coast is one of the most densely populated areas worldwide. For this reason, there are many activities located in coastal and adjacent areas to supply the population needs, such as industries, agriculture, mining operations and aquaculture (LACERDA et al., 2011; PINHEIRO et al., 2008; SOARES, 2011). Only about 46% of northeastern households have a domestic sewage collection network, PI and MA states have 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. In all four states, the main economic activities are civil construction and industrial utilities. Pulp and paper industry, food, leather and footwear, oil and natural gas extraction, metallurgical, production of oil and biofuels are the other industrial activities present in the profile of these states (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 are Itaqui (MA), Fortaleza and Pecém (CE), Natal and Terminal Salineiro de Areia Branca (RN) (GONZÁLEZ-GORBENA et al., 2015; LIMA, 1999). According to BNDES (1999), CE and RN coasts do not have many natural conditions for the implementation of new harbors (sheltered areas, bays or estuaries with deep waters). In consequence, the Itaqui harbor (MA) is the only 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. This activity is a potential source of trace metals due to accidents with the spillage products during the loading and unloading into aquatic systems, mainly the Itaqui harbor that which is the second in tons handled in the country, which 92% of the cargo corresponding 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 it has been demonstrated in the Mucuripe Harbor, CE state (Lacerda et al., 2019; Maia, 2004; Moreira et al., 2021).

Another potential source is shrimp farming, which in the Brazilian northeastern produced 98.82% of the total of 40,966,771 kg of shrimp in 2017. The states of the present study were responsible for 30,189,648 kg of shrimp, representing 74.56% of the northeastern region production, with RN state the largest producer (IBGE, 2020). Shrimp farming showed significant Hg and Cu emissions to the environment, detected in bioindicators, sediment and water.   Mercury is mostly derived from fish meal present in aquafeeds, whereas Cu comes mostly from the use of algaecides during the pond cleaning. Emission factors for Hg and Cu are among the highest among anthropogenic sources (COSTA et al., 2013; LACERDA et al., 2011; LACERDA; MARINS, 2006; LACERDA; SANTOS; MADRID, 2006; MOURA; LACERDA, 2018; PAULA FILHO et al., 2014; RIOS et al., 2016; TORRES, 2009).

According to Costa et al. (2015), Baptista Neto et al. (2013) and Duquesne et al. (2006) the disposal of domestic sewage and urban solid waste in unsuitable places, such as batteries, are important sources of Hg, Zn, Pb, Ni, Cu and Cr, these have been reported as the major trace metal sources in estuaries bordering metropolitan areas along the EBZN. Industrial discharges have cause commonly cause contamination by As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in nearshore sediments, river channels and coastal zones (CARVALHO et al., 2008; LI et al., 2013; SOUZA; SILVA, 2016), but the low industrialized nature of the EBZN decreases the relative importance of these sources. According to Costa et al. (2015) and Yunus and Chuan (2009) boats may also contribute to the trace metals inputs, as well as the fossil fuel residues since some of these elements (Zn, Cd, Cu and Pb) had a significant correlation with the petroleum markers. Unfortunately, notwithstanding the high intensity of fisheries and recreational boat activities along the EBZN, and the evidence of biological impacts of naval related substances, except TBT (BRAGA; CASTRO; ROCHA-BARREIRA, 2006; CASTRO et al., 2008; CASTRO; CASCON; FERNANDEZ, 2000) no study, to our knowledge, has addressed this source.

Emission factors of trace metals estimated to Parnaíba 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 solid waste, while the other metals showed erosion and leaching of soils as 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). Emission factor determined by Vaisman and Lacerda (2003) indicated that coal burning from Brazil are the greatest source of As and Hg. While the emission factors determined for Zn, Cu, Pb and Cd in Macaé River, were dominantly derived from non-lithogenic sources. Livestock emitted 7.4 t of Zn year^{-1}, wastewater discharge 5.1 t of Cu year^{-1}, urban solid waste emitted 4.2 t of Pb year^{-1}, and atmospheric deposition was responsible for 2.1 t of Cd year^{-1} (MOLISANI et al., 2013).

Trace Metal in Estuarine Sediments Of EZBN

Sediments act as a reservoir of trace metals that can account for more than 99% of trace metals that enter the rivers (HUANG; GE; WANG, 2012), integrating the impact of the different trace metal sources of the adjacent drainage basin to the estuaries, and through relatively long periods. Most studies on trace metal concentrations in sediments were quantified in the grain

size fraction <63 μm due to trace metals preferential association to fine materials such as clays, silt and particulate organic matter, which are the major geochemical carriers in aquatic ecosystems (Silva et al., 2015; Oliveira, 2012; Nilin, 2008; Marins et al., 2004; Nascimento, 2013; Rios, 2018). Nevertheless, in estuaries with high hydrodynamic conditions, trace metals were frequently determined in the total: <2 and <1 mm grain size fractions of the sediment (GARLIPP, 2006; PERES, 2012; SANTOS; MARINS; DIAS, 2019). Table 2 presents the average contents of trace metals in sediments of different estuaries of the Equatorial Zone of the Brazilian Northeast (EZBN).

A study developed in sediments of São Marcos Bay (MA) showed high contents during the dry season for Cu, Zn, Al and Mn, while Fe was high during the rainy season. The author concluded that Al, Fe and Mn were above the amount allowed by Brazilian legislation (CONAMA 344/04) suggesting a great availability of these elements (SOUSA, 2009). Santos et al. (2019) also found anomalous values for Mn in the same region indicating ore shipment influence. Anil River and São José estuaries (MA), located in the Maranhense Gulf, manifested anomalies values, especially for Pb, resulting mainly from domestic and hospital sewage, in the first environment, while the second estuary was derived from the lithogenic source with few anthropogenic contributions (AZEVEDO, 2019; SANTOS; MARINS; DIAS, 2019).

Paula Filho et al. (2015) established background values for trace metals in sediment cores in the largest open sea delta of the Americas, Parnaíba River Delta (PI). Most of the metals were below two threshold levels established to sediment quality guidelines, the Threshold Effect Level (TEL) that is a lower likelihood of adverse effects to the biota, and the Probable Effect Level (PEL) which there is a greater likelihood of adverse effects to the biota. Nevertheless, an anomalous value located below 30 cm from the core surface reflects a possible additional contribution of the regional urban center and the harbor. Other sediment cores (unpublished data from 2017) showed high values for Zn, while Al had a significant variation along with the core (2.0 to 6.5%), indicating the influence of the hydrodynamic variation in the deposition of lithogenic aluminosilicates through time. In a more recent study in the Parnaíba Delta, an anthropogenic influence was observed in the 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 PI continental shelf sediments, near Parnaíba River Delta. It was wrapped in a clay matrix

Table 2 Trace 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 bellow to detection limit.

Reference	Environement	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 Delta (PI)	<63 µm	-	1.4	633.0	-	-	-	-	18.0	6.8	-	-	5.9	13.4
Paula Filho et al. (2019)	Parnaíba 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
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

and observed in raspberry-shaped, which is commonly found in organic-enriched marine and estuarine sediments (AGUIAR, 2014). These studies collected sediment in different stations along with the environment, 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 CE State have been the subject of more trace metal contamination studies than the other states listed here. In the metropolitan region of Fortaleza city (MRF), Pacoti River was initially not impacted by Zn, Cu and Hg contents in the estuarine sediment (AGUIAR, 2005; VAISMAN; MARINS; LACERDA, 2005), notwithstanding, it changed some years later with an evident accumulation of Fe, Cu, Pb, Zn and Hg (Souza and Silva, 2016, Rios et al., 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 MRF, the Cocó River exhibited Hg concentrations in the bottom about 112 times higher upstream than downstream (ALMEIDA, 2015; VAISMAN; MARINS; LACERDA, 2005). 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, Cu and Hg contents in the sediment were associated with non-lithogenic source (AGUIAR, 2005; VAISMAN; MARINS; LACERDA, 2005). In addition, Nilin (2012) and Nilin et al. (2013) have strengthened studies to assess human influence on sediment quality. They identified high Zn and Cu accumulations near the river mouth, with Zn concentrations one order of magnitude higher than upstream stations. Although Hg was detected in low concentrations in this river's sediments, the estuary was considered moderately contaminated when compared to other Brazilian coastal regions.

One of the first assessment studies in sediment cores in the Jaguaribe River determined the concentration of 15 ng g^{-1} for Hg as the regional background for the Brazilian Northeastern Equatorial Coast (Marins et al., 2004). The authors also suggest the use of Hg as a proxy to indicate anthropogenic pollution for the region in reason to its absence in the Brazilian geology. Lacerda et al. (2004) compared Cu, Zn, Cd and Pb contents in the Jaguaribe river with two other estuaries located in RN coastal zone: Piranhas-Açú and Curimataú river estuaries. 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 organic matter, Fe and Mn acted as the main geochemical carriers of Cu and Zn, probably to the suboxic conditions that favor the formation of Fe-Mn oxy-hydroxide or pyritization (FeS_2), common in this environment.

Trace metal accumulations (Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in superficial sediment and cores analyzed in Curimataú River (RN) by Garlipp (2006) indicated low content in relation to other estuaries, except Mn and Cu that showed enrichment in some stations. 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). It can result from trace metal contamination by the increase of shrimp farming effluents and to river discharge during the rainy season.

The evaporation in some RN's estuaries exceeds the freshwater input, making the upstream of the river becomes a source of dense water saltier than seawater. This condition characterizes the environment as negative hyper-saline estuary, as Apodi and Conchas. These last environments showed significant contamination with Cr, Cu, Cd and Pb than the positive estuary of Potengi for Cr (SILVA et al., 2017) that exhibits increase salinity gradient seaward. The authors also indicate anthropogenic influence on a load of trace metals in addition to the hydrodynamic conditions characterized by weak tide dispersion capacity that increase the water resident time along the estuary. The high content of Pb and Zn were also identified in Ponta do Tubarão estuary (RN) which the highest metal values were detected near the urban area and anchoring boats, but the trace metal concentrations were below to the limit established by Brazilian legislation (CANTINHO, 2017).

The measurement of total 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, however, furnishes detailed information about trace metals origin, mode of occurrence, availability, mobility and transport (TESSIER; CAMPBELL; BISSON, 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; reducible fraction bound to Fe-Mn oxides and released under anoxic conditions (i.e., low Eh); oxidizable fraction bound to organic matter and sulfides which are solubilized under oxidizing

conditions; and the last fraction is the residual that holds trace metals within the crystal lattice of primary and secondary minerals, which are not expected to mobilize easily in solution.

Unfortunately for the region, little work based on the sequential extraction mentioned above exists (Figure 7). In 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. The authors identified the dominance of almost all trace metals bound to the residual fraction, except for Cr and Pb in the Paciência river estuary and Cu in Bacanga river estuary that were mostly associated with the oxidizable fraction. In the Paciência river estuary, Zn was the only element significantly related to reducible fraction. These results indicate the predominance of trace metals in non-labile fractions, except for Cr, Pb, Cu and Zn that can be mobilized from the sediment to the water column with the change of physicochemical conditions, mainly in the Paciência and Bacanga river estuaries. Also this fraction is often associated to organic matter, meaning that geochemistry of these elements can be controlled by OM.

Other studies developed in the Jaguaribe river, Oliveira (2012) and Rios (2018) applied sequential procedures to determinate trace metals in the five sediment fractions. While Torres (2009) used sequential extraction to determine the bioavailable (F1+F2+F3+F4 fractions) and not available metals (F5) in Jaguaribe and Pacoti rivers (Figure 7). Torres (2009) observed Cu contents predominant in not bioavailable fraction, while Pb was exclusively bioavailable in Pacoti estuary. The results of geochemical partition in Jaguaribe River show that Cu, Zn, Cr, Pb, Ni, Fe, Mn and Al were dominant in residual fraction, except Ba bounded to carbonates related to pH increase along with the environment. The few studies about sequential extractions in estuaries of EZBN suggest relatively low mobility of these metals in the environment related to the significant percentage in residual fractions. Although, it is notable the associations among trace metals with Fe-Mn oxides, OM and carbonates that can acts as the major geochemical carriers of trace metal along with these environments. Therefore, investigation on the quantification and qualification of geochemical carriers present in EZBN could be relevant to the comprehension of many processes of mobility, transport and fate of contaminants along the region, as observed by the complexation of Cu-OM in Cocó and Pacoti rivers. In addition, the scientific studies could indicate if the estuaries in EZBN function as a source or sinks of contaminants to adjacent marine environments,

if this mobility is related to results on these metals on the adjacent continental shelf. This type of result does not exist in the region.

Besides the different extractions and sediment fractions used to determinate the trace metals repartition, it was possible to observe a similar pattern on the spatial distribution of these element contaminations. The results indicated higher concentrations of Zn, Cu and Pb for at least one estuary of each state. Anomalous concentrations for Fe were also identified in estuaries of MA and CE states, as well high content of Mn in aquatic systems in MA and RN states. Estuaries in CE state also demonstrated a significant amount of Hg in its 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 characteristic from Barreiras formation (EL-ROBRINI et al., 2006; MORAIS, 1977; VITAL et al., 2006), and effected by the intense increase of anthropogenic activities developed on the discharge basins that aggravates the enrichment of trace metals in the coastal zone. Although, when compare to other Brazilian equatorial estuaries under constant urbanization pressure, it was possible to observe analogous and differences over the trace metal contaminations. Xavier et al. (2017) identified that even the Capibaribe estuary, which is placed in a metropole of another Northeast state of Brazil, concentrations suggest good environment quality for the sediment for Mn, Fe, Co, Ni, Cu, Zn, As and Pb. From these elements, Fe, Mn, Co, Ni and Pb were higher than found in most estuaries of EZNB. The authors affirms that Barreiras Formation was the main source that increased metals in the environment and do not clearly reflect the anthropic influence as suggested the low values of the sediment quality indices.

The other two tropical estuaries placed in the Eastern Brazil Marine Ecoregion where assessments of sources of trace metals (Fe, Al, Mn, Zn, V, Cr, Co, Cu and Pb) in their sediment are available. Vitória bay and Piraquê-Açú-Mirim estuary showed contents of major elements (Mn, Fe and Al) and Co above Apparent Effects Threshold (AET) demonstrating adverse effects in the aquatic organisms.

Figure 7 Metal fractions (%) in sediments estuaries in the Equatorial Zone of the Brazilian Northeast. Data sources from a) Nascimento (2013), b) Carvalho (2014), c)   Silva et al. (2015), d) Torres (2009), e) Oliveira (2012) and f) Rios (2018).
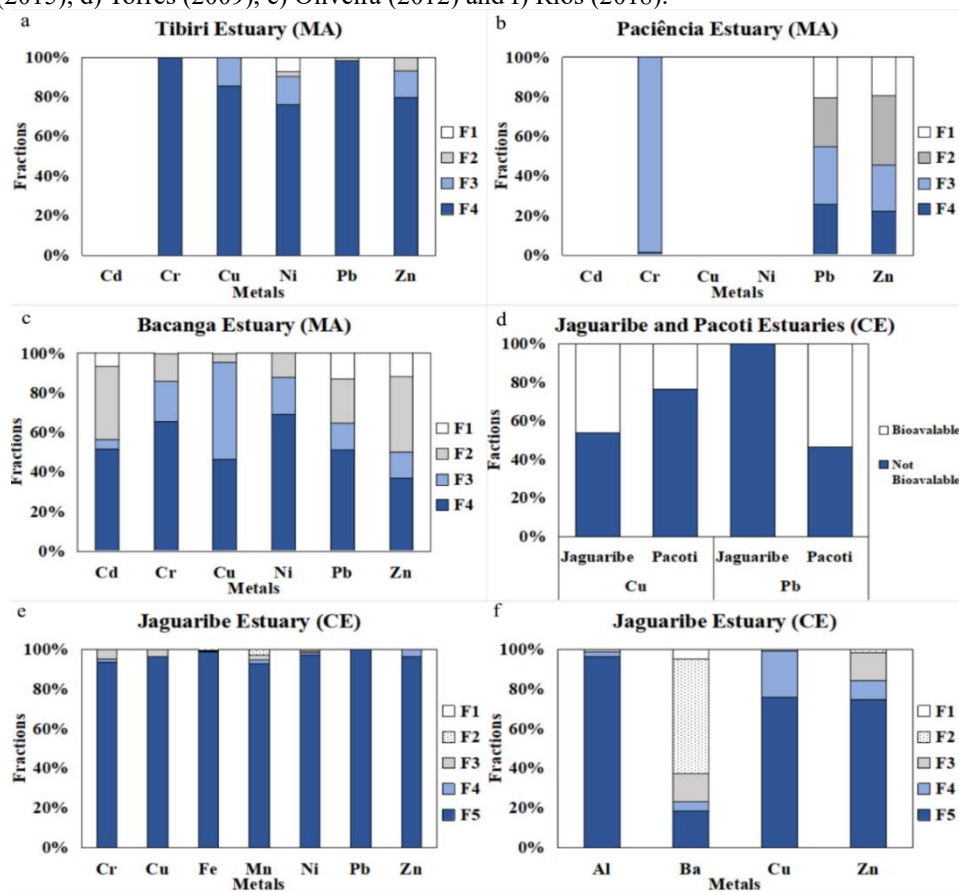
Nevertheless, as Zn exhibited good quality for the sediments of these estuaries, all the values of Zn found for EZBN's estuaries were below them. It is an interesting discovery due to Zn was found in anomalous values in estuaries of EZBN while in two tropical estuaries were not considered harmful to the environment, even Piraquê-Açú-Mirim estuary be considered a pristine estuary and the results pointed the low to moderate contamination by sewage input with the presence of eutrophic sediments (HADLICH et al., 2018). Subaé and Jaguaripe estuaries located in Todos os Santos Bay (northeast Brazil) were assessed to evaluate the sediment quality for other trace metals (Mg, Sr and V) not determinated in EZBN. They identified analogous trace metal contents for both environments, but Subaé estuary exhibited metals effects on the benthic assemblage, while Jaguaripe did not. The presence of these contaminates was related to the

intensive anthropogenic activities such as industrial and untreated domestic effluents and solid wastes.

Trace Metal In Estuarine Waters of 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, resulting usually 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 which influence the partitioning of trace metals among colloidal, dissolved and particulate fractions indicate the fate and transport of these contaminants in the environment (Robert et al., 2004; Machado et al., 2016). Suspended particulate matter (particles with size smaller than 63 µm) has high capacity to carry trace metals due to the increase of specific surface area (YAO et al., 2015). Metals in particulate fractions can be associated with Fe-Mn hydroxides, carbonates, organic matter, 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 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 EZBN due to the necessity of methods and equipment with a low limit of detection and high sensibility and selectivity, that can determine the very low content of these elements found naturally in the environment (less than 1 ppb). Available published data are presented in Table 3.

There is a great lack of data on metal concentration in EZBN waters as demonstrated in Table 3 below. São Marcos Bay (MA) and Jaguaribe River Estuary (CE) were the only environments with trace metals determined in water. São Marcos Bay is composed of diverse estuaries that discharge in it, with an important harbor complex with a large movement of ore and grains that influence trace metal contamination in the region. Furtado (2007) and Sousa (2009) reported values of dissolved Cu and Ni above the maximum allowed by Brazilian legislation (CONAMA n° 357/05), while the dissolved Al and Fe increased concentrations in the dry and rainy season, respectively, in the environment. Aluminum and Iron concentrations variability in the water column are 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 are altered by anthropogenic sources (BARBIERI, 2016). But part of the Al and Fe concentration variability may also result from the bauxite mining occurring in the Mearim river basin and to 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 previous section for São Marcos Bay.

The Jaguaribe River Estuary is a negative estuary with a 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 large fishing boats fluxes (DIAS, 2005; DIAS et al., 2009). Particulate Cu had an peculiar variation, the first studies reported Cu origin mostly from lithogenic sources, but increased of up to an order of magnitude in different locations of the estuary over time (DIAS, 2007; TORRES, 2009). This recent increase was associated with the accelerating shrimp aquaculture activity along the estuary, and the authors observed higher values near the releasing point of shrimp ponds 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 desorption of the particulate phase under salinity variation with tidal flooding, increasing the dissolved Cu fraction. The sediment can be another source for Cu in the water column because even being dominantly bound to a residual fraction in EZBN's estuaries, the element was also found associated with an oxidizable fraction of OM and sulfides which are solubilized under oxidizing conditions in the environment, as observed in the sediment section. 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 CE's state (MOUNIER et al., 2018). These complexes occur due to the attraction of the positive charge of dissolved metals to the negative charged OM, which is bound with the functional groups.

In the Jaguaribe estuary, Hg in particulate and dissolved forms showed a predominant positive correlation with geochemical continental tracers (Si, Ba and suspended particulate matter), but the dissolved fraction had some enrichment near to the launch of the shrimp farming effluent (78.3%) in comparison to particulate (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 continental runoff due to anthropogenic influence in association with global climate change. These factors could increase the estuarine residence time of water masses, and consequently, mobilize the reactive and bioavailable metal forms. This biogeochemical estuarine process has been observed to control the Hg fate (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 measure and compare 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; WANG, 2017). This parameter has valuable information to allow evaluating metal-related pollution in a water body and identify possible sites where are necessary remediation and waste management decisions.

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), Lagoa dos Patos (Rio Grande do Sul) and the Brazilian legislation (CONAMA n° 357/05) we can recognize high values for most metals determined in estuaries of the EZBN, except dissolved Cd and Mn that were 7.1 and 1.6 times lower than CONAMA values for brackish water, respectively (APRILE; BOUVY, 2010; BARBOSA; WALLNER-KERSANACH; BAUMGARTEN, 2012; CONAMA N° 357, 2005; JESUS; CRUZ, 2019; MOLISANI et al., 2007). 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; BOUVY, 2010; JESUS; CRUZ, 2019). These elements are probably available to aquatic organisms and cause harm due to high metal toxicity. The concentration dissolved Hg from lithogenic source in Sepetiba Bay (MOLISANI et al., 2007) is 11 times lower than concentration found in Jaguaribe estuary. But there aren't significant sources of Hg in Jaguaribe estuary, but there are seasonal geochemical processes that increase the Hg mobility in EZBN (LACERDA; MARINS; DIAS, 2020; LACERDA et al., 2012). These processes weren't evaluated for other metals.

Due to the important harbor zone in Lagoa dos Patos, the constant sediment dredging decreased the concentration of dissolved Pb, Cu and Zn by the dilution and dispersion of the metals accumulated in the environment over time. 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 domestic effluent and fertilizer industries contributions (BARBOSA; WALLNER-KERSANACH; BAUMGARTEN, 2012) (Barbosa et al., 2012). However, the value of dissolved Cd in Sao Marcos Bay, also with an important harbor, Itaqui harbor, was 5 times lower than Lagoa dos Patos.

The particulate Zn in EZBN estuaries was the only element with high values in comparison to Brazilian tropical estuaries, such as Rio Una (Bahia) and Paraíba do Sul (Rio de Janeiro) (CARVALHO et al., 2002; GONÇALVES; CARVALHO, 2006; JESUS; CRUZ, 2019). Jaguaribe estuary showed contents of particulate Cu and Pb lower 2 and 5 times lower than Rio Una, while particulate Al and Fe were 3 times lower than contents observed in Paraíba do Sul. In general, the concentration of trace metals in the dissolved fraction of EZBN estuaries was higher than the particulate fraction when compared to tropical urban estuaries. It evidences the high desorption of trace metal from solid to liquid phase in water column of EZBN estuaries resulting from changes in physicochemical conditions probably associated to saline intrusions in flood tide. There is therefore a need for more studies on the distribution coefficient in environmental compartments and how it may impact on local aquatic biota, especially those of commercial value for human consumption.

Table 3 Trace 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 total fraction.

Reference	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 (2005)	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	-	-	-

Organisms of EZBN as Biomonitors

Metals can be classified as essential (Fe, Mn, Zn, Cr e Cu) or toxic (Hg) to organisms, but when present in the environment in high contents most of them can cause the mortality 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 along seasons (Rainbow and Phillips, 1993). In addition, biomagnification can be a serious problem due to the contamination transfer along the food chain, especially if the concentrations reach toxic levels and reach top organisms, such as humans.

As observed, in a few studies, in the water compartment of EZBN estuaries there is a potential mobility of trace metals from particulate to dissolved fraction. It may occur due to the change of physicochemical conditions that suggest the presence of available trace metal species that contaminate the aquatic organisms.

Therefore, the National Sanitary Surveillance Agency-ANVISA (BRASIL, 2013) developed the Resolution RDC nº 42/13 derived from the Ordinance nº 685/98, which determined the maximum levels of chemical contaminants in food that may constitute a risk to human health (Table 4). Considering the legislation determinates, the maximum level of trace metal in raw fish, the present study examined the trace metal contents in the wet weight of the organisms to better comparison. When it was present in dry weight, the values were converted to wet weight by the follow equation: $[TM]_{WW} = TM_{DW} \times (100 - Moisture_{\%})/100$, where $[TM]_{WW}$ is the trace metal concentration in wet weight, $[TM]_{DW}$ is the trace metal concentration in dry weight and $Moisture_{\%}$ is the percentage of water present in the organism body. It was considered the value of 80% of fish muscles for all the organisms mentioned in the present study (KÜTTER et al., 2021)

Aquatic organisms in the MA state, bivalves (*Mytella falcata)* and fishes (*Lophiosilurus alexandri, Micropogonias furnier, Hexanematicht* hys *herzbergii* and *Bagre marinus)* showed no significant content of Cu, Pb and Cd in the muscles, except Zn in the first group with contents above to the maximum values established to foods by the Brazilian Government for use of food additives (BRASIL, 1965), but bellow to ANVISA nº 42/13 (BRASIL, 2013; CARVALHO et al., 2000; SOUSA, 2009) (Table 4), corroborate with labile Zn form identified in the MA's sediments in the previous section. The assimilation of Zn in the bivalve's

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 bivalve in CE state. Mangrove oyster (*Crassostrea rhizophorae)* usually acts as a consistent Hg regional biomonitor, reflecting the degree of anthropogenic impact over the estuary systems. In the metropolitan region of Fortaleza (CE), this organism showed a greater bioaccumulation of Hg in the estuary of the Ceará River than in other estuaries. However, it does not present a significant correlation with the size and sediment contents, that vary due to influence of the hydrodynamic on this estuarine compartment (RIOS et al., 2016; VAISMAN; MARINS; LACERDA, 2005). Notwithstanding, Almeida (2015) identified higher Hg in detritivorous fish specimens (*Pseudancistrus papariae* and *Prochilodus brevis*) than in omnivorous specimens (*Oreochromis niloticus* and *Hypostamus pusarum*) at Cocó Estuary, which the author associated to the largest weights observed in the first group. Organisms present in 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; COSTA; LACERDA, 2014; LOPES, 2012; MOURA; LACERDA, 2018; TORRES, 2009). 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 of shrimp farming effluents, but despite the biomagnification process, its contents do not present risk for human health as values were in the range accepted by ANVISA nº 42/13 (BRASIL, 2013).

Torres (2009) identified low values of Cu in bivalve (*Crassostrea rhizophorae* and *Anomalocardia brasiliana*), but the contents of Cu in the crustacean's exoskeleton (*Callinectes sapidus*) were up to twice higher than obtained in their muscles in Jaguaribe river. This variation demonstrates that shrimp may be subject to anomalous Cu levels exceeding their physiological needs, thus resulting in the development of detoxification processes in the animal. A few years later, Cu contents in muscles of bivalves (*Crassostrea rhizophorae*) exhibited values next to the limit for food in the general allowed by ANVISA nº 685/98 (SOARES, 2017). It was also notable in Torres (2009) that the increased that the increased values of Cu in the water column and the high content in the sediment at almost all EZBN estuaries, as noticed in the previous sections. Cu was

possibly associated with OM as identified in the sediment partition which could participate in organism filter-feeding diet.

A study developed in Potengi Estuary (RN) reported bioaccumulation of Fe, Zn, Cu, Cr, Pb, Cd, Ni and Ag in the oyster (*Crassostrea rhizophorae)*, as consequence of discharges of sewage and industrial effluents (SILVA et al., 2001) and higher than values allowed by ANVISA nº 685/98 and ANVISA RDC nº 42/13 (BRASIL, 1998, 2013). Carvalho et al. (2008) described the environmental quality after an ecological disaster of a shrimp farming company launched untreated effluent on the estuary, which bivalves (*Tagelus plebeius*) presented value of Pb exceeding the values of the legislation of ANVISA RDC nº 42/13 (BRASIL, 2013), with possible toxic effects with bioaccumulation and biomagnification processes.

It is remarkable to recognize that oysters and carnivorous fish and crustaceans (shrimps) had the best feedback as a biomonitor of trace metals in the EZBN's estuaries, especially for Hg, Cu, Zn and Pb. Oyster is widely used as biomonitor due to their filter-feeding and sedentary habits, which incorporate the bioavailable trace metal species from the environment (Góngora-Gómez et al., 2017; Lu et al., 2017; Rainbow and Phillips, 1993). The bioaccumulation of Hg, Cu, Zn and Pb in bivalve organisms may result from element availability as observed in EZBN estuaries mentioned previously in the water column. The carnivorous fishes are affected by feeding habits and high trophic levels (BISI et al., 2012). These species are highly consumed by the local population, although some values are below the legal limit, but with constant consumption of these organisms throughout the life of the human being, it can reach toxicity and have deleterious effects on it. The carnivorous crustaceans can be used as a biomonitor due to their detoxification processes that remove the excess of trace metal present in the muscle to the exoskeleton.

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. In consequence, some aquatic organisms can present changes in the metabolic regulatory processes in the biological system, such as 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 EZBN estuaries (Carvalho, 2014; Rios, 2018; Silva et al., 2015; Torres, 2009). These trace metal mobilities can be observed in 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 and undergo 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 are very well 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 data on the metals partition in EZBN estuarine waters.

Trace metal in organisms (wet weight) of different estuaries in the Equatorial Zone of the Brazilian Northeast (Values in µg g^{-1}, except Hg (ng g^{-1})). (a) indicates the maximum values of trace metals in fish in ANVISA RDC nº 42/13 (BRASIL, 2013), and b indicates the trace metal range allowed in food in general in ANVISA nº 685/98 (BRASIL, 1998).

Table 4 Trace metal in organisms (wet weight) of different estuaries in the Equatorial Zone of the Brazilian Northeast (Values in µg g⁻¹, except Hg (ng g⁻¹)). (a) indicates the maximum values of trace metals in fish in ANVISA RDC nº 42/13 (BRASIL, 2013), and b indicates the trace metal range allowed in food in general in ANVISA nº 685/98 (BRASIL, 1998).

Reference	Estuary	Group	Scientific name	Al	Fe	Mn	Ba	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn
Brazilian Legislation		**Fish**	-	-	-	-	-	0.05[a]	-	0.1-10[b]	50[a]	-	0.3[a]	-	-
Carvalho et al. (2000)	**Bacanga (MA)**	**Mollusc**	*Mytella falcata*	-	-	-	-	<DL	-	1240.0	-	-	<DL	-	11274
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 (2005)	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*	-	-	-	-	-	-	2.8	-	-	<LD	-	-
			Litopenaeus schimitti	-	-	-	-	-	-	4.2	-	-	<LD	-	-
		Mollusc	*Crassostrea rhizophorae*	-	-	-	-	-	-	1.5	-	-	<LD	-	-
		Seaweed	*Ulva lactuca*	-	-	-	-	-	-	0.3	-	-	<DL	-	-
	Pacoti (CE)	**Mollusc**	*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	-	-	-	-

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Author	Location	Type	Species	1	2	3	4	5	6	7	8	9	10	11	12
			Centropomus parallelus	-	-	-	-	-	-	-	25.4	-	-	-	-
			Menticirrhus americanus	-	-	-	-	-	-	-	7.6	-	-	-	-
			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)** **Jaguaribe (CE)** **Pacoti (CE)** **Cocó (CE)**	**Oyster**	*Crassostraea rhizophorae*	-	-	-	-	-	-	-	18.6	-	-	-	-
				-	-	-	-	-	-	-	15.0	-	-	-	-
				-	-	-	-	-	-	-	10.4	-	-	-	-
				-	-	-	-	-	-	-	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	-	-	-	-
		Inverterbrates	*Anomalocardia brasiliana*	-	-	-	-	-	-	-	10.2	-	-	-	-

Reference	Location	Type	Species												
			Callinectes bocourti	-	-	-	-	-	-	-	40.2	-	-	-	-	
			Callinectes danae	-	-	-	-	-	-	-	13.8	-	-	-	-	
			Callinectes exasperatus	-	-	-	-	-	-	-	4.6	-	-	-	-	
			Callinectes larvatus	-	-	-	-	-	-	-	20.8	-	-	-	-	
			Litopenaeus vannamei	-	-	-	-	-	-	-	2.8	-	-	-	-	
			Mytella charruana	-	-	-	-	-	-	-	10.4	-	-	-	-
			Pugilina morio	-	-	-	-	-	-	-	9.8	-	-	-	-
Silva et al. (2001)	Potengi (RN)	Oyster	*Crassostrea rhizophorae*	-	100	5.9	-	0.3	0.5	19.8	-	0.3	0.7	-	487.0
Carvalho et al. (2008)	Potengi (RN)	Mollusc	*Tagelus plebeius*	-	-	-	0.7	<DL	0.9	0.9	-	3.0	4.2	23.8	149.0

Assessment of the Environmental Quality of EZBN's Estuaries

Currently, trace metal studies utilize the sediment quality index as an important tool to evaluate and classify the pollution degree in the exchangeable fraction of the sediment. It indicates anomalous values in the region originated from natural and/or anthropogenic sources and allows to compare different sedimentary matrices. The most common indexes are the enrichment factor (EF) and Geoaccumulation Index (Igeo) (BARBIERI, 2016; BURUAEM et al., 2012; MARINS et al., 2004; NILIN et al., 2013; PAULA FILHO et al., 2015b; SANTOS; MARINS; DIAS, 2019). In the present study, the Geoaccumulation Index (Igeo) was applied to the trace metal contents (Figure 8). This index was proposed by Müller (1986) to measure the level of sediment contamination by inorganic environmentally relevant contaminants. It was determined by the following equation $Igeo = \log_2(Cn/1.5*Bn)$, 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 unpolluted environment and Class 6: >5 indicates very strongly polluted sediment.

There are only a few elements with regional background values determined in two estuaries of EZBN, as mentioned previously. Therefore, these values will be considered as representative for all the regions to evaluate the sediment contamination due to the similarity observed in the spatial distribution of trace metals along with the sediments of 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 values of each estuary were used to determine the index because some of the studies show only the minimum and maximum range, and others just the average values.

On the Figure 8 (Supplementary Material- Table 5), Pb and Zn showed Igeo values higher than moderate polluted (Class 2) in 53% and 25% of the EZBN estuaries, respectively. While Mn was considered unpolluted in all environments. Pb showed moderately polluted (Class 2) in Anil, São Marcos, São José, Paciencia River, Apodi and Galinhos. Bacanga indicated moderately to strongly polluted (Class 3), while Parnaíba River Delta and Curimataú estuary were found strongly polluted for this element (Class 4). Pb is a toxic metal to aquatic biota and humans (JESUS; CRUZ, 2019; KÜTTER et al., 2021). The main source of Pb for the region is mainly from

Figure 8 Geoaccumulation Index for Pb, Cu, Zn, Fe, Hg and Cr in estuarine sediments along the Equatorial Zone of the Brazilian Northeast.
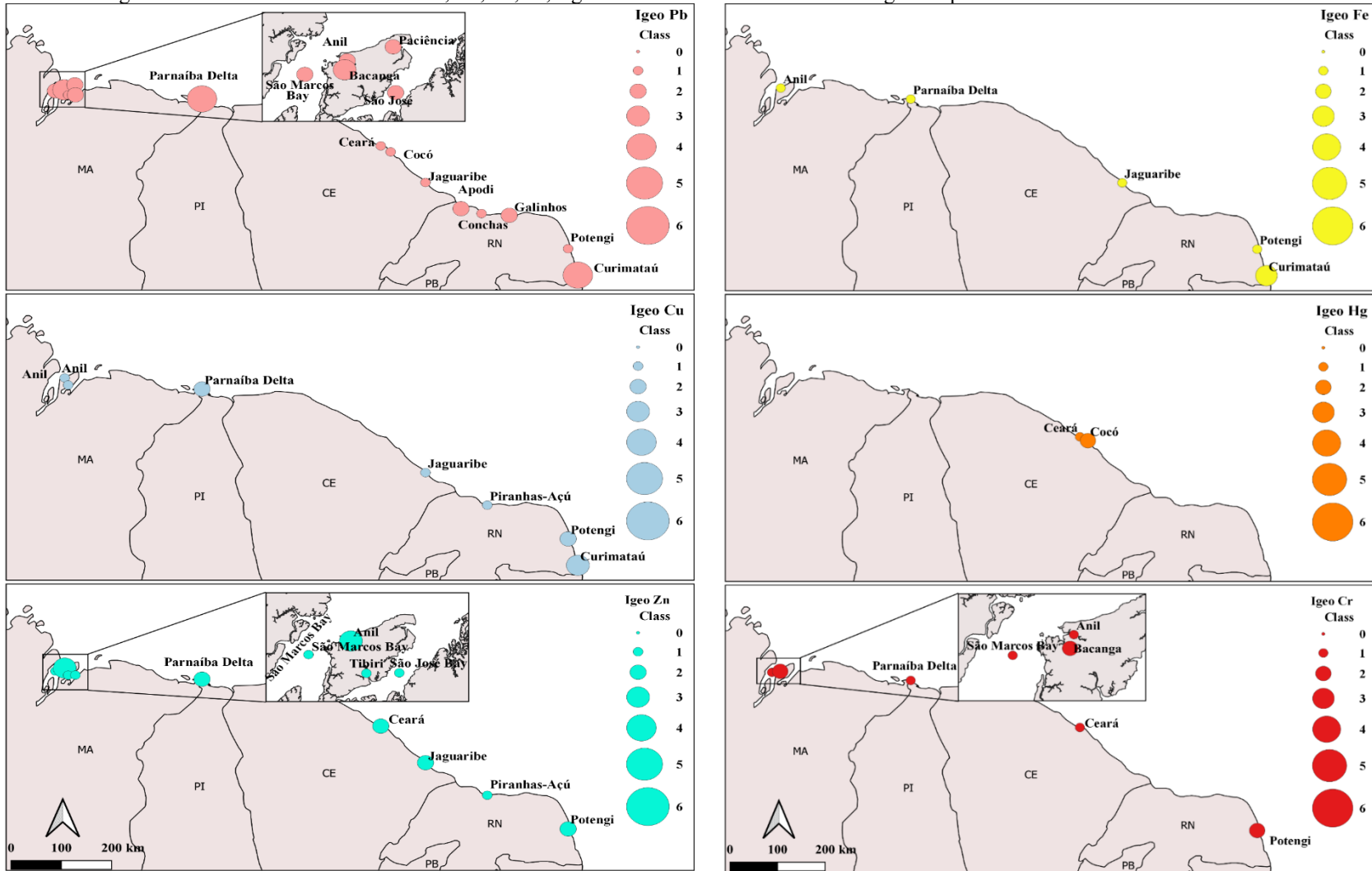
natural contribution in addition to urban runoff, inadequate disposal of solid waste and Pb in aerosols resulting from the burning of fossil fuels. Pb can be correlated with suspended particulate material which may favor the co-precipitation of Pb with Fe–Mn oxyhydroxides and $PbCO_3$ in the environment with pH > 6 (AZEVEDO, 2019; NASCIMENTO, 2013; PAULA FILHO et al., 2014; SANTOS; MARINS; DIAS, 2019), explaining the large spatial distribution of Pb in these estuarine sediments. The anomalous value of Pb could be observed bioaccumulate in oysters with values higher than Brazilian Legislation ANVISA RDC nº 42/13 (BRASIL, 2013).

For values of Zn, Parnaíba River Delta, Ceará, Jaguaribe and Potengi estuaries were classified as moderately polluted (Class 2), while Anil estuary was considered moderately to strongly polluted (Class 3). This element is an essential element that participates in the metabolism of proteins, nucleic acids, carbohydrates and lipids of the organism (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; RIOS, 2018; SILVA et al., 2015). Therefore, Zn from anthropogenic activities that are found bounded to the reducible forms in the sediments may be available as soluble species under anoxic conditions (TESSIER; CAMPBELL; BISSON, 1979). As previously mentioned, Zn was also found desorbed in the water column and lead to bioaccumulated in oysters of EZBN estuaries.

The values of Cu in the sediments of Parnaíba River Delta and Potengi estuary are classified as moderately polluted (Class 2), and moderately to strongly polluted for sediments in Curimataú (Class 3). The presence of Cu in high concentration in the water and sediment compartments can bioaccumulate and biomagnification in aquatic organisms (oyster and crustaceans) as observed in EZBN estuaries. The main sources of Cu observed for the region was natural processes of soil denudation in addition to electroplating, iron smelting, mining agriculture and inadequate disposal of wastewater and solid waste (CORREA, 2008; PAULA FILHO et al., 2014; TORRES, 2009).

Fe was considered moderately to strongly polluted in Curimataú (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; FÖRSTNER, 1984). The presence of Fe in the sediments may be related to the lithogenic source from Barreiras

Formation that is rich in Fe, Mn, Co, and Cu (XAVIER et al., 2017). Igeo for Cr classified Bacanga and Potengi estuaries as moderately polluted (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 is present in soluble species as a result of pH variation (JESUS; CRUZ, 2019).

The estuaries in CE states, Ceará and Cocó were the only environments that showed unpolluted and moderately polluted for Hg presenting in Class 1 all over the EZBN. Hg is a non-essential metal that manifested in oyster bioaccumulation and possible biomagnification in detritivores and omnivores fishes (ALMEIDA, 2015; RIOS et al., 2016; VAISMAN; MARINS; LACERDA, 2005). Stronger seawater intrusion facilitates the mobilization Hg from the sediment to the water column and Hg methylation increasing its bioavailability (DIAS et al., 2009; LACERDA et al., 2012; MARINS et al., 2004). This element was found bioaccumulated in oysters and biomagnified in carnivorous fishes and crustaceans of EZBN estuaries (COSTA, 2009; COSTA; LACERDA, 2014; LOPES, 2012; MOURA; LACERDA, 2018; RIOS et al., 2016; TORRES, 2009; VAISMAN; MARINS; LACERDA, 2005).

Therefore, the results of Igeo have a limitation that needs to be taken into consideration, since the reviewed estuaries present some different geological aspects which may affect trace metal concentrations (EL-ROBRINI et al., 2006; MORAIS et al., 2006; VITAL et al., 2006). For this, it is necessary more studies to determine the natural background levels based on sediment cores and better differentiate from natural to 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 that can qualify these systems. However, this review of results can give a snap shot of metals contaminations in the EZBN, which may help to improve new investments in environmental research in the region and to point out the authorities to develop decision-making processes to diminish trace metal inputs from anthropogenic sources and consequently reduce the bioaccumulation and biomagnification to not cause risk to human health.

Final Considerations

Trace metals in the Equatorial Zone of the Brazilian Northeast were more intensively studied in CE state, 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 effluent, domestic and industrial discharges that can alter the environmental quality of the estuaries. However, compared with studies in other Brazilian estuaries there a lack of data in metal concentrations, such as Sr, V and Mg. That are associated to anthropogenic activities that are increasing in the EZBN region.

Research on trace metals in the water is scarce but in the sediment compartment, it is very well-investigated but presents values variating two orders of magnitude in the same large-scale geological province as observed for Cu, Pb, Zn, Hg and Fe pointing out the influence of the uses of drainage basins. Sequential extractions in the sediment suggest relatively medium mobility of metals, and that Fe-Mn oxides, OM, and carbonates can act as geochemical carriers of trace metals along the estuarine gradient. Most of the organisms presented trace metal values below the maximum limit established by the Brazilian legislation, but, remarkable, oysters, and carnivorous fishes and crustaceans had the best feedback as a biomonitor for Cu, Pb, Zn and Hg in agreement with the sediment contamination degree evidenced by Igeo. Igeo exhibited anomalous values in the Curimataú estuary classifying as moderately to strongly polluted (Class 3) for Fe and Cu, and strongly polluted (Class 4) for Zn. Parnaíba River Delta also showed moderately polluted (Class 2) for Cu and Zn, and strongly polluted (Class 4) for Pb. Anomalous values may be related to lithogenic sources in addition to agriculture and inadequate disposal of wastewater and solid waste. However, more studies to determine the natural background levels based in the in ecosystems, that still do not have this data, on sediment cores are necessary to better differentiate from natural to anthropic sources. Other essential information are the identification of the dominate geochemical carriers (e.g. OM, $CaCO_3$, Al and Fe) to comprehend the mobility and reactivity of trace metals in coastal zone. Partitioning of trace metals (dissolved, colloidal and particulate phases), distribution coefficients and possible incorporation in the organisms will also turn more integrated studies to EZBN.

Supplementary Material

Table 5 Geoaccumulation index (Igeo) for trace metal (Fe, Mn, Cr, Cu, Hg, Pb and Zn) in the estuarine sediments of EZBN.

Estuaries	Igeo						
	Fe	Mn	Cr	Cu	Hg	Pb	Zn
Anil (MA)	0.51	-1.84	0.89	0.35	-	**1.85**	**2.45**
Bacanga (MA)	-	-	**1.03**	-0.20	-	**2.82**	-
São Marcos Bay (MA)	-0.80	-1.38	0.02	-1.21	-	**1.81**	0.21
Tibiri (MA)	-	-	-1.35	0.53	-	0.24	0.52
São José Bay (MA)	-0.65	-2.51	-0.14	-1.09	-	**1.44**	0.17
Paciência (MA)	-	-	-2.26	-	-	**1.46**	-2.19
Parnaíba Delta (PI)	0.47	-0.58	0.40	**1.07**	-	**3.19**	**1.18**
Ceará (CE)	-0.71	-	0.06	-0.22	**1.00**	0.68	**1.58**
Cocó (CE)	-	-	-	-	**1.94**	-	-
Jaguaribe (CE)	0.53	-1.01	-0.14	0.40	-0.24	0.42	**1.34**
Pacoti (CE)	-0.45	-	-	-0.56	-	0.20	-2.51
Curimataú (RN)	**2.63**	-4.98	-2.03	**2.66**	-	**3.31**	-0.24
Apodi (RN)	-	-	-3.08	-2.15	-	**1.27**	-1.90
Ceará-Mirim (RN)	-	-	-	-	-	-	-7.65
Conchas (RN)	-	-	-1.95	-1.00	-	0.95	-1.74
Galinhos (RN)	-	-	-2.83	-3.09	-	**1.07**	-2.29
Guamaré (RN)	-	-	-3.08	-4.35	-	-0.47	-3.65
Nísia- Floresta (RN)	-	-	-	-1.00	-	-	-1.40
Papeba (RN)	-	-	-	-	-	-	-4.19
Ponta do Tubarão (RN)	-	-	-6.15	-3.01	-2.58	-	-2.57
Piranhas-Açú (RN)	-	-	-	0.58	-	-0.40	0.63
Potengi (RN)	0.47	-	**1.67**	**1.38**	-8.33	0.76	**1.79**

5.2 TRACE METALS PARTITIONING IN PARNAÍBA DELTA WATERS, BRAZIL EQUATORIAL COAST

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Abstract

Trace metals concentrations in the particulate and dissolved fractions (Ba, Cu, Co, Cr, Pb, Ni and Zn) were determined during the dry season of the Environmental Protection Area of Parnaíba River Delta (Brazil) from subsurface water samples, to comprehend the distribution, dynamic changes of metal speciation and environmental quality index of trace metals in the particulate fraction. The trace metals in the particulate fractions exhibited a decreasing trend with the salinity increase, which particulate Ba and Zn faving a remarkable decrease. Dissolved trace metals along the environment shows heterogeneous variations with the salinity. Log(Kd) suggests a potential mobilization of Ba, Zn and Cu from particulate to available dissolved species in the water column along the mixing zone due to the physico-chemical parameter variations. The Igeo indicated moderately to heavily contamination for Zn in the particulate phase, mainly by anthropogenic activities, such as untreated domestic effluent and livestock production.

Keywords: Estuaries; Contamination; Distribution Coefficient; Dry Season.

Introduction

The Parnaíba River Delta is the largest open sea delta in the Americas, and the third in the world, after the Nile delta in Africa and the Mekong delta in Asia (GUIMARÃES-COSTA et al., 2019). The delta is dominated by wave and tides with two active channels and large mangrove creeks (AQUINO DA SILVA et al., 2019). Some of these channels are large creeks where cargo and tourist boats sail. Due to its socio-environmental importance, it is inserted into an Environmental Protection Area (APA), with an area of 313.000 ha including 10 cities over Maranhão, Piauí and Ceará states (GUZZI, 2012; IBGE, 2020; MAGALHÃES

et al., 2008). The total human population estimated on the APA is 362.449 inhabitants, of which only 1.30 - 23.50% of the domiciles have adequate sanitation over the cities in the APA (IBGE, 2020). Besides being conserved as a primitive ecosystem, the Parnaíba River Delta shows some evidence of urban and industrial contributions, with point sources of nutrients and trace metals the estuary (PAULA FILHO et al., 2015b, 2021).

The delta is placed in the third largest mangrove forest in the world, with 7 % of the global mangrove area. The states of Maranhão, Piauí and Ceará represent ~48% of Brazil's mangrove cover (DINIZ et al., 2019; FAO, 2020). The main mangrove plant genera in the region are *Rhizophora*, *Laguncularia* and *Avicennia* that can reach 40 m in height (GUZZI, 2012). Mangroves are known to be important drivers of the coastal organic and inorganic element budgets, acting usually as a sink of trace metals due to their richness in organic matter (MORI et al., 2019; THANH-NHO et al., 2018).

Trace metals evaluation in the Parnaíba River Delta (PRD) determined regional background levels (geochemical baseline) in sediments for Zn, Cu, Pb, Cr, Mn, and Fe (Paula Filho et al., 2019, 2015) . However, continuous studies in the area pointed values higher than the background for Cu, Ni, Zn and Fe (PAULA FILHO et al., 2021). The active and seasonal PRD hydrodynamic with presence of bays, large creeks and anthropogenic and natural contributors to the region besides the fate of a wave/tide dominated Delta probably inducting variations along the recent years.

The variation of physico-chemical parameters along estuaries (such as salinity, pH, turbidity, dissolved oxygen, redox potential) affect the adsorption and desorption of trace metals, causing the mobilization to the dissolved phase and the solid phases (particulate and sediment compartments) that potentially modify metals bioavailability (BIANCHI, 2007; GAULIER et al., 2021; WANG; WANG, 2016). Therefore to improve the knowledge of trace metals behavior in PRD, it is important to determinate trace metals partition to comprehend their degree of mobility and availability in aquatic environments (GUILLÉN et al., 2012; YAO et al., 2016) in a diverse estuarine environment with a major river, mangrove channels and bays that can reflect the influence of saline intrusion in times of climate changes (LACERDA; MARINS; DIAS, 2020)

Thereby, the distribution coefficients (Kd) of trace metals between particulate and dissolved fractions can suppress the lack of data and knowledge on trace metal fate in the PRD water column to assess the future environmental risks, particularly in a global scenario of sea level increase (LINDSEY, 2021), and more water scarcity in the Brazilian equatorial coast

(MARENGO; TORRES; ALVES, 2017), a region between Amazonian tropical climate and Northeastern semiarid areas (VEIGA JÚNIOR, 2000).

Besides that, it is necessary to consider that trace metals are among the contaminants that inputs to aquatic ecosystems is increasing due to intense anthropogenic sources in drainage basins from where they are transported to coastal areas through continuous, diffuse emissions or during flood events (YAO et al., 2016), that potentially increase toxicity, due to non-biodegradable properties and accumulation along the food chain by bioaccumulation and biomagnification (LI et al., 2013; NABELKOVA, 2013). The present study aims to comprehend the distribution, dynamics of changes of metal partitioning and geochemistry of seven metals (Ba, Cu, Co, Cr, Pb, Ni and Zn) in the subsurface waters of PRD.

Materials And Methods

Environmental setting and sampling

PRD is located in the Equatorial Zone of Brazil Northeast between the geographic coordinates on the longitude 41°49'10" W and latitude 2°50'15" S. It encompasses 85 islands along an area of 2,700 km^2 including a complex mosaic of ecosystems, which the east side of the delta is placed the Parnaíba River with very low declivity (up to 50 cm km^{-1}), and in direction to the west side are situated large bays with intense mangrove channels, salt marshes and sandy beaches (AQUINO DA SILVA et al., 2019; GUZZI, 2012). The vegetation of PRD is represented by coastal Caatinga (restinga), dunes with grasses, and mangroves swamp forest flooded by sea water mixed with fresh water from rivers and streams (CODEVASF, 2016). The Intertropical Convergence Zone (ITCZ) is the main system associated to precipitation ranging 50- 350 mm (INMET, 2020). The hydrodynamic is characterized by meso-tidal with amplitudes ranging from 0.2 to 4.0 m under semidiurnal regime (CHN, 2019). The basin of the Parnaíba River has multiple uses as the generation of electric energy (Boa Esperança dam), irrigation (coastal boards and Plateaus de Guadalupe) and human supply (ANA, 2020).

Subsurface water samples were taken below the surface with a 2 L Niskin water sampler, pre-cleaned with HNO_3^- and washed with Milli-Q water. The campaign were performed in December 2019 distributed at 13 stations along the PRD as observed in Figure 9.

Figure 9 Location map of 13 sampling sites along the Parnaíba River Delta in the Equatorial Zone of Brazil Northeast. [1]
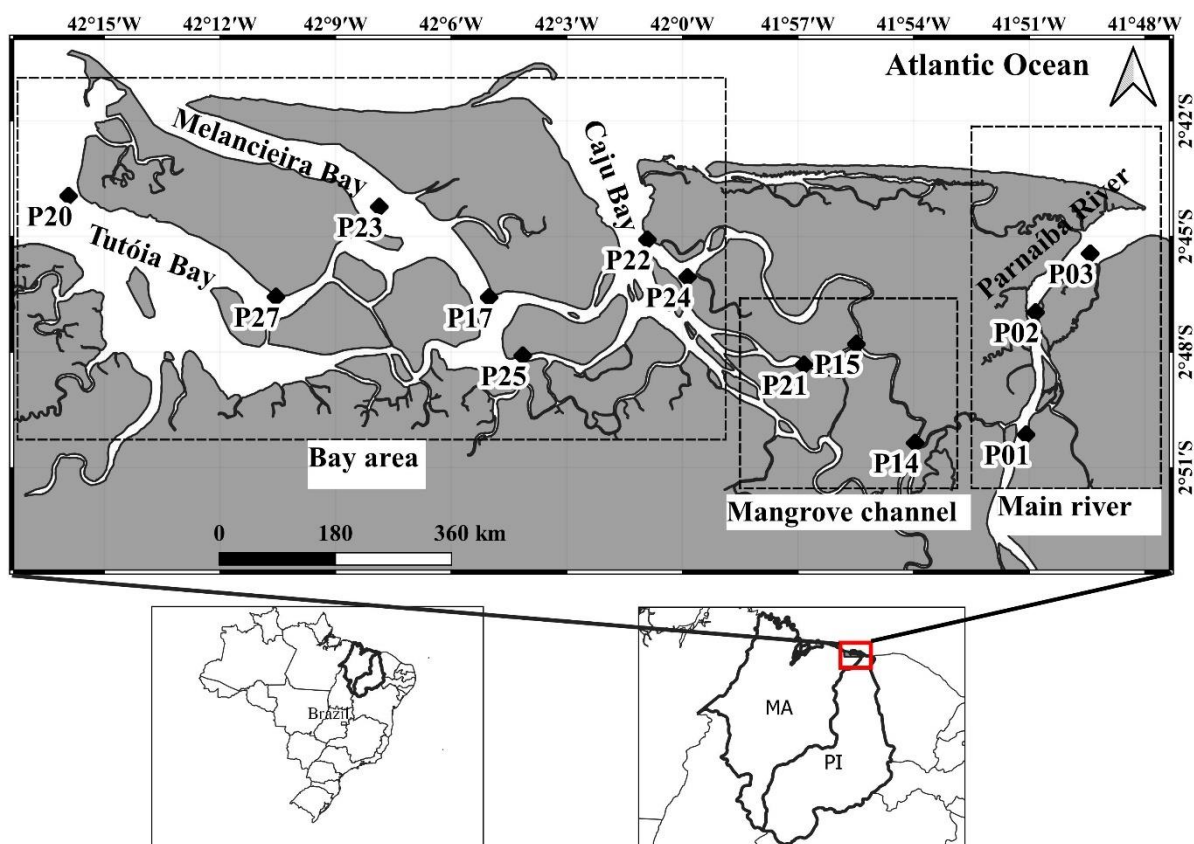
Surface water was filtrated with cellulose nitrate filters of 0.45 μm and diameter 47 mm (Figure 10), pre-cleaned with bi-distillate HCl 10% (Merck) and Milli-Q water, dried, and recorded weight. For dissolved trace metals, samples were stored in pre-cleaned (HCl 10% + Milli-Q water) high-density polyethylene (HDPE) bottles and added drops of bi-distillate HCl (37%, Merck) to reach pH 2.0. The dissolved and particulate samples were stored at 4 °C in the dark before further processing. All the apparatus were pre-cleaned with 10% HCl and rinsed with Milli-Q water. The physico- chemical parameters (temperature, salinity, dissolved oxygen (DO), and pH of the superficial water column were measured *in situ* using a handheld multi-parameter probe (YSI Professional Plus) and pH-meter (Methrom® 826). All equipment was calibrated before the sampling campaign.

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[1] The PRD division in three areas are based in salinity persistent values (Bays) or in salinity gradient values and geomorphology to Mangrove Channel and Main River, respectively. See supplementary material.

Figure 10 Activities developed during the sampling campaigns in the Parnaíba Delta River, Brazil.

Analytical procedures

The cellulose nitrate filters with retained solids were dried at 60ºC in an oven and weighted to quantify the suspended particulate material (SPM). SPM (mg L^{-1}) was determined by the equation $[(W_2 - W_1) \times 1000]/V_f$, where W_1 (g) is the initial weight of dry filter, W_2 (g) is the final weight of dry filter after filtration and V_f (mL) is the final volume of the water sample passed through the filter. After it, filters were mineralized by Ultrawave Single Reaction Chamber Microwave Digestion System (Milestone Inc) with the addition of 10 mL of aqua regia (HCl: HNO$_3$, 3:1, Fisher Scientific Trace Analysis grade) in 50 mL Teflon (PTFE). Subsequently, the substrates were filtered by a pre-cleaned online filter (0.45 µm, Whatman), and diluted with ultrapure water to 100 mL for analysis in falcon tubes. Trace metals (Ba, Cr, Co, Cu, Ni, Pb, and Zn) concentration C_M in dissolved fraction and mineralization were determined with High Resolution Inductively Coupled Plasma Mass Spectrometer instrument (HR-ICP-MS)[2]. Indium (In) was used as an internal standard for quality control. The calibration was carried out with appropriate dilutions of a multi-element stock solution. Indium (In) was used as an internal standard for quality control. Final concentrations of dissolved trace metal

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[2] Done at the Center for Marine and Environmental Research (Ruđer Bošković Institute-Croatia) thanks to Ph.D. Dario Omanović.

(MD) were corrected from dilution factor if any and directly obtain in µg L^{-1}. The coefficient of variation (CV) accepted was below 2% for all metals. The trace elements selected in the present study were Ba belongs to alkaline earth metal group; Co, Cr, Cu, Ni and Zn are transition metals, and Pb is a metal. The precision and accuracy of the metal's methodology in suspended matter was tested with certified sediment reference materials for river sediment (LGC6817 by LGC Standards Ltd) and marine sediment (PACS-2 by National Research Council of Canada). The limit of detection (LOD), the limit of quantification (LOQ) and recoveries of trace metals in the reference materials are presented in Table 6. Ba and Co have no referenced values in certified sediment materials. Trace metal in the particulate fraction was calculated following the equation: $M_P = (M_E x\ V_{ar})/W_{PM}$, Where M$_P$ (µg g^{-1}) is the trace metal in the particulate fraction, M$_E$ (µg L^{-1}) is the concentration measured in the extract of mineralization, V$_{ar}$ (L) is the volume of *aqua-regia* used on the filter mineralization, and W$_{PM}$ (g) is the weight of particulate material retained in the filter after filtration.

Table 6 Recovery values (%) for the metals in reference materials for Marine sediment (PACS-2) and River sediment (LGC6817). LOD is the limit of detection; LOQ is the limit of quantification.

Trace Metals	LOD	LOQ	PAC-2	LGC61-87
	µg L^{-1}		Recovery (%)	
Ba	0.005	0.015	-	-
Cr	0.003	0.010	77.8	112.5
Co	0.002	0.006	74.5	-
Cu	0.010	0.030	74.9	97.1
Ni	0.001	0.003	78.2	108.6
Pb	0.001	0.003	72.5	107.6
Zn	0.005	0.015	75.5	96.4

Distribution Coefficient

The distribution coefficient (Kd) is one of the most important parameters for assessing the migration potential of a contaminant present in the liquid phase that is in contact with sediment or suspended matter (NABELKOVA, 2013). It was calculated using the logarithm of the ratio of trace metal concentrations between particulate (µg kg^{-1}) and dissolved (µg L^{-1}) fractions (NABELKOVA, 2013; THANH-NHO et al., 2018).

Statistical Analysis

The Shapiro-Wilk test was used to assess the normality of physical and chemical variables in the water. When it exhibited normal distribution (parametric), homoscedasticity of variance (Bartlett's test), and one-way analysis (ANOVA) were used to compare the means of variables in different sites of the environment (Main River, Mangrove Channel, and Bay area). Although, when the data were not normally distributed, Levene's test and Kruskal-Wallis were applied. Spearmen's rank correlation method (correlation coefficient ρ) was applied to observe possible correlations among variables. All tests consider the level of significance $\alpha = 0.05$. A principal component analysis (PCA) is a multivariate method applied to investigate the distribution of trace metals with the physico-chemical, which had significative correlation with Spearmen's rank, along the different zones of the environment. All statistical analyses were performed using the software RStudio.

Results

Hydrodynamic condition and physicochemical parameters

The tide showed minimum and maximum height of 0.1 to 3.2 m during the collecting campaign. Most sample collecting occurred under flood tide conditions, except stations P14, P15, P20, P23 and P27 were over ebb tides (Figure 11).

Figure 11 Tidal variation during the collecting campaign in the Parnaíba River Delta.
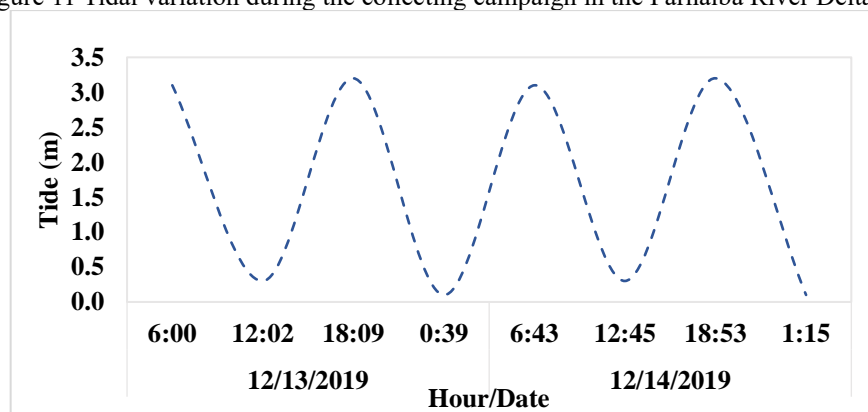
The statistical analyses applied to the physicochemical parameters in PRD to observe the similarity along the Main River, Mangrove Channel, and Bay area (One-way ANOVA and Kruskal-Wallis test) identified that only temperature was homogeneous ($p>0.05$, n=13) along all the study areas, from 29.0 - 29.9°C (29.4 ± 0.2°C) (Table 7, Supplementary Material -Figure 17).

SPM exhibited similar values in almost all the stations with an average of 34.3 ± 12.4 mg L^{-1}, except in the station in the Bay area, at the Tutóia Bay with 156.2 mg L^{-1}, in ebb tide, showing that the tide can influence significantly some points of the PRD.

Table 7 Physicochemical parameters of water column of Parnaíba River Delta.

Zone	Stations	Tide	Date	Time	Temperature (°C)	Salinity	pH	DO (mg L^{-1})	SPM (mg L^{-1})
Main River	P01	Flood	14/12/19	5:25 PM	29.7	0	7.41	6.05	28.4
Main River	P02	Flood	14/12/19	6:15 PM	29.5	17.4	8.04	5.91	23.7
Main River	P03	Flood	14/12/19	6:57 PM	29.3	36.2	8.1	5.26	21.1
Mangrove Channel	P14	Ebb	13/12/19	7:39 AM	29.2	2.3	6.78	4.01	18.2
Mangrove Channel	P15	Ebb	13/12/19	9:46 AM	29.6	11.7	6.78	3.92	33.6
Bay area	P17	Flood	13/12/19	4:42 PM	29.5	35	7.94	5.04	33
Bay area	P20	Ebb	14/12/19	10:37 AM	29.2	36.5	8.09	5.76	43
Mangrove Channel	P21	Flood	13/12/19	12:26 PM	29.9	15.3	7.18	4.09	47.7
Bay area	P22	Flood	13/12/19	4:05 PM	29.5	35	8.12	5.35	53.2
Bay area	P23	Ebb	14/12/19	7:08 AM	29	36.3	8.06	5.45	21.1
Bay area	P24	Flood	14/12/19	2:13 PM	29.6	33.3	7.71	4.33	37.1
Bay area	P25	Flood	13/12/19	1:55 PM	29.1	34.7	8.02	6	52.2
Bay area	P27	Ebb	14/12/19	9:39 AM	29.1	36.5	7.89	5.34	156.3

The Main River channel exhibited a typical longitudinal salinity and pH gradient during the dry season due to the dilution of the freshwater with seawater in the Main River, with values varying from 0.0 to 36.2 for salinity and 7.41 to 8.10 for pH. This pattern was also observed in the Mangrove Channel in direction from Main River to the Bay area. Mangrove Channel exhibited low values of DO (3.92 mg L^{-1}) and pH (6.78) at low and intermediary salinity values of 2.3 – 15.3. Whereas the Bay area showed seawater influences with high values of DO (6.00 mg L^{-1}) and pH (8.12). The values for salinity were 33.3 - 36.5, for pH were 7.71 - 8.12 and DO ranged from 4.33 - 6.0 mg L^{-1}.

Trace metal in the particulate fraction

The concentrations of trace metals extracted from the SPM ($\mu g.L^{-1}$) are given in the Table 9. The present section will present the contents of metals per gram of SPM ($\mu g.g^{-1}$) . The trace metals in the particulate fractions exhibited a desorption trend with the salinity increase, which particulate Ba, Cu, Pb and Zn had a remarkable decrease, between three and four times, except to Co, Cr e Ni, as observed in Figure 12. Main River showed a decline in trace metal contents from the P01 to P02, and a slight variation until the outer station (P03) with salinity 36.2. Mangrove Channel presented slight variation for all trace metals in intermediary salinity. Along the Bays, Cu_{MP}, Ba_{MP} and Zn_{MP} exhibited low values on the particulate fraction, while the Co_{MP}, Cr_{MP}, Pb_{MP} and Ni_{MP} did not show a clear trend with high salinities, probably because the salinity variability is very restricted in this region of the PRD.

Figure 12 Distribution of trace metals (µg g^{-1}) in the particulate fraction along the salinity gradients on the Parnaíba River Delta. MP represents metal in particulate fraction.
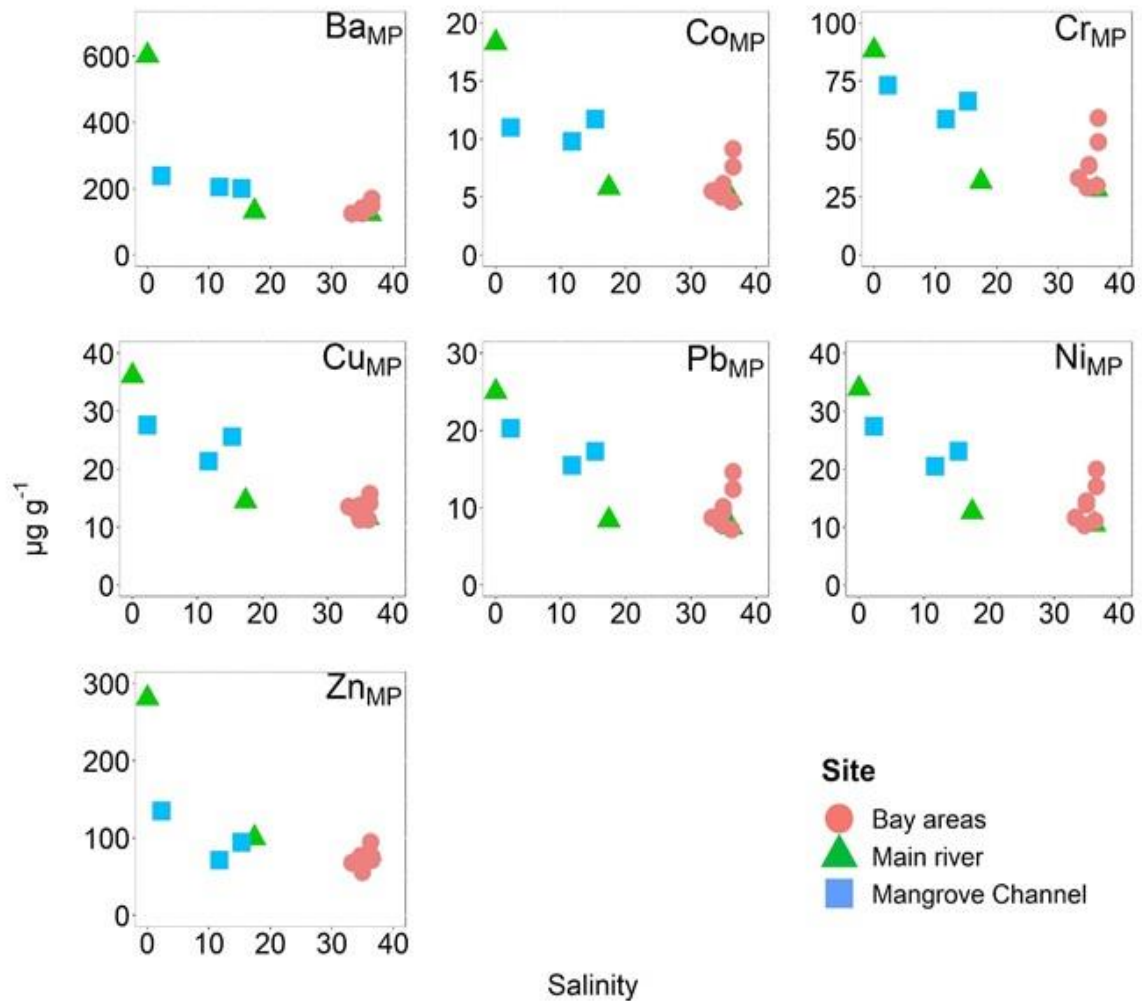
The overall mean contents of trace metals in the particulate fraction presented the follow decreasing order Ba_{MP} (190.9 ± 129.0 µg g^{-1}) > Zn_{MP} (97.6 ± 58.6 µg g^{-1}) > Cr_{MP} (47.9 ± 19.5 µg g^{-1}) > Cu_{MP} (17.6 ± 7.7 µg g^{-1}) = Ni_{MP} (17.6 ± 7.3 µg g^{-1}) > Pb_{MP} (12.6 ± 5.6 µg g^{-1}) > Co_{MP} (8.1 ± 3.2 µg g^{-1}). Spearman's rank identified a significative negative correlation between Cr_{MP} and Pb_{MP} in the particulate fraction with pH, both with $\rho = -0.7$ (p<0.05, n=13). SPM did not show a significant correlation with any trace metal in the particulate fraction. One-way ANOVA and Kruskal-Wallis test identified homogeneous variation for almost all trace metals in the study area, except Cr (p<0.05, n=13).

Dissolved trace metal fractions

Figure 13 shows heterogeneous variations and non-conservative behavior of the dissolved trace metal along the environment. In general, Ba_{MD} and Cu_{MD} have a decrease trend with salinity increase, while Cr_{MD} was the only element with high values with the increase of the salinity in the Main River (P02 and P03). It is remarkable the concentrations of all metals were above the theoretical dilution curve in the middle of the Main River (P02) with a salinity of 17.4. Ba_{MD}, Co_{MD}, Ni_{MD} and Zn_{MD} had a tendency to increase in the Mangrove Channel at intermediary salinity (11.7 and 15.3). Co_{MD}, Zn_{MD}, Cu_{MD} and Ni_{MD} also demonstrate high values at stations with the high salinity in the Bay area, such as P25 for the first two metals, and P22 for Ni_{MD}. Cu_{MD} did not exhibit a clear behavior in the Bay areas.

In general, the mean concentration of dissolved trace metal presented the following decreasing order Ba_{MD} (19.4 ± 11.9 µg L^{-1}) > Zn_{MD} (4.1 ± 2.1 µg L^{-1}) > Cu_{MD} (0.44 ± 0.13 µg L^{-1}) > Ni_{MD} (0.43 ± 0.16 µg L^{-1}) > Co_{MD} (0.15 ± 0.10 µg L^{-1}) > Cr_{MD} (0.09 ± 0.03 µg L^{-1}) > Pb_{MD} (0.05 ± 0.03 µg L^{-1}). However, most dissolved trace metal concentrations did not show significative variation with salinity gradient, except for Ba_{MD} with an inverse Spearman's correlation ($\rho = -0.8$, $p<0.05$). Ba_{MD} and Cr_{MD} also exhibited significative correlation with pH, with $\rho = -0.8$ and 0.7, respectively ($p<0.05$). One-way ANOVA and Kruskal-Wallis test identified no similarity for almost all elements in the dissolved fraction, except for Co_{MD}, Pb_{MD} and Zn_{MD} ($p>0.05$, n =13).

Figure 13 Distribution of dissolved trace metals (µg L^{-1}) along the salinity gradients on the Parnaíba River Delta. Dashed line represents the theoretical dilution curve with the station P01 (salinity 0.0) to station P03 (salinity 36.2). MD represents metal in dissolved.
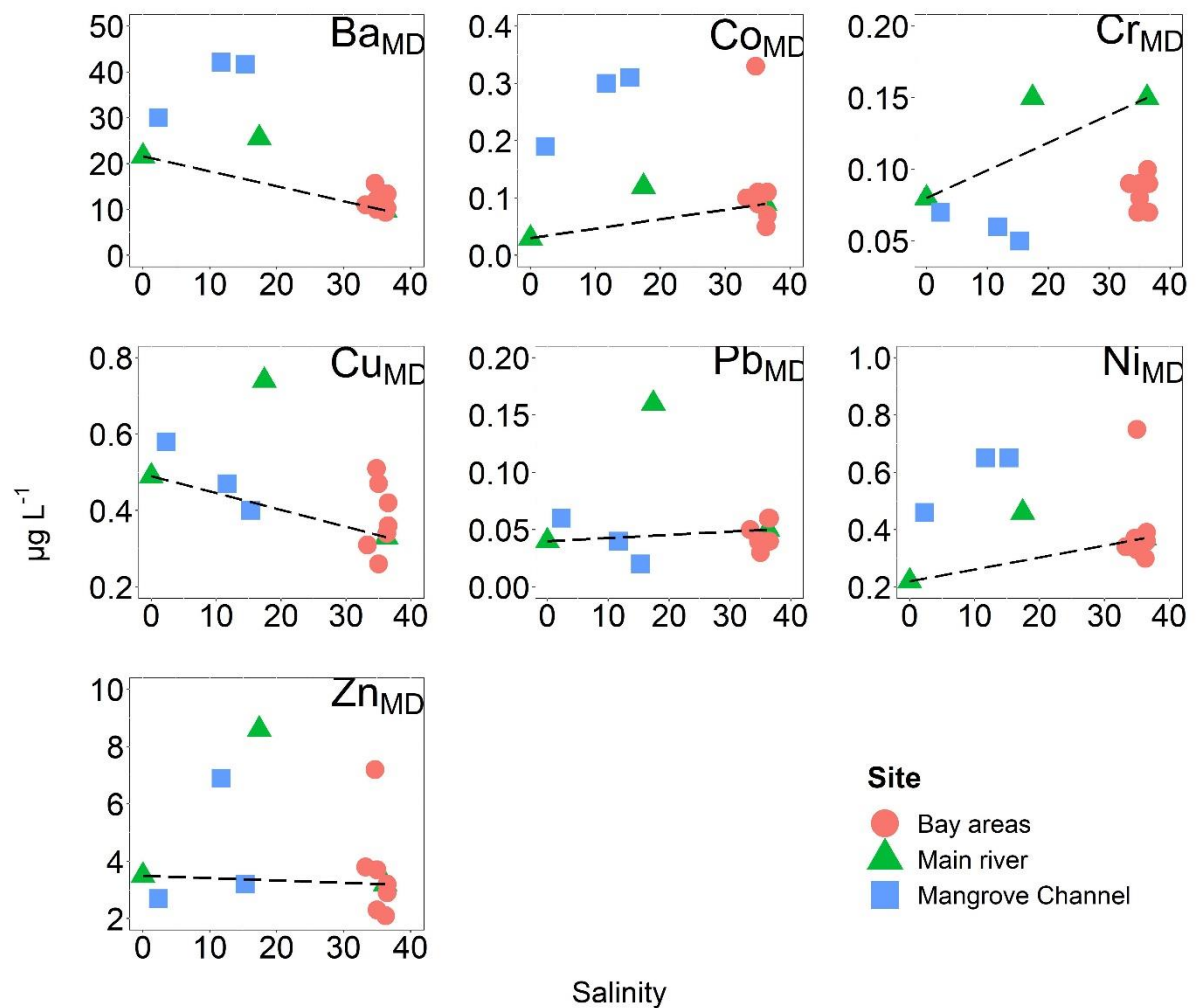
Distribution Coefficient (Log(Kd))

Log(Kd) of trace metals between dissolved and particulate fractions presented some variation along with the environment (Figure 14). ANOVA test for Ba, Cr, Cu, Ni, Pb and Zn, and Kruskal Wallis for Co identified that Log(Kd) of these elements were homogeneus among the sites, except Cr ($p<0.05$). According to Nabelkova (2013), values of Log(Kd) ≤ 3 are present preferentially in the liquid phase. Values between $3>$ Log(Kd) <5 characterize elements more easily released from solid phases, and Log(Kd) ≥ 5 represents trace metals bind into solid phases and only marginally migrate into a liquid phase.

Figure 14 Box–Whisker plots of Log(Kd) for the studied metals along the Parnaíba River Delta. Median values are the bold bars (—) with quartiles 0.25 and 0.75 in boxes; horizontal bars represent the 25% and 75% interval; and (∘) correspond to outlier values
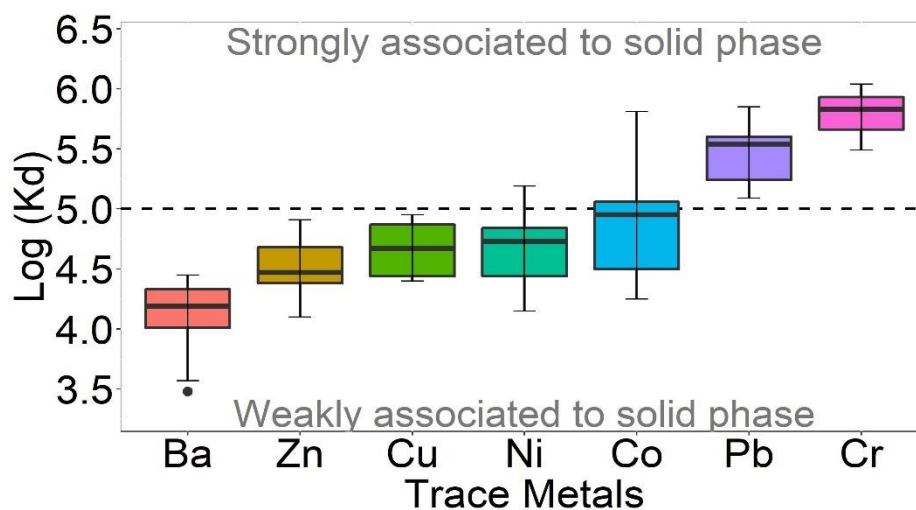
Ba, Zn and Cu exhibited a weak association with solid phase (3> Log(Kd) <5) with the range of 3.5 - 4.4, 4.1 - 4.9 and 4.4 - 4.9, respectively. Pb and Cr showed a range of Log(Kd) of 5.1 – 5.8 and 5.5 - 6.0, respectively, which indicates metal with affinity to bind or remain to a particulate fraction (Log(Kd) ≥ 5). Values of Log(Kd) for Ni (4.1 - 5.2) and presented more affinity to particulate fraction at stations P01 with salinity 0.0 with Log(Kd) ≥ 5, notwithstanding, it began to release from particulate to dissolved fraction when the salinity increased (3> Log(Kd) <5), except at station P23 in the Bay areas, in ebb tide. Log(Kd) for Co (4.2 - 5.8) maintained strongly associated to the solid phase in the Main River and most stations of Bay areas, except P17, P20 and P25. While in the Mangrove Channel, Co was observed weakly associated with the solid phase.

Spearman's rank correlation indicated significant correlation between Log(Kd) Ba with Log(Kd) Co ($\rho = 0.8$), while Log(Kd) Ni had correlation with Log(Kd) Co and Cu ($\rho = 0.7$, for both), and with Zn ($\rho = 0.8$). In addition, Log(Kd) Pb had positive correlation with Log(Kd) Cr ($\rho = 0.9$) and Cu ($\rho = 0.8$). It was also observed positive correlation between Log(Kd) of Cu and Cr ($\rho = 0.7$), and Log(Kd) of Zn and Co ($\rho = 0.7$). The mean values in descending order of Log(Kd) for trace metals along the environment follows the order Cr (5.8) > Pb (5.5) > Co (4.9) > Ni (4.7) > Cu (4.7) > Zn (4.5) > Ba (4.1).

The PCA was applied to observe the influence of the salinity and pH on the Log(Kd) of the elements along the PRD's zones (Figure 15). It accounted for 83.1% of the total variance

that explained metal partition along the zones. Factor 1 explains the 55% of the total variance and presents high loading values for Log(Kd) of Cu, Ni, Pb, Cr and Zn, while Factor 2 e 28.1% of the total variance grouping the parameters pH, salinity and Log(Kd) of Ba and Co. The PCA also suggests that the behavior of variables on the Main River and Bay area are more similar between them, while the Mangrove Channel showed different processes when compared to the rest of the environment.

Figure 15 Principal component analysis with distribution coefficients (Kd) of trace metals (Ba, Cr, Co, Cu, Ni, Pb and Zn) with physico-chemical variables along the zones on the Parnaíba River Delta.
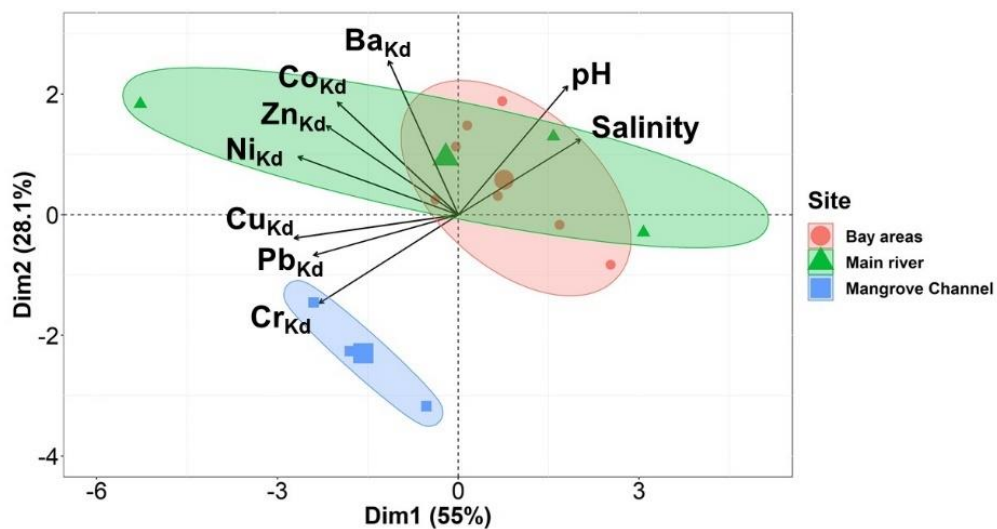
Geoaccumulation Index (Igeo)

The concentration of trace metals is not enough to identify anthropogenic input of contaminants in the environment as trace metal come from geological basement too, so it was necessary to determinate an index of sediment/particulate quality. Geoaccumulation Index (Igeo) was applied to metals in the particulate fraction by the formula $Igeo = log_2(Cn/1.5 \times Bn)$, where Cn ($\mu g.g^{-1}$) is the concentration of particulate trace metal, Bn ($\mu g.g^{-1}$) is the geochemical background value and the constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and to detect anthropogenic influence (MÜLLER, 1986). Igeo is classified as Class 0 (Igeo≤0, uncontaminated), Class 1 (0< Igeo<1, uncontaminated to moderately contaminated), Class 2 (1<Igeo<2, moderately contaminated), Class 3 (2<Igeo<3, moderately to heavily contaminated), Class 4 (3<Igeo<4,

heavily contaminated), Class 5 (4<Igeo<5, heavily to extremely contaminated) and Class 6 (Igeo≥5, extremely contaminated).

For the metals analyzed in the present study, there is the only one study reporting on regional background for Cu (6.8 µg g⁻¹), Cr (18.0 µg g⁻¹), Pb (5.9 µg g⁻¹) and Zn (13.4 µg g⁻¹) in the literature to PRD (PAULA FILHO et al., 2015b). Mean value of Al 3.8 ± 0.5% (3.4 - 4.5%) in the depth below 30 cm, of a sediment core of 50 cm collected in the region was used to normalize the Bn (Supplementary Material-Figure 18). This depth was chosen due to sedimentation rates in semi-arid estuaries of Northeastern Brazil is <0.3 cm yr⁻¹ (MARINS et al., 2004). The values of Cn were also normalized with Al values determined for each sample of the present study, with the range of 2.9 - 10.0% (6.0 ± 2.4%). Al was used as a proxy for the mineral particle-matrix to remove the lithogenic influence on the metal contents (FU et al., 2013).

The values of Igeo from all stations are presented in Figure 16. Igeo values indicated that PRD was uncontaminated to Pb, uncontaminated to moderately contaminated for Cr and Cu (0<Igeo<1), and Zn was classified as moderately contaminated (1<Igeo<2). The last element showed a noticeable Igeo values of Class 3 (2<Igeo<3) classifying the stations P01, P14, P15 and P20 as moderately to heavily contaminated. The average Igeo values were ranked as: Pb (-0.1) > Cu (0.2) = Cr (0.2) > Zn (1.6).

Figure 16 Box–Whisker plots of Igeo values for Pb, Cu, Cr and Zn at different stations in the Parnaíba River Delta. Median values are the bold bars (—) with quartiles 0.25 and 0.75 in boxes; horizontal bars represent the 25% and 75% interval; and (●) correspond to outlier values
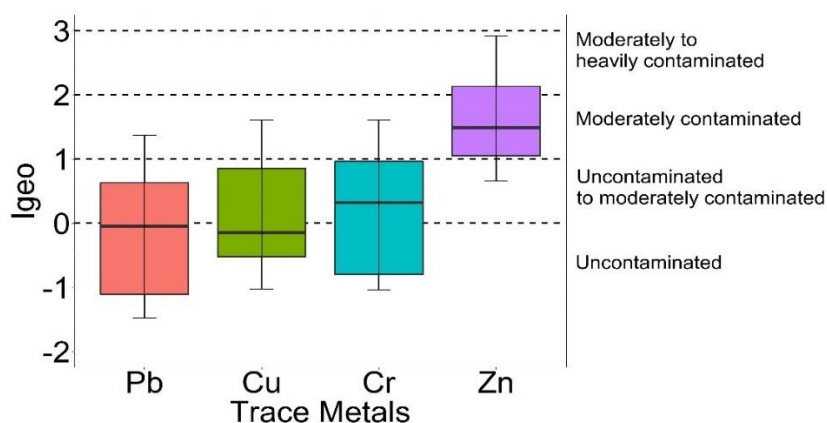
Discussion

High temperatures are common in equatorial estuaries, where almost do not show significant variation along the seasons of the year, as observed in other estuaries in Northeast Brazil (DIAS et al., 2016; SEREJO et al., 2020). The Main River has a typical longitudinal salinity and pH gradient due to the dilution of the freshwater from the river discharge, in the inner stations, and by the seawater forces at outer stations. The interaction between these different waters changes the variability of the physico-chemical variables and partitioning of trace metals along with the environment. The Mangrove Channel had low values of pH and DO due to freshwater influence, as also observed in the urbanized European Scheldt River and Chinese Jiulong River estuaries (GAULIER et al., 2021; WANG; WANG, 2016). It may be also the result of the degradation of organic matter from the Mangrove Channel by microorganisms (MILLERO, 2013) and probably lower channel hydrodynamics compared to the bays and main channel of the river. The surface of the water column presents homogeneous variations of well-oxygenated and alkaline pH in the Bay area due to strong seawater influence on the region with homogenous values for salinity, and low SPM for almost stations, except in Tutóia Bay

The Bay area showed strong seawater influences in the water column, with homogenous values for salinity, well-oxygenated, alkaline pH, and low SPM for almost stations, except in Tutóia Bay. The high value of SPM is a consequence of the push of the river plume to inside the bays and salinity transition, which part is deposited during slack water, and the rest pulled out of the Delta during the ebb-phase (AQUINO DA SILVA et al., 2019), also by additional input of material from bottom to the water column. This variation was also observed in previous studies in the area and other coastal environments in Northeast Brazil (AQUINO DA SILVA et al., 2019; SEREJO et al., 2020).

The spatial distribution of particulate metals suggests a significative continental input of these elements to the PRD. To better comprehension of trace metal behavior along the PRD, it was decided to discuss the elements in groups, such as Zn-Co- Ni, Cu-Cr- Pb, and Ba alone. Ba had a decrease trend with salinity increase for both fractions along the environment. There was noticeable desorption of Ba from particulate and dissolved fraction with the increase of salinity from 0.0 at station P01 until 2.3 - 17.4, in the Main River (P02) and Mangrove Channel (P14 and P15), respectively. The change of partition corroborates with the Log(Kd) that indicates easy release of Ba_{MP} to dissolved fraction into the subsurface water. The Ba behavior at PRD is in agreement with environments around the world with salinity increase (COFFEY et al., 1997; MORI et al., 2019). The mean value of Log(Kd) in PRD was slightly

higher than the results of geochemical speciation modeling from the literature survey of Log(Kd) determined by the Environmental Protection Agency (EPA) with a value of 4.0 (ALLISON; ALLISON, 2005). At outer stations with high salinity, Ba reached partition stabilization between particulate and dissolved fractions. The desorption phenomenon happens due to the high ionic strength and the presence of anions and cations present in the seawater tended to desorb the trace elements from particles (GAULIER et al., 2021).

The group composed of Zn, Co and Ni, Log(Kd) Ni showed significant correlation with Log(Kd) Co and Zn, which suggests a similar partition behavior along the zones. As mentioned previously, these metals arrive in the Main River strongly associated with particulate fraction, but there is an increase of desorption when the salinity reaches 17.4 (pH 8.0) at station P02, until outer station P03 with the salinity of 36.2 (pH 8.1). Over the Mangrove Channel and Bay areas, Zn, Co and Ni trend to be dominant weakly associated to the solid phase, except Co present dissolved fraction in some station of Bay areas. The increase trend of Co_{MD} was also observed in the Krka River estuary that was related to remobilization from the reduction of settled particles in hypoxic–anoxic waters (OMANOVIC et al., 2015).

Regarding the increase trend of Co_{MD} and Ni_{MD} with salinity in the Main River were divergent to the observed in Scheldt estuary with clear decreasing trends seaward (GAULIER et al., 2021). Samani et al. (2015) simulated estuarine mixing of Caspian Seawater with Navrud River water, and identified more efficient flocculation of Ni with various dissolved organic carbon concentrations at constant salinity of 2.7, while maximum flocculation rate for Zn occurs between the salinity 0.6–1.7. Besides, there are no Igeo values for Ni and Co in the solid phase for the present study, they were also weakly associated with solid phase as Zn. It can indicate a possible release of available chemical species of Ni and Co in the water column.

Zn was the only metal with a low-quality index from this group classified the anomalous content in the SPM as moderately contaminated, but the moderately to heavily contaminated classification was observed at stations P01, P14, P15 and P20. Zn is essential for the development of plants and animals, but in high concentrations can cause harmful effects to the aquatic biota (MA et al., 2020; WU; HARPER; HARPER, 2019). Nabelkova (2013) also identified Zn as the most available and hazardous in most urbanized Prague creeks, which were probably originate in runoff from heavy traffic areas in the drainage basin. Previous studies in the PRD's sediment identified minimal enrichment of Zn along the time related to the anthropic influence of the main regional urban center of Parnaíba city, such as from untreated domestic effluent and livestock activities, followed by a natural contribution from weathering of soils

(PAULA FILHO et al., 2014, 2015, 2021). Therefore, it was observed higher accumulation of Zn weakly bounded to the SPM suggesting the presence of labile forms of Zn in the subsurface water. The lower Igeo value for Zn found by in the sediment is also related to the use of Fe as a normalizer (PAULA FILHO et al., 2015a) that could present different values for Igeo when compared to the present study that used Al to normalize the trace metal contents. The drainage basin of Parnaíba River is composed by planosols rich in Fe that suffer partition under oxidation-reduction conditions (BIANCHI, 2007; CABRAL et al., 2019), while Al commonly does not show this behavior. Nevertheless, it is necessary to do sequential extraction of Zn to determinate the source of anomalous content in the SPM and sediments.

Log(Kd) for Ba, Zn, Co and Ni in PRD were systematically higher than determined by EPA with a distribution coefficient of 4.0 for Ba, 3.7 for Zn, 4.7 for Co and 4.0 for Ni, but in the environmental range, except for Cr with higher Log(Kd) compared to all. It also showed higher values (Table 8) when compared anthropogenically influenced estuaries, such as East-Hainan Rivers and higher than Bahía Blanca estuary (FU et al., 2013; LA COLLA et al., 2015). It may suggest less mobility of trace metals from SPM to subsurface water in PRD, than the other coastal environments.

Table 8 Log(Kd) of trace metals between particulate and dissolved fractions in estuaries around the world.

References	Environment	Log(Kd)						
		Ba	Cr	Co	Cu	Ni	Pb	Zn
Present study	Parnaíba River Delta	4.1	5.8	4.9	4.7	4.7	5.5	4.5
Allison and Allison (2005)	EPA (models)	4.0	4.5	4.7	4.2	4.0	5.1	3.7
Wang and Wang (2016)	Jiulong River Estuary		5.1		4.4	3.8	6	4.8
La Colla et al. (2015)	Bahía Blanca estuary		2.8		3.3	2.9	2.8	3.3
Fu et al. (2013)	East-Hainan Rivers			5.3	4.8	5.1	5.7	
Ollivier et al. (2011)	Rhône River	4.0			4.3	4.6	5.8	4.8
Luengen et al. (2007)	San Francisco Bay			4.7	4.1	4.5	5.9	5.2

Statistical analyses demonstrate a positive and significant correlation between Log(Kd) of Pb with Log(Kd) of Cr and Cu. The spatial distribution of Pb_{MP} and Cr_{MP} indicate a desorption to liquid phase, that was evidenced by the increase of Cr_{MD} with salinity, but not for Pb_{MD} in the environment. Notwithstanding, Log(Kd) for Cr and Pb demonstrated that these elements were not big a concern to the quality of the environment due to strong association to

particulate phase, which corroborates to Igeo classification of uncontaminated for Pb and uncontaminated to moderately contaminated for Cr. Furthermore, Igeo for Cu was also classified as uncontaminated to moderately contaminated, and Log(Kd) indicated that Cu was weakly associated with solid-phase all along with the stations, so Cu may start to be an issue to the water quality. The increase of Cu_{MD} in estuary mixing zones was observed in coastal environments around the world, mainly because Cu is less strongly bound to particle surfaces or predominantly associated with colloidal and dissolved organic matter (MOSLEY; LISS, 2019). Pb usually has high particle reactivity as observed in others estuaries (GAULIER et al., 2021; WANG; WANG, 2016). However, the low variability of Pb_{MD} may be explained by rapid sorption of dissolved Pb onto suspended particles and co-precipitation with Fe–Mn oxyhydroxides and aluminosilicates, organic matter and carbonate forms (DOMINGOS et al., 2015; OMANOVIC et al., 2015; SANTOS; MARINS; DIAS, 2019)

In the Mangrove Channel, these metals also prevailed in particulate fraction even during the mixing process with salinity increase. It can indicate another source for Pb, Cr and Cu in Mangrove Channel, such as metal mobilization from the bottom to water column due to slightly acid pH 6.8, which can be followed by rapid metal adsorption and flocculation as observed for Pb in the Main River. Cu and Pb in the Bay areas (salinities > 33.3) showed a slight increase in dissolved fraction, while Cr has no clear trend. This desorption of trace metal from solid into liquid phase is the consequence of the salinity increase (WANG; WANG, 2016).

Nevertheless, even with high values on dissolved fraction at station P02 of the Main River zone, Pb and Cr did not show an evident risk for the quality of the environment. These results agree with emission factors determined in the Parnaíba Basin, which Pb and Cr were mainly from natural weathering in the drainage basin, while Cu was predominant from anthropogenic sources, such as urban runoff, improper solid waste disposal, agriculture and shrimp farming (PAULA FILHO et al., 2014). Yao et al. (2016) related the high concentration of Cu_{MP} in Changjiang River to residential wastes and chemical fertilizers. The source of Pb in small urban streams of the Prague area was probably originated in runoff from heavy traffic areas (NABELKOVA, 2013). Log(Kd) for Cu, Cr and Pb in PRD also presented high values than determined by EPA and other estuaries influenced anthropogenically (Table 8) (ALLISON; ALLISON, 2005; LA COLLA et al., 2015).

Conclusion

The present study provides information about particulate and dissolved trace metal distribution along the zones of Parnaíba River Delta, where almost all trace metals in the particulate fraction suffers desorption from SPM to subsurface water when the salinity increased. Although, only Co, Pb and Zn in the dissolved fraction showed homogeneous spatial distribution along the environment. Log(Kd) suggest a potential mobilization of Ba, Zn and Cu from particulate to dissolved species in the water over the mixing zone with physicochemical parameter variations, while Pb and Cr do not present this concern due to the strong association to SPM. The environmental quality index indicates anomalous contents of Zn in the SPM that may suggest enrichment from anthropogenic activities. Results from this study can further provide information on ecological risk by metal contamination and global pollution mitigation in coastal tidal estuaries under intensive physical mixing along the equatorial coast.

Acknowledgement

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Supplementary Material

Figure 17 Distribution of temperature (ºC), salinity, pH, DO (mg L^{-1}) and SPM (mg L^{-1}) in along the Parnaíba River Delta.
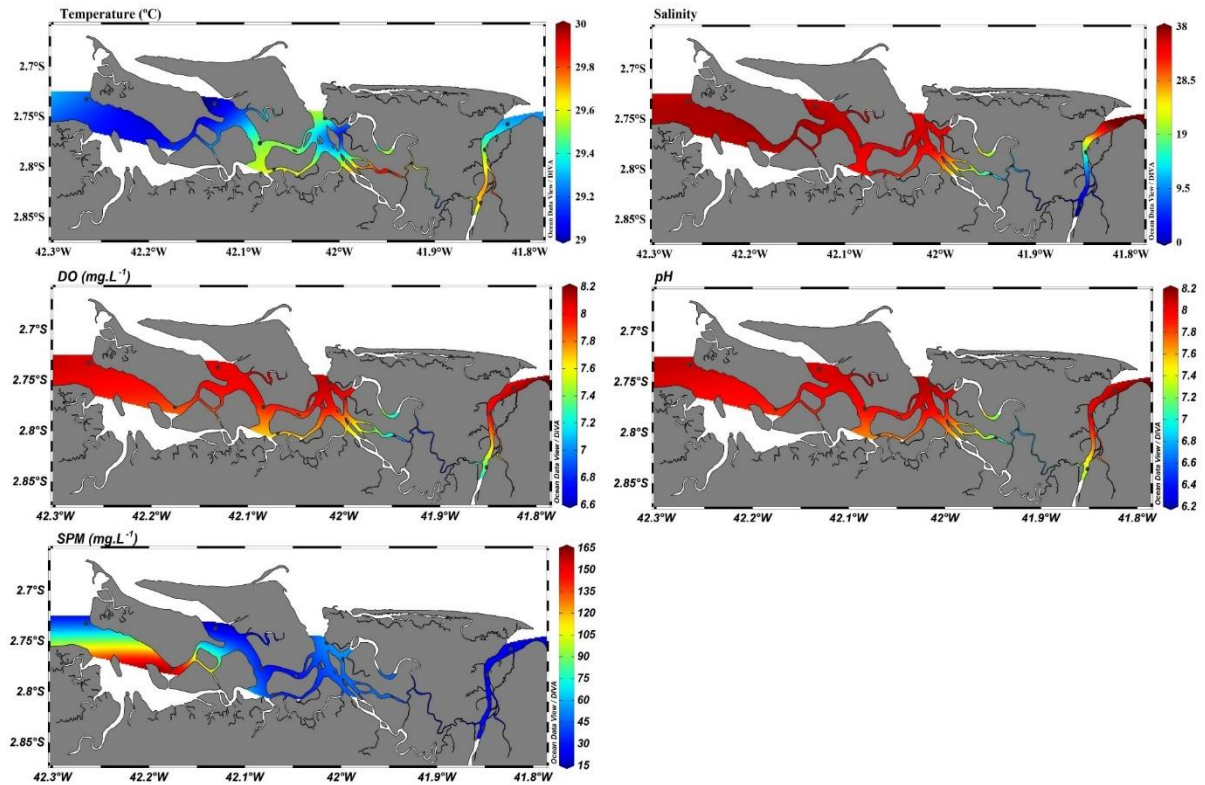
Table 9 Trace metal concentrations (µg L^{-1}) in the particulate fraction along Parnaíba River Delta.

Station	Ba	Cr	Co	Cu	Pb	Ni	Zn
				µg.L^{-1}			
P01	73.6	10.6	2.2	4.3	3.0	4.1	34.7
P02	22.0	5.4	1.0	2.5	1.4	2.1	16.6
P03	36.1	8.4	1.5	3.4	2.2	3.1	22.9
P14	26.8	8.2	1.2	3.1	2.3	3.1	15.1
P15	56.5	16.2	2.7	5.9	4.3	5.7	19.6
P17	43.6	13.3	2.0	3.9	3.3	4.8	19.1
P20	69.1	19.8	3.1	5.8	5.0	7.0	31.1
P21	72.0	23.9	4.2	9.2	6.2	8.3	33.9
P22	54.4	14.8	2.3	5.2	3.9	5.5	25.2
P23	44.3	9.1	1.4	3.5	2.2	3.4	28.4
P24	42.5	11.2	1.9	4.6	3.0	4.0	22.9
P25	37.5	8.6	1.5	3.7	2.3	3.1	22.5
P27	115.4	46.1	7.1	12.2	11.4	15.6	55.7

Figure 18 Content of Al (%) in a sediment core of Parnaíba River Delta during another collecting campaign of 2017. The cut was made every 5 cm. Mean value of Al was 3.8 ± 0.5 % (3.4 - 4.5%) in the depth below 30 cm, of a sediment core of 50 cm.

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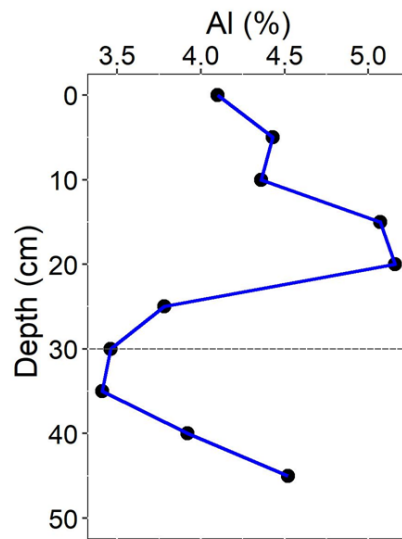
5.3 DISSOLVED ORGANIC MATTER COMPLEXATION CAPACITY AND SIGNATURES OF CHROMOPHORIC DISSOLVED ORGANIC MATTER (CDOM) IN PARNAÍBA RIVER DELTA, BRAZIL NORTHEAST

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Abstract

The characterization of dissolved organic matter (DOM) and the its interaction with metal ions in the water column were investigated in the Parnaíba River Delta, the largest open sea delta of the Americas. The application of ultraviolet-visible (UV-VIS) absorbance and fluorescence spectrophotometry methodologies provided information about the DOM source and composition through spectroscopy of chromophores present in the DOM. The variation of salinity and pH have a significant influence on CDOM geochemistry partition. The chromophoric dissolved organic matter (CDOM) is composed of humic substances from autochthone sources of marine humic substances (peak M), and a mixture compound of autochthone and allochthonous terrestrial degradation and biological activities (peak A + C), mainly from mangrove decomposition. Further, fluorescence quenching identified strong interaction between mangrove DOM complexation capacity with dissolved copper (Cu) in the Mangrove Channel suggesting less availability of trace metals in this zone of Parnaíba River Delta.

Keywords: Dissolved Organic Matter; Humic Substances; Estuary; Metal Complexation.

Introduction

Estuaries are important environments due to their significant role to process considerable quantities of terrestrial and marine organic matter (OM), and they play a controlling factor in determining fluxes of carbon to the coastal ocean and the atmosphere

(CANUEL; HARDISON, 2016). Dissolved organic matter (DOM) (<0.45μm) is the largest reduced carbon pool in aquatic environments, it plays an important role in the transport and chemical speciation of many toxic organic or inorganic chemicals and nutrient cycling throughout the environment (LIU et al., 2020; MONTEIRO et al., 2020). But this interaction depends on hydrochemical conditions of the environment, such as salinity, temperature, pH and photodegradation (CONSTANTINO et al., 2020; QU et al., 2019).

DOM sources in an estuarine environment can be from allochthonous and autochthonous materials (CONSTANTINO et al., 2020; FERRETTO et al., 2016). But currently, there is also anthropogenic inputs of DOM in the aquatic systems that can exceed natural contributions, mainly in places where there is high population density with agricultural, industrial and urban runoff. In the natural waters, DOM is composed empowered by detritic protein and humic substances (HS), where 50 - 80% of DOM is composed of HS (humic and fulvic substances) (COBLE, 1996; REDDY et al., 2014). HS are complex and heterogeneous mixtures of organic molecules resulting from the natural decomposition and transformation of organisms, that vary in their reactivity and ecological role (FELLMAN; HOOD; SPENCER, 2010; ROCKER et al., 2012). Humic acids precipitate in acid shows high aromaticity (high cyclic C compound), high molecular size (large than 2000 Da), which are more refractory in the environment. Fulvic acids maintain in acid solution, exhibit low aromaticity, low molecular size ranging between 800-2000 Da, and present more labile properties (THURMAN, 1985).

Optical methodologies has been used to determine the sources and characteristics of DOM in coastal waters (LEE; KIM; KIM, 2020), to provide useful information about the source, composition, and function of DOM in natural compartments, among which the most techniques used are the spectroscopic methods: such as Ultraviolet–visible (UV-VIS) absorbance, and 3D fluorescence (BROWN, 1977; COBLE, 2013; FERRETTO et al., 2016; HELMS et al., 2008; WEISHAAR et al., 2003; ZSOLNAY et al., 1999). UV-VIS absorbance is the radiation absorbed by DOM in the water and consequently provides the measure of chromophoric dissolved organic matter (CDOM) concentration. In addition, fluorescence typically occurs in aromatic molecules present in DOM, that absorb (chromophores) and re-emit light referred to as fluorescent chemical substances (fluorophores) (FELLMAN; HOOD; SPENCER, 2010). CDOM regulates the UV light penetration into water bodies (ZEPP et al., 2007), which attenuates the water temperature (KOSTOGLIDIS; PATTIARATCHI; HAMILTON, 2005). Considering global warming, the high amount of CDOM in equatorial zones may cause consequences for aquatic biogeochemical processes of the region. However,

the tropics show low CDOM compared to high latitudes, except in coastal zones and riverine input (NELSON et al., 2010).

Parnaíba River Delta (PRD) is the largest open sea delta of the Americas placed between the climate transition of the humid Amazonian and the dry semi-arid in the Equatorial Zone of Brazil Northeast. The Parnaíba River has 1400 km of extension with an average river discharge of 763 m³ s^{-1} (MMA, 2006a). Temperature varies between 23 to 32 ℃ and precipitation of 350 mm during the rainy season. The Environmental Protection Area (APA) of Parnaíba Delta is located throughout the states of Piauí, Ceará and Maranhão, which the last state representing 46% of 313,000 ha from the APA's area (UNIDADES DE CONSERVAÇÃO, 2021). The main resources explored in the Parnaíba Delta area are marine resources, such as maritime cargo transport and people; tourism; extraction of mangrove resources such as catching crabs; shrimp farming, rice farming and fishing; traditional agriculture made for subsistence, which is developed on the banks or inside the river (MMA, 2006a).

PRD has a coastal zone composed of a continuous system of mangroves, with the input of large amounts of freshwater, coming from extensive rivers and streams and high variations in tidal amplitudes that can reach 4.0 m under a semidiurnal regime. Mangrove forests along the states Maranhão, Piauí and Ceará represent ~48% of Brazil, being the third-largest mangrove forest with 7% of the world (DINIZ et al., 2019; FAO, 2020). A previous study identified that sediment carbon and nitrogen signatures lie in the range of freshwater or marine dissolved organic carbon and C3 terrestrial plants (SZCZYGIELSKI et al., 2014), although, there are no recent studies about DOM and its interaction with metal ions in this environment.

The biogeochemical processes between mangroves and adjacent waters are complex due to the source and sink of dissolved and particulate substances from both tides, porewater pumping, and subsurface groundwater advection (ALONGI, 2020). Due to the limited knowledge on the characterization and composition of DOM, the results of the present study will provide a better comprehension of the its dynamics in PRD waters that circulate through one of the largest mangrove forests in the world and little affected by anthropic activities, located between the transition of climate conditions.

Material And Methodology

Sampling

Collect campaigns were performed in December 2019 with a Niskin water sampler distributed at 13 stations in the PRD as described in Figure 19. Most sample collecting occurred under flood tide conditions, except stations P14, P15, P20, P23 and P27 were over ebb tides. Subsurface samples were filtrated with cellulose nitrate filters of 0.45 μm (diameter 47mm), pre-cleaned with double-destilated HCl 10%, washed with Milli-Q water, dried and weighed. Filtrated water samples were stored in high-density polyethylene (HDPE) bottles (250 mL) and added 250 μL of NaN$_3$ (1 mM final concentration). All samples were stored at 4 °C in the dark before further processing. The physicochemical parameters (temperature, salinity and pH) of the water column were measured *in situ* using a handheld multi-parameter probe (YSI Professional Plus) and pH-meter (Methrom® 826). All equipment was calibrated before the sampling campaign.

Figure 19 Location map of 13 sampling sites along the Parnaíba River Delta in the Equatorial Zone of Brazil Northeast.
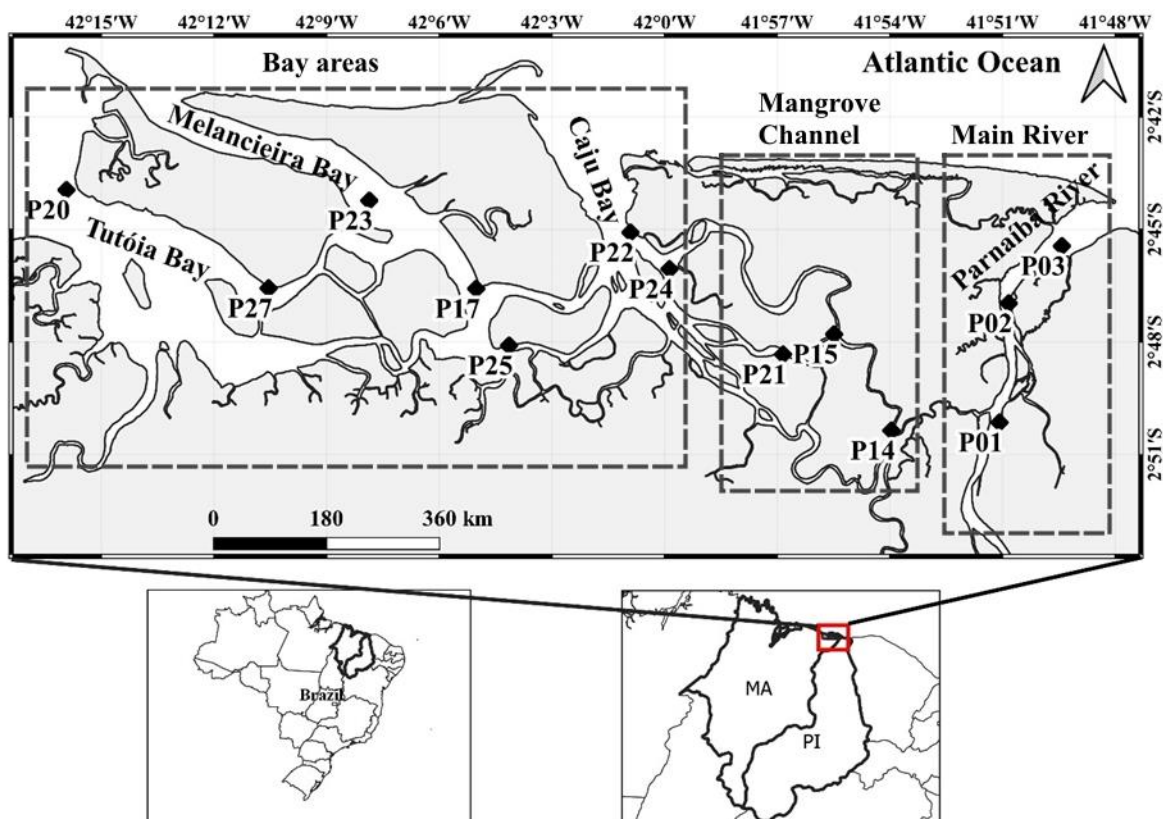
Analytical procedures

It was determined dissolved organic carbon (DOC), UV-VIS absorbance, 3D-fluorescence and complexation capacity of OM with Cu^{2+} in the surface water samples. DOC concentrations were measured by the high-temperature combustion technique using the TOC-V_{CSH} analyzer (Shimadzu), with an accuracy of 0.1 mg C L^{-1}. The equipment was calibrated using a standard solution of potassium hydrogen phthalate ($KHC_8H_4O_4$), variating of 0.1 to 10.0 mg L^{-1}.

UV-VIS absorbance spectra (200-800 nm, 0.5 nm slit) were determined using a Shimadzu-1800 spectrometer using a 10 cm quartz cell. Milli-Q water was used as a reference. The absorption coefficient a(m^{-1}) was determined by the formula a = 2.303*(A(λ)/L), where A=absorbance, λ=wavelength and L=path length of the quartz cell (m). After, the following index was determined to characterize the optical properties of DOM. The absorption coefficient at 254 nm (a_{254})) characterize the aromaticity degree of DOM (WEISHAAR et al., 2003) through Specific UV absorbance, determined by the equation $SUVA_{254} = a_{254}(m^{-1})$/DOC (mg C L^{-1}). A commonly high $SUVA_{254}$ value is associated with DOM with a high aromaticity grade. Slope ratio SR=($S_{275-295}$ nm / $S_{350-400}$ nm) is a ratio that when positive indicates increased photochemical degradation and when negative indicates aerobic activities (Helms et al., 2008). While the absorption ratio at 250 and 365 nm E_2/E_3=(at 250 nm / at 365 nm) is inversely related to the molecular size of the DOM molecules, which may indicate high molecular weight (HMW) related to the presence of HA, or low molecular weight (LMW) relating to FA (Helms et al., 2008).

The values of absorbance of the samples were also used to avoid the Inner Filter Effect (IFE) on the fluorescence signal. IFE can impact the spectra shape, change the peak position, and decrease the fluorescence intensity making the fluorescence spectra more difficult to repair (CARSTEA et al., 2020). Samples were diluted when absorbances were higher than 1 at 250 nm to produce non shifted results of fluorescence.

The DOM characterization was determined using EEMs (Excitation Emission Matrix of Fluorescence) using a HITACHI Fluorescence Spectrophotometer F4500 in 1 cm quartz cell. The instrument was set up with 2400 nm min^{-1} in the scan speed, excitation wavelength varying between 200 – 500 nm and emission wavelength range of 200 – 600 nm, with a 5 nm step. The photomultiplier voltage was set to 700 V, and the response was obtained every 100 ms. The software progMEEF version 1.3 Graphical User Interface developed by R. Redon (http://woms18.univ-tln.fr/progmeef/) was used to treat the data with an algorithm based on parallel factor analysis (PARAFAC) to decompose the EEMs into a set of fluorescent

components. The Rayleigh physical diffusion of light was treated with the method of Zepp (ZEPP; SHELDON; ANN, 2004). The best number of components was determined by Concordia percentage above 60%, according to Mounier et al. (2011).

The DOM complexation with Cu^{2+} was determined by fluorescence quenching. Fifteen quartz cuvettes (1 cm) with water samples were prepared and added solutions of copper $Cu(ClO_4)_2$. The $Cu(ClO_4)_2$ was added using logarithmic increments of concentrations from 1×10^{-3} to 1×10^{-6} mol L^{-1}, to cover a large variety of total copper concentrations, where each quartz cuvette corresponds to a point in the quenching experiment. It was also added a solution of HEPES buffer (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) + Sodium perchlorate $(NaClO_4)$ 0.2 mol L^{-1} (Sigma-Aldrich) to maintain pH 6 constant. The samples were preserved in pH 6 to avoid the trace metal speciation change, and to promote better comparison among the estuarine water samples with different salinities. All samples were allowed to equilibrate for 30 min and no precipitation was observed. The fluorescence measurement was done and decomposed into fluorescence components and contributions (If_{exp}) were determined as described above with PARAFAC. After 3D fluorescence measurements, the pH was checked to observe if occurred variation. No variations were observed during all experiments.

The model of Ryan and Weber (1982) was used to determine the 1:1 conditional stability constants (K) and the total site concentration C_L by the following equation $M + L \leftrightarrow ML$, where M is the free metal, L is a free complexing site and ML is the complex. After, K was determined by $K = [ML]/[M][L]$, where K is the conditional stability constant for pH=6, [ML] is the concentration of complexed metal, [M] is the free metal concentration, and [L] is the ~~total~~ concentration of the ligand. The total metal ion concentration (C_M) and the total ligand concentration (C_L) were defined by $C_M = [M] + [ML]$ and $C_L = [L] + [ML]$. The complexation capacity (CC) of DOM with Cu^{2+} was determined by the ratio between the total ligand concentration C_L (μmol Cu^{2+} L^{-1}) by the concentration of DOC (mg C L^{-1}) in each station of the PRD. The bias errors between the logarithm of the experimental fluorescence (If_{exp}) and logarithm calculated fluorescence (If_{cal}) was determinated by the equation $\sum\left((If_{cal} - If_{exp})/If_{exp}\right)^2$ as described in Mounier et al. (2011). The percentage of fluorescence quenching for each station was determined by the following equation: $Q(\%) = \left((If_{initial\ exp} - If_{final\ exp})/If_{initial\ exp}\right) \times 100$.

Statistical analysis

The Shapiro-Wilk test was performed to test a null hypothesis (H_0) that these parameters would take a normal distribution. When it exhibited normal distribution (parametric), homoscedasticity of variance (Bartlett's test), and one-way analysis (ANOVA) were used to compare the means of variables in different stations of the environment. Although, when the data were not normally distributed, Levene's test and Kruskal-Wallis were applied. Spearman's rank correlation coefficient (ρ) method was applied to observe possible correlations among variables. All tests considered the level of significance $\alpha=0.05$ and were performed using the software RStudio.

Results

Physicochemical parameters

To better describe the hydrodynamic of parameters along PRD was divided into three zones Main River (P01, P02 and P03), Mangrove Channel (P14, P15 and P21), and Bay areas (P17, P20, P22, P23, P24, P25 and P27) based in results of previous studies developed in the region that identified differences in the physical-chemical parameters for each zone (CHIELLE, 2019). The salinity and pH of water were not similar (One-way ANOVA and Kruskal-Wallis; $p<0.05$, n=13) along the zones Main River, Mangrove Channel and Bay areas, whereas only the temperature ($29.4 \pm 0.3°C$) was homogenous in the PRD (One-way ANOVA, $p>0.05$). Salinity and pH showed an increasing longitudinal gradient in Main River, which also increased from Mangrove Channel in direction to Bay areas. The lowest value of salinity was in the Main River at station P01 (0.0) and the highest was in the Bay areas (36.5). The minimum value of pH was identified in the Mangrove Channel at stations P14 and P15 with 6.8 for both, and the maximum 8.1 was found in the Bay area (P22).

EEMs characteristics of DOM

The decomposition by PARAFAC identified two components with CORCONDIA 73.9% (Figure 20), where the first component (C1) shows fluorescence peak with Ex_{max}/Em_{max} at 320/420 nm characterized the fluorophores as marine humic substances (peak M) that is from biological sources (COBLE, 1996). The second component (C2) showed two fluorescence peaks of humic likes. The principal exhibited Ex_{max}/Em_{max} at 280/490nm classified as peak A

(fulvic-like), whereas the second peak with Ex_{max}/Em_{max} at 370/490nm was identified as peak C, suggesting humic-like (COBLE, 1996; COBLE; DEL CASTILLO; AVRIL, 1998).

Spatial distribution of fluorescence intensity evaluated by PARAFAC showed that the DOM from the mangrove channel contributes to both components (peaks M and A+C), while the DOM from the other regions did not contribute significantly. The mangrove channel presents intermediary values of salinity (2.3-15.3) which indicates a potentially significant mixture zone of OM compounds from marine and continental sources in the surface water. Kruskal-Wallis test identified that C1 and C2 contributions were not similar among the PRD's zones (p<0.05, n=13) (Figure 20).

Figure 20 The two fluorescent components found by PARAFAC model in the water (< 0.45 μm) and their spatial distribution of fluorescence contribution for the PRD
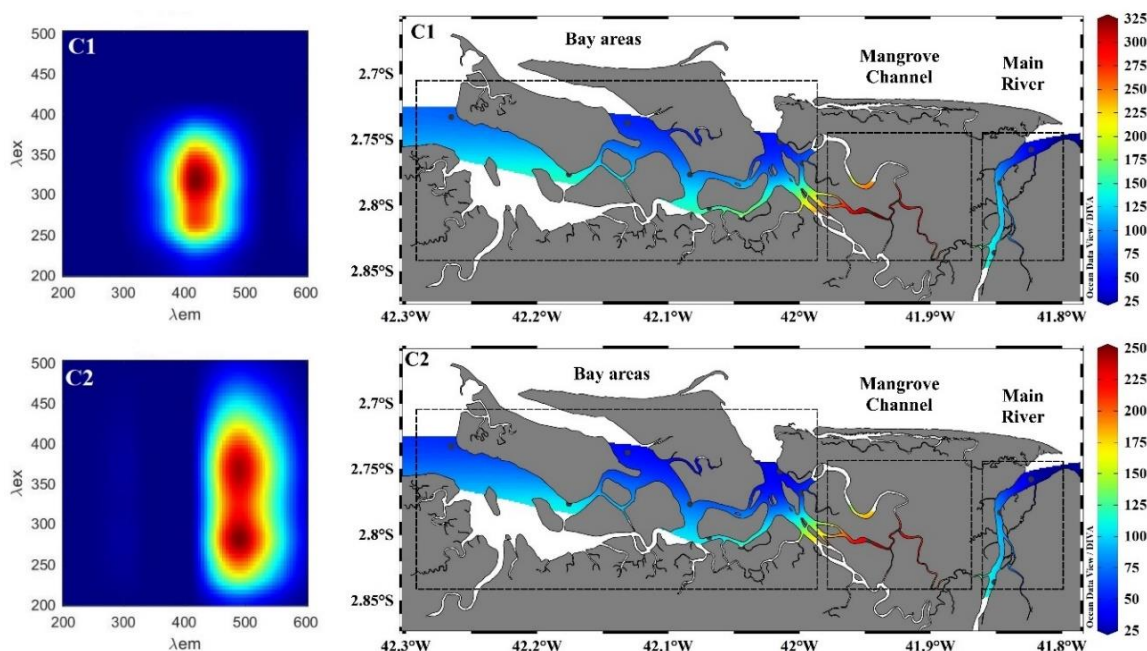
DOC concentrations

DOC concentration had an interesting variation along the environment (Figure 21 and 22), where it exhibited different behavior towards downstream of the Main River, Mangrove Channel and Bay. DOC is conservative only in Main River while in Mangrove Channel and Bay area DOC decreased with salinity increase. Most stations in Bay area exhibited the lowest DOC concentrations when compared to the other zones, mainly the station

P22 with 321.0 µmol L^{-1}, however, station near Tutóia Bay (P27) showed high value (1105.7 µmol L^{-1}), in ebb tide.

Figure 21 Spatial distribution of dissolved organic carbon (DOC µmol L^{-1}) in the PRD.
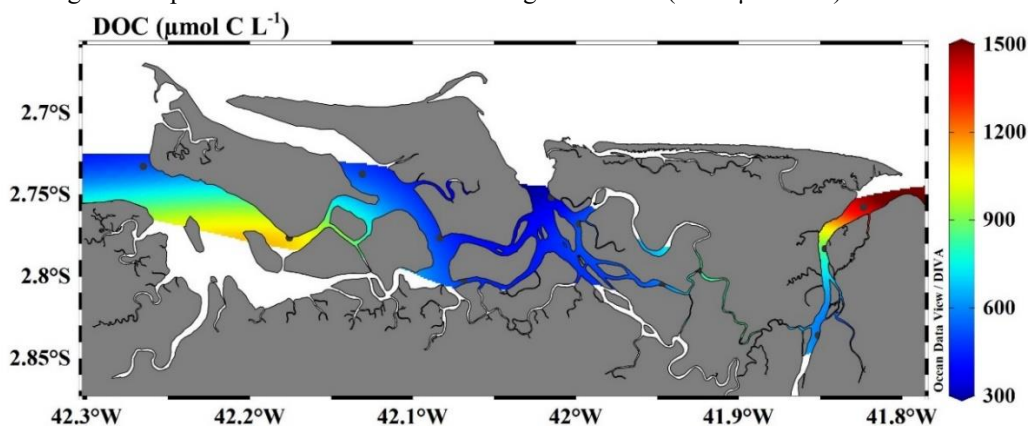
Absorbance measurements and subsequent calculations of optical properties

Optical properties of the DOM, such as the UV-visible absorption (a_{254}), specific UV absorbance ($SUVA_{254}$), Slope Ratio (SR) and E_2/E_3 ratio obtained for DOM samples are present in Figure 23. Shapiro-Wilk test showed that a_{254}, $SUVA_{254}$, SR, E_2/E_3 had normal distributions ($p>0.05$, $n=13$). One-way ANOVA (parametric data) and Kruskal-Wallis test (non-parametric data) identified that SR, $SUVA_{254}$ and E_2/E_3 were homogeneous ($p>0.05$, $n=13$), while a_{254} ($p<0.05$, $n=13$) was not similar along the zones of the environment (Figure 22).

The general values ranged from $9.9 – 24.6$ m^{-1} (16.2 ± 5.2 m^{-1}) for a_{254}, $0.6 – 3.6$ mg C L^{-1} m^{-1} (2.2 ± 0.8 mg C L^{-1} m^{-1}) for $SUVA_{254}$, $0.7 – 1.2$ (1.0 ± 0.1) for SR, and $11.0 – 157.8$ (39.2 ± 42.8) for E_2/E_3. Main River shows increased values of E_2/E_3 characterizing the rise of chromophores with low molecular weight in high salinity, reaching the value of 157.8. Although, the other parameters decrease trend with salinity gradient exhibiting a low quantity of CDOM and low aromaticity at station P03, where a_{254}, $SUVA_{254}$ and SR present values of 9.9 m^{-1}, 0.6 mg C L^{-1} m^{-1} and 0.9 respectively.

Mangrove Channel exhibited increased variation for a_{254} and $SUVA_{254\ nm}$ with the salinity, while the values of E_2/E_3 and SR presented a decrease when compared to the theoretical dilution curves. The maximum value for $SUVA_{254}$ (3.6) and a_{254} (24.6) were observed at station

P21 of this zone indicating an increase of high aromatic CDOM. Bay areas exhibited unclear pattern distribution for the optical parameters, but a_{254}, $SUVA_{254}$ and SR station were higher than the theoretical dilution curve indicating an increased production of chromophores in this zone, therefore a DOM reactivity in this region. The station P23 showed the highest value for SR (1.2) all along the zones, whereas E_2/E_3 at the same station demonstrated a high value (98.8) compared to the other stations in this zone, both with salinity higher than 35.

Figure 22 Dissolved organic carbon and optical properties of dissolved organic matter in the Parnaíba River Delta. Dashed line represents the theoretical dilution curve with the station P01 (salinity 0.0) to station P03 (salinity 36.2).
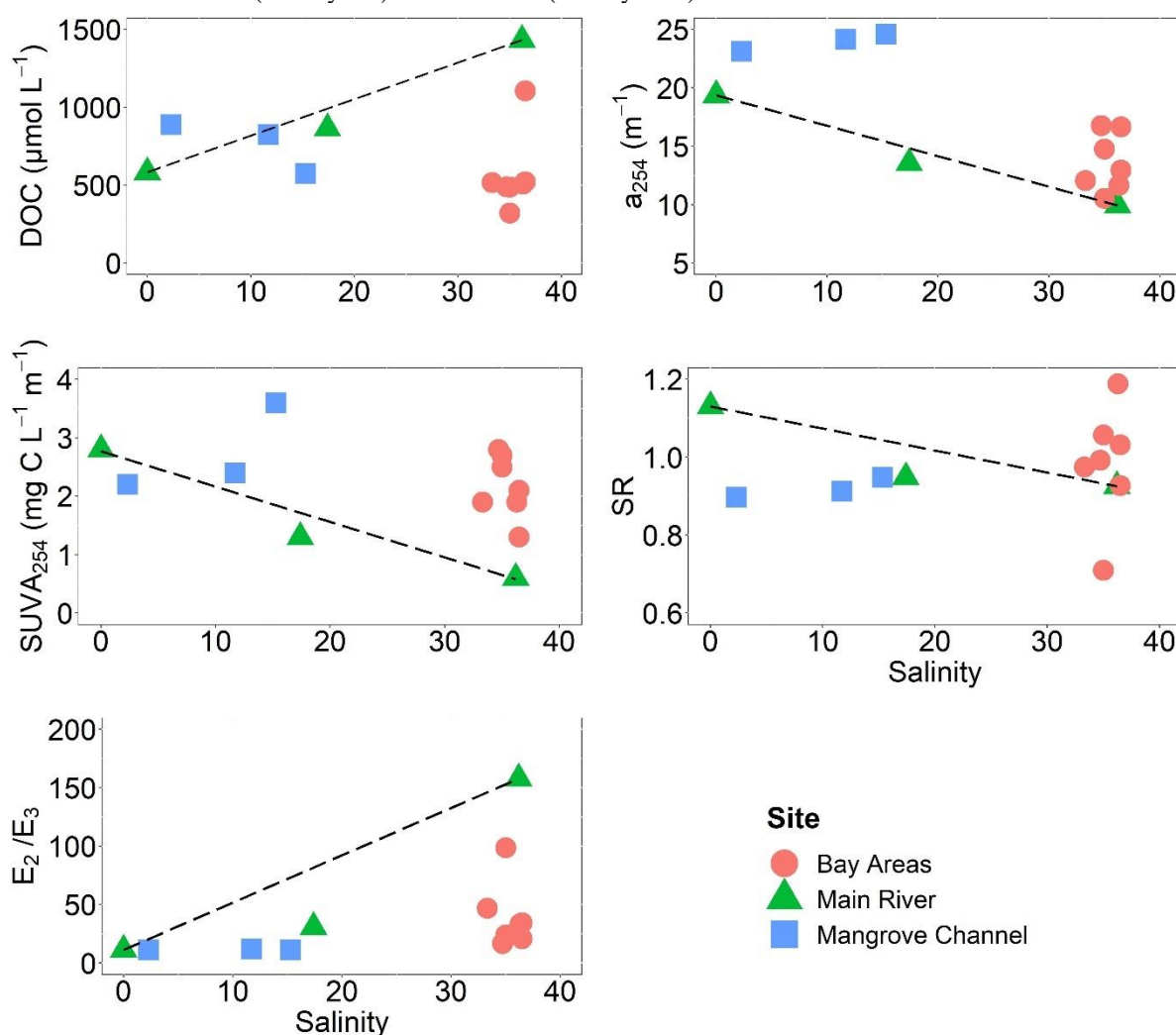
Complexation capacity (CC) of organic matter with Cu^{2+}

The results using Ryan and Weber (1982) model 1:1 showed optimizes results with bias from 0.1 to 0.3. The stability constant Log(K) exhibited the lowest values in the Bay areas

(4.7) and Main River (4.9), whereas the highest values were found in Mangrove Channel (5.2), with average values of 4.9 ± 0.4 along with PRD. It was also identified the highest average decay of fluorescence quenching over the stations in the Mangrove Channel with 78.6%, while Main River and Bay areas showed the lowest average quenching of 60.9 and 60.8%, respectively (Supplementary Material- Table 12). In general, the fluorescence quenching presents an average of 64.9 ± 10.8% over the PRD's zones. The representation of CC in the function of Log(K) (Figure 23) suggests that Mangrove Channel has an OM with greater CC and greater constant against Cu^{2+}, while the complexation dynamic of fluorophores in the Main River and Bay areas were more similar between them and weaker than Mangrove Channel. The average values of CC in each zone were 0.15 μmol of Cu^{2+} mg^{-1} C in Mangrove Channel, 0.09 μmol of Cu^{2+} mg^{-1} C in Main River and 0.08 μmol of Cu^{2+} mg^{-1} C in Bay areas, whereas the PRD average was 0.1 ± 0.07 μmol of Cu^{2+} mg^{-1} C.

Figure 23 Variation of complexation capacity (CC) of organic matter in relation with constant quenching Log(K) along the zones of Parnaíba River Delta
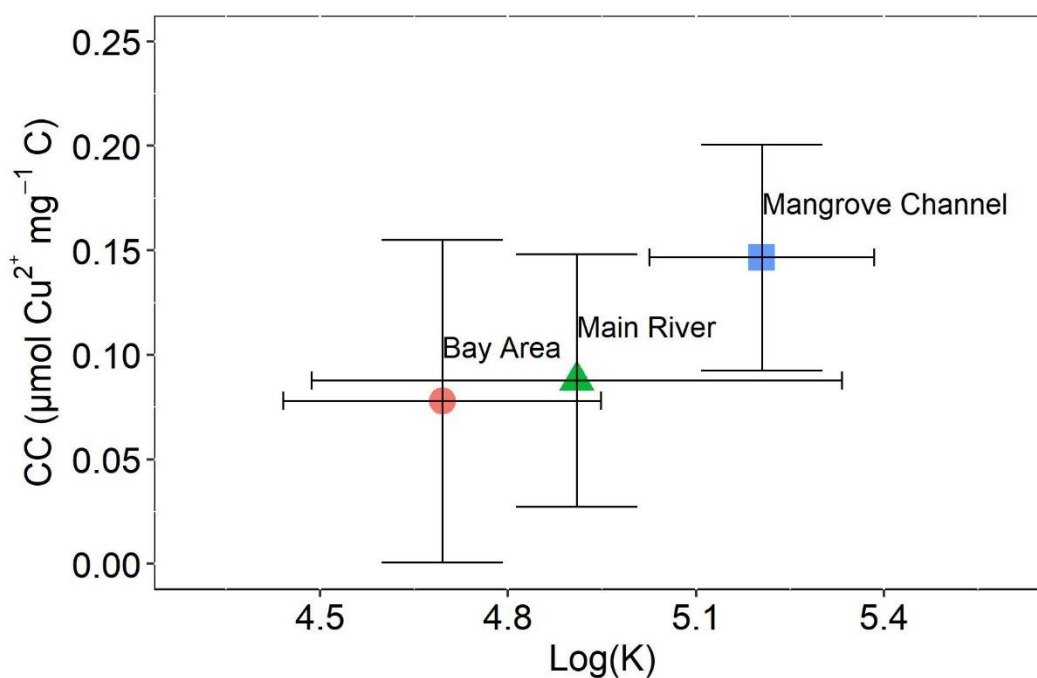
Statistical analysis

The Spearman's rank correlation was applied for all parameters, which the significant correlations accepted was $\rho > 0.7$. Salinity exhibited a negative correlation to temperature ($\rho = -0.7$) and positive with pH ($\rho = 0.8$) indicating different water mass very well

defined influencing the PRD's zones. Salinity also had a negative correlation with a_{254} (-0.7). In addition, pH had negative correlation with C1, C2 and a_{254} (ρ = -0.8, -0.8 and -0.9, respectively), and positive correlation with E_2/E_3 (ρ = 0.8). The C1 and C2 were strongly correlated between them (ρ = 0.9), and a_{254} was correlated with the components (ρ = 0.9, for both) and negatively correlated to E_2/E_3 (ρ = -0.9). E_2/E_3 was also strongly negative with a_{254} (ρ = -0.9).

The PCA was applied to observe the variability of physicochemical parameters correlated to the optical property variables with coefficient correlation $\rho>0.7$ on Spearman's rank. The multivariate method accounted 84.4% of the total variance that influences physicochemical parameters on the optical properties of DOM (Figure 24). Factor 1 explains 68.0% of the total variance and exhibits high loading values for salinity, pH, a_{254}, C1 and C2. Factor 2 describes 16.4% of the total variance and presents high loading values only for temperature and E_2/E_3. The increase of salinity and pH may influence the decrease of the other parameters (a_{254}, C1 and C2), in agreement with Spearman's correlation. The PCA also exhibited similarity between the Main River and Bay area mainly in the behavior of salinity and pH, while Mangrove Channel demonstrates distinct behavior for a_{254}, C1 and C2 along the PRD.

Figure 24 Principal component analysis (PCA) loading plot of physical and chemical parameters in the water of the Parnaiba River Delta. Big and small symbols represent zone and stations, respectively.
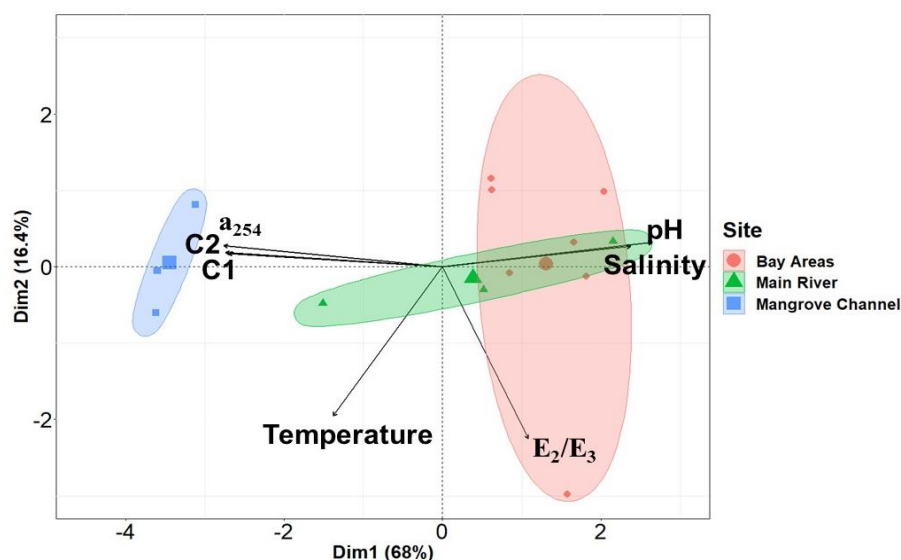
Discussion

The fluorescence components indicate that DOM in PRD is principally represented by humic substances from autochthone source (peak M) in the C1, and autochthonous and allochthonous source compounds (peak A + C) in the C2 (COBLE, 1996). Humic substances are undoubtedly mixtures that develop randomly from degradation process vegetal residue, microbial activities, or the mixture of both interactions (CHEN et al., 2003; CONSTANTINO et al., 2020). The components C1 and C2 were plotted in Chen *et al.* (2003) chart with five EEMs boundaries that characterize the organic molecules, based on literature reports, which corroborates that C1 and C2 were presented in the Region V of Humic acid-like such as near to fluorophores characterized as marine humic acid, fulvic acid-like and humic-acid like (Figure 25).

The peak M (marine humic acid) is very likely derived from biological activities such as microbial oxidation and phytoplankton degradation (COBLE, 1996; FERRETTO et al., 2016). Peak M indicates new humic-like gelbstoff, less aromatic groups and a LMW that is not preserved over long time or space scales (COBLE, 2013, 1996; FELLMAN; HOOD; SPENCER, 2010; SUN et al., 2014). However, peak M was also associated with humic substances from anthropogenic compounds from runoff, sewage discharge, and other effluents (COBLE, 2007). Whereas, peaks A and C (fulvic acid-like and humic acid-like, respectively) are derived terrestrial degradation and biological activities that produce DOM with higher concentrations of aromatic groups and HMW than peak M (COBLE, 2013; COBLE; DEL CASTILLO; AVRIL, 1998; FERRETTO et al., 2016; HELMS et al., 2008).

Figure 25 Location of EEM peaks of the fluorescence components in the water > 0.45 μm (orange color) from Parnaíba River Delta into the five EEM regions based in the literature, based in Chen et al. (2003).
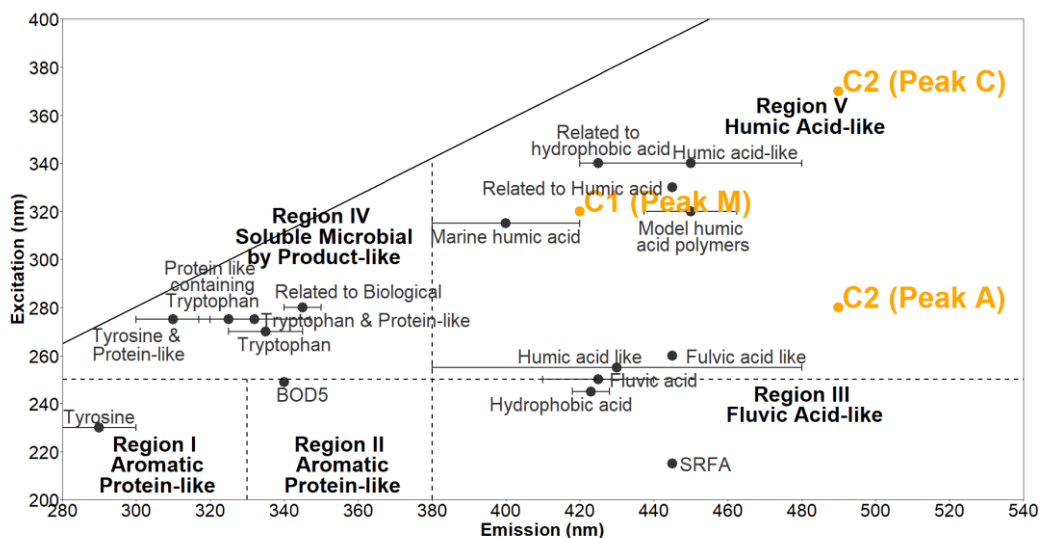
The C1 was a more blue-shifted peak for fluorescence emission intensity, whereas C2 presented a red-shifted peak that is more hydrophobic and very susceptible to photodegradation (MOUNIER et al., 2011). The anthropized estuary of Yangtze River (China) identified peak C from a diffuse source from the soil, while peak M was associated with joint effects of microbial activities (CHEN et al., 2013). According to Lee et al. (2020) peak M detected in Masan Bay (Republic of Korea) was correlated to indicate humic substances from terrestrial, anthropogenic, or agricultural sources. A study made in the French Mediterranean Coast associated the peak A with humic-like components of terrestrial DOM (FERRETTO et al., 2016).

The Main River showed changes of DOM from allochthonous origins upstream to a mixture of allochthonous and autochthonous sources downstream. The spatial distribution of DOC had an increased conservative behavior with the salinity in the Main River, which analogous behavior was identified in Pearl River (China) (54 - 116 μmol L^{-1}) related to nutrient inputs from an urban center in the estuary region of Pearl River (LIU et al., 2020). It can explain the high value of DOC in P03 near Canárias city. In addition, another possible source of the excess DOC in the outer station of the Main River may be related to an *in-situ* DOM production by biological activity, as observed in Masan Bay (LEE; KIM; KIM, 2020) and the stratified Krka River estuary (LOUIS et al., 2015). However, it was not measured chlorophyll-a to

confirm the biological activity by phytoplankton. This high DOC value may also be result from possibly contamination during sampling, storage and analysis.

Mangrove Channel exhibited a distinguish parameters variation when compared to the other PRD's zones, as represented in the PCA. The spatial distribution of fluorescence intensity contributions indicates a potentially significant mixture zone of marine and continental DOM compounds. This zone showed a small removal of DOC under seawater dilution, mainly because sampling occurred during a change of tide condition from the ebb tide, over stations P14 and P15, to flood tide at station P21. The variation reflects the reduced influence of surface runoffs, and sediment and soil leaching with the increase of salinity (XU; GUO, 2017). The behavior could also be explained if the chosen end member is not adequate for this PRD's zone. For this it should be considered that high salinity in front of the bay differ from the high salinity in front of the river mouth. Considering the geographical range, it possible but more sampling of measurement should be done to confirm this hypothesis. The outlier of DOC at station P27 (salinity 36.5) at Tutóia Bay main is associated to the increase of freshwater input from the groundwater. DOC presented higher values when compared to other aquatic environments in the same Brazilian region and around the world, as can be observed in Table 10 (CAVALCANTE et al., 2021; FELLMAN; PETRONE; GRIERSON, 2011; HELMS et al., 2008; HUGUET et al., 2010; LEE; KIM; KIM, 2020; MIDDELBURG; HERMAN, 2007; SUN et al., 2014; YANG et al., 2020), but smaller than macrotidal estuary of Gironde Estuary (France), and the anthropized Bacanga river also located in northeast Brazil (BEZERRA; TAKIYAMA; BEZERRA, 2009; HUGUET et al., 2010). This may be related to the equatorial location with high primary productivity that increase the concentration of DOC in the subsurface water (ROMERA-CASTILLO; LETSCHER; HANSELL, 2016).

Table 10 Dissolved organic carbon (DOC) reported in other environments.

Environment (Country)	DOC ($\mu mol.L^{-1}$)	Reference
Parnaíba River Delta	321– 1,432	Present study
Swan-Canning Estuary (Australia)	166 – 1,241	Fellman et al. (2011)
Masan Bay (South Korean)	100 - 200	Lee et al. (2020)
Seine Estuary (France)	133 - 554	Huguet et al. (2010)
Gironde Estuary (France)	98 - 6,035	
Estuaries in Brazil	84 – 2,006	Bezerra et al. (2009)
Estuaries in the Europe	55 - 600	Middelburg & Herman (2007)
Pearl River (China)	54 - 116	Liu et al. (2020)

Yangtze Estuary (China)	41–126	Sun et al. (2014)
Jaguaribe Estuary (Brazil)	34 - 614	Cavalcante et al. (2021)
Chesapeake Bay (USA)	26 - 108	Helms et al. (2008)

Besides DOC did not show statistical correlation with any parameters, the variation of a_{254} and $SUVA_{254}$ were in agreement with the increase of DOM *in situ* at the outer station of the Main River. The statistical analyses demonstrate an inverse correlation among physicochemical parameters (salinity and pH) with a_{254}, which the reduction of CDOM and aromacity suggests a shift from high aromatic terrestrial to low aromatic microbial DOM from freshwater until seawater (CHEN et al., 2013; XU; GUO, 2017), demonstrating the increase of autochthone source and bioavailability of the CDOM (WEISHAAR et al., 2003). Similar CDOM reduction over salinity gradient was observed from Fox River until Northern Gulf Mexico (USA) with a higher variation (~50 to 13 m^{-1}) when compared to PRD (XU; GUO, 2017). The low CDOM detected in Main River and Bay areas may be a result of photobleaching and active convection of these waters that explains the reduction of UV-Vis light absorption and fluorescence of the CDOM of aquatic environments (COBLE, 2013; ZHU; YANG; ZHANG, 2017).

According to Rosario-Ortiz et al. (2007), $SUVA_{254}$ above 3 m^{-1} mg C L^{-1} indicate high aromatic CDOM related to continental waters highly impacted by terrestrial inputs, such as agriculture runoff. Station P21 was the only place that exhibited the highest a_{254} and $SUVA_{254}$ superior to 3 m^{-1} mg C L^{-1}, but due to no evidence of significant anthropogenic influence in this zone, the high aromaticity may be related to the DOM from mangrove degradation. It corroborates with signatures of C3 terrestrial plants (mangrove) indicated by C_{org}/N_{tot} and $\delta^{13}C$ in PRD's sediment cores (SZCZYGIELSKI et al., 2014). The mangrove sediments are composed mostly of allochthonous highly-refractory OM, which is plant-derived material that decomposes slowly by microbial activities (ALONGI, 2020; CHEN et al., 2013). The OM is mobilized into the water column during the flood tide, contributing significantly to DOM composition along the PRD. High values of $SUVA_{254}$ were also identified in Bohai Sea and the northern Yellow Sea located in the coastal oceans of China related to terrestrial humic-like (YANG et al., 2020) .

Values of the E_2/E_3 ratio of absorption were inversely associated with the aromaticity displayed by $SUVA_{254}$ (CONSTANTINO et al., 2020; HELMS et al., 2008).

Therefore, the increase of E_2/E_3 values in the Main River indicates the dominance of LMW that is present in the more labile DOM (REDDY et al., 2014) with the seawater influence. Besides the lowest values, Mangrove Channel exhibited E_2/E_3 with superior values to the water column of the two Brazilian Amazonian blackwater rivers, which DOM in Carú samples were more aromatic than Rio Negro (CONSTANTINO et al., 2020).

It was developed a model to comprehend the behavior of E_2/E_3 along the environment and to detect a possible DOM third source. It was used the absorbance measured in the end-members of the salinity 0 and 36 (represent 0 and 100%, respectively). After, it was simulated the absorbance correlated to salinity contribution from the Main River, Mangrove Channel and Bay area variating from 0 to 40 to calculate the E_2/E_3 values for the environment (Figure 26). The results suggest a non-linear exponential line of the theoretical dilution curve for E_2/E_3, corroborating with the variation observed for this optical property in the Figure 23 above, and denying the hypothesis of having another source of DOM for the environment.

Figure 26 Theoretical dilution curve simulated for E2/E3. Dashed line represents the E2/E3 measured in the end-member samples, and the blue dots are the experimental simulation with the salinity gradient.
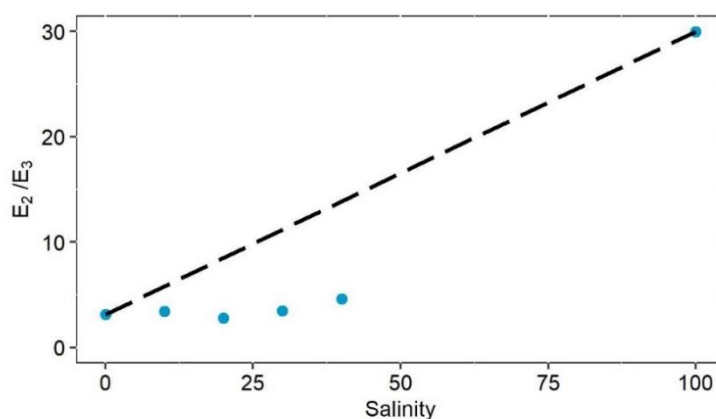
SR variation along Main River and Bay area demonstrates the shift from photobleaching process in stations with high SR values to microbial production in the lowest ones (HELMS et al., 2008). The lowest values of SR in the Mangrove Channel suggest the initial degradation of LMW compounds of CDOM that alters the molecular size of chromophores across the diverse aquatic environments (HELMS et al., 2008). These results agree with the low E_2/E_3 values indicating a more refractory CDOM with more HMW in its

structures. The values of SR in PRD were an order of magnitude smaller than found in two Brazilian Amazonian blackwater rivers with CDOM compose dominantly of allochthonous humic materials from the draining basin (CONSTANTINO et al., 2020).

Complexation reactions affect the geochemistry of metal ions, modifying their solubility, charge and redox potential which infer in availability, fate and migration of metals along with the compartments of aquatic ecosystems (BEZERRA; TAKIYAMA; BEZERRA, 2009). Cu is a metal widely used to predict CC because it is an effective quencher of the fluorescence of humic substances and shows a strong association with colloidal molecules (COSTA et al., 2011).

Mangrove Channel showed the strongest conditional Log(K) and CC ability associated with the interaction between Cu with HMW humic-like acid derived from mangrove sediments. Humic-like acids usually have greater CC than fulvic acids (NOUHI et al., 2018b). The strong bound of metal ions with humic acids occurs through interactions with the functional groups (carboxylic and phenolic) by the interaction between the negatively charged humic substances and the positively charged ions of metals (MERDY et al., 2012; MONTEIRO et al., 2020), which explains the highest fluorescence quenching of 78.6% determined by the model (MOUNIER et al., 2011). So, it suggest less available Cu in the water column and consequently presents low toxicity to aquatic organisms (KOGUT; VOELKER, 2001) in this PRD's zone.

Low Log(K) in Main River and Bay area reveals reduced strength of the interaction between DOM and Cu (MOUNIER et al., 2018) may be related to dominant low aromaticity of marine humic acid (peak M). Copper is an essential nutrient for plants and animals (MERDY et al., 2012). However, the anthropogenic enrichment of Cu from urban runoff, agriculture and shrimp farming (PAULA FILHO et al., 2014) can be a possible risk for the environment and to aquatic organisms, as observed by the low percentage of fluorescence quenching observed in these zones. The minimal values of stability constants are common in areas under strong seawater influence due to the increase of major divalent cations competition effect (LOUIS et al., 2015).

In general, values of Log(K) in PRD were in agreement with a metal-fluorophore complex composed of protein, tryptophan and humic type fluorophores observed in another estuary of northeastern Brazil Piauí River (COSTA et al., 2011). But, lower than urban environments of Itapecuru, Bacanga and Pericumã Rivers (Brazil) and Krka River (Croatia) (BEZERRA; TAKIYAMA; BEZERRA, 2009; LOUIS et al., 2015). Values of CC (μmol Cu mg^{-1} C) were bellowed to be identified in Brazilian environments (BEZERRA; TAKIYAMA;

BEZERRA, 2009; ROMÃO et al., 2003) may be associated to the use of potentiometric methods instead of fluorescence spectroscopy applied in the present study (Table 11).

Table 11 Values of stability constants (Log(K)) and complexation capacity (CC) reported in other environments.

Location	Log(K)	CC (μmol Cu mg^{-1} C)	Reference
Parnaíba River Delta (Brazil)	4.7 - 5.2	0.08 - 0.15	Present study
Brazilian estuaries (Brazil)	2.4 - 4.4	1.09 - 1.5	Romão et al. (2003)
Itapecuru, Bacanga and Pericumã Rivers (Brazil)	7.0 - 7.8	0.04 - 0.35	Bezerra et al (2009)
Piauí River (Brazil)	4.6 - 5.2	-	Costa et al (2011)
Grande Rade Bay (New Caledonia)	3.1 - 3.4	-	Merdy et al (2012)
Krka River (Croatia)	10.0-12.3	-	Louis et al (2015)

Conclusion

The Parnaíba River Delta exhibited two components composed of fluorophores from humic substances of autochthonous sources classified as marine humic-like (peak M), and a mixture of allochthonous and autochthonous sources from humic-like and fulvic-like (peak A + C). The geochemistry of CDOM is significantly influenced by salinity during the variation of hydrological conditions from flood to ebb tides. Mangrove Channel show the dominant contribution of CDOM along the environment and strong interaction with trace metal due to its quality with HMW, high aromaticity and refractory DOM from mangrove decomposition, suggesting less risk for the environment and to aquatic organisms. The results demonstrate the quality of CDOM derived from mangrove degradation may modify the availability, transport and fate of trace metal along with the Parnaíba River Delta estuaries.

Supplementary Material

Table 12 Values of stability constants conditional (Log(K), total site concentration (C_L), quenching percentage, complexation capacity (CC) determined by the fluorescence quenching from the subsurface water of Parnaíba River Delta.

Zone	Station	Salinity	Log(K)	C_L (mol/L)	Quenching (%)	CC (µmol of Cu^{2+} mg^{-1} of C)	Bias
Main River	**P01**	0.0	4.9	9.0×10^{-7}	57.2	0.1286	0.03
	P02	17.4	5.3	1.9×10^{-7}	67.4	0.0183	0.09
	P03	36.2	4.5	2.0×10^{-6}	58.2	0.1163	0.02
Mangrove Channel	**P14**	2.3	5.4	1.0×10^{-6}	81.8	0.0936	0.29
	P15	11.7	5.2	2.0×10^{-6}	78.0	0.2016	0.15
	P21	15.3	5.0	1.0×10^{-6}	76.1	0.1449	0.08
Bay area	**P17**	35.0	4.9	1.0×10^{-7}	70.8	0.0160	0.08
	P20	36.5	5.0	1.0×10^{-7}	68.5	0.0170	0.06
	P22	35.0	4.3	2.1×10^{-7}	48.2	0.0545	0.06
	P23	36.3	4.7	1.1×10^{-6}	51.4	0.1804	0.05
	P24	33.3	4.7	1.2×10^{-6}	66.2	0.1934	0.06
	P25	34.7	4.9	1.0×10^{-7}	68.7	0.0170	0.06
	P27	36.5	4.4	9.0×10^{-7}	51.6	0.0678	0.02

5.4 EVALUATION OF SIZE AND COMPOSITION OF DISSOLVED ORGANIC MATTER OF ESTUARINES WATER OF PARNAÍBA DELTA.

Introduction

Dissolved organic matter (DOM) is a major form of organic matter in aquatic environments (ZHU; YANG; ZHANG, 2017). The source and partition behavior of DOM are expected to be heterogeneous along estuaries, which are complex and dynamic systems with varying physical, chemical, and biological gradients (STOLPE et al., 2005; YI et al., 2014). The fate, transport, bioavailability and toxicity of many chemical species in the aquatic environment are highly related to the properties and molecular size of DOM (XU; GUO, 2017)

Ultrafiltration technique is wide used to separate DOM fraction based on their molecular weight or size in environmental research using a large volume of water sample, and concentrating the elements in a small volumes (LU; GAO; CHEN, 2019; WILDING; LIU; ZHOU, 2004; YAN et al., 2018). The devices separates the total DOM (<0.2 µm), colloidal fraction are the high molecular weight in (10 kDa to 0.2 µm), and truly dissolved fractions (<1 kDa) represent the low molecular weight of natural water samples (STOLPE et al., 2010; YANG et al., 2020). However this technique can have a significative loss of DOM due to adsorption on the membrane or walls of the cell during the pre- concentration process (ROMÃO et al., 2003; ZHOU; GUO, 2015).

The characterization DOM in different size fractions is needed to provide a better understanding of its dynamics in estuarine systems (YI et al., 2014). So, the present chapter aims to examine the changes in abundance and composition of DOM in different molecular weight sizes along salinity gradient of Parnaíba River Delta. Also, characterize the interaction between metal-DOM by the application of quenching fluorescence model to determinate the complexation capacity of DOM with Cu^{2+}.

Sampling and analytical procedures

Subsurface water samples were collected directly in the gallon HDPE of 20 L in December 2019 (Figure 27) for ultrafiltration process. It was a total of 6 stations following the salinity gradients ranging between 0 - 36 along the environment. On the boat, it was performed a pre-filtration with a 0.2 µm (bulk) cartridge filter to remove the suspended solid material immediately after sampling, and stored in high density polyethylene (HDPE) gallons of 20L.

Figure 27 Location map of 6 sampling sites for ultrafiltration along salinity gradient the Parnaíba River Delta in the Equatorial Zone of Brazil Northeast.
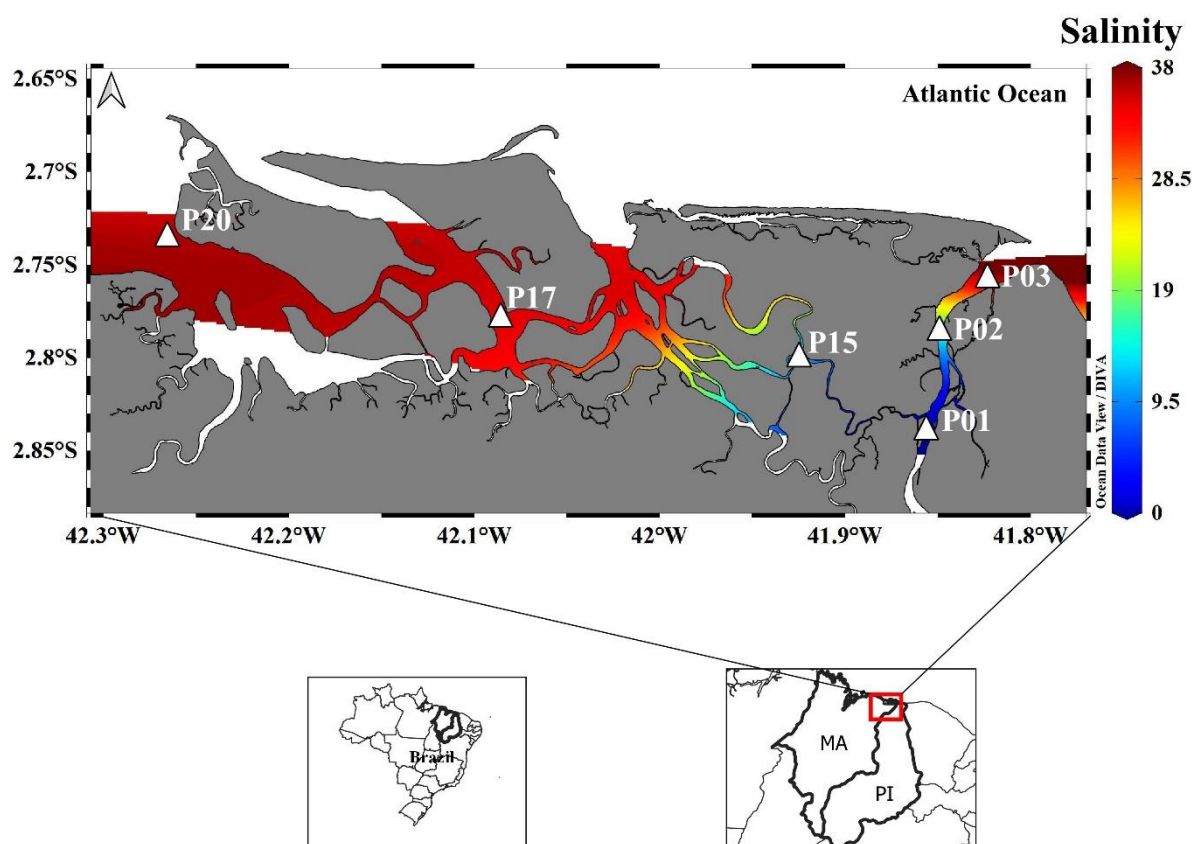
The dissolved water (< 0.2 µm), or bulk , passed thought Pellicon® Cassette Acrylic Holder and Assembly (Millipore) connected to a peristaltic pump (Millipore XX80EL000 Masterflex I/P) for tangential flow ultrafiltration. Polyethersulfone (PES) membranes with pore sizes 0.1 µm, 10 kDa and 1kDa molecular weight cut off were used (Figure 28). The initial sample container with the bulk was placed the feed hose attached to the peristaltic pump where it passed the water sample to the system with the membrane 0.1 µm. The retentate hose was deposited in the bulk sample gallon making it concentrated, while, the permeate hose was in another gallon to store the dissolved sample for further fractionation or analysis. This procedure will be done until the volume of the retentate gallon reaches approximately 10% of the initial volume. For the next membrane, the permeate gallon become the "new feed" sample of the system. It was noted the removed and maintained volume from bulk, permeate and retentate along all the procedures. The procedure was performed by the use of a single membrane to ultrafiltrate all water samples, and later, it was used the membrane with lower pore size. The

water samples were not unsalted. The system was cleaned with phosphoric acid (H$_3$PO$_4$) 0.1N and water Milli-Q with (Total Organic Carbon < 5 ppb) before and between the samples, to remove possible traces of samples and to neutralize the pH of the membranes.

Figure 28 Ultrafiltration process with the three membranes.
Source: Elaborated by the author.
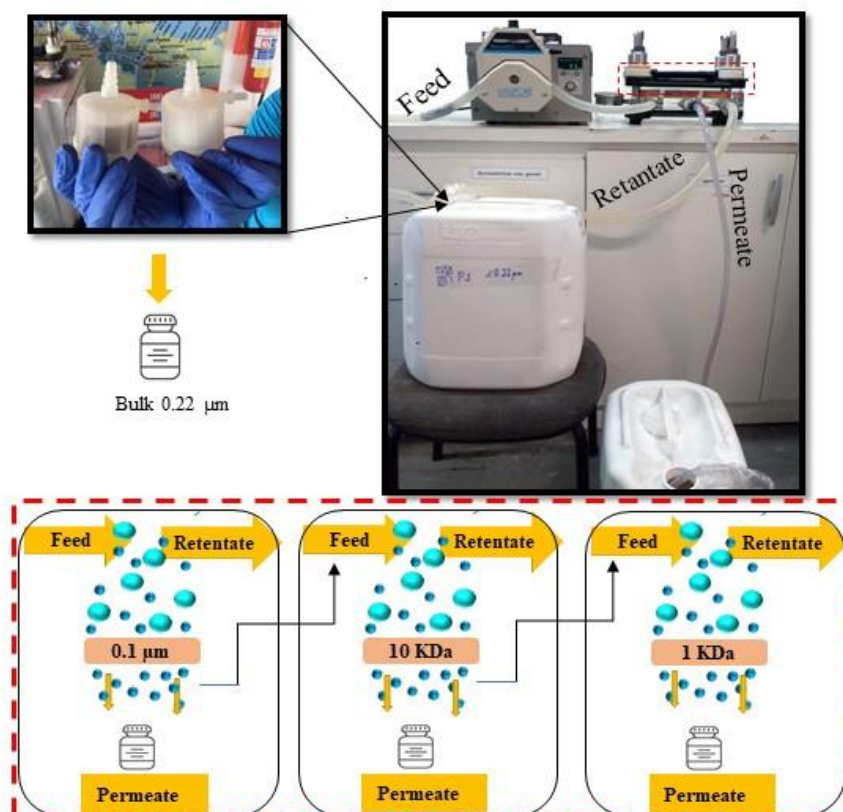
The bulk, permeate and retentate samples of each membrane into high density polyethylene (HDPE) bottles (250 mL) and added 250 µL of NaN$_3$ (1 mM final concentration). It was accounted seven subsamples for each station, totalizing 42 water subsamples from ultrafiltration procedures (Table 13). The obtained filtrates were analyzed dissolved organic carbon, fluorescence composition of DOM, and fluorescence quenching to determinate the complexation capacity of DOM with copper. The methodologies used are described in the previous Chapter 4.3, subsection 4.3.3.2 Analytical procedures.

Table 13 Ultrafiltration tangential flow membranes

Membrane	Fraction	Total

0.2 µm	Bulk	
0.1 µm	Retentate	
	Permeate	
10 kDa	Retentate	7 samples
	Permeate	
1 kDa	Retentate	
	Permeate	

The concentration factor (C$_F$) of the ultrafiltration is the ratio between the volumes of permeate and retentate to each membrane (Table 14).

Table 14 The concentration factor (C$_F$) for each membrane of ultrafiltration procedures. C$_{F1}$, C$_{F2}$ and C$_{F3}$ are C$_F$ for 0.1 µm, 10kDa and 1kDa respectively.

Stations	Salinity	Concentration factor (Cf)		
		C$_{F1}$	C$_{F2}$	C$_{F3}$
P1	0	7.4	5.2	5.0
P2	17.4	4.6	4.2	3.4
P3	36.2	12.6	4.2	3.9
P15	11.7	2.4	3.6	1.8
P17	35	8.2	4.4	3.5
P20	36.5	10.7	5.6	3.8

Final concentrations of DOC and CC were determined by $(C_R - C_P)/C_{Fn}$, where C$_P$ is the element concentrations in the permeate sample, C$_R$ is the element concentrations in the retentate sample, and C$_{F1}$ is the concentration factor of the membrane referent. It resulted DOC and CC concentrations in four fractions of 0.1-0.2µm, 10kDa-0.1µm, 1-10kDa, <1kDa. Posteriorly, the mass balance (MB) for DOC and CC were determined to verify the efficiency of the ultrafiltration system, by the follow formula: $\text{MB}(\%) = \left[\frac{(C_P x V_P)+(C_R x V_R)}{(C_B x V_B)}\right] x\ 100$, where C$_B$ is the element concentrations in the bulk sample, V$_B$ is the volume of the bulk, V$_P$ is the volume of the permeate, and V$_R$ = Volume of the retentate. According to the variability of the experiment, a balance of $100 \pm 10\%$ is accepted as good for each membrane step and for the overall balance.

Results and discussion

EEMs characteristics of DOM

The CORCONDIA resultant from the PARAFAC decomposition varied from 71.2 – 99.2%. Almost all stations exhibited two components dominant from humic substances of marine humic-like, humic-like and fulvic acid like (Figure 29 and 30), but two stations exhibited protein-like sources, accordingly to the classification of Coble (1996) and Chen et al. (2003). The fluorescence peaks characteristic from humic-like were observed in all stations with Ex_{max}/Em_{max} varying between 255-365/410-495. The marine humic-like was observed in P01, P02, P15 and P17 with Ex_{max}/Em_{max} of 310-320/410-420. The stations P01 and P03 showed fluorophores indicative of fulvic acid-like (Ex_{max}/Em_{max} 205-315/450-480) and protein-like (Ex_{max}/Em_{max} 205-240/340-350).

Figure 29 The fluorescent components found by PARAFAC in the water samples from ultrafiltration of the Parnaíba River Delta. The stations and salinities were a) P01=0.0, b) P02=17.4, c) P03=36.2, d) P15=11.7, P17= 35.0 and P20=36.5.
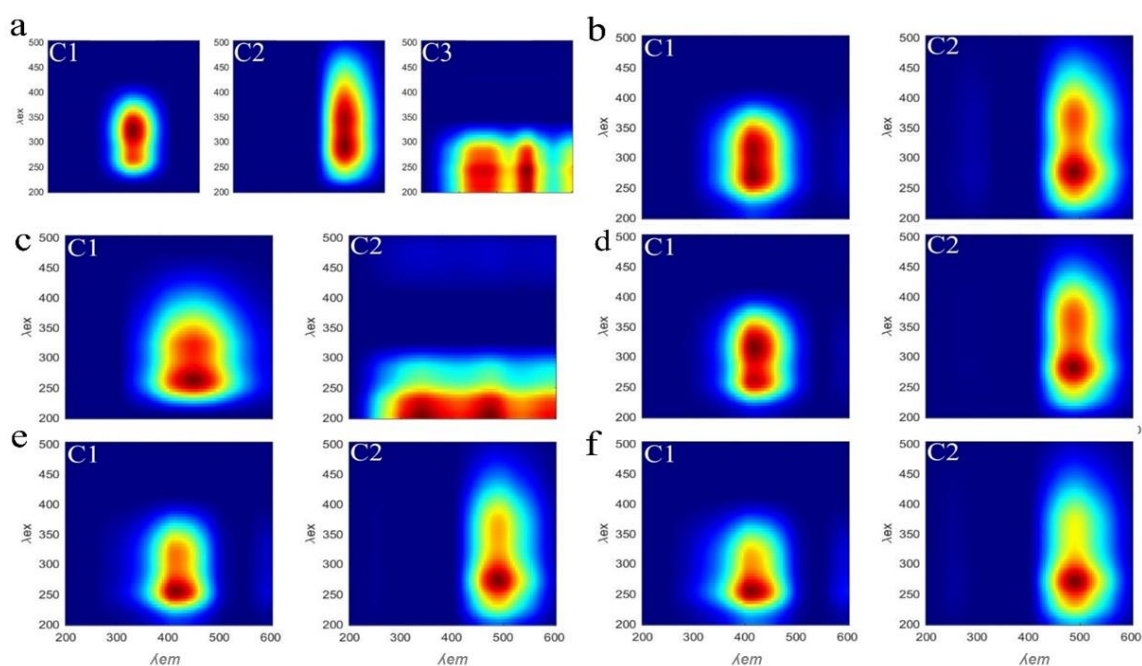
It is possible to observe protein-like peaks detected in ultrafiltration procedures that was not exhibited in the PARAFAC decomposition for samples from microfiltration with 0.45 µm filters. This phenomenon may happen because the fluorescence decomposition was made for each station with concentrated samples, while the previous decomposition from microfiltration used all stations that may overlapped the signal of fluorescence peaks.

The fluorophores are not uniformly distributed over Parnaíba River Delta zones. The fluorescence characteristics of DOM in the Main River shows more fluorophores components than the others stations from Mangrove Channel and Bay area. The protein-like is produced and consumed by microorganisms, and tend to increase in areas influenced by microorganisms with higher rates of autochthonous production (COBLE, 1996; YANG et al., 2020). It can also be used as a tracer of anthropogenic influence from untreated effluents discharged in bays, estuaries, coastal environments (HUDSON; BAKER; REYNOLDS, 2007; LEE; KIM; KIM, 2020). It may corroborate with the presence of Ilha Grande city near station P01 and Canárias city close to station P03. Protein-like fluorescence demonstrated a sharp increase in its percentage from the freshwater (14%) to the seawater endmember (78%) in Jiulong Estuary, which suggested that a protein-like fluorescent substance was relatively enriched in the DOM of the seawater end member (YI et al., 2014).

Figure 30 Location of EEM peaks of the fluorescence components in the water under ultrafiltration process into the five EEM regions based in the literature. Adapted from Chen et al. (2003).
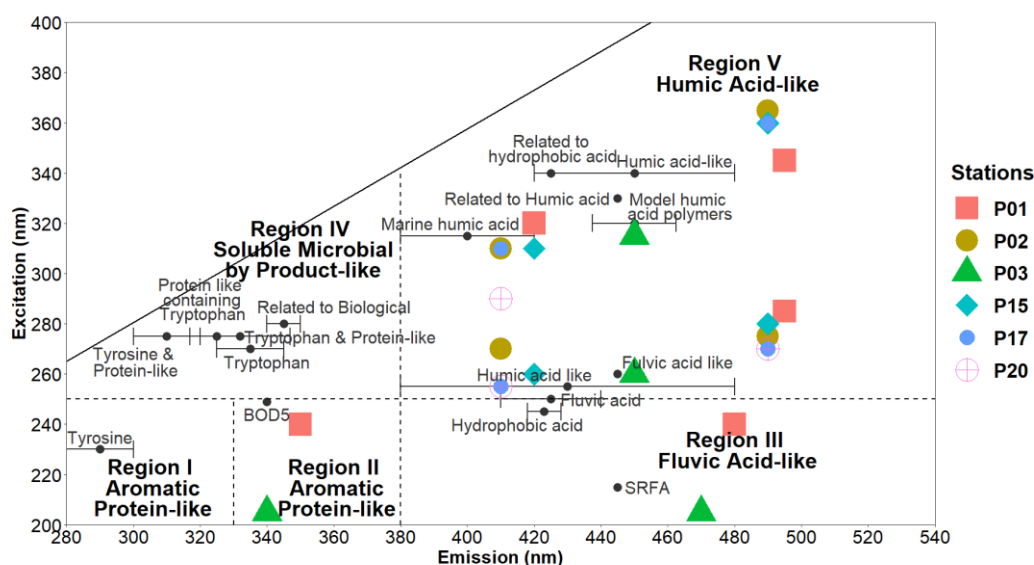
To evaluate variations in molecular size-dependent DOM composition, the florescence contribution of each membrane was used to represent their relative concentrations. The recoveries from the mass balance of C1 (marine and humic-like) and C2 (fulvic-like) contributions for each membrane are present in the Table 14 bellow, with recovery acceptable of 100 ± 10% for each membrane. Accordingly, the results indicated that mass balances of

fluorescence components at stations P17 and P20 were acceptable, although, the other stations are unreliable because they present values below the accepted limit (Table 15). Recoveries lower than 100% are likely to be attributable to loss of element between membranes.

Table 15 Minimum and maximum values of recovery from mass balance for C1 and C2 contribution from PARAFAC decomposition of each station along the Parnaíba River Delta. The symbol of (*) represent element loss and contamination over the membranes, (º) is represent element loss, and (+) means element contamination.

Stations	Salinity	Mass Balance (%)	
		C1	C2
P1	0	76.3-108.2 º	4.21-13.2 º
P2	17.4	87.09-101.7 º	82.5-101.3 º
P3	36.2	92.9-96.9	86.5-92.4 º
P15	11.7	50.9-100.4 º	48.2-97.8 º
P17	35.0	95.4-96.5	93.6-103.2
P20	36.5	93.3-108.5	93.6-103.8

The size distribution of C1 (marine and humic acid-like) and C2 (fulvic acid-like) in the Figure 31 exhibits the majority of fluorescence components occur in <1 kDa fraction (truly dissolved) in the stations P17 and P20. These results indicate different C1 size distribution along the stations, that shows the follow decrease order: <1kDa > 1-10kDa > 0.1µm-10kDa > 0.1-0.2µm for P17, and <1kDa >0.1-0.2µm > 0.1µm-10kDa > 1-10kDa at station P20. The C2 fluorescent contribution decreased according to the following order: <1kDa > 1-10kDa > 0.1-0.2µm > 0.1µm-10kDa for both stations. The different size distribution of fluorescence componentes collaborates with the salinity influence in the partitition and quality of the DOM along the PRD zones. The dominance of humic substances in LMW was also observed in in the Bohai Sea and the northern Yellow Sea (China) (YI et al., 2014).

Contrasting to the other stations, P15 exhibited high proportion of C1 and C2 at 0.1µm-10kDa fraction indicating that these fluorophores are significant in the colloidal fraction. Zhou; Guo (2015) identified in the experiment with humic and protein solutions, similar predominant size distribution of DOM samples (humic -like) in the colloidal size fraction in the <5 nm or <10 kDa size range, consistent with the size characteristics of humic substances from terrestrial DOM component. It suggests the DOM derived from mangrove decomposition characterized in previous section is dominant in colloidal fraction in the Mangrove Channel zone of PRD.

Figure 31 Proportion (%) of size distribution of C1 and C2 along salinity gradient of water column from Parnaíba River Delta.
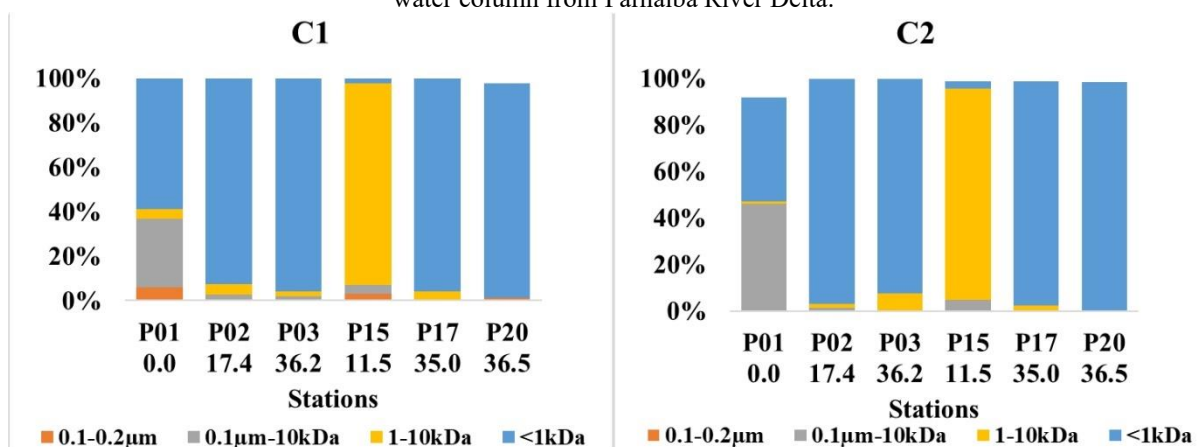
Size distributions of DOC and Complexation Capacity of DOM with Cu²⁺ with estuarine mixing

The recoveries from the mass balance of DOC and CC are present in the Table 16 bellow, with recovery acceptable is $100 \pm 10\%$ for each membrane. From all recoveries determined for the parameters, DOC presented 50% of acceptable recoveries but as it is in different molecular weight size and stations, it is difficult to analyze the mass balance of the parameter. None of the CC was inside of the recovery limit.

The loss and increase of these parameters along the fractions may result from the long period of the ultrafiltration procedures for each station in one single membrane. There are some samples that took more than 8 hours for the volume of the retentate gallon to reach approximately 10% of the initial volume, making the water sample pass many times over the ultrafiltration system. As mentioned previously, the subsurface water of PRD present dominance of DOM with high aromaticity, HMW and more refractory that may occurred the over- loading effect due to the injection of subsurface water samples with high concentration of DOC (ZHOU; GUO, 2015). Huguet et al. (2010) identified DOC losses resulted from the adsorption of some organic compounds onto the ultrafiltration membranes (principally on the 3 kDa), and after the membranes randomly release some organic compounds. A better alternative to ultrafiltration procedures is the use of Vivaspin tubes of different molecular weight size. This technique utilizes a low volume of water samples, less researcher's handling and faster to obtain the concentrated samples.

Table 16 Minimum and maximum values of recovery from mass balance for dissolved organic carbon (DOC) and complexation capacity (CC) for each station along the Parnaíba River Delta. The symbol of (*) represent element loss and contamination over the membranes, (º) is represent element loss, and (+) means element contamination.

Stations	Salinity	Mass Balance (%)	
		DOC	CC
P1	0	2.8-3132.5*	33.8-1424.8 *
P2	17.4	68.1-92.8 º	68.0-1489.3 *
P3	36.2	60.0-95.7 º	16.8-3287.7 *
P15	11.7	86.8-189.9 *	116.2-997.0 +
P17	35	64.4-195.2 *	123.3-1250.0 +
P20	36.5	80.4-98.8 *	52.6-535.1 *

The overload and lost can be confirmed by the DOC and CC proportions (%) of each molecular weight size along the stations in the Figure 32 bellow. It is possible to observe the majority proportion may be present in the truly dissolved fraction (<1kDa) for most stations. However, due to bad mass balance results it is complicated to assume the most significant molecular weight cut off for DOC and CC. Similar size distribution was observed in Seine Estuary that indicate the low percentage of DOC in HMW due to possible flocculation and sedimentation of HMW compounds with increasing salinity, or by the autochthonous production of small molecules in seawater mass (HUGUET et al., 2010).

Figure 32 Proportion (%) of size distribution of DOC and CC along salinity gradient of water column from Parnaíba River Delta
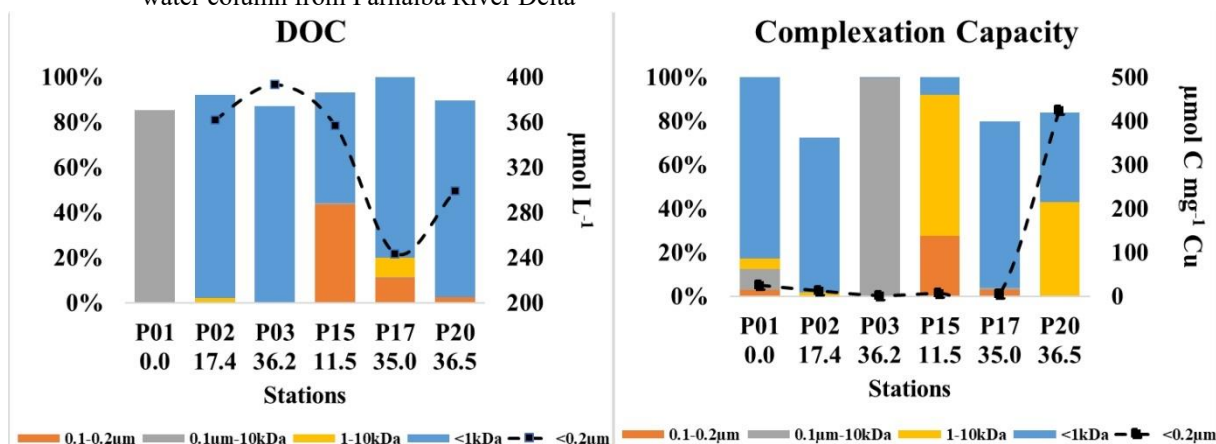
Conclusion

The DOM components resulted from PARAFAC decomposition, of water subsamples from ultrafiltration technique, identified the signal of fluorophores characteristic of protein-like in the P01 and P03 stations in the Main River and differs from components identified for PARAFAC decomposition from microfiltration. The fluorescence components of humic acid-like were predominant in the low molecular size of the truly dissolved fraction (<1kDa) in stations located in the Bay area. The presence of protein-like signal may result from concentration of this fluorophores from ultrafiltration technique and the individual PARAFAC decomposition per station, that previous decomposition used all stations that may overlapped the signal of protein-like fluorescence peak.

6.   GENERAL CONCLUSION

The present work identified complex and distinct processes and patterns along the Parnaíba Delta River (PDR) areas that characterized the importance of mangrove DOM in controlling trace metal partitioning in the subsurface waters of this equatorial estuarine system. The main channel of the Parnaíba River exhibited a typical longitudinal salinity and pH gradient due to the dilution of the freshwater from the river discharge by the seawater forces at outer stations. Salinity and pH have a significant influence on the biogeochemical behavior of trace metals and DOM processes during the variation of hydrological conditions from flood to ebb tides. Statistical analyses of physicochemical parameters identified different zones along the PRD dividing in Main Channel, Mangrove Channel and Bay areas.

The spatial distribution of trace metals in the particulate fraction showed a decreasing trend due to the rise of desorption process throughout the salinity increase. The decreasing order content of trace metals in the particulate fraction was $Ba_{MP} > Zn_{MP} > Cr_{MP} > Cu_{MP} = Ni_{MP} > Pb_{MP} > Co_{MP}$. Contrary to particulate fraction, the spatial distribution of dissolved trace metal exhibited heterogeneous variation, which Ba_{MD} showed a decrease trend with salinity increase, while Cr_{MD} increased at high salinity in the Main River. The elements in the dissolved fraction demonstrated the following decreasing order $Ba_{MD} > Zn_{MD} > Cu_{MD} > Ni_{MD} > Co_{MD} > Cr_{MD} > Pb_{MD}$.

The distribution coefficient exposes a potential mobilization of Ba, Zn and Cu from particulate to available dissolved species in the subsurface water following the physico-chemical parameter variations. The environmental quality index indicated that Zn may be a risk for PRD due to the moderate to heavily contamination in the SPM suggesting possible anthropogenic contributions, such as untreated domestic effluent and livestock activities. Cu is another metal that should be a concern for the water quality by the weak bound to solid phase, and moderate contamination observed in the particulate fraction. The complexing capacity of DOM with Zn could be interesting to determinate in future works. Additionally, future researches on sequential extractions for Cu, Zn, Ba and Pb in the sediment will detail more about the fractionation, origin, availability, mobility and transport of these elements and eventually confirm the possible contamination of the PRD with trace metals.

The dissolved organic matter (DOM) showed a composition of humic substances of mixture of biological and terrestrial origin (peaks A+C), and of marine origin (peak M) from microbial oxidation and phytoplankton degradation. The optical properties showed a

chromophoric dissolved organic matter (CDOM) characterized by high molecular weight, high aromaticity and refractory OM from mangrove decomposition, with CDOM consisting of low molecular weight, less aromatic and more labile compounds from autochthone sources that suffer microbial processes.

Main River and Bay areas exhibited similar characteristics of low stability constant Log(K) and complexation capacity of DOM with dissolved Cu indicating reduced strength of the interaction and consequently the availability of Cu the for the environment. According to these results, Cu can be a concern to the environmental quality of PRD. This was evidenced by the unclear spatial distribution of dissolved Cu in Bay areas, in which Cu was weakly bound to the solid phase and demonstrated no significant CC with DOM in Main River and Bay areas. Mangrove Channel showed strong interaction of DOM with trace metal resulted from the quality of the OM present in this zone, suggesting low availability of metal in the subsurface water.

The fluorescence composition of DOM from ultrafiltration subsamples along a salinity gradient showed "new fluorophore" signals that were not detected in previous PARAFAC decomposition from microfiltration: a protein-like signal in stations in the Main River (P01 and P03). The fluorescence components in the stations located in the Bay area showed the dominance of humic acid-like on the low molecular size of the truly dissolved fraction (<1kDa) due to the salinity influence.

Unfortunately, the recovery of mass balance for DOC and CC are often unreliable because they present values above and below the accepted limit of $100 \pm 10\%$. This occurred due to the DOM characteristics that influenced in the interaction with the membranes that caused absorption and the randomly release the organic compounds from the membranes during the ultrafiltration procedures. So, it was proposed for future studies, the use of ViVaspin tubes for ultrafiltration subsamples due the manager of low volume of water samples, less researcher's handling and faster procedure to obtain the concentrated samples. For this, another sampling campaign was carried out in the PRD in December 2021. It was applied the Vivaspin ultrafiltration methodology on the water samples along a saline gradient to determinate trace metals and DOM characterization. These results will be compared with data obtained from the waters of the Rhone Delta (France) from a sampling campaign carried out in January 2021. The main objective of this work will be to compare and examine the changes of trace metals and DOM composition in different molecular weight sizes, along the salinity gradient, of these two estuarine deltas in semi-arid conditions located in different climatic zones.

Furthermore, it is recommended future studies in the qualitative and quantitative OM characterization in the mangrove sediment to give important information about the identification of different sources and sinks and the biogeochemical processes that influence in the carbon cycles in the region. Concluding, the present study highlights the importance of mangrove DOM in controlling trace metal partitioning in the equatorial estuarine system of the Parnaíba River Delta.

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