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Article

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Interaction of Suspended Particulate Material with Cd^{2+} and Pb^{2+} in a Brazilian Lagoon Estuarine System

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The suspended particulate material (SPM) present in waters has fundamental importance for a better understanding of environmental behaviors of aquatic pollutants. This work determined the physicochemical parameters (pH, temperature, conductivity, total organic carbon and metals concentration) in water samples from Mundaú-Manguaba estuarine-lagoon system, Alagoas, Brazil. This work extracted and characterized the organic matter present in SPM in this estuary and studied the interaction of this organic matter with potentially toxic metals (Cd^{2+} and Pb^{2+}). The results of the physical-chemical parameters evaluated showed influence of the tide and also of anthropic contributions close to the estuary. In fact, the lead concentrations determined (0.10-1.32 mg L^{-1}) are well above that allowed by Brazilian legislation (< 0.010 mg L^{-1}). The organic matter present in the SPM showed a high degree of humification being similar to the organic matter extracted from water and showed strong interaction by Pb^{2+} ions.

Keywords: humic material, metals, capacity complexation

Introduction

Potentially toxic metals (PTM) can reach the aquatic environment through natural sources (rocks, minerals, etc.) and/or anthropogenic sources (industrial activities, untreated effluents, agricultural activities, etc.).[1] These metals are often in the form of (oxyhydroxides) or adsorbed/complexed to dissolved organic material.[2]

The transport and availability of contaminants in the aquatic environment is influenced by several factors such as the nature of the contaminant, the physicochemical characteristics of the waters, the natural aquatic organic material, sediment and suspended particulate matter (SPM).[3-8]

Factors such as pH, temperature, conductivity and total organic carbon content influence the availability of metals in the aquatic environment, as they affect the solubility balance of these metals and the complexation by organic matter present in the aquatic system.[9]

Several studies relate the importance of dissolved organic matter and aquatic humic substances in the availability of contaminants for the aquatic environment. However, recent studies have shown an increase in PTM levels in the SPM.[9-12] Thus, SPM studies have presented great interest due to its close relation with sediments, which may act as a temporary or long-term sink for the pollutants where it is associated.[10]

Suspended particulate material is operationally defined as material larger than 0.7 µm and is composed of aggregates of minerals, organic material and microorganisms and it plays a fundamental role in the biogeochemical cycles of aquatic environments, influencing the transport of carbon, nutrients and contaminants.[3,13]

Another interesting characteristic of this material is concerning to its contribution to the flow of carbon in the aquatic environment. According to literature, SPM contributes about 40% of the total carbon mass flow, then its application is more reliable than dissolved organic material. Besides, SPM colaborates greatly with the metabolism of microbial communities.[14,15]

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Studied have revealed that factors such as pH, conductivity and composition of the SPM, which is composed mostly by natural organic matter, play an important role in the process of adsorption of PTM and, consequently, the availability to the environment.[16]

In this context, water resources with a potential contribution from PTM should receive special attention. The Mundaú-Manguaba estuarine-lagoon system (MMELS) is one of those places with potential for environmental studies due to its high importance for the state of Alagoas, Brazil. This complex is one of the most representative ecosystems in the state and has undergone a process of degradation over the years. This is due to the speed of exploitation of its natural resources and its strategic location.[17] The generation of income and jobs is a positive aspect for the local population, but the use of resources in an intense and unsustainable way is worrying. Researches report contents of potentially toxic metals present in the complex, possibly from anthropic contributions, corroborating studies that indicate moderate contamination by domestic effluents.[18-20]

Under this perspective, this work evaluated the characteristics of the water and humic material (HM) extracted from the SPM of an estuarine lagoon region located in northeastern Brazil (Mundaú-Manguaba estuarine-lagoon system) and its influence on the availability of PTM (Cd^{2+} and Pb^{2+}) in this ecosystem.

Experimental

Chemicals and reagents

All reagents used were of high-purity grade unless otherwise stated. The acid and alkaline solutions necessary for HM extraction were prepared by dilution of 30% nitric acid (Merck, Darmstadt, Germany) and dissolution of sodium hydroxide-monohydrate (Merck, Darmstadt, Germany) in high-purity water (18.3 MΩ cm, Milli-Q systems, Millipore, Waters, Denver, USA). For calibrations and metal determinations appropriate synthetic standard (AAS multielement standard solution, Merck, Darmstadt, Germany) was employed.

Water sampling and preliminary analysis

Samples of water and SPM were collected at the Mundaú-Manguaba estuarine-lagoon system (MMELS) in the state of Alagoas (NE, Brazil) in December 2018, in a drought period. The MMELS has a total surface area of 79 km^2. Sugar cane waste effluent is transported by rivers, and urban sewages coming from Maceió (ca. 900,000 inhabitants) and other smaller cities are dumped at MMELS.[18-20]

Water samples from the MMELS were collected in polyethylene bottles previously decontaminated with a 10% (v/v) nitric acid solution. The collection points for the water samples (9 points) were defined taking into account the characteristics and anthropic activity of the sites (Figure 1). After collection, the water samples were acidified to pH 2.0 and the samples from each lagoon were combined into a composite sample.

The pH, temperature and conductivity of water samples were determined *in situ* after calibration of the equipment Multi A329 from Thermo using standard reference solutions when appropriate, following the literature[21] (precision:

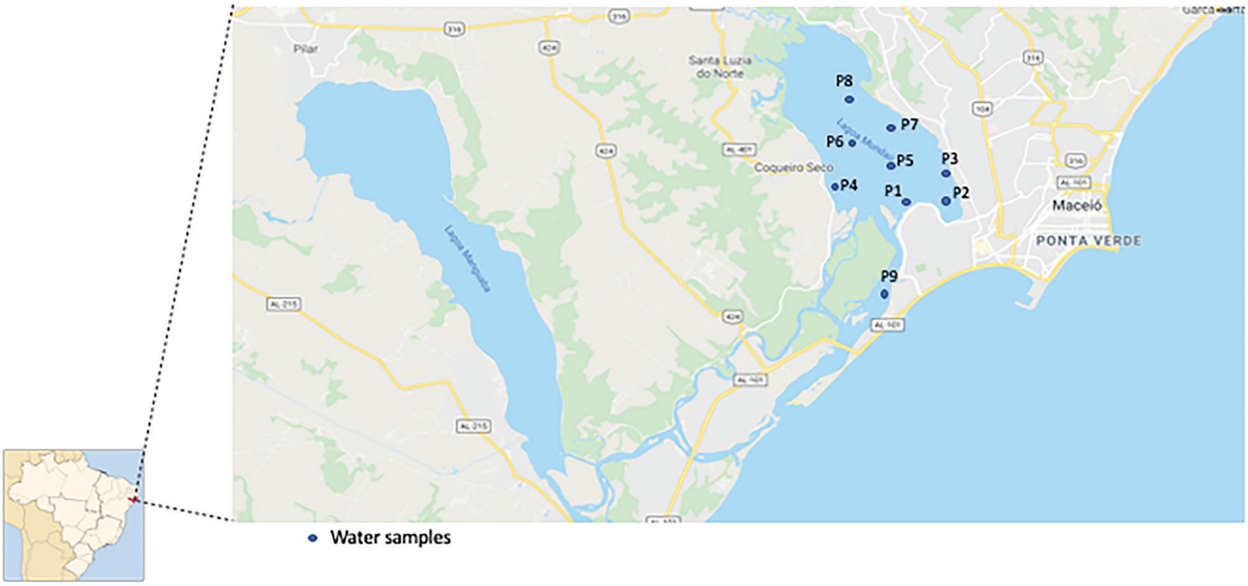

Figure 1. Water sampling in the Mundaú-Manguaba estuarine-lagoon system.

pH ± 0.002, temperature ± 0.1; conductivity ± 1). Total organic carbon (TOC) in water samples were determined using Shimadzu TOC-5000 Analyzer and infrared detection with limit of detection of 0.1 mg L^{-1} TOC. In the laboratory, the water samples were digested at 120 °C using concentrated HNO_3, and the concentrations of the metals Cd, Pb, Fe and Mn were determined by graphite furnace atomic absorption spectroscopy (GFAAS) Shimadzu model AA-6800, using multielemental calibration solutions from standard individual stocks of 1000 mg L^{-1}. These were diluted in the concentration range 0 to 5 mg L^{-1} (limit of quantification (LOQ): Cd = 0.25 µg L^{-1}, Pb = 0.30 µg L^{-1}, Fe = 0.50 µg L^{-1}, Mn = 0.20 µg L^{-1}).[22]

Extraction of humic material from suspended particulate material (HM-SPM)

The SPM was obtained after filtering the water samples using a polyethersulfone membrane (Millipore, USA) of 0.22 µm of porosity. SPM were retrieved from the filter membranes and dried at 60 °C.[3]

The humic material from suspended particulate material (HM-SPM) was extracted according to the procedure used by International Humic Substances Society (IHSS).[23] The procedure was carried at 25 ºC and NaOH (0.1 mol L^{-1}) was used as extractor in a proportion of sample and extractor of 1:10 (m/v). Thereafter, the samples were submitted under constant agitation in inert atmosphere for 4 h to reduce organic material oxidation during the extraction process.[23-25]

Characterization of HM-SPM

Molecular spectroscopy in the UV-Visible region

The E_4/E_6 is the absorbance measurements at 465 nm (E_4) and 665 nm (E_6) in molecular spectroscopy in solution with 2.0 mg of HM-SPM in 10 mL of a $NaHCO_3$ 0.05 mol L^{-1} on a DR 3900 spectrometer.[26,27]

Nuclear magnetic resonance spectroscopy of carbon 13 (^{13}C NMR)

The samples were characterized by ^{13}C NMR with crossed polarization (CP) and magic-angle spinning (MAS) in a Bruker spectrometer, Avance III 400 MHz, with a rotation of 5 kHz, the contact time of 2 ms, waiting time of 5 s and 11,000 scans.[28]

Interaction HM-MPS with Cd^{2+} and Pb^{2+}

The free metal ion concentration in the presence of the HM-SPM was quantified by using the electroanalytical technique absence of gradients and Nernstian equilibrium stripping (AGNES). This technique enables the direct determination of the free metal without the need of physical separation, while it is not hampered by adsorption of organic matter at the electrode surface presenting a limit of detection on the nanomolar range.[29,30]

An Ecochemie µAutolab III and a PGStat 12 were used in conjunction with a Metrohm 663 VA stand (Metrohm, Switzerland). The setup was controlled by the GPES 4.9 software from EcoChemie, the Netherlands. A three electrodes configuration was used comprising a Hg thin film plated onto a rotating glassy carbon (GC) disk (2 mm diameter, Metrohm) as a working electrode, a GC rod counter electrode, and an Ag/AgCl reference electrode from World Precision Instruments DRIREF-5 (electrolyte leakage < 8 × 10^{-4} µL h^{-1}).[31] A Denver Instrument (model 15) and a Radiometer analytical combination pH electrode, calibrated with Titrisol buffers (Merck, Darmstadt, Germany) were used to measure the pH of the samples. The electrochemical measurements were carried out at 25 ºC.

Metal titrations of 50 mg L^{-1} of HM-SPM were performed at ionic strength (I) 0.01 M and total metal concentration in the interval from 1×10^{-7} to 5×10^{-6} M. Cd^{2+} and Pb^{2+} titrations were carried out at pH 5.0 and 6.0. Before each metal titration, a free metal calibration was performed. The limits of detection (LOD) were calculated from the standard deviation of residuals ($3s_b/m$, s_b: standard deviation and m: average) for 12 different calibrations. The intervals for the different metals were: 0.8 to 4.0×10^{-9} M for Cd^{2+} and 1.0 to 9.0×10^{-9} M for Pb^{2+}. The measurements were performed applying the following sets of deposition potential (E_1) and deposition time (t_1): –0.67 V during 240 s for Cd and 0.53 V during 240 s for Pb^{2+}. The stripping step was performed by chronopotentiometry using an oxidizing current I_s of 2×10^{-6} A, until the potential reach –0.30 V. Prior starting the experiments, all solutions were purged under N_2 atmosphere for 15 min, assisted by mechanical stirring of the rotating electrode, 1000 rpm and for 20 s after each measurement. All measurements were performed in triplicate and no systematic variation was observed indicating that the chemical equilibrium was achieved in solution.[32]

Results and Discussion

Water characteristics

The organic matter present in the aquatic environment directly influences the physico-chemical characteristics of this environment, it can act as a buffer due to great diversity of functional groups present in its structure, as well as change the availability of these various chemical species in the environment.[33] An important and little studied source of organic material is present in SPM. SPM in estuarine regions can be characterized by complex mixtures, which are typically composed by silicates (mainly quartz), clay minerals, iron and manganese oxides and hydroxides, organic particles, such as microorganisms, diatoms and detritus vegetables.[34-36]

Table 1 lists the results of the preliminary characterization of the water samples collected from Mundaú-Manguaba estuarine-lagoon system.

Factors such as salinity, pH, organic matter and oxides affect the interaction between chemical species and are observed in an estuarine system.[39] The waters of these lagoons (estuarine system) characterized by great dynamism and have a significant influence on the tide, with the renewal of their waters estimated in 2 weeks.[40] It is worth mentioning that estuaries are transition environments that retain particulate material and in suspension including pollutants.[36] Therefore, evaluating parameters such as water pH, temperature, conductivity, TOC levels that influence the availability of metals in the aquatic environment are of fundamental importance.

The determined pH values are between 7.4-8.4 (Table 1) and are considered satisfactory for brackish waters according to the Brazilian Legislation.[41] This indicates a satisfactory range for these waters of 6.5-8.5.[41] Temperature and conductivity results (Table 1) are in accordance with the literature.[37] TOC levels (Table 1) are well above the values recommended by Brazilian legislation (TOC until 3 mg L^{-1}) and can be compared to places with high humic hydrocolloid values (Table 1).[37,38,41] TOC in natural waters is related to biodegradable and non-biodegradable organic matter, with no interference from other atoms linked to the organic structure, determining only the carbon content in its analysis. Its environmental importance refers to serving as an energy source for bacteria and algae, in addition to complex metals, being an indicator of the degree of water pollution.[40]

Wanderley *et al.*[40] evaluated some parameters in waters of this lagoon estuarine system and extracted the aquatic organic matter. The pH and TOC results corroborate the results in this study. In relation the organic matter, the authors showed that the organic matter in the Mundaú lagoon has less influence from terrestrial organic matter and a lower degree of humification than the organic matter extracted from the Manguaba lagoon.[40]

The concentration of metals in natural waters may be due to the weathering of the original rocks/soil. When the values found are above this background, the influence of human activities can be considered. Metals may be present in soluble, sparingly soluble form, adsorbed on suspended materials or complexed with natural aquatic organic matter.[37] In this study, the levels of Pb and Fe were quantified at all sampling points. The levels of Pb is in some collection points above the maximum allowed by Brazilian law (0.01 mg L^{-1}). Also, Pb levels are much higher than those determined in the literature in estuarine waters of the State of São Paulo (Table 1).[37] Fe contents are similar to values found in the literature in water rich in humic hydrocolloids (Table 1).[37] A reasonable explanation according to the literature,[42,43] shows that this fact might be associated to anthropogenic actions such as disorderly occupation, lack of basic sanitation and the presence of industries chlorochemicals, petrochemicals and intense agricultural activities. The Mn levels were determined only at the sampling points 1 to 4, being well below the values in the literature (Table 1) and most of them are below the values referenced by the Brazilian legislation for brackish

Table 1. Characterization of water samples collected at 9 collection points at Mundaú Lagoon, located in the Mundaú-Manguaba estuarine-lagoon system

Parameter	Water sample									Itapanhaú River-SP	Sal River-SE
	P1	P2	P3	P4	P5	P6	P7	P8	P9		
pH	7.4	8.2	8.3	8.4	8.1	8.3	7.7	7.8	7.9	4.4-5.2	6.9-7.6
Temperature / °C	24	25	24.5	23	22.8	23	24.5	23	24	22.2-23	28.0-29.5
Conductivity / (µS cm^{-1})	70.0	52.0	47.0	50.0	46.0	47.0	50.5	56.0	69.0	39-73.2	19.4×10^3-22.3×10^3
Total organic carbon / (mg L^{-1})	16.50	17.90	17.50	15.40	17.70	18.10	17.60	17.80	17.90	12.3-15.3	12.6-15.9
Cd^{2+} / (mg L^{-1})	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	nd	nd
Pb^{2+} / (mg L^{-1})	1.010 ± 0.030	1.320 ± 0.020	0.980 ± 0.010	1.110 ± 0.050	0.230 ± 0.050	0.150 ± 0.010	0.080 ± 0.010	0.450 ± 0.010	0.100 ± 0.01	2.5×10^{-3}-7.8×10^{-3}	nd
Mn^{2+} / (mg L^{-1})	0.110 ± 0.030	0.090 ± 0.050	0.050 ± 0.010	0.080 ± 0.010	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.425-0.249	nd
Fe^{3+} / (mg L^{-1})	0.980 ± 0.020	0.9900 ± 0.018	1.080 ± 0.200	1.120 ± 0.060	0.110 ± 0.040	0.230 ± 0.030	0.092 ± 0.050	0.546 ± 0.020	0.180 ± 0.015	0.877-0.910	nd
Reference	this study	this study	this study	this study	this study	this study	this study	this study	this study	Goveia *et al.*[37]	Garcia *et al.*[38]

LOQ: limit of quantification; nd: not determined.

waters (0.1 mg L^{-1}).[37,41] The Cd levels are below the limit of quantification (LOQ 0.25 µg L^{-1}) at all sampling points. The sampling points 1 to 4 are the ones that most receive contaminants because they are close to an area with high population density and most of them without basic sanitation (Figure 1).

Characterization HM-SPM

Several authors[3,44,45] have demonstrated the importance of the particulate matter in suspension in aquatic systems, both in the transport and accumulation of nutrients and contaminants. However, few refer to the assessment of HM present in the SPM.

After extraction, the TOC content in the humic extract of the suspended particulate material was 398.00 mg L^{-1}. HM is devoid of generic identity, without a defined chemical structure and presents several functional groups in their structure. The structure of HM is influenced by forming conditions, including weather, water characteristics, vegetation and other environmental factors.[46] Thus, different techniques to characterize the humic materials have been used, with an emphasis on aromaticity and humification index.[47]

Aromaticity and humification, as well as the levels of functional groups in the SPM, can be evaluated by the E_4/E_6 ratios and by ^{13}C NMR. Table 2 shows the E_4/E_6 ratios and levels of functional groups determined by ^{13}C NMR of the HM extracted from the SPM and other sources.

The E_4/E_6 ratio is an important indicator of the degree of condensation of the humic macromolecule and is generally associated with its aromaticity. Higher ratios are indicative of a structure having lower aromaticity.[51] According to the literature,[52] ratios lower than 4 are indicative of a greater presence of condensed aromatic structures, while values greater than 4 indicate the lack of aromaticity. E_4/E_6 ratio has an inverse relationship with the degree of condensation of aromatic rings and the degree of humification. Thus, it is observed that the HM-SPM presents a greater humification when compared to the aquatic humic substance extracted from the same lagoon.[40] He *et al.*[44] warns that the influence of the tide on the estuarine system is an important factor in the resuspension and leaching of organic matter from mangroves, which suggests that it is the dominant source of particulate organic carbon in this type of ecosystem.

The use of ^{13}C NMR is an important tool to estimate the functional groups present in the HM.[53] Integration intervals of the functional groups were performed according to the following chemical shifts: 0-60 ppm (attributed to methylene alkyl carbons bonded to methoxides and nitrogen group); 60-110 ppm (attributed to carbon atoms bonded with oxygen and alkyl groups); 110-160 ppm (attributed to aromatic groups); 160-200 ppm (attributed to the presence of carboxylic and carbonylic groups).[48] From the generated spectrum it was possible to estimate the level of functional groups present in the HM extracted from SPM (Table 2).

The results of the functional group contents show the high presence of oxygenated groups in the structure of the HM extracted from the SPM. Thus, the results from this study were compared with each other and with HM from other matrices. A higher percentage of aromaticity can infer more refractory HM. When compared to aquatic humic substances (AHS) extracted from the same lagoon there is a high similarity in the characteristics of functional groups of these two humic materials.[40]

Rocha *et al.*[54] also investigated by ^{13}C NMR the aquatic humic substances extracted from samples collected in Rio Negro-AM and observed the presence of high aromaticity with little substitution, a different profile to that observed in this study, and a ratio of 1:1 of aliphatic/aromatic groups, a result similar to that of this study.

The characterization results show that the characteristics of HM extracted from the SPM are similar to that of humic materials of aquagenic origin. The oxygenated and nitrogenous groups, electron donors, are the main responsible for the characteristics related to the complexing capacity of natural organic matter (NOM).[25,55]

Table 2. E_4/E_6 ratios and estimated content of functional groups present in the HM ratios extracted from suspended particulate matter compared to other studies

Sample	Percentage distribution of ^{13}C within indicated regions / %				E_4/E_6	Reference
	0-60 ppm	60-110 ppm	110-160 ppm	160-200 ppm		
HM-SPM	23.0	16.7	29.8	30.5	1.3	this work
HS from sediments[a]	19.9	25.6	19.9	34.7	3.2	Tadini *et al.*[48]
AHS from Rio Negro, Amazon	53.1	17.1	9.3	20.5		Oliveira *et al.*[49]
AHS from Mundaú lagoon	22.0	15.6	30.1	32.3	6.0	Wanderley *et al.*[40]
HA from sediments[b]	31.5	25.9	17.2	25.5		Mengchang *et al.*[50]

[a]From Rio Grande; [b]humic acid. HM-SPM: humic material from suspended particulate material; HS: humic substances; AHS: aquatic humic substances; HA: humic acids.

Interaction HM-SPM with Cd^{2+} and Pb^{2+}

The bioavailability and toxicity of contaminants in the environment are directly related to the way it interacts in the compartments (water, sediment and SPM).[3] Metal mobility in environmental systems is governed by a complex array of complexation, adsorption, precipitation, redox reactions and physico-chemical parameters (pH, ionic strength, solid solution ratio) which dictate the partitioning and speciation processes.[56,57]

Natural aquatic organic matter is one of the substances widely spread in aquatic systems and it control depending on the physicalchemical conditions of the systems, the transport, availability and toxicity of metallic species.[25]

An important parameter in the evaluation of the interaction between humic materials and metals is the complexing capacity (CC). This property is characterized by the maximum amount of free metallic species, which may be complexed in aqueous solution by humic material.[58]

The ultrafiltration system (UF) in tangential flow, used for determining the complexing capacity, has the major advantage in versatility for applications on the metallic ion's nature and its ligand. Furthermore, the limits of detection for metals are restricted to the sensitivities of the techniques employed in metals determination. Compared with other separation techniques, an advantage of the UF is to be faster than the dialysis and it does not disturb the complexing equilibrium according to the ion exchange chromatography.[59]

The complexing capacities determined for HM-SPM by Cd^{2+} and Pb^{2+} ions at pH 5.0 and 6.0 are shown in Table 3 with complexing capacities of other samples of HM and different metallic species.

According to Botero *et al.*,[43] the complexing capacity values provide important quantitative information regarding the affinity of metal for a particular substance or binding site. According to the results shown in Table 3, HM-SPM has a higher affinity for lead than for cadmium at both pH values. The values of the complexing capacity of the HM-SPM interaction with Cd^{2+} and Pb^{2+} followed the same trend for other NOM extracted from different matrices, with a higher value of the complexing capacity for Pb^{2+} than for Cd^{2+}. This information is important because it can be inferred that Cd^{2+} should be more available than Pb^{2+} for biota in cases of contamination by these metals.

The greater affinity of HM-SPM for Pb^{2+} ions also corroborates with the levels determined in the water samples of this lagoon and shows that this metal is in higher levels than allowed by Brazilian legislation in these waters, however, a large part of this metal is complexed to organic matter present in this ecosystem, as is the case with particulate material.

Le Meur *et al.*[3] demonstrated the importance of suspended particulate material in the transport of metals at trace levels of the Moselle River, with Pb^{2+} being the metal that demonstrated the greatest interaction with SPM.

The metals Cu^{2+} and Pb^{2+} have low mobility, due to the high affinity with OH− groups present on the surfaces of kaolinite, oxides and hydroxides of iron and aluminum.[62] In natural waters with pH ca. 7, the colloidal particles are negatively charged and can adsorb and fix the metals to the SPM.[63,64]

Monteiro *et al.*[36] evaluated metals present in the SPM of an estuarine region in southeastern Brazil, finding levels of metals Al (320832 g kg^{-1}), Pb (28.05 mg kg^{-1}), Mn (676.35 mg kg^{-1}), Cr (136.12 mg kg^{-1}) and Cu (13.76 mg kg^{-1}).

Conclusions

The particulate material present in aquatic environments has attracted attention due to its influence on the mobility of contaminants. The Mundaú-Manguaba lagoon estuary

Table 3. Complexation capabilities of HM-SPM by Cd^{2+} and Pb^{2+} at pH 5.0 and 6.0 and of different matrices and metallic species described in the literature

Chemical species	CC / (mmol g^{-1} TOC)	Origin of the humic material	Reference
Cd^{2+} pH 5.0	1.90	suspended particulate from Mundaú lagoon	this work
Pb^{2+} pH 5.0	4.00	suspended particulate from Mundaú lagoon	this work
Cd^{2+} pH 6.0	2.20	suspended particulate from Mundaú lagoon	this work
Pb^{2+} pH 6.0	8.20	suspended particulate from Mundaú lagoon	this work
Hg^{2+} pH 7.0	3.40	aquatic humic substances from Mandaú lagoon	Wanderley *et al.*[40]
Pb^{2+} pH 5.0	8.33	humic substances from peat	Santos *et al.*[60]
Cd^{2+} pH 6.0	0.15	humic material from filter cake	Santos *et al.*[61]
Pb^{2+} pH 5.0	1.60	humic substances from sediment	Botero *et al.*[43]

CC: complexing capacity; TOC: total organic carbon.

system plays a fundamental role in the state of Alagoas, once this ecosystem receives daily input from different types of contaminants. Its waters showed high levels of potentially toxic metals (Pb^{2+}) and the direct influence of the tide in the process of renewing its waters.

The HM extracted from the suspended particulate material, HM-SMP, showed a high degree of humification and high levels of oxygenated groups, thus favoring the interaction with organic and inorganic contaminants, restricting their availability.

The interaction studies between humic material Cd^{2+} and Pb^{2+} show different affinities according to pH studied. The greatest interaction occurs for Pb^{2+} ions, corroborating with the data of metals present in this ecosystem.

These results show the important influence of organic matter on SPM in the interaction with contaminants and the importance of understanding the dynamics of the interaction and the availability of contaminants in the aquatic environment.

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Author Contributions

Erismarck A. da Silva was responsible for conceptualization, data curation, formal analysis funding acquisition, investigation, writing original draft, writing-review; Andresa M. B. da Silva for data curation, formal analysis funding acquisition, investigation, validation, visualization; Jardielson S. Santos for data curation, formal analysis funding acquisition, investigation, visualization, writing original draft; Vinicius Del Colle for conceptualization, data curation, resources, software, writing original draft, writing-review and editing; Andre Gustavo R. Mendonça for conceptualization, data curation, resources, software, writing original draft; Andrea P. Fernandes: software, validation, visualization, writing original draft, writing-review and editing; Luciana C. de Oliveira for conceptualization, investigation, project administration, resources, software, validation, visualization, writing original draft; Wander G. Botero for conceptualization, investigation, project administration, resources, software, validation, visualization, writing original draft, writing-review and editing.

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