Journal of Soils and Sediments
https://doi.org/10.1007/s11368-018-2158-1

SEDIMENTS, SEC 2 • PHYSICAL AND BIOGEOCHEMICAL PROCESSES • RESEARCH ARTICLE

Dissolved humic substances supplied as potential enhancers of Cu, Cd, and Pb adsorption by two different mangrove sediments

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Received: 2 April 2018 / Accepted: 8 October 2018

Abstract

Purpose The external supply of humic substances has been recently suggested for the remediation of metal-polluted sediments; however, little is known about how to supply them and their effects on metal mobility. The study sought to investigate the sediment—metals—humic substance interaction in mangrove forest sediments. We aimed to evaluate the sediment adsorption potential in the case of large and rapid metal loads, as recently occurred in the Doce River (Brazil).

Materials and methods In each mangrove forest sampling point of the Benevente River (RB) and Vitoria bay (MO), sediments were collected randomly along the river banks at a depth of 0–10 cm. Samples were characterized in terms of pH, CEC, organic carbon, texture, specific surface area, and elemental composition. The heavy metal content was measured by mass absorption spectrophotometry. Humic substances were extracted from the sediments according to the International Humic Substances Society (IHSS) method, avoiding separation of fulvic and humic acids. Original sediments were supplemented with humic substances and six Cu, Cd, or Pb concentrations. Freundlich and Langmuir equations were employed to create adsorption isotherms.

Results and discussion The two sediments are significantly different, specifically with regard to organic carbon and Fe content, texture, and specific surface area. External humic substances increased the Cu adsorption capacity in both sediments but without an important change in Cu adsorption dynamics. Humic substances slightly increased the sediment adsorption capacity of Pb in RB sediment while they decreased in MO sediment, characterized by lower specific surface area, probably due to coverage of the active adsorption sites. Cd isotherms showed that the different characteristics of sediments alone do not affect Cd adsorption, but coupled with humic substances; Cd affinity for the soil surface increased five times in RB sediments confirming sediment-metal-humic substance interactions.

Conclusions Humic substances affect soil metal retention mainly by altering the ion affinity for sediment surface, leading to contrasting results. The Fe concentration could be important depending on specific surface area and humic substance percentage, due to its capacity to form spheroids linked to molecules of humic substances on the clay surface. Several works have been carried out on this research area, but due to the many variables and different metal ions, we recommend further studies.

Keywords Heavy metals · Isotherms · Mangroves · Organic matter

1 Introduction

Mangrove forests are widespread in tropical and subtropical regions, covering roughly 150,000 km^2, and are located mainly in 18 countries including Indonesia, Brazil, and Australia (Barbier 2016). These ecosystems are characterized by a high degree of biodiversity and represent one of the largest sinks for carbon storage among tropical forests (Donato et al. 2011). This makes them a pillar for future strategies to mitigate climate change (Atwood et al. 2017). Furthermore, as intertidal and estuarine forests, they help protect coastlines, improve

Responsible editor: Shiming Ding

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nutrient cycling and sediment accumulation, favor ecotourism (Atkinson et al. 2016), and host many fish and crustacean species during their entire life cycle (Lee et al. 2014).

Mangrove forests are often placed at the end of coastal basins characterized by high sediment delivery rates (Adame et al. 2010). Due to their root network, they can efficiently trap fine sediments (Young and Harveya 1996; Cahoon and Lynch 1997); changing water chemical conditions through the estuary promote formation and precipitation of organometallic complexes (Craig and Jenkins 2004; Bayen 2012), leading mangrove sediments to become a sink of metals which can be accumulated to toxic levels, also depending on the characteristics of each river basin and the distance from pollution sources (Perry et al. 2008; Bayen 2012). For this reason, on one hand, mangrove forests are efficient barriers against uncontrolled widespread of contaminants, but, on the other, they are suffering from increasing rates of water and sediment contamination, as a consequence of rapid industrialization and urbanization of coastal regions. Anthropic pressure erased up to 50% of mangrove areas over the past 60 years (FAO 2007). Borja et al. (2012) and Maiti and Chowdhury (2013) reported heavy metal accumulation in sediments, plant, and animal tissues of estuarine ecosystems such as mangrove areas: this is mainly caused by inadequate control of waste disposal (Chen et al. 2009; Anton et al. 2011; Wu et al. 2014). All of the abovementioned factors caused a significant forest decline, with areas characterized by several spots without canopy (Ferreira and Lacerda 2016); reducing ecosystem structural complexity; impacting fish, invertebrates, and phytoplankton populations; and increasing accumulation of heavy metals and toxic sulfides (Chen et al. 2009; Nayar et al. 2004).

Metal dynamics in sediments depends on iron oxyhydroxides, and to a lesser extent manganese oxyhydroxides, which together with clays and organic matter can adsorb heavy metals near the sediment surface by incorporation into the oxide structures or by adsorption onto particle surfaces (Clark et al. 1998). Fe-(hydro)oxides can form strong bonds with clay, silt, and sand particles, providing sorption sites for humic acids on the surfaces of these particles (Arias et al. 1996; Sei et al. 2002). These processes contribute to formation of pores (Regelink et al. 2015) and increase the potential metal ion adsorption surface (Clark et al. 1998). Miola et al. (2016) found that estuarine sediment samples characterized by significantly higher superficial Fe concentrations in the surface layer show significantly higher Cu, Zn, Pb, and Cd concentrations than samples with lower Fe content. A high proportion of Pb, Zn, Hg, and Cd is adsorbed onto clays, organic matter, and other mineral phases, and in general, they are significantly correlated with fine particle content, while oxidizable fractions of Cu, Ni, and Cr are highly correlated with organic matter content or complexed with mineral particles (Clark et al. 1998; Zhou et al. 2010).

Reforestation, also known as monospecific replantation, is considered the best way to restore these ecosystems and reactivate the food chain (Ferreira and Lacerda 2016). However, reforestation can have side effects on heavy metals in these environments: Zhou et al. (2010) found that it can increase metal accumulation in superficial sediment layers but favor the reducible and less bioavailable fractions in comparison with oxidizable fractions. On the other hand, Förstner (1989) reported that solid particles which adsorb metals can be easily re-suspended in the water flow.

Considering the slow rate of mangrove self-restoration and the moderate rate of survival in many planted regions (Primavera and Esteban 2008; Rovai 2012), a faster and more efficient restoration approach of degraded mangroves might involve the use of humic substances (Dobbss et al. 2018). The increase of natural or artificial humic substances (HS) in mangrove sediments should be studied not only with regard to the main aspect which is direct metal retention and stabilization, but also for the protective effect on seedlings and on the new canopy survival rate.

Humic substances are biomolecules formed from decomposition of animal and plant residues, resulting from soil chemical and microbial activities (Canellas et al. 2010). They are apparently high molar mass supermolecules that can be disassembled by small amounts of root organic acids, consequently releasing products of microbial activities such as auxin entrapped in their network (Pittarello et al. 2017). Humic substances are known to influence root architecture and nutrient uptake, enhancing plant yield (Nardi et al. 2009; Calvo et al. 2014; Conselvan et al. 2017, 2018).

Humic acids also increase the stability of interactions with Zn^{2+} and Cu^{2+} (Prado et al. 2006). Qi et al. (2017) reported that soil amendment by organic matter from rice straw decomposition significantly increases the surface bonded fraction of adsorbed Cu in comparison with the ion exchanged fraction, and demonstrated Cu binding to HS by forming inner-sphere complexes. Sewage discharges from the urban area of the Iguazu river basin (Curitiba region-Brazil) coated the particulate solids at downstream sites with humic substances and these probably contributed to increase the Cu adsorption on the surface of solid particulate floating in the river (Sodré et al. 2012). Stumm (1992) and Zachara et al. (1994) reported that dissolved humic substances with high molecular mass are more readily adsorbed on the existing mineral surface in freshwaters than less aromatic and lower-weight organic matter.

Based on the effects of biostimulants and their role on metal mobility, the use of organic matter and/or HS in metal-polluted sediments to foster plant growth for phytoremediation purposes has been recently suggested (Pittarello et al. 2017; Pittarello et al. 2018).

However, little information is available in terms of how much, where, and when to supply these biostimulant compounds and their effects on mobility of polluting metals. For these reasons, this work sought to investigate the sediment—metal—humic matter interaction in the case of external humic matter supply. Moreover, by testing metal concentrations up to 1000 mg L^{-1}, we intended to evaluate the sediment adsorption potential in case of a large and fast load of contaminants, as occurred in the recent ecological disaster when the Samarco mining industry dam collapsed in November 2015 (De Oliveira Neves et al. 2016).

There are many previous and recent papers describing sediment contaminations and/or sediment characteristics and/or polluted sediment recovery in mangroves of China, Vietnam, Australia, the USA, Brazil, Mexico, and other countries (Defew et al. 2005; MacFarlane et al. 2007; Noel et al. 2017). Sediments, depending on their origin and the final place of accumulation, are different in granulometry, organic matter content, time of submersion, hydrology of the river basin, exposure to pollutants, and last, but not least, kind of vegetation, leading to diverse behavior towards polluting metals (Weber et al. 1992; Noel et al. 2017; Alam et al. 2018). The specificity of this work is to try to give a preliminary result on the behavior of mangrove sediments in case of a huge and sudden load of heavy metals, employing isotherms and considering possible changes in this behavior coupled with a strong increase of humic substance content. The present work tested the hypothesis of whether humic matter supply could modify the sediment retention potential of Cu, Pb, and Cd, or if the intrinsic characteristics of the sediments, particularly in terms of Fe, organic matter content, and texture, remain prevalent in heavy metal sequestration even at high pollutant concentrations.

2 Materials and methods

2.1 Sediment sampling

Two sites in Espirito Santo State, Brazil (Fig. 1), mainly differing in terms of texture, iron, and organic matter concentration were selected for sediment sampling: (1) mangrove forest of the Benevente River (RB) (sampling points: S 20° 47′ 09″,W 40° 38′ 36″; S 20° 46′ 18″, W 40° 38′ 34″ and S 20° 45′ 49″,W 40° 39′ 44″), close to the town of Anchieta, characterized by moderate anthropic pressure and a stable and healthy mangrove population composed of *Rhizophora mangle*, *Laguncularia racemosa*, and *Avicennia germinans*, with increasing density of *A. germinans* in the inner part of river close to the sampling points (Petri et al. 2011); and (2) the inner part of the Vitoria bay mangroves, close to the Maria Ortiz neighborhood (sampling point: S 20° 15′ 16″, W 40° 17′ 51″), denominated MO (Maria Ortiz), which suffered high anthropic pressure including contamination by uncontrolled waste waters. Its recuperation started in 2011 via *Rhizophora mangle* and *Laguncularia racemosa* re-planting. These two groups of sampling points are homogeneous in terms of arboreal species composition, canopy age, tree density, proximity to river banks, and distance from a residential area (within 2 km for RB vs few meters for MO). In each sampling area, sediments were collected using a small metal shovel to easily break the root network and dig to a depth of 10 cm in a 10-m^2 area along the river bank, where four points within the area were chosen randomly. This depth was chosen as *Avicennia spp.* and is known to increase the organic matter in the first 10 cm of sediment (Lacerda et al. 1995). Sediments from each of four points were stored in plastic jars, transported to a green house, and mixed together. Sediments were spread on a thin plastic foil and left to dry for 1 week at air temperature. For measurement of the metal concentration, part of the sample was dried at 60 °C for 48 h in an oven.

2.2 Sediment characterization

All analyses were performed according to the methods described in "Manual de metodos de analise do solo" published by the Brazilian Agricultural Research Corporation (Donagema et al. 2011) and were performed in triplicate. Soil particle-size distribution was determined using the hydrometer method. The pH was measured in H_2O (soil/solution ratio equal to 1:2.5).

The redox potential was measured in fresh samples at field conditions and in dried samples, in deionized water (soil/solution ratio equal to 1:2.5) after 30 min of agitation; all measures were performed by the portable potentiometer and pH meter Digimed DM-2P.

Exchangeable K^+ was extracted using the Mehlich–1 solution and measured by flame emission spectrometry (Tecnow 700). Exchangeable Ca^{2+} and Mg^{2+} were extracted with KCl 1 mol L^{-1} and determined by titration with a 0.0125 mol L^{-1} EDTA solution. The cation exchanged capacity (CEC) was determined according to the KCl method. Potential acidity (H^++Al^{3+}) was determined by titration with 0.025 mol L^{-1} NaOH solution after extraction using 0.5 mol L^{-1} $Ca(CH_3COO)_2 2H_2O$ at pH 7. The organic carbon content (OC) was determined by the modified Walkley-Black procedure (Yeomans and Bremner 1988).

The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method (Brunauer et al. 1938) via N_2 adsorption/desorption; measurements were performed using the Quantachrome Nova 2200e® surface area analyzer.

The sediment elemental analysis (C, H, N, O, S) was performed in triplicate using the elemental analyzer CHNS-O Perkin Helmer 2400.

2.3 Sediment metal/metalloid concentration

To measure the Cd, Co, Cr Cu, Fe, Mn, Ni, and Zn content in sediments, samples were prepared according to the USEPA

Fig. 1 Sampling map: blue areas with trees identify mangrove forests subjected to more intensive submersion

method (Meyer et al. 2016) modified as follows: air-dried sediment samples were further dried for 24 h at 60 °C in an oven, then ground in a mortar with pestle to 10 mesh (2 mm); and 1 g of each sample was mixed with 5 mL of 95% pure HNO_3 (SIGMA) and warmed to 180 °C in glass tubes until sample was totally digested. After partial cooling, 2 mL of 35% concentrated H_2O_2 was added. Samples were diluted with deionized water in a ratio 1:10 *v*/*v* and analyzed in triplicate by inductively coupled plasma optical emission spectrometry, using a Shimadzu ICPE 9000 instrument. After every set of 10 samples, a standard sample of 0.20 mg L^{-1} was measured to correct for instrumental instability and matrix effect. A Fluka multielement standard solution (10 mg L^{-1}) was used as a reference to calibrate the equipment. Instrumental precision for the Cd, Fe, Co, Cr, Mn, Ni, and Zn content was ascertained using NIST SRM 2709 (San Joaquim soil) as the certified reference material. Average recovery from the CRM was 103.82 ± 6.25%.

2.4 Humic substance extraction and characterization

Sediments were ground in a mortar and to pass through a 10-mesh sieve (2 mm). From sediment, HS were extracted according to the International Humic Substances Society (IHSS) method (Swift 1996); 10% (*w*/*v*) of sediment was mixed with a 0.5 M NaOH solution. The suspension was shaken for 15 h and separated from humin after 24 h of settling. The suspension was finally centrifuged at 10000 rpm for 10 min to separate the finest clay particles; separation onto humic and fulvic acids was avoided to provide the most realistic as possible HS mixture. In order to separate them from salt, HS were dialyzed by Serva Servapor HMF MWCO 2000 dialysis tubing, against deionized water at a 1/10 volume ratio. After 3 days of dialysis, the electric conductivity of the extract was less than 10 μS m^{-1}. The pH of the HS solution was adjusted to seven and the dialyzed HS were lyophilized using a Terroni Enterprise I lyophilizer and stored at 4 °C. Full HS characterization with IR and NMR can be observed in Pittarello et al. (2018).

2.5 Isotherms of Cu, Pb, and Cd adsorption

Metal adsorption experiments were carried out individually in both RB and MO sediments in order to evaluate the affinity of the natural binding sites to copper, lead, and cadmium.

Eighteen 15-ml Falcon tubes were loaded with 100 mg of 30-mesh-sieved sediment and 7 ml of a 0.002 mol L^{-1} $CaCl_2$ solution spiked with the following metal ion concentrations: 0, 50, 250, 500, 750, and 1000 mg L^{-1}, in triplicate. The pH was adjusted to 5.8 with 0.1 mol L^{-1} NaOH for the concentrations above 50 mg L^{-1}. Ionic strength was corrected with 0.1 mol L^{-1} NaCl for solutions with metal concentrations varying between 0 and 50 mg L^{-1}. This pH range was chosen to avoid precipitation of humic substances and metal at around pH 6.5 that may occur at concentrations from 250 up to 1000 mg L^{-1}. The tubes were agitated for 24 h in a SP

Labor ALB 260 H orbital shaker at room temperature (~ 25 °C), then centrifuged at 2000 rpm for 10 min in a KC8 Kindly centrifuge. The supernatant was separated, filtered, and analyzed by microwave plasma-atomic emission spectrometry (MP-AES Agilent 4200) to measure Cd, Pb, and Cu concentrations. Quantification was carried out at 324.5 nm for Cu, 405.78 nm for Pb, and 228.802 nm for Cd. Analytical curves ($R^2 > 0.999$) were constructed with six concentration points using Cu, Cd, and Pb standard solutions (Titrisol Merck). Certified reference material NIST SRM 2709 (San Joaquin soil) was employed to ensure measurement accuracy, and the average recovery was $102.55 \pm 3.28\%$.

Identical experiments, using sediments enriched with HS, were repeated to investigate the role of HS additions on the adsorption phenomena. For each experiment, the solutions in the Falcon tubes were also enriched with 0.7 mg L^{-1} of the previously extracted dissolved humic substance. This concentration corresponds to 4.9% of HS in the sediment (*w*/*w*) and was arbitrarily chosen to provide a noticeable increase in the organic carbon content for both investigated sediments, remaining close to maximum ranges already experimented in literature (Besser et al. 2003). This also permitted the MO sediment to reach the same organic matter content of the original RB sediment, verifying the possibility that this specific increase could cause differences in metal bindings between the two sediments. After the centrifugation and filtration steps, any dissolved humic substances remaining in the supernatant was degraded using a photochemical microwaved-assisted reactor (Umex UV-EL®) according to the procedure described by Sodré et al. (2004). This step was necessary to avoid matrix effects during metal determinations using the MP-AES.

All experimental data was used to construct adsorption isotherms for each investigated metal. In our microscale experiment, only one variable, such as presence/absence of added HS, was considered. In this context, empirical models with rational basis, such as Freundlich and Langmuir, were chosen to emphasize the role of external HS addition.

Freundlich and Langmuir equations were employed to fit the data and to provide adsorption parameters. Isotherms describe the adsorption dynamics and capacity of sorbents to evaluate the feasibility of this process and play an important role in adsorption systems analysis (Kumar and Bandyopadhyay 2006). The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces, as well as in multilayer sorption.

$$q = K_F C_e^{1/n} \tag{1}$$

Equation (1) represents the non-linear form of the Freundlich equation where q stands for the milligram of metal adsorbed per gram of sorbent, C_e represents the residual metal ion concentration at equilibrium in solution, K_F is the sorption capacity and can be associated with the sorption affinity of metal cations in solution for the sediment solid phase, while $1/n$ represents the sorption intensity. A variation in the slope ($1/n$) between 0 and 1 is associated with a chemisorption process, which is more heterogeneous as the value gets closer to 0. When a slope above 1 is observed, it is consistent with cooperative adsorption (De Sà et al. 2017).

The Langmuir model can be applied for ideal and homogeneous surfaces as well as monolayer sorption.

$$q = \frac{b\,K_L C_e}{1 + K_L C_e} \tag{2}$$

Equation (2) represents the Langmuir equation where b is the maximum adsorption capacity of the adsorbent surface (mg g^{-1}), and 퐿 (L mg^{-1}) can be related to the affinity of the binding sites (Ghosal and Gupta 2017) and to the energy of adsorption (Sheikhhosseini et al. 2013). The Langmuir and Freundlich non-linear curves were constructed using the software Origin 8 Pro (Origin Lab).

2.6 Statistical analysis

The Shapiro-Wilk test for normality and Levene test for homogeneity of variance were performed. One-way ANOVA and the Games-Howell or Duncan post hoc test, depending on homogeneity of variance, were performed. All analyses were carried out using the IBM SPSS Statistics v24.0.

2.7 Data availability

Map data copyrighted Open Street Map contributors and available from https://www.openstreetmap.org

3 Results and discussion

3.1 Sediment characteristics

The sampled sediment characteristics (0–10 cm layer) of the two studied sites are significantly different (Table 1). The MO area, characterized by 4 years old *Rhizophora mangle* and *Laguncularia racemosa* canopy (the two species employed in replanting), shows organic carbon content (2.61%) close to those of bare tidal flats (0.5–2%; Pons et al. 1982), while RB sediments present 7.46% organic carbon. This value may be due to stable and dense mangrove vegetation also comprised by *Avicennia germinans* (Petri et al. 2011). Differences in organic matter contents are consistent with data reported by Lacerda et al. (1995): they underline that *Avicennia schaueriana* provides a significantly higher contribution in organic carbon accumulation in the first 10 cm of the

Table 1 Sediment characterization: sediment chemistry of samples from RB (Rio Benevente) and MO (Maria Ortiz). Values are reported with standard error. Different letters indicate statistical differences

Sediment	pH cmol dm^{-3}	H^{+}+Al^{3+}	Al^{3+}	Ca^{2+}+Mg^{2+}	K^{+}	CEC	OC %	EC mS cm^{-1}	SSA m^{2} g^{-1}
RB	6.7 ± 0.1^{a}	4.89 ± 0.45^{a}	0.20 ± 0.00^{a}	11.50 ± 0.00^{a}	1.17 ± 0.05^{a}	111.5 ± 0.00^{a}	7.46 ± 0.06^{a}	2.386^{b}	17.443^{a}
MO	6.3 ± 0.1^{b}	1.88 ± 0.21^{b}	0.20 ± 0.00^{a}	10.00 ± 0.00^{b}	0.91 ± 0.01^{a}	95.88 ± 0.00^{b}	2.61 ± 0.12^{b}	5.778^{a}	9.846^{b}

superficial sediment layer in comparison with *Rhizophora mangle*.

The pH levels of both RB and MO sediments are subneutral (6.71 and 6.32, respectively), a condition favorable for precipitation and adsorption of metals (Belzile et al. 2004; Guven and Akinci 2013).

Marchand et al. (2011) stated that the Eh of mangrove sediments depend on the organic matter, granulometry, bioturbation, forest age, root system physiology, periods of water logging, and crab burrowing. Although there are differences in canopy age, texture, and organic matter content between the samples, measurements in fresh samples show for both MO and RB suboxic conditions (15 <mV> 30), while dried samples used in the experiment show a clear oxic condition (around 115 mV). In field conditions, considering more changing variables, the redox potential is fundamental to understand the metal adsorption dynamics, nevertheless working with small amount of sample, deionized water and "ceteris paribus" experimental conditions coupled with the predominance of added known metal ions on metal concentrations in the samples and their oxidative conditions, Eh measured on fresh samples might be misleading and will not be further considered in this discussion.

Potential acidity (Table 1) is significantly higher in RB sediment (4.89 cmol dm^{-3} H^{+}+Al^{+}) compared to MO sediment (1.88 cmol dm^{-3} H^{+}+Al^{+}). RB sediment is characterized by almost two times higher clay percentage (Table 2) than that of MO and by old dense mangrove vegetation; this is in agreement with Pons et al. (1982) who reported that potential acidity is built up predominantly in kaolinite-rich sediments in tidal flats below the mean high water level, with a dense mangrove vegetation. Potential acidity in RB sediment (Table 3) covers almost the 5% CEC versus the roughly 2% in MO. We argue that higher potential acidity in RB results from higher clay percentages and/or higher H^{+} concentration.

Electric conductivity (EC) is related to the content of major cations such as K, Ca, Mg, and Na that compete for the sorption sites with heavy metals and decrease the binding of metals to humic substances (Du Laing et al. 2009). MO sediment shows an EC that is 1.5 times greater than that of RB; this can be correlated to higher Na concentration as the other major cations are found in similar concentrations.

The specific surface area (SSA) is two times higher in RB samples and it appears to be more influenced by organic carbon and clay content than Fe content, due to the ability of Fe-(hydro)oxides, clay, and humic substances to bind to each other (Arias et al. 1996; Sei et al. 2002), increasing pore formation (Regelink et al. 2015) and the potential metal ion adsorption surface (Clark et al. 1998). The higher organic carbon and clay content in RB sediment might have been able to create more linkages between clay particles and humic substances than in MO sediment, and as a consequence increase the surface for ion adsorption. On the other hand, the higher Fe content and lower pH in MO sediment do not seem to balance the lower content of organic matter and clay in terms of specific surface area**.**

The two sediments were obtained from areas subject to different anthropic pressure and contamination so a direct comparison in accumulation of metals is incorrect; nevertheless, it is interesting to note that higher clay and organic carbon percentages and specific surface area (Table 1) are associated with significantly higher concentrations of Pb, Zn, Cr, and Mn in RB sediments (Table 2); only the Fe concentration is five times higher in MO sediment, probably due to its proximity to an Fe contamination source, while Cu does not show significant differences. Cd, Co, Mo, and Ni were below the detection limit in both sediments.

Table 2 Trace elements: concentration in sediment samples of RB (Rio Benevente) and MO (Maria Ortiz). Values are in mg kg^{-1} and the standard error is reported. Different letters indicate statistical differences

Sediment	Pb mg kg^{-1}	Zn	Cu	Cr g kg^{-1}	Mn	Fe
RB	22.97 ± 0.47^{a}	24.62 ± 2.43^{a}	29.80 ± 0.51^{a}	54.56 ± 2.69^{a}	181.45 ± 5.15^{a}	20.29 ± 0.80^{b}
MO	12.92 ± 0.73^{b}	12.24 ± 0.94^{b}	24.48 ± 1.76^{ab}	10.04 ± 0.66^{b}	n.d.	108.04 ± 4.4^{a}

Table 3 Sediment texture: clay, silt, and sand percentage in Maria Ortiz (MO) and Rio Benevente (RB) sediments. VC very coarse (2–1 mm), C coarse (1–1/2 mm), M medium (1/2–1/4 mm), F fine (1/4–1/8 mm), VF very fine (1/8–1/16 mm)

	Sand					Silt	Clay
	VC %	C	M	F	VF		
MO	2	9	32	26	8	6	17
RB	2	9	36	17	4	2	30

3.2 Metal isotherms

Copper adsorption (Fig. 2, Table 4) was characterized by progressive sorption saturation on sediment sites as evidenced by L-type curves (Giles et al. 1974; Sposito 2008). R^2 values indicated that the Freundlich model fits better than the Langmuir model, suggesting a heterogeneous distribution of sorption sites. HS addition increases the concentration of adsorption sites for both sediments as evidenced by higher values of b and K_F, although significant differences were only noticed for the parameter b in RB sediments. The addition of HS does not appear to have significantly altered the heterogeneity of binding sites, as can be observed from the values of $1/n$. The findings of Besser et al. (2003) were also in agreement with our results, which suggest that Cu is both adsorbed by sediment and complexed by soluble HS.

Stronger differences between soils with and without HS addition were observed for Cd sorption (Fig. 3, Table 4); C-type isotherms (Fig. 3a, c), characterized by a constant sorption variation, were noticed for both unaltered sediments. Binding sites for Cd were characterized by high homogeneity since this metal was poorly adsorbed by physisorption, especially on MO sediment which presents the highest $1/n$ value. The Langmuir model cannot be used to fit the experimental sorption data for the unaltered soils. On the other hand, the Freundlich model fits for both sediments with and without HS.

In sediments without external HS supply, Cd adsorption appears to occur more in a cooperative way ($1/n$ value close to 1) while the adsorption dynamic does not seem to be affected by differences in Fe and organic carbon concentrations.

Humic substance addition significantly increased the number of adsorption sites in both sediments, with large differences between MO and RB sediments ($K_{\mathrm{FRB}} = 6.72$; $K_{\mathrm{FMO}} = 1.21$), and as indicated by the $1/n$ values, the

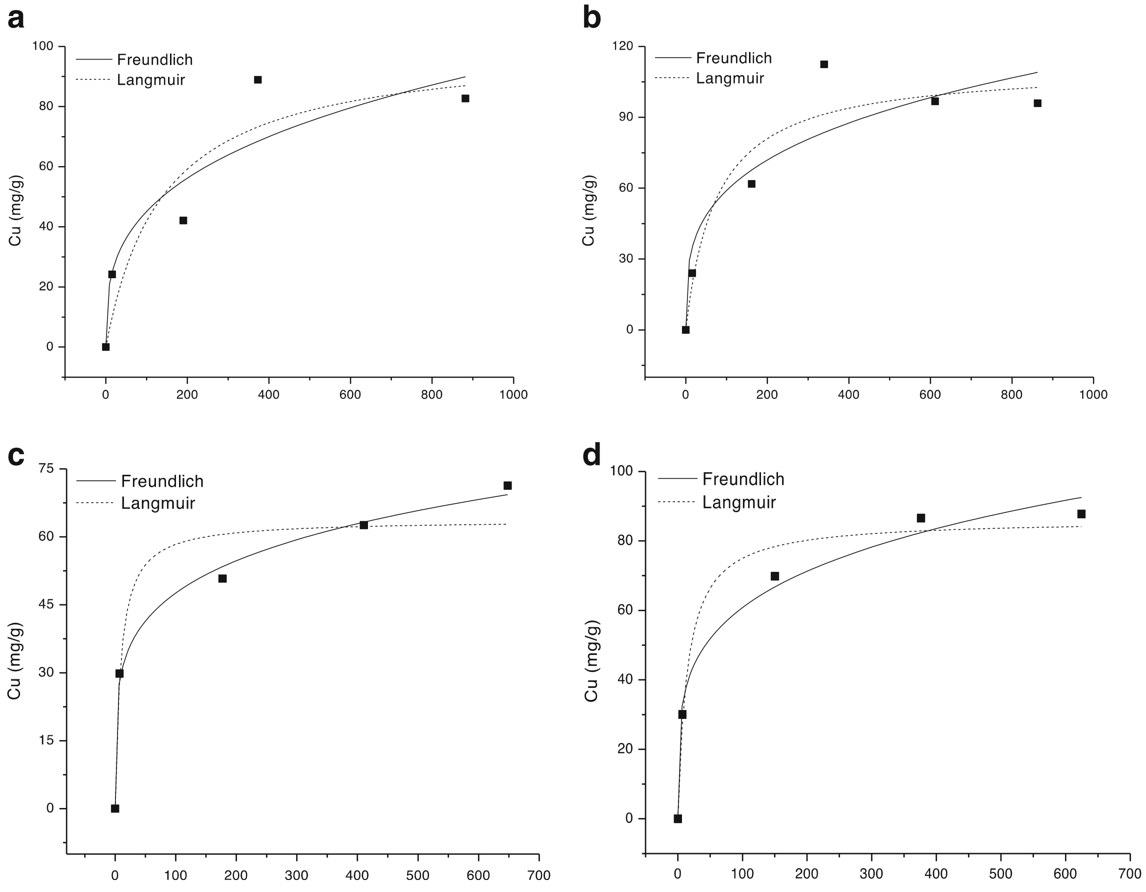

Fig. 2 Cu adsorption isotherms: Freundlich and Langmuir curves based on Cu adsorption isotherms of MO sediment (**a**), MO+HS (**b**), RB (**c**), and RB+HS (**d**). X axis: equilibrium concentrations (mg L^{-1}). Y axis: Cu adsorbed

Table 4 Isotherm equation parameters: parameters of the Freundlich and Langmuir equations. K_F = sorption capacity; $1/n$ = sorption intensity; K_L = affinity to binding sites; b = maximum adsorption capacity

Metal	Sediment	Freundlich parameters			Langmuir parameters		
		R^2	K_F	$1/n$	R^2	K_L	b
Cu	MO	0.851	10.48 ± 3.27	0.32 ± 0.13	0.835	0.01 ± 0.01	100.79 ± 27.27
	MO+HS	0.857	15.89 ± 10.58	0.28 ± 0.11	0.911	0.01 ± 0.01	111.63 ± 14.42
	RB	0.994	18.85 ± 1.95	0.20 ± 0.02	0.930	0.11 ± 0.06	63.67 ± 4.68
	RB+HS	0.987	21.16 ± 3.68	0.23 ± 0.03	0.976	0.07 ± 0.02	86.15 ± 4.09
Cd	MO	0.995	0.01 ± 0.01	1.25 ± 0.08	–	–	–
	MO+HS	0.996	1.21 ± 0.26	0.61 ± 0.03	0.979	$0.01 \pm 5 \times 10^{-4}$	143.96 ± 32.20
	RB	0.869	0.09 ± 0.02	0.96 ± 0.38	–	–	–
	RB+HS	0.856	6.72 ± 1.29	0.34 ± 0.13	0.888	0.01 ± 0.01	69.87 ± 10.78
Pb	MO	0.958	44.04 ± 16.69	0.39 ± 0.07	0.982	0.01 ± 0.004	530.89 ± 44.61
	MO+HS	0.958	38.57 ± 14.58	0.37 ± 0.07	0.964	0.04 ± 0.01	326.81 ± 29.56
	RB	0.970	54.65 ± 11.21	0.21 ± 0.04	0.971	0.05 ± 0.02	205.24 ± 11.14
	RB+SH	0.941	64.45 ± 18.36	0.23 ± 0.05	0.992	0.07 ± 0.01	264.01 ± 7.35

heterogeneity of their distribution coupled with a clear change from a Cd cooperative adsorption to a chemisorption. Our results seem to be confirmed by Postma et al. (2007) who demonstrated that Cd presents a high affinity for dissolved humic acids and that Cd ions form complexes with dissolved humic acid at low and very low pH; on the other hand, in our experiments, these phenomena also appear to happen at sub-neutral pH (5.8).

The K_F and n values in the Freundlich equation for samples supplemented with external HS suggest that HS interaction

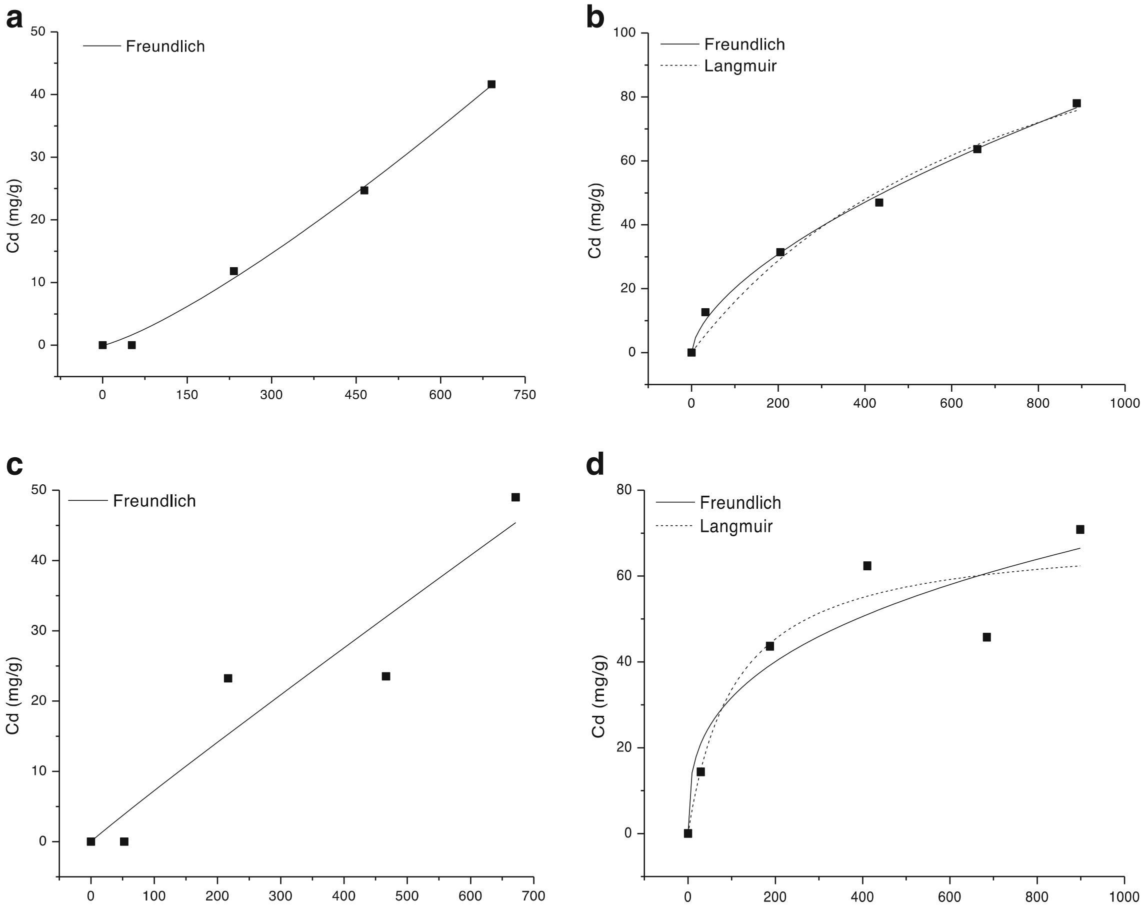

Fig. 3 Cd adsorption isotherms: Freundlich and Langmuir curves based on Cd adsorption isotherms of MO sediment (**a**), MO+HS (**b**), RB (**c**), and RB+HS (**d**). X axis: equilibrium concentrations (mg L^{-1}). Y axis: Cd adsorbed

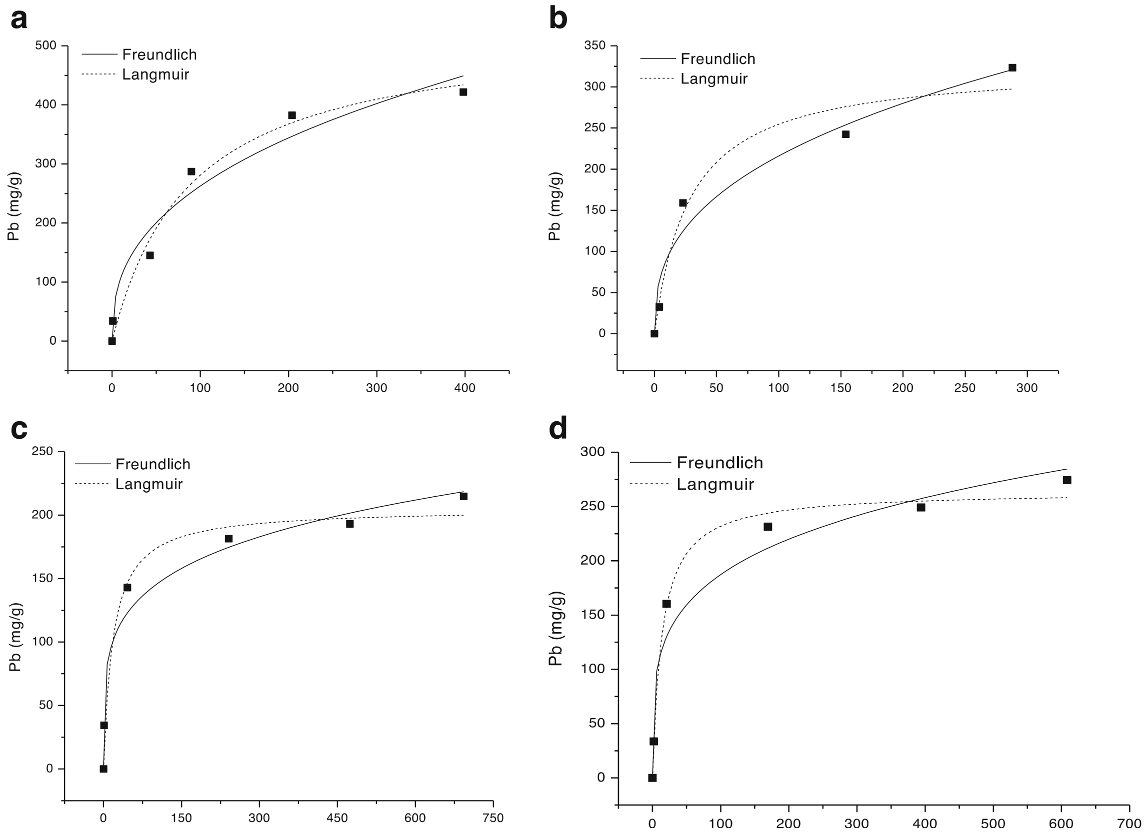

Fig. 4 Pb adsorption isotherms: Freundlich and Langmuir curves based on Pb adsorption isotherms of MO sediment (**a**), MO+HS (**b**), RB (**c**), and RB+HS (**d**). X axis: equilibrium concentrations (mg L^{-1}). Y axis: Pb adsorbed

with clay plays the main role in Cd adsorption and therefore the higher K_F, considering that MO sediment shows Fe concentration five times higher than in that of RB but a clay percentage almost 50% lower. Wijaya et al. (2016) suggested that Cd solubility aids Cd adsorption onto HS as organic particulate in sediment and confirmed that the adsorption capacity of the sediment is increased by organic matter contents. Our results support this conclusion when considering that the sediment with higher organic carbon percentage (RB) seems to magnify the effects of adding HS, in terms of K_F values.

Lead interacts strongly both with clay and organic matter and its affinity with sediment is augmented by the specific surface area more than for Cu and Cd (Clark et al. 1998; Ladonin and Plyaskina 2004); decrease in the maximum adsorption capacity (Fig. 4b) in MO+HS could be a consequence of the coverage of several active sites by HS, which on the other hand augmented Pb affinity for binding sites (K_L). Finally, in MO sediment, the HS addition caused a decrease in active sites but an increase in the binding force. In agreement with our results, Taillefert et al. (2000) and Lyven et al. (2003) reported that a heavy metal like Pb is directly bound to colloidal Fe-oxyhydroxides that are stabilized by an organic matrix. It is interesting to note that despite the decrease of K_F and K_L in MO+HS, the adsorption capacity remains three and two times higher than those of Cu and Cd, respectively.

In RB sediment, both K_L and b increase with HS addition; the lower maximum adsorption capacity in RB sediment than in MO sediment is probably explainable considering the lower Fe concentration partially balanced by higher specific surface area with HS addition increases the total number of active sites.

In both sediments, the K_F and K_L values are significantly higher than those recorded for Cu and Cd, underling the high affinity of Pb for the sediment surface irrespective of the sediment characteristics.

4 Conclusions

Two mangrove sediments with significantly different Fe, clay, and organic carbon contents, in the presence of Cd, Cu, and Pb concentrations up to 1000 mg L^{-1}, show different behaviors in terms of adsorption dynamics and ion affinity for soil active sites. The RB sediment sample shows greater higher affinity for all three ions, confirming higher capacity for metal retention in field conditions. When adding HS, extracted from RB mangroves, roughly equal to the difference between the two sediments, Cd completely changed its adsorption dynamic, from a cooperative to chemisorptive mode and significantly increased its affinity for the soil particle surface; copper and lead, due to their high affinity with every soil surface, did not show impressive changes although Cu increased its K_F and Pb presented a decrease in the b value in MO sediments.

This experiment simulated on a microscale an event of quick and high pollution of mangrove waters: in the studied conditions, starting from the isotherm model parameters, two main factors are found that affect soil responses to metal retention: ion affinity for active sites and sediment surface; the artificial addition of HS experimented in this work suggests a linear increase in sediment adsorption and complexation capacity of Cu and Cd; while Pb retention seems to depend more on clay content, one of the three main factors enhancing the specific surface area. However, a humic substance content increase simulates a desirable evolution of superficial sediment layer and suggests a desirable mix of species with the presence, where feasible, of *Avicennia spp*. The Fe content, due to the great difference in concentration between the two sediments, may be considered another important factor due to its capacity to form spheroids linked to HS molecules on the clay surface and increase the adsorbing surface area. Nevertheless, the influence on specific surface area and consequently, on sediment adsorption potential, appears to depend more on other factors in the following order: HS > metal > granulometry > Fe content.

This study can help to understand what we have to expect during a restoration and/or evolution period of a mangrove forest, in case of pollution events, starting from peculiar sediment characteristics. Many works have been carried out with regard to the role of humic matter for metal retention in sediments, but due to the many variables and different kinds of pollutants and pollution intensity, we believe more studies are needed on the microscale, mesoscale, and possibly in field conditions.

Acknowledgements The authors thank Dr. Evan Visser for the English revision.

Funding information The FAPES (Fundação de Amparo a Pesquisa do Espirito Santo/Espirito Santo State Foundation for Support to Research) has provided funds for M. Pittarello (process 69729913/2015), P. Carletti was financially supported by the University of Padova DOR1883089/18, and F. F. Sodré thanks the CNPq (480410/2012-7).

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