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Copper and Mercury Complexing Capacity of Organic Matter From a Mangrove Mud Flat Environment, Sepetiba Bay, Brazil

S. Mounier,[1] L. D. Lacerda,[2,3] R. V. Marins,[3] J. Bemaim[1]

[1] Laboratoire RCMO, Université de Toulon et du Var, BP 132, 83957 La Garde Cedex, France
[2] Departemento de Geoquimica, Universidade Federal Fluminence, Niteroí, Rio de Janeiro, Brazil
[3] Departemento de Geologia, Universidade Federal do Ceara, Fortaleza, CE, Brazil

The biochemistry of trace metals in mangrove environments has raised special attention due to the in potential role of sediments in mangrove forest as both sinks and sources of these pollutants. Harbinson 1986 a, b) and Lacerda et al (1988, 1991) reported mangroves as sinks for metals such as Cu, Zn, Cd and Pb and this property has been incorporated into coastal management planning to cope with metal smelter effluents (Lacerda 1998), oil production wastewaters (Grosso et al. 1996) and landfill leachates (Tam and Wong 1996; Clark et al, 1997). For some metals however, mangroves were shown to act as sources, such as for Mn (Carvalho et al. 1999) and Hg (Lacerda et al. 2000). The export/import rates of trace metals to and from mangroves are dependent on the reaction between the metal and the physical and chemical properties of pore waters, in particular redox reactions and complexation with organic matter. Pore water chemistry has been demonstrated to strongly affect surface waters, in particular when tidal waters flood across the sediment surface and pore water fluxes up and out from the surface of sediments (Wollanski et al. 1992). This phenomenon has been shown to enrich tidal waters in nutrients and dissolved organic carbon (Ovalle et al. 1990; Mazda et al. 1990), Mn and Hg (Carvalho et al. 1999; 2000). Notwithstanding the importance of metal complexation with organic matter to the trace metal organics in mangroves, few studies characterized the ability of mangrove organic matter to complex trace metals.

In the present study, we investigate the complexing capacity of organic matter in pore water tidal waters, for two contrasting metals Cu and Hg, for which mangrove sediment have been reported as a sink and source, respectively (Lacerda 1991).

MATERIALS AND METHODS

The study was done at the Itacurussa Experimental Forest (IEF) located along the north shore of Sepetiba Bay, approximately 100 km from Rio de Janeiro (23°S ; 44°W) The IEF is a fringe mangrove forest dominated by *Rhizophora mangle* which receives trace metal from moderately contaminated Sepetiba Bay tidal waters (see Lacerda et al. 1988 for a review). Two types of samples were collected at IEF. First, interstitial water were sampled in two field campaigns by inserting vacuum

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Correspondence to: S. Mounier

containing micro porous ceramic (0,7 μm) capped PVC tubes at different depth (5, 10, 20, 30, 40 and 50 cm) in one place into the sediment . Tidal waters (TW) were collected during a flooding event at the edge of the mangrove forest by placing seven polyethylene bottles fixed to a rod at 10 cm intervals from the sediment surface. When tidal waters full the flask, they are capped. All samples were duplicated and preserved by 100 μL spike of NaN_3 (1M) for 100 mL of sample. During transport samples were maintained at 4°C. Complexing capacity and total organic carbon were determined in a 2 month limit from sampling.

Total Organic Carbon (TOC) was done on a TOC5000 Shimadzu auto analyzer, after acid spike and oxygen bubbling for inorganic carbon (IC) removal. Sample were oxidized on platinum catalytic surface, a non-dispersive detector measured the produced carbon dioxide. Calibration curves were constructed with phthalate acid standards.

We measured the Hg complexing capacity by fluorescence quenching (CCFQ) using the quenching properties of paramagnetic metal (Ryan and Weber, 1982). Fluorescent organic matter was observed on a LS2 Perkin Elmer at an excitation wavelength of 366 nm and an emission wavelength of 450 nm. For 10 mL sub-sample, 1 mL of $NaNO_3$ (5M) was added to adjust ionic strength, and pH was maintained at about 8.0 by adding 1 to 2 mL of borate buffer. When adding volumes of Hg solution of known concentration, the fluorescence intensity decrease (the organic-Hg complex being less fluorescent than the organic matter alone). By assuming a 1:1 complexation model, it's possible to determine the complexing capacity of the sample. The Chau method (Chau, 1974) was used, although lacking precision, its high reproducibility allows robust comparison between samples.

The Cu complexing capacity (CCV) was determined by DPASV (differential Pulse Anodic Stripping Voltametry). Voltametry is a useful technique for the determination of low concentration of this metal (Weber, 1988). The procedure was similar to Hg, by adding volumes of Cu solution of known concentrations in the sample, and detecting the electro-labile copper, which is not complexed to the organic matter. Ionic strength and pH were adjusted as for Hg. A -400 mV deposition potential was used to avoid complex destruction (Weber, 1988). Scanning potential from -300 mV to 50 mV allowed the determination of the electro-labile copper. Like in CCFQ the Chau method was used to determine the complexing capacity of copper, using a 1:1 model. Total dissolved Hg concentrations were measured by atomic fluorescence spectroscopy in a Tekran 2500 AFS detector. Total dissolved copper concentrations were determined by DPASV in a metrohm 663 VA Stand. Details for the both methods are published elsewhere (Carvalho et al. 1999; Boussemart et al. 1989).

RESULTS AND DISCUSSION

Table 1 compares major chemical data from pore and tidal waters from the IEF samples. As expected, TOC concentrations are higher in pore waters, as well as Cu and Hg complexing capacity and Hg concentration. In contrast, Cu

concentrations were higher in tidal waters. The range of values of all variables measured in tidal waters is similar to those generally reported for coastal waters

Table 1. Dissolved organic carbon and Cu and Hg complexing capacity in tidal and pore waters.

	DOC (mg C.L^{-1})	Cu CC by DPASV µmol Cu.L^{-1}	Hg CC by Fluorescence quenching µmol Hg.L^{-1}	Hg (ng.L^{-1})	Cu (ng.L^{-1})
Pore Waters	4.42 - 123.4 (n=14)	8.0 - 39.3 (n=6)	5.7 - 54.8 (n=5)	<0.02 - 246 (n=11)	< 0.1 (n=5)
Tidal Waters	1.02 - 5.85 (n=12)	1.5 - 9.1 (n=12)	5.4 - 14.3 (n=7)	0.04-1.30 (n=17)	<0.1- 0.7 (n=7)

(Antelo 1998, Lacerda et al. 2000, Ovalle et al. 1991). However, comparison with pore water studies is difficult due to the highly site-specific nature of pore waters and the inexistence of such studies in mangrove dominated environments. When plotting Hg versus Cu complexing capacities for all samples, the two groups of water type appear very clearly distinct (Figure 1). Tidal waters flooding the mangroves from Sepetiba Bay exhibit a very small range in complexing capacity for both Hg (5.4-14.3 µmol.L^{-1}) and Cu (1.5-9.1 µmol.L^{-1}). The two variables are significantly positively correlated in tidal waters (Figure 1). This suggests the same origin of organic matter to tidal waters. Rezende et al. (1990), based on ^{13}C content of IEF tidal waters, also suggested a common origin of this organic matter in the phytoplankton productivity of Sepetiba Bay. Interstitial waters, on the other hand, exhibit a large range in complexing capacity for Cu (8.0-39.3 µmol.L^{-1}) and Hg (5.7-57.8µmol.L-1), but the two variables show no correlation (Figure 1).

The vertical profile of the metal complexing capacities and of TOC are shown in Figure 2. In tidal waters, samples collected close to sediments (which also represents the first tidal waters to contact the mangrove mud flat), represented the highest values of all values measured. Above 30 cm of depth, tidal waters represented lowest and constant values for all variables. In pore waters, TOC increase to very high concentrations in sediments less than 30 cm of depth, reaching a peak of 66 mg of C L^{-1} at 10 cm of depth. This concentration gradient suggest an upward diffusion of organic carbon from pore waters to tidal waters. Organic matter complexing capacity of the two sub-environments are very different. Complexing capacity for Hg and Cu seems to be inversely correlated in pore waters but significantly positively correlated in tidal water. When organic matter in pore water is Hg complexed the Cu complexing capacity is low. Apparently, at 50 cm depth, Hg (probably as Hg^{2+} Marins et al. 2000) is strongly trapped by organic matter.

Organic matter may be trapped by resurgent water from the bottom sediment, moving from the bottom to the surface. During upwelling, the organic matter may be oxidized/transformed and releases mercury at the surface. Extreme gradients of Hg concentration with near surface concentration of up to two orders of

magnitude higher have been reported in these pore waters (Marins et al. 2000). Organic matter in deep pore waters could be very enriched in sulfide based complexing sites. In fact, below 30 cm depth, pore waters are highly sulfidic (up
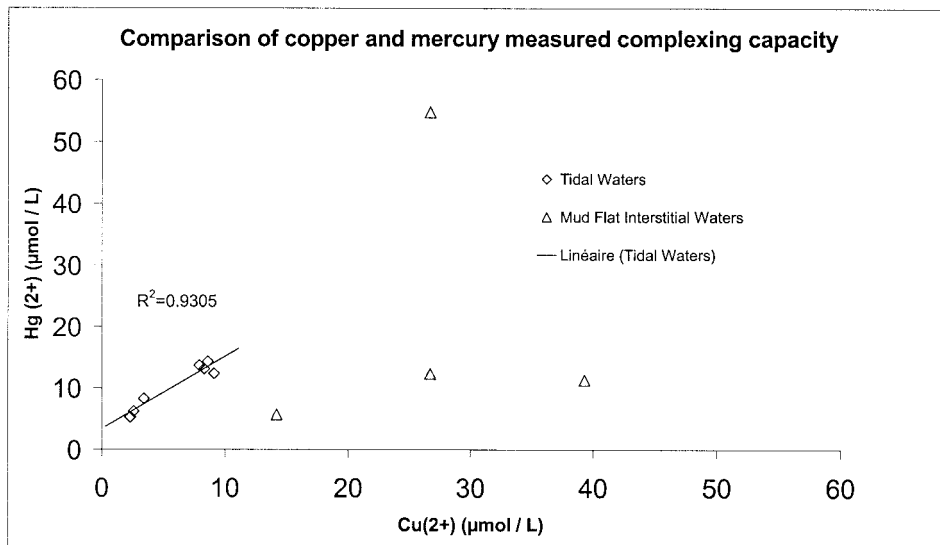
Figure 1. Comparison between complexing capacity for copper (by voltametric method) and for mercury (by fluorescence quenching method). For surface and pore water. Correlation for the low values is $r^2=0.9305$
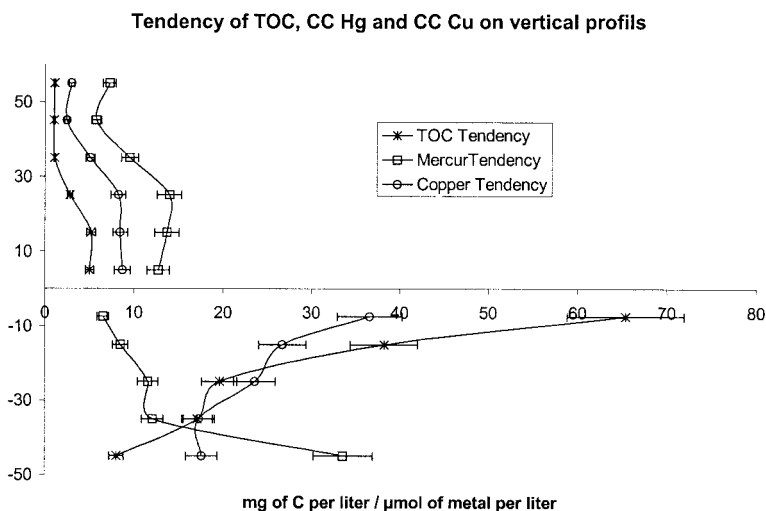
Figure 2. TOC and complexing capacity for mercury and copper tendency profile for tidal and pore water.

to 277 $\mu mol.L^{-1}$) due to the dominance of sulfate reducing metabolism at this depth. Boulegue et al. (1982) and Marins et al. (1997) suggested that under such conditions Hg would be preferentially complexed with thiol groups, by-products of this metabolism, and be fluxed upward. By oxidation, these sites could be transformed into oxygen based sites. Based on the hard and soft bases theory, the oxygen based sites show higher Cu affinity than sulfur based ones, found in deeper layers, which have higher Hg affinity.

We hypothesize that post depositional changes in the organic matter are responsible for the different complexing capacities of organic matter, which results in a different migration pattern between Hg and Cu which results in layer accumulation of Cu relative to Hg in mangrove environment.s.

By using complexing capacitiy methods, some evidence was shown of a different mechanism of transport of Cu and Hg in the mangrove systems. The Hg complexing capacity determined by fluorescence quenching method compared to the voltametric one for copper led to an original result: organic matter from the mud flat surface is more able to transport Cu ions than deep sediment one and inversely for Hg. By this way, the hypothesis of a resurgence of heavy metals from bottom sediments and transport by high complexing leaching waters is consistent with the organic carbon concentration profile and measured complexing ability. The difference between Cu and Hg behavior is also confirmed. Similar results have been reported for sediment cores from both mangroves and salt marsh areas (Marins et al. 1997; Lacerda et al. 2000).

Based on these assumptions and on the contrasting behavior of Cu CCV and Hg CCFQ, we can hypothesize that carboxylic complexing sites dominate organic matter at the surface and thiol compllexing sites dominate lower sediemnt depth as proposed previously by a few similar studies.

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