

Effect of Root Metabolism on the Post-Depositional Mobilization of Mercury in Salt Marsh Soils

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Received: 13 August 1996/Accepted: 13 January 1997

Salt marsh soils are an efficient sink for trace metals associated with particulate material in tidal waters (Nixon, 1980; Long & Mason, 1983) and have been proposed as monitors for trace metal contamination in coastal areas (Taylor, 1979), on the basis that vertical profiles provide a record of loading rates. However, the complex nature of the biogeochemical processes occurring in these soils, may prevent this use, since post-depositional mobilization of some trace metals may occur, resulting in their release to pore water, vertical movement through the soil column and exchange with overlying waters (French, 1993; Rasmussen, 1994).

Salt marsh soils are generally anoxic just below the surface, due to the consumption of oxygen in the microbial oxidation of organic matter and the poor oxygen diffusion down the soil profile. The bacterial metabolism of such soils is based on sulfate reduction (Ponnamperuma, 1972; Sikora & Keeney, 1983). Sulfide is the main product of sulphate reduction. The formation of sulfides in salt marsh soils will not only remove metals from solution, but will hold the metals in a manner that may permit their later release back into pore waters, if soil environmental conditions render deposited sulfides unstable (Feijtel *et al.*, 1988).

Plants growing on waterlogged soils avoid the toxic effects of anoxia by creating oxidized rhizospheres through oxygen translocation via well developed aerenchyma, and exudation by roots (Armstrong, 1978; Lacerda *et al.* 1993). Therefore the creation of oxidized microenvironments within an anaerobic soil, may result in the post-deposition mobilization of various substances, including trace metals, in particular those like Hg which form sulfides under anoxic, sulfidic conditions, typical of salt marsh soils (St-Cyr & Crowder, 1990; Tanizaki, 1993; Lacerda *et al.*, 1993).

Engler & Patrick (1975), demonstrated that sulphur from FeS, ZnS and CuS in anaerobic, reduced soils, was oxidized in the soil adjacent to the growing roots of rice plants and taken up. The degree of uptake was directly related to the solubility of the sulfides. In the case of Hg, the possibility of the formation vapor phases (Hg and di-methyl-Hg) and dissolved organo-Hg²⁺ and organosulfida-Hg²⁺ complexes, may facilitate remobilization through the soil column, if Hg sulfides are dissociated due to changes in the soil environmental conditions (Rasmussen, 1994), resulting in altered concentration profiles that will not provide information on Hg loading rates.

This paper presents and compares the vertical profiles of Hg in soil cores taken

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under a *Spartina alterniflora* Loisel. marsh and in adjacent mud flats without plant cover, in order to characterize the role played by this plant on the post - depositional movement of Hg through the soil column and on the possibility of using such profiles as indicators of Hg loading rates in coastal areas.

MATERIALS AND METHODS

The study was carried on in Sepetiba Bay salt marshes in March, 195. Sepetiba Bay is a moderately polluted bay approximately 60 km South of Rio de Janeiro City, SE Brazilian coast (Lat. 22°S, Long. 44°W). We selected two adjacent sites at the seaward edge side of the marsh. Both sites are subjected to the same pollution sources and show the same granulometry, inundation pattern and salinity regime. Four cores were collected in each area by inserting 60 cm long plastic tubes (9 cm in diameter) into the soil. Two additional cores were taken for organic matter content and root biomass determinations. Cores were immediately taken to laboratory and sliced no later than 6 hours from sampling.

At root depth (2 -10 cm), cores were dug in the soil and pore water was collected through a corer filled with vacuum and a porous ceramic cap, for the *in situ* determination of pH and platinum electrode redox potential, using portable electrodes. While there are inherent difficulties in interpreting Eh values determined with platinum electrodes, these values may provide a rapid and useful technique for evaluating the redox status of waterlogged soils (Sikora & Keeney, 1983). Sulfide concentrations were determined in pore waters fixed in the field with ZnOAc 5N and determined calorimetrically according to the method described in Lacerda *et al*, (1993).

Root biomass was determined by carefully sieving core slices in a 1 mm mesh nylon sieve. Dead or senescent roots were not considered. Organic matter content was determined gravimetrically after combustion at 450 °C for 16 hours (Tanizaki, 1993). Mercury concentrations in soil layers were determined after acid extraction and stannous chloride reduction, by cold vapor atomic absorption spectrophotometry, following standard procedures described in Gonçalves (1993). Reagent blanks and intercalibrated sediment samples provided by the Institute of Soil Fertility Research, Holland, were run simultaneously for precision determination of the methods used. All blanks gave Hg concentrations smaller than 30% of the lowest Hg concentrations found in samples. Intercalibration with reference samples gave values within 10% of the reported concentration.

RESULTS AND DISCUSSION

The redox potential, pH, and sulfide concentrations in pore waters collected at the root zone layer of the soil profiles, as well as organic matter content of this layer, are presented in table 1. The vertical distribution of Hg in the soil cores (mud flat and *Spartina*) and the biomass of roots are presented in Figure 1. Only average Hg concentration values from the four cores sampled are plotted. Standard deviation of the means however, were always less than 20%. Root biomass data are averages of two samples, minimum and maximum values for this variable were within 2%.

No significant difference in organic matter distribution through the cores was found. Therefore, although deposited organic matter presents high chelating and cation exchange capacity for trace metals, and some studies reported its influence upon

vertical distribution of trace metals in salt marsh soils (Taylor, 1979; Allen *et al.*, 1991; Graham *et al.*, 1993), our results show no influence of the distribution of organic matter on Hg distribution along the cores. Organic matter content at root layer depth (2.0 to 10.0 cm) ranged from 13.0 to 16.3 % along the *Spartina* core and from 16.8 to 20.8 % along the mud flat core. This suggests faster oxidation and less accumulation of organic matter in the *Spartina* core. The higher Eh and lower sulfide concentrations support the hypothesis of faster oxidation of organic matter under the conditions found under *Spartina* relative to mud flat soils. The pH distribution was also similar between the two cores, remaining close to 7.0 throughout both cores.

Table 1. Range of concentrations of organic matter in sediments and average Eh and pH and sulfide concentrations in pore waters from cores depths between 2.0 and 10.0 in mud flat and *S. alterniflora* soils from Sepetiba Bay, SE Brazil.

	Mudflat soil	<i>Spartina</i> soil
Organic matter (%)	13.0 - 16.3	16.8 - 20.8
Eh (mV)	-204 ± 95	+5 ± 102
pH	7.1 ± 0.3	6.9 ± 0.2
Sulfide (mg.l ⁻¹)	47.0 ± 16.0	0.6 ± 0.1

Mercury distribution was significantly different between the two cores, for most of the depths sampled. At the surface of cores, both soils presented low Hg concentrations, suggesting a release of Hg to the overlying waters. Mechanisms responsible for this could include the release of Hg from biogenic particles during organic matter decomposition, which is more intense on the soil-water interface; the cation exchange and Hg leaching due to sea water washing; and the resuspension of very fine, relatively Hg-richer particles due to the intertidal conditions of the samples. All these may account for the observed decrease in Hg concentrations in the first 1 cm of the soil profiles, since they would affect both vegetated and non-vegetated soils irrespectively. After an initial increase in concentrations in both cores, Hg distribution from 2 to 10 cm of depth as significantly different between the two cores. Mercury concentrations in *Spartina* cores significantly decreased from 148 to 58 mg.kg⁻¹ along this depth layer, whereas in the mud flat cores Hg concentrations increased from 113 to 137 mg.kg⁻¹. The decrease in Hg concentrations from 2 to 10 cm in the *Spartina* core occurred with an increase in root biomass from 0.20 g at 2.0 cm to 1.5 g at 10 cm of depth.

Between 2.0 and 10.0 cm in depth, oxygen excretion by *Spartina* roots results in a relatively oxic environment, although reducing conditions can also be developed. Typically, Eh values at this depth ranges from -110 to +110 mV, with an average of +5 mv (n=15) under *Spartina*. The excretion of oxygen also results in low concentrations of sulfides (average of 0.6 mg.l⁻¹, n=10). In the mud flat cores however, reducing conditions are dominant with Eh values ranging from -110 to -300 mV and an average of -204 mV (n=15). Sulfide concentration in pore water is very high reaching an average of 47 mg.l⁻¹ (n=10) (Table 1).

Beneath the soil - water interface, Hg concentrations are sulfide dependent and, at

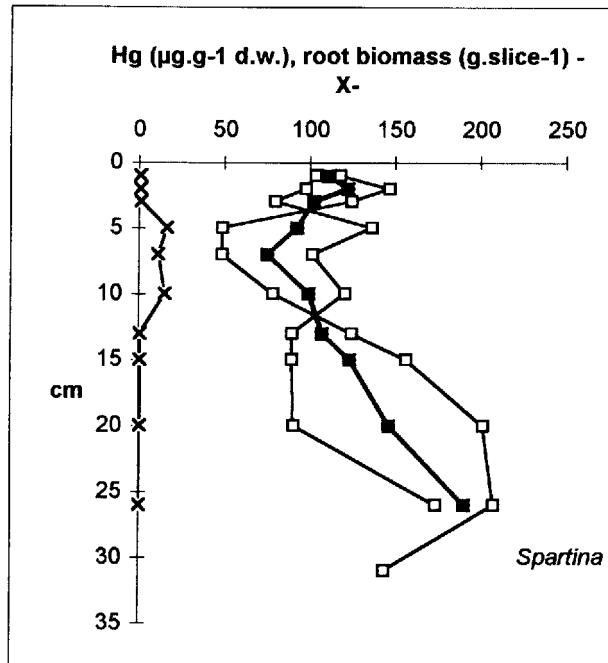
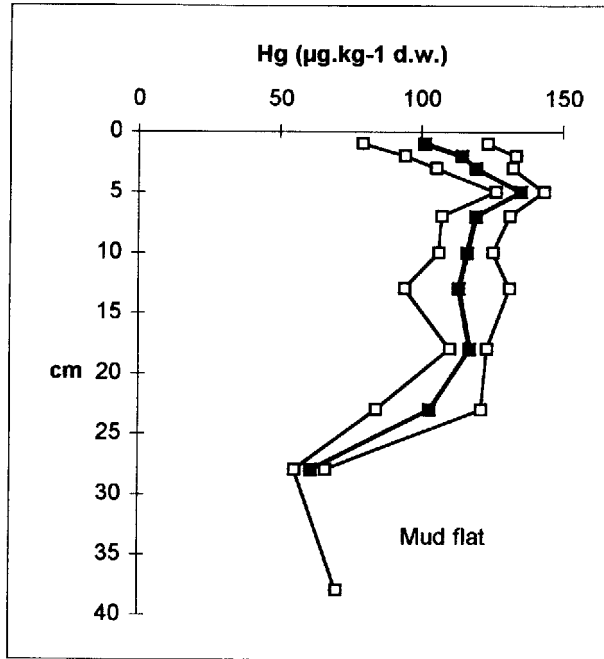


Figure 1. Vertical distribution of Hg in sediment cores collected under *Spartina alterniflora* marsh and unvegetated mud flat soils in Sepetiba Bay, SE Brazil. Values are means obtained for the same depths from four different cores collected in each site.

pH 7 and 1mM to 10 mM sulfide, Hg may precipitate as HgHS_2 and HgS_2 (Dyrssen, 1985) or coprecipitate with FeS and polysulfides (Boulegue *et al.*, 1982), starting to accumulate below this depth (Gaillard *et al.*, 1986; Feijtel *et al.*, 1988; Lacerda *et al.*, 1993). These conditions are permanently found in the mud flat soils but only occasionally under *S. alterniflora*. When anoxic conditions shift to oxic, metal sulfides dissociate. Once in pore water, metals may be complexed with water soluble organic substances and migrate through the soil column (Sikora & Keeney, 1983). Organo-sulfur molecules, which are particular resistant to oxidation and are enriched in salt marsh soils, may play an important role in the complexation, solubilization and diffusion of metals in particular of Hg (Boulegue *et al.*, 1982; Rasmussen, 1994).

Below 10 cm, Hg concentrations under *Spartina* increase with depth, from 56 to 177 mg.kg^{-1} , whereas in the mud flat cores Hg concentrations decrease from 137 to 68 mg.kg^{-1} . Since living *Spartina* roots in the studied area are restricted to the first 10 cm of soil, we assume dominant anoxia below this depth in both cores, although pore waters were not collected below 10 cm. However, other studies carried out in this site showed anoxia below the root layer (Gueiros *pers. comm.*), and this condition seems typical of salt marshes worldwide (Long & mason, 1983). Considering anoxia below root depth would suggest that the root zone layer of the *Spartina* core acts as a source of Hg to deeper layers, whereas at the mud flat soil the stability of Hg-precipitates, probably sulfides, would impede the diffusion of Hg to deeper horizons.

The effects of the metabolism of the salt marsh roots clearly result in the post-depositional mobilization of Hg. The dynamic oxic-anoxic conditions at the root depth hampers the immobilization of Hg as Hg-sulfides, resulting in the migration of soluble Hg up and down the core, and a clear enrichment at deeper layers. In the mud flat cores permanent reducing conditions result in a gradual accumulation of Hg in sub-surface layers of the sediment, and a decrease in concentrations at deeper layers, since most of the accumulation is probably of stable Hg sulfides.

In conclusion we have shown here that salt marsh plants are able to mobilize deposited Hg through the exudation of oxygen to the soil thus avoiding the development of permanent reducing conditions and the consequent immobilization of Hg as stable sulfides. Mercury remobilized through this mechanism later accumulated in deeper layers of the sediment. The metabolism of salt marsh plants induces significant changes in the Hg profile of these sediments, avoiding its correlations with loading rates. Also, since *Spartina alterniflora* is an annual species, it may create short term variability in the depositional profiles of Hg in salt marsh soils, hampering its utilization as monitors of Hg deposition and accumulation in coastal areas.

Acknowledgments. This work was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and CAPES, Brazil.

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