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## Trace metal retention in mangrove ecosystems in Guanabara Bay, SE Brazil

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## Abstract

Along contrasting environmental conditions (e.g., degree of trace metal contamination and mangrove forest structural development), sediments of Laguncularia racemosa-dominated mangrove stands in Guanabara Bay (SE Brazil) presented a trend of trace metal accumulation in forms with low potential of remobilization and biotic uptake. Concurrently, a relatively low transfer of sediment-bound metals to L. racemosa leaves was observed, which may moderate the metal export from the forests via leaf litter transport and the metal availability to enter in food chains based on leaf consumption. 2002 Elsevier Science Ltd. All rights reserved.

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The potential role of mangrove ecosystems as sinks for anthropogenic contaminants in tropical and subtropical areas has been widely recognized. There are several evidences derived from field surveys and controlled experiments of trace metal contaminants retention by sediments colonized by mangrove vegetation (Harbison, 1986; Lacerda et al., 1991; Badarudeen et al., 1996; Tam and Wong, 1996; Clark et al., 1998). It is interesting to note that most studies generally demonstrate a relatively small transference of sediment-bound metals to mangrove plants (Ragsdale and Thorhaugh, 1980; Silva et al., 1990; Chiu and Chou, 1991; Sadiq and Zaidi, 1994). This suggests a trend of small metal export from mangrove forests through plant detritus (Lacerda et al., 1988; Silva et al., 1998), as well as a small contamination of food chains based on mangrove standing biomass and detritus. However, whether metals are available for the uptake by mangrove trees and to what extent metals are transported out of mangrove forests are still debatable (Peters et al., 1997). Even if the plant material is poor in trace metals, substantial amounts of mangrove detritus can be exported from the forests to the surrounding communities, counterbalancing the low metal concentrations (Peters et al., 1997).

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It is necessary to assess the processes responsible for trace metal retention in mangrove ecosystems, but many operational limitations (including logistic, analytical, and time-scale efforts) may difficult the evaluation and monitoring of trace metal retention at the ecosystem level. Relatively simple efforts may be conducted to assess the metal retention capacity of mangrove ecosystems by determining the proportion of operationallydefined metal concentrations in sediments in forms potentially available to remobilization (through fractionation procedures). In addition, the determination of metal concentrations in mangrove plants and litter may be used to evaluate the potential of metal loss from the forest through detritus export.

We have studied the trace metal retention in mangrove ecosystems of different environmental settings of Guanabara Bay (Rio de Janeiro State, SE Brazil), a 483 km<sup>2</sup> eutrophic waterbody, affected by several urban and industrial sources of metal contaminants (Kjerfve et al., 1998). Here we present data on the ability of mangrove sediments, mainly colonized by *Laguncularia racemosa* (L.) Gaertn., retain trace metals (Zn, Pb, Cu, Ni, and Mn) in forms with low availability to remobilization and biotic uptake. It is also discussed how much L. racemosa trees transfer such elements from sediments to their leaves, as a potential mechanism whereby plants may turn the metals accumulated within sediments available to export through litter transport.

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Table 1 Structural characteristics of studied mangrove forests

Station	Tree height $(m)$	Tree density (no. / ha)	Basal area $(m^2/ha)$		
GМ	5.0	1.016	3.5		
SG	2.6	1.173	1.0		
IG	3.5	1.973	11.4		
DC	5.8	1.677	14.3		

Data from Oliveira and Lima (1997).

Four sampling stations were established along the Guanabara Bay coast, located in areas with a variable degree of exposure to metal contamination, according to previous studies (Rebello et al., 1986; Oliveira and Lima, 1997; Perin et al., 1997). Guapimirim mangrove forest (station GM;  $22^{\circ}41'40''S$ ,  $43^{\circ}01'18''W$ ) is in the northern coast of the bay, located in an environmental protection reserve, and is the highest, most protected and probably the less impacted mangrove area in Guanabara Bay. Station GM is free from point sources of metal contamination. São Gonçalo mangrove forest (station SG;  $22^{\circ}50'$ 19"S,  $43^{\circ}05'$ 45"W) is in the eastern coast of the bay, where an intermediate level of contamination is observed. Ilha do Governador mangrove forest (station IG; 22°49'24"S, 43°10'39"W) and Duque de Caxias mangrove forest (station DC;  $22^{\circ}48'33''S$ ,  $43^{\circ}17'40''W$ ) are both located in the western bay margin, the most anthropogenically-impacted area of Guanabara Bay. Sampling stations are also located in mangrove forests with a variable degree of structural development (Table 1).

In May 1997, three 30  $m<sup>2</sup>$  sampling plots were established in L. racemosa-dominated stands in each station. Five sediment samples were randomly collected in each plot by inserting 6.5 cm diameter PVC tubes to a depth of 5 cm. Leaf samples were collected from five L. racemosa trees at each plot. In the laboratory, roots were separated from the sediments. Sampled sediments and leaves were used to form composite samples for each plot. All samples were dried until constant weight  $(80 °C, 48 h)$ , ground-milled and homogenized. Leaves were digested in a concentrated nitric–perchloric acid solution. The potentially-available trace metal fraction in sediments (hereafter called weakly-bound concentrations) was estimated after an extraction in a 0.1 M HCl solution (Lacerda et al., 1987). Total metal concentration in sediments was estimated after a digestion in a concentrated nitric–perchloric acid solution. Metal concentrations were analyzed by flame atomic absorption spectrophotometry.

A ratio between weakly-bound and total concentrations (hereafter called weakly:total ratio) was used to estimate the proportion of potentially-available metal concentrations in the mangrove sediments. The metal transfer from sediments to L. racemosa leaves was evaluated through concentration factors (CFs), estimated by the ratio between leaf concentrations and the weakly-bound concentrations in the sediments. Results presented hereafter represent average values of triplicate plots for each station. An one-way ANOVA followed by a post-hoc Tukey's test was used to compare results of different stations. Whenever necessary, tests were conducted on log-transformed data to meet the assumptions of parametric analysis.

Trace metal concentrations and weakly:total ratios of surface mangrove sediments are presented in Table 2. Total metal concentrations varied significantly among stations, except for Ni. The highest total Zn concentrations were observed in station SG and highest total Pb and Cu concentrations were observed in station IG, as may be expected due to their location near urban and industrial sources of metals in Guanabara Bay. The highest Ni and Mn concentrations were observed in station GM, the sampling location more distanced from

Table 2

Total and weakly-bound trace metal concentrations ( $\mu$ g g<sup>-1</sup>), and ratio between weakly-bound and total concentrations (weakly:total ratio) in sediments

	Zn	Pb	Cu	Ni	Mn		
Total concentration							
Station GM	26.7(11.5)a	26.0(10.4)a	28.3 (18.9)ab	12.0(7.0)a	273(40)a		
<b>Station SG</b>	610(246)b	20.0(10.0)a	18.0(8.2)a	8.7(1.5)a	71.7(60.5)b		
Station IG	263(64)b	130(10.0)b	80.0(10.0)b	6.0(1.7)a	150(10)ab		
Station DC	53.3 $(15.3)a$	86.7 (56.9)ab	46.7 (37.5)ab	10.3(3.5)a	80.0(72.1)b		
Weakly-bound concentration							
Station GM	20.0(0.0)a	20.0(17.3)a	5.0(0.0)a	5.0(0.0)a	45.3 $(7.6)a$		
Station SG	53.3 (28.9)a	16.7(5.8)a	7.0(7.0)a	5.0(0.2)a	11.0(5.6)b		
Station IG	30.0(10.0)a	70.0(10.0)b	26.7(15.3)a	5.0(0.0)a	22.3(7.4)b		
Station DC	32.1(18.6)a	33.3(11.5)a	11.0(3.5)a	6.7(2.9)a	11.0(7.9)b		
Weakly: total ratio							
Station GM	0.83(0.29)a	0.67(0.29)a	0.23(0.12)a	0.52(0.18)a	0.17(0.05)a		
Station SG	0.08(0.02)b	0.89(0.19)a	0.38(0.32)a	0.87(0.23)a	0.18(0.06)a		
Station IG	0.13(0.08)b	0.54(0.04)a	0.33(0.18)a	0.55(0.16)a	0.15(0.04)a		
Station DC	0.95(0.30)a	0.52(0.42)a	0.31(0.19)a	0.59(0.11)a	0.39(0.53)a		

Values are means ( $\pm$ SD) of triplicate plot analysis. Results with the same letter are not significantly different among stations ( $p > 0.05$ ).

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	Zn	P <sub>b</sub>	Cu	Ni	Mn			
Leaf concentration								
Station GM	14.0(2.0)a	2.3(2.3)a	8.0(1.7)a	5.3 $(2.1)ab$	65.0(5.0)a			
Station SG	23.3(2.3)b	1.3(0.6)a	7.7(3.2)a	$6.7(0.6)$ ab	28.0(10.6)a			
Station IG	28.0(6.0)b	1.0(0.0)a	10.0(1.7)a	12.7(10.8)a	54.7 (39.3)a			
Station DC	31.0(1.0)b	8.9(1.2)b	7.0(2.6)a	1.8(1.9)b	49.3 (27.7)a			
CF								
Station GM	0.70(0.10)a	0.21(0.26)a	1.60(0.35)a	1.07(0.42)a	1.46(0.23)a			
Station SG	0.60(0.44)a	0.10(0.09)a	1.64(0.85)a	1.35(0.09)a	3.75(3.7)a			
Station IG	0.96(0.13)a	0.01(0.00)a	0.58(0.54)a	2.53(2.16)a	2.40(1.19)a			
Station DC	0.71(0.34)a	0.31(0.17)a	0.74(0.50)a	0.23(0.15)b	7.12 (7.71)a			

Trace metal concentrations ( $\mu$ g g<sup>-1</sup>) and concentration factors (CF = leaf concentration/sediment weakly-bound concentration) of *L. racemosa* leaves

Values are means ( $\pm$ SD) of triplicate plot analysis. Results with the same letter are not significantly different among stations ( $p > 0.05$ ).

the sources of metal contamination. These results suggest that the distribution of Zn, Pb, and Cu tended to be largely affected by human influences, while Ni and Mn distribution seems to be less affected by human activities along the bay area. For most of the metals (Pb, Cu, and Mn), weakly-bound concentrations tended to follow the variability of the total concentrations between sampling stations. As a general rule, metals maintained no significantly different weakly:total ratios among stations. In opposition, Zn concentrations showed significantly higher weakly:total ratios in station GM and station DC compared to other stations. Studied sediments presented a lower proportion of Zn weakly-bound concentrations in the stations with higher total concentrations. The same trend was observed for Pb (at a lower extent), while this did not occur for the other elements. Previous studies have found a low proportion of 'reactive' metals in mangrove sediments, which is mainly attributable to the formation of metal–sulfides and metal–organic matter complexes (Lacerda et al., 1991; Tam and Wong, 1995; Clark et al., 1998).

Table 3

L. racemosa showed less accentuated variations in leaf metal concentration among stations (Table 3) than sediments. With some exceptions, L. racemosa leaves did not present significant differences between stations. Leaves showed significantly lower Zn concentrations in station GM and significantly higher Pb concentrations in station DC than in other stations, whereas Ni concentrations in station IG were significantly higher than in station DC. Lower Zn concentration in leaves from station GM is possibly associated to the lower concentration in sediments, while for most of metals the leaf concentration seems to be not related to the metal content of sediments. Little significant variation among CFs of leaves from different stations was observed (Table 3). Only Ni had a significant difference among stations, with lower CFs in station DC than in the other stations. Observed CFs tended to be higher than those previously reported for mangrove leaves (Ragsdale and Thorhaugh, 1980; Silva et al., 1990), and suggest a general trend of higher transference of Mn, Cu, and Ni

from sediments to leaves than observed for Zn and Pb. Certainly, several processes may cause differences between this trend and that of the leaf detritus transported out the forests. For example, metal retranslocation among plant tissues before leaf fall (Zheng et al., 1997) and litter retention and mineralization in situ (Silva et al., 1998) probably change original leaf metal concentrations. Remarkably, stations where Zn (station SG) and Pb (station IG) appear to have the most important degree of contamination tend to show a lower transference of such metals from sediments to leaves than observed for other elements. A coupling between the relatively low availability in sediments and the low transfer to leaves seems to compensate the elevated contamination of Zn and Pb.

This first comparison between the studied environments indicates that, even along contrasting environmental conditions (e.g., degree of metal contamination and forest structural development), mangrove forests may maintain their sediment metal load predominantly under forms with a low potential of remobilization and biotic uptake. This preliminary approach do not permit a conclusive interpretation on the importance of metal allocation in mangrove leaves for the metal retention in the studied ecosystems, but a relatively low metal allocation in leaves appear effectively reduce the metal export through leaf litter transport, as well as the metal availability to enter in food chains based on leaf consumption. This is possibly true for many mangrove areas, since mangrove plants commonly induce changes in the sediment chemistry (e.g., due to  $O_2$  release by roots) that can prevent a potentially deleterious metal uptake and tend to show a low transfer of metals from belowground to aboveground tissues (Lacerda, 1998).

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## **References**

- Badarudeen, A., Damodaran, K.T., Sajan, K., Padmalal, D., 1996. Texture and geochemistry of the sediments of a tropical mangrove ecosystem, southwest coast of India. Environmental Geology 27, 164–169.
- Chiu, C.Y., Chou, C.H., 1991. The distribution and influence of heavy metals in mangrove forests of the Tamshui estuary in Taiwan. Soil Science and Plant Nutrition 37, 659–669.
- Clark, M.W., McConchie, D.M., Lewis, D.W., Saenger, P., 1998. Redox stratification and heavy metal partitioning in Avicenniadominated mangrove sediments: a geochemical model. Chemical Geology 149, 147–171.
- Harbison, P., 1986. Mangrove muds––a sink and source for trace metals. Marine Pollution Bulletin 17, 273–276.
- Kjerfve, B., Ribeiro, C.H.A., Dias, G.T.M., Filippo, A.M., Quaresma, V.S., 1998. Oceanographic characteristics of an impacted coastal bay: Baıa de Guanabara, Rio de Janeiro, Brazil. Continental Shelf Research 17, 1609–1643.
- Lacerda, L.D., 1998. Biogeochemistry of Trace Metals and Diffuse Pollution in Mangrove Ecosystems. International Society for Mangrove Ecosystems, Okinawa.
- Lacerda, L.D., Pfeiffer, W.C., Fiszman, M., 1987. Heavy metal distribution, availability and fate in Sepetiba Bay, SE Brazil. Science of the Total Environment 65, 163–173.
- Lacerda, L.D., Martinelli, L.A., Rezende, C.A., Mozetto, A.A., Ovalle, A.R.C., Victoria, R.L., Silva, C.A.R., Nogueira, F.B., 1988. The fate of trace metals in suspended matter in a mangrove creek during a tidal cycle. Science of the Total Environment 75, 169–180.
- Lacerda, L.D., Rezende, C.E., Aragon, G.T., Ovalle, A.R., 1991. Iron and chromium transport and accumulation in a mangrove ecosystem. Water, Air and Soil Pollution 57/58, 513–520.
- Oliveira, R.R., Lima, D.F., 1997. Caracterização biótica das estações de monitoramento dos manguezais da Ba ia de Guanabara.

Programa de despoluição dos manguezais da Baia de Guanabara. SEMA/FEEMA, Rio de Janeiro..

- Perin, G., Fabris, R., Manente, S., Rebello Wagener, A., Hamacher, C., Scotto, S., 1997. A five-year study on the heavy metal pollution of Guanabara bay sediments (Rio de Janeiro, Brazil) and evaluation of the metal bioavialability by means of geochemical speciation. Water Research 12, 3017–3028.
- Peters, E.C., Gassman, N.J., Firman, J.C., Richmond, R.H., Power, E.A., 1997. Ecotoxicology of tropical marine ecosystems. Environmental Toxicology and Chemistry 16, 12–40.
- Ragsdale, H.L., Thorhaugh, A., 1980. Trace metal cycling in the U.S. coastal zone: a synthesis. American Journal of Botany 67, 1102– 1112.
- Rebello, A.L., Haekel, W., Moreira, I., Santelli, R., Schroeder, F., 1986. The fate of heavy metals in an estuarine tropical system. Marine Chemistry 18, 215–225.
- Sadiq, M., Zaidi, T.H., 1994. Sediment composition and metal concentrations in mangrove leaves from the Saudi coast of the Arabian Gulf. Science of the Total Environment 155, 1–8.
- Silva, C.A.R., Lacerda, L.D., Rezende, C.E., 1990. Metals reservoir in a red mangrove forest. Biotropica 22, 339–345.
- Silva, C.A.R., Lacerda, L.D., Ovalle, A.R.C., Rezende, C.E., 1998. The dynamics of heavy metals through litterfall and decomposition in a red mangrove forest. Mangroves and Salt Marshes 2, 149–157.
- Tam, N.F.Y., Wong, Y.S., 1995. Spatial and temporal variations of heavy metal contamination in sediments of a mangrove swamp in Hong Kong. Marine Pollution Bulletin 31, 254–261.
- Tam, N.F.Y., Wong, Y.S., 1996. Retention and distribution of heavy metals in mangrove soils receiving wastewater. Environmental Pollution 94, 283–291.
- Zheng, W.J., Chen, X.Y., Lin, P., 1997. Accumulation and biological cycling of heavy metal elements in Rhizophora stylosa mangroves in Yingluo Bay, China. Marine Ecology Progress Series 159, 293– 301.