Evaluation of Heavy Metals in Mangrove Soil of the Graciosa River in Bahia, Brazil.

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Abstract

Mangrove soils are distributed along coastal areas with smooth topography and under constant influence of both, marine and fresh waters. Mangrove soils have specific physical, chemical and biological properties, as well as some heavy metals that in high concentrations become toxic to the environment. This work aimed to characterize a mangrove soil in South Bahia, Brazil, with focus on heavy metals. Samples of 5 layers from a profile (125 cm depth) were evaluated. In a first phase it was done the characterization of soil samples collected in a deforested (anthropic) riverine area, in 2002. For the superficial layer C1 (0-20 cm) samples of an adjacent and area under natural conditions had been also collected. Secondarily, data from the superficial layer samples under both, natural and anthropic conditions were compared, considering samples of 2002 (deforested situation) and 2007 (regenerated situation). Heavy metals concentration on the samples of 2002 were significantly different among the layers and exhibited, in general, low levels in relation to those found in no polluted soils, except for Cd and Pb that presented intermediate level. In the period between 2002 and 2007, for the superficial layers, natural and anthropic, a decrease in metals concentrations was observed, except to Ni. **Key Words:** Gleysol; Soil properties; Trace elements.

Introduction

The world has an estimated area of mangrove soils of 162,000 Km^2, distributed along the tropical and subtropical coastal areas, reaching the best development between the tropics of Cancer and Capricorn. In Bahia, Brazil, despite the few existent data, is considered that the mangrove area is of approximately 800 km^2, along almost 1,000 km of coast (Ramos, 2002).

In general, the main anthropic sources of heavy metals (added to the natural ones) have been related to urban residues (mainly Cr, Cu, Pb, Zn, Mn and Ni), fossil fuels (Cu, Ni, Pb), industries of iron and steel processing (Cr and Zn), fertilizers (Cu, Fe, Mn, Ni and Zn) and waste deposits (Zn, Mn and Pb) (Ribeiro et al., 2006).

As the behavior of heavy metals in mangroves is highly dependent of the physiochemical characteristics of their sediments, the vegetation type can modify the characteristics of the sediments, with respect to its capacity of heavy metals retention. Once those metals integrate the landscape components, the sediments represent an important tool in the evaluation of the contamination degree of those soils, because they are representative of the several processes occurred in the hydro systems of catchment.

Methods

The studied area is located in the estuary of Graciosa River (13 ° 29'56 "S and 39 ° 05'49" W). The sampling place had been deforested and received a layer of allochthonous soil. The first samples were collected in a profile close to the river, in a riverine forest, during the low tide, in November 2002. Three simple samples were collected in the layers: C_{1p} (0-20 cm, "p" indicating *anthropic layer*), C_2 (20-41 cm), C_3 (41-65 cm), C_4 (65-99 cm), C_5 (99-125 cm). A sixth sample of the 0-20 cm layer (denominated C_{1n}) was collected in the adjacent area with soil under *natural conditions*. In May 2007, a new sampling in the layer 0-20 cm was accomplished in the anthropic area, which was abandoned soon after 2002, and until this second sampling period presented an advanced regeneration process of the mangrove vegetation (*Rhizophora mangle* L.). The local soil is a Gleysols (Tropaquept).

The heavy metals analysis (Cd, Co, Cr, Cu, Zn, Ni, Mn and Fe) were done on samples of 250 mg of air dried fine soil, after passing by a sieve number 100 (145 mm). The extraction was accomplished with aqua-regia (mixture 3:1 of HCl/HNO_3), in a digester block, using the method described by McGrath and Cunliffe (1985). The determinations were made by spectrometry in inductively coupled plasma.

Results and Discussion

The concentration of heavy metals depends, among other factors, on the source material and on the process of soil formation, according Coimbra (2003). The physicochemical reactions that control the availability of heavy metals in mangrove soils include adsorption and desorption, precipitation, dissolution and complexation which are influenced by different chemical attributes such as activity of the clay fraction and organic carbon content. The pH and the redox potential are the most relevant ones because they control the chemical speciation of metals in soil solution.

The tenors of heavy metals were low (Table 1 and 2) compared to levels typically found in no polluted soils: Fe < 38 mg kg^{-1}, Cu < 60 mg kg^{-1} , Mn < 600 mg kg^{-1}, Zn < 50 mg kg^{-1}, Cr < 100 mg kg^{-1}, Cd < 0.06 mg kg^{-1}, Ni < 13 mg kg^{-1}, Pb < 20 mg kg^{-1} (Raij, 1991), except for Cd and Pb, that are medium to high.

Table 1. Heavy metal contents obtained for the Gleysol Salic Sodic (Tropaquept) at a mangrove of the estuary of Graciosa River - Bahia, in 2002

Layer	Depth (cm)	Fe	Cu	Mn	Zn	Cr	Co	Ni	Cd	Pb
		mg kg^{-1}								
C_{1n}	0-20	18.5 f	6.1 b	85.1 d	25.9 c	35.9 e	4.5 c	* b	1.5 e	* c
C_{1p}	0-20	24.8 e	7.7 a	71.5 e	9.4 d	60.2 a	6.9 a	7.0 a	1.9 d	11.6 a
C_2	20-41	28.1 d	5.2 b	99.7 c	34.8 b	46.4 c	6.2 b	* b	2.2 c	7.5 b
C_3	41-65	29.6 c	3.4 c	176.7 b	44.3 a	44.0 d	6.4 b	* b	2.5 b	* c
C_4	65-99	34.4 a	1.4 d	199.0 a	45.0 a	51.8 b	7.0 a	* b	2.8 a	* c
C_5	99-125	32,6 b	1,1 d	198.0 a	44.9 a	48.6 c	6.7 a	* b	2.8 a	* c

Averages with the same letter were not significantly different ($p < 10\%$) by Scott Knott test.
* Tenor below the detection limit for the used method.

Among the layers significant differences were detected for all the metals (Table 1 and 2). Fe, Mn, Zn, Cr, Co and Cd followed a trend of increase in depth, probably associated to the soils material of origin, strengthening the fact that the largest metal concentrations were found in the deepest layers (close to the origin rock), except to Cr, that behaved in a variable way among the layers. Cr obtained the highest concentration in the C_{1p} layer, what can be attributed to the entrance by anthropic deposited material and the use of fertilizers.

Another hypothesis would be the deposit and accumulation of these metals due to stagnation of river water during the low tide in the deepest layers (Figure 1), what contributes to the supply of small concentrations of those metals to the horizons (deepest layer) of the profile, coming from soil / rock material and upstream water bodies.

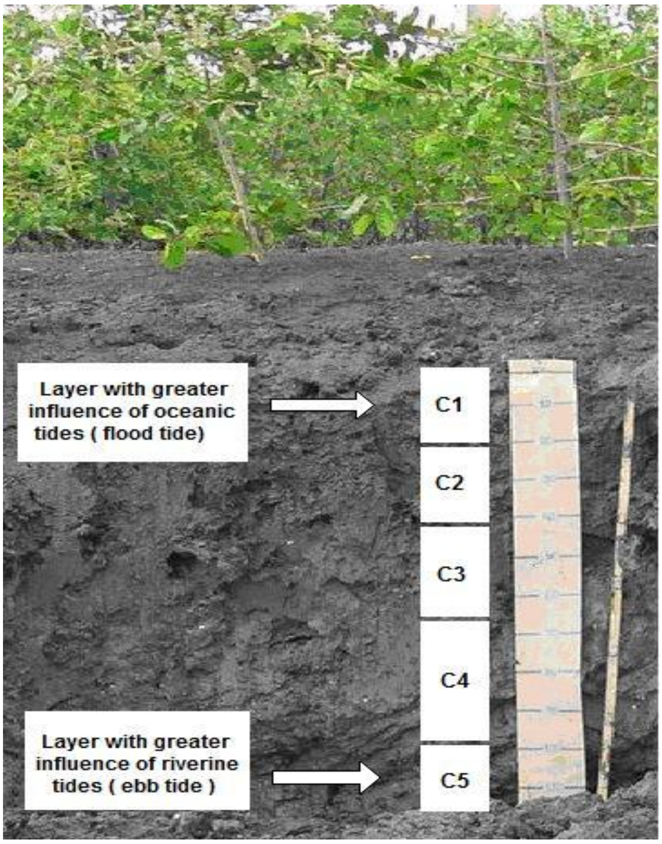

Figure 1. Influence of tides to the entrance of sediments and chemical elements in the mangrove soil.

Additionally, residual fuel oils from the daily navigation of vessels in the estuary of the Graciosa River may also be contributing to the occurrence of metals as suggested by Ribeiro *et al.* (2006), as these oils have in their composition hydrocarbons and trace metals such as nickel and copper.

The concentrations of Fe are relatively low following a trend observed by Lima (2001). The author indicates the material of origin and the environmental conditions of the region were decisive factors to the low levels of Fe found. In this case the original material is possibly poor in Fe and/or the transport of this metal in suspension from up watersheds is not very efficient, contributing to low concentrations of this metal in the soil. Hydromorphism may be the cause for fluctuations in Fe concentrations that occur in the intertidal zone, since it causes the leaching of Fe oxides to the deepest layers, as observed for this soil (Table 1). The low evolution degree and salic sodic character of the mangrove soil may also influence losses of Fe and clays, as described by Schaefer and Dalrymple (1996).

Cu follows a decreasing tendency in depth (Table 1). The levels of heavy metals showed more significant concentrations in the disturbed layer (C_{1p}) probably because the deforestation of the studied area, as well as the anthropic inputs. Lima (2001) observed this tendency of decrease with depth for the metal Cu in Gleysols of the Western Amazon.

Zn levels showed a well-defined behavior, increasing with soil depth and stabilizing in the deepest layer. The presence of this metal in soil may be related to the original material, being presented in high concentrations in magmatic rocks, as well as to the use of fertilizers and fossil fuels as discussed by Malavolta and Reichardt (1976).

The high concentrations of Cd (> 0.06 mg kg^{-1}) are probably attributed to the material of sedimentary origin, where this metal content can reach 10 mg kg^{-1}, as suggested by Malavolta and Reichardt (1976), a result reinforced by the higher concentrations of this metal in the deepest layers, close to the origin rock. In soils close to urban agglomerations, as additional sources, the residue of tires, diesel and lubricating oils, may contribute to the increment of this metal in soil.

The concentrations of Ni and Pb were below the detection limit and these metals were only detected in the disturbed layer C_{1p} for Ni and in C_{1p} and C_2 for Pb. This result can be attributed to the use of phosphoric fertilizers that contain quantities of these metals (Raij, 1991). Since Pb is a metal of little mobility, it naturally accumulates in the surface layers, as found in this soil (Table 1).

The comparison between the results obtained for the disturbed layer in 2002 and 2007 (Table 2) shows that there were significant decreases in concentrations of Fe, Mn, Zn, Cr, Co, Cd and Pb after five years of the first sampling. During this period the soil showed an increase in clay and in the flocculation degree (Table 2). Although this last factor normally does not affect the mobilization of metals in the soil as discussed by Förstner and Wittmann (1993), suggesting the association of metals preferentially to fine fractions of silt and clay size (<2 mm), which make up the sediments of mangroves. This metals/fine sediment fractions association is favored by the adsorption reactions, due to the high specific surface area of fine particles (Förstner and Wittmann, 1993). Santos (2006), however, noted that heavy metals in sediments of mangroves occur more often in soils with higher sand fraction due to the strong association of the minerals present in this fraction of the Barreiras Group sediments with metals.

The abandonment of the mangrove area and the rapid regeneration of *Rhizophora mangle* vegetation, may also have contributed to the observed metals behavior, since this plant has the capacity to mobilize metals. Only for Ni there was significant increase in the second sampling, probably because this metal is strongly adsorb by the finest fractions remaining of the soil, as observed by Malavolta and Reichardt (1976).

Table 2. Heavy metal content obtained for the Gleysol Salic Sodic (Tropaquept) at a mangrove of the Graciosa River - Bahia, in the 0-20 cm layer (natural C_{1n} and disturbed C_{1p}), for an interval of five years

Sample	Fe	Cu	Mn	Zn	Cr	Co	Ni	Cd	Pb
	mg kg^{-1}								
C_{1n} 2002	18.5 c	6.1 a	85.1 a	25.9 a	35.9 b	4.5 b	* c	1.5 b	* b
C_{1p} 2002	24.8 a	7.7 a	71.5 b	9.4 b	60.2 a	6.9 a	7.0 b	1.9 a	11.6 a
C_{1p} 2007	22.0 b	5.5 a	52.4 c	7.4 c	15.0 c	3.3 c	11.8 a	* c	* b

Averages with the same letter were not significantly different ($p < 10\%$) by Scott Knott test.
* Tenor below the detection limit for the used method.

Conclusions

The proximity of small urban agglomerates and the human activities (urban effluents, fossil fuels, and fertilizers), didn’t cause contamination by heavy metals to the studied soil, what means an environmentally conserved place on this aspect. Due to the observed middle-high concentrations, Cd and Pb should be objects of subsequent studies, focusing on analysis of their possible sources and on probable consequences to the studied ecosystem.

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