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CHARACTERIZATION OF A MANGROVE SOIL IN THE GRACIOSA RIVER ESTUARY, IN BAHIA, BRAZIL: HIGHLIGHTING HEAVY METALS AND MICROBIAL POPULATIONS

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Mangrove soils have unique properties, able to transform and sequester chemical compounds of biogeochemical and ecological importance, including heavy metals. The degeneration of mangrove soils shows the risk of releasing these metals to the environment. We search for improve the knowledge about how disturbance affects the metal fixation and microbial of mangrove soils. This study characterized a mangrove soil along the Graciosa River estuary (Bahia, Brazil), according to selected physical, chemical and microbiological properties. In 2002, soil was collected from an anthropic and from an adjacent natural site. Both sites were re-sampled in 2007, after a vegetal regeneration on the anthropic site. Significant differences between the natural and anthropic surface layers were observed for chemical and physical soil properties. In particular, heavy metals (Co, Cr, Cu, Zn, Ni, Mn and Fe) showed significant differences with depth and lower concentrations were found in the anthropic site, exception to Cd (moderately high). Between 2002 and 2007, the disturbed site showed a decrease for all observed metals, except for Ni. The data also suggest that microbial populations may be favored in the layers of the soil profile most influenced by high and low tides, C1 (0-20 cm) and C5 (99-125 cm).

Key words: Gleysol, physical and chemical characteristics, trace elements, microorganisms.

Caracterização de um solo de mangue no rio graciosa, na Bahia, Brasil: destacando metais pesados e populações microbianas. Os solos de mangue têm propriedades particulares, sendo capazes de transformar e remobilizar compostos químicos de importância biogeoquímicos e ecológicos, incluindo metais pesados. A degeneração de solos de mangue tem o risco de liberar estes metais para o ambiente. Procura-se melhorar o conhecimento sobre como as perturbações afetam a fixação de metais e a microbiota de solos de manguezal. Este estudo caracterizou um solo de manguezal no estuário do rio Graciosa (Bahia, Brasil), de acordo com algumas propriedades físicas, químicas e microbiológicas. Em 2002, o solo foi coletado a partir de um área antropizada e de outra natural adjacente. Ambas as áreas foram re-amostradas em 2007, após regeneração vegetal naquela antropizada. Diferenças significativas entre as camadas superficiais antropizada e natural foram observadas para as propriedades químicas e físicas do solo. Em particular, os metais pesados (Co, Cr, Cu, Zn, Ni, Mn e Fe) mostraram diferenças significativas com a profundidade e concentrações mais baixas foram encontradas na área antropizada, com exceção do Cd (moderadamente alto). Entre 2002 e 2007, a área antropizada mostrou diminuição para todos os metais observadas, exceto para Ni. Os dados também sugerem que as populações microbianas podem ser favorecidos nas camadas do perfil do solo mais incluenciadas pelas marés altas e baixas, C1 (0-20 cm) e C5 (99-125 cm).

Palavras-chave: Gleissolo, características físicas e químicas, elementos traços, microorganismos.

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Introduction

The world's mangroves encompass approximately 172,000 km^2 distributed along the coast of tropical and subtropical regions, and in Bahia, Brazil, their extent is estimated at 800 km^2, distributed over nearly 1,000 km of coastline (Ramos, 2002), where the largest mangrove forests are located in the cities of Caravelas, Canavieiras and between Valença and Maraú. A majority of works related to mangroves has been limited to the interaction between the distribution of vegetation and soil nutrition in this ecosystem. Few studies focus on the pedology and physical, chemical and microbiological properties of mangroves. The study and characterization of mangrove soils allow evaluations of the edaphic and ecological interaction of this ecosystem, as well as the definition of better strategies for the sustainable management of this environment. It also enables the understanding of self-regulation and evolution processes of a system under disturbance.

Urban development in coastal regions impose dual stresses on mangrove ecosystems: the clearing of mangrove forests for construction or agriculture activities, and the enrichment of mangroves with wastes, including heavy elements. The total concentration of metals in the soil, which are usually present as trace elements, can be attributed to the soil parent material as well as the impact of human activities (Paul et al., 1994). The main anthropogenic sources of heavy metals, in addition to the natural ones, have been related to urban effluents (mainly for Cr, Cu, Pb, Zn, Mn and Ni), burning of fossil fuels (Cu, Ni, Pb), beneficiation industries of iron and steel (Cr and Zn), fertilizers (Cu, Fe, Mn, Ni and Zn) and tailings deposits (Zn, Mn and Pb) (Förstner; Wittman, 1993).

Because the behavior of heavy metals in mangroves is highly dependent on physicochemical characteristics of their sediments and as the vegetation cover also influences these aspects, the type of vegetation can alter the characteristics of the sediments and hence their ability to retain heavy metals, also taking into account that sediments express the various processes that occur in the drainage basin of a water system.

The large accumulation of sediment and debris brought by the rivers and sea contributes to a constant expansion of mangroves, and the dynamic and unstable nature of their soil, due to the constant deposition of sea sand and riverine soil rejuvenation, with alluvial and lacustrine deposition (Rossi and Mattos, 2002). The mechanisms governing the dynamics of sediment in estuarine areas are directly related to hydrodynamic aspects. The effect of oceanic tides is variable along the mangrove, because some areas are inundated daily while others are only affected by large tidal variations (Herz, 1991). This variation in mangrove inundation frequency by the ocean tides can lead to differences in concentrations of salt, sediment, nutrients, heavy metals, and others. The highest salinities occur in mangroves near to the sea where there is dominance of sodium and chloride, while the mangrove forests near to rivers present a lower salt concentration (Soares et al., 2000).

In the state of Bahia, Brazil, notably in its Southern region, the lack of studies on estuarine areas is considerable. In this context, this study aimed to characterize a mangrove soil of the Graciosa River estuary in the region of Valença/Taperoá, Bahia, Brazil according to their physical, chemical (including heavy metals) and microbiological properties (quantification of fungi, bacteria and mycorrhizae). Furthermore, we compared, over an interval of five years, edaphical changes in the mangrove soil related to the regeneration of vegetation cover.

Materials and Methods

Study Site

The studied area is located at the mouth of Graciosa River, bordered by the municipal districts of Valença and Taperoá, in the South Recôncavo region of the state of Bahia (13°29'56 "S and 39° 05'49" W), at an altitude of 2 m with flat, gently undulating topography. The climate according to Thornthwaite is tropical humid, with a hydrologic index greater than 80%. Rain occurs from January to December with a maximum annual precipitation of 2,600 mm and minimum of 2,000 mm (SEI, 2003). The maximum temperature is 31.4° C, and minimum of 21.8° C with a mean temperature of 25.3° C. Abundant and regular rainfall ensure the wealth of water resources in the region.

The watershed in which the study site is located had not been well described and mapped until now.

Thereby, the following information is primary data. The drainage area of the Graciosa River watershed is of 384.9 km^2 and forms a dendritic pattern. This basin originates at the headwaters of the Juçara River, at an altitude of ca. 397 meters and reaches its lowest level on the coastal plain of Taperoá city at an elevation of 8.23 meters (SEI, 2003). It encompasses the rivers Vermelho and Sarapui-Mirim in the west, Graciosa or Engenho in the south, and Sarapui, Cachoeirinha, Ajofre and Pau da Légua in the north (Figure 1). The watershed is bounded to the east by the Atlantic Ocean, by the Una River on the north, by the Batateira/Piau River (tributaries of Una River) on the west and the Ermitão do Refugo/Camurugi River to the south.

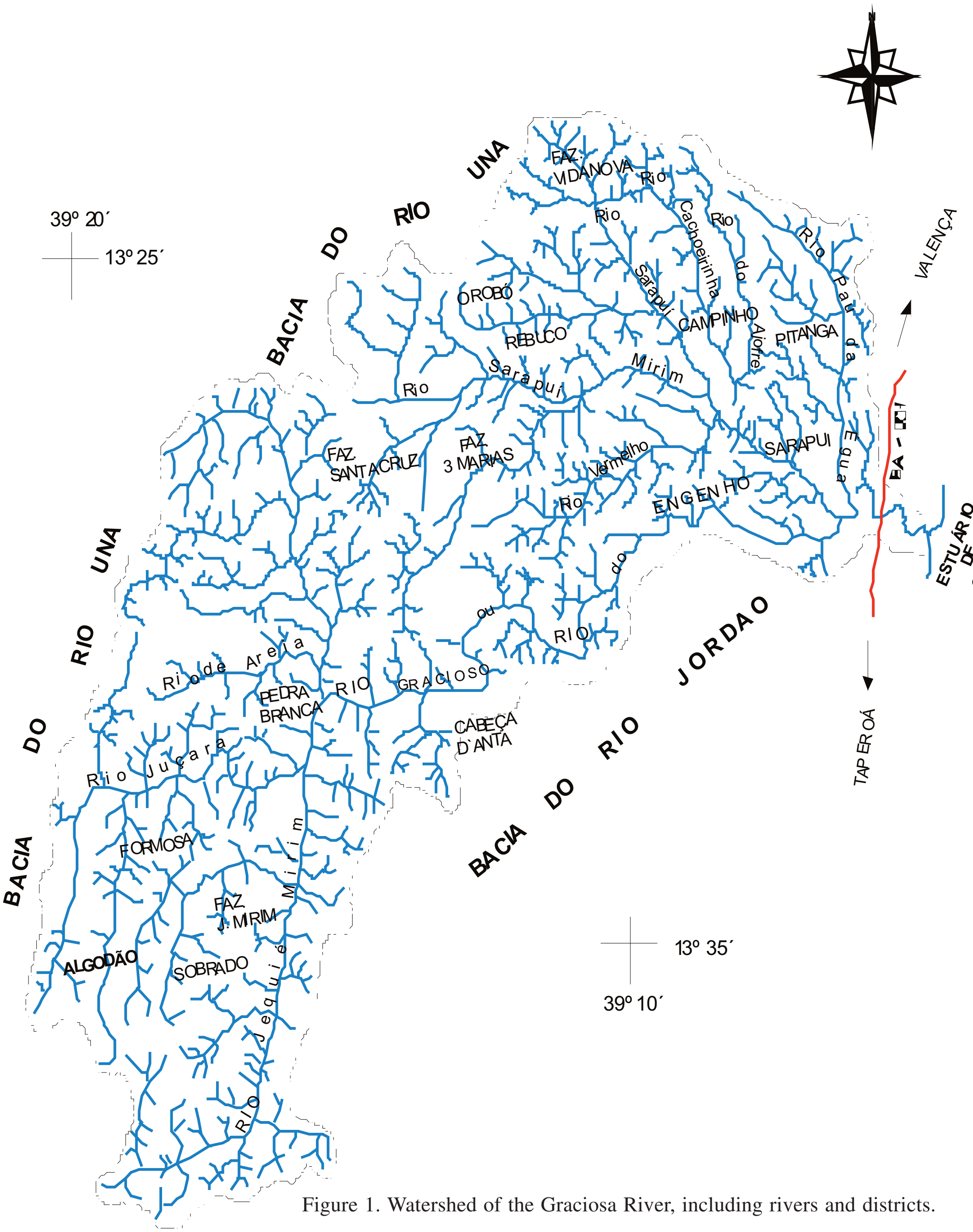

Figure 1. Watershed of the Graciosa River, including rivers and districts.

Topography of the Valença district is characterized by marine and fluvial-marine plains, interior and coastal terraces and foothills, giving rise to flat relief (with elevations ranging from 0-100 m); undulating relief (with altitudes ranging from 100 to 200 m); and strongly undulating relief (hills and mountains, with relative altitudes ranging from 300 to 400 m). Soils described in the region are composed of silicate, crystalline and amorphous minerals as well as oxides and hydroxides of aluminum, iron and titanium (Santana et al., 2005).

Economical characterization of the Graciosa River Watershed

According to data from field surveys, obtained on visits and interviews with resident farmers, rural communities, and local technicians, it was found that the Graciosa River watershed has great economic importance for the region, mainly for the cities of Taperoá and Valença. These two districts are supplied by rivers that form this basin and use its waters for various purposes: water supply, agriculture/livestock, fisheries, navigation, and tourism/leisure activities. The predominant economical activity is diverse agriculture. Agroforestry systems are commonly practiced with emphasis on the cultivation of oil palm, cocoa, coconut, rubber tree, cassava, cloves, guarana, black pepper, annatto, peach palm, mangosteen and macadamia nuts, with little use of agricultural inputs (fertilizers/pesticides). Fishing and livestock activities were also recorded, the latter being of little importance, since most of the grazing areas are degraded. Livestock, mainly cattle, is practiced in mixed pastures, in many cases, with oil palm.

Sampling

The study site was situated in a previously deforested area that had been amended with externally derived soil for the development of farming activities. The area of the study plot, of approximately 20 m x 20 m, also received the addition an unknown quantity and composition of chemical fertilizers.

The first samples were collected in November 2002, during low tide, in a trench 2 m from and parallel to the river, in a region of riparian forest. The study site was approximately 2.5 km from the mouth of the river. Simple samples were collected in triplicate in the following identified soil horizons: $C1_p$ (0-20 cm, “p” meaning *disturbed layer*), C2 (20-41 cm), C3 (41-65 cm), C4 (65-99 cm), C5 (99-125 cm). Soil samples were similarly collected in the top 0-20 cm ($C1_n$) of an adjacent and undisturbed, still forested area 30 m away. The surface horizons (0-20 cm) of both sites were sampled again in May 2007, over which time the disturbed site, since abandoned, showed advanced regeneration of specie *Rhizophora mangle* L.

Soil Classification, Physical and Chemical Properties

Pedology – The pedological description and characterization of the soil in the field was performed according to Lemos and Santos (1996) and color identification was based on the Munsell Color scheme (2000).

Physical and Chemical Properties – The physical (particle-size, equivalent humidity, particle density and bulk density) and chemical properties (pH, C, N, P, K, Ca, Mg, Na, Al concentrations) were determined using methods described in Embrapa (1997), Yeomans and Bremner (1988), Klute (1986) and Page et al. (1982). Basically the performed determinations were the following: particle-size by the pipette method; equivalent humidity by submitting a wet soil sample to a centrifugation of 1000 times the gravity; particle density by the method of alcohol and volumetric balloon; bulk density by using a cylindrical ring of 50 cm^3; pH was measured on the suspension soil:water, 1:2.5; C by oxidation through the wet way with $K_2Cr_2O_7$ in sulfur solution; N following the Kjeldahl semi-micro method of digestion/oxidation; P, K and Na by extracting in Mehlich1 and then analyzing P by spectrophotometer and K and Na by direct method of flame photometry; Al, Ca e Mg were extracted by KCl 1M, and then Al was titrated with NaOH (volumetric method) and Ca and Mg were titrated with EDTA (complexometric method).

Heavy Metals – Heavy metal concentrations (Cd, Co, Cr, Cu, Zn, Ni, Mn and Fe) were determined by aqua regia digest of soil subsamples, which had been previously sieved to < 2 mm and then crushed to a fine powder (McGrath and Cunliffe, 1985). Metal concentrations in the digests were determined by ICP spectrometry.

Bacterial and Fungal Populations – Bacterial and fungal populations were determined by the dilution plate technique described by Wollum II (1982). The number of colony-forming units (CFU) capable of growth in the particular medium was calculated by: CFU/g soil = (number of colonies x final dilution)/g dry soil.

Mycorrhizae – Spores of mycorrhizal fungi were separated from soil subsamples by decanting and wet sieving followed by sucrose centrifugation according to the method described by Sylvia (1994), as following: 25 g of soil were placed in a beaker with 2 L of water and 2-3 drops of liquid soap. The mixture was vigorously stirred for 30 seconds, and then the sand was decanted for 10-15 seconds. The supernatant was passed through sieve < 1.00 mm and < 45 µm. Spores retained on the filter were transferred to centrifuge tubes 50 ml, filled up to 2-3 cm from the top with distilled water and then centrifuged at 1500 rpm for 4 min, carefully decanting the supernatant. The supernatant organic matter adhered to the upper wall of the tubes was discarded. The tubes were filled to 2-3 cm from the top with a solution of cold sucrose 40% and centrifuged at 1500 rpm for 2 min. The centrifuge was stopped to minimize the residence time of spores in sucrose solution due to the damage by osmotic potential. The supernatant was filtered to collect the spores, which were then rinsed gently with water, and arranged in a Petri dish for subsequent observation and measurement in a composite microscope.

Statistical Analysis

The means of the microbiological parameters and heavy metals from the five layers of the disturbed site and the top layer of the undisturbed site from soils sampled in 2002 were compared using the Scott Knott test ($p < 0.10$). Average values of physical and chemical parameters and heavy metal concentrations of the disturbed soil were compared between the 2002 and 2007 sampling dates. The average values of chemical and physical parameters were also correlated with microbiological data by simple linear correlation test. Data were analyzed by the statistical software SAEG (Sistema de Análises Estatísticas e Genéticas) version 9.1 (SAEG, 2010).

Results and Discussion

Soil Characterization

The studied soil was classified as a Tropaquept (Gleissolo Sálico Sódico argissólico according the Brazilian soil classification) with the following characteristics: silty clay texture; high organic matter content; high C/N ratio; high cation exchange capacity and high base saturation; strongly acidic pH; and high expandability (data presented in the Tables 1 and 2). The sodic designation is given to soils that present, at some horizon or layer within 100 cm of the soil surface, sodium saturation e" 15% of the total cation exchange capacity (Embrapa, 2013). In this case, the undisturbed soil has in the layer C2 (20-41 cm), a sodium saturation of 16% and water-soluble salts within 100 cm of the soil surface, which defines it as salic.

Physical Parameters

From the physical analysis data obtained in 2002 (Table 1), the studied soil were dominated by the finer fractions (clay, silt). The highest concentrations of clay occurred in the most superficial layers (C1n, C1p, C2) and for silt in the deepest layers (C3, C4, C5). This textural distribution was also observed by (Clark, 1998) and may indicate a change in the sedimentation regime of the mangrove, with less transport energy and deposition of sediments in more recently deposited layers.

Observing the data for the 0-20 cm layer shown in Table 3, after a five-year interval, significant differences were found between the layers for all the physical attributes, with exception of silt and particle density, which did not differ, suggesting that the studied mangrove has a predominant deposition of finer fractions of sediments. The decrease in moisture observed in May 2007 reflects a decrease of the rainfall in the region, which corresponds, according to local farmers, to the less rainy period. While the disturbance of clearing and cultivation initiated the loss of clay, the five-year abandonment of the area permitted the accumulation of this particle size fraction.

The high silt/clay ratio observed (Table 1) suggests that the silty material deposited in the alluvial plain is in the initial stage of weathering, since the lower the silt/clay ratio is, the more weathered is soil (Embrapa, 2006). This is probably due to the recent age of the source material (sediments of the Holocene).

Frequently the mangrove soils have a gley aspect, without clear differentiation of horizons, having low concentrations of calcium, alkalis and trace elements, and high content of salts from seawater or from sulfur compounds (Marius and Lucas, 1991). Geologically, these soils exhibit composition of kaolinite, mica, illite, smectite in clay fraction and feldspar and quartz in the silt fraction. The variations in tone (pedological characterization), according to Embrapa (2006), can be explained by the higher concentration of organic matter in the surface layers and also due to changes of the redox conditions in the sediment (Fe, Mn), from oxidizing to reducing, a typical situation of wetlands and anaerobic environments. Hydromorphic conditions do not favor intensive weathering of parent material, explaining the presence of primary minerals such as potassium feldspar and muscovite, with silt from detrital allochthonous or autochthonous sources.

Table 1. Physicochemical properties of the studied mangrove soil (Tropaquept) along the Graciosa River

Horiz.	cm	Particle size				WEC ($g. kg^{-1}$)	DF (%)	BD	PD	TP (dm^3/dm^{-3})	Silt: Clay	EH ($g. kg^{-1}$)
		CS	FS	SI	C			($g\ dm^{-3}$)				
		($g.kg^{-1}$)										
C_{1n}	0–20	76	136	336	452	113	75	1.2	2.4	0.5	0.7	106.8
C_{1p}	0–20	157	198	311	334	80	76	-	2.4	-	0.9	-
C_2	20–41	114	169	328	389	75	81	1.0	2.4	0.6	0.8	156.8
C_3	41–65	74	229	359	339	41	88	1.1	2.5	0.6	1.1	124.3
C_4	65–99	58	243	365	334	42	87	1.3	2.6	0.5	1.2	105.5
C_5	99–125	80	293	395	223	38	83	-	2.6	-	1.8	-

Horiz.	OM	OC	N	C:N	pH		Sorptive Complex						SB	CEC	V	m
							Ca	Mg	K	Na	Al	H				
	($g.kg^{-1}$)				H_2O	KCL	($cmol_c\ kg^{-1}$)								(%)	
C_{1n}	117	67.9	4.1	17	5.0	4.7	7.6	16.2	1.2	4.1	0.7	7.7	29.1	37.5	78	2
C_{1p}	96	55.8	4.1	14	4.7	4.2	9.2	17.5	1.2	1.1	1.0	8.7	29.0	38.7	75	3
C_2	109	62.9	3.3	19	3.9	3.6	10.0	15.0	0.9	8.2	1.6	16.2	34.1	51.9	66	4
C_3	83	47.9	2.1	23	4.2	3.8	10.2	13.5	0.9	3.7	1.0	12.4	28.3	41.7	68	3
C_4	76	44.3	1.6	28	4.8	4.4	12.0	12.9	1.2	2.2	0.8	8.5	28.3	37.6	75	3
C_5	69	39.7	1.4	28	4.9	4.5	13.0	16.4	1.2	1.1	0.8	7.0	31.6	39.4	80	3

Horiz.	H_2SO_4 digest d = 1.47 (%)					Ki	Kr	Al_2O_3 / Fe_2O_3	P ($mg. kg^{-1}$)
	SiO_2	Al_2O_3	Fe_2O_3	$Ti\ O_2$	P_2O_5				
C_{1n}	138	100	42	5.9	-	2.14	1.70	3.85	10
C_{1p}	164	130	53	6.8	-	2.32	1.87	4.20	11
C_2	124	91	34	7.0	-	2.12	1.76	4.89	22
C_3	101	81	26	7.4	-	2.48	1.93	3.49	40
C_4	130	89	40	7.8	-	2.46	1.90	3.41	14
C_5	126	87	40	7.6	-	2.35	1.85	3.74	11

Horiz. = Pedological horizon; C_{1n} = natural layer; C_{1p} = disturbed layer; CS = coarse sand (1 to 0.2 mm); FS = fine sand (0.2 to 0.05 mm); SI = silt (0.05 to 0.002 mm); C = clay (<0.002 mm); WEC = water dispersible clay; DF = degree of flocculation; BD = bulk density; PD = particle density; TP = estimated total porosity; EH = equivalent moisture; OM = organic matter; OC = organic carbon; N = nitrogen; C/N = carbon/nitrogen ratio; SB = sum of bases; CEC (cation exchange capacity): Ca + Mg + K + Na + H + Al; V = base saturation; M = aluminum saturation; Ki = molecular ratio Silica/Alumina; Kr = molecular ratio Silica/Alumina + Ferric oxide; P = available phosphorus. (Table reproduced from Santana et al., 2004).

Table 2 - General description (a) and morphological characteristics (b) of the studied mangrove soil (Tropaquept) along the Graciosa River

(a) General description

Unit: Mangrove Soils

Current classification: Argisolic Sodic Salic Gleysol (Tropaquept)

Previous classification: Tropofluvent – Indiscriminat mangrove soil

Location: Mouth of the Graciosa River, Valenca/ Taperoa boundary along Highway BA-001

Altitude: 2 m

Situation: Lowlands

Relief: Flat

Drainage: Poorly drained

Geologic material: organic materials and mineral sediments of Proterozoic, Tertiary and Quaternary periods

Vegetation: Mangroves (*Rhizophora mangle* L.)

(b) Morphological characteristics

C1$_p$: 0-20 cm; very dark greenish grayish (3/10 GY – moist); dark grayish greenish (2.5/N – wet); dark yellowish brown (10YR 4/6 – wet); clay loam; soft, consistent massive; slightly plastic and slightly sticky, clear and wavy transition;

C1$_n$: 0-20 cm; black (n) and black (2.5 N); clay; soft, consistent massive; plastic and very sticky;

C2: 20-41 cm; very dark greenish grayish (3/3 GY); dark greenish grayish (2.5/N –wet); clay loam; soft, massive coherent; plastic and sticky, clear, wavy transition;

C3: 41-65 cm, very dark greenish grayish (3/5 GY); clay loam; soft, consistent massive; slightly plastic and sticky; clear and wavy transition;

C4: 65-99 cm; dark greenish grayish (2.5/5 G); Clay loam; free, soft, consistent massive that breaks to moderate fine to coarse sub-angular blocky; slightly plastic and sticky; clear wavy transition;

C5: 99-125 cm; greenish grayish (4/5 G); clay loam; consistent massive that breaks to moderate, coarse blocky; plastic and very sticky.

Table 3. Physical parameters obtained from the Gleysol (Tropoaquept) at a mangrove of the Graciosa River - Bahia, from 0-20 cm (natural: C1$_n$, disturbed: C1$_p$), over a five-year interval

Horizon/ year	Coarse Sand	Fine Sand	Silt	Total Clay	Natura 1 Clay	Silt: Clay	Deg. Floc. (%)	Equiv. Hum. (g/kg^{-1})	Part. Density (g cm^{-3})
	(gkg^{-1})								
C$_{1n}$ 2002	76.0^{b}	136.0^{b}	336.0^{a}	452.0^{a}	113.0^{a}	0.7^{b}	75.0^{b}	106.8^{a}	2.4^{a}
C$_{1p}$ 2002	157.0^{a}	198.0^{a}	311.0^{a}	334.0^{c}	80.0^{b}	0.9^{a}	76.0^{b}	(*)	2.4^{a}
C$_{1p}$ 2007	87.0^{b}	192.0^{a}	307.0^{a}	413.0^{b}	74.0^{c}	0.7^{b}	82.0^{a}	68.9^{a}	2.7^{a}

Averages with the same letter, in the column, were not significantly different by the Scott-Knott test ($p < 0.10$).
* Not determined.

Chemical Parameters

In general the organic matter (OM) presented high content in all layers, in special in the $C1_n$ and C2.

The pH values observed (3.9 to 5.0) were also found by Lamberti (1969) in mangrove soils of French Guiana. These results characterize this soil as strongly acid and the high levels of H and Al and the possible presence of fulvic acids (related to the OM) are the probable inducers of this acidity.

Regarding the sorptive complex, the soil has similarities between the layers as high CEC due to the large amount of OM and dominance of the cations Mg and Ca followed by Na and K, fact that gives the soil a eutrophic character.

The studied soil presented high fertility, evidenced by the usually high levels of sum of bases (SB), emphasizing Ca and Mg, high cation exchange capacity (CEC), high bases saturation (V), probably due to the low exchangeable acidity. The high ratio Ki of the soil is related to the high activity to the clay fraction, as suggested by Embrapa (2006). The high concentrations of phosphorus, mainly in the deepest horizons (C3, C4), are possibly due to higher concentration of this element at the period of sedimentation (from the parent rock or other soils), or also due to migration of this nutrient through the horizons.

In the comparison of the averages for 0-20 cm layer (Table 4), after a period of five years of advanced but partial vegetation regeneration, it was noted a decrease or a tendency to decrease in pH, Ca, Mg, K, H, C and N. The cation Na obtained significant increase in the disturbed layer in 2007 probably due to the largest influence of the saline wedge. Only Al and P remained unchanged, since the input is possibly assigned to the source material.

The high contents of OM (Table 1) observed in all layers, especially in the superficial ones ($C1_n$, C2) indicate that the studied mangrove area has well conserved vegetation, but the human intervention caused a loss of OM in the disturbed layer ($C1_p$). The conditions of mangrove soils, generally related to pH, submersion and sulfur compounds, tend to show an accumulation of OM as discussed by Cintrón-Molero and Schaeffer-Novelli (1992). The high C/N ratio (higher than average 10:1) shows a soil with less humified OM. This result probably occurs due to high soil acidity and also to the fact that mangrove areas subject to tides have higher intakes of OM compared to areas without this influence.

The geology of the watershed emphasizes the presence of lithology with predominance of enderbitics gneisses and pyroclastic associations, charnockite gneisses and quartzofeldspathic gneisses, and a lithologic association called "intermediate to basic granulitic rocks" (RADAMBRASIL, 1981). The key elements from these rocks are: TiO_2, FeO, MgO, K, Ca, Al, Na, Si and Mn.

The high contents of exchangeable bases, especially Mg, are a reflection of the seawater influence, and this concentration depends on the location in the estuary (Gamero et al., 2004; Rossi and Mattos, 2002). There is also the influence of riverine tides, carrying bases in suspension from soil and water bodies upstream to the mangrove. It can also be observed a decrease in salinity with the depth along the sediment profile, reflecting the greater influence of the salt wedge during high tide in the surface layers, as occurs for the layer C2.

This period of five years was not enough for the organic C recovery, and this decrease can also be associated with the hydrodynamic conditions at the study site, in spite of the frequent deposition of OM in

Table 4. Chemical parameters obtained for the Gleysol (Tropoaquept) at a mangrove of the Graciosa River - Bahia, from 0-20 cm (natural $C1_n$ and disturbed $C1_p$), over a five-year interval

Horizon/ year	pH (H_2O)	Ca	Mg	K	Na	Al	H	P	C	N
		$cmol_c\ dm^{-3}$						$mg\ dm^{-3}$	$g\ dm^{-3}$	
C_{1n} (2002)	5.0^a	7.6^b	16.2^a	1.2^a	4.1^b	0.7^a	7.7^a	10.0^a	67.9^a	4.1^a
C_{1p} (2002)	4.7^a	9.2^a	17.5^a	1.2^a	1.1^c	1.0^a	8.7^a	11.0^a	55.8^b	4.1^a
C_{1p} (2007)	4.0^b	3.3^c	4.9^b	0.5^b	10.5^a	0.7^a	5.1^b	8.0^a	20.5^c	0.9^b

Averages with the same letter, in the column, were not significantly different by the Scott-Knott test ($p < 0.10$)

the mangrove, as discussed by Reitermajer et al. (2011) and Alongi et al. (2000).

Heavy Metals

The levels of heavy metals showed more significant concentrations in the disturbed layer ($C1_p$) probably due to the deforestation of the studied area, as well as the inputs for the establishment of crops. In general, the heavy metals presented low levels (Table 5 and 6) compared to the typically found levels in uncontaminated soil, described by Raij (1991) as: 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}; except for Cd that was moderately high. Between the layers there were significant differences for all metals (Table 5 and 6). Fe, Mn, Zn, Co and Cd followed a trend of increase with depth, probably attributed to the source material of the soil, what is indicated by the higher concentrations found in the deepest layers (next to the matrix rock). Copper (Cu) concentrations follow a trend of reduction with depth (Table 5). Cr was the exception, with variable behavior along the depth and presented the highest concentration in the disturbed layer, what can be attributed to inputs from the deposited material and to the use of fertilizers, as indicated in the characterization of the agricultural sites.

The concentrations of Ni and Pb were below the detection limit and these metals were only detected in the disturbed layer C1p for Ni and in C1p and C2 for Pb. This result can be attributed to the use of phosphate fertilizers that contain large 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 5).

The comparison between results obtained for the disturbed layer in 2002 and 2007 (Table 6) shows that there were significant decreases in concentrations of Fe, Mn, Zn, Cr, Co, Cd and Pb after five years of the

Table 5. Heavy metal contents obtained for the Gleysol (Tropoaquept) 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, in the column, were not significantly different by the Scott-Knott test (p < 0.10).

* Concentration below the detection limit for the method used.

Table 6. Heavy metal content obtained for the Gleysol Salic Sodic argisolic at a mangrove of the Graciosa River - Bahia, in the 0-20 cm layer (natural $C1_n$ and disturbed $C1_p$), over an interval of five years

Horizon year	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, in the column, were not significantly different by the Scott-Knott test (p < 0.10).

* Concentration below the detection limit for the method used.

first sampling. During this period the soil showed an increase in clay and in the flocculation degree (Table 3). However, 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; and 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, (Förstner and Wittmann, 1993).

The abandonment of the mangrove area and the rapid regeneration of R. mangle vegetation may also have contributed to the observed changes in metals concentrations, 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 adsorbed by the finest fractions remaining of the soil, as observed by Malavolta and Reichardt (1976).

The concentration of heavy metals depends, among other factors, on the source material and on the process of soil formation. The 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. Yet the pH and the redox potential are the most relevant ones because they control the chemical speciation of metals in soil solution (Levent Tuna et al., 2007).

Another explanation would be the deposit and accumulation of these metals due to stagnation of river water during maximum ebb tide (Figure 2) in the deepest layers, contributing to the provision of small concentrations of these metals, from lithologic soil/material and upstream water bodies, to the upper horizons of the profile.

Additionally, residual fuel oils from the daily navigation of vessels in the Graciosa River estuary may also be contributing to the occurrence of metals (as suggested by Paul et al., 1994; Förstner and Wittman, 1993), as these oils have in their composition hydrocarbons and trace metals such as Ni and Cu. The concentrations of Fe are relatively low following the same trend observed by Lima (2001), that observed the pre-weathered source material and the pedoclimatic conditions of the Amazon region were driving factors for the low levels of Fe. In this study the source material is possibly poor in Fe and/or the transport of this metal in suspension from upstream water bodies is not very efficient, contributing to low concentrations of Fe in the soil. The 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 5). The low level of development of this soil and its salic sodic character may also influence loss of Fe and clays by ferrolysis as described by Schaefer and Dalrymple (1996).

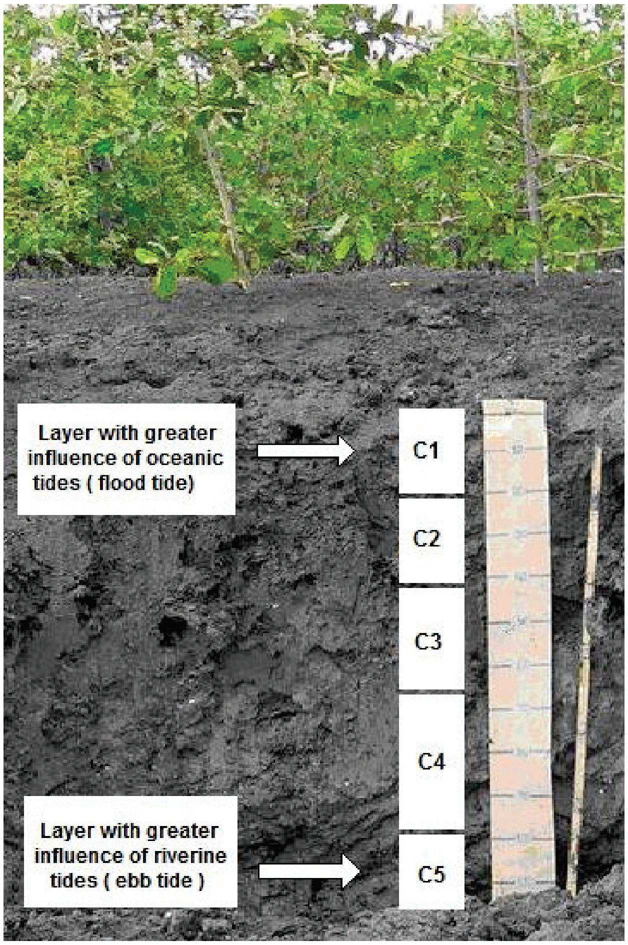

Figure 2. Location of riverine and oceanic influences on the studied mangrove soil.

Lima (2001) also observed a tendency of decrease with depth for the Copper concentration in Gleysols of the Western Amazon. Zinc concentrations 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 source material, being presented in high concentrations in magmatic rocks, as well as in fertilizers and fossil fuels as suggested 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 matrix rock. In soils close to urban areas, as additional sources, the residue of tires, diesel and lubricating oils, may contribute to the increase of this metal in soil.

Microbial Data

Mangrove vegetation, with a predominance of *R. mangle*, as well as temperature, OM input and water and nutrients availability, are some of the factors among others, that help to control the microbial composition and activities, determining their survival and growth conditions as suggested by Ovreâs and Torsvik (1998). These aspects may vary depending on the tidal cycle, the climate changes and the flora and fauna activity.

In soils of mangroves constantly flooded, there is a greater connectivity between microbial sites, since the water has a binding role between the soil aggregates, then resulting in a greater uniformity of the structure of microbial communities as suggested by (Borneman and Triplett, 1997). Biogeochemical processes, pH, type of mineral fraction, vegetation type, heavy metal contamination, sampling depth, all these factors may influence the quantification of soil microorganisms. Table 7 presents obtained data on bacteria, fungi and mycorhiza. The correlations between soil physical and chemical properties and microbial data are set in Table 8.

Bacteria - The quantification of bacteria in soil showed significant differences among the layers, with higher concentrations of these microorganisms in the layer C1n. Conversely, there was a sharp decline in the bacterial populations in layer C2, with counts near to zero. In layer C4 a marked growth of bacterial population was observed.

The greater biological activity in the superficial horizons occur due to the large amount of OM, the presence of light and oxygen and various other factors, as suggested by Borneman and Triplett (1997). The sharp decline in the bacterial populations in layer C2 may be related to the fact that these microorganisms do not support acid pH, high salinity and high concentrations of Al, parameters met in this layer (Table 1). Soil moisture and porosity (aeration) in this layer are factors that should favor the development of bacterial populations, but in this case, this wasn´t observed.

Several factors may have contributed to the marked growth of bacterial population in the layer C4: the high C/N ratio, higher pH, and lower Al and high P concentrations. Heavy metals levels in the soil did not influence the dynamics of bacteria as also observed by

Table 7. Quantification of microorganisms (bacteria, fungi and mycorrhizae) in six layers of the Gleysol at a mangrove of the Graciosa River - Bahia

Horizon	Depth (cm)	Bacteria CFU g soil^{-1} x 10 ^{6}	Fungi CFU g soil^{-1} x 10^{2}	Mycorrhiza spores/100 g soil^{-1}
C_{1n}	0-20	7.3^{a}	653.3^{a}	113.0^{a}
C_{1p}	0-20	6.2^{d}	93.3^{c}	19.0^{d}
C_{2}	20-41	* ^{f}	27.0^{d}	42.0^{c}
C_{3}	41-65	5.5^{e}	7.0^{e}	12.0^{e}
C_{4}	65-99	6.8^{b}	46.7^{d}	12.0^{e}
C_{5}	99-125	6.5^{c}	419.7^{b}	54.0^{b}

Averages with the same letter, in the column, were not significantly different by the Scott-Knott test ($p < 0.10$).

* Concentration below the detection limit for the method used.

Table 8. Correlation between the chemical and physical soil data and the microbial data

(a) Chemical properties

	Bacteria	Fungi	Mycorrhiza
OM	-0.3501	0.2817	0.5872
OC	-0.3371	0.2816	0.5846
N	-0.1497	0.2307	0.4318
C/N	0.1949	-0.0856	-0.2738
pH	0.8247	0.4081	0.0888
Ca	0.1035	0.0742	-0.0841
Mg	0.1733	0.8035	0.7938
K	0.7540	0.5544	0.2997
Na	-0.9390	-0.6537	-0.3478
P	-0.0453	-0.5986	-0.7668
Al	-0.9056	-0.1945	0.1666

(b) Physical properties

	Bacteria	Fungi	Mycorrhiza
CS	-0.1438	0.6897	0.9099
FS	0.3688	0.2548	0.0263
SI	0.2575	-0.1616	-0.4504
C	-0.3161	-0.4763	-0.2865
BD	-0.2987	-0.9325	-0.8532
TP	-0.5254	-0.9570	-0.7985
EH	-0.6608	-0.9335	-0.7272

OM = organic matter; OC = organic carbon; C/N = carbon/nitrogen ratio; P = available phosphorus; CS = coarse sand; FS = fine sand; SI = silt; C = clay; BD = bulk density; TP = estimated total porosity; EH = equivalent moisture.

Yim and Tam (2003). In this study, the pH was possibly the most important factor that adversely affected the bacterial populations.

Fungi - Significant differences were observed between the layers for fungal abundance. The high populations observed in the layers $C1_n$ and C5 related mainly with the acidic character of these layers, fact that was partially confirmed in this study since the fungi had a better development in the layers where bacterial populations were reduced, except in the surface layer (0-20 cm). Fungal populations were positively influenced by slight increasing in pH as well as by anaerobic conditions, even that the latter factor could be an inhibiting factor in some fungi populations.

The high populations observed in the layers $C1_n$ and C5 can be explained mainly by the acidic character of these layers, since soil fungi grow better in acidic conditions because they suffer less competition with bacteria (Jordan et al., 1995).

Mycorrhizae - The number of mycorrhizal spores varied between the layers of the studied soil profile, with the largest populations occurring in the undisturbed surface layer, $C1_n$. The high concentration of OM, C, N, higher luminosity, better aeration, a favorable pH and low concentrations of Na and Al are aspects that likely favored the development of these fungi in this layer, as discussed by Silveira (1992).

Flooding, often seen as inhibiting mycorrhizal growth (Silveira, 1992), did not significantly influence the population, which showed good development in the C5 layer, which remained flooded for long periods. Overall, the data suggest that the deposition of nutrients and compounds in the regions of the soil profile corresponding to the maximum and minimum tide (Figure 2), favored the growth of microorganisms adapted to the unique chemical conditions.

Conclusion

The physical and chemical properties of the studied mangrove soil were influenced by the regime of oceanic and riverine tides due to the estuarine location. Human intervention has led to a decline in the concentrations of clay and organic carbon in the soil.

The proximity of urban agglomerations and the upstream of the site – including the release of urban sewage, and use of fossil fuels and fertilizers – did not result in contamination by heavy metals (Cu, Zn, Mn, Cr, Ni, Pb, Co) in soil. Cadmium, due to its moderately high concentrations in the surface, is indicated to further studies to better understand its source and fate in this ecosystem.

The abundance of microorganisms (bacteria, fungi, mycorrhizae) was higher in the undisturbed surface layer and in the lower and intermediate layers of the disturbed site.

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