Comissão 2.3 - Mineralogia do solo

CHEMICAL PROPERTIES AND MINERALOGY OF SOILS WITH PLINTHITE AND PETROPLINTHITE IN IRANDUBA (AM), BRAZIL⁽¹⁾

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SUMMARY

Large areas of Plinthosols with ferruginous materials such as plinthite and/or petroplinthite are fairly common in the Brazilian Amazon basin. This work was carried out to investigate the chemical behavior, mineralogical composition and weathering stage of four representative soil profiles with plinthite and petroplinthite, in Iranduba, AM (Central Amazon). Three well-drained soil profiles at high elevations were studied (P1, Plinthic Vetic Ferralsol; P2 and P3, Vetic Endopetric Plinthosol) and a contrasting poorly drained soil (P4 Haplic Plinthosol), located at low elevation. After profile descriptions, soil samples were collected from each horizon, air-dried, sieved (2 mm), and analyzed for particle-size distribution, pH, exchangeable cations (Al³⁺, Ca²⁺, Mg²⁺, K⁺, and Na⁺), as well as available P and total organic carbon (TOC) content. The minerals present in the clay and sand fractions, as well as in the ferruginous materials were identified by X-ray Diffraction (XRD). The weathering stage of these soils was assessed by means of Ki and Kr indexes, and the amounts of free and amorphous Fe and Al oxides by using dithionite citrate bicarbonate (DBC) and ammonium oxalate dissolution procedures, respectively. The results showed that all soils were extremely unfertile, with pH levels ranging between strong and moderate acidity, very low sum of bases and organic matter content, and of available P. The mineralogy of the soil

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profiles was very similar, mainly of the well-drained soils, with predominance of kaolinite and quartz in the clay and sand fractions, respectively. In the poorlydrained P4, 2:1 clay particles were also observed. These profiles can be considered highly developed according to the Ki index, however, the Ki value of P4 was higher, indicating that this soil was less developed than the others. In summary, these profiles with plinthite and petroplinthite can be characterized as highly developed and infertile soils and are, with exception of P4, well-drained.

Index terms: Plinthosol, soil fertility, XRD, weathering degree, Central Amazon.

RESUMO: ATRIBUTOS QUÍMICOS E MINERALOGIA DE SOLOS COM PLINTITA E PETROPLINTITA EM IRANDUBA, AM, BRASIL

Expressivas áreas de solos com presença de materiais ferruginosos como plintita e, ou, petroplintita são muito frequentes na Bacia Amazônica brasileira. O objetivo deste trabalho foi avaliar os atributos químicos, a composição mineralógica e o grau de intemperismo de auatro perfis de solos com presenca de plintita e petroplintita, em Iranduba, AM. Três perfis de solos, como P1. Latossolo Amarelo distrófico petroplíntico; e P2 e P3. Plintossolo Pétrico concrecionário típico, ocupam posição mais elevada na paisagem apresentando boa drenagem, enquanto o perfil P4, Plintossolo Háplico alítico típico, encontra-se na área mais baixa com restrições de drenagem. Após a descrição morfológica dos perfis, amostras dos seus horizontes foram coletadas, secas ao ar, preparadas para obtenção da terra fina seca ao ar (TFSA) e posteriormente submetidas às análises químicas e mineralógicas, por meio de difratometria de raios-X (DRX) e ataque sulfúrico. As análises químicas revelaram que todos os solos apresentavam fertilidade extremamente baixa, com pH variando entre forte e moderadamente ácido, teores elevados de Al³⁺ no complexo trocável, baixos valores de soma de bases, matéria orgânica e P disponível. A mineralogia revelou similaridade entre os perfis, principalmente entre os bem-drenados, com predomínio de caulinita e quartzo nas frações argila e areia, respectivamente. No perfil com deficiência de drenagem (P4), a fração argila apresentou também mineral do tipo 2:1. Os índices Ki e Kr revelaram que os perfis bem-drenados P1, P2 e P3 são altamente desenvolvidos e quimicamente intemperizados, enquanto o P4 foi caracterizado como menos desenvolvido, quando comparado aos demais estudados. Por fim, os perfis com presença de plintita e petroplintita na região de estudo são altamente desenvolvidos e possuem fertilidade do solo extremamente baixa; com exceção do perfil P4, os solos são bemdrenados.

Termos de indexação: Plintossolo, fertilidade do solo, grau de intemperismo, DRX, Amazônia Central.

INTRODUCTION

Large areas of Plinthosols with ferruginous materials such as plinthite and/or petroplinthite are fairly common in the Brazilian Amazon basin. These ferruginous constituents are used as diagnostic properties to characterize the plinthic horizon of these soils (Soil Survey Staff, 1999; Embrapa, 2006; IUSS Working Group WRB, 2006). An estimated 7 % of Brazilian soils are Plinthosols, corresponding to an area of more than 589,000 km² (Santos et al., 2011). In the Amazon, according to Rodrigues (1996), Plinthosols cover an area of approximately 359,650 km². In the Central Amazon, these soils represent around 7.63 % (Schaefer et al., 2000), while the major areas with strong presence of plinthite and/or petroplinthite are found in the upper Solimões (Embrapa, 1986; Teixeira et al., 2010). In general, the origin of these ferruginous materials has been attributed to fluctuations of the water table, as well

as to soil drainage restrictions (Lima, 2001; Moreira & Oliveira, 2008; Benedetti et al., 2011). Plinthite is a soft, humus-poor and iron-rich material composed of clay minerals, with quartz, aluminum and other materials (Embrapa, 1999; Soil Survey Staff, 2010). Petroplinthite is developed from plinthite by oxidation and irreversible hardening of these Fe-rich materials, after being exposed to repeated wetting and drying cycles in soils (Driessen et al., 2001; IUSS Working Group WRB, 2006). In our study area in the Central Amazon, the occurrence of such soils is quite frequent; however, there is still little research on their chemical and mineralogical properties.

According to the Brazilian System of Soil Classification - SiBCS (Embrapa, 2006), the genesis of Plinthosols and other soil classes with plinthite or petroplinthite is related to alternating wetting and drying cycles over long time periods. In general, due to the high water table levels, an intense process of chemical reduction of iron compounds occurs, leading to the transport, mobilization, and concentration of these compounds in the soil systems. Consequently, when exposed to these processes, soil profiles may develop a subsurface horizon, known as plinthic horizon, associated with a waterlogging (IBGE, 2005; Embrapa, 2006; IUSS Working Group WRB, 2006).

Plinthosols are composed of mineral material with either a plinthic or a petroplinthic horizon 50 cm below the soil surface, or a plinthic horizon 100 cm deep, when underlying either an albic horizon or a horizon with stagnic properties (Embrapa, 2006; IUSS Working Group WRB, 2006). Physical and chemical limitations such as low water infiltration rates and natural fertility are often ascribed to these systems. This soil type is often associated to drainage deficiency and generally classified as inappropriate for agricultural purposes. The land suitability of Plinthosols is strongly related with the deepness, thickness and drainage of the plinthic horizon. Waterlogging and reduced water storage capacity limit the agricultural management of Plinthosols. In addition, these soils are commonly characterized as little fertile, acidic, with high amounts of exchangeable aluminum, and low cation exchange capacity (CEC) (Schaefer et al., 2000; Driessen et al. 2001; IBGE, 2005; Embrapa, 2006). Nevertheless, soils with ferruginous materials and relatively high CEC and clay activity have also been reported in the Brazilian Central Amazon by Lima et al. (2006), southwest Amazon by Martins et al. (2004) and in the State of Maranhão by Anjos et al. (2007).

The objective of this research was to investigate the chemical behavior, mineralogical composition and weathering stage of four representative soil profiles with ferruginous materials in the Central Amazon, Iranduba (AM).

MATERIAL AND METHODS

Sites and soil analysis

Four representative soil profiles in the Central Amazon were selected, containing plinthite and petroplinthite, developed on tertiary sediments of the Alter-do-Chão formation in Iranduba, State of Amazonas (map in Figure 1). The profiles P1 and P2, under agroecosystems, are located on experimental fields of Embrapa near Manaus-AM. Profile P3 is under agricultural use and P4 under secondary vegetation, near the Lago do Limão. The topographical positions of the profiles P1, P2 and P3 are higher and drainage is good. In contrast, P4 is located at a low position of the landscape, in a poorly drained area. At each site, the soil profiles were described and soil sampled from each horizon, as proposed by Santos et al. (2005). All soils were classified according to the Brazilian System of Soil Classification (Embrapa, 2006) and World Reference Base of Soil Resources (IUSS Working Group, 2006).

In the region, the annual precipitation is around 2000 mm and the mean annual air temperature and humidity are 27 °C and 87 %, respectively (RadamBrasil, 1977).

The soil samples were air-dried and sieved (2 mm) to obtain air-dried fine earth (ADFE), which was analyzed for pH (in H₂O and 1 mol L⁻¹ KCl), exchangeable cations (Al³⁺, Ca²⁺, Mg²⁺, K⁺, and Na⁺), available phosphorus (P), and total organic carbon (TOC) content, according to Embrapa (1997). From these results, the sum of bases (SB), base saturation (V) and cation exchange capacity (CEC) were computed for each profile. A number of soil morphological (horizon denomination and thickness, Munsell color) and physical properties (particle size distribution, bulk density and total porosity) were also studied, using methods described by Santos et al. (2005) and Embrapa (2006). To determine the particle-size distribution, the pipette method was applied and the volumetric ring method to measure soil bulk density. Total porosity (TP) was obtained by the following expression: Pt = 1-(Ds/Dp)x100, in which a particle density of 2.65 Mg m⁻³ is assumed (Moura et al., 1992).

Mineralogical analysis

To identify the minerals present in the clay (<2 μ m \emptyset) and sand fractions of these soils and their ferruginous constituents, the ADFE was subjected to qualitative mineral analysis, as described by Embrapa (1997). The clay material was separated by sedimentation (pipette method). The sand particles were separated by sieving and crushed afterwards in an agate mortar. X-ray diffraction (XRD) patterns of the powder materials were obtained using a SHIMADZU XRD 6000 diffractometer, with a Cu X-ray tube and scanned $(3-60^{\circ} 2\theta)$. The minerals were interpreted from the difractograms, as proposed by Chen (1977). The identification of the minerals was also confirmed by tables of the Joint Committee on Powder Diffraction Standards (JCPDS) available at Berry (1974), Brindley & Brown (1984) and Moore & Reynolds (1997).

Additionally, soil samples from topsoil and subsoil horizons of each profile were also analyzed for total Fe-, Al-, Si-, and P-content by the sulfuric acid attack (Embrapa, 1997). From the results, the weathering stage of these soils was assessed using the following indices: Ki = % SiO₂ x 1.7/% Al₂O₃ e Kr = % SiO₂ x 1.7/[% Al₂O₃ + (% Fe₂O₃ x 0.64)]. The amounts of poorly crystalline and free Fe and Al contents were also determined by ammonium oxalate (Schwertmann, 1964) and sodium dithionite citrate bicarbonate (DCB) extraction (Coffin, 1963).



Figure 1. The four geographic locations of the studied soils (P1, P2, P3 and P4) in Iranduba in the State of Amazonas: P1, Plinthic Vetic Ferralsol (Latossolo Amarelo distrófico petroplíntico); P2 and P3, Vetic Endopetric Plinthosol (Plintossolo Pétrico concrecionário típico); P4, Haplic Plinthosol (Plintossolo Háplico alítico típico).

RESULTS AND DISCUSSION

Morphological and physical properties

Based on the Brazilian Soil Classification System (Embrapa, 2006), the four soil profiles were classified as: P1, petroplinthic dystrophic Yellow Latosol (LAd); P2 and P3, concretionary Petric Plinthosol (FFc); and P4, Haplic Plinthosol (FXal), and according to the World Reference Base of Soil Resources (IUSS Working Group, 2006) as follows: P1, Plinthic Vetic Ferralsol; P2 and P3, Vetic Endopetric Plinthosol; and P4, Haplic Plinthosol.

The profile classification and soil morphological and physical properties are given in table 1. The soil horizon sequence of profile P1, used as agro-ecosystem, was A-AB-B₁-B₂-Bc₁-Bc₂-Bc₃, characterized as deep and well-drained (Embrapa, 2006). In addition, hue 10YR was observed in all horizons, as well as an increase in chroma in the deeper layers. In profile P2, the sequence of the horizons was A-Ac-AB-BA-B₁-B₂-Bc-C₁-C₂. Also, this profile P2 revealed a hue of 7.5R from the surface to the B-horizon, with predominant reddish-yellow color, and in the subsequent C and C₂ subsurface horizons reddish yellow colors (hue 2.5YR). These soil color properties indicate a well-aerated environment at a high landscape position of both profiles.

In profile P3 under agricultural use, the horizon sequence was A-B-BA-Bf₁-Bf₂-Bf₃, respectively. In this profile, a yellowish red color (5YR) was observed from the surface to the BA-horizon, and reddish yellow colors in the subsequent horizons (7.5YR) (Table 1). In profile P4, the soil horizon sequence was A-B₁-B₂-BCg-Cg₁-Cg₂, with yellowish red color (5YR) in the surface

horizon and lower chroma in a large part of the soil matrix, which may be related to iron reduction in the profile, indicating a hydromorphic process. These findings agree with those reported in other papers on soils of the Amazon region (Lima, 2001; Benedetti et al., 2011; Campos et al., 2012a).

The particle-size analysis indicated a clay content between 434 and 670 g kg⁻¹ of the profiles P1, P2 and P3, indicating clay soils (Embrapa, 2006). Profile P4 had a higher silt content than the other profiles, which varied between 218 and 317 g kg⁻¹ (Table 1), revealing a lower development stage than the other profiles. The bulk density ranged from 1.03 to 1.36 Mg m⁻³ for the higher-lying P1, P2 and P3 with good drainage, and ranged between 1.22 and 1.48 Mg m⁻³ (Table 1) for profile P4 at a lower position with poor drainage. In all soils, total porosity (TP) increased in the deeper layers, indicating an opposite tendency to that of soil bulk density. The total porosity values varied between 44 and 61 % in all soils. The lowest values were observed for P4, especially in the B_1 and B_2 horizons, suggesting low water drainage capacity of this soil.

Chemical properties

In all samples the soil $pH_{(H2O)}$ varied from 4.3 to 5.7 (Table 2), while $pH_{(KCl)}$ ranged from 3.7 to 4.4. The lowest values were found for profile P1, and the highest for profile P3. The results showed that $pH_{(H2O)}$ was higher than $pH_{(KCl)}$ at all sites and also that soil acidity decreases with depth (Table 2). Based on these pH values, the profiles can be classified as strong to moderate acidic (Embrapa, 2006). The delta pH values (pH_{KCl} - pH_{H2O}) were negative for all soils, showing that these soils were dominated by negative surface charges.

The cationic nutrient contents were rather low in all soil profiles (Table 2), i.e., the fertility of these soils is extremely low. This chemical behavior has often been observed in the highly weathered Amazonian soils, mainly in uplands where the variability of the mineral composition of the parent material is low (Radambrasil, 1977; Schaefer et al., 2000; Lima, 2001). Also, other important bioclimatic factors such as high amounts of precipitation and temperatures increased leaching and nutrient depletion from the rooting zone to deeper layers, contributing to this low chemical soil quality in the region. The cation exchange capacity (CEC) of the well-drained soil profiles P1, P2, and P3 was very low, as also observed in the topsoil of

the poorly-drained P4, where however the CEC values increased in the deeper layers (Table 2). This relatively higher CEC in deeper layers of P4 may be related to the presence of 2:1 clay silicates identified by X-ray diffraction patterns, discussed below. The values of sum of bases (SB) were extremely low in all soil profiles, with base saturation (V) generally below 50 % (Table 2), along with high exchangeable Al, as observed previously for Amazonian soils (Rodrigues, 1996; Schaefer et al., 2000; Lima et al., 2006).

In general, total organic carbon (TOC) contents are higher in the top layers, decreasing with depth (Table 2). Soil organic carbon contents varied from 0.35 to 25.2 g kg⁻¹. The lowest and highest values

Horizon	Depth	Wet color (Munsell)	Partic	le-size distri	Bulk	Total	
			Sand	Silt	Clay	density	porosity
	cm			g kg ⁻¹		Mg m ⁻³	%
	P1	- Plinthic Vetic Ferr	alsol (Latossolo	Amarelo distr	ófico petroplínt	ico)	
А	0-28	10YR 5/4	520	34	446	1.07	60
AB	28-35	10YR5/4	500	43	457	1.13	57
B_1	35-59	10YR 5/6	460	23	518	1.34	49
B_2	59-90	10YR 6/8	453	19	528	1.36	49
Bc_1	90-120	10YR 5/8	428	37	538	-	-
Bc_2	120-153	10YR 5/8	412	33	555	-	-
Bc_3	153^{+}	10YR 5/8	539	47	411	-	-
	P2 -	- Vetic Endopetric Pl	inthosol (Plintos	solo Pétrico co	oncrecionário tí	pico)	
А	0-14	7,5YR 3/2	404	70	488	1.03	61
Ac	14-29	7,5YR 3/2	442	56	536	-	-
AB	29-50	7,5YR 4/4	411	61	544	-	-
BA	50-67	7,5 YR 5/6	349	49	609	-	-
B_1	67-84	7,5YR 5/8	210	67	723	1.23	54
B ₂	84-119	7,5YR 5/8	246	46	710	-	-
вĈ	119-150	2,5YR 5/8	276	54	670	-	-
C_1	150-182	2,5YR 5/8	196	140	666	-	-
C_2	$182 - 205^+$	2,5YR 4/6	236	162	602	1.25	53
	P3 ·	- Vetic Endopetric Pl	inthosol (Plintos	solo Pétrico co	oncrecionário tí	pico)	
А	0-10	5YR 3/4	526	40	434	1.09	59
В	10-30	5YR 5/6	419	67	514	1.14	57
BA	30-41	5YR 4/6	386	56	558	1.26	52
Bf_1	41-64	7,5YR 5/8	379	42	580	1.32	50
Bf_2	64-91	7,5YR 6/8	365	28	607	1.30	51
Bf_3	91-132	7,5YR 6/8	299	47	654	-	-
		P4 - Haplic Plir	nthosol (Plintoss	olo Háplico alí	tico típico)		
А	0-24	5YR 3/2	407	259	333	1.22	54
B_1	24-39	5YR 4/1	256	266	357	1.48	44
B_2	39-62	2,5YR 4/8	291	241	467	1.45	45
BCg	62-89	10YR 8/2	140	218	641	1.38	48
Cg_1	89-101	10YR 8/1	83	317	599	-	-
Cg_2	$101 - 150^+$	5Y 8/1	86	308	605	-	-

were found in P4 and P3, respectively. The higher TOC-content in the surface layer of P3 may be related to a greater input and cycling of organic material at this site. In tropical environments, due to the high temperatures and rapid organic matter mineralization rates, the stability of organic carbon in soils is fairly low. Generally, TOC-contents are lower than 30 g kg⁻¹ in the surface layer in most soils of the Brazilian Amazon (Lima et al., 2006; Quesada et al., 2010). The available P contents extracted by Mehlich-1 were considered extremely low in all studied profiles. Normally, the P-availability in these highly developed upland soils is lower than 5 mg kg⁻¹ (Rodrigues, 1996; Lima, 2001; Quesada et al, 2010).

Mineralogical properties

In the well-drained profiles (P1, P2, and P3), the mineralogical properties are quite similar. In the clay and sand fractions, kaolinite and quartz were predominant, respectively (Figures 2 and 3). Aside from kaolinite in the clay fraction, gibbsite, goethite and titanium oxides (anatase) were also found at lower concentrations in the soil matrix. The sand fraction of all soils was fully dominated by quartz, in agreement with other papers (Horbe & Costa, 1999; Lima, 2001; Marques et al., 2002; Lima et al., 2006; Benedetti et al., 2011). In general, the dominance of kaolinite indicates that these soils are highly developed

Hz	Depth _	pH		P	к	Na	Ca ²⁺	Mg ²⁺	Al ³⁺	SB	CEC	v	тос
		H_2O	KCl				cu	8				·	100
cm		mg kg ⁻¹					cmol _c kg ⁻¹						g kg ⁻¹
P1- Plinthic Vetic Ferralsol (Latossolo Amarelo distrófico petroplíntico)													
А	0-28	4.3	3.7	4	0.57	0.20	0.01	0.01	1.90	0.78	8.38	9.30	13.05
AB	28 - 35	4.6	3.8	2	0.26	0.09	0.00	0.01	1.40	0.35	5.58	6.27	8.43
B_1	35-59	4.7	3.9	2	0.07	0.03	0.00	0.03	1.20	0.13	3.45	3.63	3.93
B2	59-90	4.8	4.2	2	0.07	0.00	0.00	0.03	0.80	0.07	2.56	2.77	3.11
Bc_1	90-120	4.8	4.1	2	0.02	0.01	0.01	0.02	0.60	0.16	2.76	5.80	3.08
Bc_2	120 - 153	4.9	4,3	2	0.07	0.01	0.00	0.01	0.40	0.10	2.26	4.42	2.38
Bc_3	153^{+}	5.1	4.3	2	0.05	0.03	0.00	0.01	0.60	0.10	1.53	6.35	1.16
P2 - Vetic Endopetric Plinthosol (Plintossolo Pétrico concrecionário típico)													
А	0-1	4.4	3.8	2	1.11	0,03	0.03	0.03	2.52	1.20	13.94	8.60	22.65
Ac	14-29	4.5	3.9	1	0.39	0,03	0.03	0.03	1.83	0.48	7.37	6.46	15.56
AB	29-50	4.4	3.9	1	0.54	-	0.02	0.01	2.00	0.58	10.24	5.62	13.30
BA	50-67	4.6	3.9	0	0.18	-	0.01	0.01	1.53	0.20	5.14	3.80	10.60
B_1	67-84	4.7	4.0	0	0.14	-	0.02	0.01	1.23	0.16	3.93	4.12	6.76
B_2	84-119	5.0	4.1	0	0.13	-	0.01	0.00	1.08	0.14	3.50	3.97	5.01
BC	119-150	5.0	4.1	0	0.05	-	0.07	0.00	1.06	0.06	3.18	1.92	3.52
\mathbf{C}_1	150-182	5.1	4.1	-	0.05	-	0.01	0.00	1.50	0.06	2.92	1.95	1.95
\mathbf{C}_2	$182 - 205^+$	5.1	4.1	-	0.08	-	0.01	0.00	1.48	0.09	2.83	3.15	1.20
		P	3 - Veti	c Endop	etric Plin	nthosol (F	lintossolo	Pétrico	concrecion	ário típio	co)		
А	0-10	4.4	3.9	3	0.64	0.32	0.04	0.02	1.62	1.02	9.94	10.22	25.25
В	10-30	4.9	4.2	2	0.35	0.19	0.02	0.01	0.85	0.57	6.43	8.91	12.20
BA	30-41	5.2	4.2	1	0.18	0.15	0.02	0.01	0.82	0.35	5.83	6.05	11.79
Bf_1	41-64	5.6	4.3	1	0.23	0.34	0.02	0.01	0,63	0.60	4.60	13.01	7.18
Bf_2	64-91	5.6	4.5	1	0.15	0.32	0.03	0.00	0,22	0.50	3.34	14.92	5.55
Bf_3	91-132	5.7	4.8	1	0.13	0.34	0.02	0.00	0,20	0.49	2.50	19.50	3.94
P4 - Haplic Plinthosol (Plintossolo Háplico alítico típico)													
Α	0-24	4.5	3.8	2	1.25	0.97	0.27	0.13	3.15	2.62	11.73	22.34	20.20
B_1	24-39	4.6	3.8	1	0.38	0.72	0.16	0.11	5.47	1.37	8.39	16.33	9.14
B_2	39-62	4.7	3.8	1	0.38	0.33	0.15	0.12	6.90	0.98	9.27	10.57	4.62
BCg	62-89	4.8	3.8	1	0.38	0.41	0.11	0.14	6.77	1.04	10.61	9.80	3.95
Cg_1	89-101	4.8	3.7	1	0.62	0.58	1.20	0.11	10.30	2.51	14.71	17.60	0.59
Cg_2	101-150+	4.9	3.7	1	0.62	0.76	0.13	0.11	10.27	1.62	13.74	11.79	0.35

Table 2. Chemical properties of four soils studied in Iranduba (AM)

Hz: horizont.

and weathered. In turn, the poorly-drained P4 show a different stage of development, basically due to the presence of 2:1 clay minerals (Figure 4). According to Schaefer et al. (2000) and Lima (2001), the strong drainage deficiency within the soil profile associated to high water table levels, limit the pedological



Figure 2. X-ray diffractogram of clay fraction of the A and B1 horizons, the A, B1 and C1 horizons, and the A, Bf1 and F layers of the well-drained P1, P2 and P3 profiles, respectively: Kt, Kaolinite; Gb, Gibbsite; Gt, Goethite; and Qtz, Quartz.



Figure 3. X-ray diffractogram of sand fraction of the A and B1 horizons, and the A, B1 and C1 horizons, and the A, Bf1 and F layers of the well-drained P1, P2 and P3 profiles, respectively: Qtz, Quartz.

processes resulting in underveloped soils in the landscape.

Goethite and hematite were observed as major iron compounds of ferruginous materials such as petroplinthite in P1, P2, and P3 profiles (Figure 5). Other components such as gibbsite, kaolinite and 2:1 clay particles were also observed. The presence of these particular iron compounds is strongly associated to the genesis process (Resende et al., 2005). Soils with



Figure 4. X-ray diffractogram of clay fraction of the A, B₁ and the Cg₁ horizons of the poorly drained P4: Kt, Kaolinite; Gb, Gibbsite; Gt, Goethite; Qtz, Quartz, and 2:1 clay mineral.



Figure 5. X-ray diffractogram of petroplinthites of the Bc₁ horizon, the Ac and BC horizons, and Bf₁ and F layers of the well-drained P1, P2 and P3 profiles, respectively: Kt, Kaolinite; Gb, Gibbsite; Hm, Hematite; Gt, Goethite; and 2:1 clay mineral.

drainage deficiency could lead to chemical reduction of iron compounds, (Fe⁺³ to Fe⁺²), transport and precipitation, leading to the formation of these ferruginous materials in the profile, over time (Anjos et al., 1995; Duarte et al., 2000; Anjos et al., 2007; Moreira & Oliveira, 2008). The plinthic materials in P4 consisted mainly of kaolinite and quartz, whereas 2:1 clay silicates, and iron and aluminum oxides were observed at lower levels (Figure 6).





The highest amounts of free iron extracted by sodium dithionite citrate bicarbonate (DCB) (Fe_d) were found at well-drained sites (P1, P2, and P3), as well as in their plinthic materials (Table 3). The lowest Fe_d amounts were found in P4. Santos & Batista (1996) also observed these characteristics in their investigations in the north of Brazil.

The higher Fe_o/Fe_d ratio revealed the dominance of poorly crystalline iron oxides in the whole profile P4 and also in the topsoil layers of other profiles (Table 3). According to Ghidin et al. (2006), high amounts of amorphous iron are very common in reduced environments, in line with this behavior of the poorly drained P4. In other profiles, this fact was probably related to the higher organic matter contents of the topsoil layers. It is known that organic carbon interacts with iron oxides, and that it could consequently slow down their crystallization process in soils (Schwertmann et al., 1986).

In the profiles P1, P2, and P4, the total iron (Fe_t) extracted by sulfuric acid attack and expressed in oxide form contents was low (Fe₂O₃ < 80 g kg⁻¹, Table 3), but medium (80 < Fe₂O₃ < 180 g kg⁻¹) in P3, according to the criteria utilized by Embrapa (2006). These values were in agreement with such a characteristic normally observed for these Amazonian

 $\begin{array}{l} \mbox{Table 3. Values of Silicium-, Aluminum-, Iron-, and P-oxides extracted by the sulfuric acid attack, Ki and Kr indexes, Fe-dithionite (Fe_{(d)}), Fe-oxalate (Fe_{(o)}), F_{(o)}/F_{(d)} ratio, and Al_2O_3/Fe_2O_3 of four soils studied in Iranduba (AM) \end{array}$

Hz	Depth	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	$\mathbf{Fe}_{(\mathbf{o})}$	$\mathbf{Fe}_{(\mathbf{d})}$	$Fe_{(o)}/Fe_{(d)}$	Ki	Kr	Al ₂ O ₃ /Fe ₂ O ₃		
cm				g ł	kg ⁻¹								
	P1- Plinthic Vetic Ferralsol (Latossolo Amarelo distrófico petroplíntico)												
А	0-28	144.9	137.0	48.7	00.4	01.5	01.3	1.15	1.80	1.47	4.42		
Bc_1	90-120	164.8	159.8	52.6	00.5	00.5	01.3	0.38	1.75	1.45	4.77		
Petroplinthite													
Bc_1	90-120	126.0	127.4	630.0	00.4	00.7	06.7	0.10	1.68	0.40	0.31		
P2 - Vetic Endopetric Plinthosol (Plintossolo Pétrico concrecionário típico)													
А	0-14	145.3	137.9	54.1	00.5	02.0	01.3	1.54	1.79	1.43	4.00		
B_1	67-84	240.2	212.4	78.2	00.4	00.5	01.5	0.33	1.92	1.56	4.26		
Petroplinthite													
Ac	14-29	88.4	116.5	660.2	00.3	01.0	05.7	0.18	1.29	0.28	0.28		
P3 - Vetic Endopetric Plinthosol (Plintossolo Pétrico concrecionário típico)													
А	0-10	96.3	137.6	92.6	06.8	02.0	01.3	1.54	1.19	0.83	2.33		
Bf_1	41-64	146.6	186.4	120.8	00.7	00.8	01.2	0.66	1.34	0.95	2.42		
Petroplinthite													
Bf_1	41-64	128.0	202.7	489.2	01.3	00.8	06.3	0.13	1.07	0.42	0.65		
P4 - Haplic Plinthosol (Plintossolo Háplico alítico típico)													
А	0-24	111.8	98.5	37.6	00.4	04.0	00.8	5.00	1.93	1.55	4.11		
\mathbf{B}_1	24-39	133.3	106.2	35.6	00.3	03.7	00.8	4.62	2.13	1.76	4.69		
	Plinthite												
\mathbf{B}_1	24-39	254.7	196.6	136.7	00.2	00.8	01.3	0.62	2.20	1.52	2.26		

Hz: horizont.

soils (Lima, 2001; Campos et al., 2011; Silva et al., 2011; Campos et al., 2012a,b). In contrast, the total iron oxide contents found in the ferruginous materials were higher than 180 g kg⁻¹, revealing a high concentration of Fe-oxides in these ferruginous concretions, formed after a period of time of wetting and drying processes in these soil systems.

The Si/Al ratio of all soils and their ferruginous materials ranged from 1.19 to 2.13 and 1.07 to 2.20, respectively (Table 3). According to (Embrapa, 2006), these soils can be characterized as highly developed and chemically weathered. In general, soils with Ki index lower than 2.2 imply that the clay fraction is dominated by low activity clay particles (kaolinite, and iron and aluminum oxides), well-developed and drained profiles in the landscape. The Ki index was higher in the poorly-drained profile P4 (Table 3), particularly in the plinthic horizon and also in the plinthites, confirming that P4 is less developed and chemically weathered than the profiles P1, P2, and P3 and their plinthic materials.

CONCLUSIONS

1. In the Central Amazon, soil profiles with ferruginous materials (i.e., plinthite and petroplinthite) have extremely low chemical fertility with low nutrient and total organic carbon contents; high acidity, low cation exchangeable capacity (CEC), and high exchangeable Al contents.

2. According to the XRD analysis, the mineralogical characteristics of these soils are quite similar. The soil composition is basically dominated by kaolinite in the clay fraction, followed by goethite, gibbsite and titanium oxides (anatase). The sand fraction is dominated by quartz. The poorly-drained P4 also contained 2:1 clay minerals.

3. Iron oxides such as goethite and hematite are the major constituents of the ferruginous materials, e.g., petroplinthite, and the plintic material of P4 contained mostly kaolinite, quartz and 2:1 silicates. Profile P4 contained significant amounts of amorphous iron oxides, according to its Fe_0/Fe_d ratio. The lower Ki index revealed that the well-drained profiles (P1, P2, and P3) can be characterized as highly weathered and developed, while P4 is less developed.

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