

## Forms of soil organic phosphorus at black earth sites in the Eastern Amazon<sup>1</sup>

Formas de fósforo orgânico do solo em sítios de terra preta na Amazônia Oriental

Adriane da Rocha Costa<sup>2\*</sup>, Mário Lopes Silva Júnior<sup>2</sup>, Dirse Clara Kern<sup>3</sup>, Maria de Lourdes Pinheiro Ruivo<sup>3</sup> and Raphaël Marichal<sup>4</sup>

**ABSTRACT** - Soils containing archaeological black earth (ABE) are formed by the continuous deposition of organic residue, and maintain their high fertility even after years of cultivation. The aim of this study was to characterise and quantify the forms of organic phosphorus in areas of archaeological black earth (ABE), with a view to understanding the dynamics of the element and contributing to the development of sustainable practices of land use. Samples of 10 profiles were used from Latosols, Argisols and Gleysols located in the eastern Amazon with an anthropogenic A-horizon (ABE), using adjacent, non-anthropogenic soils as reference. The samples relative to the A, transitional and B-horizons, were subjected to sequential fractionation of P in an acid base extraction, and to further physicochemical characterisation. The acid-extracted P fraction in the A1 and B-horizons predominated over the basic-extractant labile and soluble fractions in all areas, displaying the highest percentages for the inorganic form. An increase in the labile organic phosphorus content (Pol) was found in the A1-horizon, with a reduction between the A and B-horizons of 97.6%. The amount of total phosphorus (TP) was significantly higher (6,778 mg dm<sup>-3</sup>) in the A-horizons of the ABE in comparison with the soil in the reference area (168 mg dm<sup>-3</sup>). The predominance of inorganic phosphorus over organic phosphorus was found for the total fraction, while the opposite occurred with the labile fractions. Most of the total labile P is therefore accumulated in the organic fractions of the soil, and represents an active means of supplying the nutrient to plants as it mineralises.

**Key words:** Sequential fractionation. Anthropogenic soils. Labile phosphorus. Pyrogenic carbon.

**RESUMO** - Os solos com Terra Preta Arqueológica (TPA) são formados pela deposição contínua de resíduos orgânicos e mantêm sua fertilidade elevada mesmo após anos de cultivo. O objetivo do trabalho foi caracterizar e quantificar as formas de fósforo orgânico em sítios de Terra Preta Arqueológica (TPA), visando compreender a dinâmica desse elemento e contribuir com o desenvolvimento de práticas sustentáveis de uso do solo. Foram utilizadas amostras de 10 perfis com horizonte A antrópico (TPA) em Latossolos, Argissolos e Gleissolo, usando como referência solos adjacentes não antropogênicos, localizados na Amazônia Oriental. As amostras referentes aos horizontes A, horizonte de transição e B, foram submetidas ao fracionamento sequencial do P, em extrato ácido e básico e demais caracterizações físico-químicas. A fração de P em extrato ácido nos horizontes A1 e B predominou sobre as frações lábeis e solúvel em extrato básico em todas as áreas, apresentando os maiores percentuais observados na forma inorgânica. Verificou-se o aumento do conteúdo de fósforo orgânico lábil (Pol) no horizonte A1, com redução entre os horizontes A e B de 97,6%. O fósforo total (PT) apresentou teores significativamente elevados (6.778 mg dm<sup>-3</sup>) nos horizontes A de TPA em comparação com o mesmo horizonte no solo de referência (168 mg dm<sup>-3</sup>). Na fração total observou-se o predomínio do fósforo inorgânico sobre o fósforo orgânico, enquanto que nas frações lábeis ocorreu o inverso. Portanto, a maior parte do P total lábil está acumulado nas frações orgânicas do solo, representando uma forma ativa para o fornecimento do nutriente aos vegetais à medida que se mineraliza.

**Palavras-chave:** Fracionamento sequencial. Solos antrópicos. Fósforo lábil. Carbono Pirogênico.

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\*Autor para correspondência

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<sup>2</sup>Departamento de Solos e Nutrição Mineral de Plantas, Universidade Federal Rural da Amazônia, Av. Presidente Tancredo Neves, 2501, Terra Firme Belém-Pará, Brasil, 66.077-830 adrianedarocha@yahoo.com.br, mario.silva@ufra.edu.br

<sup>3</sup>Museu Paraense Emílio Goeldi, kern@museu-goeldi.br, ruivo@museu-goeldi.br

<sup>4</sup>CIRAD, UPR Systèmes de pérennes, F-34398 Montpellier, France, raphael.marichal@gmail.com

## INTRODUCTION

In the Amazon, anthropogenic soils known as Archaeological Black Earth (ABE), display high fertility related to the addition of organic residue and the presence of pyrogenic carbon resulting from biomass pyrolysis at temperatures over 600 °C, whose partial oxidation produces carboxyl groups that contribute to an increase in CEC, with a long-term increase in nutrient levels (FRASER *et al.*, 2011; GLASER; BIRK, 2012; HOLLIDAY; GARTNER, 2007; KERN *et al.*, 2010; SANTOS *et al.*, 2013; SILVA *et al.*, 2012).

The anthropogenic A horizon occurs in discontinuous patches throughout the Amazon area over several orders of soil, such as Latosols Argisols, Gleysols and Neosols (SMITH, 1980). Sites can vary from 0.3 to 5 hectares (ha) in size, reaching hundreds of hectares in areas near rivers (COSTA; COSTA; KERN, 2013; KERN *et al.*, 2010). These soils are generally eutrophic in character, with high levels of nutrients in a form assimilated by plants, mainly calcium (Ca) and phosphorus (P), whose available content may be up to 3000 mg dm<sup>-3</sup> (BARROS *et al.*, 2012; CAMPOS *et al.*, 2011; GLASER; BIRK, 2012; KERN *et al.*, 2010; LIMA *et al.*, 2002). Farmers recognize the benefits of ABE to agricultural production, and use these areas mainly for subsistence farming (ARROYO-KALIN *et al.*, 2010; FRASER *et al.*, 2011). However, such sites are considered to be areas of cultural heritage of mandatory preservation, according to Federal Law No. 3924 of 26 July 1961.

In anthropological research, P can inform about past human occupation, and the duration and intensity of human activities (HOLLIDAY; GARTNER, 2007; SATO *et al.*, 2009; SOUZA *et al.*, 2009). Moreover, P is a key nutrient in agricultural areas, whose deficiency in the soil directly affects crop development (DUDA *et al.*, 2006; DUDA *et al.*, 2013.).

In Brazilian soils, such as Latosols, P is present mainly in forms which are unavailable to plants (GUERRA *et al.*, 1996; MERLIN; HE; ROSOLEM, 2013), especially forms of inorganic P with high-energy binding to the mineral fraction and to stable organic forms (EBERHARDT *et al.*, 2008; NOVAIS; SMYTH, 1999; SÁNCHEZ-ALCALÁ *et al.*, 2014). After fertilization of these soils with superphosphate, around 85 to 90% of the P is unavailable to plants during the first year of application due to adsorption and precipitation with Fe, Al and Ca (GICHANGI; MNKENI; BROOKES, 2009). Management strategies are necessary to improve P usage efficiency in the soil, thereby reducing the high costs of adding mineral phosphate fertilizers.

The intake of organic material may contribute to a higher concentration of P in the soil and to an increase in the bioavailability of this nutrient in the long term for plants and soil organisms (BUSATO; CANELLAS; VELLOSO, 2005; MALIK; MARSCHNER; KHAN, 2012; NOGUEIRA *et al.*, 2008; NOVAIS; SMYTH, 1999). In humid tropical soils, 32% of the total phosphorus (TP) on average is found in organic form, of which from 5 to 86% may be in the labile organic fraction (GUERRA *et al.*, 1996; HOLLIDAY; GARTNER, 2007), underlining the importance of this fraction to the availability of P in weathered soils (XAVIER *et al.*, 2009).

Partelli *et al.* (2009) found a stock of total organic P (Pot) accounting for up to 56.9% of the soil TP in organic coffee plantations. On the other hand, Duda *et al.* (2013) observed levels of labile organic phosphorus (Pol) which ranged from 50 to 91% in relation to labile inorganic phosphorus (Pil) in 14 classes of soils in Brazil. Mendoza *et al.* (2012) reported that in a Gleysol, even with a predominance of the organic fraction, inorganic P displayed a higher stock of potentially available P.

The disposal of organic residue of plant and animal origin by past civilizations, associated with the intense use of fire, promotes an increase in total phosphorus (TP), changes the dynamics of the soil fractions and consequently the availability of P. The aim of this research was to characterise and quantify the forms of organic phosphorus in Archaeological Black Earth, using as a reference adjacent undisturbed areas, and generate information about the fertility potential of Latosols, Argisols and Gleysols in the tropics.

## MATERIAL AND METHODS

The study was carried out at sites located in the eastern Amazon, in soils of the Order of Latosols Argisols and Gleysols (Table 1). The areas were defined as: a) of anthropogenic origin, Archaeological Black Earth (ABE); and b) soils adjacent to these sites, with no occurrence of anthropogenic processes (AD). Soil samples were collected as per the methodology proposed by Santos *et al.* (2005). The same horizons were selected, having different depths in each profile (A1, AB, BA, B).

The following were determined: pH in KCl 1 mol L<sup>-1</sup> in the proportion of 1:2.5; potential acidity (H<sup>+</sup> + Al<sup>+3</sup>) extracted with calcium acetate 0.5 mol L<sup>-1</sup> at pH 7.0; exchangeable Ca and Mg extracted with KCl 1 mol L<sup>-1</sup>; K and P extracted with Mehlich-1 (Table 2). The organic carbon (OC) was obtained by the Walkley-Black method and converted to organic matter (OM) by a correction factor of 1.724. Particle size analysis consisted of the separation

**Table 1** - Characterisation of the Archaeological Black Earth sites at the sampling locations

Site	Location	Coordinates	Soil	------(cm)-----				Vegetation
				A1	AB	BA	B	
TP2 ABE	Juruti	2°10'36.92"S	Latosol	0-10	80-130	130-150	>150	Rainforest
TP2 AD		56°06'16.93"W		0-10	20-55	55-80	80-100	Alluvial Forest
BJ 8 ABE	Bom Jesus do Tocantins	5°06'42.24"S	Latosol	0-3	42-73	73-88	88-110	Palm Trees
BJ 8 AD		48°40'27.35"W		0-10	10-22	22-32	32-52	Secondary Forest
OP3 ABE	Ourilândia do Norte	6°31'45.80"S	Argisol	0-10	28-37	37-48	48-68	Grasses
OP3 AD		51°03'32.30"W		0-6	6-19	19-30	30-49	
Jab. ABE	Bragança	01°03'13"S	Gleysol	16-42	68-90	90-124	>124	Grasses
Jab. AD		46°45'56"W		18-28	28-42	42-60	>60	Secondary Forest
S.Raim. ABE	Region around Caxiuanã	01°45'36.0"S	Argisol	0-21	21-40	40-61	61-90	Subsistence Farming (Manihot esculenta)
S.Raim. AD		51° 26'34.3"W		0-14	14-40	40-63	63-92	

TP2, Terra Preta 2; BJ8, Bom Jesus do Tocantins; OP3, Onça Puma 3; Jab., Jabuti; S.Raim., S.Raimundo

**Table 2** - Chemical and granulometric characteristics of the soils studied in ABE and AD <sup>(1)</sup>

Site <sup>(2)</sup>	Horiz. <sup>(3)</sup>	pH	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	H+Al	CTCef	V	OM	Sand	Silt	Clay
		KCl	------(cmol <sub>c</sub> dm <sup>-3</sup> )-----						(%)	------(g kg <sup>-1</sup> )-----		
TP2 ABE	A1	4.3	0.06	4.8	1.2	0.2	8.93	68	27.24	761	144	74
	AB	5.1	0.02	2.5	0.6	0.2	6.62	47	14.95	743	102.5	134
	BA	4.7	0.02	1.7	0.4	0.3	3.81	57	7.07	670	175.5	134
	B1	4.6	0.02	1.6	0.4	2.7	3.53	58	5.57	657	168	154
TP2 AD	A1	4.4	0.05	0.3	0.2	1.5	2.10	29	11.59	729	176.5	74
	AB	4.2	0.02	0.3	0.2	2.7	7.16	8	7.22	664	181	134
	BA	4.5	0.02	0.3	0.1	2.8	5.73	8	3.37	647	198	134
	B1	4.1	0.02	0.3	0.2	2.5	4.52	12	1.87	578	227.5	174
BJ8 ABE	A1	5.6	0.31	8.8	3.6	0.1	13.81	93	43.1	703	162.5	114
	AB	5.1	0.05	2.7	0.6	0.1	4.23	80	18.01	646	159.5	174
	BA	5.1	0.04	2.4	0.3	0.1	3.61	77	13.83	647	158	174
	B1	5.1	0.04	2.4	0.4	0.1	3.70	77	9.29	585	180.5	214
BJ8 AD	A1	5.0	0.19	6.6	0.7	0.1	9.57	79	38.39	491	274	214
	AB	5.0	0.08	2.9	0.8	0.1	5.32	72	8.27	447	278	254
	BA	5.0	0.06	1.8	1.0	0.1	4.05	71	5.59	366	299	314
	B1	5.1	0.07	1.8	1.0	0.1	3.91	75	4.95	351	314	314
OP3 ABE	A1	6.9	0.39	16.1	1.6	0.1	19.02	96	64.21	497	288	194
	AB	5.2	0.07	5.0	2.4	0.1	9.81	76	29.38	499	246.5	234
	BA	4.7	0.05	2.3	1.0	0.1	4.86	69	9.56	377	248.5	354
	B1	5.3	0.13	2.6	0.6	0.1	5.19	65	14.38	387	238.5	354
OP3 AD	A1	5.2	0.23	7.4	1.6	0.1	11.64	80	58.31	458	387	134
	AB	4.9	0.14	4.4	0.8	0.1	7.24	75	27.28	630	255	94
	BA	5.3	0.14	3.0	0.9	0.1	5.92	69	19.85	577	308.5	94
	B1	5.2	0.22	2.9	0.9	0.1	5.93	69	19.06	386	239	354

Continued Table 2

Jab. ABE	A1	4.3	0.11	8.8	0.3	1.2	18.15	52	67.30	779	126	74
	AB	5.0	0.06	5.1	1.2	2.2	11.04	61	33.73	859	86.5	34
	BA	5.1	0.05	2.3	0.3	1.7	4.34	66	5.97	888	37.5	54
	B1	5.3	0.04	2.9	0.7	2.1	5.27	72	3.84	854	51.5	74
Jab. AD	A1	4.1	0.08	0.8	0.9	0.2	9.94	19	62.37	752	113.5	114
	AB	3.9	0.04	0.3	0.2	0.3	6.18	9	9.25	851	74.5	54
	BA	4.0	0.03	0.3	0.2	0.1	4.18	13	1.82	898	27.5	54
	B1	4.0	0.03	0.3	0.2	0.2	4.35	13	2.83	849	56	74
S. Raim. ABE	A1	5.1	0.13	9.7	2.4	0.1	18.30	67	46.94	570	195.5	214
	AB	4.6	0.04	2.0	0.4	0.1	5.65	62	8.89	373	92	514
	BA	4.5	0.08	1.7	0.6	0.1	3.90	66	4.92	275	110.5	594
	B1	4.7	0.03	1.9	0.4	0.1	3.34	70	4.85	280	185.5	514
S.Raim. AD	A1	3.8	0.06	0.4	0.1	2.2	8.55	7	38.94	605	100	274
	AB	3.9	0.04	0.4	0.1	2	6.56	9	23.19	469	96.5	414
	BA	4.0	0.04	0.4	0.1	1.9	5.37	11	6.24	413	52	514
	B1	4.0	0.02	0.3	0.1	1.5	3.11	15	14.00	403	62	514

<sup>(1)</sup>Analyses performed as per methodologies shown in EMBRAPA (1997). <sup>(2)</sup>TP2, Terra Preta 2; BJ8, Bom Jesus do Tocantins; OP3, Onça Puma 3; Jab., Jabuti; S.Raim., S.Raimundo; <sup>(3)</sup>Horiz., Horizon; Source: Costa (2011)

and quantification of the granulometric fractions by the pipette method (EMBRAPA, 1997).

The TP was determined by nitro-perchloric digestion ( $\text{HNO}_3$ :  $\text{HClO}_4$ ) 1:1.5 (v/v), following the methodology proposed by Olsen and Sommers (1982). The Pol was obtained by extraction with  $\text{NaHCO}_3$  0.5 mol  $\text{L}^{-1}$  (BOWMAN; COLE, 1978). As per Bowman (1989), acid extract inorganic phosphorus ( $\text{Pi H}^+$ ) was obtained from the addition of 2 mL of concentrated  $\text{H}_2\text{SO}_4$ , then 50 mL  $\text{NaOH}$  0.5 mol  $\text{L}^{-1}$  were added to the centrifuge tube containing the extraction residue so as to obtain the soluble base extract phosphorus ( $\text{Pi OH}^-$ ). The total labile phosphorus fractions (Ptl), both acid extract ( $\text{Pt H}^+$ ) and base extract ( $\text{Pt OH}^-$ ), were determined by nitro-perchloric digestion of 15 mL of the aliquots removed from the supernatant resulting from the extractions with  $\text{NaHCO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  respectively. The phosphorus contained in the extracts was quantified by spectrophotometry (MURPHY; RILEY, 1962). The Po content of each fraction is the result of the difference between the Pt and Pi contents.

The chemical attributes (MO,  $\text{H}^+\text{Al}$ , V%, pH), the granulometric fractions (sand, clay) and the P fractions: total organic and inorganic phosphorus (Pot; Pit - the sum of their respective fractions), organic phosphorus and total labile (Pol; Ptl - sum of the labile fractions), available P and total P (TP), were statistically evaluated by principal component analysis (PCA), with the Pearson

linear correlation coefficient (r) between them also being calculated. Only 12 variables were selected so as to remove any redundant data, retaining the original information.

The PCA was centred and normalised, and the results obtained by eigenvalue decomposition of the correlation matrix. The principal components 1 and 2 were selected according to the percentage of explained variance, where the accumulated variance of the components should be less than 70% (CARVALHO *et al.*, 2004). The R software was used in the analysis (IHAKA; GENTLEMAN, 1996).

## RESULTS AND DISCUSSION

The acid extract organic phosphorus content ( $\text{Po H}^+$ ) between the studied orders of soil are described in Table 3. The highest levels of  $\text{Po H}^+$  were found in the A1 horizon, at the Jabuti ABE and Onça Puma 3 ABE sites. Intermediate levels were obtained at the Juruti 2 ABE and S. Raimundo ABE sites and, as with the remaining sites, at levels higher than in the areas of AD.

In the A1 horizon, the  $\text{Po H}^+$  fraction varied between 33.0 and 60.4% of the total organic P (Pot), predominating over the labile fractions and base extract, and following the same pattern in the B horizon. According to Novais and Smyth (1999), the acid extract

**Table 3** - Available phosphorus, forms of phosphorus and total soil phosphorus at ABE and AD sites<sup>(1)</sup>

Site		Pavl.	Pil	Ptl	Pol	Pi H <sup>+</sup>	Pt H <sup>+</sup>	Po H <sup>+</sup>	Pi OH <sup>-</sup>	Pt OH <sup>-</sup>	Po OH <sup>-</sup>	TP
		-----mg dm <sup>-3</sup> -----										
TP 2 ABE	A1	55	61.44	197.73	136.29	712.78	1003.91	291.13	70.37	125.14	54.77	1350.94
	AB	55	58.03	153.75	95.72	376.95	512.58	135.63	67.68	122.54	54.86	806.37
	BA	42	50.77	125.24	74.47	350.12	472.18	122.06	47.77	92.26	44.49	709.70
	B1	48	21.65	33.27	11.62	45.48	59.24	13.76	7.33	14.89	7.56	114.52
TP2 AD	A1	5	6.21	24.62	18.41	32.25	43.58	11.33	6.38	11.00	4.62	84.60
	AB	1	5.99	15.19	9.20	32.17	41.65	9.48	5.52	10.02	4.49	77.04
	BA	1	8.21	17.81	9.60	30.21	39.58	9.37	5.24	9.27	4.04	71.31
	B1	4	5.23	8.24	3.01	14.17	18.13	3.96	2.13	3.86	1.74	29.72
BJ 8 ABE	A1	20	31.74	134.18	102.44	343.81	476.00	132.19	51.13	93.59	42.46	719.94
	AB	4	38.25	83.65	45.40	131.27	177.58	46.31	23.26	42.37	19.11	325.91
	BA	11	37.46	113.50	76.04	223.27	301.02	77.75	34.90	65.00	30.10	500.03
	B1	19	36.40	111.46	75.06	275.51	360.28	84.77	39.69	74.90	35.21	576.14
BJ 8 AD	A1	4	8.44	25.35	16.91	50.59	68.17	17.58	8.42	15.23	6.82	117.17
	AB	2	7.29	15.28	7.99	25.25	33.46	8.21	4.51	8.23	3.72	63.30
	BA	1	7.14	14.53	7.39	36.58	47.09	10.51	5.37	10.04	4.67	77.20
	B1	1	6.78	12.80	6.02	33.69	43.12	9.43	4.45	8.29	3.84	63.80
OP3 ABE	A1	169	214.53	924.28	709.75	1919.60	2763.21	843.61	360.81	635.45	274.64	4367.04
	AB	11	111.16	396.84	285.68	1099.39	1495.56	396.17	171.75	314.27	142.52	2238.44
	BA	13	79.08	186.69	107.61	379.75	500.40	120.65	57.00	106.64	49.64	820.32
	B1	4	71.50	156.46	84.96	327.09	429.81	102.73	47.78	91.60	43.82	704.61
OP3 AD	A1	3	74.58	256.20	181.62	558.14	755.36	197.22	105.77	182.36	76.59	1221.06
	AB	2	69.25	251.24	181.99	555.95	732.00	176.05	101.19	179.54	78.35	1180.17
	BA	1	70.11	248.02	177.91	541.58	701.26	159.68	87.57	153.42	65.85	1115.24
	B1	1	79.54	195.84	116.30	492.52	624.15	131.63	69.30	126.04	56.74	969.57
Jab. ABE	A1	1138	284.14	1292.58	1008.44	3165.60	4458.59	1292.99	572.27	987.36	415.09	6778.75
	AB	999	242.23	953.64	711.41	2585.47	3510.48	925.01	211.65	671.33	459.68	5164.06
	BA	961	224.31	894.37	670.06	2485.53	3347.52	861.99	404.29	728.84	324.55	4991.05
	B1	943	325.19	897.42	572.23	2286.78	2969.85	683.06	344.75	647.30	302.55	4540.73
Jab. AD	A1	41	13.89	32.94	19.05	76.39	103.04	26.65	13.09	21.96	8.86	168.92
	AB	4	6.52	11.03	4.51	26.44	34.63	8.19	4.25	7.38	3.13	56.78
	BA	1	6.32	10.63	4.31	23.02	29.84	6.82	3.59	6.36	2.77	48.93
	B1	4	7.05	10.27	3.22	24.34	31.00	6.67	3.66	6.61	2.94	50.82
S.Raim. ABE	A1	90	93.64	322.13	228.49	595.93	823.67	227.75	101.18	175.54	74.36	1360.28
	AB	53	11.28	24.61	13.33	57.22	76.77	19.55	9.06	16.36	7.31	125.85
	BA	39	10.42	22.74	12.32	55.30	73.39	18.08	8.78	15.64	6.85	120.31
	B1	1	8.97	14.41	5.44	39.08	51.42	12.33	6.02	10.96	4.94	84.29
S.Raim. AD	A1	13	15.79	41.25	25.46	119.95	161.48	41.53	20.85	34.41	13.56	264.72
	AB	1	11.94	25.75	13.81	91.70	118.77	27.07	14.71	25.31	10.60	194.70
	BA	3	5.47	11.03	5.56	68.69	89.82	21.12	11.07	19.14	8.07	147.24
	B1	27	6.21	10.64	4.43	43.16	54.99	11.83	6.67	11.72	5.05	90.15

<sup>(1)</sup> Pavl., available phosphorus; Pil, labile inorganic phosphorus; Ptl, total labile phosphorus; Pol, labile organic phosphorus; Pi H<sup>+</sup>, acid extract inorganic phosphorus; Pt H<sup>+</sup>, acid extract total phosphorus; Po H<sup>+</sup>, acid extract organic phosphorus; Po OH<sup>-</sup>, base extract organic phosphorus; Pt OH<sup>-</sup>, base extract total phosphorus; Pi OH<sup>-</sup>, base extract inorganic phosphorus; TP, total phosphorus

solubilises the forms bound to P-Ca. These results may be associated with the high levels of biogenic apatite, widely found in the form of animal and fish bones in ABE, which are rich in P and Ca (FRASER *et al.*, 2011; LIMA *et al.*, 2002; SATO *et al.*, 2009; SOUZA *et al.*, 2009).

The levels of Po H<sup>+</sup> in the ABE also predominated over the respective areas of AD in the remaining horizons, tending to decrease with increasing depth. In the Onça Puma 3 area of AD, higher levels of Po H<sup>+</sup> were seen from the BA horizon in the case of an Argisol with the horizon sequence A1 - textural B, tending to greater subsurface P retention due to the increase in clay content. Souza *et al.* (2009), in an ABE of a clayey to very clayey texture, found the highest levels of total P (TP) and the highest levels of the main form of P (P-Ca).

There was no correlation between Po H<sup>+</sup> and the clay content of the soils in the A1 horizon ( $p < 0.05$ ;  $n = 15$ ,  $r = 0.05$ ), even though this variability was not more than 10 to 20%, in the textural classes the accumulation in this fraction followed the sequence Sandy Loam (Gleysols) > Sandy Clay Loam (Argisols) > Sandy Loam (Latosols) > Sandy Clay Loam (Argisols) > Sandy Loam (Latosols).

On first examination, the greater Po H<sup>+</sup> content at the Jabuti site may be understood as a consequence of the anoxic condition common in the soils of those areas (Gleysols). In such cases, the water saturation associated with the input of labile organic matter results in the use of forms of Fe<sup>3+</sup> as final electron acceptors. As a result, dissolution of the Fe oxides (III) takes place and the release of P-associated in the soil solution, which in turn may create forms of P-Ca (MENDOZA *et al.*, 2012).

The results for Pt H<sup>+</sup> expressed the highest percentage of P in inorganic form, as also seen by Bowman (1989). This increase in the Po-H<sup>+</sup>/Pt-H<sup>+</sup> ratio in the ABE plays an important role, since this fraction acts as a P reserve compartment for plants in the short and medium term, in the form of fulvic acids (BOWMAN, COLE, 1978; DUDA *et al.*, 2013; XAVIER *et al.*, 2009).

The higher levels of base extract organic P (Po OH<sup>-</sup>) in the areas of Terra Preta were also seen in the A1 horizon of the sites at Jabuti and Onça Puma 3 ABE (Table 3), with a lower value found at the BJ 8 ABE site, showing a significant reduction for AD. The values for Po OH<sup>-</sup> varied between 11.4 and 23.7% of the Pot, being generally lower than the acid extract fraction, with a reduction of up to 49.0%.

The Po OH<sup>-</sup> fraction may be associated with humic acids or undergo sorption at the surface by compounds of Fe and Al, suggesting an increase of these compounds with depth (OLSEN; SOMMER, 1982). These compounds are stable and of difficult availability, corresponding to

a more advanced and polymerised material, the humic acids, hindering the access of microorganisms and plants (NOVAIS; SMYTH, 1999). However, for Busato, Canellas and Velloso (2005), in low fertility soils of the tropical humid region, humic acids make up an important, readily available reserve of organic P.

In the ABE there is a predominance of highly humidified fractions (humins and humic acid - HAF) and lower levels of the fulvic acid fraction (FAF), resulting in high HAF/FAF ratios (BARROS *et al.*, 2012; CAMPOS *et al.*, 2011; LIMA *et al.*, 2002). It is possible that in this study, the humic acids of the soils, in comparison to the fulvic acids, are not enriched with P.

The levels of labile organic P (Pol) were higher in the A1 horizons of the ABE soils found at the Jabuti and Onça Puma 3 sites, with the lowest levels found at the BJ 8 site (Table 3). In general, there was an increase in Pol content in the A1 horizon, with a reduction between the A and B horizons of up to 97.6%, indicating the contribution of organic matter (OM) to this P fraction.

In relation to the total labile P (Ptl), the percentage of Pol varied between 31.4% in the B horizon of the soil under AD at the Jabuti site, and 78.0% in the A1 horizon of the ABE at the same site. There was a predominance of Pol over labile inorganic P (Pil) at all sites and in the areas of ABE and AD, which in most of the horizons was over 50% of the Ptl (Figure 1a). The addition of organic material, including crop residues and other biogenic rural and urban waste, increase P availability in the soil (BOWMAN; COLE, 1978; DUDA *et al.*, 2013; GUERRA *et al.*, 1996; PARTELLI *et al.*, 2009). In this study the available P was positively correlated with the Po fractions ( $r = 0.77$ ).

Malik, Marschner and Khan (2012), comparing the lability of P after the addition of inorganic and organic P to the soil, noted that the latter is less prone to sorption and precipitation due to the lower concentration of water-soluble P and the stimulation of microbial activity through the addition of C. The competition between organic and phosphate anions for the same adsorption sites on the surface of oxides may increase P availability for plants (XAVIER *et al.*, 2009).

In the adjacent areas, the Argisols displayed the highest levels of Pol (181.62 and 25.46 mg dm<sup>-3</sup>). These results agree with those found by Duda *et al.* (2006) and Guerra *et al.* (1996), in which the highest levels of Pol were found in the surface horizon and in the more clayey soils, however in the present study no significant correlation was seen between this P fraction and clay content ( $r = 0.14$ ).

There was a reduction in TP of 40.3 and 54.7% in the transitional horizons (AB) of the A1 horizon at the

sites at Terra Preta 2 ABE and BJ 8 ABE respectively, where the areas had the lowest levels for TP (Table 3), in line with the levels found in tropical Latosols, generally with a TP of around 200 mg dm<sup>-3</sup> (DUDA *et al.*, 2013; GUERRA *et al.*, 1996).

In the Argisols corresponding to the ABE Onça Puma 3 and S. Rimundo sites, the TP levels were higher than those found in the Latosols, but no significant correlation was found between TP and the clay fraction ( $r = 0.14$ ). This increase in TP content may be related to the predominant vegetation in these areas; for example, the site at Onça Puma 3, vegetated with Marandu grass (*Brachiaria brizantha*), which has a high demand for P and high biomass production that favours incorporation of the element into the plant tissue and increases organic residue and reserves in the soil (DUDA *et al.*, 2013; MERLIN; HE; ROSOLEM, 2013). Studies by Nogueira *et al.* (2008) showed no difference between the Pol fraction in an area of native forest and an area of intensive farming, where the spontaneous growth of grass in the latter area may have facilitated the maintenance of OM in the soil.

At the S. Raimundo site, a decrease of 90.8% in Pol was seen from the A1 horizon (1360.28 mg dm<sup>-3</sup>) to the AB horizon (125.85 mg dm<sup>-3</sup>), probably a result of the management applied in the cultivation of cassava. Souza *et al.* (2009), evaluating the forms of phosphorus

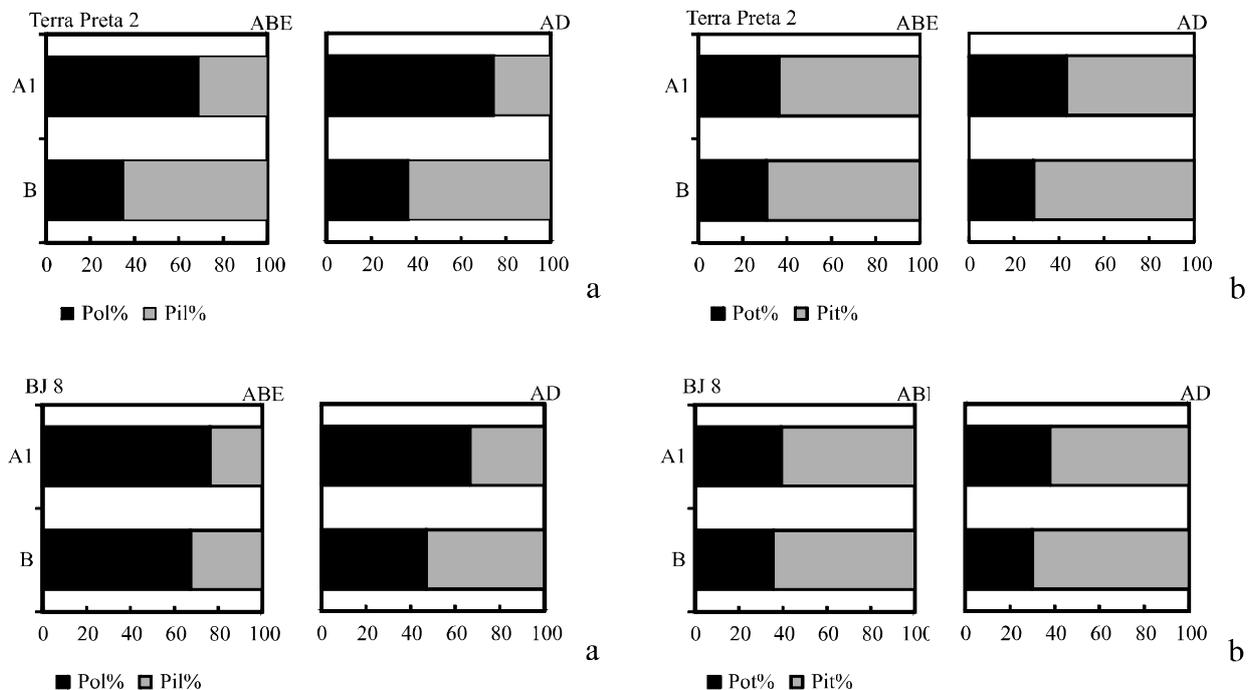
found in cultivated black earth sites in the Brazilian Amazon, found TP levels of 1001.1 mg dm<sup>-3</sup> in a Latosol and 2043.0 mg kg<sup>-3</sup> in an Argisol at a depth of 0-20 cm.

The highest TP levels were found in the A1 horizon at the Jabuti ABE site, decreasing with increasing depth; there was a positive correlation with the OM in both the ABE and the AD areas ( $r = 0.9$ ;  $r = 0.99$ ) respectively, indicating a contribution from different sources of P to the high levels of nutrients quantified in the ABE, such as the biogenic apatite widely found in these soils (COSTA, 2011; GLASER; BIRK, 2012; KERN *et al.*, 2010).

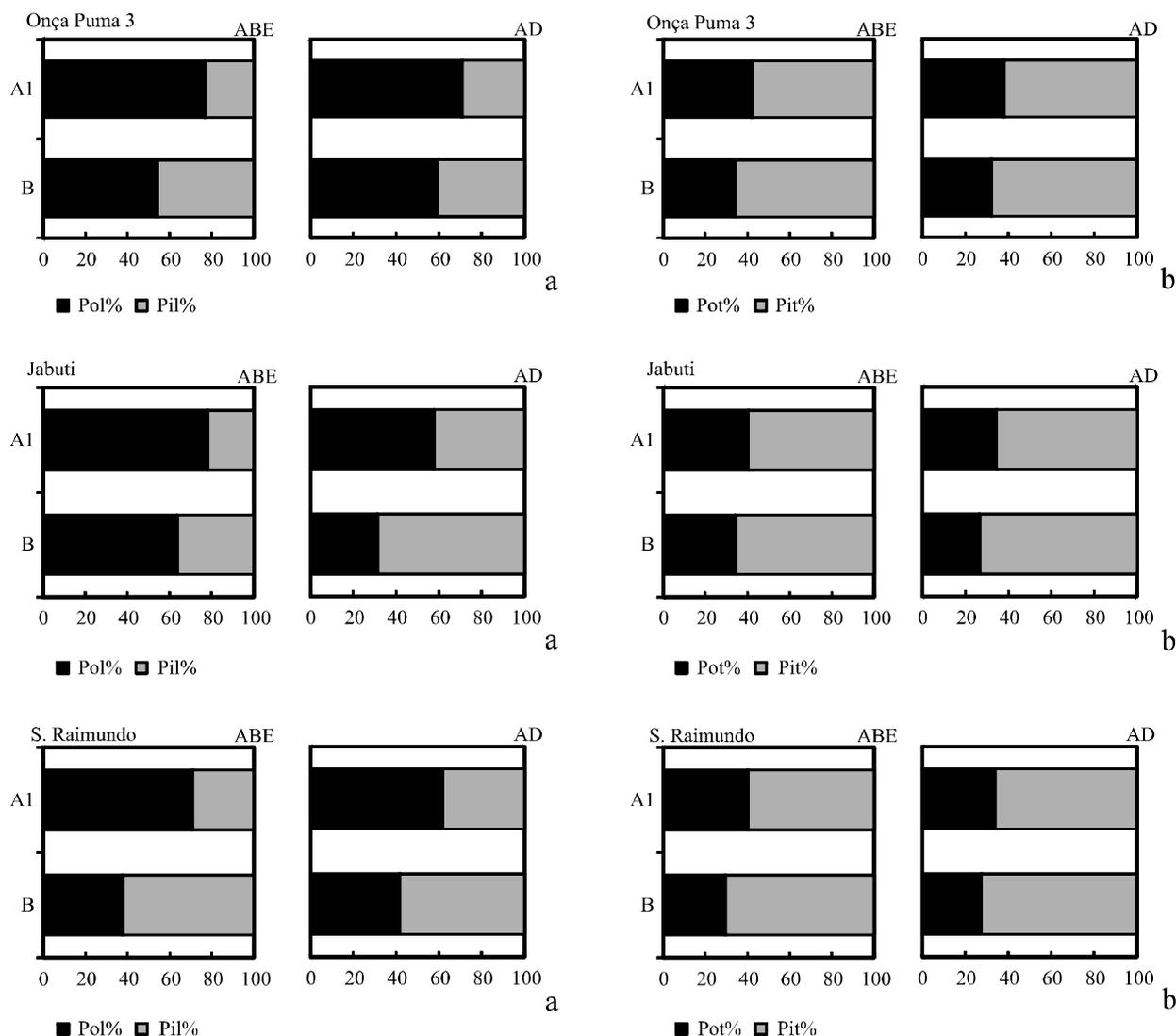
With the percentage distribution of total organic P (Pot) and total inorganic P (Pit), a predominance of Pit was found in all sites and in an area of ABE and AD, accounting on average for 65.3% of the TP, whereas Pot represented on average 34.82% of the TP (Figure 1b), a percentage value higher than that found by Busato, Canellas and Velloso (2005) of 25%, and by Guerra *et al.* (1996), where the average contribution of this fraction was 27% for 17 soil samples.

The results of the Principal Component Analysis (PCA) showed that the forms of P in the soil were strongly correlated with the first ordination axis (Figure 2), and together with the chemical attributes and granulometric fractions, made it possible to differentiate the ABE and adjacent areas.

**Figure 1a** - Distribution of labile organic P (Pol) and labile inorganic P (Pil) relative to the total labile P (Ptl) in the A1 and B horizons of the ABE sites and adjacent areas



**Figure 1b** - Distribution of total organic P (Pot) and of total inorganic P (Pit) relative to the total soil P (TP) in the A1 and B horizons of the ABE sites and adjacent areas



Distribution of the selected variables with a cumulative variation of 76.53% can be seen for the F1 and F2 axes, with the F1 axis explaining 55.63 and the F2 axis 20.9% of this variance (Table 4).

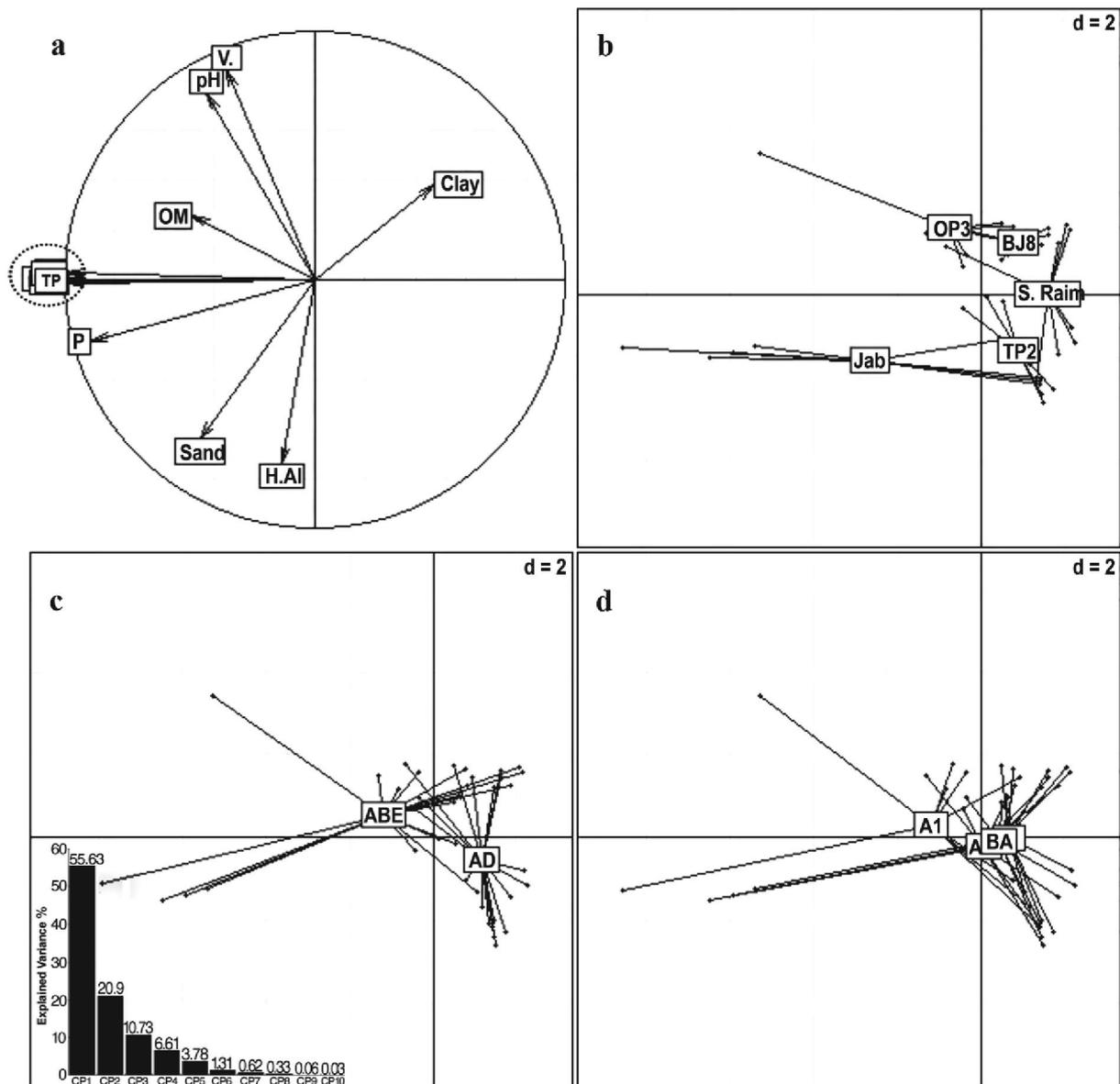
From the graphic dispersion it could be seen that there was a difference between the sites under study in relation to the variables shown in the PCA. The sites at S. Raimundo, Terra Preta 2 and BJ 8, differ from the others mainly in the forms of P, potential acidity (H+Al) and clay content respectively (Figure 2b). These sites had the lowest levels of P in the areas of ABE and AD; at the BJ 8 site, the levels of P correlate positively with the clay content ( $r = 0.72$ ).

The greatest values for H+Al were found at the Terra Preta 2 site, reaching levels of 2.7 in the ABE B horizon, and of up to 2.8  $\text{mg dm}^{-3}$  in the BA horizon of the AD area, showing the persistence of the geochemical characteristics of these soils, rich in Fe and Al oxides, as noted by Costa, Costa and Kern (2013) in studies in the area. The availability of P in weathered soils is partly controlled by the predominance of amorphous clays of Fe and Al of low crystallinity and high specific surface area, which at low pH are positively charged and tend to adsorb phosphate anions (EBERHARDT *et al.*, 2008; GICHANGI; MNKENI; BROOKES, 2009; SÁNCHEZ-ALCALÁ *et al.*, 2014).

The site at Onça Puma 3 displayed a correlation with CP1 for OM, and a correlation with CP2 for pH and V%, with high levels of OM in the A1 horizon (64.21 g kg<sup>-1</sup>) and the greatest values for pH and V% between sites, of 6.9 and 96% respectively. In the area of AD, high values for these attributes were also seen at

a low pH (5.2). In soils under systems of high biomass production, besides the addition of bases to the soil (Ca, Mg and K) as a result of nutrient cycling, the free Al<sup>3+</sup> and H<sup>+</sup> ions are complexed in the anionic organic compounds, buffering or raising the pH (GICHANGI; MNKENI; BROOKES, 2009).

**Figure 2** - Principal Component Analysis (PCA) carried out for soil attributes and forms of P on the ABE sites and adjacent areas for five different locations, in the A1, AB, BA and B horizons. (a) Correlation circle between the soil chemical variables, forms of P and granulometric fractions. (b) Ordination diagram of the samples by site ( $p = 0.001$ , observation = 0.35). (c) Ordination diagram of the samples by horizon ( $p = 0.001$ , observation = 0.17). (d) Ordination diagram of the samples by area studied (ABE, AD) ( $p = 0.001$ , observation = 0.15)



a) Total organic phosphorus (Pot); Total inorganic phosphorus (Pit); total labile phosphorus (Ptl); labile organic phosphorus (Pol); available phosphorus (P); total phosphorus (TP); organic matter (OM); pH in KCl; Base saturation (V%); Potential acidity (H + AD); Sandy; Clay; b) Sites: TP2, Terra Preta 2; BJ8, Bom Jesus do Tocantins; OP3, Onça Puma 3; Jab, Jabuti; S. Raim, S. Raimundo; c) Areas: Archaeological Black Earth (ABE); Adjacent area (AD); d) Horizons: A1; AB; BA; B

**Table 4** - Correlation of soil-attribute data used in the Principal Component Analysis (PCA) between the first two principal components, and classification of the attribute scores by contribution

Attribute	Score		Coordinates		Rank <sup>1</sup>
	PC1	PC2	PC1	PC2	
Pot	-0.382	0.002	-0.988	0.003	1
Pit	-0.382	-0.007	-0.987	-0.012	2
Ptl	-0.383	0.019	-0.989	0.03	11
Pol	-0.382	0.017	-0.987	0.027	10
P	-0.345	-0.158	-0.892	-0.249	9
PT	-0.383	-0.002	-0.989	-0.004	12
pH	-0.167	0.473	-0.432	0.749	6
MO	-0.189	0.163	-0.489	0.258	8
V%	-0.136	0.532	-0.352	0.843	5
H+Al	-0.05	-0.469	-0.129	-0.742	4
Sand	-0.176	-0.404	-0.455	-0.64	7
Clay	0.184	0.241	0.476	0.381	3
Autovalor	6.68	2.51	-	-	-
Accumulated variance (%)	55.63	76.53	-	-	-

<sup>1</sup>Classification of attributes by contribution to the construction of PC1

All the forms of phosphorus were correlated with PC1, explaining 55.63% of the cumulative variance, the fractions are shown superimposed graphically, all highly represented by proximity to the unit circle, with Pot having the greatest participation in the construction of CP1 (Table 4). The P fractions are shown in relation to the site at Jabuti, which has the highest TP content (6778.75 mg dm<sup>-3</sup>) in the area of ABE, and high levels of available P in all the horizons, ranging from 1138 to 943 (A1 and B). It was not possible to see the individual influence of the P fractions by means of the PCA however, due to their being strongly related.

The sand fraction and potential acidity were best explained by CP2 and also related to the site at Jabuti. The potential acidity in this area increased with the increase in depth, varying from 1.2 to 2.1 cmol<sub>c</sub> dm<sup>-3</sup>. High values were seen for the sand fraction, on average 845 g kg<sup>-1</sup> in the ABE. The greatest concentration of this granulometric fraction is commonly reported in anthropogenic soils associated with the formation of stable organo-mineral material with a size equal to that of sand, where the use of fire and deposition of organic residues may be responsible for this transformation (BARROS *et al.*, 2012). However, in the present study there did not appear to have been any changes in soil granulometry at the Jabuti site, since the adjacent areas show an average content of 837.5 g kg<sup>-1</sup>.

The A1 horizon and the area of ABE correlated in the main with CP1, relating to the forms of P, the OM, and to a lesser extent the pH and V%, which are better explained by CP2 (Figures 2c and 2d). The A horizon is identified, among other properties, by the dark coloration resulting from the decomposition of organic material and in the form of charcoal left over from such cultural practices as clay ovens and firing ceramics for use in agriculture, among others (CAMPOS *et al.*, 2011; SMITH, 1980). This horizon stood out from the others, mainly due to the OM and the high levels of P in the fractions under study.

At the sites at Terra Preta 2 and Jabuti, high levels were also seen for the forms of P and for TP at depth, that may result from wildlife activity (bioturbation) (ARROYO-KALIN *et al.*, 2010; LIMA *et al.*, 2002) or the significant transfer of P to deeper horizons through leaching due to the high sand content found in these areas. Silva *et al.* (2012), characterising the BJ 8 site by attribute, observed an increase from 20 mg dm<sup>-3</sup> in the A1 horizon to 50 mg dm<sup>-3</sup> in the B2 horizon.

The organic matter content in the ABE was higher at all sites compared to the areas of AD, agreeing with the levels of 46.50 mg dm<sup>-3</sup> found by Silva *et al.* (2012), but less than those found by Campos *et al.* (2011) of 75.39 mg dm<sup>-3</sup>, and Santos *et al.* (2013) of 112.75 mg dm<sup>-3</sup>.

In the ABE, the eutrophic characteristic of the soils is often reported, highlighting the contribution of Ca to the high base saturation. In turn, the high levels of P are used as one of the criteria for classifying the anthropogenic horizons that should show over 200 mg TP dm<sup>-3</sup>, as seen at all the sites in this study (GLASER; BIRK *et al.*, 2012; LIMA *et al.*, 2002).

The chemical attributes and the P content of these soils show that the Amerindian peoples were able to make persistent changes in favour of the conservation and improvement of the agricultural potential of the weathered soils of the Amazon, representing a model for sustainability in tropical regions.

## CONCLUSIONS

1. Anthropogenic action increases the TP content of ABE sites in relation to the surrounding area, with a predominance of the form of acid extract organic phosphorus (Po H<sup>+</sup>), giving anthropogenic soils a high level of resilience in the availability of phosphorus for plants;
2. Most of the total labile P (Ptl) accumulates in organic soil fractions and represents an active means of supplying the nutrient to plants.

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