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## STUDY OF THE EXTRACTABLE PHOSPHATE IN THE ARCHAEOLOGICAL BLACK EARTH

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### ABSTRACT

**A**rchaeological Black Earth (ABE), an Anthrosol commonly found in several areas of central Amazonia, is an important register of ancient human occupation in the Amazonian region. ABE is known for its high concentration of nutrients, mainly phosphorus and calcium as well as fragments of ceramic relic (CRF). Due to the lack of a standard method for phosphorus estimating, this work has developed a comparative study using Mehlich (M1), Mehlich-3 (M3), Bray-1 (B1), and Olsen (OL) solutions on the ABE and its CRF. ABE and CRF samples were collected at depth ranging from 0.00-0.20 cm from eight archaeological sites in Manaus, Parintins, Itacoatiara, and Barreirinha (Amazonas, Brazil). The performances of the



extractants were compared via phosphate concentration obtained from ABE (fraction <2mm) and CRF powder using the ammonium molybdate method. The phosphorus contained in the M1, M3, B1, and OL extracts categorized the ABE site into three groups. The phosphate concentration of the M1, M3, B1, and OL extracts suggested differences in phosphorus availability depending on the ABE site. Generally, ancient ceramics have been disregarded as a component for evaluating soil fertilization, but our results have shown that CRF is an important source of phosphorus just as ABE is.

**KEYWORDS:** Soil analysis, Extraction procedure, Soil mineralization.

### INTRODUCTION

Despite the numerous opportunities which the study of soils at archaeological sites provides, as well as the wealth of scientific approaches available for soil analysis, there remain several persistent challenges associated with making inferences about past human activity from soils (Walkington, 2010). In the Amazon Basin, within a landscape of infertile soils, fertile Anthrosols of pre-Columbian origin occur (ABE). These soils are

characterized by great amounts of charred organic matter (black carbon, biochar) and high nutrient stocks (Birk et al., 2011). Frequently, the considerable amount of CRF commonly found in archaeological sites upholds the ideas of the pedogenesis of the ABE as well as the occupation of Amerindians throughout the Amazonian region. ABE is widely distributed in Amazonian region as patches and due to its high fertility, mainly phosphorus and calcium, it is important to the family farmer (Smith, 1980; Glaser et al., 2001). It can be assumed that phosphorus and calcium sources have their origins in the biogenic apatite of fish, mammals, and turtle bones as well as human bones. The ABE possesses several phosphorus concentration levels, ranging from 68.60 to

13,870.00 mg kg<sup>-1</sup> (Lima et al., 2002; German, 2003). However, only the chemical and physical properties of the ABE have been studied and its phosphorus potential limited to the use of M1, M3 (Lima et al., 2002; Rebellato, 2007), B1 (Eden et al., 1984), citrate (Macedo, 2009), and ion-exchange resin (Cunha, 2005; Santos et al., 2013). From what is known, phosphorus transformations such as adsorption/desorption, dissolution/precipitation, mineralization/immobilization, and others were common and diverse in paddy soil. In spite of having enormous amount of knowledge of the complexity of the soil-plant system, a search for better methods to determine the availability of phosphorus in plants still has to be carried out. A large number of chemical extractions have been suggested for worldwide soil analysis in routine soil testing. Preliminary ABE findings have demonstrated an unquestionable lack of the study of extractable phosphorus. The selection of a phosphorus chemical extractant depends on the phosphorus species in the soil. Several soil properties using chemical extraction have been reported to show the influence and availability of phosphorus for plants. Indeed, the best extractable phosphorus solution should be selected depending on the mineralogy of the soil. The choice of chemical extractions should consider available Fe, Al, and Mn oxides, clay mineral composition, CaCO<sub>3</sub>, organic matter, soil pH and sorption capacity of phosphorus, and others.

Generally, M1 is adopted to extract phosphorus on acid and low cation exchange capacity soils; M3 is a multi-nutrient extractant suitable for a wide range of soils; B1 is used only to extract phosphorus on acid soils with moderate CEC, and OL was originally developed as a phosphorus extract for alkaline soils and is now also used for acid and neutral soils. These chemical extractants have different critical values considered optimum for plant growth and responses to addition of the phosphorus (Summer, 1999). Previous ABE findings have shown anomalous values for extractable phosphorus concentration depending on the sampling site for M1 and M3. For M1, phosphorus concentration is from 3.00 to 1991.00 mg kg<sup>-1</sup> (Lima et al., 2005; Silva et al., 2012) and M3 1.70 to 1991.00 mg kg<sup>-1</sup> (Lima et al., 2002; Rebellato, 2007). These findings show that M1 and M3 depending on ABE sampling site have plausible critical values; i.e., available phosphorus concentration is under or above for plants depending on the chemical extractant used. An explanation for such anomalous findings is the relationship between the phosphorus and calcium estimated with M1 and M3. According to Souza et al. (2009) the higher concentration of phosphorus bound to calcium (P-Ca) form in ABE is due to limited alteration and reaction of primary bone apatite. Lima et al. (2002) also suggested that most of the phosphorus in the ABE is amorphous/low crystalline forms, associated with bone apatite from fish bones. The micromorphology and electron microprobe analysis of ABE showed P-Ca and phosphorus bound to aluminum (P-Al) forms originated from animal and fish bones (Schaefer et al., 2004). Usually, the P-Ca amount is higher than P-Al and phosphorus bound to iron (P-Fe) (Souza et al., 2009b).

Chemical acid extractants such as M1 and M3 have demonstrated problems when used to determine phosphorus in some soils varying in pH values and calcium carbonate concentration (Mallarino, 1997). The aim of this paper was to analyse the extractable phosphate concentration in M1, M3, B1 and OL chemical extractants applied to ABE, and CRF samples in order to compare phosphorus concentration.

## MATERIAL AND METHODS

### Sampling

Eight ABE samples from the cities of Barreirinha, Itacoatiara, Manaus, and Parintins, in Amazonas, Brazil (the location and soil properties are shown in Table 1) were studied. At each ABE site, the samples for phosphate analysis were collected in zigzag according to the 1999 EMBRAPA recommendations at a depth ranging from 0 to 20 cm. Each ABE sample was mixed, and divided into four parts, with one of the parts being chosen randomly for this study.

### Phosphate analysis

Phosphate concentration was analyzed in the M1, M3, B1 and OL extracts according to the method proposed by Pierzynski (2000). For phosphate extraction with M1, M3, and B1, the ratio 1:10 for ABE (or CRF) to extractor, respectively, was used, using a shaker (brand Orbital 141) for 5 min with a rotation of 240 rpm. For phosphate extraction with OL, a ratio of 1:20 (soil/ceramic: extractor) and a stirring time of 30 min were used.

After centrifugation at 3000 rpm for 5 min, the extractors (supernatants) were obtained. The concentration of phosphorus present in the extractors were analyzed using the ammonium molybdate method in a spectrophotometer (Shimadzu Model UV- 1650PC) at a wavelength of 885 nm.

**Table 1 – Location, physicochemical and mineralogical characteristics of ABE sites.**

Code	Archaeological Black Earth Site							
	*Tpa	*Tpl	*Tpi	*Tph	*Tpm	*Tpp	*Tpg	*Tpnc
S	03°16'15.3 2"	02°47'40.6 1"	03°18'56.1 1"	58°48'57.4 5"	02°54'16.7 3"	02°40'29.6 6"	02°59'14.0 9"	02°59'34.2 4"
O	58°53'16.7 9"	57°10'09.8 0"	58°48'57.4 5"	56°43'36.5 7"	56°47'37.1 3"	56°46'57.7 3"	56°49'01.1 2"	59°58'48.6 0"
Soil Propriety								
pH <sub>(H<sub>2</sub>O)</sub>	6.34	6.30	6.00	5.84	5.81	5.51	5.36	5.16
C (g/kg)	47.48	33.44	26.59	24.97	23.68	22.52	22.66	7.02
K (cmol <sub>c</sub> /dm <sup>3</sup> )	97.00	118.00	155.00	39.00	19.00	16.00	17.00	5.00
Ca (cmol <sub>c</sub> /dm <sup>3</sup> )	10.68	10.20	8.46	5.40	3.83	3.73	3.11	0.09
Mg (cmol <sub>c</sub> /dm <sup>3</sup> )	2.14	1.12	1.56	0.47	0.69	0.27	0.43	0.02
Al (cmol <sub>c</sub> /dm <sup>3</sup> )	ND	ND	ND	ND	ND	ND	0.26	0.86
Fe (mg/dm <sup>3</sup> )	86.00	81.00	162.00	68.00	19.00	26.00	49.00	26.00
Zn (mg/dm <sup>3</sup> )	19.64	62.19	24.58	19.85	10.73	6.97	2.99	1.23
Mn (mg/dm <sup>3</sup> )	413.70	86.72	122.15	50.57	37.29	33.11	40.32	11.70
Cu (mg/dm <sup>3</sup> )	1.81	1.30	1.84	11.44	0.73	0.63	0.48	0.61
P total (mg/kg)	3446.00	7947.00	3623.00	2753.00	2903.00	2930.00	2937.00	3023.00
Sand (g/kg)	25.27	50.02	30.66	65.18	71.42	72.01	69.75	84.43
Silt (g/kg)	31.40	25.95	19.00	14.87	7.48	12.89	9.60	2.92
Clay (g/kg)	43.33	24.03	50.34	19.95	21.10	15.10	20.65	12.65
Textural class	Clay loam	Sandy clay loam	Silt loam	Sandy loam	Sandy clay loam	Sandy loam	Sandy loam	Sandy clay loam
**Mineralogy	Kao, Qz, It, Ant, Ab, Kf	Kao, Qz, It, Ant, Ab, Kf	Kao, Qz, It, Ant, Ab, Kf	Kao, Qz, It, Ant	Kao, Qz, It, Ant	Kao, Qz, It, Ant	Kao, Qz, It, Ant	Kao, Qz, It, Ant, Gb

ND = non-detected. \*Tpa = São José do Amajari; Tpl = Terra Preta do Limão; Tpi = São Pedro de Iracema; Tph = Hospital Jofre Cohen; Tpm = Marajó; Tpp = Parananema; Tpg = Gregoste; Tpnc = Nova Cidade. \*\*Kao = kaolinite; Qz = quartz; It = illite; Ant = anatase; Ab = albite; Kf = Potassium feldspar; Gb = gibbsite.

## RESULTS AND DISCUSSION

The total phosphorus concentration for ABE have shown great variation between minimum and maximum values depending on the archaeological site (Table 2). Great variation in total phosphorus concentration values was also seen in our results. Anomalous phosphorus concentration is an important indicator of anthropogenic sources, mainly prehistoric human activity. Indeed, the total phosphorus in ABE studies especially gives insights into patterns of human occupation (Rodrigues e da Costa, 2015). Research shows that the total phosphorus concentration in ABE is a product of the mineralization of organic to inorganic phosphate with

formation of precipitated and/or insoluble phosphorus compounds. Human activity modifies several physical and chemical properties of the soil, such as pH, amount of carbon, phosphorus, nitrogen, and carbonates in deposits.

**Table 2– Total phosphorus concentration of references and this work.**

City	Site	Total phosphorus (mg kg <sup>-1</sup> )			Reference
		Min.	Max.		
*Rio Preto da Eva	Jiquitaia	1801	2043	1922 (n=2)	Souza et al. (2009)
*Manacapuru	Laranjal	1001	3005	2003 (n=2)	
*Iranduba	Hatahara	3070	13,870	8580 (n=3)	Lima et al. (2002)
**Melgaço	Manduquinha	943	8877	3001 (n=4)	Costa e Kern (1999)
**Água azul do Norte e Orilândia do Norte	Onça Puma 3	1518	2147	1870 (n=4)	Garcia et al 2015
Barreirinha	Tpl			7947 (n=1)	This work
Itacoatiara	Tpa and Tpi	3446	3623	3535 (n=2)	
Parintins	Tph, Tpm, Tpp and Tpg	2753	2937	2881 (n=4)	
Manaus	Tpnc			3023 (n=1)	
Summary		943	13,870	3593 (n=23)	

n = number of samples. \*Amazon. \*\* Para.

Figure 1 shows the phosphorus concentration extracted by M1, M3, B1, and OL for each ABE site. Estimated phosphate concentration from extractors varied depending on the solution used and ABE site: M1 ranged from 32.50 to 1800.00 mg kg<sup>-1</sup>; M3 from 60.00 to 500.00 mg kg<sup>-1</sup>; B1 from 57.50 to 450.00 mg kg<sup>-1</sup> and OL from 16.00 to 144.00 mg kg<sup>-1</sup>. These values are higher than levels found in non-anthropogenic Amazon soils (ultisols and oxisols), in which the phosphate concentration varies from 0.20 to 26.00 mg kg<sup>-1</sup> (Campos et al., 2011b, 2012), showing the anthropogenic influence on the genesis of ABE.

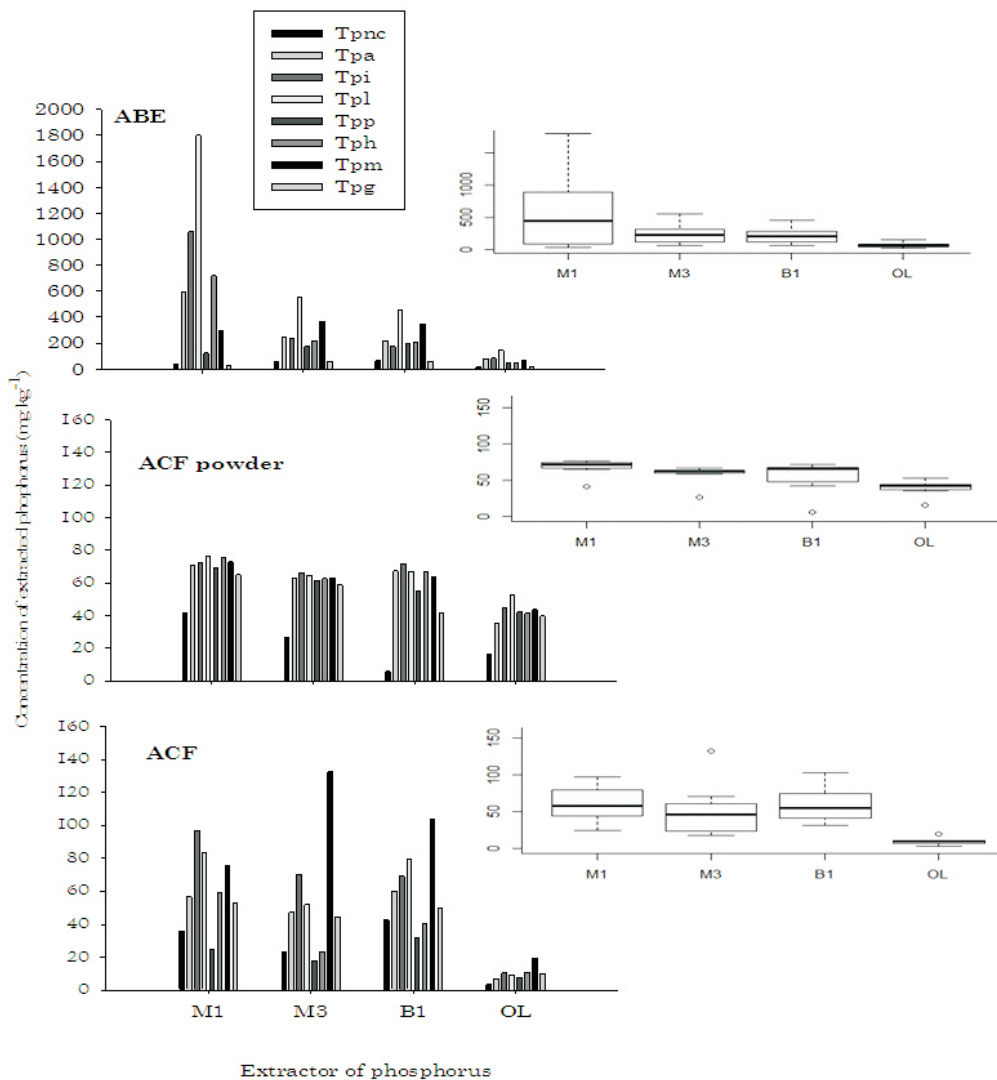
The phosphate concentration suggests the existence of three ABE groups according to the order of extraction: i) Tpa, Tpl, Tpi, and Tph showing M1 > M3 > B1 > OL; ii) Tpm and Tpg showing M3 > B1 > M1 > OL; and iii) Tpp and Tpc showing B1 > M3 > M1 > OL (Figure 1). Additionally, the coefficient of variation values for all sampling sites shows that M1 (104.70%) is higher than M3 (67.40%), B1 (61.80%) and OL (64.50%). Correspondingly, the coefficient of variation shows that the variability in extracting phosphate ABE soil was similar for the M3, B1, and OL extractors. Clearly, for the Tpa, Tpl, Tpi and Tph sites, the average extracted with M1, M3, B1, and OL, for the amounts of total phosphorus were: 23.80%, 7.10%, 6.10% and 2.00%, respectively. This shows that M1 overestimates phosphate quantities extracted in relation to M3, B1, and OL by the following percentages: 16.70%, 17.70%, and 21.80%.

Mean values of phosphate extraction in ABE sites for this work and references are shown in Figure 2 (Smith, 1980; Ruivo et al., 2004; Cunha, 2005; Lima et al., 2005; Falcão e Borges, 2006; Moreira, 2007; Cannavan, 2007; Neves Junior, 2008; Macedo, 2014; Souza et al., 2009; Macedo, 2009; Campos et al., 2011b, 2012a; Corrêa et al., 2011; Lemos et al., 2011; Barros et al., 2012; Silva et al., 2012; Oliveira et al., 2014). It is possible to note that the results of this work are similar to those found in the references for ABE phosphate extraction, and generally, it can be seen that M1 has tendency extraction. Depending on the point of collection, the M1 can overestimate the phosphate amounts available on the same site. This leads to anomalous results, expressing higher standard deviation than average. Variations of phosphate measures are also due to the different locations of occurrence of ABE. In this sense, it is possible to observe little variation for some sites (Apui, Rio Preto da Eva and Novo Aripuana) and wide variation for others (Anori, Codajas, Coari and this work). This behavior shows that M1 has to

be used cautiously to establish an evaluation criterion for phosphate availability in ABE, especially considering that 76.60% of all work done on anthropogenic soils have used this extractor. M3 was utilized only by Lima et al. (2002) and Rebellato (2007) at the Iranduba sites (AM), with phosphate ranging from 55.00 to 1991.00 mg kg<sup>-1</sup> and averaging 636.70 mg kg<sup>-1</sup> (n=17). B1 was only used at an ABE site in Colombia with a value found at 71.00 mg kg<sup>-1</sup> (Eden et al., 1984). Anion exchange resin was only used by Oliveira et al. (2015), Santos et al. (2013) and Aquino et al. (2016), ranging from 6.10 to 432.70 mg kg<sup>-1</sup> and an average of 151.10 mg kg<sup>-1</sup> (n=14). Studies using OL in ABE soil were not found.

Evidently, the preference for operational species is an important variable in the estimation of the extracted phosphorus. Phosphorus estimation has a relationship with the pH value used for the four extractors. M1 uses pH value of 1.20, M3 of 2.50, B1 of 2.60 and OL of 8.50. As the dissolved orthophosphate forms (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>) are the principle of phosphorus estimation, therefore the content of dissolved phosphorus differs depending on the pH values. In addition, as acidity increases, M1 > M3 > B1 > OL, the estimated phosphorus also increases suggesting orthophosphate is easily dissolved from the ABE. This explains the high content of released phosphorus in M1 suggesting weak bonds between phosphorus and aluminum, iron, and calcium (Moreira et al., 2009).

Figure 1 – Phosphorus content extracted by M1, M3, B1 and OL.



ABE M1 (average = 583.80, median = 447.50); M3 (average = 238.80, median = 223.80); B1 (average = 214.10, median = 198.80), OL (average = 63.30, median = 59.00)

CRF Powder M1 (average = 71.70, median = 68.00); M3 (average = 58.40, median = 62.80); B1 (average = 55.00, median = 65.30), OL (average = 39.50, median = 41.80)

CRF M1 (average = 60.70, median = 58.00); M3 (average = 51.40 median = 45.80); B1 (average = 59.50, median = 54.90), OL (average = 9.70, median = 9.50)

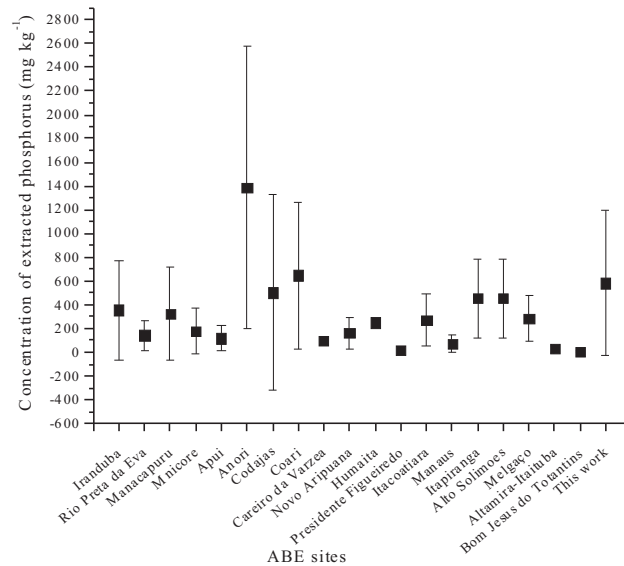
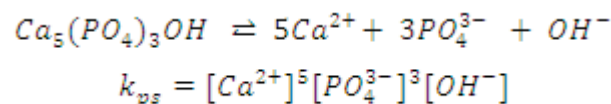


Figure 2 – Mean values of phosphate extraction for ABE sites in the states of Amazonas and Paramade by references and this work. Number of samples according to the city: Iranduba (n = 13); Rio Preto da Eva (n = 12); Manacapuru (n = 19); Manicore (n = 6); Apui (n = 3); Anori (n = 3); Codajas (n = 4); Coari (n = 5); Careiro da Vaezea (n = 3); Novo Aripuana (n = 4); Humaita (n = 2); Presidente Figueiredo (n = 2); Itacoatiara (n = 3); Manaus (n = 6); Itapiranga (n = 3); Alto Solimões (n = 3); Melgaço (n = 29); Altamira-Itaituba (n = 6); Bom Jesus do Tocantins (n = 3); This Work (n = 8).

Research shows that the total and available phosphorus in ABEarises from biogenic apatite (Lima et al., 2002). However, heavyweathering, as well as high degradation of organic matter in the Amazonian region,transformedthe biogenic apatite into amorphous/low crystalline forms(Souza et al., 2009).Maritan and Mazzoli (2004) affirm the dominanceof hydrated Fe-phosphate and hydrated Ca-phosphate, with respectively ideal formulas  $Fe_3(PO_4)_2 \cdot 8H_2O$  and  $Ca_2Fe_3(PO_4)_3 \cdot 0.2 \cdot 3H_2O$ , as the main forms existent in thearcheologicalfragment.Indeed,the weathering/dissolution in archaeological soils depends on the action of organic (fulvic and humic) and carbonicacids(White andHannaus, 1983).The increase of acidity caused by organic matter release  $Ca^{2+}$ changingthe solubility of the apatite. The chemical reaction of the hydroxyapatite dissolution/precipitation process also has an effect on the pH:



The released orthophosphate could react with aluminum and/or iron present in the soil solution and precipitate as orthophosphate of iron/aluminum.The process of dissolution/precipitation is more effective depending on the weathering stage. Commonly, the following order: P-Ca P-Al P-Fe P-occluded prevails during the weathering of apatite(Hsu and Jackson, 1960). This order explains the three groups observed for theextractionof phosphorus with M1 (Figure 1). The first group represents the primary weathering stage due to



the high content of phosphorus extracted by M1; i.e. the P-Ca operational form is most prevalent. The calcium content of the physical and chemical soil properties confirms this. The calcium content is close to the extracted phosphorus for M1. Groups two and three represent more advanced weathering stages than the first group; i.e. the P-Fe and P-Al operational forms have content close to P-Ca.

The low phosphorus content extracted by the OL method revealed that the major part of the phosphorus in the ABE links to calcium. The capacity of OL operational phosphorus confirms this. The OL method is preferential for extracting the P-Al, and Fe-P operational form.

Research reveals three hypotheses to explain high phosphorus mobility. Firstly, high phosphorus mobility occurs due to the high content of organic matter (Souza et al., 2009). Secondly, this mobility may also result from high phosphorus inputs at the surface, surpassing the plant uptake capacity, and increasing the potential for leaching losses (Lima, 2001). Thirdly, human actions have promoted the changing of the chemical characteristics of anthropogenic horizons by leaching, mainly the high content of phosphorus (Campos et al., 2011).

### PHOSPHORUS IN CRF

The phosphate concentrations in CRF powder and CRF vary with both the collection site and the type of extractor used. This shows that the phosphorus forms extracted by the extractors M1, M3, B1, and OL are in different proportions for CRF. Generally, M1 showed the highest phosphate levels in whole and sprayed ceramics, as can be seen for the values of the mean and median of the phosphate amounts obtained with M1, M3, B1, and OL (Figure 1). With CRF spraying an increase of phosphate extraction occurred in some samples and a decrease in others, with the use of M1, M3, and B1. On the other hand with CRF spraying the extraction increased with OL. Studies show that the major forms of phosphate extracted by the extractors M1, M3, and B1 are P-Ca, P-Al, and P-Fe, likewise OL preferably extracts P-Al and P-Fe (Van Raij, 1998). Consequently, larger quantities of phosphate obtained in CRF using M1, and CRF powder with OL, suggests that the ceramic surface layer has higher amounts of P-Ca and the inner layer has a mixture of P-Ca, P-Al, and P-Fe, the latter two being in larger quantities. It cannot be ruled out that the spraying process destroys some of the matrix structures of the ceramic, increasing the contact surface of the sample with the extractor. Furthermore, phosphorus is considered a dopant, precipitated or stuck on the surface of ceramics during firing (Ionescu et al., 2011). Collomb and Maggetti (1996) reported that the high phosphorus concentration in archaeological ceramic is a result of incorporating phosphorus-rich substances such as urine or fecal material, and is used to increase the plasticity of the raw material. The phosphate adsorption on the surface pores, existing in archaeological ceramics, is another way to increase the concentration of this element. Phosphate adsorption occurs during cooking of food. Maritan and Mazzoli, (2004) in their study of archaeological ceramic microstructures explain this process by:

- Phosphorus aggregates are located in specific microstructural sites;
- The phosphorus adheres perfectly to the surrounding groundmass;
- Phosphorus crystals have patchy distribution within each single aggregate;

The orientation of the phosphorus crystals is not related to the margins of the aggregates (i.e., they do not grow from the margin towards the center of the aggregate).

Given the above contamination of archaeological ceramics, phosphorus adsorbed may be one explanation for the behavior obtained by extractors with CRF powder (Figure 1). The OL was the only extractor that had an increase in phosphate concentration with the spraying of ceramics. This may suggest the occurrence of larger amounts of P-Al and P-Fe in the pores of the ceramic (inside the ceramic). Costa et al. (2011) shows that 0.50 to 2.90% P<sub>2</sub>O<sub>5</sub> corresponds to P-Al as a possible phosphate mineral found in ceramic ABE fragments. However, XRD generally does not detect the presence of phosphorus in the mineral matrix of the ceramic withdrawn from ABE. Costa et al. (2004) have reported that the abnormal phosphorus concentrations in archaeological ceramic matrix may be derived from the incorporation of food cooking and/or ABE soil transfer.

The distribution of the phosphate concentration for CRF powder was more homogeneous than for CRF pieces (Figure 1). This suggests saturation of phosphorus, which is adsorbed on the matrix of archaeological ceramics. Therefore, ceramic fragments are a major source for the maintenance of fertility of the soil of the ABE.

According to Duma (1972) the pores of pieces transfer phosphorus to the ground. Moreover, this process has certainly contributed to the increase of phosphate extraction from the ABE as well as the higher P<sub>2</sub>O<sub>5</sub> concentration ceramic fragments as reported by Silva et al. (2012). On the other hand, the weathering process can reduce the amounts of phosphorus both in the soil matrix as well as in CRF.

## CONCLUSIONS

The results showed that the four extractors used for ABE site phosphate extraction exhibited extraction differences revealing the classification of three groups of soils according to the descending order of the phosphate content: Tpa, Tpl, Tpi, and tph; tpm and Tpg and Tpp and Tpa.

M1 was the extractant that showed the greatest variability between ABE site extractions, showing increased sensitivity in the variation of their physical and chemical properties, especially the content of P-Ca. The OL extractor was the only phosphate extractant that did not have great variation of quantities between the ABE sites, and can be an alternative to the extractors which overestimate the phosphate in anthropogenic soils.

Both for the ABE as well as the CRF, the P-Ca is the predominant form of phosphate due to the decomposition of organic matter and cooking food. The higher phosphate concentrations found in the CRF powder form, suggests that phosphorus release depends on the increased contact surface of the CRF with the extractor.

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