

**QUÍMICA E MINERALOGIA
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DO SOLO E NUTRIÇÃO
DAS PLANTAS**

P adsorption and desorption capacities of selected Andisols from the Azores, Portugal

Capacidade de adsorção e de desorção de P em Andossolos dos Açores, Portugal

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ABSTRACT

Phosphorous adsorption maxima (*P-ads max*) and the amounts of P desorbed (*P-des*) using Langmuir equation and eight successive extractions with 0.01M CaCl₂, were determined on sixteen horizons of Andisols from the Azores, Portugal. Results showed that the values of *P-ads max* and the proportions of P desorbed (*P-des*) were highly influenced by allophane, Al_o, Al_d, and Fe_d contents, and by the values of Al_o + ½ Fe_o and ferrihydrite + allophane. *P-des* were negatively correlated with these constituents, but not with allophane. Vitrandic Haplustepts and Typic Udivitrands, and Typic Hapludands containing low amounts of allophane, Al_o, Al_d, and Fe_d showed low values of *P-ads max*, but high *P-des* values. Phosphate ions applied as fertilizer on these soils are highly available for plant use, but maybe easily lost through surface runoff, subsurface drainage and soil erosion. They may require restricted amounts of P fertilizer, and P losses should be controlled to minimize eutrophication of nearby water bodies. Conversely, Typic Placudands containing large amounts of allophane, and Acrudoxic Hydrudands and

Typic Hapludands containing large amounts of organic C showed high values of *P-ads max*, but low *P-des*, indicating unavailability of P when retained by these soils. Large amounts of slow P-releasing fertilizer may be required for better crop use.

RESUMO

A adsorção máxima de P (*P-ads max*) e a quantidade de P desorvido no solo (*P-des*), foram determinadas em 16 horizontes superficiais e subsuperficiais de Andossolos dos Açores, Portugal, usando equação de Langmuir e oito extracções sucessivas com cloreto do cálcio. Os valores de *P-ads max* mostraram uma correlação positiva com os teores de Al_o, Al_d, Fe_d, alofana, ferrihidrite + + alofana, e com valores de Al_o + ½ Fe_o. Por outro lado, os resultados de *P-des*, mostraram uma correlação negativa com os mesmos constituintes, excepto com alofana. *Vitrandic Haplustepts*, *Typic Udivitrands* e *Typic Hapludands* mostraram um valor de *P-ads max* baixo, mas com elevado teor de *P-des*. Iões fosfato adicionados como fertilizante neste tipo de solos ficam disponíveis para utilização pelas plantas, mas provavel-

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mente, serão facilmente perdidos por drenagem e erosão do solo. Estes solos podem necessitar de quantidades limitadas de fertilizante de fósforo, com controlo das perdas deste elemento para minimizar a eutroficação dos cursos de água das proximidades. Por outro lado, os *Typic Placudands* com elevado teor de alofana e os *Acrudoxic Hydrudands*, com elevado teor de carbono orgânico, têm elevado valor de *P-ads max* e baixo teor de *P-des*, indicando indisponibilidade do P quando retido por estes solos. Neste caso, poderá ser preferível o uso de grandes quantidades de fertilizante de libertação lenta de P.

INTRODUCTION

Most Andisols contain large amounts of active Al and Fe, ferrihydrite, allophane and organic C, which were found strongly correlated with the capacity of the soil to adsorb P (Bache & Williams, 1971; Shoji *et al.*, 1993; Mozaffari & Sims, 1994). The predominance of these constituents in most Andisols of the Azores (Auxtero *et al.*, 2001, 2002, 2004; Madeira *et al.*, 2003) is supposed to influence their capacity to adsorb and desorb P. The capacity of the soil to adsorb and desorb P has been successfully described by adsorption and desorption isotherms. Several quantitative measurements of P adsorption by soils other than Andisols have been described (Olsen & Watanabe, 1957; Chardon & Blaauw, 1998; Maguire *et al.*, 2001; Villapando & Graetz, 2001). Phosphorous adsorption measurement using the Langmuir equation, which estimates P adsorption maxima, presents distinct advantage over other equations (Woodruff & Kamprath, 1965; Lopez *et al.*, 1990; Pierzynski, 2000; Comfort & Eghball, 2002). Phosphorous desorption studies for non-andisols have also been reported

(Delgado & Torrent, 2000; Villapando & Graetz, 2001). So far, information regarding the capacity to adsorb P using Langmuir equation and to desorb P using successive extractions with weak salt (0.01M CaCl₂), for sound P management of Andisols from the Azores is not yet available.

Having this in view, a study was conducted on eight pedons of Andisols from the Azores to 1) determine the values of P adsorption maxima and the amounts of P desorbed, and 2) assess the influence of soil constituents on P adsorption and desorption.

MATERIALS AND METHODS

Soils

Soil samples from surface and subsurface horizons representing eight pedons of Andisols from the Azores were used according to their chemical composition (Tables 1 and 2). Their chemical composition have been reported in detail elsewhere (Ricardo *et al.*, 1977; Pinheiro *et al.*, 2001; Auxtero *et al.*, 2001, 2002, 2004; Madeira *et al.*, 2001, 2003). They are: (a) Andic Haplustepts, containing significant amounts of 1:1 layer silicate minerals, predominantly halloysites (Pediton FA26); (b) Typic Hapludands, having significant amounts of layer silicate minerals (halloysite), little amounts of organic C and allophane (Pediton FA10); (c) Acrudoxic Hapludands, containing little amounts of 2:1 layer silicate minerals and little organic C, but significant amounts of allophane (Pediton FA12); (d) Acrudoxic Hydrudands, having significant amounts of organic C, significant amounts of allophane and negligible amounts of 2:1 layer minerals (Pediton PI14); (e) Acrudoxic Hydrudands, containing very high organic C, negligible amounts of 2:1 layer miner-

als and no allophane (Pedom PI12); (f) Typic Placudands, having high organic C in the surface horizon and with rather high allophane content, but with very little organic C in the subsurface horizon (Pedom FA20); (g) Vitrandic Haplustepts, containing very little organic C and halloysite as the predominant mineral in the clay fraction (Pedom SMI55); and, (h) Typic Udivitrands, having significant amounts of organic C in the Ah horizon and low amounts of 1:1 layer silicate minerals (Pedom SMisc).

Laboratory procedures

Measurements were done on air-dried soil samples passed through a 2 mm sieve prior to analysis and results are expressed on air-dried soil basis. Soil reaction (pH) was measured in H₂O and 1M KCl using a soil to solution ratio of 1:2.5 and 1:5 for 1 M NaF. Total organic C content of the soil samples was determined by wet oxidation following the Springer method (De Leenheer and Van

Hove, 1958). Dithionite-citrate-bicarbonate extractable Al (Al_d) and Fe (Fe_d) were determined following the procedures of Mehra and Jackson (1960). The oxalate and pyrophosphate extractable Al (Al_o, Al_p), Fe (Fe_o, Fe_p) and Si (Si_o, Si_p) were determined using the method of Blakemore *et al.* (1987). Al, Fe and Si from extracts were quantified by atomic absorption spectroscopy. The Al:Si atomic ratio for the soil allophane was estimated from (Al_o-Al_p)/Si_o values, multiplied by the atomic ratio of Al/Si (Parfitt, 1986). Ferrihydrite was calculated as the product of Fe_o*1.72 (Childs, 1985).

P adsorption maxima

P adsorption maxima (*P-ads max*) were calculated using the linear form of the Langmuir equation (Woodruff & Kamprath, 1965): $C/Ads\ P = C/ads\ max + 1/k\ ads\ max$, where *C* is the equilibrium P concentration (mg L⁻¹), *Ads P* is the amount of P adsorbed (g kg⁻¹), *ads max* is the adsorption maximum, and *k* is a constant related

TABLE 1 - Environmental conditions and taxonomic classification of the studied pedons. LT-lithology; PM-pyroclastic materials of acidic (a) or basic (b) composition; Alt – altitude; MAP – mean annual precipitation; MAT – mean annual temperature; S - slope

<i>Pedons</i>	LT	Sub-group (SSS, 1999)	Alt (m)	MAP (mm)	MAT (°C)	S (%)	Vegetation
Faial Island							
FA 26	PMa	Andic Haplustepts	115	1100	17	10	Pasture
FA10	PMa	Typic Hapludands	110	1100	17	5	Pasture
FA 12	PMa	Acrudoxic Hapludands	230	1400	16	18	Forest
FA20	PMa	Typic Placudands	750	2000	13	20	Pasture
Pico Island							
PI 12	PMb	Acrudoxic Hydrudands	640	3000	13	20	Pasture
PI 14	PMb	Acrudoxic Hydrudands	840	3000	12	20	Pasture
São Miguel Island							
SMI55	PMa	Vitrandic Haplustepts	70	1000	17	5	Agric. Land
SMisc	PMa	Typic Udivitrands	500	2000	15	10	Pasture

TABLE 2- Mineralogical composition (MC), contents of organic carbon (OC), Si, Al and Fe, extracted by oxalate (O), by pyrophosphate (P) and by dithionite (D), ferrihydrate (Fer) and allophane (A) contents, and values of $Al_o + \frac{1}{2} Fe_o$

Pedons	Hor	Depth (cm)	MC	(g kg ⁻¹)										
				OC	Si _o	Al _o	Al _o	Fe _o	Fe _d	Al _p	Fer	A	Fer + A	Al _o + $\frac{1}{2}$ Fe _o
FA 26	Ah	0-20	1VHK	32.0	8.3	14.8	8.2	9.1	14.1	3.5	15.7	50	65.7	19.4
	Bw1	20-50	1VHK	13.7	10.3	15.3	7.0	9.1	16.5	1.9	15.7	80	95.7	19.9
Andic Haplustepts														
FA10	Ap	0-20	2VHK	36.8	14.5	30.0	10.0	20.1	19.9	4.8	34.6	100	134.6	40.1
	Bw	20-65	2VHK	25.3	15.6	29.6	8.6	19.6	19.9	4.0	33.7	90	123.7	39.4
Typic Hapludands														
FA 12	Ah	0-25	2VHK	41.0	16.5	43.0	39.5	18.0	21.6	12.0	31.0	120	151.0	52.0
	Bw	30-55	2VHK	20.2	19.7	37.4	14.1	17.9	17.5	4.9	30.8	120	150.8	46.4
Typic Placudands														
FA20	Ap	0-15	2VK	110.6	10.9	31.1	15.5	14.0	25.6	10.8	24.1	80	104.1	38.1
	BC	35-52	2VK	14.1	65.9	100.8	50.4	15.6	37.7	4.6	26.8	400	426.8	108.6
Acruudoxic Hydudands														
PI 12	Ah1	0-16	AB	268.7	3.4	25.2	12.0	41.8	63.3	30.6	71.9	0	71.9	46.1
	Bw1	27-50	AB	187.0	2.7	25.3	41.5	54.8	78.9	38.7	94.3	0	94.3	52.7
PI 14	Ah	0-20	3VH	83.0	20.3	45.1	37.8	32.5	59.6	16.4	55.9	120	175.9	61.4
	Bw	20-40	3VH	60.8	18.9	47.5	44.0	27.0	58.2	15.7	46.4	130	176.4	61.0
Vitrandic Haplustepts														
SMI55	Ap	0-12/15	1H2M	9.7	0.8	3.2	1.4	3.6	3.7	0.5	6.2	12	18.2	5.0
	Bw	12/15-40/45	1H2M	9.3	1.1	2.7	1.4	3.7	3.6	0.3	6.4	10	16.4	4.6
Typic Udivitrands														
SMI5c	Ap	0-3	nd	98.6	0.1	3.3	2.2	1.8	1.3	2.4	3.1	10	13.1	4.2
	Bw	15-25	nd	5.8	0.3	1.5	1.0	0.4	0.5	0.5	0.7	10	10.7	1.7

Symbols: H- halloysite, K- kaolinite, V- vermiculite, M- montmorillonite, 1- significant amounts, 2- low amounts, 3- negligible amounts, AB- no layer silicate minerals, nd- not determined

to the binding energy of the adsorbent for the adsorbate. The values of $C/Ads\ P$ were plotted against C and a linear curve is fitted to the scattered points to obtain $y = a + bC$. The inverse value of b ($1/b$) obtained from this linear fit represents the Langmuir adsorption maximum of P ($P-ads\ max$). The amount of $Ads\ P$ ($g\ kg^{-1}$) was determined by the method of Fox and Kamprath (1970) using four replicates for each sample. This was done by adding 10 ml of 0.01M $CaCl_2$ solutions containing various concentrations of phosphate as KH_2PO_4-P to 1 g of soil in 50 ml plastic centrifuge tubes equilibrated for 6 days at room temperature. Two drops of chloroform were added to each sample to suppress microbial growth (Bache & Williams, 1971; Self-Davis *et al.*, 2000). The suspensions were shaken for 30 min twice a day within the equilibration period using reciprocal shaker. After equilibration, the samples were centrifuged for 10 min and filtered. The P content in the supernatant solution was determined by the molybdate blue color (MBC) method (Murphy and Riley, 1962).

Phosphate not recovered in the solution was assumed to be retained by the soils, and was calculated as $P\ Ads = (C_i - C_f) VW$, where $P\ Ads$ is the added P adsorbed ($g\ kg^{-1}$), C_i is the amount of P added ($mg\ L^{-1}$), C_f is the amount of P in solution after equilibration ($mg\ L^{-1}$), V is the volume of solution (L), and W is the air dried weight of the soil (kg).

P desorption

P desorption was studied by equilibrating two samples of 2 g of soil with 20 ml of 0.01 M $CaCl_2$ solutions containing the Langmuir $P-ads\ max$ concentration of phosphate as KH_2PO_4-P in 50 ml plastic centrifuge tubes equilibrated for 6 days at room temperature. Two drops of chloro-

form were added to each sample to suppress microbial growth (Bache & Williams, 1971; Self-Davis *et al.*, 2000). The suspensions were shaken for 30 min twice a day within the equilibration period using reciprocal shaker. After equilibration, the samples were centrifuged for 10 min and filtered. The P content in the supernatant solution, determined by the MBC method, represented the initial value for adsorbed P . Phosphorous saturated soils were then extracted eight times successively, by adding 20 ml of 0.01 M $CaCl_2$ to these saturated soils, followed by 2 h of shaking using a reciprocal shaker. Samples were then centrifuged for 10 min and filtered. The P content in the supernatant solution for each extraction was determined by the MBC method. P desorbed ($P-des$) was calculated as the difference between the $P-ads\ max$ and the sum of P obtained after eight successive extractions.

RESULTS AND DISCUSSION

P adsorption

The values of P adsorption maxima ($P-ads\ max$) calculated from soils equilibrated with various concentrations of P for six days, using the linear Langmuirian fit of P adsorption isotherms for each soil, are given in Table 3. These values were extremely variable and ranged from 0.03 to 52.40 $g\ kg^{-1}$. The lowest values of $P-ads\ max$ (0.03 to 0.57 $g\ kg^{-1}$) were observed in the A_p horizon of Typic Hapludands (pedon FA10), and in both surface and subsurface horizons of Vitrandic Haplustepts (pedon SMI55) and Typic Udivitrands (pedon SMI5c). The highest values of $P-ads\ max$ (47.62-52.40 $g\ kg^{-1}$) were obtained in the A_h horizon of Acrudoxic Hydrudands (pedon PI14)

having significant amounts of organic C (60.8-83.0 g kg⁻¹) and allophane (120-130 g kg⁻¹), and in the BC horizon of Typic Placudands, containing low amounts of organic C (14.1 g kg⁻¹) and high allophane content (400 g kg⁻¹). Values of *P-ads max*

TABLE 3 - Values of P adsorption maxima (*P-ads max*) and P desorbability (*P-des*) of surface and subsurface horizons of selected Andisols from the Azores

Pedons	Horizons	<i>P-ads max</i> (g kg ⁻¹)	<i>P-des</i> (%)
FA 26	Ah	3.44	20
	Bw1	1.12	23
FA10	Ap	1.61	5
	Bw	0.03	13
FA 12	Ah	19.61	34
	Bw	3.45	29
FA20	Ap	2.27	28
	BC	47.62	21
PI 12	Ah1	8.33	8
	Bw1	19.23	4
PI 14	Ah	52.40	18
	Bw	6.25	25
SMI55	Ap	0.04	100
	Bw	0.10	99
SMIsc	Ap	0.15	99
	Bw	0.57	69

for the other pedons (FA26, FA12, PI12), Ap horizons of pedons FA10 and FA20, and Bw horizon of pedon PI14 showed values between 1.12 and 19.61 g kg⁻¹. The wide range of observed values of *P-ads max* is in agreement with the data reported by Van Ranst *et al.* (2004), for andisols developed on volcanic ash along the Sundra arc crossing Java Island, Indonesia, and by Madeira *et al.* (2006), for European volcanic soils. That range of values is mostly in relation with the vari-

ability of studied soils regarding their colloidal (both mineral and organic) constitution.

The values of *P-ads max*, calculated using the Langmuir equation, were related to amounts of Al and Fe extracted by the oxalate (Al_o, Fe_o), dithionite (Al_d, Fe_d) and pyrophosphate (Al_p, Fe_p), and to amounts of allophane and ferrihydrite using correlation analysis. These relationships are shown in Table 4. The values of *P-ads max*, as reported by Van Ranst *et al.* (2004) and Madeira *et al.* (2006), were positively correlated with Al_o contents ($r = 0.74$; $p < 0.001$). In spite of the strong adsorbing ability observed for the allophane-rich horizon (pedon FA20), the positive correlation between allophane contents and with the values of *P-ads max* ($r = 0.64$; $p < 0.01$) was weaker than that obtained with Al_o. This indicates that constituents other than allophane may play an important role in P adsorption of studied Andisols. In fact, the correlation of Al_d with the values of *P-ads max* ($r = 0.77$; $p < 0.001$) was stronger than the correlation with Al_o, suggesting that in the absence of allophane, Andisols can adsorb large amounts of P. As P adsorption values were not significantly correlated with Al_p constituents, that is, with Al- and Fe-humus complexes (Wada & Gunjigake, 1979), our data suggest that allophane-like and imogolite may be active constituents in the adsorption of P in the studied Andisols.

When accounted alone, Fe_o was not correlated with the values of *P-ads max*, suggesting that amorphous ferruginous constituents play a negligible role in P adsorption. On the other hand, the positive correlation between Fe_d and *P-ads max* values ($r = 0.55$; $p < 0.05$), although lower than that observed for other soil constituents, suggests that crystalline iron oxides are more important for P adsorption than amorphous

TABLE 4 - Relationships between values of P sorption maxima (P-ads max) and soil constituents

Equations	r values	p
$P_{ads\ max} = -3.78 + 0.50 Al_o$	0.74	<0.001
$P_{ads\ max} = -3.11 + 0.73 Al_d$	0.77	<0.001
$P_{ads\ max} = -6.44 + 0.45 (Al_o + \frac{1}{2} Fe_o)$	0.76	<0.001
$P_{ads\ max} = 2.18 + 0.75 Si_o$	0.68	<0.01
$P_{ads\ max} = 1.26 + 0.11$ allophane	0.64	<0.01
$P_{ads\ max} = -6.89 + 0.41$ ferrihydrite + 0.64 allophane	0.76	<0.01
$P_{ads\ max} = 0.14 + 0.37 Fe_d$	0.55	<0.05

iron constituents. This is in agreement with the fact that the correlation between P sorbed values and those of $Al_o + \frac{1}{2} Fe_o$ (a criteria for classifying Andisols) was similar ($r = 0.76$; $p < 0.001$) to the correlation between values of P-ads max and Al_o contents. However, combining allophane and ferrihydrite contents, 76% of the variation in the P-ads max was accounted. As inferred from the correlation analysis, there was no significant relation between the values of P-ads max and organic C content, suggesting a negligible influence of this constituent in P adsorption of studied soils.

According to our study, in the Ah horizon of Acrudoxic Hydrudands (Pedin PI14) and the BC horizon of Typic Placudands (pedon FA20), P may be strongly held in unavailable forms for crop use, and an efficient P fertilizer management is required on these soils. Conversely, in the pedons SMI55 (Vitrandic Haplustepts) and SMISc (Typic Udivitrands) with low values of P-ads max, applied P through fertilizers is highly available for plants, but prone to be easily leached, and risks of P losses from soil may occur.

Amounts of P desorbed

In most studied soils, P desorbed (P-des) increased following eight successive extractions with calcium chloride ($CaCl_2$). This was shown by the decrease in the amounts of P adsorbed remaining in all soils (Figure 1), which was strongly vari-

able among them. In the Ap horizon of Vitrandic Haplustepts (pedon SMI55), the totality of the added P (100%) was desorbed after the first extraction with $CaCl_2$ (Figure 1A). After eight successive extractions with $CaCl_2$, 99% of added P in the Bw horizon of this soil was desorbed, whereas in Typic Udivitrands (pedon SMISc), these proportions were 69 to 99%, respectively in surface and subsurface horizons (Figure 1A). The large proportions of P-des observed for these soils suggest a high probability of P losses through soil erosion, surface runoff and subsurface drainage. If not controlled, P transfer may cause eutrophication of nearby water bodies. We may emphasize that this behaviour is also in relation with large amounts of extractable P by the Bray 2 test ($582.50\ mg\ kg^{-1}$) exhibited by these soils due to fertilizer application (Auxtero *et al.*, 2005; J. Pinheiro, personal communication).

Horizons of Acrudoxic Hydrudands (pedon PI12) with high contents of organic C ($187.0-268.7\ g\ kg^{-1}$), Al_o ($25.2\ g\ kg^{-1}$), Fe_o ($41.0-54.8\ g\ kg^{-1}$) and Fe_d ($63.3-78.9\ g\ kg^{-1}$), and the Ah horizon of Typic Hapludands (pedon FA10), with lower contents of organic C ($36.8\ g\ kg^{-1}$), Fe_o ($20.1\ g\ kg^{-1}$) and Fe_d ($19.9\ g\ kg^{-1}$), and similar contents of Al_o ($30.0\ g\ kg^{-1}$) showed lower P-des than the other pedons (4 to 8% of the total P added). Other pedons showed a P desorbability ranging from 13 to 29% (Figure 1B and 1C).

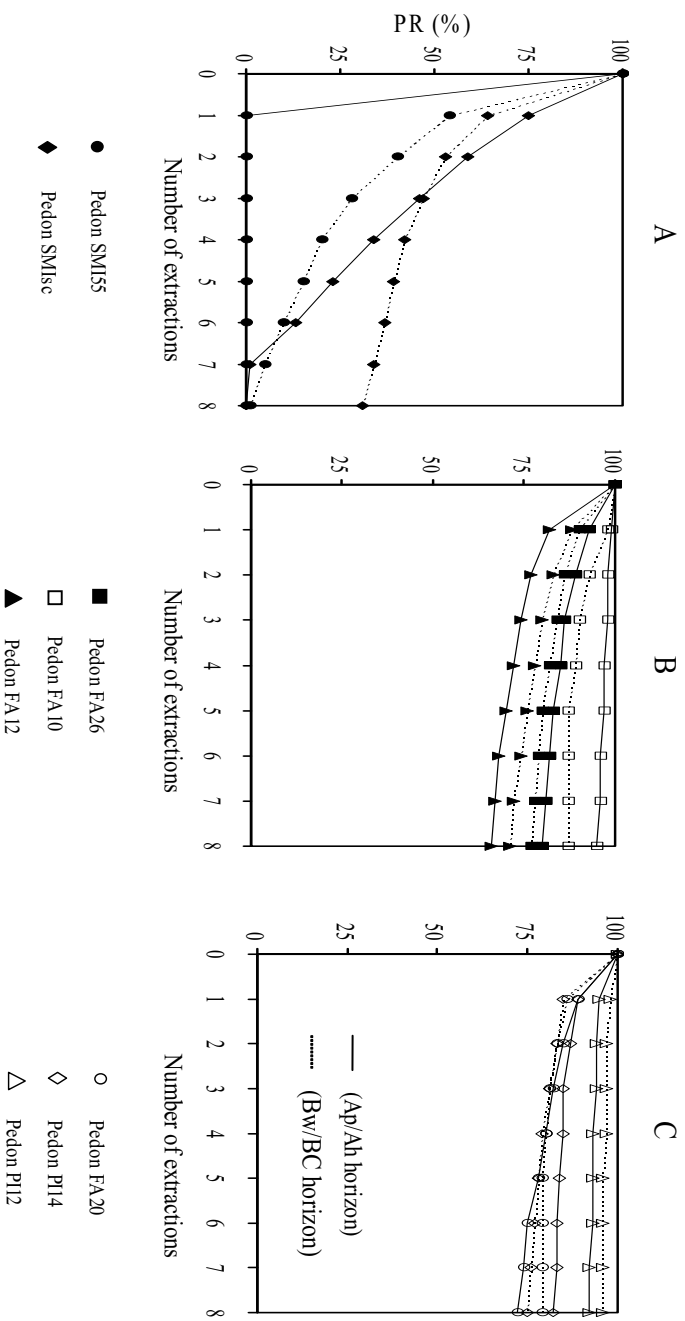


Figure 1 - Proportions of P remaining (PR) in the soil (%) following eight successive extractions with 0.01 M CaCl_2 in the Ap/Ah and Bw/BC horizons of selected Andisols from the Azores (bars of standard deviation are too small to be shown)

TABLE 5 - Relationships between P desorbed (*P-des*) and soil constituents

Equations	r values	p
$P\text{-des} = 66.04 - 1.60 \text{ Fe}_o$	-0.70	<0.01
$P\text{-des} = 62.73 - 0.92 \text{ Fe}_d$	-0.67	<0.01
$P\text{-des} = 67.42 - 0.80 (\text{Al}_o + \frac{1}{2} \text{Fe}_o)$	-0.66	<0.01
$P\text{-des} = 58.56 - 0.75 \text{ Al}_o$	-0.54	<0.05
$P\text{-des} = 52.61 - 1.63 \text{ Al}_p$	-0.53	<0.05
$P\text{-des} = 76.16 - 0.70 \text{ ferrihydrite} - 0.35 \text{ allophane}$	-0.78	<0.01
$P\text{-des} = 55.48 - 0.99 \text{ Al}_d$	-0.51	<0.05

The amounts of P desorbed (*P-des*) following eight successive extractions with calcium chloride were related to soil constituents. In contrast to *P-ads max*, the amounts of P desorbed (*P-des*) showed negative correlations with soil colloidal constituents (Table 5). Significant negative correlations with Al_p ($r = -0.53$; $p < 0.01$), Al_d ($r = -0.51$; $p < 0.05$) and Al_o ($r = -0.54$; $p < 0.05$) contents were observed. These data indicate that reactivity of Al bound with humus (Al_p) was similar to constituents related to Al_o and Al_d . Unlike the values of *P-ads max*, the amounts of P desorbed were not significantly correlated with allophane, suggesting a negligible role of these materials in P desorption.

As observed for the values of *P-ads max*, we can also use the values of $\text{Al}_o + \frac{1}{2} \text{Fe}_o$ to discriminate the studied soils regarding their ability to desorb P. A stronger significant negative correlation was shown between the amounts of *P-des* and the values of $\text{Al}_o + \frac{1}{2} \text{Fe}_o$ ($r = -0.66$, $p < 0.01$) (Table 4). This difference is in agreement with the high correlation coefficient observed between the amounts of *P-des* and Fe_o or ferrihydrite contents ($r = -0.70$; $p < 0.01$) (Table 4). As the correlation coefficient between *P-des* and Fe_d was slightly lower ($r = -0.67$; $p < 0.01$) than that observed for ferrihydrite, ferruginous amorphous constituents may be more important than the crystalline ones in reducing P desorbility from studied soils. Allophane content was not correlated with the *P-des*, but the highest

correlation for P desorption was obtained combining ferrihydrite and allophane contents (78%) (Table 5). As shown in our study, Fe constituents (Fe_o and Fe_d) have stronger negative influence in P desorption than Al constituents (Al_o and Al_d), indicating the stronger influence of Fe constituents than Al in desorption of P. P bound to ferruginous materials are more stable than those bound to Al, because they are less soluble than amorphous Al materials (P. Buurman, personal communication). In fact, the lowest *P-des* (4%) (Figure 1C) was observed in the subsurface horizon of Acrudoxic Hydrudands (PI12), containing the highest Fe_o (54.8 g kg^{-1}), Fe_d (78.9 g kg^{-1}) and ferrihydrite (94.3 g kg^{-1}) contents, suggesting that P is strongly held by these soils. Conversely, Vitrandic Haplustepts (pedon SMI55) and Typic Udivitrands (pedon SMIsc) containing low amounts of those constituents (Table 2), showed much greater amounts of desorb P than other soils. Following eight successive extractions with CaCl_2 , the observed amounts of added P desorbed were 69 to 100% (Figure 1A), suggesting that sorbed P may be easily available for crops, but on the other hand it may be easily transferred to nearby water bodies.

CONCLUSIONS

Values of *P-ads max* were positively correlated with allophane, Al_o , Al_d , and Fe_d

contents, and with the values of $Al_o + \frac{1}{2} Fe_o$ and ferrihydrite + allophane, while *P-des* values were negatively correlated with similar constituents, except allophane.

Andisols having low amounts of allophane, Al_o , Al_d and Fe_d , that is, Vitrandic Haplustepts, Typic Udivitrands, and Typic Hapludands, showed low values of *P-ads max*, but high *P-des* values. Applied P fertilizers may be easily available for plant use, but also easily lost from soil through surface runoff, subsurface drainage and soil erosion. Hence, P fertilizers should be applied in restricted amounts to avoid P losses risks and to minimize eutrophication of nearby water bodies.

On the contrary, Andisols containing high amounts of allophane, Al_o , Al_d and Fe_d , like Acrudoxic Hapludands, Acrudoxic Hydrudands and Typic Placudands, have strong ability to adsorb P, but low ability to desorb P. These soils have strong ability to retain P, which may become unavailable for plant use, and may require large amounts of slow P-releasing fertilizers for best crop response.

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REFERENCES

- Auxtero, E., Sousa, E., Madeira & M., Pinheiro, J. 2001. Cation and anion exchange properties of some Andisols of the Azores, Portugal, by compulsive exchange method. Comparison with other methods. *Rev. Ciências Agrárias*, **24** (3/4): 121- 133.
- Auxtero, E., Madeira, M. & Sousa, E. 2002. Assessment of pH-dependent charge of selected Andisols from Faial Island (Azores), Portugal. *Rev. Ciências Agrárias*, **25** (3/4): 123- 137.
- Auxtero, E., & Madeira, M. 2004. Variable charge characteristics of selected Andisols from the Azores, Portugal. *Catena*, **56**: 111-125.
- Auxtero, E., Madeira, M. & Sousa, E. 2005. Extractable P as determined by different test and P adsorption capacity of selected Andisols from the Azores, Portugal. *Rev. Ciências Agrárias*, **XXX-VIII**(2): 121-132.
- Bache, B.W. & Williams, E.G. 1971. A phosphate sorption index for soils. *J. Soil Sci.*, **22**(3): 290-301.
- Blakemore, L. C., P. L. Searle & B. K. Daly. 1987. Soil bureau laboratory methods: A methods for chemical analysis of soils. New Zealand: Soil Bureau Scientific Report 80.
- Chardon, W. J. & Blauuw, D.1998. Kinetic Freundlich equation applied to soils with a high residual phosphorus content. *Soil Sci.*, **163**(1): 30-35.
- Childs, C. W. 1985. Towards understanding soil mineralogy: II. Notes on ferrihydrite. NZ Bureau Scientific Report No. **80**. Lower Hutt, NZ, p. 103.
- Comfort, S. D. & Eghball, B. 2002. Phosphorus leaching from manure applications. *Manure matters*, **2**(8): 1-3.
- De Leenheer, L. & Van Hove, J. 1958. Determination de la teneur en carbone organique des sols. Études critiques des metodes tritrimétriques. *Pédologie*, **8**: 39-77.

- Delgado, A. & Torrent, J. 2000. Phosphorus forms and desorption patterns in heavily fertilized calcareous and limed acid soils. *Soil Sci. Soc. Amer. J.*, **64**: 2031-2037.
- Fox, R.L. & Kamprath, E.J. 1970. Phosphate sorption isotherms for evaluating the phosphate requirements of soils. *Soil Sci. Soc. Amer. Proc.*, **34**: 902-907.
- Lopez, S.C., Barbaro, N.O. & Tramontini, S. R. 1990. Effect of previous fertilization on P adsorption. Measurement of surface P by isotopic exchange. *Soil Sci.*, **150(3)**: 594-601.
- Madeira, M., Pinheiro, J. Monteiro, F., Fonseca & M. Medina, J. 2001. Características e classificação dos Solos da Ilha do Faial (Arquipélago dos Açores). *Rev. Ciências Agrárias*, **25 (3/4)**: 53-66.
- Madeira, M., Auxtero, E. & Sousa, E. 2003. Cation and anion exchange properties of Andisols from the Azores, Portugal, as determined by the compulsive exchange and ammonium acetate methods. *Geoderma*, **117**: 225-241.
- Madeira, M., Fuleky, G. & Auxtero, E. 2007. Phosphate sorption of European volcanic soils. In Bartoli, F., Bururman, P., Arnolds, O., Stoops, G. & Garcia-Rodeja, E. (eds) *Soils of Volcanic Regions of Europe*. Elsevier. (in press).
- Maguire, R.O., Foy, R.H., Bailey, J.S. & Sims, J.T. 2001. Estimation of the phosphorus sorption capacity of acidic soils in Ireland. *European J. Soil. Sci.*, **52**: 479-487.
- Mehra, B.P. & Jackson, H.L. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Min.*, **7**: 317-327.
- Mozaffari, M. & Sims, J.T. 1994. Phosphorus availability and sorption in an Atlantic coastal plain watershed dominated by animal-based agriculture. *Soil Sci.*, **157**: 97-107.
- Murphy, J. & Riley, J.P. 1962. Modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, **27**: 31-36.
- Olsen, S.R. & Watanabe, F.S. 1957. A method to determine phosphorus adsorption of soils as measured by the Langmuir isotherm. *Soil Sci. Soc. Am. Proc.*, **21**: 144-149.
- Parfitt, R.L. 1986. Towards understanding soil mineralogy. Part III. Notes on allophanes. *New Zealand: Soil Bureau Laboratory Report 10A*.
- Pierzynski, G.M. (ed). 2000. *Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Waters*. Southern Cooperative Series Bull. no. 396, USDA-CSREES Regional Committee, USA.
- Pinheiro, J., Madeira, M., Monteiro, F. & Medina, J. 2001. Características e classificação dos Andossolos da Ilha do Pico (Arquipélago dos Açores). *Rev. de Ciências Agrárias*, **24 (3/4)**: 48-60.
- Ricardo, R., Madeira, M., Medina, J., Marques, M & Furtado, A. 1977. Esboço pedológico da Ilha de São Miguel (Açores). *Anais do Instituto Superior de Agronomia*, **XXXVII**: 275-385.
- Self-Davis, M.L., Moore, P.A., Jr. & Joern, B.C. 2000. Determination of water and/or dilute salt-extractable P. In Pierzynski, G.M. (ed) *Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Waters*. Southern cooperative series bull. no. 396, USDA-CSREES Regional Committee, USA.
- Sharpley, A.N. 1983. Effect of soil properties on kinetics of phosphate desorption. *Soil Science Society of America Journal*, **47**: 462-467.
- Shoji, S., Nanzyo, M. & Dahlgren, R. 1993. Productivity and utilization of volcanic ash soils. Volcanic ash soils. Genesis,

- properties and utilization. The Netherlands: Elsevier Science Publishers.
- SSS (Soil Survey Staff). 1999. *Soil Taxonomy. A Basic System of Soil Classification for Making and Interpreting Soil Survey*, 2nd ed. Agriculture Handbook Number **436**. USDA and NRCS, Washington, D. C.
- Van Ranst, E., Utami, S.R., Vanderdeelen, J., Shamshuddin, J. 2004. Surface reactivity of Andisols on volcanic ash along the Sunda arc crossing Java Island, Indonesia. *Geoderma*, **123**, 193-203.
- Villapando, R.R. & Graetz, D.A. 2001. Phosphorus sorption and desorption properties of the spodic horizon from selected Florida spodosols. *Soil Sci. Soc. Am. J.*, **65**: 331-339.
- Wada, K. & Gunjigake, N. 1979. Active aluminium and iron and phosphate adsorption in Ando soils. *Soil Sci.*, **128** (6): 331-336.
- Woodruff, J.R. & Kamprath, E.J. 1965. P adsorption maxima measured by the Langmuir isotherm and the relationship to P availability. *Soil Sci. Soc. Amer. Proc.*, **29**: 148-150.