Phosphorus desorbability in soils with andic properties from the Azores, Portugal

Desorção de fósforo em solos com propriedades ândicas do Arquipélago dos Açores (Portugal)

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ABSTRACT

Desorbability of phosphorus (P *des*) at P sorption maxima in eighteen horizons (surface and subsurface) of soils with andic properties from the Azores, Portugal, was determined by eight successive extractions using distilled water (H_2O), calcium chloride ($CaCl_2$), Bray 2 (B2), Mehlich 3 (M3), Egnér-Riehm (ER) and Olsen (OL) methods.

The highest proportions of P *des* by the B2, M3, ER and OL methods (29-100%) were obtained in soils with weak andic properties (Vitrandic Haplustepts, Typic Haplustepts and Andic Haplustepts), indicating that P can be easily lost from these soils to nearby water bodies, through surface runoff and subsurface drainage. In contrast, low proportions of P *des* (4-57%) by these methods were obtained in allophane-rich (Acrudoxic Hydrudands and Typic Placudands) and non-allophanic soils (Acrudoxic Hydrudands and Alic Hapludands), indicating that large amounts of P can be sorbed in an unavailable form by these soils. Of the six methods used, the proportions of P *des* obtained by H_2O and $CaCl_2$ were consistently lower than those obtained by the B2, M3, ER and OL methods. The proportion of P *des* obtained by the B2 method was highly correlated with other methods (M3, ER and OL) suggesting that the B2 is also an effective method to extract P in most of the studied soils. The proportions of P *des* obtained by different methods were negatively correlated with Fe_o and $Fe_{d,}$ correlatios being stronger than with Al_o, Al_d, Al_p and Fe_p contents. This indicates that Fe_o-and Fe_d plays an important role in desorbability of P in studied soils.

RESUMO

A proporção de P desorvido no solo (P *des*) após oito extracções sucessivas com água destilada (H_2O), cloreto do cálcio ($CaCl_2$) e pelos métodos Bray 2 (B2), Mehlich 3 (M3), Egnér-Riehm (ER) e Olsen (OL) foi determinada em dezoito horizontes (superficiais e subsuperficiais) de pedónes representativos de Andossolos dos Açores, enriquecidos com P no seu máximo desorção. As proporções de P *des* por estes extractantes foram comparadas e correlacionadas com os constituintes coloidais do solo. Observou-se uma grande

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variação da proporção de P*des* para qualquer dos extractantes, consoante a constituição coloidal do solo. As proporções de P *des* obtidas pela H_2O e $CaCl_2$ foram bastante menores do que as observadas para os outros extractantes, em qualquer dos horizontes dos solos estudados. Os Vitrandic Haplustepts, Typic e Andic Haplustepts, que apresentam reduzido teor de alofana e em que as propriedades ândicas estão fracamente expressas, mostraram elevada proporção de P*des* (29-100%) pelos métodos de B2, M3, ER e OL. Os fosfatos aplicados como fertilizantes neste tipo de solos ficarão facilmente disponíveis para as plantas, mas, provavelmente, serão facilmente perdidos por drenagem e erosão do solo. Assim, a aplicação de fertilizante de fósforo nesses solos deverá ser a estritamente necessária e em quantidades limitadas, de modo a minimizar as perdas de P e naturalmente a eutroficação dos cursos de água e lagoas das proximidades. Pelo contrário, tanto os horizontes superficiais como subsuperficiais dos outros pédones (Typic Placudands, Acrudoxic Hydrudands, Acrudoxic Hapludands e Alic Hapludands) mostraram uma baixa proporção de P *des*, sugerindo uma forte retenção e indisponibilidade do P quando aplicado a estes solos. Nestas circunstâncias, será preferível a aplicação de grandes quantidades de fertilizante de libertação lenta e contínua de P. Dos seis métodos estudados, as proporções de P *des* usando H_2O e $CaCl_2$ foram inferiores às obtidas com B2, M3, ER e OL. O P *des* obtido com B2, M3, ER e OL mostrou uma forte correlação entre eles. B2 revelou-se o extractante mais eficaz na remoção de P na maioria dos solos em estudo. As proporções de P *des* observadas para os extractantes mostraram uma correlação negativa com os teores de Al_d, Al_o, Al_p, Fe_o, Fe_d, and Fe_p e com os valores de Al_o + ½ Fe_o, e de retenção de P. Contudo, a correlação entre as proporções de P*des* obtidas com $CaCl_2$, B2, M3, ER e OL com componentes ferruginosos (Fe_o, Fe_d) foi mais forte do que com componentes de Al (Al_o, Al_d).

INTRODUCTION

Most Andisols contain varying amounts of allophane, imogolite, ferrihydite, and Al- and Fe-humus constituents (Shoji *et al.*, 1993; Buurman *et al.*, 2004). These constituents are of particular interest regarding phosphorus (P) chemistry in soils with andic properties, as they may play an important role in P sorption-desorption processes-and P availability (Negrín et al., 1996; Bache and Williams, 1971; Shoji et al., 1993; Mozaffari and Sims, 1994). Phosphorus sorbed by these constituents may be also unavailable for plants. In the other hand, in soils with low amounts of those constituents P desorbed may be lost through surface runoff and subsurface drainage, which may contribute to the eutrophication of natural water courses (van der Zee and van Riemsdijk, 1986; Turner and Haygarth, 2000).

In the Azores (Portugal), large differences in the proportion of the above mentioned colloidal constituents have been reported for soils with andic properties (Madeira *et al*, 2002, 2007; Pinheiro *et al.*, 2001). It is expected that such differences may affect the capacity of these soils to sorb and desorb P (Auxtero *et al.*, 2005). While studies on P sorption capacity by the soils from the Azores have been carried out (Auxtero et. al., 2005, 2007; Auxtero and Madeira, 2008), information on their ability to desorb P using different methods of extraction has not yet been documented. Also, it is admitted that desorbability of P may be dependent upon their colloidal constituents.

In the Azores, concentration of P may be high in areas where fertilizers and manures have been continuously applied. However, its availability to plants may rendered low in soils with strong capacity to sorb P. In contrast, in soils with low P-sorbing capacity, large quantities of P may be lost through erosion, surface runoff and subsurface drainage which may cause eutrophication of natural water bodies (van der Zee & van Riemsdijk, 1986; Turner & Haygarth, 2000). Information about this subject may be useful for sound fertilizer management and to improve soil and water quality.

Desorbability of P using water (H_2O), dilute salt calcium chloride ($CaCl_2$), and Mehlich 3 (M3), Bray and Olsen (OL) methods has been commonly used for non-Andisols (Sharpley *et al.* 1981; Pote *et al.*, 1996). However, so far these methods have not yet been used for soils with andic properties. Assessment of relationships between the proportions of P desorbed by different methods with contents of soil colloidal constituents will be useful for understanding soil behaviour in relation with fertilizer management. Having this in view, a study was conducted to determine the ability of H_2O, $CaCl_{2,}$ B2, M3, ER and OL methods to desorb P from representative soils from the Azores, and to correlate the proportion of P desorbed with the content of soil colloidal constituents.

MATERIALS AND METHODS

Soils

Nine pedons from Faial (FA), Pico (PI), Santa Maria (Sm) and São Miguel (SM) islands, Azores (Portugal), were selected according to their classification and main chemical characteristics (Table 1). The pedons were: (i) FA8 (Typic Haplustept); (ii) FA26 and FA11 (Andic Haplustepts) having weakly expressed andic properties, containing significant amounts of 1:1 layer silicate minerals and allophane, and organic C not greater than 6%; (iii) FA12 (Acrudoxic Hapludand) containing high amounts of allophane, negligible amounts of 2:1 layer silicate minerals and organic C content quite similar to Andic Haplustepts; (iv) PI12 (a non-allophanic Acrudoxic Hydrudand) having very high organic C content greater than 23%, and Fe_o and Fe_d contents greater than 4% and 6%, respectively; (v) PI14 (an allophanic Acrudoxic Hydrudand), having 12 to 14 % of allophane, organic C content greater than 5% and negligible amounts of layer silicate minerals; (vi) FA20 (Typic Placudand) having a BC horizon poor in organic C, but with rather high Al_o and allophane contents; (vii) SM55 (Vitrandic Haplustept) having a negligible allophane content and dominated by 2:1 layer silicate minerals; and (viii) Sm21 (Alic Hapludand) a non-allophanic Andisol containing large amounts of extractable Al by 1 N KCl (2.79-5.67 $cmol_{(+)}\,kg^{-1}$).

Laboratory procedures

Determinations were done on air-dried soil samples passed through a 2 mm sieve prior to analysis. Total organic C content of soil samples was determined by wet oxidation following the Springer method (De Leenheer & Van Hove, 1958). Dithionite-citrate-bicarbonate extractable Al (Al_d) and Fe (Fe_d) were determined following the procedures described by 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

TABLE 1- **Contents of organic C (OC), Al and Fe extracted by the oxalate (Al_o and Fe_o) and by the dithionite (Al_d and Fe_d) and allophane (A) (g kg^{-1}), and values of Al ($cmol_{(+)}$ kg^{-1}) extracted by 1M KCl (Al_e), Al_o + ½ Fe_o, P sorption maxima (mg kg^{-1})(P*sm*) and phosphorus retention percentage (PR) in the studied soils. Symbols: H - halloysite, K - kaolinite, V - vermiculite, M - montmorillonite; 1- significant amounts, 2- low amounts, 3- negligible amounts, AB- layer silicate minerals absent, nd- not determined**

Pedons	**Hor (cm)**	**MC**	**OC**	**Al_o**	**Al_d**	**Al_p**	**Fe_o**	**Fe_d**	**Fe_p**	**A**	**Al_o + ½ Fe_o**	**Al_e**	**P*sm***	**PR**
Typic Haplustepts														
FA8	Ap	1VKH	24.0	5.5	3.1	1.1	12.9	9.2	0.9	20	12.0	0	1667	35
	Bw	1VKH	5.9	2.7	2.4	0.3	10.8	7.6	0.3	10	8.1	0	25	23
Andic Haplustepts														
FA26	Ah	1VKH	32.0	14.8	8.2	3.5	9.1	14.1	1.4	50	19.4	0.01	3448	98
	Bw1	1VKH	13.7	15.3	7.0	1.9	9.1	16.5	0.9	80	19.9	0	1124	72
FA11	Ah1	nd	46.4	24.0	7.9	3.4	12.8	7.7	0.7	70	30.4	0	8333	81
	Ah2	nd	29.4	18.7	1.8	2.4	14.4	2.8	0.6	40	25.9	0	1786	76
Acrudoxic Hapludands														
FA12	Ah	2VHK	41.0	43.0	39.5	12.0	18.0	21.6	5.0	120	52.0	0.31	19608	98
	Bw	2VHK	20.2	37.4	14.1	4.9	17.9	17.5	1.4	120	46.4	0.09	3448	98
Sm21	Ah1	nd	53.7	12.0	12.0	8.9	16.3	39.9	12.2	10	20.2	3.47	15385	97
	Ah2	nd	51.1	11.4	13.0	9.0	15.2	40.3	12.7	10	19.0	5.49	4000	99
Typic Placudands														
FA20	Ah1	2VK	110.6	31.1	15.5	10.8	14.0	25.6	9.4	80	38.1	0.67	2273	92
	BC	2VK	14.1	100.8	50.4	4.6	15.6	37.7	0.9	400	108.6	0	47619	93
Acrudoxic Hydrudands														
PI12	Ah1	AB	268.7	25.2	12.0	30.6	41.8	63.3	45.4	0	46.1	2.31	8333	96
	Bw1	AB	187.0	25.3	41.5	38.7	54.8	78.9	57.5	0	52.7	0.80	19231	99
PI14	Ah	3VH	83.0	45.1	37.8	16.4	32.5	59.6	23.6	120	62.1	0	52400	98
	Bw	3VH	60.8	47.5	44.0	15.7	27.0	58.2	20.9	130	61.0	0	6250	99
Vitrandic Haplustepts														
SM55	Ap	1H2M	9.7	3.2	1.4	0.5	3.6	3.7	0.2	10	5.0	0	48	20
	Bw	1H2M	9.3	2.7	1.4	0.3	3.7	3.6	0.2	10	4.6	0	111	17

were quantified by atomic absorption spectrophometry. 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).

Duplicate samples from each P saturated soils at P sorption maxima (P *sm*) concentration were equilibrated at room temperature for 6 days and they were subjected to eight successive extractions thereafter using water (H_2O), 0.01M calcium chloride ($CaCl_2$), Bray 2 (B2), Mehlich 3 (M3), Egnér-Riehm (ER) and Olsen (OL) methods. Values of P *sm* reported elsewhere (Auxtero *et al.*, 2005), were used in this study. P extraction using H_2O and $CaCl_2$ involved shaking of sample for 1 h and 2 h, respectively, at soil to solution ratio of 2:20 (Self-Davis *et al.*, 2000). P extraction using the B2 was obtained by shaking 2 g soil manually, with 20 ml of 0.03 N NH_4F + 0.1 M HCl solution at pH 2.6, for 40 sec (Bray & Kurtz, 1945). P from the M3 was extracted using a soil to solution: 0.013 M HNO_3 + 0.02 M CH_3OOH + 0.015 M NH_4F + 0.025 M NH_4NO_3 + 0.001 M EDTA ratio of 2:20 at pH 2.5, shaken for 5 min (Mehlich, 1984). P extracted by the ER was obtained by shaking 1 g of soil with 20 ml of 0.1 M NH_4-$CH_3CHOHCOOH$ + 0.4 M CH_3COOH + $(NH_4)_8Mo_7O_{27}.4H_2O$ + $K(SbO)C_4H_4O_6.1/2\ H_2O$ solutions at pH 3.7 to 3.8, for 2 h (Riehm, 1958). A 2:20 soil to solution: 0.5 M $NaHCO_3$ ratios at pH 8.5 were used to extract P using Olsen (OL), shaken for 30 min (Olsen *et al.*, 1954). P in filtered extracts was determined by the molybdenum blue (MB) method of Murphy and Riley (1962), using a spectrophotometer at 882 nm. P desorbability (P *des*) expressed in percentage was calculated from the ratio between the amount of P obtained in each extraction and the amount of P at P *sm*.

Relationships between P *des* by studied extractants and soil constituents were determined using coefficients obtained from the correlation and regression analyses. Differences in the proportions of P *des* by studied extractants were analyzed using Statistica software (Statsoft, 2004). The Tukey multiple range test was used to compare the differences among means of P *des* obtained by each method.

RESULTS AND DISCUSSION

The proportions of P desorbability (P *des*) after the first and from the second to eighth extractions using water (H_2O), calcium chloride ($CaCl_2$), Bray 2 (B2), Mehlich 3 (M3), Egnér-Riehm (ER) and Olsen (OL) extractants of studied pedons are shown in Table 2. After the first extraction, the proportions of P*des* by H_2O (2-100%) and by $CaCl_2$ (2-100%) differed widely among studied soils, with values being positively correlated ($r = 0.92$, $p < 0.001$). In the surface horizon of Vitrandic Haplustepts (pedon SM55), all methods desorbed 100% of added P, while 19-100% of added P was desorbed in the subsurface horizon. We may note that this soil has very low capacity to sorb P (with values of P *sm* between 48-111 mg kg^{-1}) as reported in previous studies (Auxtero *et al*., 2005; Auxtero *et al*., 2008).

Similar trend was observed in the horizons of Typic Haplustepts (pedon FA8) and Andic Haplustepts (pedons FA11 and FA26), where the proportions of P *des* obtained by H_2O and $CaCl_2$ ranged from 10-45% and 6-28%, respectively, after eighth extractions. We may consider both proportions desorbed by H_2O and $CaCl_2$ as P held in solution at field conditions (McDowell & Sharpley, 2003; Pote *et al*., 1996). A wide variation of P desorbed through surface runoff by these soils may be also expected. High proportions of P *des* (100%) by H_2O and by other extractants observed in the surface horizon of pedon SM55 and much greater proportions of P *des* shown by pedons FA8, FA26 and FA11, suggests that P desorbed may be highly available for plants, but also can be easily lost to nearby water systems.

The proportions of P *des* obtained by the B2, M3, ER and OL extractants in all studied pedons following eight successive extractions also varied widely (7-100%) and they were consistently higher than those estimated for H_2O and $CaCl_2$ (Table 2). In fact the proportions of P *des* obtained by the former have discriminated better the studied soils than those proportions of P *des* obtained by H_2O and $CaCl_2$. After the first extraction, the range of P *des* by the B2, M3, ER and OL for non-Andisols (pedons SM55, FA8 and FA26) were 80-100, 48-100, 72-100 and 29-100%, while for Andisols was 14-82, 7-77, 15-85 and 8-55%, respectively (Table 2). Of these four extractants, the M3 extractant showed better discrimination of P *des*. In non-Andisols, the proportion of P *des* by those extractants in pedon FA11 (an Andic Haplustepts), which contain higher proportion of Al_o and Fe_o, was higher than the others, and this proportion was close to those observed for studied subgroups of Andisols. This suggests that the pedon FA11 behaves like Andisols in regard P desorbability. As P may not be readily desorbed compared to other non-Andisols, we may expect low availability of P to plants. After the first extraction, the proportions of P *des* obtained by H_2O,

$CaCl_2$, B2, M3, ER and OL in non-allophanic Andisols (pedons Sm21 and PI12) ranged from 2-17, 2-23, 14-52, 7-36, 15-38 and 8-34%, respectively. It is probable that high proportion of P on these soils remains bound to Al- and Fe- humus complexes. In fact, most of the lowest proportions of P *des* obtained by studied methods after the first extraction were observed in the subsurface horizon of pedon PI12 (2-8%), having no allophane but with high amounts of organic C (187.0-268.7 g kg^{-1}), Fe_o (41.8-54.8 g kg^{-1}) and Fe_d (63.3-78.9 g kg^{-1}) and also higher contents of Al_p (30.6-38.7 g kg^{-1}) and Fe_p (454.4-57.5 g kg^{-1}). However, as observed for pedon Sm21, also a non-allophanic Andisol, the proportion of P *des* obtained by these extractants after the first extraction was much greater than that estimated for the pedon PI12. This may be attributed to higher Al and Fe contents in pedon PI12 (12.0-78.9 g kg^{-1}) than in pedon Sm21 (11.4-40.3 g kg^{-1}). After the eighth extraction, the proportion of P*des* obtained by B2 and M3 was doubled (40-62% and 30-78%, respectively). This suggests that P bound to Al and Fe constituents were mostly desorbed due to the acidity of solution and F^- ion reactions with Al and Fe components of the soil (Madeira *et al.*, 2007). The correlations (r) of P *des* between extractants after the first extraction were different from those obtained at the eighth extraction. We may consider the proportion of P *des* after the first extraction, as the proportion of extractable P that may desorb and can be available to plants. After the first extraction, the proportions of P *des* obtained

TABLE 2- **P desorbability (P*des*) after the 1st and 2nd to 8th extractions by water (H_2O), 0.01M calcium chloride ($CaCl_2$), Bray 2 (B2), Mehlich 3 (M3), Egnér-Riehm (ER) and Olsen (OL) of P enriched Andisols from the Azores**

Pedons	Hor	1st Extraction						2nd-8th Extractions					
		H_2O	$CaCl_2$	B2	M3	ER	OL	H_2O	$CaCl_2$	B2	M3	ER	OL
FA8	Ap	26^a	32^b	100^c	100^c	99^c	52^d	45^a	19^b	0	0	1^c	48^d
	Bw	21^a	25^a	100^b	89^b	72^c	49^d	45^a	28^b	0	11^c	28^d	36^e
FA26	Ah	14^a	7^b	97^c	53^d	86^e	30^f	13^a	6^b	3^b	47^c	14^d	36^e
	Bw1	11^a	10^a	80^b	48^c	80^b	29^d	14^a	13^a	20^b	52^c	20^b	38^d
FA11	Ah1	23^a	36^b	63^c	54^d	47^e	29^f	16^a	14^b	37^b	46^c	39^b	25^d
	Ah2	36^a	22^b	44^c	77^d	52^e	37^f	10^a	11^a	56^c	23^d	43^e	30^f
FA12	Ah	17^a	18^a	64^b	35^c	62^b	30^d	18^a	16^a	36^b	65^c	38^b	30^b
	Bw	20^a	12^b	58^c	24^d	63^e	55^c	36^a	17^b	42^c	$76d^c$	37^c	45^c
Sm21	Ah1	17^a	23^b	31^c	36^d	38^e	34^f	14^a	15^a	62^b	62^b	37^c	41^d
	Ah2	8^a	5^a	52^b	22^c	31^c	30^c	13^a	5^b	48^c	78^d	41^c	36^e
FA20	Ah1	13^a	11^b	82^c	46^d	85^c	50^e	24^a	17^b	18^b	54^c	15^b	50^c
	BC	12^a	14^a	34^b	25^b	45^c	21^d	7^a	7^a	66^b	20^c	34^d	33^d
PI12	Ah1	2^a	5^a	38^b	25^c	19^d	13^e	5^a	3^a	62^b	30^c	33^c	17^d
	Bw1	5^a	2^a	14^b	7^a	15^b	8^a	6^a	2^b	40^c	48^d	8^e	11^f
PI14	Ah	9^a	11^b	16^c	16^c	17^d	13^b	8^a	7^a	43^b	16^c	10^d	7^d
	Bw	14_a	15^a	34^b	19^a	25^c	30^d	19^a	10^a	65^b	54^c	6^d	36^e
SM55	Ap	100^a	100^a	100^a	100^a	100^a	100^a	0	0	0	0	0	0
	Bw	19^a	46^b	100^c	100^c	100^c	100^c	42^a	53^b	0	0	0	0

Means in the same horizon followed by different superscript are significantly different at $p < 0.05$ level by Tukey test

Table 3 - **Relationships between the values of P desorbability (P*des*) obtained using distilled water (H_2O), 0.01M calcium chloride ($CaCl_2$), Bray 2 (B2), Mehlich 3 (M3), Egnér-Riehm (ER) and Olsen (OL) extractants after the first extraction of P enriched Andisols at sorption maximum from the Azores**

Equations	r values	p
Distilled water		
P*des*H_2O= 1.34 + 0.87 P*des* $CaCl_2$	0.92	<0.001
P*des*H_2O = 0.04 + 0.42 P*des* M3	0.61	<0.01
P*des*H_2O = −0.17 + 0.36 P*des* ER	0.50	<0.05
P*des*H_2O = −2.27 + 0.57 P*des* OL	0.69	<0.01
$CaCl_2$		
P*des*$CaCl_2$= −1.19 + 0.38 P*des* B2	0.50	<0.05
P*des* $CaCl_2$ = −3.08 + 0.51 P*des* M3	0.71	<0.001
P*des* $CaCl_2$ = −2.16 + 0.42 P*des* ER	0.55	<0.01
P*des* $CaCl_2$ = −5.95 + 0.71 P*des* OL	0.80	<0.001
Bray 2		
P*des* B2 = 23.22 + 0.79 P*des* M3	0.82	<0.001
P*des* B2 = 6.59 + 0.95 P*des* ER	0.93	<0.001
P*rec* B2 = 28.29 + 0.84 P*des* OL	0.71	<0.001
Mehlich 3		
P*des* M3 = −0.84 + 0.86 P*des* ER	0.81	<0.001
P*des* M3= 11.43 + 0.94 P*des* OL	0.77	<0.001
Egnér-Riehm		
P*des* ER = 22.30 + 0.89 P*des* OL	0.77	<0.001

by H_2O were positively correlated with those obtained by $CaCl_2$ ($r = 0.92$, $p < 0.001$), the M3 ($r = 0.61$, $p < 0.01$), ER ($r = 0.50$, $p < 0.01$) and OL ($r = 0.69$, $p < 0.01$) extractants (Table 3). The correlations (r) of P *des* by $CaCl_2$ with these extractants were 0.71, 0.57 and 0.80, respectively. The proportion of P *des* obtained by the B2 method were positively correlated with the M3 ($r = 0.82$, $p < 0.001$), ER ($r = 0.93$, $p < 0.001$) and OL ($r = 0.71$, $p < 0.001$) methods, and those of M3 method were correlated with those obtained by the ER ($r = 0.81$, $p < 0.001$) and by the OL ($r = 0.77$; $p < 0.001$).The proportion of P*des* by the ER extractant was also positively correlated with that by the OL ($r = 0.77$, $p < 0.001$). After the eighth–extraction, the proportions of P *des* obtained by H_2O and $CaCl_2$ methods remained lower than those obtained by the other methods. In our study, the proportions of P *des* obtained by the B2, M3 and ER (acidic extractants) were greater than those obtained by the OL method in most surface and subsurface horizons of studied pedons, being mostly greatest using the B2 method. Higher ability of the B2 to extract P bound to Al and Fe compounds than that by the M3 and ER methods, may be ascribed to the stronger concentration of NH_4F (0.03 N)and the lower pH (2.6) of the B2 solution than those of the M3 and ER solutions. At very acid pH conditions, there is a greater reactivity of F^- ions to dissolve P bound to Al, Fe and Ca compounds (Sims, 2000).

The proportions of P *des* by studied extractants were negatively correlated with soil constituents and PR values (Table 4). The proportions of P *des* obtained by H_2O and $CaCl_2$ were not correlated with Al_o content, and correlations with Al_d, Al_p, Fe_o, Fe_d, Fe_p and $Al_o + ½ Fe_o$ contents, and PR values, were weaker than those observed for the B2, M3, ER and OL methods. The correlations (r, $p < 0.001$) between the proportions of P *des* by studied methods with Fe_o (−0.52 to −0.79) and Fe_d (−0.55 to −0.81) contents were stronger than those observed for Al_o (−0.55 to −0.62) and for Al_d (−0.56 to −0.71) constituents. This suggests that both amorphous and crystalline forms of iron constituents may play an important role on P desorption exhibited by studied soils. The correlation (r) between values of P *des* obtained by each method and Fe_d contents ($r = −0.58$, $p < 0.001$) was close to that with Fe_o ($r = −0.62$, $p < 0.001$) contents. The stronger negative correlations of P *des* obtained by each method with Fe constituents (Fe_o, and Fe_d) rather than with Al_o, and allophane, suggests that Al constituents may play a lesser role on P desorption.

Table 4 - **Correlation of P desorbability (P*des*) by distilled H_2O, 0.01N $CaCl_2$, Bray 2 (B2), Mehlich 3 (M3), Egnér-Riehm (ER) and Olsen (OL) extractants with contents of Al and Fe by ammonium oxalate (Fe_o, Al_o), dithionite (Fe_d, Al_d) and pyrophosphate (Al_p, Fe_p), values of Al_o + ½ Fe_o, and P retention (PR) after the first extraction of P enriched Andisols at sorption maximum from the Azores**

Extractants	Correlation coefficients (r)								
	Soil constituents								
	Al_o	Al_d	Al_p	Fe_o	Fe_d	Fe_p	Al_o + ½ Fe_o	PR	OC
H_2O	ns	ns	ns	ns	ns	ns	ns	–0.59**	ns
$CaCl_2$	ns	ns	–0.47*	0.51*	−0.48*	ns	ns	–0.74***	ns
B2	–0.55**	–0.69***	–0.69***	–0.76***	–0.83***	–0.66**	–0.71***	–0.73***	–0.51*
M3	–0.59**	–0.73***	–0.68***	–0.69***	–0.78***	–0.61**	–0.67***	–0.91***	–0.51*
ER	ns	–0.60**	–0.73***	–0.79***	–0.85***	–0.72***	–0.61**	–0.70***	–0.59**
OL	ns	–0.56**	–0.59**	–0.67**	–0.61**	–0.54**	–0.52*	–0.79***	–0.50*

*Significant at 5% level; **significant at 1 % level; ***significant at 0.1 % level; ns-not significant.

The correlations of Fe_p (−0.53 to 0.72) and Al_p (−0.59 to−0.73) were not too different from that of either Al_o and Fe_o or Al_d and Fe_d, indicating that the reactivity of Al and Fe bound with humus was similar regarding P *des* as reported by other authors (Villapando and Graetz, 2001). The correlations between the proportions of P *des* and values of Al_o + ½ Fe_o were intermediate (between between −0.52 and −0.91), indicating that proportions of P *des* of the studied soils (−0.58 and −0.71) with those observed for Al and Fe constituents. In our study, the strongest correlations of P *des* obtained by the studied methods were observed, with values of P retention (PR) decreasing relative to their ability to sorb P (Table 2). Similar pattern of correlation was maintained even after the eighth extraction, but at lower extent. Our data also showed that the lowest proportion of P *des* by studied methods (2-15%) after the first extraction (Fig. 1C), observed in the subsurface horizon of pedon PI12 (Acrudoxic Hydrudands) maybe related to high contents of Fe_o (54.8 g kg^{-1}) and Fe_d (78.9 g kg^{-1}) on these soils. This result emphasizes the important role of Fe constituents on P desorption by studied soils rather than of Al constituents on these soils.

Organic C content also showed a negative correlation with P *des* obtained by the B2, M3, ER and OL methods (between −0.50 and −0.59) after the first extraction. This correlation was no longer shown after the eighth extraction, as most of the poorly ordered oxihydroxides Al and Fe bound to organic matter has probably been dissolved from the soils. When organic C content is accounted alone, it gave significant positive correlations (r, $p < 001$) with Fe_o (0.81) and Fe_d (0.74) constituents, suggesting close relationship of organic C to these constituents on the desorbability of P. Increase in the availability of P by blocking potential sites of Fe for sorption has been reported to be highly related to the role of organic C, thereby increasing P desorbability (Krull *et al*., 2005).

CONCLUSIONS

The proportion of P desorbability (P *des*) obtained by H_2O, $CaCl_2$, B2, M3, ER and

OL methods following eight successive extractions, varied widely with soil type and were strongly influenced by soil colloidal constituents. Of the six methods, the proportions of P *des* obtained by H_2O and $CaCl_2$ methods were consistently lower that those obtained by the B2, M3, ER and OL. The proportions of P *des* obtained by the B2, M3, ER, and OL methods were highly correlated, and the B2 was most efficient in extracting P in most of the studied soils. Low P *des* were observed in both allophane-rich Acrudoxic Hydrudands and Typic Placudands and non-allophanic Acrudoxic Hydrudands and Alic Hapludands. In contrast, Vitrandic Haplustepts, Typic Haplustepts, and Andic Haplustepts, with weak andic properties showed high P *des*. P is easily released on these soils and fertilizers should be applied as strictly necessary, in order to minimize losses of P through surface runoff and subsurface drainage to nearby water systems. In contrast, Alic and Acrudoxic Hapludands, Acrudoxic Hydrudands and Typic Placudands, which showed low P *des*, need an efficient application of P fertilizer to help increase the supply of P for plant use. P release for crop use in these soils can be quite difficult and large amounts of P fertilizer using efficient application method may be expected. The proportions of P *des* by studied methods showed significant negative correlation with P retention values, contents of Al_d, Al_o, Al_p, Fe_o, Fe_d, Fe_p, and values of $Al_o + ½\ Fe_o$. Correlations of the proportions of P*des* by $CaCl_2$, B2, M3, ER and OL with iron constituents (Fe_o, Fe_d) were stronger than with Al constituents (Al_o, Al_d).

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