Predicting the degree of P saturation of selected Andisols from the Azores (Portugal) by the acidified ammonium oxalate and the Mehlich 3 methods

Avaliação do grau de saturação de P nos Andossolos dos Açores (Portugal) pelos métodos do oxalato de amónio e de Mehlich 3

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ABSTRACT

Extractable aluminium (Al), iron (Fe), and phosphorus (P) were assessed on twenty eight soil horizons from a representative range of Andisols from the Azores, using the acidified ammonium oxalate method (Al_o, Fe_o and P_o) and the Mehlich 3 method (Al_{M3}, Fe_{M3} and P_{M3}). The degree of P saturation (DPS) by these two methods (DPS_o and DPS_{M3}) was also estimated.

The amounts of Al_o and Al_{M3} were positively correlated, while the amounts of Fe_o and Fe_{M3} were negatively correlated. On the other hand, the amounts of P_o and P_{M3} were not significantly correlated. Soils with high allophane content, showed higher values of Al_o, Al_{M3}, and P_o, while non-allophanic Andisoils, containing large amounts of organic C, showed higher values of Fe_o than other studied soils.

Values of DPS_o were greater than those of DPS_{M3} and highly correlated. DPS_o values were negatively correlated with the contents of Al and Fe extracted by dithionite (Al_d, Fe_d), by pyrophosphate (Al_p and Fe_p), and also with P retention (PR) values. A negative correlation was observed between DPS_{M3} values and Fe_p and Al_d contents, and PR values. High values of DPS_o and DPS_{M3}, observed in soils with low amounts of allophane, low amounts of organic C, and with less pronounced andic properties (Typic Haplustepts, Vitrandic Haplustepts and Andic Haplustepts), may indicate high P susceptibility to surface runoff and leaching. In contrast, P losses through water runoff and leaching may be negligible in Andisols with large amounts of extractable Al by the 1N KCl (Alic Hapludands) and high allophane content (Typic Placudands), and with low values of DPS_o and DPS_{M3}.

RESUMO

Os teores de alumínio (Al), ferro (Fe) e fósforo (P) foram determinados em vinte e oito horizontes superficiais e subsuperficiais de Andossolos dos Açores, usando os métodos do oxalato de amónio (Al_o, Fe_o e P_o) e de Mehlich 3 (Al_{M3}, Fe_{M3} e P_{M3}). O grau de saturação de P (DPS) foi também avaliado por estes dois métodos (DPS_o e DPS_{M3}).

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Observou-se uma correlação positiva entre as quantidades de Al_o e Al_{M3} e uma correlação negativa entre as quantidades de Fe_o e Fe_{M3}. Por outro lado, as quantidades de P_o e P_{M3} não foram significativamente correlacionadas. Os solos com elevado teor de alofana mostraram valores de Al_o, Al_{M3}, e P_o mais elevados, enquanto que os solos não alofânicos e com elevado teor de carbono orgânico, mostraram teores de Fe_o superiores aos dos outros solos estudados.

Os valores de DPS_o foram bastante superiores aos de DPS_{M3}, mostrando-se fortemente correlacionados entre si. Os valores de DPS_o mostraram uma correlação negativa com os teores de Al e Fe extraídos pelo ditionite (Al_d, Fe_d) e pelo pirofosfato (Al_p e Fe_p), e com os valores da percentagem de retenção de P no solo (PR). Do mesmo modo, os valores de DPS_{M3} também mostraram uma correlação negativa com aqueles constituintes, excepto com o Al_p e Fe_d. Os valores mais elevados de DPS_o e DPS_{M3} foram obtidos nos solos com baixos teores de alofana e de carbono orgânico, e com características ândicas pouco marcadas (Typic Haplustepts, Vitrandic Haplustepts e Andic Haplustepts), sugerindo uma elevada susceptibilidade de perda de P por escoamento superficial e lixiviação. Pelo contrário, nos Andossolos com elevado teor de Al extractável pelo KCl 1N (Alic Hapludands) e com elevado teor de alofana (Typic Placudands), que mostraram baixo valor de DPS_o e DPS_{M3}, o P será pouco susceptível aos efeitos do escoamento superficial e da lixiviação.

INTRODUCTION

Losses of dissolved and particulate phosphorus (P) from agricultural soils is of major environmental concern in the Azores. High concentrations of P in soil solution is supposed to pollute nearby water bodies, affecting the surface water quality due to eutrophication of aquatic environments. Presumably, the potential release of P to water across a wide range of Andisols from the Azores would be greatly influenced by the differences in the amounts of organic C, allophanic materials, and layer silicate minerals. So far, information related to the extent of P accumulation on these soils and environmental impact of P in water pollution is not yet available.

The degree of P saturation (DPS), as an indicator for the risk of potential P losses from agricultural soils through runoff and leaching under field conditions, has been predicted by the acidified ammonium oxalate method for soils of the Netherlands (Van der Zee & Van Riemsdijk, 1988; Maguire et al., 2001), and for soils of the USA (Sharpley *et al.*, 1996). This method defines DPS as the ratio of the amount of P already sorbed to the P sorption capacity (Van der Zee *et al.*, 1988; Schoumans, 1995). According to Pautler & Sims (2000), soils have defined capacity to sorb P, and when a critical P sorption saturation level is attained, there is a great probability of P release to the surface or ground water. P sorption saturation limit of 25 % (that is, groundwater P concentration of greater than 0.1 mg P L^{-1} in soil solution) was established as a threshold for ground water quality status in the Netherlands (Schoumans, 1995). Besides the acidified ammonium oxalate method, the DPS has also been predicted using the Mehlich 3 single extraction method, as described by Maguire & Sims (2002) for soils of the USA. So far, a study on the determination of the DPS by the acidified ammonium oxalate and the Mehlich 3 methods for the Andisols from the Azores has not yet been carried out.

Having this in view, this study was conducted to 1) determine the DPS using the acidified ammonium oxalate and the Mehlich 3 methods, 2) determine the relationships between soil properties and DPS values, and 3) compare the acidified ammonium oxalate and Mehlich 3 methods to predict the DPS for representative Andisols from the Azores.

MATERIALS AND METHODS

Soil samples

Eight soil groups with a range of chemical properties, representing the Andisols of the Azores at different environmental conditions, were selected for this study (Table 1). These soils and their main characteristics are: 1) Andic Haplustepts (pedon FA8) and (2) Typic Haplustepts (pedons FA26, FA27) which have weakly marked andic properties; 3) Typic Hapludands (pedons FA11, SJ4) contain significant amounts of 1:1 layer silicate minerals, and allophane, and organic C not greater than 6%; 4) Acrudoxic Hapludands (pedons FA12, FL27), contain large amounts of allophane, negligible amounts of 2:1 layer silicate minerals, and organic C content quite similar to Typic Hapludands; 5) Acrudoxic Hydrudands, which show non-allophanic character, and have an organic C content greater than 23%, and Fe_o and Fe_d contents greater than 4% and 6%, respectively (pedon PI12), or which have high allophane content, organic C content greater than 6% and negligible amounts of layer silicate minerals (pedons P16 and PI14); 6) Typic Placudands (pedon FA20), have BC horizon poor in organic C, but with rather high Al_o and allophane contents; 7) Vitrandic Haplustepts (pedon SMI55) are dominated by 2:1 layer silicate minerals and have very

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

Pedon	LT	**Sub-group** (SSS, 1999)	**Alt** (m)	**MAP** (mm)	**MAT** (ºC)	**S)** (%)	**Vegetation**
		Faial Island					
FA8	Pa	Andic Haplustepts	50	900	17	5	Agric. land
FA26	Pa	Typic Haplustepts	115	1100	17	10	Pasture
FA27	Pa	Typic Haplustepts	50	900	17	5	Agric. land
FA11	Pa	Typic Hapludands	50	1000	17	5	Forest
FA12	Pa	Acrudoxic Hapludands	230	1400	16	18	Forest
FA20	Pa	Typic Placudands	750	2000	13	20	Pasture
		São Jorge Island					
SJ4	Pb	Typic Hapludands	410	1500	15	5	Pasture
		Flores Island					
FL27	Pb	Acrudoxic Hapludands	560	2000	14	10	Forest
		Pico Island					
PI6	Pb	Acrudoxic Hydrudands	640	3000	12	20	Pasture
PI12	Pb	Acrudoxic Hydrudands	640	3000	13	20	Pasture
PI14	Pb	Acrudoxic Hydrudands	840	3000	12	20	Pasture
		São Miguel Island					
SMI55	Pa	Vitrandic Haplustepts	70	1000	17	5	Agric. land
		Santa Maria Island					
SM21	Basalt	Alic Hapludands	350	1200	16	35	Pasture
SM32	Pb	Alic Hapludands	390	1400	16	10	Forest

TABLE 2- **Mineralogical composition (MC), contents of organic carbon (OC) and allophane, Al and Fe extracted pyrophosphate (p) and dithionite-citrate-bicarbonate (d), Al extracted by 1N KCl (Al_e), and values of P retention (PR)**

Pedon	**Hor**	**MC**	**OC**	**pH H_20**	**pH KCl**	**pH NaF**	**Al_p**	**Fe_p**	**Fe_d**	**Al_d**	**Al_e**	**PR**	**Allophane**
			(g kg^{-1})		(1 M)	(1 M)	«	(mmol kg^{-1})			cmol $_{(+)}$ kg^{-1}	(%)	
FA8	Ap	1VKH	24.0	6.7	5.3	9.1	164.73	100.10	16.11	100.10	0	35	2
	Bw	1VHK	5.9	7.3	5.4	9.0	136.08	77.49	5.37	77.49	0	23	1
FA26	Ah	1VHK	32.0	5.8	4.7	10.7	252.46	264.77	25.07	264.77	0.01	98	5
	Bw	1VHK	13.7	6.7	4.8	10.7	295.43	226.03	16.11	226.03	0	72	8
FA27	Ah	nd	18.9	6.8	5.0	9.0	132.50	193.74	14.32	193.74	0	57	4
	Bw	nd	19.4	6.9	5.3	9.8	123.55	196.96	89.53	196.96	0	58	4
FA11	Ap	nd	46.4	5.7	5.2	10.2	137.87	255.09	12.53	255.09	0	81	7
	Bw	nd	29.4	6.8	5.7	10.2	50.13	58.12	10.74	58.12	0	76	4
SJ4	Ah	nd	86.4	5.6	4.8	11.0	325.87	723.28	213.07	723.28	0.46	98	8
	Bw	nd	76.3	6.1	5.0	11.2	345.57	781.40	327.66	781.40	0.01	100	15
FA12	Ah	2VHK	41.0	5.4	4.9	11.5	386.75	1275.43	89.53	1275.43	0.31	98	12
	Bw	2VHK	20.2	5.6	5.2	11.2	313.34	455.28	25.07	455.28	0.09	98	12
FL27	Ah	nd	80.6	4.9	4.9	11.0	363.47	752.34	211.28	752.34	0.28	94	11
	Bw	nd	58.3	5.7	5.3	11.1	329.45	745.88	171.89	745.88	0.04	100	13
SM21	Ah1	nd	53.7	5.2	4.3	10.1	714.41	387.47	218.44	387.47	3.47	87	1
	Ah2	nd	51.1	5.1	4.2	10.2	721.58	419.76	227.39	419.76	5.39	88	1
SM32	Ah	nd	73.0	5.1	4.3	10.6	948.97	649.02	458.37	649.02	2.79	96	1
	AB	nd	76.2	4.7	4.4	10.9	897.05	668.39	576.54	668.39	4.94	92	1
FA20	Ah1	2VK	110.6	5.5	4.5	11.1	458.37	500.48	168.31	500.48	0.67	97	8
	BC	2VK	14.1	6.9	5.7	11.4	675.02	1627.38	16.11	1627.38	0	99	40
PI12	Ah1	AB	268.7	4.8	4.3	10.5	1133.39	387.47	812.89	387.47	2.31	96	0
	Bw1	AB	187.0	5.5	4.7	11.1	1412.71	1340.01	1029.54	1340.01	0.80	99	0
PI6	Ah	nd	190.9	4.7	4.5	10.9	1149.51	1291.57	664.28	1291.57	3.89	95	7
	2Bw2	nd	92.7	5.8	5.6	10.9	1788.72	1733.94	503.13	1733.94	0	99	29
PI14	Ap	3VH	83.0	6.3	5.2	9.9	1067.14	1220.54	422.56	1220.54	0	97	12
	Bw	3VH	60.8	6.5	5.1	10.4	1042.08	1420.73	374.22	1420.73	0	98	13
SMI55	Ap	1H2M	9.7	6.7	5.5	7.9	66.25	45.21	3.58	45.21	0	20	1
	Bw	1H2M	9.3	6.6	5.5	8.0	25.07	35.52	64.46	35.52	0	17	1

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 low allophane content; and 8) Alic Hapludands (pedons SM21, SM32) contain large amounts of extractable aluminium by 1 N KCl (2.79-5.67 $cmol_{(+)}$ kg^{-1}). The chemical properties of selected soils are shown in Table 2. Detailed chemical characteristics of the selected soils have also been reported elsewhere by Ricardo *et al.* (1977), Pinheiro *et al.* (2001), Madeira *et al.* (2002, 2003) and Auxtero *et al.* (2004, 2005).

Laboratory procedures

Prior to analysis, all soil samples were air-dried and ground to pass through a 2 mm sieve. All soils were analyzed for total organic C by wet oxidation of Springer and Klee method (De Leenheer and Van Hove, 1958). Soil reaction (pH) was measured in H_2O and 1M KCl using a soil to solution ratio of 1:2.5, and 1:5 for 1 M NaF. Analytical data for the extractable P were obtained from three replicates. Mehlich 3 (M3) P, Fe and Al (P_{M3}, Fe_{M3} and Al_{M3}) were extracted by shaking 2 g of soil with 20 ml of M3 solution (0.20M CH_3COOH, 0.25M NH_4NO_3, 0.015M NH_4F, 0.013M HNO_3, 0.001M EDTA at pH 2.5) for 5 min (Mehlich, 1984). The acidified ammonium oxalate P, Fe and Al (P_o, Fe_o and Al_o) were extracted by shaking 1 g of soil in 50 ml plastic centrifuge tube with 40 ml of 0.2M acid ammonium oxalate at pH 3 for 4 h in the dark (Blakemore *et al.*, 1987). The solutions were then centrifuged and filtered. An aliquot of 10 ml from each filtered extract was transferred to a digestion tube and was added with H_2SO_4 and HCl (1 ml, respectively). The solution was digested in a hotplate digester at 250 ºC for 40 min. Digested samples were then washed with distilled water in a 50 ml volumetric flask. Filtered P from the acidified ammonium oxalate and the M3 extracts were analyzed colorimetrically by the molybdate blue color method of Murphy and Riley (1962) using spectrophotometer at 880 nm, while Fe and Al were measured using the atomic absorption spectrophotometer.

Calculation of the degree of P saturation

The degree of P saturation from the acidified ammonium oxalate (DPS_o) was calculated as DPS_o (%) = $P_o/PSC*100$ (Schoumans, 2000; Van der Zee & Van Riemsdijk, 1988), where PSC (P sorption capacity) = $(Al_o + Fe_o)*0.5$, P_o is the molar concentration of the acidified ammonium oxalate extractable P (mmol kg^{-1}), Al_o and Fe_o are the molar concentrations of the acidified ammonium oxalate extractable Fe and Al (mmol kg^{-1}).

The degree of P saturation determined by the Mehlich 3 method (DPS_{M3}) was calculated from single extraction as DPS_{M3} (%) = $P_{M3}/(Al_{M3} + Fe_{M3})*100$ (Maguire & Sims, 2002), where P_{M3} is the molar concentration of the Mehlich 3 extractable P (mmol kg^{-1}), Al_{M3} and Fe_{M3} are the molar concentrations of the Mehlich 3 extractable Fe and Al (mmol kg^{-1}).

RESULTS AND DISCUSSION

Al and Fe extracted by the acidified ammonium oxalate and the Mehlich 3 methods

The amounts of Al extracted by the acidified ammonium oxalate (Al_o) and by the Mehlich 3 (Al_{M3}) methods, in the horizons of studied pedons, are shown in Table 3. The amounts of Al_o (100.1-3736.1 mmol kg^{-1}) were much greater than those of Al_{M3} (20.7-46.5 mmol kg^{-1}), and the amounts of Al extracted by both methods (Al_o and Al_{M3}) were positively correlated (r = 0.49; $p < 0.05$).

TABLE 3 - **The amounts of P, Al and Fe extracted by the acidified ammonium oxalate method (P_o, Al_o and Fe_o) and by the Mehlich 3 (P_{M3}, Al_{M3} and Fe_{M3}), and values of Al_o/Al_{M3} and Fe_o/Fe_{M3} ratios of selected Andisols from the Azores**

Pedon	Horiz	Al_o	Fe_o	P_o	Al_{M3}	Fe_{M3}	P_{M3}	Al_o/Al_{M3}	Fe_o/Fe_{M3}
		(mmol kg^{-1})							
FA8	Ap	203.85	230.98	26.45	25.80	2.10	1.00	8	110
	Bw	100.07	193.38	23.91	23.06	1.56	0.44	4	124
FA26	Ah	548.55	162.94	30.51	36.27	0.76	0.09	15	214
	Bw	567.09	162.94	23.50	35.03	1.01	0.11	16	161
FA27	Ah	452.19	179.04	31.71	35.81	0.66	0.08	13	271
	Bw	433.65	171.89	35.56	35.36	0.74	0.08	12	232
FA11	Ap	889.55	229.19	34.74	32.71	0.67	0.09	27	342
	Bw	693.11	257.83	17.46	27.89	1.15	0.18	25	224
SJ4	Ah	1549.30	515.67	37.76	37.03	0.62	0.01	42	832
	Bw	1971.83	608.77	39.02	40.49	0.54	0	49	1127
FA12	Ah	1593.77	322.29	37.77	44.33	0.25	0	36	1289
	Bw	1386.21	320.50	14.72	44.42	0.79	0	31	406
FL27	Ah	1697.55	476.28	33.02	38.67	0.71	0	44	671
	Bw	1786.51	555.06	31.24	38.67	0.71	0	46	782
SM21	Ah1	444.77	291.85	0.64	41.22	0.96	0	11	304
	Ah2	422.54	272.16	26.83	44.12	0.94	0	10	290
SM32	Ah	670.87	440.47	0.56	45.46	1.45	0	15	304
	AB	652.34	648.16	0.23	45.46	1.45	0.10	14	447
FA20	Ah1	1152.71	250.67	39.70	38.00	1.29	0.55	30	194
	BC	3736.10	279.32	5.49	45.32	0.94	0.19	82	297
PI12	Ah1	934.03	748.43	33.41	38.07	0.56	0	25	1336
	Bw1	937.73	981.20	29.69	44.78	0.38	0.02	21	2582
PI6	Ah	1971.83	460.16	32.30	44.03	0.42	0	45	1096
	2Bw2	3732.39	581.92	26.77	39.06	0.36	0	96	1616
PI14	Ap	1671.61	608.77	31.27	35.75	0.69	0	47	882
	Bw	1760.56	483.44	11.55	39.69	0.60	0.02	44	806
SMI55	Ap	118.61	64.46	8.23	20.65	0.97	0.30	6	66
	Bw	100.07	66.25	26.24	22.86	1.13	2.06	4	59

Soils with low organic C content (5.9-9.3 g kg^{-1}), with weakly marked andic properties, and having significant amounts of clay minerals (halloysite/kaolinite) (Table 2), that is, Typic Haplustepts, showed the smallest amount of Al_o (100.1 mmol kg^{-1}). Similar amount was also observed in the subsurface horizons of Vitrandic Haplustepts (pedon SMI55) and Typic Haplustepts (pedon FA8). In their surface horizons, also with low organic C content (9.7 -24.0 g kg^{-1}), low amounts of Al_o were also observed, varying from 118.6 to 203.9 mmol kg^{-1}. The amounts of Al_o in Andic Haplustepts (pedons FA26 and FA27) and Typic Hapludands (subsurface horizon of pedon FA11), containing significant amounts of allophane (4-8%) and organic C (13.7-32.0 g kg^{-1}), were greater (433.7-693.1 mmol kg^{-1}) than those observed in the Vitrandic Haplustepts and Typic Haplustepts.

Soil horizons containing large amounts

of allophane (29-40 %), that is, Acrudoxic Hydrudands (pedon PI6) and Typic Placudands (BC horizon of pedon FA20), showed the greatest amounts of Al_o (3732.4-3736.1 mmol kg^{-1}). Such amounts dropped to 1152.7-1971.8 mmol kg^{-1}, with decreasing amounts of allophane in the soil (7%-15%), as observed in Acrudoxic Hapludands (pedons FA12 and FL27), Acrudoxic Hydrudands (pedon PI14 and Ah horizon of pedon PI6), surface horizons of Typic Hapludands (pedon SJ4) and Typic Placudands (pedon FA20). Non-allophanic Andisoils (Alic Hapludands, pedons SM21 and SM32), with less than 1 % of allophane content, but with great amounts of organic C (51.1-76.2 g kg^{-1}) and large amounts of extractable Al by 1 N KCl (2.8-5.4 $cmol_{(+)}$ kg^{-1}), showed Al_o amounts (422.5-670.9 mmol kg^{-1}) more than the double of those observed for Typic Haplustepts and Vitrandic Haplustepts. Moreover, in non-allophanic Andisols, such as Acrudoxic Hydrudands (pedon PI12), which contains very large amounts of organic C (187.0-268.7 g kg^{-1}) and having extractable Al by 1 N KCl from 0.80 to 2.31 cmol $_{(+)}$ kg^{-1}, were also extracted great amounts of Al_o (934.0 -937.7 mmol kg^{-1}).

Amounts of Al_o were positively correlated with P retention (PR) values (r = 0.61; $p < 0.001$). The presence of reactive –OH groups from Al_o constituents was supported by a significant positive correlation (r = 0.68; $p < 0.01$) between this constituent and pH values measured in 1 M NaF (Table 4).

The amounts of Al extracted by the Mehlich 3 method (Al_{M3}) did not discriminate the studied soils. Data in Table 3 showed that the magnitude of Al_{M3} values in the studied soils (27.9-45.5 mmol kg^{-1}) were not strongly different among them, but greater amounts were observed in soils with high content of allophane. The amounts of Al_{M3} extracted from non-allophanic soils (pedon PI12), with very high organic C content, were similar (38.1-44.8 mmol kg^{-1}) to those measured in other soils. As observed for Al_o, Vitrandic Haplustepts and Typic Haplustepts also showed the smallest amounts of Al_{M3} (20.7-25.8 mmol kg^{-1}), while the BC horizon of pedon FA20 (Typic Placudands), rich in allophane, exhibited the largest amounts. The amounts of Al_{M3} and organic C were positively correlated (r=0.40 $p < 0.01$) (Table 4), suggesting the effect of organic C on amounts of extractable Al by the M3 in soils containing great amounts of organic C (45.3 mmol kg^{-1}). Similar amounts (45.5 mmol kg^{-1}) were also observed in Alic Hapludands (pedon SM32).

Values of the Al_o/Al_{M3} ratio were positively correlated with Al_p (r = 0.50; $p < 0.01$), Al_d (r = 0.82; $p < 0.01$), Fe_p (r = 0.82; $p < 0.01$) and allophane (r = 0.90; $p < 0.01$) contents. The values of this ratio also showed positive correlation with those of PR (r = 0.59; $p < 0.001$) and pH NaF (r = 0.65; $p < 0.001$), but not with pH values

TABLE 4 – **Coefficient of correlations** (r) **between the amounts of Al and Fe extracted by the acidified ammonium oxalate (Al_o, Fe_o) and by the Mehlich 3 (Al_{M3}, Fe_{M3}) methods, and soil constituents. (ns-not significant)**

	OC	allophane	pH NaF	PR
Al_o	ns	0.92 ($p < 0.001$)	0.68 ($p < 0.001$)	0.61 ($p < 0.001$)
Al_{M3}	0.40 ($p < 0.01$)	ns	0.82 ($p < 0.001$)	0.86 ($p < 0.001$)
Fe_o	0.76 ($p < 0.001$)	ns	0.55 ($p < 0.01$)	0.63 ($p < 0.001$)
Fe_{M3}	−0.39 ($p < 0.01$)	ns	−0.45 ($p < 0.01$	−0..52 ($p < 0.01$

measured in H_2O or KCl. This suggests the predominance of Al_o in soils containing great amounts of allophane.

The amounts of Fe extracted by the acid ammonium oxalate method (Fe_o) and by the Mehlich 3 (Fe_{M3}) are shown in Table 3. In contrast to other studied soils, largest amounts of Fe_o (748.4-981.2 mmol kg^{-1}) were measured in non-allophanic soils (pedon PI12), containing very high amounts of organic C (187.0-268.7 g kg^{-1}). This suggests that organic C content may have an important role on the extractability of Fe by the acid ammonium oxalate, which is in agreement with a strong positive correlation ($r = 0.76$, $p < 0.001$) between amounts of Fe_o and organic C content (Table 4). Consistent with our data for the amounts of Al_o and Al_{M3}, Vitrandic Haplustepts also showed the smallest amounts of Fe_o (64.5-66.3 mmol kg^{-1}).

The amounts of Fe extracted by the M3 were very small in all studied soils (0.25-2.10 mmol kg^{-1}) and were also much lower than those observed for Fe_o (Table 3). In contrast to the smallest amounts of Al_o and Al_{M3} obtained for Typic Haplustepts, the largest amounts of Fe_{M3} (1.56-2.10 mmol kg^{-1}) were measured on these soils, while pedon FA12 showed the smallest amounts of Fe_{M3} (0.25 mmol kg^{-1}). In pedon SM21, Ah horizon of pedon FA20 and Bw horizons of pedons FA26, FA11 and SMI55, the amounts of Fe_{M3} were greater than 1.0 mmol kg^{-1}. Amounts of Fe_{M3} smaller than 1.0 mmol kg^{-1} were extracted in other horizons of the studied pedons.

Amounts of Fe_o were negatively correlated with those of Fe_{M3} ($r = -0.40$; $p < 0.01$). In all studied soils, the amounts of Fe extracted by the acidified ammonium oxalate method (Fe_o) were much greater than those obtained by the Mehlich (Fe_{M3}). Similarly to the Al_o/Al_{M3} ratio, the values of the Fe_o/Fe_{M3} ratio (Table 3) were correlated with Al_p ($r = 0.70$, $p < 0.01$) and Fe_p ($r = 0.69$, $p < 0.001$) contents, and with values of PR ($r = 0.52$, $p < 0.01$) and pH in NaF ($r = 0.53$, $p < 0.01$), but were not significantly correlated with allophane contents.

P extracted by the acidified ammonium oxalate and the Mehlich 3 methods

The amounts of P determined by the acidified ammonium oxalate (P_o) and by the Mehlich 3 (P_{M3}) methods are shown in Table 3. The amounts of P_o were not significantly correlated with those of P_{M3}.

Alic Hapludands (pedon SM32 and Ah horizon of pedon SM21), showed the smallest amounts of P_o (0.23-0.64 mmol kg^{-1}); and greater amounts of P_o (5.49-8.23 mmol kg^{-1}) were measured in the Ap horizon of pedon SMI55 and in the BC horizon of pedon FA20, than in Alic Hapludands. The largest amounts of P_o (39.02-39.70 mmol kg^{-1}) were observed in the Bw horizon of pedon SJ4 and in the Ah horizon of pedon FA20. Amounts of P_o, greater than 30 mmol kg^{-1}, were measured in both surface and subsurface horizons of pedons FA27, SJ4, FL27, PI12, PI6, and PI14, and in surface horizon of pedons FA26, FA11, FA12 and FA20.

Most horizons of studied pedons, such as pedons SJ4, FA12, FL27, SM21, PI12, PI6, PI14 and Ah horizon of pedon SM32, showed negligible and nil amounts of P_{M3}. In contrast to the amounts of Al_o and Al_{M3}, amounts of P_{M3} were greater in the subsurface horizon of pedon SMI55 (2.06 mmol kg^{-1}) than in the surface horizon of pedon FA8 (1.00 mmol kg^{-1}). Pedons FA26, FA27, FA20, FA11, Ap horizon of pedons FA8 and SMI55, and subsurface horizon of pedon SM32, also showed small amounts of P_{M3} (0.08-0.55 mmol kg^{-1}).

The amounts of P_o were not correlated with contents of Al_o and Fe_o. Conversely, the amounts of P_{M3} showed negative correlation with the amounts of Al_{M3} ($r = -0.58$, $p < 0.001$) and positive with the amounts of Fe_{M3}. ($r = 0.53$, $p < 0.01$).

Values of DPS_o and DPS_{M3}

Values of P saturation degree determined by the acidified ammonium oxalate (DPS_o) and by the Mehlich 3 (DPS_{M3}) methods are given in the Table 4. As observed for the amounts of Al_o and Al_{M3}, and Fe_o and Fe_{M3}, values of DPS_o (0-32 %), were mostly greater than those estimated for DPS_{M3} (0-9 %). Values of DPS_o showed a positive correlation with those of DPS_{M3} ($r = 0.86$; $p < 0.001$). The largest values of DPS_o (9-32 %) were estimated in soils containing very small amounts of allophane, low organic C content and with weakly marked andic properties (pedons FA8 and SMI55, FA27 and surface horizon of pedon FA26). Soils containing large amounts of extractable Al by 1 N KCl (pedon SM32 and Ah horizon of pedon SM21), or with very largest amounts of allophane (BC horizon of pedon FA20), showed the smallest values of DPS_o (0-0.3 %). Values of DPS_o, between 1 and 8 %, were measured in pedons FA11, SJ4, FA12, FL27, PI12, PI6 and PI14, in surface horizons of pedons SM21 and FA20, and in the subsurface horizon of pedon FA26.

Values of DPS_{M3} between 1 and 9 % were observed in pedons FA8, SMI55, subsurface horizons of pedon FA11 and pedon SM32, being the highest value found in the Bw horizon of pedon SMI55 (9%). In other horizons of studied pedons, DPS_{M3} values were nil.

Values of DPS_o showed significant a negative correlations with contents of Al_p ($r=-0.53$, $p < 0.01$), Fe_d ($r=-0.39$; $p< 0.01$) and Fe_p ($r = -0.57$; $p < 0.001$) (Table 6); a significant negative correlation between DPS_o and the amounts of Al_d was also obtained ($r = -0.57$; $p < 0.05$). Values of DPS_{M3} also showed a negative correlation with the amounts of Fe_p ($r = -0.40$, $p < 0.001$) and Al_d.($r = -0.40$, $p < 0.001$). This indicates that P bound with organo-metallic complexes of Fe (Fe_p) and Al (Al_p) may have similar reactivity with Al_d and Fe_d constituents. Values of both DPS_o and DPS_{M3} were not significantly correlated with allophane, suggesting that con-

TABLE 5 - **Values of the degree of saturation determined by the acidified ammonium oxalate (DPS_o) and by the Mehlich 3 (DPS_{M3}) methods of selected Andisols from the Azores**

Pedon	Hor	DPS_o	DPS_{M3}
		(%)	
FA8	Ap	12	4
	Bw	16	2
FA26	Ah	9	0
	Bw	6	0
FA27	Ah	10	0
	Bw	12	0
FA11	Ap	6	0
	Bw	4	1
SJ4	Ah	4	0
	Bw	3	0
FA12	Ah	4	0
	Bw	2	0
FL27	Ah	3	0
	Bw	3	0
SM21	Ah1	0	0
	Ah2	8	0
SM32	Ah	0.10	0
	AB	0.04	1
FA20	Ah1	6	0
	BC	0.27	0
PI12	Ah1	4	0
	Bw1	3	0
PI6	Ah	3	0
	2Bw2	1	0
PI14	Ap	3	0
	Bw	1	0
SMI55	Ap	9	1
	Bw	32	9

stituents other than allophane (e. g. extractable Al) strongly affect DPS_o and DPS_{M3} values.

Significant negative correlations were observed between DPS_o and P retention values (PR) ($r = -0.82$, $p < 0.001$), and between DPS_{M3} and PR ($r = -0.71$, $p < 0.001$), suggesting that soils with less ability to retain P may show high DPS_o and DPS_{M3} values. This is in agreement with data from Vitrandic Haplustepts and Typic Haplustepts, that is, those showing lower PR values (17-35%) (Table 2), also showed higher DPS_o (9-32 %) and DPS_{M3} (1-4 %) than other studied soils.

The studied soils were better discriminated by DPS_o values than by those of DPS_{M3}. High values of DPS_o (32 %) and DPS_{M3} (9 %) estimated in Vitrandic Haplustepts suggest that potential P losses through runoff and leaching under field conditions can be higher than in other studied soils. In our study, the DPS_o value obtained for Vitrandic Haplustepts (32 %) was above the limit (above 25 %) established for non-andisols. According to Van der Zee (1988), Lookman *et al.* (1996), Pote *et al.* (1996), Sharpley *et al.* (1996) and Sims *et al.* (1998), soils with degree of saturation above 25 %, may pose great risks of P loss through surface runoff and leaching.

TABLE 6 – **Relationships between the degree of P saturation determined by the acidified ammonium oxalate (DPS_o) and by the Mehlich 3 (DPS_{M3}) methods, and soil constituents**

Equations	r values	p
$DPS_o = 9.98 - 0.007\ Al_p$	−0.53	< 0.01
$DPS_o = 0.10 - 0.0001\ Al_d$	−0.57	< 0.05
$DPS_o = 0.10 - 0.0001 Fe_p$	−0.57	< 0.01
$DPS_o = 0.08 - 0.001\ Fe_d$	−0.39	< 0.01
$DPS_o = 0.22 - 0.002\ PR$	−0.82	< 0.001
$DPS_{M3} = 0.02 - 0.0001 Fe_p$	−0.40	< 0.001
$DPS_{M3} = 0.02 - 0.0001\ Al_d$	−0.40	< 0.001
$DPS_{M3} = 0.04 - 0.005\ PR$	−0.71	< 0.001

CONCLUSIONS

In most studied soils, the Mehlich 3 method (DPS_{M3}) showed lower ability to estimate the degree of P saturation than the acidified ammonium oxalate method (DPS_o). However, DPS_{M3} may be more appropriate to discriminate soils containing low amounts of allophane, low amounts of organic C and weakly marked andic properties (Typic Haplustepts, Vitrandic Haplustepts and Andic Haplustepts).

Values DPS_o were positively correlated with those of DPS_{M3}. Values of DPS_o were negatively correlated with amounts of Al and Fe extracted by dithionite (Al_d, Fe_d) and by pyrophosphate (Al_p and Fe_p), and with values of P retention. Additionally, values of DPS_{M3} were negatively correlated with the amounts of Fe_p, Al_d and values of PR.

Typic Haplustepts, Vitrandic Haplustepts and Andic Haplustepts showed high degree of P saturation (either DPS_o or DPS_{M3}), indicating potential risk of P losses through surface runoff and leaching. In contrast, risk of P losses through surface runoff and leaching may be considered low in Alic Hapludands, and Typic Placudands, having high allophane content, which showed low degree of P saturation by DPS_o, This is also true for Acrudoxic Hapludands, containing significant amounts of allophane or great amounts of organic C, which showed low degree of P saturation by DPS_{M3}.

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