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SOIL AVAILABLE PHOSPHORUS TESTS IN VOLCANIC SOILS USED IN CANARY ISLANDS (SPAIN) LABS: A SHORT REVIEW

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Introduction

Although soil available P levels not greater than 20-30 mg kg^{-1} are not recommended, in volcanic soils higher levels could have positive impacts. In Canary Islands, values exceeding 100 mg kg^{-1} have been reported without any negative effect on plant growth (Negrín *et al.*, 1993a and 1993b, Domínguez *et al.*, 2001). Indeed, it is widely recognised that the usual calibrations relating extractable P to expected yield and fertiliser requirements are not adequate for these types of soils (Fox, 1980). This can be attributted to the high retention capacity usually shown by soils of volcanic origin (Wada, 1995). Sorbed P may be present at considerable quantity (absolute terms) in Andisols but relative to adsorption capacity the quantity of sorbed P is small.

The resulting low degree of soil P saturation, defined as the portion of the soil binding sites covered with P indicates the potential desorbability of soil P (Beauchemin & Simard, 2000), determines a low solubility and P uptake by plant. This is closely related to P solubility in these types of soils. The impact of arable management systems on soil quality and nutrient movement from soil to water must be also considered as another variable governing P solubility and, therefore, P availability in volcanic soils.

In young vitric Andisols from Nicaragua, under ecological and conventional management, Joergensen & Castillo (2001) have found that the halting of application of easily soluble mineral P fertilisers resulted in decreasing amounts of total P and extractable soils under ecological management.

Soil P retention capacity is characterised by the percent P sorption from a 1000 mg l^{-1} P solution. Values higher than 90% are common in soils of western Canary Islands and usually remain after fertilisation. Soil components responsible for P retention dynamic in Andisols and Andic soils are (1) amorphous or short-range-ordered aluminosilicates such as allophane and imogolite, (2) iron and aluminium oxy-hydroxides, especially of low crystallinity and (3) organomineral complexes of Al (Fe) of the type AH-Al(Fe)-OH (AH: humic or fulvic acid). In turn, greatest irreversibility of P sorption reaction has been observed in Al-rich allophane and Fe-oxy-hydroxides volcanic soils.

Various ways of estimating available P for crops in variable charge soils have been used in Canary Islands. The objective of this study is to review different soil P tests that have been used in these islands as indicator for available P in Andisols and Andic soils.

Soil test for phosphorus

Fertiliser recommendations for crops are based on soil P tests. Soil test phosphorus (STP) is an indication of how much P is available for plant use. Tunney *et al.* (1997) showed that STP could be considered as an indicator when a concentration of dissolved P may be in runoff water due the increasing P losses from agricultural soils. Other researchers have investigated STP to assess the capacity of a soil to retain P against leaching (Sims *et al.*, 2000; Maguire *et al.*, 2001). Different types of chemical extractants are used to extract plant-available P from soil. They are of interest because can be used for routine analysis. These extractants have been selected in field experiments, because they have shown to give a reasonable correlation between extracted P and uptake, dry-matter yield and crop response to added fertiliser P. Except for water, chemical extractants break down the soil matrix and recover variable amounts of P from differents P pools (available and unavailable forms of soil P).

More than ten different soil extractants are used to STP around the world (Hanotiaux & Vanoverstraeten, 1990). The principal consecuence of the large number of STP is that the results of soil test and, consequently, fertiliser recommendations for P cannot be compared between regions even soil type, farming and climatics conditions are similars.

Moreover, some STP may be more suited to certain soil type or land management. STPs are used also to classify P levels in low, medium, high and very high. A review of literature (i.e. Tunney *et al.*, 1997; Hanotiaux & Vanoverstraeten, 1990) shows that using the same test, there are important differences in this classification due to the fact that each P fertiliser recomendation scheme uses the same approach in each region or country in order to quantify the ability of different soils to maintain an adequate level of P in the soil solution for optimum uptake by the crop (a measure of soil-P buffer capacity).

Olsen P test is the most widely used STP in Canary Islands. Other STPs, such as water extraction techniques and anion exchange membranes, have been used as alternative tests to volcanic soils. In recent years, infinite sinks from Fe oxide-impregnated paper, isotopic exchange and oxalate extraction have also been introduced in the Canary Islands labs.

Olsen Extraction

Olsen P test (pH=8.5, solution:soil ratio=20, 0.5M $NaHCO_3$, time=0 min) (Olsen *et al.*, 1954) is considered as a STP more suitable for neutral, alkaline and weakly weathered acid soils. In Canary Islands, this STP has been used in different edaphic and environmental conditions. Bicarbonate extract promote the desorption of P from Al and Fe hydrous oxide surfaces.

In soil derived of volcanic ash dominated by allophanic or organomineral materials, Negrín e*t al.* (1995) have found that centrifugation temperature of bicarbonate extracts had an important influence on the extracted compounds, especially soluble C and P fractions (Table 1 and Figure 1); the results pointed to the existence of inorganic colloidal matter (allophane, ferrihydrite) together with Al(Fe)-humus complexes in Olsen extracts. The authors also questioned the conventional classification of inorganic and organic P by fractionation in these types of soils by (1) the existence of colloidal materials (allophane, ferrihydrite) together with Al(Fe)-humus complexes, (2) the overestimation of inorganic P during the acid hydrolysis of the bicarbonate extract and (3) the important fraction of soluble organic P (33 to 93%) hydrolysed by acid phosphatase.

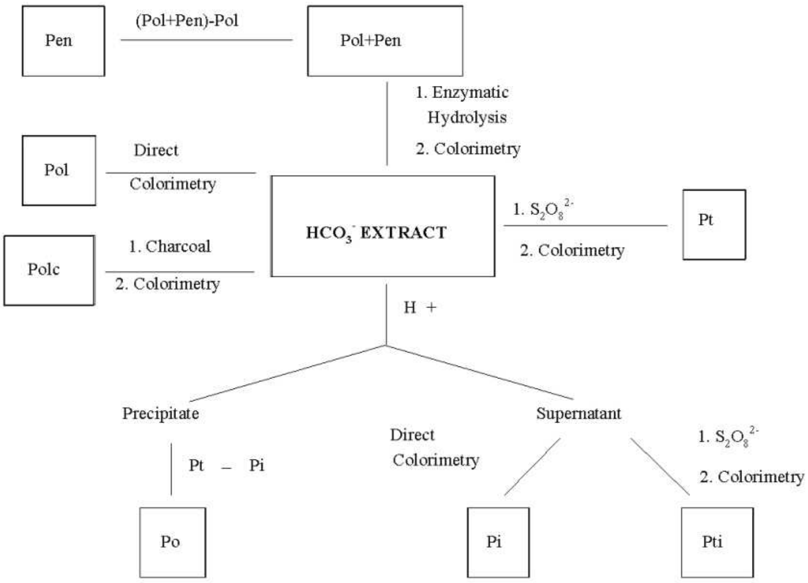

Figure 1. Operational definition of P fractions defined during the study and analysis of bicarbonate extracts (from Negrín *et al.*, 1995).

Table 1. P fractionation and phosphatase-hydrolysed P (Pen) in bicarbonate soil extracts (mg kg^{-1}). For P fraction[a] see Figure 1 (adapted from Negrín *et al.*, 1995)

A) Centrifuged extracts at 4ºC.

Soil[b] Classification	Hor.	Pol	Polc	Pt	Pi	Po	Pti	Pf	Ph	Pen
Cultivated Typic Hapludands		134	90	143	136	7	140	4	3	4
Typic Hapludands (I)	A1	12	1.0	38	10	28	27	16	12	26
	Bw2	12	2.2	35	11	24	22	10	14	16
Typic Hapludands (II)	A1	7	1.9	20	5	15	13	8	7	11
	Bw	10	1.2	17	9	8	12	3	5	5
Hydric Fulvudands	Bw3	12	0.3	21	9	12	12	3	9	4

B) Centrifuged extracts at 20ºC.

Soil Classification	Hor.	Pol	Polc	Pt	Pi	Po	Pti	Pf	Ph	Pen
Cultivated Typic Hapludands		148	110	275	139	137	189	50	87	63
Typic Hapludands (I)	A1	27	1.6	50	24	26	36	12	14	18
	Bw2	36	3.3	73	34	39	59	25	14	36
Typic Hapludands (II)	A1	31	2.8	69	28	42	56	28	13	35
	Bw	30	1.9	66	25	41	45	20	21	30
Hydric Fulvudands	Bw3	30	0.5	70	28	51	42	14	37	33

[a] P-symbols: ol (Olsen), olc (Olsen after charcoal), t (total), i (inorganic), o (organic), ti (total after acid treatment), f (fulvic), h (humic) and en (enzyme). [b] Soil Survey Staff (1992).

These results were interpreted in terms of soluble ternary complexes of organic or inorganic P with Al(Fe)-humus complexes (Figure 2). The bioavailability of organic P, together with the need for standardisation of Olsen P test in Andic soils, could explain the lack of response to P fertilisation observed in some type of Andisols in spite of their P-retention capacities.

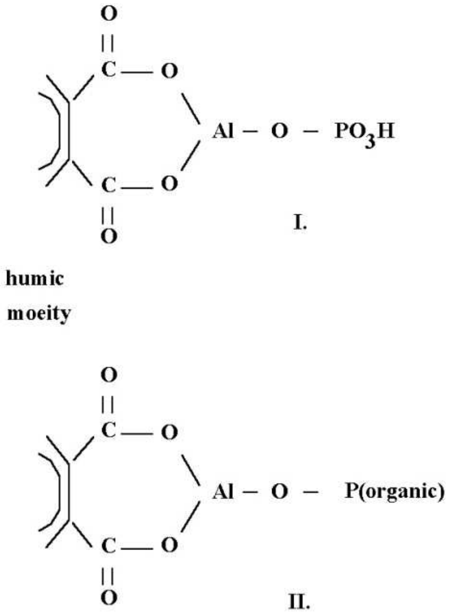

Figure 2. Complexes proposed for interaction between humic-Al compounds and orthophosphate (I) and organic P (II) (after Negrín *et al.*, 1995).

Water Extraction

STP based on water extraction (pH of soil, solution: soil ratio=60, distilled water standing then shaking, time=22+1 h) (Sissingh, 1971) have a potential interest in environmental and agricultural issues and can provide a good indication of P availability in a wide range of soils (principally well fertilised or alkaline soils), although it may fail due to below detection limits for soils poor in P (Salcedo *et al.*, 1991).

The study of desorption of P by this test is of interest for research on plant nutrition and water quality (Schoenau & Huang, 1991), and in models to predict the runoff of soluble P from soil (Sharpley, 1983). However, caution must be exercited in using current terminology for forms of P in water to study P transfer from agricultural land. Haygarth & Sharpley (2000) suggested a methodological classification of P forms in water by operational definitions of analytical methods and size of filter used.

In Andisols and andic soils from Canary Islands, Negrín *et al.* (1993a) found that these soils can release much P, Al, and soluble C when water : soil ratio (w:s) is large. This result was confirmed by Negrín *et al.* (1996) and Negrín *et al.* (1998) in a serie of forest soils and cultivated areas. In the first report, the authors observed a release of soluble P when increasing w:s from 2.5 to 75, while soluble C decreased significantly. A uniform partition between dialysable and non-dialysable P in dialysed 2.5 extracts (molecular weight cutoff of 1000) was also reported (Table 2).

The results were explained by the corresponding difference in soluble C and were consistent with the existence of soluble P-Al-fulvic acid complexes and organic P partition between solid and solution soil phases. The study of solubility diagrams suggested that dissolution of Al phosphates could explain most of P release to water as free orthophosphate (Figure 3).

The authors indicated that both solubility mechanisms and organic P partition between solid and soil solution phases may be considered to reflect the main sources of P in Andisols: Al-Phosphate and organic-Al-P complexes.

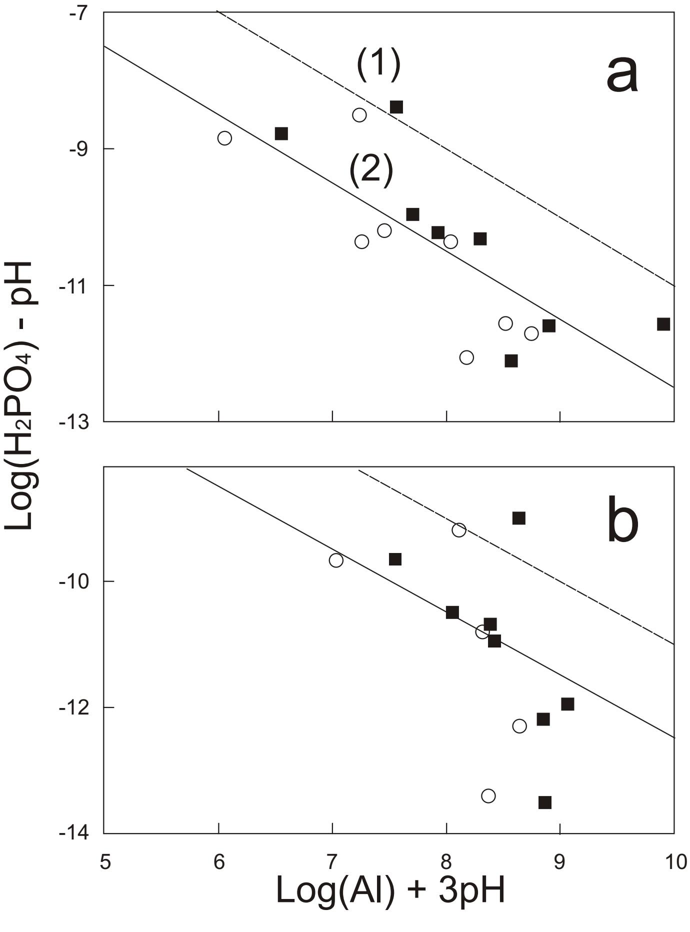

Figure 3. Aluminium phosphate solubilities in soil water extracts. a, 2.5 dm^3 kg^{-1}; b, 75 dm^3 kg^{-1}. (1) Amorphous analogue; (2) Variscite; ?, dialysates (from Negrín *et al.*, 1996).

Table 2. Analysis of P, Al and DOC in dialysate and outer solutions of the 2.5:1 extracts[a] (adapted from Negrín *et al.*, 1996)

Soil Classification[b]	pH	Al-4 /µmol dm^{-3}	DAl /µmol dm^{-3}	DRP /µmol dm^{-3}	DP /µmol dm^{-3}	DOC /mg dm^{-3}	DDOC /mg dm^{-3}	ΔP:ΔDOC[c]
Cultivated Typic Hapludands (I)	4.30	1.4	0.4	33.9	27.7	15.7	10.0	1:30
Cultivated Typic Hapludands (II)	4.20	24.5	13.2	63.9	46.5	37.3	9.8	1:50
Cultivated Andic Xerorthents	7.44	0.7	0.5	315.5	253.2	141.8	11.3	1:60
Cultivated Typic Hapludands (III)	6.86	0.4	0.2	8.4	7.1	24.6	13.1	1:300
Uncultivated Andic Haplumbrets	5.81	0.8	0.4	32.3	28.1	33.2	24.3	1:70
Cultivated Typic Hapludands (IV)	5.36	0.9	0.2	13.9	10.7	82.3	66.3	1:170
Uncultivated Typic Haplohumults	6.02	2.1	0.9	3.2	3.2	14.2	13.1	1:190
Uncultivated Hydric Fulvudands	5.20	0.7	0.4	17.1	14.5	16.5	11.3	1:60

Symbols:[a]Monomeric Al (Al-4), Dissolved reactive P (DRP), Dissolved organic C (DOC), DAl, DP, DDOC (Dialysable Al, P and DOC respectively). [b]Soil Survey Staff (1992). [c]Molar ratios.

Anion Exchange Membrane

Anion exchange resin membrane (AEM) test (pH of soil, solution: soil ratio= 40, one strip of 8 cm^2 of strongly basic AEM, time= 16-18 h) has been used under field conditions to measure soil solution P in soils with a large P-retention capacity (Cooperband & Logan, 1994). In these soils, AEM can compete with soil colloids for soil solution P.

Other studies suggest that soil mineralogy and P retention properties are able to influence on AEM capacity to sorb P from soil solution (Fernandes & Warren, 1996; Skogley & Dobermann, 1996). Recently, Cooperband *et al.* (1999) found that AEM sorption of inorganic and organic P can be close to 100% of total soluble P if concentrations are large, and may be closer to 90% to recovery more complex P compounds (phytate P).

Research performed in Canary Islands with Andisols using AEM showed that: (i) membranes remained usually dark after different washing procedure following the reactions with soils suspensions, and (2) organic C, Al, Si, and Fe were always present in significant amounts. Hernández-Moreno & Negrín (1998) studied P extraction by AEM, in two Andisols from a greenhouse experiment with corn (*Zea mays*) at four levels of P (0, 50, 100 and 200 mg P kg^{-1}).

The sequential elution of membranes with 1M NaCl and 0.5 M $NaHCO_3$ showed (1) more P was extracted in the later, (2) Fe and Si were detected in NaCl eluents, (3) Al and organic C were found in the bicarbonate eluents and (4) closely relationships between P fractions, and Al(Fe) and organic C in the AEM eluents corresponding to the different P treatments (Table 3 and Figure 4).

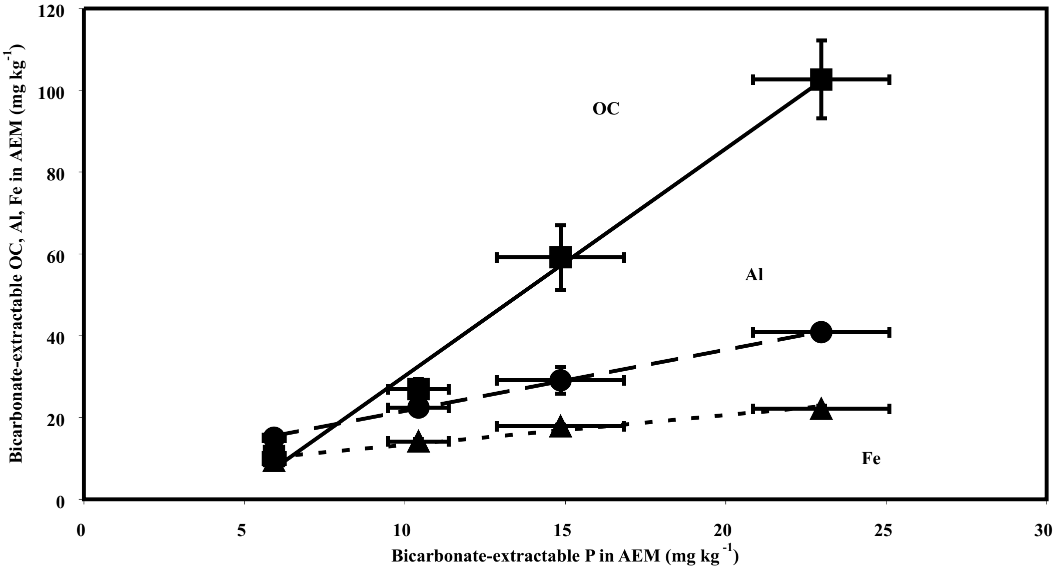

Figure 4. Relationships between organic carbon (OC), Al, and Fe in bicarbonate eluates of AEM from Typic Hapludands (I) sample (means±SE) (adapted from Negrín *et al.*, 1998).

Table 3. P fractionation in AEM eluates from two cultivated Typic Hapludands [a] (mean±SD) (adapted from Hernández-Moreno & Negrín, 1998) [b]

Soil 1	mg kg^{-1}								
Treatment(mg P kg^{-1} soil)	Cl-P	Cl-Fe	Cl-Si	Bi-P	Bi-Pc	Bi-OC	Bi-Al	Bi-Fe	Bi-Si
0	6.4±0.7	9.8±0.3	613±42	5.7±0.6	0.22±0.04	10.1±1.1	14.9±0.5	9.3±0.3	74.7±7.8
50	17.4±1.8	15.8±0.5	650±29	10.4±0.9	0.43±0.03	27.0±2.4	22.4±1.4	14.2±0.5	70.5±6.2
100	27.0±1.7	22.1±0.4	617±26	14.9±2.0	0.56±0.02	59.2±7.9	29.1±3.2	17.9±0.4	75.8±6.7
200	44.3±2.0	29.0±0.4	623±18	23.0±2.1	0.73±0.02	103±10	40.9±1.8	22.1±0.8	81.8±4.5
Soil 2	mg kg^{-1}								
Treatment (mg kg^{-1} soil)	Cl-P	Cl-Fe	Cl-Si	Bi-P	Bi-Pc	Bi-OC	Bi-Al	Bi-Fe	Bi-Si
0	11.8±0.9	7.2±0.5	814±50	16.6±0.9	0.33±0.02	29.7±1.6	23.2±1.3	10.5±0.5	118±3
50	22.3±0.7	13.9±0.6	880±22	21.2±0.8	0.65±0.03	55.0±2.0	32.3±1.9	18.5±0.7	127±9
100	40.0±1.1	19.7±0.6	845±38	31.0±2.0	0.96±0.02	111±7	42.5±2.3	25.9±0.5	122±8
200	58.0±1.4	25.8±0.4	867±42	40.0±1.1	1.32±0.05	192±6	52.6±1.5	29.0±0.7	124±5

[a] Soil Survey Staff (1992).

[b] Symbols: Cl-P, Cl-Fe and Cl-Si (NaCl-extractable P, Fe, Si in AEM respectively), Bi-P, Bi-Pc, Bi-OC, Bi-Al, Bi-Fe and Bi-Si (Bicarbonate-extractable P, after charcoal P, organic carbon, Al, Fe, Si in AEM respectively).

These results suggest that the adherence of soil particles to AEM could not be a contamination in the sense of aleatory adherence. Therefore, phosphate adsorption mechanism involved for P extraction by AEM for Andisols can not be only a simply anion exchange processes due to the reaction of a large portion of inorganic P added with complexes of the type humus-Al(Fe)-OH (to humus-Al(Fe)-P). In conclusion, the use of AEM as STP in volcanic soils appears to have some limitations, further testing may provide an understanding of P dynamics in these large P-fixing systems.

Conclusions

The inconsistencies of STP when applied to Andisols seem to be due to P sinks in these soils (Al(Fe) phosphates and P-Al(Fe)-humus complexes), which seem to influence the partitioning of P between soil and solution.

In a further study using isotope exchange kinetics and an infinite sink, Frossard *et al.* (2000) indicated that the understanding of physico-chemical and biological soil processes involved in inorganic P release from the solid phase and its measurement is useful in the development of strategies to reduce P losses from agriculture soils and the development of appropriate techniques to reduce P availability in high status soils.

This is of the special importance in soil use and management practices of Andisols and Andic soils in which changes in soil P cycling by abiotic and biotic processes, soil organic P dynamic and the irreversibility of P sorption reaction are aspects concerning P availability for crops. The development and evaluation of new soil available P tests are needed in these soils considering the dominant components and volcanic ash-based substrates responsible for P retention.

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