



Phosphorus fertilizer recovery from calcareous soils amended with humic and fulvic acids

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Abstract

Precipitation of Ca phosphates negatively affects recovery by plants of P fertilizer applied to calcareous soils, but organic matter slows the precipitation of poorly soluble Ca phosphates. To study the effect of high molecular weight organic compounds on the recovery of applied P, a mixture of humic and fulvic acids was applied to calcareous soils with different levels of salinity and Na saturation which were fertilized with 200 and 2000 mg P kg⁻¹ as NH₄H₂PO₄. Recovery was measured as the ratio of increment in Olsen P-to-applied P after 30, 60 and 150 days, and associated P forms were studied using sequential chemical fractionation and ³¹P NMR spectroscopy. Application of the humic-fulvic acid mixture (HFA) increased the amount of applied P recovered as Olsen P in all the soils except in one soil with the highest Na saturation. In soils with high Ca saturation and high Olsen P, recovery increased from < 15% in the absence of amendment to > 40% at a 5 g HFA kg⁻¹ amendment rate (30 days incubation and 200 mg P kg⁻¹ fertilizer rate). This is ascribed to inhibition of the precipitation of poorly soluble Ca phosphates, consistent with the sequential chemical extraction (reduction of the HCl extractable P) and P concentration in 0.01 M CaCl₂ (1:10 soil:solution ratio) extracts. ³¹P NMR spectra revealed that in non-amended samples, most spectral shifts were due to poorly soluble P compounds (carbonate apatite); on the other hand, at the 5 g HFA kg⁻¹ rate, significant amounts of amorphous Ca phosphate and dicalcium phosphate dihydrate (DCDP) were identified. The increase in the recovery of applied P due to HFA reveals a positive effect of the application of organic matter as soil amendments on the efficiency of P fertilizers and also explains that manures and other organic sources of P were more efficient increasing available P than inorganic P fertilizers in calcareous soils.

Abbreviations: CB – citrate-bicarbonate; CBD – citrate-bicarbonate-dithionite; DCDP – dicalcium phosphate dihydrate; HAF – humic and fulvic acid mixture; HAP – hydroxyapatite; OCP – octacalcium phosphate; TCP – tricalcium phosphate

Introduction

Adsorption and precipitation processes in soils result in only part of applied P fertilizer remaining available to plants. The apparent recovery of applied fertilizer is usually low in the first cropping year following application, and residual P plays a major role in agricultural soils by supplying P to plants (Barrow, 1980; Matar

et al., 1992). In calcareous soils, precipitation of insoluble Ca phosphates is believed to be a major factor in the loss of availability of applied P (Sample et al., 1980), although the relative contribution of adsorption and precipitation processes to P fixation in calcareous soils seems to depend on P application rate (Afif et al., 1993; Castro and Torrent, 1995). An initial low soil P status may constrain agricultural use, especially in calcareous soils, where a sizeable fraction of ap-

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plied P can precipitate as poorly soluble Ca phosphates (Delgado and Torrent, 2000; Duiz et al., 1997).

Organic matter applied to soil as amendment (e.g., manure or compost) is important in increasing productivity in agricultural soils with low levels of organic carbon, for example through well-documented effect of humic substances on plant growth and nutrition (Adani et al., 1998; Fernández-Escobar et al., 1996). These amendments may influence P dynamics in soils. For example, there is evidence of competitive adsorption between low molecular weight organic acids and phosphate, thus delaying P adsorption on active surfaces (Geelhoed et al., 1999; Staunton and Leprince, 1996; Violante and Gianfreda, 1993), which accounts for the increased P fertilizer efficiency in soils amended with organic matter (Shi and Thompson, 2000; Xie et al., 1995). Organic compounds may also affect the rate and form in which P precipitates in calcareous soils. Organic acids inhibit the precipitation of hydroxyapatite (HAP) (Inskeep and Silverthoath, 1988) and favour the formation of dicalcium phosphate dihydrate (DCPD) over other, more thermodynamically stable and less soluble phosphates (Grossl and Inskeep, 1991). High molecular weight organic acids are more effective inhibitors of HAP precipitation than are low molecular weight acids (Inskeep and Silverthoath, 1988). Thus, the addition of organic compounds such as humic and fulvic acids to soil may increase the efficiency of applied P fertilizer in calcareous soils by increasing the fraction of applied P that remains as highly soluble Ca phosphates (Fixen et al., 1983; Havlin and Westfall, 1984).

The main purpose of this work was to study the recovery of applied P fertilizer from soils amended with a mixture of humic and fulvic acids using chemical extraction (viz. Olsen P, a bicarbonate-extraction which is a valuable estimate of available P in calcareous soils) to examine the effect of this amendment on the efficiency of applied fertilizer increasing the available P pool in soils. The speciation of P in soils may contribute to explain the mechanism by which organic amendments affect recovery of applied P. Speciation has usually been studied by indirect methods such as sequential chemical fractionation (Delgado and Torrent, 2000; Xie et al., 1995). In this work, we also used ^{31}P NMR spectroscopy, which is effective to study P speciation in heavily fertilized acid (Lookman et al., 1996) and calcareous soils (Delgado et al., 2000).

Materials and methods

Soils

Soil samples were collected at six different sites in the Guadalquivir River Valley, Southwestern Spain. These calcareous soils had similar properties and were classified as Aeric Endoaquepts (Soil Survey Staff, 1998). The main difference among soils in the studied area is their salinity and Na saturation. Detailed information about the area and its soils can be found elsewhere (Domínguez et al., 2001; Moreno et al., 1981). Agricultural uses include cropping of sugar beet (*Beta vulgaris* L.) and cotton (*Gossypium hirsutum* L.) Samples were collected from the Ap horizon (0–30 cm), air-dried and ground to <2 mm before analysis.

Soil analyses

Particle size was determined using the pipette method following treatment with an HOAc-NaOAc buffer (pH 4.75) to remove carbonates (Gee and Bauder, 1986). Soil pH was measured in water (1:2.5 soil:water ratio). Organic carbon was determined by dichromate oxidation (Walkley and Black, 1934), and cation exchange capacity (CEC) using 1 M NH_4OAc buffered at pH 7. Following extraction with 1 M NH_4OAc (three consecutive washes), exchangeable Na, K and Mg were determined using flame photometry for K and Na, and atomic absorption spectroscopy for Mg. Due to the presence of CaCO_3 , the exchangeable Ca was estimated as the difference between the CEC and the sum of the other exchangeable cations. The total CaCO_3 equivalent was determined by the weight loss upon treatment with 6 M HCl, and 'active' CaCO_3 (ACCE) by the method of Drouineau (1942). The 1:1 extract obtained using the procedure of Rhoades (1996) was analysed for electrolytic conductivity, cations (using flame photometry for Na and K, and atomic absorption spectroscopy for Ca and Mg). Field capacity of the soil was determined by using a column (3.75 cm diameter, 15 cm long) in which soil was packed to a bulk density of 1.25 kg dm^{-3} , value reported by Moreno et al. (1981) for typical soils of the area, and moistened and allowed to freely drain for 48 h.

Minerals in the clay fraction were studied by X-ray diffraction, using Co $K\alpha$ radiation in a D5000 Siemens diffractometer.

P forms in soil

Plant-available P was estimated according to Olsen et al. (1954), except that the active carbon treatment was avoided and centrifuging was used instead of filtering. Phosphorus fractionation was carried out following the sequential scheme of Olsen and Sommers (1982). The process involves four consecutive extractions with (i) NaOH + NaCl, (ii) citrate-bicarbonate (CB), (iii) citrate-bicarbonate-dithionite (CBD), and (iv) HCl. All extractions were for 16 h (by exception, the HCl extraction lasted only 1 h). Following Solís and Torrent (1989), the CBD extraction was conducted at 298 K for 16 h. All extractions were carried out in duplicate at 298 K, and only molybdate reactive P was determined in the extracts according to Murphy and Riley (1962).

NaOH-P represents mainly P adsorbed on 'active surfaces' (no Fe- and Al-phosphates may exist in calcareous soils) (Ruíz et al., 1997). In calcareous soils, most of NaOH-P is reprecipitated or re-adsorbed for release in the following step. CB-P is related to adsorbed P and highly soluble precipitated phosphates; CBD-P is related to P adsorbed on high energy sites plus P occluded within Fe oxides; and HCl-P is P precipitated as poorly soluble Ca phosphates (mainly hydroxyapatite + fluorapatite) (Delgado and Torrent, 2000; Delgado et al., 2000; Ruiz et al., 1997).

Experimental design

A commercial liquid mixture of humic and fulvic acids (Solfer húmicos®, Valencia, Spain) was used as organic amendment. The mixture contained 11% humic and 4% (w/w) fulvic acids, plus a negligible amount of total P. Recovery of applied fertilizer was examined in relation to applied amendment by conducting an experiment involving four factors and two replicates per treatment. The factors studied were the six soils, two fertilizer application rates (200 and 2000 mg P kg⁻¹), four amendment application rates (0, 1, 2 and 5 g of mixture per kg of soil) and three incubation times (30, 60 and 150 days). The lower fertilizer rate was similar to that typically applied to highly intensive horticultural crops in the area. The higher was used to simulate the effect of the actual distribution of P fertilizer in the soils, to which it is applied as granules that release large amounts of P in a restricted soil volume. Similar rates of P fertilizer have been used by several authors in field (Hooker et al., 1980) and laboratory experiments (Afif et al., 1993; Castro and Torrent, 1995).

On the assumption of a bulk density of 1.25 kg dm⁻³ (Moreno et al., 1981) and a mixing depth of 25 cm, 1 and 2 g kg⁻¹ of amendment are equivalent to 3 and 6 Mg ha⁻¹. This range spans the amount of humic and fulvic acids potentially formed in the soil from applied manure and compost at the rates usually employed in the area. The highest rate (5 g kg⁻¹) was intended to simulate a non-uniform distribution of this amendment in the soil.

Experiments were performed at 298 K, placing 30 g of soil in a Petri dish and adding the amendment and fertilizer. During the experiment, the soil was maintained at field capacity. The water content was maintained constant by replacing the amount of water lost every 4 days, followed by carefully mixing of the soil. The P fertilizer used was reagent grade NH₄H₂PO₄. The fertilizer and amendment were applied dissolved/mixed in the irrigation water and the soil carefully mixed. At 30 days, one-third of the mass of incubated soil was removed, dried and ground to pass through a 2-mm sieve. This was repeated at 60 and 150 days.

Following collection and processing, soil samples were analysed for the P availability (Olsen P) and for the P fractions by using the above-described methods. All determinations were carried out in duplicate. The amount of applied P fertilizer recovered was determined from the increase in Olsen P after fertilization. The increase in the different P forms was also estimated. The P concentration in the extract obtained with 0.01 M CaCl₂ (1:10 soil:extractant ratio) was also determined as an estimate of the intensity factor concerning plant nutrition (Delgado and Torrent, 1997)

³¹P NMR study

Solid-state ³¹P NMR spectra were recorded according to Delgado et al. (2000) on a Bruker ACP-400 spectrometer at 161.975 MHz, at room temperature. Operating conditions for ³¹P NMR were: excitation pulse 5 μs (π/2 pulse); recycle time 10 s, line broadening 20 Hz. A sufficient number of scans was used to give a high signal-to-noise ratio (18 000 to obtain each spectra). ³¹P chemical shifts were measured relative to 85% (w/w) H₃PO₄. Spectra were recorded using samples from soils LB4 and LB5 fertilized with 2000 mg P kg⁻¹ and amended with 0 and 5 g kg⁻¹ of the mixture.

Table 1. General properties and P forms in the soils

Soil	Clay content (g kg ⁻¹)	pH (H ₂ O)	Organic carbon (g kg ⁻¹)	CCE ^a (g kg ⁻¹)	ACCE ^a (g kg ⁻¹)	CEC ^a (cmol _c kg ⁻¹)	Exchangeable cations				EC ^b (dS m ⁻¹)	SAR ^b mmol _c ^{1/2} L ^{1/2})	P fractions ^c (mg kg ⁻¹)				
							Ca	Mg	K	Na			Olsen P	NaOH-P	CB-P	CBD-P	HCl-P
LB1	630	7.8	7.9	211	126	41.1	27.2	10	2.8	1.1	0.9	1.2	21	6	99	60	446
LB2	530	7.5	6.7	260	136	36.9	24.5	9	2.2	1.2	3.3	0.9	34	4	129	97	511
LB3	570	8.1	7.6	273	133	36.8	12.6	18.6	2.2	3.4	1.0	6.0	16	6	69	59	394
LB4	650	8.0	10.8	213	125	41.4	23.6	10.3	2.9	4.6	1.6	6.9	13	6	70	29	414
LB5	550	7.6	7.6	255	131	34.3	20.1	11.3	2.2	0.7	2.1	0.6	36	5	160	107	556
LB6	520	7.8	7.6	267	123	32.7	18.8	10.2	2.3	1.4	1.1	1.8	26	8	117	79	530

^a ACCE – active calcium carbonate equivalent; CCE – calcium carbonate equivalent; CEC – cation exchange capacity.

^b EC – Electrolytical conductivity; SAR – Na adsorption ratio, both in the 1:1 soil:water extract.

^c P fractions according to Olsen and Sommers (1982); CB – citrate-bicarbonate; CBD – citrate-bicarbonate-dithionite.

Statistical analyses

Statistical analyses including curve fitting (Simplex procedure) and regression analysis were performed using CoStat (CoHort Software, 1988).

Results

The studied soils were calcareous, with pH ranging from 7.5 to 8. Clay was the dominant size fraction. Illite ranged from 65 to 76% of the clay fraction, and smectite and kaolinite from 7 to 20%. Their properties, including available P content and P fractions as determined according to Olsen and Sommers (1982), are summarised in Table 1. Olsen P ranged from 13 to 43 mg kg⁻¹. The dominant P fraction was HCl-P, which ranged from 69 to 81% of the combined forms, indicating that most P was associated to poorly soluble Ca phosphates (hydroxyapatite and fluorapatite). The electrical conductivity and sodium adsorption ratio (SAR) of the 1:1 soil:water extract varied widely among soils (Table 1).

Recovery of applied P (based on Olsen P) is given as the 'recovered P-to-applied P' ratio, i.e.

$$\frac{(\text{Olsen P after fertilization} - \text{Initial Olsen P})}{(\text{Applied P})} \quad (1)$$

Less than 15% of applied P was recovered as Olsen P from the soils with high Ca saturation and high initial Olsen P (LB2, LB5) after 30 days at the lower P application rate when no amendment was used (Figure 1). Recovery from soils with a high Na saturation (more than 9% of exchangeable Na percentage –ESP) (LB3, LB4) was much greater (about 60% in LB4 at

30 days) (Figure 1). Values for recovery from high Ca soils was similar to those reported by Afif et al. (1993) and Castro and Torrent (1995) for other calcareous soils from Mediterranean regions at similar fertilizer rates. In soils with initial high Ca saturation, precipitation of low soluble Ca phosphates may be the dominant contribution to P fixation (Delgado et al., 2000; Ruiz et al., 1997; Tunesi et al., 1999). This may account for the low recovery of P fertilizer in non-amended high Ca soils. Also, the ratio of recovered P-to-applied P was in general lower at the higher P fertilizer rate (especially at 150 days), consistent with the results of Afif et al. (1993) and Castro and Torrent (1995), except the LB4 (high Na – low P) that exhibited less marked differences between the two fertilizer rates (Figure 1).

Fertilizer recovery decreased with increasing incubation time at both P fertilizer rates (Figure 1). Precipitation of Ca phosphates in calcareous soils may significantly contribute to the decrease in P recovery with time (Castro and Torrent, 1998; Matar et al., 1992). This effect was smaller in the highest Na soil (LB4, Figure 1), probably because precipitation of Ca phosphates was less favourable in this soil due to its lower Ca activity in the solution.

Application of the humic + fulvic acids mixture (HFA) increased the recovery of applied P (measured as the increase in Olsen P in relation to applied P) in all the soils except LB4, which had the highest Na saturation (Figure 1). The effect was apparent at all incubation times (Figure 1 shows the recovery at 30 and 150 days). At 30 days, the increase in P recovery due to the amendment was higher in LB2 and LB5, which were the soils with a high Ca saturation and the highest initial Olsen P. In these soils, the proportion of

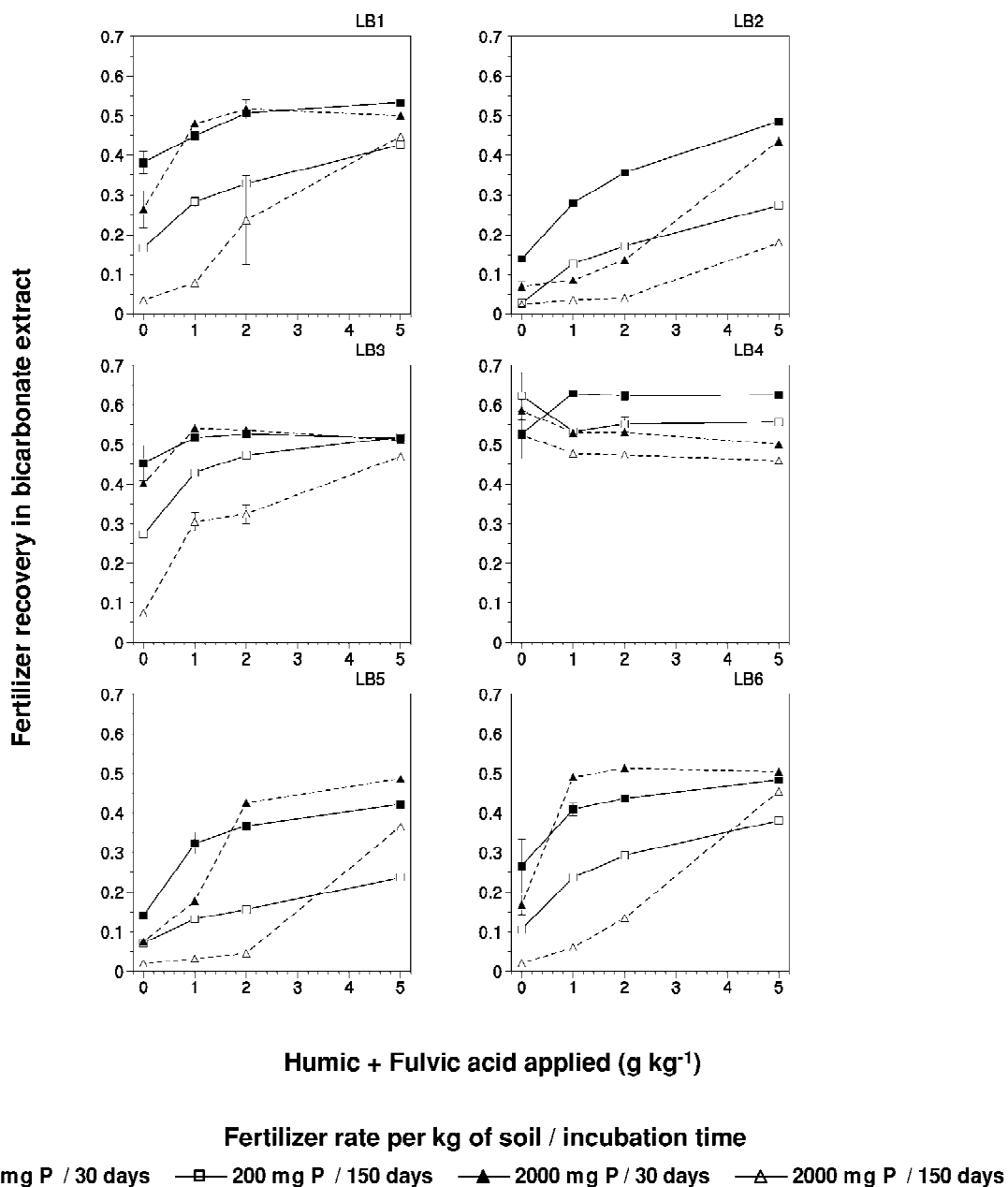


Figure 1. Recovery of applied P fertilizer measured as the increment in the $[(\text{Olsen P after fertilization} - \text{Initial Olsen P})/(\text{Applied P})]$ ratio as a function of the humic + fulvic rate at the two fertilizer rates at 30 and 150 days. Error bars indicate one standard deviation on each side of the mean.

applied P that was recovered increased from less than 15% in the absence of amendment to more than 40% at a 5 g HFA kg^{-1} amendment rate (30 days incubation time and the lowest P fertilizer ratio) (Figure 1). At 150 days, the increase in P recovery due to amendment was significant in all the soils except the one with

the higher Na saturation (LB4, Figure 1). The higher increase in P recovery at 150 days was observed in LB6, where P recovery increased from 2% with no amendment to 45% at the 5 g HFA kg^{-1} amendment rate (Figure 1).

Table 2. Distribution of applied P into the fractions given by the sequential fractionation scheme of Olsen and Sommers (1982) at the two inorganic P fertilizer rates used in soils amended with different amounts of humic + fulvic acids^a

Incubation time (days)	Humic + fulvic mixture applied (g kg ⁻¹)	200 mg P kg ⁻¹ applied			2000 mg P kg ⁻¹ applied		
		CB-P	CBD-P	HCl-P	CB-P	CBD-P	HCl-P
30	0	0.64 ± 0.06	0.17 ± 0.02	0.19 ± 0.07	0.46 ± 0.04	0.13 ± 0.01	0.41 ± 0.03
	1	0.71 ± 0.03	0.14 ± 0.01	0.15 ± 0.03	0.64 ± 0.05	0.15 ± 0.01	0.22 ± 0.05
	2	0.73 ± 0.03	0.13 ± 0.01	0.13 ± 0.03	0.68 ± 0.03	0.14 ± 0.01	0.18 ± 0.04
	5	0.75 ± 0.03	0.13 ± 0.01	0.12 ± 0.03	0.76 ± 0.01	0.14 ± 0.01	0.10 ± 0.02
60	0	0.66 ± 0.05	0.16 ± 0.01	0.17 ± 0.06	0.33 ± 0.04	0.11 ± 0.01	0.56 ± 0.04
	1	0.75 ± 0.04	0.16 ± 0.01	0.10 ± 0.04	0.58 ± 0.05	0.15 ± 0.01	0.27 ± 0.05
	2	0.76 ± 0.03	0.15 ± 0.01	0.10 ± 0.03	0.65 ± 0.04	0.13 ± 0.01	0.22 ± 0.04
	5	0.83 ± 0.03	0.15 ± 0.01	0.02 ± 0.03	0.76 ± 0.02	0.12 ± 0.01	0.12 ± 0.02
150	0	0.48 ± 0.05	0.13 ± 0.01	0.38 ± 0.06	0.23 ± 0.03	0.10 ± 0.01	0.67 ± 0.04
	1	0.60 ± 0.04	0.17 ± 0.01	0.23 ± 0.05	0.44 ± 0.05	0.16 ± 0.01	0.40 ± 0.05
	2	0.65 ± 0.03	0.17 ± 0.01	0.18 ± 0.03	0.51 ± 0.04	0.15 ± 0.01	0.34 ± 0.04
	5	0.74 ± 0.03	0.18 ± 0.01	0.08 ± 0.03	0.71 ± 0.03	0.13 ± 0.01	0.16 ± 0.03

^aMeans and standard errors for the six soil population. CB, CBD – citrate-bicarbonate and citrate-bicarbonate-dithionite. CB-P, CBD-P, and HCl-P are steps in the sequential fractionation scheme of Olsen and Sommers (1982).

A substantial fraction of applied P was recovered as HCl extractable P (HCl-P) according to the Olsen and Sommers fractionation scheme (1982), especially when no amendment was applied (Table 2). This indicates that precipitation of poorly soluble Ca phosphates (mainly HAP; Lindsay et al., 1989) may contribute significantly to the lack of recovery of applied P. Precipitation of this type of compound was more marked at the higher P fertilizer rate (Table 2). Recovery as HCl-P increased with time, the increase being roughly equivalent to the decrease in CB-recovered P; the latter fraction includes the precipitated phase that is more soluble than HAP in addition to P adsorbed on active surfaces (Delgado and Torrent, 2000; Ruiz et al., 1997) (Table 2).

Application of HFA decreased recovery as HCl-P and increased recovery as CB-P (Table 2). With no amendment applied, the proportion of HCl recovered P increased by 100% from 30 to 150 days at 200 mg P kg⁻¹ fertilizer rate, and by 63% at a 2000 mg P kg⁻¹ rate; on the other hand the increase in poorly soluble phosphates with time at the highest HFA rate was not significant, especially at the lower P fertilizer rate (Table 2). Thus, the application of the organic amendment reduced the decrease in CB recovered P and the increase in HCl recovered P with time (Table 2).

P concentration in 1:10 soil:0.01 M CaCl₂ extracts after 150 days incubation increased markedly as the

HFA rate increased (Table 3). At the higher P application rate, P concentration when amendment dose increased from 0 to 5 g HFA kg⁻¹ increased by more than an order of magnitude. This suggests a change in the phase in equilibrium with the solution.

Ca phosphates have been successfully detected in soil samples using NMR spectroscopy (Lookman et al., 1996), although overlapped peaks in the spectra hinder the identification of specific compounds (Delgado et al., 2000). Figure 2 shows the ³¹P NMR spectra for two soils (LB4 and LB5), representing differences in P recovery and amendment effect. All chemical shifts in the NMR spectra ranged from –0.1 to 7 ppm and can be ascribed to different forms of Ca related phosphorus. Most of the peaks for non-amended samples can be attributed to carbonate apatite; however, in soils with high Ca saturation and P content (e.g., LB5, Figure 2), there is evidence of the presence of tricalcium phosphate (TCP) (peak at 4.2 ppm) and OCP (peak at 3.4 ppm with shoulder peak at –0.1 ppm) (Hinedi et al., 1992; Rothwell et al., 1980). Samples amended with 5 g HFA kg⁻¹ had spectra with more peaks (generally broader) and stronger spin sidebands than non-amended samples. This effect can be ascribed to the presence of more Ca phosphates and to a higher proportion of low crystalline compounds (amorphous Ca phosphate – ACP) (Hinedi et al., 1992). Further evidence for the presence of ACP

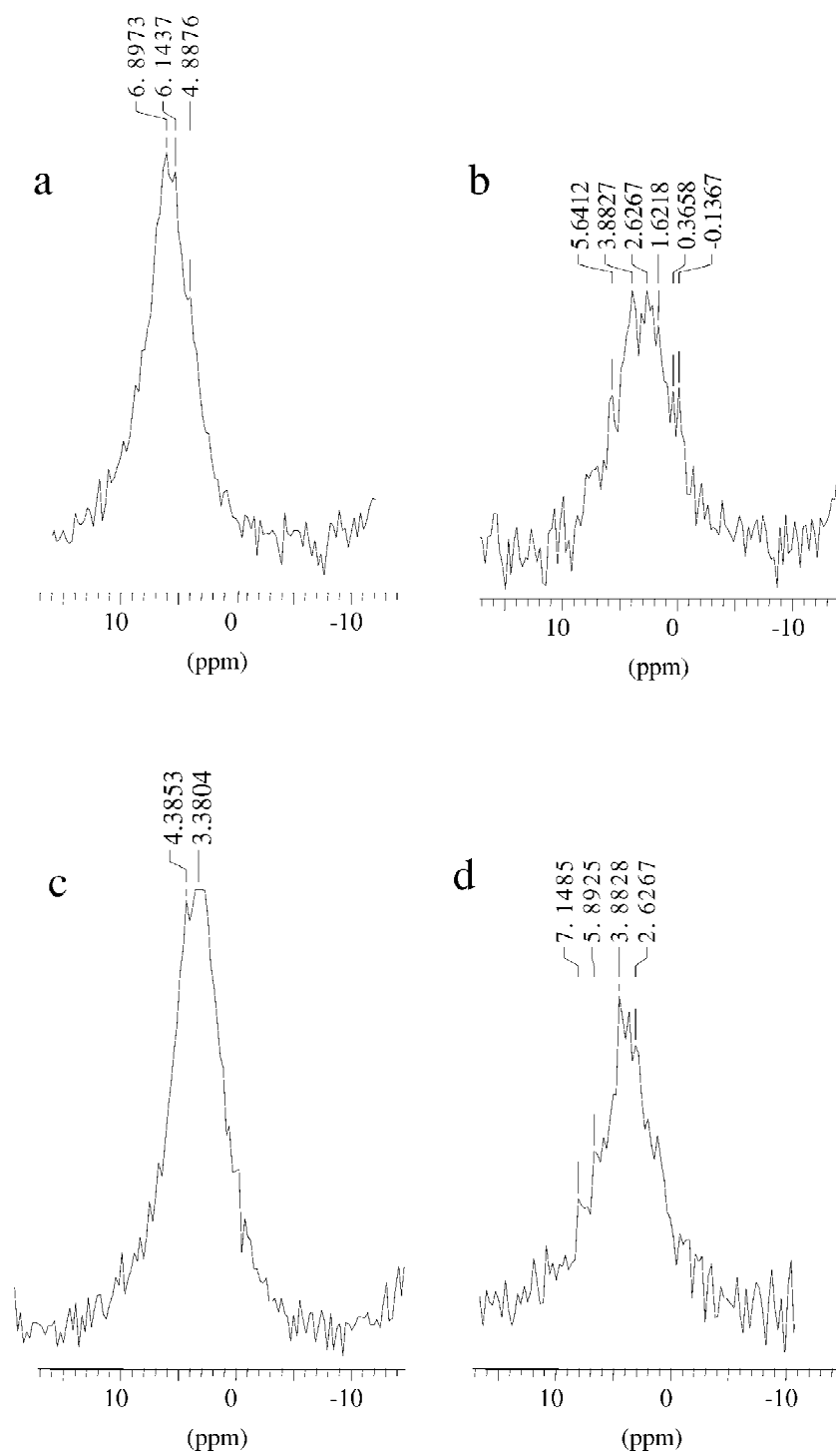


Figure 2. ^{31}P NMR spectra for LB4 and LB5 soil samples fertilized with 2000 Mg P kg⁻¹: (a) LB4 with no humic + fulvic acid mixture applied; (b) LB4 amended with 5 G kg⁻¹ of mixture; (c) LB5 with no humic + fulvic acid mixture applied; (d) LB5 amended 5 g kg⁻¹ of mixture.

Table 3. P concentration (mg L^{-1}) in the 1:10 soil: 0.01 M CaCl_2 extract after 150 days incubation of soils amended with different rates of humic + fulvic acids

Humic + fulvic mixture applied (g kg^{-1})	200 mg P kg^{-1} applied		2000 mg P kg^{-1} applied	
	Mean \pm SE	Range	Mean \pm SE	Range
0	0.47 ± 0.19	0.06 – 1.95	0.30 ± 0.12	0.06 – 1.17
1	0.68 ± 0.17	0.14 – 1.88	3.22 ± 1.50	0.09 – 14.34
2	0.81 ± 0.18	0.18 – 1.94	3.37 ± 1.44	0.09 – 13.84
5	1.01 ± 0.15	0.43 – 1.89	10.98 ± 1.50	1.04 – 15.41

is provided by spectral peaks at 2.6 ppm in samples amended with 5 g HFA kg^{-1} (Figure 2). This peak can be also ascribed to hydroxyapatite (Rothwell, 1980), but the observed half-height line, greater than 4 ppm, allows one to ascribe it to ACP (Hinedi et al., 1992). The LB4 (higher Na saturation) amended sample also exhibited evidence of the presence of DCDP and OCP, two P forms that may contribute to the available P pool in the soil (Delgado and Torrent, 2000).

Discussion

According to chemical fractionation data, the effect of HFA increasing the recovery of applied P is mainly related to the interference on Ca phosphate precipitation. Application of the commercial HFA decreased recovery as HCl-P (related to poorly soluble Ca phosphates) and increased recovery as CB-P (adsorbed + soluble Ca phosphates) (Table 2). This is consistent with the well-documented inhibition of HAP precipitation in the presence of high molecular weight acids (Inskeep and Silvertooth, 1988); by exception, precipitation of a more soluble precipitated phase may be not inhibited. In this sense, Grossl and Inskeep (1991) found DCDP to precipitate on seed crystals with adsorbed C, and the precipitation of other, more thermodynamically stable, phosphates (OCP, HAP) to be more strongly inhibited by soluble C. This is consistent with a kinetically favoured formation of soluble forms over other less soluble phosphates, which increases the amount of P recovered by bicarbonate. Adsorption of humic and fulvic acids onto seed crystals not only reduces precipitation but also the dissolution and reprecipitation as less soluble forms with time. Thus, an organic amendment, which incorporates humic and fulvic acids to soil, not only increases the fraction of applied P that remains available after fertilization, but also inhib-

its the long-term P reactions resulting in the lack of recovery of applied P with time.

Direct evidence for the presence of more soluble Ca phosphates as a consequence of the use of humic + fulvic amendment is provided by the ^{31}P NMR spectra. According to the NMR spectra, amended samples contain more soluble Ca phosphates (ACP, DCDP) whereas non-amended samples appear to contain carbonate apatite as the dominant P form. These results are consistent with the increased chemical recovery of applied P and the increased P concentration in the soil extracts, which reflect improved efficiency of applied P, and also support that the interference on Ca phosphate precipitation is a major mechanism involved in the effect of humic and fulvic acids increasing P recovery.

Total area of the spectra of the amended soils was smaller than non-amended soils, suggesting some type of interference. The effect is similar to that described by Delgado et al. (2000), where the area of the spectra and the estimated amount of total P in soils decreased as the content in poorly crystalline Fe oxides increased. This was ascribed to an increased paramagnetic interference of Fe as the proportion of Fe associated to poorly crystalline compounds increased. In this case, the effect could be related to an increased paramagnetic interference due to complexation of Fe by the applied organic compounds. Formation of organic-metal (mainly Fe) compounds also contributes to explain a higher recovery of applied P through the dissolution of metal oxides (Ohno and Crannell, 1996) or the adsorption of P by these organic-metal compounds decreasing the amount of P that precipitates as Ca phosphates. The presence of P bound to organic-metal compounds could be also a possible explanation for smaller NMR spectra areas.

The effect of humic and fulvic acids on P recovery contributes to explain why organic amendments

increase plant available P in soils more than inorganic P fertilizers (Erich et al., 2002). This is important to increase crop production in soils where the low available P level is a limiting factor for crop production (Buerkert et al., 2001) but also to preserve agricultural productivity with a minimum environmental risk associated with P additions, since an accurate plant nutrition can be maintained with lower P application rates using manure or other organic sources of P instead of fertilizers.

Conclusions

Organic amendments consisting of a mixture of humic and fulvic acids increased recovery of applied P by bicarbonate (Olsen P). This is the result of the precipitation rate of poorly soluble Ca phosphate being decreased by the organic amendment. The ^{31}P NMR analysis revealed the presence of amorphous Ca phosphate in amended samples. By contrast, carbonate apatite seemed to be the dominant form in non-amended samples. These results account for a higher efficiency of applied P fertilizer in organically amended soils.

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