

Phosphorus Forms and Desorption Patterns in Heavily Fertilized Calcareous and Limed Acid Soils

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ABSTRACT

Phosphorus desorption from fertilized soils is significant for agriculture and the environment. This study was aimed at characterizing the forms in which P occurs in calcareous and limed acid soils and their influence on P desorption patterns. The P forms of two limed acid and three calcareous soils of Europe were characterized by chemical extraction, isotopic exchange, and sequential fractionation. Phosphate desorption was studied using resins and goethite as ion sinks. Total P ranged from 705 to 1400 mg kg⁻¹. Isotopic exchange revealed more surface-adsorbed P in the limed acid than in the calcareous soils. Calcium phosphates predominated in the calcareous and Al and Fe phosphates in the limed acid soils; one limed acid soil contained significant amounts of Ca phosphates. The mixed cation and anion exchange resins (ACER) were more effective in desorbing P than the anion exchange resin (AER) and goethite. The desorption curves indicated significant differences in the degree of homogeneity of the P desorption reactions, the greatest and lowest degree of homogeneity corresponding with calcareous soils. The proportion of ACER-extractable P that was plant-available P was >50% for the limed acid and <20% for the calcareous soils. The proportion of ACER-extractable P that was released to 0.002 M CaCl₂ was >60% for the limed acid and <40% for the calcareous soils. Plant P availability was thus poorer in the calcareous soils than in the limed acid soils.

FOR DECADES, most agricultural soils in Europe have been fertilized with P for optimum crop yields. Upon application to soil, fertilizer P undergoes several chemical reactions that influence its availability to plants. Generally, surface adsorption and precipitation processes contribute to its binding to the solid phase from which it may be released subsequently. These two types of processes cannot be differentiated in most cases. But soil properties and fertilizer P management practices affect the relative distribution of adsorbed P and the P precipitated with different cations (Afif et al., 1993). In calcareous soils, P is mainly bound to adsorption surfaces at low (<10^{-4.5} M) concentrations of orthophosphate in solution (Borrero et al., 1988; Tunesi et al., 1999), whereas it is mainly precipitated as Ca phosphates at higher concentrations (Castro and Torrent, 1998; Tunesi et al., 1999). In acid soils, Fe and Al phosphates are the typical precipitation products (Lindsay, 1979; Pierzynski et al., 1990). However, some heavily fertilized acid soils contain significant amounts of Ca phosphates (Lookman et al., 1996), and hydroxyapatite (HA) has been found as a product of the dissolution of superphosphates in acid and slightly acid soils (Kumar et al., 1994). Pierzynski et al. (1990) showed that P-rich particles re-

sulting from fertilizer dissolution in acid soils included not only Al and Fe but also Si and Ca. Calcium phosphates precipitate when large doses of P are applied to limed acid soils (Muurman and Peech, 1968).

Hydroxyapatite is the most stable Ca phosphate formed in soils, which should occur in calcareous soils (Freeman and Rowell, 1981). However, the precipitation rate to this stable phase is slow. It is generally preceded by the precipitation of more soluble, metastable phases, which slowly evolve to the stable phase and control the solution P concentration for long periods. Such phases include dicalcium phosphate dihydrate, octacalcium phosphate, and tricalcium phosphate in order of decreasing solubility (Lindsay, 1979; Fixen et al., 1983). Small concentrations of these products in the soil matrix preclude their identification by direct methods (e.g., x-ray diffraction). Phase diagrams derived from pure minerals and other indirect methods are hence used for this purpose (Olsen and Khasawneh, 1980; Fixen and Grove, 1990). These phase diagrams suggest that a fraction of these Ca phosphates may be available to plants (Fixen et al., 1983; Havlin and Westfall, 1984).

Estimating the content and solubility of the different Ca and other metal phosphate species that precipitate in calcareous and limed acid soils is far from simple. Soil P fractionation, though often used, is considered a poorly selective method for different forms of P in soil (Olsen and Khasawneh, 1980), and no more precise information can be expected from simple extraction techniques (Fixen and Grove, 1990).

The first objective of this study was to characterize the inorganic P forms in different heavily fertilized calcareous and limed acid soils. To this purpose, we combined data obtained from P fractionation, simple chemical extraction and isotopic exchange. The second objective was to characterize the P desorption patterns to P sinks (resins and goethite) and their relationship with the P forms. Finally, the possible agricultural and environmental implications of the different forms in which P occurs in calcareous and limed acid soils were considered. In the following, the term desorption is used to encompass all processes that result in release of P from the soil solid phase.

MATERIALS AND METHODS

Soils

Three calcareous soils (a Typic Xerofluvent [E1] and a Typic Calcixerert [E2] from Spain, and a Vertic Calcixerert

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Abbreviations: ACER, mixed anion and cation exchange resin; AER, anion exchange resin; CB, citrate-bicarbonate; CC, citric acid-Na citrate; CBD, citrate-bicarbonate-dithionite; HA, hydroxyapatite; d (subscript), extracted by citrate-bicarbonate-dithionite; IEP, isotopically exchangeable P; o, (subscript), extracted by oxalate.

Table 1. Properties of the soils studied.

Soil	Location	Classification	Clay	Organic C	CaCO ₃	pH (CaCl ₂)	Fe _d †	Fe _o †	Al _o †	Mineralogy of the clay fraction‡
D1	Germany	Typic Hapludoll	200	24	0	6.4	6.0	2.0	1.4	I,S,K,Q,F
D2	Germany	Mollic Epiaqualf	150	13	0	6.7	8.6	3.1	1.2	I,S,Ch,K,Q
E1	Spain	Typic Xerofluvent	170	7	240	7.8	4.0	0.7	0.5	I,S,F,K,C,Q
E2	Spain	Typic Calcixerent	450	9	340	7.7	2.8	0.8	1.0	S,I,K,C,Q
I3	Italy	Vertic Calcixerent	300	12	140	7.6	6.1	1.7	1.7	S,I,Ch,K,C,Q

† Fe_d, citrate-bicarbonate-dithionite soluble Fe; Fe_o, oxalate-soluble Fe; Al_o, oxalate-soluble Al.

‡ In order of abundance. C, calcite; Ch, chlorite; F, feldspar; I, Illite; K, kaolinite; Q, quartz; S, smectite.

[I3] from Italy) and two limed acid soils (a Typic Hapludoll [D1] and a Mollic Epiaqualf [D2] from Germany) were used in this study. The soils ranged widely in properties and represented important European agricultural areas having a long history of P fertilization. Selected physical, chemical, and mineralogical properties of the soils are reported in Table 1. More detailed characterization of the soils is given elsewhere (Barberis et al., 1996; Delgado and Torrent, 1997, 1999).

Characterization of Soil Phosphorus Forms

Total P and organic P were determined as described by Barberis et al. (1996). Isotopically exchangeable P (IEP) was determined in suspensions with a solution/soil ratio of 10:1 (Delgado and Torrent, 1997). This solution was prepared to match the concentration of the different cations in the saturation extract of the soil using Cl salts. The suspension was shaken on a reciprocating shaker at a frequency of 3 Hz for 6 d before adding a known amount of carrier-free ³²P. Then, the suspension was shaken for another day, centrifuged, and molybdate-reactive P and ³²P were determined in the supernatant according to Murphy and Riley (1962) and by Cerenkov counting, respectively. The IEP was calculated on the assumption of isotopic equilibrium between the solid and liquid phases.

Plant-available P was estimated as described in detail by Delgado and Torrent (1997). Briefly, 2.8 kg of each soil was P-depleted by growing eight successive crops for a total period of 18 mo to reach either a solution P concentration of 0.01 mg L⁻¹ or an Olsen P (Olsen et al., 1954) value of 6 mg kg⁻¹. Then, plant-available P was estimated by interpolating or extrapolating cumulative P uptake to these exhaustion levels. Phosphorus released in 0.002 M CaCl₂ was measured by preparing eight solution/soil suspensions ranging from 10:1 to 10 000:1 (Delgado and Torrent, 1999), which were stirred occasionally during 340 d. Molybdate-reactive P in solution was measured and the P released in CaCl₂ was defined as the amount of P calculated by interpolation or extrapolation to a solution P concentration of 0.01 mg L⁻¹. The rationale for using this concentration was that it represents the threshold for significant algal growth in fresh waters (Golterman and de Oude, 1991).

The Olsen and Sommers (OS) (1982) sequential fractionation scheme was applied to 0.8 g of soil in 40 mL of extracting solution to obtain the NaOH-, citrate-bicarbonate- (CB-), citrate-bicarbonate-dithionite- (CBD-), and HCl-extractable P fractions. Detrital (lithogenic) apatite was considered to be HCl-extractable P in a procedure similar to the OS fractionation scheme. However, before HCl extraction, the soils were treated with 0.2 M citric acid–Na citrate buffer at pH 6 and then with acetic acid–Na acetate buffer at pH 4 to remove the more soluble and pedogenic hydroxyapatite (Ruttenberg, 1992). Direct extractions with 0.25 M Na citrate–0.1 M NaHCO₃ (CB) and 0.2 M citric acid–Na citrate buffer at pH 6 (twice) (CC) were performed by shaking a suspension of

1 g of soil in 50 mL of extracting solution for 16 h on a reciprocating shaker oscillating at a frequency of 3 Hz. All extractions were carried out in triplicate.

Kinetics of Phosphorus Desorption

Soil P was desorbed by ion exchange resins saturated with HCO₃⁻, Cl, and NH₄⁺ and Cl (mixed), and goethite. To study the kinetics of P desorption to an AER saturated with HCO₃⁻, nylon bags holding 2.2 g of 0.3 to 0.8 mm Dowex 1 × 4 resin were used (Sigma Chemical, St. Louis, MO). A 2-g soil sample and a resin bag were suspended in 100 mL of deionized water in 120-mL polyethylene flasks placed on a reciprocating shaker oscillating at 1.3 to 1.6 Hz. At 1, 4, 8, 12, 16, and 25 d, the resin bags were recovered and replaced with a bag containing fresh HCO₃⁻-AER.

In the experiments with Cl-AER, a soil sample containing 0.25 mg of desorbable P (estimated by 25-d extraction with HCO₃⁻-AER) was placed in a 60-mL polyethylene bottle. The bottle contained the resin bag and 30 mL of a solution that matched the concentrations of Ca, Mg, K, and Na in the soil saturation extract with Cl as counterion; cation concentrations were previously determined by atomic absorption spectrophotometry (Ca and Mg) or flame photometry (K and Na). The bottle was then placed on a reciprocating shaker at 1.3 to 1.6 Hz. The resin bags were replaced with other bags containing fresh Cl-AER at 15 times ranging from 0.17 to 1920 h. In both sets of experiments, the resin bags were eluted with 0.5 M HCl to remove the adsorbed P.

The kinetics of phosphate desorption to ACERs was studied in polyethylene bottles containing the same amount of soil as in the experiment with Cl-AER, 100 mL of deionized water, and cation exchange resin (2.8 mL of Duolite 255, NH₄ form; Sigma Chemical) and anion exchange resin (4.0 mL of IRA 402, Cl form; Sigma Chemical) in separate nylon bags. The bottles were shaken as for Cl-AER, and the resin bags were replaced with bags containing fresh resin at 12 times ranging from 1 to 1440 h. The adsorbed P and cations were eluted with 1 M NH₄Cl at pH 2.

Goethite with a surface area of ≈40 m² g⁻¹, prepared according to Guzmán et al. (1994), was the other sink used for P desorption. A dialysis bag containing 2 g of soil in 50 mL of water was immersed into a Nalgene bottle with 450 mL of water containing 0.46 g of goethite. Before use, the dialysis bag (Visking tube 36/32, pore size between 12 000 and 15 000 Da) was washed with 0.5 M NaOH, rinsed with water, and allowed to stand overnight in deionized water. Bottles were shaken in an orbital shaker rotating at 1.3 Hz. Subsamples (4 mL) of the goethite suspension were taken at 16 times ranging from 48 to 672 h. The goethite subsamples were dissolved with 4 mL of 11.5 M HCl and analyzed for P and Fe using inductively coupled plasma-optical emission spectroscopy. All desorption experiments were carried out in duplicate at a temperature of 25 ± 1°C. In all solutions, molybdate

reactive phosphate was analyzed according to Murphy and Riley (1962).

Curve Fitting and Statistical Analyses

The Johnson-Mehl or Avrami equation (Goss, 1987) given below was used to describe P desorption to various sinks as a function of time.

$$q = q_{\max}\{1 - \exp[-(kt)^n]\} \quad [1]$$

In Eq. [1], q is the amount of P desorbed at time t , q_{\max} is the maximum amount of P that can be desorbed, and k and n are constants. This equation yields a sigmoidal curve when q/q_{\max} is plotted against $\ln t$. At $t = 1$, q/q_{\max} increases with increasing k^n , and the slope of the curve increases with increasing n . Fitting of Eq. [1] to the P desorption data was done by the Simplex procedure (CoHort Software, Minneapolis, MN).

Comparison of extraction data means among soils were made with the Student's t test. In the tables, figures followed by the same letter are not significantly different at the $P = 0.05$ level. Unless otherwise stated, the term significant, when used in the text, also refers to the 0.05 level.

RESULTS AND DISCUSSION

Forms of Soil Phosphorus

Total Phosphorus

Various chemical methods used in this study that, according to literature, serve to characterize different forms of P in soils, as well as the suggested correspondence between P forms and methods are summarized in Table 2. This correspondence will be used in the following sections, taking account of the fact that P forms are not discretely separable; they rather constitute a continuum in properties and solubility.

The different P extraction data are given in Table 3. Total P in soil ranged from 705 to 1400 mg kg⁻¹, from which <25% was in organic form. Olsen P was greater than its critical limit of 10 to 20 mg P kg⁻¹ soil for common field crops. This reflects the long fertilizer application history of the fields with P doses greater than crop P uptake. It is difficult to quantify the contribution of fertilizer to total P. One possible way to estimate the amount of P in excess of plant uptake in the calcareous soils is to consider that the background Olsen P was <5 mg kg⁻¹, as it is usually observed in unfertilized soils. Then, the amount of Olsen P in excess of this value can be considered as the product of fertilizer P by the recovery factor for the Olsen extractant. If we take an average recovery factor of 0.1, as suggested by the work of Castro and Torrent (1995) for a large population of calcareous soils, the fertilizer P is $(46 - 5)/0.1 = 390$ mg kg⁻¹ for E1, $(19 - 5)/0.1 = 140$ mg kg⁻¹ for E2, and $(35 - 5)/0.1 = 300$ mg kg⁻¹ for I3, so a substantial portion of total P in the calcareous soils seems to be due to fertilization with P. The recovery factor is likely to be different in the limed acid soils, but their high Olsen P values suggest even greater values for the residual fertilizer P.

Adsorbed Phosphate

The IEP represents surface-adsorbed P. The ratio between IEP and the sum of P fractions in the OS

Table 2. Forms of soil P and their extraction.

Method†	Description of P forms
Total P	All forms of P, including structural P and P occluded in soil minerals.
Organic P	Phosphorus in organic compounds. Generally, it is defined operationally as the difference in acid-extractable P between intact and ignited samples.
IEP	Surface P, which includes the phosphate adsorbed on mineral surfaces plus some phosphate pertaining to the external layers of metal phosphates (Olsen and Khasawneh, 1980). IEP is usually measured at 1 d of exchange.
OS fractionation scheme‡	
NaOH	Phosphate adsorbed on mineral surfaces, phosphate released by the hydrolysis of Fe and Al phosphates and by the hydrolysis of phosphated organic Fe and Al complexes (Chang and Jackson, 1957; Syers et al., 1972).
CB	Labile pedogenic Ca-rich phosphates and (in calcareous soils) phosphate read-sorbed by calcite in the NaOH step (Chang and Jackson, 1957; Williams et al., 1971).
CBD	Reductant-soluble P, mostly P occluded in Fe oxides (Chang and Jackson, 1957).
HCl	Ca phosphates, including lithogenic apatite but excluding some labile pedogenic Ca phosphates that are partly dissolved in the preceding CB and CBD steps (Chang and Jackson, 1957).
Direct extractions	
Olsen P	Some portion of the labile pool of plant-available P extracted by NaHCO ₃ (Olsen et al., 1954).
CB-P	Most of the phosphate adsorbed on mineral surfaces and part of the pedogenic, relatively labile Fe, Al, and Ca phosphates (Ruiz et al., 1997).
CC-P	Most adsorbed phosphate, Ca phosphates (excluding lithogenic apatite), and (due to the citrate complexing capacity) a small proportion of the Fe and Al phosphates (Ruttenberg, 1992; Ruiz et al., 1997).
NaOH-P 	Fe and Al phosphates and phosphate adsorbed on high-affinity surfaces that is not desorbed by citrate (Chang and Jackson, 1957; Ruiz et al., 1997).

† CB, citrate-bicarbonate; CBD, citrate/bicarbonate/dithionite; CC, 0.2 M citric acid-Na-citrate at pH 6; IEP, isotopically exchangeable P.

‡ P fractionation scheme of Olsen and Sommers (1982).

|| P specifically released by NaOH = ([NaOH-P + CB-P] in the OS fractionation scheme) - CB-P (direct extraction).

fractionation scheme was 0.25 for D1, 0.18 for D2, 0.04 for E1 and E2, and 0.08 for I3 (values significantly different among soils, except for E1 and E2). This ratio indicates that the calcareous soils contain a smaller proportion of extractable P in adsorbed form than do the limed acid soils. This is consistent with the observation that P applied to calcareous soils is adsorbed not only on the high-affinity sites of the Fe and Al oxides but also on calcite surfaces, where it slowly transforms into Ca phosphates (Freeman and Rowell, 1981; Castro and Torrent, 1998). The lowest values for this ratio are found in E1 and E2, the soils with the smallest Fe and Al oxide contents, as indicated by dithionite-extractable Fe (Fe_d), and oxalate-extractable Fe and Al (Fe_o, Al_o). Much of the P applied to E1 and E2 was adsorbed on carbonate surfaces and was likely to be transformed

Table 3. Phosphorus extraction data.[†]

Soil	Total P	Organic P	IEP [‡]	Plant-available P	P released to 0.002 M CaCl ₂ [§]	P fractions				Lithogenic apatite	Olsen P	CB-P ^{‡‡} #	CC-P ^{‡‡} #	NaOH-P ^{‡‡} #
						NaOH	CB [‡]	CBD [‡]	HCl					
D1	1168	205	200	350	756	88	323	214	177	802	105	307	513	104
D2	890	221	99	160	187	127	155	157	110	549	48	159	213	123
E1	1400	30	51	79	192	8	233	120	842	1203	46	183	898	58
E2	705	135	26	26	72	4	103	42	441	590	19	76	264	31
I3	1035	145	58	53	112	15	179	130	434	758	35	77	373	117

[†] Data are means of three replicates. SE (not shown) is <6% of the mean in all cases.

[‡] CB, citrate-bicarbonate; CBD, citrate-bicarbonate-dithionite; CC, 0.2 M citric acid-Na-citrate at pH 6; IEP, isotopically exchangeable P.

[§] P released in a dilute soil suspension at 340 d (extrapolated to an equilibrium concentration of 0.01 mg P dm⁻³).

^{||} Sequential P fractionation scheme of Olsen and Sommers (1982); ∑fractions, sum of the four fractions.

[#] Direct extractions.

^{‡‡} P specifically released by NaOH = ([NaOH-P + CB-P] in the OS fractionation scheme) - CB-P (direct extraction).

into Ca phosphate. By contrast, P applied to D1 and D2 tended to remain in adsorbed form because these soils contain no carbonate and show substantially greater amounts of Fe and Al oxides than E1 and E2. Soil I3 shows an intermediate ratio because it contains carbonate but also Fe and Al oxides in proportions similar to D1 and D2. In summary, the partitioning of P applied to soil into P adsorbed on variable-charge surfaces and P precipitated as Ca phosphate seems to depend on the relative amounts of carbonate and Fe and Al oxides.

Metal Phosphates

Pedogenesis and fertilization with P result in different secondary metal phosphates precipitating in soil. In the three calcareous soils, calcium phosphates predominate over other P forms. This idea is supported by (i) the large HCl-P values, usually assigned to these minerals (Chang and Jackson, 1957), and (ii) the dramatic increase in the amount of P extracted directly by citrate when pH is changed from 8.5 (CB extractant) to 6 (CC extractant) (Table 3), consistent with the pH-dependent solubility of Ca phosphates (Lindsay, 1979). In these soils, HCl-P (Ca phosphates) was ≈80% of the sum of fractions in the OS fractionation scheme. According to the assumptions indicated in Table 2, one can estimate the amount of pedogenic Ca phosphates (i.e., excluding lithogenic apatite) in the calcareous soils by subtracting IEP from the amount of P extracted by citrate at pH 6 (CC). The resulting estimates of pedogenic Ca phosphates are 847 mg kg⁻¹ for E1, 238 mg kg⁻¹ for E2, and 315 mg kg⁻¹ for I3. The estimates for E2 and I3 are smaller than the corresponding HCl-extractable P values less lithogenic apatite, probably because HCl dissolves pedogenic Ca phosphates that are only poorly soluble at pH 6, as is the case with HA (Lindsay, 1979).

In the two limed acid soils, HCl-P is <25% of the sum of fractions in the OS scheme, so Ca or Ca-rich phosphates are secondary to other P forms. The amount of P extracted increased significantly when the pH of the extracting solution decreased from 8.5 (CB) to 6 (CC). This increase, which was 205 mg kg⁻¹ for D1 and 54 mg kg⁻¹ for D2, is likely to be due to dissolution of Ca phosphates, which are much more soluble at pH 6 than at pH 8.5 (Lindsay, 1979). However, in contrast to the Ca phosphates that precipitate in calcareous soils, these Ca phosphates are likely to include substantial amounts of Al, Fe, Si, and other elements, as noted in some acid soils by Pierzynski et al. (1990).

Phosphorus specifically extracted by NaOH, which is assigned to Fe and Al phosphates (Table 2) were >100 mg kg⁻¹ for D1, D2, and I3, but <60 mg kg⁻¹ for E1 and E2 (Table 3). This is consistent with the higher likelihood of Fe and Al phosphates precipitating in soils free of or containing little carbonate and containing significant amounts of Fe and Al oxides. Indeed, the ratio between P extracted by NaOH and the sum of fractions in the OS scheme is positively and significantly correlated with the Fe and Al oxides contents (data not shown).

Desorption of Phosphorus to Different Sinks

Equation [1] provided a good description of P desorption to different sinks. Its constants are given in Table 4 (HCO₃⁻ and Cl-saturated AER, and ACER) and Table 5 (goethite). The values of q_{max} differed widely among soils and P sinks. Generally, the ACER was the most, and goethite was the least, efficient P sink. Because $q_{max} > IEP$, sinks probably promoted dissolution of metal phosphates. This idea is consistent with the more relative effectiveness of the ACER, because the cation exchange resin reduces cation activity in solution, thus decreasing the ionic product and favoring metal phosphate dissolution. Moreover, the q_{max} values for ACER differed by <30% from CC-P, which includes a substantial portion of the metal phosphates (Table 2). The contribution of metal phosphates to the ACER- q_{max} is also supported by the lower effectiveness of goethite relative to resins. In the goethite experiments, cations were not removed from solution, so metal phosphate dissolution was hindered by the progressive increase in solution cation concentration.

The different contribution of Ca and Ca-poor phosphates to ACER-P in calcareous and limed acid soils is supported by the comparison between ACER- q_{max} (Table 4) and CC-P (Table 3). In the calcareous soils, ACER- $q_{max} < CC-P$, whereas ACER- $q_{max} > CC-P$ in the limed acid soils. This suggests that, relative to the former, the latter soils contain more Al and Fe phosphates, which are less soluble than various Ca-phosphates at pH 6 (Lindsay, 1979).

Aharoni and Sparks (1991) showed that the plot of q/q_{max} against $\ln t$ in a chemical reaction gives a sigmoid curve, which is increasingly linear and decreases in slope (i.e., the n constant of Eq. [1] decreases) with increasing reaction heterogeneity. In P desorption to ACER (the most effective P sink), both the shape of the curve (Fig. 1) and its maximum slope (calculated from Eq. [1], not shown) indicate that E1 is the least and E2 is the most heterogeneous soil. The homogeneity in the desorbable P forms in E1 probably indicates the presence of pedogenic Ca phosphates of similar solubility. This soil has been continuously and heavily fertilized, so it is likely to remain oversaturated with respect to the same Ca phosphate phase, which would be the one to precipitate. Heterogeneity in E2 may be due to the presence of Ca phosphates of widely different solubility because this soil has received less, and irregular P fertilizer than either E1 or I3. So, its solution may have been oversaturated with respect to different Ca phosphates at different times.

Data in Fig. 1 show that the two limed acid soils are intermediate between E1 and E2 in degree of homogeneity. Therefore, these soils contain P forms (Ca, Ca-containing, and Al and Fe phosphates) moderately contrasting in desorption (dissolution) rates.

The ratio of the P desorbed after the first day of reaction (q_{slow}) to q_{max} (q_{slow}/q_{max} , Tables 4 and 5), which measures the relative importance of the slow desorption, is significantly lower (higher ordinates at $\ln t = 0$, Fig. 1) for the limed acid than for the calcareous soils. So,

Table 4. Constants of equation $q = q_{max} [1 - \exp[-(kt)^n]$ for P desorption by different resins.

Soil	HCO ₃ ⁻ -AER [†]				Cl-AER [†]				ACER [‡]						
	q_{max} mg P kg ⁻¹	k	n	R^2	$q_{slow}/q_{max}^{\ddagger}$	q_{max} mg P kg ⁻¹	k	n	R^2	$q_{slow}/q_{max}^{\ddagger}$	q_{max} mg P kg ⁻¹	k	n	R^2	$q_{slow}/q_{max}^{\ddagger}$
D1	423	0.65	0.41	0.99***	0.43a	434	2.48	0.43	0.99***	0.25a	621	3.80	0.47	0.99***	0.15a
D2	285	0.15	0.30	0.99***	0.56b	147	0.80	0.36	0.99***	0.39b	300	1.33	0.48	0.99***	0.48b
E1	416	0.13	0.45	0.99***	0.66c	719	0.01	0.30	0.99***	0.81c	882	0.53	0.74	0.99***	0.52c
E2	197	0.25	0.47	0.99***	0.58b	117	0.05	0.33	0.99***	0.68d	208	0.08	0.33	0.99***	0.63d
I3	180	0.19	0.42	0.99***	0.60bc	146	0.31	0.37	0.98***	0.52f	301	0.39	0.64	0.99***	0.61cd

*** Significant at the 0.001 probability level.

† ACER, mixed anion and cation exchange resin; AER, anion exchange resin.

‡ q_{slow} = amount of P desorbed after 1 d. In this column, values followed by the same letter are not significantly different at the 0.05 probability level.

Table 5. Constants of equation $q = q_{\max} \{1 - \exp[-(kt)^n]\}$ for P desorption by goethite.

Soil	q_{\max}	k	n	R^2	$q_{\text{slow}}/q_{\max}^\dagger$
	mg P kg ⁻¹				
D1	475	0.54	0.70	0.93***	0.39a
D2	162	0.44	0.67	0.97***	0.48ab
E1	138	0.38	0.57	0.79***	0.52ab
E2	67	0.26	0.58	0.84***	0.63bc
I3	66	0.29	0.64	0.89***	0.61bc

*** Significant at the 0.001 probability level.

† q_{slow} = amount of P desorbed after 1 d. In this column, values followed by the same letter are not significantly different at the 0.05 probability level.

the limed acid soils (particularly D1) showed a greater proportion of quickly desorbed P than did the calcareous soils. Firstly, this can be attributed to the greater proportion of surface P in the limed acid soils. Secondly, the concentration of P in solution (Table 3) was higher for the limed acid than for the calcareous soils, which indicates that the former contained more phosphate adsorbed on sites of lower affinity, and thus more easily desorbed than the latter.

By subtracting IEP from ACER-P at 1 d, one can estimate the amount of metal phosphates that are readily dissolved in a system with effective ion sinks. This yields 326 mg kg⁻¹ for D1, 106 mg kg⁻¹ for D2, 359 mg kg⁻¹ for E1, 47 mg kg⁻¹ for E2, and 69 mg kg⁻¹ for I3. If we then subtract from these values the corresponding amounts of pedogenic Ca phosphates estimated above, we obtain 121 mg kg⁻¹ for D1, 52 mg kg⁻¹ for D2, -488 mg kg⁻¹ for E1, -191 mg kg⁻¹ for E2, and -246 mg kg⁻¹ for I3. These contrasting, significantly different figures suggest that the metal phosphates of limed acid soils (Fe and Al phosphates and/or Ca phosphates) dissolve faster than the Ca phosphates of calcareous soils.

Available Phosphorus in Relation to Phosphorus Forms

The limed acid soils contained more plant-available P than the calcareous soils. Plant-available P constituted >50 and <20% of the ACER- q_{\max} in the former and latter soils, respectively. This can be attributed to (i) the greater content in surface P (as estimated by IEP) of the former relative to the latter soils and (ii) the aforementioned idea that the metal phosphates in the limed acid soils are more soluble, and thus can supply more P to plants, than the Ca phosphates in the calcareous soils. This is further supported by the fact that the excess of plant-available P over IEP is significant only for the limed acid soils (150 mg kg⁻¹ for D1 and 61 mg kg⁻¹ for D2) and E1 (28 mg kg⁻¹); albeit in the latter soil this excess is only 3% of the ACER- q_{\max} . The differences in Ca phosphate homogeneity and rate of dissolution between E1 and I3, on one side, and E2 on the other do not seem, therefore, to be reflected in major differences in plant availability.

The high correlation between plant-available and Olsen P ($r = 0.98$; $P < 0.01$) is consistent with the good performance of Olsen's test in neutral and alkaline soils as an indicator of plant-available P. However, the ratio Olsen P/plant-available P is significantly higher in the

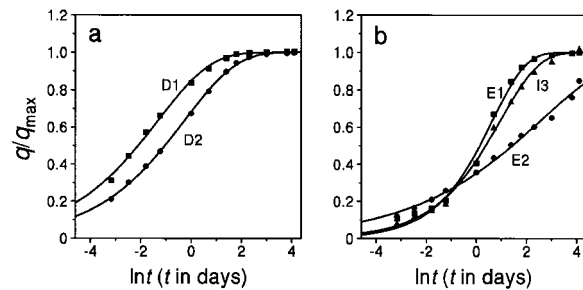


Fig. 1. Time course of P desorption to mixed cation and anion exchange resins (ACER), plotted as the ratio between the amount of P desorbed (q) and the maximum amount of desorbable P (q_{\max}) against $\ln t$ for (a) the limed acid and (b) the calcareous soils. The q_{\max} value was calculated by fitting the Johnson-Mehl equation to the data.

calcareous than in the limed acid soils (means of 0.30 and 0.66, respectively). This suggests that bicarbonate tends to somewhat overestimate plant-available P in the former, probably by dissolving a portion of some plant-unavailable Ca phosphates.

The amount of P released to 0.002 M CaCl₂ (Table 3) was significantly greater than plant-available P for all soils except D2. This is probably due to the lower phosphate and Ca concentrations in the 0.002 M CaCl₂ relative to the soil solution, which results in more desorption of adsorbed phosphate and dissolution of metal phosphates in 0.002 M CaCl₂. Finally, P released to 0.002 M CaCl₂ constituted a greater proportion of the ACER- q_{\max} in the limed acid than in the calcareous soils (1.22 for D1, 0.62 for D2, 0.22 for E1, 0.35 for E2, and 0.37 for I3; all values are significantly different except those of E2 and I3). This is likely to be caused by the lower solubility of the Ca phosphates in the calcareous soils relative to the metal phosphates in the limed acid soils and by the presence of Ca in the equilibrium solution.

SUMMARY AND CONCLUSIONS

The calcareous soils (E1, E2, and E3) contain less surface P than the limed acid soils (D1 and D2), probably because of differences in the extent and nature of the P-adsorbing surfaces. Substantial amounts of metal phosphates have accumulated in all soils as a result of pedogenesis and P fertilizer application in excess of plant uptake. Aluminum and Fe phosphates predominate in the limed acid soils and Ca phosphates in the calcareous soils. One limed acid soil (D1) contains substantial amounts of Ca or Ca-rich phosphates.

The ACER was a more effective sink than AER and goethite to desorb P. Phosphate desorption kinetics were described by the Johnson-Mehl equation, which indicated that the degree of homogeneity of P forms differed among soils. Seemingly, pedogenic Ca phosphates of similar solubility predominate in E1, whereas E2 contains balanced amounts of Ca phosphates of different solubility. The limed acid soils and I3 are intermediate in degree of homogeneity of the P forms.

Plant-available P was >50 and <20% of the ACER-extractable P in the limed acid and the calcareous soils, respectively. This difference can be partly attributed to

the higher solubility of some metal (Fe and Al and/or Ca) phosphates in the limed acid soils relative to the Ca phosphates in the calcareous soils. Plant-available P was highly correlated with Olsen P, but Olsen's extractant tended to overestimate plant-available P in the calcareous relative to the limed acid soils. The amount of P released to 0.002 M CaCl₂ was greater than plant-available P and represented >60 and only <40% of the ACER-extractable P in the limed acid and calcareous soils, respectively.

In summary, the metal (Fe, Al, and Ca) phosphates present in the limed acid soils are more soluble than the Ca phosphates of the calcareous soils. This makes the calcareous soils inferior to the limed acid soils in terms of plant availability of soil P.

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