/ / 0 2

0038-075C/03/16805-368–375
Soil Science
Copyright © 2003 by Lippincott Williams & Wilkins, Inc.

May 2003
Vol. 168, No. 5
Printed in U.S.A.

PHOSPHATE SORPTION BY PACIFIC NORTHWEST CALCAREOUS SOILS

A.B. Leytem and D.T. Westermann

Understanding phosphorus (P) sorption of calcareous soils is important for the development of successful fertilizer and manure management practices. This study was conducted to identify soil chemical properties controlling P sorption in semiarid calcareous soils of the Pacific Northwest. Sorption isotherms of 18 primarily calcareous soils ranging widely in soil physical and chemical properties were constructed by equilibrating 4 g of soil with 40 mL of 0.01M $CaCl_2$ containing between 0 and 700 mg P L^{-1} for 24 h. The P sorption isotherms at low to medium P concentrations fit the Freundlich isotherm ($r^2 \geq 0.93$). The slope of the isotherm generally increased abruptly at high P concentrations, suggesting Ca-P precipitation. The maximum P sorption prior to Ca-P precipitation was closely related to organically complexed Fe and Mn ($R^2 > 0.98$), suggesting that such complexes may regulate P sorption in these soils. The equilibrium P concentration at the point where Ca-P precipitation begins to dominate was closely related to pH and organic carbon. A better understanding of the role of organically complexed metals in controlling P sorption in calcareous soils is needed to determine how P solubility is affected by organic matter additions and how this will ultimately impact the plant availability and potential off-site transport of P from these soils. (Soil Science 2003;168:368–375)

Key words: phosphorus, calcareous soils, organic matter, NTA-extractant.

IN the arid agricultural region of the Pacific Northwest, the accumulation of calcium carbonate ($CaCO_3$) is believed to govern soil P reactions, whereas in acid soils, P solubility is controlled by Fe and Al (Lindsay, 1979). Sharpley et al. (1984) found that extractable P was negatively correlated to $CaCO_3$ concentrations following addition of fertilizer to 20 calcareous soils. In addition, the decrease in P availability between 30 and 180 days after fertilizer application was correlated to $CaCO_3$ content (Sharpley et al., 1989). In contrast, some studies have found that P sorption in calcareous soils is more closely related to iron oxide and clay content (Hamad et al., 1992; Ryan et al., 1985; Solis and Torrent, 1989), as well as to aluminum oxides (Castro and Torrent, 1998), than to $CaCO_3$ content. Furthermore, Robbins et al. (2000) found that the addition of organic carbon as manure or other waste products seemed to enhance the solubility and extractability of added ortho- and organic-P. Thus, it becomes apparent that there may be many mechanisms regulating P sorption and solubility in calcareous soils.

The objective of this study was to identify soil properties related to sorption and precipitation of applied phosphate in calcareous Pacific Northwest agricultural soils. We use the term *phosphate sorption* to encompass all processes that remove P from solution (e.g., surface adsorption and precipitation). A wide range of solution P concentrations were used to maximize the amount of P sorbed by the soils and to determine the effects of varying soil properties on the P-sorption processes.

MATERIALS AND METHODS

Eighteen soil samples were taken from surface (0–30 cm) horizons of mainly arid, calcare-

USDA-ARS, NWISRL, 3793N 3600E Kimberly, ID, 83341. Dr. Leytem is corresponding author. E-mail: leytem@nwisrl.ars.usda.gov

Received Oct 30, 2002; accepted Feb. 3, 2003.

DOI: 10.1097/01.ss.0000070911.55992.0e

ous agricultural soils in the Pacific Northwest region. Many of the soil samples collected are not currently mapped and, therefore, soil series information was not available. Samples were air-dried and ground to pass through a 2-mm sieve prior to analysis.

Soil Analysis

Particle size was determined by the hydrometer method (Gee and Bauder, 1986). Organic carbon (OC) was determined using the method of Walkley and Black (1934). pH was measured in a saturated paste using a combination electrode (Robbins and Wiegand, 1990). Cation exchange capacity (CEC) was obtained by saturation with 1*M* NaOAc at pH 7, followed by ethanol washing, Na displacement with NH_4OAc, and analysis of Na by AA (United States Salinity Laboratory Staff, 1969). Calcium carbonate equivalent (CCE) was determined with the titrimetric method of Allison and Moodie (1965). Sodium bicarbonate extractable P was determined using the method of Olsen et al., (1954). Oxalate-extractable Fe (Fe_{ox}), Al (Al_{ox}), and Mn (Mn_{ox}) were obtained by extraction with 0.2*M* ammonium oxalate at pH 3 to obtain a measure of the amorphous Fe, Al, and Mn in the soils (Jackson et al., 1986). Organically complexed Fe (Fe_{nta}), Al (Al_{nta}), and Mn (Mn_{nta}) were obtained by extraction with 0.1*M* sodium nitrilotriacetate (NTA) at pH 8.3, with a soil solution ratio of 1:200 and filtration through 0.45 μm (Yuan et al., 1993). Oxalate and NTA extractable Fe, Al, and Mn were quantified by ICP-OES detection. Other soil properties measured included: citrate-dithionate extractable Fe; total Al, Fe, and Ca by microwave digestion in acid; and soluble Ca and Mg in a saturated paste as well as electrical conductivity. However, these properties were not correlated to P sorption and are, therefore, not presented in this paper.

Sorption Isotherms

Phosphate sorption isotherms were obtained by mixing 4 g of soil with 40 mL of 0.01 *M* $CaCl_2$ containing varying amounts of KH_2PO_4 for 24 h at a constant temperature of 22 °C. The initial P concentrations in the $CaCl_2$ solutions were 0, 1.25, 5, 12.5, 25, 50, 75, 100, 200, 300, 500, and 700 mg P L^{-1}. After agitation, the suspensions were allowed to settle for 30 min, and an aliquot was then filtered (0.45 μm) and analyzed for P by ICP-OES. The amount of phosphate sorbed was calculated from the difference between initial and final quantities of P in solution. All isotherms were performed in duplicate.

Sorption parameters were calculated using the Freundlich isotherm as follows: $q = Ac^b$, where q is the amount of P found in the solid phase of a soil at concentration c, and A and b are positive-valued parameters, with b constrained to lie between 0 and 1. The parameters A and b are estimated by plotting log q against log c. Log A and b are calculated as the y intercept and slope, respectively, of the linear regression between log q and log c (Sposito 1989). Freundlich isotherms were calculated for soils at low to medium P concentrations (equilibrium P concentrations of 0 to 150 mg P L^{-1}) as the equation does not apply to adsorption data obtained for high values of c (Sposito, 1984).

Statistics

All statistical analyses were performed using the PROC REG procedure in SAS (SAS Institute, 1989). Relationships significant at the 0.05, 0.01, and 0.001 probability levels are marked in the text as *, **, and ***, respectively.

RESULTS

Soil Properties

The soils examined in this study varied widely in the chemical properties that commonly affect P sorption in soils (Tables 1 and 2). Clay and OC concentrations ranged from 0 to 246 g kg^{-1} and from 0.4 to 25.7 g kg^{-1}, respectively. Most of the

TABLE 1

Selected soil properties

Soil No.	Clay	OC†	pH	CEC‡	CCE§
	—— g kg^{-1} ——			$cmol_c kg^{-1}$	g kg^{-1}
1	146	13.5	7.9	14	496.0
2	162	8.0	7.5	22	19.7
3	132	8.2	7.9	14	114.3
4	246	5.3	6.4	16	40.0
5	157	25.7	4.9	18	0.0
6	62	4.3	7.1	13	13.7
7	145	13.0	7.6	19	91.0
8	0	0.4	8.6	5	15.0
9	40	5.4	7.6	13	18.3
10	35	4.2	6.8	11	11.0
11	110	16.0	7.7	19	38.0
12	155	2.6	7.8	12	86.0
13	180	7.5	7.6	16	170.0
14	125	6.4	7.5	14	186.0
15	115	9.4	7.7	19	25.0
16	130	11.8	7.9	20	55.0
17	25	5.0	7.3	7	5.0
18	120	6.6	7.8	17	12.0

†Organic carbon

‡Cation-exchange capacity

§Calcium carbonate equivalent

TABLE 2

Soil properties related to phosphorus and phosphorus sorption

Soil No.	Olsen P†	Al_{ox}‡	Fe_{ox}‡	P_{ox}‡	Mn_{ox}‡	Al_{nta}§	Fe_{nta}§	Mn_{nta}§	P_{nta}§
	mg kg^{-1}				g kg^{-1}				
1	18.8	0.96	0.97	0.46	0.25	0.54	0.46	0.29	0.23
2	28.0	1.02	2.02	0.40	0.40	0.77	0.62	0.25	0.19
3	12.6	0.78	0.59	0.36	0.20	0.46	0.30	0.20	0.22
4	19.0	0.74	0.56	0.27	0.32	0.64	0.44	0.19	0.08
5	67.8	1.30	1.98	0.45	0.46	1.11	1.03	0.30	0.22
6	9.3	0.62	1.64	0.26	0.26	0.14	0.19	0.06	0.04
7	45.7	0.79	0.65	0.45	0.36	0.19	0.14	0.29	0.24
8	1.2	0.34	0.75	0.13	0.09	0.26	0.26	0.03	0.05
9	12.2	0.66	0.99	0.24	0.19	0.26	0.28	0.08	0.07
10	31.7	0.56	2.05	0.43	0.17	0.31	0.61	0.08	0.14
11	25.1	0.77	0.55	0.47	0.33	1.18	0.80	0.32	0.41
12	2.8	0.43	0.55	0.28	0.16	2.35	1.35	0.14	0.14
13	4.0	0.65	0.45	0.32	0.24	0.85	0.50	0.27	0.16
14	51.1	0.65	0.58	0.43	0.18	0.43	0.30	0.21	0.32
15	41.8	0.92	0.29	0.47	0.31	0.32	0.16	0.23	0.43
16	51.9	0.98	0.60	0.45	0.37	0.32	0.16	0.24	0.29
17	14.5	0.27	0.75	0.13	0.13	0.16	0.15	0.07	0.15
18	24.1	0.76	0.55	0.24	0.30	0.66	0.39	0.19	0.16

†Bicarbonate extractable phosphorus

‡Al_{ox}, Fe_{ox}, Mn_{ox}, P_{ox} ammonium oxalate extractable Al, Fe Mn, P

§Al_{nta}, Fe_{nta}, Mn_{nta}, P_{nta} NTA extractable Al, Fe, Mn, P

soils had a pH greater than 7.0; there was one acidic soil (pH 4.9). The CEC ranged from 5 to 22 $cmol_c$ kg^{-1}, and the $CaCO_3$ equivalent of the soils varied from 0 to 496 g kg^{-1}. Bicarbonate extractable P (Olsen P) ranged from 1.2 to 51.9 mg kg^{-1}. Amorphous Al, Fe, Mn, and P concentrations varied from 0.27 to 1.30 g kg^{-1}, 0.29 to 2.02 g kg^{-1}, 0.09 to 0.46 g kg^{-1}, and 0.13 to 0.47 g kg^{-1}, respectively. Organically complexed Al, Fe, Mn, and P (NTA-extractable) varied from 0.16 to 2.35 mg kg^{-1}, 0.14 to 1.35 mg kg^{-1}, 0.03 to 0.32 mg kg^{-1}, and 0.04 to 0.43 mg kg^{-1}, respectively.

P-Sorption Isotherms

Figure 1 shows the P-sorption curves for three soils of dissimilar behavior. The P-sorption isotherms for all soils at low to medium equilibrium P concentrations (0–150 mg P L^{-1}) fit the Freundlich isotherm well ($r^2 = 0.926$–0.998; $P < 0.01$). At equilibrium concentrations greater than 150 mg P L^{-1}, there was a difference in the relationship between log q and log c. The majority of the soils studied (11 soils) had P-sorption isotherms similar to Soil 1 (Fig. 1a), where at equilibrium concentrations greater than 150 mg P L^{-1} there was a sharp increase in the slope of the curve, suggesting that the precipitation of Ca-P dominated the process (Cole et al., 1953; Fig. 1a and Fig. 2). The change in slope at this inflection point was pronounced in Soils 12, 14, and 16 (Fig. 1b), with a curve similar to an S-type curve, which may suggest different precipitation products. Three soils did not have an abrupt change in slope, although there seemed to be a difference in the curve at low versus high equilibrium P concentrations (Soils 2, 9, and 15; Fig. 1c). In Soil 10, the sorption curve was an L-type curve at low concentrations, reached a maximum, and then abruptly decreased in sorption.

Figure 2 shows P sorption isotherms plotted on logarithmic scales for two soils that vary in their sorption properties and the properties measured in order to establish the nature of the sorption processes. The initial region of the curves was essentially linear, conforming to a Freundlich equation. The slope b of the initial region was determined by linear regression. The equilibrium P concentration (C_t) was determined at the inflection point where the curve increased abruptly and the corresponding amount of P sorbed (X_t) at C_t was determined (Fig. 2a). Two of the soils did not have an inflection point on the log-log plots of the data, and, therefore, we were unable to calculate the C_t and X_t values for these soils; b values for these soils were calculated as before (Soils 9 and 10; Fig. 2b).

The values of the Freundlich and related parameters for the 18 soils are listed in Table 3. The

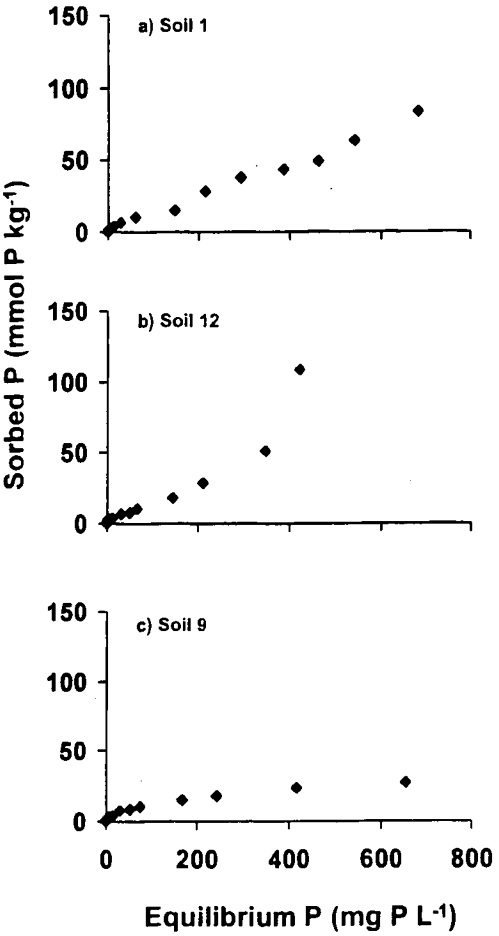

Fig. 1. P-sorption isotherms for selected soils with varying sorption characteristics; a) Soil 1, b) Soil 12, and c) Soil 9.

Freundlich A value varied from 0.6 to 1.6 (mean 1.2, standard deviation (SD) 0.51), and the *b* value varied from 0.34 to 0.71 (mean 0.52, SD 0.10). The equilibrium P concentration at which precipitation processes seemed to dominate the sorption process (C_t) varied from 49 to 619 mg P L^{-1} (mean 173, SD 145), whereas the amount of P sorbed at C_t (X_t) ranged from 4 to 32 mmol kg^{-1} (mean 17, SD 8).

Pearson correlation coefficients were calculated between the various parameters of the P-sorption curves and soil properties for all soils studied (except in the case of C_t and X_t where these values could not be determined on two of the soils; Table 4). These correlations were also performed on the subset of 11 soils that had similarly shaped curves (Table 4). The slope of the initial region of the isotherms (*b*) and the y-intercept (A) were not correlated with any soil property. The concentration C_t where precipitation begins to dominate the sorption process was significantly correlated to OC and pH in the 16 soils and was significantly correlated to OC, pH, Al_{ox}, Mn_{ox}, and Fe_{nta} in the subset of 11 soils. The amount of P sorbed (X_t) at the inflection point was significantly correlated to OC, CEC, Al_{ox}, Mn_{ox}, and Mn_{nta} in the 16 soils and to OC, CEC, clay, Al_{ox}, Mn_{ox}, Al_{nta}, Fe_{nta}, and Mn_{nta} in the subset of 11 soils.

Forward stepwise regressions were performed for C_t and X_t with a listing of all independent variables measured for the subsets of 16 and 11 soils. The stepwise regressions on the subset of 16 soils selected the equations $C_t = 1335.5 - 155.9$ pH ($R^2 = 0.78^{***}$) and $X_t = 1.1 + 0.08\ Mn_{nta}$ ($R^2 = 0.68^{***}$). The stepwise regressions on the subset of 11 soils selected the equations $C_t = 994.1 - 115.6\ pH + 0.18\ Fe_{nta}$ ($R^2 = 0.93^{***}$) and $X_t = 0.46 + 0.01\ Fe_{nta} + 0.06\ Mn_{nta}$ ($R^2 = 0.98^{***}$). The measure of X_t in these instances may not be a true representation of the maximum amount of P sorbed, because it does not include a measurement of initial P present before

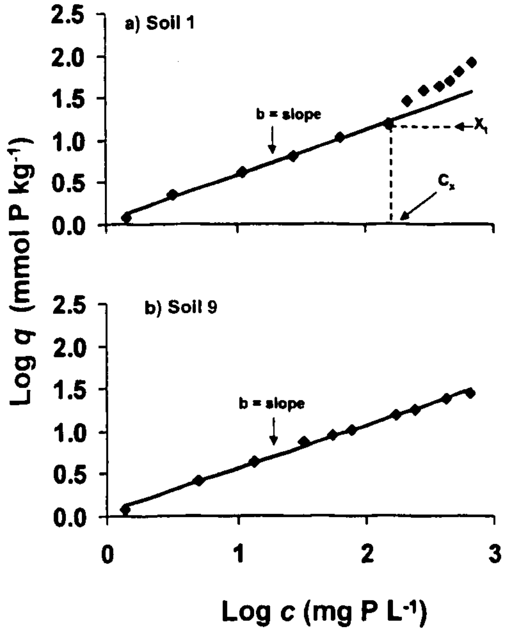

Fig. 2. Log-log plot of P-sorption isotherms for selected soils and measured properties of the log-log plot: a) Soil 1 and b) Soil 9.

TABLE 3

Values of the phosphate sorption curve parameters

Soil No.	Values of curve parameters				
	A	b	r^2	C_t	X_t
	mmol kg^{-1}			mg L^{-1}	mmol kg^{-1}
1	1.1	0.53	0.99	150	22
2	0.8	0.61	0.99	94	14
3	1.6	0.49	0.99	131	15
4	1.4	0.42	0.99	371	15
5	2.2	0.46	0.98	619	28
6	1.1	0.34	0.99	169	9
7	0.8	0.53	0.99	150	17
8	0.6	0.44	0.93	95	4
9	1.1	0.51	0.99	NC	NC
10	0.9	0.46	0.98	NC	NC
11	0.9	0.58	0.99	263	26
12	1.5	0.42	0.99	69	9
13	2.3	0.51	0.99	126	22
14	1.8	0.60	0.99	49	18
15	0.8	0.71	0.99	94	20
16	0.8	0.69	0.99	56	32
17	0.7	0.41	0.93	187	5
18	0.8	0.60	0.99	166	16

equilibration with added P. To account for the initial P present in the soils and examine the relationship between the estimated total P sorbed and soil characteristics, we added two measurements of initial soil P to X_t to provide an estimate of total P sorbed. Olsen P, which is correlated to Al_{ox}, Mn_{ox}, and OC, was added to X_t to give an estimate of total P sorbed. Since Olsen P is highly correlated with the characteristics predicted to affect P sorption, we felt that this might be a good estimate of initial P. We then used the formula $X_t + P_{nta} + 0.5P_{ox}$ to provide another measure of total sorbed P. Since the organically complexed metals seem to be best correlated to P sorption, the P associated with these metals was added to X_t as well as a fraction of the oxalate extractable P. Laboratory tests examining the potential overlap between the ammonium oxalate extractable metals and NTA extractable metals showed little overlap in extraction for Al and Fe, but the extracts did have a common pool of Mn and P (Fig. 3). When soils were extracted with NTA before extraction with ammonium oxalate, there was little change in oxalate extractable Fe and Al in soils with low organic matter content compared with those extracted in ammonium oxalate alone. Soil 5, which has a greater OC content (27.5 g kg^{-1}), did show some overlap between the two pools. The P and Mn concentrations in the ammonium oxalate extracts were approximately 40 to 50% less when the soils were first extracted with NTA. This suggests that there is a labile pool of P and Mn that is subject to extraction by both methods and is common between the two. To avoid overestimating total initial P associated with amorphous and organically complexed metals, we added the P_{nta} and 50% of the P_{ox} to X_t to account for this overlap.

Forward stepwise regressions calculated using these new values of total sorbed P (X_t + Olsen P and $X_t + P_{nta} + 0.5P_{ox}$) on the subset of 11 soils selected Mn_{nta} and Fe_{nta} as independent variables for X_t + Olsen P, and Mn_{nta}, Fe_{nta}, and clay for $X_t + P_{nta} + 0.5P_{ox}$ (Table 5).

TABLE 4

Pearson correlation coefficients (r) between two parameters of the P-sorption isotherms and soil properties for soils with definable values (n = 16) and soils with similar curve shapes (n = 11).

Soil Property‡	Parameter of the curve†			
	C_t (n = 16)	X_t (n = 16)	C_t (n = 11)	X_t (n = 11)
OC	0.65**	0.78***	0.71*	0.85***
Clay	0.27 NS	0.48 NS	0.41 NS	0.65**
pH	−0.89***	−0.28NS	−0.94***	−0.43 NS
CEC	0.16 NS	0.72**	0.39 NS	0.83***
Al_{ox}	0.42 NS	0.78***	0.67*	0.85***
Fe_{ox}	0.34 NS	−0.01 NS	0.60 NS	0.15 NS
Mn_{ox}	0.49 NS	0.71**	0.73**	0.77**
Al_{nta}	0.16 NS	0.09 NS	0.59 NS	0.85***
Fe_{nta}	0.36 NS	0.14 NS	0.77**	0.82**
Mn_{nta}	0.27 NS	0.85***	0.36 NS	0.95***

†Significant at * $P < 0.05$, ** $P < 0.01$ and *** $P < 0.001$, respectively

NS = not significant

‡Abbreviation as in Table 1

DISCUSSION

The dominant P sorption processes in the initial region of the sorption curves are likely to be associated with variable charged surfaces such as oxides, clay surfaces, and organically complexed metals, but there was no indication of an interaction with $CaCO_3$. This is particularly true when a discernable inflection point between sorption and probable Ca-P precipitation was present, as seen in the subset of 11 soils. These findings are similar to those of other studies on calcareous soils, where the calculated sorption at the inflection point was significantly correlated with oxides and clays rather than with varying amounts of $CaCO_3$ (Castro and Torrent, 1998; Zhou and Li, 2001). The steep slopes of the

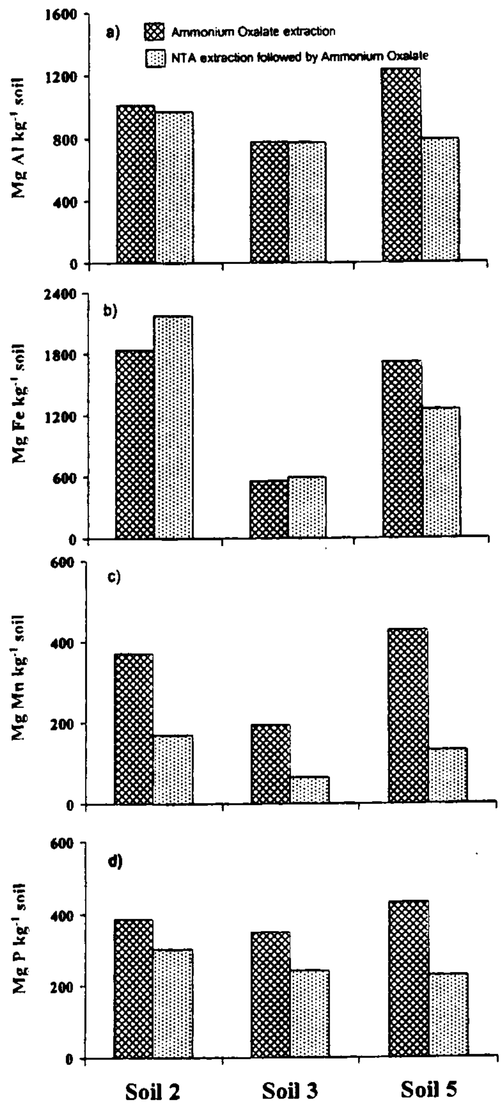

Fig. 3. Comparison of extractable a) Al, b) Fe, c) Mn, and d) P with Ammonium oxalate extraction vs pretreatment with NTA and subsequent extraction with Ammonium oxalate.

TABLE 5

Stepwise regression independent variables selected for the subset of 11 soils

Total P sorption estimates†	Regression parameters	R^2‡
X	Mn_{nta}, Fe_{nta}	0.98***
X + Olsen P	Mn_{nta}, Fe_{nta}	0.98***
X + P_{nta} + 0.5 P_{ox}	Mn_{nta}, Fe_{nta}, clay	0.98***

†Abbreviation as in Table 1

‡Significant at *** $P < 0.001$

isotherms after the inflection point can probably be attributed to the precipitation of Ca-phosphates. Studies of pure calcium carbonate-phosphate systems indicate that at low P concentrations, there is surface adsorption of P on $CaCO_3$ surfaces, with a curve shape similar to a Langmuir monolayer sorption isotherm, and the P sorbed on these surfaces is easily exchangeable (Boischot, 1950; Cole et al., 1953). At high P concentrations there is a sharp change in the calcium concentration where precipitation occurs; P sorbed in this phase is mostly nonexchangeable. The higher concentrations required for precipitation indicate that a degree of nucleation is necessary before precipitation becomes appreciable.

Regression analysis of X_t as well as two measurements of total sorbed P consistently list organically complexed Fe and Mn as the main factors affecting the P sorption capacity. The relationship between organically complexed Fe + Mn and the P sorption maximum is most closely fitted with a quadratic equation (r^2 = 0.93***, Fig. 4). Although regression does not elucidate actual interactions of soil properties, the continual selection of organically complexed metals does suggest that these metals are an important component of P sorption at low to medium P concentrations. This may be caused by P complexation with organic matter through metal bridges, or OC may be interfering with Ca-P and metal oxide precipitation by coating the surfaces of carbonates and retaining P in these surface complexes through metal interactions.

The value of C_t, the threshold concentration needed for Ca-P precipitation, was greater in all soils than the corresponding threshold needed for precipitation in pure $CaCO_3$ systems ($>3 \times 10^{-4}$ *M*) (Cole et al., 1953). This behavior was

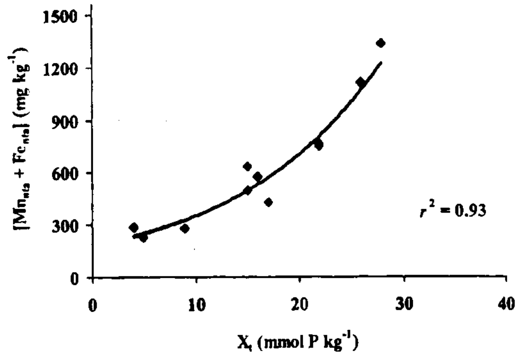

Fig. 4. Relationship in soils of [Mn_{nta} + Fe_{nta}] to X_t for the subset of 11 soils.

also seen by Castro and Torrent (1998) in calcareous Vertisols and Inceptisols, suggesting that some soil components interfere with the nucleation of Ca-phosphates in solution or on the mineral surfaces to delay the precipitation reaction. In the 16 soils evaluated, C_t was significantly correlated to OC, whereas in the subset of 11 soils it was significantly correlated to OC, Al_{ox}, Mn_{ox} and Fe_{nta}. The positive correlation of C_t to OC suggests that either soluble OC or OC associated with the $CaCO_3$ surfaces may be interfering with precipitation of Ca-phosphates at low P concentrations in these soils. Inskeep and Silvertooth (1988) showed that OC slowed the rate of precipitation of Ca-phosphates from solution. They found that humic and fulvic acids inhibited hydroxyapatite (HAP) precipitation by the adsorption of OC onto the seed crystals. Furthermore, it was only necessary to have fractional surface coverage of the seed crystals to inhibit HAP precipitation sufficiently. The formation of Al and Mn oxide coatings formed on the calcium carbonate surfaces may hinder precipitation of Ca-P, but they also serves as sorption sites. Blokhuis et al. (1968) found that impregnation of carbonates by Fe and Mn oxides are common in some calcareous Vertisols. Hamad et al. (1992) also found that Fe oxide coatings on $CaCO_3$ were prevalent and more involved in P sorption than the $CaCO_3$ in the soils studied.

Regression analysis of C_t identified pH as the factor controlling potential precipitation of Ca-P in these soils. It is not likely that pH controls this process by itself. As pH increased in these soils, the equilibrium concentration needed to initiate Ca-P precipitation decreased (Fig. 5). This relationship is likely dictated by the continual deprotonation of the OC functional groups and hydroxide groups on the carbonate surfaces as pH increases, which creates a negative charge on both the carbonate surfaces and organic matter, causing electrochemical repulsion. Essentially, as pH is increased, the interactions between carbonate surfaces and organic matter decrease, thereby reducing interference from OC in the Ca-P precipitation process.

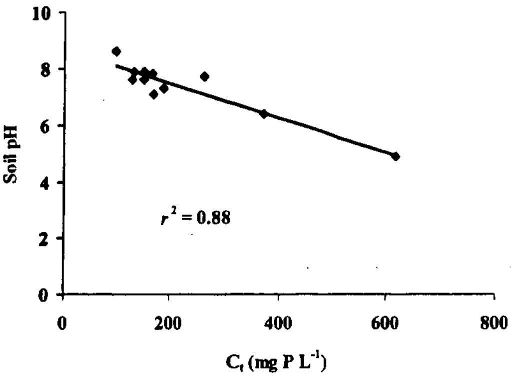

Fig. 5. Relationship in soils of soil pH to C_t for the subset of 11 soils.

In summary, both amorphous and organically complexed metals seemed to be more important to P sorption than $CaCO_3$ concentration in the soils studied. In addition, these organically complexed and amorphous metals were involved in the inhibition of Ca-P precipitation. What is unclear is the role that organically complexed metals play in the sorption of P and the possible interference with Ca-P precipitation. It is possible that OC-metal complexes in solution interact with soluble P, forming a cationic bridge between the OC and P and thus removing it from solution. It is also possible that these OC-metal associations exist on the surfaces of carbonates, clays, and possibly even amorphous metals, thereby providing sites for sorption of P.

By better understanding what soil properties are affecting P sorption, as well as the inflection point at which Ca-P precipitation processes begin to control P solubility, we will be better able to predict the potential P release for plant uptake or loss through surface runoff and leaching. If organic materials are added as a nutrient source, it is beneficial to know at what concentrations they can be applied in order to maximize plant uptake of P while reducing the formation of insoluble Ca-P minerals. On the other hand, when manure or other organic materials containing P are land applied strictly for disposal, we may want to manage their application to promote precipitation of stable P complexes and, therefore, lessen the amount of P potentially lost in runoff and leaching.

REFERENCES

Allison, L. E., and C. D. Moodie. 1965. Carbonate. *In* Methods of Soil Analysis, Part 1, 1st Ed. C.A. Black et al. (eds.). Am. Soc. Agron., Madison, WI, pp. 1379–1396.

Blokhuis, W. A., T. Pape, and S. Slager. 1968. Morphology and distribution of pedogenic carbonate in some Vertisols of the Sudan. Geoderma 2:173–200.

Boischot, P., M. Coppenet, and J. Herbert. 1950. Fixation de l'acide phosphorique sur le calcaire des sols. Plant Soil 2:311.

Castro, B., and J. Torrent. 1998. Phosphate sorption by calcareous Vertisols and Inceptisols as evaluated from extended P-sorption curves. Eur. J. Soil Sci. 49:661–667.

Cole, C. V., S. R. Olsen, and C. O. Scott. 1953. The nature of phosphate sorption by calcium carbonate. Soil Sci. Soc. Am. Proc. 17:352–356.

Gee, G. W., and J. W. Bauder. 1986. Particle size analysis. *In* Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods. Am. Soc. Agron., Madison. WI., pp. 383–411.

Hamad, M. E., D. L. Rimmer, and J. K. Syers. 1992. Effect of iron oxide on phosphorus sorption by calcite and calcareous soils. J. Soil Sci. 43:273–281.

Inskeep, W. P., and J. C. Silvertooth. 1988. Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic, and tannic acids. Soil Sci. Soc. Am. J. 52:941–946.

Jackson, M. L., C. H. Lim, and L. W. Zelazny. 1986. Oxides, hydroxides, and aluminosilicates. *In* Methods of Soil Analysis, Part 1, 2nd Ed. Agron. Monogr. No. 9. A. Klute (ed.). ASA and SSSA, Madison, WI, pp. 101–150.

Lindsay, W. L. 1979. Chemical Equilibria in Soils. John Wiley & Sons, New York.

Olsen, S. R., C. V. Cole, F. S. Watatanabe, and L. A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ 939. US Govt. Print. Office, Washington, DC.

Robbins, C. W., L. L. Freeborn, and D. T. Westermann. 2000. Organic phosphorus source effects on calcareous soil phosphorus and organic carbon. J. Environ. Qual. 29:973–978.

Robbins, C. W., and C. L. Wiegand. 1990. Field and laboratory measurements. *In* K.K. Tanji (ed.). Agricultural Salinity Assessment and Management. Am. Soc. Civil Eng., New York, pp. 201–219.

Ryan, J., D. Curtin, and M. A. Chema. 1985. Significance of iron oxides and calcium carbonate particle size in phosphate sorption by calcareous soils. Soil Sci. Soc. Am. J. 49:74–76.

SAS Institute. 1989. SAS/GRAPH User's Guide, Version 5 edition. SAS Inst., Cary, NC.

Sharpley, A. N., C. A. Jones, C. Gray, and C. V. Cole. 1984. A simplified soil and plant phosphorus model: II. Prediction of labile, organic, and sorbed phosphorus. Soil Sci. Soc. Am. J. 48:805–809.

Sharpley, A. N., U. Singh, G. Uehara, and J. Kimble. 1989. Modeling soil and plant phosphorus dynamics in calcareous and highly weathered soils. Soil Sci. Soc. Am. J. 53:153–158.

Solis, P., and J. Torrent. 1989. Phosphate sorption by calcareous Vertisols and Inceptisols of Spain. Soil Sci. Soc. Am. J. 53:456–459.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, New York.

Sposito, G. 1989. The Chemistry of Soils. Oxford University Press, New York.

United States Salinity Laboratory Staff. 1969. Diagnosis and Improvement of Saline and Alkaline Soil. L. A. Richards, ed. USDA Agricultural Handbook No. 60, pp. 100–101.

Walkley, A., and I. A. Black. 1934. An examination of the degtjareff method for proposed modification of the chromic acid titration method. Soil Sci. 37:29–38.

Yuan, G., L. M. Lavkulich, and C. Wang. 1993. A method for estimating organic-bound iron and aluminum contents in soils. Commun. Soil Sci. Plant Anal. 24:1333–1343.

Zhou, M., and Y. Li. 2001. Phosphorus-sorption characteristics of calcareous soils and limestones from the southern Everglades and adjacent farmlands. Soil Sci. Soc. Am. J. 65:1404–1412.