

Path and Multiple Regression Analyses of Phosphorus Sorption Capacity

H. Zhang,* J. L. Schroder, J. K. Fuhrman, N. T. Basta, D. E. Storm, and M. E. Payton

ABSTRACT

Soil P saturation indices and P Langmuir adsorption maximum (S_{\max}) are two environmental soil tests that provide valuable information for the proper management P in soils to avoid the overapplication of P. The objectives of this study were to determine S_{\max} and develop P saturation indices for 28 Oklahoma benchmark soils and to use path analysis and multiple regression to examine the relationships between S_{\max} and soil properties. Soil samples were analyzed for pH, clay content, oxalate extractable P (P_{ox}), Al (Al_{ox}), Fe (Fe_{ox}), and Mehlich-3 (M3) extractable P (P_{M3}), Al (Al_{M3}), Fe (Fe_{M3}), Ca (Ca_{M3}), and Mg (Mg_{M3}). The S_{\max} value and saturation indices based on oxalate and M3 extractions were determined. The S_{\max} value ranged from 34 to 500 mg kg⁻¹ and was highly correlated with clay content ($r = 0.79$), organic C ($r = 0.80$), Al_{ox} ($r = 0.88$), and Fe_{ox} ($r = 0.83$). Soil pH was not correlated ($p > 0.05$) with S_{\max} . Path analysis showed significant direct effects ($p < 0.01$) between Al_{ox} and S_{\max} and between Fe_{ox} and S_{\max} but these relationships were highly influenced by indirect effects of Al_{ox} and Fe_{ox} . Multiple regression agreed well with path analysis and found that the combination of Al_{ox} and Fe_{ox} were the two most important soil properties related to S_{\max} of the soils studied. Significant relationships existed between Al_{M3} ($r = 0.54$) and S_{\max} and between Fe_{M3} ($r = 0.54$) and S_{\max} . Three P saturation indices studied were highly correlated ($p < 0.05$) with each other. Our results show that S_{\max} of Oklahoma soils may be predicted with oxalate extractable Al and Fe or M3 extractable Al, Fe, and Ca.

ALTHOUGH P is considered to be relatively immobile in the soil system (Johnson et al., 1997), there are mechanisms for P to leave the soil through plant uptake, loss in surface runoff, erosion of sediment, and leaching through the soil profile. If P is applied to the soil in excess of the crop requirement, P will generally build up in the soil, which increases the chances of P loss from the soil system (Sharpley et al., 1999). The N/P ratio of animal manures ranges from 1:1 to 4:1 (Zhang et al., 2004) and is generally less than the N/P ratio 8:1 taken up by most crops and pastures (USDA, 2001). The land application of animal manure to meet crop N needs often results in an overapplication of P, thus leading to an accumulation of P in the soil (Sharpley et al., 1999). Agricultural runoff is now considered a primary non-point source of P pollution because many point sources are largely under control (Daniel et al., 1994) and may lead to eutrophication of water bodies (Sharpley et al., 1999). To prevent P accumulations in soil, manure should be applied according to the P needs of the crop, and then supplemented with N fertilizer to accommo-

date the N needs of the crop (Daniel et al., 1994). Unfortunately, this is not always economically or practically feasible (Sharpley et al., 1996).

Many agricultural fields contain soil P levels that exceed crop requirements resulting from long-term manure application. In these situations, the environmental fate of P must be assessed. One tool that has been used in the evaluation of the environmental fate of P is soil P saturation. Phosphorus saturation is defined as the amount of P sorbed divided by the P sorption capacity of the soil. The concept of P saturation is meaningful as it estimates the degree to which P sorption sites have been filled and indicates the potential desorbability of soil P (Beauchemin and Simard, 1999). Phosphorus saturation has been highly correlated with P desorption such that P desorption increases with higher degrees of P saturation (Sibbesen and Sharpley, 1997). Phosphorus saturation is viewed as an environmental indicator of soil P because it has been found to be a good indicator of P availability to runoff and leachate (Kleinman and Sharpley, 2002).

Several approaches for the estimation of P saturation have been reported (Sharpley, 1995; Schoumans, 2000; Kleinman and Sharpley, 2002). One common approach is to determine acidified ammonium oxalate extractable P, Al, and Fe (P_{ox} , Al_{ox} , Fe_{ox}), and then calculate a degree of P saturation (DPS) (Schoumans, 2000). According to Schoumans (2000), DPS by the acid ammonium oxalate method is equal to the ratio of the amount of oxalate-extractable P divided by the P sorption capacity. It is assumed that the sum of the oxalate extractable Al and Fe equals the P sorption capacity. A critical DPS of 25% has been established for Dutch soils (Sharpley et al., 1996). Above this limit, the risk of P losses to leaching and surface runoff becomes unacceptable to the Dutch government and further applications of manure may be prohibited. However, this method may not be applicable to high pH soils, especially calcareous soils because the carbonates in calcareous soils tend to neutralize the acidic extracting solution (Loeppert and In-skeep, 1996; Kleinman and Sharpley, 2002). Furthermore, Al and Fe oxides are less significant for P sorption in high pH soils than acid soils (Lindsay, 1979).

A disadvantage of the definition of DPS is that its calculation depends on the P sorption capacity of the soil, which varies from horizon to horizon but is usually assessed by $0.5 (Al_{\text{ox}} + Fe_{\text{ox}})$ (Schoumans, 2000). How-

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Abbreviations: Al_{M3} , Mehlich-3 extractable Aluminum; Al_{ox} , oxalate extractable aluminum; DPS, degree of phosphorus saturation; Fe_{M3} , Mehlich-3 extractable iron; Fe_{ox} , oxalate extractable iron; M3, Mehlich-3; PSI, phosphorus saturation index; P_{ox} , oxalate extractable phosphorus; P_{M3} , Mehlich-3 extractable phosphorus; P_{sat} , phosphorus saturation; PSI_{M3} , phosphorus saturation index calculated with Mehlich-3 data; PSI_{ox} , phosphorus saturation index calculated with oxalate data; r , simple correlation coefficient; R^2 , coefficient of determination; S_{\max} , phosphorus adsorption maximum; U , uncorrelated residue value.

ever, it is possible to eliminate this assessment of P sorption capacity and to calculate an independent P saturation index (PSI) as shown in Eq. [1]:

$$\text{PSI}_{\text{ox}} = \frac{P_{\text{ox}}}{\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}} \quad [1]$$

where P_{ox} , Al_{ox} , and Fe_{ox} are expressed in mmol kg^{-1} soil.

Another approach proposed by Sharpley (1995) for the estimation of P saturation uses Mehlich-3 (M3) P (Mehlich, 1984) and the adsorption maximum (S_{max}) from P adsorption isotherms. It is referred to as P_{sat} and is defined as:

$$P_{\text{sat}} = \frac{P_{\text{M3}}}{S_{\text{max}}} \quad [2]$$

where P_{M3} is M3 extractable P, S_{max} is P Langmuir adsorption maximum and are expressed in milligrams per kilogram (mg kg^{-1}) of soil. Mehlich-3 extraction is widely used to assess the amount of P available to a plant during the growing season. It works well in soils with a wide range of pH (Mallarino, 1997).

Still another approach offered by Kleinman and Sharpley (2002) is similar to the acid ammonium oxalate approach but involves extraction of P, Al, and Fe with M3 as shown in Eq. [3].

$$\text{PSI}_{\text{M3}} = \frac{P_{\text{M3}}}{\text{Al}_{\text{M3}} + \text{Fe}_{\text{M3}}} \quad [3]$$

where P_{M3} , Al_{M3} , and Fe_{M3} are M3 extractable P, Al, and Fe, respectively, and are expressed in millimole per kilogram (mmol kg^{-1}) of soil.

Phosphorus adsorption characteristics are influenced by one or a combination of chemical and mineralogical properties of soil such as clay type and content, Fe and Al oxides, organic C (OC), pH, and CaCO_3 (Burt et al., 2002). Soil properties that have been correlated with P adsorption in soils include soil pH (Brennan et al., 1994; Dodor and Oya, 2000), OC and clay content (Singh and Tabatabai, 1977; Sanyal et al., 1993; Dodor and Oya, 2000), clay content, and Al and Fe oxide content (Sanyal et al., 1993; Dodor and Oya, 2000; Börling et al., 2001). Often, these properties are interrelated and autocorrelated (Basta et al., 1993), which makes it difficult to determine the components that contribute most to P adsorption in soils (Syers et al., 1973). Therefore, simple correlation analysis inadequately explains the relationships because correlation does not imply that a direct cause-and-effect relationship exists (Wright, 1921). Rather, the correlation analysis and the resulting coefficient may be influenced by indirect effects.

Path analysis is a statistical technique that partitions correlations into direct and indirect effects and distinguishes between correlation and causation (Wright, 1934; Afifi and Clark, 1984). Path analysis has been used extensively in agronomic studies (Gravois and Helms, 1992; Pantone et al., 1992; Cramer and Wehner, 2000; Zheng et al., 2002; Garcia del Moral et al., 2003) and to investigate relationships between soil properties and adsorption of heavy metals (Basta et al., 1993; Krishnasamy and Mathan, 2001). Several studies have used ei-

ther simple correlation to examine relationships between individual soil properties and P sorption maxima or multiple regressions to evaluate the effect of different combinations of soil properties on P adsorption (Singh and Tabatabai, 1977; Sanyal et al., 1993; Brennan et al., 1994; Dodor and Oya, 2000; Börling et al., 2001). However, to the best of our knowledge, none have utilized path analysis to examine the contributions of the different soil properties to correlations established between soil properties and P adsorption. The objectives of this study were to (i) characterize P adsorption maximum (S_{max}) of major benchmark soils from Oklahoma; (ii) use path analysis to investigate the relationships between S_{max} and major soil properties; and (iii) to determine the relationships between different P saturation indices. The study will also provide useful information about S_{max} and P saturation indices in Oklahoma soils, which may be used by environmental managers to avoid overapplication of P and minimize eutrophication of water bodies.

MATERIALS AND METHODS

Study Soils

Twenty-eight Oklahoma benchmark soils originally classified by Gray and Roozitalab (1976) and which had not received P additions as manure or commercial fertilizers within 3 yr of collection were chosen for P characterization to identify factors affecting their P sorption capacity. The soils were originally collected by Scott (1994). One sample per soil type was chosen for the study. Oklahoma has a diverse paleoclimate and geology with soils that represent many of the world soil orders (Table 1). Soils in this study represent the diversity of soils found in Oklahoma along with the major land resources areas (Fig. 1). The soils were sampled from the surface horizon (A horizon or plow layer) then air-dried and ground to pass a 2.0-mm sieve.

Soil Properties

Soil properties (clay content, OC content, and soil pH) analyzed by Scott (1994) were utilized in the study. Soil pH was measured in 1:2 soil/0.01 M CaCl_2 suspension (McLean, 1982). Soil organic C content was determined by acid dichromate digestion according to Heanes (1984). Clay content was determined by the hydrometer method (Gee and Bauder, 1986).

Adsorption Isotherms

Phosphorus adsorption isotherms were determined according to the method of Graetz and Nair (2000). One gram of soil sample was equilibrated with 25 mL of varying concentrations of P in 0.01 M CaCl_2 solution in 50-mL centrifuge tubes. The concentrations of the solutions were 0.0, 0.5, 1.0, 5.0, 10.0, 15.0, and 20.0 mg P L^{-1} . The tubes were shaken for 24 h on an end-to-end shaker at 150 oscillations per min. The samples were then centrifuged for 10 min at $5211 \times g$ and the supernatant decanted. The P in solution was then quantified colorimetrically using the ascorbic acid method (Kuo, 1996). The amount of P adsorbed was determined by the difference between the initial and final amounts of P in solution. Duplicate analyses were conducted on all study soils.

Phosphorus adsorption isotherms were determined with the linearized form of the Langmuir equation Eq. [4].

Table 1. Classification and general properties of 28 Oklahoma benchmark soils.

Soil	Classification	pH [†]	Clay		OC [‡]	Mehlich-3 P [§]
			g kg ⁻¹			
Bernow	Glossic Paleudalfs	4.3	110	14.0	14.0	11
Burleson	Udic Haplusterts	5.9	420	11.0	11.0	30
Carnasaw	Typic Hapludults	5.7	210	28.0	28.0	6.0
Clarksville	Typic Paleudults	5.5	260	20.0	20.0	20
Cobb	Typic Haplustalfs	5.5	160	4.00	4.00	70
Dalhart	Aridic Haplustalfs	7.3	120	4.00	4.00	12
Darnell	Udic Haplustepts	5.4	110	5.00	5.00	4.0
Dennis	Aquic Argiudolls	5.7	250	16.0	16.0	4.0
Dougherty	Arenic Haplustalfs	5.2	80.0	7.00	7.00	69
Durant	Udertic Argiustolls	6.7	270	25.0	25.0	5.0
Easpur	Fluventic Haplustolls	5.9	220	6.00	6.00	5.5
Grant	Udic Argiustolls	6.0	260	8.00	8.00	14
Kirkland	Udertic Paleustolls	5.7	350	11.0	11.0	29
Lebron	Fluvaquentic Hapludolls	7.9	590	20.0	20.0	34
Mansic	Aridic Calcicustolls	8.1	350	14.0	14.0	20
Osage	Typic Epiaquerts	5.6	660	30.0	30.0	34
Parsons	Mollic Albaqualfs	6.5	300	14.0	14.0	17
Pond Creek	Pachic Argiustolls	5.2	280	10.0	10.0	31
Pratt	Lamellic Haplustalfs	6.3	70.0	4.00	4.00	2.5
Renfrow	Udertic Paleustolls	6.4	250	14.0	14.0	5.5
Richfield	Aridic Argiustolls	7.4	460	8.00	8.00	17
St. Paul	Pachic Argiustolls	6.9	280	11.0	11.0	5
Sallisaw	Typic Paleudalfs	5.5	220	12.0	12.0	140
Stigler	Aquic Paleudalfs	5.6	280	23.0	23.0	120
Summit	Oxaquic Vertic Argiudolls	7.6	580	25.0	25.0	5.5
Tillman	Typic Paleustolls	6.4	340	7.00	7.00	26
Woodward	Typic Haplustepts	7.7	200	11.0	11.0	3.5
Zaneis	Udic Argiustolls	5.7	210	12.0	12.0	3.5
Mean		6.2	280	13.0	13.0	27
Median		5.9	260	12.0	12.0	16
Minimum		4.3	70.0	4.00	4.00	2.5
Maximum		8.1	660	30.0	30.0	140

[†] Soil pH was measured in 1:2 soil/0.01 M CaCl₂ suspension (McLean, 1982).

[‡] Organic C.

[§] Molybdate reactive P analyzed on spectrophotometer.

$$\frac{C}{S} = \frac{l}{kS_{\max}} + \frac{C}{S_{\max}} \quad [4]$$

where S equals the total amount of P retained, mg kg⁻¹; C equals concentration of P after a 24-h equilibrium, mg L⁻¹; S_{\max} equals P sorption maximum, mg kg⁻¹; k equals a constant related to the bonding energy, L mg⁻¹ P. S_{\max} was calculated by regressing C/S versus C , where C is the equilibrium solution P concentration and S is adsorbed P. The reciprocal of the

slope of the linear regression is S_{\max} (Olsen and Watanabe, 1957; Syers et al., 1973).

Soil Extractions

Acid ammonium oxalate extractable P, Al, and Fe were determined by shaking duplicate 1.5-g samples of soil with 30 mL of 0.5 M (COONH₄)₂ · H₂O at pH 3.0 in 50-mL centrifuge tubes (Schoumans, 2000). Samples were shaken for 2 h,

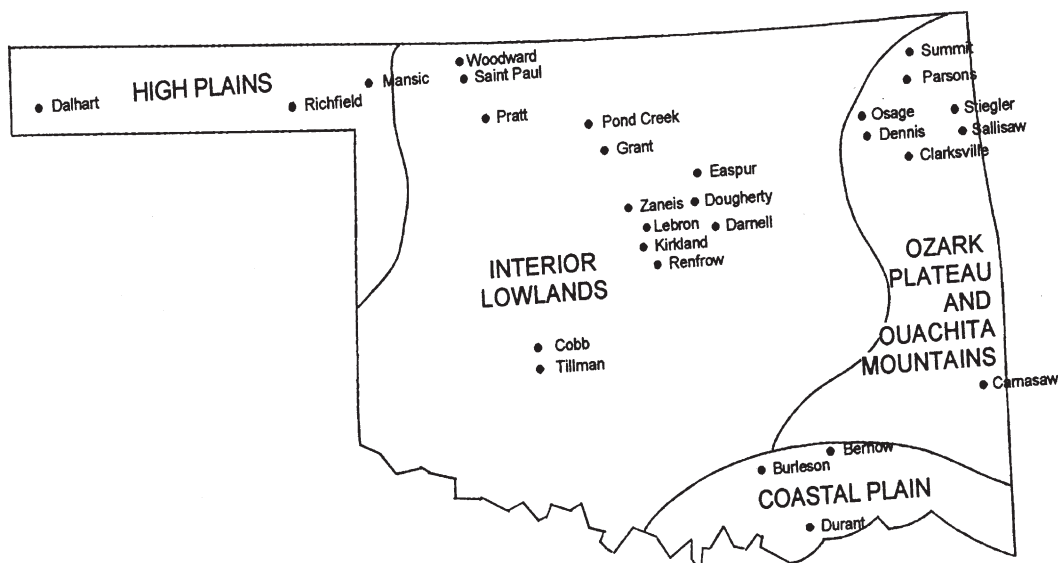


Fig. 1. Locations of the 28 Oklahoma benchmark soils used in this study along with delineation of major land resource areas.

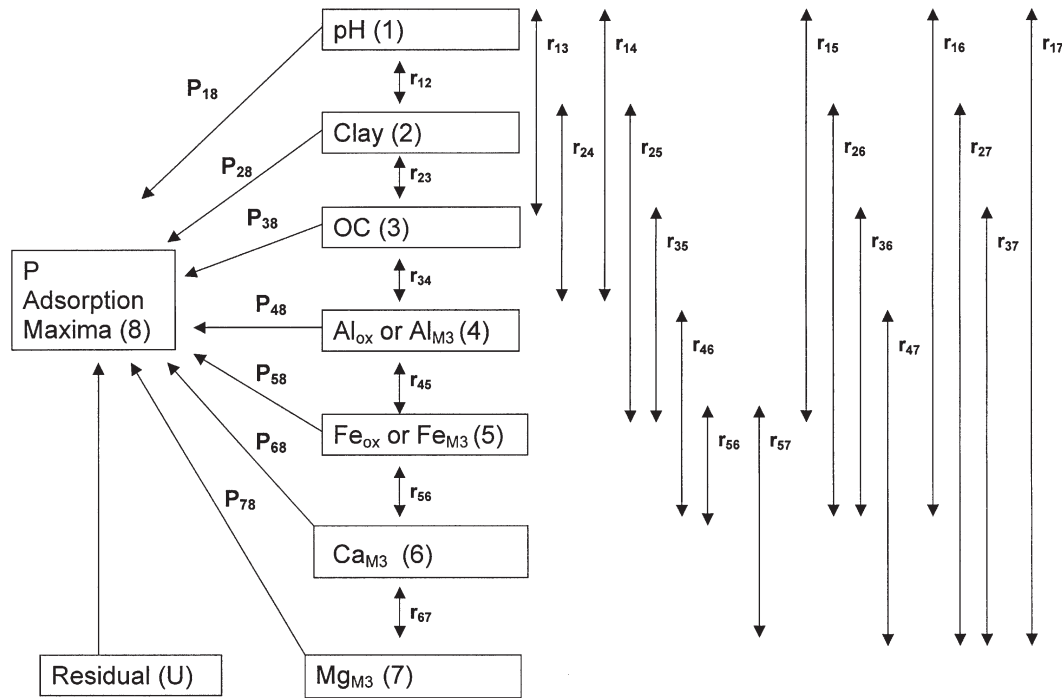


Fig. 2. Path diagram for the relationship between soil properties and P adsorption by soil. The direct effects (P_{ij}) of soil properties on P adsorption maxima (S_{max}) are represented by single-headed arrows while the indirect effects ($r_{ij}P_{ij}$) of soil properties are shown by double-headed arrows. Subscript designations for soil properties and P adsorption are identified numerically as follows: (1) pH = soil pH; (2) clay = clay content; (3) OC = organic carbon content; (4) Al_{ox} = acid ammonium oxalate extractable Al and Al_{M3} = Mehlich-3 extractable Al; (5) Fe_{ox} = acid ammonium oxalate extractable Fe and Fe_{M3} = Mehlich-3 extractable Fe; (6) Ca_{M3} = Mehlich-3 extractable Ca; (7) Mg_{M3} = Mehlich-3 extractable Mg; and (8) S_{max} = P adsorption maxima.

in the dark, on an end-to-end shaker at 150 oscillations per minute and centrifuged for 10 min at $5211 \times g$. Supernatants were analyzed for P, Al, and Fe using a TJA-9000 inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Mehlich-3 extractable P, Al, Fe, Ca, and Mg were determined by shaking duplicate 2.0-g samples of soil and 20 mL of M3 solution in 50-mL centrifuge tubes for 10 min on an end-to-end shaker (150 oscillations per minute). The samples were then centrifuged at $5211 \times g$ for 10 min and supernatants were analyzed by ICP-AES. Duplicate analyses were conducted on the study soils.

Calculation of PSI_{ox} , PSI_{M3} , and P_{sat}

Phosphorus saturation indexes based on ammonium oxalate and M3 extractions were calculated using Eq. [1] and [3], respectively. P saturation with respect to S_{max} (P_{sat}) was calculated using Eq. [2]. Phosphorus saturation indices were expressed as percentages.

Statistical Analyses

Statistical analyses were performed using PC SAS Version 8.2 (SAS institute, 2001). Two different statistical techniques (backward-stepwise regression analysis and path analysis) were utilized to evaluate the effect of soil properties on S_{max} . Backward-stepwise regression analysis was used to generate empirical models capable of predicting S_{max} based on soil properties. The backward-stepwise regression was used to identify crucial soil properties that explain most of the variation in S_{max} . Soil properties that did not explain a significant part of the variation (i.e., $p > 0.05$) were not used as independent variables in the multiple regression equation.

Path analysis differentiates between correlation and causation by partitioning simple correlation coefficients between

independent variables (soil properties) and dependent variables (S_{max}) into direct and indirect effects (Afifi and Clark, 1984; Basta et al., 1993). Path analysis provides a numerical value for both direct and indirect effects, thus indicating the relative strength of causal relationships (Loehlin, 1987). Direct effects are referred to as path coefficients and are standardized partial regression coefficients (Basta et al., 1993).

Two path analysis models similar to those used by Basta et al. (1993) were also used to evaluate the relationships between S_{max} and soil properties (Fig. 2). The direct effects of soil properties on S_{max} are represented by single-headed arrows while coefficients of intercorrelations between soil properties are shown by double-headed arrows. Indirect effects of soil properties on S_{max} are determined from the product of one double-headed arrow and one single-headed arrow. The independent variables of the first model were soil pH, clay content, OC content, and Al_{ox} and Fe_{ox} . The second model examined the relationships between S_{max} and soil pH, clay content, OC content, Al_{M3} , Fe_{M3} , Ca_{M3} , and Mg_{M3} (Fig. 2). For both models, direct and indirect effects were obtained from multiple linear regression of soil properties on S_{max} and simple correlations between soil properties (SAS Institute, 2001). Additionally, an uncorrelated residue (U) was calculated for both models using the following equation.

$$U = \sqrt{1 - R^2} \tag{5}$$

where R^2 is the coefficient of determination. Path analysis results were determined from the following equations (Williams et al., 1990):

$$\begin{aligned} r_{18} &= P_{18} + r_{12}P_{28} + r_{13}P_{38} + r_{14}P_{48} + r_{15}P_{58} + \\ &\quad r_{16}P_{68} + r_{17}P_{78} \\ r_{28} &= r_{12}P_{18} + P_{28} + r_{23}P_{38} + r_{24}P_{48} + r_{25}P_{58} + \end{aligned} \tag{6}$$

$$r_{26}P_{68} + r_{27}P_{78} \quad [7]$$

$$r_{38} = r_{13}P_{18} + r_{23}P_{28} + P_{38} + r_{34}P_{48} + r_{35}P_{58} + r_{36}P_{68} + r_{37}P_{78} \quad [8]$$

$$r_{48} = r_{14}P_{18} + r_{24}P_{28} + r_{34}P_{38} + P_{48} + r_{45}P_{58} + r_{46}P_{68} + r_{47}P_{78} \quad [9]$$

$$r_{58} = r_{15}P_{18} + r_{25}P_{28} + r_{35}P_{38} + r_{45}P_{48} + P_{58} + r_{56}P_{68} + r_{57}P_{78} \quad [10]$$

$$r_{68} = r_{16}P_{18} + r_{26}P_{28} + r_{36}P_{38} + r_{46}P_{48} + r_{56}P_{58} + P_{68} + r_{67}P_{78} \quad [11]$$

$$r_{78} = r_{17}P_{18} + r_{27}P_{28} + r_{37}P_{38} + r_{47}P_{48} + r_{57}P_{58} + r_{67}P_{68} + P_{78} \quad [12]$$

where r_{ij} is the simple correlation coefficient between soil property and P adsorption, P_{ij} are path coefficients (direct effects), and $r_{ij}P_{ij}$ are the indirect effects of soil property on P adsorption. Subscript designations are: (1) pH, (2) clay content, (3) OC content, (4) Al_{ox} or Al_{M3}, (5) Fe_{ox} or Fe_{M3}, (6) M3 extractable Ca (Ca_{M3}), (7) M3 extractable Mg (Mg_{M3}), and (8) S_{max} (Fig. 2).

The path analysis results can be summarized in a concise table, which consists of a matrix with the main diagonal representing direct effects and off-diagonal elements representing indirect effects (Williams et al., 1990). The position of each element in the matrix corresponds to its position in the normal equations presented above.

RESULTS AND DISCUSSION

Soil Characteristics

The selected soil samples had a wide range of chemical and physical properties. Soil pH ranged from 4.3 to 8.1, clay content from 70 to 660 g kg⁻¹, and OC from 4 to 30.0 g kg⁻¹ (Table 1). Overall, the soils were moderately acidic (median pH = 5.9), low in OC (median OC = 12 g kg⁻¹), and low in soil test P (median M3 P = 16 mg kg⁻¹ and ranged from 2.5 to 140 mg P kg⁻¹ soil; agronomic optimum M3 P = 30 to 50 mg kg⁻¹; SERA-IEG-6, 2001).

Phosphorus extracted by the acid ammonium oxalate method varied by soil and ranged from 26 to 750 mg P kg⁻¹ soil with a median value of 120 mg P kg⁻¹ soil (Table 2). Ranges for Al_{ox} extracted by this method were from 140 to 2000 mg Al kg⁻¹ soil while Fe_{ox} ranged from 120 to 9600 mg Fe kg⁻¹ soil. On average, M3 extracted approximately 22% of the P, 64% of the Al, and 8% of the Fe extracted by ammonium oxalate method. Our results are similar to those of Sims et al. (2002) who reported that M3 extracted approximately 84% of the Al and 19% of the Fe extracted by acid ammonium oxalate in soils typical of the Mid-Atlantic USA. The P sorption data were satisfactorily described by the linearized Langmuir equation with correlation coefficients ranging from 0.95 to 0.98. Phosphorus sorp-

Table 2. Phosphorus sorption characteristics for 28 Oklahoma benchmark soils.

Soil	Acid ammonium oxalate				Mehlich-3							
	P†	Al†	Fe†	PSI _{ox} ‡	P†	Al†	Fe†	Ca†	Mg†	PSI _{M3} §	S _{max}	P _{sat} #
	mg kg ⁻¹			%	mg kg ⁻¹							
Bernow	68.0	290	670	9.70	31.0	280	340	93.9	20.5	6.10	110	28.0
Burleson	150	1100	1600	7.20	43.0	690	160	2910	560	4.90	240	18.0
Carnasaw	71.0	1200	1600	3.20	16.0	690	160	862	154	1.80	240	7.00
Clarksville	200	1200	1200	9.60	50.0	860	140	839	139	4.70	280	18.0
Cobb	110	510	360	14.0	68.0	600	46.0	621	66.9	9.50	100	68.0
Dalhart	48.0	260	150	12.0	14.0	290	36.0	638	88.7	4.00	64.0	22.0
Darnell	50.0	270	240	12.0	24.0	350	69.0	176	40.3	5.60	60.0	40.0
Dennis	90.0	900	2200	4.00	16.0	660	130	1120	357	1.90	240	7.00
Dougherty	120	190	280	31.0	69.0	190	130	134	28.1	24.0	92.0	75.0
Durant	68.0	800	2300	3.10	14.0	480	130	3270	209	2.20	200	7.00
Easpur	73.0	420	580	9.10	20.0	410	84.0	967	237	3.80	120	17.0
Grant	87.0	620	640	8.20	23.0	600	88.0	1110	287	3.20	170	14.0
Kirkland	130	860	1300	7.30	37.0	700	150	1650	476	4.10	160	23.0
Lebron	420	1100	1100	23.0	38.0	100	70.0	6040	503	24.0	250	15.0
Mansic	390	780	230	38.0	26.0	81.0	13.0	7450	185	26.0	182	14.0
Osage	550	1600	9600	7.70	45.0	820	480	3940	648	3.80	500	9.00
Parsons	160	770	2700	6.80	22.0	550	130	1760	239	3.10	290	8.00
Pond Creek	120	730	800	9.70	39.0	700	130	1070	138	4.50	220	18.0
Pratt	26.0	140	120	12.0	5.00	210	35.0	277	52.2	2.00	34.0	15.0
Renfrow	65.0	640	860	5.40	13.0	550	71.0	1470	323	2.00	170	8.00
Richfield	170	1100	670	11.0	22.0	620	52.0	3360	643	2.90	180	12.0
St. Paul	120	890	470	9.30	13.0	530	50.0	1880	414	2.10	180	7.00
Sallisaw	420	1200	1300	21.0	180	810	150	501	92.7	18.0	230	78.0
Stigler	750	1200	4000	21.0	180	800	270	1560	108	17.0	240	75.0
Summit	120	2000	3400	2.80	13.0	640	90.0	6310	406	1.60	430	3.00
Tillman	150	720	820	12.0	31.0	550	88.0	1200	509	4.60	110	28.0
Woodward	150	950	220	12.0	12.0	360	27.0	2280	261	2.90	170	7.00
Zaneis	62.0	800	890	4.40	14.0	600	71.0	996	197	2.00	160	9.00
Mean	176	830	1440	11.7	39.0	526	121	1950	264	6.70	194	23.0
Median	120	800	840	9.70	24.0	575	89.0	1160	223	3.90	180	15.0
Minimum	26.0	140	120	2.80	5.00	81.0	13.0	93.9	20.5	1.60	34.0	3.00
Maximum	750	2000	9600	38.0	180	860	480	7450	648	26.0	500	78.0

† Analyzed by ICP-AES.

‡ Phosphorus saturation index calculated from acid ammonium oxalate data (oxalate P/oxalate Al + oxalate Fe).

§ Phosphorus saturation index calculated from Mehlich-3 data (Mehlich-3 P/Mehlich-3 Al + Mehlich-3 Fe).

|| P adsorption maxima calculated from Langmuir adsorption isotherms.

Phosphorus saturation calculated from Mehlich-3 data and adsorption isotherms.

tion maximum (S_{\max}) estimated by Langmuir adsorption isotherms ranged from 34 to 500 mg P kg⁻¹ soil with a median of 180 mg P kg⁻¹ soil.

Path Analysis and Multiple Regression—Ammonium Oxalate

Results for the path analysis of P adsorption are shown in Table 3. Simple correlation coefficients (r) between pH, clay content, OC, Al_{ox}, Fe_{ox}, and S_{\max} are presented for comparison with path analysis results. The uncorrelated residual value (U) was low (0.28) while the coefficient of determination (R^2) was high (0.92) indicating that the path analysis model explained the majority of variation in P adsorption by soil. Significant correlation coefficients ($p < 0.01$) were found between clay content ($r = 0.79$), OC ($r = 0.80$), Al_{ox} ($r = 0.88$), Fe_{ox} ($r = 0.83$), and S_{\max} (Table 3). A significant correlation ($p > 0.05$) was not found between S_{\max} and soil pH. Our results are similar to those of other researchers who reported nonsignificant relationships existed between soil pH and S_{\max} (Brennan et al., 1994; Dodor and Oya, 2000). Additionally, the results of our study are consistent with the findings of others (Singh and Tabatabai, 1977; Sanyal et al., 1993; Dodor and Oya, 2000) in that clay content and OC are both well correlated with P S_{\max} . Furthermore, several researchers have found significant relationships between Al_{ox} and S_{\max} and between Fe_{ox} and S_{\max} (Sanyal et al., 1993; Dodor and Oya, 2000; Börling et al., 2001).

Path analysis partitions each r value into one direct effect and four indirect effects. Partitioning by path analysis showed significant direct effects by Al_{ox} ($r = 0.47$) and Fe_{ox} ($r = 0.32$) on S_{\max} . However, the direct effects of clay and OC content on P sorption were not significant ($p > 0.05$). Examination by path analysis revealed that the indirect effects of Al_{ox} ($r = 0.38$) and Fe_{ox} ($r = 0.20$) were important contributors to the corre-

lation between clay and S_{\max} . Similarly, the indirect effects of both Al_{ox} ($r = 0.36$) and Fe_{ox} (0.23) contributed greatly to the correlation between OC and S_{\max} . Aluminum and Fe oxides exist in soil as discrete crystals, coatings on clay and humic substances and as mixed gels. They play an important role in adsorption in soil because of their high specific surface areas and reactivity (Sparks, 2003). The ammonium oxalate solution extracts amorphous Al and Fe oxides, which are the most reactive oxides in soil because of their size and consistently high surface areas (Loeppert and Inskeep, 1996). Therefore, it was not unexpected that there would be a significant intercorrelation between clay and Al_{ox} and also between clay and Fe_{ox}. Our results suggested that the correlation between OC and P adsorption was indirect and represented P adsorbed by Al and Fe associated with organic matter. This concept is supported by a study by Borggaard et al. (1990) who found that P adsorption was not influenced by the removal of organic matter with H₂O₂.

Stepwise multiple regression identified a two-term model based on Al_{ox} and Fe_{ox} that explained 91% of the variation in S_{\max} (Table 4). The multiple stepwise regression agreed well with path analysis and identified the same two terms whose direct effects were identified as significant by path analysis. Our results agree with those of Börling et al. (2001) who used a multiple regression model and reported that the combination of Al_{ox} and Fe_{ox} were the two most important soil properties related to P adsorption in soil.

Several researchers have suggested that acid ammonium oxalate extractions are not appropriate for calcareous soils where calcium dominates P sorption reactions because oxalate is precipitated as a calcium salt and oxalic acid reacts with calcium carbonate to change the pH of the buffer solution (Loeppert and Inskeep, 1996; Schoumans, 2000; Kleinman and Sharpley, 2002). There-

Table 3. Path analysis direct effects (diagonal, underlined) and indirect effects (off diagonal) of soil pH, clay (g kg⁻¹), organic carbon (g kg⁻¹), and Fe and Al extracted by acid ammonium oxalate or Mehlich-3 on P adsorption for 28 Oklahoma benchmark soils.

Response	Acid ammonium oxalate						$r $	$R^2\#$	U
	pH	Clay	OC†	Al _{ox} ‡	Fe _{ox} ‡				
S_{\max}									
pH	<u>-0.04</u>	0.07	0.01	0.13	-0.04	0.13	0.92**	0.28	
Clay	-0.02	<u>0.16</u>	0.07	0.38	0.20	0.79**			
OC†	0.00	0.08	<u>0.13</u>	0.36	0.23	0.80**			
Al _{ox} ‡	-0.01	0.12	0.10	<u>0.47**</u>	0.20	0.88**			
Fe _{ox} ‡	0.01	0.10	0.10	0.30	<u>0.32**</u>	0.83**			
Response	Mehlich-3						$r $	$R^2\#$	U
	pH	Clay	OC†	Al _{M3} §	Fe _{M3} §	Ca _{M3} §			
S_{\max}									
pH	<u>0.17</u>	0.30	0.01	-0.12	-0.09	-0.02	-0.12	0.13	0.90
Clay	0.07	<u>0.72**</u>	0.15	0.09	0.05	-0.02	-0.27	0.79**	0.32
OC†	0.01	0.41	<u>0.27**</u>	0.12	0.10	-0.01	-0.08	0.81**	
Al _{M3} §	-0.07	0.20	0.10	<u>0.32**</u>	0.07	0.01	-0.09	0.54**	
Fe _{M3} §	-0.09	0.21	0.15	0.13	<u>0.17</u>	0.02	-0.05	0.54**	
Ca _{M3} §	0.12	0.57	0.12	-0.06	-0.01	<u>-0.03</u>	-0.17	0.54**	
Mg _{M3} §	0.06	0.60	0.07	0.08	0.02	-0.01	<u>-0.32</u>	0.50**	

** $p < 0.01$.

† Organic carbon.

‡ Extracted with acid ammonium oxalate solution.

§ Extracted with Mehlich-3 solution.

|| Simple correlation coefficient.

Coefficient of multiple determination.

Table 4. Multiple regression formulae describing the relationship between soil properties and P sorption maxima (S_{\max}) for 28 Oklahoma benchmark soils.

Response	Independent variables	Equation	Statistics
S_{\max}	pH, clay g kg ⁻¹ , OC g kg ⁻¹ †, Al _{ox} ‡, Fe _{ox} ‡, Clay g kg ⁻¹ , OC g kg ⁻¹ , Al _{ox} ‡, Fe _{ox} ‡, OC g kg ⁻¹ †, Al _{ox} ‡, Fe _{ox} ‡	Acid ammonium oxalate model	
		$y = 48.8 - 0.49(\text{pH}) + 0.11(\text{clay g kg}^{-1}) + 1.83(\text{OC g kg}^{-1}) + 0.01(\text{Al}_{\text{ox}}) + 0.002(\text{Fe}_{\text{ox}})$	$R^2 = 0.92, n = 28, p < 0.001$
		$y = 23.7 + 0.08(\text{clay g kg}^{-1}) + 1.76(\text{OC g kg}^{-1}) + 0.01(\text{Al}_{\text{ox}}) + 0.002(\text{Fe}_{\text{ox}})$	$R^2 = 0.91, n = 28, p < 0.001$
		$y = 31.0 + 1.35(\text{OC g kg}^{-1}) + 0.01(\text{Al}_{\text{ox}}) + 0.002(\text{Fe}_{\text{ox}})$	$R^2 = 0.91, n = 28, p < 0.001$
	Al _{ox} ‡, Fe _{ox} ‡	$y = 36.2 + 0.02(\text{Al}_{\text{ox}}) + 0.002(\text{Fe}_{\text{ox}})$	$R^2 = 0.91, n = 28, p < 0.001$
S_{\max}	pH, clay g kg ⁻¹ , OC g kg ⁻¹ †, Al _{M3} §, Fe _{M3} §, Ca _{M3} §, Mg _{M3} §, pH, clay g kg ⁻¹ , OC g kg ⁻¹ †, Al _{M3} §, Fe _{M3} §, Mg _{M3} §, Clay g kg ⁻¹ , OC g kg ⁻¹ †, Al _{M3} §, Fe _{M3} §, Mg _{M3} §, Clay g kg ⁻¹ , OC g kg ⁻¹ †, Al _{M3} §	Mehlich-3 model	
		$y = -158 + 1.81(\text{pH}) + 0.50(\text{clay g kg}^{-1}) + 3.70(\text{OC g kg}^{-1}) + 0.01(\text{Al}_{\text{M3}}) + 0.02(\text{Fe}_{\text{M3}}) - 0.001(\text{Ca}_{\text{M3}}) - 0.02(\text{Mg}_{\text{M3}})$	$R^2 = 0.90, n = 28, p < 0.001$
		$y = -153 + 1.73(\text{pH}) + 0.48(\text{clay g kg}^{-1}) + 3.63(\text{OC g kg}^{-1}) + 0.02(\text{Al}_{\text{M3}}) + 0.02(\text{Fe}_{\text{M3}}) - 0.02(\text{Mg}_{\text{M3}})$	$R^2 = 0.90, n = 28, p < 0.001$
		$y = -43.4 + 0.52(\text{clay g kg}^{-1}) + 4.39(\text{OC g kg}^{-1}) + 0.01(\text{Al}_{\text{M3}}) + 0.006(\text{Fe}_{\text{M3}}) - 0.02(\text{Mg}_{\text{M3}})$	$R^2 = 0.89, n = 28, p < 0.001$
		$y = -44.5 + 0.52(\text{clay g kg}^{-1}) + 4.78(\text{OC g kg}^{-1}) + 0.01(\text{Al}_{\text{M3}})$	$R^2 = 0.89, n = 28, p < 0.001$

† Organic carbon.

‡ Extracted with acid ammonium oxalate solution.

§ Extracted with Mehlich-3 solution.

fore, path analysis and multiple regression were conducted after the removal of six soils with pH >7.0 from the data set. Removal of the high-pH soils did not significantly change the results of the path analysis or the multiple regressions. After the removal of the high-pH soils, the simple correlations between S_{\max} and soil properties were: clay content ($r = 0.83$), OC ($r = 0.77$), Al_{ox} ($r = 0.87$), and Fe_{ox} ($r = 0.86$) (data not shown). Our results differ from those of Kleinman and Sharpley (2002) who evaluated 62 soils (37 acidic soils and 25 alkaline soils) and separated them into acidic and alkaline groups before doing correlation analysis. They reported highly significant relationships existed between Al_{ox} and P adsorption and between Fe_{ox} and P adsorption for acidic soils. They did not report the correlations for the combined soils; but examination of their data set shows that significant relationships existed between Al_{ox} and P adsorption and between Fe_{ox} and P adsorption which were greatly improved by the removal of the alkaline soils. Unlike their study, removal of the soils with pH >7 did not improve the relationships for our study. The differences between the two studies were most likely due to the number of alkaline soils. Approximately 21% of our soils were alkaline while approximately 40% the soils examined by Kleinman and Sharpley (2002) were alkaline. Additionally, only one of our study soils was pH >8 yet approximately 23% of their soils were pH >8 where Ca would dominate P sorption reactions (Lindsay, 1979). Although, a direct measurement of carbonates was not performed in either of the studies, Ca_{M3} was measured in both studies. Their soils contained an average of approximately 9000 mg kg⁻¹ Ca_{M3} as compared with a mean of 1950 mg kg⁻¹ Ca_{M3} in our study soils (Table 2) suggesting their soils contained much greater concentrations of carbonates than our study soils. Additionally, M3 extractable Ca in our soils ranged from 94 to 7450 mg Ca kg⁻¹ soil while Ca_{M3} in their soils ranged from 452 to 33 400 mg Ca kg⁻¹ soil. Therefore, the difference between the two studies was most likely the result of the fact that their soils contained greater

concentrations of carbonates when compared with our study soils.

Path Analysis and Multiple Regression—Mehlich-3

Results for the M3 path analysis model are summarized in Table 3. Simple correlation coefficients (r) between pH, clay content, OC, Al_{M3}, Fe_{M3}, Ca_{M3}, Mg_{M3}, and S_{\max} are presented for comparison with path analysis results. Similar to the ammonium oxalate model, U was low (0.32) and R^2 was high (0.90), indicating the model constructed in this study explained most of the variation in P adsorption by soil. Significant correlations ($p < 0.01$) existed between S_{\max} and clay and between S_{\max} and OC as previously noted (Table 3). A significant correlation ($p > 0.05$) was not found between S_{\max} and soil pH as previously noted. Significant relationships ($p < 0.01$) were also found between Al_{M3} ($r = 0.54$), Fe_{M3} ($r = 0.54$), Ca_{M3} ($r = 0.54$), Mg_{M3} ($r = 0.50$), and S_{\max} . Our results are similar to those found by Tran et al. (1990) who reported a significant relationship ($r = 0.77$) between Al_{M3} and P adsorption for 82 Quebec soils. However, they did not report the relationship between Fe_{M3} or Ca_{M3} and P adsorption in their study.

The M3 path analysis model found different direct and indirect effects from those of the acid ammonium oxalate path analysis model (Table 3). In contrast to the acid ammonium oxalate path analysis model, the M3 model showed significant direct effects by clay ($r = 0.72$) and OC ($r = 0.27$) on S_{\max} . A significant direct effect of Al_{M3} on S_{\max} also existed ($r = 0.32$), while a nonsignificant direct effects ($p > 0.05$) were found between Fe_{M3}, Ca_{M3}, Mg_{M3}, and S_{\max} . Mehlich-3 extracted only about 8% of the Fe extracted by the oxalate method. This has also been shown by several other researchers (Maguire and Sims, 2002; Sims et al., 2002). Perhaps the low extraction efficiency of M3 affected the Fe inputs for the M3 path analysis model and changed the outputs for the direct effects of the model, thus

allowing discrepancies to exist among the models. The existence of the significant direct effect between Al_{M3} and S_{max} suggested that the M3 extractant was similar to the acid ammonium oxalate extractant in that it extracted Al from the same non-crystalline pool in soil. Indeed other researchers have reported significant relationships between Al_{ox} and Al_{M3} but not between Fe_{ox} and Fe_{M3} (Tran et al., 1990; Fernandez Marcos et al., 1998). Path analysis revealed that the indirect effect of clay was an important contributor to the relationships between Ca_{M3} and S_{max} and between Mg_{M3} and S_{max} .

Stepwise multiple regression agreed well with path analysis. Stepwise multiple regression revealed the best model was a combination of the three same terms (clay, OC, and Al_{M3}) whose direct effects were found significant by path analysis. The combination of these terms explained 89% of the variation in S_{max} .

Again, the soils with $pH > 7.0$ were removed and path analysis and multiple regression were conducted. Removal of the high-pH soils significantly changed the simple correlations found with path analysis by improving the relationships between Al_{M3} ($r = 0.73$), Fe_{M3} ($r = 0.67$), Ca_{M3} ($r = 0.70$), and S_{max} (data not shown). Our results agree somewhat with those of Kleinman and Sharpley (2002) who reported highly significant and improved relationships between Al_{M3} and S_{max} in acidic soils, when they separated soils into acidic and alkaline groups for correlation analysis. However, Kleinman and Sharpley (2002) reported a nonsignificant relationship between Fe_{M3} and S_{max} .

Removal of the high-pH soils did not change the results of the path analysis or the multiple regression for the M3 model. Clay, OC, and Al_{M3} were still the only significant direct effects and were also identified by multiple regression as the three most important soil properties related to P adsorption in soil.

Correlations between Phosphorus Saturation Indices

The P saturation index (PSI) is the amount of extractable P ($mmol\ kg^{-1}$) divided by the sum of the extractable Al and Fe ($mmol\ kg^{-1}$). This saturation index was estimated using both acid ammonium oxalate (PSI_{ox}) and M3 (PSI_{M3}) as extractants. The two different PSIs produced different values. The PSI_{ox} ranged from 2.8 to 38% and PSI_{M3} ranged from 1.6 to 26% (Table 2). Median values were 9.7% for PSI_{ox} and 3.9% for PSI_{M3} . Additionally, a third saturation index (P_{sat}) based on M3 P and S_{max} was calculated for the study soils. The P_{sat} value ranged from 3 to 78% with a median of 15%.

Phosphorus saturation index using acid ammonium oxalate was highly correlated ($p < 0.01$, $r = 0.87$) with PSI_{M3} for all 28 study soils (Fig. 3). Removal of soil samples with $pH > 7.0$ did not improve the correlation between PSI_{ox} and PSI_{M3} (data not shown). Our results are consistent with other researchers who have reported highly significant relationships between PSI_{ox} and PSI_{M3} (Kleinman and Sharpley, 2002; Maguire and Sims, 2002; Sims et al., 2002). Phosphorus saturation was not significantly related ($p > 0.05$) to PSI_{ox} when all 28 soils were

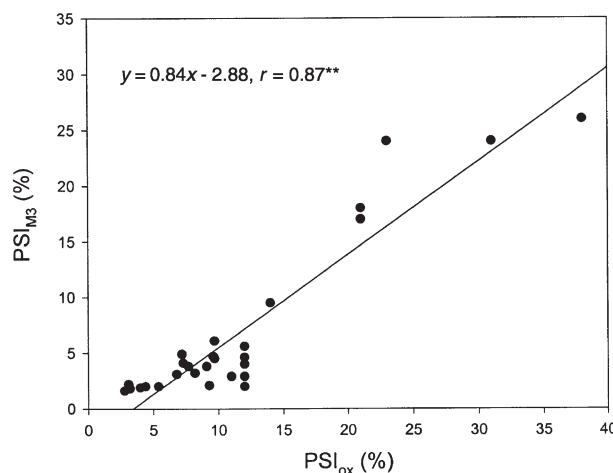


Fig. 3. Relationship between P saturation indexes using acid ammonium oxalate (PSI_{ox}) and Mehlich-3 (PSI_{M3}) as extractants for 28 Oklahoma benchmark soils. $**p < 0.01$.

included (Fig. 4A). However, removal of soils with $pH > 7.0$, produced a highly significant relationship ($p < 0.01$, $r = 0.79$) between P_{sat} and PSI_{ox} (Fig. 4B). A nonsignificant relationship ($p > 0.05$) was also observed between P_{sat} and PSI_{M3} (Fig. 4C), but removal of soils with $pH > 7.0$ resulted in a highly significant correlation between P_{sat} and PSI_{M3} ($p < 0.01$, $r = 0.85$) (Fig. 4D). Close examination of Fig. 4A through 4D showed that two outliers (the Lebron and Mansic soils) which had a high pH (approximately 8), high PSI_{ox} , high PSI_{M3} , and a low P_{sat} greatly influenced the regression. These outliers appear in the lower right corners of Fig. 4A and Fig. 4C and their removal considerably improved the relationships between P_{sat} and PSI_{ox} and between P_{sat} and PSI_{M3} . The Lebron and Mansic soils had much greater concentrations of Ca_{M3} as compared with the other study soils (Table 2) suggesting that the soils contained greater concentrations of carbonates as compared with the other study soils which may have interfered with the M3 and oxalate extractions of Al and Fe and influenced the regression analysis.

The degree of P saturation estimates how close the soil is to saturation and is viewed as an environmental indicator of soil P based on the fact that more P is released from soil to runoff or leaching as the degree of P saturation increases (Sharpley, 1995; Kleinman and Sharpley, 2002). Considerable research has been conducted on the use of PSI_{ox} as an environmental soil test (Hooda et al., 2000; Pautler and Sims, 2000; Maguire et al., 2001; Maguire and Sims, 2002; Sims et al., 2002). Our results indicate that other measurements of P saturation are well correlated with PSI_{ox} and may serve useful in identifying soils with increased risk for P loss.

CONCLUSIONS

Understanding the P sorption capacity of a soil can help to estimate the amount of P that a soil is capable of holding. Soil properties (clay content, OC content, Al_{ox} , and Fe_{ox}) were highly correlated with S_{max} . Path analysis indicated that the direct effects for clay and OC were not significant and that these relationships

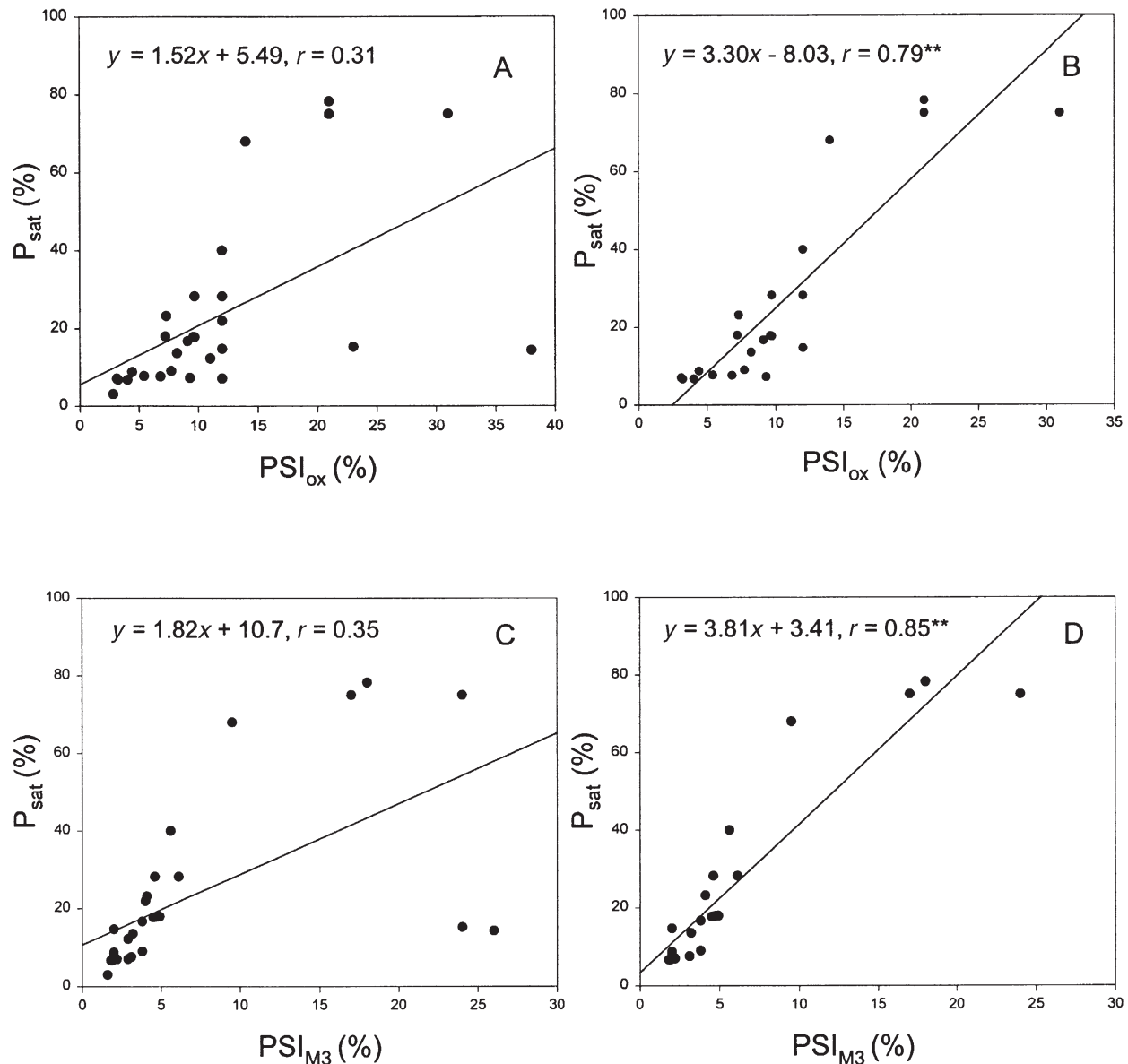


Fig. 4. Relationships between a P saturation index calculated from Mehlich-3 extractable P and S_{\max} (P_{sat}), and (A) a P saturation index calculated from acid ammonium oxalate extractable data (PSI_{ox}) for all 28 soils; (B) PSI_{ox} for soils with $\text{pH} < 7.0$; (C) a P saturation index calculated from Mehlich-3 extractable data (PSI_{M3}) for all 28 soils; or (D) PSI_{M3} for soils with $\text{pH} < 7.0$. ** $p < 0.01$.

were highly influenced by the indirect effects of Al_{ox} and Fe_{ox} . Multiple regression also found that the combination of Al_{ox} and Fe_{ox} were the two most important soil properties related to P sorption in soil. Therefore, Al_{ox} and Fe_{ox} were more important soil properties for the direct estimation of P sorption than clay and OC. It also appeared that pH did not affect the relationship between Al_{ox} and S_{\max} or between Fe_{ox} and S_{\max} . Thus, P sorption in Oklahoma soils may be estimated using the more economical and time saving oxalate extraction instead of time-consuming adsorption isotherms.

Aluminum, Fe, and Ca extracted by M3 were better correlated with S_{\max} after the removal of the high-pH soils indicating pH affected the relationships. Thus, M3 extractions of Al, Fe, and Ca may be used to estimate P adsorption in Oklahoma soils. Mehlich-3 is a very common method used by many laboratories and repre-

sents an alternative to the ammonium oxalate method. Many testing facilities use ICP-AES for their analyses and including Al, Fe, and Ca analyses on M3 extracts would be a relatively easy extra step for many soil-testing laboratories.

Phosphorus saturation is increasingly viewed as an environmental indicator of soil P because it has been found to be a good indicator of P availability to runoff and leachate (Kleinman and Sharpley, 2002). Conversely, P saturation is usually estimated from data not readily available through testing laboratories. Our results show that PSI_{ox} was highly correlated with PSI_{M3} for all 28 soils. Furthermore, P_{sat} was highly correlated with PSI_{ox} and with PSI_{M3} when two outliers containing large amounts of M3 extractable Ca were removed from the data set. Several researchers have shown that PSI_{ox} is related to P in surface runoff and to leachable P. The

results of our study indicate that two other measurements of P saturation (PSI_{M3} and P_{sat}) were well correlated with PSI_{ox} and may serve useful in identifying soils with increased risk for P loss. In particular, the correlation between PSI_{ox} and PSI_{M3} showed the potential use of the M3 extractant for estimating P saturation in soils, which provides useful information about the risk of runoff and leaching P in soils. Therefore, over-application of P can be limited.

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