PHOSPHORUS SORPTION AND DESORPTION CHARACTERISTICS OF SELECTED OKLAHOMA SOILS

By

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Chapter I

WATER SOLUBLE P DETERMINATION IN SOILS AND ITS RELATIONSHIP TO MEHLICH 3 P

ABSTRACT

Phosphorus (P) is one of the most important nutrients for growing crops. However, mismanagement of fertilizer or manure P can be detrimental to environmental quality. This study evaluated the effectiveness of several variations of water soluble P in order to determine a method that would be easily adopted by commercial testing laboratories. Water soluble P was measured for ten soils using four different soil:solution ratios (1:2, 1:5, 1:10, 1:50) and four different extraction times (10 min., 30 min., 1 hr., 15 hr.). Additionally, varying concentrations of $CaCl_2$ were used for the extracting solution. The average amount of P extracted increased as the extraction time was increased and also as the soil to solution ratio decreased. The addition of $CaCl_2$ to the extracting solution decreased the amount of P extracted compared with deionized water. Water soluble P was well correlated with Mehlich 3 P for a wide range of soils ($r^2 = 0.88$). A better correlation between water soluble P and Mehlich 3 P was found when the soils were grouped by pH. Using a 1:10 soil to solution ratio and a 10 minute extraction time is an easy and reliable method to determine water soluble

P. This extraction, along with the pH of the soil, should provide a good idea as to the potential risk a soil has to lose P to the surrounding environment.

INTRODUCTION

Phosphorus (P) is considered one of the most important plant nutrients in plant/soil systems. The concentration of P in plant tissue ranges from 0.1 to 0.4%. The primary role of P in plants is for energy storage and transfer (ADP and ATP). Phosphorus is also associated with increased root growth in most plants (Tisdale et al., 1993). P is generally applied to agricultural land as either commercial fertilizer or manure. Orthophosphates ($H_2PO_4^-$ and HPO_4^{2-}) are the common plant available forms of P found in the normal pH range of agricultural soils (Lindsay et al., 1989). There have been several tests developed to determine the amount of P available to a plant during the growing season. The major extraction methods include: the Mehlich 3 (Mehlich, 1984), Bray P1 (Bray and Kurtz, 1945), and Olsen (Olsen et al., 1954). These soil P tests are based on an index of the percent sufficiency for a growing plant. They are each better suited for different geographic regions and soil properties. Bray I is used for acid soils, while the Olsen method is commonly used for high pH soils. Mehlich 3 is suitable for a wide range of soil pH.

Phosphorus is often the limiting nutrient for plant growth in aquatic systems (Sharpley et al., 1994. Increased levels of P in aquatic systems can cause eutrophication, which may lead to hypoxic conditions in water systems. Prior to the United States Clean Water Act of 1972, the main source of phosphorus pollution was attributed to point sources (industry, sewage, drainage pipes, etc.). Now, agricultural runoff is considered to be a primary source of P pollution (Daniel et al., 1994), since many point sources are largely under control.

Water soluble P in soils has been studied in great detail because it represents the amount of P that is readily available to plants and algae. Water soluble P is perhaps a better environmental indicator compared to other soil test methods developed for crop production. Bioavailable P in runoff has been well correlated with soil test P levels and water soluble P (Pote et al., 1996). Extractants for soluble P in soils have included distilled H_2O and 0.01 M $CaCl_2$ in distilled H_2O. The 0.01 M $CaCl_2$ approximates the ionic strength of the soil solution. $CaCl_2$ solution in general does not extract as much P from the soil as distilled H_2O.

Currently, there is not a widely accepted standard method for the determination of water soluble phosphorus (P). Previous studies have used different procedures to determine water soluble P (Olsen and Sommers, 1982; Pote et al., 1996; Thompson et al., 1960), namely by using different soil:solution ratios or different extraction times. Some methods used large soil:solution ratios and long extraction times, such as, 1:20/1hr (Mackay et al., 1984), 1:105/15hr (Thompson et al., 1960), 1:100/15hr (van Diest, 1963), and 1:60/1hr (van der Paauw, 1965), while others used smaller soil:solution ratios and shorter extraction times; 1:10/5min (Olsen and Sommers, 1982), 1:10/5min (Kuo and Jellum, 1987), 1:1.25/1hr (Olsen and Watanabe, 1970), and 1:10/1hr (Kuo, 1996). It is difficult to compare the effectiveness of the different water soluble P methods because all of these studies used different soils. Also, other methods have used a solution of $CaCl_2$ as an extracting solution (Kuo, 1996) to aid in filtration, which in turn has an effect on the amount of P extracted. However, Chapman et al. (1997) did investigate the effect of soil:solution ratio on the fractions of P extracted with water. Additionally, Hesketh and Brooks (2000) studied the effect of soil:solution ratio on $CaCl_2$ extractable P of selected European soils. This study will investigate the effect of soil to solution ratio, shaking time, and electrolyte concentration on water soluble P extractions in order to develop a convenient and efficient method for determining water soluble P, and to determine the relationship of water soluble P and Mehlich 3 extractable P.

MATERIALS AND METHODS

Ten Oklahoma soils were chosen to develop a convenient and efficient method for water soluble P determination. Soils varied in physical and chemical properties (pH, texture, etc.), as well as Mehlich 3 extractable phosphorus content (Table 1).

To determine the water soluble P content of the soils, a known weight of soil sample (air dried, passed 2mm sieve) was placed in 50 mL centrifuge tubes along with a known volume of deionized water. The tubes were capped and placed on an end-to-end shaker and shaken for a specified time at 150 oscillations per minute. The tubes were then centrifuged at 10,000 rpm (14,470 x g) for 10 min. The clear supernatant was then analyzed colorimetrically for phosphorus using the molybdate blue method (Kuo, 1996).

Various ratios of soil to extracting solution and the extracting times were compared. The soil:solution ratios used were 1:2, 1:5, 1:10, and 1:50. The actual mass of soil and volume of water used was 10 g & 20 mL, 4 g & 20 mL, 2 g & 20mL. and 0.75 g & 37.5 mL, respectively. The extraction times were 10 min., 30 min., 1 hr., and 15 hr. for each of the soil:solution ratios. The effect of the extracting solution was also investigated. This was done by using deionized water, tap water, and three concentrations of $CaCl_2$ as the extracting agent. The concentrations of $CaCl_2$ used were 0.005M, 0.01M, and 0.02M. Mehlich 3 P was determined by extracting 1 g of soil with 10 mL of Mehlich 3 solution and shaking for five minutes.

The relationship between water soluble P and Mehlich 3 extractable P was also investigated. Based on the preliminary results, the soil to water ratio of 1:10, and shaking time of 10 minutes was chosen to determine soil water extractable P, which is similar to the method used for Mehlich 3 P. The relationship between water soluble and Mehlich 3 extractable P was established on a large number of soil samples with a wide range of soil properties. This was done by placing two grams of soil (air dried, passed 2mm sieve) into 50 mL centrifuge tubes. Twenty mL's of deionized water were added to the tubes. The tubes were then capped and shaken on an end-to-end shaker for 10 minutes. The tubes were then centrifuged at 10,000 rpm (14,470 x g) for 10 minutes to obtain a clear supernatant. Phosphorus content was determined colorimetrically using the ascorbic acid method (Kuo, 1996).

For all of the P extractions, high speed centrifugation was chosen to obtain a clear supernatant instead of filtration (0.45μm). Preliminary results did not show a difference between the two methods. For the sake of this study, the centrifugation proved to be the most efficient method.

RESULTS AND DISCUSSION

Effect of Extraction Time and Soil:Solution Ratio on Water Soluble P

There have been many studies that use different water soluble P methods. However, there are very few studies comparing different water soluble P tests. Water soluble P extracted with 4 shaking times and 4 soil to solution ratios is presented in Figure 1. In general, the amount of P extracted increased as shaking time increased and as soil to solution ratios decreased. However, the increase with shaking time depended on the soil to solution ratio. For the 1:2 ratio, there was an increase in P extracted by 9%, 17%, and 23% when extraction time increased from 10 min. to 30 min., 1 hr., and 15 hr., respectively. When comparing extraction times for the 1:50 ratio, the increase was nearly 100% from 10 min. to 15 hr. Table 2 shows the average relative amount of P extracted for all samples normalized to the 1:10 soil to solution ratio and ten minute extraction time. These results were consistent with the findings of Chapman et al. (1997) in which the amount of extracted P per unit weight of soil increased as the soil:solution ratio decreased. It is likely that the solutions had not reached an equilibrium concentration in the shorter extraction times. Therefore, the P in solution will increase until the solution reaches equilibrium if given enough time.

It appears the lower soil:solution ratios approach an equilibrium concentration sooner than the higher soil:solution ratios. As the soil:solution ratio decreased, the amount of P extracted increased. The amount of P extracted using 1:50 soil:solution ratio was 4.3, 4.4, 4.8, and 7 times that using 1:2 soil:solution ratio shaking for 10 min., 30 min., 1 hr., and 15 hr., respectively. This is because there is a greater proportion of solution that can extract more P before the solution reaches equilibrium. All of the water soluble P methods that vary the extraction time and soil:solution ratio were strongly correlated with the Mehlich 3 extractable P (Figure 3).

Studies have shown that water soluble P methods using long extraction times and high soil:solution ratios (15 hr. and 1:105) are correlated with plant growth (Thompson et al., 1960; van Diest, 1963). However, these methods may not be suitable for environmental impact assessment. During a rainfall event, surface runoff is in contact with the soil for only a short period of time. A shorter extraction time and a lower soil:solution ratio (e.g., 10 min. & 1:10) may better simulate P in the surface runoff under natural environmental conditions. Additionally, the shorter extraction time and lower soil:solution ratio are well correlated with Mehlich 3 P levels. Therefore water soluble P may also be used as an indicator of a soil's ability to support plant growth. A soil to water ratio of 1:10 and shaking for 10 minutes can be easily adapted by commercial and university soil testing laboratories since these are similar to existing agronomic P test procedures.

Effect of $CaCl_2$ Concentration on the Amount of P Extracted

Five extraction solutions differing in salt concentrations were used to extract soluble P. As the concentration of $CaCl_2$ in the extracting solution increased, the amount of P extracted decreased (Figure 2). The most noticeable difference is that deionized (DI) water extracted the most P. There were differences in the rest of the extracting solutions, however, these were subtle compared to the DI water extraction. The lower levels of P extracted by other solutions containing electrolytes may be due to a cation effect in which the Ca^{2+} is increasing the P sorption capacity of the soil. Therefore, you would find less P in solution with increased concentrations of Ca^{2+}. There have been several studies that try to explain this effect (Helyar et al., 1976; Bowden et al., 1980). Regardless of the mechanism, they all concluded that the P sorption capacity increases with an increase in Ca^{2+} concentration. However, the difference between 0.005M $CaCl_2$ and the 0.02M $CaCl_2$ is small and not significant.

This would be especially helpful for rainfall simulation studies. In these studies, you do not always have the luxury of choosing the best water source. Many times you pump the water out of the nearest pond you can find. With knowledge of this effect $CaCl_2$ has on water soluble P, one could better compare results from rainfall simulation studies that utilized different water sources.

Relationship between water soluble P and Mehlich 3 extractable P

Over one hundred Oklahoma soils varying in physical and chemical properties, and P content were used to develop a relationship between water soluble P and Mehlich 3 P (Figure 3). The water soluble P (1:10 soil:solution, 10 min., DI H_2O) is highly correlated with Mehlich 3 P ($r^2 = 0.88$, $p < 0.001$). Deionized water appears to extract only about 6% of the amount of P that the

Mehlich 3 extracts. For instance, if a soil has a Mehlich 3 P level of 160 mg/kg, you could expect it to have a water soluble P level of about 10 mg/kg. This extrapolates to about 1 mg/L P in the extracting solution. Using 1 mg/L as a suggested upper limit for P in runoff water (Sharpley et al., 1996), 160 mg/kg of Mehlich 3 P in the soil would be the critical upper limit assuming the 1:10 soil:solution ratio/10 min. extraction is a reasonable indicator of the amount of P that would be released during a runoff event. However, this was originally established for point source discharge from wastewater treatment facilities and may not be applicable to non-point sources of P pollution. In addition, this does not include other factors of P sorption such as soil texture or pH. For instance when comparing a sandy soil to a clay soil, both of which have a Mehlich 3 P level of 160 mg/kg, the sandy soil will have a much greater chance of releasing P to the environment than the clay soil. This difference is because soil texture affects P sorption capacity of soils (Chapter 2). Therefore, the Mehlich 3 P level alone may not be an adequate indicator for establishing upper limit threshold values for P.

Effect of pH on the relationship between water soluble P and Mehlich 3 P

The effect of pH on the relationship between water soluble P and Mehlich 3 P is shown in Figure 4. Soils were grouped into three pH ranges: low (pH<5.5), neutral (pH 5.5-7.0), and high (pH>7.0). Water soluble P (1:10, 10 min.) was correlated with Mehlich 3 P for all three pH ranges, however the slope of the correlation was different for each pH region. This implies that at a given water soluble P level, a soil will have a different corresponding Mehlich 3 P level depending on the pH of that soil. Using the above stated critical water soluble P level of 10 mg/kg (equivalent to 1 mg L^{-1} in the extractant of a 1:10 ratio/10 min. extraction), you could expect Mehlich 3 P levels of 208, 143, and 371 mg kg^{-1} (or 416, 286, 742 lbs./acre in the top six inches of the soil) for low, neutral, and high pH ranges, respectively. Therefore, if a soil has a high or low pH, it can have a higher Mehlich 3 P level before it reaches the critical water soluble P level than if it were a neutral pH soil. This increase in sorption capacity for low and high pH soils is possibly due to increased amounts of Al and Fe compounds in low pH soils and increased amounts of Ca and Mg in high pH soils. These cations or their compounds are likely to bind with P and reduce P desorption. The effect of pH on water soluble P may be consistent with the findings of Pote et al. (1996) in which they found a Captina silt loam soil with a pH of 5.0 to have a good correlation between Mehlich 3 P and dissolved reactive P in runoff. They determined that 1.0 mg P L^{-1} in runoff was correlated to about 260 mg kg^{-1} of Mehlich 3 P. Based on the relationship we found with pH and Mehlich 3 P, you could expect a low pH soil with a Mehlich 3 P level of 208 mg kg^{-1} to have a water soluble P level of 10 mg kg^{-1} or 1 mg L^{-1} in solution. Water soluble P is more of a physical extraction where the water extracts the easily desorbable P by "washing" it away from the soil. Water soluble P is more dependent on soil texture. Mehlich 3 P is a chemical extraction that removes the phosphorus by dissolving minerals in the soil with strong acid and by displacing P in the soil with fluoride. The Mehlich 3 extraction determines the amount of P that would be available during the growing season of the crop, whereas the water soluble extraction determines the amount of P that is immediately available. This information may help influence management decisions for land application of manure based on soil pH and water soluble P.

CONCLUSIONS

Increasing the extraction time of water soluble P from 10 minutes, 30 minutes, 1 hour, to 15 hours caused an increase in the amount of P extracted. Decreasing the soil:solution ratio from 1:2, 1:5, 1:10, to 1:50 caused an increase in the amount of P extracted as well. The addition of $CaCl_2$ in the extracting solution caused a decreasing trend in the amount of P extracted. Knowledge of these differences should help researchers to better compare results of past studies in which differing methods were used to determine water soluble P in soils.

Additionally, it is necessary to have a standardized method for water soluble P for environmental risk assessment for use in future studies. Water soluble P extracted with a 1:10 soil:solution ratio, 10 minute extraction time, using deionized water is a suitable test for determining the impact a soil may have on the environment. This procedure should be easily adaptable to most commercial and university soil testing labs if a water soluble P test is needed to better manage P fertilization. The relationship between water soluble P and Mehlich 3 extractable P is affected by soil pH, which in turn may affect management decisions on the application of P nutrient sources. Having either a very low or very high soil pH may allow the soil to have a higher agronomic soil P level without having added risk to the surrounding environment.

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Table 1 Chemical and physical properties of soils used.

Soil	Texture	M3 P (mg/kg)	pH	% Clay
Darnell	fine sandy loam	4	5.4	11
Dalhart	fine sandy loam	12	7.3	12
Pond Creek	silt loam	31	5.2	28
Dougherty	loamy fine sand	69	5.2	8
Lebron	clay	80	7.6	59
Sallisaw	loam	142	5.5	22
Stigler	silt loam	236	6.3	28
Soil 1*	silt loam	330	5.9	8
Soil 2*	loam	425	6.4	13
Soil 3*	silt loam	540	6.4	8

* Randomly selected from the soil testing lab. Soil types and location were unknown.

Table 2 Average P extracted with 4 shaking times and 4 soil:solution ratios normalized to that of 1:10 and 10 min. shaking.

Shaking	**Soil:Solution Ratio**			
Time	1:2	1:5	1:10	1:50
10 min.	0.4	0.6	**1.0**	1.7
30 min.	0.4	0.8	1.3	1.9
1 hr.	0.5	0.9	1.4	2.2
15 hr.	0.5	1.0	1.7	3.4

Table 3 Correlation coefficients (r^2) between water soluble P and Mehlich 3 extractable P for four soil:solution ratios at four shaking times.

Extraction	Soil:Solution Ratio			
Time	**1:2**	**1:5**	**1:10**	**1:50**
10 min.	0.95	0.88	0.92	0.83
30 min.	0.96	0.97	0.95	0.83
1 hr.	0.96	0.96	0.96	0.90
15 hr.	0.95	0.96	0.96	0.96

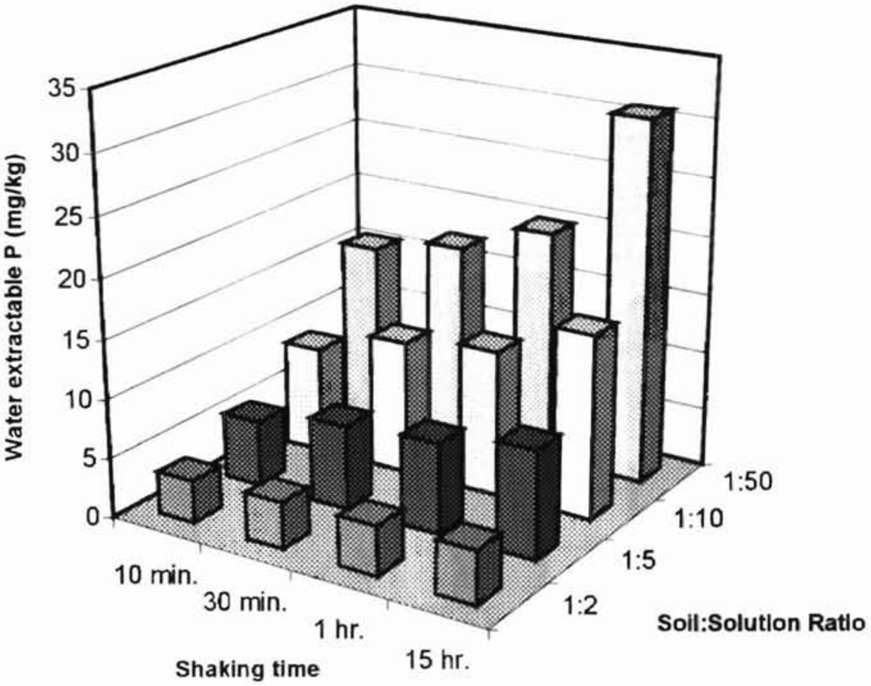

Figure 1 Effect of shaking time and soil to solution ratio on the amount of water extractable P.

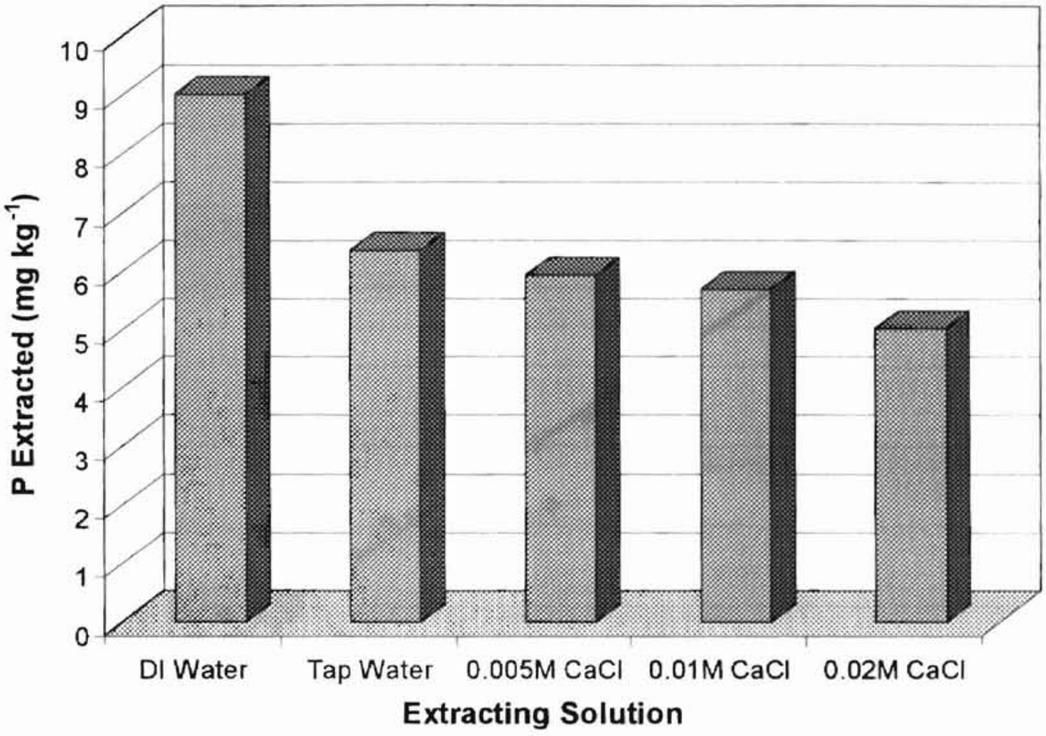

Figure 2 Effect of $CaCl_2$ concentration on average amount of P extracted for ten soils using 1:10 soil to solution ratio and 10 minute extraction time.

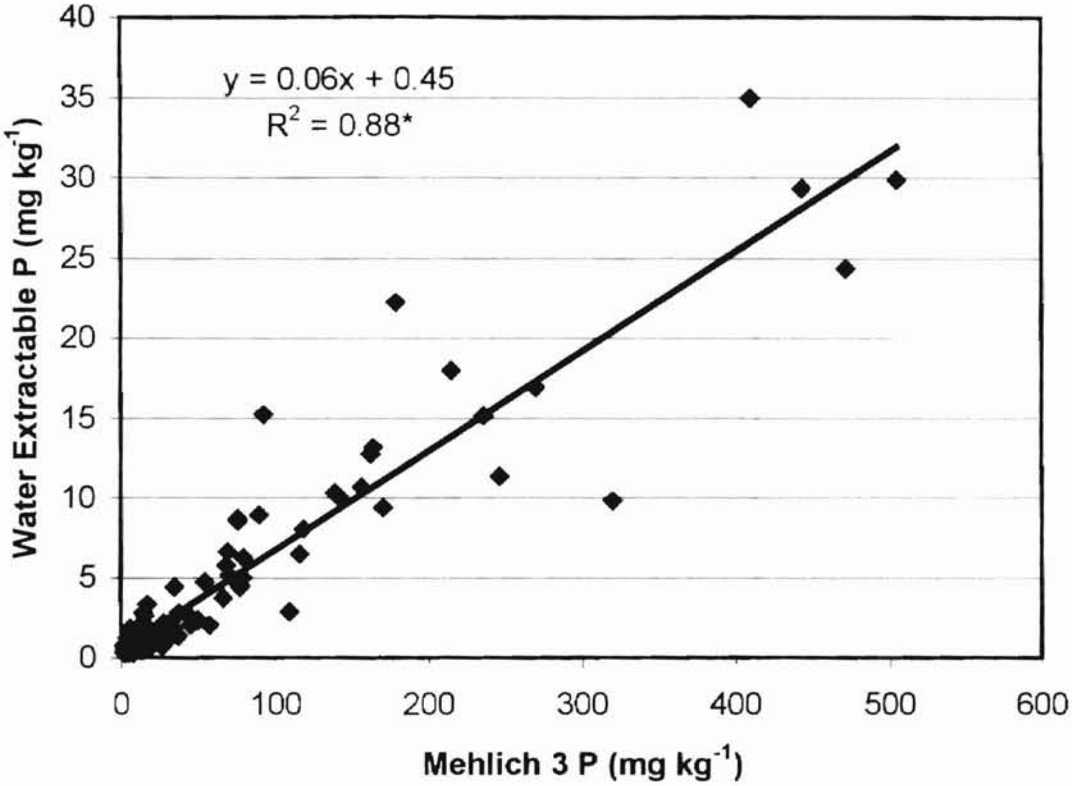

Figure 3 Correlation between water soluble P (1:10 ratio/10 min. extr.) and Mehlich 3 P for several Oklahoma soils. (* denotes significance at the 0.05 level)

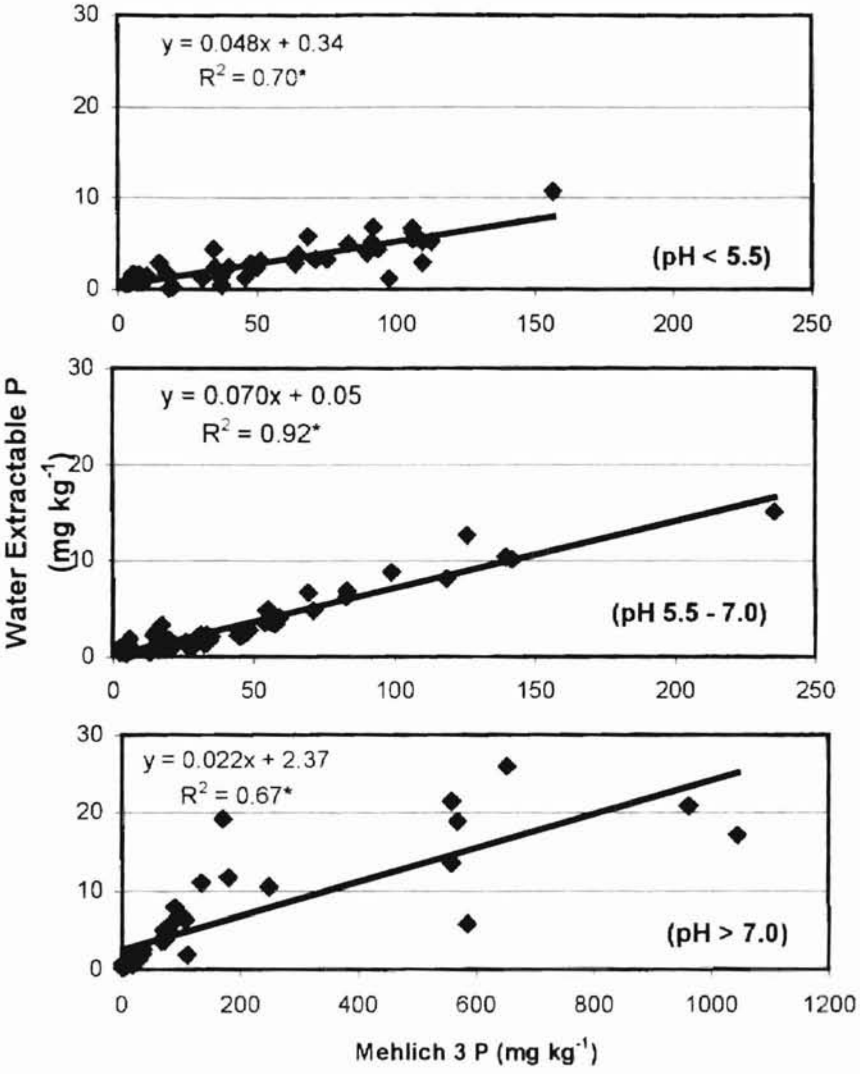

Figure 4 Relationship between water soluble P and Mehlich 3 P for low (top), neutral (middle), and high (bottom) pH ranges. (* denotes significance at the 0.05 level)

CHAPTER II

PHOSPHORUS SORPTION CAPACITY AND SATURATION INDEXES OF SELECTED OKLAHOMA SOILS

ABSTRACT

The phosphorus (P) sorption capacity of a soil helps to estimate its ability to assimilate the amount of P added and its potential to lose P to receiving water bodies. The purposes of this study were to determine the P sorption capacity and saturation indexes of predominant Oklahoma soils and to assist in identifying a threshold value at which additions of P to the soil would not be in the best interest to the surrounding environment. Several chemical and physical properties were determined from twenty-eight benchmark soils in order to characterize the P status of those soils. Phosphorus sorption maximum determined from a Langmuir adsorption isotherm was well correlated with: clay content of the soils ($r^2 = 0.63$), percent clay & percent organic carbon ($r^2 = 0.87$), sum of acid ammonium oxalate extractable iron and aluminum ($r^2 = 0.78$), and the sum of Mehlich 3 extractable iron and aluminum for acidic soils ($r^2 = 0.74$). P adsorption isotherm maximums ranged from 34 to 497 mg kg^{-1}. A phosphorus saturation index (PSI) using Mehlich 3 as the extracting solution was found to be well correlated with a PSI using acid ammonium oxalate ($r^2 = 0.80$). The oxalate PSI ranged from 2.8 to 38% and Mehlich 3 PSI ranged from 1.6 to 26%. P sorption capacities are highly correlated with clay content, soil organic matter,

and extractable aluminum and iron. Therefore, the P S_{max} of a soil can be easily predicted by many readily available soil properties.

INTRODUCTION

Although P is considered to be relatively immobile/stable in the soil system, there are mechanisms for P to leave the soil system through plant uptake, desorption into 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 build up in the soil, which increases chances of P loss from the soil system. Phosphorus accumulation commonly occurs in animal-based agriculture where animal manure is applied to meet the crop nitrogen needs of a specific yield goal. The N:P ratio of animal manure is generally lower than the N:P ratio for crop needs. Nitrogen based animal manure land application often results in an excessive application of phosphorus, which leads to an accumulation of phosphorus in the soil. To prevent this accumulation, manure should be applied according to the phosphorus needs of the crop, then supplemented with nitrogen fertilizer to accommodate the N needs of the crop (Daniel et al., 1994). Unfortunately, this is not always economically feasible for all producers due to increased costs with multiple fertilizer applications (Sharpley et al., 1996) or limited land available for land application.

Phosphorus is generally considered an immobile nutrient in the soil (Johnson et al., 1997) relative to mobile nutrients such as nitrate and chloride. This is because phosphorus reacts with various soil components and the solubility is influenced by many factors in the soil. These factors include: pH, soil texture, soil organic matter (SOM), iron, aluminum, and calcium contents.

Soil pH

Soil pH determines the forms and solubility of phosphorus compounds. It also has an effect on the other ions found in the soil solution. For instance, a greater concentration of soluble Al can be found in lower pH soils. At higher pH values, there is generally a greater concentration of Ca^{2+} in the soil due to the presence of calcium carbonates. The pH of a soil also influences the surface charge property of variable charged clays, which in turn affects chemical adsorption. Olsen and Watanabe (1957) found that per unit surface area, acid soils held more P and with greater bonding energy than those of alkaline soils. Soil pH varies from 4.0 to 8.5 in most agricultural fields, therefore, the solubility of P varies as well.

Surface Area

Clay content of a soil has a great effect on P sorption due to the large reactive surface area. Generally, the greater the specific surface area of a clay, the more P it can sorb. Soils across Oklahoma have wide differences in clay type and content, therefore, the P sorption capacities of those soils can be very different. As a result, the mobility of soil P should be different for soils with different textures.

Soil organic matter (SOM) has a highly reactive surface that is able to influence many soil properties and may react with phosphorus. There have been several studies which showed a positive correlation with organic carbon and phosphorus sorption (Singh and Tabatabai, 1977; Sanyal et al., 1993; Dodor and

Oya, 2000). However, the mechanism of the reaction between P and soil organic matter is not well understood.

Iron and Aluminum

Soluble and exchangeable aluminum (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$) and iron (Fe^{3+}) are able to react with P to form aluminum phosphate ($AlPO_4$) and iron phosphate ($FePO_4$). Over time, these minerals transform soluble P into less available or insoluble forms (Juo and Ellis, 1968). Several studies have found positive relationships between acidified ammonium oxalate extractable Al and Fe, and P sorption (Adams et al., 1987; Dodor and Oya, 2000; Sanyal et al., 1993). In these studies, the extracted Al and Fe is assumed amorphous and to react with P in the soil.

Sorption Models

Several models have been used to characterize P adsorption. Perhaps the two most popular models are the Langmuir and the Freundlich (Bohn et al., 1985) equations. They are both equilibrium adsorption models and assume precipitation of minerals does not take place. Both equations use the equilibrium P in solution vs. the amount of P sorbed by the soil. However, the Langmuir model has an advantage over the Freundlich in that it produces an adsorption maximum (Olsen and Watanabe, 1957).

Another approach used to characterize P sorption is to determine acidified ammonium oxalate extractable P, Al, and Fe (Schoumans, 1998). The P saturation is the ratio of the amount of oxalate-extractable P and the P sorption capacity, which is assumed to be the sum of oxalate extractable Al and Fe in the soil. It is assumed that the phosphorus adsorbs only to the Al and Fe oxides. A critical P saturation of 25% with this method has been established for Dutch soils (Sharpley et al., 1996). Above this limit, the risk of P losses to leaching and surface runoff become unacceptable. 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. Furthermore, Al and Fe oxides are less significant in high pH soils than acid soils. Sharpley (1996) has also proposed a P saturation model using Mehlich 3 soil test P and the adsorption maximum from P adsorption isotherms. It is defined as (extractable soil P / P sorption capacity)*100, where both variables are unit masses of P per unit mass of soil.

Many current guidelines for the application of P are an arbitrary number based on grossly exceeding the crop requirement of phosphorus, not the potential environmental impact of excessive P. The objective of this study is to determine a scientifically based value for soil P in order to minimize off-site water quality impact by utilizing easily obtainable information and properties of the soil. This will be done by characterizing the P sorption capacities of several Oklahoma soils and using physical properties of the soils to predict it's sorption maximum. Chemical extractions (Mehlich 3 and acid ammonium oxalate) will also be used to predict the sorption maximum. Phosphorus saturation indexes will be used to evaluate the P loading of the soils.

MATERIALS AND METHODS

Twenty-eight Oklahoma benchmark soils (Gray and Roozitalab, 1976) were chosen for P characterization to identify factors affecting their P sorption capacity. The soils chosen represent the diversity of soils found in Oklahoma along with the major land resources areas (Figure 1). The soils were sampled from the surface horizon (A horizon or plow layer) then air-dried and ground to pass a 2mm sieve.

Phosphorus adsorption isotherms were determined using the Langmuir model to predict the P sorption maximum of the soils. One gram of soil sample was equilibrated with 25 mL of varying concentrations of P in 0.01M $CaCl_2$ solution in 50 mL centrifuge tubes. The concentrations of the solutions were 0, 0.5, 1, 5, 10, 15, and 20 mg/L phosphorus. The tubes were shaken for 24 hours on an end-to-end shaker at 150 oscillations per minute. The samples were then centrifuged for 10 minutes at 10,000 rpm (14,470 x g). 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.

Acid ammonium oxalate extractions were performed to determine the amounts of amorphous aluminum (Al), iron (Fe), and phosphorus (P) in the soils (Schoumans, 1998). Thirty mL of acid ammonium oxalate solution were added to 1.5 grams of soil in 50 mL centrifuge tubes. The extracting solution was made by dissolving 16.2 g of ammonium oxalate monohydrate $[(COONH_4)_2.H_2O]$ and

10.8 g of oxalic acid dihydrate [$(COOH)_2.2H_2O$] in one liter of water and adjusted to pH 3.0 by addition of ammonium oxalate or oxalic acid. The tubes were shaken for two hours, in the dark, on an end-to-end shaker at 150 oscillations per minute. They were then centrifuged at 10,000 rpm for 10 minutes to obtain a clear supernatant. The solutions were then analyzed for P, Al, and Fe using a TJA-9000 inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Mehlich 3 (Mehlich, 1984) solution was also used to extract P, Al, and Fe. The Mehlich 3 extraction is widely used to assess the amount of P available to a plant during the growing season. It works well in a wide range of pH values. For this study we try to use the M3 extractable P, Al, and Fe to develop a saturation index similar to the acid ammonium oxalate method, but without additional analytical costs. The soils were tested using 2 grams of soil and 20 mL of M3 in 50 mL centrifuge tubes. They were shaken for 10 minutes on an end-to-end shaker (150 opm). The samples were then centrifuged at 10,000 rpm for 10 minutes. The solutions were analyzed for P, Al, and Fe using ICP-AES.

Water soluble P was extracted using 2 grams of soil (air dried, passed 2mm sieve) and 20 mL of deionized water in a 50 mL centrifuge tube. The samples were shaken for 10 minutes on an end-to-end shaker (150 opm). The samples were then centrifuge for 10 minutes at 10,000 rpm. The solutions were then analyzed for P colorimetrically using the ascorbic acid method (Kuo, 1996).

Soil OM and clay content were obtained from an Scott (1994). The general soil properties are shown in Table 1.

RESULTS AND DISCUSSION

General properties of soils used in study

This study utilized a group of soils with a wide range of soil properties. Table 1 and Table 2 list some of the chemical and physical properties of the soils used along with the mean, maximum, and minimum values for each property. Soil pH ranged from 4.3 to 8.1, clay contents ranged from 7% to 66%, and organic carbon contents ranged from 0.4% to 3.0%. Additionally, the amount of extractable phosphorus in the soils varied greatly as well, with water soluble P ranging from 0.4 mg kg^{-1} to 10 mg kg^{-1} and Mehlich 3 extractable P ranging from 2.5 mg kg^{-1} to 140 mg kg^{-1}. Five soil orders were represented. The majority of the soils were mollisols with 14 soils, and alfisols with eight soils. There were also two vertisols, two ultisols, and two inceptisols. Given this wide range of soil properties, any relationships found with this set of soils should be applicable to a variety of soils.

Effects of soil OM and clay content on P S_{max}

The relationship between P sorption maximum (P S_{max}), percent clay, and percent OC can be seen in Figure 2, which gives an example of P sorption isotherms for three selected soils. As the percent clay and OC increased, a corresponding increase in P S_{max} was observed. For example, the Parsons soil which has a P S_{max} of 289 mg kg^{-1}, also has 30% clay and 1.4% OC. Whereas the Dalhart soil has a P S_{max} of 64 mg kg^{-1} with 12% clay and 0.35% OC. Tables 1 and 2 show the P S_{max}, percent clay, and percent OC for all of the soils used in the study. Again, the same positive relationship between the three variables can be observed. Using this data, percent clay was correlated ($r^2 = 0.63$) with the P S_{max} of the soils in the following regression model.

$S_{max} = 5.5(\% \text{ Clay}) + 40 \qquad r^2 = 0.63 \qquad$ [Eq. 1]

When we expanded this to a multiple regression to include the variables of percent clay and percent organic carbon (OC), confidence was increased for the correlation with P S_{max}.

$S_{max} = 5.9(\% \text{ Clay}) + 32.4(\% \text{ OC}) - 0.35 \qquad r^2 = 0.87 \qquad$ [Eq. 2]

These results are consistent with the findings of others (Sanyal et al., 1993; Singh and Tabatabai, 1977; Dodor and Oya, 2000) in that clay content and OC are both well correlated with P Sorption maximum derived from the Langmuir equation. We questioned whether percent clay and percent organic carbon were correlated and were possibly causing a false increase in our ability to predict P S_{max}, which was of concern for Sanyal et al. (1993). However, we graphed percent clay vs. percent OC and found that they were not correlated to one another (Figure 3) for the soils used in this study ($r^2 = 0.31$). Using these results, one should be able to obtain a fairly good estimate of the P S_{max} of a soil simply based on the two physical characteristics of percent clay and percent organic carbon. Both of which may possibly be roughly extrapolated from a County Soil Survey.

Effect of extractable Al & Fe on P S_{max}

The acid ammonium oxalate method is currently being used for Dutch soils to determine when additions of P should not continue due to potential adverse effects to the environment (Sharpley et al., 1996). This determination is done by using a saturation index in which the P sorption capacity is assumed to be the sum of the acid ammonium oxalate extractable Al and Fe (Al_{OX} + Fe_{OX}) for a particular soil. The sum of Al_{OX} and Fe_{OX} was plotted vs. P for all of the soils used in the study(Figure 4). The sum of the Al_{OX} and Fe_{OX} was correlated with the P S_{max} ($r^2 = 0.78$). Similar results were found by Dodor and Oya (2000) and Sanyal et al. (1993), however these studies correlated both Al_{OX} and Fe_{OX} with P S_{max} separately but not the sum of Al and Fe. Instead of performing a phosphorus adsorption isotherm, which may take several days, you can more easily determine the amount of oxalate extractable Fe and Al and estimate P S_{max} for a soil with a single extraction.

The sum of the Mehlich 3 extractable Fe and Al (Fe_{M3} + Al_{M3}) was also plotted vs. P S_{max} (Figure 5). This plot was constructed using all of the soils in the study. A significant linear trend is seen in the data ($r^2 = 0.39$). However, when only acid soils (pH < 7.0) were used Fe_{M3} + Al_{M3} were well correlated with P S_{max} ($r^2 = 0.74$). An approach similar to this was used by Khiari et al. (1999) where Mehlich 3 extractable Al was used to describe the P sorption capacity of 24 Canadian soils. The work of Khiari et al. (1999) was based on the strong correlation between P S_{max} and Al_{M3} found by Giroux and Tran (1996) for 58 soils in Quebec. However, all of the soils used in Khiari et al. (1999) were at pH 7 0 or below, and they did not verify their results with actual P S_{max} levels. This relationship between P S_{max} and extractable Al and Fe is useful in that a commonly performed soil test (Mehlich 3) can estimate P S_{max} in acidic soils, simply by analyzing two additional elements (Fe and Al), which is easily done with an ICP-AES. Although given the variability of Oklahoma soils, $Al_{M3} + Fe_{M3}$ alone may not be able to accurately predict the P S_{max} for all soils in Oklahoma due to the amount of calcareous and high pH soils found in the state. This inability for $Al_{M3} + Fe_{M3}$ to predict P S_{max} for high pH soils is likely due to low and/or variable amounts of Mehlich 3 extractable Al and Fe in high pH soils.

Phosphorus Saturation Indexes

The phosphorus 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 and Mehlich 3 as extractants. The acid ammonium oxalate method for determining the phosphorus saturation index (PSI_{OX}) was highly correlated ($r^2 = 0.80$) to the phosphorus saturation index utilizing Mehlich 3 (PSI_{M3}) as the extractant (Figure 6). For the soils used in this study, the PSI_{OX} ranged from 2.8 to 38% while the PSI_{M3} had a range of 1.6 to 26% (Table 2).

For Dutch soils, when P occupies twenty-five percent of the sorption capacity, based on the acid ammonium oxalate extraction, the soil is considered high in P and should not receive further additions of P. The PSI used in the Netherlands also uses an alpha value in the equation that is multiplied by the sum of the oxalate extractable Al and Fe. This alpha value is experimentally determined to help determine the relationship between the P S_{max} and oxalate extractable Al and Fe (Sims, 1998). Both saturation indexes utilized for our study use the amount of P extracted, divided by the sum of the aluminum and iron of each extraction [P/(Al + Fe)]. For simplicity in comparisons, we did not use an alpha value in our determinations of PSI since it is a constant and would have the same effect on the relationships but yield a different number. Given the relationship in Figure 6, a PSI_{OX} value of 25% would be equivalent to a PSI_{M3} value of about 18%. If you were to add an alpha value to the determination of PSI_{OX}, then you would simply adjust the PSI_{M3} with the same alpha.

Khiari et al. (1999) used Mehlich 3 extractable P and Al as an agro-environmental diagnosis tool. However, they did not verify that the Mehlich 3 extractable Al was correlated with the P S_{max}; instead they based their findings on the results of Giroux and Tran (1996).

The oxalate extraction is not a routine test, however Mehlich 3 is a very common soil test used by many soil testing laboratories. Many testing facilities use ICP-AES for their analyses. Given these two facts, it should be very easy for soil testing labs to provide a phosphorus saturation index for acidic and neutral soils.

CONCLUSIONS

Understanding the P sorption capacity of a soil can help to estimate the amount of P that a soil is capable of holding. The traditional method of determining the P S_{max} by performing a P adsorption isotherm is laborious and time consuming. Soil physical properties were well correlated with the S_{max} for the soils used in the study. This was seen when based on texture (% clay) and clay content & organic carbon content. Using this relationship, the P sorption capacity of a soil could be estimated from soil properties that could be easily obtainable from reference sources such as County Soil Survey Manuals.

Additionally, chemical extractions were highly correlated with P S_{max}. The sum of the Mehlich 3 extractable Fe and Al and the sum of the oxalate extractable Fe and Al were both well correlated with P S_{max}. The relationship between Mehlich 3 extractable Al and Fe and P S_{max} could allow labs to easily determine the P sorption capacity of a soil while performing a routine soil analysis. However, these methods did not work as well for high pH soils. Possibly, a relationship between extractable Ca and Mg can be found for the P S_{max} for high pH or calcareous soils.

The use of phosphorus saturation indexes can further help to characterize the P status of soils. These indexes provide valuable information about the amount of P in the soil relative to the P sorption capacity. This knowledge can help to better manage application of P to soil systems.

The results of this study confirm that the P sorption capacity of Oklahoma soils is influenced by many variables. Additionally, the P S_{max} can be predicted by many of these variables. Therefore, setting guidelines concerning the application of P to a soil should not be based solely on the agronomic soil test level for a particular soil, but rather a combination of the variables that affect the P dynamics of the soil system.

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Table 1 Classification and general properties of soils used for this study.

Soil	Classification	pH	Clay (%)	OC (%)	H_2O-P* (mg/kg)	M3-P* (mg/kg)
Bernow	Glossic Paleudalfs	4.3	11	1.4	1.4	11
Burleson	Udic Haplusterts	5.9	42	1.1	1.5	30
Carnasaw	Typic Hapludults	5.7	21	2.8	1.8	6
Clarksville	Typic Paleudults	5.5	26	2.0	1.7	20
Cobb	Typic Haplustalfs	5.5	16	0.4	6.6	70
Dalhart	Aridic Haplustalfs	7.3	12	0.4	1.3	12
Darnell	Udic Haplustepts	5.4	11	0.5	0.7	4
Dennis	Aquic Argiudolls	5.7	25	1.6	0.7	4
Dougherty	Arenic Haplustalfs	5.2	8	0.7	5.7	69
Durant	Udertic Argiustolls	6.7	27	2.5	0.7	5
Easpur	Fluventic Haplustolls	5.9	22	0.6	0.5	5.5
Grant	Udic Argiustolls	6	26	0.8	0.7	14
Kirkland	Udertic Paleustolls	5.7	35	1.1	1.4	29
Lebron	Fluvaquentic Hapludolls	7.9	59	2.0	1.5	34
Mansic	Aridic Calciustolls	8.1	35	1.4	0.7	20
Osage	Typic Epiaquerts	5.6	66	3.0	1.4	34
Parsons	Mollic Albaqualfs	6.5	30	1.4	0.7	17
Pond Creek	Pachic Argiustolls	5.2	28	1.0	1.2	31
Pratt	Lamellic Haplustalfs	6.3	7	0.4	0.4	2.5
Renfrow	Udertic Paleustolls	6.4	25	1.4	0.7	5.5
Richfield	Aridic Argiustolls	7.4	45	0.8	1.0	17
St. Paul	Pachic Argiustolls	6.9	28	1.1	0.4	5
Sallisaw	Typic Paleudalfs	5.5	22	1.2	10	140
Stigler	Aquic Paleudalfs	5.6	28	2.3	8.0	120
Summit	Oxyaquic Vertic Argiudolls	7.6	58	2.5	0.4	5.5
Tillman	Typic Paleustolls	6.4	34	0.7	1.5	26
Woodward	Typic Haplustepts	7.7	20	1.1	0.5	3.5
Zaneis	Udic Argiustolls	5.7	21	1.2	0.5	3.5
Mean		6.2	28	1.3	1.9	26.4
Maximum		8.1	66	3.0	10	140
Minimum		4.3	7	0.4	0.4	2.5

* Molybdate reactive P analyzed on a spectrophotometer.

Table 2 Phosphorus sorption characteristics of soils used for study.

Soil	S_{max}	Acid Ammonium Oxalate				Mehlich 3			
		P*	Al*	Fe*	PSI-Ox	P*	Al*	Fe*	PSI-M3
	mg/kg	mg/kg			%	mg/kg			%
Bernow	110	68	290	670	9.7	31	280	340	6.1
Burleson	240	150	1100	1600	7.2	43	690	160	4.9
Carnasaw	240	71	1200	1600	3.2	16	690	160	1.8
Clarksville	280	200	1200	1200	9.6	50	860	140	4.7
Cobb	100	110	510	360	14	68	600	46	9.5
Dalhart	64	48	260	150	12	14	290	36	4.0
Darnell	60	50	270	240	12	24	350	69	5.6
Dennis	240	90	900	2200	4.0	16	660	130	1.9
Dougherty	92	120	190	280	31	69	190	130	24
Durant	200	68	800	2300	3.1	14	480	130	2.2
Easpur	120	73	420	580	9.1	20	410	84	3.8
Grant	170	87	620	640	8.2	23	600	88	3.2
Kirkland	160	130	860	1300	7.3	37	700	150	4.1
Lebron	250	420	1100	1100	23	38	100	70	24
Mansic	182	390	780	230	38	26	81	13	26
Osage	500	550	1600	9600	7.7	45	820	480	3.8
Parsons	290	160	770	2700	6.8	22	550	130	3.1
Pond Creek	220	120	730	800	9.7	39	700	130	4.5
Pratt	34	26	140	120	12	5	210	35	2.0
Renfrow	170	65	640	860	5.4	13	550	71	2.0
Richfield	180	170	1100	670	11	22	620	52	2.9
Saint Paul	180	120	890	470	9.3	13	530	50	2.1
Sallisaw	230	420	1200	1300	21	180	810	150	18
Stigler	240	750	1200	4000	21	180	800	270	17
Summit	430	120	2000	3400	2.8	13	640	90	1.6
Tillman	110	150	720	820	12	31	550	88	4.6
Woodward	170	150	950	220	12	12	360	27	2.9
Zaneis	160	62	800	890	4.4	14	600	71	2.0
Mean	194	176	830	1430	11.6	38.5	525	121	6.9
Maximum	500	750	2000	9600	38	180	860	480	26
Minimum	34	26	140	120	2.8	5	81	13	1.6

* Total dissolved concentrations in solution, analyzed on an ICP-AES.

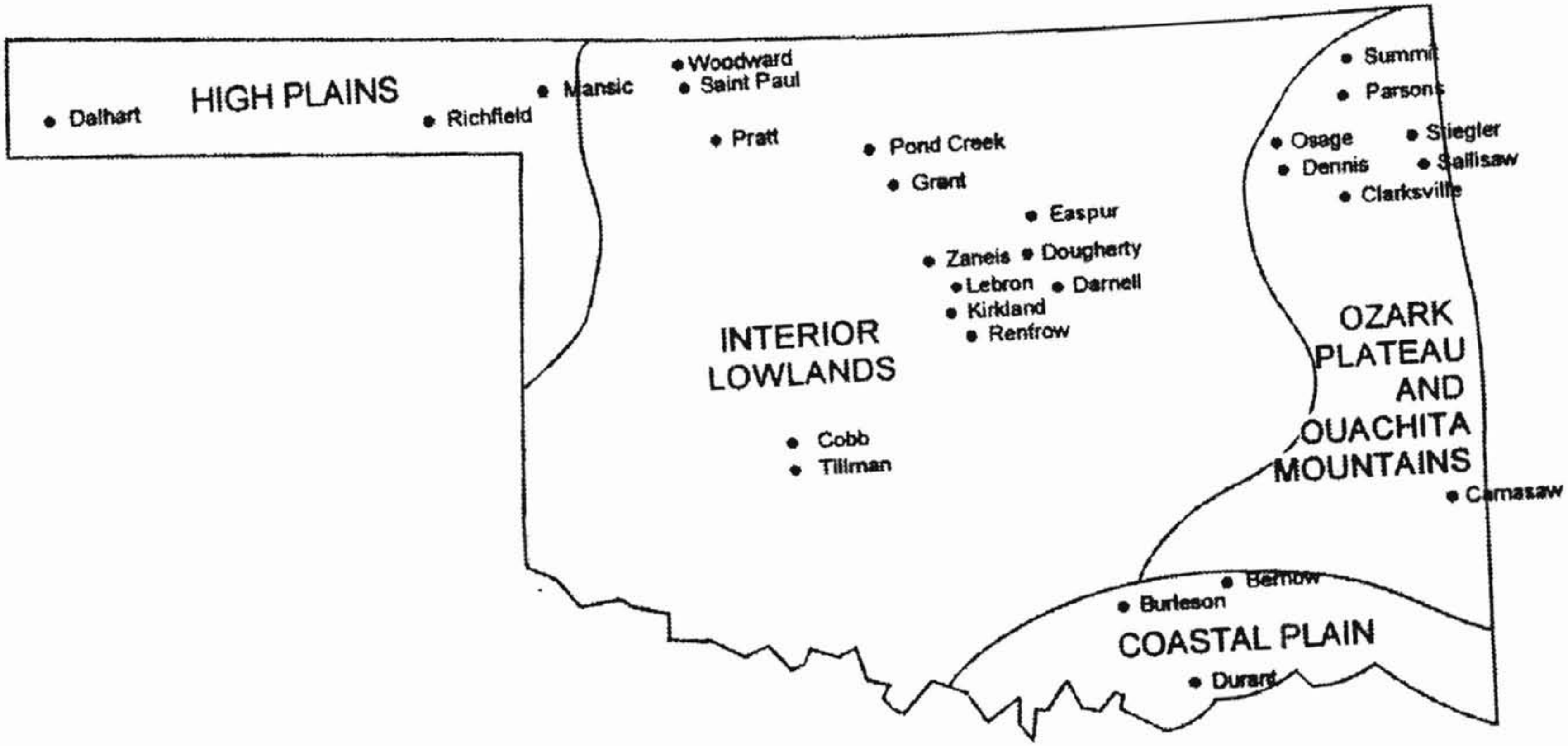

Figure 1 Locations of the 28 Oklahoma benchmark soils used in this study along with delineation of major land resource areas.

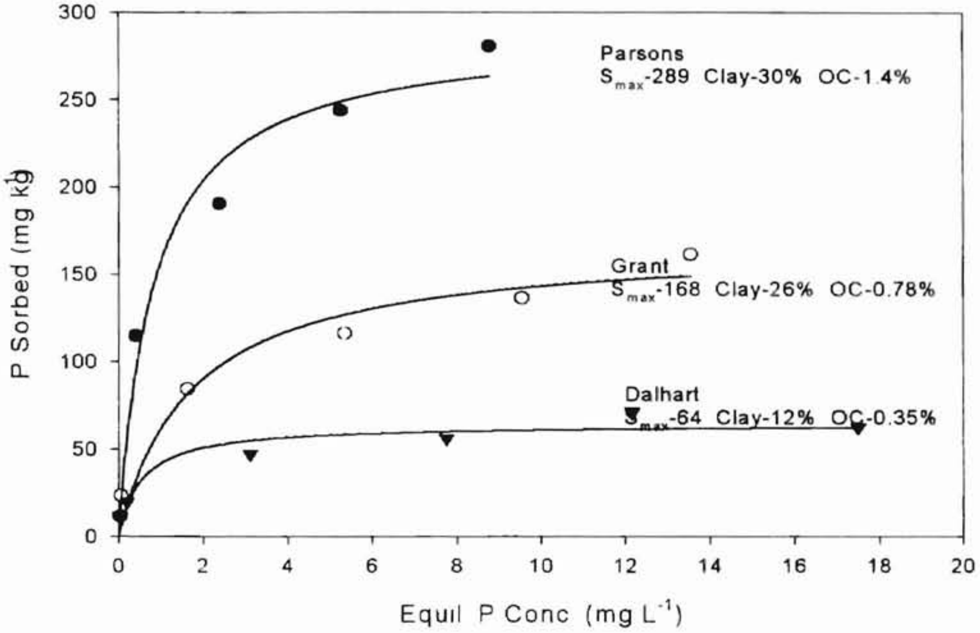

Figure 2 Phosphorus adsorption isotherms for three selected soils showing the relationship between S_{max}, % clay, and % OC.

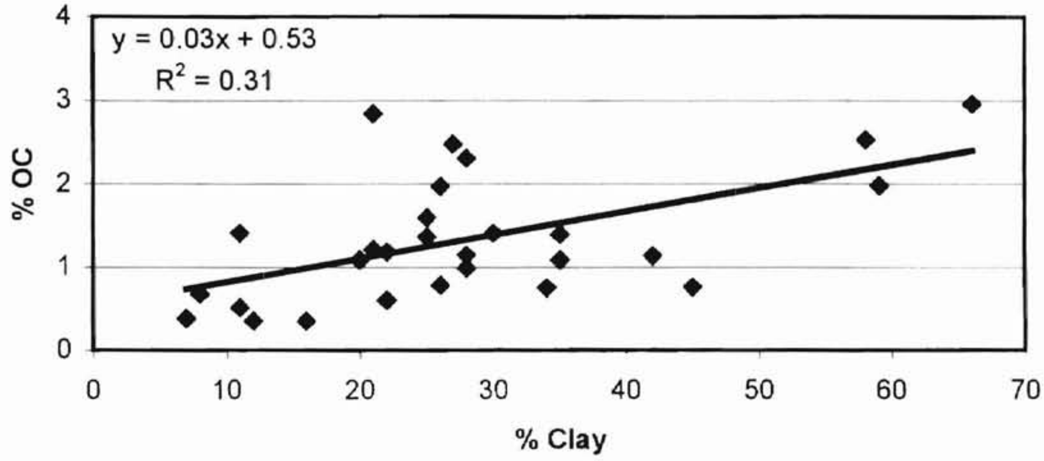

Figure 3 Relationship between percent organic carbon and percent clay for all soils used in the study (not significant at the 0.05 level).

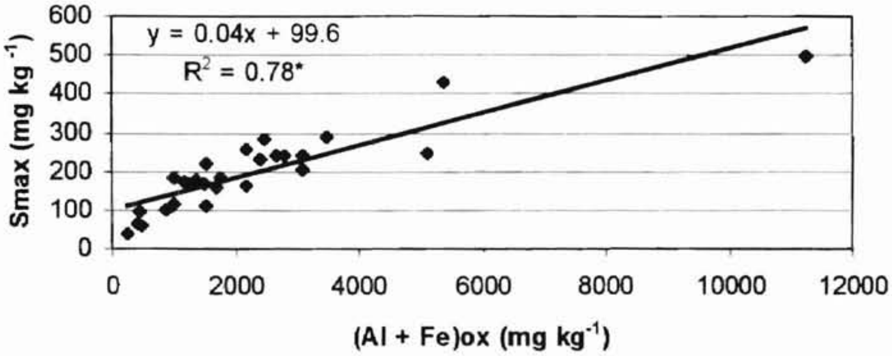

Figure 4 Relationship between P Smax as derived from a sorption isotherm and the sum of acid ammonium oxalate extractable iron and aluminum. (* denotes significance at the 0.05 level)

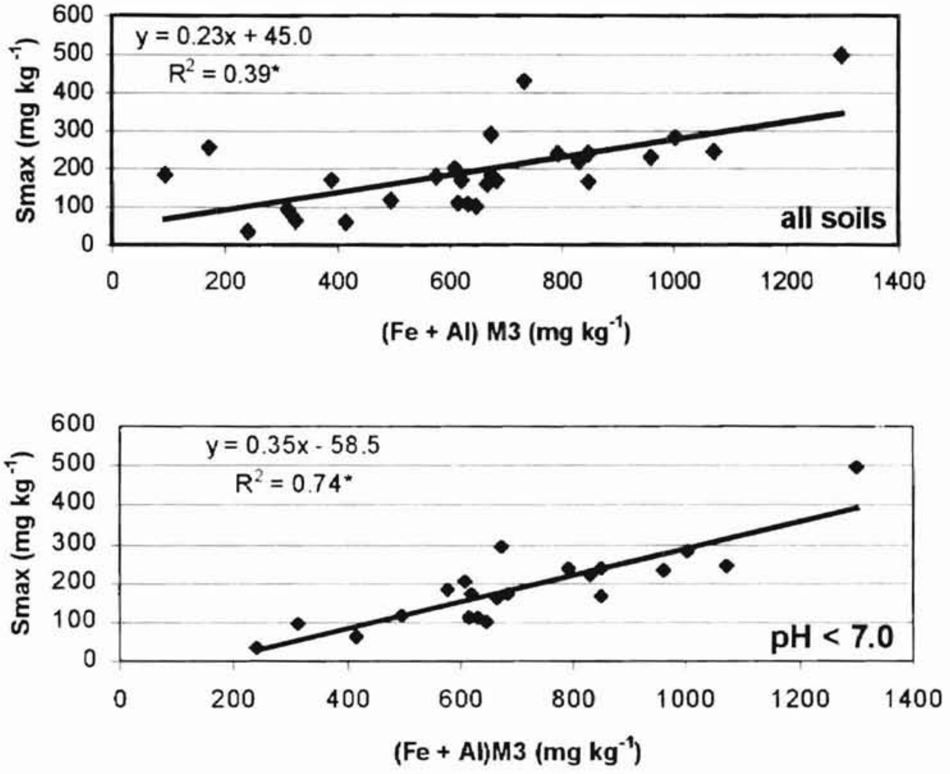

Figure 5 Relationship between P Smax as derived from a sorption isotherm and the sum of Mehlich 3 extractable iron and aluminum for all soils used in the study and for only the acidic soils in the study. (* denotes significance at the 0.05 level)

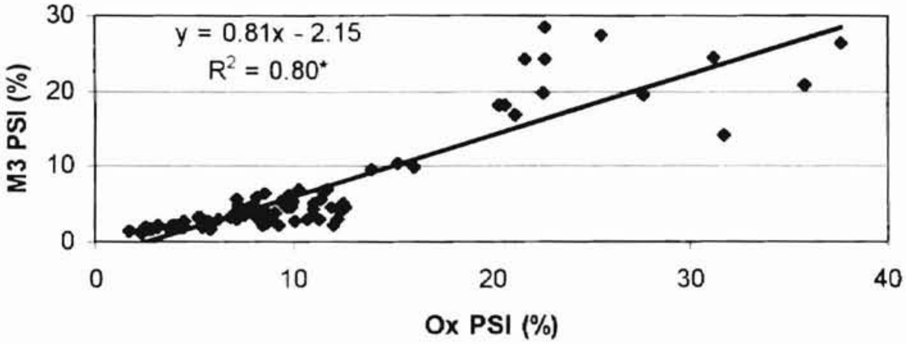

Figure 6 Relationship between phosphorus saturation indexes using Mehlich 3 and acid ammonium oxalate as extractants. PSI is defined as [mmol P/(mmol Fe + mmol Al)]. (* denotes significance at the 0.05 level)

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