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PHOSPHORUS SORPTION AND DESORPTION IN  
CALCAREOUS SOILS FROM ARIZONA

by

Lindbergue Araujo Crisostomo

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A Dissertation Submitted to the Faculty of the  
DEPARTMENT OF SOILS, WATER AND ENGINEERING  
In Partial Fulfillment of the Requirements  
For the Degree of  
DOCTOR OF PHILOSOPHY  
WITH A MAJOR IN AGRICULTURAL CHEMISTRY AND SOILS  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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## ABSTRACT

Phosphorus sorption and desorption were investigated on four calcareous Arizona soils, treated and untreated with sulfuric acid. Application of sulfuric acid in amounts necessary to neutralize 0, 20, 40, 60, 80, and 100 percent of acid titratable basicity (%ATB) tended to decrease the soil pH and to increase soluble salts, DTPA extractable iron,  $\text{NH}_4\text{OAc}$  extractable aluminum, exchangeable calcium, Al-P fractions, and water soluble P.

The sorption of added inorganic P was calculated using the Langmuir adsorption equation. The adsorption maxima for Avondale, Pima, and Laveen soils were similar in values (172, 167, and 187  $\mu\text{g P/g}$ ), but that for Guest was much lower (91  $\mu\text{g P/g}$ ). This difference can be attributed to the low content of calcium carbonate and high content of soluble salts of the Guest soil. When P sorption data were plotted according to the linear form of Langmuir equation, two linear relationships were observed for Pima and Laveen soils, and three for Avondale and Guest soils. One peculiar characteristic of the Guest soil was desorption of P at lower concentrations of P added for equilibration. When soils were treated with sulfuric acid to neutralize 20 percent ATB, all soils tended to desorb P at concentrations of P added for equilibration lower than 5  $\mu\text{g/ml}$ . Above that value all soils tended to sorb P in amounts higher than the untreated ones, but with a low index of bonding energy. When soils treated with

sulfuric acid (0 and 20 percent ATB) were incubated with quantities of P equivalent to one and two times the adsorption maximum ( $1b$  and  $2b$ ) were equilibrated with P solutions (5 to 20  $\mu\text{g}/\text{ml}$ ), the amounts of P sorbed increased slightly, but the index of bonding energy decreased. The increase in  $b$  maximum was dependent on the amounts of P applied, acid treatment, moisture regime, and soil series. The amounts of P desorbed were also dependent on the amounts of P added, acid treatment, moisture regime, and soil series. In general, higher percentages of P desorbed were obtained from soils treated with sulfuric acid (20 percent ATB) and at  $1b$  P level.

Addition of P and P plus manure tended to shift the isotherms to the right due to an increase of P in equilibrium solution. When P in equilibrium solution obtained with P-free water was added to sorbed P as "correction" of water soluble P, it tended to shift the isotherms up and the x-intercept to the left. Higher association was observed between P extracted by the  $\text{CO}_2$  and  $\text{NaHCO}_3$  methods and yields of alfalfa and lettuce, but not with the yields of carrots and sugar beets. Phosphorus in equilibrium solution (intercept of isotherms with x-axis) was highly associated with P extracted by both  $\text{CO}_2$  and  $\text{NaHCO}_3$  methods, as well as with the yields of alfalfa and lettuce. The amounts of P sorbed at a concentration of P in equilibrium solution of 0.2  $\mu\text{g}/\text{ml}$  was negatively associated with the yields of alfalfa and lettuce.

## INTRODUCTION

Phosphorus (P) is an essential element for plant growth and the amounts and nature of soil available forms have long been of interest to soil scientists.

Today we are facing increasing fertilizer costs, which are due principally to the high cost of energy and a shortage of natural P resources. With this in mind, soil scientists and agronomists must strive to improve the use of high cost fertilizers in order to obtain maximum production without waste.

The chemical complexity of P in solution as well as in the soil has been given attention by scientists in order to understand the behavior of that element in the soil-water-plant system. When a soluble form of P is applied to a soil, it is progressively converted into more stable form by reactions with Ca, Al, and Fe. These reactions occur primarily in the soil solution. These stable phosphate forms are less soluble, and consequently less available to plants.

Recently, considerable attention has been given to the phenomena of P adsorption, desorption, and equilibrium between the solid and solution phases. These phenomena are mainly affected by the chemical and physical characteristics of a given soil.

The factors of utmost importance that govern the flow of P to plant roots are:

1. Intensity factor: the ability of a soil to regenerate P to the soil solution as it is used by the plants;
2. Capacity factor: the ability of a soil to provide P to the solution as depletion occurs;
3. Quality factor: considered as the portion of P easily subjected to chemical change;
4. Quantity factor: the quantity of P retained by the soil at a specified condition of intensity.

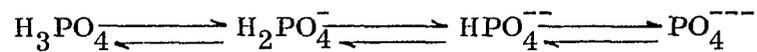
Each soil has different characteristics of P adsorption, desorption, and equilibria. The sorption isotherm procedure is considered by some soil scientists as a reliable method for describing changes in P depletion and enrichment that occur in each soil.

The purpose of this study was to examine the applicability of the sorption isotherm procedure in predicting sorption and desorption of P in calcareous soils with and without sulfuric acid amendment. Relationships existing between the P sorption isotherm, yield, and P extracted by sodium bicarbonate and CO<sub>2</sub>-saturated water were studied.

## LITERATURE REVIEW

Phosphorus chemistry in soils has been studied extensively by soil scientists (Fuller and Ray 1967). In general, two categories of P are recognized to be present in most soils, namely organic and inorganic, each one with many forms. Although organic forms play an important role in soils, emphasis in this study will be given to the inorganic category. Most inorganic P is present in soils as salts of orthophosphoric acid, which can be classified as fluoro-, hydroxy-, and oxiphosphates of iron, calcium, aluminum, magnesium, manganese, and titanium (Larsen 1967).

In solution, orthophosphoric acid dissociates according to the equation:



The concentrations of the various phosphate ions in pure solution are intimately related with the pH value of the medium.

Buehrer (1932), studying the physico-chemical relationships of soil phosphates, observed that with ordinary pH values (6 - 8) the predominant ion is  $\text{H}_2\text{PO}_4^-$ . He also reported phosphate ion concentrations are affected by the presence of  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  which favor the formation of a series of phosphate compounds of varying solubility.

When inorganic soluble P is added to soil, its concentration in soil solution is markedly reduced due to fixation (Dean 1949; Wild 1949). Fixation

mechanisms vary with soil pH, clay content and type of mineral, and the dominant cation present.

### Phosphorus Fixation in Acid Soils

In acid soils, iron and aluminum hydroxides and oxides account for much of the phosphate fixation (Dean 1934; Brown 1935; Toth 1937; Kittrick and Jackson 1956; Hsu 1964). Besides iron and aluminum oxides, the aluminum layer silicates are also responsible for phosphate fixation (Low and Black 1950; Taylor and Gurney 1962; Taylor, Gurney, and Moreno 1964) where the edge  $\text{Al}(\text{OH})_2$  groups react with phosphate.

Metzger (1940) observed phosphate fixation decreased from 78 to 12 percent as the active iron was removed in a pH range where the reaction was feasible. The products of reaction of phosphate with iron and aluminum are iron and aluminum phosphates ( $\text{FePO}_4$  and  $\text{AlPO}_4$ ), which accounted for almost all of the fixed P. There is evidence from the results of potentiometric titration by Swenson, Cole, and Sieling (1949) that two hydroxyls and one phosphate ion react with one metal ion to form  $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_2\text{H}_2\text{PO}_4$  or  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_2\text{H}_2\text{PO}_4$ , within the range of pH of acid soils dominated by  $\text{H}_2\text{PO}_4^-$ . Haseman, Lehr, and Smith (1950), with the aid of electron and X-ray diffraction techniques, observed that in the presence of common soil cations, the compounds formed by reaction of phosphate with iron and aluminum were iron and aluminum oxy- and hydroxyphosphates.

Haseman, Brown, and White (1950) equilibrated gibbsite, goethite, kaolinite, illite, and montmorillonite with different concentrations of P at various pH values and temperatures. They observed two distinct sorption stages occurred with time. The first stage was characterized by a rapid rate as a result of the reaction of phosphate with active iron and aluminum. The second stage was slower and occurred after aluminum and iron were released by weathering. This double stage hypothesis was also supported by Low and Black (1950). These authors suggested that the surface silicon tetrahedra are replaced by phosphorus tetrahedra in the first stage and precipitation of Al-phosphate occurred in the second stage as a consequence of P induced surface clay decomposition. Coleman (1945), working with montmorillonite and kaolinite clays, observed that within a pH range of five to seven, the amounts of phosphate fixed were about the same for both minerals over a one-month period.

#### Phosphorus Fixation in Calcareous and Alkaline Soils

According to McGeorge and Breazeale (1931), the formation of carbonate-phosphate compounds in which one mole of calcium carbonate is combined with three moles of tricalcium phosphate accounts for the low P availability in calcareous soils. They suggested that soil or rock phosphate solubility is greatly reduced when calcium carbonate is present in the solid phase.

Boisshot, Coppenet, and Hebert (1950) reported that soluble phosphate is fixed on the surface of calcium carbonate by a sorption phenomenon, not by

precipitation. The phosphate fixed in this manner can be used by the plants as it returns to the soil solution by a desorption phenomenon. Cole, Olsen, and Scott (1953) confirmed the findings of Boischot et al. (1950). They reported that when soluble phosphate is placed in contact with calcium carbonate in calcareous soils, phosphate is rapidly taken from the solution by the solid particles of calcium carbonate. Two different types of behavior were suggested: one operating at low concentration and the other operating at high concentration of phosphate. At lower concentration, sorption may be explained by the Langmuir adsorption isotherm where P is adsorbed as a monolayer over the surface of calcium carbonate particle. This sorption phenomenon is proportional to the amount of calcium carbonate present and is independent of the concentration of neutral salts (0.01-0.10M KCl or NaCl) in the pH range from seven to ten. At higher levels of phosphate concentration, the amount of phosphate sorbed is independent of calcium carbonate surface area and the reaction proceeds as the phosphate concentration of solution has been reduced below a certain critical value.

Working with calcareous soils, Burd (1948) pointed out that in highly buffered soils some calcium phosphate compounds of low solubility were formed as the soil was treated with phosphate fertilizers. This occurs because calcium compounds in the soil are potentially soluble, releasing calcium ions which react with phosphate, forming less soluble Ca-phosphate compounds. He also observed that the concentration of phosphate in solution increased as that of calcium decreased. This fact can be used to explain the role of calcium in fixation of soluble native or added P to calcareous soils.

Buehrer (1932) suggested that phosphate solubility in calcium saturated soil is directly proportional to hydrogen ion concentration and inversely proportional to the calcium ion concentration. On the other hand, in sodium dominated soils, the solubility of phosphate is much higher than in calcium dominated soils (Gardner and Kelley 1940; Ravikovitch 1939).

Pratt and Thorne (1948) observed that at pH values between four to ten, the phosphate solubility was higher in sodium than in calcium clay suspensions.

Chang and Jackson (1958) found that in the majority of calcareous soils, P is present as calcium phosphate although some can exist in the aluminum and iron fractions. These workers believed that when phosphate fertilizers are added to calcareous soils, P combines easily with calcium and aluminum and not with iron because those ions are more active. As iron phosphate is less soluble than calcium and aluminum phosphates, it tends to accumulate in soils.

Sen Gupta and Cornfield (1962), working with six calcareous soils from England, reported that the "inert" phosphate, apatites and non-apatitic calcium phosphate fractions accounted for most of the inorganic fraction when expressed as percentage of the total soil P. They also reported that in the presence of calcium carbonate, non-apatitic forms are slowly converted to apatitic form.

The fixation of P in soils without excessive amounts of calcium and magnesium in the system is carried out by substitution of phosphate ions for hydroxyl ions, i. e., by anion exchange phenomenon (Dean and Rubins 1947).

The anion exchange capacity is highly correlated with the amount of clay and specific surface area. It was also observed that as the free iron oxides were removed from the soil, the anion exchange capacity decreased, but not in proportion to the amount of iron dissolved.

#### Role of Organic Matter in Phosphate Fixation

The role of organic matter in fixation of soil P has been emphasized by many soil scientists. The idea is based on the fact that during the process of organic matter mineralization, there is a release of  $\text{CO}_2$  and organic acids and reactions with fulvic and humic acids which results in the formation of organo-metallic phosphates (Sinha 1972).

Harter (1969), using the Chang and Jackson (1958) procedure for fractionation of soil P, found that P extracted with 0.5N  $\text{NH}_4\text{F}$  was not associated with aluminum in the soil, but was bonded to organic matter. He suggested that P in the  $\text{NH}_4\text{F}$  fraction was primarily from soil organic matter. Some type of anion exchange may be involved where hydroxy groups are replaced by phosphate ions. It was also postulated that after certain periods of time, the P released is transformed into less soluble iron and aluminum phosphates or incorporated into organic matter.

Swenson et al. (1949) found that several organic anions are effective in preventing formation of aluminum and iron phosphate compounds. They also claimed that the effectiveness was higher for those anions capable of forming stable complexes with iron and aluminum.

Struthers and Sieling (1950), working with nine organic acids, some found extensively in soils, observed that each acid differed in its effectiveness in preventing phosphate fixation by iron and aluminum at different pH values. They also observed that the effectiveness for iron is different from that for aluminum, for each acid, and it increased with the number of hydroxyl and carboxyl groups and with the chain size. The short chain acids were more efficient in preventing phosphate fixation than the long ones.

Midgley and Dunklee (1945), in greenhouse and field experiments, observed that plant response was better when P was applied mixed with manure, rather than separately. This response was more pronounced for soils capable of fixing high amounts of P. When the P source was mixed with manure, they suggested that several effects could occur, such as: (a) reduction of superphosphate solubility; (b) immobilization of P by microorganisms and slow release to the plants; (c) adsorption of phosphate ions by active humates.

#### Role of Exchange Reactions on Phosphate Fixation

The exchange reaction is a phenomenon where one ion replaces another. Two types of exchange reactions were recognized by Kolthoff (1936), one involving counter ions and the other involving lattice ions. The counter ion exchange involves those ions held at the surface of the crystals as a result of imbalanced charges. The lattice exchange involves ions that are part of the crystal structure, which are replaceable due to their position at the edges and corners.

Coleman (1945) observed an increase in pH as phosphate ions were adsorbed by clays, suggesting an exchange of phosphate ions for hydroxyl ions. This was recognized by Dean and Rubins (1947), who also observed that the anion exchange capacity of some soils increased with clay content and surface area.

In the opinion of Fried and Dean (1955), three different mechanisms are involved in retention of phosphate by soils, i. e. , (a) counter ion exchange; (b) precipitation; and (c) exchange of phosphate ions for ions on the surface of solid particles.

Krishnamourthy and Overstreet (1950) observed that the counter ion exchange is a rapid reaction that takes place in minutes. As such, it could not be the primary mechanism for phosphate retention. They confirmed that phosphate fixation is not a typical precipitation. In conclusion, it seems probable that phosphate fixation is an exchange reaction between phosphate ions and ions on the surface of the particle.

#### Phosphate Availability to Plants

Since obtaining the knowledge that plants take up mineral nutrients, many soil and plant scientists have been looking for easy and fast chemical methods capable of measuring the amounts of available plant nutrient. In soil testing laboratories, a known amount of soil is usually treated with a given amount of extracting solution and the quantity of the element extracted is then measured. Many tests were designed to simulate plant root action.

### Chemical Extractants

In 1894, Dyer developed a chemical method using one percent citric acid, which he supposed to be successful in extracting available soil P. Later, in 1930, Truog proposed the use of 0.02N  $H_2SO_4$  buffered at pH 3.0 with  $(NH_4)_2SO_4$ , in an attempt to simulate action of plants in removing available P from the soil.

Puri and Asghar (1936) proposed a method using a water saturated  $CO_2$  solution. This method was based on the fact that  $CO_2$  is released by plant roots as they respire. When  $CO_2$  is released in the soil solution, carbonic acid, a weak acid, is formed and is capable of dissolving some phosphate compounds. McGeorge and Breazeale (1931), working with calcareous soils, observed that  $CO_2$  in the soil solution did not increase the solubility of phosphates, and in certain cases it tended to decrease it.

Morgan (1941) proposed the use of what he called "Universal Soil Extraction Solution" which could be used for extraction of available P and other elements. This method was used for some time in the United States and abroad. Later, Bray and Kurtz (1945) developed two extractants known as Bray-1 (0.03N  $NH_4F$  + 0.025N HCl) and Bray-2 (0.03N  $NH_4F$  + 0.1N HCl) for extraction of adsorbed, and acid-soluble and adsorbed soil P, respectively. These methods were used in acid soils with some success, i. e., in most cases they were well correlated with plant yield.

Due to a lack of methods for evaluating available P in both acid and alkaline soils, Olsen, Cole, Watanabe, and Dean (1954) developed the sodium

bicarbonate method, which is based on the tendency of increasing the solubility of calcium phosphate by lowering the calcium activity in solution. They reported a very high association between P extracted by 0.5N sodium bicarbonate at pH 8.5 and "A" values for all of their experiments. Besides that, it was also observed that this method compared very well with the Bray, Truog, water soluble, and CO<sub>2</sub>-soluble P methods, which were correlated with "A" values from six experiments.

#### Phosphate Potential

Schofield (1955), studying phosphate potential in dilute calcium chloride solutions previously equilibrated with soils, suggested that the measurement of labile P of the soil could be based on the measurement of Ca<sup>++</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> activities. He proposed using the sum of  $\frac{1}{2}pCa + pH_2PO_4$  as an index of available phosphate. White and Beckett (1964), pursuing this further, concluded that labile P in soil is not in equilibrium, and that the equilibrium potential depends on the soil:solution ratio and duration of shaking. Larsen (1965) reported that the phosphate potential decreased with an increase in CaCl<sub>2</sub> concentration from 0.002 to 0.05M. On the other hand, when CaHPO<sub>4</sub> was allowed to form, the phosphate potential was independent of CaCl<sub>2</sub> concentrations.

#### Phosphate Fractionation

Soil phosphorus is present principally as fractions of Fe-P, Al-P, and Ca-P. The relation of each one of these fractions to plant nutrition is not yet well known. Inferences related with utilization of these forms have been

made based on the solubility products of pure compounds and plant growth, having precipitated iron and aluminum phosphates as P source. However, there is little proof of existence of these compounds in soils (Smith 1965). The above author, using fractionation studies of soil P, reported that aluminum phosphate was the main source of plant available P, and an increase in Fe-P fraction tended to decrease plant growth. On the other hand, Al-Abbas and Barber (1964) and Fassbender, Muller, and Balerdi (1968) concluded that Fe-P and Al-P in acid soils are the principal sources of P. According to Olsen et al. (1954) and Kurtz (1953), the Ca-P fraction becomes more important at pH values close to or above neutrality.

Sen Gupta and Cornfield (1962) reported that in calcareous soils iron, aluminum, and non-apatitic calcium phosphates accounted for a smaller proportion of total soil P, while in acid soils, those fractions are dominant.

Rauschkolb (1963), using P fractionation procedure in some calcareous soils from Arizona, reported that yield was best correlated with ammonium chloride fraction than with the Fe- and Al-P fractions.

#### Adsorption Isotherms

Adsorption isotherms can be defined as the relation between the amount of substance adsorbed by an adsorbant and equilibrium concentration of the substance at constant temperature (Prutton and Maron 1953). Adsorption isotherm equations were developed primarily to explain the adsorption of gases by solids.

Today, some of these equations are being used to study the adsorption of liquids or ions in solutions by solid particles (Boyd, Schubert, and Adamson 1947; Jackson, Whittig, and Pennington 1950).

The Freundlich equation is considered empirical in nature, but has been used by many workers to describe P adsorption by soils and solid mineral particles. Davis (1935) observed that P sorption could be expressed by Freundlich's equation ( $\Delta P = kP_E^{\frac{4}{3}}$ ), and that the amount of P sorbed was affected by the soil:solution ratio. Kurtz, DeTurk, and Bray (1946) reported that at low P concentrations, adsorption did not fit Freundlich's equation, and that the amount of P sorbed was a function of P in solution and was higher in the presence of soluble salts.

Low and Black (1950), working with kaolinite, concluded that phosphate sorption followed a "typical adsorption curve", represented by equation  $x/m = kc^{\frac{1}{n}}$ . This finding was confirmed by Russel and Low (1954) who observed that when the exchange complex was saturated with aluminum, the adsorption was increased, suggesting a reaction of aluminum with P.

Besides the Freundlich equation, that proposed by Langmuir (1918) has been used to describe P adsorption by soils and soil minerals (Olsen and Watanabe 1957; Hsu and Rennie 1962; Gunary 1970; Udo and Uzu 1972; Syers, Browman, Smillie, and Corey 1973; Rajan 1973; and many others).

The linear form of the Langmuir equation generally used is:

$C/x/m = 1/kb + C/b$ , where:

$C$  = concentration of P in equilibrium solution ( $\mu\text{g P/ml}$ );

$x/m$  = amount of P sorbed by the soil ( $\mu\text{g P/g}$ );

$b$  = adsorption maximum;

$k$  = constant related with the bonding energy of the adsorbent for the adsorbate.

It has been suggested that each soil has a characteristic isotherm line and  $\underline{b}$  and  $\underline{k}$  values.

Although P adsorption generally fits the Langmuir equations, a curvature of the adsorption line has been observed. Gunary (1970), studying P sorption in 24 soils, found good agreement between P sorption and the Langmuir isotherm plot; however, a slight curvature in the isotherm was observed. To fit this curvature, he expanded the original equation by adding a square root term, for which no theoretical foundation has been obtained.

In the findings of Syers et al. (1973), when P sorption data are plotted according to the Langmuir equation, two linear relationships are obtained. This indicates the existence of two different population sites, each one with a different P affinity. For this reason, they proposed a modification of the original equation  $x/m = kbc/(1+kc)$  to  $x/m = k^i b^i c^i / (1+k^i c) + k^{ii} b^{ii} c^{ii} / (1+k^{ii} c)$ , where the superscript i and ii represent the first and second portion of the adsorption line, respectively.

Woodruff and Kamprath (1965) found a decrease in adsorption maxima in acid soils as exchangeable aluminum was neutralized. On the other hand, P absorption by the plants increased with P saturation according to the adsorption maximum, i. e. , the highest yield was obtained when P was added to reach

50 percent of P saturation for most of the soils. Coleman, Thorup, and Jackson (1960) reported a decrease in phosphate sorption by removal of exchangeable aluminum by salt leaching. They observed that montmorillonite saturated with potassium, calcium, or sodium by salt leaching sorbed little phosphate. However, aluminum saturated montmorillonite sorbed phosphate in quantities equivalent to the exchangeable aluminum, but only under conditions where aluminum hydrolysis was feasible. In soils low in exchangeable aluminum but with large quantities of aluminum and iron oxides and hydroxides, P sorption was not affected by salt leaching. This suggests that P sorption involving exchangeable aluminum ions leads to the formation of a substance with the composition of variscite.

Olsen and Watanabe (1957) found a close relationship between the P adsorption maximum and surface area for acid and alkaline soils. The acid soils sorbed more P per unit of surface area with a higher bonding energy than alkaline soils.

Phosphate sorption by soils is influenced by conditions such as time of equilibration, temperature, soil:solution ratio, etc. Fox and Kamprath (1970) found that a reasonably stable equilibrium was attained after six days, with rapid shifting of isotherm lines during the first days of equilibration. These findings were confirmed by Gardner and Jones (1973), who observed that equilibrium was reached more rapidly at 20C than at 5C. On the other hand, Beckwith (1965) reported that 16 hours was sufficient for some Australian soils.

Another factor responsible for discrepancies among the results of sorption is the P solution used for equilibration. Olsen and Watanabe (1957) used water while Ozanne and Shaw (1968), Gardner and Jones (1973), Fox and Kamprath (1970) used P in 0.01M CaCl<sub>2</sub> solution, at pH 7. On the other hand, Beckwith (1965) and Fox, Plucknett, and Whitney (1968) used 0.1M sodium acetate solution at pH 5.2. Besides that, Beckwith (1965) washed the soil with the sodium acetate solution prior to equilibration.

Phosphorus isotherms can provide the basis for making phosphate fertilizer recommendations in unusual circumstances where traditional chemical extractants are not satisfactory. From a semilog plot of P in equilibrium solution versus the amount of P sorbed by the soil, Beckwith (1965) concluded that 0.2 µg P/ml in equilibrium solution could be used as standard for estimating P needs of some Australian soils. This 0.2 value was used by Fox et al. (1968) and Fox and Kamprath (1970) for some Hawaiian soils. Ozanne and Shaw (1967) reported that a concentration of 0.3 µg P/ml would be appropriate for some crops. They observed that values of 0.2 to 0.3 µg P/ml gave good results for grass and that an increase in P above 0.3 was responsible for a decrease in yield. Therefore, they selected 0.3 as being sufficient for maximum yield and this value could be measured better than lower concentrations. In 1962, Andrew (cited by Beckwith 1965) reported that the critical level for optimum growth of legumes lies between 0.1 and 0.2 µg P/ml in equilibrium solution.

### The Use of Sulfuric Acid in Calcareous Soils

Deficiencies of phosphorus, zinc, copper, iron, and manganese sometimes are observed in calcareous soils. These deficiencies in general are due to low solubility and availability of those elements caused by high pH and calcium content. Brown (1961) reported that iron chlorosis of sorghum growing in calcareous soils is caused by nutrient imbalance due principally to calcium and P.

Treatment of calcareous soils with sulfuric acid has been used to overcome P and micronutrient deficiencies in some crops (Christensen and Lysterly 1954; Mathers 1970; Ryan, Miyamoto, and Stroehlein 1974).

Sulfuric acid is also used to correct alkalinity problems to improve water permeability of soils and to improve the quality of irrigation waters.

Thorne (1944) working with calcareous soils, reported that application of sulfuric acid did not affect the yields of alfalfa, barley, and corn growing in calcareous soils treated with sulfuric acid. Similar results were obtained by Mathers (1970) where he observed that 560 kg  $\text{FeSO}_4$ /ha or 560 kg  $\text{H}_2\text{SO}_4$ /ha produced about the same yield response on grain sorghum. Working with cotton, Christensen and Lysterly (1954) reported an increase in yield, as well as an increase in magnesium, sulfur, and P contents absorbed by the plants. Ryan and Stroehlein (1974) observed an increase in P taken up by tomato plants growing in acidified calcareous soils.

In relation to soil chemical characteristics, Pratt (1961) reported that acidification of soil tends to increase the solubility of P without affecting aluminum until the pH is lowered from neutral to 4.2. He pointed out that further

decrease in soil pH decreased P solubility. It was also reported that  $H_2SO_4$  soluble P fraction tended to decrease with acidification while  $NH_4F$ -P and NaOH-P tended to increase. Similar trends were observed by Ryan, Crisostomo, and Stroehlein (1975) when calcareous Arizona soils were treated with  $H_2SO_4$ , although the pH did not drop below 6.0. In 1974, Ryan, Miyamoto, and Stroehlein reported an increase in DTPA extractable manganese and iron when calcareous soils were treated with  $H_2SO_4$ . They also reported that water soluble fractions increased when 100 percent or more of acid titratable basicity was neutralized. Johnson and Low (1967) reported that emergence of sugar beet seedlings was improved and soil crusting controlled when the soil was treated with  $H_2SO_4$  immediately after planting. Similar results with wheat were obtained by Yacoubi (1973). Acid treatment was reported to improve water penetration (Miyamoto and Stroehlein 1974). In relation to quality of irrigation water, Miyamoto, Prather, and Stroehlein (1974) and Miyamoto, Ryan, and Stroehlein (1974) reported that  $H_2SO_4$  treatment tends to decrease bicarbonate concentration, reduce the precipitation of calcium carbonate, and reduce the loss of ammonia by volatilization. On the other hand, this treatment tends to decrease the SAR of waters and consequently lower the sodium hazard of irrigation waters.

## MATERIAL AND METHODS

### General

Composite samples of the plow layer (0-30 cm) were collected in different locations in the State of Arizona, each representing four soil series: Avondale, Pima, Laveen, and Guest. The soils were air dried, mixed thoroughly, ground to pass a 1.0 mm sieve, and stored at room temperature.

Soil pH values and total soluble salts were determined on the saturated pastes and saturated extracts, respectively, using procedures described by the U. S. Salinity Laboratory Staff (1954). The acid titratable basicity (ATB) was measured by the procedure of Miyamoto, Bohn, and Renthal (1973). Available iron was extracted with the DTPA (diethyleneamine pentacetic acid) procedure of Lindsay and Norvell (1969). Aluminum was extracted with 1N ammonium acetate, pH 4.8, according to McLean (1965). Exchangeable calcium was extracted with 1N ammonium acetate, pH 7.0 (Chapman 1965). Atomic absorption was used to determine the concentrations of aluminum, iron, and calcium in solution. Available P was extracted using saturated CO<sub>2</sub> (Puri and Asghar 1936) and 0.5N sodium bicarbonate pH 8.5 (Olsen et al. 1954) methods. The phosphomolybdate blue color was developed using the Murphy and Riley (1962) reagents, as modified by Watanabe and Olsen (1965). Phosphorus concentration was determined using a Coleman Model 6/20A spectrophotometer at 700mu

wavelength. Inorganic phosphate fractionation was performed according to Peterson and Corey (1966).

### Phosphorus Sorption and Desorption Studies

#### Experiment 1

In this experiment, six 200 g lots of each soil were placed in beakers and treated with 5N H<sub>2</sub>SO<sub>4</sub> so that 0, 20, 40, 60, 80, and 100 percent of ATB was neutralized. Sufficient water was added to maintain the soil at saturation for 48 hours. After that time, the soil was dried, ground, and sieved to pass 1.0 mm screen.

Duplicate 1.50 g soil samples were weighed into 50 ml Nalgene centrifuge tubes, and 30 ml equilibrating solution added. To minimize biological activity, two drops of toluene were added per tube. The samples were equilibrated for six days at room temperature on a reciprocating shaker, and shaken vigorously 30 minutes twice daily. The equilibrating solutions containing 0, 1.0, 2.5, 5.0, 7.5, 10.0, and 20.0 µg P/ml as KH<sub>2</sub>PO<sub>4</sub> were made with deionized water adjusted to pH 7.0 with NaOH. After equilibration, the samples were centrifuged at 15,000 rpm (approximately 29,000 x g) using a high speed refrigerated centrifuge (Sorvall Model RC-2). Aliquots of the supernatant were pipetted and P concentrations were then determined.

The amount of P sorbed was calculated by difference between the initial and final concentrations in equilibration solutions, to which the quantity of

P at equilibrium in P free water was added. Phosphorus in equilibrium solution (C) was plotted on log scale against P sorbed on linear scale.

A linear plot of P in equilibrium solution (C) versus the ratio of P in equilibrium to P sorbed (C/x/m) was made to calculate the adsorption maximum for each soil without acid treatment. The slope and intercept of the curve from the above plot were calculated by the least squares method, using a programmed Olivetti-Underwood Programa 101 calculator. The adsorption maximum  $\underline{b}$  and the index of bonding energy  $\underline{k}$  were calculated as  $1/\text{slope}$  and  $\text{slope}/\text{intercept}$ , respectively (Olsen and Watanabe 1957; Udo and Uzu 1972; Syers et al. 1973).

## Experiment 2

One kilogram of each soil treated with  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB) were incubated in plastic bags for ten weeks at 75 percent of field capacity and sealed to avoid water loss. Another set of one kilogram samples were transferred into plastic trays placed in a greenhouse, and subjected to wetting-drying cycles for ten weeks. Both sets received P as  $\text{KH}_2\text{PO}_4$  in order to reach one and two times the adsorption maximum ( $1\underline{b}$  and  $2\underline{b}$ ) as calculated in Experiment 1 for acid untreated soil. After that time, each sample was dried, ground to pass a 1.0 mm sieve and stored at room temperature.

New adsorption isotherms were determined for each sample using P concentrations of 0, 5, 10, 15, and 20  $\mu\text{g P/ml}$ . New regression equations and values of  $r$ ,  $\underline{b}$ , and  $\underline{k}$  were calculated for these data as well as for 0 and 20 percent ATB treatments in Experiment 1.

### Experiment 3

In this experiment, duplicate 1.50 g soil samples from Experiment 2 were transferred into 50 ml Nalgene centrifuge tubes and 30 ml of deionized water added. The tubes were weighed, then were shaken vigorously for eight 30-minute periods over a 22-hour interval, centrifuged, and aliquots of the supernatant taken for P determination. The rest of the supernatant was discarded. Phosphorus extractions were repeated on the same samples until the concentration of P in the supernatant was approximately equal to P in equilibrium solution when the original soil was equilibrated with deionized water (Experiment 1).

### Phosphorus Requirement

Phosphorus requirement for Laveen soil was determined using P-sorption isotherms, sodium bicarbonate and CO<sub>2</sub> methods. This study was carried out on composite samples of the plow layer collected from field plots at the University of Arizona Experiment Farm at Mesa, Arizona. One field has been used for P research for 14 years and the second for three years. For the first field, the main P treatments were: (a) no P application over 14 years; (b) 146 kg P/ha, applied in 1969/71; (c) 577 kg P/ha, applied since 1959, but zero in 1969/71/73; and (d) 724 kg P/ha, applied since 1959, but none in 1973. Each treatment was replicated five times and the yields of carrots, lettuce, and sugar beets grown during 1973/74 were taken from plots that received adequate nitrogen.

In the second field the main treatments were: (a) control; (b) 196 kg P/ha; (c) 196 kg P/ha plus stimulex; (d) 98 kg P/ha; and (e) 196 kg P/ha plus 22 ton manure/ha. Each treatment was replicated three times, and the yield was computed on a total of five cuttings.

## RESULTS AND DISCUSSION

### General

Some chemical characteristics of soils treated with  $H_2SO_4$  at the rate of 0, 20, 40, 60, 80, and 100 percent of ATB are presented in Table 1. The pH of the four soils varied from 8.1 to 5.5 for 0 and 100 percent ATB treatments, respectively. The Guest soil was affected the most, showing the lowest buffering capacity. In relation to soluble salts, as indicated by electrical conductivity, the general trend was towards an increase in EC as the acid titratable basicity was neutralized. This can be attributed to dissolution of some less soluble compounds by the acid itself or as consequence of the decrease in soil pH.

A slight increase in exchangeable calcium was noticed (Table 1) which was dependent on the amount of acid added. This can be attributed to dissolution of calcium carbonate which tends to increase the water soluble calcium. On the other hand, DTPA extractable iron and  $NH_4OAc$  extractable aluminum were slightly affected at lower acid rates up to 40 percent ATB, but highly affected at rates above 60 percent ATB. Ryan, Miyamoto, and Stroehlein (1974) observed similar effects on DTPA extractable iron for other calcareous soils from Arizona. They also observed that water soluble iron content was affected with acid treatments higher than 100 percent ATB.

Table 1. Characteristics of Four Soils Treated with  $H_2SO_4$ . -- 0 to 100 percent ATB neutralized.

Soil	ATB %	pH	EC	$Ca^{++}$	Al	Fe	P	Clay %
		Saturation Ext.	Paste Ext.	Ext.	$NH_4OAc$ Ext.	DTPA Ext.	Water Ext.	
		mmhos/cm			ug/g			
Avondale	0	8.1	1.00	125	5.0	22	2.00	25.6
	20	7.7	3.53	275	8.4	38	25.80	
	40	7.0	4.29	425	13.0	38	49.60	
	60	6.7	4.54	425	40.0	53	83.80	
	80	6.5	4.79	450	120.0	182	77.20	
	100	6.4	5.36	475	230.0	690	9.60	
Pima	0	8.1	1.09	175	3.6	22	1.80	27.6
	20	7.7	2.88	275	10.0	40	25.60	
	40	6.9	3.04	375	18.0	46	50.80	
	60	6.5	3.31	425	22.0	50	93.80	
	80	6.2	3.37	450	46.0	93	121.20	
	100	6.1	3.44	450	142.0	401	98.80	
Laveen	0	8.0	1.18	150	4.0	22	2.00	21.6
	20	7.6	3.33	375	8.0	36	12.00	
	40	6.9	3.89	525	18.0	42	21.00	
	60	6.8	4.14	525	40.0	77	41.40	
	80	6.5	4.31	575	112.0	210	57.60	
	100	6.3	4.60	600	336.0	1060	1.60	
Guest	0	8.2	1.67	150	5.0	27	10.00	27.6
	20	7.7	4.62	250	13.0	50	41.00	
	40	6.7	4.76	275	38.0	73	66.20	
	60	6.5	5.08	300	102.0	216	68.20	
	80	6.2	5.16	300	156.0	400	62.20	
	100	5.5	6.25	325	206.0	738	60.00	

The acid treatment up to 80 percent ATB tended to increase the water soluble P. Beyond that level, there was a tendency to decrease this P fraction. This decrease in water soluble P can be due to an increase in iron and aluminum which should be precipitated as Fe- and Al-P. To confirm this hypothesis, P fractionation of 0 and 100 percent ATB treatments were performed. The data presented in Table 2 show a substantial increase in  $\text{NH}_4\text{Cl}$ - and Al-P fractions, and a decrease in Ca-P fraction. On the other hand, the Fe-P fraction showed some increase, but only for Laveen soil. The association between decrease in water soluble P and increase in Al- and Fe-P fractions as measured by linear regression showed r values of 0.720 and 0.246, respectively. It seems probable that the increase in P sorption of acid treated soils is due primarily to formation of Al-P compounds. Similar results for other calcareous soils were obtained by Ryan, Crisostomo, and Stroehlein (1975).

### Phosphorus Sorption and Desorption Studies

#### Experiment 1

When P in equilibrium solution (C,  $\mu\text{g P/ml}$ , log scale) versus amounts of P sorbed ( $x/m$ ,  $\mu\text{g P/g}$ ) for four soils (Tables A1 to A4) were plotted on semilog paper, shifting of isotherm lines, indicating an increase in water soluble P, was observed for  $\text{H}_2\text{SO}_4$  treated soils when the amounts of  $\text{H}_2\text{SO}_4$  added increased up to 80 percent ATB (Figs. 1 to 4). This shifting to the right can be explained by dissolution of some phosphate compounds by the acid, increasing the amount of soluble P, consequently increasing the amount of P in

Table 2. Inorganic Phosphate Fractions for Four Calcareous Soils Treated with Sulfuric Acid. -- 0 and 100 percent ATB neutralized.

Soil	ATB	Phosphate Fractions				
		NH <sub>4</sub> Cl-P	Al-P	Fe-P	Reductant	Ca-P
		Soluble-P				
	%	ug/g				
Avondale	0	6	62	20	50	180
	100	44	408	12	25	75
Pima	0	10	62	90	45	160
	100	80	456	90	22	80
Laveen	0	8	50	8	25	135
	100	10	204	62	23	60
Guest	0	10	36	48	48	230
	100	52	384	44	28	135

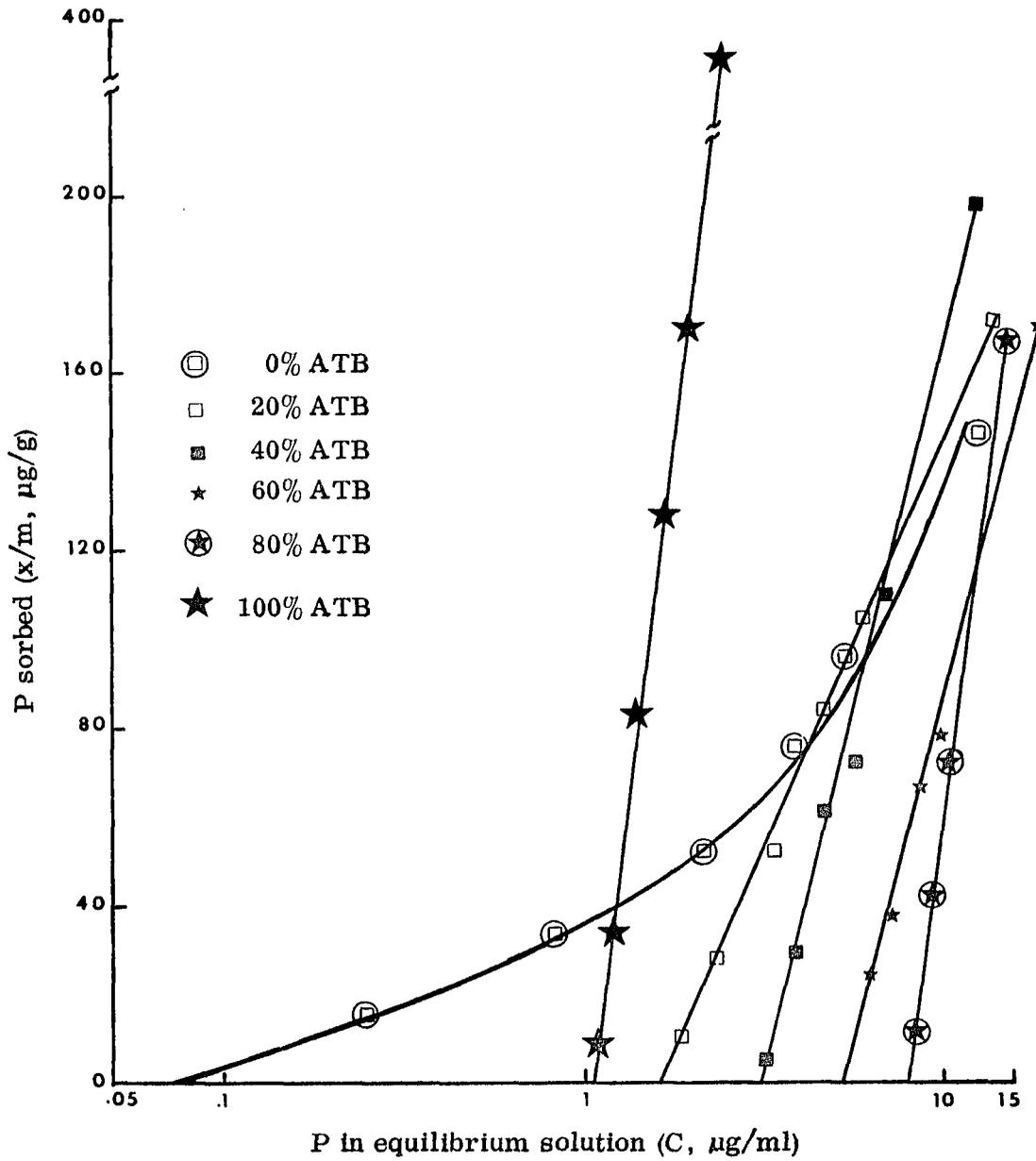


Figure 1. Phosphorus adsorption isotherms of Avondale soil treated with different quantities of  $H_2SO_4$  to neutralize various levels of ATB.

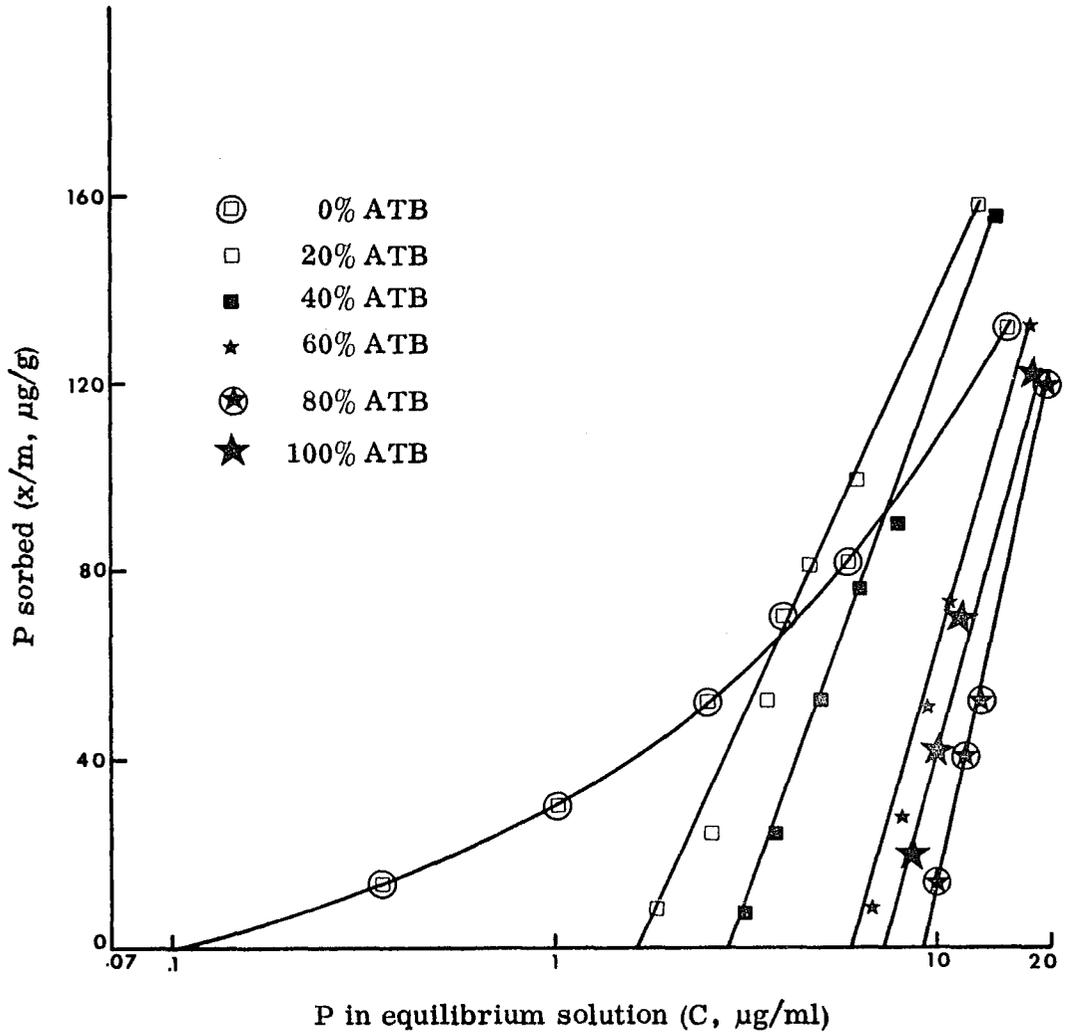


Figure 2. Phosphorus adsorption isotherms of Pima soil treated with different quantities of  $H_2SO_4$  to neutralize various levels of ATB.

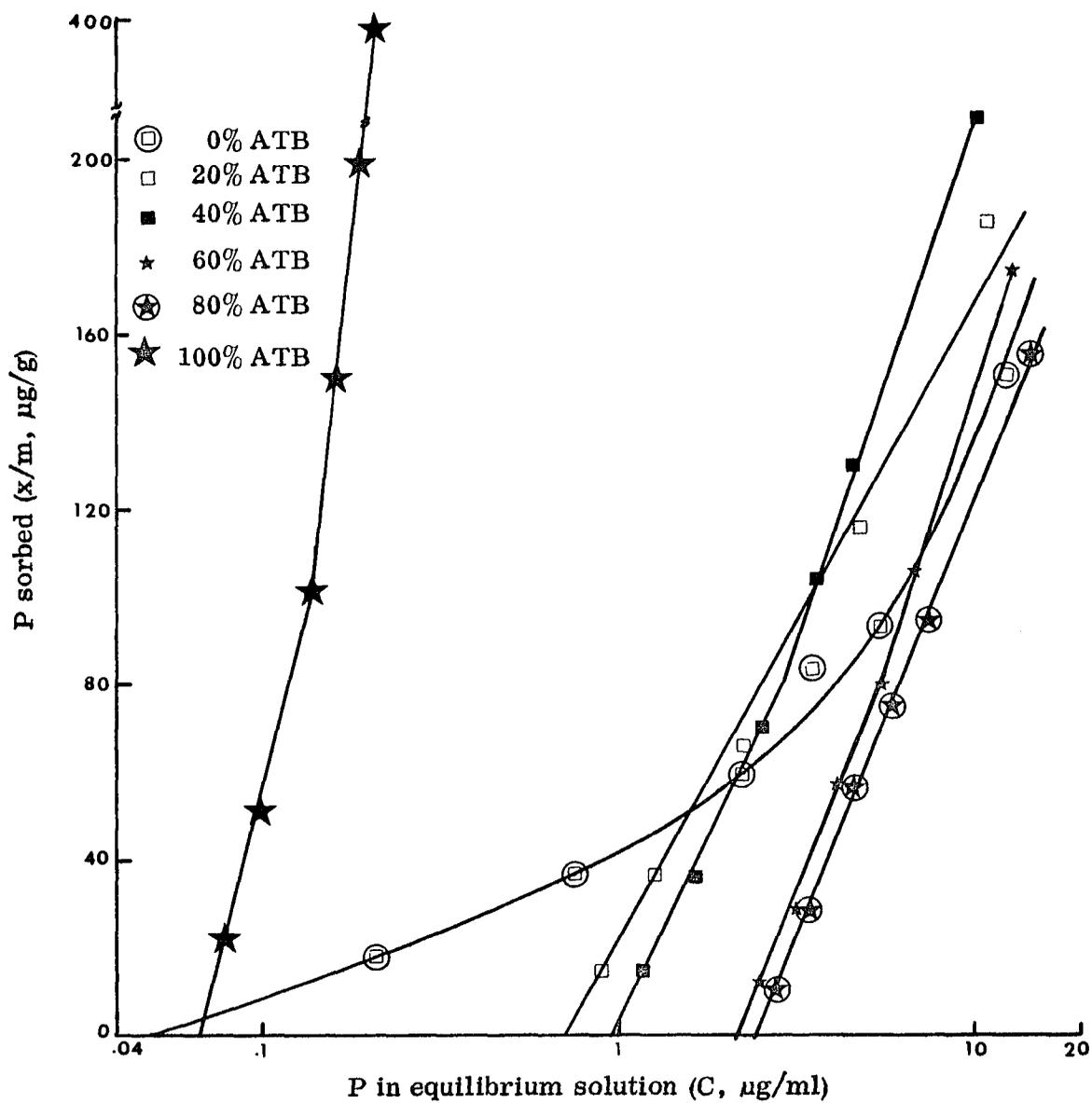


Figure 3. Phosphorus adsorption isotherms of Laveen soil treated with different quantities of  $H_2SO_4$  to neutralize various levels of ATB.

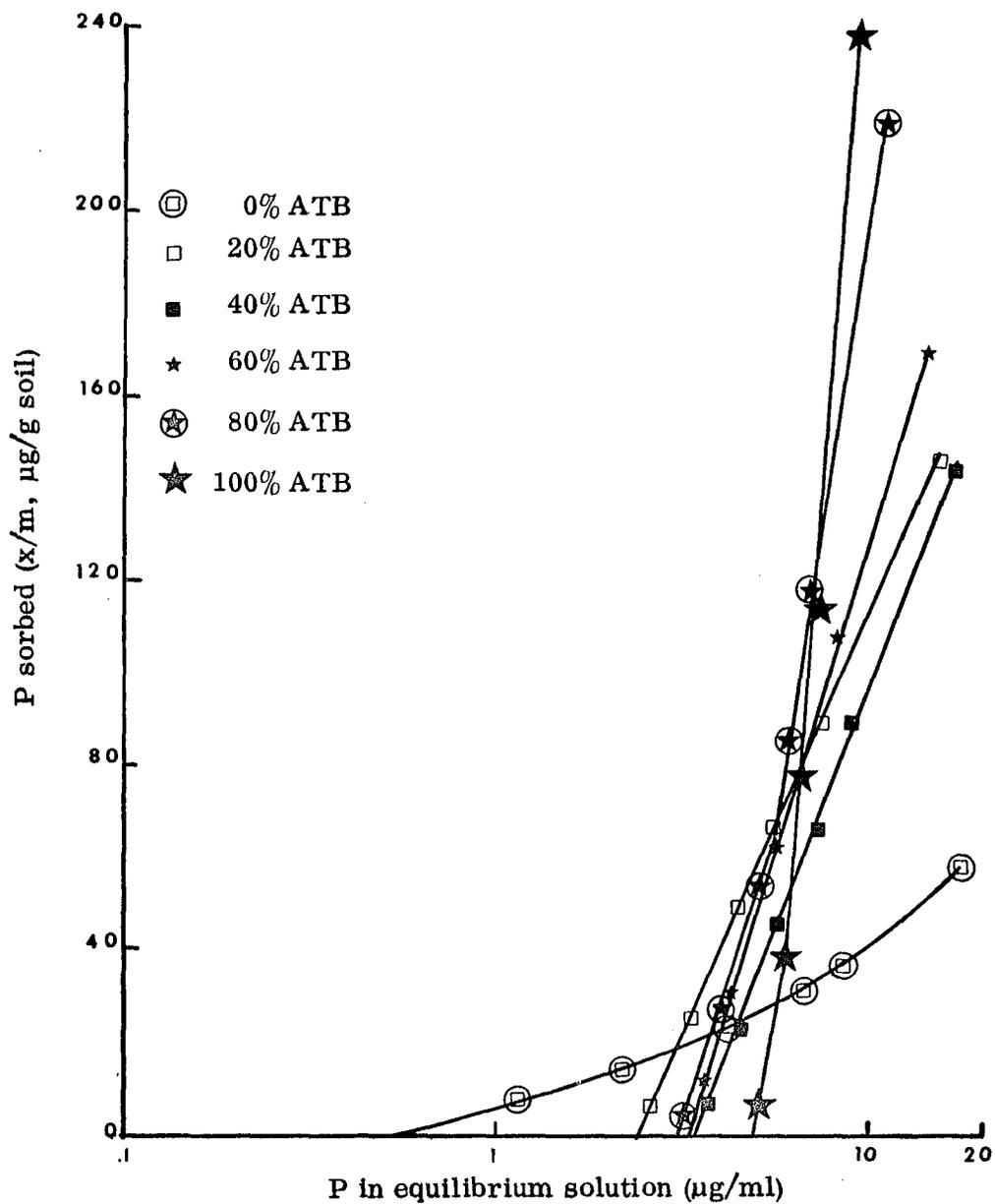


Figure 4. Phosphorus adsorption isotherms of Guest soil treated with different quantities of  $H_2SO_4$  to neutralize various levels of ATB.

equilibrium solution. This was observed at lower levels of P added in the equilibrium solutions up to 10  $\mu\text{g P/ml}$ , but small differences were observed at the 20  $\mu\text{g P/ml}$  level. This increase of P in equilibrium solution with acid addition can be due to solubilization of less soluble P compounds and competition between sulfate and phosphate ions for sorption sites, which is dependent on sulfate and phosphate activities. On the other hand, as the amount of  $\text{H}_2\text{SO}_4$  added increased, there was an increase in DTPA-Fe and  $\text{NH}_4\text{OAc-Al}$  which tended to react with phosphate ions forming less soluble P compounds decreasing the amounts of P in equilibrium solution. At 100 percent ATB acid addition a reversion of isotherm lines towards the origin was observed, which was more accentuated on Laveen soil. The data from Table 1 suggest that this reversion is related to the high increase in  $\text{NH}_4\text{OAc}$  extractable Al and DTPA extractable Fe. This idea is corroborated by the increase in Al-P fraction of all soils and Fe-P fraction of Laveen soil where the reversion was more substantial (Table 2).

If 0.2-0.3  $\mu\text{g P/ml}$  in the equilibrium solution is taken as an index of P adequacy for crop growth (Beckwith 1965; Fox et al. 1968; Fox and Kamprath 1970), the addition of  $\text{H}_2\text{SO}_4$  in amounts necessary to neutralize 20 percent of ATB should release P for plant use. Ryan and Stroehlein (1974) reported an increase in P uptake by tomato plants growing in calcareous soils treated with  $\text{H}_2\text{SO}_4$ . Besides the effect on P availability, there was an increase in DTPA extractable iron, which should be useful in correcting iron deficiency for some crops.

Using the data from Table 3, the adsorption maximum for each soil (0 percent ATB treatment) was calculated using the Langmuir equation:  $C/x/m = 1/kb + C/b$ . The capacity to sorb added P varied from soil to soil as represented by the adsorption maximum values  $\underline{b}$  presented in Table 4. At higher levels of P addition (20  $\mu\text{g P/ml}$ ) the P sorption percentages were 35, 32, 37, and 12 percent, respectively, for Avondale, Pima, Laveen, and Guest soils. Phosphorus sorption capacity seems to be related to percentage of  $\text{CaCO}_3$  equivalent and DTPA extractable iron, but independent of the clay content.

Although very high correlation coefficients were obtained when the linear form of the Langmuir equation was used, data plotted on Fig. 5 showed a significant curvature of isotherm lines. Due to this curvature, the isotherm lines were divided in two or three straight line portions to which different P affinities can be attributed. The Pima and Laveen soils showed clearly the existence of two population sites, each one with different P affinity; in other words, an increase in adsorption maxima with a decrease in slope. This is in agreement with the suggestions of Syers et al. (1973) for acid soils. Avondale and Guest soils showed three different population sites. In the Avondale soil the P affinity as measured by the  $\underline{b}$  maximum increased for each site with an increase in P added initially for equilibration. The Guest soil presented one site where desorption occurred, as shown by a negative slope from 1 to 2  $\mu\text{g P/ml}$  in equilibrium solution. Above that P concentration, two straight lines with positive slopes were observed, showing an increase in  $\underline{b}$  maximum with an increase in P added for equilibrium.

Table 3. Concentrations of P in Equilibrium Solution (C,  $\mu\text{g/ml}$ ), Ratios of P in Equilibrium to Sorbed P (C/x/m) for Four Soils after Equilibration with 0 to 20  $\mu\text{g P/ml}$ .

Initial Conc.	Avondale		Pima		Laveen		Guest	
	C	C/x/m	C	C/x/m	C	C/x/m	C	C/x/m
	$\mu\text{g/ml}$		$\mu\text{g/ml}$		$\mu\text{g/ml}$		$\mu\text{g/ml}$	
0	0.10	--	0.09	--	0.10	--	0.50	--
1.0	0.25	.015	0.35	.024	0.21	.012	1.13	.153
2.5	0.84	.024	1.06	.035	0.76	.021	2.06	.110
5.0	2.18	.042	2.47	.047	2.17	.037	4.31	.181
7.5	3.74	.048	4.04	.057	3.52	.043	6.51	.218
10.0	5.34	.056	6.01	.074	5.45	.058	8.72	.240
20.0	13.13	.094	13.69	.107	12.59	.084	17.64	.308

Table 4. Regression Equations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ) versus Ratios of P in Equilibrium to Sorbed P (C/x/m), Adsorption Maxima  $\underline{b}$ , Indexes of Bonding Energy  $\underline{k}$ , and Correlation Coefficients  $\underline{r}$  for Four Soils, Calculated after Equilibration with 0 to 20  $\mu\text{g P/ml}$ .

Soils	Regression Equations	$\underline{b}$ $\mu\text{g/g}$	$\underline{k}$ $\text{ml/g}$	$\underline{r}$
Avondale	$Y = 0.00581X + 0.02131$	172.12	.2726	.985**
Pima	$Y = 0.00599X + 0.02953$	166.94	.2028	.981**
Laveen	$Y = 0.00533X + 0.02041$	187.62	.2611	.948**
Guest	$Y = 0.01089X + 0.12859$	91.83	.0847	.941**

\*\*Significant at 0.01 level.

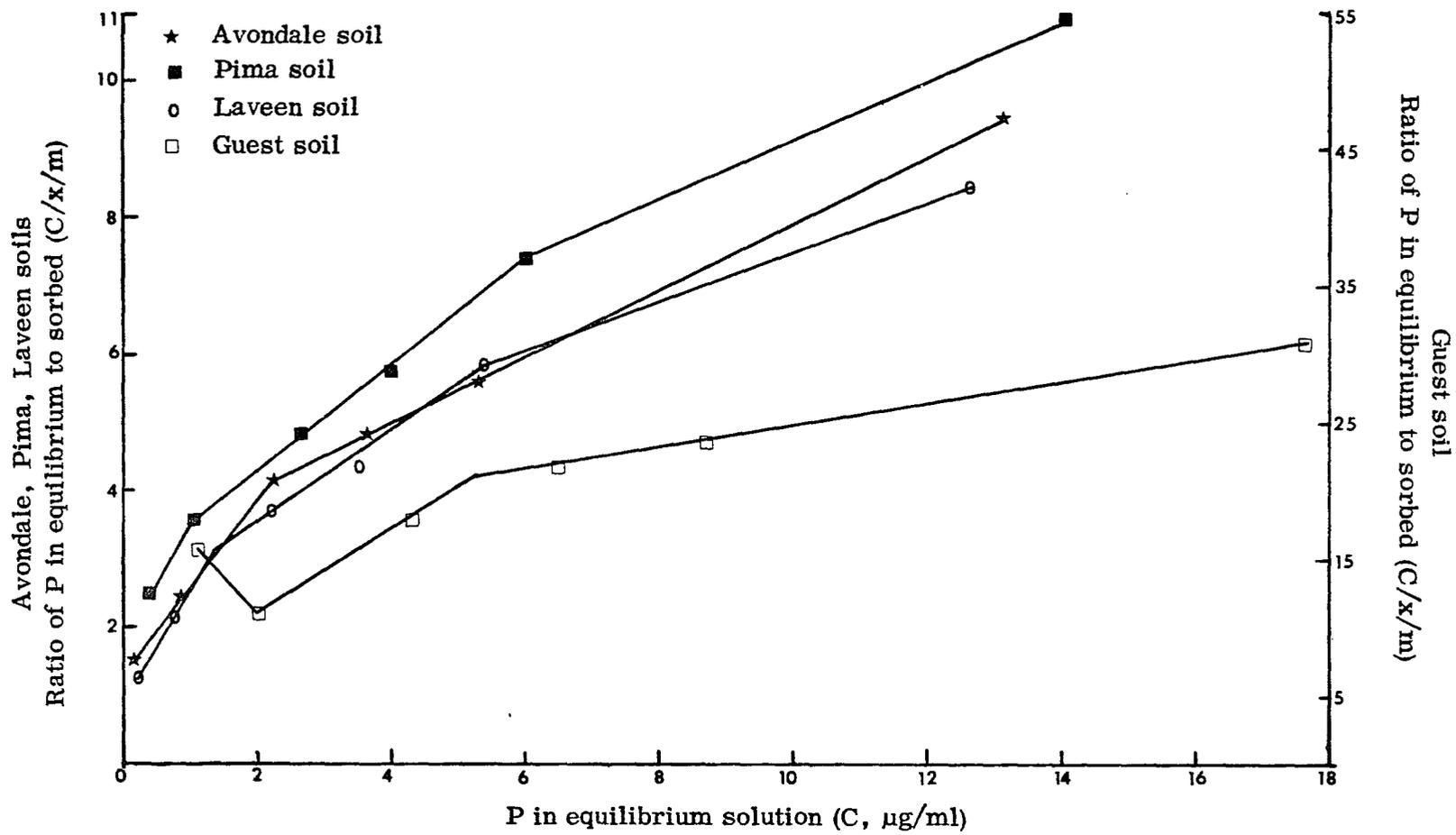


Figure 5. Phosphorus sorption data for four untreated soils plotted according to the linear Langmuir equation.

For acid treated soils (20 percent ATB) the general characteristics of isotherms (Fig. 6) are very different from that of untreated soils. Two regions of P desorption and one of P sorption were observed. Initially, these soils tended to desorb P with a high intensity, being followed by a low intensity, after which sorption was the dominant phenomenon. These transformations from sorption to desorption on acid treated soils were probably due to changes in chemical, physical, and mineralogical characteristics of the original soil.

When the sorption data within the range of 5 to 20  $\mu\text{g P/ml}$  were calculated according to Langmuir's equation, an increase in adsorption maxima and a decrease in the indexes of bonding energy (Table 5) were observed for each soil receiving  $\text{H}_2\text{SO}_4$  (20 percent ATB). This increase in adsorption maxima should be attributed to an increase in exchangeable calcium, DTPA extractable iron, and  $\text{NH}_4\text{OAc}$  aluminum. The percentage of increase in  $\underline{b}$  maxima varied from soil to soil and were 144, 135, 51, and 328 percent for Avondale, Pima, Laveen, and Guest soils, respectively. These increases in  $\underline{b}$  maxima seems to be related more to increases in exchangeable calcium than to DTPA-Fe or  $\text{NH}_4\text{OAc}$ -Al. The correlation coefficients were 0.928, 0.642, and 0.847, respectively, for increases in calcium, iron, and aluminum. As the  $\underline{b}$  maxima increased due to acid treatment, the indexes of bonding energy  $\underline{k}$  decreased. This means that additional P sorbed is not retained as strongly as in the original soil.

Thipathi, Tandon, and Tyner (1970), working with some calcareous soils from India, reported that on the average, the Ca-P fraction was dominant

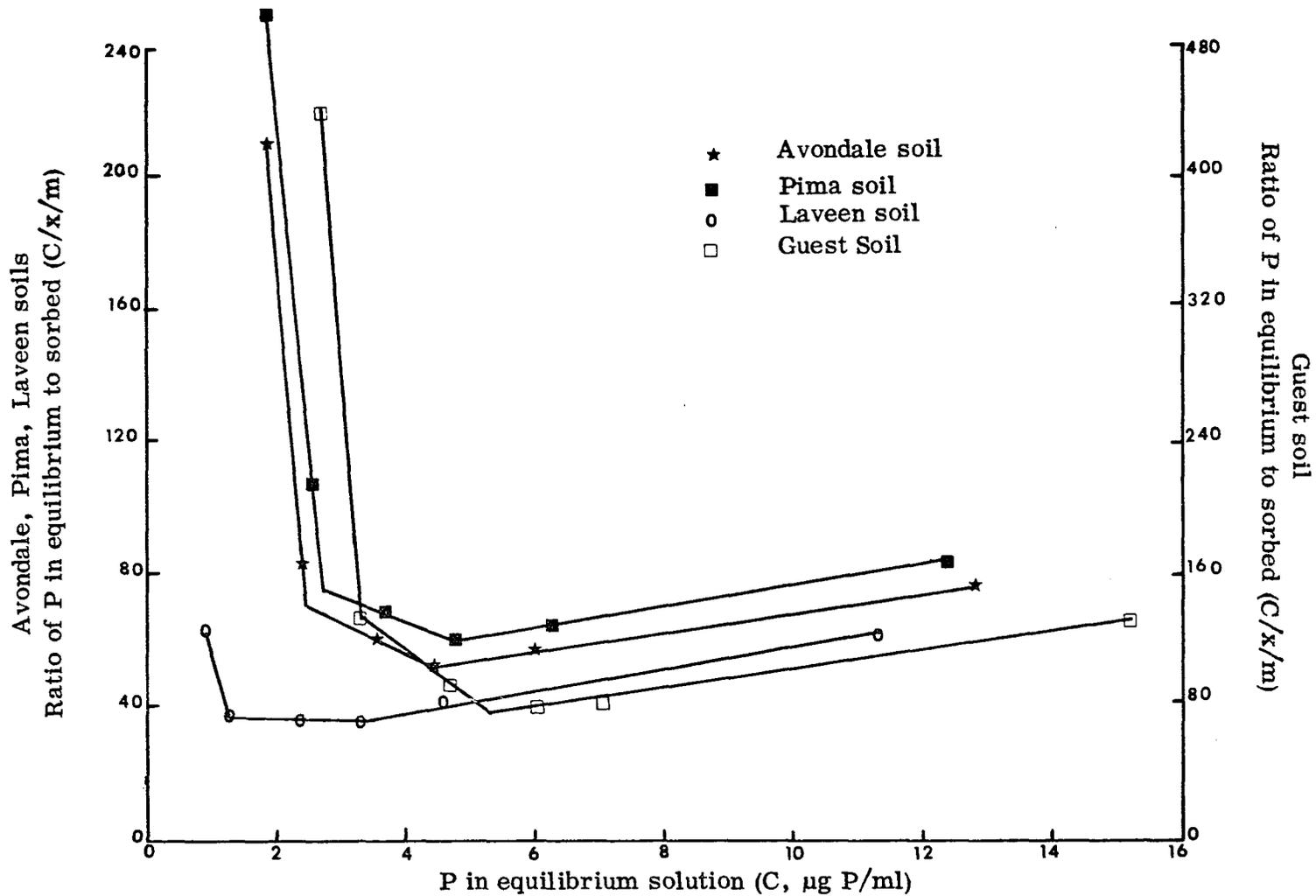


Figure 6. Phosphorus sorption data for four soils treated with  $H_2SO_4$  (20 percent ATB) plotted according to the linear Langmuir equation.

Table 5. Regression Equations of P in Equilibrium Solutions (C,  $\mu\text{g}/\text{ml}$ ) versus Ratios of P in Equilibrium to Sorbed P ( $C/x/m$ ), Adsorption Maxima  $\underline{b}$ , Indexes of Bonding Energy  $\underline{k}$ , and Correlation Coefficients  $\underline{r}$  for Four Soils Treated with  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB), Calculated after Equilibration with 0 to 20  $\mu\text{g}$  P/ml.

Soils	ATB	Regression Equations	$\underline{b}$	$\underline{k}$	$\underline{r}$
	%		$\mu\text{g}/\text{g}$	$\text{ml}/\text{g}$	
Avondale	0	$Y = 0.00508X + 0.02774$	196.85	.1831	.998**
	20	$Y = 0.00208X + 0.04796$	480.77	.0434	.889
Pima	0	$Y = 0.00523X + 0.03695$	191.20	.1415	.989*
	20	$Y = 0.00222X + 0.05361$	450.45	.0414	.865
Laveen	0	$Y = 0.00446X + 0.02929$	224.21	.1523	.985*
	20	$Y = 0.00295X + 0.02715$	338.98	.1086	.991**
Guest	0	$Y = 0.00896X + 0.15463$	111.61	.0579	.980*
	20	$Y = 0.00209X + 0.07602$	478.47	.0275	.754

\*Significant at 0.05 level.

\*\*Significant at 0.01 level.

(41 percent) while Fe-P, and Al-P fractions were 4.7 and 4.0 percent, respectively, of the total P content. Similar results were reported by Rauschkolb (1963) for other calcareous soils from Arizona. Their results were similar to those found for acid untreated calcareous soils in this study, however, there was a tendency toward an increase in the Al-P fraction due to acid treatment.

### Experiment 2

Phosphorus sorption data for four soils treated with  $H_2SO_4$  (0 and 20 percent ATB), and incubated with P ( $1b$  and  $2b$  levels) at two different moisture regimes are presented in Tables B1 to B4. For the same soil, different values of  $b$  are  $k$  were obtained which were dependent on the level of P applied, acid treatment and moisture regime (Tables 6 to 9).

### Effect of P Addition

The effect of P addition on adsorption maxima did not follow the same trend for all soils. For Avondale soil there was a tendency to decrease  $b$  maxima by increasing the amount of P added before incubation (Table 6). On Pima and Guest soils (Tables 7 and 9) there was practically no difference between  $1b$  and  $2b$  treatments. On the other hand, the  $b$  maxima for Laveen soil (Table 8) tended to increase with an increase in P. Comparing plots of isotherm lines obtained from original soils with those from  $1b$  and  $2b$  treatments, some parallelism was observed. Bache and Williams (1971) observed the same kind of parallelism for soils that received different levels of P fertilizers. The isotherms from Avondale soil ( $1b$  and  $2b$ ) tended to move up when compared with

Table 6. Regression Equations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ) versus Ratios of P in Equilibrium to Sorbed P ( $C/x/m$ ), Adsorption Maxima  $\underline{b}$ , Indexes of Bonding Energy  $\underline{k}$ , and Correlation Coefficients  $\underline{r}$  for  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB) Treated Avondale Soil Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum Added ( $\underline{1b}$  and  $\underline{2b}$ ), Calculated after Equilibration with 5 to 20  $\mu\text{g P/ml}$ .

Treatments		Regression Equations	$\underline{b}$ $\mu\text{g/g}$	$\underline{k}$ $\text{ml/g}$	$\underline{r}$
CM <sup>†</sup>	$\underline{1b}$	$Y = 0.00310X + 0.10273$	322.58	.0302	.874
	$\underline{2b}$	$Y = 0.00344X + 0.10846$	290.69	.0319	.945
CM <sup>‡</sup>	$\underline{1b}$	$Y = 0.00181X + 0.05310$	552.49	.0431	.961*
	$\underline{2b}$	$Y = 0.00198X + 0.06217$	335.57	.0479	.988**
WD <sup>†</sup>	$\underline{1b}$	$Y = 0.00283X + 0.10073$	341.29	.0291	.822
	$\underline{2b}$	$Y = 0.00326X + 0.12370$	206.75	.0263	.792
WD <sup>‡</sup>	$\underline{1b}$	$Y = 0.00097X + 0.05333$	1030.93	.0189	.899
	$\underline{2b}$	$Y = 0.00172X + 0.05071$	581.39	.0339	.931
Control <sup>†</sup>		$Y = 0.00508X + 0.02774$	196.85	.1831	.998**
Control <sup>‡</sup>		$Y = 0.00208X + 0.04796$	480.77	.0434	.889

<sup>†</sup>0 percent ATB neutralized.

<sup>‡</sup>20 percent ATB neutralized.

\*Significant at 0.05 level.

\*\*Significant at 0.01 level.

Table 7. Regression Equations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ) versus Ratios of P in Equilibrium to Sorbed P (C/x/m), Adsorption Maxima  $\underline{b}$ , Indexes of Bonding Energy  $\underline{k}$ , and Correlation Coefficients  $\underline{r}$  for  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB) Treated Pima Soil Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum Added ( $\underline{1b}$  and  $\underline{2b}$ ), Calculated after Equilibration with 5 to 20  $\mu\text{g}$  P/ml.

Treatments		Regression Equations	$\underline{b}$	$\underline{k}$	$\underline{r}$
			$\mu\text{g/g}$	$\text{ml/g}$	
CM <sup>†</sup>	$\underline{1b}$	$Y = 0.00253X + 0.07268$	395.26	.0348	.817
	$\underline{2b}$	$Y = 0.00297X + 0.06550$	336.70	.0453	.966*
CM <sup>‡</sup>	$\underline{1b}$	$Y = 0.00153X + 0.04391$	653.09	.0348	.992**
	$\underline{2b}$	$Y = 0.00155X + 0.04037$	645.16	.0384	.988*
WD <sup>†</sup>	$\underline{1b}$	$Y = 0.00513X + 0.04501$	194.93	.1139	.995**
	$\underline{2b}$	$Y = 0.00405X + 0.03399$	246.91	.1191	.999**
WD <sup>‡</sup>	$\underline{1b}$	$Y = 0.00109X + 0.04148$	917.43	.0263	.974*
	$\underline{2b}$	$Y = 0.00090X + 0.02866$	1111.11	.0314	.987*
Control <sup>†</sup>		$Y = 0.00523X + 0.03695$	191.20	.1415	.989*
Control <sup>‡</sup>		$Y = 0.00222X + 0.05361$	450.45	.0414	.865

<sup>†</sup>0 percent ATB neutralized.

<sup>‡</sup>20 percent ATB neutralized.

\*Significant at 0.05 level.

\*\*Significant at 0.01 level.

Table 8. Regression Equations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ) versus Ratios of P in Equilibrium to Sorbed P ( $C/x/m$ ), Adsorption Maxima  $\underline{b}$ , Indexes of Bonding Energy  $\underline{k}$ , and Correlation Coefficients  $\underline{r}$  for  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB) Treated Laveen Soil Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum Added ( $\underline{1b}$  and  $\underline{2b}$ ), Calculated after Equilibration with 5 to 20  $\mu\text{g P/ml}$ .

Treatments		Regression Equations	$\underline{b}$ $\mu\text{g/g}$	$\underline{k}$ $\text{ml/g}$	$\underline{r}$
CM <sup>†</sup>	$\underline{1b}$	$Y = 0.00404X + 0.05699$	247.52	.0709	.976*
	$\underline{2b}$	$Y = 0.00333X + 0.09504$	300.30	.0350	.993**
CM <sup>‡</sup>	$\underline{1b}$	$Y = 0.00167X + 0.03663$	598.80	.0456	.987*
	$\underline{2b}$	$Y = 0.00070X + 0.05326$	1428.57	.0131	.999**
WD <sup>†</sup>	$\underline{1b}$	$Y = 0.00327X + 0.09676$	305.81	.0338	.998**
	$\underline{2b}$	$Y = 0.00196X + 0.12234$	510.20	.0160	.697
WD <sup>‡</sup>	$\underline{1b}$	$Y = 0.00158X + 0.06634$	632.91	.0238	.996**
	$\underline{2b}$	$Y = 0.00170X + 0.07421$	588.24	.0229	.993**
Control <sup>†</sup>		$Y = 0.00446X + 0.02929$	224.21	.1523	.985*
Control <sup>‡</sup>		$Y = 0.00295X + 0.02715$	338.98	.1086	.991**

<sup>†</sup>0 percent ATB neutralized.

<sup>‡</sup>20 percent ATB neutralized.

\*Significant at 0.05 level.

\*\*Significant at 0.01 level.

Table 9. Regression Equations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ) versus Ratios of P in Equilibrium to Sorbed P ( $C/x/m$ ), Adsorption Maxima  $\underline{b}$ , Indexes of Bonding Energy  $\underline{k}$ , and Correlation Coefficients  $\underline{r}$  for  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB) Treated Guest Soil Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum Added ( $\underline{1b}$  and  $\underline{2b}$ ), Calculated after Equilibration with 5 to 20  $\mu\text{g P/ml}$ .

Treatments		Regression Equations	$\underline{b}$ $\mu\text{g/g}$	$\underline{k}$ $\text{ml/g}$	$\underline{r}$
CM <sup>/</sup>	$\underline{1b}$	$Y = 0.00435X + 0.17235$	299.88	.0252	.978*
	$\underline{2b}$	$Y = 0.00513X + 0.08222$	194.93	.0624	.983*
CM <sup>≠</sup>	$\underline{1b}$	$Y = 0.00293X + 0.05792$	341.30	.0506	.999**
	$\underline{2b}$	$Y = 0.00228X + 0.06435$	438.60	.0354	.972*
WD <sup>/</sup>	$\underline{1b}$	$Y = 0.00640X + 0.07659$	156.25	.0836	.994**
	$\underline{2b}$	$Y = 0.00600X + 0.08709$	166.66	.0689	.989*
WD <sup>≠</sup>	$\underline{1b}$	$Y = 0.00308X + 0.03996$	324.67	.0771	.994**
	$\underline{2b}$	$Y = 0.00301X + 0.03326$	332.22	.0939	.990**
Control <sup>/</sup>		$Y = 0.00896X + 0.15463$	111.61	.0579	.980*
Control <sup>≠</sup>		$Y = 0.00209X + 0.07602$	478.47	.0275	.754

<sup>/</sup>0 percent ATB neutralized.

<sup>≠</sup>20 percent ATB neutralized.

\*Significant at 0.05 level.

\*\*Significant at 0.01 level.

the original soil, however,  $1b$  lines were higher than  $2b$ . On the other three soils the general trend was  $1b$  to be equal or lower than  $2b$ . The principal effect of P addition was in moving the isotherms up from their original positions to higher and relatively parallel ones, but the same fundamental sorption characteristics remained.

#### Effect of Moisture Regimes

The moisture regimes did not seem to affect P sorption of acid untreated soils. However, on acid treated soils some differences were observed for all, except Guest soil. In Avondale and Pima soils the  $b$  maxima increased, as the soil was subjected to wetting-drying cycles at both  $1b$  and  $2b$  P levels. On the other hand, a similar difference was observed for  $2b$  P level for Laveen soil. Sufficient data were not available to explain these differences. However, some speculation can be made. The increase in  $b$  maxima due to wetting-drying cycles can be attributed to precipitation of some P compounds which are not dissolved by subsequent wetting. A decrease in  $b$  maxima with this moisture regime could be due to a blockage of sorption sites at lower levels of P or due to rapid water loss which causes some reduction of surface area due to clay shrinkage. The increase in  $b$  maxima at constant moisture could be due to a constant precipitation of P in less soluble forms or to an increase in sorption surface due to clay swelling.

### Experiment 3

Phosphorus desorption data for four soils are presented in Tables C1 to C4. Each soil has shown specific trends in desorbing added P, which was dependent on the amount of P added initially for equilibration, acid treatment, and moisture regimes. Higher values of P desorbed were obtained from Avondale soil, and the lowest were obtained from the Pima soil.

#### Effect of P Addition

In general, the highest percentage of P recovery at the end of the experiment was obtained from 1b P level, which was dependent on the acid treatment and moisture regimes. The highest percentage of P released at the end of the experiment was observed on Avondale and Guest soils. These soils also released the highest percentage of added P during the first extraction. As the amount of P added for equilibration increased from 1b to 2b there was a decrease in the amount of P released by successive extractions. An exception to this was observed on Laveen soil where the variation was almost insignificant.

The reasons why 1b treatment is more effective in releasing P than 2b is not understood. One assumption is that at 2b level, more P is initially in solution. As the sorption sites are being filled, more P is left in solution at level 2b, which could react with calcium, aluminum, and iron, forming initially more or less soluble compounds. With time, these initial compounds could be transformed to more stable and less soluble P compounds. Besides that, higher

P levels could favor the replacement of silicon tetrahedra for phosphate in the clay particle. The phosphate in this position is unavailable for desorption.

#### Effect of Acid Treatment

In general, the acid treatment tended to increase the total or percentage of P released. During the first extraction, the acid treatment tended to reduce the amount of P released; however, it kept the P level in solution at higher values as compared with untreated soil. This can be attributed to dissolution of calcium carbonate and consequently release of calcium. The calcium released could react with phosphate during the incubation process which leads to formation of dicalcium phosphate which is more soluble. The acid treatment tends also to increase Fe- and Al-P fractions which are less soluble than Ca-P compounds.

#### Effect of Moisture Regimes

Comparing totals and percentages of P released at the end of the experiment, it can be concluded that wetting-drying cycles tended to reduce P desorption. While constant moisture showed higher values, it is not feasible to maintain this condition in the field. The reasons why soils subjected to wetting-drying conditions desorb less P is not well understood. Probably, during the wetting-drying cycles, a portion of P not sorbed could be precipitated and transformed to less soluble compounds due to chemical transformations or coprecipitation with calcium carbonate. This condition would not be favorable when the soil is constantly wet.

## Phosphorus Requirement

### General

From semilog plots of P in equilibrium solution (C) versus P sorbed by the soil (x/m), the amounts of P sorbed at any value of C can easily be calculated by interpolation. In general, values of 0.2 to 0.3  $\mu\text{g P/ml}$  in equilibrium solution have been reported as being sufficient for crop growth (Beckwith 1965; Ozanne and Shaw 1967, 1968; Fox et al. 1968; Fox and Kamprath 1970).

In the present report, the amount in equilibrium solution obtained after equilibration of soil with P-free deionized water was added to sorbed P, which was called "correction". This approach was proposed to avoid the use of isotopic exchange for determination of surface P, as suggested by Olsen and Watanabe (1957), as well as washing the soil prior to equilibration, as proposed by Beckwith (1965). In nature, this correction is equivalent to washing the soil prior to equilibration. This portion of P is only a fraction of exchangeable P; however, the isotopic exchange is subjected to failures due to soil/solution ratio and rate of shaking the suspension.

Some features of sorption isotherms are illustrated by the results presented in Figs. 7 and 8 for five soil samples taken from field plots on Laveen soil that received different levels of P fertilizers and manure. These isotherms were obtained by plotting P in equilibrium solution versus P sorbed in the laboratory. Comparing the isotherms shown in Fig. 7, it can be observed that the main effect of the "correction" was in shifting the isotherms up from their

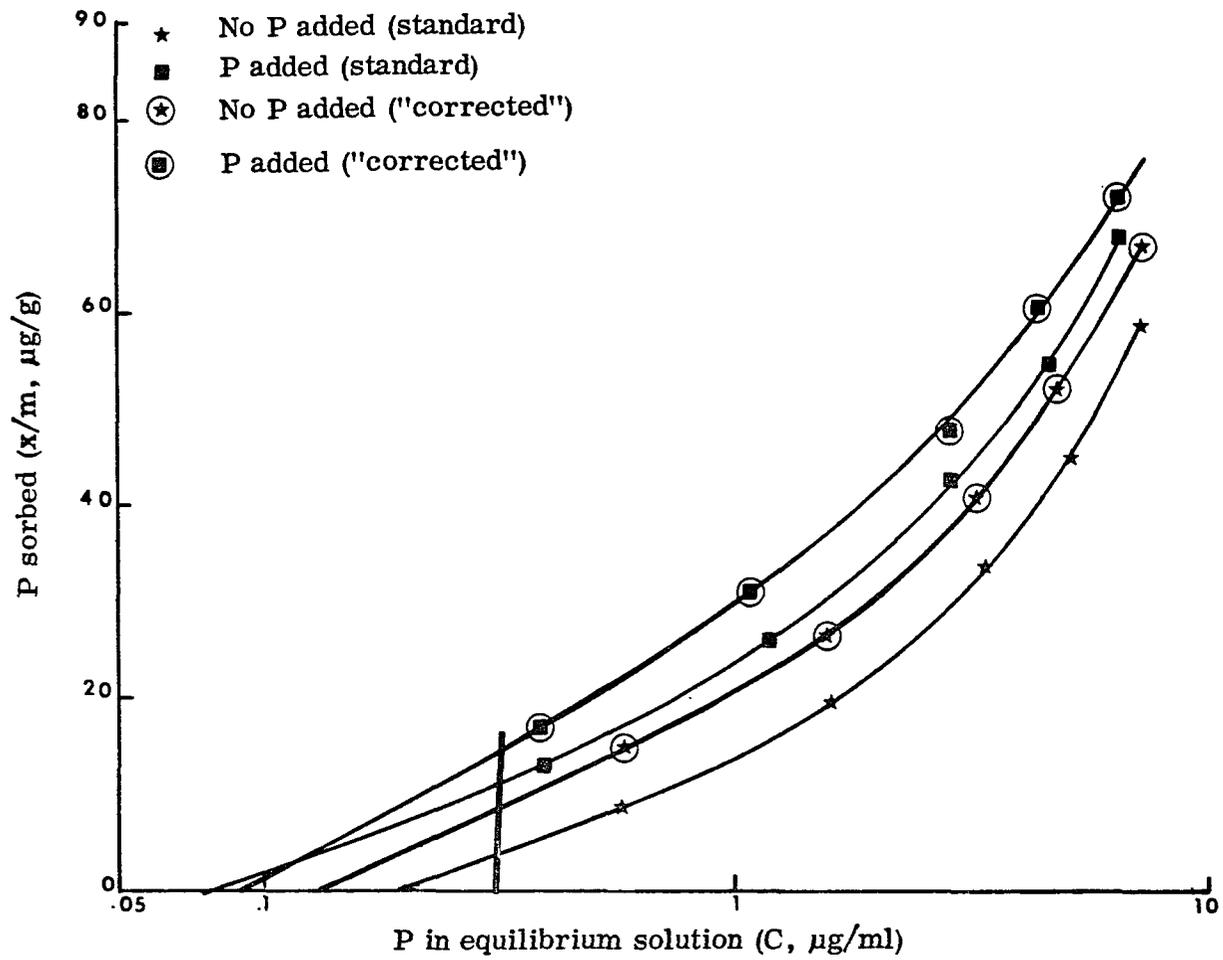


Figure 7. "Corrected" and standard isotherms from fertilizer plots on Laveen soil from Mesa Experiment Farm.

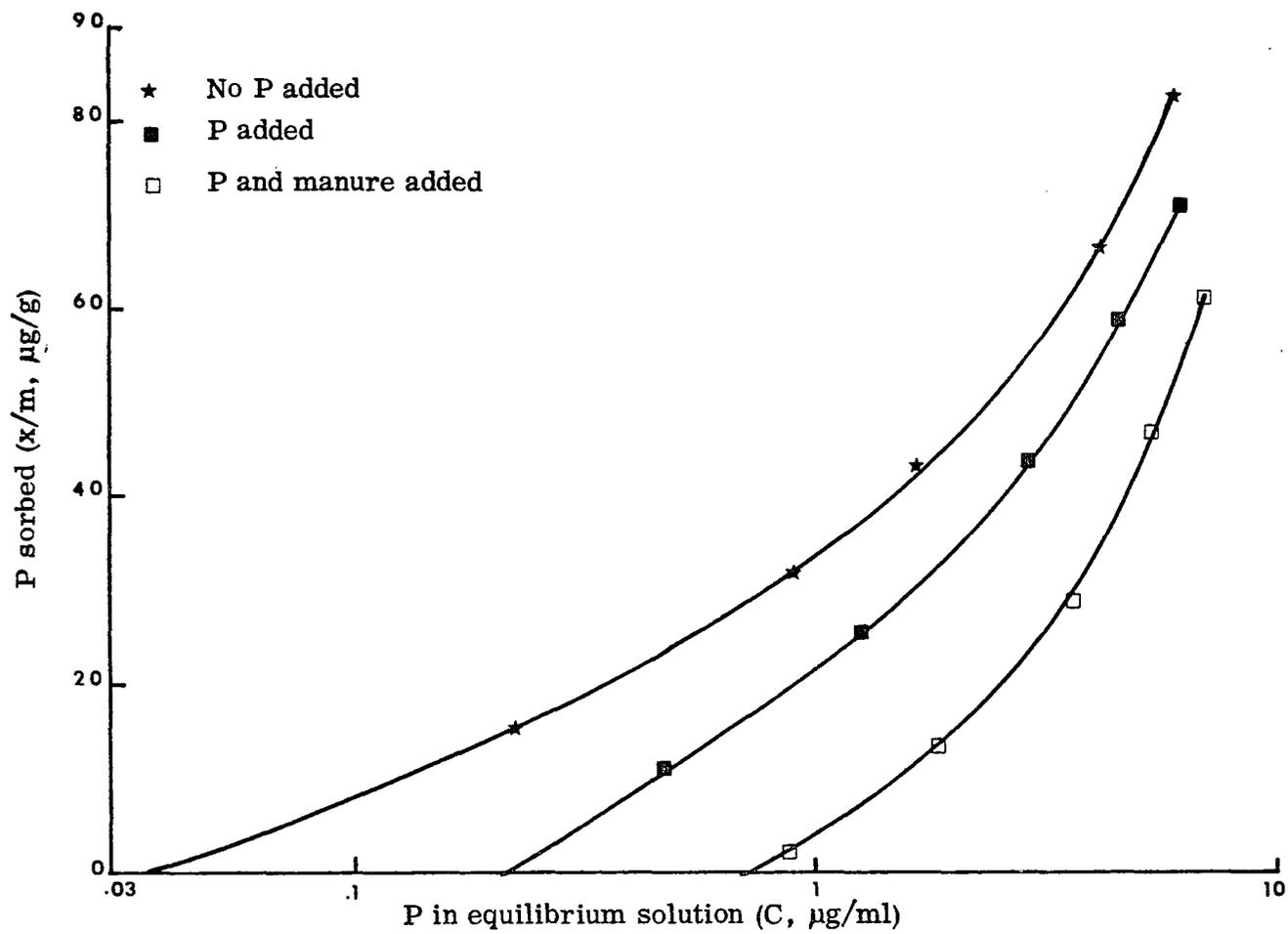


Figure 8. Isotherms from fertilizer plots on Laveen soil from Mesa Experiment Farm.

original position. This is in agreement with the findings of Bache and Williams (1971); however, no superimposition was noticed as was claimed by the above workers. On the other hand, the "correction" tended to shift the x-intercept to the left. This shifting up tended to increase the amount of P sorbed at a determined value of  $\underline{C}$ , as shown by a vertical bar at a  $\underline{C}$  value of  $0.2 \mu\text{g P/ml}$  (Fig. 7).

The isotherms presented in Fig. 8 show the effect of P and P plus manure application on P sorption of Laveen soil. These results indicate that P application to a soil tends to increase the amount of P in equilibrium solution and tends to decrease the amount of P sorbed with the same concentration of P in equilibrium solution. On one side, manure acts as a P source, and on the other side, it decreases P sorption by the mineral particles of the soil.

Midgley and Dunklee (1945) suggested several effects due to manure application, such as: reduction of phosphate solubility; immobilization of P by microorganisms and slow release of P to soil solution; and adsorption of phosphate ions by active humates. Abbott and Tucker (1973) reported an increase in P extracted by sodium bicarbonate in soils treated with manure, as well as the amount of P taken up by barley. Hannapel, Fuller, Bosma, and Bullock (1964) reported that the movement of P in calcareous soils was increased by application of organic matter, which was attributed to an enrichment of organic P forms in the soil solution.

## Evaluation of Laboratory and Field Results

Phosphorus in equilibrium solution, P extracted by CO<sub>2</sub> and bicarbonate methods, and yields of alfalfa, carrots, lettuce, and sugar beets cropped on Laveen soil are shown on Tables D1 to D3. The analyses of variance of yields have shown no difference to P application on carrots and sugar beets; however, some statistically significant differences were observed for lettuce and alfalfa at the 0.05 level. The F values were significant, but differences between means was not shown by the LSD procedure.

Table 10 presents the linear correlation coefficients for association of P sorbed at a value of 0.2 µg P/ml in equilibrium solution, P in equilibrium solution, P extracted by the CO<sub>2</sub> and NaHCO<sub>3</sub> methods, and yields. A reasonable degree of association as shown by high and positive correlation coefficient was observed between the CO<sub>2</sub> and NaHCO<sub>3</sub> methods, although different amounts and fractions of soil P were extracted. Holanda (1972), working with other calcareous Arizona soils, reported a high degree of association between P extracted by those two methods.

Soil P extracted by the CO<sub>2</sub> and NaHCO<sub>3</sub> procedures was significantly associated with yields of lettuce and alfalfa; however, a lack of relation was observed for carrots and sugar beets. Although some differences exist in the amounts of P extracted by CO<sub>2</sub> and NaHCO<sub>3</sub>, i. e., increasing with the increase of P applied over 14 years, this did not affect the yield of carrots and sugar beets. This presence of absence of response seems to be highly related with

Table 10. Correlation Coefficients for Measures of Available P Versus Yields of Carrots, Lettuce, Sugar Beets, and Alfalfa on Laveen Soil, Mesa Experiment Farm.

Methods	Crops			
	Carrots	Lettuce	Sugar Beet	Alfalfa <sup>+</sup>
C x NaHCO <sub>3</sub> <sup>‡</sup>	.563***	.563***	.614***	.957***
C x CO <sub>2</sub> <sup>‡</sup>	.799***	.799***	.666***	.961***
NaHCO <sub>3</sub> x CO <sub>2</sub>	.674***	.674***	.957***	.987***
C x yield <sup>‡</sup>	.266	.626***	.095	.444*
NaHCO <sub>3</sub> x yield	.330	.502**	.012	.590**
CO <sub>2</sub> x yield	.242	.558**	.070	.584**
x/m x yield <sup>‡</sup>	-.041	-.501**	-.016	-.765***

<sup>+</sup>F Value for treatments significant at 0.05 level.

<sup>‡</sup>C = P in equilibrium solution.

<sup>‡</sup>x/m = P sorbed at 0.2 µg/ml in equilibrium solution.

\*Significant at 0.1 level.

\*\*Significant at 0.05 level.

\*\*\*Significant at 0.01 level.

plant species, i. e. , with the plant capacity to absorb P, since carrots and lettuce were cropped side by side in the same plots.

Jones (1959) reported that tomato yields were better correlated with P extracted by the  $\text{CO}_2$  than by the  $\text{NaHCO}_3$ . On the other hand, Holanda (1972) observed that P extracted by both  $\text{CO}_2$  and  $\text{NaHCO}_3$  was better associated with plant yield when grown in soils that had not received P than in those that had received it. Olsen et al. (1954) reported a good agreement between P extracted by  $\text{CO}_2$  and  $\text{NaHCO}_3$  with "A" values for some of their field and greenhouse experiments.

The relationships between yield, P extracted by  $\text{CO}_2$  and  $\text{NaHCO}_3$  versus sorption isotherms were also evaluated. The r values in Table 10 show a high degree of association between P extracted by  $\text{CO}_2$  and  $\text{NaHCO}_3$  with P in equilibrium solution, when no "correction" for the initial water soluble P was taken into account. In this section, P in equilibrium solution is defined as the amount of P calculated when the isotherms intercept the x-axis. That association seems to be related with P fertilization history because the alfalfa experiment which received P recently presented the highest correlation coefficient. This indicates that P in equilibrium solution tends to decrease with time due to chemical transformations to which the more soluble forms of P are subjected. On the other hand, these transformations do not seem to affect the  $\text{CO}_2$  and  $\text{NaHCO}_3$  extractable P as they do P in equilibrium solution.

When yield is taken into account, some association was observed between P in equilibrium solution and yields of alfalfa and lettuce, but not for carrots and sugar beets. The association with alfalfa was significant at 0.10 level, however, it increased to 0.05 level when manure treatment was excluded from the linear regression analysis. A high and positive association was observed between that parameter and total P taken up by alfalfa. When yield of alfalfa was plotted versus P in equilibrium solution, a value higher than 0.1  $\mu\text{g}$  P/ml was found to be adequate for 95 percent of maximum yield. This kind of response was not obtained for the other three crops because the value of P in equilibrium solution from no P treatment was higher than 0.15  $\mu\text{g}/\text{ml}$ , which seems to be sufficient to support the plants need.

One of the advantages of the adsorption isotherms procedure over chemical extractants, as claimed by Beckwith (1965), Ozanne and Shaw (1967, 1968), Fox et al. (1968), and Fox and Kamprath (1970), is the possibility of calculating the amount of P sorbed for each soil. Considering 0.2  $\mu\text{g}$  P/ml in equilibrium solution as adequate for most crops, the amount of P sorbed at that value could be considered as the P requirement. The values of P sorbed were significantly and negatively associated with the yields of alfalfa and lettuce. In other words, higher yields were obtained when small or no P was sorbed at 0.2  $\mu\text{g}$  P/ml in equilibrium solution.

The sorption isotherm method seems to be useful for predicting P needs. However, more research using various calcareous soils and crops must be done to prove its validity.

## SUMMARY AND CONCLUSIONS

Application of sulfuric acid in amounts necessary to neutralize 0, 20, 40, 60, 80, and 100 percent of ATB affected some characteristics of the four soils studied. Soil pH values were initially 8.0 to 8.2 but decreased to levels ranging from 6.1 to 5.5 with acid rates calculated to neutralize 100 percent ATB. The decrease in pH seemed to be related to the buffering capacity of each soil. On the other hand, the treatments increased the amounts of soluble salts, exchangeable calcium, DTPA extractable iron, and  $\text{NH}_4\text{OAc}$  extractable aluminum. The amounts of water soluble P tended to increase with the quantities of sulfuric acid added up to 60-80 percent ATB, above which there was a decrease in that form of soil P.

Phosphorus adsorption isotherms obtained by plotting P in equilibrium solution versus P sorbed tended to shift to the right with an increase in sulfuric acid added. This shifting was due to an increase of water soluble P. When 60-80 percent of ATB was neutralized, the isotherms tended to return to their original position, which seems to be related to an increase in water soluble iron and aluminum and formation of Al-P compounds, principally. Taking 0.2 to 0.3  $\mu\text{g}$  P/ml in equilibrium solution as a critical level for plant growth, addition of sulfuric acid in amounts necessary to neutralize 20 percent ATB can be considered sufficient to release P and iron for plant use.

The adsorption maxima (b) of soils treated with sulfuric acid (20 percent ATB) was higher than the normal soils, but the P sorbed was less strongly bonded. When soils treated with sulfuric acid (0 and 20 percent ATB) were incubated with P in quantities sufficiently to reach 1b and 2b, the new adsorption maxima were dependent on the amounts of P applied, moisture regimes, and acid treatment. Some parallelism among the isotherm lines were observed for each untreated soil; however, this was not observed for acid treated ones. In normal soils the principal effect of P addition is to shift the isotherms up, showing, however, the same fundamental sorption characteristics.

The amounts of P desorbed from each soil was dependent on the rate of acid applied, moisture regimes, and amounts of P added for equilibration prior to incubation. In general, higher percentages of P recovery were obtained from 1b P level and from acid treated soils subjected to constant moisture.

When the P obtained without P in equilibrium solution was added to sorbed P as a "correction", it tended to shift the isotherms up and the x-intercept to the left. This "correction" effect was smaller for untreated soil than for those treated with sulfuric acid. On the other hand, this "correction" tended to increase the amounts of P sorbed at the same value of P in equilibrium solution.

The application of P fertilizer or P plus manure tended to increase the concentration of P in equilibrium solution and to shift the isotherms to the right. Consequently, the quantity of P sorbed at a determined value of P in equilibrium solution decreased.

Although the amounts and P fractions extracted by the  $\text{CO}_2$  and  $\text{NaHCO}_3$  methods were quite different, a significant association was observed between them. Phosphorus extracted by both methods were highly associated with the yields of alfalfa and lettuce, but not with the yields of carrots and sugar beets. On the other hand, positive association was observed between each of these methods and P in equilibrium solution obtained by the sorption isotherm procedure.

A significant and positive association was observed between P in equilibrium solution and yields of lettuce and alfalfa, but none with the yields of carrots and sugar beets. A negative and significant association was observed between P sorbed at  $0.2 \mu\text{g P/ml}$  in equilibrium solution and the yields of lettuce and alfalfa.

The adsorption isotherm method seems to be useful for the prediction of P needs, however, more extensive studies using various soils and crops are suggested.

APPENDIX A

PHOSPHORUS IN EQUILIBRIUM SOLUTION  
AND PHOSPHORUS SORBED BY FOUR SOILS

Table A1. Concentrations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ) and Amounts of P Sorbed (x/m,  $\mu\text{g/g}$ ) after Equilibration with 0 to 20  $\mu\text{g P/ml}$  by Avondale Soil Treated with  $\text{H}_2\text{SO}_4$ . -- 0 to 100 percent ATB.

Initial Conc. $\mu\text{g P/ml}$	% ATB											
	0		20		40		60		80		100	
	C	x/m	C	x/m								
0	0.10	--	1.29	--	2.48	--	4.19	--	3.86	--	0.48	--
1.0	0.25	17.00	1.85	8.80	3.22	5.20	5.50	--	5.86	--	1.01	9.40
2.5	0.84	35.20	2.38	28.20	3.75	24.60	5.96	14.80	6.50	--	1.24	34.80
5.0	2.18	52.40	3.47	56.40	4.36	62.40	7.32	37.20	8.36	10.00	1.39	81.80
7.5	3.74	77.20	4.54	85.00	6.38	72.00	8.46	64.40	9.22	42.80	1.70	125.60
10.0	5.35	95.00	6.08	104.20	7.05	108.60	10.24	78.80	10.19	73.40	2.03	169.00
20.0	13.13	139.40	12.87	168.40	12.67	196.20	15.92	165.20	14.50	167.20	3.80	333.60

Table A2. Concentrations of P in Equilibrium Solutions (C,  $\mu\text{g}/\text{ml}$ ) and Amounts of P Sorbed (x/m,  $\mu\text{g}/\text{g}$ ) after Equilibration with 0 to 20  $\mu\text{g}$  P/ml by Pima Soil Treated with  $\text{H}_2\text{SO}_4$ . -- 0 to 100 percent ATB.

Initial Conc. $\mu\text{g}$ P/ml	% ATB											
	0		20		40		60		80		100	
	C	x/m										
0	0.09	--	1.28	--	2.54	--	4.69	--	6.06	--	4.94	--
1.0	0.35	14.80	1.90	7.60	3.19	7.00	6.03	--	7.53	--	7.25	--
2.5	1.06	30.60	2.58	24.00	3.85	23.80	6.77	8.40	9.76	--	8.41	--
5.0	2.47	52.40	3.65	52.60	8.31	27.60	8.31	27.60	10.29	15.40	9.05	17.80
7.5	4.04	71.00	4.47	80.80	6.29	75.00	9.63	51.20	11.61	39.00	10.49	39.00
10.0	6.01	81.60	6.34	98.80	8.11	88.60	10.99	74.00	13.38	53.60	11.40	70.80
20.0	13.69	128.00	13.39	157.80	14.70	156.80	18.07	132.40	20.08	119.60	18.96	119.60

Table A3. Concentrations of P in Equilibrium Solutions (C,  $\mu\text{g}/\text{ml}$ ) and Amounts of P Sorbed (x/m,  $\mu\text{g}/\text{g}$ ) after Equilibration with 0 to 20  $\mu\text{g}$  P/ml by Laveen Soil Treated with  $\text{H}_2\text{SO}_4$ . -- 0 to 100 percent ATB.

Initial Conc. $\mu\text{g}$ P/ml	% ATB											
	0		20		40		60		80		100	
	C	x/m	C	x/m								
0	0.10	--	0.60	--	1.05	--	2.07	--	2.38	--	0.08	--
1.0	0.21	17.80	0.89	14.20	1.28	15.40	2.47	12.00	2.77	12.20	0.08	20.00
2.5	0.76	36.80	1.32	35.60	1.74	36.20	3.22	27.00	3.47	28.20	0.10	49.60
5.0	2.17	58.60	2.34	65.20	2.58	69.40	4.23	56.80	4.49	57.80	0.14	98.80
7.5	3.52	81.60	3.32	95.60	3.55	100.00	5.58	79.80	6.03	77.00	0.17	148.20
10.0	5.45	93.00	4.76	116.80	4.51	130.80	6.79	105.60	7.60	95.60	0.19	197.80
20.0	12.59	150.20	11.35	185.00	10.54	210.20	13.38	173.80	14.60	155.60	0.39	393.80

Table A4. Concentrations of P in Equilibrium Solution (C,  $\mu\text{g/ml}$ ) and Amounts of P Sorbed (x/m,  $\mu\text{g/g}$ ) after Equilibration with 0 to 20  $\mu\text{g P/ml}$  by Guest Soil Treated with  $\text{H}_2\text{SO}_4$ . -- 0 to 100 percent ATB.

Initial Conc. $\mu\text{g P/ml}$	% ATB											
	0		20		40		60		80		100	
	C	x/m	C	x/m	C	x/m	C	x/m	C	x/m	C	x/m
0	0.50	--	2.05	--	3.31	--	3.41	--	3.11	--	3.00	--
1.0	1.13	7.40	2.74	6.20	3.90	8.00	3.75	13.20	3.73	7.60	4.66	--
2.5	2.06	18.80	3.30	25.00	4.69	22.40	4.40	30.00	4.30	26.20	5.25	5.00
5.0	4.31	23.80	4.64	48.20	6.06	45.00	5.50	58.20	5.42	53.80	6.13	37.40
7.5	6.51	29.80	6.01	70.80	7.45	67.20	6.74	83.40	6.23	87.60	6.59	78.20
10.0	8.72	35.60	7.50	91.00	8.82	89.80	8.02	107.80	7.10	120.20	7.35	113.00
20.0	17.64	57.20	15.21	136.80	16.12	143.80	14.90	170.20	12.88	204.60	10.14	257.20

APPENDIX B

RESULTANT PHOSPHORUS CONCENTRATIONS  
AFTER TREATMENT OF THE FOUR SOILS

Table B1. Concentrations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ), and Ratios of P in Equilibrium to Sorbed P (C/x/m) for Avondale Soil Treated with  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB), Incubated with P at One and Two Times the Adsorption Maximum (1b and 2b), and Subjected to Constant Moisture (CM) and Wetting-Drying Cycles (WD) for Ten Weeks.

Initial Conc. $\mu\text{g P/ml}$		$\text{CM}^{\dagger}$		$\text{CM}^{\ddagger}$		$\text{WD}^{\dagger}$		$\text{WD}^{\ddagger}$	
		C	C/x/m	C	C/x/m	C	C/x/m	C	C/x/m
0	1b	2.35	--	1.79	--	2.24	--	1.72	--
	2b	5.06	--	3.29	--	3.93	--	2.21	--
5	1b	5.29	.128	3.77	.062	5.11	.126	3.59	.058
	2b	7.35	.136	5.02	.077	6.79	.159	3.90	.060
10	1b	8.70	.119	6.54	.062	8.46	.112	6.24	.057
	2b	11.20	.145	8.42	.086	10.24	.139	6.69	.060
15	1b	12.77	.139	9.88	.071	12.62	.136	9.38	.064
	2b	15.26	.159	12.27	.102	14.65	.171	9.73	.065
20	1b	17.10	.161	13.28	.078	16.80	.155	12.27	.065
	2b	19.57	.178	15.92	.108	18.96	.191	13.38	.076

$\dagger$ 0 percent ATB neutralized.

$\ddagger$ 20 percent ATB neutralized.

Table B2. Concentrations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ), and Ratios of P in Equilibrium to Sorbed P (C/x/m) for Pima Soil Treated with  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB), Incubated with P at One and Two Times the Adsorption Maximum (1b and 2b), and Subjected to Constant Moisture (CM) and Wetting-Drying Cycles (WD) for Ten Weeks.

Initial Conc. $\mu\text{g P/ml}$		$\text{CM}^{\dagger}$		$\text{CM}^{\ddagger}$		$\text{WD}^{\dagger}$		$\text{WD}^{\ddagger}$	
		C	C/x/m	C	C/x/m	C	C/x/m	C	C/x/m
0	1b	1.46	--	1.08	--	0.53	--	0.73	--
	2b	2.12	--	1.30	--	0.52	--	0.55	--
5	1b	4.04	.038	2.98	.048	3.00	.059	2.72	.045
	2b	4.41	.081	3.04	.046	2.58	.044	2.13	.031
10	1b	7.30	.088	5.73	.053	6.54	.082	5.17	.046
	2b	7.55	.083	5.53	.048	5.63	.057	4.11	.032
15	1b	11.00	.101	8.62	.058	10.19	.095	7.96	.051
	2b	11.30	.097	8.41	.053	9.17	.072	6.34	.034
20	1b	15.00	.116	11.56	.061	14.50	.120	10.65	.053
	2b	15.21	.110	11.56	.059	12.98	.086	8.82	.037

$\dagger$ 0 percent ATB neutralized.

$\ddagger$ 20 percent ATB neutralized.

Table B3. Concentrations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ), and Ratios of P in Equilibrium to Sorbed P (C/x/m) for Laveen Soil Treated with  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB), Incubated with P at One and Two Times the Adsorption Maximum (1b and 2b), and Subjected to Constant Moisture (CM) and Wetting-Drying Cycles (WD) for Ten Weeks.

Initial Conc. $\mu\text{g P/ml}$		$\text{CM}^{\dagger}$		$\text{CM}^{\ddagger}$		$\text{WD}^{\dagger}$		$\text{WD}^{\ddagger}$	
		C	C/x/m	C	C/x/m	C	C/x/m	C	C/x/m
0	1b	1.43	--	1.14	--	2.18	--	1.88	--
	2b	3.95	--	2.39	--	4.38	--	3.26	--
5	1b	3.91	.077	2.80	.042	4.99	.114	4.09	.073
	2b	6.30	.118	3.90	.056	7.00	.147	5.15	.083
10	1b	7.10	.082	5.22	.044	8.67	.124	7.25	.078
	2b	9.98	.126	6.64	.058	10.39	.130	8.46	.088
15	1b	10.85	.097	8.16	.051	12.62	.138	10.49	.082
	2b	13.99	.141	9.48	.060	14.44	.146	12.00	.096
20	1b	15.21	.122	11.05	.055	16.70	.152	14.00	.089
	2b	18.18	.157	12.37	.062	18.75	.166	15.50	.100

$\dagger$ 0 percent ATB neutralized.

$\ddagger$ 20 percent ATB neutralized.

Table B4. Concentrations of P in Equilibrium Solutions (C,  $\mu\text{g/ml}$ ), and Ratios of P in Equilibrium to Sorbed P (C/x/m) for Guest Soil Treated with  $\text{H}_2\text{SO}_4$  (0 and 20 percent ATB), Incubated with P at One and Two Times and Adsorption Maximum (1b and 2b), and Subjected to Constant Moisture (CM) and Wetting-Drying Cycles (WD) for Ten Weeks.

Initial Conc. $\mu\text{g P/ml}$		$\text{CM}^{\dagger}$		$\text{CM}^{\ddagger}$		$\text{WD}^{\dagger}$		$\text{WD}^{\ddagger}$	
		C	C/x/m	C	C/x/m	C	C/x/m	C	C/x/m
0	<u>1b</u>	2.15	--	1.05	--	1.34	--	0.78	--
	<u>2b</u>	2.84	--	1.33	--	1.55	--	0.73	--
5	<u>1b</u>	5.71	.198	3.49	.068	4.07	.090	2.89	.050
	<u>2b</u>	5.47	.198	3.80	.075	4.61	.119	2.64	.043
10	<u>1b</u>	9.88	.218	6.74	.078	8.26	.134	5.73	.057
	<u>2b</u>	9.17	.125	6.94	.079	8.42	.134	5.22	.047
15	<u>1b</u>	14.04	.226	10.24	.088	12.42	.158	9.00	.066
	<u>2b</u>	13.30	.146	10.29	.085	12.57	.158	8.47	.058
20	<u>1b</u>	18.55	.257	14.00	.099	16.73	.181	12.90	.081
	<u>2b</u>	17.84	.178	14.19	.099	17.13	.194	12.17	.071

$\dagger$ 0 percent ATB neutralized.

$\ddagger$ 20 percent ATB neutralized.

APPENDIX C

PHOSPHORUS DESORPTION FROM THE  
FOUR TREATED SOILS

Table C1. Phosphorus Desorbed on Successive 22-hour Extractions from  $H_2SO_4$  (0 and 20 percent ATB) Treated Avondale Soil, Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum (1b and 2b).

Ext. No.	CM <sup>†</sup>		CM <sup>‡</sup>		WD <sup>†</sup>		WD <sup>‡</sup>	
	1b	2b	1b	2b	1b	2b	1b	2b
1	54.13	99.75	33.22	61.23	46.02	77.45	32.85	39.94
2	27.17	48.46	29.81	29.06	24.74	36.90	27.78	37.51
3	13.15	24.74	22.10	37.51	12.57	21.29	23.72	32.24
4	10.24	17.94	16.32	24.02	9.48	15.21	17.59	24.53
5	7.45	13.03	12.01	18.01	6.74	10.90	12.77	18.10
6	5.43	9.48	8.36	13.53	5.43	10.24	9.99	14.80
7	5.17	8.21	7.45	11.00	5.17	7.71	8.21	12.01
8	4.41	7.45	6.69	9.99	4.66	7.20	7.20	10.49
9	4.16	6.44	5.69	8.47	3.90	5.93	6.18	8.72
10	3.65	5.17	4.92	7.45	3.80	5.17	5.32	7.71
11	3.40	4.82	4.16	6.18	3.14	4.82	4.66	6.94
12	2.89	4.66	4.00	5.83	2.89	4.41	4.51	6.44
13	2.74	4.26	3.65	5.53	2.89	4.41	4.00	5.58
14	2.69	4.26	3.55	5.42	2.89	3.90	4.00	5.53
15	2.69	4.00	3.50	4.82	2.79	3.65	3.70	4.82

<sup>†</sup>0 percent ATB neutralized.  
<sup>‡</sup>20 percent ATB neutralized.

Table C2. Phosphorus Desorbed on Successive 22-hour Extractions from  $H_2SO_4$  (0 and 20 percent ATB) Treated Pima Soil, Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum (1b and 2b).

Ext. No.	CM <sup>†</sup>		CM <sup>‡</sup>		WD <sup>†</sup>		WD <sup>‡</sup>	
	<u>1b</u>	<u>2b</u>	<u>1b</u>	<u>2b</u>	<u>1b</u>	<u>2b</u>	<u>1b</u>	<u>2b</u>
1	30.82	45.01	22.10	27.37	9.94	11.15	12.77	10.54
2	15.11	18.96	18.96	22.71	6.27	6.79	13.38	10.64
3	9.83	13.08	15.41	18.15	4.73	5.54	11.05	9.33
4	7.20	9.48	11.25	13.03	3.55	4.31	8.06	7.86
5	5.53	7.20	8.36	9.73	3.55	4.01	6.18	6.34
6	4.31	5.32	6.44	7.71	2.64	3.55	5.32	5.17
7	4.16	5.17	5.93	6.69	2.38	3.40	4.41	4.66
8	4.16	5.17	5.69	6.18	2.38	3.40	4.16	4.41
9	3.80	4.92	5.17	5.17	2.38	3.30	3.65	4.16
10	3.40	4.16	4.31	4.66	2.03	2.89	3.40	3.65
11	3.24	4.00	4.00	4.41	1.93	2.89	3.40	3.65
12	2.99	3.90	3.90	4.16	1.88	2.89	3.04	3.60
13	2.48	2.99	3.40	3.90	1.78	2.84	2.43	3.60
14	2.38	2.89	3.35	3.65	1.67	2.79	2.38	2.55
15	2.35	2.89	3.35	3.60	1.67	2.79	2.34	2.50

<sup>†</sup>0 percent ATB neutralized.  
<sup>‡</sup>20 percent ATB neutralized.

Table C3. Phosphorus Desorbed on Successive 22-hour Extractions from  $H_2SO_4$  (0 and 20 percent ATB) Treated Laveen Soil, Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum (1b and 2b).

Ext. No.	CM <sup>†</sup>		CM <sup>‡</sup>		WD <sup>†</sup>		WD <sup>‡</sup>	
	1b	2b	1b	2b	1b	2b	1b	2b
1	30.62	79.88	20.28	46.43	42.58	86.57	35.88	64.27
2	15.21	42.98	19.67	38.32	19.67	44.50	26.76	49.06
3	9.83	28.08	18.96	35.18	12.88	23.21	23.82	41.76
4	6.79	18.96	13.38	25.55	8.82	13.89	14.70	28.08
5	6.18	14.80	10.49	20.38	6.69	11.00	11.51	19.87
6	4.16	10.85	7.05	14.80	5.47	9.48	8.47	16.07
7	3.65	9.48	6.18	12.52	4.41	7.20	6.94	12.01
8	3.40	7.96	5.42	10.49	3.90	6.18	5.69	9.73
9	2.89	7.05	4.41	8.47	3.40	5.17	4.61	7.96
10	2.74	6.18	3.90	7.45	3.09	4.56	4.00	6.94
11	2.38	5.17	3.40	6.03	2.48	4.26	3.40	6.18
12	2.13	4.87	3.19	5.83	2.38	3.90	3.04	5.53
13	1.88	3.75	2.54	4.87	2.18	3.40	2.74	4.92
14	1.83	3.65	2.54	2.77	2.08	3.29	2.74	4.77
15	1.78	3.65	2.48	4.41	2.03	2.99	2.54	4.16

<sup>†</sup>0 percent ATB neutralized.

<sup>‡</sup>20 percent ATB neutralized.

Table C4. Phosphorus Desorbed on Successive 22-hour Extractions from  $H_2SO_4$  (0 and 20 percent ATB) Treated Guest Soil, Incubated for Ten Weeks at Both Constant Moisture (CM) and Wetting-Drying Cycles (WD) with One and Two Times P Adsorption Maximum (1b and 2b).

Ext. No.	CM <sup>†</sup>		CM <sup>‡</sup>		WD <sup>†</sup>		WD <sup>‡</sup>	
	1b	2b	1b	2b	1b	2b	1b	2b
1	46.43	57.17	21.29	25.75	31.83	35.89	14.60	14.19
2	17.94	13.58	17.44	20.48	11.86	13.38	13.58	13.08
3	5.93	6.56	10.47	15.00	4.92	5.53	8.45	8.77
4	4.06	4.26	8.57	9.38	3.50	3.80	6.54	8.47
5	3.14	3.14	7.45	7.20	3.50	3.40	4.41	6.08
6	2.48	2.48	4.46	4.97	2.13	2.48	3.90	4.51
7	2.13	2.13	3.65	4.26	1.88	2.38	3.65	3.90
8	2.13	2.08	2.65	4.06	1.88	2.38	3.40	3.65
9	1.88	2.13	3.30	3.65	1.88	2.38	3.40	3.80
10	1.72	1.78	2.79	2.95	1.78	2.38	2.96	3.40
11	1.72	1.78	2.79	2.79	1.57	2.13	2.89	3.24

<sup>†</sup>0 percent ATB neutralized.  
<sup>‡</sup>20 percent ATB neutralized.

APPENDIX D

CROP YIELDS AND SOIL TEST VALUES  
FROM THE LAVEEN SOIL

Table D1. Values of P in Equilibrium Solutions (C, at  $x/m =$  )  $\mu\text{g P/g}$ ), P Sorbed ( $x/m$ , at  $C = 0.2 \mu\text{g P/ml}$ ), P Extracted by  $\text{NaHCO}_3$  and  $\text{CO}_2$  Methods, and Yield of Alfalfa.

Treat.	Rep.	P-eq. soln.		P-sorbed		P extrac. by		Yield*
		$C^{\dagger}$	$C^{\ddagger}$	$x/m^{\dagger}$	$x/m^{\ddagger}$	$\text{NaHCO}_3$	$\text{CO}_2$	
		$\mu\text{g/ml}$		$\mu\text{g/g}$				$\text{ton/ha}$
1	1	.034	.030	11.0	14.5	2.84	0.22	7.76
	2	.038	.035	13.0	14.0	2.74	0.44	8.50
	3	.038	.035	13.0	14.0	2.74	0.44	8.50
2	1	.250	.160	--	2.0	11.56	1.74	13.52
	2	.220	.130	--	3.5	13.99	1.82	14.17
	3	.180	.080	1.0	6.0	10.85	1.82	13.22
3	1	.056	.045	11.0	12.0	4.46	0.82	13.89
	2	.120	.076	5.0	8.0	9.33	1.42	13.95
	3	.090	.050	6.0	9.0	7.81	1.57	13.26
4	1	.072	.056	8.0	9.0	5.07	0.85	12.22
	2	.080	.070	9.0	14.0	4.46	0.76	12.00
	3	.052	.024	10.0	13.0	5.07	0.78	12.80
5	1	.760	.300	--	--	20.07	3.34	13.35
	2	.720	.250	--	--	24.74	4.18	13.29
	3	.760	.250	--	--	24.03	4.52	14.25

$\dagger$  Values calculated from "corrected" isotherms.

$\ddagger$  Values calculated from standard isotherms.

\*Total of five cuttings (dry matter).

Table D2. Values of P in Equilibrium Solutions (C, at  $x/m = 0 \mu\text{g P/g}$ ), P Sorbed ( $x/m$ , at  $C = 0.2 \mu\text{g P/ml}$ ), P Extracted by  $\text{NaHCO}_3$  and  $\text{CO}_2$  Methods, and Yields of Carrots and Lettuce.

Treat.	Rep.	P-eq. soln.		P-sorbed		P extrac. by		Carrots	Lettuce
		$C^{\dagger}$	$C^{\ddagger}$	$x/m^{\dagger}$	$x/m^{\ddagger}$	$\text{NaHCO}_3$	$\text{CO}_2$		
		$\mu\text{g/ml}$		$\mu\text{g/g}$				ton/ha	heads/ha
A	1	.094	.190	4.0	6.0	6.29	1.77	33.66	12582
	2	.040	.120	6.5	11.0	5.78	1.71	39.54	10962
	3	.024	.040	10.0	13.0	4.26	1.08	38.64	11772
	4	.070	.150	4.0	8.0	9.83	2.46	36.62	11691
	5	.030	.045	9.0	11.0	4.76	1.49	35.17	9342
B	1	.098	.200	4.0	6.0	9.12	2.21	39.54	12069
	2	.040	.140	8.0	11.0	7.81	1.65	42.45	11691
	3	.030	.110	6.0	11.0	7.10	2.01	30.74	13905
	4	.054	.150	4.0	8.5	10.39	2.46	33.66	12069
	5	.045	.110	4.5	9.0	8.31	2.19	36.62	10152
C	1	.080	.200	3.0	7.0	13.89	2.58	45.42	12789
	2	.060	.200	3.5	8.0	11.05	2.41	32.98	12204
	3	.052	.180	0.5	8.0	11.35	3.02	33.66	15582
	4	.046	.160	3.5	8.5	11.86	2.66	38.28	12789
	5	.080	.086	4.0	7.0	13.89	1.74	38.08	11016
D	1	.066	.220	3.0	10.0	14.90	3.47	45.42	12744
	2	.080	.220	3.0	7.0	17.23	3.08	40.99	13905
	3	.047	.200	2.0	9.0	14.39	3.27	35.17	13608
	4	.052	.160	3.5	8.0	13.38	2.84	45.42	12123
	5	.076	.100	7.0	10.0	15.41	1.48	35.17	12069

$\dagger$  Values calculated from "corrected" isotherms.

$\ddagger$  Values calculated from standard isotherms.

\*Yield with adequate level of nitrogen.

Table D3. Values of P in Equilibrium Solutions (C, at  $x/m = 0 \mu\text{g P/g}$ ), P Sorbed ( $x/m$ , at  $C = 0.2 \mu\text{g P/ml}$ ), P Extracted by  $\text{NaHCO}_3$  and  $\text{CO}_2$  Methods, and Yield of Sugar Beets.

Treat.	Rep.	P-eq. soln.		P-sorbed		P extrac. by		Yield*
		$C^{\dagger}$	$C^{\ddagger}$	$x/m^{\dagger}$	$x/m^{\ddagger}$	$\text{NaHCO}_3$	$\text{CO}_2$	
		$\mu\text{g/ml}$		$\mu\text{g/g}$				$\text{ton/ha}$
A	1	.070	.250	0.5	7.0	12.87	2.58	79.0
	2	.052	.120	4.0	8.0	8.31	1.76	79.5
	3	.050	.068	5.0	10.0	5.27	1.46	68.8
	4	.064	.100	5.0	8.0	7.81	2.05	75.7
	5	.046	.060	6.0	9.5	4.97	1.33	61.3
B	1	.084	.250	--	5.5	14.39	2.96	49.3
	2	.050	.074	6.0	9.0	5.78	1.39	75.5
	3	.078	.092	7.5	9.0	7.81	2.09	80.8
	4	.110	.180	0.5	4.0	5.27	1.86	81.0
	5	.074	.130	3.0	6.0	6.79	1.84	85.5
C	1	.050	.150	0.5	8.0	13.89	2.58	75.2
	2	.078	.092	0.5	6.0	8.31	1.86	69.0
	3	.068	.120	3.5	6.5	15.41	2.89	77.0
	4	.068	.200	1.5	7.0	12.37	2.58	81.2
	5	.060	.130	2.0	4.0	9.33	2.22	77.7
D	1	.050	.150	0.5	10.0	15.41	2.84	71.5
	2	.072	.160	2.0	9.0	6.79	1.39	77.7
	3	.090	.170	1.5	7.5	15.71	3.09	83.5
	4	.110	.220	0.5	4.0	14.39	2.96	88.6
	5	.096	.130	3.0	7.0	11.35	2.33	61.9

$\dagger$  Calculated from "corrected" isotherms.

$\ddagger$  Calculated from standard isotherms.

\*Yield with adequate level of nitrogen.

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