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# PHOSPHORUS ADSORPTION STUDIES WITH AN ACID, ALUMINOUS SOIL

## AND ALUMINUM HYDROXIDE SUSPENSIONS

By

James Thomas Sims

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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#### ABSTRACT

## PHOSPHORUS ADSORPTION STUDIES WITH AN ACID, ALUMINOUS SOIL AND ALUMINUM HYDROXIDE SUSPENSIONS

#### BY

#### JAMES THOMAS SIMS

Phosphorus adsosrption by aluminum hydroxides (A1-OH) often limits crop production in areas of the world dominated by highly weathered, acid, aluminous soils. Understanding how the pH at which the A1-OH is precipitated, the age and extent of growth of A1-OH polymers, and soil solution ionic strength will affect reactivity of A1-OH for P is essential if successful soil fertility programs are to be developed.

Changes were evaluated in the adsorption and availability of P in an acid, aluminous soil following liming to neutralize 1N KCl exchangeable  $A1^{3+}$  (minimal liming) or to a pH of 6.8 as determined by the SMP buffer. Phosphorus adsorption by "pure" A1-OH suspensions was examined as a function of pH of A1-OH precipitation, aging and ionic strength. Langmuir adsorption isotherms were utilized to ascertain changes in P adsorption in the soil and A1-OH suspensions. A greenhouse bioassy was conducted to evaluate changes in P availability for crop uptake due to liming and incubation treatments.

Results of the soil study confirm minimal liming is the most effective approach, from both agronomic and economic standpoints. Minimal liming optimized P uptake and minimized the P adsorption maxima (Langmuir b). The SMP approach did not improve P uptake despite the application of three times as much lime, and also markedly reduced exchangeable Mg. Aging of adsorbate surfaces in the soil reduced their bonding intensity for P (Langmuir k), as did increasing soil pH. Reductions were noted in Al extractability with time and imposition of wet/dry cycles during incubation. Development of ordered, less soluble Al-OH polymers with fewer nonstructural OH groups capable of ligand exchange with P is postulated as the mechanism underlying these observations. Increases in pH dependent negative surface charge and P adsorption by free CaCO<sub>3</sub> may be involved.

Aging of Al-OH suspensions reduced their capacity for P adsorption and while Al-OH precipitated at pH 5.5 initally adsorbed more P than that precipitated at 7.0, the difference became insignificant within three months. Reducing the ionic strength of the suspensions by dialysis produced gibbsite and a decrease in Al-OH P adsorption maxima, further evidence that the polymerization/crystallization process is an important control of Al-OH reactivity for P.

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#### INTRODUCTION

Phosphorus (P) adsorption by highly weathered, acid, aluminous soils seriously limits crop production in regions of the world that offer the greatest opportunity to improve agricultural productivity. Soils of this type develop in areas where favorable climatic conditions (warm temperatures, adequate to excessive rainfall) exist that are conducive to the growth of from two to four crops per year. However, soil fertility limitations, particularly the deleterious effects of soil acidity, may prevent optimization of crop yields.

Extremely acid soils (pH < 5.0) contain appreciable quantities of exchangeable aluminum (A1) that may inhibit crop growth, either through direct toxicity or by reducing the availability of P, an essential plant nutrient. Traditionally, ground limestone has been applied to reduce A1 toxicity and increase P availability. In temperate regions rates have been designed to raise soil pH to near neutrality (pH 6.5 to 7.0). Recent research has indicated that for acid, aluminous soils this may in fact be overliming and that rates of lime sufficient to neutralize one to one and a half times the exchangeable A1 are adequate from a soil fertility standpoint.

Although liming eliminates precipitation of P by Al, the formation of aluminum hydroxides (Al-OH) in the soil following the application of limestone often results in fixation of P in a manner such that it is no longer available for crop uptake. The determination of the most

efficient combination of lime and P fertilizer, from both agronomic and economic points of view, is a topic of considerable importance to the soil scientist in areas where Al is a dominant factor in the chemistry of the soil solution.

The overall objective of this study was to examine the effect of two liming philosphies in terms of their relative effects on P adsorption and availability for crop use. Comparisons were made between the application of lime sufficient to neutralize exchangeable Al (minimal liming) and that required to produce a near-neutral soil pH as determined by a buffer method. Additionally examination of P adsorption by artificially prepared Al-OH was studied in the laboratory in an attempt to elucidate the mechanisms involved, with particular emphasis on changes in the nature of the adsorption process with time.

The results of this experimentation will hopefully provide information of use in designing crop production systems for areas of the world plagued by manageable soil fertility problems. The soil chemist sees these problems, not as obstacles, but as challenges and dedicates research efforts to developing solutions. It is hoped that this research may play some part in such a solution.

### CHAPTER I

#### LITERATURE REVIEW

The enhancement of agricultural productivity has been a major concern of professionals in numerous fields of scientific endeavor. As with progress in any other discipline, success in agriculture requires identification of the primary components involved in the system of interest. Subsequently, the interaction and effects of these components on previously defined goals, in this case food production, can be determined. Numerous parameters are involved in the growth of food crops, among the most important of which is the plant-soil interaction, particularly in the realm of availability for plant uptake of critical plant nutrients. The nature of the soil-plant interface and the chemistry of essential and non-essential elements in this region are areas of extreme complexity and profoundly effect plant growth and development. The plant root is the biological conduit through which nutrients are transferred from the soil into the plant for metabolic The environment in which roots exist is commonly referred to as use. the soil matrix and may be defined as soil particles (sand, silt, clay) surrounded by a thin aqueous film where the interaction of biological and mineralogical activity occurs. It is in this aqueous phase that native and applied (fertilizer) minerals undergo a variety of transformations (dissolution, precipitation, polymerization,

crystallization) that affect their ability to be utilized by the plant. As in any chemical solution factors such as pH, Eh, temperature, pressure, extent of complexing and ionic strength must be taken into consideration. Equilibrium reactivity and reaction rate kinetics may then be applied to the system in an attempt to determine present behavior and predict future states. The study of soil chemistry may be viewed as an attempt to synthesize all of these variables and develop a cohesive model that can function as an integral part of a larger system. The focus of this overall system involves increasing food production through inputs from all disciplines concerned with the plant and soil sciences.

Operating within this context soil chemists have isolated many reactions that are significant controls on the availability of essential plant nutrients. One of the principal non-essential elements that is involved in plant nutrition is Al the major acidic metallic element in the pH range commonly found in acid (pH < 7.0), agricultural soils. Aluminum is of importance for several reasons, having been identified as the primary source of soil acidity in acid mineral soils and as a force for the immobilization of P in a form that is sparingly available for crop uptake. To fully understand the role of Al in the chemistry of the soil solution, particularly its interaction with P, a vital plant nutrient, requires a thorough knowledge of the chemical behavior of Al in pure aqueous systems. Extrapolation of Al chemistry in pure water into the more complex soil solution can only be done when this theoretical background can be combined with empirical data gathered from careful research utilizing a wide variety of soil types.

Aluminum is a group III element, possessing three electrons in its outer shell, and an atomic diameter of 0.57 angstroms. It is a trivalent metallic element exhibiting ionic and covalent character in compound formation. The size of the Al atom is almost exactly the same as the void space at the center of six closely packed oxygen (0) atoms, hence Al is commonly found in sixfold coordination with 0 in the octrahedral layer of primary and secondry minerals. In terms of abundance within the earth's crust, Al is the second most plentiful oxide, the third most plentiful element and the most abundant metallic element. Common primary mineral sources of Al include micas, feldspars Secondary minerals that contain Al are the and cryolite. aluminosilicate clays and ores such as bauxite. Values of Al in surface soils relative to other elements are of virtually the same magnitude as in the earth's crust, with lesser quantities noted in those soils that are predominantly sand or have experienced intensive weathering (Ultisols, Oxisols). It is the weathering process that initiates removal of Al from mineral structures and introduces it into the soil solution. At pH values less than 4.0 hydrogen (H) ions enter into the mineral structure and dissolve Al into the soil solution. Once in this aqueous medium Al enters into an octahedral arrangement with six water molecules,  $A1(H_20)_6^{3+}$  (6). These water molecules are oriented with their negative charge centers  $(0^-)$  directed toward the Al ion and the positively charged sides  $(H^+)$  facing outward. The strength of the charge on the  $A1^{3+}$  ion tends to weaken the forces of attraction between the H and O atoms, making the protons  $(H^+)$  relatively easy to dislodge (20). In essence Al acts as a weak acid capable of sequential

dissociation of H ions as the pH of its environment is increased above 3.5. Most natural systems exist under pH conditions that favor dissociation of these H ions and the generally accepted sequence ofreactions associated with increasing pH is:

$$A1(H_20)_6^{3+} = A1(H_20)_5(0H)^{2+} + H^+$$

 $A1(H_2O)_5(OH)^{2+} = A1(H_2O)_4(OH)_2^{1+} + H^+$ 

 $A1(H_2O)_4(OH)_2^{1+} = A1(H_2O)_3(OH)_3^{O} + H^+$ 

$$A1(H_{2}O)_{3}(OH)_{3}^{O} = A1(H_{2}O)_{2}(OH)_{4}^{1-} + H^{+}$$

Upon hydrolysis the Al-OH species formed do not remain as distinct individual ions but undergo a polymerization process that involves the formation of polynuclear complexes. The initial step involves dimerization according to the reaction :

 $2 \text{ A1}(\text{H}_2\text{O})_6^{3+} = 2 \text{ A1}(\text{H}_2\text{O})_5(\text{OH})^{2+} + 2 \text{ H}^+$ 

$$2 \text{ A1}(\text{H}_{2}\text{O})_{5}(\text{OH})^{2+} = \text{A1}_{2}(\text{H}_{2}\text{O})_{8}(\text{OH})_{2}^{4+} + 2 \text{H}_{2}\text{O}$$

The key to dimer formation and subsequent polymerization is the establishment of the double hydroxide (OH) bridge characteristic of both these polymers and the crystalline aluminum hydroxides  $(A1(OH)_3)$  such as gibbsite. Hsu (25) has demonstrated that the OH/A1 ratio affects the

rate of polymerization and in some cases the crystalline end product that develops. Rapid polymerization and the formation of bayerite was found with OH/A1 = 3.05, while for OH/A1 of 1.8 to 2.7 gibbsite formed at a much slower rate. Although polymerization may continue in many stereochemical configurations, the most statistically probable is that of a ring containing six Al octahedra, i.e.,  $A1(H_20)_{12}(OH)_{12}^{6+}$ . The basis for ring formation and further coalescence of these rings into larger polymers is the same deprotonation-dehydration reaction written above for dimerization. Characterization of the polymers may be conducted by the procedure of Bersillon et al. (5), in which soluble Al species are separated on the basis of OH/A1 ratio and surface charge. Four categories are identified by this technique: (i) high OH/Al polymers with a residual positive charge of 0.33 or less per Al atom, (ii) medium OH/Al polymers, (iii) low OH/Al polymers, and (iv) monomeric Al ions. This separation procedure offers considerable promise for studying the mechanisms of gibbsite crystallization from aqueous solutions and perhaps in the soil solution as well. Within the ring structure and larger polymers the OH groups are generally classified as structural OH or nonstructural OH referring to their location and potential reactivity. Structural OH groups are those located in the double OH bridges linking Al ions together and are viewed as less reactive than the nonstructural OH which are located along the perimeter of the polymer. Reactivity of protons or other anions with these two classes of OH groups will be quite dissimilar. The nonstructural OH may be visualized in terms of chemisorption or anion exchange capacity and should be easily neutralized by H ions or replaced by anions of suitable

size and charge. Structural OH cannot react until a simultaneous break of at least two OH-Al bonds occurs within a double OH bridge. Hence the reactivity of structural OH is thought to be slower and subject to a more complex rate law than nonstructural OH. Aging of these precipitated A1-OH polymers can produce changes in reactivity as well. Evidence exists that Al-OH gels precipitated from soluble Al salts by addition of a base are initially highly random structures that convert to a more thermodynamically stable system upon aging (51). The ultimate end product of the aging process is usually a crystalline form of Al(OH); such as gibbsite, bayerite, or pseduo-boehmite (25). Characterization of these gels during the aging process has been done in terms of X-ray diffraction, electron micrographs, acid reactivity, pH and other chemical and physical parameters (50,51,52). Results of these investigations may be combined into an aging model that attributes much of the change to the aforementioned deprotonation-dehydration reaction. According to this model polymerization occurs between adjacent Al-OH particles with the release of H causing a continual decline in system pH, stabilizing at approximately 3.8. Infrared studies, x-ray diffraction patterns, and electron micrographs are all consistent with a gradual conversion of amorphous Al-OH into a crystalline material with mineralology that varies slightly according to the precise conditions of initial precipitation (pH, type of Al salt, temperature, etc.)

Anion substitution may be a critical factor in determining polymer growth and pH in natural systems. The concentration of anions such as chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and bicarbonate (HCO<sub>3</sub><sup>-</sup>) has been shown to correlate with polymer size, pH and acid reactivity of Al-OH gels

precipitated under controlled conditions (52,72). Ross and Turner (69) concluded that the ability of monovalent anions to enhance crystallization of Al-OH was inversely related to anion size and structural complexity. Their results show that  $Cl^-> NO_3^-> ClO_4^-$  in terms of ease of incorporation into the gel structure and subsequent acceleration of the rate of crystallization. In the case of Cl a negative correlation exists between anion concentration and polymer size. Presumably Cl ions occupy edge positions on the Al-OH colloidal particles and inhibit further polymerization at these sites by preventing the establishment of double OH bridges. In addition, the pH of the system increases with Cl content as nonstructural OH ions are displaced into the external solution.

Acid reactivity is frequently used as an indicator of the degree of structural order in Al-OH polymers (51). Acid reactivity profiles determined for Al-OH gels by Nail et al. (52) possessed three phases: (i) an initial fast reacting portion whose contribution decreased as the gel ages (ii) a portion that reacts with acid according to apparent first order kinetics, at a rate that decreases with age and (iii) a slow, second order portion believed to be highly ordered material. Freshly precipitated gels exhibit a high degree of reactivity whereas gels aged for as little as thirty days show marked decreases in their ability to react in acid (i.e. neutralize external acidity). Larger polymer size and incorporation of nonstructural OH into double OH bridges that are more resistant to acid attack are cited as causes for the decreased reactivity with age. Anions such as Cl may also contribute to this phenomenon by their inhibition of the incorporation

of OH into double OH bridges. Research by Hem et al. (21) provided evidence that loss of acid reactivity is dependent upon pH of precipitation, with Al gels precipitated at relatively high pH values (7.7-9.2) showing highest rates of loss of reactivity. They concluded that changes in acid reactivity on aging were not due to differential crystallization but could be attributed to the stabilizing effect of Cl ions, with high Cl activity correlated with retention of acid reactivity throughout the aging process.

The implications of anion adsorption by Al-OH polymers are twofold. In one instance, anions that are present at the time of precipitation and subsequent polymerization may be incorporated into the developing polymeric structure. Inclusion of anions (Cl) may have a significant effect on the physical and chemical nature of the polymer as it ages. Of perhaps greater import is the adsorption of anions that enter the system following the intial precipitation process. Certain anions ( $H_2PO_4^-$ ,  $NO_3^-$ ) are directly involved in many biochemical processes critical to plant metabolism. The interaction between these anions and precipitated amorphous Al-OH polymers can have considerable influence on the participation of these nutrient elements in numerous essential biochemical systems. Examination of the mechanisms of anion adsorption is therefore of prime importance in interpreting the role of Al-OH polymers in the availability of plant nutrients.

Adsorption of anions by Al-OH gels has been postulated to occur by three mechanisms (22):

- Nonspecific adsorption: anions adsorbed only by positively charged surfaces, loosely held in the diffuse layer.
- 2) Specific adsorption of anions of completely dissociated acids such as sulfate, fluoride, and carbonate; based on chemical adsorption, involving ligand exchange with water.
- 3) Specific adsorption of anions of incompletely dissociated acids such as  $H_2PO_4^-$  and  $HSiO_4^-$ .

Nonspecific adsorption is defined as an electrostatic attraction between the anion and positively charged sites on the Al-OH polymer. Specific adsorption, however, evolves from ligand exchange that produces direct coordination of the anion with  $A1^{3+}$ , usually through an 0 atom. Several factors have been cited (72) as important in terms of anion adsorption: (i) anions with smaller size will be adsorbed more strongly, (ii) the more deformable the anion, the greater the interaction, and, (iii) the charge of the anion is directly related to the strength of interaction. Research on the mechanism of P adsorption by A1-OH polymers has utilized cation and anion exchange resins, precipitated Al-OH gels, artificially prepared gibbsite and pure clay minerals such as kaolinite. Although there is not universal agreement on the nature of the adsorption process, a common mechanism suggested involves P replacement of exposed OH groups on the polymer surface. Ligand exchange with water molecules coordinated to Al ions on the polymer surface has also been postulated, and would result in a coordinate covalent bond being formed between Al and an 0 atom in the P anion (78). Resolution of the precise nature of the adsorption process is an area currently receiving extensive research, particularly with regard to the effect of ambient pH and the

pH of gel precipitation.

Application of the principles of Al-OH polymer behavior in the pure systems mentioned thus far to the soil solution is the next step in relating the chemistry of soil Al to availability of nutrients for plant growth. Upon release from soil minerals in the weathering process Al exists initially as a trivalent ion coordinated with six waters  $(A1(H_20)_6^{3+})$ . At pH values below 5.0 this trivalent ion may remain in solution, but is more commonly found adsorbed onto soil cation exchange sites where it may be viewed as a source of potential acidity and as a possible reactant in the precipitation of minerals such as variscite  $(AlPO_4 \cdot 2H_20)$  (41). Additionally, complexation of Al with organic matter may be of considerable importance in regulating the quantity of exchangeable and solution Al in the soil. Bloom (7) maintains that exchange of Al from carboxyl sites on organic matter is the most important factor in the control of soil solution Al activity at pH values less than 5.5 in acid soils low in aluminous chlorite and permanent charge exchage capacity. According to Bloom, the solubility of crystalline minerals or amorphous aluminosilicates has little direct influence on solution Al. Exchange of Al by H ions and hydrolysis of Al found on organic matter exchange sites are defined as major sources of pH buffering in these soils.

Successful management of agricultural soils requires neutralization of excessive soil acidity through the application of limestone. Consequently, research in the area of determining lime requirements that minimize the detrimental effects of soil acidity while maintaining adequate nutrients is of pressing importance. Numerous

analytical techniques have been used to estimate the lime requirement for highly weathered, acid, aluminous soils (3, 37, 42, 61, 62, 73). Evans and Kamprath (10) found that lime requirements based on Al concentration in the soil solution correlated well with maximum corn growth in coastal plain soils of widely varying organic matter content. They cautioned against overliming due to yield depressions noted at pH values greater than 5.3 and speculated that nutrient imbalances under overliming could have been responsible. Reeve and Sumner (65) developed the exchangeable Al index (EAI) for estimating lime requirement on South African oxisols, but also stated that solution Al was more applicable to a wider range of soils. Recently Farina, et. al. (11) compared exchangeable Al and pH as indicators of lime requirement for corn grown on a wide variety of temperate and tropical soils and found that Al saturation was a valuable index as well. The use of pH alone proved to be a poor measure of lime requirement and indeed the authors raised serious questions about the validity of the long held view that nutrient availability is maximized at near neutral pH values (6.0 and above). The depressive effects on yield of liming to near neutrality they observed have been seen in numerous experiments (2, 13, 36, 39, Kamprath (32) has elucidated possible reasons for this yield 59). depression, among them precipitation of calcium phosphates, boron (B), manganese (Mn) and zinc (Zn) deficiencies and reduction in soil aggregate stability which may increase the susceptibility of the soil to erosion. Keeney and Corey (35) found that organic matter content and soil pH were well correlated with lime requirement in acid Wisconsin soils, while clay content and exchangeable Al were of little importance.

It should be noted, however, that exchangeable Al values in these soils were extremely low (< 1.0 meq/100g), which may explain the unimportance of Al as a lime index. Subsequently Pionkee and Corey (60) examined the relations between Al, pH, clay and organic matter in 127 acid Wisconsin soils, in an effort to determine how liming affects the chemistry of soil Al. They devised a reaction scheme for Al that predicted the partitioning of soil Al between the solution, exchangeable, polymerized and organic matter complexed forms, at a constant pH. Additionally, they described the conversion between exchangeable and nonexchangeable Al (that found as Al polymers and Al-OM complexes) as a function of pH. They found that nonexchangeable Al is progressively converted to exchangeable Al below a pH (in KCl) of 4.1, primarily due to the replacement of Al in Al-OM complexes with H ions. Based on the work of these researchers and others, the application of lime to neutralize between one and two times the 1N KC1 exchangeable A1 seems to be an acceptable approach to the minimization of the negative effects of excessive acidity in these soils. The use of 1N CuCl<sub>2</sub> exchangeable Al as a lime requirement index offers promise as well, particularly in those soils where the Al-organic matter interaction may be important (31). Overliming (to pH > 5.5) should be avoided and regarded as a waste of economic and natural resources.

Although these liming approaches eliminate the direct toxic effects of Al acidity on plants and minimize precipitation reactions with applied P from fertilizer materials, they do not completely resolve the issue of deleterious Al-P interactions. Addition of lime to soils containing appreciable amounts of  $Al^{3+}$  initiates a series of reactions similar to those discussed previously in the consideration of the aqueous chemistry of Al. As pH increases, amorphous Al-OH polymers are precipitated as continuous layers or discontinuous islands on the surfaces and interlayers of clay minerals. Complexation with soil organic matter may occur as well (1). These polymerized Al-OH species act as a sink for anion adsorption, particularly chemical adsorption of soluble P. The (Al-OH)-P interaction does not follow solublility product principles, rather it must be viewed as an adsorption reaction and characterized thermodynamically as such. As a result of this continued reaction between Al-OH and P, even under conditions of adequate lime to neutralize Al toxicity, research is needed to develop soil fertility programs that will optimize P fertilization in acid, aluminous soils.

As noted earlier, research is in progress at numerous locations in an attempt to further understanding of the nature of the P adsorption process in agricultural soils where Al-OH polymers are a significant factor in immobilization of applied P. Taylor and Ellis (78) , utilizing an anion exchange resin, investigated the mechanism of P adsorption at equilibrium P concentrations low enough to insure that precipitation was unlikely to occur. Their results indicate the existence of "one-point" and "two-point" attachment processes by which P could be bound to anion exchange sites. Two-point attachment is seen as coordination of two O atoms in a  $HPO_4^{2-}$  molecule to two positive sites on the exchange surface. Bonding of this type would be expected to be quite stable as the distance between the two oxygen atoms (2.85 to 3.20 angstroms) is very close to the distance between two Al atoms on the edge face of a kaolinite crystal. Although H<sub>2</sub>PO<sub>4</sub> ions may exist in solution during the initial phase of adsorption, deprotonation occurs to produce  $HPO_4^{2-}$  and adsorption through two-point attachment. Adsorption of  $H_2PO_4^-$  (one point attachment) occurs after steric accommodation of  $HPO_4^{2-}$  ions is essentially complete and dominates the latter phase of the adsorption process. Research has been conducted by Robarge and Corey (68) using a cation exchange resin to hold positively charged Al-OH polymers during adsorption of P. Data from their work support the contention of Hsu (27) that P is chemisorbed onto the Al-OH species and in addition show that the adsorption capacity of the polymer for P is saturated at a Al/P ratio of 2:1. At higher P levels in solution it is probable that the solubility product of some aluminum phosphate compound is exceeded and precipitation reactions occur. Hsu (25, 26, 27, 28) has been involved in some of the most valuable research in this area, investigating P adsorption in acid soils, and crystalline and amorphous Al-OH species. According to Hsu, availability of adsorbed phosphate is related to surface reactivity of amorphous A1-OH. Hsu postulates that P will not be available for plant uptake until near total saturation of the adsorbent surface has occurred and that precipitation reactions between Al and P will not occur at pH values greater than 5.0 due to the paucity of Al ions in solution. Ryden et al. (70) examined P sorption on allophanic soils of New Zealand and determined that the overall sorption process could be divided into three regions, each of which could be characterized by a distinct Langmuir isotherm. Regions I and II were dominated by chemisorption, with  $-OH_2^+$  and OH undergoing ligand exchange with H<sub>2</sub>PO<sub>4</sub>. In Region III, "more physical sorption" was the

dominant process with P retained as a potential-determining ion outward of the plane of chemisorbed P. Later work by these researchers (71) identified the "more physically sorbed " P with the labile P pool in soils due to the ease of desorption, dependence on ionic strength and isotopic exchangeability of this form of sorbed P. Parfitt (57), compared the adsorption process for P on an oxisol with results from model systems and concluded that P reacted with exposed A1(OH)H<sub>2</sub>O on kaolinite edges and Al-OH species to form a binuclear or bidentate P complex. At higher solution concentrations Parfitt postulated that new adsorption sites could be created by the adsorption process itself by disruption of the 001 face on gibbsite or by adsorption of a second P layer on edge sites. Van Riemsdijk and Lyklema (80), working with P adsorption by gibbsite under conditions of constant P supersaturation, found that P can sorb in excess of the maximum monolayer exchange capacity. Concomitant with this excess sorption they noted an increase in total surface area and the formation of a surface coating on the gibbsite particles. The authors reasoned that although the P uptake had some characteristics of simple adsorption, it was in fact precipitation, quite probably of potassium aluminum phosphate. The possible implications of interaction between Al-OH compounds and soil organic matter (OM) has been investigated by Bloom (6). Utilizing an Al substituted peat he found numerous similarities between P adsorption and precipitation in Al-peat and in acid soils. Results from his research indicate that precipitation of amorphous AlH2PO4(OH)2 and the formation of Al-peat-phosphate complexes are likely to be important in removal of P from the soil solution.

Langmuir isotherms have been used by many authors to characterize P adsorption in acid soils. Olsen and Watanabe (56), in some of the earlier research with this approach, pointed out that the main advantage of Langmuir technique is the ability to calculate k (bonding strength) and b (adsorption maxima) values that may be used to compare sorption between soils. Their research identified two phases of P adsorption, a rapid initial reaction due to exchange of  $H_2PO_4^-$  for OH on the surface of soil particles, and a slow second reaction due to the gradual increase in crystal growth of precipitated aluminum phosphates. The initial reaction was defined as chemical adsorption involving primary valence bonds, the extent of this reaction being represented by the Langmuir b value. Woodruff and Kamprath (81) related plant dry weight to the adsorption maximum, b, under different liming conditions. They found liming reduced b for all soils with those soils having the greatest saturation of exchangeable Al showing the greatest decline. In terms of P supply to the plant, it was found that soils with higher b values were able to supply sufficient P for growth at lower saturation of the adsorption maximum than soils with low b values. Fox and Kamprath (12) evaluated the validity of using P sorption isotherms to determine P fertilizer requirements for soils of varying mineralogy, texture and fertilization history. They concluded that this method provided information on P capacity and intensity factors, an approach more closely related to plant needs than the study of the solubility of P compounds in the soil. Additionally, they suggested that the concentration of P in solution is the overriding factor in P nutrition for crops because of its relation to concentration gradients responsible

for the movement of P to plant roots. Rajan and Fox (63) used Langmuir isotherms to separate P sorption in Hawaiian and Indian soils into two regions, similar to the approach of Olsen and Watanabe (56). Adsorption in Region I was dominated by high energy sites and accompanied by pH increases suggesting replacement of OH groups. In Region II low energy sites were dominant and sorption was thought to occur by P competition for OH groups linking Al atoms (ol groups), resulting in disruption of the oxide structure and creation of new adsorption sites. Ellis (9) utilized 35 soil profiles from Michigan and South Africa to evaluate differences in Langmuir k and b constants associated with clay and sesquioxide content. Soils with higher k and b values were those containing the greatest percentage of clay and Al and Fe hydroxides. He also emphasized the value of the Langmuir approach in predicting the amount of P that must be applied to the soil to maintain the concentration of P in solution at a level optimum for plant growth. Ellis also pointed out that as the adsorption maxima became progressively more saturated by P, the intensity of binding decreased and P became more available for crop uptake and leaching. Gebhardt and Coleman (16) using allophanic tropical soils, postulated three separate reaction mechanisms to explain P retention. Under low pH (2.3 to 3.0), high P conditions, precipitation was likely as the solubility product of variscite-like compounds was exceeded. At higher pH values specific, inner sphere adsorption of  $H_2PO_4^-$  on protonated surfaces can occur, with the P adsorbed tightly bound, but still able to be released by reaction of the soil with other specifically adsorbed anions. Finally, co-adsorption of P with sodium (Na) through either: (i) specific

adsorption on a non-protonated surface through donation of a proton of the adsorbed H2PO4 anion or (ii) OH displacement by H2PO4, with co-adsorption of Na to maintain electroneutrality. Munns and Fox (48) researched the slow reaction that continued after P adsorption on tropical soils. Based on their results they maintained that the major agronomic significance of this slow reaction was that the equilibrium attained in the soil may be more influential than the rate at which it was attained. Specifically, the equilibrium condition, modified to account for crop removal and other losses, could become the most useful index of P fertility. Equilibrium isotherms used to evaluate this parameter would not be rapid soil tests (minimum six days shaking time), but could be used as background information to supplement short-term isotherms. The interaction between lime induced pH changes and P adsorption by highly weathered acid soils has also received considerable research. Smyth and Sanchez (75) noted that in soils with pH dependent surface charge, liming or P fertilization increased the negative charge character of soil colloids. This could reduce cation leaching, but may increase anion movement due to decreases in soil positive charge. They also cited contradictory literature showing decreases (55, 57) and increases (2) in P sorption as pH increased. Common mechanisms for decreased sorption include: (i) increased competition of OH with H<sub>2</sub>PO<sub>4</sub>for specific adsorption sites on mineral surfaces, (ii) increased anion repulsion due to the previously mentioned increase in negative charge. Increases in P sorption as pH increased were associated with reactions of added P with freshly precipitated Al and Fe hydroxides. Mokwunye (47) studied the influence of pH on P sorption in African soils and

maintained that as pH was increased from 3 to 7 sorption also increased, but that from pH 7 to 9 sorption was constant. He speculated that the primary factor governing P sorption in these soils was the activity of amorphous Al-OH which increased beyond pH 5. The mechanism involved in this phenomenon was the existence of weakly held OH groups on the edge of Al-OH polymers that were involved in ligand exchange with  $H_2PO_4^{-}$ . Research by Friesen et al. (14) on Nigerian Ultisols supports this concept. Their data show that a decline in soil solution P associated with liming was due to the formation of additional reactive surfaces upon precipitation of Al-OH. However, desorption of P was found to increase on soils receiving high P and high lime treatments, indicating a weaker bonding energy of adsorbed P in limed soils.

Exhaustive experimentation has also been conducted in the agronomic aspect of Al-P interaction in soils. Research of this type generally centers around crop response to P in aluminous soils that have been adjusted to various pH values by addition of lime. Sumner (77), working with two highly weathered acid oxisols and a factorial combination of lime and P found that freshly precipitated Al-OH represented a highly effective and extensive surface for P adsorption. Yield depressions were noted at high lime levels and attributed to a reduction in availability of P due to the presence of the amorphous Al-OH surface and to a decrease in P solubility at higher pH values. Earlier work by Reeve and Sumner (64) confirmed that while liming tended to reduce precipitation of P by exchangeable Al, chemisorption by Al-OH precipitated on sesquioxide surfaces was still a major factor in reduced P availability. Mendez and Kamprath (45) attributed improvements in plant growth upon liming to neutralization of the toxic effects of exchangeable Al and not to improved P solubility in the soil. Again, higher P adsorption capacities in these soils were associated with the presence of amorphous Al-OH compounds. Further refutation of the concept that liming increases P availability in acid soils comes from Amarasiri and Olsen (2). Data from their work attributes inactivation of P to freshly precipitated Al-OH that may either adsorb or physically occlude applied P. Precipitation of P by soluble  $Al^{3+}$  is thought to occur but at much slower rates than the adsorption/occlusion process. Yost et al. (83) conducted research on P response by corn on acid soils from the Cerrado region of central Brazil. The emphasis in their experimentation was the effect of rate and placement of P on P availability for the crop. For the initial crop, broadcast applications gave highest yields primarily due to a more uniform distribution of P in the soil which promoted even distribution of roots and greater use of available soil water. Subsequent crops, however, yielded better under band fertilization, implying that losses of P from the system were balanced best by repeated localized fertilizer applications. Overall, the authors felt the best P fertility program involved a combination of an initial broadcast treatment, followed by periodic banding to maintain adequate P in the soil solution. Later work by these same authors (82) on the residual value of P applications in the same soil found considerable residual value of banded P in terms of plant availability than where the same quantity of P was mixed with a greater volume of the same soil (broadcast). These authors also stated that declines in soil test P with time were best described by logarithmic functions and that

the fact that  $NH_4F$  extractable P declined faster than NaOH extractable suggested a conversion of applied P to less soluble Fe phosphates. Ayodele and Agboola (4) also examined the residual value of P fertilizers, using Alfisols, Ultisols and Oxisols of western Nigeria. They developed the concept of fractional recovery (FR) of applied P and attempted to evaluate how FR changed with time as a function of several soil parameters. The influence of clay and organic matter on FR became less significant with time, while that of Fe and Al oxides increased suggesting a predominance of precipitation (or adsorption) in P fixation. Their data strongly support the concept that the residual value of applied P in tropical soils may be of considerable agronomic importance and that generalizations about P fixation by tropical soils may often be invalid. Kamprath (34) also reached this conclusion in an experiment that evaluated the residual value of high P rates on soils known to fix large quantities of P. A marked residual effect of P applied 7-9 years before was noted for corn, indicating that added P is not irreversibly lost. For lower initial P applications a maintenance rate of 22 pounds per acre, banded, was found to be adequate for high corn yields. Soybean response to liming on Brazilian oxisols was investigated by Martini et al. (44). They cited numerous reasons for avoiding liming tropical soils to near neutrality, among them: (i) an economic and resource waste, (ii) problems with nutrient leaching, fixation and imbalance, (iii) rapid organic matter decomposition, (iv) a degradation of soil aggregates, and (v) an increased incidence of soil borne diseases. Their research data confirms the fact that the quantity of lime required to neutralize exchangeable Al was adequate for optimum crop growth and that, while no detrimental effects on yield were noted due to overliming, there was no significant increase in yield beyond pH 5.5.

Toxic effects of soluble Al on plant roots have been noted in very acid soils (pH < 5.0). It is also possible that precipitation of P by Al $^{3+}$  within plant roots may be a contributing factor in reduced plant growth under these conditions (40). Gonzalez-Erico et al. (17) investigated the effect of Al on root growth in an Oxisol from central Brazil. Roots in nonlimed zones were thickened, poorly branched, and suberized, typical symptoms of Al damage. Their data show that liming reduced Al saturation and solution Al and that root proliferation and soil water utilization increased markedly, particularly when subsoil liming was conducted. Friesen et al. (15) found that liming an acid Ultisol promoted profuse growth of very fine second and third order lateral roots and resulted in a doubling of root length. The positive effects of lime and P noted in this study were attributed to increased exploitation of soil and fertilizer P as a result of improved root growth. The authors concluded that overall, elimination of the toxic effects of Al on crop growth should be the major goal of liming in these highly weathered soils.

Identification of specific aspects of the Al-P interaction that require further research should center on application of the principles developed in pure systems to agronomic situations. With this attitude in mind, a dual-focused research project was developed. The agronomic phase involved evaluation of P adsorption and availability for plant uptake following the application of lime to a highly weathered, acid,

aluminous soil. Concurrently, an effort was made to ascertain the effect of aging and pH of precipitation on P adsorption by Al-OH gel suspensions. Alterations in the chemical and physical nature of Al-OH due to these treatment factors are quite readily related to liming practices used in acid agricultural soils. The rate of lime applied will influence the pH at which amorphous Al-OH precipitates and consequently, the nature of the compound that develops. The time of lime application relates the age of the precipitate to its reactivity for applied P. It may be advisable to delay fertilization with soluble P sources until polymerization of Al-OH species has reduced their surface reactivity. Data generated from these studies should provide information of practical and theoretical value that can be applied to management programs for acid soils requiring P fertilization. Additionally, this research will serve as a framework for continued experimentation as to how the role of Al-OH compounds can be minimized in terms of immobilization of P necessary for satisfactory crop growth.

Soil chemistry seeks to combine the theoretical and the practical to resolve difficulties in agriculutral productivity. Research of the type discussed in this dissertation illustrates the necessity of understanding the chemistry of the soil solution as a prerequisite to maximizing crop yield, the ultimate aim of agronomic professionals.

#### CHAPTER II

## ADSORPTION AND AVAILABILITY OF PHOSPHORUS FOLLOWING THE APPLICATION OF LIMESTONE TO AN ACID, ALUMINOUS SOIL

Introduction and Literature Review

Fixation of phosphorus (P) by soil aluminum (A1) seriously limits the attainment of maximum yields in areas dominated by highly weathered, acid, aluminous soils. Although the precise mechanism involved in P fixation is disputed, it seems clear that adsorption by aluminum hydroxides (A1-OH) is a major factor in reduced P availability for crop uptake, particularly when these soils are limed to greater than pH 5.0. Since application of limestone to neutralize excessive acidity and to reduce associated  $A1^{3+}$  toxicity is essential to improve crop growth on soils of this type, the lime-Al-P interaction is an area that has received considerable research interest. Liming approaches have varied (3, 10, 31, 33, 65, 73), but recent research suggests that application of sufficient lime to neutralize the toxic effect of  $A1^{3+}$  is the most efficient and economical approach. Limestone applications that increase soil pH beyond 5.5 have been associated with yield decreases and liming these acid, aluminous soils to near neutrality (pH 6.5 to 7.0) should be viewed as overliming and as a practice to be avoided (32, 36, 39, 59, 77) . Martini et al. (44), citing such factors as nutrient imbalances,
leaching and fixation, as well as increased organic matter decomposition, soil aggregate degradation and incidence of soil borne diseases, cautioned against liming Oxisols beyond pH 5.7. Farina et al. (11), raised serious questions about the concept of maximized nutrient availability at pH values near neutrality. Their results and those of others (2, 13, 38) plainly indicate that fertility programs adapted for highly weathered soils should be based on a minimal liming approach, with elimination of the inhibitory effects of toxic Al<sup>3+</sup> on plant growth the major objective. Additional lime applications can be economic and resource wastes and may in fact reduce yields.

Maximum crop yields require optimization of the plant's P nutritional status, hence the effect of different liming practices on P sorption by soil components and subsequent availability for the plant is of critical importance. Reeve and Sumner (64), in research with South African Oxisols, found that the elimination of the direct toxic effects of  $A1^{3+}$  by liming did not alleviate the fixation of P. They attributed the inability of lime to improve P availability to chemisorption of P on sesquioxide surfaces that quite probably were produced by the reaction of  $Al^{3+}$  with lime, which then resulted in the formation of amorphous Al-OH. Ellis (9) evaluated P adsorption in 35 soil profiles of Michigan and South Africa and determined that the accumulation of exchangeable Al and amorphous Fe and Al oxides was the dominant factor involved in P fixation. Numerous other authors have elucidated the importance of Al-OH precipitated upon liming these soils on P availability for crop uptake (2, 16, 45, 55, 57, 63, 75). Additionally, the effects of soil pH (45, 47, 48, 81), organic matter

(6) and ionic strength (70), lime and fertilization placement practices (17, 34, 75, 82, 83) and crop type (58) on the availability of P have been examined and related to yield.

Despite the varied and intensive nature of the research effort, questions still remain. In particular, will the reactions of precipitated A1-OH with P remain constant with time or will changes associated with aging of these compounds alter their reactivity for applied P? The development of liming and fertility programs that will maximize P availability for crop use requires an answer. The timing of limestone application may have considerable influence on the availability of added P due to changes upon aging in the chemical reactivity of A1-OH precipitated by liming. Interactions between lime rate, P adsorption, and time must be evaluated as well. The objective of this study was to characterize changes noted with time on the adsorption and availability of P under two liming systems commonly used in areas where acid, aluminous soils predominate.

### Materials and Methods

Surface (0-15 cm) and subsurface (15-30 cm) samples of a Tatum soil, a clayey, mixed thermic, typic Hapludult were used in this study. Selected characteristics of the soil are summarized in Table 1.

Initially, an incubation study was conducted for eight months using a 3 x 2 (lime rate x incubation environment) factorial combination of treatments arranged in a completely randomized design with two replications. At the conclusion of the incubation study three P rates were superimposed on the initial treatment combinations producing a 3 x 2 x 3 factorial split plot design that was subsequently utilized in a greenhouse bioassay for P uptake. Statistical analyses of data from these two experiments included analysis of variance and determination of least significant difference (l.s.d.) values. Three lime rates were selected: no lime (0), lime sufficient to neutralize exchangeable Al as determined by extraction with IN KCl (KCl), and lime to produce a soil pH of 6.8 as determined by the Shoemaker-McLean-Pratt buffer test (SMP) (73) (Table 2). Incorporation of lime involved mixing 2000 grams of air dry soil with appropriate quantities of reagent grade CaCO3 in a V-mixer. Soils were incubated at constant field moisture capacity (FMC) (Environment 1) and at FMC combined with air drying at two week intervals, followed by rewetting to FMC (Environment 2). Soil moisture content at one-third bar tension as determined by the pressure plate

Depth	Texture	рН <sub>₩</sub> +	рН <sub>8</sub> +	CEC	Exch Al	Al Sat.	Bray Pl
CM				me	q/100g	%	mgP/kg
0-15	cl	4.4	3.3	6.4	4.8	78.2	0.3
15-30	с	4.8	3.5	6.4	5.8	79.1	0.2

Table 1. Selected characteristics of the Tatum soil.\*

Table 2. Treatment combinations utilized during the incubation and greenhouse studies.

Depth	Lime	Environment	Sample Date	Phosphorus
-cm-	-mt/ha-		months	mg P/kg
0				
0-15	0	1) Moist Incubation	One	0
15-30	0	(FMC)		75
				150
<u>KC1</u>				
0-15 15-30	5.4 6.5			
		2) Moist Incubation	Eight	0
SMP		(FMC) +		150
0-15 15-30	17.2 19.0	14 Air Dry Cycles		300

method was selected to approximate FMC. Surface and subsurface soil samples each received all treatment combinations producing a total of 24 experimental units: 2 soil horizons x 3 lime rates x 2 incubation environments x 2 replications.

Immediately following treatment application the soil was placed in plastic containers and brought to FMC with distilled, de-ionized water. All containers were then sealed in polyethylene bags to minimize evaporative water loss and arranged in a completely randomized design in a constant temperature chamber at 27C. Weekly checks were made to ensure that the soils remained between 90 to 100% of FMC throughout incubation.

Soil samples (200 g) were taken at one and eight months following initiation of incubation. Measurements of soil acidity included pH in water, pH in 1N KC1, and exchangeable acidity as determined by titration of a 1N KC1 soil extract with standardized NaOH. Soil to solution ratios for acidity measurements were 1:1, 1:2.5, and 1:5, respectively. Soils were also extracted at a soil to solution ratio of 1:5 with 1N NH4OAc (pH 4.8) and 1N KC1 for determination of A1 by the aluminon method (42). Phosphorus was extracted from the soil with a solution of .03N NH4F + .025N HC1 (Bray P1) and determined analytically by the method of Murphy and Riley (49) modified for use with a Technicon Auto Analyzer II. Exchangeable bases (Ca, Mg, and K) were extracted with 1N NH4OAc (pH 7.0) using a soil:solution ratio of 1:10. Calcium and Mg were then determined by atomic absorption spectrophotometry and K was measured by flame emission.

Phosphorus adsorption isotherms were conducted initially and at both sample dates. Two gram soil samples from each treatment combination

were shaken for 24 hours with 50 ml of six solutions of appropriate P concentrations. Phosphorus solutions were prepared by dilution of a  $1000 \text{ mg} \cdot 1^{-1}$  P (as K<sub>2</sub>HPO<sub>4</sub>) stock solution in .01M CaCl<sub>2</sub>. After shaking, pH of all samples was measured, soil suspensions were filtered through number 2 Whatman paper and P determined on the Technicon Auto Analyzer II.

Following the conclusion of the incubation phase of the study a greenhouse bioassy (method of Stanford and Dement (76)) was begun to ascertain the effect of incubation on the availability for crop uptake of applied P. Air dry soil from each experimental unit was subdivided into three 240 gram split plot experimental units, each receiving in solution form a designated quantity of P as  $Ca(H_2PO_4)_2$ . After incorporation of the  $Ca(H_2PO_4)_2$  solutions a 40 g subsample was removed from each split plot unit and placed in separate containers to be used in characterization of the soil at the beginning of the bioassay. All split plot experimental units as well as the 40 g subsamples, were placed in sixteen ounce plastic cottage cheese cups, watered to FMC, sealed in zip-loc bags and incubated for two weeks at 27C.

Initiation of crop growth began while the soils were undergoing incubation. This process involved removing the bottom from 72 plastic cups identical to those containing the soil samples and inserting each cup into another intact cup. Five hundred grams of silica sand were then weighed into these cups and 40 oat seeds (<u>Avena Sativa</u>, L., cv. Korwood) were spread evenly on the surface and covered with another 160 g of silica sand. Fifty ml of Hoaglands minus-P nutrient solution (23) and 40 ml of distilled water were then added and arranged in a completely randomized design in the greenhouse. During the next two

weeks distilled water or Hoaglands solution were added as necessary to maintain sufficient available nutrients and the initial moisture content of the sand. Seventeen days after seeding, the oats were approximately 20 cm in height and had developed an extensive root system. At this point the bottom, intact cups were removed and the inner cups with their exposed root mats were placed into the cup containing the incubated soils. To determine the background levels of nutrients in plant tissue, control cups were included that consisted of a rooting zone composed entirely of silica sand. Aerial portions of the oats were harvested at 39 days after seeding (22 days after contact with the incubated soil), and plant tissue oven dried at 55C for 3 days. Tissue samples were weighed and ground in a stainless steel Wylie mill with a 40 mesh screen. One gram tissue samples were digested for elemental analysis using a 4:1 HNO3:HClO4 acid mixture. Phosphorus in the tissue digest was measured on the Technicon Auto Analyzer II. Calcium and Mg were determined using atomic absorption spectrophotometry and K by flame emission.

Characterization of the soils at the initiation of the greenhouse bioassay was done utilizing the previously mentioned 40 gram subsamples. Phosphorus was assessed by three methods, extraction with (1) pH 8.5, .05 M NaHCO<sub>3</sub> (Olsen), (2) .03N NH<sub>4</sub>F + .025N HCl (Bray) and (3) .025N  $H_2SO_4$  + .05N HCl (double acid) using soil to solution ratios of 1:25, 1:4 and 1:4, respectively. The concentration of P in all soil extracts was determined as described previously.

Certain analyses were performed solely for the purpose of initial characterization of the surface and subsurface samples. Cation exchange capacity was determined at a soil to solution ratio of 1:5 by four

sequential extractions with  $1N \ NH_4OAc$  (pH 7.0), followed by washing with a mixture of water and ethanol to remove excess  $NH_4^+$  and by one extraction with  $1N \ NH_4C1$  (pH 7.0). Ammonium was then determined on the filtered extract by use of a Technicon Auto Analyzer II. Organic matter was measured by use of a Leco Model 750-100 Carbon Analyzer and texture determined by the hydrometer method (8).

## Results and Discussion

Initial characterization (Table 1) of the soil used in this study confirms its suitability for research on lime induced changes in P adsorption. The Tatum soil is a highly weathered, acid, aluminous Ultisol, with a low native P content. Exchangeable Al values for this soil are higher than reported in many cases for Oxisols of the humid tropics where Al is often a serious soil fertility problem. The Al saturation values noted are in the yield limiting range outlined by Evans and Kamprath (18), and indicate a positive response to lime should be expected.

The KCl lime rate was approximately 82% efficient in eliminating exchangeable Al and achieved a 66% reduction in extractable Al (Table 3). Liming on the basis of the SMP buffer totally eliminated exchangeable Al, but reduced extractable Al by only 78%, an almost insignificant gain over the KCl rate, particularly when the fact that over 3 times as much lime was applied is considered. Several other pertinent conclusions can be drawn based on the Al data. The decrease in exchangeable and extractable Al seen with time and the imposition of wet/dry cycles during incubation (Environment 2) suggests that changes occurring due to these treatment factors reduce the solubility of soil Al. Although the criteria of statistical significance is not met for

Depth	Sample Da	te <u>Env</u>	vironment	: 1	<del>,</del>	Environmen	t 2
		0	KC1	SMP	0	KC1	SMP
-cm-	Months		Ext	ractable	Al (meq	/100g)	
0-15	1	3.40	1.11	•72	3.05	1.03	•68
	8	2.71	1.11	•40	2.57	•95	• 37
15-30	1	5.00	1.76	1.63	4.99	1.61	1.56
	8	4.75	1.49	1.61	4.48	1.33	1.50
			Exc	hangeabl	e Al (me	q/100g)	
0-15	1	4.24	.53	0	3.92	•51	0
	8	3.98	•83	0	3.36	.95	0
15-30	1	5.93	1.09	0	5.83	.96	0
	8	5.27	•86	0	4.88	.80	0
				Al Satur	ation (%	<u>)</u>	
0-15	1	75.7	9.7	0	74.0	9.8	0
	8	74.6	14.5	0	66.7	17.2	0
15-30	1	79.4	14.3	0	78.1	12.1	0
	8	73.3	11.2	0	72.1	10.4	0
Extracta	able Al :	L.S.D. (Rov L.S.D. (Col	vs) = lumns) =	.25 (0-1 .09 (0-1	5); .15 5); .15	(15-30). (15-30).	
Exchange	eable Al:	L.S.D. (Row L.S.D. (Col	vs) = lumns) =	•31 (0-1 •05 (0-1	5); .18 5); .08	(15-30). (15-30).	
Al Satu	ration :	L.S.D. (Row L.S.D. (Col	vs) = lumns) =	3.1 (0-1 0.4 (0-1	5); 1.2 5); 0.6	(15-30). (15-30).	

Table 3. The effect of lime rate, length of incubation and environment on extractable (pH 4.8, 1N NH4Oac) and exchangeable (1N KC1) Al and per cent Al saturation in a Tatum soil.

every comparison, this seems to be a case when a consistent trend exists that may offer insight into changes in the nature of Al compounds in the soil. Ammonium acetate (pH 4.8, 1N) has been shown to dissolve A1-OH from soils that have been recently limed (62). It is quite probable that a similar reaction occurs with IN KC1 given the pH which this extractant induces in the soil (Table 4). Aging of freshly precipitated, amorphous Al-OH is known to result in polymerization and eventual crystallization that make the Al ions involved difficultly extractable. Amedee and Peech (3) have shown that freshly precipitated A1(0H)3 is readily soluble in IN KCl and that the lower the pH of the KCl, the greater the solubility. Their results also indicated that gibbsite, the end product of Al-OH polymerization, was virtually insoluble in IN KCl, providing support for the concept of reduced Al extractability as A1-OH ages. Given this set of circumstances, it is not unrealistic to assume that either aging of Al-OH polymers in the soil, or changes induced by the stress of wetting and drying may reduce the activity of Al in the soil solution.

The Al saturation data (Table 3) points out the value of lime in reducing the dominance of  $Al^{3+}$  in the cation suite. Additionally, it indicates that the much more economically efficient KCl lime rate will produce a base saturation level quite satisfactory for crop growth (approximately 80% Ca + Mg + K) (1).

Soil pH values (Table 4) correspond quite well with those cited by Kamprath (33) for liming to neutralize KCl exchangeable Al, but indicate that use of the SMP buffer produces a pH regime that can only be defined

Depth	Sample Date	Envi	ronmen	<u>t 1</u>	Env	ironmen	t 2
		0	KC1	SMP	0	KC1	SMP
-cm-	Months			<u>р</u> Н (Н	20)		
0-15	1	4.57	5.57	7.53	4.58	5.55	7.63
	8	4.51	4.99	7.47	4.51	4.75	7.62
15-30	1	<b>4.9</b> 0	5.67	7.45	4.85	5.65	7.57
	8	4.97	5.59	7.97	4.85	5.55	7.93
				<u>рН (1</u>	<u>N KC1)</u>		
0-15	1	3.33	3.86	6.63	3.33	<b>3.9</b> 0	6.73
	8	3.41	3.74	6.74	3.37	3.61	6.76
15-30	1	3.49	3.87	6.28	3.47	3.87	6.43
	8	3.52	3.88	7.02	3.50	3.88	6.97
рн (н <sub>2</sub> 0)	) : L.S.D. L.S.D.	(Rows) (Columns)	= .15 = .06	(0-15); (0-15);	.09 (15-30). .04 (15-30).		
рН (1N )	KC1): L.S.D. L.S.D.	(Rows) (Columns)	= .05 = .02	(0-15); (0-15);	.04 (15-30). .12 (15-30).		

Table 4. The effect of lime rate, length of incubation and environment on pH ( $H_2O$ ) and pH (IN KC1) in a Tatum soil.

as overlimed. The use of reagent grade CaCO3, which will react more extensively than agricultural limestone, may explain the high pH values noted for this treatment. It also indicates, as noted by Kamprath (33) that perhaps 1.5 times the quantity of exchangeable Al may be the most appropriate lime rate for these acid soils when agricultural limestone is utilized. As mentioned previously, research by several authors has confirmed the inadvisability of liming highly weathered soils to a pH beyond 5.5. The pH results obtained in this study strengthen the value of 1N KC1 as a lime requirement index, if only in terms of producing a suitable soil pH for crop growth.

The exchangeable base status of the soil was altered markedly by addition of lime (Table 5). Exchangeable Ca values obtained at the KCl lime rate are adequate from a plant nutrition standpoint, but those observed for the high lime treatment may produce nutrient imbalances (Ca/K, Ca/Mg) described by some authors (2, 10, 32). This becomes especially evident when the exchangeable Mg data are considered. Increasing soil pH to approximately 5.5 by the KCl lime rate effects a 25% reduction in exchangeable Mg, but the SMP approach virtually eliminates exchangeable Mg in the soil. Grove et al. (19) observed a similar phenomenon with acid soils of Georgia and South Africa. They attributed this Mg-fixation to the adsorption and possible solid diffusion of soluble Mg into newly precipitated and amorphous Al-OH polymers created upon liming acid soils. Regardless of the precise mechanism involved, Mg availability and uptake will be seriously limited under overlimed conditions which will adversely affect plant growth and

Dej	pth	Sample Date	Env	ironment	1		Environmen	t 2
			0	KC1	SMP	0	KC1	SMP
-ci	<b>n</b>	Months			me	q/100g	یہ جو حوال جار جہ چہ جو حو حو	, ang ang ang ang ang
					Ca			
0-	-15	1	•26	4.09	11.31	•30	3.93	11.41
		8	•22	4.02	11.69	• 37	3.75	10.89
15-	-30	1	•21	5.65	12.61	•21	5.70	12.61
		8	.17	5.82	12.49	• 28	5.77	12.13
					Mg			
0-	-15	1	.15	.11	•01	.13	.11	•01
		8	.15	•12	•02	.17	•14	•02
15-	-30	1	•41	•28	•05	•41	•33	.03
		8	•43	•35	.03	•45	• 37	•02
					<u>K</u>			
0-	-15	1	.15	.15	.13	•15	.17	•12
		8	.16	•17	•11	.16	.15	.10
15-	-30	1	.22	•23	.19	•22	•23	.19
<del>6</del>		8	.23	.23	.13	•23	.26	.15
Ca	:	L.S.D. (Rows)	<b>=</b> .65	(0-15);	.56 (15-	30).		
		L.S.D. (Columns)	= .30	(0-15);	.23 (15-	30).		
Mg	:	L.S.D. (Rows) L.S.D. (Columns)	= .02 = .01	(0-15); (0-15);	.03 (15- .01 (15-	30). 30).		
K	:	L.S.D. (Rows) L.S.D. (Columns)	= .02 = .01	(0-15); (0-15);	.02 (15- .01 (15-	30). 30).		

Table 5. The effect of lime rate, length of incubation and environment on exchangeable (pH 7.0, 1N NH40ac) Ca, Mg, and K in a Tatum soil.

Depth	Sample Date	Envir	Environment 1			Environment 2		
		0	KC1	SMP	0	KC1	SMP	
-cm-	Months			<b>n</b>	ng/kg			
0-15	1	•25	.21	•06	•26	.15	•31	
	8	.28	•54	.82	• 55	1.00	1.06	
15-30	1	•11	.10	•0 <b>9</b>	•15	.11	.13	
	8	•02	•02	.01	•04	•04	•04	
TCD	(Powe) = 60	(0-15)	08 (1	5-30)				

Table 6. The effect of lime rate, length of incubation and environment on Bray (.03N  $NH_4F$  + .025 N HC1) extractable P a Tatum soil.

L.S.D. (Rows) = .60 (0-15); .08 (15-30). L.S.D. (Columns) = .21 (0-15); .03 (15-30).

metabolism. Though not as striking, the exchangeable K data indicate a similar loss of K when the soil was overlimed. The implications of distorted Ca/Mg and Ca/K ratios in the soil are significant and suggest another reason to avoid excessive liming with soils of this type.

Soil P showed little significant response to lime (Table 6), but the increase in Bray P noted between the one and eight month sample dates in the surface horizon is of some importance. When combined with the decreases noted in exchangeable and extractable Al, it appears that the native P in the soil may become more available as the surfaces responsible for P fixation (Al-OH polymers) age. This is supported by research in pure Al-OH systems which shows a decrease in P sorption capacity of Al-OH with time (Sims, Chapter II, this dissertation).

Results of the adsorption studies (Table 7) are useful in interpreting changes in the ability of the Tatum soil to fix P. The Langmuir k (bonding energy) constant was seen to decrease with lime rate and time after lime application. The response to lime rate may be explained by the development of pH dependent negative charge as soil pH increased from 4.5 to 7.5. Anion repulsion by the negatively charged surfaces in the soil would be enhanced under these conditions, thus contributing to the lower k values observed. Smyth and Sanchez (75) measured surface charge in a Brazilian Oxisol under varying lime rates and found significant increases in negative soil charge and decreases in positive soil charge as pH increased. These authors also speculated that at higher pH increased OH competition with P ions for specific adsorption sites may occur which could also be involved in the decreased

Depth	Sample Date	Env	lronment	1	En	vironment	2
		0	KC1	SMP	0	KC1	SMP
-cm-	Months		<u>k</u>	(1 mol-1	x 104)		
0-15	1	22.7	22.8	18.2	25.1	21.0	14.6
	8	15.1	14.9	7.7	15.4	13.7	7.8
15-30	1	21.1	31.1	11.3	24.2	18.1	7.7
	8	18.3	6.5	4.7	17.0	6.7	3.9
				b (mg	/100g)		
0-15	1	36.4	19.6	21.3	35.2	19.8	20.7
	8	41.6	22.1	23.7	38.4	21.3	20.8
15-30	1	61.6	37.5	47.7	61.1	37.1	50.1
	8	68.3	42.2	54.3	68.4	41.6	55.4

Table 7. The effect of lime rate, length of incubation and environment on Langmuir k and b constants in a Tatum soil.

b : L.S.D. (Rows) = 1.9 (0-15); 4.9 (15-30). L.S.D. (Columns) = 0.5 (0-15); 1.3 (15-30). k values noted. The more marked decline in K values with time (relative to lime rate) supports the earlier contention that aging of adsorbate surfaces reduces their reactivity for P. The fact that the lowest k values seen were those at the high lime rate, eight month sample suggests a complementary effect of negative surface charge and A1-OH polymerization on intensity of P binding by soil components.

Examination of the adsorption maxima (Langmuir b) data may seem somewhat confusing at first, in light of the previous discussion. Liming to neutralize KCl exchangeable Al does produce an approximate 58% reduction in the capacity of the soil to fix P, but the application of more lime (SMP) creates a greater sink for P, particularly in the subsoil. This can be explained if the exchangeable Al data is reconsidered. At the KCl lime rate all exchangeable Al was not neutralized (Table 2), hence the additional lime supplied by the SMP treatment could have precipitated more amorphous Al-OH which could then provide additional sites for P sorption. The possibility of P adsorption by free CaCO3 that may be present in the overlimed treatment has been discussed by Griffin and Jurinak (18) and may also contribute to the increased b values noted. The seemingly contradictory nature of the b data centers around the increases noted with time. Should the concept of reduced A1-OH reactivity with aging discussed earlier be correct, the adsorption maxima would be expected to decrease between one and eight months. A plausible explanation for the increase observed is that the continued polymerization of Al-OH with time creates a more extensive surface capable of sorbing greater quantities of P. It is also possible that  $A1^{3+}$  released during incubation may form additional

Al-OH surfaces capable of sorbing P or may precipitate added P directly. If this is accepted, it seems obvious that a slight change in the quantity of P sorbed (b) will occur due to aging, but that the loss of reactivity for P postulated will be reflected primarily in a reduction of the intensity of bonding (k). Reduced bonding energies associated with more ordered Al-OH polymers or crystalline Al(OH)<sub>3</sub> may be due to decreased steric accomodation of P anions. "One-point attachment" of  $H_2PO_4^-$  was shown by Taylor and Ellis (78) to attain lower heats of adsorption than two point attachment of  $HPO_4^{2-}$ , and the presence of sterically favorable sites on adsorbate surfaces was cited as a key factor in determining the mode of attachment and hence the bonding intensity.

### Phosphorus Availability and Crop Uptake

At the conclusion of the incubation study, changes in P availability due to the treatment combinations used was evaluated by a crop bioassay technique. Phosphorus uptake data (Table 8) illustrate the validity of the KCl liming approach. Increases in P uptake were seen with P rate, as would be expected, but of greater interest is the response to lime rate. Raising soil pH to approximately 5.5 (KCl) increased P uptake by 32 and 48% in the surface horizon and 56 and 119% in the subsoil for the intermediate and high P rates respectively. No additional increase in P uptake was seen for the SMP rate, despite the application of over 3 times as much lime. This is strong evidence for

Depth	P Rate	En	Environment 1			Environment 2		
		0	KC1	SMP	0	KC1	SMP	
-cm-	mg/kg				mg/pot	یہ جہ وہ جہ میں چہ مو جھ سے تھ س	هی خود خود جو ها هو هو در و	
0-15	0	2.99	2.69	2.94	3.01	3.13	2.57	
	75	4.52	5.96	5.55	4.67	7.02	5.93	
	150	6.49	9.64	9.75	8.34	10.45	9.79	
15-30	0	2.74	3.01	2.87	2.28	2.85	2.84	
	150	5.09	7.95	7.95	3.69	7.27	6.74	
	300	5.65	12.39	12.63	6.53	12.58	11.18	
L.S.D.	(Rows) = 1.33	3 (0-15	); 2.45	(15-30).				

,

Table 8. The influence of lime, incubation environment and P rate on P uptake by oats grown on a Tatum soil.

L.S.D. (Columns)= 0.48 (0-15); 0.89 (15-30).

the economic and agronomic efficiency of minimal liming of highly weathered acid soils.

Simple correlation coefficients were determined between P measured by three common extractants and P tissue concentration, P uptake and plant dry matter yield (Table 9). Although all extractants correlated well with the P parameters, the double acid mixture commonly used in many southeastern states was the least effective, particularly in the subsoil. The excellent results obtained with Olsen's 0.5 M, pH 8.5 NaHCO3 indicate further research with this extractant would be appropriate, even in acid soils of the southeast. This is especially true when the work of Holford (24) is considered. His results indicate that Olsen P extracted quantities of P that correlated well with labile P over a wide range of soil orders. Additionally, his data showed a much better correlation of Olsen P with plant uptake than Bray P or double acid extractable P, and that Olsen P compensates well for the widely different buffering capacities seen in many agricultural soils.

Extractant	P Concentration	P Uptake	Dry Weight
-		r	
Olsen	.921**	•910**	•488 <b>**</b>
Bray	•925 <b>**</b>	<b>。</b> 907**	•431 <sup>*</sup>
Double Acid	•865 <b>**</b>	•829 <b>**</b>	•325
		<u>15-30 cm</u>	
Olsen	<b>.</b> 693**	<b>•694</b> **	•323
Bray	•579**	•582 <b>**</b>	•258
Double Acid	.394*	•389*	.135

Table 9. Simple correlation coefficients between three P extractants and P content in oats, P uptake by oats and plant dry matter yield.

**\*\***Significant at .01 level of probability.

\*Significant at .05 level of probability.

### CHAPTER III

# CHANGES IN PHOSPHORUS ADSORPTION ASSOCIATED WITH AGING OF ALUMINUM HYDROXIDE SUSPENSIONS

Introduction and Literature Review

Aluminum hydroxide (Al-OH) is a term generally used to refer to the reaction products of Al<sup>3+</sup> formed upon addition of a base to the system of interest. Major Al-OH ions in the pH range found in most soils include: Al(OH)  $\cdot$  (H<sub>2</sub>O)<sub>5</sub><sup>2+</sup>, Al(OH)<sub>2</sub>  $\cdot$  (H<sub>2</sub>O)<sub>4</sub><sup>1+</sup>, Al(OH)<sub>3</sub>  $\cdot$  (H<sub>2</sub>O)<sub>3</sub><sup>O</sup> (amorphous or crystalline) and occasionally, at higher pH values Al(OH)<sub>4</sub>  $\cdot$  (H<sub>2</sub>O)<sub>2</sub><sup>1-</sup>. The presence of these forms of Al is common in highly weathered acid soils (Ultisols, Oxisols), particularly those that have been limed to pH 5.0 or more. The importance of Al-OH compounds in P fixation has been cited by numerous investigators (2, 16, 26, 28, 45) with the emphasis, in many cases, on the reactions of amorphous or freshly precipitated Al-OH with added (fertilizer) P. However, understanding the nature and extent of the reactions of all forms of Al-OH with P has important implications for the development of soil fertility programs in soils dominated by Al.

In the case of Al-OH, as in many areas of soil chemistry or fertility, research in pure systems is essential to isolate features of the soil that may be important when considering the soil as a whole.

Hem and Roberson (20) outlined the nature of Al-OH complexes in dilute solution in an extensive review of the chemistry of Al in natural waters. The polymerization model described by these authors is based on a deprotonation-dehydration reaction scheme:

$$2 \text{ A1}(\text{H}_20)_6 = 2 \text{ A1}(\text{H}_20)_5^+ + \text{H}^+$$

$$2 \text{ A1(H}_{2}\text{O})_{5(\text{OH})}^{2+} = \text{A1}_{2}(\text{H}_{2}\text{O})_{8}(\text{OH})_{2}^{4+} + 2 \text{H}_{2}\text{O}$$

Dimerization as described here is followed by development of a polymeric ring with six Al ions bound together by double OH bridges. Enlargement of the polymer with time (aging) occurs by incorporation of nonstructural (edge) OH groups into the polymer as structural OH in the double OH bridge. The nature of the bonding of nonstructural OH is such that it should be replaceable by other anions (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) and be quickly neutralized by H ions. The weaker bonding forces involved with nonstructural OH as opposed to structural OH have significance in terms of P adsorption by the Al-OH polymer. A steady and significant decline in P sorption should be seen during the aging process as nonstructural OH decreases at the expense of structural, bridging OH. The necessity of breaking two OH-Al bonds to effect ligand exchange of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> for a structural OH reduces the likelihood of P sorption under these conditons.

The polymerization process will be affected by factors such as the pH of initial precipitation (21), the type and activity of counteranions present (69, 72) and the ionic strength of the system (5, 68). Hsu (25)

has shown that the conversion of meta-stable A1-OH solutions to crystalline polymorphs of A1(OH)<sub>3</sub> is a function of the OH/A1 ratio at precipitation of the A1 salt. Ratios of 3.05 were associated with rapid formation of bayerite and lower ratios (1.8 to 2.7) caused a gradual development of gibbsite. Nail et al. (50, 51, 52) in a series of papers related the initial structure, aging process and acid reactivity of A1-OH gels to the counteranion present during precipitation (C1) and further elaborated on Hem's model for A1-OH polymer growth.

Adsorption of P by Al-OH has been evaluated in laboratory studies by several authors. Robarge and Corey (68) examined the effect of ionic strength, pH and neutral salt cation on the adsorption of P in an Al-resin system. Results of this study indicated that Al-OH species akin to those in limed acid soils may have a short-term effect on P concentration in the soil solution. However, the instability of these species with respect to gibbsite and other Al minerals over long time periods may alter the initial equilibria attained. Hsu and Rennie (28) postulated that weakly held nonstructural OH groups could be exchanged for H<sub>2</sub>PO<sub>4</sub>, but that the total surface OH available for participation in the reaction may not be constant. The incorporation of edge OH into the larger polymer may be overcome at very high P concentrations, according to these authors and others (57, 63), with disruption of the polymer during the adsorption process resulting in the creation of new sites for further adsorption. Hsu and Rennie also maintained that the primary factor responsible for governing the availability of P in solution was the activity of Al in all its forms, i.e., Al<sup>3+</sup>, polymerized Al-OH and crystalline A1(OH)<sub>3</sub>. Whether the reaction was precipitation of  $H_2PO_4^-$ 

by  $A1^{3+}$  (low pH, high P conditions) or adsorption of  $H_2PO_4^-$  by polymeric Al-OH compounds, P removal from solution is a direct function of total Al activity. Unfortunately, the activity of Al compounds in the soil or in a laboratory suspension is rarely constant, even in a "closed system". The aging/polymerization process alone alters the reactivity of Al-OH for P and must be considered as an underlying process that interacts with externally induced changes in pH, ionic strength or cation/anion composition in solution. Availability of P in the soil solution for crop uptake will thus be affected by alterations in all of these parameters, common occurences in agricultural systems that utilize liming, fertilization and irrigation practices.

The intent of this study was to minimize the number of factors involved that may have affected the reactivity of precipitated Al-OH for P and to simply examine the changes in P sorption associated with aging/polymerization and reduction of ionic strength by dialysis. The only treatment variable introduced was the pH of initial precipitation, with pH values selected to correspond with those found in acid soils limed to: (i) neutralize exchangeable aluminum (pH 5.5) or (ii) "near-neutrality" (pH 7.0).

#### Materials and Methods

Aluminum hydroxide suspensions (gels) were precipitated from a solution of  $.356\underline{M}$  AlCl<sub>3</sub> by addition of 13% (v/v) NH4OH at a rate of 120 ml/min until the pH of the suspension reached 4.0-4.5, then dropwise to the desired pH, (5.5 or 7.0). The system was maintained at this pH with continuous stirring for 30 minutes. Following precipitation, the gels were filtered under suction through number 4 Whatman filter paper, resuspended in distilled water and filtered again in the same manner. Filtration was designed to remove excess NH<sub>4</sub>Cl from the system that could inhibit Al-OH polymerization. After completion of the filtration process, gels were suspended in distilled water at a 1:3 gel to water ratio, and placed in a constant temperature chamber at 27C.

Physical and chemical characterization of the gels was done initially and after one, three, six and twelve months of incubation. Additionally, dialysis of gels against distilled water was conducted following initial precipitation and at the one month sample date, with dialyzed gels subjected to all analyses as non-dialyzed. The dialysis process involved pipetting a 50 ml aliquot of gel suspension into 3.33 cm Fisher Dialyzer Tubing and immersing the tubing in 1750 ml of distilled water for three days with daily changing of the water.

Physical characterization of the gels included the use of x-ray diffraction to detect the development of crystalline compounds as the gels aged or were dialyzed. Thin layer samples were rotated with respect to an X-ray beam (Cu radiation) and deflections recorded with a scanning goniometer, utilizing a Geiger-Muller counter tube in conjunction with a scaler-ratio meter with an automatic recorder. Qualitative identification of these compounds was accomplished using a Model JSM 35C JEOL scanning electron microscope.

At each sample date several chemical analyses were used to determine changes in gel nature and P reactivity with aging. Measurement of pH and Cl activity were made using a Model 801 Orion Ionalyzer and appropriate ion sensitive electrodes. The equivalent Al oxide content of the gels was assayed by EDTA titration (79). Acid reactivity of gels was evaluated by adding six 10 ml aliquots of gel suspension to six plastic cups, each containing 50 mls of standardized HCl acid. The cups were then shaken in a water bath at 37C for 0.5, 3, 6, 12, 24, and 48 hours. At each time interval the gel-acid suspension was titrated with standardized NaOH to a pH of 3.5 to determine the me's of unreacted acid. A pH of 3.5 was chosen for the potentiometric endpoint because above this pH Al freed from the polymerized Al-OH during the shaking process will react with added OH groups and confound the determination of unreacted acid. Acid reactivity was then expressed as a percentage of the theoretical acid consuming capacity (TACC) of each gel, defined as:

TACC = Weight of gel (g) x Assay of gel as  $% Al_{2}O_{3} \times 6^{*}$ (Molecular weight of  $Al_{2}O_{3} = 102$ )

where:

TACC = meq of  $H^+$  that will theoretically be consumed by the gels

Weight of gel (g) = (volume of gel suspension) x (% solids gel)

\*This is based on the assumption that each mole of Al<sub>2</sub>O<sub>3</sub> reacts with 6 moles of hydrogen according to the following equation:

 $A1_{2}O_{3} + 6 H^{+} = 3 H_{2}O + 2 A1^{3+}$ 

Therefore, acid reactivity at time t may be expressed as:

Capacity and intensity of the gels for P adsorption was measured through use of Langmuir isotherms. Two ml samples of each gel were added to 100 ml of six P solutions of an appropriate concentration range. Phosphorus solutions were prepared by dilution of a 1000 mg $\cdot$ 1<sup>-1</sup> P stock solution (as K<sub>2</sub>HPO<sub>4</sub>) in .01<u>M</u> CaCl<sub>2</sub>. The solutions were then shaken at 200 rpm for 72 hours, centrifuged at 10,000 rpm for 30 minutes, and filtered under suction using a 0.22 micron millipore filter. Phosphorus content of the filtrate was measured using a Technicon AutoAnalyzer II, and the method of Murphy and Riley (49), with P adsorption expressed as the difference between initial and final P concentration values. Only data with an equilibrium P concentration of less than 3 mg·1<sup>-1</sup> were used, in order to eliminate the possibility of precipitation of P by Ca or Al. The isotherms were conducted with and without pH adjustment in order to compare adsorption at the ambient pH with that following readjustment to the pH of initial precipitation. Adjustment of pH involved daily addition, during the shaking process, of .015 <u>M</u> Ca(OH)<sub>2</sub> or .01 N HCl, as necessary, to maintain suspension pH at either 5.5 or 7.0.

## Results and Discussion

X-ray diffraction patterns representative of the changes detected in Al-OH suspensions with aging are presented in Figure 1. Initially the Al-OH precipitate was X-ray amorphous, but within 3 months a well-defined peak located at 4.84 angstroms confirmed the development of gibbsite  $(A1(OH)_3)$ . X-ray patterns obtained following dialysis of the Al-OH suspensions provide evidence that reduction of ionic strength enhances gibbsite formation. Removal of excess Cl- ions that may inhibit development of double OH bridges and hence polymerization, has been suggested as the basis for this ionic strength effect (51). The pH of initial precipitation had no effect on the type of crystalline A1(OH)3 compound that developed. The small difference in OH/A1 ratio at precipitation (2.54 for pH 7.0, 2.43 for pH 5.5) may explain this when the work of Hsu (25) discussed earlier is considered. Evidently the development of different A1(OH) 3 polymorphs requires either greater disparity in initial OH/Al ratio, or different conditions during inucubation or precipitation (temperature, ionic strength, counteranion, etc.).

Scanning electron micrographs (SEM) illustrate visually the development of more ordered material during the aging process or upon reduction of ionic strength through dialysis (Figure 2). Although these



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Figure 1. X-ray diffraction patterns for aluminum hydroxide suspensions: (A) pH 7.0, one month sample, dialyzed, (B) pH 7.0 3 month sample, (C) pH 7.0, inital sample.





SEM photos are somewhat qualitative, the hexagonal nature of the crystalline material seen in Figure 2d is characteristic of gibbsite.

Examination of the pH and Cl data obtained helps clarify the nature of chemical changes that occurred during the aging process (Table 1). As would be expected, the release of H ions associated with polymer growth is reflected in a decrease in pH with time, stabilizing within 3 months at approximately 3.8. The rapid decline in pH in the first 3 months of incubation, followed by a near steady state condition afterwards indicates that hydrolysis is virtually complete within this time period. Chloride activity increases with time as Cl ions occupying edge sites on Al-OH polymers are expelled from the compound during formation of double OH bridges. Response to the pH of precipitation followed expected trends. The A1-OH suspensions precipitated at a more acid pH (pH 5.5) remained at a slightly lower pH throughout the experiment, while the Cl activity for this treatment was slightly higher. The greater  $Cl^{-}$  activity for Al-OH precipitated at pH 5.5 occurs because of the less ordered nature of A1-OH at this pH which results in less occlusion of Cl ions within the polymeric structure, hence a greater Cl activity in suspension.

Acid reactivity profiles have been utilized to estimate changes in reaction rate and equilibrium reactivity for Al-OH gels (52). This technique may be viewed as an indirect measurement of the proportion of nonstructural, easily neutralized OH groups found in the gel suspension. Aging of Al-OH suspensions results in a conversion of easily neutralized OH to structural OH that requires longer time intervals to neutralize

рН	of precipitation	Time				
		Initial	1	3	6	12
				ths		
				рН		
рН	7.0	5.98	5.42	3.87	3.88	3.65
pН	5.5	4.99	4.73	3.63	3.69	3.59
рН	7.0Dialyzed	5.03	5.61			
pН	5.5Dialyzed	4.47	4.88			
			<u>C1</u>	(eq•g <sup>-1</sup> )		
рН	7.0	.198	•222	•255	.248	.289
pН	5.5	•222	• 304	• 321	•285	•405
рН	7.0Dialyzed	.0002	•0002			
рН	5.5Dialyzed	.0001	.0001		~-	
pН	: L.S.D.: (Ro	ws)= .07; (C	olumns)= .:	22		

Table 1. The influence of pH of initial precipitation, aging and dialysis on the pH and Cl activity of Al-OH suspensions.

Ċ1 : L.S.D.: (Rows)= .04; (Columns)=.13

pH of precipita	ation	Time	
	1	6	12
		months	
	<u>k</u>	$(1 \text{ mol}^{-1} \times 10^4)$	
(+) pH adjustme	ent		
рН 7.0	•55	1.05	•65
рН 5.5	•96	3.51	8.42
(-) pH adjustme	ent		
рН 7.0		2.86	3.27
рН 5.5		• 55	1.13
Dialyzed			
рН 7.0	•88		
рН 5.5	1.31		
		<u>b (mgg<sup>-1</sup>)</u>	
(+) pH adjustme	ent		
рН 7.0	137.3	40.0	30.1
рН 5.5	164.9	38.3	33.1
(-) pH adjustme	ent		
рН 7.0		37.3	27.8
рН 5.5		42.5	39.3
Dialyzed			
рН 7.0	24.8		
рН 5.5	16.3		
k : L.S.D. (p	distment) = 1.81		
L.S.D. (I	oH of precipitation) = 2	2.45	
b : L.S.D. (p	oH adjustment) = 3.8		
L.S.D. (t	ime) = 4.6	. 7	
L.S.D. (I	oH of precipitation) = 8	5•/	

Table 2. The influence of pH of initial precipitation, aging and dialysis on Langmuir k and b constants for P adsorption by Al-OH suspensions.


FIGURE 3. ACID REACTIVITY PROFILES FOR pH 7.0 AL (OH) 3 GELS.



FIGURE 4. ACID REACTIVITY PROFILES FOR pH 5.5 AL (OH) 3 GELS.



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external acidity. This mechanism is substantiated by Nail et al. (52) who attributed decreases in acid consuming capacity with time to a decreased rate of reactivity rather than to a change in equilibrium reactivity. Results indicate that Al-OH precipitated at pH 5.5 is more effective at acid neutralization initially and at one month, but that by three months aging there is little difference in acid reactivity between treatments (Figure 3, 4). Dialysis of the Al-OH suspensions, initially and at one month, produced distinctly different acid reactivity profiles (Figure 5). The reduction in ionic strength associated with dialysis gave a much less reactive material immediately after precipitation than that dialyzed after one month aging. It appears that the development of order that occurred in the first month inhibited completion of the dialysis process and resulted in the formation of a more reactive A1-OH material. Response to dialysis as a function of the initial pH of precipitation, as measured by acid reactivity, varied with sample date. At present no explanation is offered for this phenomenon.

Results for the Langmuir k (bonding energy) and b (adsorption maximum) constants are presented in Table 2. No significant differences in k values were noted throughout the experimental period for Al-OH precipitated at pH 7.0 when pH was adjusted. Bonding energy was seen to increase for the pH 5.5 system (with adjustment) at all sample dates. Isotherms conducted without pH adjustment resulted in increased k values for the pH 7 system, relative to those with adjustment, while decreases were seen for the pH 5.5 treatment. Introduction of OH groups into the suspension during the pH adjustment process would be expected to produce lower k values due to increased competition of OH with  $H_2PO_4^{-1}$ ions for adsorption sites on the Al-OH polymer. Although this was observed for the pH 7 treatment, the increase in k values for the pH 5.5 system due to pH adjustment is somewhat difficult to explain. Adsorption maxima values (with pH adjustment) decreased markedly between the one and six month sample dates for both pH of precipitation treatments (Table 2). The initially greater b values for the pH 5.5 treatment can be attributed to the presence of more edge (nonstructural) OH in this less ordered material that are capable of exchange with  $H_2PO_4^{-1}$  ions. By the six month sample no significant differences were detected between treatments, indicating that comparable states of polymerization existed, a fact seen in the gel acid reactivity profiles as well. Minor differences, significant in only one case (pH 5.5, 12 month sample), in b values were noted due to the pH adjustment process.

Isotherms were also conducted at the one month sample date following dialysis of the Al-OH suspensions. The reduction in ionic strength affected by dialysis produced a much less reactive material in terms of adsorption maxima, regardless of the pH of precipitation (Table 2). No significant change was noted in the bonding energy of Al-OH for P due to dialysis.

To summarize the adsorption data:

(i) reduction in Al-OH polymer capacity for P adsorption with aging or is reflected in marked decreases in b values during the first 3 months. Adjustment of pH had no effect on b. (11) reducing the ionic strength of the Al-OH suspension by dialysis resulted in the development of gibbsite. Associated with gibbsite formation was an 80 to 90% decrease in P adsorption maxima, further evidence that the polymerization/crystallization process significantly inhibits P retention by Al-OH surfaces. (111) the bonding energy (k) values obtained indicate a rather low intensity in the bonding of P to Al-OH surfaces in suspension. Differences due to the pH of initial precipitation and the adjustment of pH are contradictory and more research is needed to elucidate the mechanisms behind the observed data.

## CHAPTER IV

## SUMMARY AND CONCLUSIONS

Evaluation of P adsorption by Al-OH in the soil and in a pure system, and the implications of this reaction for P availability for crop uptake resulted in the following conclusions:

1) The concept of minimal liming of highly weathered acid soils is strongly supported by this study. Use of liming rates recommended by the SMP buffer method resulted in overliming that failed to increase P uptake by oats despite the application of three times as much lime as needed to neutralize exchangeable Al.

2) Aging of adsorbate surfaces in the soil reduced their bonding intensity for P, as does increasing soil pH. The development of more ordered A1-OH polymers that offer reduced steric accomodation of P anions may be a factor in this lessened bonding energy. The increase in pH dependent negative surface charge at higher pH values may also contribute by enhancing anion repulsion.

3) The quantity of P adsorbed decreased significantly when minimal liming was used, but increased with overliming. Development of more extensive Al-OH surfaces or possible adsorption of P by free CaCO<sub>3</sub> may be the basis for this observation. Increases in b values noted with time may be due to continued polymerization of Al-OH as  $Al^{3+}$  was released from soil minerals during incubation.

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4) Decreases in Al extracted by two methods was noted upon aging and introduction of wet/dry cycles during incubation, suggestive of the presence of less soluble Al-OH polymers that may also be less reactive for P.

5) Evaluation of P extractants as predictors of P uptake indicate that the Olsen and Bray methods work extremely well, but that the double acid technique may be less effective than currently believed.

6) Reduction in exchangeable Mg and K under overlimed conditions indicate the possiblity that nutritional imbalances (Ca/Mg, Ca/K) may exist that could adversely affect crop growth.

7) Aging of Al-OH suspensions reduced their capacity for P adsorption. Aluminum hydroxide precipitated at pH 5.5 did sorb significantly more P initially, but within three months no difference was noted from the suspension precipitated at pH 7.0. Reduction in the quantity of edge OH available for ligand exchange with P anions due to their incorporation into the developing Al-OH polymers (double OH bridges) is postulated as the basis for this phenomenon. Decreases in acid reactivity of the Al-OH suspensions were also noted with time confirming the loss of easily neutralized external OH as polymer growth and crystallization occurred.

8) The intensity of bonding of Al-OH suspensions for P was small and significant variations were detected only for those suspensions precipitated at pH 5.5 where k values increased upon aging.

9) Aging or reducing the ionic strength of the Al-OH suspensions by dialysis resulted in the formation of gibbsite  $(Al(OH)_3)$ . Decreases in P adsorption maxima greater than that obtained after two years aging

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were seen following dialysis, providing further evidence that the polymerization and cystallization processes will decrease the reactivity of Al-OH for P. The reduced capacity of Al-OH for P adsorption following dialysis may explain differences in P retention noted for seemingly similar highly weathered soils. A soil that has developed under lower ionic strength conditions may contain Al-OH compounds that are less effective in sorbing applied P. The influence of previous cultivation, fertilization and irrigation practices should be considered when evaluating the potential of soils of this type for P fixation.

10) Consistent but minor changes were noted in Langmuir k and b values due to pH adjustment during the adsorption isotherm process. At present no explanation is offered for these changes, and it is believed that further research is needed over wider pH ranges in order to elucidate specific mechanisms.

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APPENDIX

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Depth	P Rate	? Rate		nvironment	L	I	Environment	2
			0	KC1	SMP	0	KC1	SMP
-cm	-mg/kg-	-						
					Dry v	weight (g)		
0-15	0		3.15	3.08	3.21	3.07	3.17	2.89
	75		3.34	3.23	3.35	3.01	3.63	3.71
	150		3.14	3.37	3.53	3.37	3.49	3.73
15-30	0		2.90	3.27	3.21	2.68	3.21	3.17
	150		3,13	3,51	3,10	3.09	3.25	3, 57
	300		2.91	3.45	3.25	3.35	3.50	3.53
					<u>P co</u>	ontent (%)		
0-15	0		.095	.087	.091	•098	.099	.089
	75		.135	.185	.167	.155	.193	.160
	150		•206	•287	•277	•247	• 300	•263
15-30	0		.095	.092	.089	.085	.089	.089
	150		.163	. 227	.257	.120	. 225	.189
	300		.195	.361	.389	.196	.363	.319
Dry weight		•	L.S.D.	(Rows) =	- 51	(0-15), 5	5 (15-30).	
biy weight		•	L.S.D.	(Columns)=	•91 •21	(0-15); .29	(15-30).	
P content		•	L.S.D.	(Rows) =	. 035	$(0-15) \cdot .09$	2 (15-30).	
. concent		•	L.S.D.	(Columns)=	.017	(0-15); .03	35 (15-30).	

Table Al. The influence of lime, incubation environment and P rate on plant dry weight and P content for oats grown on a Tatum soil.

$NH_4F +$	.025N 1	HC1 (B	ray), and	.025N 1	$H_2SO_4 +$	.05N HC1 (Doul	ble Acid).	
Depth	P Rate	e	Environment l		Envir	Environment 2		
			0	KC1	SMP	0	кс1	SMP
-cm-	mg/k	g	4					
			mg/kg					
						Olsen		
0-15	0		3.3	3.9	2.7	3.5	3.3	3.1
	75		31.1	30.2	29.2	35.1	29 <b>.9</b>	34.9
	150		55 <b>.9</b>	54.2	57 <b>.9</b>	67.0	64.5	57.7
15-30	0		0	0	0	0	0	0
	150		39.2	42.5	30.3	48.3	35.2	27 <b>.9</b>
	300		78.3	65.0	66.7	91.3	61.3	74.5
						Bray		
0-15	0		0.1	0.2	0.3	0.1	0.2	0.8
	75		13.8	14.1	12.6	13.2	12.9	14.1
	150		43.3	46.9	40.2	51.4	52.0	37.7
15-30	0		0	0	0	0	0	0
	150		23.7	29.7	6.9	36.7	25.2	6.9
	300		73.6	80.2	43.5	108.2	78.7	35.1
					De	ouble Acid		
0-15	0		0.1	0	0	0.1	0.1	0
	75		3.5	2.5	0.9	3.4	2.7	1.1
	150		7.2	6.9	4.3	7.3	7.5	4.6
15-30	0		0	0	0	0	0	0
	150		3.3	1.9	0.1	4.0	1.7	0.2
	300		8.9	6.9	2.4	10.5	6.2	1.9
01sen	: ]	L.S.D.	(Rows)	= 9.7	(0-15);	12.8 (15-30)	•	
	1	L.S.D.	(Columns)	= 3.6	(0-15);	5.1 (15-30).		
Bray	: ]	L.S.D.	(Rows)	= 8.9	(0-15);	10.9 (15-30)	•	
	]	L.S.D.	(Colums)	= 3.8	(0-15);	3.7 (15-30)	•	
Double	Acid: 1	L.S.D.	(Rows)	= 1.0	(0-15);	1.4 (15-30).		
	]	L.S.D.	(Columns)	= 0.4	(0-15);	0.7 (15-30).		

Table A2. The influence of lime, incubation environment and P rate on P extracted from a Tatum soil by pH 8.5, 0.5M NaHCO<sub>3</sub> (Olsen), .03N NH<sub>4</sub>F + .025N HC1 (Brav), and .025N H<sub>2</sub>SO<sub>4</sub> + .05N HC1 (Double Acid).

Depth P Rate		Er	vironment	1	Env	Environment 2		
		0	KC1	SMP	0	KC1	SMP	
-cm-	mg/kg-	-						
				рН	(H <sub>2</sub> 0)			
0-15	0	4.33	4.76	7.59	4.33	4.71	7.53	
	75	4.27	4.71	7.33	4.21	4.72	7.39	
	150	4.27	4.69	7.31	4.29	4.73	7.36	
15-30	0	4.86	5.37	7.77	4.67	5.37	7.77	
	150	4.61	5.24	7.63	4.57	5,18	7.64	
	300	4.45	5.24	7.57	4.47	5.17	7.53	
				рН ()	IN KCI)			
0-15	0	3.30	3.58	6.69	3.29	3.61	6.74	
	75	3.33	3.58	6.65	3.31	3.61	6.71	
	150	3.35	3.61	6.61	3.35	3.62	6.63	
15-30	0	3.43	3.81	7.02	3.42	3.76	6.94	
	150	3.44	3.79	6.95	3.43	3.79	6.90	
	300	3.39	3.79	6.81	3.41	3.77	6.79	
рН (Н <sub>2</sub>	0) :	L.S.D. (Rov L.S.D. (Col	vs) = .: lumns)= .(	15 (0-15); 05 (0-15);	.17 (15-	30). 30).		
рН (1N	i KC1) :	L.S.D. (Rov L.S.D. (Col	vs) = .04 Lumns)= .02	8 (0-15); 2 (0-15);	.11 (15-3 .02 (15-3	0). 0).		

Table A3. The influence of lime, incubation environment and P rate on pH (H<sub>2</sub>O) and pH (IN KC1) in a Tatum soil.

Depth P Rate		Envi	ronment 1		Environment 2		
		0	KC1	SMP	0	KC1	SMP
-cm-	mg/kg						
			Exchar	ngeable	Al (meq	/100g)	
0-15	0	3.39	1.03	0	2.95	0.93	0
	75	3.33	1.06	0	3.26	0.99	0
	150	3.29	1.06	0	3.19	0.99	0
15-30	0	4.97	0 <b>.97</b>	0	4.81	0.89	0
	150	5.06	1.08	0	4.86	1.01	0
	300	5.10	1.06	0	4.87	1.03	0
			<u>A1</u>	satura	tion (%)		
0-15	0	68.9	18.1	0	59.8	16.5	0
	75	63.2	18.1	0	61.2	16.9	0
	150	63.2	17.1	0	59.7	16.6	0
15-30	0	72.5	13.5	0	71.1	13.2	0
	150	67.3	14.5	0	65.1	15.1	0
	300	63.0	13.5	0	59.8	13.1	0
Exchan	geable Al	: L.S.D.	(Rows)	= .21	(0-15);	.07 (15-30).	
	-	L.S.D	. (Columns)	) = .06	(0-15);	.04 (15-30).	
Al sat	uration	: L.S.D.	(Rows)	= 4.4	(0-15);	1.8 (15-30).	
		L.S.D	. (Columns)	) = 0.6	(0-15);	0.9 (15-30).	

Table A4. The influence of lime, incubation environment and P on exchangeable (1N KC1) A1 and percent A1 saturation in a Tatum soil.

Depth	P Rate	E	Environment l		Envir	Environment 2	
		0	KC1	SMP	0	KC1	SMP
-cm-	mg/kg		~~~~~	%			
				<u>Ca</u>	L		
0-15	0 75 150	.31 .39 .41	•40 •53 •55	•45 •59 •58	• 37 • 47 • 49	•45 •49 •52	•47 •59 •57
15-30	0 150 300	•26 •39 •41	•41 •51 •57	•42 •51 •53	•33 •33 •45	•41 •57 •62	•39 •53 •46
				Mg	_		
0-15	0 75 150	.18 .19 .19	•18 •20 •21	.17 .18 .19	.20 .21 .21	•19 •20 •21	•17 •17 •17
15-30	0 150 300	.17 .21 .22	•19 •21 •21	.19 .19 .19	•19 •19 •21	•18 •21 •21	.17 .19 .16
				K			
0-15	0 75 150	1.15 1.13 1.11	1.23 1.36 1.41	1.25 1.27 1.19	1.25 1.30 1.24	1.29 1.29 1.31	1.24 1.18 1.17
15-30	0 150 300	1.16 1.21 1.25	1.41 1.38 1.43	1.36 1.57 1.49	1.49 1.21 1.36	1.37 1.39 1.42	1.25 1.37 1.47
Ca :	L.S.D L.S.D.	• (Rows) (Columns)	= .05 (0-15) = .02 (0-15)	5); .13 ( ; .06 (1	15-30). 5-30).		
Mg :	L.S.D. L.S.D.	(Rows) (Columns)	= .02 (0-15) = .01 (0-15)	; .05 (1 ; .027 (	5-30). 15-30).		
к :	L.S.D. L.S.D.	(Rows) (Columns)	= .17 (0-15) = .09 (0-15)	; .20 (1 ); .08 (1	5-30). 5-30).		

Table A5. The influence of lime, incubation environment and P rate on Ca, Mg and K content in oats grown on a Tatum soil.

Depth P Rat		Rate Environment			En		2
		0	KC1	SMP	0	KC1	SMP
-cm-	mg/kg-						
		meq/	'100g			-	
				<u>_</u>	a		
0-15	0	•35	3.95	11.15	.55	4.01	10.53
	75	• 58	4.07	11.03	•75	4.17	10.53
	150	•77	4.37	11.54	•93	4.31	10.96
15-30	0	.29	5.35	12.38	• 36	4.96	11.54
	150	•75	5.44	12.73	.89	4.85	12.19
	300	1.18	5.99	12.95	1.45	5.87	12.42
				M	lg		
0-15	0	.13	.13	.01	.19	.11	0
	75	.13	•12	.01	.19	.13	0
	150	•14	.13	.01	.19	•11	•01
15-30	0	•40	.35	0	.43	.35	0
	150	•41	.33	.01	•45	.37	Ō
	300	•41	•35	•01	•47	• 37	•01
				K	<u>.</u>		
0-15	0	•17	.16	.11	.18	.17	.10
	75	.15	.15	.10	.17	.16	.09
	150	.15	.15	•11	.16	.16	.10
15-30	0	•23	•26	.15	.25	. 26	.18
	150	•23	.23	.15	•25	.26	.19
	300	•23	•24	•16	•25	•27	.19
Ca :	L.S.D.	(Rows) =	.75 (0-15)	66 (15	-30)-		
	L.S.D.	(Columns) =	.31 (0-15)	; .31 (15	-30).		
Mg :	L.S.D.	(Rows) =	.05 (0-15)	.03 (15	-30).		
5	L.S.D.	(Columns) =	.01 (0-15)	; .01 (15	-30).		
κ :	L.S.D.	(Rows) =	.02 (0-15)	02 (15	-30)-		
- •	L.S.D.	(Columns) =	.01 (0-15)	): .01 (15	-30)		

Table A6. The influence of lime, incubation environment and P rate on exchangeable (pH 7.0.  $1N NH_2Oac$ ) Ca. Mg. and K Tatum soil

	Lime rate				
P Rate	0	KC1	SMP		
mg/kg		Dry weight (g)			
0	2.85	3.46	3.17		
150	3.11	3.75	3.51		
300	3.05	3.78	3.75		
		P content (%)			
0	.111	.097	.113		
150	.195	.167	•253		
300	.367	•359	.375		
		<u>P uptake (mg/pot)</u>			
0	3.15	3.33	3.60		
150	6.05	6.23	8.89		
300	11.21	13.43	13.87		

Table A7. The influence of lime and P rates on plant dry weight, P content and P uptake for oats grown on a Bradson soil.

Table A8. The influence of lime and P rates on P extracted from a Bradson soil by pH 8.5, 0.5 M Na HCO<sub>3</sub> (Olsen), .03N NH<sub>4</sub>F + .025N HCl (Bray) and .025N H<sub>2</sub>SO<sub>4</sub> + .05N HCl (Double Acid).

	Lime rate					
P Rate	0	KC1	SMP			
mg/kg		mg/kg				
		<u>Olsen</u>				
0	9.3	5.9	16.1			
150	34.5	25.7	22.5			
300	54.2	50.6	42.5			
		Bray				
0	1.0	0.3	0.3			
150	10.4	6.7	2.3			
300	21.9	15.9	7.5			
		Double Acid				
0	0.1	0	0.1			
150	0.5	0.3	0.2			
300	1.0	0.9	0.5			

		Lime rate	
P Rate	0	KC1	SMP
mg/kg		%%	
		Ca	
0	• 34	•45	•56
300	•45 •55	•57	•67
		Mg	
0	.19	•17	.19
150	•21	.19	.19
300	•21	•20	.19
		<u>K</u>	
0	1.93	1.77	1.93
150	1.87	1.75	2.07
300	1.99	1.82	1.76

Table A9. The influence of lime and P rates on Ca, Mg and K content in oats grown on a Bradson soil.

Table AlO. The influence of lime and P rates on exchangeable (pH 7.0, 1N NH4OAc) Ca, Mg, and K in a Bradson soil.

	Lime rate				
P Rate e	0	ксі	SMP		
mg/kg		meq/100g			
		Ca			
0	.38	1.82	9.70		
150	•70	2.33	10.11		
300	1.15	2.65	10.11		
		Mg			
0	•11	.15	•12		
150	•09	•17	•14		
300	•11	.17	.15		
		<u>K</u>			
0	•63	.79	.75		
150	• 57	.81	•75		
300	•65	.79	.75		

		Lime rate	
P Rate	0	KC1	SMP
mg/kg		рН (Н <sub>2</sub> 0)	
0	4.45	4.44	6.81
150	4.43	4.39	6.77
300	4.57	4.47	6.72
		pH (1N KC1)	
0	4.07	4.14	6.12
150	4.00	4.10	6.07
300	4.01	4.07	6.04

Table All. The influence of lime and P on pH ( $H_2O$ ) and pH (lN KC1) in a Bradson soil.

Table Al2. The influence of lime and P rates on exchangeable (1N KC1) Al and percent Al saturation in a Bradson soil.

Lime rate				
P Rate	0	KC1	SMP	
mg/kg				
	]	Exchangeable Al (meq/	100g)	
0	1.82	1.29	0	
150	1.83	1.31	0	
300	1.50	1.17	0	
		Al saturation (%)		
0	56.2	30.1	0	
150	53.5	27.4	0	
300	41.0	23.5	0	

	Lime rate			
Incubation Length	0	KC1	SMP	
months		Extractable Al (meq/100g)		
1		2.02	1.01	
8		2.41	.79	
		Exchangeable Al (meq/100g)		
1		•72	0	
8		1.14	0	
		Al saturation (%)		
1		17.3	0	
8		25.5	0	

Table Al3. The effect of lime rate and incubation length on extractable (pH 4.8,  $1N NH_4OAc$ ) and exchangeable (1N KC1) Al and percent Al saturation in a Bradson soil.

Table Al4. The effect of lime rate and incubation length on exchangeable (pH 7.0, 1N NH4Oac) Ca, Mg, and K in a Bradson soil.

	Lime rate			
Incubation Length	0	KC1	SMP	
months		meq/100g	و من هي هي خلي خلي الي الي الي الي الي الي الي الي الي ا	
		Ca		
1		1.97	10.17	
8		1.99	10.17	
		Mg		
1		•15	.11	
8		•17	.15	
		<u>K</u>		
1		•78	•72	
8		.78	.72	

	Lime rate					
Incubation Length	0	KC1	SMP			
months						
		рн (н20)				
1		4.68	7.07			
8		4.47	6.81			
		pH (1N KC1)				
1		4.25	6.41			
8		4.16	6.15			
		Bray P (mg/kg)				
1		.13	.13			
8		•28	•28			

Table Al5. The effect of lime rate and incubation length on pH ( $H_2O$ ), pH (1N KC1) and .03 N NH<sub>4</sub>F + .025 N HC1 extractable (Bray) P in a Bradson soil.

Table Al6. The effect of lime rate and incubation length on Langmuir k and b values in a Bradson soil.

	<del></del>	·				
Incubation Length	0	KC1	SMP			
months						
		<u>k (1mol<sup>-1</sup> x 10<sup>4</sup>)</u>				
1		40.8	17.1			
0		h (mg/100g)	/•J			
		<u>b (mg/100g)</u>	<i></i>			
8		57.8 70.1	64.9 73.9			

pH of precipitation	Time (months)				
	Initial	1	3	6	12
	<u>Nondialyzed</u>				
рН 7.0	58 <b>.9</b>	59.7	60.1	57.5	5 <b>9.</b> 0
рН 5.5	55.5	56.5	57.7	53.5	55.6
	Dialyzed				
рН 7.0	64.4	84.0			
рН 5.5	77.1	76.3			

Table A17. Al oxide contents of dialyzed and nondialyzed A1-OH suspensions as a function of pH of precipitation and incubation length.

Table Al8. Percent solids of nondialyzed and dialyzed Al-OH suspensions as a function of pH of precipitation and incubation length.

pH of precipitation	ion Time (mont)				<b>IS</b> )	
	Initial	1	3	6	12	
				-%		~~
			Nondia	alyzed		
рН 7.0	1.59	1.54	1.55	1.58	1.50	
рН 5.5	1.71	1.62	1.65	1.71	1.61	
	Dialyzed					
рН 7.0	0.96	0.75				
рН 5.5	0.67	0.82			-	

Time (months)								
12	13	15	18	24				
<u>k (+ pH adjustment (<math>1mo1^{-1} \times 10^{5}</math>)</u>								
	•34	1.01	•36	•60				
	<u>k (- pH ad</u>	justment (1mol <sup>-1</sup> x )	10 <sup>5</sup> ))					
		.58	•53	1.11				
	<u>ь (+ </u>	Hadjustment (mg/g)	<u>))</u>					
	33.2	31.4	36.6	29.3				
b (- pH adjustment (mg/g))								
		31.7	30.3	28.8				
		рН						
3.74	3.72	3.59	3.73	3.56				
<u>Cl (eq/g)</u>								
•305	•355	•332	•305	.342				
Al oxide content (%)								
55.5	52.8	58.8	55.1					
Solids content (%)								
1.72	1.79	1.63	1.68					

Table Al9. Selected characteristics of a separate Al-OH suspension precipitated at pH 7.0 and aged for two years.

