

THE FATE OF APPLIED PHOSPHORUS ON A PIEDMONT SOIL  
AND ITS EFFECT ON LOBLOLLY PINE GROWTH  
TWENTY YEARS AFTER APPLICATION

by

John L Torbert Jr.

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APPROVED:

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J.A. Burger, Chairman

-----  
M.M. Alley

-----  
D.Wm. Smith

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## INTRODUCTION

Trees are a renewable natural resource. With an increasing demand on all natural resources, the supply of most materials dwindles and the search continues for new sources. Unlike coal and other minerals, timber can be produced perpetually. The American forester is replacing old forests, often understocked and comprised of low value trees, with new stands of better quality and improved growth rates. More efficient forest management becomes especially important as forest sites are sacrificed to food production and numerous other non-agricultural uses.

Intensive forestry is probably most prevalent in the pine plantations of the Southeast. These forests are providing an increasingly large amount of the nation's forest products. The single most important southern tree is loblolly pine (Pinus taeda L.). Much research is devoted to improving the growth of this species.

The growth of a tree is dictated by two factors, its genetics and its environment. Loblolly pine tree improvement programs have developed superior genotypes that grow faster and develop better form than native trees.

Millions of genetically improved seedlings are produced each year in nurseries. These superior genotypes will increase forest production and help meet the wood and fiber needs of the future.

Although genetic improvement boosts the efficiency with which a tree uses its site, environmental conditions are the ultimate factors determining growth. Usually a tree cannot realize its true growth potential due to some limiting factor of its environment. More often than not, an inadequate supply of water or nutrients restricts growth. From a practical standpoint, there is not much the forester can do to rectify a water shortage. There is no practical way to increase precipitation, and irrigation is rarely economically feasible. Nutrient deficiencies, however, can often be corrected with the addition of one or more nutrient elements.

In agriculture, fertilization is often required when crops need more nutrients than the soil can supply. Without fertilization, the plants will not attain their full growth potential. Although trees are not quite as demanding for nutrients as agronomic crops, there are many cases where forest fertilization can improve growth. It is important that foresters learn to identify situations where fertilization is helpful. To prevent unnecessary expenses,

it is equally important to distinguish sites which do not need improvement.

Much fertilization research has been undertaken with loblolly pine and slash pine (Pinus elliotti L.) The North Carolina State Forest Fertilization Cooperative (NCSFFC) at North Carolina State University and the Cooperative Research in Forest Fertilization (CRIFF) at the University of Florida have contributed to the understanding of how fertilization affects southern pines. Besides these industry-university research efforts, state and federal foresters are also involved with fertilization research.

Generally, the nutrients most experimented with are nitrogen (N) and phosphorus (P). Deficiencies of other nutrients are rare, especially in the South. Almost all studies show some response to N application. Nitrogen tends to produce a short term increase in growth along with increased needle weight and a darker green foliage. Inorganic nitrogen fertilizer reactions in soil are relatively straight forward and fairly well understood. Unless applied N is immobilized biologically or leached from the soil system, most of it will remain available to plants until the supply is depleted.

Phosphorus behaves in a more complicated manner. In some cases, particularly on the Coastal Plain, P application

produces drastic growth increases, while under seemingly similar circumstances on the Piedmont, P has no effect on loblolly pine. It is not uncommon for a forest company owning land on both the Coastal Plain and Piedmont to apply the same management techniques to all sites without really understanding the potentials of each soil. Since all sites do not respond similarly to P addition, it becomes important to be able to identify which sites are P deficient and which are not.

In view of all the uncertainties pertaining to P fertilization for loblolly pine on the Piedmont, a study was needed to elucidate the factors controlling response to P applied on Piedmont soils. The foundations for such a study were established in 1959 on the Virginia Piedmont in the form of a P fertilization trial. Phosphorus was applied at rates up to 670 kg P/ha to eliminate the argument that not enough P was added in past trials to produce a response. Growth of this stand was evaluated at age 10 by Moschler et al (1970), at which time there was no significant growth response to treatment. Evaluation of this study at age 20, when the trees were approaching rotation age, established whether or not P fertilization at time of planting results in increased production.

Piedmont soils often have a high phosphorus retention capacity. Phosphorus reacts readily with iron (Fe) and aluminum (Al) at low soil pHs to form P compounds which are mostly unavailable for growth. The reaction of applied P with Fe and Al needed to be evaluated in light of the limited and insignificant response at age 10. A 20 year evaluation of the growth of the stand as affected by treatment, and an evaluation of the fate of this applied phosphorus after 20 years, provided additional insight to phosphorus fertilization of loblolly pine on the Piedmont.

The objectives of this study were:

- 1) To determine the long-term effect of liming and various P fertilizer treatments on soil and foliar P levels and their effect on loblolly pine growth.
- 2) To examine the soil chemistry in an attempt to account for the applied P, and make inferences concerning the suitability of each treatment for long-term pine nutrition.

## LITERATURE REVIEW

### Introduction to Loblolly Pine Phosphorus Fertilization

#### Role of phosphorus in loblolly pine nutrition

A twenty year old loblolly pine plantation requires approximately  $5.5 \text{ kg P}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$  (Switzer and Nelson, 1972). Despite high levels of total soil P in natural ecosystems, P is often the growth limiting element due to low plant availability. Phosphorus readily reacts with Al, Fe, and Ca, which are often plentiful in soils, to produce P compounds which are unavailable for plant growth.

Although trees require less P than N or K, it is as essential for growth. Phosphorus is indispensable to all life due to its genetic role as a part of RNA molecules. In addition, all life requires the energy transformations governed by the phosphate bonds in ATP. Phosphorus is critical for juvenile growth and is required for establishment of the pine stand. Unlike N which is most demanded after several years of growth, P when needed, should be provided at the time of establishment.



### Identifying phosphorus deficiencies

A severe phosphorus shortage can be identified by deficiency symptoms. There will be few branches and needles will be short and drop sooner than usual. Such trees have a sparse and tufted appearance and under extreme conditions needles will be purple. However, pines seldom exhibit such clear-cut deficiency symptoms. On most forest soils, the result of insufficient P is simply reduced growth. To meet the production goals of today's forest industry, it is important to identify marginally deficient sites where no outward deficiency symptoms exist.

Soil and foliar tests are most often used to detect soils in need of P fertilization. Foliar tests have generally been more reliable for predicting responsive sites (Wells and Crutchfield, 1973). The foliar concentration is an expression of the interaction of all factors affecting the plants' ability to take up nutrients. Wells and Metz (1963) discuss the variability of foliar levels within a single tree as affected by age, season, and position in the crown. In order to compare one stand with another and to meaningfully correlate foliar data with growth responses, it is necessary to standardize the foliage sampling technique. Pritchett et al. (1975) explained the factors involved and suggested guidelines to follow for sampling southern pine

needle tissue. Dominant or codominant trees should be sampled in early autumn, collecting the last fully elongated flush of needles from the top third of the south side of the crown.

Although foliar analyses are the most predictable indicators of P deficiencies, a soil test for nutrient determinations has several advantages over foliar analyses (Pritchett, 1979). It is easier to sample soil than to sample foliage from older stands when samples must come from near the top of the tree. For a soil test, several samples can quickly be taken with a push tube and composited. Perhaps most important, soil tests can be performed and fertilization prescriptions made before the time of planting. If loblolly pine does not already exist on the site, it would be necessary to wait a few years after planting to do a foliar analysis. Because of the importance of P early in the rotation, this could be most unfortunate in areas suspected of being deficient. Detailed information about soil tests for P are given in a later section.

It is important that the results of foliar analyses and soil tests be correlated with growth. Assuming no other factors are limiting, as levels increase, growth should also increase until a critical point is reached. When foliar or soil levels rise above this critical level, an economic

growth response to added P will not occur and the tree may undergo luxury P consumption. When a foliar or soil test indicates that P levels are below the critical level, P fertilization can be expected to increase growth.

Phosphorus fertilizers used to correct deficiencies

Many types of phosphate fertilizers are available, but only a few are commonly used in forestry applications, namely, ground rock phosphate (GRP) and triple superphosphate (TSP), also known as concentrated superphosphate. Rock phosphate (fluroapatite:  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ) is mined as a raw mineral and often ground and applied in its original form. The phosphorus content of apatite is usually about 18%, and is essentially 100% water insoluble. This form of P comes into solution only over a long period of time and only under acidic conditions. Rock phosphate is not often used in agriculture where annual crops are grown on near neutral soils. This fertilizer has more appeal to foresters growing pines, where a long term crop and acidic soils are involved. Because GRP releases its P slowly, this fertilizer may be most important for soils with either very high or low P fixing capabilities (Pritchett, 1979).

Triple superphosphate, about 20% P, is produced by treating apatite with phosphoric acid. Triple superphosphate is an orthophosphate which unlike GRP is about 90% water soluble. Due to its high solubility, high analysis, and good physical properties, TSP is often used when the soil P-fixing capacity is not extreme.

When N is required along with P, some fertilizer forms such as ammoniated superphosphate, produced by reacting ammonia with superphosphate, or ammonium phosphnate, formed by treating ammonia with phosphoric acid, are applied. The ammoniated superphosphates tend to have lower P contents and solubilities than superphosphates without N, but this may be beneficial in forested systems where continued release of P is often desirable.

### Phosphorus fertilization trials

The literature contains numerous examples of successful P applications to coarse textured Coastal Plain soils. Pritchett (1969) and Wells and Crutchfield (1973) report southern pine responses to P fertilization on these soils. Ballard and Pritchett (1975) prescribe application rates on Coastal Plain sites based on levels of extractable P and drainage class.

A consensus of the literature suggests that trees will respond to P applications when soils have double acid extractable P levels less than 4 or 5 ppm and when needle tissue levels are less than 0.10% P (Fowells & Drauss, 1959; Wells and Crutchfield, 1973; Trew, 1981). When soil and foliar levels fall below these critical levels, P application can have a positive effect on southern pine growth. Crutchfield (1977) reported a 400% increase in volume per hectare following P application to a loblolly pine plantation on a Coastal Plain soil with an extractable P level of 2.0 ppm and foliar levels of 0.07%.

Phosphorus fertilization studies on Piedmont sites have not shown the same marked response as those on the Coastal Plain. Maki (1960) fertilized two established loblolly pine plantations on the North Carolina Piedmont. A 5-year-old plantation on a Georgeville silt loam and a 10-year-old

stand on an Alamance silt loam each received up to 40 kg P/ha every year, broadcast as superphosphate, along with various rates of N and K for nine years. Nitrogen increased diameter and needle length but no growth increases were attributable to P. Foliar concentrations of control plants were 0.11%. Since foliar levels of control trees were above the critical level, no growth response should have been expected. Although growth was not improved by P application, average foliar levels of 0.16% for treated trees showed that there was a significant increase in P uptake.

Haines and Haines (1979) fertilized 4-year-old loblolly pine on a Cecil sandy clay in the North Carolina Piedmont. Over a 3 year period, 198 kg N/ha, 7 kg P/ha and 26 kg K/ha were added, with all the P applied in the second year. Tree diameter and volume were significantly increased as a result of the N, but no response to P was apparent. Foliar P levels averaged 0.12% before treatment and were not significantly increased by fertilization. Soil extractable P went from 3 to 6 ppm with no corresponding growth response. This implies that the critical level of 4-5 ppm extractable P for Coastal Plain soils does not apply to this Piedmont site since the soil level went from below the critical level to above with no growth response.

Menge et al. (1977) fertilized 11-year-old loblolly pines with 25 kg P/ha and various N levels on a sandy loam in the Piedmont. Although P with N increased growth, no response could be attributed to P alone. Again, control tree foliar levels of 0.11% indicate that this site was not P deficient for loblolly pine, although extractable soil levels were below the critical level at 3 ppm.

Wells and Crutchfield (1973) conducted nine studies on Piedmont sites. Phosphorus was broadcast as triple superphosphate at planting at rates of 56 to 224 kg P/ha. Fertilization significantly increased foliar levels of treated trees at age 3 but did not increase growth.

Phosphorus fertilization work is currently being carried out by the North Carolina State Forest Fertilization Cooperative (NSFFC). Twenty-six plots on Piedmont soils which received P treatments at time of establishment showed no significant response to P at age 5 (NCSFFC, 1978).

Comparison of data from a Coastal Plain and Piedmont study with certain common characteristics (Table 1) helps to illustrate the uncertainty that exists pertaining to fertilizing with P on the Piedmont. Crutchfield (1977) gives data for a 10-year-old fertilization trial on a South Carolina Coastal Plain soil. Moschler et al. (1970) reported the 10-year results for the Piedmont fertilization



Table 1. Comparison of Coastal Plain and Piedmont Loblolly Pine Fertilization trials.

Stand Characteristic	Coastal Plain (Crutchfield, 1977)	Piedmont (Moschler et. al., 1970)
<u>Control Plots</u>		
Age (yrs)	10	10
Height (m)	7.5	7.7
Diameter (cm)	11.2	9.6
Volume/tree (m <sup>3</sup> )	0.3	0.3
Extractable Soil P (ppm)	2.0	2.0
Foliar P (%)	0.07	0.11
<u>Fertilized Plots</u>		
Rate TSP application (kg P/ha)	56	170
Volume increase/tree (%)	300	6
Volume increase/ha (%)	400	6

trial at Orange, Virginia with which the present study deals.

Analysis of the data shows that for both studies, growth rates of control plots are similar. Heights of Coastal Plain trees are 7.5 meters and essentially the same as control trees on the Piedmont sites. Diameters are somewhat greater on Coastal Plain sites, but considering differences in tree form, individual tree volumes are reported as 0.3 m<sup>3</sup> for both studies. At age 10, double acid extractable P in both control plots are 2.0 ppm P which would indicate a deficiency based on soil information alone. Both sites received TSP applications at time of planting.

The Coastal Plain site received 56 kg P/ha. Ten years after treatment, fertilized trees were 50% taller, 50% greater in diameter, and 300% greater in individual tree volume than control trees. Furthermore, due to an increase in survival realized by fertilization, Crutchfield estimated volume on a per hectare basis to have increased by 400%.

By comparison, fertilization on the Piedmont soil which had the same level of extractable P and an application rate three times greater than that on the Coastal Plain, did not significantly increase growth. Individual tree volume of treated trees averaged only 6% more than the controls. This is a drastic difference from the 300% increase realized on

the Coastal Plain study. In addition, fertilization on the Piedmont had no effect on survival or volume per hectare.

These results can be explained by comparing foliar levels of control trees for the two studies. Foliar levels on the Coastal Plain were only 0.07% P, which is below the foliar critical level of 0.1%, suggesting that P application should improve growth. Indeed, P application did improve growth, and foliar levels of treated trees were greater than 0.1% P after 10 years. On the other hand, Piedmont control plot foliar levels were 0.11% which was above the critical level, indicating that despite a low soil P level of only 2.0 ppm, pines were capable of extracting enough P for adequate growth.

From all the literature pertaining to P trials with loblolly pine on the Piedmont, it seems that although a critical foliar level of 0.1% P may be valid for the Piedmont, a critical soil level of 4.0 ppm is not.

## Phosphorus Fixation

### Introduction

Phosphorus fixation is the conversion of P from a soluble form to an insoluble form which is unavailable for plant uptake. The ability of a soil to fix P is largely related to its clay content. Generally, the chemistry of soils high in clay, especially the most weathered soils high in kaolinite, is such that conditions are favorable for P fixation. Coastal Plain soils do not have as great a clay content as Piedmont soils and, therefore, generally have lower P-fixing capabilities.

The high P-fixation capacity of many Piedmont soils is often a problem in agriculture because agronomic crops require much greater soil P levels than pines. Although P is often added to increase the soil solution concentration for plant growth, only about 10% of the applied P will enter the plant-animal life cycle (Ozanne 1980), despite the fact that very little P will be leached from the system. Approximately 90% of the applied P undergoes reactions with Al, Fe, and Ca to form insoluble compounds which are not available for plant use.

Phosphorus fixation is a complex phenomenon which is not completely understood. The literature is confusing and often contradictory as to the exact mechanisms by which P is

fixed. Most information deals with P fixation in acid soils separately from basic soils. Although the principles are the same, exact mechanisms differ since calcium compounds play the predominant role in P fixation in basic soils. In acid soils, where pines occur naturally, Al and Fe are primarily responsible for removing applied phosphorus from solution.

Source of phosphate ions to be fixed

The major form of soil phosphate available for fixation following fertilization is the orthophosphate ion ( $\text{H}_2\text{PO}_4^-$ ). Orthophosphates are derived from the dissolution of most commonly used fertilizers, such as GRP, TSP and ordinary superphosphate, mono and diammonium phosphates, and phosphoric acid. In acid soils,  $\text{H}_2\text{PO}_4^-$  predominates while  $\text{HPO}_4^{2-}$  is the most common phosphate ion in basic soils. The pK for hydrolysis of  $\text{H}_2\text{PO}_4^-$  is 7.2 which means that at pH 7.2  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  exist in equal proportions.

Pyrophosphates ( $\text{H}_2\text{P}_2\text{O}_6$ ) $^{2-}$  derived from fertilizers like ammonium polyphosphate are metastable in soils and eventually hydrolyze to orthophosphate. Pyrophosphates are sometimes used to deter the fixation of P because it takes time for the orthophosphate ion to form.

### Source of Al and Fe involved in P fixation

Iron and Al play major roles in removing P from solution in acid soils. Yuan et al. (1960) showed that 90% of applied P ends up in combination with Al and Fe. Iron and Al are reactive as both ions in solution and as polymers of hydrous oxides. The many forms of Fe and Al oxides and hydroxides are collectively known as sesquioxides, and although their exact compositions may vary, they are thought to behave similarly towards P.

These Al and Fe hydroxides are termed amorphous when they are undetectable to x-ray diffraction techniques. Allophane, an intermediate product of weathering, is an amorphous alumino-silicate gel common in soils. It usually contains some hydrated  $Al_2O_3$  and  $Fe_2O_3$ , and  $SiO_2$ . Upon aging, amorphous material tends to crystallize. Gibbsite  $Al_2(OH)_6$  is a crystalline aluminum hydroxide and has definite characteristics that enable it to be identified via x-ray diffraction techniques. Iron compounds such as hematite ( $Fe_2O_3$ ) and goethite ( $FeOOH$ ) can exist as freshly deposited amorphous coatings or become crystalline with time and accumulation.

Hydrous oxides are amphoteric, meaning that their surface charge can be either negative or positive depending on pH. Iron and Al go from their trivalent forms,

$Al, Fe(H_2O)_6^{+3}$ , at very low pH to large hydroxyl polymers  $Al, Fe(OH)_6^{-3}$  at high pH's. The dissociation constants are much lower for iron, which does not exist as  $Fe^{+3}$  in solution above pH 2. According to Bohn et al. (1979),  $Al(OH)^{+2}$  exists within a very small pH range and is not common in soils. Trivalent aluminum is predominant below pH 4.7 and monovalent aluminum,  $(Al(OH)_2^+)$ , is in abundance from pH 4.7 to 6.5.

Iron and Al available for reaction with P can come from several sources. In all cases, release of these ions is accelerated by a decrease in pH, as occurs in the zone surrounding a dissolving pellet of monocalcium phosphate. Aluminum and some Fe, which has been isomorphically substituted for Al, can be released from the crystal structure of layer silicates. Aluminum and Fe hydrous oxides will break down from large polymers to trivalent ions as pH decreases. Aluminum is much more likely than iron to exist in trivalent form under conditions normally found in soils. However, since the pH around fertilizer granules can temporarily get down to 1.5, Fe hydroxides can easily dissolve releasing  $Fe^{+3}$  which may react with phosphate to produce a new compound. A third source of  $Al^{+3}$  and  $Fe^{+3}$  is the dissolution of phosphate minerals such as variscite  $Al(OH)_2H_2PO_4$ , strengite  $(Fe(OH)_2H_2PO_4)$  and baranadite



(Fe,Al(OH)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>) at levels in accordance with the solubility product principle (Lindsay and Moreno, 1960).

Phosphorus fixation (adsorption vs. precipitation)

Phosphorus fixation can be viewed as occurring by two broad processes: precipitation and adsorption. Sometimes it is a fine line that determines by which process fixation is occurring. At lower pH's, when the activities of Al and Fe are high, there is a greater tendency for P to precipitate out of solution as colloidal variscite-baranaditestrengite type materials (Brady 1974). At a more neutral pH, fixation is likely to occur at the surfaces of sesquioxides by adsorption mechanisms (Fig. 1).

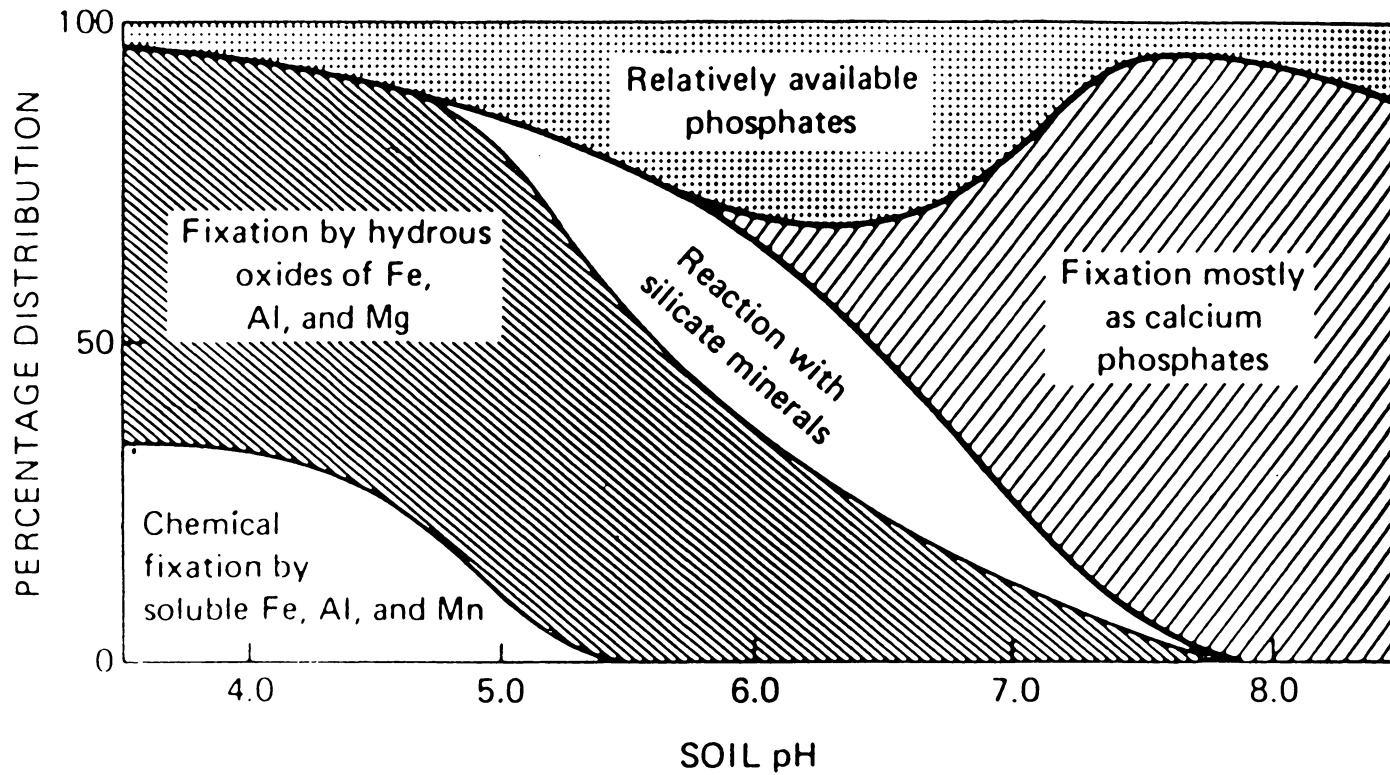


Figure 1. Inorganic fixation of added phosphorus at various soil pH values (from Brady, 1974)

### Fixation by adsorption

The adsorption phase of P fixation occurs primarily at the surface of sesquioxides. There may also be some adsorption onto layer silicate surfaces. Adsorption onto Fe and Al hydrous oxides actually involves at least three separate mechanisms which occur in sequential order. The first two involve a ligand exchange between  $\text{H}_2\text{PO}_4^-$  and  $\text{OH}_2$  and OH-groups at the hydrous oxide surface. These are termed chemisorption reactions because of the high-energy nature of the bond. The third sorption mechanism involves a low energy, electrostatic non-specific anion attraction to the hydroxide surface which has a low density diffuse positive charge. This low energy absorption is the predominant form of fixation from solutions with a high P concentration. All three reactions proceed rapidly after P is added to solution. The slow rate of increased P fixation results from occlusion of phosphorus and an increase in the amount chemisorbed. The important thing to realize about these reactions in comparison to precipitation reactions is that the Al and Fe are not moved from their initial positions where they are coordinated with hydroxyl groups.

Sample et al. (1980) give a good treatise on the subject of P fixation and adsorption reactions for soils and Fe oxide gel. Parliff et al. (1977) describe similar

occurrences at the edges of gibbsite and goethite and predict similar reactions for all sesquioxide surfaces.

The development of adsorption theories are largely based on interpretation of phosphorus adsorption isotherms (Q/I curves), and transformations of these curves with the Langmuir equation. Phosphorus Q/I curves are derived after equilibrating soil samples with a series of solutions containing a range of P concentrations. The quantity of P sorbed (Q) from solution is plotted against the equilibrium solution concentration (C). In order to quantitatively describe certain P sorbing characteristics and make comparisons with other soils, data from Q/I curves are often fitted to the Langmuir equation:

$$C/Q = 1/B \cdot K + C/B$$

B = sorption capacity

C = equilibrium solution concentration (ppm)

K = affinity parameter

Q = P sorbed from solution (ppm)

Although originally derived to describe the adsorption of a monolayer of gas onto a metal surface, this equation is often used to describe P fixation reactions (Veith and

Sposito, 1977). The value  $K$  gives an indication as to the bonding energy of  $P$  for the soil. The sorption maxima is often estimated by  $B$ .

The understanding of adsorption mechanisms came about from the realization that  $P$  adsorption isotherms ( $Q/I$  curves) and the derived Langmuir equations consist of at least three different linear ranges (Figure 2). This had largely gone unnoticed in the past due to an insufficient number of data points, particularly at the very low concentration range. Syers et al. (1973) and Ryden et al. (1977b) worked with soils of widely contrasting fixation properties. Although the soils fixed different quantities of phosphorus, all isotherms had the same shape, and for each curve, three Langmuir equations could be fitted. Each equation corresponded to one of the three linear regions of the  $Q/I$  curve indicating three different fixation mechanisms. The  $K$  value for each equation were the same for similar regions on all soils indicating that in all soils the same three fixation processes were involved. Furthermore,  $K$  values for the first two linear ranges were similar, and equal to or higher than reported values derived for cations chemisorbed from solutions. The  $K$  value for the third region was much lower, indicating a low energy type of  $P$  sorption.

It was also observed that as P is adsorbed in region I, a more negative charge develops at the surface as evidenced by an increase in the amount of Na<sup>+</sup> adsorbed from solution. Adsorption in region II did not result in any surface change, but region III sorption resulted in a more negative surface. The increased charge was about one equivalent for each mole of sorbed phosphorus. These researchers also observed that adsorption in region II resulted in a sharp increase in pH, but regions I and III were unaffected (Parfitt et al, 1975).

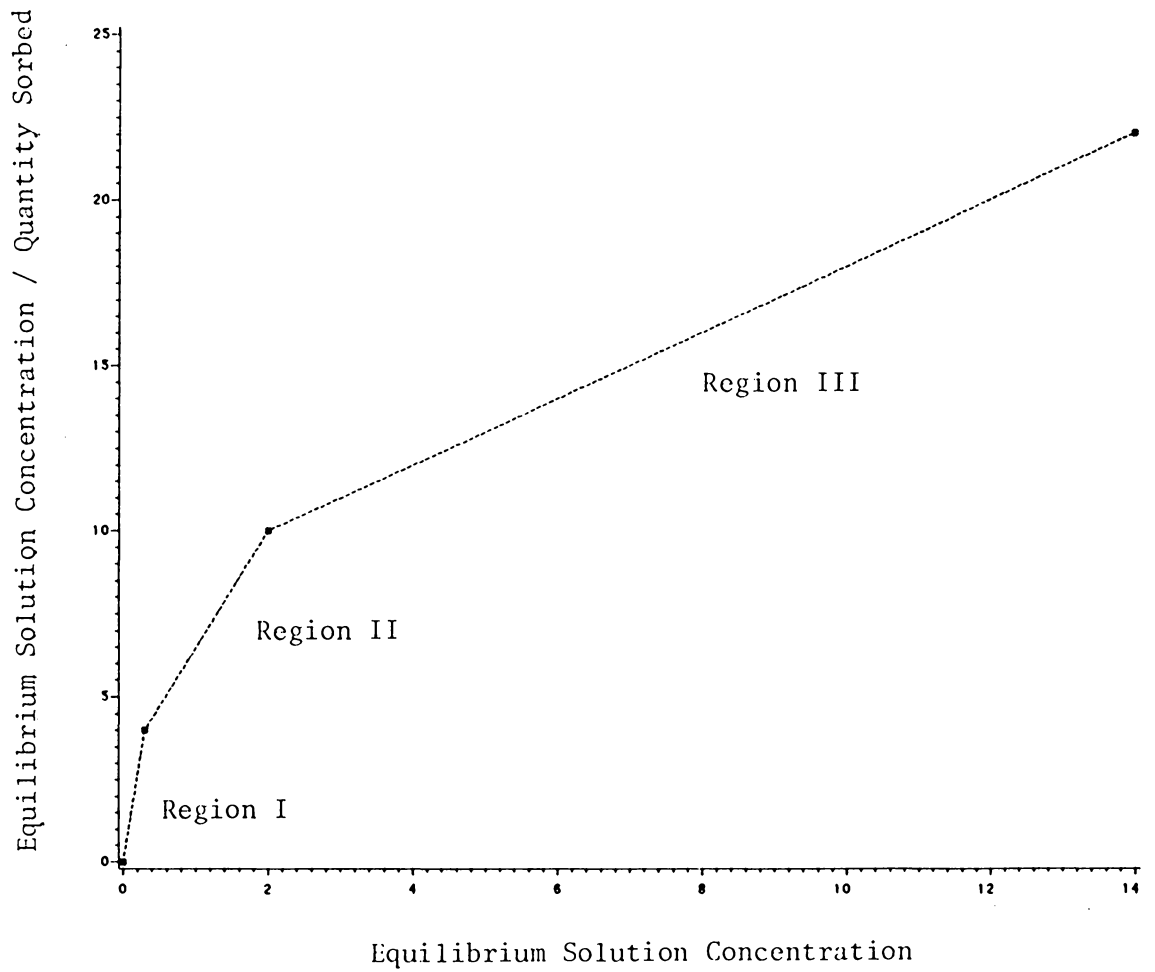


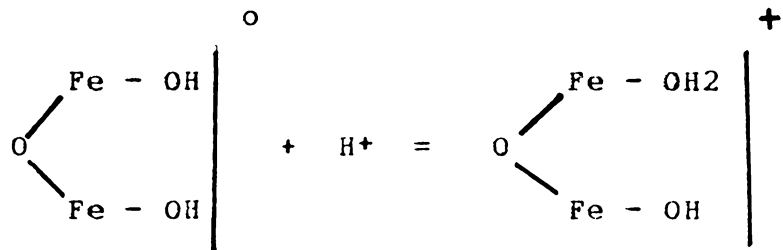
Figure 2. Typical Langmuir equation depicting three linear ranges of phosphorus sorption.



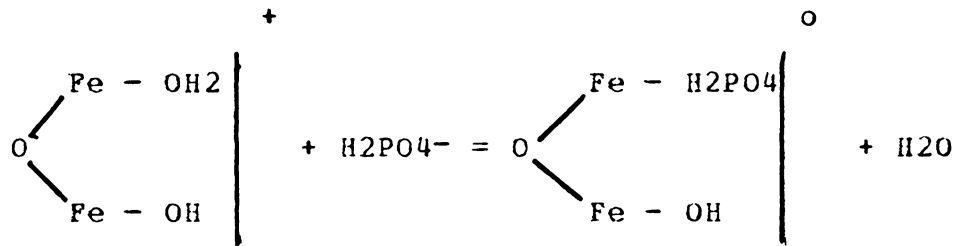
Adsorption at Regions I, II, and III (Rapid Reaction)

Under acidifying conditions, a mineral such as goethite with a relatively neutral surface may undergo a reaction whereby one of the hydroxyl groups becomes protonated (Eq. 1). When P is added to solution the first fixation reaction (Region I) occurs immediately as the phosphate ion with a negative charge displaces the water with a neutral charge (Eq. 2).

Equation 1. Protonation of mineral surface



Equation 2. Adsorption of P at Region I

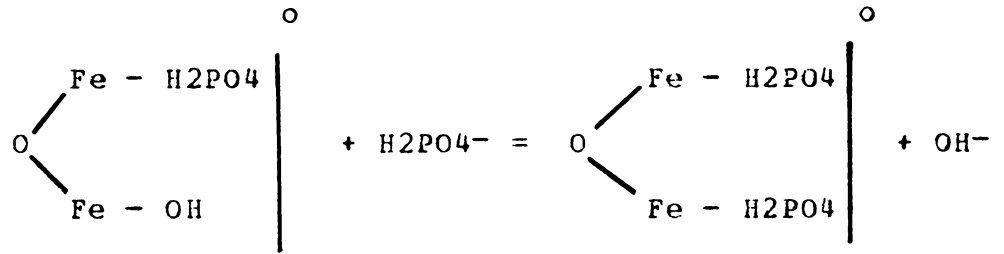


The net effect is the chemisorption of a phosphate ion and a decrease in surface charge by one equivalent for each mole of P adsorbed. There is no change in pH because neither hydroxyls nor hydronium ions are produced.

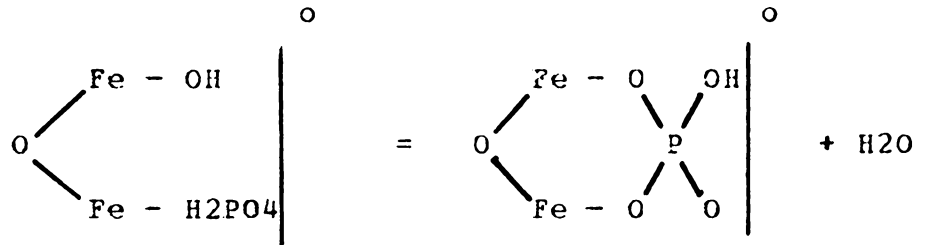
When these protonated sites have exchanged for phosphorus, chemisorption occurs at region II by the ligand exchange method proposed by Hingston et al. (1974) (Eq. 3). Adsorption at region II does not create a surface charge because hydroxyl groups with a negative charge are exchanged for the negative phosphate groups. However, the displacement of these hydroxyls induces the pH change that has been measured.

Other experiments, Parfitt et al. (1975) have determined the existence of a binuclear complex with phosphate at the surface of a ferric gel following addition of a low concentration phosphate solution. This could occur following adsorption at region I via a condensation reaction (Eq. 4).

Equation 3. Adsorption of P at Region II

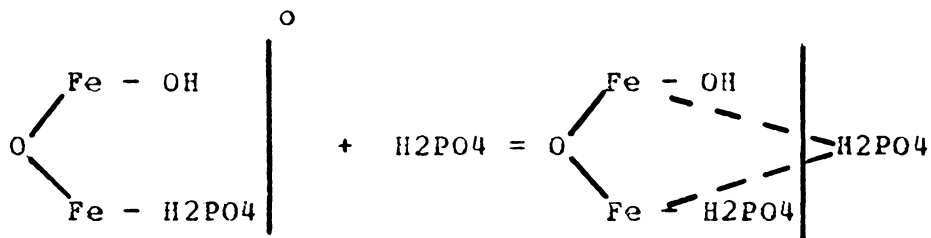


Equation 4. Formation of binuclear complex following P adsorption at Region I.



Sorption in region III (Eq. 5) results in an increased negative surface charge with no pH change. The low K value derived for region III further implies that a weak, more physical type of bonding takes place. This probably results from some small attraction of the complexed Al or Fe for the phosphate following rearrangement of the surface structure.

Equation 5. Physical Adsorption at Region III.



The effect of pH on these adsorption mechanisms is an increase in adsorption as pH decreases from near neutral. As would be expected, this total increase was due to increased sorption in region I alone. An increase in hydronium ions resulted in protonation of more hydroxyls and, therefore, more sites were included in region I at a lower pH. Ryden et al. (1977a) only examined pH down to 6.0. It seems logical that at lower pH values the increased sorption in region I will come at the expense of region II as more hydroxyl groups become water groups for region I sorption.

An increase of ionic strength with NaCl resulted in increased sorption in regions II and III, but region I was unaffected. This is probably due to a decreased ionic double layer which in effect brings the phosphates closer to the surface and makes them more likely to react.

Slow adsorption reaction (occlusion)

It is generally known that P sorption increases with time and this increase is known as the slow rate reaction for adsorption mechanisms. Ryden et al. (1977b) explain that sorption increases with time as phosphates, initially adsorbed at the surface, penetrate deeper into the sesquioxide whose surface sites are then occupied by phosphates from solution. It is important to note that this increased sorption only occurs in amorphous material. The phenomenon did not occur on pure crystalline synthetic goethite. Ryden et al. (1977b) and Parfitt et al. (1977) report that P sorption does not occur on crystalline gibbsite and goethite except at the outermost surfaces unless flaws in the surface are present.

Ryden et al. (1977b) showed that for 24-48 hours after initial P fixation all sorbed P could be extracted with NaOH solution. However, with increased time some of the chemisorbed P diffuses into the hydrous oxide. This occurred on soils, iron oxide gel (100% amorphous), and natural goethite (which contained 7.4% amorphous material as a result of grinding). This P which makes its way beyond the surface is said to be occluded and cannot be extracted with NaOH. A citrate-dithionite bicarbonate (C-DB) combination is needed to extract occluded P. With time, the

amount of fixed P extractable with C-DB increases. Phosphorus associated with the synthetic 100% crystalline goethite was always 100% extractable with NaOH, as no P could diffuse into its highly organized crystalline structure. With time, as P becomes occluded, the total amount of chemisorbed P relative to the amount physically adsorbed increases.

Diffusion into sesquioxides is not the only manner in which occlusion occurs. Any P at a surface (whether adsorbed or precipitated) can become occluded if conditions develop whereby new layers of Fe or Al hydrous oxides are formed on top of the fixed P.

### Adsorption onto layer silicates

The mechanisms of sorption onto clay minerals are not clear and are probably not as important in magnitude as fixation onto sesquioxide surfaces. Part of the confusion dealing with layer silicate fixation is that adsorption often credited to clay particles, was, in fact, due to Fe oxide impurities coating the clay. It is possible that some phosphate is held to clay surfaces by linkage with exchangeable  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  (Pissarides et al, 1968). The adsorption of P was greater on clays saturated with divalent cations than clays with  $\text{K}^+$ ,  $\text{NH}_4^+$ , or  $\text{Na}^+$ .

Rajan and Fox (1975) have proposed two regions of fixation on layer silicates based on binary Langmuir equations derived from isotherms. Adsorption at region I resulted in a release of sulfate and silicate and increased pH. This suggests P was replacing adsorbed silicate, sulfate, and hydroxyl groups. Adsorption in region II occurred at higher phosphorus concentrations and resulted in a sharp increase of silicate but not sulfate, suggesting that the crystal structure was becoming disorganized and that silicates were being replaced. Sample et al. (1980) reported several other instances where destruction of kaolinite at high phosphorus concentrations have occurred.

### Fixation by precipitation

Phosphates in solution, if not adsorbed to an oxide surface, may react with Fe and Al ions in solution and precipitate as discrete particles:  $Al, Fe^{+3} + H_2PO_4^- + 2H_2O = 2H^+ + Al, Fe(OH)_2 \cdot H_2PO_4$ . The precipitation reactions are dependent on the activities of Al and Fe and are more predominant at lower pH's. The products formed are usually very similar to variscite  $Al(OH)_2 \cdot H_2PO_4$ , baranadite  $Al, Fe(OH)_2 \cdot H_2PO_4$ , or strengite  $Fe(OH)_2 \cdot H_2PO_4$ .

Haseman (1950) and Cole and Jackson (1955) offer some of the earlier evidence pertaining to formation of variscite and strengite compounds in acid soil solution. Essentially, these compounds are precipitated out of solution when activities of the involved ions exceed the solubility product values.

Juo and Ellis (1968) as well as others have shown that Al-P and Fe-P precipitate as discrete colloidal particles. Initially, this colloidal material is amorphous, but with time it crystallizes to pure variscite and strengite. The rate of crystallization proceeds much more rapidly for Fe-P. Under autoclave conditions it took Fe-P 12 hours to crystallize to strengite, while it took colloidal Al-P 40 days to form variscite. In a 35 C waterbath, strengite was forming after nine months but the aluminum phosphate was still 100% amorphous.



In their amorphous forms, Fe-P has a much greater surface area than Al-P (27.5 m<sup>2</sup>/g compared to 10.5 m<sup>2</sup>/g) (Juo and Ellis, 1968). Upon crystallization, the surface area of strengite decreased to less than 10% its original surface area (1.98 m<sup>2</sup>/g) while variscite increased to 24.9 m<sup>2</sup>/g. Variscite has a larger surface area because of its irregular surfaces (Juo and Ellis 1968). This means Fe-P has more surface area than Al-P in colloidal form, but after crystallization Al-P has a greater surface area.

The stability of precipitated compounds in solution depends on their solubility constants, the activities of common ions, and the ionic strength of the soil solution. In general, Fe-P and Al-P are less soluble with increasing acidity. Increased activity of Fe and Al from some other non-phosphate soil component will also decrease their solubilities, but an increase in ionic strength from other soil ions will increase the solubility of the P compounds.

Initial deposits of colloidal material are much more soluble than variscite and strengite (Lindsay and Moreno 1960). With time, as crystallization occurs, they become more stable and release of P is less likely. Strengite is more stable than variscite, and it has been observed by many, that with time, the amount of strengite increases at the expense of variscite.

For the most part, the reaction of P with Al and Fe to form colloidal particles is immediate. However, there is a slow rate of reaction via precipitation that occurs as clays (particularly kaolinite) decompose and the released Al or Fe reacts with phosphate (Low and Black, 1947).

Part of the confusion in the literature as to whether or not fixation is occurring by adsorption or precipitation phenomenon results because both processes are so interrelated. Precipitation occurs on the same surfaces as adsorption, especially under acidifying conditions as Al or Fe is released from hydroxyls or hydrous oxides. As soon as the ion leaves the surface, it can combine with a phosphate ion and return to the surface as  $\text{Fe}(\text{OH})_2 \cdot \text{H}_2\text{PO}_4$ , having the same structural formula as the surface layer of P saturated Fe-hydroxide.

Kittrick and Jackson (1955) have electron micrographs showing how Al and Fe oxide surfaces react with a P phase. This experiment occurred before the chemisorption theory was presented (Hingston, 1974; Parfitt, 1975) and they concluded that their photos were direct evidence of variscite and strengite precipitation. They conclude that all P was fixed by a precipitation mechanism, and the P concentration in solution was lower than would be expected by solubility product values due to common ion effects. This may be

partially true but undoubtedly some (if not most) of this fixed P is chemisorbed, and the P concentration in solution is lower than would be expected by solubility product values because adsorbed P is not subject to the solubility product principle.

### Availability of fixed P

Availability of soil P varies according to the form of soil P and is altered by time and environmental conditions. Availability of precipitated phosphorus is governed by the solubility product principle. When a portion of a phosphate mineral dissolves, the availability of the remaining undissolved compound is unchanged; it is still subject to the same solubility product values. However, in the case of non-specifically adsorbed phosphorus, remaining phosphorus becomes more unavailable as some phosphates are removed from the surface. The availability of precipitated P depends on the concentration in solution, while the availability of adsorbed P depends on surface concentrations.

Another trend in the availability of fixed P is a tendency to become less available with time. This results from crystallization or occlusion in the case of precipitated P and occlusion of adsorbed P. Hsu (1965) and others report that freshly precipitated amorphous Al- and Fe-P are moderately available for plant growth. Senewiratne (1961) reports that colloidal Fe-P was 78% as available as soluble P, while crystalline strengite was unavailable for growth. Juo and Ellis (1968) found the amorphous P available for growth, strengite completely unavailable, and variscite only slightly available. They conclude that as

colloids, surface area is not important since Al and Fe forms were equally available while the Fe had a much larger surface area. However, surface area is more important with crystalline minerals. The variscite which was more available had a much larger surface area. Strengite would also be expected to be less available because of its lower solubility. Another factor involved is the rate of crystallization. Many reports that Al-P forms are more available are probably due to the slower conversion of the amorphous form to variscite. This allows the Al-P to remain more soluble longer than Fe-P.

Adsorbed P becomes more unavailable as chemisorption occurs deeper into the structure. The unavailability of this occluded form is evidenced by the required use of a harsh citrate-dithionite solution to extract it. Occlusion of precipitated forms can also occur as hydroxides formed over deposits of individual particles.

The availability of the various forms of soil P depends on environmental conditions. Phosphorus is most available in the pH range 5.5-6.5. In this range, solubilities of variscite and strengite are high and low levels of trivalent Al and Fe prevent readsorption as a precipitate. Fixation by chemisorption decreases as pH increases since a higher OH concentration in solution reduces the extent to which P will

undergo ligand exchange with hydroxyl groups of Al and Fe polymers. As pH's increase above 7.0, P availability is reduced by precipitation and adsorption with Ca compounds.

Oxidation-reduction conditions have an effect on the availability of phosphorus fixed with Fe. Under wet conditions  $Fe^{+3}$  is reduced to  $Fe^{+2}$ . The solubility of strengite is greatly increased and phosphorus enters solution. This will occur under moderate reducing conditions. If the reducing conditions are very strong the iron phosphate will re-precipitate as vivianite.

Mycorrhizae may also affect the availability of certain forms of fixed phosphorus. They reportedly have the ability to extract relatively unavailable forms of phosphorus. This could result from exuded by-products such as oxalic acid. According to Nagarajah et al. (1970) oxalate can displace phosphate from the surfaces of gibbsite and goethite, allowing the root to take up the phosphorus.

## Phosphorus Extractions

### Introduction to soil extractants

Soil extractions are often performed to determine whether or not a sufficient supply of nutrients exists for plant growth. Phosphorus extractions estimate the small fraction of total soil P available to plants. Bray (1948) suggests that a good soil test should meet three criteria: The extractant should 1) remove all or a proportional part of the available forms of P from soils with varying properties, 2) be quick and accurate, and 3) the amount of P extracted should be correlated with growth and response to P application. The perfect extractant would remove from the soil the same amount of P as would the roots of the plants. Factors affecting the amount of P extracted by a plant include the needs of the plant, characteristics of its root system, status of the soil P and soil moisture and temperature.

### Soil phosphorus characteristics

Several soil P properties affecting the P supply to plants include the soil solution concentration (intensity), the amount of P in the soil (quantity), and the relationship between quantity and intensity (buffering capacity). Phosphorus in the soil solid phase that is in equilibrium with the soil solution is known as labile P. Labile P can readily replenish the P absorbed by roots from solution. Non-labile P such as occluded or organic forms cannot readily replace solution P. The buffering capacity is essentially an indicator of labile P levels.

To gain a complete picture of a soil's P status, intensity, quantity, and buffering capacity must be examined. Humphreys and Pritchett (1971) found that these three parameters accounted for 85% of the variability in foliar P levels for slash pine fertilized on the Coastal Plain. The solution intensity affects the diffusion rate of P to the plant root. In solutions with higher P levels, a greater concentration gradient develops around the rooting zone as P is absorbed by the plant. Consequently, the depleted zone will be replenished more rapidly by other P in solution. Soils with a high buffering capacity require larger additions or deletions of soil P to affect a change in intensity levels.



Unfortunately, there is no single soil test that can evaluate all three parameters. Weak extracts such as water or neutral salt solution tend to estimate the intensity factor. Stronger extractants such as acids, bases, or complexing agents extract phosphorus representing the quantity term. Kamprath and Watson (1980) suggest that the single most effective soil test would be a strong extractant that measures the portion of soil P controlling the soil solution levels (labile P).

### Mechanisms of P extraction

Many different solutions have been used to extract P. The amount of P removed depends on the form of P in the soil and the extraction mechanisms of the active ions involved. As mentioned before, most P is fixed in some combined form with Al, Fe, or Ca, although some P exists either in solution, on exchange sites, or in combination with other minor soil constituents such as manganese. Within a given soil P fraction, there are often numerous compounds differing in their availability to plants and solubility in various reagents. For example, among the Fe-P forms, freshly precipitated colloidal material is very available to plants whereas crystalline strengite is almost completely unavailable (Ballard 1973).

There are basically four reaction types by which P can be extracted from the solid phase of a soil system (Kamprath and Watson 1980):

a) Dissolution with acids. The hydronium ion at a pH between 2 and 3 is especially effective at dissolving Ca-P releasing the P into solution. As pH decreases, P adsorbed onto Al and Fe hydroxides is released as these polymers are broken down into smaller units.

Acids used as extractants can be classified as either strong acids (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) or weak acids (citric,

lactic, acetic, oxalic). Russell and Prescott (1916) discovered that weak acids such as citric and oxalic extracted more P than equivalent concentrations of strong acids, such as HCl or HNO<sub>3</sub>. Furthermore, with the strong acids, more P was extracted in ten minutes than 24 hours. This results from refixation of extracted P which is greater for strong acids. At low pH's more trivalent Al and Fe is available to form a precipitate with P in solution that had originally been in a Ca-P or adsorbed form. This reactive aluminum comes from the breakdown of aluminum hydroxy polymers and the crystal lattice of clays. Once the P is refixed from solution as an Al-P precipitate, its solubility is dictated by the solubility product principle and it will not return to solution unless the pH is increased.

b) Dissolution with bases. An increase in OH<sup>-</sup> concentration will result in a release of sorbed P for several reasons. Dissolution of P minerals such as variscite and strengite increases in accordance with the solubility product principle as pH rises. With more hydroxyls in solution, some of the chemisorbed P will undergo exchange with OH groups and be released to solution. When the hydroxide concentration is great enough, P can also be released from break down of organic compounds.

c) Anion replacement. Anions such as acetate, citrate, lactate, bicarbonate and sulfate can displace phosphates that are adsorbed on the surfaces of  $\text{CaCO}_3$  or sesquioxides. These anions are often present when extracting with weak acids and probably are more important in the extraction process of acid soils than the hydronium ion with which they are associated. Their presence on the surfaces of hydrated aluminum and iron oxides reduces re-adsorption of displaced P.

Ballard (1973) reported that bicarbonate ions extract P in the order  $\text{Al-P} > \text{Fe-P} > \text{Ca-P}$  and that acetate ions extract somewhat more calcium phosphate in the order  $\text{Al-P} > \text{Ca-P} > \text{Fe-P}$ . Kurtz et al. (1946) concur and report that the bicarbonate ion is more effective at extracting P from acid soils than the acetate ion. However, the differences could be due to a pH effect rather than selectiveness of the various anions. The acetate solutions with a pH of 4.8 would not be as effective at dissolving precipitated Al-P and Fe-P as would the sodium bicarbonate solution at a pH of 8.5. In addition, the higher hydronium activity in the acetate solutions would more readily dissolve calcium phosphates and could lead one to the impression that acetate ions can more readily displace adsorbed P from calcium compounds than the bicarbonate ion.

d) Complexing of cations. The flouride ion complexes strongly with Al releasing P fixed as Al-P. With decreasing pH, the flouride ion becomes less specific and begins to extract Fe-P. Organic ions, such as citrate and lactate can also complex with Al ions (Kamprath and Watson, 1980).

### Classification of soil test extractants

Numerous solutions have been used to extract soil nutrients. These can be classified into one of several categories based upon the mechanisms of extraction involved.

a) Dilute concentrations of weak acids. One of the earliest solutions used was that proposed by Dyer (1894). He theorized that a good estimate of available nutrients could be attained by extracting with a solution of the same pH as root sap, which he calculated to be equivalent to a 1% citric acid solution. Dilute citric acid was a popular extractant through the 1920's (Breland and Sierra, 1962). Acetic acid buffered to pH 4.8 with ammonium acetate is another weak acid commonly used. As mentioned earlier, the organic anions involved in these solutions act to release P by complexing with binding cations or displacing P from adsorption sites.

b) Dilute concentrations of strong acids. Truog (1920) introduced the use of 0.002 N  $H_2SO_4$  solution buffered to pH 3.0 with ammonium sulfate. The most commonly used soil extractant in the Southeast is the North Carolina double acid extract, 0.05 N HCl + 0.025 N  $H_2SO_4$ , reported by Mehlich (1953). The pH of this extract is about 1.3. These strong acid extractants are especially effective at removing P from the Ca-P fraction. On soils recently fertilized with

GRP, the double acid extractant overestimates available P by readily dissolving the fertilizer compound which would normally dissolve only very slowly and become available to plants over a long period of time (Ballard, 1975; Moschler et al (1970).

c) Dilute acids with a complexing agent. Bray and Kurtz (1945) report using two different solutions which have come to be called the Bray 1, 0.025 N HCl + 0.03 N NH<sub>4</sub>F, and the Bray 2, 0.1 N HCl + 0.03 N NH<sub>4</sub>F. These solutions not only extract P from the Ca-P fractions, but also remove much of the Al-P. The low pH of the solution tends to break up Al and Fe hydroxyl polymers, releasing adsorbed P. Before this released P can be refixed by precipitation with trivalent Al, the Al<sup>+3</sup> is complexed with the fluoride ions.

Mehlich (1978) reported a new extractant, 0.2 N NH<sub>4</sub>Cl + 0.2 N HOAc + 0.15 N NH<sub>4</sub>F + 0.012 N HCl, which is being used in the North Carolina State Soil Testing Laboratory. This new solution has come to be known as the new Mehlich extractant, and continually extracts more nutrients than the double acid method (Lea et al. 1980). This solution seems to make use of weak acids, strong acids, and complexing agents. The major role of the weak acids in this case is probably to provide organic ions which prevent reabsorption of P extracted by the other components of the extractant.

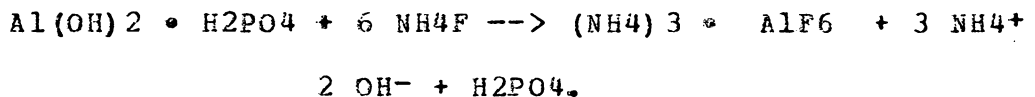
d) Buffered alkaline solutions. Olsen (1954) developed an alkaline extraction, 0.5 N NaHCO<sub>3</sub> buffered to pH 8.5, which utilizes the bicarbonate ion. This extractant effectively removed Al-P and Fe-P. The Olsen method was originally intended for use on calcareous soils because acid extracts overestimated available P by dissolving Ca-P compounds that were not available to plants.



### Phosphorus fractionation

Chang and Jackson (1956) originated, and Peterson and Corey (1966) modified, a fractionation scheme to separate all the soil P into its various forms. The procedure is based on the selective response of each P fraction to various extractants and involves the systematic extraction of a single soil sample with a number of reagents each designed to remove a specific form of P. The theory on which the P fractionation method was designed hinges on the assumption that variscite, strengite, and apatite are the predominant forms of Al-P, Fe-P, and Ca-P in the system.

Solution and loosely bound P is removed first with a neutral extracting solution, namely 1 N NH<sub>4</sub>Cl. This initial step also removes extractable Ca<sup>+2</sup> and Al<sup>+3</sup> from the soil and reduces the likelihood of re-fixation of extracted P in later steps. Aluminum-phosphates are removed by extraction with 0.5 N NH<sub>4</sub>F adjusted to a pH 8.2 by the following reaction:



The pH of the solution is raised to 8.2 to prevent extraction of Fe-P. Iron-P is removed in the third step with 0.1 N NaOH:  $\text{Fe(OH)}_2 \cdot \text{H}_2\text{PO}_4 + \text{NaOH} \rightarrow \text{Fe(OH)}_3 + \text{Na}^+ +$

H<sub>2</sub>PO<sub>4</sub>. This extractant is not specific for Fe-P but will also remove Al-P if present; however, it is assumed that all Al-P was removed by NH<sub>4</sub>F. Reductant P, that which is bound in iron oxide concretions, is removed through an involved sodium dithionite-sodium citrate extraction. The dithionite is a strong reducing agent and converts Fe to the ferrous form. The sodium citrate is a strong complexer with Fe<sup>+2</sup> and binds with the Fe releasing P. Once these Fe coatings are dissolved, occluded P which was buried underneath is extracted with NaOH. This occluded P can also be separated into its Al and Fe components by using an NH<sub>4</sub>F solution before NaOH. Finally, Ca-P is removed with a sulfuric acid extractant.

## METHODS AND MATERIALS

### Study Area

This study, initiated in March 1959, was part of a larger project representing a joint effort between the Forestry and Agronomy Departments at Virginia Polytechnic Institute and State University to determine the effect of fertilization and liming of specific soil types on forest production and wood quality. This particular experiment was established under the supervision of the Virginia Agricultural Experiment Station in Orange, Virginia. The study area is located on the Virginia Piedmont near Fredericksburg along Route 624 approximately two miles south of Rhoadsville. The land was provided by Continental Forest Industries, Inc. and Westvaco Corporation donated genetically improved one-year-old loblolly pine seedlings from their Summerville, South Carolina nursery.

Prior to establishment of this fertilization trial, the site supported a mixed hardwood forest. The soil is an eroded Tatum silt loam, classified as a clayey, mixed, thermic Typic Hapludult and is considered one of the more infertile soils in Virginia due to its inherent acidity and

low levels of available nutrients. It has been described as moderately deep and friable without restrictive layers (Moschler et al. 1970). A thorough description of the soil profile is given in Table 2. The study area was nearly level.

Table 2. Profile characteristics of Tatum silt loam in Orange County, Virginia.

Horizon	Depth (cm)	Color	Texture	Structure	Consistence	Gravel or Clay Skins	Boundary	Vegetation
O1	0-1.3							Pine Needles
A1	0-2.5	10YR3/4	1 to sil	fine gr.	friable	quartzite <sup>1</sup>	clear smooth	fine roots matted
A2	2.5-20	10YR5/6	1 to sil	fine gr.	friable	quartzite	clear smooth	many fine roots
B1 <sub>t</sub>	20-35	7.5YR5/8	sil	weak fine sbk	friable	quartzite	clear smooth	fine roots common
B21 <sub>t</sub>	35-51	2.5YR5/6 and 5YR5/8	60% clay estimate	moderate fine sbk	firm, slightly plastic	few patchy clay skins	gradual smooth	occasional fine roots
B22 <sub>t</sub>	51-99	2.5YR4/8	60% clay estimate	moderate fine and moderate sbk	firm, slightly plastic	thin clay skins common occasional fine schist fragment	gradual smooth	occasional fine roots
B3 <sub>t</sub>	99-137	2.5YR streaked w/ yellowish red	sil	weak medium sbk	friable to firm	few medium clay flaws	gradual smooth	
C	137-183	multicolored	breaks easily into silty soil materials, very fine mica common					
R	183	hard hard	sericite schist rock					

si = silt                      gr = granular  
 c = clay                      sbk = subangular blocky  
 l = loam  
 1/ Occasional fine red fragment

### Study Design

The study design was a randomized block design with four replications of nine treatments (Figure 2). Plot size was approximately 80 m<sup>2</sup>. Twenty-five test trees, selected for uniformity in height, were planted in each plot at a spacing of 2.13 meters. In addition, a row of border trees was planted around each plot. Therefore, sample trees from adjacent plots were at least 6.39 meters apart and separated by two rows of buffer trees.

The study was designed to accommodate nine different treatments; however, only six received P and lime applications (Table 3). Lime and fertilizer were broadcast applied at the time of planting unless otherwise noted. Ground dolomitic limestone was applied at a rate of 4.5 T/ha. Two ground rock phosphate (GRP) treatments at 670 and 170 kg P/ha allowed for a comparison of application rates, as well as a comparison with triple superphosphate (TSP) which was also applied at a rate of 170 kg P/ha. TSP and lime were combined at the rates mentioned above to study the possibility of an additive response.

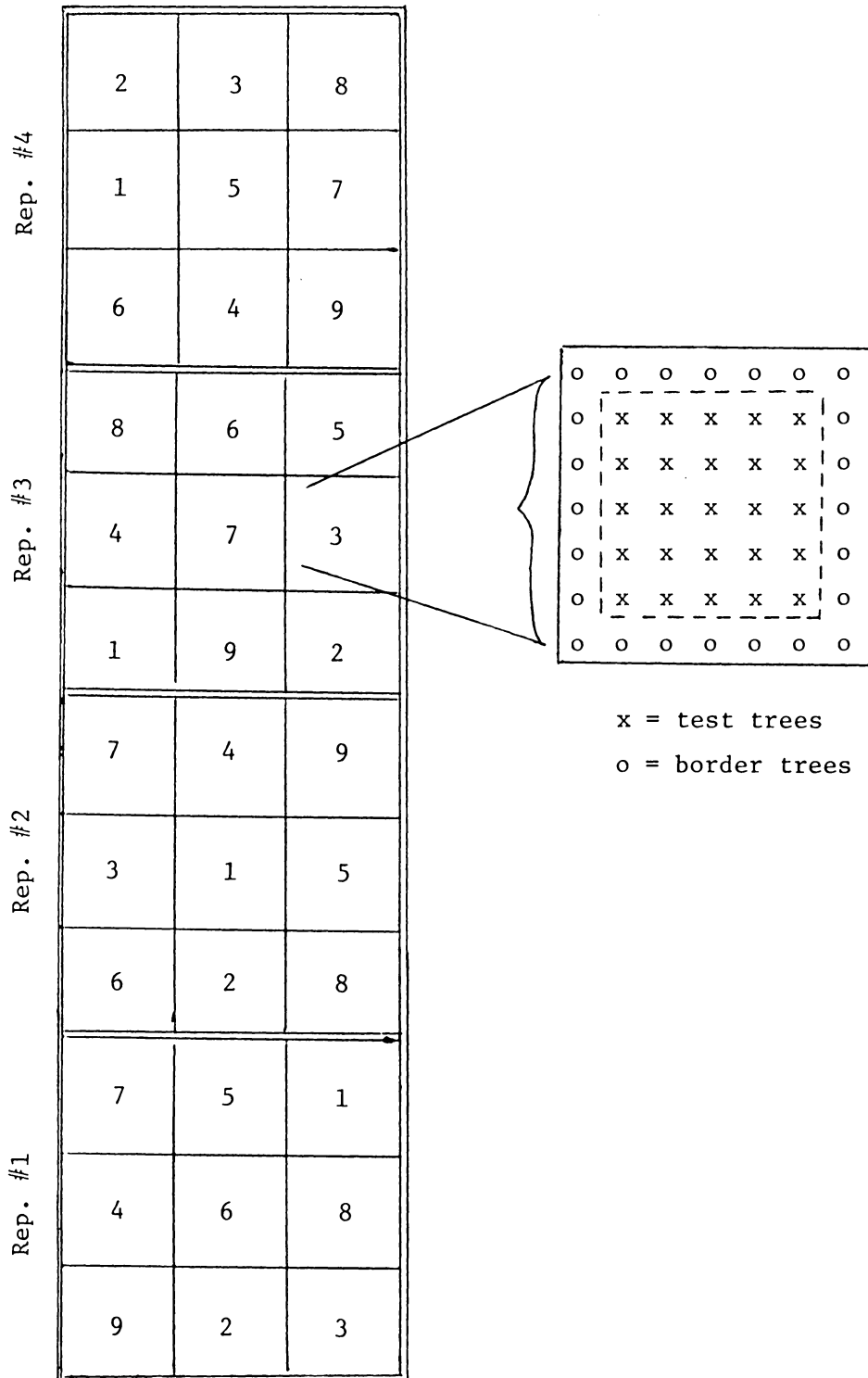


Figure 3. Plot design for loblolly pine fertilization study in Orange County, Virginia.

Table 3. Fertilization treatments applied to loblolly pine in Orange County, Virginia.

Treatment	Source	Phosphorus Rate	Limestone Rate	Nitrogen Rate
		(Applied March 1959)	(Applied March 1959)	(Applied March 1963)
		(kg/ha)	(T/ha)	(kg/ha)
Control	--	--	--	--
Nitrogen	NH <sub>4</sub> NO <sub>3</sub>	--	--	56
Lime	--	--	4.48	--
Low level GRP	30% ground rock phosphate	160	--	--
High level GRP	30% ground rock phosphate	670	--	--
TSP	18% triplesuperphosphate	160	--	--
TSP + lime	18% triplesuperphosphate	160	4.48	--
TSP + lime + N	18% triplesuperphosphate NH <sub>4</sub> NO <sub>3</sub>	160	4.48	56
TSP + lime + N	18% triplesuperphosphate NH <sub>4</sub> NO <sub>3</sub>	160	4.48	56



To increase experimental flexibility, the original plan included two control treatments and three TSP plus lime plots. These spare treatments were established so that additional treatments could be superimposed at a later time. At age four, 56 kg N/ha as ammonium nitrate was added to a replication of control and TSP plus lime plots.

Although nine treatments were originally established (Table 2), this study was evaluated based only on six different P and/or lime treatments, since no effects on growth or foliar levels were evident due to the limited N treatment. Therefore, analysis of the study includes eight replications for the control, twelve replications for the TSP lime treatment, and four replications for all others.

Following tree planting, hardwood sprouts were eliminated by hand each year until they no longer competed for light. However, a severe infestation of fireweed (Erechtites hieracifolia) during the first few years was not controlled. This species was especially prevalent on the plots receiving TSP. Trees were sprayed the first three years with DDT to prevent tip moth injury.

### Field Procedures

In 1979, at age 20, the Virginia Division of Forestry, with help from the Virginia Agricultural Experiment Station in Orange, measured total height, diameter and crown condition. Since a severe ice storm damaged many tops that winter, the length of the broken tops was added to tree height. When the broken top could not be found or measured, total height was estimated.

Loblolly pine foliage was collected in early September 1980, from four or five codominant or dominant trees at the center of each plot. All of the most recent fully elongated needles including fascicle sheaths from the south side of the top third of the crown were collected.

The surface soil (A horizon) was sampled to 20 cm at 5 cm intervals. An additional sample representing the B1 horizon was taken at 20-35 cm. Each sample consisted of a composite of 50 subsamples.

### Laboratory Procedures

Foliage samples were dried at 65 C and ground in a Wiley mill to pass a 20 mesh screen.

Total foliar nitrogen was determined using standard micro Kjehldal techniques (Bremner, 1965) by the Virginia Soil Testing Lab at VPI&SU.

Phosphorus, K, Ca, and Mg were extracted with 10 ml of 6 N HCl from 0.5 g of tissue following ignition in a muffle furnace at 450 C for 10 hours. The Murphy-Riley ascorbic acid technique (Watanbe and Olsen, 1965) was used to analyze the extracts for P, and cation levels were determined using an atomic adsorption spectrophotometer. Each tissue sample was analyzed in triplicate for P and cations.

Soil samples were air dried and crushed through a 2 mm sieve then extracted in duplicate for available P, Ca, K, Mg, Fe, and Al with the double-acid Mehlich, (1953) and the new Mehlich (Mehlich, 1978) solutions; Soil extracts were analyzed with the same procedures used for the tissue analyses, and Fe and Al were also determined via atomic adsorption spectrophotometry; Soil pH was measured with a glass electrode in the supernatant of a 1:1 soil-water mixture with an Orion Ionalyzer; Total P was determined on duplicate samples by perchloric acid digestion according to Sommers and Nelson (1972).

A modified Change and Jackson P fractionation as described by Peterson and Corey (1966) was performed on all soil samples. The reductant and occluded steps were omitted. Phosphorus in all fractionation extracts was determined by the ascorbic acid method described above. When P in the  $\text{NH}_4\text{F}$  extracts was analyzed, a 0.8 M boric acid solution was used instead of water to prevent interference of the  $\text{F}^-$  ion with color development.

Phosphorus adsorption isotherms were derived for each soil by equilibrating five gram soil samples in 0.01 N  $\text{CaCl}_2$  solutions ranging from 0-200 ppm P.

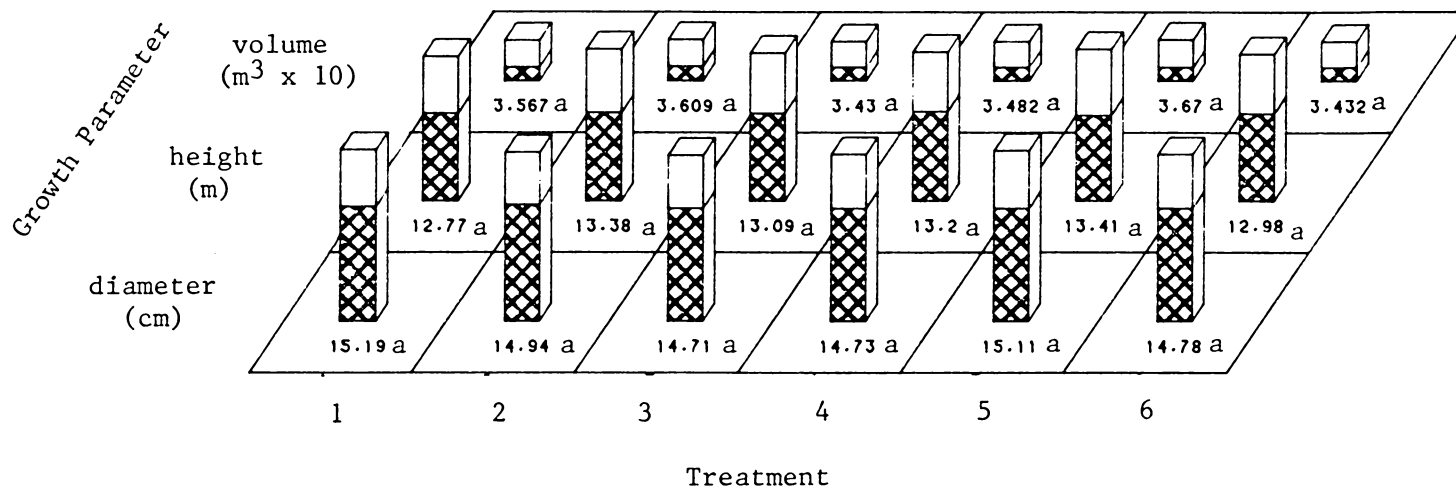
Total soil acidity was determined from duplicate samples by potentiometric titration of 2 g of soil extracted with 1 N  $\text{KCl}$ .

## RESULTS

### Treatment Effects On Tree Growth

Twenty years after establishment of the study, the loblolly pine plantation consisted primarily of pulpwood and small, sawtimber sized trees and demonstrated no growth response to treatment (Figure 4). In addition to the 20 year measurements, growth from age 10 to 20 in terms of height, diameter, volume, and percent survival was examined to evaluate the possibility that some treatments may have had delayed effects, but no differences were apparent.

The average height of dominant trees in the stand was approximately 14.9 meters (49 feet). Overall, average tree height was 13.1 meters (43 feet) with a diameter of 14.9 cm (6 inches) and a volume of 0.353 m<sup>3</sup> (12.5 ft<sup>3</sup> outside bark diameter). Average survival was almost exactly 50% (Figure 5) leaving approximately 1500 trees per hectare (600/acre) to produce a total tree volume of about 530 m<sup>3</sup>/ha (7478 ft<sup>3</sup>/acre), and a basal area of 11.0 m<sup>2</sup>/ha (118 ft<sup>2</sup>/acre).



LEGEND

▨ 10 years

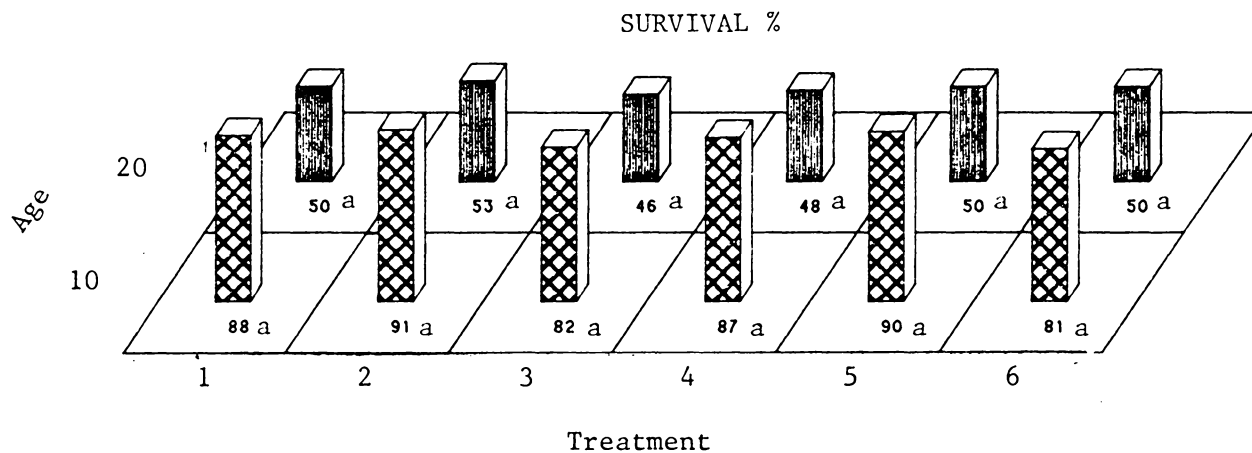
□ 20 years

1 = control  
 2 = high rate GRP (670 kg P/ha)  
 3 = low rate GRP (160 kg P/ha)

4 = TSP (160 kg P/ha)  
 5 = TSP + lime (160 kg P + 4.48 T lime/ha)  
 6 = lime (4.48 T lime/ha)

Values within a row followed by the same letters are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 4. Average tree height, diameter, and volume by treatment at ages 10 and 20 for loblolly pine fertilization study in Orange County, Virginia.



TREATMENT LEGEND

- |                                 |  |
|---------------------------------|--|
| 1 = control                     | 4 = TSP (160 kg P/ha)                      |
| 2 = high rate GRP (670 kg P/ha) | 5 = TSP + lime (160 kg P + 4.48 T lime/ha) |
| 3 = low rate GRP (160 kg P/ha)  | 6 = lime (4.48 T lime/ha)                  |

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 5. Percent survival by treatment at age 10 and 20 for loblolly pine fertilization study in Orange County, Virginia.

## Foliar Analysis

### Nitrogen

Foliar levels at stand ages 1, 10, and 20 are presented for N, P, K, Ca, and Mg in Table 4. No treatment differences occurred with respect to foliar N levels at any age. The average N content decreased with stand development to an average value of 1.12% at age 20.

### Phosphorus

Although P and lime application had no impact on growth, these amendments affected the uptake of soil P as evidenced by foliar P levels which were significantly higher on fertilized plots (Table 4). The highest foliar levels at age 20 (0.134%) occurred where GRP was applied at the high rate of 670 kg P/ha. Application of 160 kg P/ha as GRP resulted in foliar levels (0.122%) which were higher than the TSP treatment (0.111%). Where lime was applied in conjunction with TSP, foliar levels were slightly higher than TSP alone (0.115%), but where lime was applied without P, foliar levels (0.099%) were somewhat lower than the control. Control trees had a foliar concentration of 0.105% P, which is somewhat above the commonly accepted critical level of 0.1% P. At ages 1 and 10, all P treatments had significantly higher foliar P levels than the control. At



Table 4. Foliar nutrient levels at age 1, 10, and 20 by treatment at various ages for loblolly pine fertilization study in Orange County, Virginia.

Treatment	Nutrients														
	N			P			K			Ca			Mg		
	Ages			Ages			Ages			Ages			Ages		
	1	10	20	1	10	20	1	10	20	1	10	20	1	10	20
	----- (%) -----														
Control	1.68a <sup>1</sup>	1.17a	1.13a	.148b	.107b	.105cd	.71a	.44a	.66a	.24a	.13a	.15a	.05a	.08b	.10b
High rate GRP (670 kg P/ha)	1.17a	1.16a	1.12a	.180a	.129a	.134a	.73a	.47a	.70a	.29a	.14a	.15a	.06a	.07b	.09bc
Low rate GRP (160 kg P/ha)	1.71a	1.22a	1.12a	.180a	.134a	.122ab	.70a	.45a	.68a	.23a	.13a	.14a	.04a	.08b	.09bc
TSP (160 kg P/ha)	1.66a	1.16a	1.12a	.190a	.128a	.111bc	.73ab	.46a	.69a	.25a	.15a	.15a	.06a	.07b	.08c
TSP + lime (160 kg P) (4.48 T/ha)	1.51a	1.16a	1.11a	.17ab	.129a	.115b	.63b	.44a	.62a	.26a	.15a	.14a	.06a	.11a	.11a
lime (4.48 T/ha)	1.64a	1.16a	1.14a	.145b	.106b	.099d	.67ab	.45a	.65a	.27a	.14a	.16a	.07a	.10a	.11a

<sup>1</sup>values within a column followed by the same letter are not significantly different ( $\alpha=0.05$ ) according to Duncan's Multiple Range Test.

age 20, foliar levels of all P treatments were still significantly greater, except for the TSP treatment without lime.

#### Cations (K,Ca,Mg)

There were no treatment effects on K or Ca foliar levels after 20 years. Average foliar levels were approximately 0.67% K and 0.15% Ca. However, foliar Mg levels of limed plots (0.11%) were significantly greater than on unlimed soils. The lowest Mg level occurred where TSP was applied without lime (0.08%) and was significantly lower than the control (0.10%).

## Soil Analysis

### Soil pH

Average A horizon soil pH for each treatment at various years is presented in Table 5. The average A horizon soil pH under the stand has decreased during the past 20 years (Table 5). At time of plantation establishment, the average A horizon (0-20 cm) pH was about 4.5 and decreased to 4.1 in control plots after 20 years. The upper A horizon (0-10 cm) is more acidic (pH 3.9) than the lower half (pH 4.3), after 20 years (Figures 6 and 7).

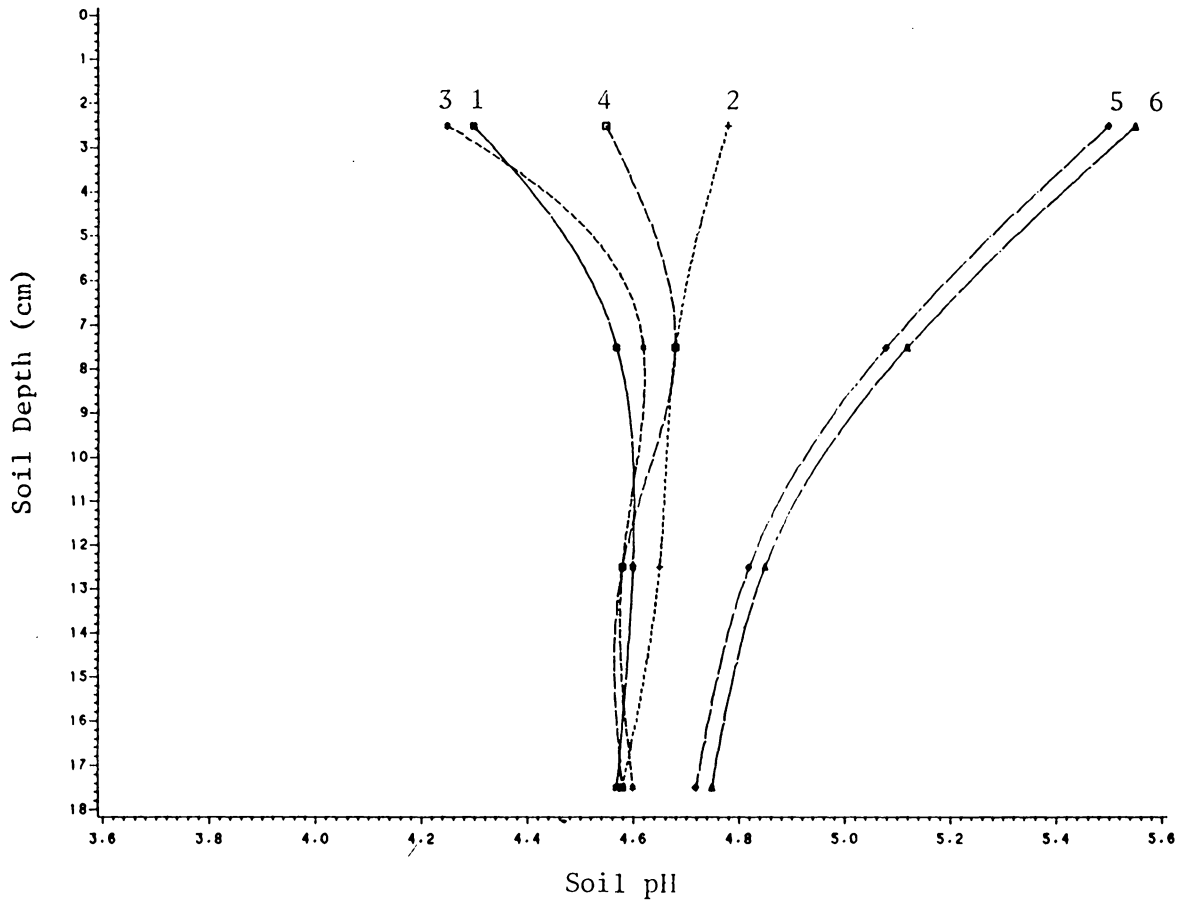
Liming resulted in a significantly higher pH through the B horizon even after 20 years. Limed plots with and without P had virtually the same pH throughout the profile, and in all cases were significantly greater than the unlimed plots. Average A horizon pH for limed plots was 4.9 compared to 4.1 on control plots at age 20.

Phosphorus fertilization also increased soil pH but not as much as liming (Table 5). Ground rock phosphate at 670 kg P/ha produced a significant increase in average A horizon pH by 0.24 units. Both 160 kg P/ha treatments had virtually the same pH values through the B horizon and are only slightly higher than the control.

Table 5. Average A horizon soil pH levels on Tatum silt loam by treatment at various stand ages for loblolly pine fertilization study in Orange County, Virginia.

Treatment	Soil pH			
	0 yr	2 yr	10 yr	20 yr
Control	4.5a	4.8b	4.5b	4.1b
High rate GRP (670 kg P/ha)	4.5a	4.8b	4.7b	4.3b
Low rate GRP (160 kg P/ha)	4.5a	4.8b	4.6b	4.2b
TSP (160 kg P/ha)	4.5a	4.8b	4.6b	4.2b
TSP + lime (160 kg P + 4.48 T lime/ha)	4.5a	5.4a	5.0a	4.8a
Lime (4.48 T lime/ha)	4.5a	5.2a	5.1a	4.9a

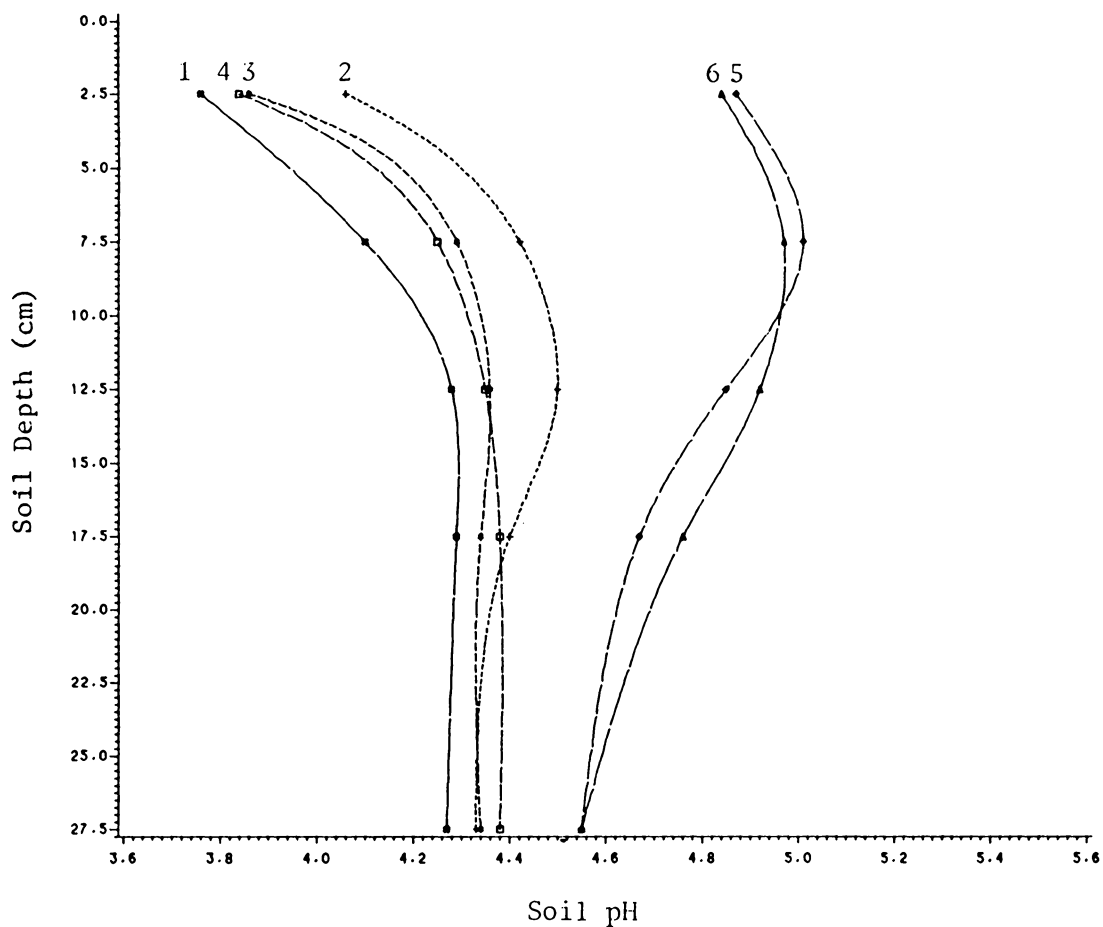
Values within a column followed by the same letter are not significantly different ( $\alpha=0.05$ ) according to Duncan's Multiple Range Test.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◆—◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲—▲ 6 = lime (4.48 T lime/ha)

Figure 6. Soil pH by treatment and depth at stand age 10 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- ◻—◻ 4 = TSP (160 kg P/ha)
- ◊—◊ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲—▲ 6 = lime (4.48 T lime/ha)

Figure 7. Soil pH by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.

Extractable soil K,Ca,Mg

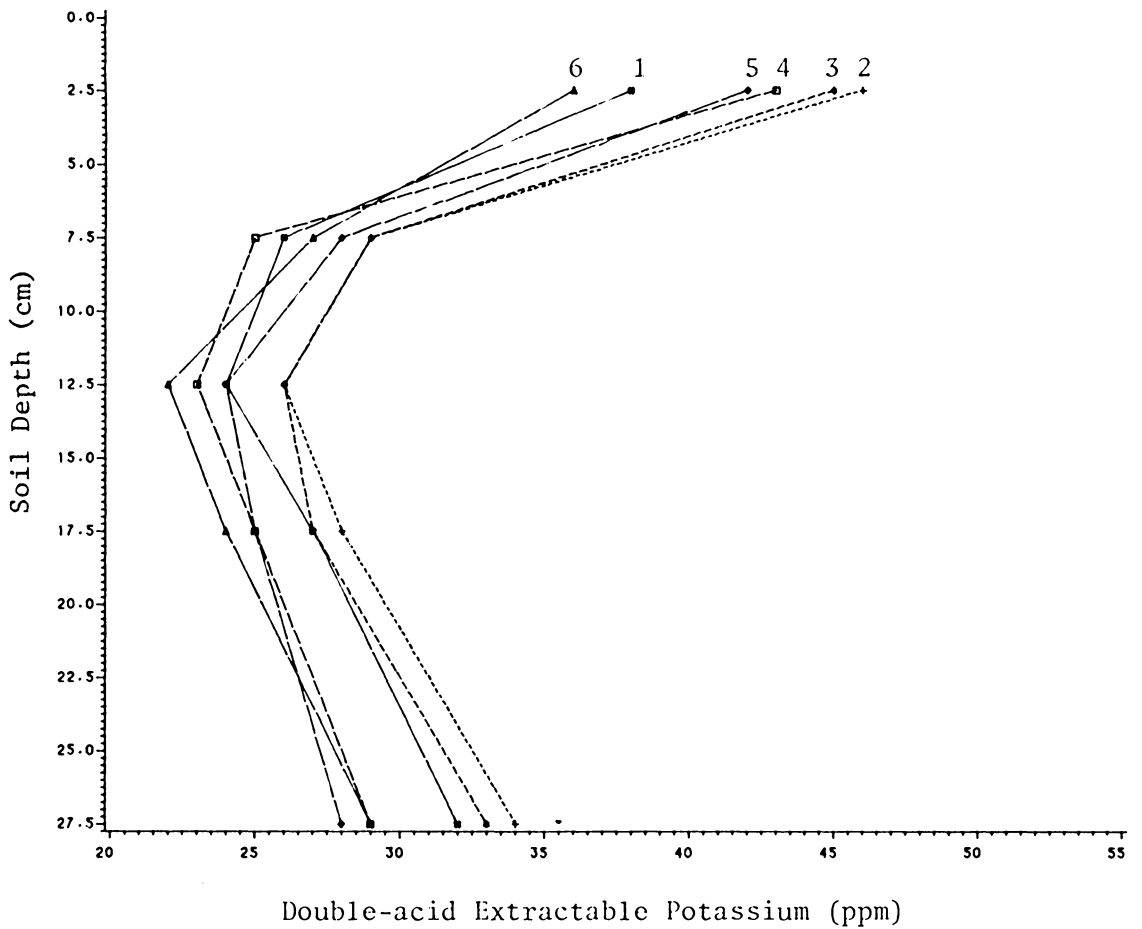
Two different solutions were used to extract K, Ca, and Mg. They were the dilute double acid (0.05 N HCl + 0.025 N H<sub>2</sub>SO<sub>4</sub> and the new Mehlich (0.2 N NH<sub>4</sub>Cl + 0.2 N HOAc + 0.015 N NH<sub>4</sub>F + 0.012 N HCl) solutions. Data for year 20 is presented for each nutrient and extractant by treatment and depth in Figures 8-13. Nutrient levels were generally highest in the surface 5 cm, lowest in the lower portion of the A horizon and intermediate in the B horizon. The Mehlich solution consistently extracted more K, Ca, and Mg than the double acid solution. Average A horizon levels are presented in Figures 14-16 along with double acid extraction values from stand age 10.

Potassium levels were not affected by treatment and generally averaged about 30 ppm double acid extractable K in the A horizon (Figure 14). The greatest treatment effects occurred with respect to Ca levels (Figure 15). Both lime treatments have the highest double acid extractable Ca levels and where TSP accompanied lime, the A horizon Ca values (347 ppm) at stand age 20 are significantly higher than lime alone (244 ppm). The ordering of Ca levels for other treatments generally follows a pattern according to how much Ca was added during treatment: high rate GRP (177 ppm) > low rate GRP (59 ppm) > control (44 ppm) > TSP (43

ppm). Liming also produced a significant increase in extractable Mg levels at stand age 20 (Figure 16). Unlimed soils averaged about 10 ppm Mg whereas limed plots were near 50 ppm double acid extractable Mg.

Table 6 contains correlation data ( $r^2$ ) for the relationships between extractable soil nutrients and soil pH. There was a significant relationship between soil pH and Ca and Mg, but not with K. Table 7 contains data for the relationship between soil nutrients and foliar levels. Extractable soil Mg was the only cation consistently related to foliar levels at all depths.

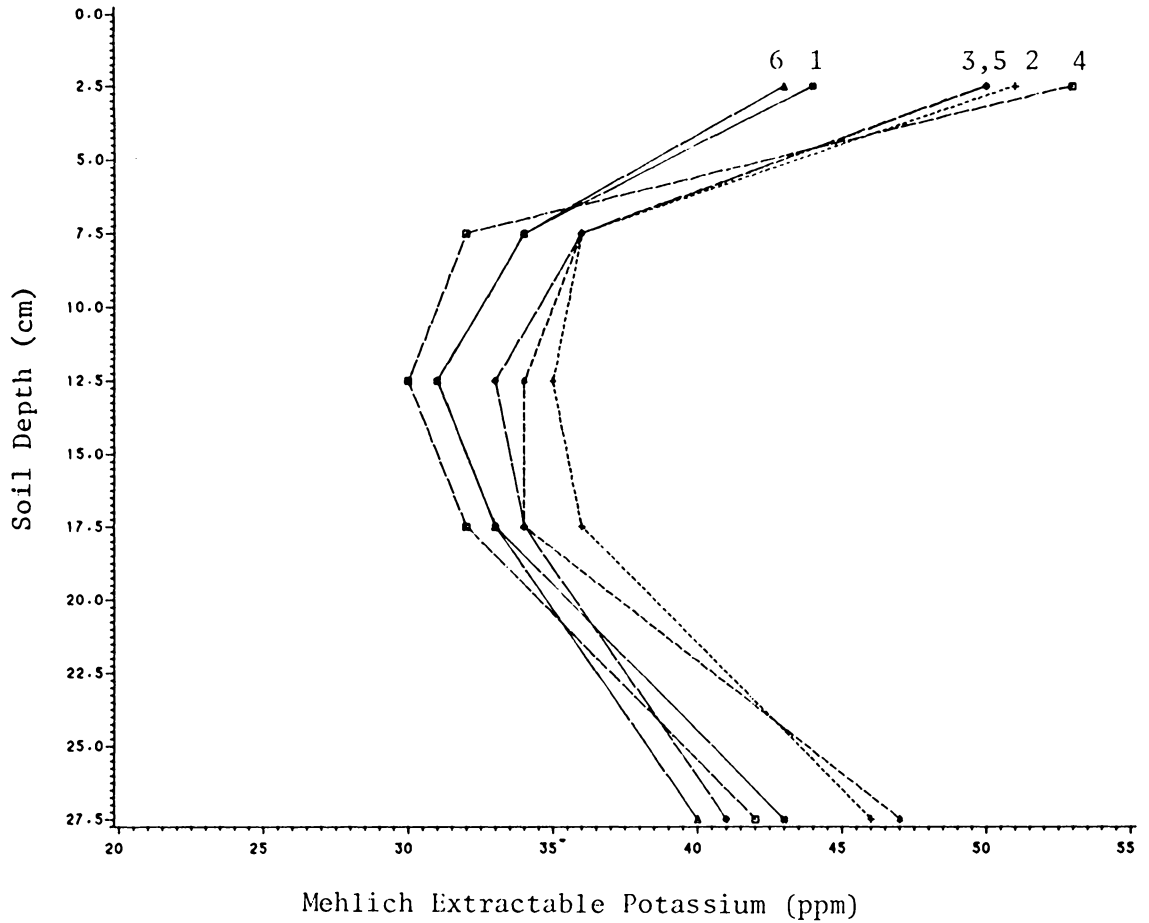




## TREATMENT LEGEND

- ◆◆◆ 1 = control
- 2 = high rate GRP (670 kg P/ha)
- ◆◆◆ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◆◆◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ◆◆◆ 6 = lime (4.48 T lime/ha)

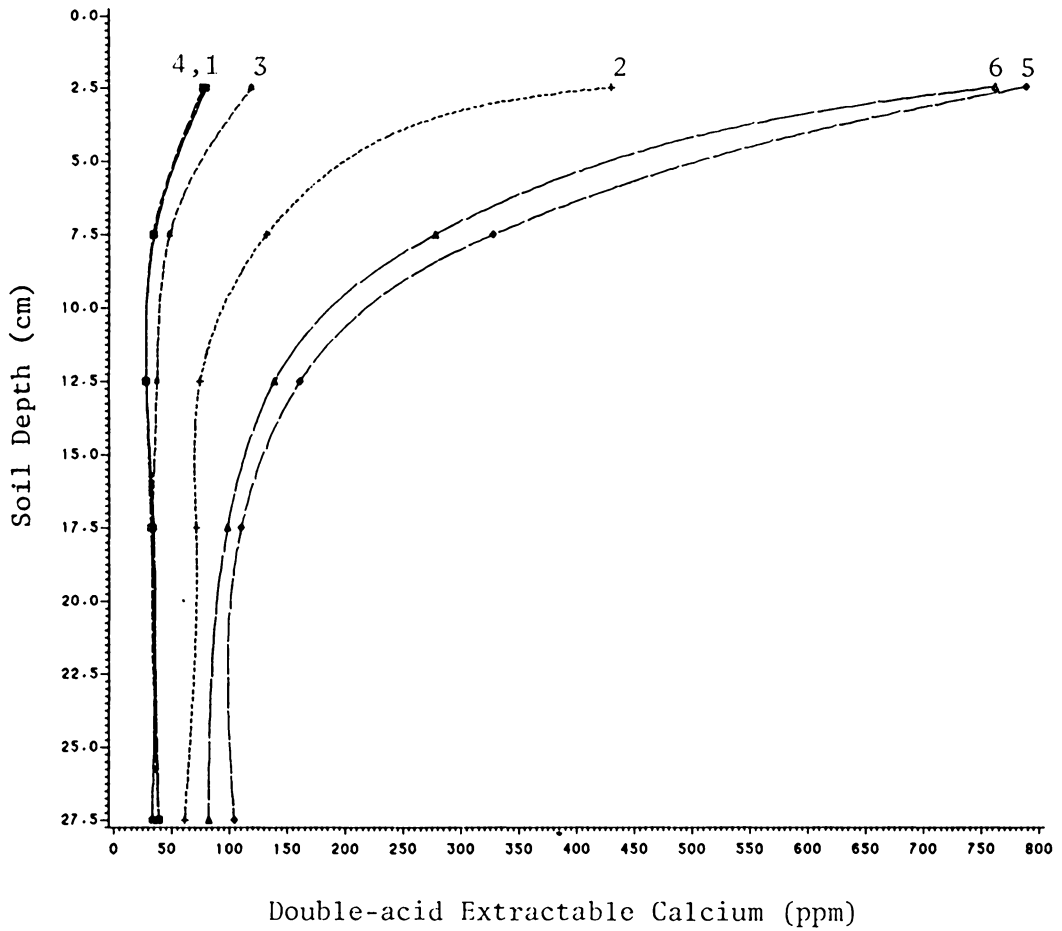
Figure 8. Double-acid extractable soil potassium by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ▲—▲ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▼—▼ 6 = lime (4.48 T lime/ha)

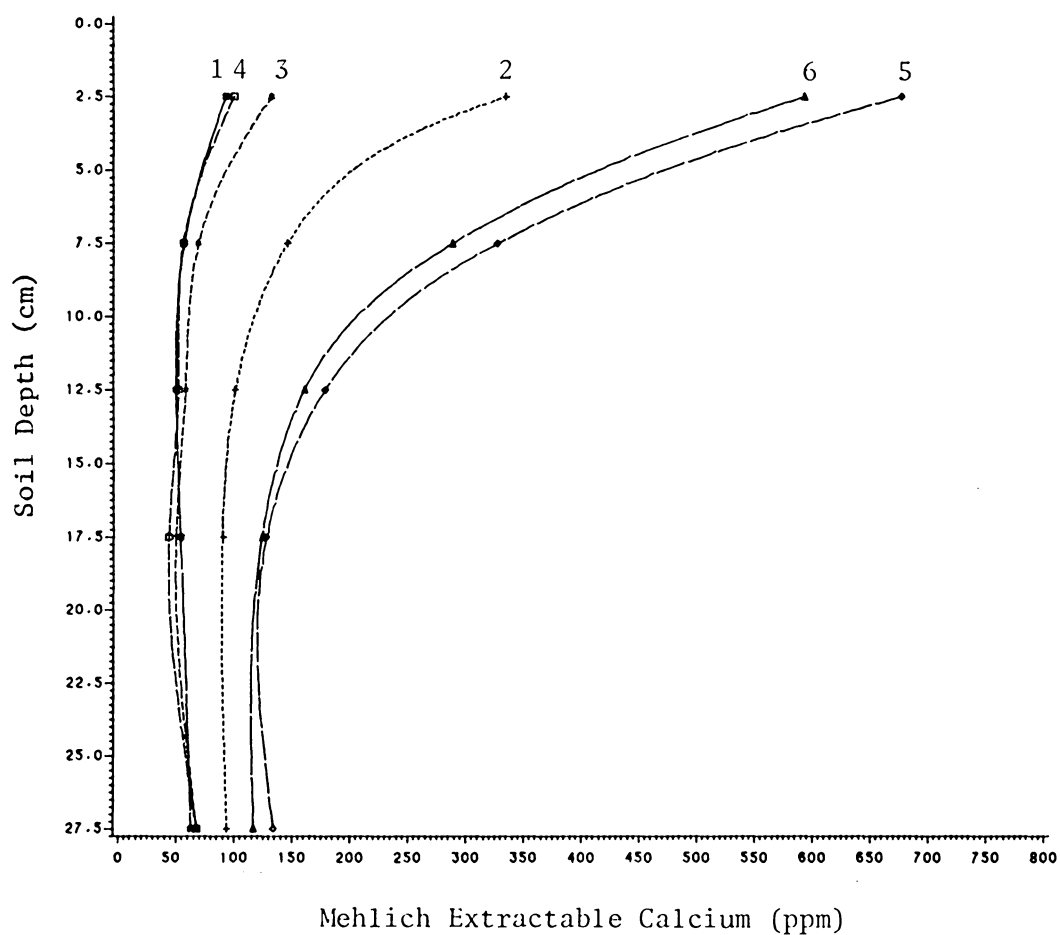
Figure 9. Mehlich extractable soil potassium by treatment and depth of stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◆—◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ◆—◆ 6 = lime (4.48 T lime/ha)

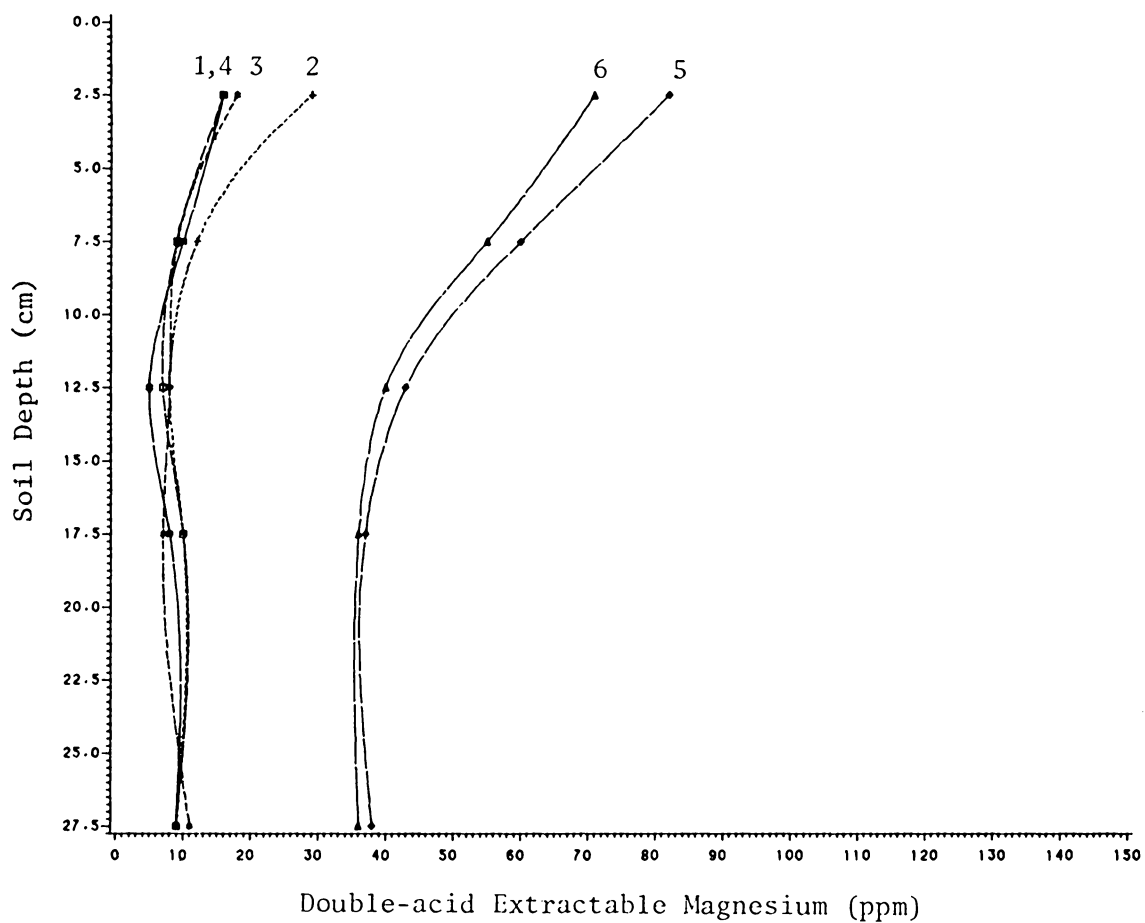
Figure 10. Double-acid extractable soil calcium by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- ⊖—⊖ 4 = TSP (160 kg P/ha)
- ◆—◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ⊖—⊖ 6 = lime (4.48 T lime/ha)

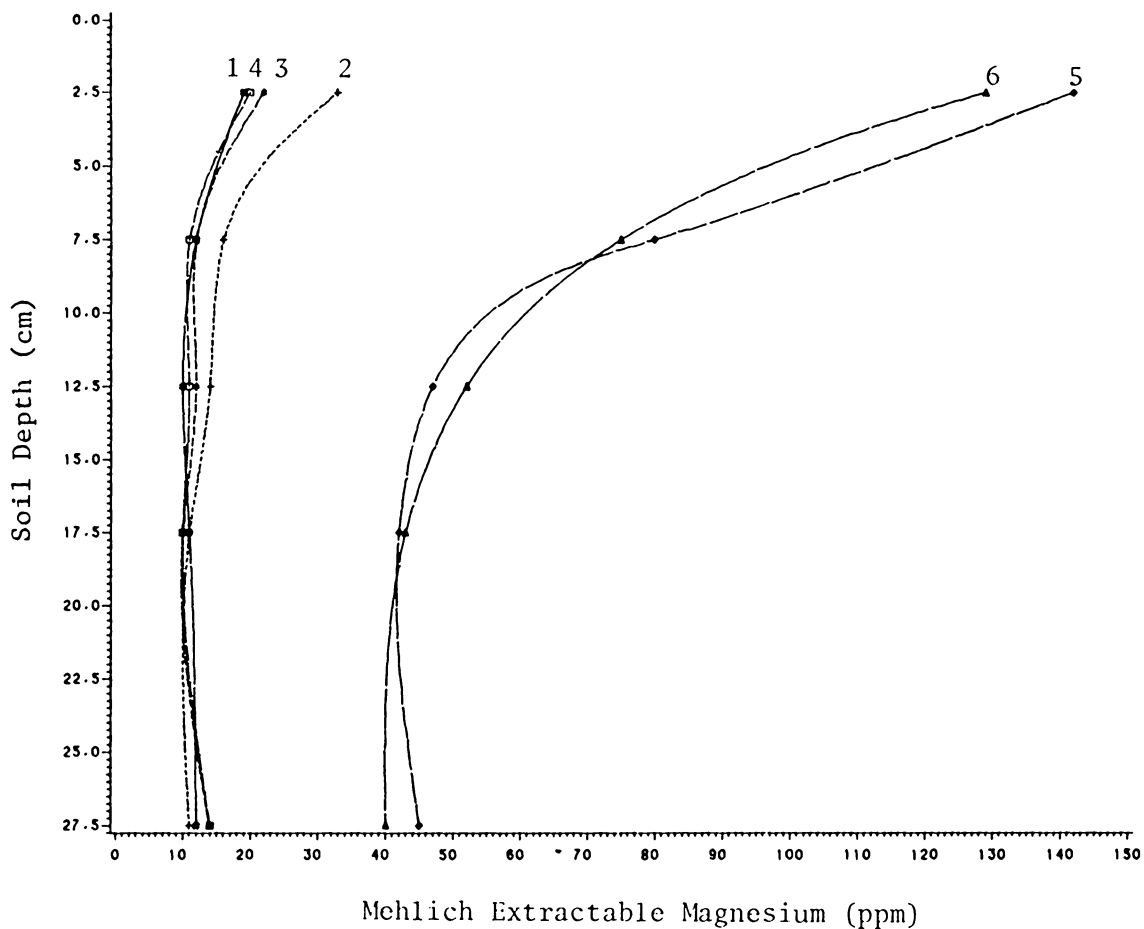
Figure 11. Mehlich extractable soil calcium by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +-+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ▲—▲ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ★—★ 6 = lime (4.48 T lime/ha)

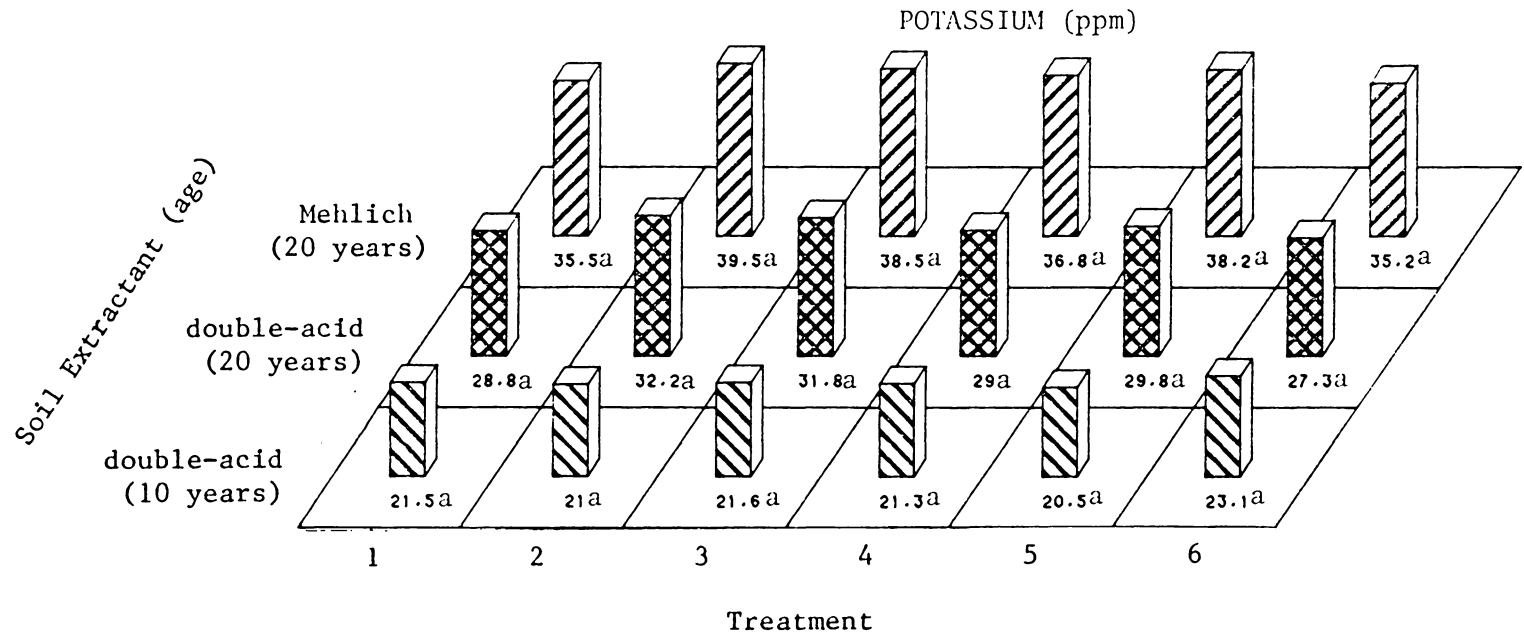
Figure 12. Double-acid extractable soil magnesium by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◊—◊ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲—▲ 6 = lime (4.48 T lime/ha)

Figure 13. Mehlich extractable soil magnesium by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.

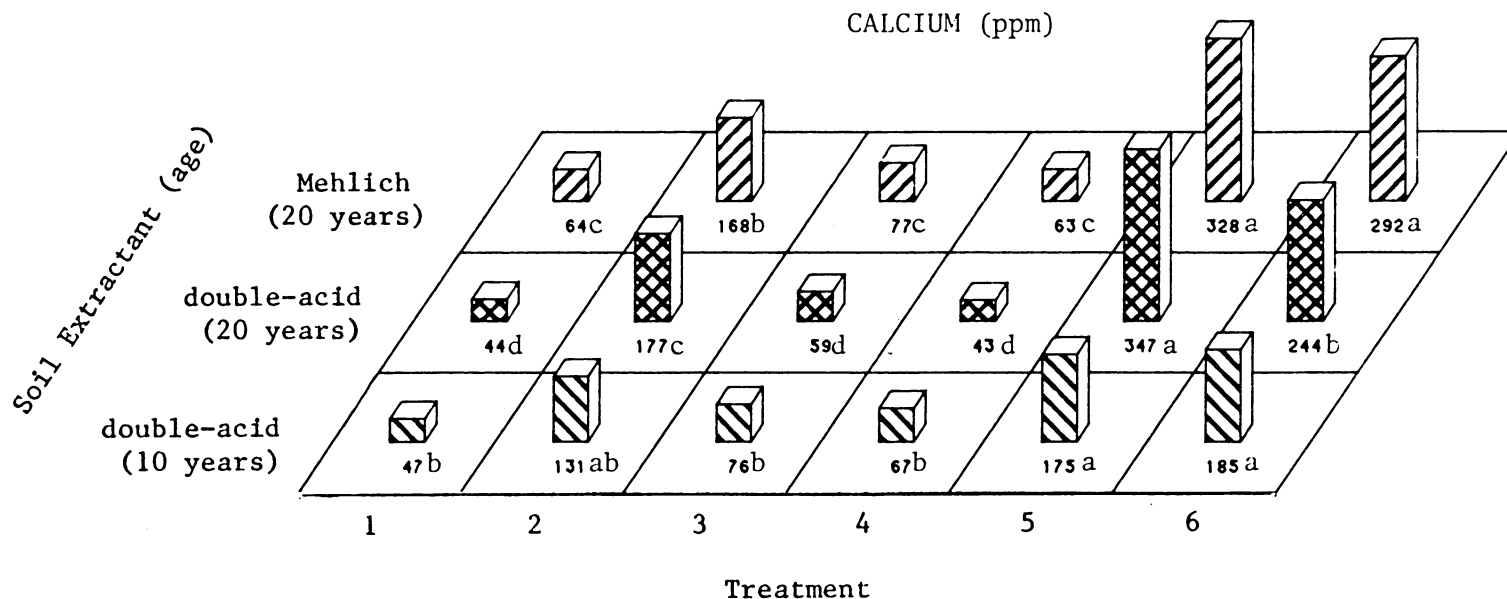


TREATMENT LEGEND

- |                                 |  |
|---------------------------------|--|
| 1 = control                     | 4 = TSP (160 kg P/ha)                      |
| 2 = high rate GRP (670 kg P/ha) | 5 = TSP + lime (160 kg P + 4.48 T lime/ha) |
| 3 = low rate GRP (160 kg P/ha)  | 6 = lime (4.48 T lime/ha)                  |

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 14. Average A horizon extractable potassium as extracted by the double-acid and Mehlich solutions at age 20 and the double-acid solution at age 10 for loblolly pine fertilization study in Orange County, Virginia.



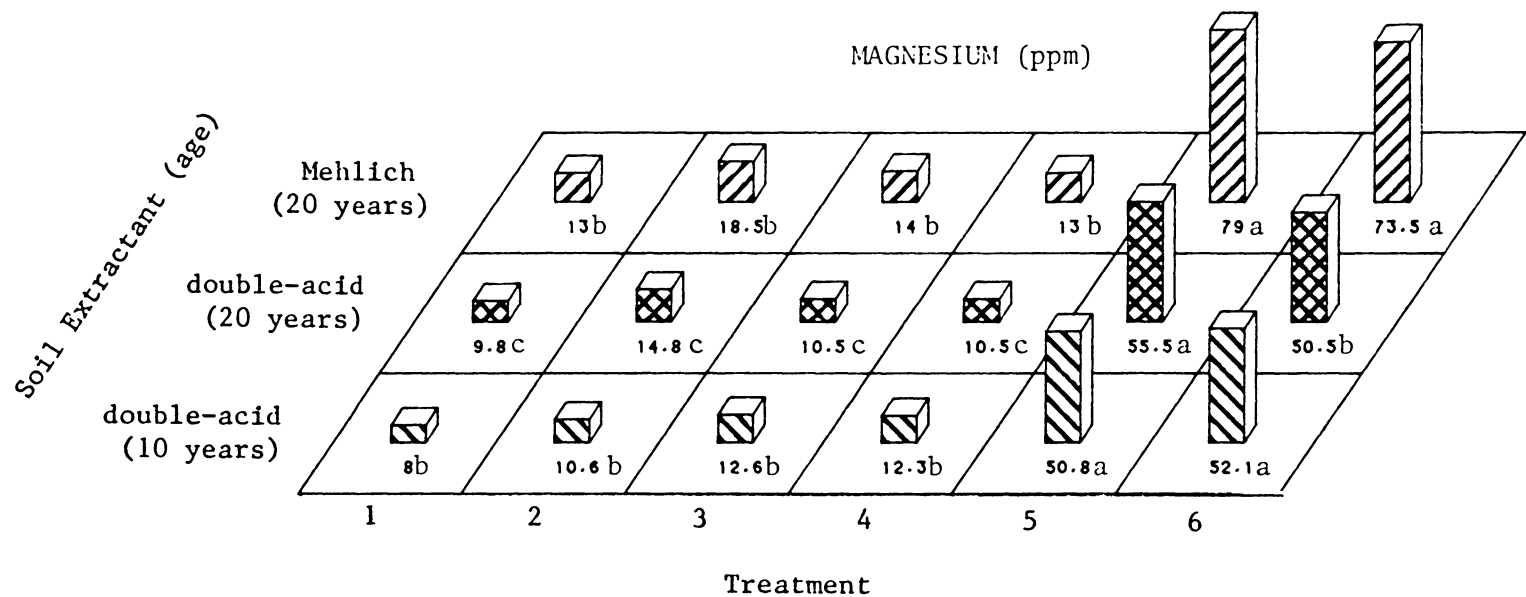
TREATMENT LEGEND

- |                                 |  |
|---------------------------------|--|
| 1 = control                     | 4 = TSP (160 kg P/ha)                      |
| 2 = high rate GRP (670 kg P/ha) | 5 = TSP + lime (160 kg P + 4.48 T lime/ha) |
| 3 = low rate GRP (160 kg P/ha)  | 6 = lime (4.48 T lime/ha)                  |

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 15. Average A horizon extractable calcium as extracted by the double-acid and Mehlich solutions at age 20 and the double-acid solution at age 10 for loblolly pine fertilization study in Orange County, Virginia.





TREATMENT LEGEND

- |                                 |  |
|---------------------------------|--|
| 1 = control                     | 4 = TSP (160 kg P/ha)                      |
| 2 = high rate GRP (670 kg P/ha) | 5 = TSP + lime (160 kg P + 4.48 T lime/ha) |
| 3 = low rate GRP (160 kg P/ha)  | 6 = lime (4.48 T lime/ha)                  |

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 16. Average A horizon extractable magnesium as extracted by the double-acid and Mehlich solutions at age 20 and the double-acid solution at age 10 for loblolly pine fertilization study in Orange County, Virginia.

Table 6. Simple correlation ( $r^2$ ) between pH and double-acid and Mehlich extractable soil nutrients ( $\alpha=0.1$ ) on Tatum silt loam in Orange County, Virginia.

Depth (cm)	Soil Nutrients											
	P		K		Ca		Mg		Fe		Al	
	double acid	Mehlich	double acid	Mehlich	double acid	Mehlich	double acid	Mehlich	double acid	Mehlich	double acid	Mehlich
	----- (r <sup>2</sup> ) -----											
0 - 5	ns	ns	ns	ns	.79	.81	.90	.87	.70	.46	.71	.41
5 - 10	ns	ns	ns	ns	.91	.91	.90	.91	.44	.28	.56	.22
10 - 15	ns	ns	ns	ns	.84	.78	.86	.80	.23	ns	.15	.15
15 - 20	ns	ns	ns	ns	.69	.57	.82	.73	.14	ns	.27	.13
20 - 35	ns	ns	ns	ns	.52	.36	.58	.54	.09	ns	.15	.16
-----												
0 - 10	ns	ns	ns	ns	.85	.88	.92	.92	.64	.45	.70	.45
10 - 20	ns	ns	ns	ns	.80	.72	.87	.79	.20	ns	.21	.20
-----												
0 - 20	ns	ns	ns	ns	.86	.88	.92	.91	.60	.33	.64	.45

Table 7. Simple correlation ( $r^2$ ) between loblolly pine foliar nutrient levels and double-acid and Mehlich extractable soil nutrient levels at various depths ( $\alpha=0.1$ ) of Tatum silt loam in Orange County, Virginia.

Depth (cm)	Soil Nutrients							
	P		K		Ca		Mg	
	double acid	Mehlich	double acid	Mehlich	double acid	Mehlich	double acid	Mehlich
	----- (r <sup>2</sup> ) -----							
0 - 5	.36	.38	.25	.13	.16	.11	.49	.39
5 - 10	.40	.50	ns	ns	.10	.09	.51	.44
10 - 15	.37	.40	ns	ns	ns	ns	.46	.38
15 - 20	.43	.44	ns	ns	ns	ns	.46	.38
20 - 35	.44	.31	ns	.11	ns	ns	.45	.36
-----								
0 - 10	.37	.41	.16	.09	.14	.11	.49	.42
10 - 20	.39	.42	ns	ns	ns	ns	.47	.39
-----								
0 - 20	.38	.43	.08	ns	.13	.10	.49	.42

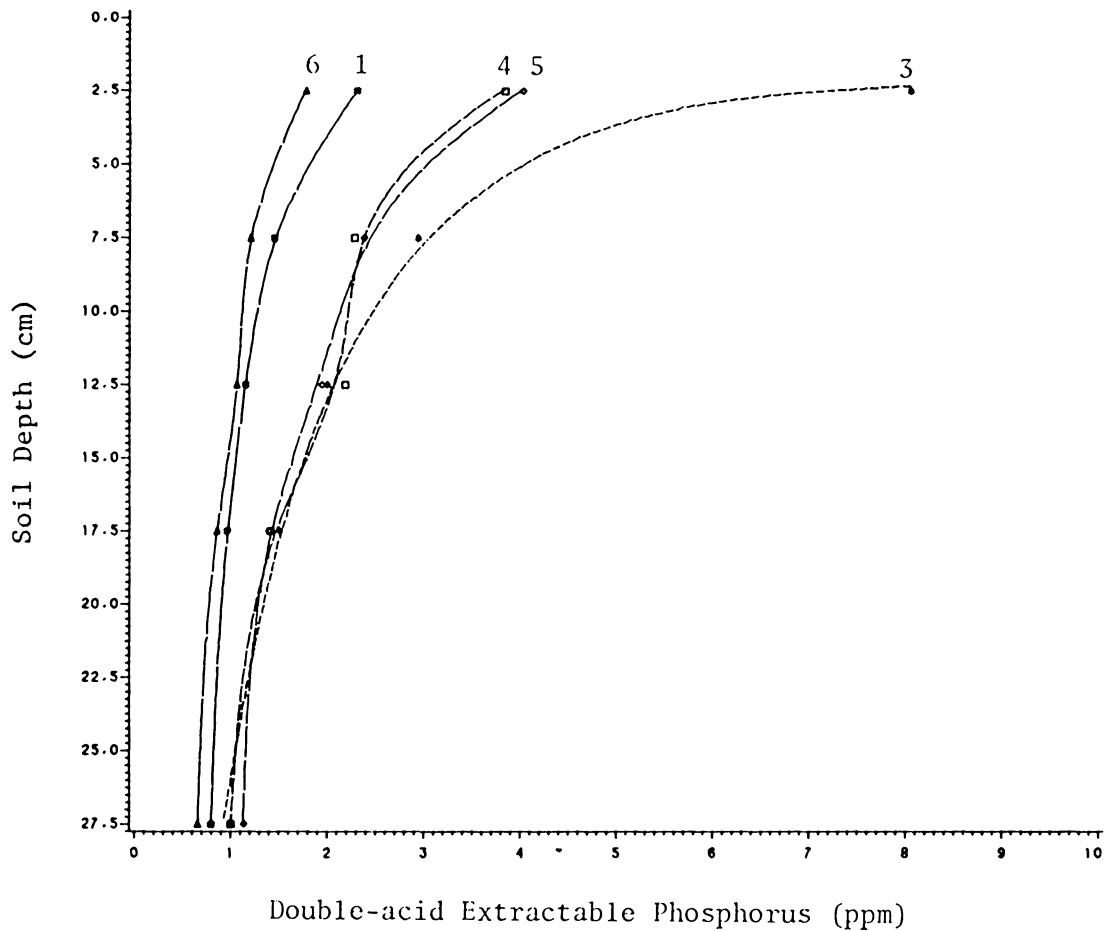
### Extractable P

Figures 17 and 18 contain data for double acid and Mehlich extractable P by depth for all treatments except the high rate GRP application. Since extractable P values were nearly a magnitude higher for this GRP treatment; data by depth for the two extractants is presented in Figure 19. Extractable P is greatest in the surface 5 cm and decreases continually with depth. Mehlich values are greater than double acid except at the surface of GRP treated soils.

Average A horizon soil P levels by each extractant are presented in Figure 20 along with the 10 year double acid values. Extractable soil P levels of the A horizon were significantly affected by treatment (Figure 20). Several treatment differences are significant when A horizon values are compared for double acid extracts at age 20 (Figure 20). Untreated plots had only 1.5 ppm P. The limed plot without TSP had 1.2 ppm P. The only treatments with significantly greater P levels than the control were the GRP plots. The extractable level for the low GRP treatment (3.6 ppm) was significantly higher than all other treatments except the high rate GRP treatment.

There was a significant correlation between extractable P and foliar P at all soil depths for both extractants (Table 7). Based on A horizon values, correlations are

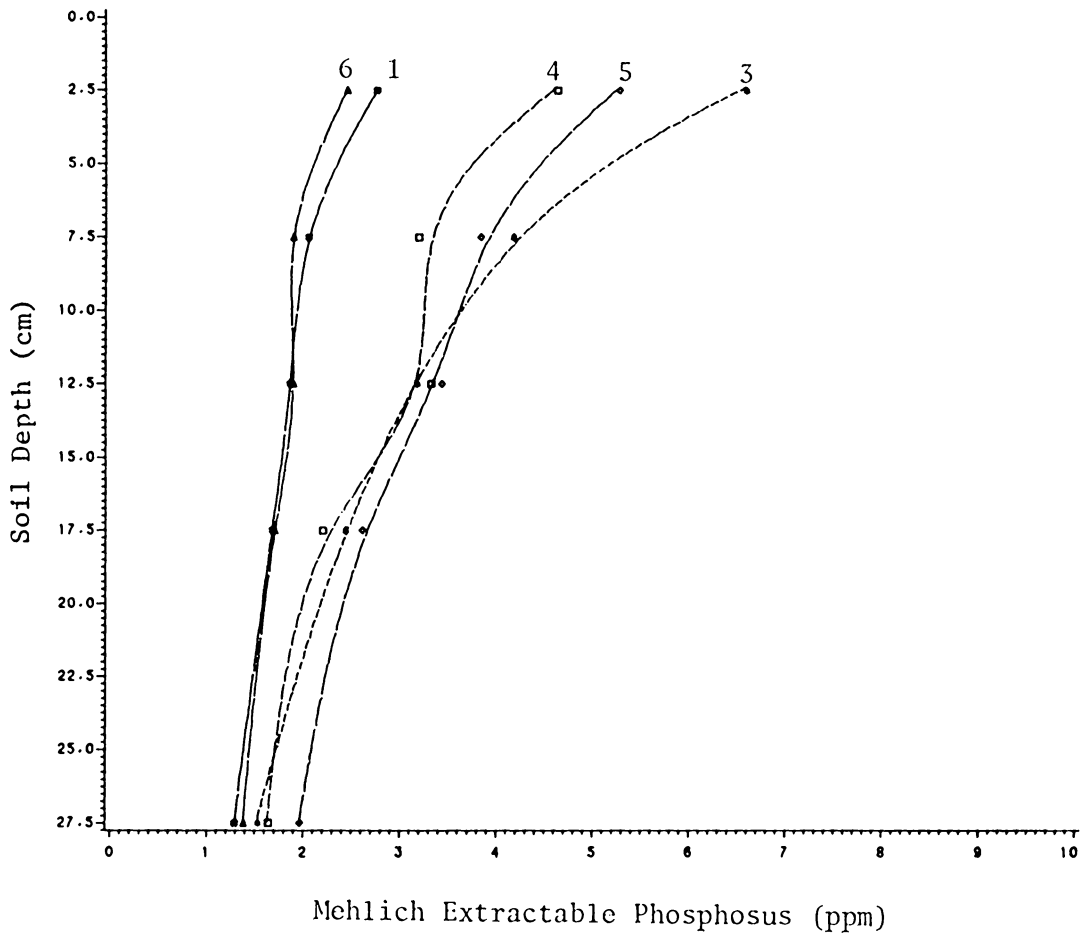
somewhat better for the Mehlich ( $r^2 = .43$ ) than the double acid ( $r^2 = .38$ ). Better correlations were found when high rate GRP plots were not included in the relationship. Figure 21 depicts the relationship between foliar and soil extractable P when high rate GRP plots were excluded.



## TREATMENT LEGEND

- 1 = control
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- ◻—◻ 4 = TSP (160 kg P/ha)
- ◊—◊ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲—▲ 6 = lime (4.48 T lime/ha)

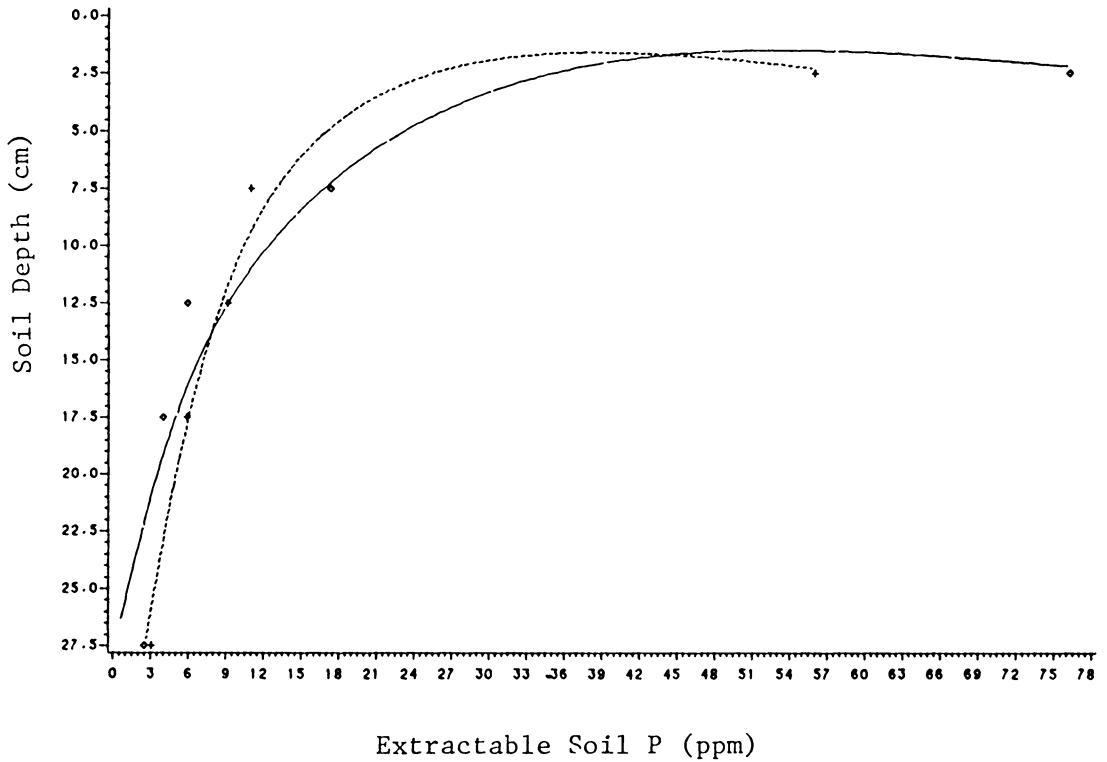
Figure 17. Double-acid extractable soil phosphorus by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia (excluding 670 kg P/ha GRP).



## TREATMENT LEGEND

- 1 = control
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ▲—▲ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ★—★ 6 = lime (4.48 T lime/ha)

Figure 18. Mehlich extractable soil phosphorus by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia (excluding 670 kg P/ha GRP).



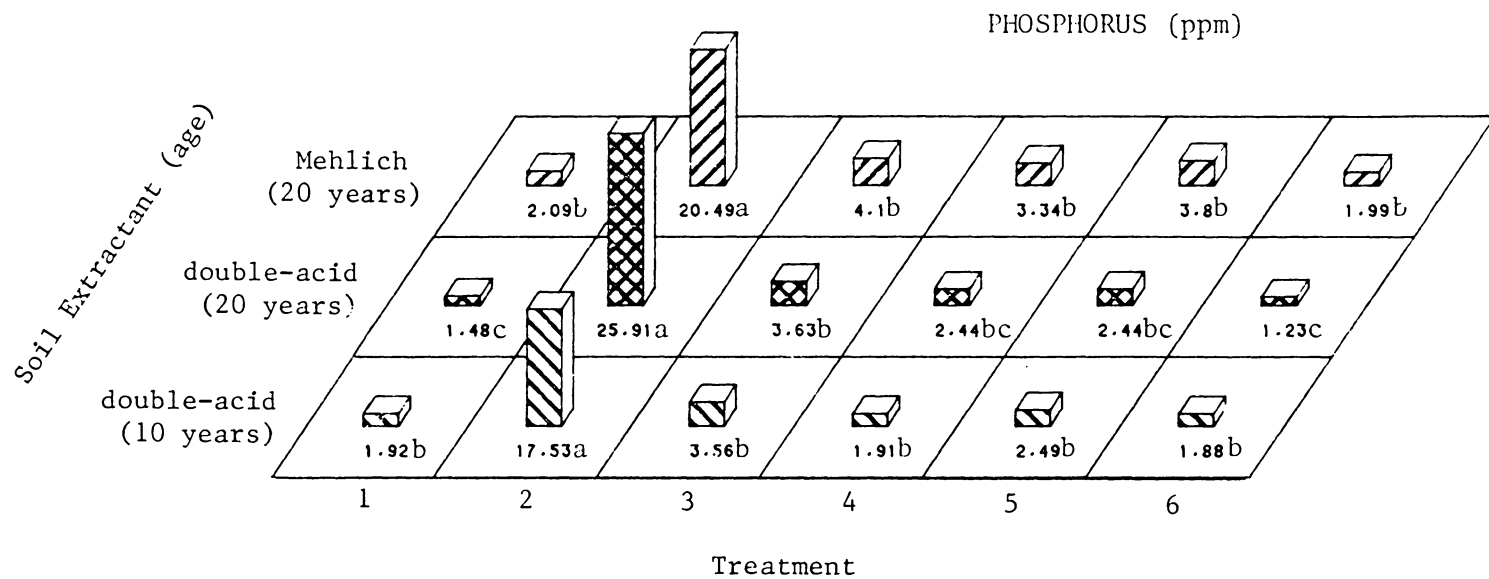
## EXTRACTANT LEGEND

◆◆◆ double-acid

+ + + Mehlich

Figure 19. Double-acid and Mehlich extractable soil phosphorus for the high rate GRP (670 kg P/ha) treatment at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



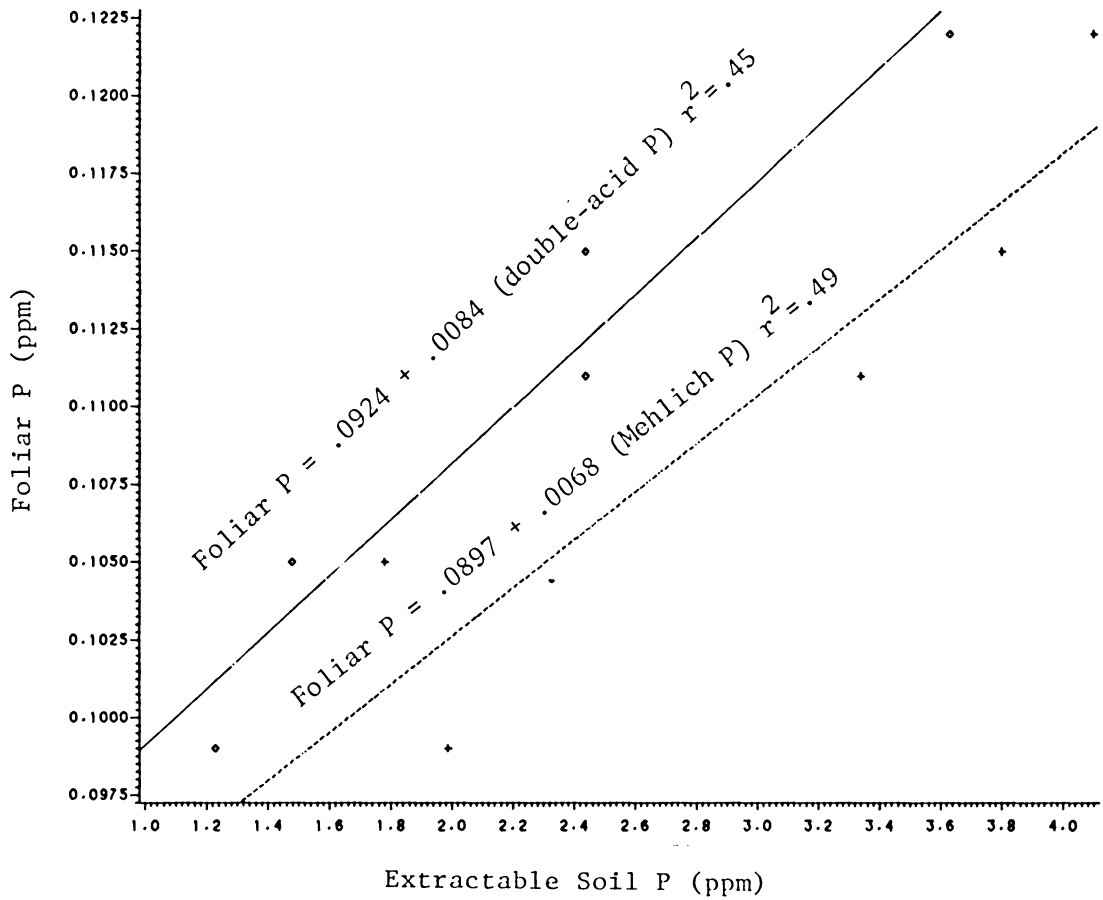


TREATMENT LEGEND

- |                                 |  |
|---------------------------------|--|
| 1 = control                     | 4 = TSP (160 kg P/ha)                      |
| 2 = high rate GRP (670 kg P/ha) | 5 = TSP + lime (160 kg P + 4.48 T lime/ha) |
| 3 = low rate GRP (160 kg P/ha)  | 6 = lime (4.48 T lime/ha)                  |

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 20. Average A horizon extractable phosphorus as extracted by the double-acid and Mehlich solutions at age 20 and the double-acid solution at age 10 for loblolly pine fertilization study in Orange County, Virginia.



## EXTRACTANT LEGEND

◆—◆ double-acid

+--+ Mehlich

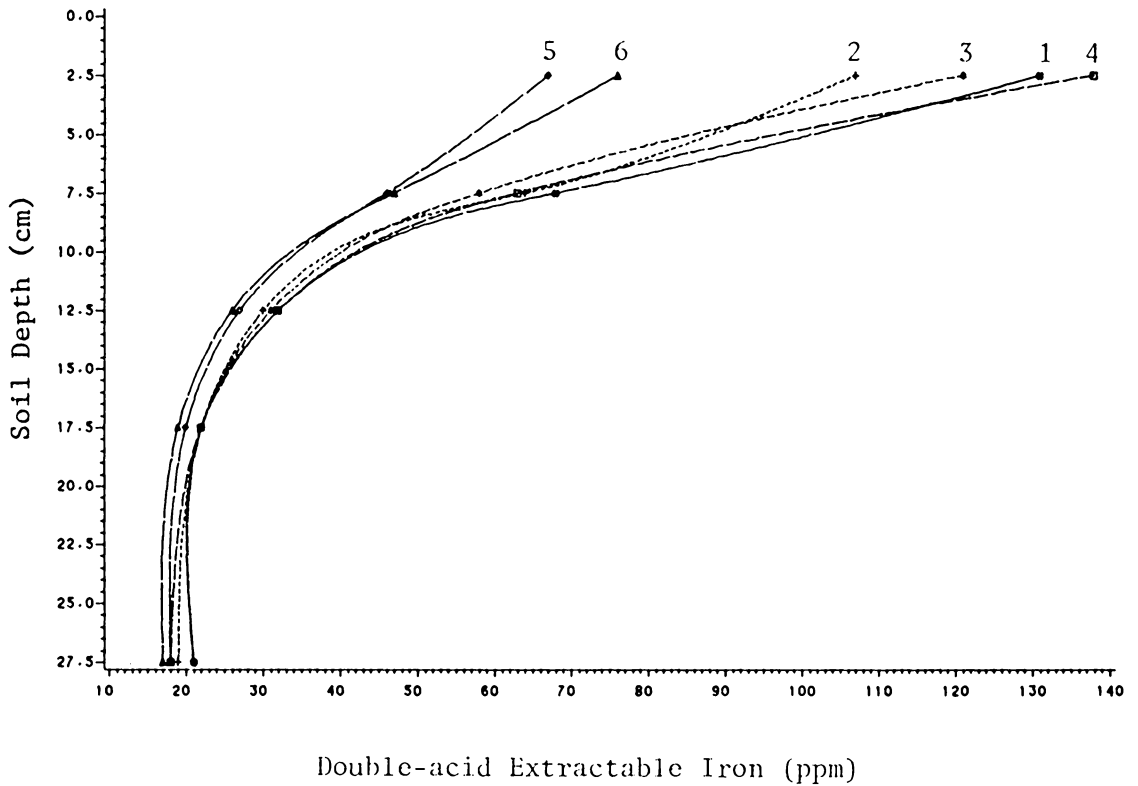
Figure 21. Loblolly pine foliar phosphorus (ppm) versus double-acid and Mehlich extractable soil phosphorus (ppm) at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.

### Extractable Fe and Al

Extractable Fe and Al levels are depicted by depth and treatment in Figures 22-25, and A horizon values are compared by treatment for the double acid and Mehlich extracts at age 20, and the double acid at age 10 in Figures 26 and 27, respectively. Extractable Fe is almost 4 times higher at the surface 5 cm than below 10 cm (Figure 22 and 23). The lowest extractable levels were found in the B horizon. Liming resulted in a significant decrease in extractable Fe levels. Unlimed soils averaged about 60 ppm in the A horizon (Figure 26), whereas limed soils averaged about 40 ppm.

Generally, double acid soil nutrient values are greater than the Mehlich values at soil depths above 10 cm. At the lower depths the Mehlich solution consistently extracted slightly more than the double acid. There was an inverse relationship between pH and extractable Fe which was strongest for the double acid extract (Table 6). The relationship became insignificant for Mehlich values below 10 cm depth.

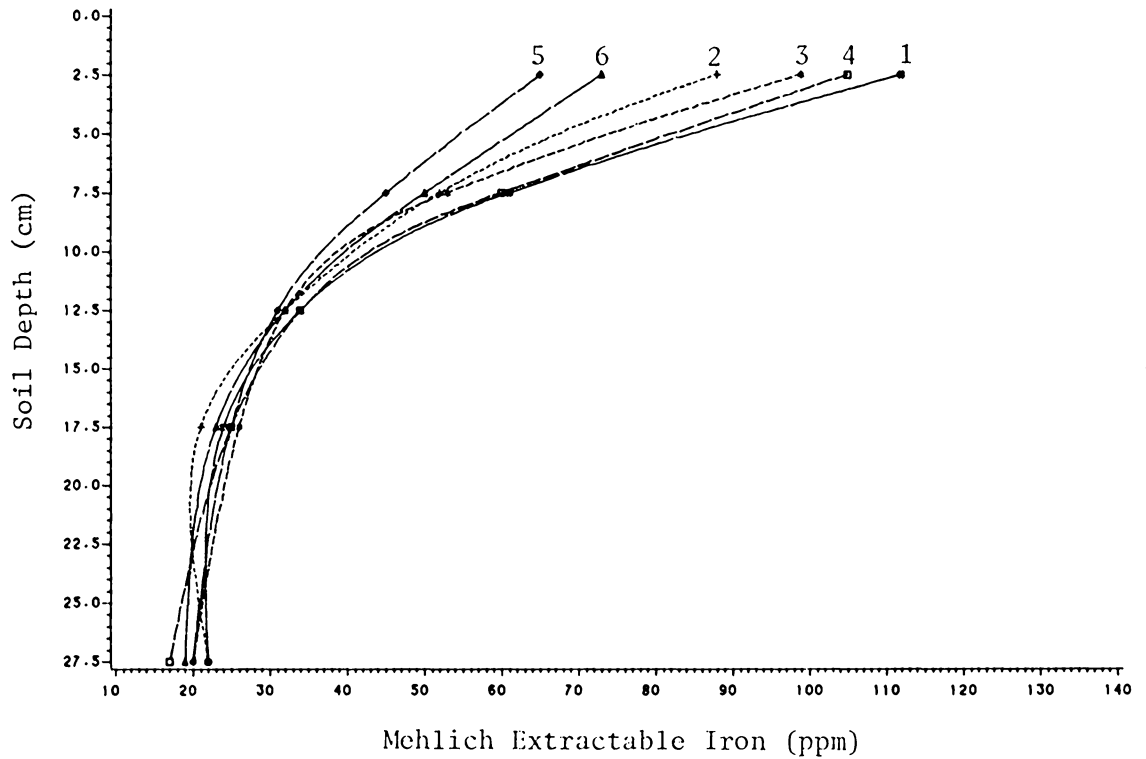
Similar to Fe, double acid extractable Al tended to decrease with depth (Figure 24). Unlimed soils averaged 420 ppm double acid extractable Al in the A horizon, while the limed plots were significantly lower and averaged 340 ppm Al (Figure 27).



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- ⊖—⊖ 4 = TSP (160 kg P/ha)
- ◊—◊ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ⊕—⊕ 6 = lime (4.48 T lime/ha)

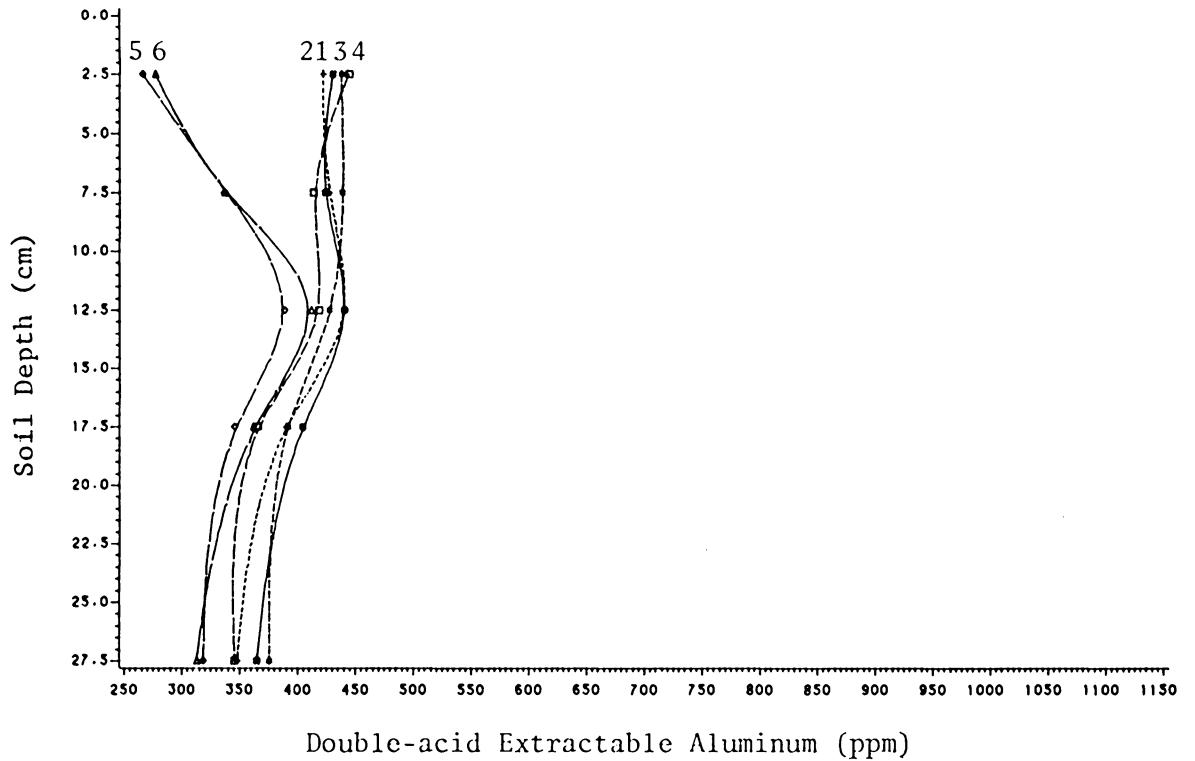
Figure 22. Double-acid extractable soil iron by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +--+ 2 = high rate GRP (670 kg P/ha)
- 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◆-◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲-▲ 6 = lime (4.48 T lime/ha)

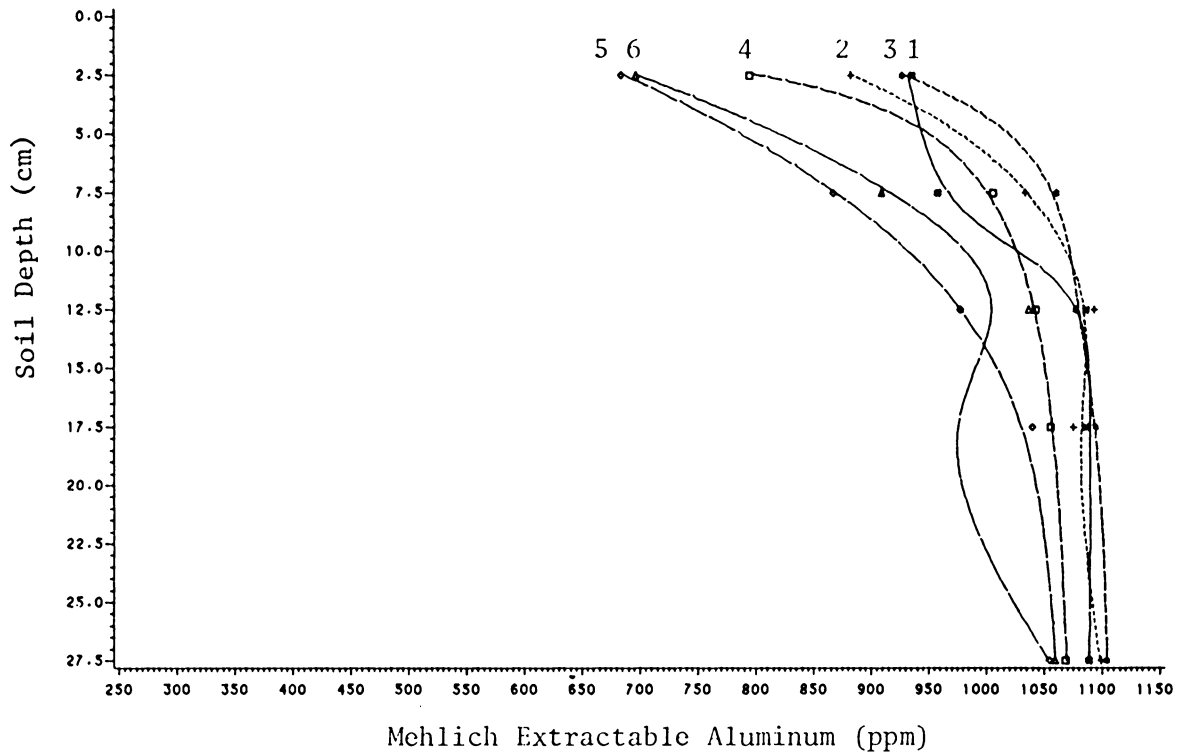
Figure 23. Mehlich extractable soil iron by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- 2 = high rate GRP (670 kg P/ha)
- 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- 6 = lime (4.48 T lime/ha)

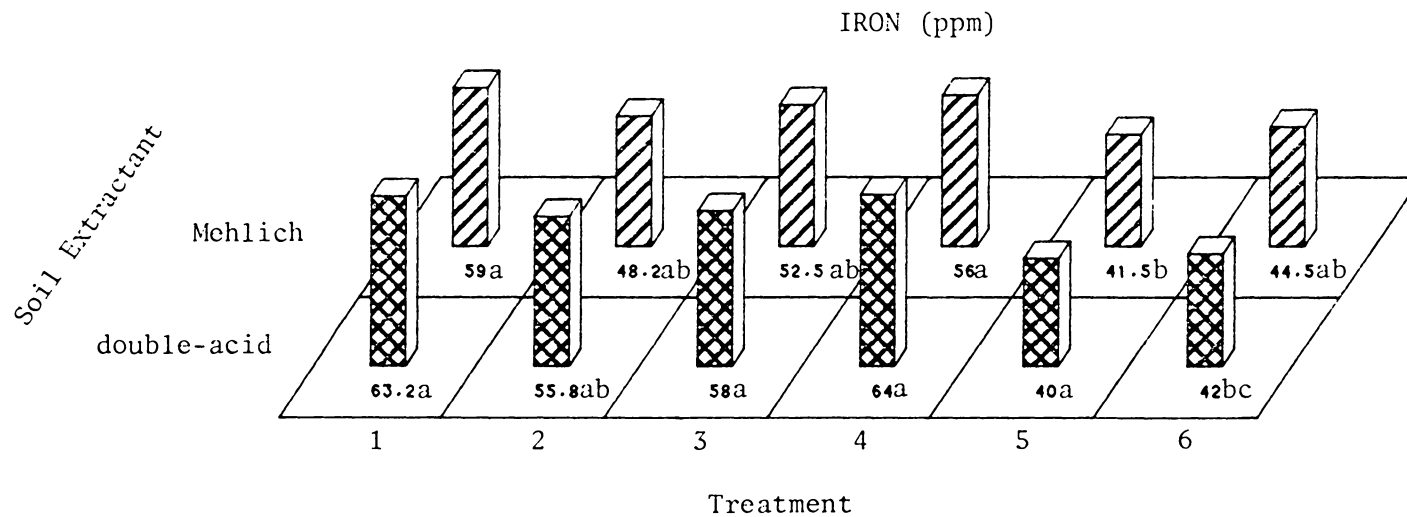
Figure 24. Double-acid extractable soil aluminum by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ▲—▲ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◆—◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- 6 = lime (4.48 T lime/ha)

Figure 25. Mehlich extractable soil aluminum by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



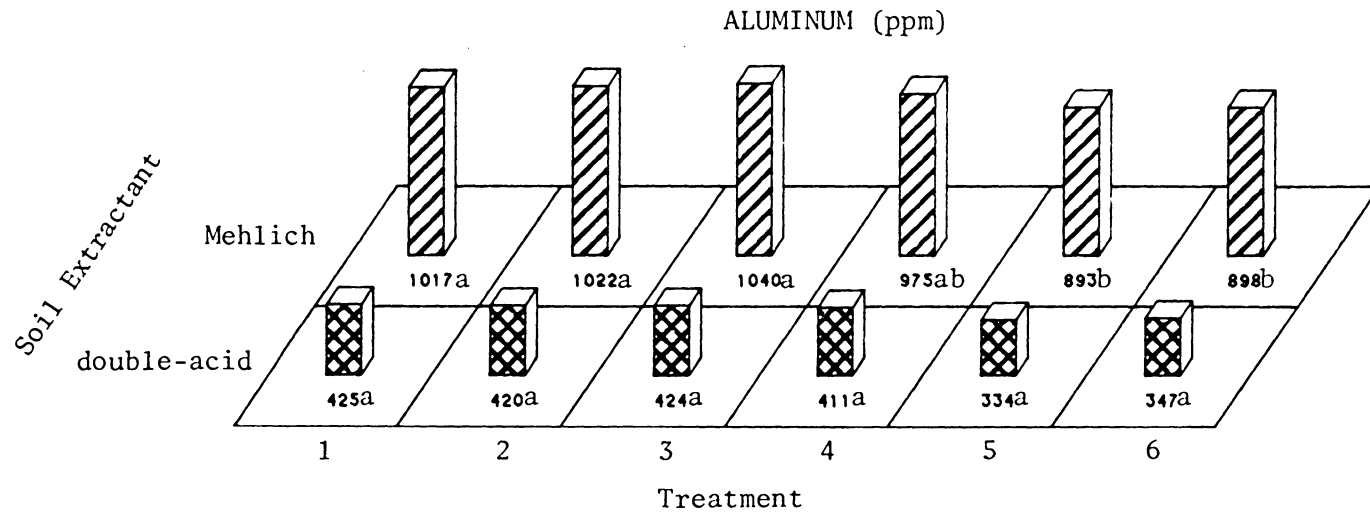
TREATMENT LEGEND

- |                                 |  |
|---------------------------------|--|
| 1 = control                     | 4 = TSP (160 kg P/ha)                      |
| 2 = high rate GRP (670 kg P/ha) | 5 = TSP + lime (160 kg P + 4.48 T lime/ha) |
| 3 = low rate GRP (160 kg P/ha)  | 6 = lime (4.48 T lime/ac)                  |

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 26. Average A horizon extractable iron as extracted by the double-acid and Mehlich solutions at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.





TREATMENT LEGEND

- |                                 |  |
|---------------------------------|--|
| 1 = control                     | 4 = TSP (160 kg P/ha)                      |
| 2 = high rate GRP (670 kg P/ha) | 5 = TSP + lime (160 kg P + 4.48 T lime/ha) |
| 3 = low rate GRP (160 kg P/ha)  | 6 = lime (4.48 T lime/ha)                  |

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

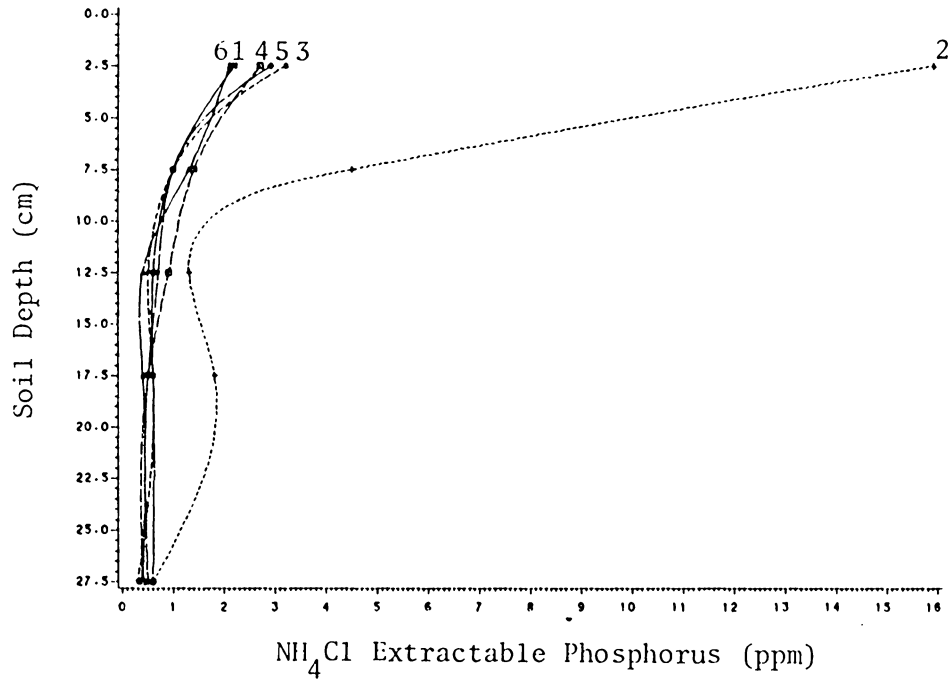
Figure 27. Average A horizon extractable aluminum as extracted by the double-acid and Mehlich solutions at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.

Mehlich extractable Al levels were two or three times greater than the double acid values. The relative difference between the two extractants was greatest at the lower depths. Unlike all other nutrients extracted, Mehlich Al levels continually increased through the profile (Figure 25).

### Phosphorus fractionation

A modified Chang and Jackson fractionation (Peterson and Corey, 1966) allowed for a comparison of the various forms of plant available soil P by treatment. The fractions often regarded as readily soluble P (saloid-P), aluminum phosphates (Al-P), iron phosphates (Fe-P), and calcium phosphates (Ca-P) are summarized by depth in Figures 28-31. Total soil P is depicted in Figure 32. The A horizon averages for the same fractions are compared by treatment in Figure 33. Data pertaining to the ratio of Al-P to Fe-P at each depth is included in Table 8.

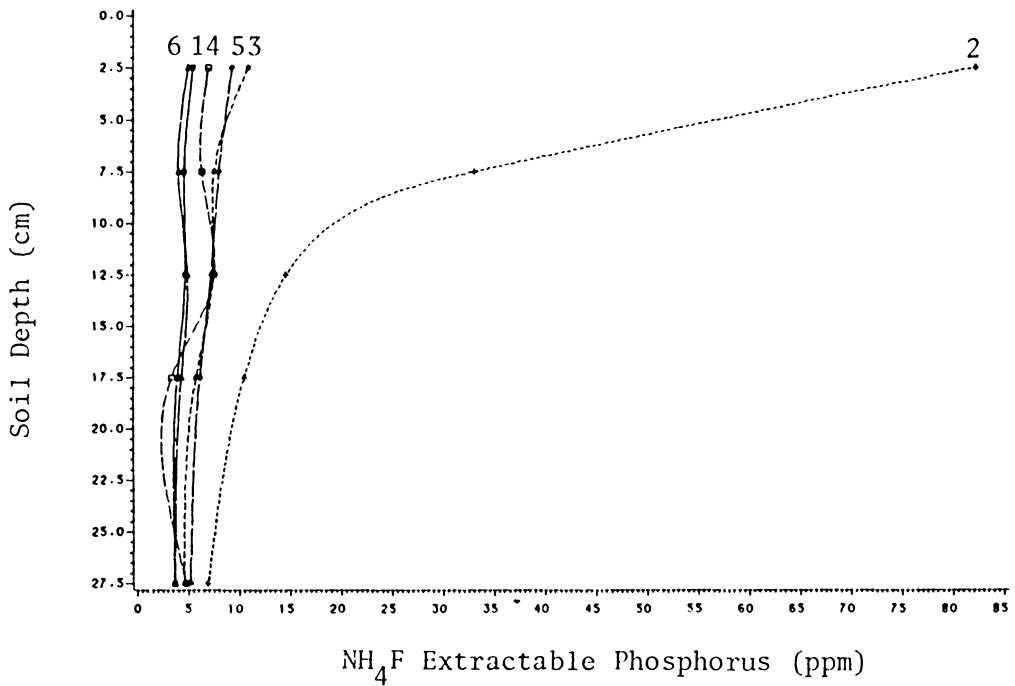
It is obvious from Figure 33 that most soil P existed in forms other than those determined by the fractionation. Of the 134 ppm total soil P in the control A horizon, about 110 ppm existed in a form other than that measured with the Chang and Jackson fractionation. The difference between total P and fractionated P is assumed to be the occluded and organic forms. Most of the fractionated P in the control soil was removed with NaOH and described as Fe-P (16.6 ppm). Along with the Al-P (4.6 ppm) extracted by NH<sub>4</sub>F, these two fractions dominated the total amount of P extracted. The saloid-P (1.1 ppm) and Ca-P (1.2 ppm) made up a very small portion of the P pool.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◆—◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ◆—◆ 6 = lime (4.48 T lime/ha)

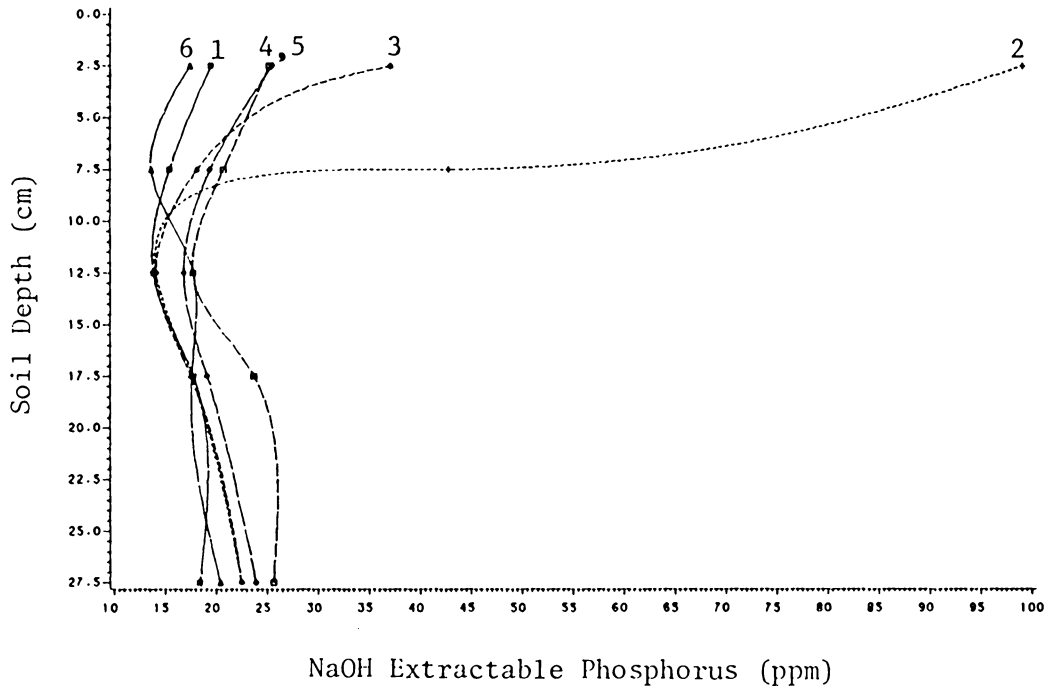
Figure 28.  $\text{NH}_4\text{Cl}$  extractable soil phosphorus (saloid-P) by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- ⊖—⊖ 4 = TSP (160 kg P/ha)
- ◀—▶ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲—▲ 6 = lime (4.48 T lime/ha)

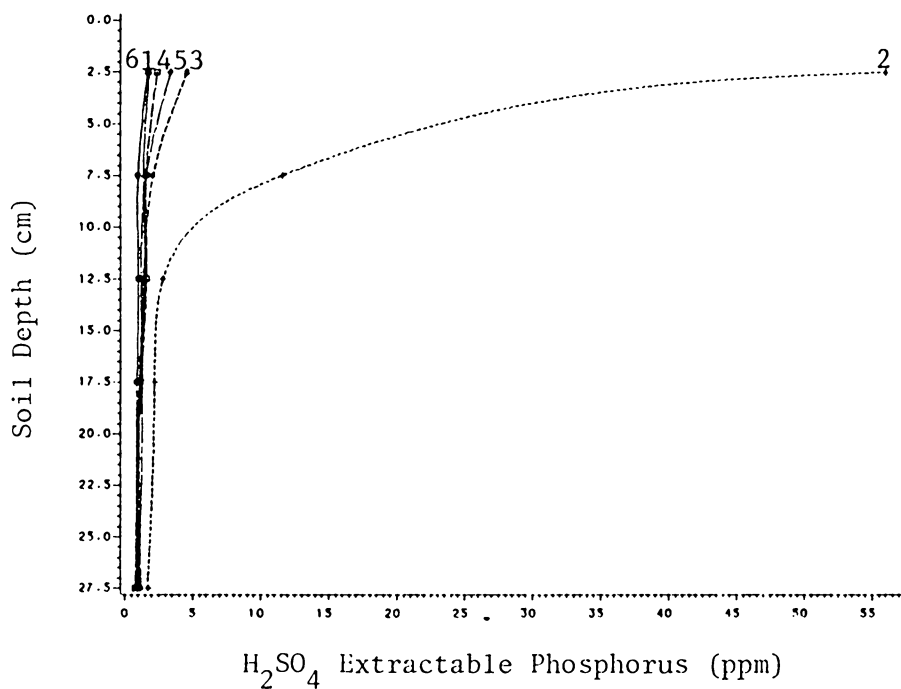
Figure 29.  $\text{NH}_4\text{F}$  extractable soil phosphorus (Al-P) by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- ◆—◆ 3 = low rate GRP (160 kg P/ha)
- ◻—◻ 4 = TSP (160 kg P/ha)
- ◊—◊ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲—▲ 6 = lime (4.48 T lime/ha)

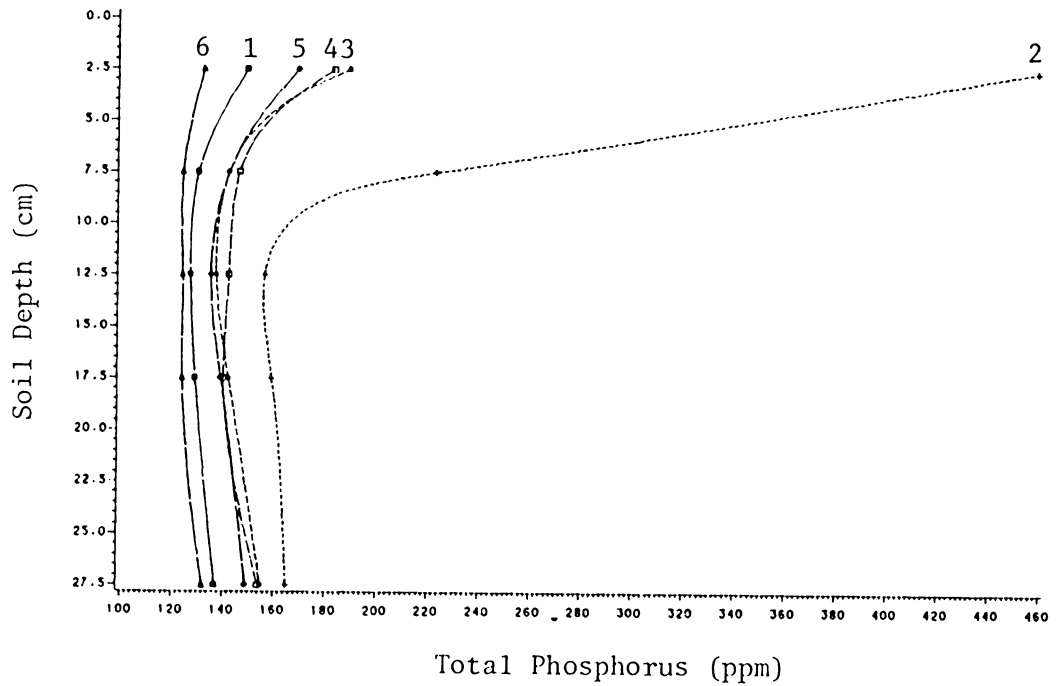
Figure 30. NaOH extractable soil phosphorus (Fe-P) by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- ◆—◆ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- ▲—▲ 6 = lime (4.48 T lime/ha)

Figure 31. H<sub>2</sub>SO<sub>4</sub> extractable soil phosphorus (Ca-P) by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.

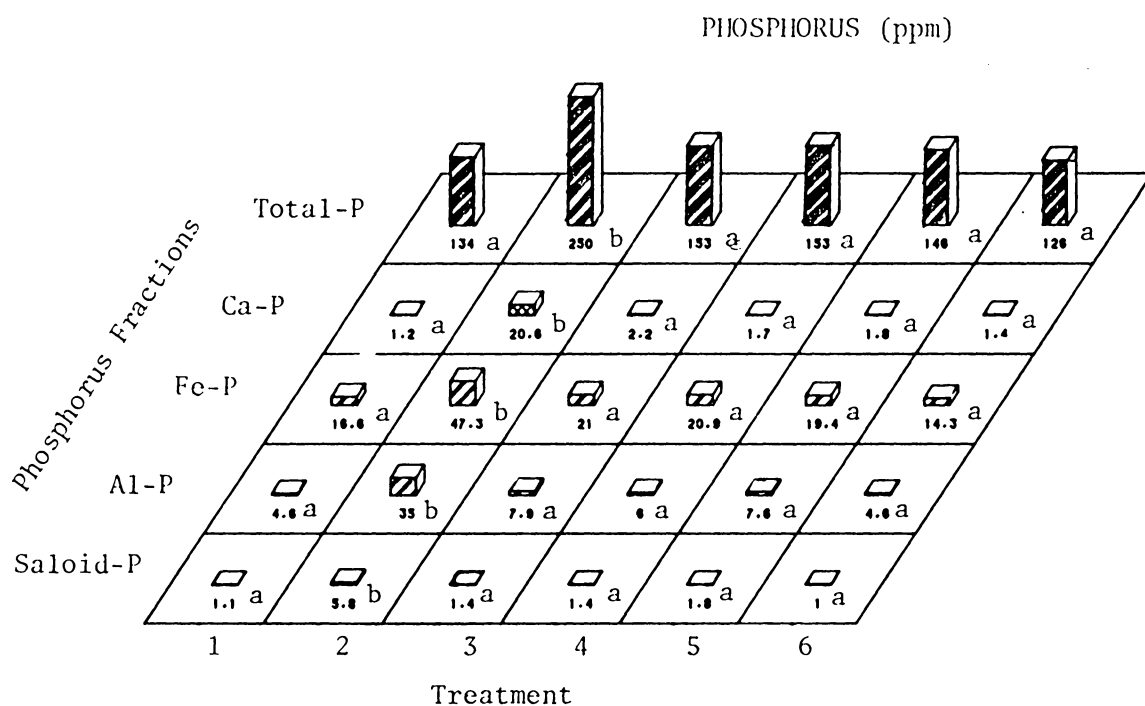


## TREATMENT LEGEND

- 1 = control
- +—+ 2 = high rate GRP (670 kg P/ha)
- 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- +—+ 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- +—+ 6 = lime (4.48 T lime/ha)

Figure 32. Total soil phosphorus by treatment and depth at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.





## TREATMENT LEGEND

- 1 = control
- 2 = high rate GRP (670 kg P/ha)
- 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- 6 = lime (4.48 + lime/ha)

Values within a row followed by the same letter are not significantly different at the 0.05 level according to Duncan's Multiple Range Test.

Figure 33. Average A horizon soil phosphorus fraction levels by treatment at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.

Table 8. Ratio of  $\text{NH}_4\text{F}$  extractable soil phosphorus (Al-P) to NaOH extractable soil phosphorus (Fe-P) by treatment and depth on Tatum silt loam in Orange County, Virginia.

Treatment	Soil Depth (cm)					A horizon
	0-5	5-10	10-15	15-20	20-35	
	----- (Al-P:Fe-P) -----					
Control	.30	.32	.32	.25	.51	.28
High rate GRP (670 kg P/ha)	.86	.82	.65	.47	.24	.66
Low rate GRP (160 kg P/ha)	.32	.44	.48	.40	.21	.41
TSP (160 kg P/ha)	.26	.33	.46	.08	.18	.30
TSP + lime (160 kg P + 4.48 T lime/ha)	.36	.42	.47	.25	.22	.40
Lime (4.48 T lime/ha)	.31	.34	.27	.27	.20	.31

The only treatment with a significantly higher total P level than the control was the high rate GRP treatment with 250 ppm P (Figure 33), which was slightly more than 100 ppm P higher than the rest of the treatments. This GRP treatment had higher levels of all forms of P and represented the only significant treatment of the various P fractions. Levels of the various forms, saloid-P (5.8 ppm), Al-P (35.0 ppm), Fe-P (47.3 ppm) and Ca-P (20.6 ppm) were all significantly higher than the other treatments. The sum of these various P fractions (108.7 ppm) accounted for only 43% of the total P.

Where no P was applied or where TSP was applied without lime, the ratio of Al-P to Fe-P (0.30) in the A horizon (Table 8) indicated that there was approximately three times as much Fe-P as Al-P. Where GRP was applied at the high rate, Al-P became relatively more important and a higher ratio (0.66) existed. The low rate GRP and TSP with lime had a ratio (0.40) closer to control values.

Regression coefficients for the relationships between A horizon averages of the various soil P fractions (Table 9) as well as the relationships between the different P fraction levels at various depths with foliar P (Table 10) were determined. All forms of soil P were significantly related to foliar P levels. The strongest relationship

between A horizon levels and foliar P existed for  $\text{NH}_4\text{F}$  extractable P ( $r^2=.42$ ) and NaOH extractable P ( $r^2=.40$ ). The A horizon average of  $\text{NH}_4\text{F}$  extractable P was also most highly correlated with double acid extractable P ( $r^2=.98$ ) and Mehlich P ( $r^2=.97$ ).

Table 9. Simple correlation ( $r^2$ ) between A horizon levels of soil phosphorus fractions and extractable soil phosphorus on Tatum silt loam in Orange County, Virginia.

P Fraction	Extractable Soil P							
	Total P	H <sub>2</sub> O-P	Al-P	Fe-P	Ca-P	Al-P:Fe-P	double acid-P	Mehlich-P
	----- (r <sup>2</sup> ) -----							
Total-P	---	.45	.56	.57	.45	.18	.97	.98
H <sub>2</sub> O-P	.45	---	.91	.71	.85	.45	.94	.91
Al-P	.56	.91	---	.77	.83	.54	.98	.97
Fe-P	.57	.71	.77	---	.54	.14	.76	.71
Ca-P	.45	.85	.83	.54	---	.50	.87	.86
Al-P:Fe-P	.18	.45	.54	.14	.14	---	.50	.57

Table 10. Simple correlation ( $r^2$ ) between various soil phosphorus fractions and loblolly pine foliar phosphorus levels ( $\alpha=0.1$ ) by soil depth on Tatum silt loam in Orange County, Virginia.

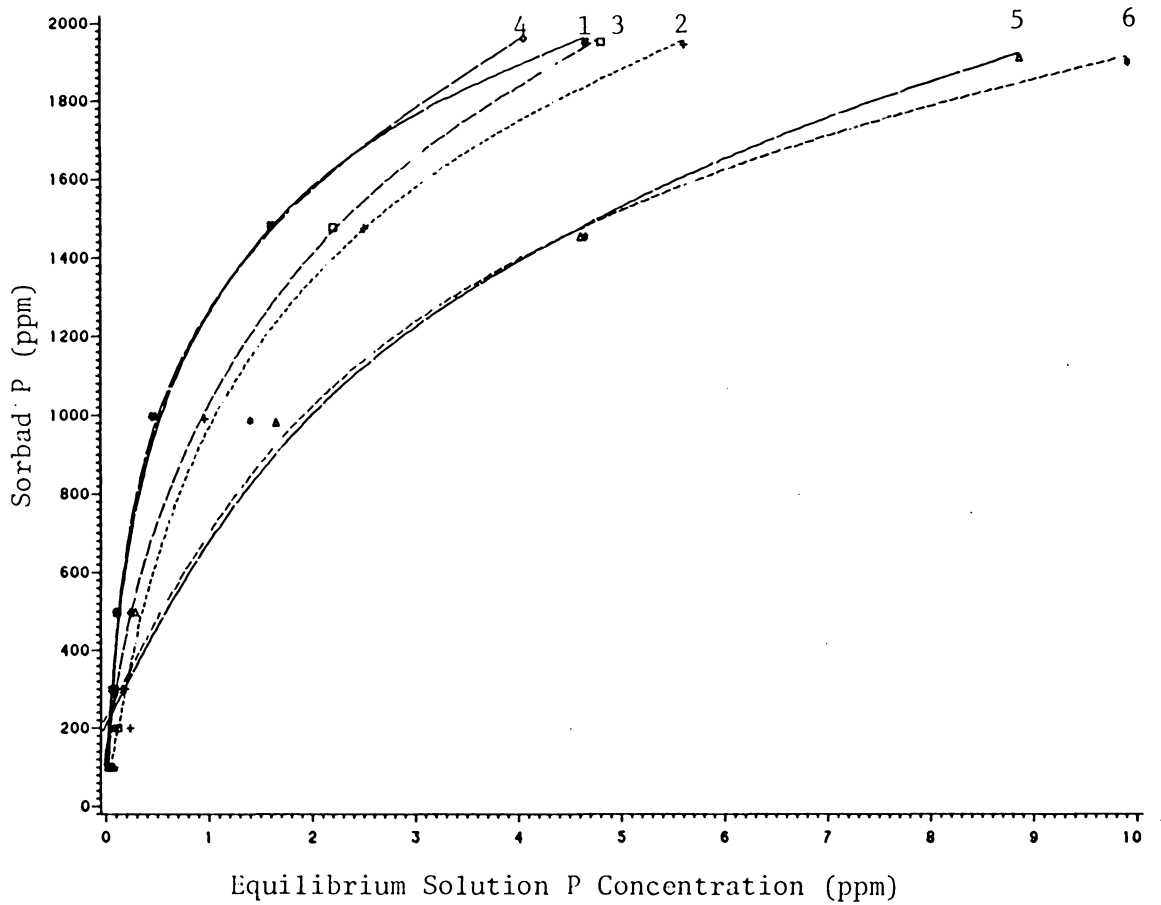
Depth (cm)	Soil P Fraction					
	H <sub>2</sub> O-P	Al-P	Fe-P	Ca-P	Total-P	Al-P : Fe-P
	----- (r <sup>2</sup> ) -----					
0 - 5	.37	.36	.52	.32	.27	.27
5 - 10	.15	.44	.42	.29	.16	.25
10 - 15	.16	.37	.10	.12	ns	.15
15 - 20	.27	.46	ns	.19	ns	.26
20 - 35	ns	.45	.12	.14	ns	ns
-----						
0 - 10	.33	.39	.45	.30	.23	.25
10 - 20	.28	.44	.10	.18	ns	.18
-----						
0 - 20	.35	.42	.40	.30	.13	.26

### Phosphorus adsorption isotherms (Q/I Curves)

Quantity-intensity (Q/I) curves for the six treatments are presented in Figure 34. The adsorption maximum is calculated as the point where the slope of the line approaches zero. The sorption maximum was not realized within the range of equilibrium solution concentrations used, but it was in excess of 2000 ppm. The specific sorbing capacity, interpreted as the intercept with the vertical axis was approximately 200 ppm.

Liming had the greatest effect on P sorption. The slope of the curve which represents the soil's P buffering capacity decreased with liming. Although sorption maxima were not quantifiable from these data, liming seemed to have decreased the amount of added P that can be removed from solution.

Applied phosphorus had a slight effect on the Q/I curves when applied as GRP, but not as TSP. The effect was more pronounced when GRP was applied at the high rate.



## TREATMENT LEGEND

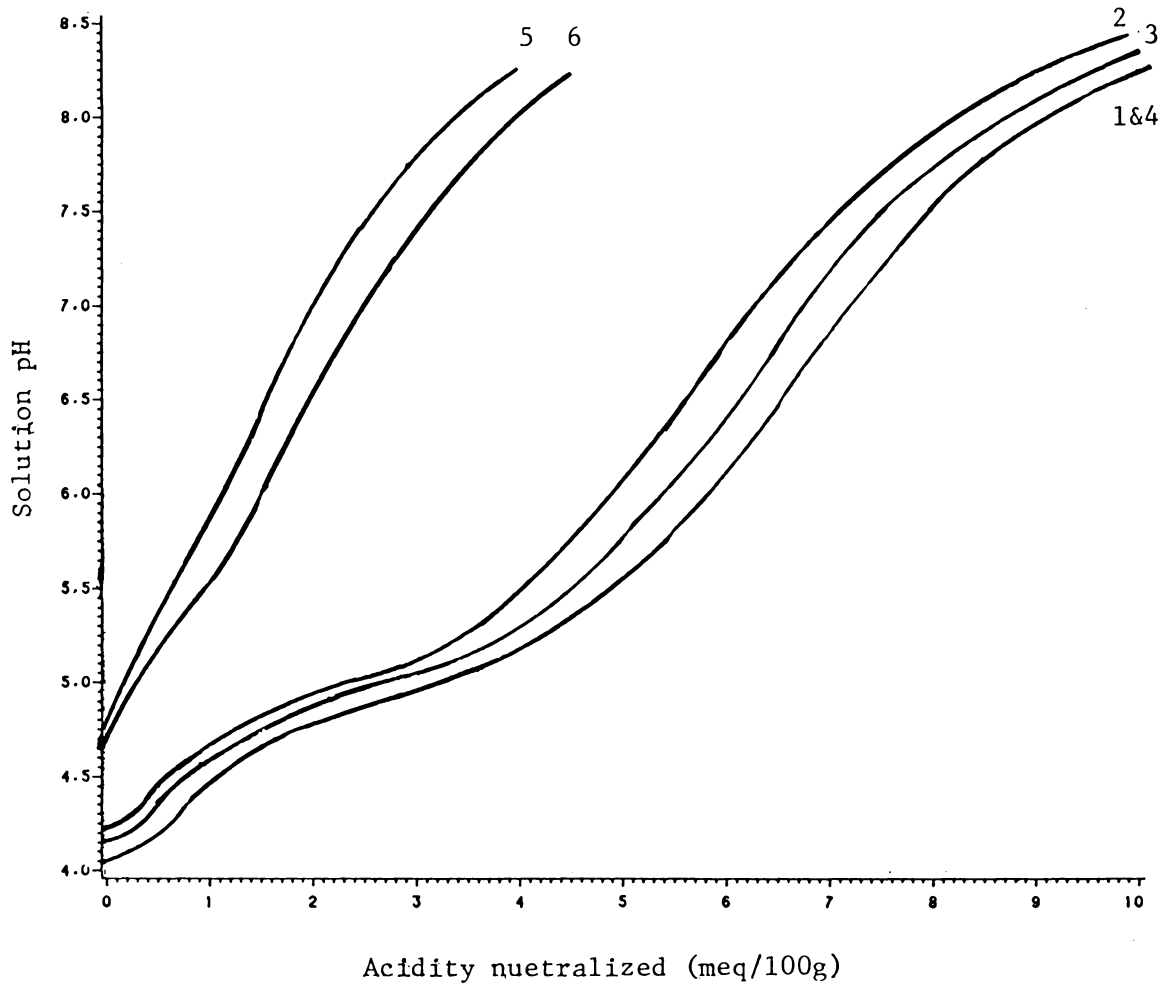
- 1 = control
- +—+—+ 2 = high rate GRP (670 kg P / ha)
- 3 = low rate GRP (160 kg P / ha)
- ◇—◇—◇ 4 = TSP (160 kg P / ha)
- △—△—△ 5 = TSP + lime (160 kg P + 4.48 T lime / ha)
- ▲—▲—▲ 6 = lime (4.48 T lime / ha)

Figure 34. Phosphorus absorption isotherms (Q/I curves) by treatment at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.



Potentiometric titration of soil acidity

Comparison of titration curves for A horizons of the control and limed soils show some striking differences in soil acidity which can be related to Al in the system (Figure 35). Even after 20 years, the effect of liming has been a reduction of soil acidity by more than half, from approximately 10 meq/100 grams to about 4 meq/100 grams. Liming neutralized nearly 6 meq/100 grams of trivalent or highly reactive Al hydroxyls in the soil. The treatment effects on soil acidity closely parallel those observed with Q/I curves. Although the greatest effect occurred in response to liming, P caused a slight decrease in soil acidity particularly when applied as GRP. The effect was greatest where GRP was applied at the high rate.



## TREATMENT LEGEND

- 1 = Control
- 2 = high rate GRP (670 kg P/ha)
- 3 = low rate GRP (160 kg P/ha)
- 4 = TSP (160 kg P/ha)
- 5 = TSP + lime (160 kg P + 4.48 T lime/ha)
- 6 = Lime (4.48 T lime/ha)

Figure 35. Potentiometric titration of soil acidity at stand age 20 for loblolly pine fertilization study in Orange County, Virginia.

## DISCUSSION

### Growth Analysis

Although it was believed prior to establishment of the study that added P might improve growth, there was no response to any treatment. Fertilized trees had essentially the same heights, diameters, and individual tree volumes as untreated trees (Figure 4).

Based on the 10 and 20 year growth analysis of this study, as well as a non-response to P in other research mentioned earlier, it seems that a P deficiency is not the immediate limitation to loblolly pine growth on many Piedmont soils. In fact, notes taken for early annual progress reports suggest that some P treatments had a detrimental effect on the pines. In the early years there was severe competition by fireweed (Erechtites hieracifolia) on TSP plots. At age two, growth was observed to be best on control plots and worst on TSP plots because of the fireweed. By age five, trees on TSP plots were stunted and crooked. At age 15 these trees were still showing some deformity but, overall their growth form improved. Apparently, an adequate amount of P was available to the

trees, but the application greatly stimulated the growth of the herbacious competition. Despite attempts to control competition by hand in the early years, the vigorous growth of the fireweed, induced by fertilization, was a hinderence to the pines.

Dominant tree heights which averaged almost 13 meters correspond to a site index (base age 50) of about 70 for Piedmont soils (Burkhart, 1981). Site index 70 is a moderate value within the range of productivities found on the Piedmont. The greatest loblolly pine growth occurs on soils with poor surface drainage, a deep surface layer, and a firm subsoil (USDA, 1965). Site indices of 80-100 (base age 50) are common on non-eroded soils such as the Durham, Georgeville, Appling, Cecil, Davidson, and Lloyd series. Productivity decreases greatly with removal of the A horizon. The least productive sites are those with an eroded surface and plastic subsoil characteristic of the Iredell, Orange, and Whitestone where site indices can be as low as 40.

According to the Soil Conservation Service estimate (1971), the Tatum series should provide a site index of 75-85 (base age 50) for loblolly pine. The particular site involved in this study was an eroded phase of the Tatum; therefore, the lower range of productivity should be expected due to a limited A horizon.

Reduction of the A horizon would increase the emphasis placed on the B horizon for root development. Loblolly pine root development is impeded by fine textured and plastic subsoils thereby reducing the trees ability to absorb water and nutrients. Bilan (1971) reports that a slight increase in sand content of a clayey soil doubled the horizontal root growth of loblolly pine seedlings. Since the Tatum soil is well drained, reduced root growth would be particularly detrimental for water uptake.

### Foliar Analysis

Erosion of the surface layer decreased the inherent fertility of the site and it is possible that some other nutrient, namely N, may have been the immediate growth limiting factor thereby preventing a growth response to added P. Foliar analyses are useful for ascertaining nutrient deficiencies since nutrient levels in the tissue are an expression of the interaction of all the factors affecting nutrient uptake.

Nitrogen is often deficient in forest soils of the Southeast and most fertilization studies have demonstrated some response to added N. A N deficiency should be especially suspect on an eroded soil where much of the organic matter has been lost. Foliar N levels in this study (table 4) averaged 1.12 % and were not affected by treatment. These levels are somewhat below the 1.2% N critical level established by other fertilization trials on Coastal Plain and Piedmont sites. This suggests that a marginal N deficiency may exist in the stand after 20 years. It appears that N is becoming increasingly deficient as the stand ages. Foliar levels at age one averaged 1.65% which is well above the critical level, but decreased to an average of 1.17% at age 10, decreasing subsequently to 1.12% at age 20. Pritchett (1979) explained that N deficiencies often

aren't apparent until sometime after stand closure due to immobilization of N in the forest floor.

Despite the insignificant growth response to added P, the effects of treatment on P uptake were evaluated. Foliar P levels provided a comparison of the effects of various treatments on P uptake. Availability of soil P was assumed to be greater in plots where trees had correspondingly higher foliar P levels.

Average foliar P in untreated trees was 0.105% (table 4) which is above the critical range of 0.08 to 0.10% P consistently reported in the literature. These tissue levels indicate that P is not restricting growth and consequently no growth response to added P should have been expected. Judging from foliar levels there seems to be a long term benefit to be derived by using GRP instead of TSP for providing P for loblolly pine uptake. Since the superphosphates are essentially 100% water soluble, all the applied P entered the soil system and began to be fixed by the soil shortly after application. After 20 years, most of this P had been removed from the soil or fixed into plant unavailable forms. Consequently, the foliar levels of TSP plots without lime (0.111%) are only slightly different from untreated plots (0.105%). Rock phosphate on the other hand dissolves slowly, and the 160 kg P/ha applied as apatite

took years to enter the soil solution. Therefore, much of this P has not had as long to become fixed and after 20 years there is still enough P in a form available for uptake such that foliar levels are significantly greater (0.122%) than control plots (0.105%).

Since TSP enters the soil solution rapidly, foliar levels at age one seemed to be greater than levels in GRP treated trees (0.19 vs 0.18%), but the difference was not significant. Furthermore, both P sources were so effective at increasing foliar levels, that either could have provided necessary P for early growth had there been a deficiency. The greater amount of available P from TSP did not aid pines but was enough for fireweed to get out of control.

Differences in application rate of GRP were not significant in the first 20 years but will probably become significant at age 25 or 30 years. In the same manner that GRP plots with 160 kg P/ha have greater foliar levels than TSP plots, the high rate GRP treatment will have significantly higher foliar levels when P from the low rate GRP has had time to equilibrate with the soil. Even after 20 years, the high rate apatite treatment is still releasing undissolved P into solution long after all the fertilizer from the low rate treatment dissolved. Although foliar levels between GRP treatments are not yet significantly



different, the difference appears to be greater at age 20 than they were at age 10, and as high rate GRP foliar levels increase and the low rate values decrease, it seems probable that the difference in foliar levels between application rates will become significant.

Although P availability is known to increase with pH on acid soils, liming on its own did not increase the uptake of P by loblolly pine on this Tatum soil. At ages 1, 10, and 20, P levels were actually slightly lower on limed soils (0.099%) than control soils (0.105%). Although growth effects were insignificant, the lowest tree volume occurred on the limed soil which also had the lowest foliar P levels. Gilmore (1978), working with 15 year old loblolly pines on a silt loam in Illinois, also found no effect on foliar P levels when lime was applied at much higher rates than were involved in this study. He did observe a decrease in height due to liming which he attributed to restricted root development somehow induced by liming.

Although liming alone seems to have no long term beneficial effect on P uptake, there may be some value to liming in conjunction with TSP application, as evidenced by foliar levels. As already mentioned, most P from the TSP treatment seems to have been fixed into unavailable forms and TSP foliar levels (0.111%) are not statistically

different from control plots (0.105%) after 20 years. However, where lime was applied with TSP, more P seems to be available for plant uptake; foliar levels on these plots (0.115%) were greater than the controls. As will be explained later, lime is capable of neutralizing much of the reactive Al which would otherwise combine with added P removing it from solution. Furthermore, a higher pH induced by liming may reduce the rate of transformation to the more unavailable forms of P such as Fe-P or occluded P.

Powers (1974) reported foliar critical levels for conifers as 0.40% K, 0.12% Ca, and 0.05% Mg, and Ballard (1979) reported loblolly pine critical levels of 0.30% K, 0.10% Ca, and 0.05% Mg. Foliar analyses for the major cations, K, Ca, Mg (Table 4) established that these nutrients existed at adequate levels in the tissue and should not be limiting growth.

Uptake of these cations seems to have been little affected by treatment with the exception that lime induced significantly greater Mg levels compared to all unlimed plots (Figure 16); this was probably due to increased levels of soil Mg added by dolomitic limestone. Although the difference is not significant, foliar K levels appeared to be lower on limed plots. As will be discussed later, liming can often decrease the availability of soil K.

Switzer et al. (1968) reported that accumulation of N, P and K is greatest in the early years of loblolly pine development; consequently, foliar concentrations of these nutrients should be greatest at age one and lowest at age 20. He also showed that other nutrients such as Mg and Ca follow the opposite trend. Comparisons of N and P data (table 4) from this trial show that this had been the case. However, it is interesting that the 10 year K foliar levels were much lower than age 1 and 20. The initial levels measured in year 1 were higher than the 20 year levels by about 0.05% (Table 4) which should be expected. Foliar Mg levels for all treatments were lowest at age one and increased to the values determined at age 20. On the other hand, calcium levels in the foliage showed an increase from age 10 to 20 which would be expected; however, values reported at age one were almost twice as great as those found at 20 years and are not readily explainable.

Soil Analysis

Judging from foliar concentrations, it is apparent that the greatest effect of these treatments has been on P uptake. Although increased P uptake in this study did not correspond to greater growth, it should not be assumed that an adequate supply of P exists in this soil and that P will never pose a nutritional problem. Alleviation of other growth limiting factors may increase tree growth to the point where P does become limiting. Consequently, it was important to evaluate the effect of these treatments on P uptake in order to gain some insight which may be useful once other steps are taken to correct other growth limiting problems. The resulting effect of these treatments on foliar levels can be explained only by examining the soil chemistry with special emphasis on those characteristics pertaining to P fixation.

Soil pH

The rates and direction of almost all soil P reactions are influenced by pH. Phosphorus availability is usually greatest near pH 5.5-6.5. At lower pH's, precipitation and adsorption reactions with exchangeable Al and Fe or their hydroxyl forms remove P from solution. As pH's rise above neutral, similar types of fixation occur with Ca compounds.

Soil pH values measured at age 10 and 20 show similar treatment effects at all depths (Figures 6 and 7), and several conclusions can be drawn by comparing these values to the pH of 4.5 that existed before the study. The inherent pH of the soil study area has decreased during the last 20 years due to conversion from a hardwood stand to a loblolly pine plantation. The average A horizon pH was about 4.5 at time of establishment and has decreased to 4.1 after 20 years (table 5). The upper A horizon is significantly more acidic than the lower region (3.9 vs. 4.3). The greatest decrease in pH has occurred during the past 10 years during which time canopy closure occurred and a thick litter layer developed. Liming buffered the effect of species conversion on pH change. A horizon values of control plots decreased 0.4 pH units whereas limed plots decreased by only 0.2 pH units.

Although P availability is generally regarded to increase with pH towards neutrality, there seems to be no direct relationship between pH and P uptake in this study. At ages two and ten, the pH of limed treatments was much higher than the control (table 5), yet foliar levels for the two treatments were essentially the same (table 4). After 20 years the pH difference between limed and control soils are greater than ever, yet the foliar P on limed plots is actually lower than the control situation.

Although liming seems to have no merit on its own for increasing the long term uptake of P for pine, it may be beneficial when combined with P fertilization. Liming was shown to reduce or alter the fixation reactions of applied P (Figure 25), rendering the P available for a longer period of time. After 20 years, foliar levels of trees on TSP plots were not significantly greater than untreated trees unless lime was also applied.

Extractable soil K, Ca, Mg

Extractable K, Ca, and Mg were determined for these soils because along with N and P they are taken up in relatively large amounts. Although it is apparent from the foliar levels that these nutrients were not limiting growth, the lime and P treatments had some effect on their levels and availability in the soil.

Phosphorus application often increases the CEC of a soil for a variety of reasons (Bertsch, 1980). A ligand exchange reaction between adsorbed phosphates with neutral octahedrally coordinated water molecules creates a more negative surface charge. Furthermore the neutralization of positive charges at the surface with hydroxyls allows for a greater expression of negative charges.

Unfortunately, the full effect of treatments on availability of these nutrients cannot be evaluated due to the nature of the extractants. A neutral salt extraction would have provided better data on the exchangeable levels of these cations. Exchangeable ions are those which are easily displaced and capable of replacing nutrients lost from solution. Due to the acidifying nature of the extractants involved these reagents will not only remove the exchangeable nutrients, but will also dissolve forms which would normally not be readily available to plants.

As a general observation, nutrient levels are highest at the surface, decreasing in concentration to about 15 cm and then increasing into the B horizon. This pattern reflects the importance of nutrient cycling in forest soils. Nutrients absorbed by roots are passed into various components of the tree and eventually returned to the surface through the litter layer. Nutrients released from organic matter at the surface slowly move through the A horizon and accumulate in the B horizon.

The Mehlich solution always extracted more cations than the double acid method which is consistent with the findings of other researchers (Lea et al., 1980; Mehlich, 1978). The  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{F}$  constituents of the Mehlich extractant are effective at displacing cations from the exchange complex. The  $\text{NH}_4$  ion which is about the same size as a hydrated  $\text{K}^+$  ion can effectively displace K from specifically adsorbed interlayer positions of 2:1 type layer silicates. A greater solution-soil ratio involved with the Mehlich procedure also contributes to higher extractable levels. The relationships between soil nutrient levels extracted by the double acid and Mehlich solutions are depicted graphically in the appendix (Figures A1-A6).

Potassium levels (Figure 14) did not show any treatment effect and were not related to pH (Table 6) or foliar levels



(Table 7). However, there was a general tendency for liming, due to increased Ca and Mg concentrations in the soil solution, to result in an increased K saturation of the exchange complex and a decreased solution K in accordance with Schofield's Ratio Law (Beckett, 1964a,b). The increased pH from liming can also decrease solution K by promoting hydrolysis of interlayer Al in 2:1 minerals creating K specific fixation sites. A decrease in solution K by such mechanisms could not be detected by the powerful extracting solutions involved in this study, but reduced K availability was partially reflected by the foliar K values which were lowest on the two limed treatments (Table 4).

Since all treatments involved Ca addition as either dolomitic limestone or fertilizer, it is not surprising that the greatest treatment effect occurred with respect to Ca levels (Figures 10, 11, and 15). Both lime treatments had the highest Ca levels, and where TSP accompanied lime addition, the A horizon Ca values were significantly higher than liming alone. The ordering of Ca levels for other treatments generally follows a pattern depending upon how much Ca was added as fertilizer.

Liming resulted in significantly higher extractable Mg levels since dolomitic limestone contains an appreciable amount of Mg. As expected, a significant correlation

existed between pH and extractable Mg and Ca (Table 6) There was also a significant relationship between foliar Mg and soil extractable levels, which did not exist for Ca (Table 7). However, this significant relationship resulted entirely from increased foliar Mg levels on limed plots. For unlimed treatments, soil and foliar levels did not even follow the same trends.

### Extractable soil P

The double acid extraction is the most commonly used procedure for determining available soil P levels in the Southeast. Of the three soil P factors mentioned earlier (intensity, quantity and buffering capacity), extractable P is probably a good estimator of the quantity term. Double acid and Mehlich P represents P in the soil which should be slowly available throughout the growing season to replace solution P removed by plants and microbes, or lost through leaching. Sources of P removed by these extractants should include not only the readily exchangeable forms, but also P held with weak binding forces to adsorption surfaces, some of the more tightly bound chemisorbed P, and some of the amorphous and crystalized P existing as a precipitate. Occluded forms which become available only over a long period of time, if ever, probably do not contribute to the levels of extractable P. A harsher reagent such as a dithionite-citrate-bicarbonate combination is required to dissolve the Fe oxide coatings covering occluded P.

As was the case for cation extraction, the Mehlich solution extracted more P than the double acid in nearly all cases. At very low levels of soil P, the differences between the two extractants were minor. In the surface 10 cm of soil in the GRP treatments, double acid values were

higher because there was more Ca-P of which the more acidic double acid solution is was an effective solvent. Several factors were involved in the higher P extracting capacity of the Mehlich solution besides the greater solution-soil ratio already mentioned. Fluoride ions in the Mehlich solution complex more strongly with Al than P (Hsu, 1977), releasing adsorbed P from sesquioxide surfaces and reducing refixation with reactive Al in solution. In a similar manner, acetate ions can compete with P for adsorption sites reducing refixation of dissolved P.

The average value extracted from the control plots was only 1.5 and 2.1 ppm for the double acid and Mehlich extractants, respectively (Figure 20). Only one treatment had extractable A horizon levels greater than 4.0 ppm. The high rate GRP application averaged almost 26 ppm. This treatment was significantly higher than all other treatments at every depth and by both extraction procedures. As will be discussed shortly, the extractable P determined for this GRP treatment probably overestimates the quantity of P actually available for growth. The first 5 cm contains 56 ppm extractable P which exists largely as still undissolved GRP and is not currently available for plant growth.

Average A horizon extractable P was higher when 160 kg P/ha was applied as GRP (3.63 ppm) compared with TSP (2.44

ppm). Generally, where P was applied at 160 kg P/ha, extractable P levels were higher for GRP treatments at the surface 10 cm, and TSP was greater at lower depths. Since TSP dissolves immediately after application, it had longer to move through the soil than the GRP which probably took years to completely enter the soil system. Where lime was applied with TSP, extractable P was equal to the levels where TSP was applied alone. However, where lime was applied without P, extractable levels were lower than the control.

Although P availability is generally considered to be a function of pH, increasing in acid soils to a pH near 5.5 or 6, there was no correlation between pH and extractable P in this study (table 6). This non-correlation should not be interpreted to mean that pH is not important to P availability, but more likely reflects the ability of these extractants to remove P which is slowly available over a long period of time. Readily soluble P (saloid-P) is probably much more susceptible to pH changes than the quantity of P removed by these extracts.

On Coastal Plain soils where P deficiencies are most pronounced, 3-5 ppm double acid extractable P is generally considered the average critical value below which southern pine growth will be limited by a P deficiency. Lea et al

(1980) compared double acid and Mehlich values on Coastal Plain soils and ascertained that a critical level as determined by the Mehlich extractant should be 5-6 ppm P. The relationship between Mehlich and double acid P extracted for this study is depicted in the appendix (Figure A4) and shows that at low P levels both solutions extract nearly the same amount.

It is obvious from the average A horizon values derived by double acid and Mehlich extractions (Figure 20) as well as the fact that foliar P levels clearly are not deficient, that the critical levels found to be valid on Coastal Plain sites are not applicable to this Piedmont soil.

The relationship between foliar P and extractable soil P is depicted in Figure 21, where the 670 kg P/ha GRP treatment was excluded. Assuming that a 1000 ppm foliar P level is a valid critical level for loblolly pine on this site, it can be seen that critical soil levels corresponding to this foliar level are much lower than on Coastal Plain soils. Whereas values of about 4.0 ppm (double acid) or 5.0 to 6.0 ppm (Mehlich) are considered critical on the Coastal Plain, values in the order of only 1.0 and 1.5 ppm seem applicable on this Piedmont soil.

Sanchez and Uehara (1980) report that lower levels of solution P are required for plant growth on fine textured

soils as compared to sandy soils. Phosphorus movement is restricted on Coastal Plain soils to diffusion through thin water films on soil particles. To establish a concentration gradient strong enough to move an adequate amount of P to the depleted zone around a root, the solution concentration needs to be higher on these coarse textured soils. Furthermore, the roots in Piedmont soils should be in closer contact with a greater quantity of soil P since fine textured soils have a much greater total surface area than sandy soils for a given volume. Apparently a greater amount of extractable P is required on Coastal Plain soils to compensate for the slower diffusion rates and greater distances required for diffusion to the pine roots.

Adepoju et al (1982) worked with the residual effect of added P on plant uptake and stated that an estimate of available P depends upon soil characteristics and the nature of soil compounds that have accumulated. The ratio of P taken up by plants to extractable soil P tended to be lower on the finer textured soils suggesting that critical extractable levels should be lower on these types of soils than on sandier soils.

Extractable soil Fe and Al

Extractable Fe and Al were determined because they are the most important elements involved with P fixation in acid soils. Both were extracted by the double acid and Mehlich procedures (Figures 22-27). Again it is regrettable that a neutral salt extraction was not also used since levels of exchangeable Fe and Al are important to P fixation by precipitation reactions. The harsh reagents used also removed Fe and Al from polymers and some crystal lattice structures in addition to the exchangeable forms.

Within the normal pH range of soils, exchangeable  $Fe^{+3}$  does not exist. Since pK values for the first two hydrolysis reactions are 2.9 and 3.3 (Bohn et al., 1979) most Fe in soils above pH 4 will exist as some form of neutralized  $Fe(OH)_3$  either as crystalline goethite or an amorphous form. Exchangeable  $Al(H_2O)^{+3}$  is common in acid soils since hydrolysis of Al occurs at much higher pHs than Fe. A commonly derived value for the pK of Al is about 4.5. Since many of the pH's involved in this study were below 4.5, there was probably a lot of exchangeable Al which can react readily with P.

On unlimed soils extractable Fe was almost four times higher at the surface than below 10 cm (Figure 22 and 23). The steady decrease in depth across all treatments seems odd



since Fe is often thought to increase with depth, especially into the B horizon where clays and sesquioxides accumulate. Average A horizon values were near 50 ppm Fe while the B horizon was only about 20 ppm. It is necessary to keep in mind that these extractable levels represent neither exchangeable nor total Fe, but were largely derived from Fe hydrous oxides which released Fe under acidifying conditions. The high surface Fe levels that decreased rapidly with depth probably resulted from two factors: Fe released by organic matter at the surface, and neutralization of the extractants by the soil taken from lower depths.

The greater quantities of Fe near the surface probably correspond to organic matter content and represent the effect of nutrient cycling from lower parts of the profile to the surface through the litter layer. Although Fe is only a micronutrient in plants, such Fe levels could have developed at the surface because of the long time period involved and the immobility of Fe. Since this soil has remained unplowed and nutrient cycling has occurred through the life of the current pine stand as well as the previous hardwood stand, over fifty years have elapsed during which litter layers have continually released small amounts of Fe to the soil. This Fe probably reacted immediately to form immobile hydrous oxides due to the low pK values involved.

Apparently these Fe products which may resemble amorphous  $\text{Fe}(\text{OH})_3$  were more readily extracted by the acid solutions involved, even though more total Fe may exist in some less soluble sesquioxide form further below the surface.

There was an inverse relationship between pH and extractable Fe which is most striking for double acid values. This may partially reflect the difficulty of extracting the more neutralized forms of Fe which exist at higher pH's, but could also be related to the soil's ability to partially neutralize the extractants. Due to the low pK of Fe hydrolysis reactions, the pH of these solutions must be very low to be efficient extractors. At the surface where pH's were generally lower, the double acid extracted relatively large amounts of Fe. At greater depths, the higher pH's and greater base saturation tended to neutralize acidity of the extractant, thereby reducing its ability to dissolve Fe-hydroxides. The Mehlich solution was not as subject to buffering by the soil since it has a higher ionic strength and solution-soil ratio; consequently, Mehlich Fe values were not as strongly related to pH. At lower depths where the pH range was narrow, there was no significant relationship between Mehlich Fe and pH (Table 6). At the surface where neutralization by the soil was minimal, double acid values were higher than Mehlich values because the pH

of the double acid solution is almost one unit lower than the Mehlich. Where double acid was neutralized at lower depths, the Mehlich values tended to be slightly higher.

The only treatment effect on extractable Fe resulted from liming and the effect was greater for double acid extracted Fe. A significant relationship between double acid extracted Fe and Ca ( $r^2 = .59$ ) and Fe and Mg ( $r^2 = .61$ ) indicated the influence of liming. Liming probably decreased extractable Fe due to a combination of the formation of less soluble polymers and the buffering effect on the extractants.

Since the hydrolysis reactions of Al have a higher pK than Fe, more Al can be expected to exist in a readily exchangeable form. Dissolution of Al hydroxyls does not require as low a solution pH as Fe-hydroxyls; therefore, the buffering capacity of the soil did not affect the Al extracting ability of the double acid as greatly as with Fe. Consequently, although double acid extractable Al decreased with depth in a fashion similar to Fe, the relative differences were not as great (Figure 19).

As was the case with Fe, the soil pH had a significant impact on extractable Al levels as shown by a strong relationship between double acid extracted Al and pH, extractable Ca, and extractable Mg, especially at the

surface where a wider pH range existed. Higher pH's lead to formation of larger, more neutralized Al hydroxides and amorphous or crystalline gibbsite materials which are not as readily extracted as exchangeable Al (Coleman and Thomas, 1967). Furthermore, a higher pH should tend to increase the neutralization of the extractant, but this is probably not as important as with Fe since the solution pH does not have to be as low.

Since the Mehlich solution is more resistant to being neutralized, the relationship between Mehlich Al and pH was not as strong as with the double acid. Unlike the case with extractable Fe, the relationship between Mehlich Al and pH is significant at the lower depths (table 6) illustrating the effect of pH on polymerization. The relationship did not exist for Fe since the pHs involved were well above the Fe hydrolysis pK values.

The most striking difference between the two extractants was that the Mehlich Al values increased with depth and the double acid values decreased (Figure 19). The tendency for Mehlich Al to increase with depth seems more logical since Al should increase with clay content and sesquioxides at lower levels. Apparently, the Mehlich solution is much more effective at extracting Al and less influenced by the soils buffering capacity. It is partially

understandable that the solution should extract more Al since (1) the  $\text{NH}^+$  in solution can displace Al from the exchange complex; (2) a greater solution soil ratio assures that more total Al can be removed from the soil; (3) enough HCl is present to make the solution acidic enough to dissolve Al hydroxyls; and (4) acetic acid provides resistance to neutralization. Yet it seems odd that the Mehlich values are so much higher than the double acid since the Mehlich solution also contains  $\text{F}^-$  ions which react instantly with  $\text{Al}^{+3}$  to remove it from solution. Apparently not enough  $\text{F}^-$  is included to react with all the Al extracted.

Liming was the only treatment having an effect on extractable Al. This was probably due to neutralization of the reactive exchangeable Al into a less soluble gibbsite form.

### Phosphorus fractionation

P fractionations are often used as a method to determine the fate of applied P to a soil (Chang and Chu, 1961; Chu et al., 1962; Volk and McLean, 1963; Singh et al., 1969). Usually some form of a Chang and Jackson (1956) fractionation is used to break the soil P into one of four groups: saloid-P, Al-P, Fe-P, and Ca-P. Whichever category correlates best with plant uptake or growth is often considered to be the fraction most plant available.

Olsen and Khasawneh (1980) discuss some of the problems involved with the P fractionation. Originally, the scheme was based on the assumption that Al-P, Fe-P, and Ca-P exist primarily as variscite, strengite, and hydroxyapatite. Although one of the major criticisms concerned the non-selectiveness of a neutral  $\text{NH}_4\text{F}$  solution for Al-P (Pife 1959a,b), the problem was generally corrected by modifying the procedure to include an  $\text{NH}_4\text{F}$  solution adjusted to pH 8.2 (Peterson and Corey, 1966) as performed in this study.

Although results derived by the modified Chang and Jackson procedure are reasonable for soils near equilibrium, too many researchers have ignored the assumptions upon which the procedure was based. Most compounds formed following addition of P to the soil system are not the same ones for which the fractionation scheme was developed. Failure to

consider the P compounds involved often leads to erroneous conclusions as to what forms of P are actually involved in each fraction (Olsen and Khasawneh, 1980). Many researchers have learned to avoid mistakingly placing P in a wrong category by referring to  $\text{NH}_4\text{F}$  extractable P instead of Al-P, or NaOH-P instead of Fe-P, etc. Although this may protect the researchers from making inaccurate statements, it doesn't really help to explain the status of soil P.

Following P fertilization in acid soils, taranakites  $(\text{NH}_4, \text{K})_3\text{H}_6\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$  are commonly formed (Lindsay et al., 1962). As Al-P, one should expect to be able to extract it with  $\text{NH}_4\text{-F}$ . Ballard (1973) found that, although  $\text{NH}_4\text{F}$  was an effective extractor of P from pure taranakite, much would be readsorbed in the presence of soil so that only about 80% was extractable by  $\text{NH}_4\text{F}$ . The rest would probably come out in the NaOH fraction and be mislabeled as Fe-P. Wavellite  $(\text{Al}_3(\text{PO}_4)_2\text{OH}_3 \cdot \text{H}_2\text{O})$  is an Al-P that forms after a period of time in fertilized acid soils without high K concentrations. According to Barwood (1979), wavellite is only 20% soluble in  $\text{NH}_4\text{F}$  and the other 80% is removed in the NaOH extract. Ballard (1973) reports that only 4% of wavellite is extracted with  $\text{NH}_4\text{F}$ . Another very important fertilizer reaction-product in soils with only a slight amount of acidity is crandalite  $(\text{CaAl}_3(\text{PO}_4)_2\text{OH}_3 \cdot \text{H}_2\text{O})$ , an Al-

Ca-P combination. In a typical fractionation scheme Barwood (1979) extracted less than 5% of the P with  $\text{NH}_4\text{F}$ , almost 80% with  $\text{NaOH}$ , and about 20% with  $\text{HCl}$ . Therefore it seems that by disregarding the forms of P which exist in recently fertilized soils, much of the Fe-P reported in the literature is actually Al-P that was not extracted by  $\text{NH}_4\text{F}$ . Furthermore, not all Fe-P is extracted by the  $\text{NaOH}$ . Although increasing the  $\text{NH}_4\text{F}$  solution to pH 8.2 prevented the removal of P from strengite, which is considered the most common form of crystalline Fe-P, Ballard (1973) showed that about 60% of amorphous Fe-P is still extracted by  $\text{NH}_4\text{F}$ .

Nevertheless, keeping all the discrepancies in mind and realizing that much P is held via adsorption mechanisms on Al-hydroxyls, which should behave similarly to variscite and dissolve in  $\text{NH}_4\text{F}$  (Hsu, 1977; Ballard, 1973), data for a modified Chang and Jackson fractionation are presented in Figures 14-17 and 23. Considering that 20 years have elapsed since fertilization, more time has been allowed for equilibration of applied P, in the case of applied TSP. Taylor and Gurney (1964) reported the conversion of recently formed taranakite and Ca-Al-P to non-crystalline Al-P which were reported to be good available P sources for plants. Therefore, classification of the various forms of P is probably more valid than in cases where fractionations were performed shortly after fertilization.



Saloid-P (NH<sub>4</sub>Cl extractable)

Ammonium chloride extractable P (Figure 28) is probably the closest estimate of P intensity that can be made since it should be readily exchangeable. For most treatments, average A horizon values were between 1.0 and 2.0 ppm (Figure 33). The trend of NH<sub>4</sub>Cl extractable P levels exactly followed that of foliar P. A similar pattern also existed for NH<sub>4</sub>F-P and NaOH-P. The correlation between NH<sub>4</sub>Cl-P and foliar P ( $r^2 = .35$ ) was somewhat less than that for NH<sub>4</sub>F-P and NaOH-P, but the significance of the relationship for NH<sub>4</sub>Cl-P may be downplayed by the narrow range of values involved and the level of variability associated with a P fractionation procedure. It seems logical to assume that this NH<sub>4</sub>Cl-P fraction is most important for supplying plants with P, and other fractions are more important for gradually replacing this P which the plants remove. The relationship between all fractions were significant (Table 8), but the correlation between NH<sub>4</sub>Cl-P and NH<sub>4</sub>F-P was stronger ( $r^2 = .91$ ) than that with NaOH-P ( $r^2 = .71$ ) or Ca-P ( $r^2 = .85$ ).

It is interesting to note that more P existed as exchangeable P than double acid extractable P in the top 10 cm of the limed soil (Figure 17 and 28). Apparently, much of the P in this soil was loosely bound, and when extracted

with double acid, much was re-fixed with reactive Al produced by the extraction process from dissolution of Al minerals. The re-fixation problem did not occur in the Mehlich solution where the  $F^-$  ion reacts with  $Al^{+3}$  before P.

The only significant treatment effect occurred from application of 670 kg P/ha GRP where the A horizon levels were almost 6 ppm (Figure 33). Even though the differences are insignificant, saloid-P levels of all other P treated soils appeared to be higher than unfertilized soils (Figure 33) as were extractable P levels (Figure 20). Fertilization with P resulted in a greater quantity of P capable of maintaining somewhat higher levels of P in the soil solution after 20 years.

#### Al-P (NH<sub>4</sub>F extractable)

The NH<sub>4</sub>F solution at pH 8.2 is theoretically the extractant for Al-P. Despite all the problems discussed with the fractionation of fertilized soils, it may not be too presumptuous to refer to the NH<sub>4</sub>F-P involved in this study as predominantly Al-P. Although Ballard (1973) showed that amorphous Fe-P is soluble in alkaline NH<sub>4</sub>F, crystalline strengite is not. It's impossible to determine how much Fe-P is in amorphous form from data generated in this study, but since Juo and Ellis (1968) reported that amorphous Fe-P converts rapidly to crystallized strengite, it was likely

that most Fe-P in this study existed as strengite and was not extracted by  $\text{NH}_4\text{F}$ . Furthermore, although taranakite, wavellite, and crandalite are initial Al-P fertilizer reaction products not completely soluble in  $\text{NH}_4\text{F}$ , much time had elapsed during which many of these forms could have converted to variscite. It was more likely that these intermediate products were more prevalent in the high rate GRP treatment where some P had recently dissolved from its apatite form.

Values for  $\text{NH}_4\text{F}$ -P are reported in Figure 29 by depth, and Figure 33 as A horizon averages. As was the case for every other P fraction in this study, only the high rate GRP treatment was significantly higher than the rest. The control soil A horizon contained 4.6 ppm  $\text{NH}_4\text{F}$  extractable P whereas the 670 kg P/ha treatment had 35.0 ppm. The other treatments range from about 6.0-8.0 ppm P (Figure 33).

It has often been reported that there is a tendency for applied P to be initially fixed as Al-P and to convert with time to Fe-P (Hsu, 1965; Juo and Ellis, 1968). In this study, Al-P levels were higher when 160 kg P/ha was applied as GRP than TSP. It could be argued that since TSP is completely water soluble and has had several years more time to equilibrate with the soil, more of the Al-P had converted to the Fe-P form. Where lime was applied with TSP, there

was 1.6 ppm more Al-P and 1.5 ppm less Fe-P, which could support the suggestion that liming decreases the conversion of Al-P to Fe-P.

Phosphorus extracted as Al-P may have been the most important single contributor to the nutrition of loblolly pine in this soil. It already been pointed out that the Al-P fraction was most strongly correlated to the readily exchangeable P (Table 8). Furthermore, this fraction was most related to double acid- and Mehlich extracted P (Table 8), as well as foliar P (Table 9), indicating that this  $\text{NH}_4\text{F}$  extracted P fraction might be the best single estimate of the P quantity factor used to supply the long term P requirements.

#### Fe-P (NaOH extractable)

Although it was probably safe to assume that most  $\text{NH}_4\text{F}$  extractable P is Al-P, it is not necessarily valid to claim that all the NaOH-P is Fe-P, or think that all the Al-P was extracted by  $\text{NH}_4\text{F}$ . The NaOH probably includes some Al-P or Al-Ca-P, produced as fertilizer reaction products. Of the four involved in this study, the NaOH fraction was by far the largest.

Non-treated soils contained about 17 ppm NaOH extracted P in the A horizon (Figure 33). The only significantly higher treatment was the high level GRP which had about 47

ppm P. Both the 160 kg P/ha treatments had about 21.0 ppm P regardless of source. Liming the unfertilized and fertilized plots decreased NaOH-P slightly. Iron surfaces would be less reactive at higher pH's and not able to fix as much P.

There was a significant correlation ( $r^2=.40$ ) between this fraction in the A horizon with foliar P (Table 10). The relationship was strongest at the surface where extractable Fe levels were highest, and almost non-existent below 10 cm. Of all fractions, Fe-P was the least correlated with extractable P (Table 9).

#### Ca-P (H<sub>2</sub>SO<sub>4</sub> extractable)

On acid soils, Ca-P is not generally considered to be an important source of soil P due to its low levels. Calcium phosphates tend to dissolve readily and P is converted to an Al-P or Fe-P form. In this study, Ca-P levels were about the same as saloid-P with about 1 ppm existing in the A horizon of control soils (Figure 33). When 160 kg P/ha was applied, levels of Ca-P were closer to 2 ppm. The most important information to be gleaned from the Ca-P data was that much of the P applied as GRP at the high rate still seems to be in its original form. At the surface, there were 56.0 ppm P as Ca-P at the high rate of GRP and only 5.0 ppm at the low rate. Its hard to say exactly how much of the Ca-P was still original apatite.

With high Ca concentrations and an increased pH, some P released from apatite may form some other Ca-P form or an Al-Ca-P form such as crandalite. However, since the soil pH of the 0-5 cm depth of the high rate GRP treatment was lower than the 5-10 cm depth (Figure 7), it seems that any P existing as Ca-P above the level found from 5-10 cm must be attributable to undissolved apatite. Based on this assumption, approximately 45 ppm P as GRP existed at the surface 5 cm. Assuming an acre furrow slice weighs two million kilograms per hectare, this undissolved GRP represents between 20 and 30 kg P/ha. After twenty years most, but not all, of the GRP dissolved.

Considering the low levels of Ca-P in the soil, it is doubtful that this fraction played much of a role in the nutrition of loblolly pine on this site, except possibly on the GRP plots. The relationship between Ca-P and foliar P was barely significant (Table 10).

Ratio of Al-P to Fe-P

The ratio between Al-P and Fe-P values (Table 8) was examined for each treatment because the Al-P fraction seems to be the most important source of P to this stand, and there is a reported tendency for Al-P to convert to Fe-P over time. Where no P was added or where TSP was added without lime, the values for the A horizon were essentially the same (0.30). There was about three times more Fe-P than Al-P. This apparently represented an equilibrium ratio for the soil. The TSP treatment had twenty years to react and had probably neared equilibrium. Consequently, this was the only fertilizer treatment with foliar levels not significantly higher than the control.

The highest and only significantly different ratio existed on the high rate GRP treatment (0.66). About twice as much Al-P existed as Fe-P on this treatment. If there was a tendency for Al-P to convert to Fe-P with time, then the ratio should have been high on this treatment, since P was still being added from the apatite at the surface and initially forming Al-P.

Where 160 kg P/ha GRP or 160 kg P/ha TSP with lime was applied, the ratio (0.40) was between the equilibrium and high rate GRP treatment. It is understandable why the TSP treatment with lime would be higher than TSP alone. A

higher pH tends to slow the conversion of Al-P to Fe-P by increasing the solubility of Fe-P (Hsu, 1965). In the case of GRP application, less time has been involved for all the P to equilibrate. With time, both of these treatments should approach the equilibrium ratio existing on untreated plots. Total soil P

Total soil P was determined for each treatment by depth (Figure 32) and A horizon averages were compared to the levels of the other four P fractions determined in this study (Figure 33). There was much more P in the soil than can be extracted with  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{F}$ ,  $\text{NaOH}$ , or  $\text{H}_2\text{SO}_4$ . Most soil P existed in organic or occluded form and was not readily available to plants. Total P levels were highest at the surface, decreased to 15 cm, and then increased again in the B horizon.

Organic P at the surface was released only through microbial decomposition. Once this P was released, it was probably refixed into an Fe or Al form. A decrease in organic matter with depth is reflected by the decreasing levels of total P from the surface to 15 cm. At lower levels, P accumulated due to a higher sesquioxide content and consequently total P levels increased again in the B horizon.



Occluded P is formed when P which exists on the surfaces of Fe or Al hydroxyls, or as a precipitate, is covered by a newly formed layer of Fe or Al hydroxyls. Phosphorus can also become entrapped beneath the surface of an amorphous Fe or Al gel when adsorbed surface P diffuses into the structure. The relative amount of P in an occluded form was much higher in the B horizon as evidenced by total P levels which were higher than other P fractions. Furthermore, Mehlich extractable P levels which were shown to be little affected by soil buffering capacity, were lower in the B horizon than the A horizon. Therefore, even though more P existed in the B horizon, it was largely in a form not available to plants. Correlation between extractable P and foliar P was lowest for the B horizon and top 5 cm of the A horizon (Table 10), suggesting that occluded and organic P were not of immediate importance to loblolly pine nutrition. These two forms of P can probably be considered non-labile and available only over the long run.

As with all P fractions examined, only the high rate GRP treatment had a significantly higher total P level in the A horizon. B horizon treatment differences were not significant. In the A horizon, the 670 kg P/ha GRP treatment had only 66 ppm P, or about 150 kg P/ha more total P than the control (Figure 33). The 160 kg P/ha treatments

had only about 40 kg P/ha more than the control. It was difficult to account for the rest of the added P. Some probably moved to lower horizons, but the differences among treatments in the B horizon account for only a small amount of added P. Erosion should not have been a factor since the terrain is nearly level and a hardwood litter layer existed at the time of planting. Differences in total P uptake by plants may account for some P not in the soil. As noted already, foliar P levels in the loblolly pines were higher on fertilized plots and it seems probable that P levels in other species were also increased. Without having done a foliar analysis on all the understory which has a high species diversity, it is impossible to account for all added P; however, a considerable portion could exist in the biomass as well as being incorporated into the litter layer.

It is important to understand that while extractable soil P levels in this soil are below critical values generally considered to be deficient on the Coastal Plain, the total levels of soil P in this Piedmont soil were 3 to 4 times higher than most Coastal Plain forest soils. Pritchett and Comerford (1982) reported that the Bladen fine sandy loam and the Rutledge loamy fine sand, which responded to P fertilization with increased slash pine growth, had total P levels of only 74 and 48 ppm. Other soils which did not

respond had lower levels near 50 ppm. These sandy soils do not have a sufficient quantity of clays and sesquioxides to maintain high levels of soil P against leaching. Apparently, Coastal Plain P deficiencies result from a combination of lower total soil P levels, and the requirement for a greater solution P concentration than was found on this Piedmont soil.

### Phosphorus adsorption isotherms (Q/I Curves)

Phosphorus adsorption isotherms provide information about the P sorbing characteristics of the soil. Maximum P adsorption is indicated where the slope of the curve approaches zero. The rate of P sorption is indicated by the slope. Where a steeper slope exists, applied P is sorbed by the soil at a greater rate, deterring an increase in soil solution P concentration.

Data for this study (Figure 34) show that this Tatum soil was capable of sorbing large amounts of P. The derived curves did not indicate the maximum sorbing capacity, but it seems to have been in excess of 2000 ppm for all treatments.

The Bladen and Rutledge soils of the Coastal Plain, already mentioned to be responsive to P application, had sorption maxima of only 280 and 116 ppm (Humphreys and Pritchett, 1971). Other Coastal Plain soils involved with their study had even lower sorption capacities. Unable to retain added P, these soils can be readily leached.

Several years after application phosphorus often has a residual effect of decreasing the sorption maximum and buffering capacity to produce a Q/I curve which lies nearly parallel but beneath the control soil (Bertsch, 1980). Applied P, retained on fixation sites for several years, reduces the adsorption or precipitation of subsequent P

additions. Presumably with time this P is removed by plants or transformed to occluded forms such that the soil returns to its original P sorption capacity.

In this study both the GRP treatment curves are somewhat below the control soil, whereas the TSP treatment and control are practically identical. These curves provide further evidence that GRP produced a more long term impact on soil P availability than TSP. Comparison of Al-P : Fe-P ratios suggested that the transformation of applied P towards the control situation had proceeded further for the TSP treated soils. The Q/I curves show that where P was applied 20 years ago as TSP, the P fixing characteristics of the soil appeared to have returned to initial conditions, whereas in the case of GRP, some P still existed on fixation sites reducing adsorption of added P and allowing for a greater increase in solution concentration.

As would be expected, GRP at the high rate had a more pronounced effect on the sorption characteristics than at the low rate. A combination of more added P and less time for this P to undergo transformations resulted in more fixation sites being occupied after 20 years.

The greatest impact on the P sorbing characteristics of this soil resulted from liming. The sorption maximum for both limed plots appeared to be reduced as had the buffering

capacity. This liming effect resulted from reduced levels of available Fe and Al to react with applied P (Figures 26 and 27).

### Potentiometric titration of soil acidity

It appeared that soil Al was an important factor in affecting the availability of applied P to loblolly pine. Of the four soil P categories examined, the Al-P group seemed to be the most important. It was most highly related to foliar P (Table 10), readily exchangeable P (Table 9), and extractable P (Table 9). Furthermore, liming was shown via the Q/I curves to have an impact on P fixation even after 20 years. It is well known that liming is particularly effective at reducing soil acidity via neutralization of Al compounds. Therefore the forms and levels of Al in the soil which affect P sorbing characteristics were examined by potentiometric titration.

Inflection points on the titration curves (Figure 35) indicated changes in the predominant form of Al contributing to soil acidity. On unlimed soils the first inflection point occurred at a pH near 4.5 which is approximately the pK for the first hydrolysis reaction of trivalent Al. Below pH 4.5 most Al exists in an exchangeable trivalent ion form. As pH increases above 4.5 more Al reacts with hydroxyl groups to form hydroxy polymers such as partially neutralized coatings or interlayer material. As pH rises, the polymeric groups become more neutralized, larger, and less exchangeable as they approach a form similar to gibbsite. The inflection

points near pH 6 to 6.5 represent a point where most Al has reacted with hydroxyls and hydrolysis of other materials such as organic matter are becoming the greatest contributors to total soil acidity.

Analysis of the titration curves from this study (Figure 35) confirmed earlier speculations regarding the effect of treatment on P adsorption. Treatment effect on soil acidity closely paralleled the observed effects on Q/I curves (Figure 34). Liming had a great effect on reducing soil acidity, whereas P application had only a minimal impact. Liming reduced total acidity to only about half of that of other treatments (4-5 meq/100 grams versus 10 meq/100 grams). Almost all the acidity attributable to exchangeable Al below pH 4.5 on the control soil (1.5 meq/100 grams) was neutralized by liming. The level of soil acidity between pH 4.5 and 6.5 on the limed plots (1.5 meq/100 grams), predominantly due to hydrolysis of Al hydroxides, was reduced to about one third the level found on control soils (4.5 meq/100 grams). These reductions in soil Al forms corresponded to the decreased sorbing ability of these soils as evidenced by the Q/I curves.

As was the case with sorption characteristics, P application had only a slight effect on soil acidity compared to liming after 20 years. Once again the greatest



P effect without liming occurred where GRP was applied at the high rate. At equivalent rates of application, GRP had slightly decreased soil acidity while TSP had no effect. These results compare directly with treatment effects on Q/I curves (Figure 34). After 20 years, levels of Al contributing to total soil acidity on the TSP plots returned to the same state as untreated soils. Presumably these factors are the same ones largely responsible for P sorption and the ratio of Al-P : Fe-P.

The GRP treatments decreased soil acidity while TSP didn't because of the time factor involved with transformations of applied P. Where 670 kg P/ha was applied, less time was available for reaction of a greater amount of applied P and consequently this P treatment had the greatest effect on soil acidity. Another factor involved with GRP treatments which may serve to reduce soil acidity and P sorbing characteristics is inclusion of the F<sup>-</sup> ion. The GRP (fluoroapatite) releases an appreciable amount of F<sup>-</sup> ions to the soil system along with P. According to Hsu (1977), the OH<sup>-</sup> and F<sup>-</sup> ions are effective competitors with P for Al binding sites. These F<sup>-</sup> ions may be partially responsible for lower levels of reactive Al in the GRP treatments which contributed to soil acidity or P sorbing reactions. A combination of slower dissolution rates, a greater level of

applied P, and the inclusion of the F<sup>-</sup> ion may have caused the high rate GRP treatment to have the greatest long term effect on loblolly pine P uptake, extractable soil P levels, P sorption characteristics, and soil acidity.

## CONCLUSION

A loblolly pine lime and P fertilization trial was evaluated 20 years after establishment on a Piedmont silt loam known to be P deficient for agronomic crops. Neither P fertilization nor liming had an effect on tree growth. Foliar analysis revealed that P levels of untreated trees were above 0.1% and that a P deficiency was not the immediate growth limiting factor even though surface horizon double acid extractable P levels were only 1.5 ppm.

Foliar N levels slightly below 1.2% after 20 years may have indicated a marginal N deficiency and it seems probable that added N would have improved growth as has been the case in most Piedmont studies. Physical site conditions may also have limited growth. Site indices are often lower on eroded Piedmont soils with plastic subsoils due to restricted root system development.

Although P was not the growth limiting factor on this site, the effects of the various treatments on P uptake were important. By eliminating the immediate growth limiting factors, it is possible that a P deficiency could have

become a factor restricting further growth. Under such circumstances, treatment to increase P uptake could have resulted in significant growth responses.

The study provided a comparison of TSP and GRP as P sources and afforded an evaluation of liming as it affected long term P uptake and loblolly pine growth. Characteristics of the soil related to its P fixing capabilities were also evaluated to help explain treatment effects on P uptake.

In this high P-fixing, acid, Piedmont soil, GRP was a more effective source than TSP after 20 years for supplying P to loblolly pine. At equivalent rates of application, extractable soil P and foliar P levels were higher where GRP was applied. The slow release of P from GRP reduced the amount of time during which much of the P could become occluded or transformed to crystalline Fe-P over the life of the stand. The timed release of P into solution virtually assured that there will always be a supply of P in exchangeable or readily available forms such as amorphous Al-P precipitate, until all the GRP had dissolved. Fluoride ions released by GRP were more competitive than P ions for exchangeable Al and possibly chemisorption sites thus reducing the P fixing capacity of the soil and increasing the availability of added P to plants.

Although P uptake by the stand was greater on TSP plots than GRP plots during the first two years (which is when P fertilization would be especially important), tissue levels on GRP plots were increased significantly over tissue levels of untreated trees and would probably be enough to correct a P deficiency had one existed. Furthermore, the increased availability of P on TSP plots during the first several years dramatically improved fireweed growth to the point where a severe competition problem developed on TSP plots but not where GRP was applied.

Disregarding financial considerations, application of GRP at 670 kg P/ha was more effective at increasing soil P levels and P uptake in the long run than where only 160 kg P/ha was applied. After 20 years, some of the GRP at the higher application rate still existed in its original form and was releasing P to the soil solution.

The availability of soil P was shown to be highest when a greater proportion of soil P was extractable in  $\text{NH}_4\text{F}$ , and to decrease as transformations proceeded which converted some of this soil P to a NaOH extractable form. The availability of added P as GRP should be expected to decrease with time as the ratio of Al-P :Fe-P approached that found in plots where no P was applied or where P was applied as TSP.

Liming with 4.48 T/ha resulted in a significantly higher surface-horizon pH 20 years after application. Although liming alone did not increase loblolly pine P uptake, it did reduce the P sorbing ability of the soil by neutralizing some of the reactive forms of Al. There was some evidence to suggest that liming may prolong the availability of P applied as TSP by slowing the transformations to the more unavailable forms. After 20 years, the TSP plots which also received lime had an Al-P :Fe-P ratio similar to that of the low rate GRP treatment, and foliar levels were significantly higher than the control. Where TSP was applied without lime, the Al-P :Fe-P ratio was almost the same as for the control, and there was no significant foliar level difference compared to unfertilized trees.

The recently developed Mehlich soil extractant was evaluated and, within the scope of this study, found not to offer any advantages over the double acid extraction method for routine use in forest soils. The Mehlich solution was a more effective extractor of soil P and other nutrients but did not seem to be as sensitive to subtle differences in soil levels as was the double acid. More significant differences in soil P resulted by comparison of double acid levels. Correlations of Mehlich and double acid extractable

P levels with the various soil P fractions and foliar P were nearly identical. The Mehlich did not overestimate the amount of available P when undissolved GRP still existed as did the double acid, but considering the simplicity and the well established nature of the double acid method in routine soil analyses in the Southeast, there was no evidence based on this study to suggest that the Mehlich solution be used instead.

This study showed that the critical levels of extractable soil P established through Coastal Plain studies were not applicable to this Piedmont soil. Data suggested that a deficiency should not occur until double acid extractable levels fall below 1 ppm. Considering the high levels of total soil P and the high P buffering capacity of this Tatum silt loam, a P deficiency should not develop for loblolly pine under current site conditions.

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APPENDIX



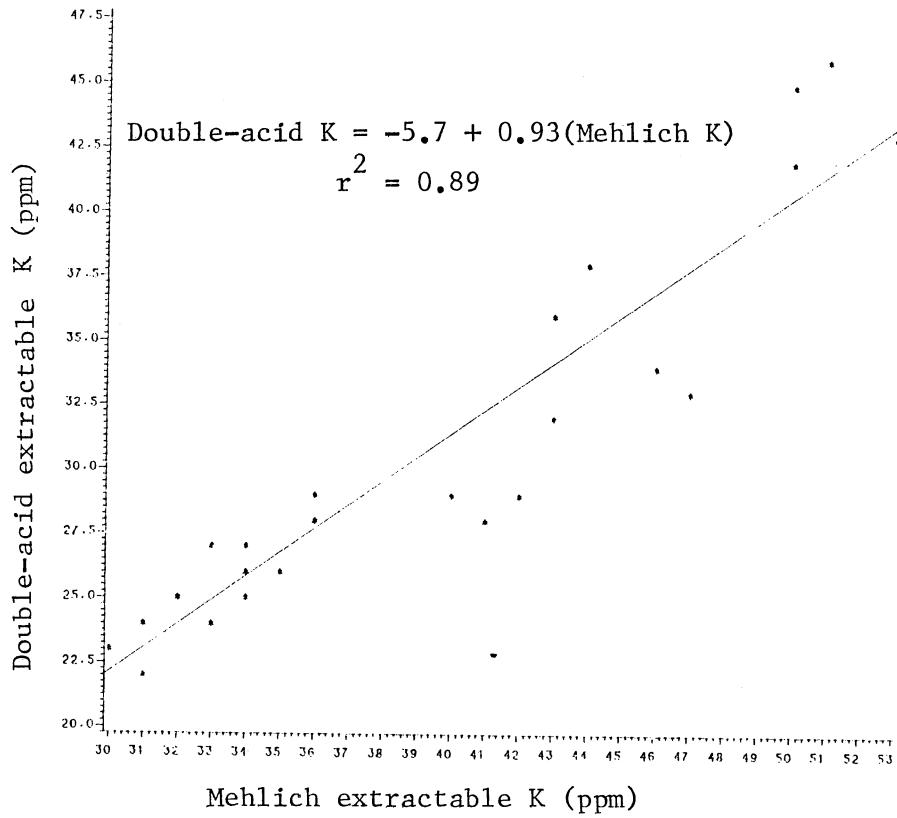


Figure A1. Relationship between double-acid and Mehlich extractable soil potassium on a Tatum silt loam in Orange County, Virginia.

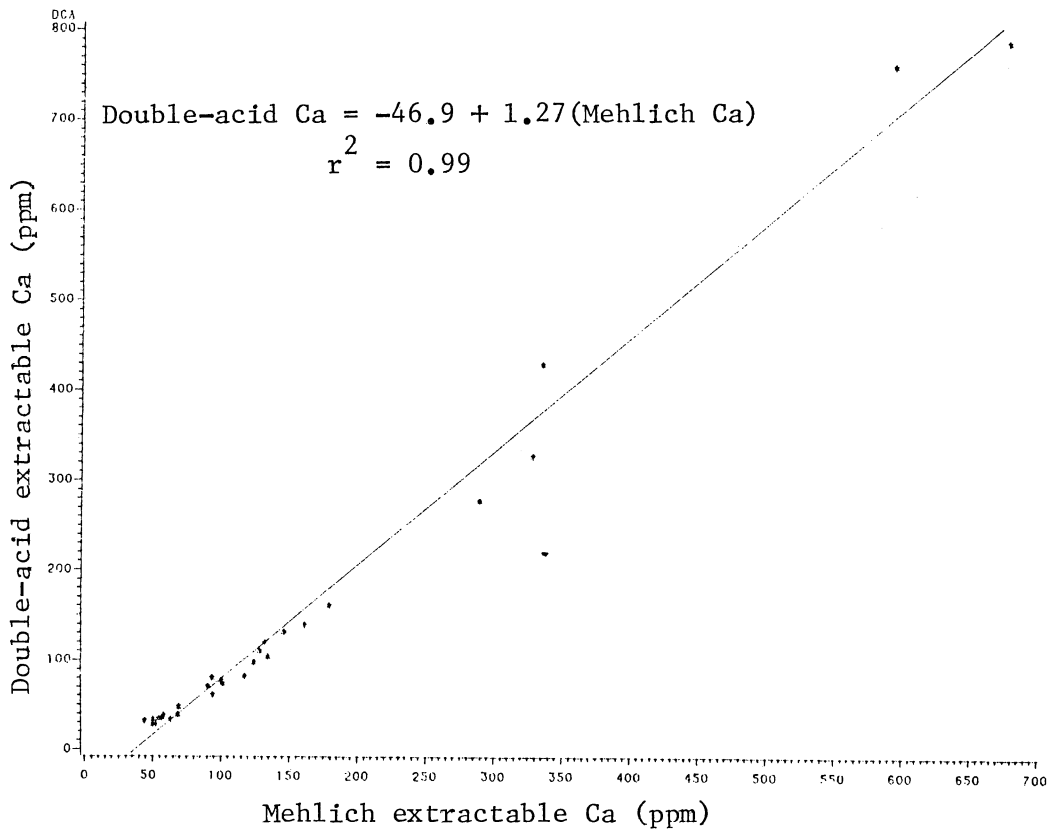


Figure A2. Relationship between double-acid and Mehlich extractable soil calcium on a Tatum silt loam in Orange County, Virginia.

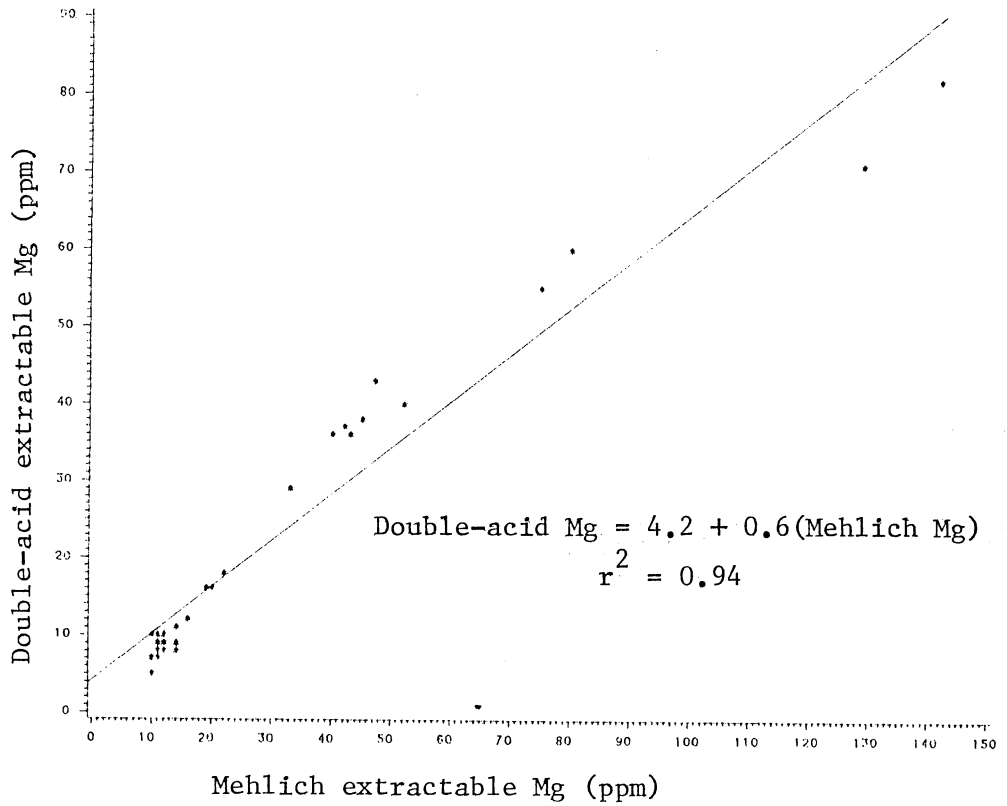


Figure A3. Relationship between double-acid and Mehlich extractable soil magnesium on a Tatum silt loam in Orange County, Virginia.

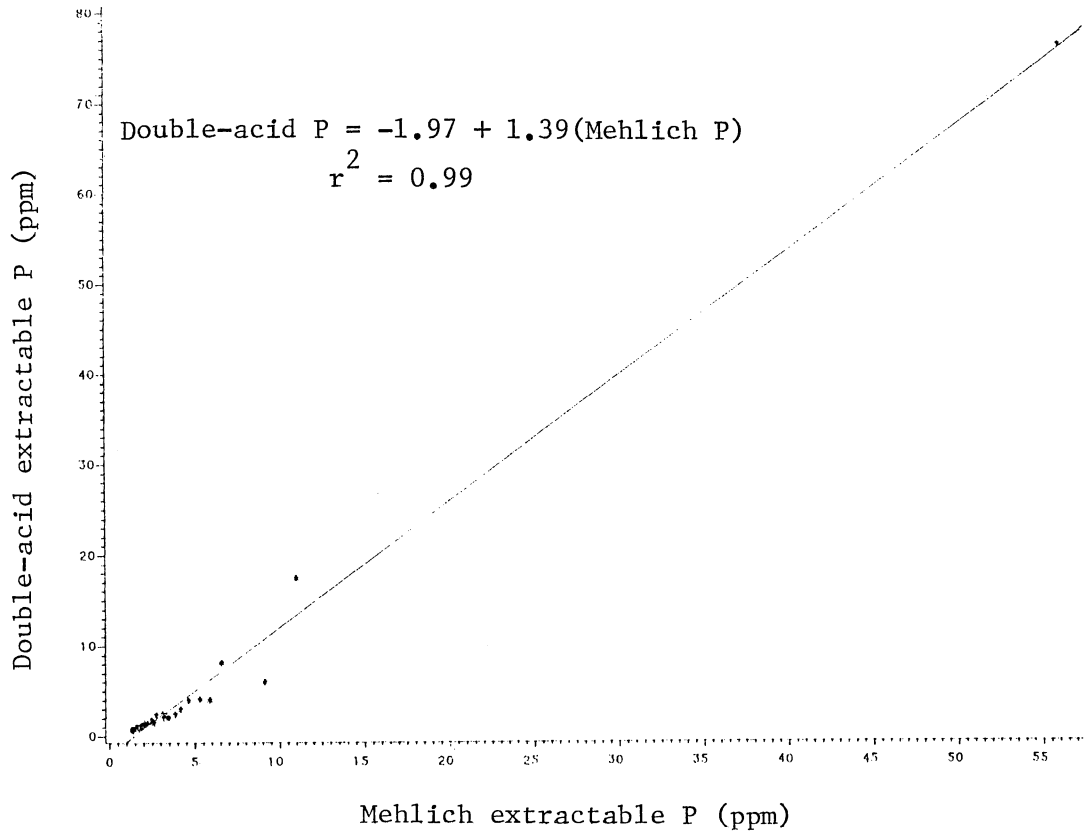


Figure A4. Relationship between double-acid and Mehlich extractable soil phosphorus on a Tatum silt loam in Orange County, Virginia.

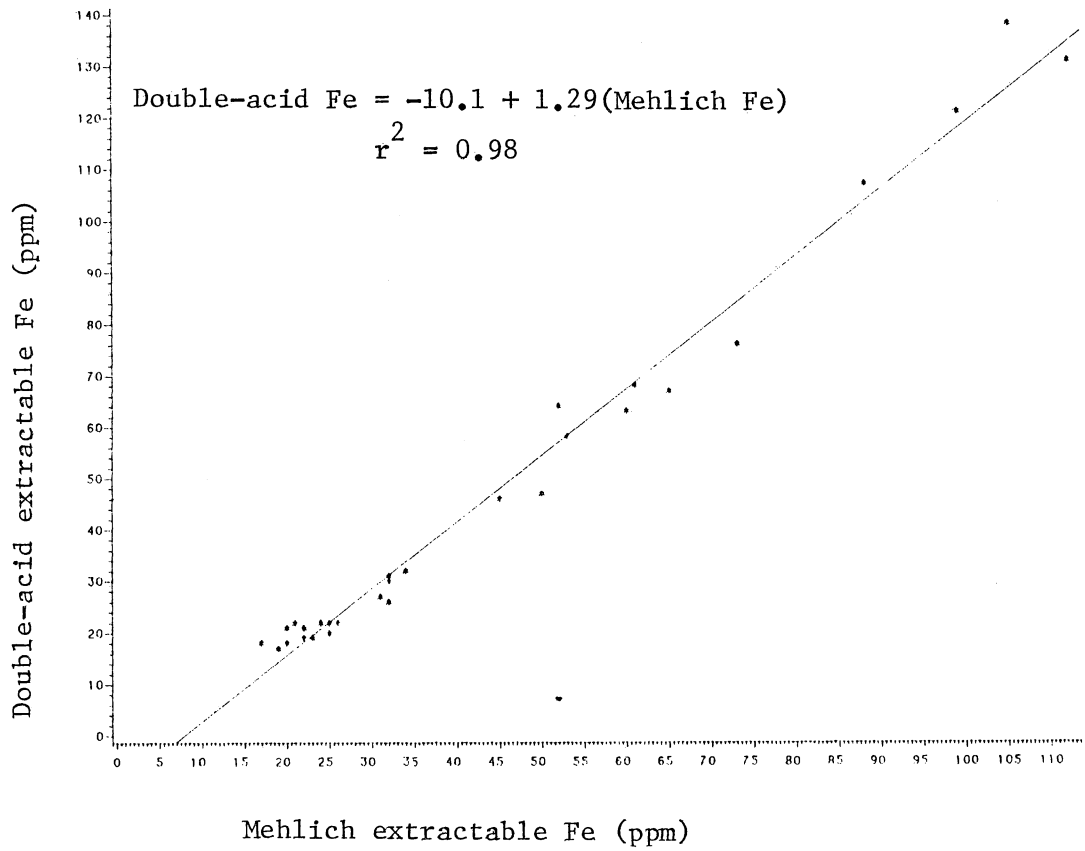


Figure A5. Relationship between double-acid and Mehlich extractable soil iron on a Tatum silt loam in Orange County, Virginia.

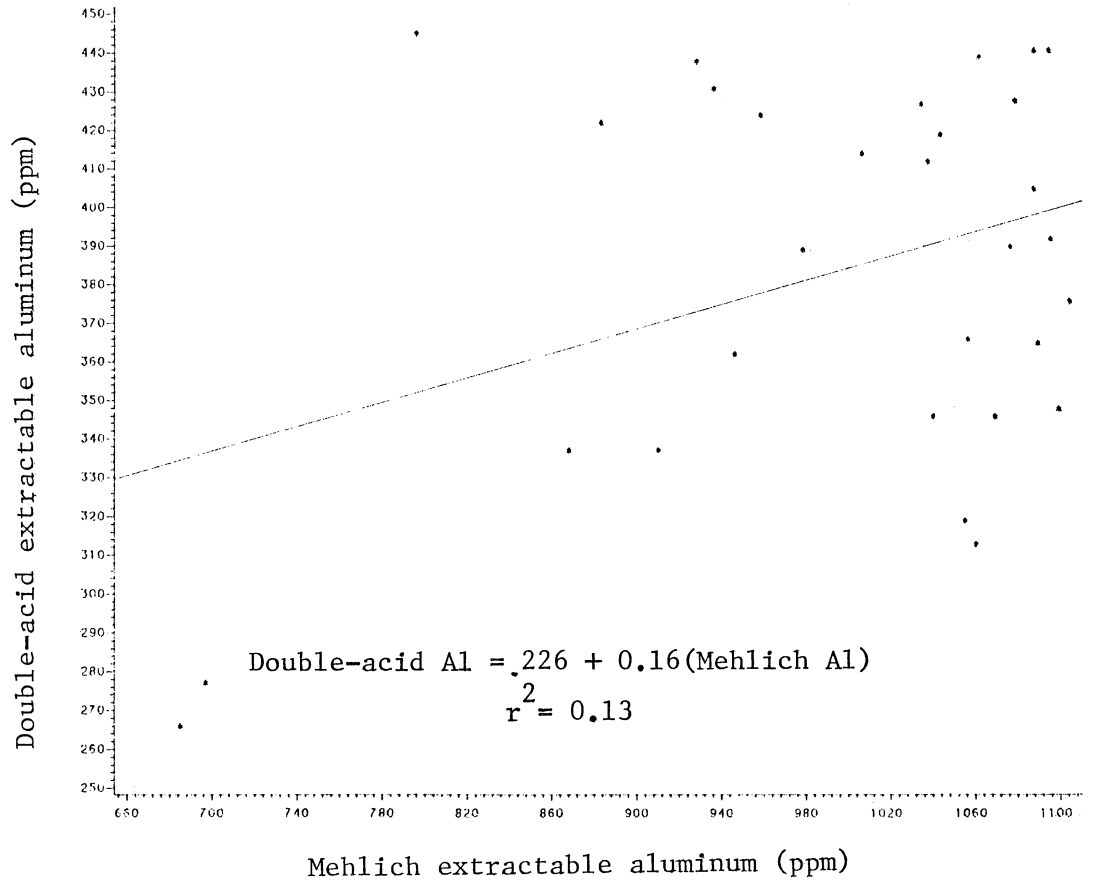


Figure A6. Relationship between double-acid and Mehlich extractable soil aluminum on a Tatum silt loam in Orange County, Virginia.

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THE FATE OF APPLIED PHOSPHORUS ON A PIEDMONT SOIL  
AND ITS EFFECT ON LOBLOLLY PINE GROWTH  
TWENTY YEARS AFTER APPLICATION

John L. Torbert Jr.

ABSTRACT

A loblolly pine phosphorus fertilization trial was evaluated 20 years after establishment on a Tatum silt loam in the Virginia Piedmont. Triple superphosphate (TSP) was applied at 160 kg P/ha and ground rock phosphate (GRP) was applied at both 160 kg P/ha and 670 kg P/ha. Lime (4.48 T/ha) was applied with and without the TSP treatment. Tree growth was not significantly affected by treatment and foliar phosphorus levels were above 0.10% indicating that a deficiency was not the immediate growth limiting factor. Double-acid-extractable soil phosphorus critical levels established for the Coastal Plain do not appear useful for diagnosing tree requirements for this Piedmont soil. A critical level of 1.0 ppm double-acid-extractable phosphorus would be more applicable to this soil. GRP was more



effective than TSP after 20 years at increasing phosphorus uptake, probably due to a slower dissolution rate and the inclusion of  $F^-$  ions which reacted with soil Al to reduce phosphorus fixation. Although an increase in the A horizon pH persisted for 20 years, there was no increase in phosphorus uptake as a direct response to this higher pH. Liming may have some long-term merit when applied in conjunction with a water soluble phosphorus fertilizer such as TSP by reducing the transformations of applied phosphorus to unavailable forms.