

**RELATIONSHIPS OF SOIL TEST PHOSPHORUS WITH SOIL PROPERTIES
AND PHOSPHORUS FORMS**

by

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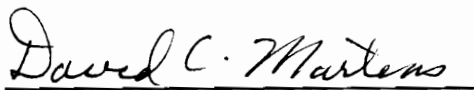
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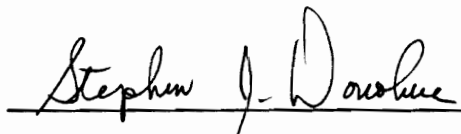
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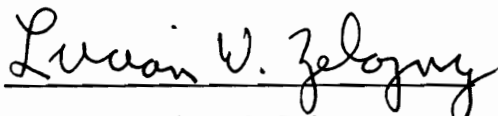
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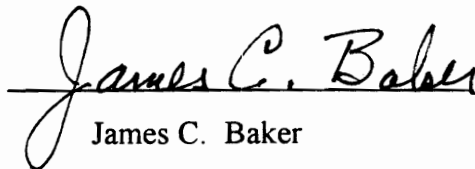
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Crop and Soil Environmental Sciences

(ABSTRACT)

A comprehensive approach to soil P management in agricultural systems requires a balance between nutritional enhancement of the soil and a reduction in adverse consequences on the environment. Evaluation of forms in which P is present in the soil, dynamics of P transformation across these forms, determinants of spatial and temporal distribution of P pools in the soil, and impacts of agricultural practices on the rate and direction of these reactions were the key objectives of the present investigation.

Phosphorus extracted by the four widely used soil extractants, i.e., Bray 1, Mehlich 1, Mehlich 3, and Olsen, represented less than 25 percent of the total P content in 43 Virginia soils from the Coastal Plain, Piedmont, and Ridge and Valley regions. Correlation between Bray 1 (1 minute and 5-minute shaking), Mehlich 1, and Mehlich 3

extractable P was high; correlation of these extractants was poor with the Olsen procedure which extracted the lowest soil P contents. The Mehlich 3 procedure was more reliable in the extraction of labile P than the Mehlich 1 procedure in soils with a wide range of pH values. The Mehlich 3 procedure was less prone to extraction of plant unavailable, structurally adsorbed phosphorus, particularly in dithionite-citrate-bicarbonate extractable Al_2O_3 rich soils, than the other procedures. The process of P extraction by different extractants under varying physical and chemical conditions was satisfactorily explained by an acid-catalyzed nucleophilic substitution reaction mechanism. This mechanism satisfactorily links the solubilization of P from Al and Fe surfaces to the strength of nucleophilic agents such as OH^- , CH_3COO^- , Cl^- , F^- , and H_2O , and to the acidity of the supernatant solution.

Inorganic P fractionation was determined by the modified Chang and Jackson (1957) procedure of Peterson and Corey (1966) with several modifications, and the organic P analyzed by the Bowman (1989) method. The total P content of the 43 soils in this study ranged from 0.02% to 0.4%. Twenty six percent of the total P was in the labile to moderately labile pool, 49% in the non-labile pool, and 25% in the organic fraction. The distribution pattern of Fe-P, reductant soluble P, occluded P, residual P, and organic P fractions was directly related to soil Fe_2O_3 and clay contents. The Al-P content was not markedly influenced by the clay content or pH. It was concluded that Fe-P, a dominant labile P form in agricultural soils was transformed over time to reductant soluble P, the dominant P form in the soils. The reductant soluble P fraction, which increases with P

fertilization and has higher solubility under reduced conditions, through erosion poses a major potential eutrophication threat to surface waters. The eutrophication potential is high in the Piedmont and high clay soils.

Phosphorus adsorption in the Davidson and Tatum soils from the Piedmont physiographic region was well explained by the two-site-Langmuir adsorption model. The adsorption maxima was slightly (5%) decreased by long-term P fertilization over three decades. All soil inorganic and organic P fractions were increased by fertilizer application with the reductant soluble fraction increasing by 61 and 57 percent in the Davidson and Tatum soils, respectively. The residual effects of long-term application of P fertilizer increased labile P contents extracted by soil test methods, and in the Davidson soil the uptake from the residual fertilizer P was sufficient to maintain the tissue P concentrations of young corn seedlings at the sufficiency range.

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CHAPTER 1

INTRODUCTION

Phosphorus (P) management in agricultural systems escalated in importance over the past few years due to several reasons. Phosphorus is an essential plant nutrient and hence, proper management of soil and applied P is vital for successful crop production. Environmentally based P management programs have become critically important lately due to the need to reduce the impact of P from agricultural soils on eutrophication. Achieving these goals should take into consideration the chemical, physical, and biological P reactions in soils. Methods of determination of available P in an agronomic context do not measure the quantity of P available to a crop, but instead measure a pool that is related to the plant available portion. Therefore, a comprehensive approach to soil P determination should take into consideration the forms in which P is present in the soil, the dynamics of P transformation across different forms, and changes in the pool size of P over time as determined by various adsorption/desorption reactions. Phosphorus reactions in soils are affected by physical and chemical properties (pH, clay content, Fe and Al oxides, organic matter, etc.), genesis (parent material, weathering), agricultural practices (P application techniques, tillage), and P source (manures, chemical fertilizers).

Several test methods are employed to estimate the plant availability of soil P. The tests widely used in the United States are Bray 1, Mehlich 1, Mehlich 3, and Olsen

methods. The Mehlich 1 extractant is generally used for soil P determination in mid-Atlantic region soils. However, due to the relatively low reliability of Mehlich 1 to indicate P availability in some soils, and the gaining popularity of the Mehlich 3 extractant as a universal extractant for multiple nutrients has stimulated interest on evaluating alternative procedures. The study reported in chapter two was initiated to compare the extractable P levels by Bray 1, Mehlich 1, Mehlich 3, and Olsen methods and to evaluate the relationships between the physical and chemical properties of soils and the amounts of P extracted by each of these procedures. A possible mechanism of P solubilization by different ions in the extractant solutions was addressed in this research.

Soil P levels are controlled by the native P and soil amendments, such as synthetic fertilizers and manures. Although long-term fertilization and manure application has resulted in extremely high soil test P levels in some USA soils, P deficiency and response to P application are often observed in agronomic plants. Therefore, procedures that reliably predict available P from different soil P forms and soils with diverse properties are needed to evaluate the levels of available soil P. The investigation reported in chapter three was undertaken to study the distribution of various forms of inorganic and organic P in soils with diverse properties and to determine the relative contribution of different P forms to Bray 1, Mehlich 1, Mehlich 3, and Olsen extractable P.

Soil management and fertilization are likely to affect P availability to plants because chemical properties in the soil environment govern P adsorption/desorption, transformation, and availability during long-term cultivation. Properties such as soil

texture and sesquioxide content are not markedly changed by management and fertilization. Changes in P sorption, availability, and transformation in soils from long-term fertilization has agricultural and environmental management implications. The effects of long-term P application on the phosphate adsorption, on the role of soil physiochemical and mineralogical properties in controlling P adsorption, and on the effects of long-term P applications on soil P transformation and extractability by various soil test methods were investigated in chapter four with two soils that were fertilized for more than three decades.

CHAPTER 2

EVALUATION OF MEHLICH 3 EXTRACTANT TO ESTIMATE THE AVAILABLE PHOSPHORUS IN VIRGINIA SOILS

ABSTRACT

The Mehlich 3 extractant, which is considered as an alternative to Mehlich 1 for soil P determination in Virginia, has not been adequately evaluated for the major soil series in the state. Mehlich 3 extractable P quantities in 43 Virginia soils were compared to the Mehlich 1, Bray 1, and Olsen methods in this study. For all soils, Bray 1 (5 minute) extracted highest P quantities followed by Mehlich 3, Bray 1 (1 minute), Mehlich 1, and Olsen procedures. The correlations between Mehlich 3, Mehlich 1, and Bray 1 (1 minute and 5 minutes) were high ($R^2 = 0.92, 0.98$ and 0.96). The Mehlich 3 procedure was more reliable than the Mehlich 1 procedure in soils with a wide range of pH values, because Mehlich 1 dissolved plant unavailable Ca-P in the acid soils and, thus, overstated extractable P levels.

The relationship between Olsen extractable P and Mehlich 3 extractable P improved markedly when considered in soil groups with similar clay content. In clayey fine soils, the Mehlich 3 solution extracted less P due to F^- depletion by reaction with NH_4^+ exchangeable Al^{3+} . In soils containing ditionite-citrate-bicarbonate extractable

Al_2O_3 , Mehlich 3 was less prone to extraction of structurally adsorbed P than Bray 1 (5 minute) or Olsen procedures. Mehlich 3 extractable P contents are more reliable because it overcomes the Ca-P extraction problem of the Mehlich 1. The Mehlich 3 procedure is found most appropriate for laboratory testing for different Virginia soils because it performs better than other extractants in accurately determining extractable P contents in these soils, and can also be used simultaneously to determine other soil nutrients.

An acid-catalyzed nucleophilic substitution reaction mechanism was introduced to explain soil P solubilization from Al and Fe surfaces. This mechanism satisfactorily demonstrates the roles of the nucleophilic agents such as OH^- , CH_3COO^- , Cl^- , F^- , and H_2O in the four extracting solutions under varying soil physical and chemical conditions. The degree of P solubilization by different extractants is reflected by the strength of nucleophile and the acidity of the supernatant solution.

2-1 INTRODUCTION

The presence of adequate quantities of nutrients in forms accessible to plant roots in soil solution is essential to attain optimum crop growth and thereby desired yields. Availability of nutrients in soils can be measured by various soil testing methods. Soil test procedures have been developed to rapidly assess and group soils by the amount of nutrients required for optimum crop yield. Soil testing today is an important part of best management practices aimed at reducing non-point source pollution. It is advocated that soil test interpretations be used for nutrient recommendations to avoid over-fertilization which may degrade surface water quality (Anderson and Flaig, 1995). Therefore, soil testing has an increasing demand from environmental, agronomical, and economical standpoints.

The development of soil test methods for P has been affected markedly by the expanding knowledge in soil P chemistry and mineralogy. Of particular relevance are developments in such areas as the influence of other soil factors on P availability, mechanism of phosphate sorption by plants, and new analytical techniques. Analytical techniques for soil P have undergone frequent improvements. The wide range of analytical methodologies in use, in conjunction with the voluminous literature on the assessment of the P status of soils and the availability of P, illustrates the importance of the unresolved problems in the soil test procedures for available P. Changes in the soil

environment influence the soil physical and chemical properties, i.e., the degree of weathering and agricultural practices change the diversity of soil P forms and their relative proportions in relation to the parent materials. Hence, predicting the quantity of plant available portion of extractable P is not an easy assignment in dynamic and complex systems such as agricultural soils.

The amount of soil solution P, known as the intensity factor, may range from 0.3 to 3.0 kg P ha⁻¹. A rapidly growing crop absorbs about 1 kg P ha⁻¹ per day (Mengel and Kirkby, 1987). Hence, it is necessary that soil solution P be replenished by other P pools, mainly labile and other nonlabile pools, usually known as the quantity factor. Thus, P in soil solution is regulated by the release of adsorbed P from mineral surfaces, mineralization of organic P, and dissolution of solid P minerals.

Residual and indigenous inorganic soil P reside in several chemical combinations attached mostly to the divalent and trivalent cations which are sparingly soluble in water. Predominant forms of these compounds are orthophosphates (H_2PO_4^- , HPO_4^{2-}) of Al, Fe, and Ca. The Al bound P (Al-P) and Fe-bound P (Fe-P), such as variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) respectively, are predominant inorganic end products of P formed during soil genesis and P fertilization in acid soils (Chang and Chu, 1961; Chang and Jackson, 1958; Hawkins and Kunze, 1963; Taylor et al., 1963). Aluminum-P, Fe-P, and Ca bound P (Ca-P) are prevalent in neutral soils (Chang and Chu, 1961). In most

mineral soils, from 20 to 60 % of total P is present in organic P forms such as inositol P, nucleic acids, and phospholipids (Tissen et al., 1994).

Orthophosphate ion bonding to the mineral surfaces encompasses monodentate ligand formation through an Al-O-P bond of considerable covalent character (Corbridge, 1974). The H_2PO_4^- from the Al-O-P bond is labile P and can be readily desorbed from the mineral surfaces. When two Al-O molecules are bonded to a H_2PO_4^- , a stable six member ring complex (chelate) is formed and this H_2PO_4^- , which is multi-dentate, is considered to be chemisorbed and nonlabile (Kyle et al., 1975; Tisdale et al., 1993). Adsorption and desorption studies with ^{32}P on kaolinite showed that all of the P which is held to the surface by one bond is isotopically exchangeable and remains as labile P (Kaikafi et al., 1967). Structural models of the surface reaction of P on different forms of Fe oxides and hydroxides, such as goethite, hematite, lepidocrocite, β -Ferric hydroxide and non-crystalline ferric hydroxide gel were studied with infrared spectroscopic techniques (Pratt et al., 1975). They found that replacement of two surface OH^- ions or H_2O molecules and then coordination of H_2PO_4^- to two different Fe^{3+} ions resulted in a bi-nuclear surface complexation through two of the oxygen atoms of the H_2PO_4^- . Studies on desorption behavior of phosphates with gibbsite and goethite showed that surface complexes between Al^{3+} and phosphate are more labile than those of Fe^{3+} and phosphate (Hingston et al., 1974).

Extractants have been developed to solubilize Ca-P, Al-P, Fe-P, and organic P from different pools which are accessible to plant roots through the soil solution. An effective P extracting solution solubilizes a portion of P from the labile pool (Halford, 1980), i.e., from the pool that is in quasi-equilibrium with soil solution P (Mattingly, 1965). The labile soil P is affected by many soil characteristics such as CaCO_3 content, amount of clay, crystalline and non-crystalline Al and Fe oxides, extractable Al, and Ca, and the type of clay (Kuo et al., 1988). Dalal and Hallsworth, (1976) explained that the availability of soil P is governed by soil solution P concentration, amount of solid phase P that is capable of entering into the soil solution (capacity factor), dissolution or desorption rate, and diffusion. Phosphorus solubility diagrams show that the degree of solubility of different P forms varies with soil pH and that Ca-P, Fe-P, and Al-P dissolve to some extent through the entire range of pH (Lindsay and Moreno, 1960).

For an effective P test the extractant should remove a reproducible and consistent proportion of the plant available P (Thomas and Peaslee, 1973). Soil P extractants tried as indicators of the available P status of soils are water, acids, bases, salts, buffered solutions, and electro dialysis and ion exchange resins (Nelson et al., 1953). Water or dilute salt solutions are used to measure only solution phase soil P (Kamprath and Watson, 1980; Luscombe et al., 1979). Currently used P extraction methods consist of strong acids such as HCl, HNO_3 , and H_2SO_4 ; weak acids such as acetic, citric, and lactic acids; or some combination of them. A very weak acid fails to extract sufficient amounts

of nutrients from the labile solid phase and, as a result, does not reflect the ability of a soil to replenish nutrients removed by plants from the soil solution. Strong acids may remove solid phase nutrients that are not available to plants.

Amounts of P solubilized by different extractants vary according to the form of soil P, properties of the soils, and chemistry of the extracting solution. Chloride and NO_3^- from the strong acids in concentrations from 0.002 to 0.075 M have very little effect on P extraction, but SO_4^{2-} from H_2SO_4 reduces readsorption of dissolved P by the acid solution (Nelson et al., 1953). The carboxyl group of the weak organic acids can form chelated complexes with the polyvalent cations such as Al^{3+} and Fe^{3+} and, hence, desorb P. The dissociated organic acids compete for adsorption sites and, thus, prevent readsorption (Kamprath and Watson, 1980).

Four basic reaction mechanisms have been proposed to explain P release from soil by extractants. They are acid dissolution, ion exchange, cation complexation with bonded P, and cation hydrolysis (Kamprath and Watson, 1980). Ballard (1974) summarized the solubilization of soil P forms by the principal ions in the soil test extractants as follows: H_3O^+ extracts P in the order $\text{Ca-P} > \text{Al-P} > \text{Fe-P}$; OH^- in the order $\text{Fe-P} > \text{Al-P}$; HCO_3^- ions in the order $\text{Al-P} > \text{Fe-P} \geq \text{Ca-P}$; F^- in the order $\text{Al-P} > \text{Fe-P} > \text{Ca-P}$; and acetate ions in the order $\text{Al-P} \geq \text{Ca-P} > \text{Fe-P}$.

The most extensively used soil test P methods in the United States are the Mehlich 1 (M1), Bray 1, Olsen, and Mehlich 3 (M3) procedures (Cox, 1994). Overall,

Bray 1 usage dominates in the midwest, M1 in the southeast, and Olsen in western region United States. Mehlich 3 is used in the south, central and, to a lesser extent, in the eastern United States (Allen et al., 1994).

Literature reveals that quantities of P extracted by these soil testing methods are correlated very well among each other and that the relationship between available and extractable P under variable soils can be improved by grouping soils by texture, buffering capacity, pH, or soil taxonomy (Cox and Lins, 1984; Holford, 1980; Martens et al., 1969; Sharpley et al., 1987). Cox and Lins (1984) showed that use of clay content along with extractable P provides the greatest improvement in soil test interpretations. Acid fluoride extractable (Bray 1) P contents were inversely related to the clay content in Davidson clay loam, Groseclose silt loam, and Wellston fine sandy loam (Martens et al., 1969). Studies with 120 uncultivated and cultivated soils indicated that labile P was most closely predicted by the Olsen procedure in calcareous soils and by the Bray 1 method in slightly and highly weathered soils (Sharpley et al., 1987).

2-1.1 Mehlich 1 Method

The M 1, 0.05 M HCl and 0.0125 M H₂SO₄, extraction method was developed by Nelson et al. (1953) for determination of available P in highly weathered acidic sandy soils of the southeastern United States. These soils have exchange capacities <10 cmol(c) kg⁻¹, pH levels <6.5, and relatively low organic matter contents (<5.0%). This method

was subsequently extended for determination of extractable K, Ca, and Mg (Mehlich, 1978). The order of P extraction by the M 1 solution is as follows: Ca-P> Al-P> Fe-P (Thomas and Peaslee, 1973).

Because the M 1 procedure readily extracts Ca-P, the procedure overestimates available P in acidic rock phosphate-amended soils (Yost et al., 1982). Thus, use of this method is not recommended for either calcareous or acid soils with recently applied rock phosphate (Barnes and Kamprath, 1975). The M1 procedure underestimates available P in alkaline calcareous soils due to acid neutralization by free CaCO₃ (Tran et al., 1990). Furthermore, the M1 procedure underestimates P availability for soils high in Fe oxides and clay due to neutralization of the acidic extraction solution by these soil constituents (Cajuste and Kussow, 1974; Thomas and Peaslee, 1973; Singh, 1965). However, this mixed acid solution solubilizes relatively greater amounts of Fe-P. Therefore, the M1 procedure is suitable for Piedmont and mountain region soils that have strong P fixing capacities (Olsen and Sommers, 1982).

To the contrary, Mehlich (1984) found that, in greenhouse and field studies, M1 extractable P did not correlate well with crop growth for soils from the Mountain, Piedmont, Coastal Plain or Tidewater regions. This finding probably reflects neutralization of extraction solution in acid soils with a high buffer capacity. Overall, the M1 procedure is efficient in the removal of Ca-P which has not been demonstrated to be well correlated with the plant availability of P (Martens et al., 1969).

An increase in the extraction time and the soil-extraction solution ratios increase the amount of Mehlich 1 extractable P (Daughtery et al., 1973; Cajuste and Kussow, 1974). Often, these increased P quantities do improve correlations with plant growth or uptake. Hence, the higher extractable P quantities do not necessarily reflect higher P availability to plants (Daughtory et al., 1973). Increased shaking times or soil solution ratios increase the reaction time and surface area exposed for reactions. Greater soil-extraction solution content may lead to release of P forms that are not usually present in the root zone in a plant accessible form.

2-1.2 Bray 1 Method

The Bray 1 extraction solution, which consists of 0.025 M HCl and 0.03 M NH_4F , reliably estimates the ability of Illinois soils to renew soil solution P for plant growth (Bray and Kurtz, 1945). Also, extractable P by this method predicts crop response to applied fertilizer on both acid and neutral soils adequately (McLean et al., 1979; Vaughn and Jones, 1980). Bray 1 solution is not buffered, and hence, the P solubilizing capacity of the extractant is decreased in clay and silty clay soils with a moderately high degree of base saturation or free CaCO_3 (Randall and Grava, 1971). Therefore, this method is recommended for soils that have a $\text{pH} < 6.8$ with a silty clay loam or finer texture.

Desorption of Al-P is influenced by F^- which has a high affinity for Al^{3+} and, thus, forms different Al-F complexes and thereby decreases the Al^{3+} activity in the soil solution

(Dickman and Bray, 1941; Bray and Kurtz, 1945; Chang and Jackson, 1957; Mehlich, 1978). In slightly acid to neutral soils, the Bray 1 extractant solubilizes some Al-P and Ca-P which are highly correlated to labile P (Tandon and Kurtz, 1968). Hence, AlPO_4 dissolves to resupply Al^{3+} ions and P into the solution. Jardine and Zelazny (1987) reported that F^- forms strong bonds with Al which do not readily dissociate until OH^- successfully competes with F^- at higher levels of soil pH. Maida (1978) reported that Bray 1 extracted Al-P and Ca-P, but not Fe-P, in Malawi soils.

Inclusion of 0.025 M HCl in the Bray 1 method results in the solubilization of Ca-P (Jackson, 1958). However, P solubilization is less effective in calcareous soils due to the neutralization of acid by CaCO_3 followed by deactivation of F^- by formation of insoluble CaF_2 (Blancher and Caldwell, 1964; Smillie and Syers, 1972; Nesse and Grava, 1986). Mehlich (1978) showed that precipitation of CaF_2 may also occur in neutral and acid soils. It was also shown that the advantages of F^- , when added to HCl to control selective extractability of P, did not apply to Ca-P unless the pH of the extractant is held below about pH 2.9. To achieve appropriate solubilization of Ca-P in calcareous soils wide soil:extractant ratio or a considerably higher buffer capacity is required than is inherent in Bray 1. Therefore, research has been directed toward modification of the Bray 1 extractant to extend its use to Ca^{++} saturated and calcareous soils. The modifications include changes in soil:solution ratios, filtering techniques, and shaking

times (Agboola and Omeute, 1980; Breland and Sierra, 1962; Hanlon and Johnson, 1984; Smith et. al., 1957; Randall and Grava, 1971).

2-1.3 Olsen Method

The Olsen extractant, which consists of 0.5 M NaHCO_3 buffered at pH 8.5 was developed for the extraction of available P in neutral and calcareous soils (Olsen et al., 1954). This method was designed to control the ionic activity of Ca^{2+} through the precipitation of CaCO_3 during the extraction process. Solubilization of P in Ca-P increases by precipitation of Ca^{2+} as CaCO_3 . The reagent extracts some P from the surfaces of Al and Fe hydroxides and oxides, through replacement of H_2PO_4^- with OH^- which represses the Al^{3+} and Fe^{3+} activities by formation of aluminate complexes and by precipitation of Fe as the oxides, respectively (Jackson, 1958). In the acid and calcareous soils, secondary or co-precipitation reactions are decreased because the Al^{3+} , Ca^{2+} , and Fe^{3+} activities remain low in the extract (Olsen and Dean, 1965.).

The Olsen method is recommended for soils with medium to high CEC values, high base saturation, moderate to high amounts of Ca-P, and free CaCO_3 (Thomas and Peaslee, 1973). There is some evidence that the buffered NaHCO_3 extractant performs reasonably well for prediction of available P in acid soils (Smyth and Sanchez, 1982). High OH^- concentration in the NaHCO_3 solution can cause removal of adsorbed P from Al-P and Fe-P (Maida, 1978). In comparison to other soil test methods, the Olsen

method removes a constant proportion of the labile pool P from soils with a wide range of texture and buffer capacities (Holford, 1980). Wolf et al. (1985) reported that, in southeastern soils grouped by textural classes, the best predictors of labile P were Olsen and M1. In contrast, Novais and Kamparth (1978) reported that the Olsen method was less suitable than either the M1 or Bray 1 methods for predicting P availability in Coastal Plain soils.

2-1.4 Mehlich 3 Method

The M 3 multi-nutrient extractant (0.2M CH₃COOH, 0.25M NH₄NO₃, 0.015 M NH₄F, 0.013 M HNO₃ and 0.0001M EDTA) was developed by Mehlich (1984). He developed the procedure with a relatively high buffer capacity to improve laboratory efficiency of soil testing and to provide a soil test solution with extracting properties applicable to a wide range of soils. Acetic acid decomposes apatite to a lesser extent than equivalent mineral acids, and, hence was used in the M 3 extractant. Ammonium fluoride was added to the M 3 solution to quantitatively mimic Bray 1. M 3 and Bray 1 extracted similar amounts of P from soils in Pennsylvania, and southern and mid-Atlantic states (Beegle and Oravec, 1990; Mehlich, 1984). Bray 1 extractable P quantities decreased when the shaking time was shortened from 5 to 1 minute (Tran et al., 1990; Cox et al., 1993). Reduced shaking time limits the exposure duration of soil surfaces to reactions and, thereby, causes lower P extraction.

The amounts of P extracted by M 3 and Bray 1 extractants are influenced by the dynamics of different soil P forms and by chemical, physical, and biological properties of soils. Bray 1 extractable P quantities were larger than M 3 P in 91 soils from the southeastern, north central, and northeastern United States (Wolf and Baker, 1985). In Atlantic Coastal Plain soils, levels of Bray 1, and M 3 extracted P were closely correlated ($R^2=0.97$), and the response to applied P and the magnitude of extractability were Bray 1 > M 3 (Gascho et al., 1990).

Tran et al. (1990) reported that, in very acid soils with large amounts of either noncrystalline Al (oxalate extractable Al > 0.6%) or M 3 extractable Al (> 1500 mg kg⁻¹), the M 3 procedure extracts 15-30% less P than Bray 1. The NH₄F concentration in Bray 1 is twice that of M 3. The higher F⁻ concentration in Bray 1 leads to extraction of more P from noncrystalline Al-P than does M 3 (Tran et al., 1990). The M 3 procedure extracted 66% and 12% more P than the Bray 1 method from volcanic and loess soils, respectively (Michaelson et al., 1987). The high buffering capacity of M 3 compared to Bray 1 may lead to extraction of higher amounts of P from these soils.

Relationships between P extracted by M 3 and other extractants vary with the experimental procedure and the type of soil. Comparative studies involving M 3 and M 1 indicated greater P extraction by the M 3 method (Sims, 1989; Wolf and Baker, 1985; Gascho et al., 1990). The relatively high amount of M 3 extractable P is due to the F⁻

ions that enhance P removal from Fe and Al phosphates. Kraske et al. (1989) found that M 1 solubilizes more P than either M 3 or Bray 1 in mineral forest soils.

2-1.5 Comparison of Phosphorus Soil Tests

To avoid complications from the diverse nature of soil P and to interactions between extractants and soil, studies have been conducted with synthetic forms of soil nutrient compounds, with and without soils, to understand the reactions and performances of the soil tests. The relative availability of P to sudan grass (*Sorghum vulgare sudanese*) from the synthetic compounds was in the following order: colloidal Al-P = colloidal Fe-P > variscite > strengite (Juo and Ellis, 1968). Ballard (1974) studied the solubility of P in colloidal Al and Fe phosphates, strengite, wavellite, K taranakite, and mono and dicalcium phosphates, with and without soils. He compared nine different extractants including M 1, Bray 1, and 0.5 M NaHCO₃ at pH 8.5, and found that strengite and wavellite were insoluble in all of the extractants. Sodium bicarbonate at pH 8.5 solubilized more P from colloidal Fe phosphate than from colloidal Al phosphate or K taranakite. Bray 1 solubilized less P from colloidal Fe phosphate than from colloidal Al phosphate. Mehlich 1 solubilized more P from colloidal Al phosphate and K taranakite than from colloidal Fe-P, but less than extractants with complexing agents such as F⁻. In the presence of soils, the extracted P quantities decreased in all extractants except NaHCO₃. Lower P recovery in soils from Bray 1 was attributed to preferential

complexation of F^- with soil Al^{3+} . In the presence of soils, 0.5 M $NaHCO_3$ dissolved substantial amounts of P from colloidal Fe phosphates. This relationship was attributed to complexation of Fe^{3+} by ionized organic functional groups in soils (Ballard, 1974; Schnitzer, 1969).

Since the quantity of P extracted by different extractants was influenced by the forms of soil P, the degree of crystallinity of Al-P and Fe-P, and the soil characteristics the P extraction efficiency may change with the type of soil. Differences in parent material and soil formation lead to diverse physical, chemical, and mineralogical properties in Virginia soils (Perkins et al., 1973). Soils in Virginia are classified into 600 to 610 taxonomically different soil series (Baker, J.C., 1995, personal communication). The majority of the ultisols in the Piedmont region are developed from igneous and metamorphic rocks. Coastal Plain ultisols are derived from unconsolidated marine and river sediments, while soils in the valley and ridge areas are derived from the consolidated sedimentary rocks, limestone, shale, and sandstones. These soils contain non-crystalline and crystalline Al and Fe oxy-hydroxides, allophane, saprolite, gibbsite, and goethite in which the P is mainly present in Al-P and Fe-P forms. Kaolinites dominate the clay-sized fraction in the majority of these soils. However, large amounts of 2:1 minerals such as vermiculite and some intergrade mica are often present in some soils.

A correlation study between P uptake and extractable P in Wellston fine sandy loam, Davidson clay loam, and Groseclose and Nason silt loam indicated that, except in the Groseclose soil, P uptake by oat plants (*Avena sativa*) was related more closely to Bray 1 than Mehlich 1 extractable P (Martens et al., 1969). Phosphorus levels extracted by the two methods were related equally to plant uptake in the Groseclose soil. It was also observed that Al-P levels in the four soils were more closely correlated to Bray 1 extractable P than to Fe-P and Ca-P. In the Groseclose soil, the major source of M 1 extractable P was Al-P. However, neither Bray 1 nor M 1 extractants were able to predict P availability accurately on newly cleared Atlantic Coastal Plain soils (Bertch, 1980).

The M 1 extractant is generally used to estimate available P in Virginia soils. However, the lessened reliability of M 1 to indicate P availability in some Virginia soils has generated an interest for an alternative extractant. Thus, research is underway to evaluate M 3 as an extractant for soil P in Virginia. In order to validate the suitability of M 3 as an alternative to M 1, it is necessary to conduct expensive and time consuming greenhouse correlation and field calibration studies that are supported by interpretations and recommendations based on field research. Before proceeding to conduct such costly studies, as a interim measure, it is advisable to carry out laboratory evaluations with a wide range of soils and existing extractant solutions. Factors such as the soil type, environmental conditions, and the physical and chemical properties of the soils affect P extractability. Therefore, this study was initiated with the following objectives: 1) to

compare the amounts of Mehlich 3 extractable P content with Mehlich 1, Bray 1, and Olsen P from a wide range of soils. 2) to evaluate the relationships between the physical and chemical properties of soils and the amount of P extracted by the Mehlich 3, Mehlich 1, Bray 1, and Olsen P methods, and 3) to determine the possible mechanisms of P solubilization by different ions in the Mehlich 3, Mehlich 1, Bray 1, and Olsen P extractant solutions.

2-2 MATERIALS AND METHODS

Research was conducted to study the effects of soil type, physical and chemical properties, and environmental conditions on P extractability. Bray 1, Mehlich 1, Mehlich 3, and Olsen extraction methods which are widely used for P determination were examined. Forty-three soil samples were collected from the Ap horizon of the cultivated soils in the Piedmont, Atlantic Coastal Plain, and Ridge and Valley regions for this research. The soils varied widely in chemical and physical properties as shown by their taxonomic classifications (Table 2-1).

2-2.1 Soil Analysis

Soil samples were air-dried and screened to pass a 2 mm sieve. The soil pH (H_2O) was determined in a 1:1 v/v of soil:water mixture (McLean, 1982). The organic matter (OM) content was determined by the Walkley-Black (1934) method, and particle size distribution by the pipette procedure (Day, 1965). Total Fe, Al, and Mn as oxides and hydroxides were extracted with the dithionite-citrate-bicarbonate (DCB) extraction procedure as described by Mehra and Jackson (1960), and exchangeable Al with 1M KCl (Barnishel and Bertsch, 1982). Aluminum, Fe, and Mn in solution from these analyses were determined by inductively-coupled argon plasma spectroscopy.

Table 2-1. Taxonomic information for the 43 soils used in the study.

Soil Series	Taxonomic Class	Physiographic Region*
Altavista	fine-loamy, mixed, thermic Aquic Hapludults	CP
Appling	clayey, kaolinitic, thermic Typic Kanhapludults	P
Bojac	coarse-loamy, mixed, thermic Typic Hapludults	CP
Cecil (2) [†]	clayey, kaolinitic, thermic Typic Kanhapludults	P
Christian	clayey, kaolinitic, mesic Typic Hapludults	RV
Craven	clayey , mixed, thermic Aquic Hapludults	CP
Davidson (5)	clayey, kaolinitic, thermic Rhodic Kandiudults	P
Dothan	fine-loamy, siliceous, thermic Plinthic Kandiudults	P
Dragston	fine-loamy, mixed, thermic Typic Endoaquults	CP
Dyke	clayey, mixed, mesic, Typic Rhodudults	P
Emporia (2)	fine-loamy, siliceous, thermic Typic Hapludults	CP
Fauquier	fine, mixed, mesic Ultic Hapludalfs	P
Groseclose	clayey, mixed, mesic Typic Hapludult	RV
Guernsey	fine, mixed, mesic Aquic Hapludalfs	RV
Hayter (2)	fine-loamy, mixed, mesic Ultic Hapludalfs	RV
Kempsville	fine-loamy, siliceous, thermic, Typic Hapludults	CP
Lodi (2)	clayey ,mixed , mesic Typic Hapludult	RV
Mayodan	clayey, kaolinitic, thermic, Typic Hapludults	P
Myatt	fine-loamy, siliceous, thermic Typic Ochraqults	CP
Norfolk	fine-loamy, siliceous, thermic Typic Kandiudults	CP

Contd.....

Soil Series	Taxonomic Class	Physiographic Region*
Rains	fine-loamy, siliceous, thermic Typic Paleaquults	CP
Rumford (3)	coarse-loamy, siliceous, thermic Typic Hapludults	CP
Sassafras	fine-loamy, siliceous, mesic Typic Hapludults	P
Slagle	fine-loamy, silicious, thermic Aquic Hapludults	CP
Starr	fine-loamy, mixed, thermic Fluventic Dystrochrepts	P
State	fine-loamy, mixed, thermic Typic Hapludults	CP
Tarboro	mixed, thermic Typic Udipsamments	CP
Tatum (4)	clayey, mixed, thermic Typic Hapludults	P
Uchee	loamy, sliceous, themic Arenic Hapludults	CP
Wagrums	loamy, sliceous, themic Arenic Kandudults	CP

* P = Piedmont; CP = Coastal Plain; RV = Ridge & Valley

† = Numbers within parenthesis show the number of soils when a soil series is represented by more than one soil.

2-2.2 Soil Test P Analyses

Levels of Mehlich 3 , Mehlich 1, Bray 1, and Olsen extractable P were determined in duplicate for the 43 soils and, hence, all values in figures and tables are averages of two replicates. Analytical details for the procedures are described in Table 2-2.

Although M 1, M 3, and Bray 1 (5-minute) analyses were conducted and results presented on a volume basis, per scoop soil weights were measured to facilitate conversion of extraction levels to a weight basis. Weight basis was used for Olsen and Bray 1 (1-minute) analyses. In all cases soil P was extracted in 100 ml polyethylene centrifuge tubes with a reciprocal shaker at recommended speeds for each procedure. After centrifugation, supernatants were filtered through Whatman no. 42 filter paper. Solution pH values were measured for each procedure immediately after filtration of extractants. Phosphorus extracted by each method was determined colorimetrically by the molybdate blue-ascorbic acid method (Murphy and Riley, 1962) with a Hitachi Model 100-20 spectrophotometer.

2-2.3 Statistical Analyses

Simple and multiple correlation analyses were used to evaluate the relationships among the amounts of P extracted from different methods and the chemical and physical properties of the soils. Linear correlation procedures were used to compare the amounts of M 3 extractable P (means of the duplicate reading) with amounts of M 1, Bray 1

(1-minute), Bray 1 (5-minute), and 0.5 M NaHCO₃ at pH 8.5. Stepwise multiple regression was performed to identify the relative effects of soil properties on amount of extractable P. Regression analyses were performed with M 3 extractable P as the dependent variable, and M 1, Bray 1, Olsen extractable P levels, and the soil parameters such as pH, KCl exchangeable Al, percent OM, clay, DCB extractable Fe₂O₃, and Al₂O₃ contents as independent variables. The regression analyses were performed using the GLM procedure (Myers, 1992).

2-3 RESULTS AND DISCUSSION

2-3.1 Soil Properties

Forty three soils representing three physiographic regions in Virginia were used in the study: 19 soils were from the Coastal Plain, 17 from the Piedmont, and seven from the Valley and Ridge region. The soils belong to 30 different series and occurs within Ultisol, Alfisol, Inceptisol, and Entisol orders (Table 2-1). Over 80% of the soils were Ultisols. Selected physical and chemical characteristics of the individual soils are shown in the Appendix 1 and summarized by major categories in Table 2-3. According to the USDA soil classification (1993), 15 soils are considered extremely to strongly acidic (pH 3.5 to 5.5), 20 are slightly to moderately acidic (pH 5.6 to 6.5), and eight are neutral (pH 6.6 to 7.5). The clay content in the Coastal Plain soils ranged from 0.7 - 12.1%, which is less than the lower boundary, i.e., 17%, for a coarse loamy soil (Soil Taxonomy Guide, 1994). The Piedmont region soils were high in clay content, i.e., 30% of the Piedmont soils contained 35 - 60% clay and are categorized as clayey fine soils. The average clay content of the valley and ridge soils was 10.8% (Appendix 2-1).

The levels of DCB extracted Fe_2O_3 averaged 3.8% and ranged from 0.3 to 16.7% (Table 2-3). This procedure extracts both noncrystalline and crystalline Fe and substituted structural Al (Boero and Schwertmann, 1989; Skjemstad et al., 1989; Fontes et al., 1991). Starr, Fauquir, and Davidson series soils from the Piedmont region

Table 2-3. Characteristics of the 40 soil samples used for the study.

Variable	Mean	Range		Standard Deviation
		Minimum	Maximum	
pH (1:1, soil:H ₂ O)	5.9	4.0	7.4	0.7
Clay (%)	16.0	0.7	48.9	13.9
Organic Matter (%)	2.2	0.4	5.0	1.1
1 M KCl exchangeable Al (mg Al kg ⁻¹)	16.4	0.6	372.5	58.6
DCB extractable Fe ₂ O ₃ (%)	3.8	0.3	16.7	4.8
DCB extractable Al ₂ O ₃ (%)	0.5	0.1	1.5	0.4
DCB extractable Mn (mg Mn kg ⁻¹)	806.3	7.3	4933.0	1365.3

contained the highest Fe_2O_3 contents in the range 10 to 16.7% (Appendix 2-1). The Coastal Plain soils had the lowest levels of Fe_2O_3 , which ranged from 0.3 to 0.9%. DCB extractable Al_2O_3 in all soils ranged from 0.1 to 1.5% and averaged 0.5%. Soils from the Piedmont region had the highest Al_2O_3 contents, i.e., from 0.2 to 1.5%. Exchangeable Al ranged from 0.6 to 372.5 mg kg^{-1} , and 40% of the soils had values greater than 5 mg kg^{-1} . A soil from the Tatum series had the highest Al content, 372.5 mg kg^{-1} (Appendix 2- 1).

Three soil series from the Coastal Plain region, i.e., Rains, State and Altavista, had extractable P quantities that were well above the maximums reported for Virginia soils in a previous study by Sims (1993), and hence, were excluded from subsequent analyses. The amounts of Mehlich 3, Bray 1, Mehlich 1, and NaHCO_3 extractable P quantities in these soils are shown in Table 2-4.

2-3.2 Mehlich 3 Extractable P and Soil Properties

Extractable P content and ranges were compared for the 40 soils as one set and then separated by physiographic region, clay content, and pH group for further comparisons. Twenty four of the 40 soils had M 3 extractable P contents less than the mean, i.e., 76.8 mg dm^{-3} (Fig. 2-1). Mehlich 3 extractable P content in the soils ranged from 2.6 to 188.3 mg dm^{-3} and the mean was 76.8 mg dm^{-3} (Table 2-5). Mean P contents in the soils grouped by physiographic regions and soil clay contents had a greater

Table 2-4. The amounts of Mehlich 3, Bray 1, Mehlich 1, and 0.5 M NaHCO₃ extractable P in the three soil series.

Soil series	Extractable P Methods				
	Mehlich 3 P (mg P dm ⁻³)	Bray 1 P* (mg P kg ⁻¹)	Bray 1P** (mg P dm ⁻³)	Mehlich 1 P (mg P dm ⁻³)	NaHCO ₃ P (mg P kg ⁻¹)
Altavista	673.0	305.2	990.6	327.9	171.6
Rains	268.0	135.2	250.0	116.4	103.8
State	536.0	267.3	695.3	189.8	63.3

* Shaking time = 1 minute

** Shaking time = 5 minutes

Table 2--5. Mehlich 3 and Bray 1 extractable P values in soils grouped according to the physiographic region, texture, and pH.

Soil	N*	Mehlich 3 P (mg P dm ⁻³)		Bray 1 P (1min) (mg P kg ⁻¹)		Bray 1 P (5 min) (mg P dm ⁻³)	
		Mean	Range	Mean	Range	Mean	Range
All	40	76.8	2.6 - 188.3	53.1	3.2 - 113.4	101.9	7.9 - 268.2
Physiographic region							
Coastal Plain	16	129.1	45.4 - 188.3	79.6	29.1 - 113.4	165.3	52.9 - 268.2
Piedmont	17	28.6	2.6 - 163.8	22.3	3.2 - 88.3	42.4	7.9 - 202.1
Valley & Ridge	7	74.0	23.6 - 166.1	49.6	15.9 - 97.6	101.6	28.2 - 232.4
Texture							
clay <17%	28	94.9	9.6 - 188.3	59.7	6.9 - 113.4	123.3	11.8 - 268.2
clay 17.1 - 35%	6	41.0	6.9 - 163.8	32.5	6.7 - 88.3	53.6	7.9 - 202.1
clay 35.1 - 60%	6	28.2	2.6 - 72.2	27.3	3.2 - 55.2	50.3	9.1 - 142.1
pH							
3.5 - 5.5	14	69.7	2.6 - 188.3	49.8	3.2 - 112.2	90.7	7.9 - 264.2
5.6 - 6.5	18	81.1	6.9 - 88.4	57.2	8.6 - 113.4	114.0	7.9 - 268.2
6.6 - 7.5	8	79.7	16.7 - 163.8	49.6	12.2 - 88.4	94.2	24.7 - 202.1

* Number of soils in a group.

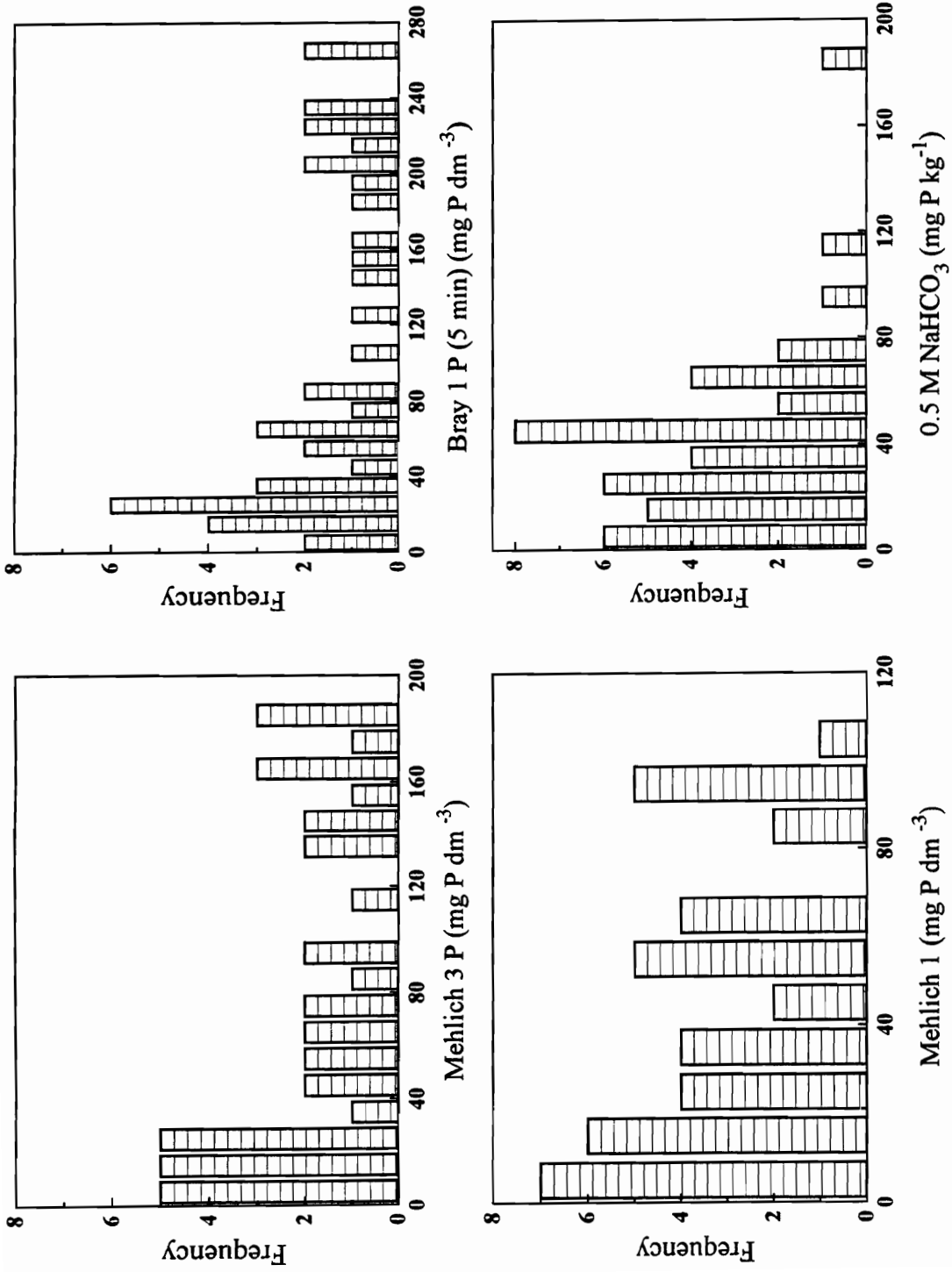


Fig. 2-1. Frequency distribution of extractable P in 40 soils by the Mehlich 3, Bray 1, Mehlich 1, and NaHCO₃ methods.

variation than soils grouped by soil pH. Extractable P contents declined with an increase in the soil clay content.

Simple correlation between Mehlich 3 extractable P content and soil physical properties are shown in Table 2-6. Extractable P contents show an inverse relationship with the percent clay content ($r = 0.51$, $p = 0.01$). Dissolution of clay by acids in the extractant solution, i.e., pH 2.5, may lead to greater acid neutralization in soils with high clay contents (Kittrick and Jackson, 1955; Martens et al., 1969; Pratt and Garber, 1964). The lowering of H^+ activity due to this acid neutralization may decrease both the solubilization of Ca-P and the rate of Al and Fe-dissolution. Another feasible explanation for the lowering of P extraction is the reprecipitation and readsorption of dissolved P by structural Al^{3+} and Fe^{3+} released through clay dissolution.

Exchangeable Al quantity in the Coastal Plain soils was positively correlated ($r = 0.60$, $p = 0.05$) with M 3 extractable P (Table 2-6). The low concentration of Al and Fe oxides in the Coastal Plain soils suggests that most of the P in these soils could be present in recently precipitated or early transitional stages of variscite and strengite formation rather than adsorbed forms. Therefore, a larger portion of this P may be loosely bound with exchangeable Al. The CH_3COO^- and F^- from buffered M 3 solution form strong complexes with exchangeable Al and thereby release P to the solution. Furthermore, EDTA in the M 3 solution decreases reprecipitation of dissolved P by formation of chelated complexes with Al.

Table 2-6. Correlation coefficients (r) between Mehlich 3 extractable P values and selected soil properties of the 40 soils.

Soil category	N*	Al ⁺ (mg Al kg ⁻¹)					OM			Clay (%)	Al ₂ O ₃	Fe ₂ O ₃
		Al ⁺ (mg Al kg ⁻¹)	OM	Clay	Al ₂ O ₃	Fe ₂ O ₃						
All	40	-	-0.32*	-0.51**	-0.40*	-	-	-	-0.40*	-	-0.40*	
Physiographic region												
Coastal Plain soils	16	-0.51*	0.60*	-	-	-	-	-	-	-	-	
Piedmont soils	17	0.58*	-	-	-	-	-	-	-	-	-	
Valley & Ridge	7	-	-	-	-	-	-	-	-	-	-	
Texture												
Clay < 17%	28	-	-	0.54**	-	-	-	-	-	-	-	
Clay 17.1 - 35%	6	0.82*	-	-	-	-	-	-	-	-	-	
Clay 35.1 - 60%	6	-	-	-	-	-	-	-	-	-	-	
pH												
3.5 - 5.5	14	-	-0.63*	-0.69**	-0.60*	-	-	-	-0.60*	-	-0.54*	
5.6 - 6.5	18	-	-	-0.44*	-	-	-	-	-	-	-	
6.6 - 7.5	8	-	-	-	-	-	-	-	-	-	-	

* Significant at p = 0.05.

** Significant at p = 0.01.

- Not statistically significant at p = 0.05.

+ Exchangeable Al.

Mehlich 3 extractable P and pH were positively correlated ($r = 0.58$, $p = 0.05$) in the Piedmont soils (pH 4.0 - 7.3), and negatively correlated ($r = 0.51$, $p = 0.05$) in the Coastal Plain soils (pH 4.9 - 6.9) (Table 2 6). Piedmont soils had higher percent Al_2O_3 and Fe_2O_3 contents than Coastal Plain soils (Appendix 2-1). The solubility of Al-P and Fe-P increases with an increase in pH (Lindsay and Moreno, 1960). Therefore, extractability of P attached to oxides and hydrous-oxides of Al and Fe increases with increasing pH. The positive correlation between pH and M 3 extractable P contents could be due to extraction of these P forms by M 3. The relatively small quantities of DCB extractable Al and Fe oxides in the Coastal Plain soils suggest that the P contribution from noncrystalline and crystalline Al and Fe is likely to be small. A portion of extractable P is supplied by Ca-P which has a greater solubility at low pH. Similarly, figure 2-2 shows that the quantity of exchangeable Al is higher at low pH ($r = - 0.81$, $p = 0.01$). Thus, the positive correlation between exchangeable Al content and M 3 P referred to earlier suggests that M 3 extractable P quantity will decrease with pH.

2-3.3 Mehlich 3 vs. Bray 1 Extractable P

The amounts of P extracted by the Mehlich 3 method with a standard 5-minute shaking time and the Bray 1 method with 1-minute (1m) and 5-minute (5m) shaking times are given in Table 2-5. Mehlich 3 extracted 31 percent more P than Bray 1 with 1-minute shaking time. When the shaking time was increased to 5 minutes, Bray 1

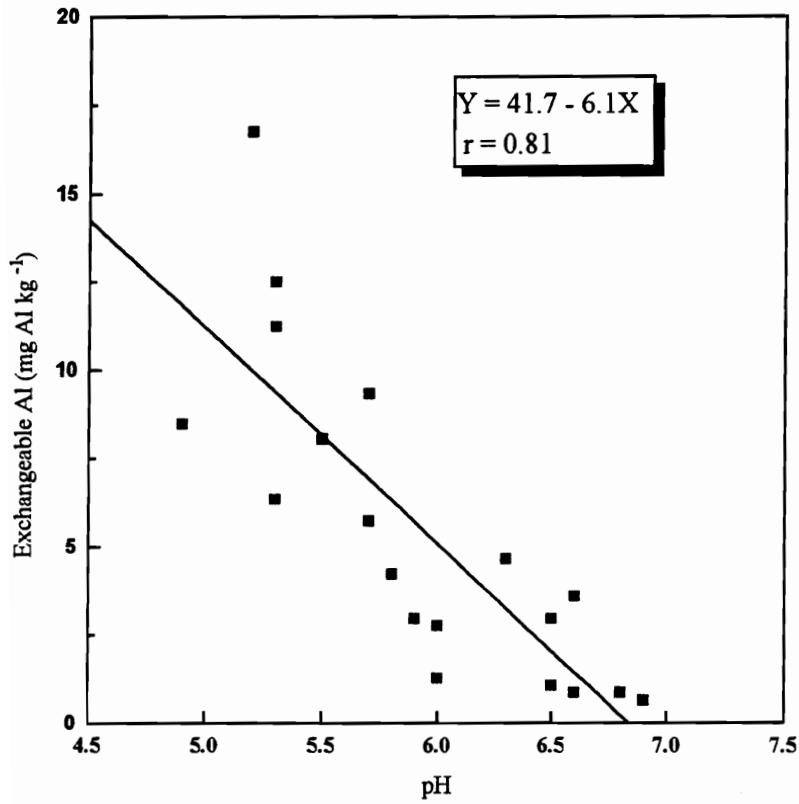


Fig. 2-2. The relationship between the amount of exchangeable Al (Y) and pH (X) on Coastal Plain soils.

extracted P levels were 33% higher than M 3. The sharp increase in Bray 1 (5m) extractable P quantities is explained by a two-fold higher F^- concentration in Bray 1 than in M 3 extraction solution. Bray 1 (5m) extracted P quantities in 11 soils were above the highest quantity of P extracted by the M 3 procedure (Fig. 2-1).

Amounts of Bray 1 and M 3 extractable P are strongly correlated at either 1 or 5 minute shaking times for the Bray 1 procedure (Fig. 2-3). For each unit increase in Bray 1 (5m) content, M 3 P content increased by 0.72 units, while with Bray 1(1m) the rate of increase in M 3 was 1.67. The amounts of Bray 1 P extracted by 1-minute and 5-minute shaking times (Fig. 2-4) correlated closely ($R^2 = 0.97$). The overall quantity of Bray 1 (5m) extractable P was 47 percent greater than Bray 1 (1m) extractable P. Increased shaking time increases the reaction time and the surface area exposed for reactions, and thereby, led to greater dissolution of P.

The magnitude of increase in P solubility for the 5-minute and 1-minute shaking time was relatively low in Piedmont soils and also in the soils high in clay contents (Table 2-5). The larger surface area of clay, Fe_2O_3 , and Al_2O_3 in these soils may require a longer reaction time to extract P. Furthermore, greater reprecipitation of dissolved P by Fe^{3+} and Al^{3+} can also be taking place in these soils.

Several soils from different regions and series had similar M 3 and Bray 1 extractable P quantities (Appendix 2-1 and 2-2). Cecil soil in the Piedmont region which had 5.1 mg kg^{-1} KCl extractable Al and 4.9 percent DCB extractable Fe_2O_3 , contained

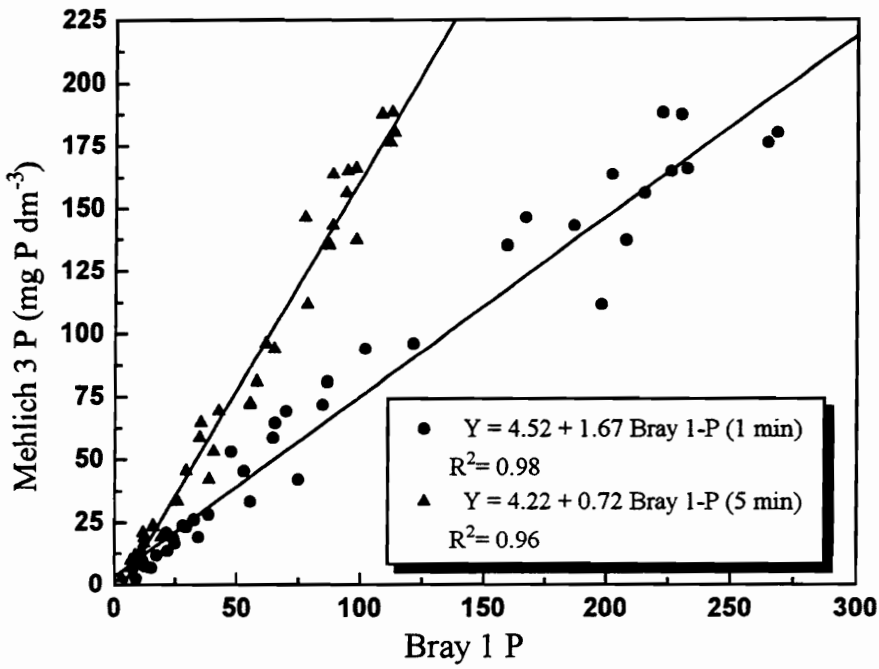


Fig. 2-3. Relationships between Mehlich 3 P (Y) and Bray 1 P (X) with 1(mg P kg⁻¹) and 5 (mg P dm⁻³) minutes shaking times.

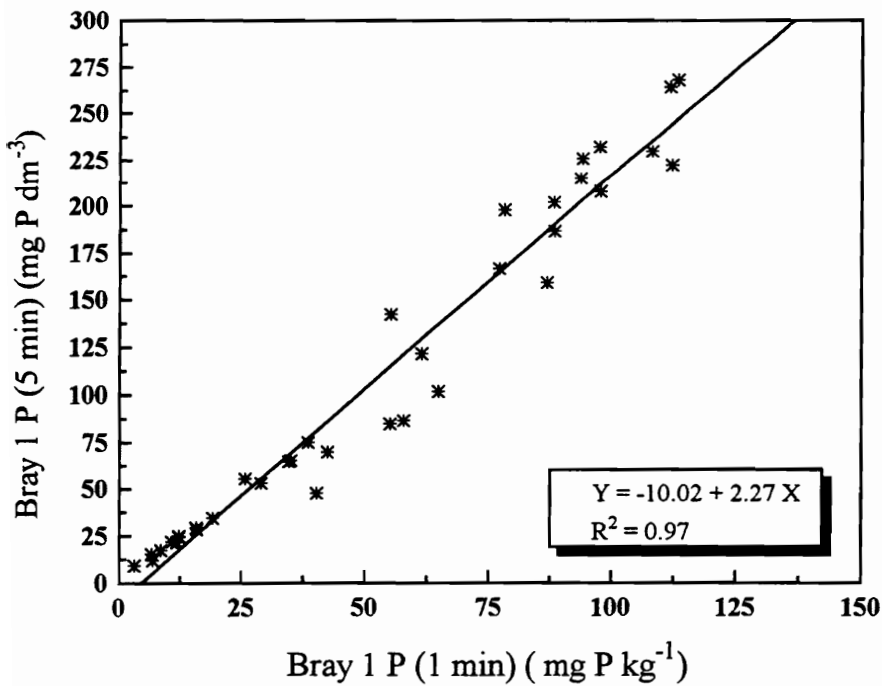


Fig. 2-4. Effect of shaking time of 5 min (Y) and 1 min (X) on levels of Bray 1 P.

identical amounts of M 3 and Bray 1 (1m) extractable P. Tatum and Davidson soils, also from the Piedmont region had similar quantities of extractable P by the M 3 and Bray 1 (1m) methods. Dragston, and Myatt series soils from the Coastal Plain region, which had neutral pH values and low organic matter and clay contents, and the Dothan series soil from the Piedmont region contained similar extractable P by the M 3 and Bray 1 (5m) procedures. The ability of CH_3COO^- than F^- to extract more P from sources such as Fe-P in the Cecil, Dragston, Dothan, and Myatt soils may compensate for selectively higher extraction of Al-P by F^- in Bray 1.

The results from the literature on comparison of amounts of P extracted by the M 3 and Bray 1 methods require close scrutiny due to use of different soil-solution ratios and shaking times. In the present study, standard procedures with a 1:7 (w/v) soil to solution ratio and a 1-minute shaking time for the Bray 1 method and with a 1:10 (v/v) ratio for the M 3 method were compared with a 1.7:20 (v/v) ratio and a 5-minute shaking time for the Bray 1 method. Results from the previous studies that are comparable to the present study are summarized in Table 2-7. A number of studies indicated greater amount of M 3 extractable P than by Bray 1 with a 1-minute shaking time (Tran et al., 1990; Cox et al., 1993). In others, similar or greater quantities of P were extracted by M 3 and Bray 1 (5m) methods (Mehlich, 1984; Beegle and Orave, 1990; Wolf and Baker, 1985). As pointed out earlier, soils that had similar quantities of M 3 and Bray 1 (1m)

Table 2-7. Literature on evaluation of Mehlich 3 and Bray 1 extractable P procedures.

Shaking Time		Soil : Ssolution Ratio		Soils Location	Results	Reference
1 minute	5 minute	Bray 1	Mehlich 3			
		x	x	Coastal Plain	B1>M3>M1	Gascho et al. (1990)
		x	x	Oklahoma State	M3 = B1	Hanolon and Johnson (1984)
x			x	Quebec	M3>B1>M1	Tran et al. (1990)
		x	x	Pennsylvania State	M3≥B1	Beegle and Oravec (1990)
		x	x	Southern and Mid-atlantic States	M3≥B1	Mehlich (1984)
		x	x	Southeastern, north central and northeastern US	B1>M3>M1 >Olsen	Wolf and Baker (1985)
		x	x	Alaska	M3>B1	Michaelson et al. (1987)
x			x	Grenada	M3>M1>B1	Cox et al. (1993)

*measurement type is not given.

extractable P would have contained forms of P that could be extracted by CH_3COO^- , which is present in M 3 but not in the Bray 1 extractant.

The relationships between M 3 and Bray 1 (1m) and Bray 1 (5m) extractable P quantities as affected by the soil characteristics are shown in Tables 2-8 and 2-9. The DCB extractable Al_2O_3 content which consists of noncrystalline, crystalline and a portion of exchangeable Al had a negative coefficient for the relationship between M 3 and either Bray 1(1m) and Bray 1 (5m). The negative relationship suggests that Bray 1(1m) and Bray 1(5m) extract more Al-P than M 3. Similarly Tran et al. (1990) reported that oxalate extractable, noncrystalline Al had a negative influence on the P amounts extracted by M 3 and Bray 1(1m). The Bray 1 solution has a two-fold higher F^- concentration than M 3 which causes higher selective extractability for Al-P. High electronegativity of the F^- causes a high affinity with Al which leads to the formation of stable Al-F complexes and thereby increases P release from Al-P. The stability constant of the Al^{3+} and F^- complex ($K_1 = 6.71$) is higher than that of the Fe^{3+} and F^- complex ($K_1 = 5.16$) at 25 °C (Hogfeldt, 1982). Therefore, it is likely that F^- in the Bray 1 solution extracts higher quantities of Al-P. Variscite, which is the ultimate P transformation product of Al, has a surface area of $24.9 \text{ m}^2 \text{ g}^{-1}$ which is 12 times greater than that of strengite, the ultimate Fe-P product (Juo and Ellis, 1968). Due to the large surface area exposed to F^- attack, even relatively more stable forms of Al-P, which are in the advanced stages of transition,

Table 2-8. Relationships between Mehlich 3 (Y) and Bray 1(1 min) extractable P contents as affected by soil properties.

Soil	N*	Regression Equation	Coefficient of Determination (R ²)
All	40	Y = - 4.52 + 1.67 Bray 1 P	0.977**
Physiographic region			
Coastal Plain soils	16	Y = - 1.68 + 1.64 Bray 1 P	0.950**
		= 16.55 + 1.65 Bray 1 P - 87.29 Al ₂ O ₃ [†]	0.968 **
Piedmont soils	17	Y = - 5.50 + 1.81 Bray 1 P	0.973**
Valley & Ridge soils	7	Y = - 8.52 + 1.66 Bray 1 P	0.965**
		= 9.28 + 1.75 Bray 1 P - 98.05 Al ₂ O ₃ [†] + 10.7 Fe ₂ O ₃ [†]	0.997**
Texture			
clay < 17%	28	Y = - 3.96 + 1.66 Bray 1 P	0.976**
		= 13.11 + 1.66 Bray 1 P - 101.16 Al ₂ O ₃ ^{††} + 11.86 Fe ₂ O ₃ [†]	0.989 **
clay 17.1 - 35%	6	Y = - 10.43 + 1.96 Bray 1 P	0.994**
		= 5.11 + 2.10 Bray 1 P - 2.39 Fe ₂ O ₃ [†]	0.999**
clay 35.1 - 60%	6	Y = - 1.27 + 1.27 Bray 1 P	0.982**
pH			
3.5 - 5.5	14	Y = - 5.55 + 1.68 Bray 1 P	0.991**
		= 7.91 + 1.65 Bray 1 P - 50.02 Al ₂ O ₃ [†] + 3.61 Fe ₂ O ₃ [†]	0.994 **
5.6 - 6.5	18	Y = - 2.89 + 1.64 Bray 1 P	0.966**
		= 7.03 + 1.61 Bray 1 P - 34.53 Al ₂ O ₃ [†] + 2.21 Fe ₂ O ₃ [†]	0.975**
6.6 - 7.5	8	Y = - 7.39 + 1.76 Bray 1 P	0.960**
		= 9.25 + 1.72 Bray 1 P - 99.58 Al ₂ O ₃ [†] + 12.43 Fe ₂ O ₃ [†]	0.993**

* Number of soils in a group.

** contribution of the 1st variable is significant at p = 0.01.

† Contribution of the second variable is significant at p = 0.05 (†) or P = 0.01(††).

Table 2-9. Relationships between Mehlich-3 (Y) and by Bray 1(5 min) extractable P contents as affected by soil properties.

Soil	N*	Regression Equation	Doefficient of Determination (R ²)
All	40	Y = 4.22 + 0.72 Bray 1 P	0.960**
		= 9.23 + 0.70 Bray 1 P - 0.89 Fe ₂ O ₃ [†]	0.964**
		= 11.47 + 0.70 Bray 1 P - 10.59 Al ₂ O ₃ [†]	0.964**
<u>Physiographic region</u>			
Coastal Plain soils	16	Y = 25.57 + 0.63 Bray 1 P	0.933**
Piedmont soils	17	Y = -1.62 + 0.76 Bray 1 P	0.976**
		= 4.15 + 0.77 Bray 1 P - 0.24 clay [†]	0.983**
Valley & Ridge soils	7	Y = -13.25 + 0.60 Bray 1 P	0.929**
		= 35.36 + 0.58 Bray 1 P - 0.03 Mn [†]	0.980**
<u>Texture</u>			
clay < 17%	28	Y = -9.83 + 0.69 Bray 1 P	0.951**
		= 11.21 + 0.71 Bray 1 P + 1.49 clay [†] - 56.32 Al ₂ O ₃ [†]	0.966**
clay 17.1 - 35%	6	Y = -3.21 + 0.82 Bray 1 P	0.996**
		= 3.82 + 0.85 Bray 1 P + 2.99 Fe ₂ O ₃ [†] - 33.28 Al ₂ O ₃ [†]	0.999**
clay 35.1 - 60%	6	Y = 2.72 + 0.51 Bray 1 P	0.980**
<u>pH</u>			
3.5 - 5.5	14	Y = 0.33 + 0.76 Bray 1 P	0.978**
5.6 - 6.5	18	Y = 5.09 + 0.68 Bray 1 P	0.956**
6.6 - 7.5	8	Y = 8.82 + 0.76 Bray 1 P	0.964**

* Number of soils in a group.

** contribution of the 1st variable is significant at p = 0.01.

† Contribution of the second variable is significant at p = 0.05 (†).

may react with F^- in the Bray 1 solution and, thereby, extract larger quantities of P.

Bertch (1980) found that newly cleared Coastal Plain soils in Virginia extracted inflated amounts of Bray 1 P which were not well correlated with plant available P, whereas, Bray 1 P quantities from Davidson clay loam, Nason silt loam and Wellston fine sandy loam soils from the Virginia were well correlated with plant uptake (Martens, 1969).

Relationships of M 3, Bray 1 (1m), and Bray 1 (5m) extractable P and clay content in coarse loamy soils (<17% clay) are illustrated in Fig. 2-5A and 2-5B. The quantity of P extracted by all 3 methods decreased with an increase in the clay content. The rate of decrease was highest for the Bray 1 (5m). The decrease in P extractability by acid extractants with an increase in clay is attributed to acid neutralization, which lowers solubility, destruction and dissolution of clay particles, and to the need for a larger volume of extractants to attack the larger surface area of the clay particles (Martens, et al. 1969; Thomas and Peaslee, 1973). Furthermore, it is likely that some of the P dissolved by the extractant is reprecipitated by structural Al released from dissolved clay particles. However, the relationship between M 3 and Bray 1 (5m) extractable P contents in the coarse loamy (clay <17%) soils was positively influenced by the clay content (Table 2-9). The buffering action of the M3 extraction solution may cause an increase in P extraction by prevention of acid neutralization reactions.

In the case of Piedmont soils, which had a high average clay content (28%), the relationship between M 3 and Bray 1 (5m) extractable P quantities were negatively

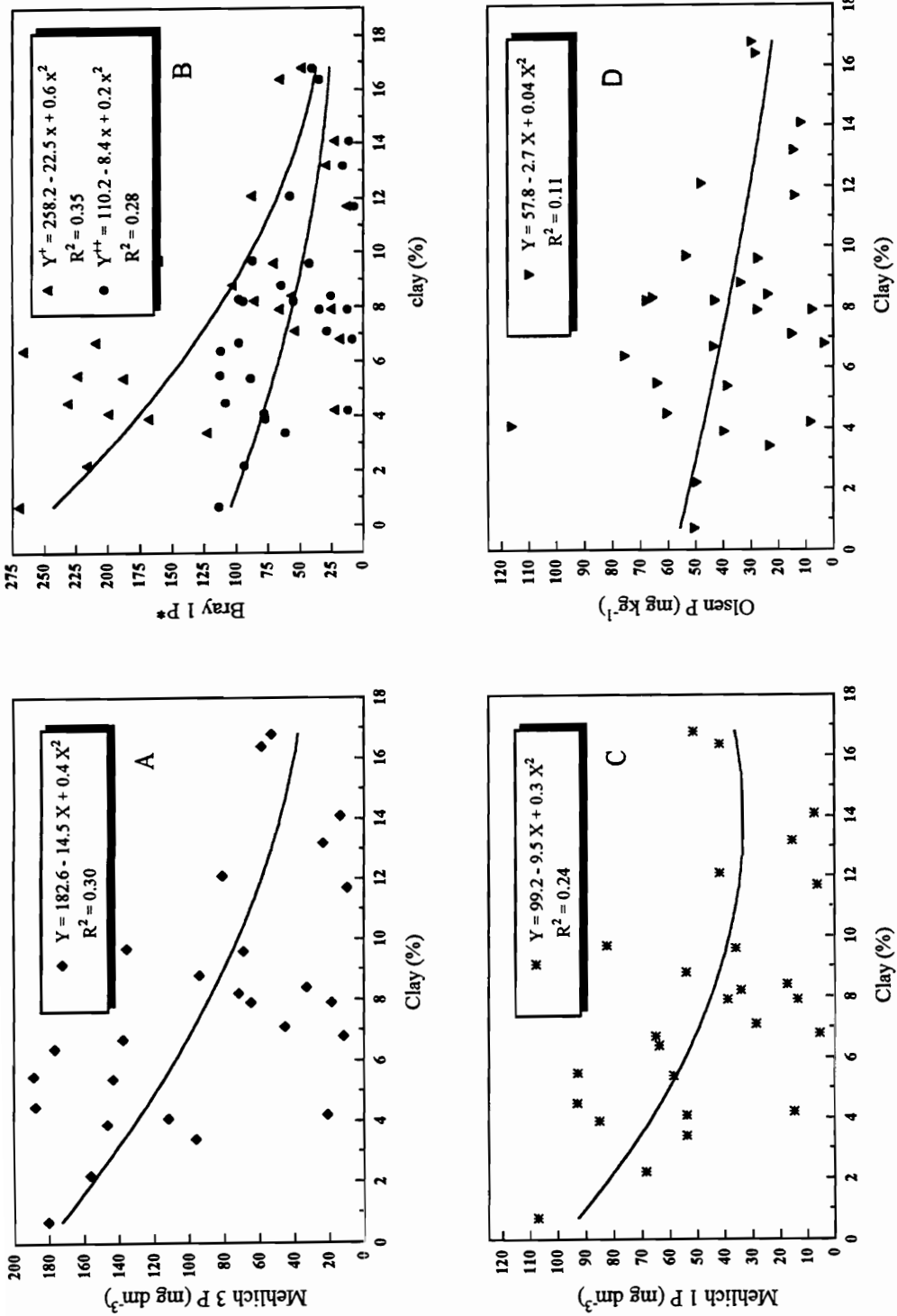


Fig. 2-5. Relationships between Mehlich 3, Bray 1, Mehlich 1, and Olsen extractable and clay content in soils with <17% clay (x).
* Bray (1 min) = mg kg⁻¹, Bray 1 (5 min) = mg dm⁻³ and Y⁺ = Bray 1 (5 min), Y⁺⁺ = Bray 1 (1 min).

influenced by the clay content (Table 2-9). This relationship suggests that Bray 1 (5m) is capable of extracting more P as compared with M 3 from high clay soils. Bray 1 (5m) procedure extracts 2.1 units of P per each one percent increase in the clay content compared with the extraction rate of 1.6 units of P by M 3 extractant in the fine loamy (17.1-35% clay) soil group (Fig. 2-6).

There are possible explanations for the higher P extractability by Bray 1(5m), than by M 3, from high clay soils. The differences in F^- concentration in the two extraction solutions can cause the differential M 3 and Bray 1 P extraction in the high clay soils. Since the F^- concentration in the Bray 1 solution is twice that of M 3 solution, relatively more Al can be complexed with F^- in the Bray 1 solution. Therefore, more reprecipitation and readsorption reactions can take place in the M 3 solution which extracted lower amounts of P than Bray 1-(5m). This contention is supported by Tran et al., (1990). They reported that, in very acid soils with a large amount of either oxalate extractable (noncrystalline) Al (>0.6%) or M 3 extractable Al (> 1500 $\mu\text{g g}^{-1}$), the M 3 procedure extracts 15 - 30% less P than Bray 1 P.

At low extraction solution pH values (M 3, pH = 2.5 and Bray 1, pH = 2.6), destruction of clay minerals by M 3 and Bray 1 extractants releases Al, Fe, Ca, and Mg to the soil solution (McBride, 1994). The higher NH_4^+ concentration in M 3 has a tendency to release more exchangeable Al into the solution. Skeen and Summer (1967) found that,

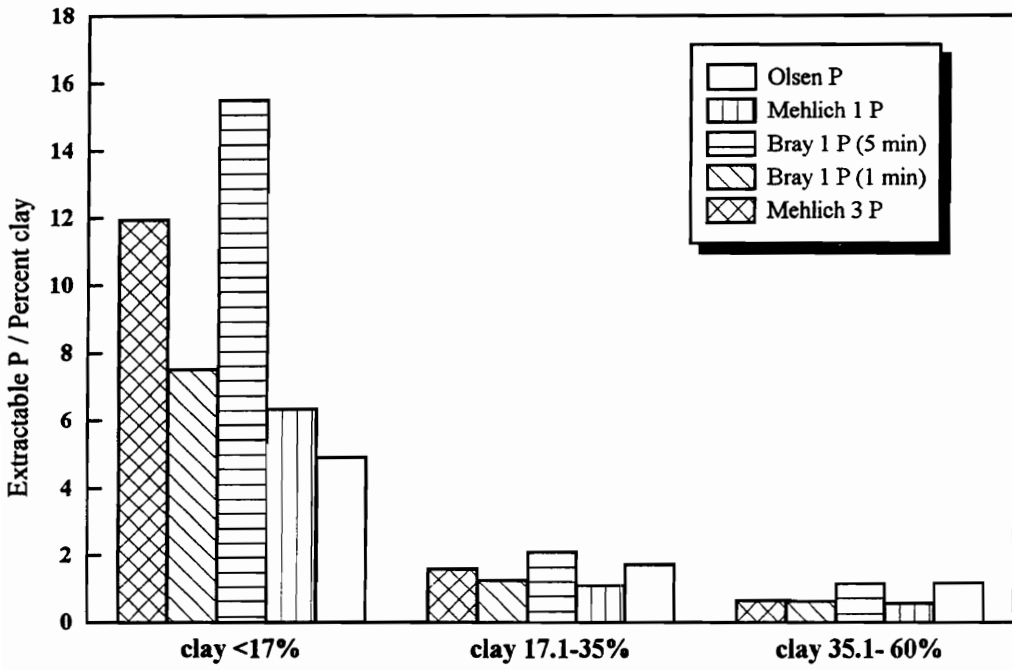


Fig. 2-6. The quantity of extractable P per one percent of clay by the Mehlich 3, Bray 1, Mehlich 1, and Olsen methods.

with 0.2 M KCl, NH₄Cl, and NaCl and with 0.1 M CaCl₂ and MgCl₂, the amount of Al released from structural, nonexchangeable, and exchangeable components was influenced by the cations in the order NH₄⁺ > K > Ca > Mg > Na. Thus, lower P extractability from high clay soils by M 3, than by Bray (5m), may be caused by consumption of F⁻ by reaction of NH₄⁺ exchangeable Al³⁺ to form Al-F in the M 3 extract.

The lower extraction of P from high clay soils by M 3 than by Bray 1 (5m) is further explained by the changes in the pH levels in the reaction solutions. In the two soil groups with high clay content, the supernatant of the Bray 1 (5m) extraction had a higher pH (pH 4.0 and 4.2) than from the M 3 extractant (pH 3.1 and 3.3) (Table 2-10). In the Piedmont soils, the supernatant of Bray 1 (5m) had a higher pH (3.7) than the more highly buffered M 3 supernatant (pH 3.0). A pH increase in the supernatant increases P solubilization from Al and Fe-P (Lindsay and Moreno, 1960). In summery, high F ion concentration, less NH₄⁺ in the Bray 1 solution, and higher pH values in the soil extraction solution are complementary activities favoring high amount of extractable P by Bray 1 (5m) .

Narrow differences in M 3 and Bray 1 (1m) extractable P occur in soils grouped according to soil pH (Table 2-5). The clay contents of the three soil groups ordered by pH were quite similar (Appendix 2-1). Slightly to moderately acidic (pH 5.6-6.5) soils had the highest amount of M 3 extractable P among the three pH groups. The average with exchangeable Al content in this group of soils was 3.5 mg kg⁻¹. On the average,

Table 2-10. Extraction solution pH values after shaking with soil for the Mehlich 3, Bray 1, Mehlich 1, and Olsen procedures grouped by physiographic regions, texture and pH.

Soil	N*	Mehlich 3 P			Bray 1 P (5 min)			Mehlich 1 P			Olsen P	
		Mean	Range		Mean	Range		Mean	Range		Mean	Range
All	40	2.9	2.3 - 3.6		3.4	2.7 - 4.4		1.5	1.3 - 2.4		8.8	8.8 - 8.9
Physiographic region												
Coastal Plain	16	2.8	2.3 - 3.2		3.1	2.8 - 3.7		1.4	1.3 - 1.6		8.8	8.8 - 8.8
Piedmont	17	3.0	2.5 - 3.6		3.7	2.7 - 4.4		1.6	1.3 - 2.4		8.8	8.8 - 8.9
Valley & Ridge	7	3.0	2.8 - 3.2		3.2	3.0 - 3.5		1.5	1.4 - 1.6		8.8	8.8 - 8.8
Texture												
clay <17%	28	2.8	2.3 - 3.2		3.1	2.7 - 3.7		1.4	1.4 - 1.6		8.8	8.8 - 8.9
clay 17.1 - 35%	6	3.1	2.8 - 3.6		4.0	3.2 - 4.4		1.7	1.4 - 2.4		8.8	8.8 - 8.8
clay 35.1 - 60%	6	3.3	3.0 - 3.3		4.2	3.6 - 4.4		1.7	1.5 - 1.8		8.8	8.8 - 8.8
pH												
3.5 - 5.5	14	2.9	2.5 - 3.3		3.2	2.7 - 4.3		1.5	1.3 - 1.7		8.8	8.8 - 8.8
5.6 - 6.5	18	2.9	2.7 - 3.3		3.4	2.8 - 4.4		1.5	1.4 - 1.8		8.8	8.8 - 8.9
6.6 - 7.5	8	3.1	2.3 - 3.6		3.6	3.0 - 4.4		1.7	1.4 - 2.4		8.8	8.8 - 8.8

* Number of soils in a group.

from extremely to strongly acidic soils (pH 3.5-5.5), M 3 extracted 12 mg P dm⁻³ less P than from the slightly to moderately acidic soils. Exchangeable Al averaged 41.5 mg kg⁻¹ in the extremely to strongly acidic soils. Low amounts of M 3 extractable P in this group could be attributed to reprecipitation of dissolved P by high exchangeable Al contents.

The relationship between M 3 and Bray 1(1m) extractable P contents of the soils grouped by pH were positively influenced by Fe₂O₃ (Table 2-8). The average Fe₂O₃ contents of the soils grouped by pH decreased slightly (4.6, 3.4, and 3.2) with an increase in pH (Appendix 1). The Fe³⁺ released following P solubilization with M 3 can form complexes with CH₃COO⁻, F⁻, and EDTA and with Bray 1 can form complexes with F⁻ and Cl⁻. Iron forms very stable complexes with organic ligands and the synthetic EDTA compounds. Fluoride ions in both M 3 and Bray 1 solutions can release P from Fe-P by forming trivalent fluoroferrate ion which is stable in acid solutions, but unstable in neutral to alkaline solutions (Turner and Rice, 1952). The stability constant of acetic acid ligand complexes with Fe is 6.5 and with Al is 3.8 (Young and Bache, 1985). The stability constant of the Fe³⁺ and EDTA complex is 26.3 and of the Al³⁺ and EDTA complex is 19.0 (Lindsay, 1979). Natural ligands in the soil also form more stable complexes with Fe³⁺ than with Al³⁺ (Young and Bache, 1985). Thus, organic acids prevent readsorption and precipitation of dissolved P by M 3. Organic ligands, i.e., CH₃COO⁻ and EDTA, in the M 3 solution are comparable to those in the natural soil system and increase P extractability by the M 3 procedure.

2-3.4 Mehlich 3 vs. Mehlich 1 Extractable P

The means and ranges of Mehlich 1 extractable P for the 40 soils according to the physiographic regions, clay contents, and pH groups are given in Table 2-11. The quantity of M 3 extractable P was 47% greater than that of M 1 (Table 2-5 and 2-11), except in the Cecil, Davidson, and Tatum soils from the Piedmont region which contained similar amounts of M 3 and M 1 extractable P (Appendix 2-2). The increased extractability of P by M 3 relative to M 1 reflects the presence of F^- , CH_3COO^- , and EDTA in the M 3 but not in the M 1 extraction solution. High affinity of F^- for Al^{3+} enhances the solubility of P primarily from Al-P compounds, and high affinity of CH_3COO^- and EDTA for Fe^{3+} solubilize Fe-P. Extraction of larger amounts of P by M 3 relative to M 1 were previously reported for 91 noncalcareous agricultural soils from the US (Wolf and Baker, 1985), 400 soils from Delaware and the Atlantic Coastal Plain (Sims, 1989), and 82 soils from Quebec, Canada, (Tran et al., 1990).

A relatively close relationship ($R^2 = 0.92$, $p = 0.01$) was obtained between M 3 and M 1 extractable P for the 40 soils (Fig. 2-7). The relationship was improved by the inclusion of soil pH (1:1, H_2O :soil) values in the equation (Table 2-12). The influence of the pH variable was negative except in the slightly to moderately acidic group (pH 5.6-6.5). The negative relationship probably indicates that Ca-P was extracted relatively more easily by M 1 than by M 3 in extremely to strongly acidic (pH 3.5-5.5) and in neutral soils (pH 6.6-7.5). The high acidity of the M 1 extractant (pH = 1.35) and the

Table 2-11. Mehlich 1, and Olsen extractable P values in soils grouped according to the three physiographic regions, texture, and pH.

Soil	N*	Mehlich 1 P (mg P dm ⁻³)		Olsen 1 P (mg P kg ⁻¹)	
		Mean	Range	Mean	Range
All	40	43.3	1.5 - 107.0	41.9	3.5 - 185.2
Physiographic region					
Coastal Plain	16	66.2	28.5 - 107.0	45.2	15.4 - 76.0
Piedmont	17	21.4	1.5 - 97.6	36.9	3.5 - 185.2
Valley & Ridge	7	44.1	15.5 - 95.5	46.2	14.7 - 116.7
Texture					
clay <17%	28	50.6	5.5 - 107.0	39.0	3.5 - 116.7
clay 17.1 - 35%	6	28.2	6.2 - 97.8	44.8	5.5 - 185.2
clay 35.1 - 60%	6	24.7	1.5 - 61.5	52.1	6.2 - 98.5
pH					
3.5 - 5.5	14	34.2	1.5 - 93.0	36.3	6.2 - 76.0
5.6 - 6.5	18	48.9	5.5 - 107.0	42.0	3.5 - 116.7
6.6 - 7.5	8	46.9	17.23 - 97.8	51.4	24.2 - 185.2

* Number of soils in a group.

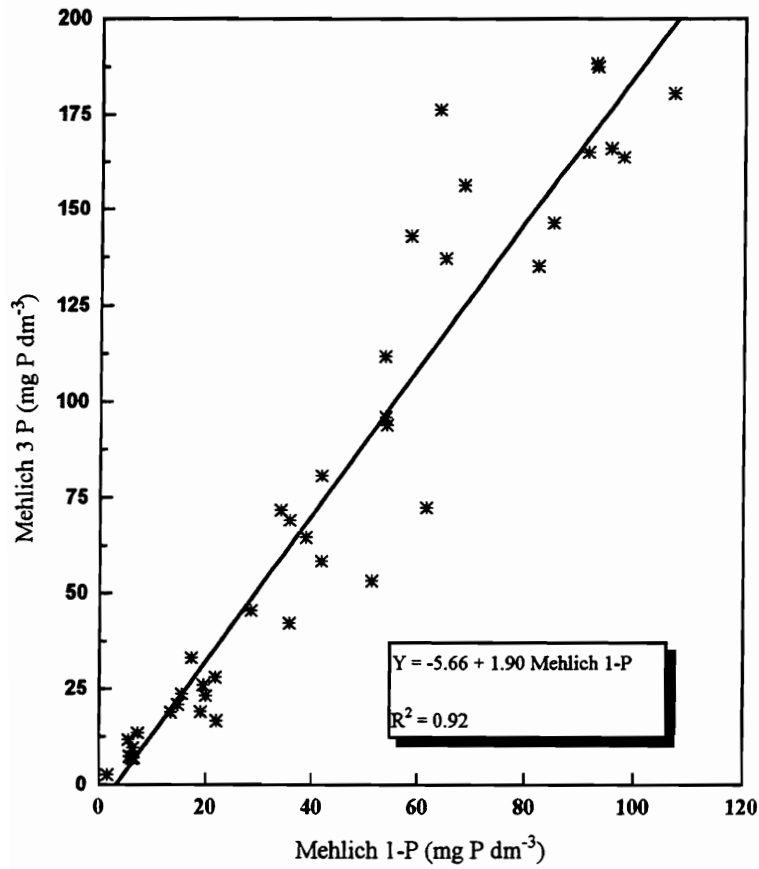


Fig. 2-7. The relationship between the amounts of Mehlich 3 (Y), and Mehlich 1(X) extractable P.

very low pH of the supernatant (Table 2-10) suggest that M 1 may dissolve considerably more Ca-P compounds than those that supply P to plants. These results conform with the data from a previous study with Virginia soils from four soil series (Martens et al., 1969). They observed that the M 1 procedure extracted more Ca-P from soils treated with rock phosphates and than from controls, and that, M 1 extracted P from rock phosphate treatments was not well correlated to plant uptake.

The correlation between M 3 and M 1 P in the soil group with less than 17 % clay content was improved by inclusion of DCB extractable Al_2O_3 content in the equation (Table 2-12). The positive sign of the regression coefficient for Al_2O_3 in the equation indicates a higher capacity of M 3 solution to extract Al-P, i.e., the soil P was shown to be highly correlated to plant uptake (Martens et al., 1969). The coefficient of determination of the multiple regression relating to M 3 and M 1 P was also increased when exchangeable Al^{3+} was included in the equation for Coastal Plain soils in the pH group 5.6-6.5 (Table 2-12). Under the very acidic condition of the M 3 soil solution, which has a pH of 2.94, Al^{3+} has a higher affinity for F^- than OH^- which is similar in size to F^- . Formation of bonds with F^- decreases the activity of the Al^{3+} in solution and, thus curtails the reprecipitation of dissolved P and enhances the P extractability power of the M 3 extractant.

The correlation between M 3 and M 1 extractable P in the <17% clay group is positively influenced ($p = 0.01$) by the organic matter content (Table 2-12). This positive

Table 2-12. Relationships between Mehlich 3 (Y) and Mehlich 1 extractable P contents as affected by soil properties.

Soil	N*	Regression Equation	Coefficient of determination (R ²)
All	40	Y = - 5.66 + 1.90 Mehlich 1 P = 51.13 + 1.85 Mehlich 1 P - 7.89 pH [†] - 0.49 clay [†]	0.923** 0.944**
<u>Physiographic region</u>			
Coastal Plain soils	16	Y = 9.75 + 1.80 Mehlich 1 P = 5.78 + 1.58 Mehlich 1 P + 3.34 Al ^{††}	0.806** 0.917**
Piedmont soils	17	Y = - 4.39 + 1.62 Mehlich 1 P 3.74 + 1.60 Mehlich 1 P - 0.34 clay [†]	0.954** 0.970**
Valley & Ridge soils	7	Y = - 2.37 + 1.64 Mehlich 1 P = 86.12 + 1.59 Mehlich 1 P - 10.59 pH [†] - 2.07 clay [†]	0.905** 0.986**
<u>Texture</u>			
clay < 17%	28	Y = 1.39 + 1.91 Mehlich 1 P = - 94.20 + 1.82 Mehlich 1 P - 15.59 pH ^{††} + 11.22 OM ^{††} - 25.88 Fe ₂ O ₃ [†] + 170.15 Al ₂ O ₃ ^{††}	0.906** 0.951**
clay 17.1 - 35%	6	Y = - 8.15 + 1.74 Mehlich 1 P	0.996**
clay 35.1 - 60%	6	Y = - 0.80 + 1.17 Mehlich 1 P = 43.64 + 1.32 Mehlich 1 P - 8.09 pH ^{††}	0.974** 0.999**
<u>pH</u>			
3.5 - 5.5	14	Y = - 8.87 + 2.36 Mehlich 1 P	0.958**
5.6 - 6.5	18	Y = - 4.62 + 1.77 Mehlich 1 P = - 79.39 + 1.71 Mehlich 1 P + 11.46 pH [†] + 3.22 Al ^{††} - 1.02 Fe ₂ O ₃ [†]	0.976** 0.992**
6.6 - 7.5	8	Y = - 4.5 + 1.80 Mehlich 1 P = 437.79 + 2.20 Mehlich 1 P - 66.93 pH [†]	0.812** 0.944**

* Number of soils in a group.

** contribution of the 1st variable is significant at p = 0.01.

† contribution of the second variable is significant at p = 0.05 (†) or p = 0.01(††).

relationship can be explained by several different reactions involving organic matter, i.e., the formation of chelate complexes with Ca, Fe, and Al with the release of phosphate to the solution, the competition between humate and phosphate ions for adsorbing surfaces thereby prevention of readsorption and precipitation of dissolved P, and the formation of protective coating over sesquioxides thereby further reducing P precipitation.

The regression relationship between M 3 and M 1 extractable P contents in the slightly to moderately acidic (pH 5.6-6.5) group was negatively influenced ($p = 0.05$) by DCB extractable Fe_2O_3 content (Table 2-12). Extremely low pH values of the M 1 solution in the absence (pH = 1.35) and presence of soil suggest a high ability to solubilize Fe-P compounds (Table 2-10). Under acidic conditions, though $\text{Fe}(\text{OH})_3$ is solubilized, the solubility product of $\text{Fe}(\text{OH})_3$ is so low ($k_{sp} = 3.8 \times 10^{-38}$) that nearly complete precipitation of $\text{Fe}(\text{OH})_3$ takes place, which lower the activity of the Fe^{3+} in the M 1 soil solution. The precipitation does not occur in the presence of certain organic acids which are available in the M 3 solution (Svehla, 1982). Moreover, SO_4^{2-} ions in the M 1 solution can dissolve more Fe-P than M 3 because $\text{Fe}(\text{SO}_4)_2^-$ has a high formation constant (5.38) (Lindsay, 1979). This evidence supports the assertion of dissolution of non-labile mineral P by the M 1 method that have been advanced by other researchers (Holford, 1980; Mehlich, 1978). Therefore, it can be assumed that M 3 extracts a relatively even quantity of Fe-P compared to M 1 solution.

The high clay group soils, the extraction power of M 3 is not markedly different from M 1 (Table 2-11). Also, the clay content negatively influenced the relationship between M 3 P and M 1 P (Table 2-12). Acid neutralization by clay dissolution and destruction are common reasons for lowering of extractable P by both methods. This relationship is illustrated by Figure 2-4a and 2-4c. The M 3 extractant has a high capacity to solubilize P due to the presence of F^- , CH_3COO^- , and EDTA. A more feasible explanation for the above relationship would be that the NH_4^+ in the M 3 solution releases more exchangeable Al from the clay surfaces to the solution (Skeen and Summer, 1967) and thereby decreases the solubility of especially Al-P and increases reprecipitation and readsorption of dissolved P.

2-3.5 Mehlich 3 vs. Olsen Extractable P

The average amounts and ranges of Olsen extractable P for the 40 soils according to the physiographic regions, clay contents and pH groups are given in Table 2-11. The results show approximately similar quantities of Olsen extractable P among the various physiographic regions, pH groups and clay categories. These results are consistent with previous comparative studies that show little effect of textures and buffer capacities on levels of Olsen extractable P which leads to extraction of a constant proportion of the labile pool P by the procedure (Thomas and Peaslee, 1973; Halford, 1980; Wolf and Baker, 1985). Overall, the quantity of M 3 extractable P contents were on the average

46% higher than amounts solubilized by Olsen P (Table 2-5 and 2-11). The ability of F^- and CH_3COO^- in the M 3 extractant to decrease Al^{3+} , Ca^{2+} , and Fe^{3+} activities could be stronger than the ability of Olsen extractant to lower activities of Al^{3+} , Ca^{2+} , and Fe^{3+} at high pH. The lower Al^{3+} , Ca^{2+} , and Fe^{3+} activities in the M 3 solution would dissolve more P than Olsen extractant at high pH.

Relationships determined by simple linear regression and multivariate regression analyses of P contents for M 3 and Olsen extractable P and soil properties are given in the Table 2-13. Mehlich 3 and Olsen extractable P did not correlate closely ($R^2 = 0.38$) when all soils were included in the data set (Fig. 2-8). The low correlation probably reflects extraction of different forms of soil P by the two procedures.

Olsen extractable P contents in the Piedmont region and from fine-loamy and clayey-fine soils (clay >17.1%) were higher than M 3 extractable P contents when the soils were grouped by the physiographic region and by the clay content (Table 2-5 and 2-11). In the Piedmont region, the Olsen extractable P contents were 40% higher than M 3 P. The Olsen extractable P contents in the clayey-fine (clay 35.1-60%) soils were 85% above M 3. Although, overall, M 3 and Olsen extractable P had a relatively low correlation, much higher correlations occurred when soils were grouped according to physiographic regions and clay contents (Table 2-13). The relationship between M 3 and Olsen extractable P quantities was negatively influenced by the clay content irrespective of the soil group.

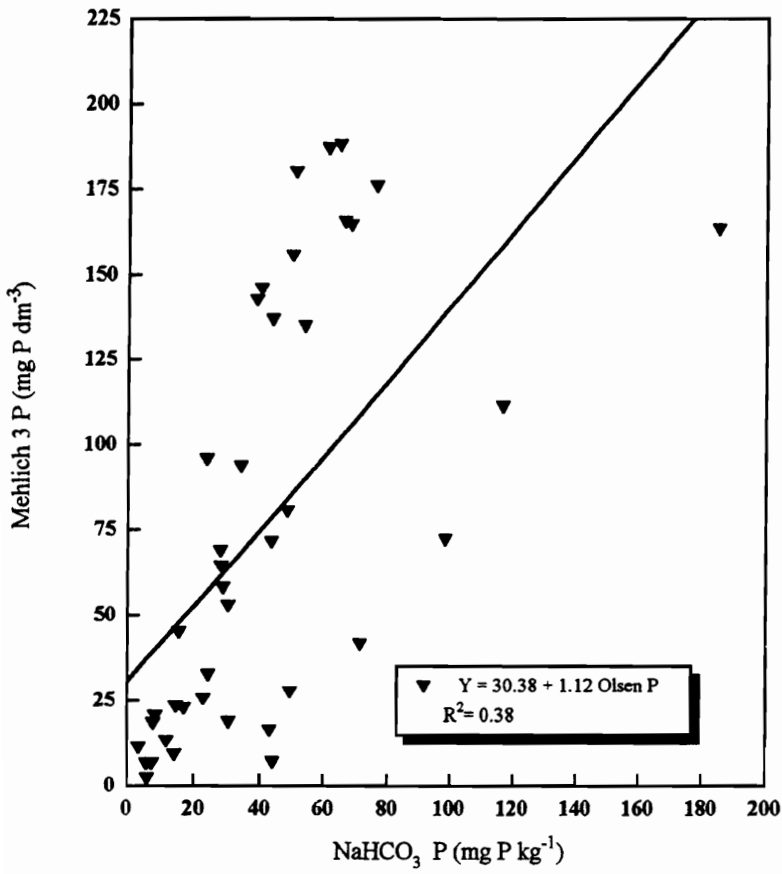


Fig. 2-8. The relationship between the amounts of Mehlich 3 (Y) and 0.5 M NaHCO₃ (X) extractable P.

There are several possible explanations for the high P extraction capacity of Olsen in the soils high in clay. Unlike the M 3 solution, the NaHCO_3 solution does not destroy and dissolve the clay fraction because the soil extraction solution pH on the average is 8.8, whereas M 3 procedure had average soil extraction solution pH value of 2.9 (Table 2-10). Therefore, reprecipitation of dissolved P by Al^{3+} and Fe^{3+} from destroyed and dissolved clay particles does not occur with the NaHCO_3 extractant to the same extent as with M3. Also, in the M 3 solution, some dissolved P can be reprecipitated by exchangeable Al^{3+} released from the clay particles by NH_4^+ which is more active than Na^+ in the Olsen extractant (Skeen and Summer, 1967).

Dithionite-citrate-bicarbonate extractable Al_2O_3 , and Mn, contents have a negative influence on the relationships between M 3 and Olsen P (Table 2-13). In some instances Fe_2O_3 and organic matter contents also show a similar trend. The results observed above are in agreement with those of Tran et al., (1990) who observed that oxalate extractable Fe and organic matter contents have significantly negative effects on the relationship between M 3 and Olsen P. The 30- minute shaking time of the Olsen method provides ample time to react with clay minerals which have a large surface area. This longer reaction time allows release of P from oxides and hydrated oxides of Al, and Fe and Mn.

Table 2-13. Relationships between Mehlich 3 (Y) and Olsen extractable P contents as affected by soil properties.

Soil	N*	Regression Equation	Coefficient of Determination (R ²)
All	40	Y = 30.38 + 1.12 Olsen P	0.380**
		= 66.49 + 1.49 Olsen P - 99.20 Al ₂ O ₃ ^{††}	0.759**
		= 47.12 + 1.40 Olsen P - 7.56 Fe ₂ O ₃ ^{††}	0.698**
		= 39.12 + 1.38 Olsen P - 0.02 Mn ^{††}	0.633**
		= 66.78 + 1.23 Olsen P - 2.56 Clay ^{††}	0.696**
		= 72.88 + 1.12 Olsen P - 19.11 OM [†]	0.481**
Physiographic region			
Coastal Plain soil	16	Y = 23.82 + 2.33 Olsen P	0.704**
		= 51.13 + 2.58 Olsen P - 7.51 Fe ₂ O ₃ ^{††}	0.819**
		= 75.99 + 2.23 Olsen P - 7.89 Clay ^{††}	0.929**
Piedmont soils	17	Y = 0.34 + 0.82 Olsen P	0.894**
		= 9.25 + 0.94 Olsen P - 1.86 Fe ₂ O ₃ ^{††}	0.941**
		= 16.14 + 0.97 Olsen P - 26.60 Al ₂ O ₃ ^{††}	0.952**
		= 5.84 + 0.93 Olsen P - 0.01 Mn ^{††}	0.965**
		= 14.02 + 0.90 Olsen P - 0.64 Clay ^{††}	0.962**
		= - 58.77 + 0.83 Olsen P + 11.24 pH ^{††} + 3.64 OM [†] - 0.31 Fe ₂ O ₃ [†] - 0.01 Mn ^{††}	0.988**
Valley & Ridge soils	7	Y = 26.74 + 1.02 Olsen P	0.524**
		= 91.40 + 1.40 Olsen P - 40.62 Fe ₂ O ₃ ^{††}	0.842**
		= 71.51 + 1.34 Olsen P - 0.10 Mn ^{††}	0.915**

Contd....

Soil	N*	Regression Equation	Coefficient of Determination (R ²)
Texture			
Clay < 17%	28	Y = 23.63 + 1.85 Olsen P	0.579**
		= 52.35 + 2.09 Olsen P - 41.35 Fe ₂ O ₃ ^{††}	0.842**
		= 73.40 + 2.18 Olsen P - 221.39 Al ₂ O ₃ ^{††}	0.814**
		= 55.61 + 1.77 Olsen P - 14.37 OM [†]	0.646**
		= 71.63 + 1.60 Olsen P - 4.89 Clay ^{††}	0.669**
		= 32.64 + 2.14 Olsen P - 0.10 Mn ^{††}	0.795**
clay 17.1 - 35%	6	Y = 1.99 + 0.87 Olsen P	0.992**
		= 17.95 + 0.94 Olsen P - 19.90 Al ₂ O ₃ ^{††}	0.999**
clay 35.1 - 60%	6	Y = - 12.89 + 0.79 Olsen P	0.880**
pH			
3.5 - 5.5	14	Y = 26.62 + 2.63 Olsen P	0.687**
		= 28.46 + 2.42 Olsen P - 79.50 Al ₂ O ₃ ^{††}	0.900**
		= - 7.59 + 2.69 Olsen P - 0.03 Mn ^{††}	0.911**
		= 36.37 + 2.09 Olsen P - 2.50 Clay ^{††}	0.867**
		= 89.92 + 1.65 Olsen P + 3.61 Fe ₂ O ₃ [†] - 165.90 Al ₂ O ₃ [†]	0.950**
5.6 - 6.5	18	Y = 36.36 + 1.10 Olsen P	0.343**
		= 66.98 + 1.47 Olsen P - 96.90 Al ₂ O ₃ ^{††}	0.680**
		= 47.89 + 1.48 Olsen P - 8.10 Fe ₂ O ₃ ^{††}	0.658**
		= 60.36 + 1.33 Olsen P - 2.26 Clay ^{††}	0.635**
		= 41.25 + 1.36 Olsen P - 0.02 Mn [†]	0.564**
6.6 - 7.5	8	Y = 47.72 + 0.63 Olsen P	0.461**
		= 71.07 + 1.37 Olsen P - 113.07 Al ₂ O ₃ [†]	0.825**
		= 48.31 + 1.43 Olsen P - 13.06 Fe ₂ O ₃ [†]	0.821**

** contribution of the 1st variable is significant at p = 0.01.

† contribution of the second variable is significant at p = 0.05 (†) or p = 0.01(††).

The influence of DCB extractable Al_2O_3 and Fe_2O_3 on the relationship between M 3 extractable P and Olsen P is negative (Table 2-13). This negative relationship suggests that, for soils high in these P forms, the M 3 procedure has a lower P solubilizing capacity than the Olsen method. Solubilization of Al-P occurs at high pH (Jardine and Zelazny, 1987) and the high soil extraction pH in the Olsen procedure, which is about 8.8 in all the soils (Table 2-10), could lead to extraction of more Al-P. Also, the high pH would in fact favor P dissolution from Al_2O_3 and Fe_2O_3 surfaces through the decrease in surface positive charge. Soil P solubility in the alkaline NaHCO_3 procedure is consistent with lowering of the activities of Fe, Al, and Ca which are responsible for P reprecipitation in the extraction solution as described by Olsen and Dean, (1965). It seems possible that the lower amount of P extracted by the M 3, from soils with high amounts of Al_2O_3 and Fe_2O_3 than by Olsen method, are due to more reprecipitation and readsorption of dissolved P by M 3. During the formation of variscite, different transitional stages of crystalline forms of Al-P in the soil can be expected to have a larger surface area than Fe-P forms. As shown by Juo and Ellis (1968), variscite, an Al-P mineral, has 12-times more surface area than the Fe-P mineral, strengite. Therefore, the 30-minute shaking time in the Olsen method may lead to extraction of more Al-P than Fe-P.

In the present study, when Fe_2O_3 is included as a second variable to the equation relating M 3 and Olsen P, a highly positive correlation ($R^2 = 0.95$, $p = 0.01$) is obtained in

the extremely to strongly acidic (pH 3.5-5.5) soil group (Table 2-13). This positive correlation can be attributed to complexation of Fe^{3+} by the organic compounds, such as CH_3COO^- and EDTA, in the M 3 solution to form very stable compounds, with consequent release of P. Ballard, (1974) and Schnitzer, (1969) showed that the solubility of colloidal Fe-P is greater than the solubility of colloidal Al-P because Fe forms complexes with the organic functional groups in the soil.

Furthermore, the multiple regression analyses reveals that the DCB extractable Mn has a significantly negative effect on the relationship between M 3 and Olsen P (Table 2-13). Manganous P forms such as MnHPO_4 and $\text{Mn}_3(\text{PO}_4)_2$ in the soil are very insoluble, but can be solubilized under low Eh conditions because solubility of these compounds are redox dependent (Lindsay, 1979). The Mn^{2+} in the NaOH solution precipitates as $\text{Mn}(\text{OH})_2$ which is rapidly oxidized on exposure to air and synthesized to insoluble hydrated manganese dioxide [$\text{MnO}(\text{OH})_2$]. This [$\text{MnO}(\text{OH})_2$] is responsible for lowering Mn^{2+} activity in the solution (Svehla, 1982). Therefore, it is reasonable to hypothesize that NaHCO_3 at pH 8.5 displaces more adsorbed P from Mn-P than does the M 3 solution. Dissolution of the nonlabile pool of Mn-P in alkaline NaHCO_3 solution probably causes an overestimation of available P by the Olsen method.

The organic matter contents of the soils range from 0.4 - 5.0 % (Table 2-3). The multiple regression indicated that, at constant levels of Olsen P, M 3 P decreases with an increase in organic matter (Table 2-13). Alkalinity in the NaHCO_3 extraction method

extracts P from both inorganic and organic P compounds in soils, but may extract more of quick-releasing inorganic P (Bowman and Cole, 1978). The dark brown color of NaHCO_3 soil extractions is caused by organic P compounds. The organic P content in the upper 15 cm is calculated to be 898 kg ha^{-1} based on 1% P content and a 4% organic matter content (Tisdale et al., 1993). The availability of organic P depends on the mineralization rate which is controlled by various factors such as C/P ratio and the factors associated with microbial degradation. Therefore, the plant availability of all the P extracted from organic matter by NaHCO_3 is not predictable and could be an overestimation.

2-3.6 Comparison of Extractable P by Volume-Volume, and Weight-Volume Basis

The bulk densities and the amounts of extractable P by M 1, M 3, Bray 1(5 min) procedures on the volume/volume (v/v) and weight/volume (w/v) bases for all soils and by textural classes are shown in Table 2-14. The v/v basis extractable P quantities, by all three extraction procedures, are greater than the w/v basis in the coarse-loamy (clay < 17%) soil group and in the group with all soils. The extractable P quantities by v/v and w/v basis are not different ($p = 0.05$) in the fine-loamy and clayey-fine loamy (clay >17.1%) soil groups.

The weight of equal soil volumes differ according to their bulk densities. Fine-textured soils such as silt loams, clays and clay loams generally have lower bulk densities

Table 2-14. Comparison of volume and weight basis extractable P by texture.

Texture	N*	Bulk density		Extractable P					
		(g cm ⁻³)		Mehlich 1 P		Mehlich 3 P		Bray 1 P(5 min)	
		(g cm ⁻³) median	Range	volume (mg P dm ⁻³)	weight (mg P kg ⁻¹)	volume (mg P dm ⁻³)	weight (mg P kg ⁻¹)	volume (mg P dm ⁻³)	weight (mg P kg ⁻¹)
All (soils)	40	1.3	1.1 - 1.6	43.3	32.5	76.8	57.9	101.9	75.1
Clay < 17%	28	1.4	1.2 - 1.4	50.6	36.7	95.0	68.1	123.3	88.0
Clay 17.1-35%	6	1.2	1.1 - 1.2	28.2	23.5	41.0	37.7	53.6	47.8
Clay 35.1-60%	6	1.2	1.1 - 1.2	24.7	21.9	28.2	26.9	50.3	44.9

* No. of soils in the group.

than sandy soils (Fig.2-9). Thus, when the extractable nutrient quantities are expressed on the weight basis, the extracted amounts are depreciated more in the soils with a sandy texture. The weight-based extractable P quantities in the coarse-loamy soils and in all soils were lower than the volume-based quantities (Table 2-13). The lower weight-basis extractable P quantities in all-soils category is explained by the large representation (70%) of coarse-loamy soils in the total sample.

The difference between volume and weight based analytical results increases with the use of larger soil volumes. The scoop volumes used for extraction by the three methods ranged from 0.85 cm³ to 4.0 cm³. Thus, the differences in extractable P quantities across different methods observed under volume-based extractions are also not comparable with weight-based measurements. Mehlich (1973) showed that results based on the use of a volume sample (scooped) but calculated on an assumed weight of soil changed the values in inversion of assumed volume-weight. Therefore, results based on weight measurements may be compared following conversion to volume basis.

2-3.7 Possible Nucleophilic Reaction Mechanisms on P Extractability

Several possible structural models have been introduced to explain orthophosphate ion bonding to the mineral surfaces. Ligand exchange of phosphates (PO₄³⁻) for surface oxides and hydroxides of Al and Fe is explained by monodentate, bidentate, and binuclear models of surface adsorbed P (White, 1980; Praffitt et al., 1975;

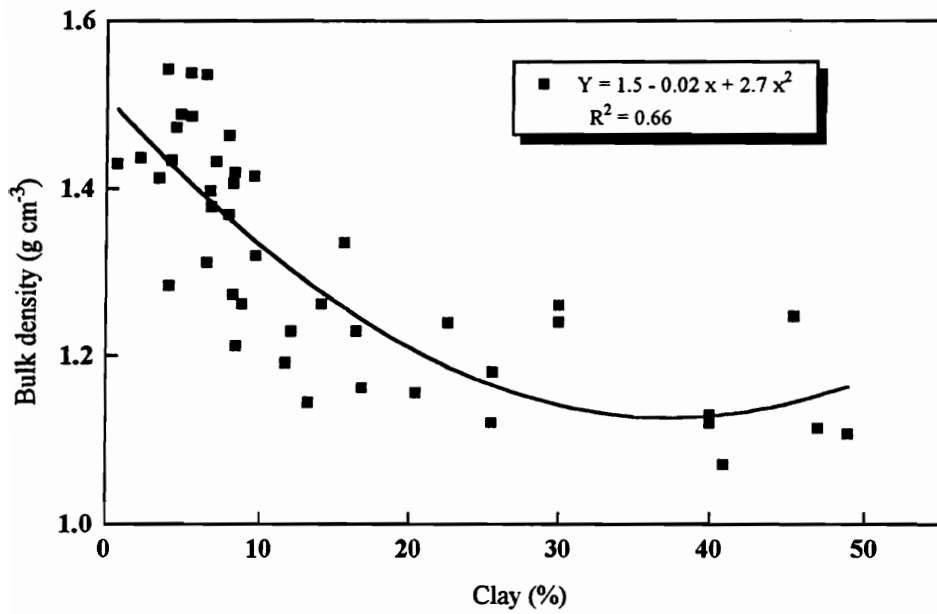


Fig. 2-9. Relationship between bulk density (Y) and percent clay (X) contents of the 43 soils.

Kyle et al., 1975; Kaikafi et al., 1967). Structural models of these P forms are shown in Figure 2-10.

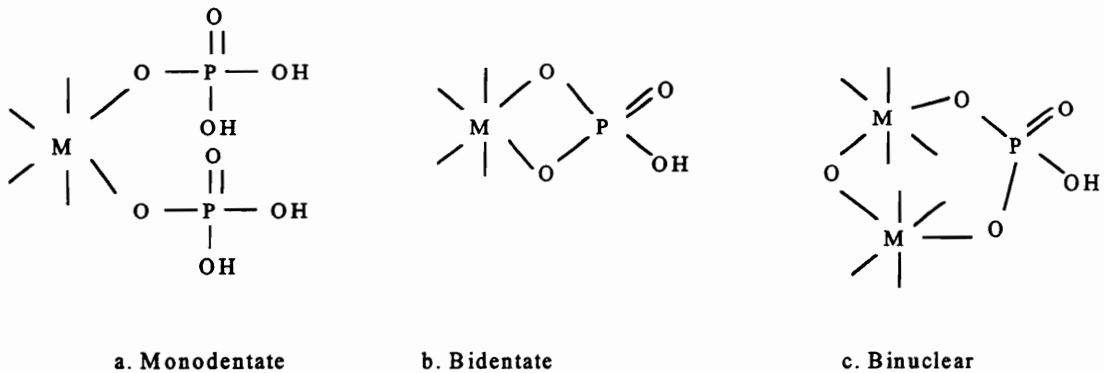


Fig. 2-10. Structural models of ligand exchange of H_2PO_4^- on metal surface hydroxide (M = Al or Fe).

The bidentate P complex is more stable than the binuclear complex, and the monodentate structure is the least stable. The greater stability of bidentate than the monodentate complex is generally explained by the difference in entropy of formation. Thus, the H_2PO_4^- from the M-O-P bond is considered labile P as it can be readily desorbed from the mineral surfaces (Hingston et al., 1974; Tisdale et al., 1993).

Mehlich 3, Bray 1, Mehlich 1, and 0.5 M NaHCO_3 (pH 8.5) contain anions such as Cl^- , F^- , SO_4^{2-} , HCO_3^- , CH_3COO^- , NO_3^- , and OH^- . Apart from these anions, H_2O molecules are also available in the solutions. Among these constituents, Cl^- , F^- , CH_3COO^- , OH^- and H_2O are good nucleophiles, i.e., negative ions or molecules that have an unshared pair of electrons. Further, a negatively charged ion is always a much

stronger nucleophile than its conjugate acid (Solomons, 1992). Thus, among the nucleophiles that are prominent in the alkaline NaHCO_3 solution, OH^- is a stronger nucleophile than H_2O .

In a protic solvent such as H_2O , the nucleophile with a larger atom is stronger (Solomons, 1992). Thus, within the same group in the periodic table, the larger Cl^- ions are more nucleophilic than strongly solvated smaller ions such as F^- which is a constituent of the Bray 1 solution. Since the charge in smaller size nucleophiles is more concentrated, the molecules of protic solvents more easily form hydrogen bonds. These hydrogen bonds lower the reactivity of the F^- ion. The greater reactivity of nucleophiles with larger nucleophilic atoms is not entirely related to solvation. Larger atoms are more polarizable (Solomons, 1992) and, hence, can donate a greater degree of electron density to the substrate than a smaller nucleophile whose electrons are more tightly held. According to Solomons (1992), the relative nucleophilicities of the nucleophiles which are in the M 1, M 3, Bray 1, and NaHCO_3 extractants, can be ranked in the order; $\text{OH}^- > \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{F}^- > \text{H}_2\text{O}$.

In a nucleophilic substitution reaction, the nucleophile seeks an electron deficient center. The labile pool P which consists of surface adsorbed P of mainly monodentate nature does not have a positively charged center to proceed with the nucleophilic reaction. Therefore, a positive charge must be created on the metal ion (Al or Fe) in a substrate that bears a H_3PO_4 leaving group. Hydrogen ions (H^+) in the acidic M 1, M 3,

and Bray1 solutions protonate the phosphate group and, thereby, polarize the M-O bond as depicted in the figure 2-11.

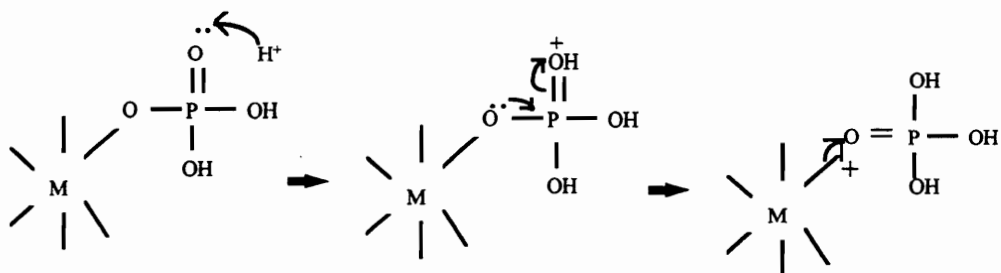


Fig. 2-11. Polarization of the trivalent metal ion through protonation of terminal oxygen atom of the (P=O) orthophosphate ion.

The attachment of H^+ to the unshared electron pair of the O atom creates a positive center on the metal ion which becomes a substrate for the nucleophile. Thereafter, the nucleophile reacts with the substrate Al or Fe phosphate by replacing the orthophosphate substituent as orthophosphoric acid. Since the substitution reaction is initiated by protonation of terminal oxygen atom of the orthophosphate ion, the reaction can be categorized as an acid catalyzed nucleophilic substitution reaction. The final reaction steps are demonstrated in the Figure 2-12.

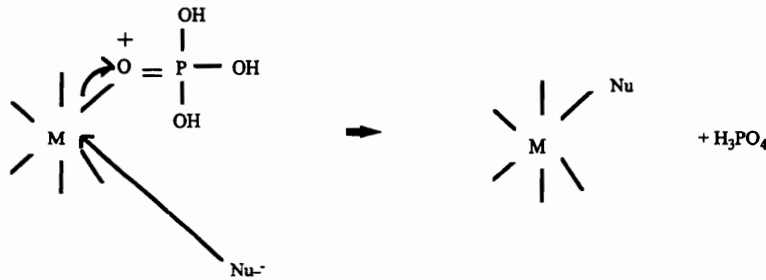


Fig. 2-12. Final step of the acid catalyzed nucleophilic substitution reaction.

To sustain this type of reaction, the leaving group substituent must be able to exit as a relatively stable, weakly basic molecule or ion (Solomons, 1992). The pK_1 , pK_2 , and pK_3 values of the tribasic orthophosphoric acid are 2.12, 7.22, and 12.33 respectively (Berkheiser et al., 1980). Thus, the H_3PO_4 and $H_2PO_4^-$ ions are very stable in the low pH range. The extraction solutions from M 1, M 3 and Bray 1 have very low pH values (Table 2-10). Therefore, the leaving group H_3PO_4 can remain in the M 1 solution as H_3PO_4 and $H_2PO_4^-$, and in Bray 1 and M 3, solutions as above ions and their NH_4^+ salts. The reaction can be expected to move in a forward direction as long as the leaving group of the nucleophilic substitution reaction remains in a stable form.

Nucleophiles in the Bray 1 solution are Cl^- , F^- , and H_2O . Though, the Cl^- ion is a stronger nucleophile than the F^- ion, more P is dissolved by F^- than Cl^- . Under very acidic conditions, Al combines with the F^- ions and forms a strong complex because F^- ion has a high affinity to Al^{3+} . Stability constants of F^- complex with Al and Fe, i.e., 6.71 and 5.16,

are 8-9 times greater than the stability constant of FeCl_3 , which is 0.77. The Al and F^- complexes are solubilized at a high solution pH (Jardine and Zelazny, 1987).

Nucleophiles in the M 1 solution are Cl^- and H_2O and in the M 3 solution are CH_3COO^- , F^- , and H_2O . Acetate ions form very stable complexes with Fe than Al. The stability constant of CH_3COO^- with Fe is 6.5 and with Al is 3.76 (Young and Bache, 1985).

Fluoride ions in both M 3 and Bray solutions can release P from Fe-P by nucleophilic substitution, because the trivalent fluoroferrate ion is stable under acidic conditions (Turner and Rice, 1952).

The SO_4^{2-} ions in the M 1 solution and NO_3^- ions in the M 3 solution do not act as nucleophiles to dissolve P because the charge is distributed in the molecule. But the SO_4^{2-} ion in the M 1 solution facilitates P dissolution through formation of Al and Fe sulfates. The relatively high formation constant of $\text{Fe}(\text{SO}_4)_2^-$, i.e., 5.38, influences formation of more $\text{Fe}(\text{SO}_4)_2^-$ than $\text{Al}(\text{SO}_4)_2^-$, which has a formation constant of 1.90 (Lindsay, 1979). Jardine and Zelazny (1987) found that SO_4^{2-} ions form strong bonds with mononuclear and polynuclear Al which do not readily dissociate until high solution pH values. The SO_4^{2-} ions in the M 1 solution can form Al and Fe sulfates and, thereby, prevent readsorption and reprecipitation of dissolved P in the solution.

Bicarbonate (HCO_3^-) ions in the alkaline NaHCO_3 solution are weak nucleophiles for P solubilization. Therefore, the solubility of P by NaHCO_3 takes place mainly by lowering of Ca^{2+} , Al^+ , Fe^{3+} ion activity under high pH conditions in the soil solution

(Olsen and Dean, 1965). Strongly bound mononuclear or polynuclear Al^{3+} and H_2PO_4^- are not dissolved until the solution attains high pH levels (Jardine and Zelazny, 1987). The OH^- and H_2O molecules in the NaHCO_3 solution are sufficiently negatively charged to participate in nucleophilic reactions. The pH values of the supernatant of NaHCO_3 extraction are shown in Table 2-10. The average pH value of the supernatant was 8.8. These high pH values facilitate precipitation of Al and Fe hydroxides formed following the nucleophilic attack of OH^- forming H_2PO_4^- . This postulation agrees with the finding that OH^- ions of the NaHCO_3 solution remove some Al-P and Fe-P (Maida, 1978).

The alkaline 0.5 M NaHCO_3 solution dissolves some forms of organic P in soil (Bowman and Cole, 1978; Hedley, 1982). Hydroxide ions and H_2O molecules in the solution act as nucleophiles for the reaction to dissolve organic P compounds. The reaction mechanism for inositol hexa phosphate (phytic acid) which is prominent in the soil is demonstrated in Figure 2-13. The reaction probably occurs through nucleophilic attack on the phosphate group.

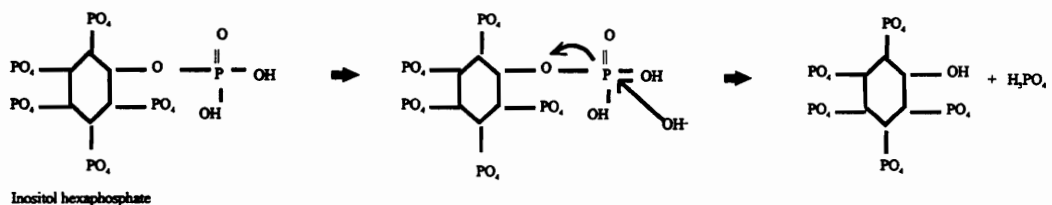


Fig. 2-13. Reaction mechanism for dissolution of phytic acid P by nucleophilic substitution under alkaline condition.

The amounts of water extractable P are relatively small compared to amounts extracted by other soil extractants (Frossard et al., 1996). The water molecules function as a weak nucleophile to release P from Al and Fe surfaces. The rate and quantity of P solubility are affected by the pH (active acidity) of the soil because to initiate a nucleophilic substitution reaction a positive charge has to be created on the Al or Fe surface.

The acid catalyzed nucleophilic substitution reaction mechanism which is introduced to explain P solubility by M 1, M 3, Bray 1, and Olsen methods fall within the four basic mechanisms (Kamprath and Watson,1980). These mechanisms encompass acid dissolution, ion exchange, cation complex and cation hydrolysis. The reasons for the decrease in P extractability due to neutralization of acidic extractions (Martens et al., 1969; Thomas and Peaslee, 1973) are not explained in the literature. It is possible that the decrease in acidity lowers the release of H_2PO_4^- by limiting the supply of H^+ needed to create a positive center on the metal ion, i.e., a prerequisite for the positive center to serve as a substrate for the nucleophilic substitution reaction.

2-4 CONCLUSIONS

The study compared amounts of Mehlich 3 extractable P with quantities of Mehlich 1, Bray 1, and Olsen extractable P in 40 Virginia soils. The relationships between amounts of P extracted by the different methods and the soil physical and chemical properties were also studied. When all the soils were considered as a group, the highest extractable P quantities were obtained by the Bray 1 (5 m) procedure followed by the M 3, Bray 1 (1 m), M 1, and Olsen procedures. The M 3 extractable P quantities were well correlated ($R^2 = 0.92, 0.98$ and 0.96) with M 1, Bray 1 (1 m), and Bray 1 (5 m) extractable P quantities, but the correlation was low ($R^2 = 0.38$) with Olsen extractable P contents.

The correlation between Mehlich 3 and Olsen extractable P contents improved markedly when the soils were classified according to physiographic regions or textural groups based on the clay content. In the clayey fine soil group, the highest amounts of P were extracted by the Olsen method followed by Bray 1 (5m), M 3, Bray 1 (1m), and M 1 methods. The increased P extraction potential of F^- in the M 3 solution was decreased in high clay soils due to consumption of F^- by reaction with NH_4^+ exchangeable Al^+ to form Al-F. As M 3 extractable P contents are inversely related with the soil clay levels, when M 3 is used in the extraction, separate soil test calibrations should to be performed for soils grouped by the clay content.

When the soils were grouped by pH, M 3 extractable P quantities varied marginally compared with soil classification by physiographic regions or the texture.

This relationship is caused by the high buffering capacity of the M 3 extractant which is not affected by soil acidity. The relationship between M 3 and M 1 extractable clay contents was negatively affected by pH indicating that Ca-P was extracted relatively more easily by M 1 than by M 3 in relatively more acidic soils. The Ca-P extracted by M 1 may not be plant available. Therefore, the M 3 extractant can be used to estimate extractable P in soils with greater accuracy than the M 1 procedure in a group of soils with a wide pH range.

In soils containing DCB extracted noncrystalline, crystalline, or substituted Al, M 3 extractable P contents were lower than Bray 1 (5 m) and Olsen extractable P contents indicating lower extraction of fixed P by M 3. Bray 1 extractant has a two-fold higher F^- concentration compared to M 3 which causes higher extraction of Al-P. This makes M 3 a better P extractant in soils containing larger quantities of DCB extractable Al_2O_3 .

The mechanism of P solubilization in the soil is explained by acid-catalyzed nucleophilic substitution reactions that solubilize P from Al and Fe surfaces by the nucleophiles such as OH^- , CH_3COO^- , Cl^- , F^- and H_2O and the extracting agents in the four extracting solutions. The changes in P extractability under varying soil physical and chemical conditions can be explained by this mechanism. The degree of P solubilization by different extractants is reflected by the strength of nucleophile and the acidity of the supernatant solution.

Mehlich 3 performs as well as Bray 1(5 m) in determining extractable P quantities in a wide range of soils due to the inclusion of more complexing radicals for trivalent cations. However, the use of Bray 1 procedure is limited to the determination of extractable soil P. Given the suitability of M 3 as a universal extractant for the simultaneous determination of many other plant nutrients, it can be used to determine the extractable P contents in Virginia soils.

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Appendix 2-1. Physical and chemical properties of 43 soils

Soil Series	Physio. Region	pH	OM	Clay	Fe ₂ O ₃	Al ₂ O ₃	Mn	Exch. Al
					%		mg kg ⁻¹	
Altavista	CP	5.3	1.5	4.8	0.73	0.26	127.3	6.3
Appling	P	4.8	2.4	14.1	1.57	0.43	96.3	50.7
Bojac	CP	6.3	0.7	8.2	0.88	0.26	61.8	4.7
Cecil	P	5.6	1.6	7.9	0.79	0.22	100.0	8.1
Cecil	P	5.4	1.7	22.6	4.94	0.74	234.5	5.1
Christia	RV	5.7	1.9	16.4	2.26	0.37	758.0	1.1
Craven	CP	5.5	3.8	12.1	0.64	0.25	161.8	8.1
Davidson	P	6.5	3.1	47.0	15.31	1.04	1001.5	3.0
Davidson	P	6.4	2.9	25.6	10.96	1.40	3778.5	1.7
Davidson	P	5.4	2.5	40.0	16.74	1.48	3795.0	3.8
Davidson	P	5.4	2.5	40.0	16.74	1.48	3795.0	4.0
Davidson	P	5.4	4.6	40.9	10.68	0.92	1526.5	13.6
Dothan	P	6.2	1.6	4.2	0.33	0.15	32.7	1.5
Dragstow	CP	6.9	1.1	9.6	0.63	0.28	7.3	0.6
Dyke	P	6.9	1.6	45.4	7.90	1.04	4933.0	1.3
Emporia	CP	6.5	2.0	9.7	0.84	0.31	23.7	1.1
Emporiia	CP	6.5	1.4	3.4	0.39	0.19	30.9	3.0
Fauquier	P	7.3	3.0	25.5	11.06	1.38	2584.5	1.3
Groseclo	RV	5.1	3.3	13.2	1.33	0.26	580.0	29.9
Guernsey	RV	6.3	2.2	4.1	3.20	0.68	1139.5	4.0
Hayter	RV	6.6	2.9	8.4	2.61	0.55	794.5	3.4
Hayter	RV	5.7	3.4	8.3	0.94	0.27	67.3	4.9
Kenusvil	CP	6.0	1.0	7.1	0.52	0.18	145.4	1.3
Lodi	RV	5.2	3.9	8.2	1.92	0.56	456.2	29.7
Lodi	RV	7.4	2.6	16.8	1.90	0.45	450.8	1.1
Mayadan	P	6.1	1.4	6.8	0.68	0.23	20.0	2.8
Myatt	CP	6.8	1.1	7.9	0.33	0.11	7.3	0.8
Norfolk	CP	5.8	1.9	3.9	0.36	0.18	9.1	4.2
Rains	CP	6.0	2.4	15.6	0.56	0.22	9.1	2.8
Rumford	CP	5.3	1.6	4.5	0.28	0.16	10.9	11.2
Rumford	CP	5.3	1.7	5.5	0.28	0.18	10.9	12.5
Rumford	CP	6.6	1.0	5.4	0.46	0.19	163.6	0.8

(Contd.)

Sassefra	CP	5.7	2.6	6.7	0.73	0.33	198.1	9.3
Slagle	CP	6.6	3.5	8.8	0.56	0.32	241.8	3.6
Starr	P	6.1	2.2	48.9	9.46	1.11	4198.5	1.1
state	CP	5.7	2.4	6.5	0.56	0.34	130.9	5.7
Tarboro	CP	5.4	0.4	6.4	0.83	0.30	132.7	16.7
TATUM	P	6.2	2.2	30.0	6.51	0.75	178.1	4.0
Tatum	P	6.2	1.9	30.0	6.51	0.75	178.1	4.0
Tatum	P	5.5	2.7	20.4	6.33	0.70	192.7	14.6
Tatum	P	4.0	5.0	11.7	1.40	0.34	116.3	372.5
Uchee	CP	4.9	1.1	2.2	0.25	0.14	20.0	8.5
Wagrums	CP	5.9	1.2	0.7	0.26	0.14	18.2	3.0

Appendix 2-2. Extractable P by different methods for 43 soils

Soil Series	Physio. Region	Olsen	Bray 1	Mehlich 3	Mehlich 1	Bray 1
		_____ mg kg ⁻¹ _____	_____	_____ mg dm ⁻³ _____	_____	_____
Altavista	CP	171.0	258.0	536.1	189.8	695.3
Appling	P	12.0	10.9	13.6	7.3	21.8
Bojac	CP	68.1	94.2	165.0	91.3	225.9
Cecil	P	7.9	12.2	18.8	13.5	24.1
Cecil	P	7.5	6.7	7.0	6.5	15.3
Christia	RV	28.5	34.7	58.6	41.8	64.7
Craven	CP	48.4	57.8	80.9	41.8	86.5
Davidson	P	98.5	55.2	72.5	61.5	142.1
Davidson	P	30.3	19.2	19.1	19.0	34.4
Davidson	P	44.0	5.8	7.3	5.7	12.7
Davidson	P	49.4	16.8	28.0	21.7	38.6
Davidson	P	6.2	3.2	2.6	1.5	9.1
Dothan	P	8.5	11.8	21.0	14.8	21.5
Dragstow	CP	27.8	42.4	69.2	35.8	69.7
Dyke	P	43.1	12.2	16.7	22.0	24.7
Emporia	CP	53.8	86.9	135.3	82.3	159.1
Emporiia	CP	23.6	61.4	96.2	53.8	121.5
Fauquier	P	185.2	88.3	163.8	97.8	202.1
Groseclo	RV	14.7	15.9	23.7	15.5	28.2
Guernsey	RV	116.7	78.1	111.7	53.7	197.9
Hayter	RV	24.2	25.8	33.1	17.3	55.6
Hayter	RV	66.0	97.6	166.1	95.5	232.4
Kenusvil	CP	15.4	29.1	45.5	28.5	52.9
Lodi	RV	43.4	55.1	71.8	34.0	84.7
Lodi	RV	30.1	40.3	53.2	51.3	47.6
Mayadan	P	3.5	8.6	11.7	5.5	17.4
Myatt	CP	27.9	35.1	64.7	38.8	65.3
Norfolk	CP	40.0	77.1	146.4	85.0	166.8
Rains	CP	103.8	134.1	268.7	116.4	250.0
Rumford	CP	60.9	108.2	187.5	93.0	230.0
Rumford	CP	64.4	112.2	188.3	92.8	222.4
Rumford	CP	38.7	88.4	143.1	58.5	186.8

(Contd.)

Sassefra	CP	43.7	97.8	137.2	65.0	207.9
Slagle	CP	33.9	64.8	94.2	54.0	101.8
Starr	P	71.3	38.6	42.1	35.8	74.7
state	CP	63.3	305.2	673.0	327.9	990.6
Tarboro	CP	76.0	111.8	176.3	63.8	264.7
TATUM	P	22.8	13.9	26.0	19.5	32.6
Tatum	P	5.9	6.3	6.9	6.2	7.9
Tatum	P	17.0	15.7	23.2	20.0	29.4
Tatum	P	14.3	6.9	9.6	6.3	11.8
Uchee	CP	49.9	93.7	156.2	68.5	215.0
Wagrums	CP	50.8	113.4	180.4	107.0	268.2

CHAPTER 3

DISTRIBUTION AND AVAILABILITY OF DIFFERENT PHOSPHORUS FRACTIONS IN VIRGINIA SOILS

ABSTRACT

Continual application of phosphorus (P) fertilizers have raised soil test P levels in most areas in the United States. Recent occurrences of severe eutrophication problems have renewed interest on a better understanding of the transformation and dynamics of plant nutrients including P. This study was carried out to evaluate the distribution of different inorganic and organic soil P forms and their contribution to Bray 1, Mehlich 1, Mehlich 3, and Olsen extractable P contents in the Coastal Plain, Piedmont, and Ridge and Valley soils in Virginia. Inorganic P fractionation was accomplished by the modified Chang and Jackson (1957) procedure of Peterson and Corey (1966) with several modifications, while the organic fraction was determined by the following Bowman (1989) method.

The total P content of the soils ranged between 0.02% and 0.4%, with 26% of the total P in the labile to moderately labile pool, 49% in the non-labile pool, and 25% in the organic fraction. The ranking of the P fractions within the labile to moderately labile pool was Fe-P > Al-P > Ca-P > NH₄Cl-P and the non-labile pool was residual P > reductant

soluble P > occluded P. The distribution pattern of Fe-P, reductant soluble P, occluded P, residual P, and organic P in the soil was primarily determined by the Fe_2O_3 and clay contents. The Al-P content was not markedly influenced by the clay content or pH.

The reductant soluble P was the dominant P form in the soils. It was concluded that Fe-P, a dominant labile form in agricultural soils was transformed to reductant soluble form over time. Although it is not important agriculturally, the reductant soil P fraction has increased availability under reduced conditions, and hence, is a potential P source for eutrophication in surface waters. Accordingly, the Piedmont soils and high clay soils seem to have a higher eutrophication potential.

Extractable P contents for soil tests were as follows: Bray 1 > M 3 > M 1 > Olsen. The levels of P solubilization by the procedures other than the Olsen method were negatively influenced by the clay, Al_2O_3 , Fe_2O_3 , and organic matter contents. Multiple regression data suggested selective extraction from Al-P fraction by the Bray 1 extractant; Al-P and Fe-P fractions by M 3 method; Al-P, Ca-P, and organic P fractions by M 1 procedure; and NH_4Cl -P, Fe-P, Ca-P and organic P fractions by the Olsen technique. The Olsen extractable P content was not related to Al-P ($p = 0.05$).

3-1 INTRODUCTION

Agronomic and environmental aspects of soil P transformation and dynamics has renewed interest on the impact of agricultural practices on P movement in soil. In recent years, the role of P in the aquatic ecosystems has emerged due to problems created by excessive plant growth on surface waters. Research has demonstrated that the soil test P levels in the surface soil and dissolved P in the runoff water are highly linearly correlated (Oloya and Logan, 1980; Sharpley et al., 1981).

Soil P levels are controlled by the native P and soil amendments, such as synthetic fertilizers, plant residues, and animal manures, because atmospheric desorption of P is of a low magnitude. Extremely high soil test P levels have been reported for United States soils following long-term fertilization and manure applications (Sims, 1993).

Nonetheless, effects of P deficiency and responses to P application are often observed in U.S. soils (Cope, 1981; Harrison et al., 1987). Hence, it is necessary to understand P dynamics and transformation in the soils with diverse properties to ensure adequate P availability to plants and to control environmental problems such as eutrophication.

Soil tests are used to estimate plant available P and fertilizer requirements. Application of fertilizer increases the amounts of plant available P in soil measured by soil tests (McCollum, 1991). However, most of the soil tests measure only a portion of inorganic P and ignore the less available P pools. In highly weathered soils, a better

measure of potential plant available P may be provided by the less available pools. Water soluble P applied to soil readily dissolves and increases soil solution P which is available to plants in the immediate vicinity of the root zone. After initial stages, reaction products of fertilizer P are transformed to various forms of sparingly soluble inorganic compounds by reaction with soil mineral constituents (Sample et al., 1980). In addition, some of the soil applied P is converted to soil organic P through plant, animal and microbial residues (Anderson, 1980; Dalal, 1977). Thus, fractions of inorganic and organic P not measured by soil tests may accumulate in the soil.

3-1.1 Forms of Soil Phosphorus

The forms of P vary considerably from soil to soil (Ahmed and Islam, 1975; Sharpley, 1984). Soil solution P concentrations are buffered by various inorganic and organic P forms which are the major P reservoirs in soil. Hence, the forms, relative proportions, and ultimate reaction products of P are governed by soil mineralogy, which can be related more or less systematically to the nature of the parent material and the degree to which this material has been altered by weathering (Tisdale et al., 1993). The P-accompanying cations, which have different degrees of mobility and physical and chemical properties, are simultaneously changed with agricultural practices and with soil environmental iterations. Among the soil properties, pH is the most important determinant of the forms, distribution and quantity of soil P (Sample et al., 1980).

Stevenson (1994) classified P compounds in soils into three groups, i.e., inorganic P compounds in which the P is combined with Al, Ca, Fe, Mg, and clay minerals; organic and inorganic P compounds associated with the cells of microorganisms and soil biomass; and organic compounds of the soil humus.

3-1.1.1 Inorganic P

Soil inorganic P is a heterogeneous mixture of Al, Ca, and Fe phosphates, occluded or encapsulated by Fe oxides and hydrated oxides (Chang and Jackson, 1957; Smeck, 1985). Occluded P refers to P physically encapsulated by minerals which are structurally devoid of P and are sheltered from interaction with more reactive P forms. Phosphorous encapsulated by primary or secondary silicate minerals referred to as residual inorganic P is among the hardest to extract (Smeck, 1985). In acid soils, inorganic P exists as precipitates of secondary minerals, such as aluminum bound P (Al-P) and iron bound P (Fe-P), and as adsorbates to surfaces of Al and Fe oxide and clay minerals. In neutral and calcareous soils, inorganic P precipitates as Ca bound secondary P minerals (Ca-P) or is adsorbed to surfaces of clay minerals and CaCO_3 (Tisdale et al., 1993). In acid soils, initial reaction products of fertilizer P are transformed into stable crystalline forms such as strengite and variscite (Taylor et al., 1963). Formation of strengite from crystallization of colloidal Fe phosphate is much faster than formation of variscite from colloidal Al phosphates (Hsu, 1982; Juo and Ellis, 1968). Inorganic P

compounds in soils are extremely sensitive to small changes in soil properties (Supak, 1969). Hsu and Jackson (1960) found that, as soil weathers, the pH decrease causes transformation of Ca-P to Fe-P.

3-1.1.2 Organic P

The levels of organic P in soils vary enormously. In most mineral soils, organic P accounts from 20 to 60 percent of total P (Tiessen et al., 1994). Generally organic P is higher in clay soils than in coarse-textured soils, but lower than in humus soils (Dalal, 1977). The availability of organic P is regulated by the biological and biochemical reactions during the mineralization process. During plant material decomposition, microorganisms rapidly mineralize a portion of the organic P and incorporate a portion of plant P into cell tissue P which later is mineralized (Birch, 1961). The quantity of P mineralization was positively related to the quantity of P initially present in soils (Blair et al., 1978).

Soil organic P does not have a direct affect on the P nutrition of plants for it must be mineralized before absorbed (Sanyal and De Datta, 1991). Tran and N'dayeggamie (1995) reported that there was no correlation between plant uptake of P and organic P fraction. However, easily mineralizable organic P extracted by the Olsen (NaHCO_3) procedure and water soluble organic P may contribute to plant uptake during the growing season (Bowman and Cole, 1978b; Gahoonia and Nielson, 1992). Sharpley and Smith

(1983) reported that cultivation and fertilizer P application tended to increase the amount of total P and decrease organic P in the surface soil horizons. Therefore, turnover rates of organic P may become important for P nutrition of plants (Friesen and Blair, 1988).

Research on the effects of factors that control transformation of organic P in the soil-plant eco-system has shown that only a small portion of the total soil organic P is released to soil solution annually (Stewart and Tiessen, 1987).

The absolute change in the soil organic P pool under growing crops is usually very small in comparison to the total P pool and, consequently, observations over several years are necessary to detect changes (Friesen and Blair, 1988). Sequential extraction of inorganic and organic P fractions showed that in 65 years of continuous wheat-wheat-fallow rotation decreased total P in a cultivated soil by 29 percent as compared with an adjacent area under permanent pasture. Of the total P lost, 74 percent was organic and residual P. Twenty two percent of the total P lost originated from extractable organic P forms and 52 percent from the non-extractable residual P fraction. Mineralization and accumulation of organic P is regulated by creation of favorable environments for microbial growth and activity. Thus, addition of lime decreases organic P accumulation and increases its mineralization (Condrón and Goh, 1989).

Organic P consists of two basic forms, i.e., Di-ester and mono-ester. Di-esters contain structural phosphate in macro molecules, i.e., nucleic acids and phospholipids. Mono-esters account for less than one-half of the organic P in bacteria, fungi, and plants

(Anderson, 1980; Beever and Burns, 1980). Inositol phosphate, one of the mono-ester P forms, comprises about 60 percent of the total organic P (Tate, 1984). Several inositol phosphate esters such as mono-, di-, tri-, and hexa (phytic acid) have been identified (Anderson, 1980). Calcium and Mg associated inositol phosphates are found in plant materials while the soil combined forms are associated with Al^{3+} and Fe^{3+} in the acid soils, and Ca^{2+} in the calcareous soils (Stevenson, 1994). Inositol phosphates are less mobile than soil phospholipids and tend to accumulate in soils (Cole et al., 1977). Gil-Sotres et al. (1990) reported that the orthophosphate mono-ester, which includes inositol phosphates, was the dominant organic P source of soil extracts.

3-1.2 Fractionation Procedures

Phosphorus fractionation provides qualitative information about various P forms in P compounds such as apatite, strengite, and variscite and in compounds related to different transitional stages of P bound to Al, Ca, Fe and Mg. Phosphorous fractionation procedures are based on the ability of certain chemical reagents to solubilize different forms of soil P. Because of the dynamic and the complex nature of soil mineralogy and chemistry, separation of P into discrete forms is difficult. Numerous fractionation procedures have been developed for elucidation of the chemical nature and transformation of the soil P and sediment inorganic phosphates (Chang and Jackson,

1957; Hedley et al., 1982; Peterson and Corey, 1966; Williams et al., 1967, 1971a, 1971b).

Soil P fractionation applies chemical extraction/digestion techniques to a single sample in sequence to solubilize different forms of P compounds one group at a time. The most popular approach is that of Chang and Jackson (1957), which sequentially separates soluble P with NH_4Cl , Al-P compounds with NH_4F (pH 7.0), Fe-P compounds with NaOH , Ca-P with H_2SO_4 , and reductant soluble and occluded-P with $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of citrate. With the advancement of P chemistry, modifications of this approach involve use of different chemical extractants, pH change of extractants, and extraction sequence change (Olsen and Khasawneh, 1980; Olsen and Sommers, 1982; Hedley et al., 1982; Tiessen and Stewart, 1983; Sharpley, 1986; Weil et al., 1988). Some of the current fractionation schemes reflect a greater emphasis on the organic P fractions (Headley et al., 1982; Sharpley, 1986).

A recent P fractionation approach involves use of ^{32}P in isotopic exchange techniques (Wolf et al., 1986; Olsen and Khasawneh, 1980; Fardeau, 1993; Frossard et al., 1996). The isotopic exchange kinetics experiment, based on physiological and agronomic principles, modeled inorganic soil P into four pools. The central pool comprises P in soil solution plus free P with the same mobility as solution P. Phosphate present in the central pool can be exchanged with P in the other three pools, i.e., P in the solid phase. The latter forms were classified into 1 minute to 1 day, 1 day to 12 weeks,

and >12 weeks based on the time needed to exchange with solution P (Fardeau, 1993 cited in Frossard et al., 1996). Isotopic exchange techniques for P fractionation are not recommended for soils with high amorphous Fe contents and, consequently, high P fixation capacities, because accurate measurements of labile pool P is difficult (Wolf et al., 1986).

There are no direct measurements of soil organic P. It is estimated indirectly as the weight difference prior to and after an oxidative treatment of a soil. Fractionation procedures have been developed to separate the organic P in soil extracts into acid and base extractable components through sequential extraction (Bowman, 1989). Over the past decade, ^{31}P -nuclear magnetic resonance (NMR) spectroscopy has been introduced to obtain qualitative and quantitative measurements of organic P in alkaline soil extracts (Adams and Byrne, 1989; Gil-Sotres et al., 1990).

3-1.3 Extractability of Different Forms of P by Soil Test Methods

The forms of P identified with each chemical extractant has characteristics associated with plant availability and the chemistry of the soil (Tiessen and Meir, 1993). The soil extractants solubilize a portion of all the different P forms. The solubilizing capacity of each P form is reflected by the surface area and the degree of crystallization (Juo and Ellis, 1969). Fertility levels are commonly characterized by the quantity (Q) of P extracted by chemical extractants (Kamprath and Watson, 1980).

Kamprath and Watson (1980) reviewed P extraction studies that used various soil test methods to extract different forms of P from soils in widely different regions. They observed that P extracted by the 0.025 M HCl + 0.03 M NH₄F (Bray 1) solution and 0.5 M NaHCO₃ (Olsen) procedure were correlated with Al-P, and by the 0.05 M HCl + 0.125 M H₂SO₄ (Mehlich 1) solution was correlated with Ca-P. However, when the Ca-P quantity was low, the Mehlich 1 solution extracted both Ca-P and Al-P. Correlation studies between different soil P forms and plant uptake showed that the amount of P supplied by Al-P, Ca-P and Fe-P varies from soil to soil (Singh et al., 1966; Al-abbas and Barber, 1964a). Similar correlation studies between the availability of soil P and the forms of P extracted by Mehlich 3 solution are not available in the literature.

Traditional soil tests to formulate P fertilizer recommendations are often based on greenhouse correlation and field calibration studies. Bollard and Gilkes (1992) showed that the quantity of P extracted by soil test methods and the P taken up by crop under standard conditions provide only a crude prediction of plant uptake and yield. Therefore, in order to accurately characterize the available soil P, there is a need for a method that provides a good prediction of available P from different P forms and diverse soil properties. This investigation was undertaken with following objectives: 1) to study the distribution of different forms of inorganic and organic P in soils with diverse properties, and 2) to determine the relative contribution of different P forms to Bray 1, Mehlich 1, Mehlich 3, and Olsen extractable soil P.

3-2 MATERIALS AND METHODS

Research was carried out to investigate the distribution of different forms of inorganic and organic P in soils with diverse properties and to determine the relative contribution of different P forms to soil test extractable P. Soil test P was measured by the Bray 1, Mehlich 1, Mehlich 3, and Olsen extraction methods which are widely used for P determination. Forty-three soil samples were collected from the Ap horizon of the cultivated soils in the Piedmont, Atlantic Coastal Plain, and Ridge and Valley regions. The soils varied widely in physical and chemical properties as shown by their taxonomic classifications (Table 3-1).

3-2.1 Soil Analysis

Soil samples were air-dried and screened to pass a 2 mm sieve. The soil pH (H_2O) was determined in a 1:1 of soil:water mixture (v/v) (McLean, 1982). Soil organic matter (OM) content was determined by the Walkley-Black (1934) method, and particle size distribution by the pipette procedure (Day, 1965). Total Fe, Al, and Mn as oxides and hydroxides were measured with the dithionite citrate-bicarbonate (DCB) extraction procedure as described by Mehra and Jackson (1960) and exchangeable Al with 1 M KCl extraction (Barnishel and Bertsch, 1982). Aluminum, Fe, and Mn in solution from these analyses were determined by inductively-coupled argon plasma spectroscopy. Soils were

Table 3-1. Taxonomic information according to the soil orders for the 43 soils used in the study.

Soil Series	Taxonomic Class	Physiographic Region*
<u>Alfisol</u>		
Fauquier	fine, mixed, mesic Ultic Hapludalfs	P
Guernsey	fine, mixed, mesic Aquic Hapludalfs	RV
Hayter (2)	fine-loamy, mixed, mesic Ultic Hapludalfs	RV
<u>Entisols</u>		
Tarboro	mixed, thermic Typic Udipsamments	CP
<u>Inceptisols</u>		
Starr	fine-loamy, mixed, thermic Fluventic Dystrochrepts	P
<u>Ultisols</u>		
Altavista	fine-loamy, mixed, thermic Aquic Hapludults	CP
Appling	clayey, kaolinitic, thermic Typic Kanhapludults	P
Bojac	coarse-loamy, mixed, thermic Typic Hapludults	CP
Cecil (2) [†]	clayey, kaolinitic, thermic Typic Kanhapludults	P
Christian	clayey, kaolinitic, mesic Typic Hapludults	RV
Craven	clayey , mixed, thermic Aquic Hapludults	CP
Davidson (5)	clayey, kaolinitic, thermic Rhodic Kandiudults	P
Dothan	fine-loamy, siliceous, thermic Plinthic Kandiudults	P
Dragston	fine-loamy, mixed, thermic Typic Endoaquults	CP
Dyke	clayey, mixed, mesic, Typic Rhodudults	P
Emporia (2)	fine-loamy, siliceous, thermic Typic Hapludults	CP
Groseclose	clayey, mixed, mesic Typic Hapludult	RV
Kempsville	fine-loamy, siliceous, thermic, Typic Hapludults	CP

Contd.....

Soil Series	Taxonomic Class	Physiographic Region*
Lodi (2)	clayey, mixed, mesic Typic Hapludult	RV
Mayodan	clayey, kaolinitic, thermic, Typic Hapludults	P
Myatt	fine-loamy, siliceous, thermic Typic Ochraquults	CP
Norfolk	fine-loamy, siliceous, thermic Typic Kandudults	CP
Rains	fine-loamy, siliceous, thermic Typic Paleaquults	CP
Rumford (3)	coarse-loamy, siliceous, thermic Typic Hapludults	CP
Sassafras	fine-loamy, siliceous, mesic Typic Hapludults	P
Slagle	fine-loamy, silicious, thermic Aquic Hapludults	CP
State	fine-loamy, mixed, thermic Typic Hapludults	CP
Tatum (4)	clayey, mixed, thermic Typic Hapludults	P
Uchee	loamy, siliceous, thermic Arenic Hapludults	CP
Wagrum	loamy, siliceous, thermic Arenic Kandudults	CP

* P = Piedmont; CP = Coastal Plain; RV = Ridge & Valley

† = Numbers within parenthesis show the number of soils when a soil series is represented by more than one soil.

grouped by pH and percent clay contents according to the USDA soil classification (1993).

3-2.2 Extractable P Analysis

Levels of Mehlich 3, Mehlich 1, Bray 1, and Olsen extractable P were determined in duplicate in the 43 soils and, hence, all values in figures and tables are averages of two replicates. Analytical details for the procedures are described in Table 3-2. In all cases soil P was extracted in 100 ml polyethylene centrifuge tubes with a reciprocal shaker at recommended speeds for each procedure. After centrifugation, supernatant was filtered through Whatman no. 42 filter paper. Phosphorous extracted by each method was determined colorimetrically by molybdate blue-ascorbic acid method (Murphy and Riley, 1962) with a Hitachi Model 100-20 spectrophotometer.

3-2.3 Sequential Fractionation of Inorganic P

Soil P fractionation was carried out by the modified Chang and Jackson (1957) procedure of Peterson and Corey (1966) with several modifications. A diagrammatic representation of the sequential extraction procedure with the modification is given in Fig. 3-1. The extraction of reductant soluble P was carried out by shaking the soil residue mixture after step 3 of the fractionation with 25 ml of 0.3 M Na-citrate and 1 g of $\text{Na}_2\text{S}_2\text{O}_4$ for 5 minutes, and then by heating in a water bath at 75°C until the color

Table 3-2. Soil test P methods that were related to soil P forms in the study.

Method	Chemical Composition	Soil:Solution Ratio	Time of Extraction	Reference
Mehlich 3	0.015 M NH_4F + 0.25 M NH_4NO_3 + 0.2 M CH_3COOH + 0.013 M HNO_3 + 0.001 M EDTA	1:10 (v/v)	5 min	Mehlich (1984).
Mehlich 1	0.05 M HCl + 0.025 M H_2SO_4	1:4 (v/v)	5 min	Nelson, & Mehlich (1953).
Bray 1	0.03 M NH_4F + 0.025 M HCl	1:70:20 (v/v)	5 min	The Council on Soil Testing and Plant Analysis (1980).
Olsen	0.5 M NaHCO_3	1:10 (w/v)	30 min	Olsen et al. (1954).

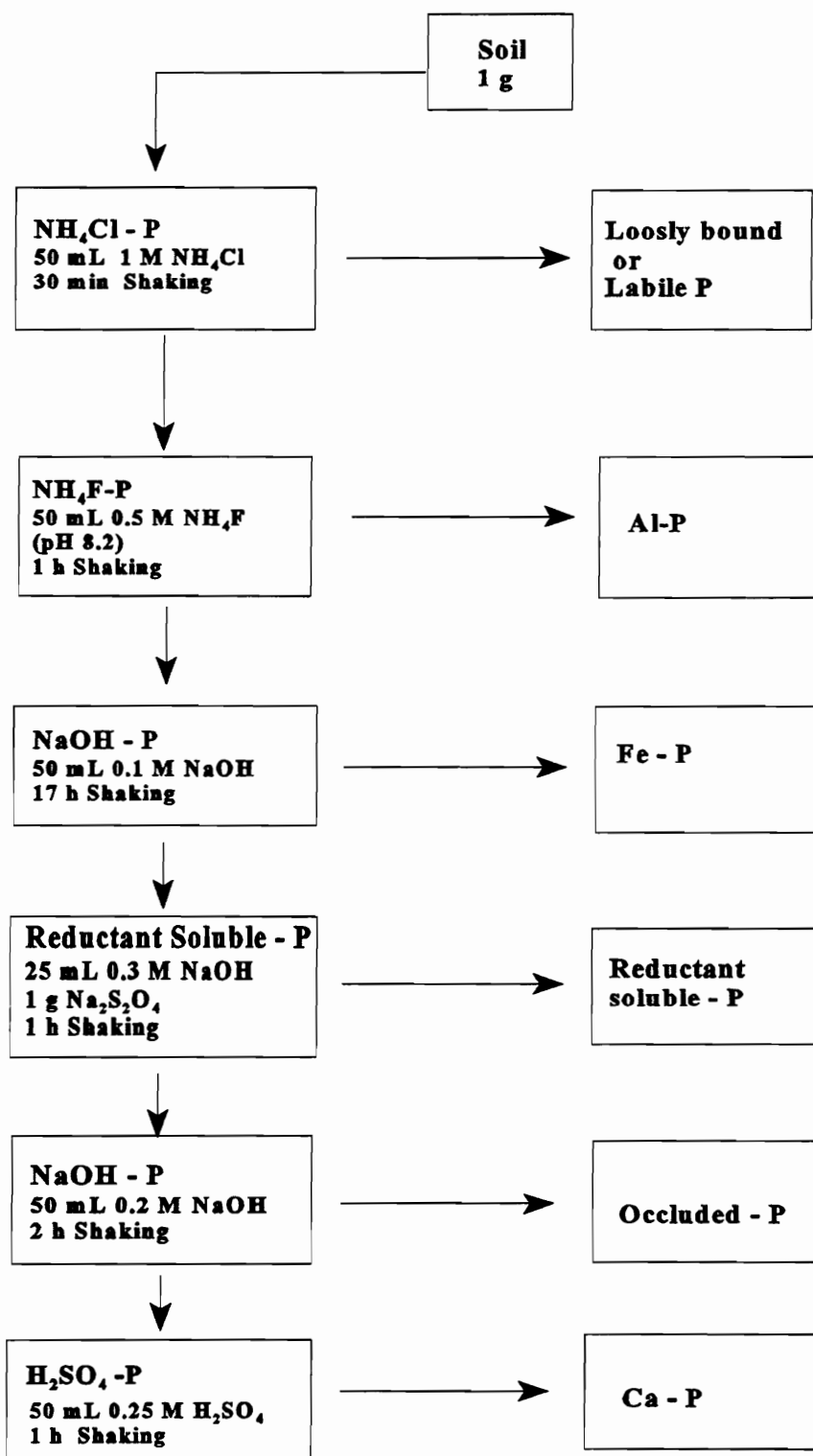


Fig. 3-1. Fractionation scheme for the extraction of different inorganic P forms.

disappearance. After cooling, the sample was brought back to the original weight by deionized water addition. Then samples were shaken for 1 hr to extract the reductant soluble P fraction.

After each extraction the suspensions were centrifuged for 10 minutes at 2000 rpm in 100 ml screw capped tubes. Then the supernatant was filtered through Whatman no. 42 filter paper in preparation for P determinations. After each extraction, excess reagents were removed from soil samples by two successive washing with 25 ml of super saturated NaCl solution. Samples were centrifuging at $14,500 \times g$ for 5 min. to remove the NaCl solution.

3-2.4 Sequential Fractionation of Organic P

Soil organic P was fractionated by the sequential extraction procedure reported by Bowman (1989). This procedure extracts two forms of organic P such as acid extractable organic P (AEOP) and base extractable organic P (BEOP). The fractionation sequence for organic P is shown in the diagram in Fig. 3-2. The fractions were calculated as follows:

AEOP = Total acid extractable P - Acid extractable inorganic P (AEIP),

BEOP = Total base extractable P - Base extractable inorganic P (BEIP),

Total organic P (TOP) = AEOP + BEOP, and

Total P (TP) = Total acid extractable P (TAEP) + Total base extractable P (TBEP).

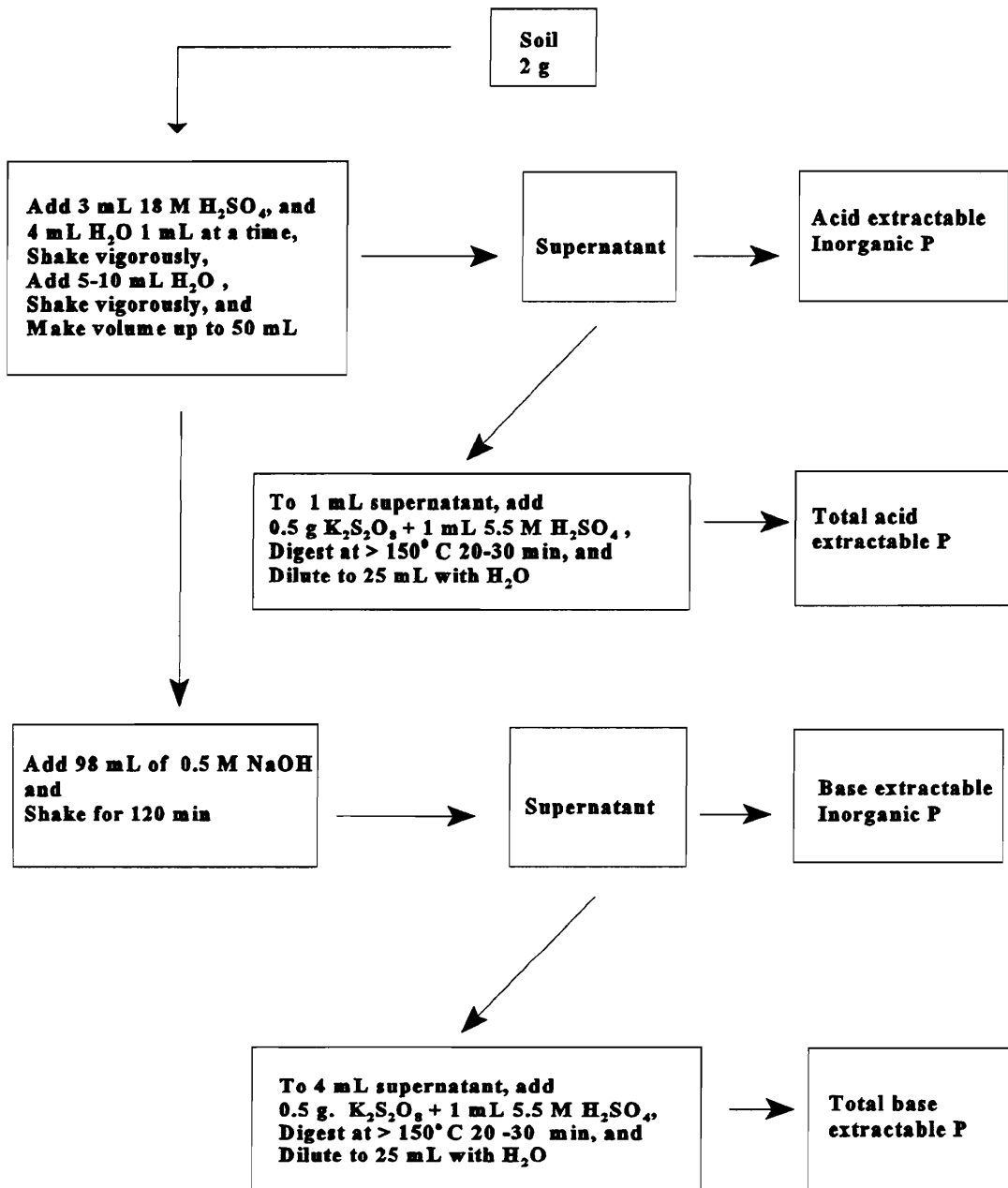


Fig. 3-2. Fractionation Scheme for Organic P determination.

3-2.5 Determination of P

All P fractions, except the reductant soluble P fraction, were determined colorimetrically by an ascorbic acid reduction method (Murphy and Riley, 1962), with the modifications indicated in Table 3-3. The pH of all acid or alkali filtrates was corrected to 5.5 prior to P determination. The reductant soluble fraction was determined using 24-5.7.3 method described in Olsen and Sommers (1982).

3-2.6 Statistical analyses

Simple and multiple correlation analyses were used to evaluate relationships among the forms of P extracted from different chemical extraction methods and the chemical and physical properties of the soils. Linear correlation procedures were used to compare the amounts of different P forms (means of the duplicate reading) with amounts of P extracted by M 3, M 1, Bray 1(1 m), Bray 1 (5m), and 0.5 M NaHCO₃ (pH 8.5) procedures. Multiple regression analyses were performed with the extractable P quantities as the dependent variable and the various P fractions and soil parameters (i.e., pH and amounts of KCl exchangeable Al, and percent OM, clay, DCB extractable Fe₂O₃, and Al₂O₃) as independent variables. The regression analysis was performed by GLM procedures (Myers, 1992).

Table 3-3. Modified P determination procedures for NaOH and NH₄F fractions.

Fraction	Procedure
0.1 M NaOH - P 0.2 M NaOH - P	<p>1. <u>Decoloration</u> -</p> <p>Step I. Mix 5 mL supernatant with 0.5 mL NaOCl (4 - 6% NaOCl) and allow to stand for 1 hour.</p> <p>Step II. To eliminate extra oxidant (NaOCl), add 10 mL of 10% ascorbic acid and allow to stand for 10 min.</p> <p>Determine P in the decolorized 0.1 M NaOH and 0.2 M NaOH extracts.</p>
NH ₄ F - P	<p>1. <u>Decoloration</u> - (as above)</p> <p>2. <u>Elimination of F⁻ interference</u> - Add 10 mL of 1.5% H₂BO₃ solution and allow to stand for 30 min. Read NH₄F - P.</p>

3-3 RESULTS AND DISCUSSION

3-3.1 Soil Properties

The 43 soils used in the study comprise 4 orders and 30 soil series (Table 3-1). Selected physical and chemical properties of the individual soils summarized by major categories are shown in Table 3-4. Soil pH values ranged from 4.0 to 7.4. However, the mean pH values of the soils grouped by physiographic regions and textural classes were evenly spread. Exchangeable Al contents were much higher in the extremely to strongly acidic soil group than in the soils with lower acidity and in the <17% clay group than in the high clay soils. The DCB extractable Mn content is distributed in the reverse order of that of exchangeable Al with the highest Mn contents reported in the low acidic (>6.6%) and high clay (>35.1%) groups. High clay soils (>35%) have the highest DCB extractable amorphous and crystallized Fe_2O_3 , Al_2O_3 , and Mn_2O_3 , and, OM contents. The average OM, Al_2O_3 , and Fe_2O_3 contents are higher in the soils in the Piedmont region than in the Coastal Plain or Valley and Ridge regions. The high Al_2O_3 and Fe_2O_3 contents in the Piedmont soils are explained by the high clay content in these soils.

3-3.2 Different Forms of P

Average P quantities associated with 7 inorganic P fractions and the organic fraction extracted by sequential procedures are given in Table 3-5. The inorganic sequential extraction procedure employs NH_4Cl to extract labile P as well as to leach out

Table 3-4. Physical and chemical properties of the 43 soils grouped according to the physiographic region, texture, and pH.

Soil	N*	pH	Al*		Mn	OM	Clay	Al ₂ O ₃	Fe ₂ O ₃
			(mg kg ⁻¹)						
All	43	5.9	15.5	15.5	756.2	2.2	15.5	0.5	3.5
Physiographic region									
Coastal Plain soils	19	5.9	5.5	5.5	79.5	1.7	6.8	0.2	0.5
Piedmont soils	17	5.8	29.0	29.0	1574.2	2.5	27.2	0.8	7.5
Valley & Ridge	7	6.0	10.8	10.8	606.6	2.9	10.6	0.5	2.0
Texture									
Clay < 17%	31	5.9	19.8	19.8	197.5	2.1	8.0	0.3	0.9
Clay 17.1 - 35%	6	6.2	5.1	5.1	1191.1	2.4	25.7	1.00	7.7
Clay 35.1 - 60%	6	6.0	4.5	4.5	3208.3	2.8	43.7	1.2	12.8
pH									
3.5 - 5.5	15	5.2	39.1	39.1	750.4	2.6	16.4	0.6	4.3
5.6 - 6.5	20	6.1	3.6	3.6	604.0	2.0	14.6	0.5	3.1
6.6 - 7.5	8	6.9	1.6	1.6	1147.8	2.1	16.0	0.5	3.2

* Exchangeable Al

Table 3-5. Different forms of P in relation to physiographic regions, texture, and pH groups in 43 soils.

Soil	N*	(mg P kg ⁻¹)							
		Labile P	AlP	FeP	Reductant soluble P	Occluded P	Ca P	Organic P	Residual P
All	43	5.8	118.3	123.1	215.4	30.4	48.8	277.6	309.7
Physiographic region									
Coastal Plain	19	7.8	171.2	79.6	78.1	6.1	42.5	168.2	230.3
Piedmont	17	3.5	84.5	174.2	400.5	65.3	52.9	392.4	397.5
Valley & Ridge	7	5.7	68.4	117.5	138.6	11.5	56.1	295.8	314.1
Texture									
Clay < 17%	31	6.4	116.4	80.3	89.7	7.9	44.3	182.2	230.8
Clay 17.1 - 35%	6	5.8	117.3	193.4	470.1	51.1	60.1	333.5	444.3
Clay 35.1 - 60%	6	2.5	107.1	274.6	610.2	125.7	60.5	714.4	618.8
pH									
3.5 - 5.5	15	4.0	105.7	106.1	264.0	27.8	53.0	298.3	266.5
5.6 - 6.5	20	6.1	121.3	127.8	194.9	26.7	43.8	279.8	330.1
6.6 - 7.5	8	8.1	118.0	143.6	287.9	44.3	53.5	233.4	366.7

* Number of soils in a group.

exchangeable Ca^{2+} that can interfere with the subsequent step, which uses NH_4F (pH 8.2) extraction to solubilize Al specifically associated with inorganic P (Al-P). Then NaOH is used to qualitatively extract Fe bound P (Fe-P), and dithionite citrate to solubilize reductant soluble P. Phosphorus occluded in gibbsite and residual reductant-soluble P were extracted with 0.2 M NaOH. Calcium associated P (Ca-P) was extracted with H_2SO_4 . The residual P contents, possibly associated with primary and secondary silicate minerals (Smeck, 1985) were calculated by subtracting the organic and inorganic P contents from total P (i.e., AEP + BEP) in Table 3-6.

3-3.2.1 Labile P

Readily available, labile P contents have the lowest concentration of the eight different P forms (Table 3-5). Labile P amounts to only 0.6 percent of the total P content in the soils (Fig. 3-3). Soil labile P contents ranged between 0.7-28.4 mg P kg^{-1} with 38 soils having less than 10 mg P kg^{-1} labile P (Fig. 3-4). It is reported that successive extraction of soil by 1 M NH_4Cl solubilizes Ca and Mg associated P (Nair et al., 1995). Therefore, the labile P extracted by NH_4Cl probably consists of a portion of P weakly or loosely attached to Ca and Mg. Labile P content was strongly correlated with Al ($r = 0.74$, $p = 0.01$) and Ca-P ($r = 0.49$, $p = 0.01$) contents (Table 3-7). These relationships suggest that mainly Al-P is extracted by NH_4Cl .

Table 3-6. The amount of total, inorganic and organic P in 43 soils grouped by physiographic regions, pH, and clay content.

Soil	N*	Total P			Organic P			Inorganic P*		
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	
All		1126.5	199.5 - 3858.3	277.6	35.4 - 1230.9	543.7	101.1 - 2583.4			
Physiographic region										
Coastal Plain	19	783.0	398.8 - 2019.6	168.2	35.4 - 642.9	354.6	129.5 - 1156.1			
Piedmont	17	1551.8	199.5 - 3828.3	392.4	64.9 - 1230.9	786.0	101.1 - 2583.4			
Valley & Ridge	7	1001.5	807.5 - 1367.6	295.8	50.9 - 698.6	397.8	286.3 - 609.8			
Texture										
Clay < 17%	31	756.6	199.5 - 2019.6	182.2	35.4 - 698.6	345.0	101.1 - 1156.1			
Clay 17.1 - 35%	6	1675.4	717.2 - 3858.3	335.5	148.6 - 477.4	897.6	356.6 - 2583.4			
Clay 35.1 - 60%	6	2460.3	1740.1 - 2897.3	714.4	328.6 - 1230.9	1195.3	857.7 - 1574.9			
pH										
3.5 - 5.5	15	1071.3	298.8 - 2897.3	298.3	64.9 - 1250.9	566.5	173.4 - 1345.1			
5.6 - 6.5	20	1121.5	199.5 - 2806.3	279.8	50.9 - 698.7	520.6	101.1 - 1574.9			
6.6 - 7.5	8	1221.1	414.5 - 3858.3	233.6	35.4 - 433.5	655.3	129.5 - 2583.4			

* Total extracted inorganic P.

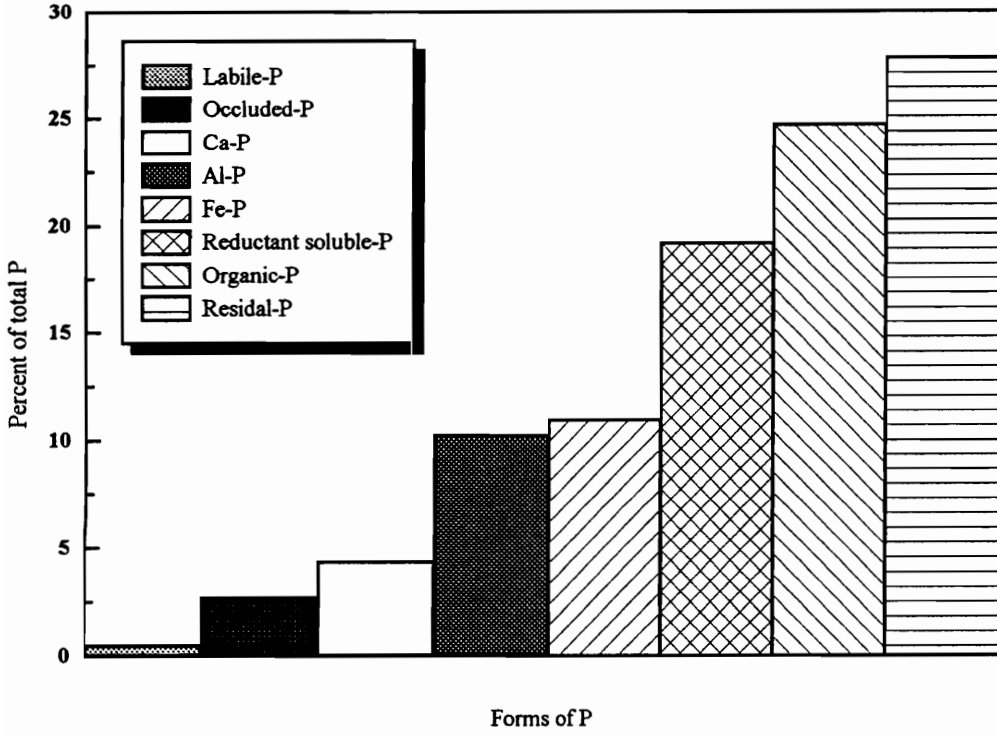


Fig. 3-3. Different P forms expressed as a percent of total P in 43 soils.

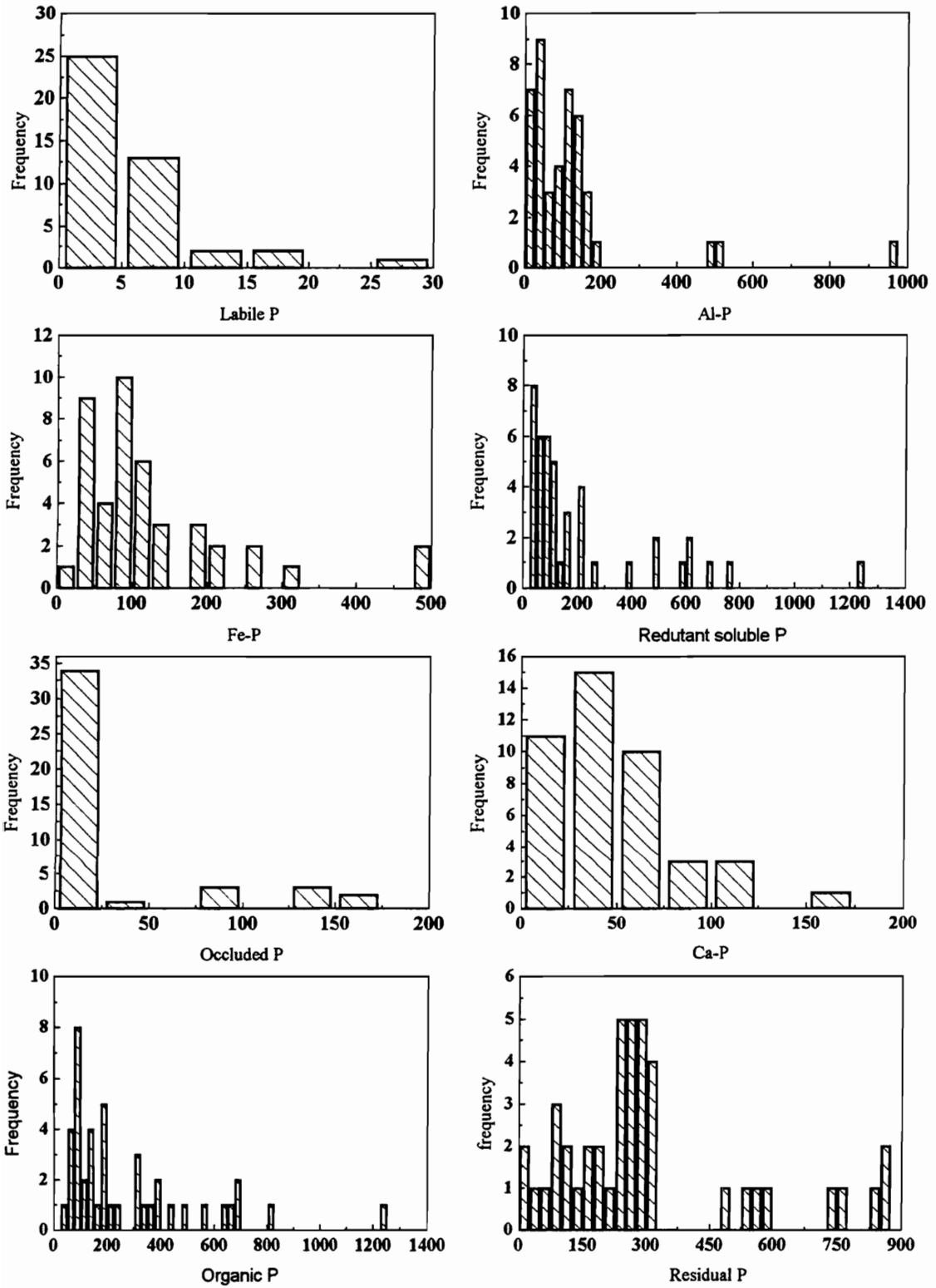


Fig. 3-4. Frequency distribution of different forms of P (mg P kg⁻¹) in the 43 soils.

Table 3-7. Simple correlation coefficients related to different forms of P contents.

P forms (mg P kg ⁻¹)	(mg P kg ⁻¹)										
	Labile P	Al-P	Fe-P	ReS-P	Oc-P	Ca-P	OP	AEIP	BEIP	AEOP	BEOP
Labile P	-	0.74**	-	-	-	0.49**	-	0.39*	0.34*	-	-
Al-P	0.74**	-	0.35*	-	-	0.62*	-	0.58**	0.34*	-	-
Fe-P	-	0.35*	-	0.88**	0.84**	0.55**	0.48**	0.92**	0.81**	0.47**	-
ReS-P	-	-	0.88**	-	0.95**	0.53**	0.62**	0.90**	0.88**	0.63**	-
Oc-P	-	-	0.84**	0.95**	-	0.51**	0.58**	0.87**	0.88**	0.58**	-
Ca-P	0.49**	0.62**	0.55**	0.53**	0.51**	-	-	0.65**	0.49**	-	-
OP	-	-	0.48**	0.62**	0.58**	-	-	0.54**	0.42**	0.99**	-
AEIP	0.39*	0.58**	0.92**	0.90**	0.87**	0.65**	0.54**	-	0.82**	0.54**	-
BEIP	0.34*	0.34*	0.81**	0.88**	0.88**	0.49**	0.42**	0.82**	-	0.43**	-
AEOP	-	-	0.47**	0.63**	0.58**	-	0.99**	0.54**	0.43**	-	-
BEOP	-	-	-	-	-	-	-	-	-	-	-

* Correlations are significant at $p = 0.05$ (*), $p = 0.01$ (**), or non significant at < 0.05 (-).

3-3.2.2 Calcium P

The mean Ca-P content in the soils was 48.8 mg kg⁻¹ (Table 3-5) and 4.4% of the total P content (Fig. 3-3). The Ca-P content of the soils ranged between 1.0 to 173.8 mg kg⁻¹ with more than 90% soils having Ca-P contents below 100 mg kg⁻¹ (Fig. 3-4). The low Ca-P contents suggest possible conversion of Ca-P compounds to other P forms. Apatite, which is the primary phosphate mineral in the parent material is unlikely to remain unchanged with soil weathering. A combination of different types of Ca containing P fertilizers i.e., mono-calcium phosphate, di-calcium phosphate, etc., and soil constituents, such as Al(OH)₂, Fe₂O₃, and CaCO₃, produce a variety of P reaction products (Lindsay et al., 1962). There is a relatively low Ca²⁺ activity in acid soils compared with Al³⁺ and Fe³⁺ activities and, hence, there is gradual conversion of Ca-P into Al-P and Fe-P.

3-3.2.3 Aluminum P

The average quantity of Al-P for all soils is 118.3 mg P kg⁻¹ (Table 3-5) and constitutes 10.8% of total P (Fig. 3-3). Ninety percent of the soils contain Al-P contents below 200 mg P kg⁻¹, and the highest value was 950 mg P kg⁻¹ (Fig. 3-4). The Coastal Plain soils have an average Al-P content of 171.2 mg P kg⁻¹ which is the highest amount extracted for any group. Following fertilizer application, orthophosphate induced weathering of aluminosilicate minerals may yield amorphous-analog Al which is converted to Al-P (Karathanasis, 1983). Low Fe₂O₃ and clay contents in the moderately

acidic Coastal plain soils (Table 3-4), may favor retention of Al-P. The Piedmont and Ridge and Valley soils have Al-P contents of about 50 percent of that in Coastal Plain soils. Average Al-P contents of the soils in various textural groups and pH categories are quite similar (Table 3-5).

The soils that are high in exchangeable Al (i.e., Piedmont soils and Valley and Ridge soils) are extremely to strongly acidic (pH 3.5-5.5) and have low Al-P contents. High Al^{3+} and P contents and low pH favor greater crystallization and formation of variscite (Hsu, 1982b). Crystallized variscite probably does not dissolve in 0.5 M NH_4F (pH 8.2) because, as shown by Ballard (1974) wavellite, which is a synthetic crystalline Al-P compound, was insoluble in NH_4F .

Aluminum P content was closely correlated with Ca-P and Fe-P (Table 3-7). These relationships suggest that gradual conversion of Ca-P towards to Fe-P. It has been also reported that, with time, there is a gradual conversion of Al-P to Fe-P (Chang and Jackson, 1957; Hsu, 1964; Yuan et al., 1960). The rate of this reaction is enhanced at low pH due to increased Al^{3+} and Fe^{3+} activities under acidic conditions (Shelton and Coleman, 1968; Martens et al., 1969). Aluminum P is the form that commonly correlates with plant uptake and, therefore is the most important P form in agriculture (Martens et al., 1969; Juo and Ellis, 1968; Susuki et al., 1963).

3-3.2.4 Iron P

The average Fe-P content in the soils was 123.1 mg kg^{-1} (Table 3-5), which constituted 11 percent of the total P content (Fig. 3-3). Iron-P contents ranged between $15 - 485 \text{ mg kg}^{-1}$, but a majority of the soils had less than 150 mg kg^{-1} Fe-P (Fig. 3-4). Soils in the Coastal Plain region had the lowest Fe-P contents. Iron-P contents positively correlated ($p = 0.01$) with soil clay, and DCB extractable Fe, Mn, and Al (Table 3-8). The rate of increase in Fe-P content is 5.5 mg kg^{-1} for one percent increase in the clay content, and 16.2 mg kg^{-1} for one percent increase in Fe_2O_3 content (Fig. 3-5). These relationships reflect the close association between Fe_2O_3 and soil clay, and the ability of Fe_2O_3 to readily adsorb P. The Fe_2O_3 content of a soil was shown to be an index of the weathering intensity of a soil (Feldman, 1995). The strong correlation between contents Fe_2O_3 and Fe-P explains the high Fe-P concentrations in highly weathered Piedmont soils and high clay soils. In some P availability studies, Fe-P has been found to correlate more closely to plant uptake than other forms (Al-Abbas and Barber, 1964).

According to Hsu (1982a), under conditions of low pH and high Fe^{3+} and P contents, meta-strengite and strengite formation is accelerated. The occurrence of strengite type compounds in soils has never been observed. Lindsay and Vlek (1977) suggested that the contents of these compounds are too low to be detected by ordinary techniques. Another likely explanation is that the conversion of Fe-P to reductant-soluble P and occluded P by soil weathering prevents strengite formation.

Table 3-8. Simple correlation coefficients relating different P forms and soil physical and chemical parameters.

P forms (mg P kg ⁻¹)	pH	Exch.Al. (mg kg ⁻¹)	OM	Clay	Fe ₂ O ₃ Al ₂ O ₃		Mn (mg kg ⁻¹)
					(%)		
Labile P	-	-	-	-	-	-	-
Al-P	-	-	-	-	-	-	-
Fe-P	0.34*	-	-	0.69**	0.71**	0.79**	0.78**
Re S-P	-	-	-	0.77**	0.87**	0.89**	0.75**
Oc-P	-	-	-	0.83**	0.85**	0.85**	0.87**
Ca-P	-	-	-	-	0.30*	0.36*	-
OP	-	-	0.64**	0.72**	0.69**	0.62**	0.53**
AEIP	-	-	-	0.64**	0.75**	0.79**	0.70**
BEIP	--	-	-	0.56**	0.69**	0.74**	0.68**
AEOP	-	-	0.67**	0.72**	0.70**	0.63**	0.54**
BEOP	-	-	-	-	-	-	-

* Correlations are significant at $p = 0.05$ (*) or $p = 0.01$ (**).
 Correlations are not significant at $p = 0.05$ (-).

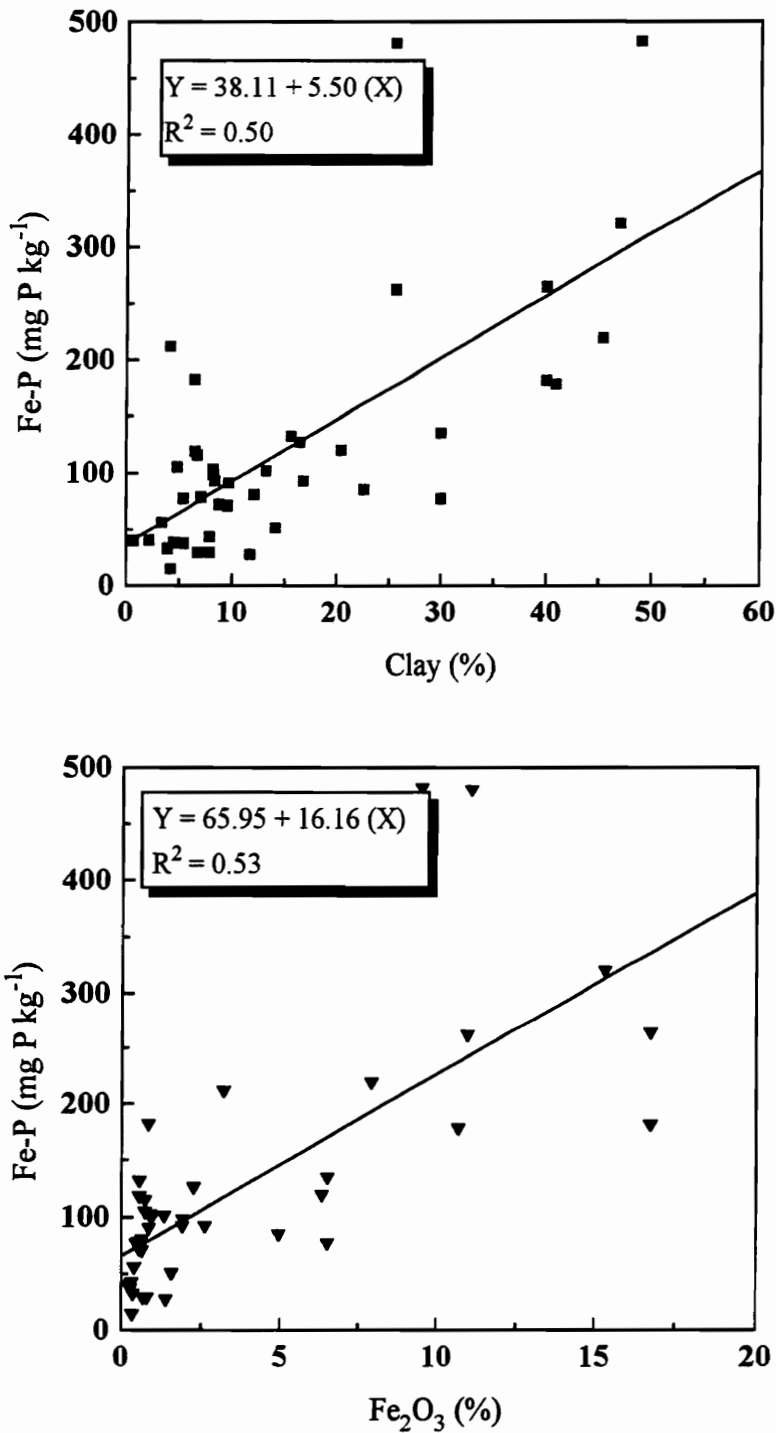


Fig. 3-5. Relationships between Fe-P (Y) with clay (X) and Fe_2O_3 (X) in the 43 soils.

3-3.2.5 Reductant Soluble-P

Reductant Soluble-P (Re S-P) which was the dominant inorganic P form in the soils, accounted for 19.2 percent of the total P fraction (Fig. 3-3) and averaged 215.4 mg P kg⁻¹ (Table 3-5). Piedmont soils and high clay soils contained very high average reductant soluble P values in the range of 28-1250 mg kg⁻¹ (Fig. 3-4). The majority of these soils had P values less than 200 mg kg⁻¹. There were high positive correlations between reductant soluble P contents and soil clay, Fe₂O₃, Al₂O₃, and MnO₂ contents (Table 3-8). The rate of increase in reductant soluble P content was 15 mg kg⁻¹ for one percent increase in clay content and 45 mg kg⁻¹ for one percent increase in Fe₂O₃ content (Fig. 3-6).

Table 3-7 shows that reductant soluble-P contents are strongly correlated with Fe-P ($r = 0.88$, $p = 0.01$), occluded P ($r = 0.95$, $p = 0.01$) and Ca-P ($r = 0.53$, $p = 0.01$) contents. With soil aging, high soil clay, Fe₂O₃, and other soil mineral contents favor encapsulation of phosphate minerals and, thus, increase the reductant soluble-P and occluded P contents. Transformations of inorganic P moves in one direction with primary P minerals being converted to occluded P via intermediate soluble, labile, secondary mineral forms (Smeck, 1985). Thus, these results (Table 3-5) confirm that the presence of high Fe-P contents and Fe₂O₃ favors an increase in the reductant soluble-P fraction. Soil P retained in the soil in the reductant soluble form becomes more plant available as Eh decreases. In the highland soils, which are not subjected to periodic changes in oxidation status, reductant soluble P will continue to accumulate over time.

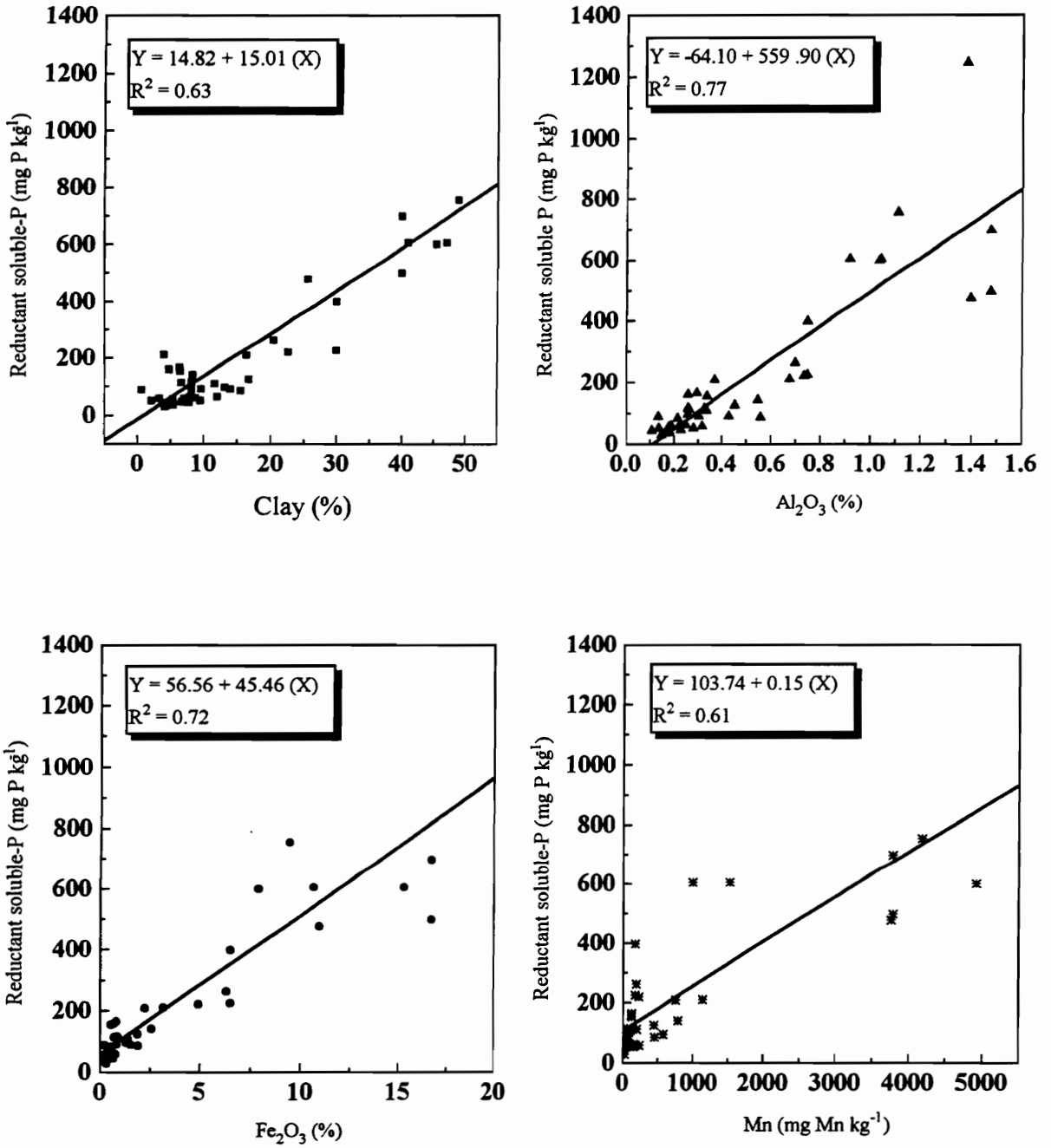


Fig. 3-6. Relationships between reductant soluble P (Y) with clay (X), Fe₂O₃ (X), Al₂O₃ (X), and Mn in the 43 soils.

3-3.2.6 Occluded P

The amounts of 0.2 M NaOH fractionated occluded P (Oc-P) associated with crystalline Al hydroxides and oxides (gibbsite) are shown in Table 3-5. The average occluded P content in the 43 soils was 30.4 mg kg^{-1} with the lowest being 6.1 mg kg^{-1} in the Coastal Plain soils. The majority of the soils had less than 25 mg kg^{-1} occluded P with a range from $2.5 - 175 \text{ mg kg}^{-1}$ (Fig. 3-4). Occluded P constituted 2.7% of total P, which was only higher than labile P with a concentration of 0.6% (Fig. 3-3). The low occluded P contents reflect the slow process of conversion of primary P minerals in the soil to occluded P (Smeck, 1985).

The simple correlation coefficients between P forms and chemical and physical properties of soils indicate that occluded P has strong positive relationships with clay ($r = 0.83$), Fe_2O_3 ($R = 0.85$), and Al_2O_3 ($r = 0.85$) contents (Table 3-8). Occluded P increased curvilinearly with an increase in clay ($R^2 = 0.75$) and Al_2O_3 ($R^2 = 0.74$) contents (Fig. 3-7). The rate of increase in occluded P content is 46.4 mg kg^{-1} for one percent increase in Al_2O_3 and 0.6 mg kg^{-1} for one percent increase in Fe_2O_3 (Fig. 3-7). Occluded P content was strongly correlated to Fe-P ($R^2 = 0.75$, $p = 0.01$) and reductant soluble P ($R^2 = 0.87$, $p = 0.01$) (Fig. 3-8) which may be a reflection of greater levels of Oc-P, Fe-P, and ReS-P with higher P additions to the soils.

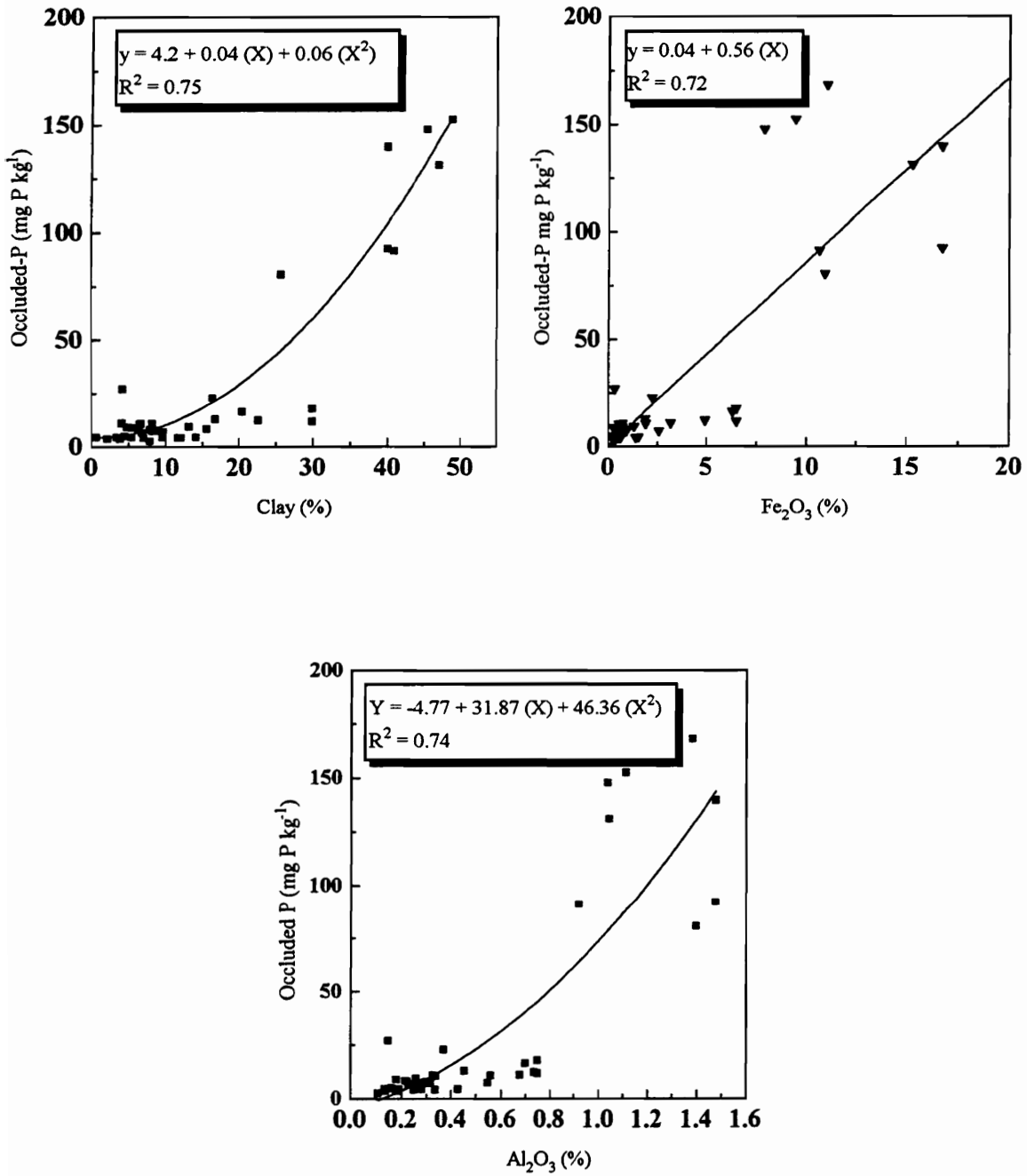


Fig. 3-7. Relationships between occluded-P (Y) with clay (X), Fe₂O₃, and Al₂O₃ in the 43 soils.

3-3.2.7 Organic P

The organic P (OP) fraction consists of 24.7% of the total P (Fig. 3-4) in the 43 soils with an average of 277.6 mg kg⁻¹ (Table 3-5). The total amount of organic P in the soil is in agreement with data in the literature where the organic P ranged from 20 to 60% of the total P (Allen, 1994). Over 30% of the soils contained organic P contents in the range from 300 - 1350 mg kg⁻¹ (Fig. 3-4). The acid extractable organic P fraction (AEOP) averaged 261.1 mg kg⁻¹ and the balance, i.e. 16.5 mg kg⁻¹, was base extractable (BEOP) fraction (Table 3-9).

Correlations between total organic P, AEOP, and BEOP with soil chemical and physical properties are given in Table 3-8. Total organic P and AEOP contents are strongly positively correlated ($r = 0.99$, $p = 0.05$). The two P fractions are also positively correlated with OM, clay, Fe₂O₃, and Al₂O₃ (Table 3-8). But none of the factors correlated ($p = 0.05$) to BEOP. The organic P content increased by 110.6 mg kg⁻¹ for each one percent increase in OM, and by 13.5, 36.9 and 392.3 mg kg⁻¹ for a percent increase in clay, Fe₂O₃, and Al₂O₃ respectively (Fig. 3-9). Soils with high Fe and Al contents strongly adsorb organic P, especially inositol hexaphosphate (Chang et al., 1990, 1992; Saxena, 1979). Inositol hexaphosphate is adsorbed by soil Fe₂O₃ more strongly than orthophosphates (Anderson et al., 1974). Therefore, it is likely that a high proportion of organic P in these soils are present as inositol hexaphosphate. The organic P content of the soils increases with soil clay content and, in high clay soils, nearly 30 percent of the total P is organic P (Table 3-6).

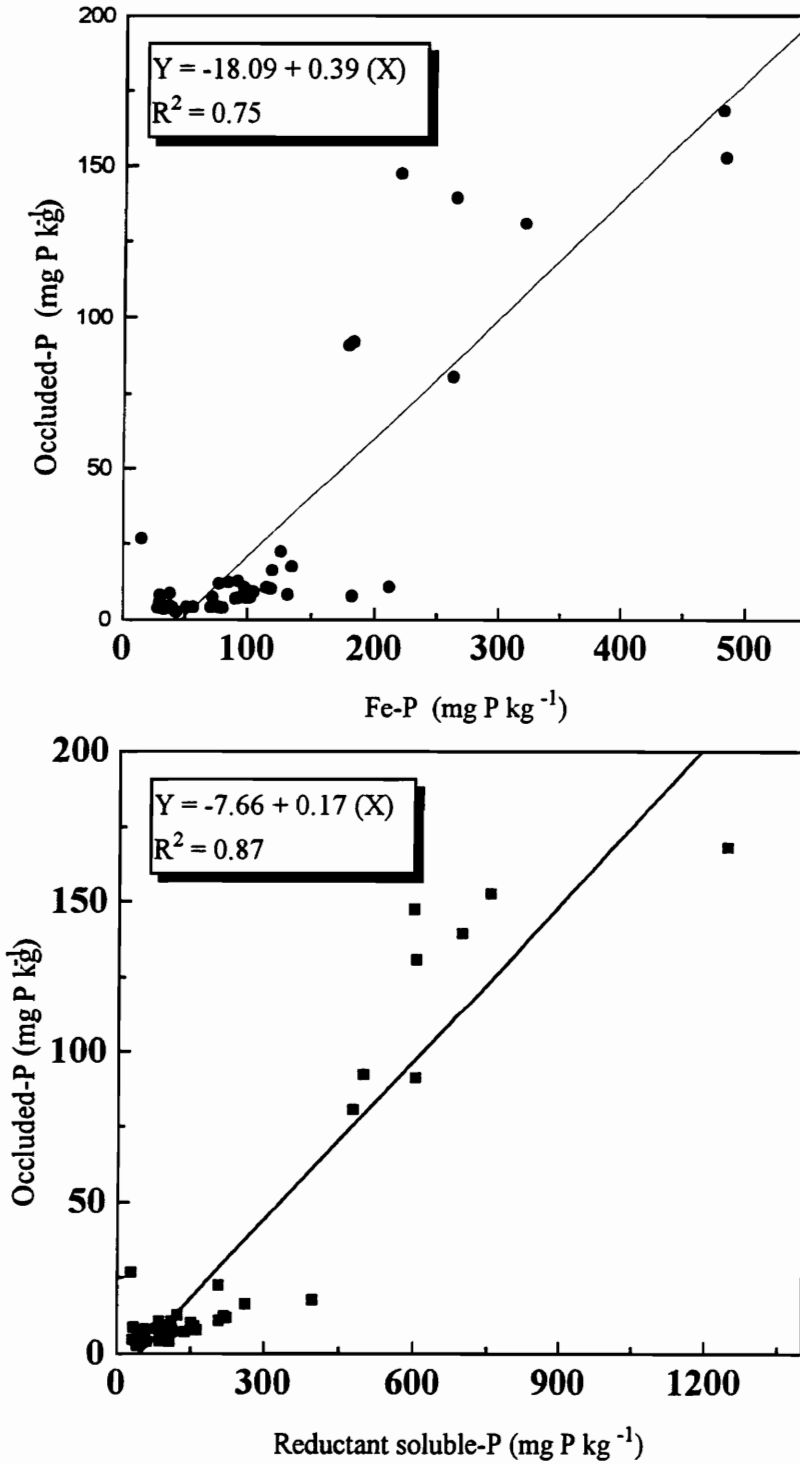


Fig. 3-8. Relationships between Occluded-P (Y) with Fe-P (X) and reductant soluble-P in the 43 soils.

Table 3-9. Acid and base extractable inorganic, and organic P in relation to physiographic regions, texture and pH groups in 43 soils.

Soil	N*	AEIP			BEIP			AEOP			BEOP		
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range		
All		736.2	90.0 - 2925.0	108.7	19.6 - 500.0	261.1	24.4 - 1184.4	16.5	1.8 - 242.5				
<u>Physiographic region</u>													
Coastal Plain	19	544.1	250.0 - 1607.5	70.7	44.1 - 171.6	149.0	24.4 - 634.4	19.3	1.8 - 242.5				
Piedmont	17	999.0	90.0 - 2925.0	160.5	19.6 - 500.0	377.9	62.5 - 1184.4	14.5	1.8 - 61.2				
Valley & Ridge	7	619.3	475.0 - 1087.5	86.5	46.6 - 117.6	282.1	37.5 - 690.0	86.5	46.6 - 117.6				
<u>Texture</u>													
Clay < 17%	31	498.1	90.0 - 1607.5	76.3	19.6 - 245.1	166.4	24.4 - 690.0	15.8	1.8 - 242.5				
Clay 17.1 - 35%	6	1163.8	487.5 - 2925.0	178.1	68.6 - 500.0	326.4	14.06 - 475.0	7.2	2.4 - 14.5				
Clay 35.1 - 60%	6	1538.8	925.0 - 2022.5	207.1	112.7 - 281.9	685.2	322.5 - 1184.4	29.2	6.0 - 61.2				
<u>pH</u>													
3.5 - 5.5	15	672.4	177.5 - 1805.0	100.6	46.6 - 281.9	288.8	63.1 - 1184.4	9.5	1.8 - 46.5				
5.6 - 6.5	20	735.0	90.0 - 2022.5	106.7	19.6 - 245.1	268.3	37.5 - 690.0	11.5	1.8 - 61.2				
6.6 - 7.5	8	858.8	335.0 - 2925.0	129.0	44.1 - 500.0	191.3	24.4 - 418.8	42.1	4.3 - 242.5				

(mg P kg⁻¹)

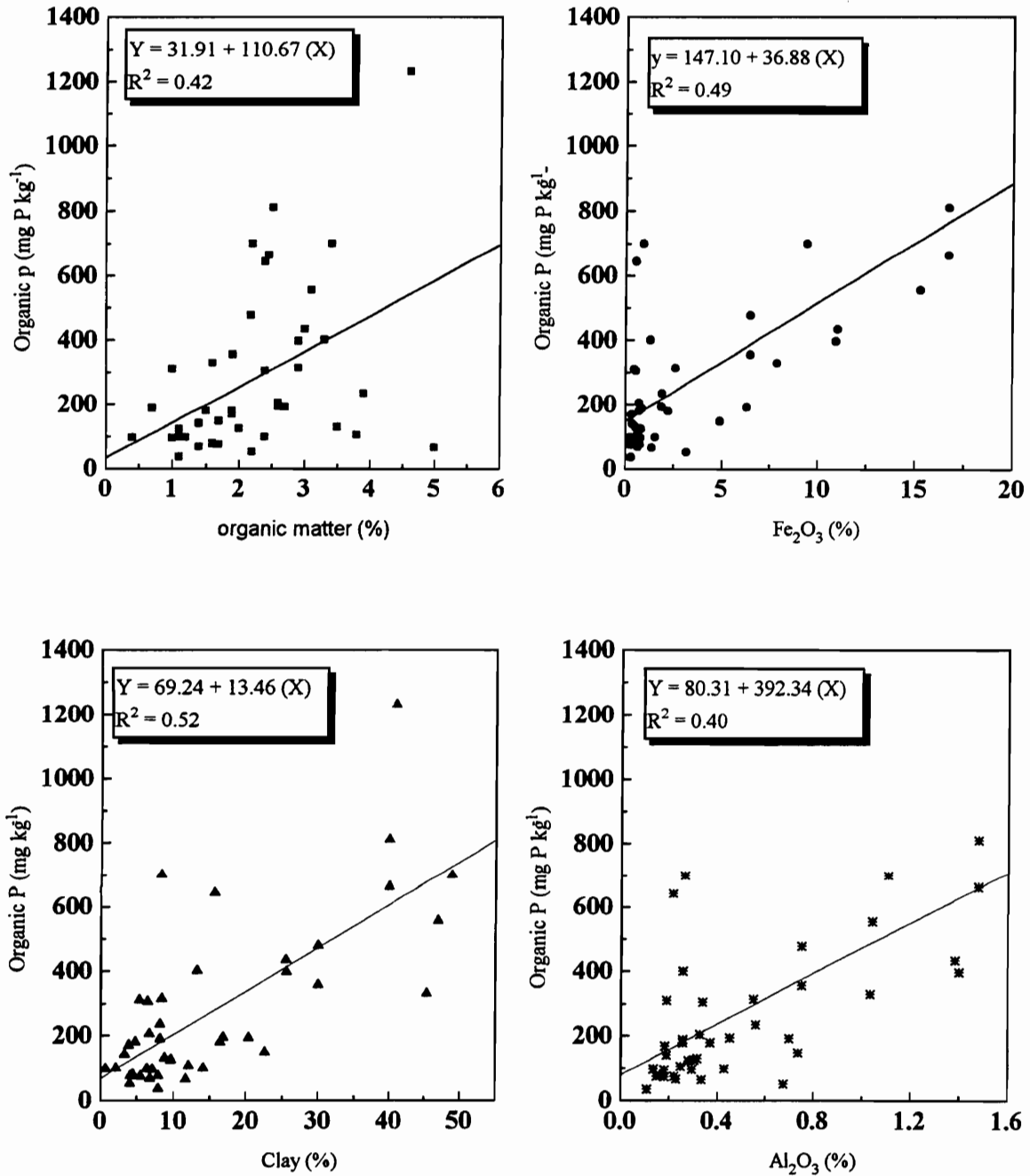


Fig. 3-9. Relationships between organic P with OM, clay, Fe₂O₃, and Al₂O₃ in the 43 soils.

3-3.2.8 Residual P

The residual P fraction contained the largest portion of P in the soils (Table 3-5), and accounted for 28% of the total P (Fig. 3-3). The average residual P quantity for the 43 soils was 314.7 mg kg⁻¹. Thirty four of the 43 soils had less than 300 mg kg⁻¹ residual P and the highest Rs- P content was 868 mg kg⁻¹ (Fig. 3-4). Residual P increased with clay content which may indicate a higher P level in parent material in finer-textured soils as shown in Table 3-5.

According to the Smeck (1985) residual inorganic P, that is P encapsulated by primary or secondary silicate minerals, is extracted by HF dissolution or by Na₂CO₃ fusion. In this study, residual P was computed as the difference between the sum of total inorganic P fractions from the sequential extraction and the organic P fractions i.e., the total acid extractable (18 M H₂SO₄) and base extractable (0.5 M NaOH) P contents in the soils. Based on the high possibility of silicate mineral dissolution it seems likely that, as proposed by Smeck (1985), the residual P is encapsulated and structurally held in primary silicate minerals such as feldspar, mica, quartz and secondary silicate minerals like kaolinite and gibbsite. Kaolinite and gibbsite are weathering product of primary silicate mineral such as feldspar (Rice, 1985; Bryant and Dixson, 1963).

3-3.2.9 Total P

The average total P content was 0.02 - 0.4% in the 43 soils (Table 3-6). This range compares well with the values reported in the literature which are between 0.02 -

0.5% (Lindsay et al., 1989). The dominant P form is inorganic P which amounts to 48% of total P without considering residual form of P, which was equivalent to 36% of inorganic P (Table 3-5 & 3-6). The distribution pattern of total P, organic and inorganic P contents do not vary among the pH groups (Table 3-6). The largest amounts of total, organic and inorganic P occurred in the Piedmont and high clay soils. The average total inorganic P content was 540.7 mg P kg⁻¹ with a range from 101.1 - 2583.4 mg P kg⁻¹ (Table 3-6). The highest inorganic P content of 1195.3 mg P kg⁻¹ was in the clayey fine group.

3-3.3 Relationships Between Forms of Soil P and Soil Test P

3-3.3.1 Bray 1 Method

The means and ranges of Bray 1 extractable P for the 43 soils according to the physiographic regions, clay contents, and pH groups are given in Table 3-10. Bray 1 extractable P contents in the soils ranged from 7.9 to 990.6 mg dm⁻³ and averaged 139.8 mg dm⁻³. Bray 1 procedure extracts the larger amounts of P than the Mehlich 3, Mehlich 1, and Olsen procedures. Amounts of Bray 1 extractable P represent only a relatively small portion of the total soil P and inorganic P fractions, i.e., 12.4 and 25.7 % respectively (Table 3-6 & 3-10). Extraction of small and different amounts of P by the soil tests may indicate that the procedures selectively solubilize specific soil P fractions or a varying portions of the soil P fractions.

Table 3-10. Extractable P by Mehlich 3 and Bray 1, Mehlich 1 and Olsen methods in soils grouped according to the physiographic region, texture, and pH.

	N*	Mehlich 3 P (mg P dm ⁻³)		Bray 1 P (mg P dm ⁻³)		Mehlich 1 P (mg P dm ⁻³)		Olsen P (mg P kg ⁻¹)	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range
All	43	105.9	2.6 - 673.0	139.8	7.9 - 990.6	55.1	1.5 - 327.9	46.8	3.5 - 185.2
Physiographic region									
Coastal Plain	19	176.5	45.5 - 673.0	221.1	52.9 - 990.6	89.2	28.5 - 327.9	55.9	15.4 - 171.0
Piedmont	17	28.6	2.6 - 163.8	42.4	7.9 - 202.1	21.4	1.5 - 97.8	36.9	3.5 - 185.2
Valley & Ridge	7	74.0	23.7 - 166.1	101.6	28.2 - 232.4	44.2	15.5 - 95.5	46.2	14.7 - 116.7
Texture									
clay <17%	31	128.5	9.6 - 673.0	163.8	11.8 - 990.6	66.1	5.5 - 327.9	46.2	3.5 - 171.0
clay 17.1 - 35%	6	41.0	6.9 - 163.8	53.6	7.9 - 202.1	28.2	6.2 - 97.8	44.8	5.9 - 185.2
clay 35.1 - 60%	6	28.2	2.6 - 72.2	50.3	9.1 - 142.1	24.7	1.5 - 61.5	52.1	6.2 - 98.5
pH									
3.5 - 5.5	15	100.8	2.6 - 536.1	131.0	9.1 - 695.3	44.5	1.5 - 189.8	45.3	6.2 - 171.0
5.6 - 6.5	20	120.1	6.9 - 673.0	164.6	7.9 - 990.6	66.2	5.5 - 327.9	46.1	3.5 - 116.7
6.6 - 7.5	8	79.7	16.7 - 163.8	94.2	24.7 - 202.1	46.9	17.3 - 97.8	51.4	24.2 - 185.2

* Number of soils in a group

Simple correlations between inorganic P, (i.e., labile P, Al-P, Fe-P, and Ca-P, and organic P fractions) and Bray 1 extractable P for the 43 soils are given in Table 3-11. Coefficients of simple correlation show that Bray 1 extractable P contents are positively related to labile P ($r = 0.64$, $p = 0.01$), Al-P ($r = 0.89$, $p = 0.01$) and, Ca-P ($r = 0.38$, $p = 0.05$), but not with Fe-P. The strong correlation between Bray 1 extractable P and Al-P suggests that Al-P is the major source of Bray 1 extractable P. Dissolution of Al-P in the Bray 1 solution is influenced by F^- which has a high affinity for Al^{3+} and, thus, forms Al-F complexes which are stable in acidic solution (Bray and Kurtz, 1945; Lindsay and Walthall, 1989). Complex formation decreases the Al^{3+} activity in the Bray 1 extraction solution which lowers readsorption and reprecipitation reactions and increases the amount of extractable P. Also, the larger surface area and the relatively low rate of crystallization of Al-P may increase its solubilization by the Bray 1 extractant.

The relationship between Bray extractable P and Al-P contents of the soils are shown in Fig. 3-10. Bray 1 extractable P content was increased by 1.33 units for each unit increase in Al-P. Data from three soils, i.e., the Altavista and State series from the Coastal Plain region and the Fauquier series from the Piedmont region, are not shown in the graph as they contained exceptionally high Al-P and extractable P levels as compared with other soils. However, regression results are reported for the 43 soils as the three soils displayed the same relationship as others (Table 3-12).

Relationships between different P forms and Bray 1 extractable P in the presence of soil characteristics are shown in Table 3-12. The amount of P extracted by Bray 1

Table 3-11. Simple correlation coefficients (r) between soil P forms and soil test extractable P contents by four methods.

P forms (mg P kg ⁻¹)	Mehlich 3	Bray 1	Mehlich 1	Olsen P
	(mg P dm ⁻³)			(mg P kg ⁻¹)
Labile P	0.66**	0.64**	0.69**	0.75**
Al-P	0.88**	0.89**	0.88**	0.71**
Fe-P	0.14*	-	-	0.55*
Ca-P	0.36*	0.38*	0.58*	0.57**
OP	-	-	-	0.34*
AEIP	-	-	-	0.62**
BEIP	-	-	-	0.47**
AEOP	-	-	-	0.35*
BEOP	-	-	-	-

* Correlations are significant at $p = 0.05$ (*) or $p = 0.01$ (**).
Correlations are not significant at $p = 0.05$ (-).

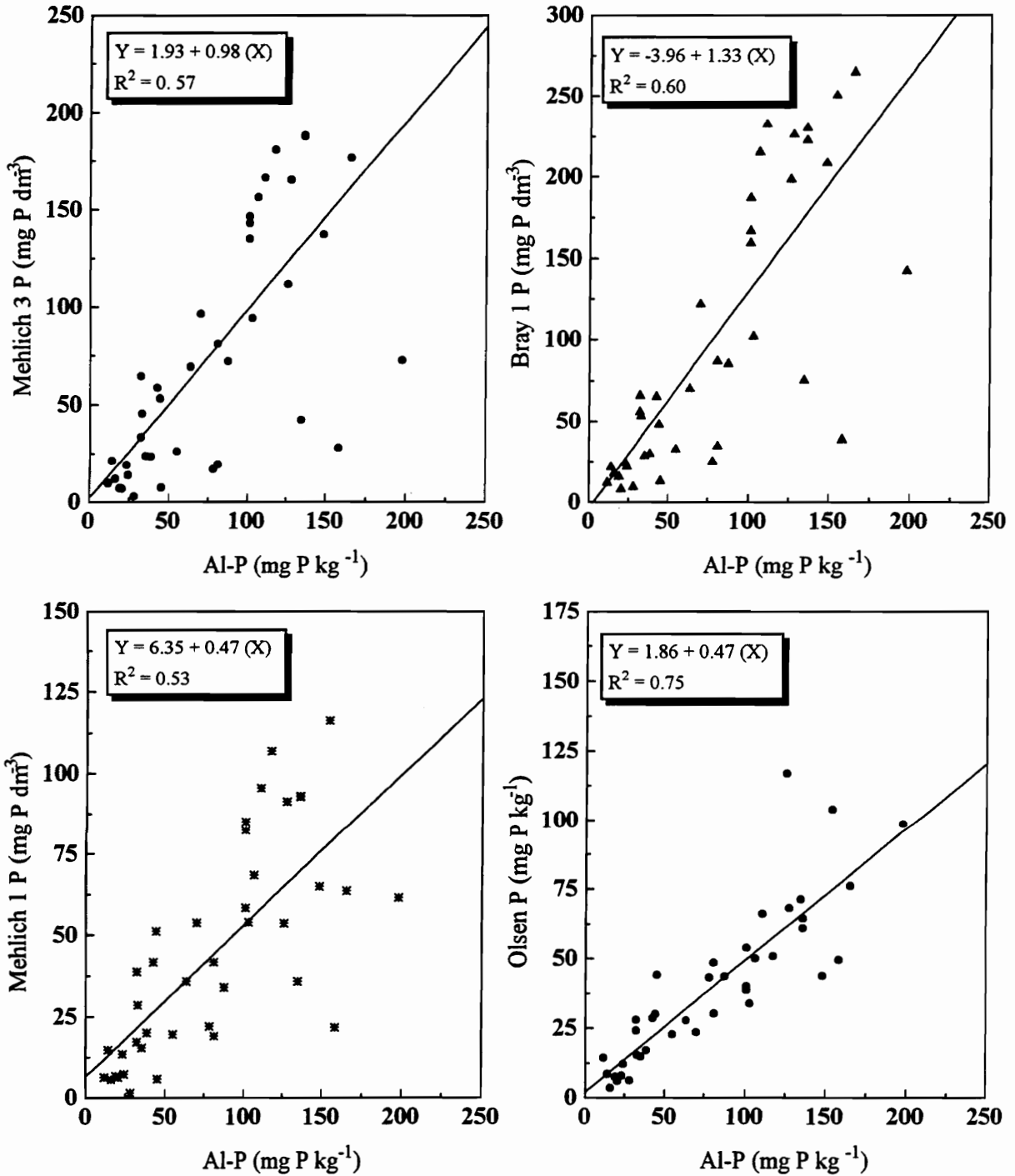


Fig. 3-10. Relationships between extractable P by Mehlich 3, Bray 1, Mehlich 1, and Olsen methods with Al-P in the 40 soils.

Table 3-12. The relationships between Bray 1 extractable P (Y) and different forms of P as affected by soil properties for 43 soils.

P Form	Regression Equation	Coefficient of Determination (R ²)
Labile P	Bray I P = 18.23 + 21.11 Labile P	0.40**
	(Y) = 449.00 + 23.92 Labile P - 75.56 pH [†]	0.48**
Al-P	= 8.31 + 1.14 Al-P	0.80**
	= 48.13 + 1.16 Al-P - 11.72 Fe ₂ O ₃ ^{††}	0.89**
	= 69.91 + 1.12 Al-P - 3.81 Clay ^{††}	0.88**
	= 70.00 + 1.14 Al-P - 27.54 OM [†]	0.82**
	= 34.15 + 1.16 Al-P - Mn ^{††}	0.88**
Ca-P	= 65.59 + 2.71 Ca-P - 16.40 Fe ₂ O ₃ ^{††}	0.31*
	= 108.50 + 2.50 Ca-P - 5.85 Clay [†]	0.33**
AEIP	= 53.10 + 0.31 AEIP - 39.66 Fe ₂ O ₃ ^{††}	0.53**
	= 147.28 + 0.36 AEIP - 540.02 Al ₂ O ₃ ^{**}	0.59**
	= 140.48 + 0.23 AEIP - 11.11 Clay ^{**}	0.47**

* Contribution of the first variable is significant at p = 0.05 (*) or p = 0.01 (**).

† Contribution of the second variable is significant at p = 0.05 (†) or P = 0.01(††).

solution is decreased by Fe_2O_3 , OM, MnO_2 , and, clay contents. It can be postulated that the consumption of H^+ due to reactions with Fe_2O_3 and clay decreases the ability of Bray 1 to extract P from mainly Al-P. Furthermore, organic acids can limit H^+ activity by acting as a buffering agent.

Bray 1 extractable P is not closely related to Ca-P as to Al-P (Table 3-11).

Calcium-P extraction is affected by HCl in the Bray 1 extractant. The extraction power of HCl is weakened by neutralization with Fe_2O_3 and clay and, thereby, lowers the contribution of Ca-P to Bray 1 extractable P. The Fe-P content in the 43 soils is not correlated with Bray 1 extractable P content (Table 3-11). A high correlation is observed between Fe-P and Bray 1 P contents in the Piedmont soils ($r = 0.76$, $p = 0.01$) and the fine-loamy (17.1-35%) soil groups ($r = 0.94$, $p = 0.01$) (Tables 3-13, 3-14, and 3-15). However, Bray 1 extractable P quantities in these soil groups are not higher than those in the other groups (Table 3-10). Hence, Fe-P extraction could be limited by neutralization of H^+ in the Bray 1 solution by high clay and Fe_2O_3 contents in these soils (Table 3-4).

Multiple regression results between soil P forms, and soil test methods and soil physical and chemical parameters for the 43 soils are shown in Table 3-16. Aluminum P is the only soil P fraction that is significantly correlated with the Bray 1 P content. This relationship reiterates the selective extractability of Al-P by F^- in Bray 1 extractant which has a high affinity to Al.

Table 3-13. Correlation coefficients (r) for relationships between forms of P and extractable P by four methods in different physiographic regions.

Method	Labile P	Al-P	Fe-P	Ca-P	Organic P
	(mg P kg ⁻¹)				
<u>Coastal Plain soils</u>					
Mehlich 3 P (mg dm ⁻³)	0.74**	0.98**	-	0.70**	-
Bray 1 P (mg dm ⁻³)	0.73**	0.99**	-	0.72**	-
Mehlich 1 P (mg dm ⁻³)	0.73**	0.96**	-	0.73**	-
Olsen P (mg kg ⁻¹)	0.57*	0.98**	0.42**	0.42**	-
<u>Piedmont soils</u>					
Mehlich 3 P (mg dm ⁻³)	0.94**	0.97**	0.71**	0.81**	-
Bray 1 P (mg dm ⁻³)	0.85**	0.94**	0.76**	0.81**	-
Mehlich 1 P (mg dm ⁻³)	0.86**	0.95**	0.77**	0.81**	-
Olsen P (mg kg ⁻¹)	0.87**	0.98**	0.84**	0.84**	-
<u>Ridge & Valley soils</u>					
Mehlich 3 P (mg dm ⁻³)	-	0.87**	-	-	-
Bray 1 P (mg dm ⁻³)	-	0.91**	-	-	-
Mehlich 1 P (mg dm ⁻³)	0.78**	0.68**	-	-	-
Olsen P (mg kg ⁻¹)	-	0.91**	0.84**	-	-

Significant at $p = 0.05$ (*) or $p = 0.01$ (**).
not significant at $p = 0.05$ (-).

Table 3-14. Correlation coefficient (r) for relationships between forms of P and extractable P by four methods in different clay groups.

Method	Labile P	Al-P	Fe-P	Ca-P	Organic P
	(mg P kg ⁻¹)				
<u>Clay <17 %</u>					
Mehlich 3 P (mg dm ⁻³)	0.77**	0.97**	-	0.48*	-
Bray 1 P (mg dm ⁻³)	0.76**	0.95**	-	0.50*	-
Mehlich 1 P (mg dm ⁻³)	0.79**	0.95**	-	0.45*	-
Olsen P (mg kg ⁻¹)	0.66**	0.61**	0.56*	-	0.43*
<u>Clay 17.1- 35.0 %</u>					
Mehlich 3 P (mg dm ⁻³)	0.99**	0.99**	0.99**	0.98**	-
Bray 1 P (mg dm ⁻³)	0.99**	0.99**	0.94**	0.98**	-
Mehlich 1 P (mg dm ⁻³)	0.98**	0.99**	0.94**	0.98**	-
Olsen P (mg kg ⁻¹)	0.99**	0.99**	0.95**	0.98**	-
<u>Clay > 35.1 %</u>					
Mehlich 3 P (mg dm ⁻³)	0.99**	0.9*2*	-	0.79*	-
Bray 1 P (mg dm ⁻³)	0.99**	0.86*	-	0.73*	-
Mehlich 1 P (mg dm ⁻³)	0.97**	0.90**	-	0.81*	-
Olsen P (mg kg ⁻¹)	0.89**	0.87**	-	0.78*	-

Significant at p = 0.05 (*) or p = 0.01 (**).

Not significant at p =0.05 (-).

Table 3-15. Correlation coefficient (r) for relationships between forms of P and extractable P by four methods in different soil pH groups.

Method	Labile P	Al-P	Fe-P	Ca-P	Organic P
	(mg P kg ⁻¹)				
<u>pH 3.5 - 5.5</u>					
Mehlich 3 P (mg dm ⁻³)	0.92**	0.95**	-	-	-
Bray 1 P (mg dm ⁻³)	0.91**	0.95**	-	-	-
Mehlich 1 P (mg dm ⁻³)	0.90**	0.92**	-	-	-
Olsen P (mg kg ⁻¹)	0.89**	0.97**	-	-	-
<u>pH 5.6 - 6.5</u>					
Mehlich 3 P (mg dm ⁻³)	0.79**	0.93**	-	0.48*	-
Bray 1 P (mg dm ⁻³)	0.78**	0.96**	-	0.53*	-
Mehlich 1 P (mg dm ⁻³)	0.83**	0.94**	-	0.51**	-
Olsen P (mg kg ⁻¹)	0.47*	0.40*	0.53*	0.39*	0.42*
<u>pH 6.6 - 7.5</u>					
Mehlich 3 P (mg dm ⁻³)	0.74*	0.73*	-	-	-
Bray 1 P (mg dm ⁻³)	0.73*	0.74*	-	-	-
Mehlich 1 P (mg dm ⁻³)	0.88**	0.86**	0.65*	0.72*	-
Olsen P (mg kg ⁻¹)	0.93**	0.99**	0.95**	0.91**	0.64*

significant at $p = 0.05$ (*) or $p = 0.01$ (**)

not significant at $p = 0.05$ (-).

Table 3-16. Results of multiple regression between soil test method and soil P forms, chemical, physical characteristics in 4 soils.

Parameter	Bray 1 P	Mehlich 3 P	Mehlich 1 P	Olsen P
Intercept	283.05	214.7	42.8	62.74
Labile P	-2.07	0.98	0.65	3.45 ^{††}
Al-P	1.36 ^{††}	0.92 ^{††}	0.40 ^{††}	0.04
Ca-P	-0.72	-0.57	0.20 [†]	0.01 [†]
Fe-P	0.07	0.03 [†]	-0.10	0.23 ^{††}
Organic P	-0.23	0.09	0.04 [†]	0.12 [†]
pH	-27.82	-22.72	-0.95	-8.05
OM	-0.25	-4.27	0.09	2.61
Clay	-0.14	-0.61	-0.30	0.87
Exch. Al	-0.18	-0.17	-0.06	-0.01
Fe ₂ O ₃	-1.30	-3.99	-0.49	2.15
Al ₂ O ₃	-96.1	-63.11	-48.72	-25.25
Mn	0.01	0.01	0.003	0.01
R ² (p = 0.01)	0.92	0.93	0.90	0.67

Contribution is significant at p = 0.05 (†) or p = 0.01 (††).

3-3.3.2 Mehlich 3 P

Amounts of P extracted by M 3 method from all soils by physiographic regions, clay contents, and pH groups are given in Table 3-10. The average M 3 extractable P content was 105.9 mg dm^{-3} with a range of $2.6\text{-}673.0 \text{ mg dm}^{-3}$. The Coastal Plain soils had the highest mean P content of 166.5 mg dm^{-3} with a range from $45.5\text{-}673.0 \text{ mg dm}^{-3}$, and the Piedmont soils had the lowest amount of M 3 extractable P among all groups, which was 42.4 mg dm^{-3} with a range from $7.9\text{-}202.1 \text{ mg dm}^{-3}$.

Simple correlation coefficients show that M 3 P and forms of soil P (Table 3-11) was positively correlated to labile P ($r = 0.66$, $p = 0.01$), Al-P ($r = 0.88$, $p = 0.01$), and, Ca-P ($r = 0.36$, $p = 0.05$). M 3 extractable P contents were more closely related to Al-P fraction than to either labile P or Ca-P. The buffered M 3 extractant consists of potential tri-valent, cation-complexing radicals such as F^- , CH_3COO^- , and, EDTA which solubilizes P. High reactivity of Al-P with the various complexing radicals explains the solubilization of P from Al-P by the M 3-P procedure. Overall M 3 extractable P content is increased by 0.98 units for each unit increase in Al-P (Fig. 3-10).

The relationships between M 3 extractable P and different forms of P under various soil characteristics are given in Table 3-17. The coefficients of Fe_2O_3 , OM, Al_2O_3 , and clay in the regressions with Al-P are negative. The negative relationship suggests that the extractable capacity of Al-P by M 3 solution is lowered by these soil constituents. Lower Al-P extraction probably is due to depletion of the M 3 reagents by

Table 3-17. Relationships between Mehlich 3 extractable P (Y) and forms of P as affected by properties for 43 soils.

P Form	Regression Equation	Coefficient of Determination (R²)
Labile P	M 3 P = 15.04 + 15.78 Labile P	0.43**
	(Y) = 320.66 + 17.77 Labile P - 53.60 pH [†]	0.51**
Al-P	= 12.74 + 0.80 Al-P	0.77**
	= 71.25 + 0.84 Al-P - 123.15 Al ₂ O ₃ ^{††}	0.91**
	= 62.06 + 0.79 Al-P - 3.05 Clay ^{††}	0.87**
	= 45.56 + 0.82 Al-P - 9.67 Fe ₂ O ₃ ^{††}	0.89**
	= 59.53 + 0.80 Al-P - 20.88 OM ^{††}	0.80**
	= 33.64 + 0.82 Al-P - 0.03 Mn ^{††}	0.86**
Fe-P	= 140.57 + 0.54 Fe-P - 6.53 Clay ^{††}	0.23**
Ca-P	= 39.44 + 1.36 Ca-P	0.13*
	= 58.48 + 1.90 Ca-P - 12.95 Fe ^{††}	0.33**
	= 90.69 + 1.73 Ca-P - 4.47 Clay [†]	0.33**
AEIP	= 49.58 + 0.22 AEIP - 29.37 Fe ^{††}	0.54**
	= 119.24 + 0.25 AEIP - 399.07 Al ₂ O ₃ ^{**}	0.60**
	= 113.47 + 0.16 AEIP - 8.06 Clay ^{**}	0.46**

* Contribution of the first variable is significant at p = 0.05 (*) or p = 0.01 (**).

† Contribution of the second variable is significant at p = 0.05 (†) or P = 0.01(††).

reaction with Fe_2O_3 , OM, Al_2O_3 , and clay and, to more readsorption and reprecipitation of dissolved Al-P.

The correlation coefficient between Ca-P and M 3 extractable P contents was low ($r = 0.36$, $p = 0.05$) when the 43 soils were considered in one group (Table 3-11). This low correlation suggests that M 3 has a low ability to solubilize Ca-P. It is possible that most of the F^- in the M 3 solution is used to solubilize Al-P in preference to Ca-P and that CH_3COO^- controls the solubility of Ca-P through its pH buffering action. The low solubilization of Ca-P by M 3 is further decreased as the soil Fe_2O_3 and clay neutralize acidity required for solubilization of Ca-P (Table 3-17). The simple correlations between Ca-P and M 3 extractable P is improved when the soils are grouped according to physiography or clay (Table 3-14). When the soils are grouped by similar properties, correlations between extracted P contents and soil P contents are improved due to the homogeneity within the group.

The relationships between Fe-P and M 3 P are similar to those with Ca-P. The correlation coefficients between M 3 and Fe-P were quite low for all soils (Table 3-11), but increased dramatically in the Piedmont and fine loamy (17.1-35% clay) soil categories (Table 3-13 & 3-14). Generally, the larger the fraction of soil P as Fe-P, the lower the portion extracted by M 3 solution (Table 3-5 & 3-10). This relationship suggests that H^+ activity of the M 3 extractant is quickly neutralized in the presence of high Fe_2O_3 , Al_2O_3 , and clay contents in the soils. Surface complexations of phosphate on Fe^{3+} are observed to be less reversible and labile than those involving Al (Hingston, 1974).

Multiple correlation involving all soil parameters and P fractions show significant positive relationship with Al-P ($p = 0.01$) and Fe-P ($p = 0.05$) contents (Table 3-16). However, the coefficient associated with Fe-P (0.03) is quite small as compared with Al (0.92) despite the fact that the average Fe-P and Al-P contents in the soils were similar (Table 3-5). The M 3 solution has a selective extractability to Al due to F^- . The ability of M 3 solution to extract some Fe-P can be attributed to the presence of CH_3COO^- and EDTA which can form strong complexes with Fe.

3-3.3.3 Mehlich 1 P

The amounts of Mehlich 1 extractable P when the soils were considered in a single group and in several categories grouped by physiographic regions, clay contents, and pH groups are presented in the Table 3-10. Mehlich 1 extracted an average P content of 55.1 mg dm^{-3} from all soils and ranged from 1.5 to 327.9 mg dm^{-3} . The Coastal Plain, coarse loamy (clay < 17 %) and slightly to moderately acid (pH = 5.6 to 6.5) soil groups had greater M 1 extractable P quantities than in the other soil groups. These soils are low in Fe_2O_3 and clay contents which to decrease P extraction by M 1.

The simple correlation coefficient between M 1 extractable P and different P forms (Table 3-11) show a positive relationship with labile P ($r = 0.69$, $p = 0.01$), Al-P ($r = 0.88$, $p = 0.01$), and Ca-P ($r = 0.58$, $p = 0.01$) for the 43 soils. Previous studies have reported solubilization of Ca-P by the acidic 1 extractant (Thomas and Peaslee, 1973; Kamprath and Watson, 1980). The low correlation between M 1 and Ca-P may reflect

the low amounts of Ca-P in the 43 soils (Table 3-5). The correlation between M 1 extractable P and Ca-P is negatively influenced by Fe_2O_3 and clay (Table 3-18). These relationships suggest that Fe_2O_3 and clay neutralize the acidity in the reagent and thereby reduce the H^+ activity lowering Ca-P solubility.

The high correlation coefficient between Al-P and M 1 extractable P ($r = 0.88$, $p = 0.01$) shows that the contribution from Al-P to M 1 extractable P is greater than from Ca-P and labile P (Table 3-11). Solubilization of Al-P by SO_4^{2-} in the acidic M 1 solution is moved in a forward direction by the formation of $\text{Al}_2(\text{SO}_4)_3$. Jardine and Zelazny (1987) found that SO_4^{2-} forms strong bonds with mononuclear and polynuclear Al which do not readily dissociate until high levels of solution pH. Simple regression shows that Al-P contributes 0.47 P units for each unit increase in M 1 P concentration (Fig. 3-10). The amounts of Al-P extracted by M 1 were decreased by Fe_2O_3 , Al_2O_3 , Mn oxides and clay contents (Table 3-18). These soil constituents decrease H^+ activity which is necessary to solubilize P. Furthermore, Al and Fe increase reprecipitation reactions. Hence, when the soils are grouped by physiography, clay and pH contents, the correlation coefficients between Al-P and M 1-P are increased sharply (Table 3-13, 3-14, & 3-15). There likely is less masking of the relationship between Al-P and M 1 by Fe_2O_3 , Al_2O_3 , MnO_2 , and clay in correlations in the grouped soils as compared with the 43 soils.

Aluminum-P, Ca-P and organic P contents in the soils are positively correlated with the M 1 extractable P content (Table 3-16). The lower coefficients associated with

Table 3-18. The relationships between Mehlich 1 extractable P (Y) and forms of P as affected by soil properties for 43 soils.

P Form		Regression Equation	Coefficient of Determination (R ²)
Labile P	Mehlich 1P	= 12.87 + 7.52 Mehlich 1 P	0.48**
	(Y)	= 107.11 + 7.94 mehlich 1 P - 16.53 pH [†]	0.52**
Al-P		= 13.65 + 0.36 Al-P	0.78**
		= 26.66 + 0.36 Al-P - 3.83 Fe ₂ O ₃ ^{††}	0.88**
		= 32.57 + 0.35 Al-P - 1.17 Clay ^{††}	0.86**
		= 37.15 + 0.37 Al-P - 49.47 Al ₂ O ₃ ^{††}	0.90**
		= 32.57 + 0.35 Al-P - 0.11 Mn ^{††}	0.85**
Ca-P		= 23.82 + 0.42 Ca-P	0.31*
		= 31.66 + 0.42 Ca-P - 5.32 Fe ₂ O ₃ ^{††}	0.43**
		= 108.50 + 2.50 Ca-P - 5.85 Clay [†]	0.49**
AEIP		= 26.56 + 0.10 AEIP - 13.03 Fe ₂ O ₃ ^{††}	0.57**
		= 57.62 + 0.12 AEIP - 178.43 Al ₂ O ₃ [†]	0.64**
		= 54.52 + 0.07 AEIP - 3.50 Clay ^{††}	0.46**

* Contribution of the first variable is significant at p = 0.05 (*) or p = 0.01 (**).

† Contribution of the second variable is significant at p = 0.05 (†) or P = 0.01(††).

Ca-P and organic P suggest a lower contribution of these fractions to M 1 extractable P.

The high acidity of M 1 extractant solution could lead to solubility of some AEOP.

3-3.3.4 Olsen P

The mean Olsen extractable P content in the 43 soils is 41.8 mg kg⁻¹ with a range of 3.5 to 185.2 mg kg⁻¹ (Table 3-10). Olsen extractable P contents have the lowest mean values of the four soil test methods. Mean Olsen P values were highest in the Coastal Plain soils, and in the soil groups with high clay contents and soil pH levels.

Olsen P values were positively correlated with all labile P fractions (Table 3-11). The Olsen extractant, NaHCO₃ at pH 8.2, has a favorable media for Al-P extraction for which the solubilization increases at higher pH levels (Jardine and Zelazny, 1987). Olsen extraction solution lowers the activities of Al²⁺, Fe³⁺, and Ca²⁺ by formation of aluminate complexes, and by precipitation of Fe as the oxides and Ca as CaCO₃ respectively (Olsen et al., 1954; Jackson, 1958). Release of P from Ca-P and Fe-P due to the precipitation reactions accounts for the positive correlation between Olsen-P and both Ca-P and Fe-P.

The influence of soil properties on relationships between Olsen extractable P and various P fractions are different than those for the Bray 1, M 1 and M 3 extractants (Table 3-19). In general, the correlations between P sources and Olsen P are considerably lower than with the other extractants. The correlation between Fe-P and Olsen P were improved by inclusion of Al, Fe, Mn and clay contents in regression equations. Olsen procedure is the only extractant that was significantly correlated with the organic P

Table 3-19. Relationships between Olsen extractable P (Y) and forms of P as affected by properties for 43 soils.

P Form		Regression Equation	Coefficient of Determination (R ²)
Labile P	Olsen P	= 15.31 + 5.47 Labile P	0.56**
	(Y)	= 6.56 + 5.71 Labile P + 2.07 Fe ₂ O ₃ [†]	0.62**
		= 2.16 + 5.62 Labile P + 24.42 Al ₂ O ₃ [†]	0.62**
		= 8.90 + 5.64 Labile P + 0.01 Mn [†]	0.62**
		= 2.87 + 5.88 Labile P + 0.65 Clay [†]	0.61**
Al-P		= 23.89 + 0.20 Al-P	0.50**
Fe-P		= 22.10 + 0.20 Fe-P	0.29**
		= 19.98 + 0.34 Fe-P + 0.38 Fe ₂ O ₃ ^{††}	0.41**
		= 30.45 + 0.38 Fe-P - 61.72 Al ₂ O ₃ ^{††}	0.43**
		= 15.83 + 0.35 Fe-P + 0.02 Mn ^{††}	0.41**
		= 31.28 + 0.39 Fe-P - 2.08 Clay ^{††}	0.54**
Ca-P		= 14.54 + 0.66 Ca-P	0.32**
AEIP		= 16.37 + 0.4 AEIP	0.39**
		= 27.08 + 0.08 AEIP - 0.97 Clay [†] - 52.64 Al ₂ O ₃ [†]	0.68**
BEIP		= 30.60 + 0.30 BEIP - 1.04 Clay [†]	0.31**

* Contribution of the first variable is significant at p = 0.05 (*) or p = 0.01 (**).

† Contribution of the second variable is significant at p = 0.05 (†) or P = 0.01(††).

fraction (Table 3-8). Alkalinity in the Olsen extractant is able to extract P from organic compounds (Bowman and Cole, 1978; Headley, 1982).

Olsen extractable P contents are positively correlated with labile-P, Fe-P, Ca-P and organic P contents in the multiple regressions (Table 3-16). The increased solubility of Fe-P can be attributed to Fe forming stable complexes with soil organic acids at the high pH induced by Olsen extractant (Ballard, 1974).

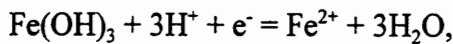
3-3.4 Environmental Implications of Different P Forms

The reductant soluble P which contains a large proportion of inorganic P in soils has little importance as a source of plant available P except under rice cultivation. Availability of P from reductant soluble forms depends on the removal of iron oxides and hydrated oxides coatings. Under reduced conditions, as in the flooded soils, the availability of reductant soluble P increases (Willett, 1989).

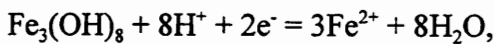
The average reductant soluble P contents in the 43 soils under study were estimated to be 215.4 mg kg⁻¹ which is about 40 percent of the total inorganic P content (Table 3-5 & 3-6). If a large share of this P fraction becomes available following reduced conditions in the water bodies, the amount of P available for aquatic plant growth is likely to be significant. Even a strong extractant such as Bray 1 extracted only about 26% of the total inorganic soil P content (Table 3-6 & 3-10). Therefore, the relative contribution of reductant soil P in increasing the P sink in water bodies can be substantially higher than that indicated by the extractable soil P data.

Truman et al. (1993) estimated that seasonal soil in run-off loss from a Coastal Plain soil with a 3% slope ranged from 153 to 1232 kg/ha. At this level of soil loss, the amount of reductant soil P to reach water body could range from 0.03 to 0.26 kg/ha. Reductant soluble P was shown to be highly correlated with the clay and Fe_2O_3 contents (Fig. 3-6). Since soil clay is transported in run off loss, the amount of reductant soil P accumulating in water bodies is likely to be even higher than predicted by Truman et al. (1993).

Increased solubilization of Fe oxide and hydrous oxide encapsulations under reduced conditions can be explained by chemical equilibria equations of the following form:



for reduction in the early stages of flooding, and



in soils under prolonged reduced conditions (Ponnamperuma et al., 1967). Increased solubility of Fe^{2+} leads to solubilization of encapsulated Fe-P. Furthermore, increased pH in stagnant water bodies leads to solubilization of Fe-P and Al-P from soil particles. The combined effect of these reactions may lead to an aggravated eutrophication.

3-4 CONCLUSIONS

This investigation was undertaken to study the distribution of soil P among different inorganic and organic P forms and their contribution to P quantities extracted by Bray 1, M 1, M 3, and Olsen methods. The total P content in the 43 soils varied from 0.02 to 0.4%. Twenty-six percent of the total P was present as the labile P to moderately labile P pool in the order Fe-P > Al-P > Ca-P > labile (NH₄Cl) P. The non-labile P pools accounted for 49% of the total P with residual P > reductant soluble P > occluded P. The remainder of the total P (25%) was organic P.

Iron oxide and clay contents in the soils greatly influenced the distribution of soil P among various fractions. A wide range of DCB extractable Fe₂O₃ (0.3-17%) and clay (0.7-49%) contents, which are heavily altered by weathering, were observed in the soils. Coastal Plain soils which had low Fe₂O₃ and clay contents had a dominant Al-P fraction. Soils in the Piedmont region, which were high in Fe₂O₃ and clay contents, had a Al-P content nearly a half of that of Coastal Plain soils. The Al-P content was not markedly affected by the soil texture or pH. Iron-P, which was the dominant labile P fraction in the Piedmont soils, was positively influenced by the soil clay content. Calcium-P and labile (NH₄Cl) P contents were unaffected by soil group, texture or pH.

In the non-labile P fractions, reductant soluble P and occluded P were the dominant forms in the Piedmont soils. The levels of these P fractions increased with clay content, but were unaffected by the changes in pH. The residual P fraction behaved

similar to the other two non-labile fractions and increased with clay content and pH. The dominant soil P sink was reductant soluble P. The results suggests that Fe-P, which is the premier labile P sink, is gradually transformed to reductant soluble P.

The organic P content in the Piedmont soils was high relative to other soils, and increased with clay content. The extractable P contents by the four extraction solutions ranked Bray 1 > M 3 > M 1 > Olsen P. Aluminum P had significant positive correlations ($p = 0.01$) with Bray 1 ($R^2 = 0.60$), M 1 ($R^2 = 0.53$), M 3 ($R^2 = 0.57$), and Olsen ($R^2 = 0.75$) extractable P contents. Extractable P contents by procedures other than the Olsen extractant were negatively influenced by the clay, Al_2O_3 , Fe_2O_3 and organic matter contents, which suggests that high concentrations of these soil constituents decreased the extractability power. The Olsen method strongly linearly correlated with the all labile pool P fractions, although the extraction levels were rather small. Mehlich 1 extractable P content correlated with the Ca-P fraction ($r = 0.58$) in the labile pool.

Soil test relationships with soil P fractions and soil physical and chemical properties were evaluated by multiple regression analysis. The results suggested that Bray 1 selectively extracts Al-P ($p = 0.01$) as indicated by the high affinity shown by F^- in the Bray 1 extractant towards Al-P. Mehlich 3 extractant showed significant relationships with Al-P ($p = 0.01$) and Fe-P ($p = 0.05$) and M 1 with Al-P ($p = 0.01$), Ca-P ($p = 0.05$), and organic P ($p = 0.05$). Olsen extractable P contents were related to NH_4Cl P ($p = 0.01$), Fe-P ($p = 0.01$), Ca-P ($p = 0.05$), and organic P ($p = 0.05$), but not to soil Al-P content. The other radicals in M 3 extractant, i.e., CH_3COO^- and EDTA, may increase P

extraction by forming strong complexes with Fe from Fe-P and some Al from Al-P. The results suggest that potential eutrophication problems are high with Piedmont and high clay soils due to high reductant soluble P and Fe-P contents and to high soil P levels in these soils.

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CHAPTER 4

PHOSPHATE ADSORPTION AND TRANSFORMATION IN PIEDMONT SOILS THAT RECEIVED LONG-TERM PHOSPHORUS APPLICATIONS

ABSTRACT

Phosphorus (P) adsorption is an important determinant in agricultural production and environmental quality. The study and usage of adsorption curves are aided by interpretation of soil constituents involved in adsorption, postulation of the nature and mechanism of the adsorption process, and prediction of fertilizer requirements to attain optimum yields. In this study, the phosphorus adsorption behavior, and the sizes and changes in the native and residual P forms were studied with Langmuir and two-site Langmuir models in two soil series that received P applications for over three decades, i.e., Davidson clay loam (clayey, kaolinitic, thermic, Rhodic Paleudults), and Tatum silt loam (clayey, mixed, thermic, Typic Hapludults).

Phosphorus adsorption data for the two soils were explained quite well by the two-site Langmuir model as evidenced from the lowest residual sums of squares. phosphorus adsorption maxima in the non-fertilized treatments were 4,007 mg/kg in the

Davidson soil and 2,179 mg/kg in the Tatum soil. The maximum P sorption capacity was decreased slightly (5%) by P fertilization. The Davidson soil, which had a low pH (5.4), higher amounts of clay (40%), dithionite-citrate-bicarbonate extractable iron oxides (16.7%), and aluminum oxides (1.5%) had higher P adsorption levels than the Tatum soil. Application of P fertilizer did not decrease the P adsorption power of the soil due to the transformation of adsorbed P into non-labile forms, such as reductant soluble P and occluded P. The lack of decreasing P adsorption may be a result of freeing original sites and the creating of new sites due to weathering.

All soil inorganic and organic P fractions increased following P fertilizer applications in the field. Of the non-labile P forms, the reductant soluble P fraction increased by 61% in the Davidson soil and by 57% in the Tatum soil. For the P fractions in the labile to moderately labile P pool, Al-P and Ca-P contents had the largest increase due to fertilizer P application. However, relative to the total P content, the Fe-P fraction dominated all labile to moderately labile P fractions in both soils. Bray 1, Mehlich 1, Mehlich 3, and Olsen extractable P contents were greater in the fertilized soil than in the non-fertilized soil. Residual P effects in the fertilized Davidson soil were adequate to maintain corn tissue P concentrations in the sufficiency range.

4-1 INTRODUCTION

Plants take up all essential mineral nutrients except carbon and oxygen from soil. Both plants and soil microorganisms actively compete for meager levels of soil solution phosphorus (P) present as orthophosphates, the level of which is controlled by adsorption, precipitation, and desorption processes. Adsorption of phosphates on soil colloids takes place through an inner-sphere complexation process (McBride, 1994; Sposito, 1989). Thus, a reasonable fraction of adsorbed phosphate is rapidly converted to non-labile forms that are not extracted by P soil test methods. Of the adsorbed phosphates, only the mononuclear fraction is considered to be labile and exchangeable with ^{32}P within a specific time (Okajima et al., 1983; Frossard et al., 1993). Thus, rapid dissolution of the labile pool P recharges the soil solution P against uptake by growing plants and the soil biota.

Literature demonstrates the importance of P adsorption in agricultural use and in environmental quality such as for eutrophication. The motivation of this study and usage of adsorption curves are identification of soil constituents involved in adsorption, postulation of the nature and mechanism of the adsorption process, and prediction of fertilizer requirements to attain optimum yields (Fox and Kamprath, 1970; Adams et al., 1987; Barrow, 1987).

Soils are known to vary widely in their capacities to supply P to crops, due to differences in parent materials and climate as well as the heterogenous nature of soil

components that leads to complex reactions between added fertilizer P and soil constituents. Phosphorus adsorption/desorption, transformation, and availability are influenced by the clay content, free Al and Fe oxides, pH, the ionic strength of soil solution, organic matter, and the mineralogy of the soil (Bolan et al., 1986; Borggaard et al., 1990; Fan et al., 1993; Sanyal and De Datta, 1991; White, 1981).

Properties such as soil texture and the sesquioxide content will not be markedly changed by management and fertilization. The chemical properties of the soil environment such as soil pH, organic matter, cation exchange capacity, and extractable nutrient contents are altered by long-term cultivation (Mullins, 1991). Thus, soil management and fertilization are likely to affect P sorption and P dynamics in soils both directly and indirectly. The long-term application of soluble phosphate fertilizer is considered to reduce P adsorption capacity because the reactive sites would be partially occupied. Failure of the adsorption maxima to be decreased by long-term P addition would imply the transformation to P minerals to non-exchangeable forms. Therefore, it would be beneficial to investigate how P sorption, availability and transformation in the agricultural soils is affected by long-term P fertilization. The objectives of the present study are 1) to evaluate changes in phosphate adsorption caused by long-term application of P fertilizer, 2) to investigate the role of soil physio-chemical and mineralogical properties in controlling P adsorption, and 3) to study the effect of long term P applications on soil P transformation and extractability by the Mehlich 1, Mehlich 3, Bray 1, and Olsen P procedures.

4-1.1 Adsorption Isotherms

The relationship between the amount of P adsorbed per unit weight of soil and the equilibrium P concentration in soil solution at constant temperature is described by adsorption isotherms (Sanyal and De Datta, 1991). Most adsorption equations were originally developed to explain gas adsorption to solid surfaces, and hence, application to soils has been limited. However, several equilibrium based models have been introduced to describe P adsorption by soils and soil constituents (Olsen and Watanabe, 1957; Syers et al., 1973). Among them, Langmuir, Freundlich, Temkin, and the Brunauer-Emmett-Teller (BET) models have received wide acceptance. In recent years, the Langmuir adsorption and Freundlich equations have become popular among soil and environmental chemists.

4-1.1.1 Langmuir Adsorption Isotherm

Langmuir (1918) theory explains adsorption of gaseous molecules onto planar solid surfaces based on the following assumptions: 1) the isosteric heat of adsorption $[\Delta H]$ is constant regardless of the extent of surface coverage, 2) the molecules are specifically adsorbed with no interaction between them, and 3) the adsorption maximum occurs with monolayer adsorption at reactive sites (Bohn et al., 1985). As originally proposed, the equation was of the form,

$$n = \frac{V_m bP}{(1+bP)} \quad 3.1$$

where,

n = the amount of gas adsorbed per unit area,

P = the equilibrium gas pressure,

V_m = the adsorption capacity (the adsorption maximum), and

b = coefficient related to the bonding energy of gas to solid surface.

In application to soil systems, single adsorption sites can provide a close approximation to reality. The linear form of the Langmuir equation can be utilized by disregarding desorbed ions (Olsen and Watanabe, 1957). It has the form,

$$\frac{C}{x/m} = \frac{1}{V_m b} + \frac{C}{V_m} \quad 3.2$$

where,

b and V_m are defined as before,

C = the equilibrium concentration of P in solution ($\mu\text{g P/mL}$), and

x/m = P adsorbed per unit mass of soil ($\mu\text{g P/g soil}$).

The rigorous conditions under which the Langmuir equation is derived are rarely satisfied in practice. A linear isotherm implies mono-layer adsorption, and such a result

was previously taken as evidence against a precipitation reaction, though recent research has shown the fallacy of this theory (Veith and Sposito, 1977). Generally, a close fit to the Langmuir equation is obtained at low concentrations of P ($< 15 \text{ mg P L}^{-1}$) (Sanyal and De Datta, 1991). It was also shown that the calculated adsorption maximum for lower concentration range was often exceeded at higher concentrations (Harter, 1984). The curvi-linear relationship between wide ranges of concentration indicates that the bonding energy is not a constant, but rather a function of adsorption, due to penetration of sorbed P into subsurface layers and crystalline hydrous Fe oxides (Sanyal and De Datta, 1991).

Deviation from linearity with a Langmuir model has been interpreted as evidence that P adsorption sites have different binding characteristics (Muljadi et al., 1966a, b, c; Syers et al., 1973; Taylor and Ellis, 1978). Phosphorus adsorption studies on kaolinite, gibbsite, and pseudobehmite identified three linear regions in Langmuir plots (Muljadi et al., 1966a, c). This data led to the postulation that three sites exist have different affinity for P, i.e., the first region at low concentrations had the strongest affinity and totally irreversible reaction, the second region had partially reversible reactions, and occurred at intermediate initial P concentrations, and the third region had totally reversible reactions and was postulated to have purely electrostatic bonds. Two distinctly different regions observed in the Langmuir plots were attributed to the differences in binding energy to a bi-dentate attachment of phosphate at low concentrations and a mono-dentate attachment at the higher P concentrations on the resin surfaces (Taylor and Ellis, 1978).

The nonlinearity of the simple Langmuir model and the non-uniformity of site population, and thereby multi-layer adsorption, violate the assumptions for the original model and the applicability to a soil-solution system. Hence, the two-site Langmuir model for soil-solution systems has been introduced with satisfactory results (Syers et al., 1973; Ram et al., 1987; Mehadi and Taylor, 1988). The two surfaces are characterized by different bonding energy and adsorption maximum. The two-site Langmuir equation is written as,

$$\frac{x}{m} = \frac{V_{m1}b_1c}{1+b_1c} + \frac{V_{m2}b_2c}{(1+b_2c)} \quad 3.3$$

Where,

x/m = P adsorption capacity, per gram of soil at C concentration of P ($\mu\text{g Pg soil}^{-1}$),

b = coefficient related to the free energy of transfer of P from solution to soil,

V_m = the adsorption maximum for monolayer coverage ($\mu\text{g Pg soil}^{-1}$),

and the subscripts represent to the discrete energy sites, i.e., V_{m_n} represents the adsorption capacity due to sites of the n th discrete energy.

Though the modification of the Langmuir model solves the problem of multiple sites with heterogeneity, it does not overcome the problem of lateral interaction which is assumed to be have constant adsorption energy and coupled adsorption-desorption (White and Zelazny, 1986).

4-1.1.2. BET Adsorption Isotherm

The BET equation has also been used with some success to describe P adsorption by soils (Griffin and Jurinak, 1973; Taylor and Ellis, 1978). The BET equation is different from the Langmuir equation by the fact that it allows for multi-layer adsorption of ions. The form of the BET equation is as follows:

$$\frac{C}{\frac{x}{m} (C_0 - C)} = \frac{1}{V_m b} + \frac{b-1}{V_m b} \left(\frac{C}{C_0} \right) \quad 3.4$$

where, C, x/m and V_m are as defined for the Langmuir equation, b is related to binding energy of the first adsorbed layer only, and C₀ is the concentration of P required to cause precipitation of the most likely solid form of P. Injudicious selection of a C₀ may give erroneous results.

4-1.1.3 Freundlich equation

The Freundlich adsorption equation has been used quite extensively to describe P adsorption and to obtain chemical kinetic data of adsorption reactions (Kuo and Lotse, 1974). Also, the Freundlich equation gave a better fit than the original Langmuir model at higher equilibrium soil P concentrations (Sanyal et al., 1993). This better fit may be due to the fact that empirical Freundlich equation implies that the affinity for adsorption decreases exponentially with increasing surface saturation which is closer to reality than theory for the Langmuir equation (Sposito, 1984). The equation can be written as,

$$\frac{x}{m} = kC^{\frac{1}{n}} \quad 3.5$$

where x/m = P adsorbed (mg P kg^{-1}), k and n are constant terms, and C = equilibrium concentration of P in solution (mg P L^{-1}). Some researchers show little interest for this model due to the lack of an adsorption maximum parameter.

4-1.2 Physio-Chemical and Mineralogical Factors Affecting P Adsorption

Generally, P adsorption results from a fast initial adsorption reaction at low concentrations followed by slower diffusion control process (precipitation) at higher concentrations (Barrow, 1985). Soils and soil constituents are adsorbents with different binding strengths and surface areas which influence P adsorption. Thus, degree of P adsorption is affected by the chemical changes of the soil environment as well as by the amount of P fertilizer added and time. Research during the past three decades has focused on elucidation of adsorption mechanisms and on factors that influence P adsorption.

4-1.2.1 Organic Matter

The relationship between P adsorption and soil OM content has received much attention. Soil OM is involved in P retention by ligand exchange (i.e., H_2PO_4^- for OH^-) in a process similar to hydrous oxides and aluminosilicates, but humic substances are

normally negatively charged and, therefore, OM may retain less P than Al and Fe compounds (Sample, 1980). Several studies showed a positive correlation between OM content and P sorption (Mizota et al., 1982; Hinga, 1973; Sanyal et al., 1990). In acid soils, the positive relationship is often attributed to the formation of Fe and Al chelates which provide an active surface for P adsorption on soil OM and hydrous sesquioxides (Saunders, 1965). In the presence of OM, the crystallization of Fe and Al oxides is lowered (Schwertmann, 1966; Gerke, 1993). As the surface area available for adsorption is decreased with crystallization, the addition of organic matter increases P adsorption capacity.

Sibanda and Young (1986) found that addition of humic substances decreased phosphate adsorption. It seems likely that, in soils, sites suitable for both phosphates and organic anions, adsorption of organic anions can block phosphate reaction and, thereby, reduce P adsorption (Hue, 1990; Moshi et al., 1974). Research on transient organic acids of microbial or root exudate origin has shown that acids with a short chain length and high carboxyl density reduce P adsorption most effectively by competition for adsorption sites (Nagarajah et al., 1970).

4-1.2.2 Effect of pH

In principle the maximum quantity of phosphate adsorption is determined by the number of available bonding sites which is a function of soil pH. A strong inverse relationship was observed between P adsorption and pH due to high Al and Fe activity of

soils (Adams and Odom, 1985; Bolan et al., 1988; Mehadi and Taylor, 1988). When the pH increases the charge and the electrostatic potential of positive pH dependent adsorption sites decreases and thereby, lowers P adsorption.

In contrast, positive relationships between P adsorption and pH have been observed (Barrow, 1987; Haynes, 1982). This relationship may be attributed to high Ca activity in the soil solution at higher levels of pH which precipitates P as Ca-P. Thus, in limed soils, dilute CaCl₂ used as an electrolyte increases P adsorption (Amarasiri and Olsen, 1973; Naidu, 1990).

4-1.2.3 Clay Content

A direct relationship between P adsorption and clay content has been reported in several studies. High specific surface area of the clay particles leads to the increase in P adsorption (Bennoah and Acquaye, 1989; Loganathan et al., 1987). Tropical soils that contain 1:1 lattice clay conditions may contribute adsorption sites for enhanced P adsorption at low pH (Sanyal et al., 1993). The adsorption for P on kaolinite has been intensively studied decades ago (Black, 1942; Kittrick and Jackson, 1956; Muljadi et al., 1966c). The edge faces of kaolinite are favorable sites of P adsorption. Thus, aluminum phosphate is formed through adsorption of P on kaolinite (Low and Black, 1950). In addition, at high concentrations where monolayer coverage of the highly reactive sites is to be exceeded, there is also evidence to suggest that P solution can dissolve phyllosilicates, mostly kaolinite, to release Al and Si, with the subsequent precipitation of

Al-P (Low and Black, 1950; Rajan and Fox, 1975). Major P immobilizing components such as hydrous oxides of Fe and Al are found as fine coatings on clay particles. The large surface area of these particles enhances P adsorption by the Fe and Al hydrous oxides, which implies a secondary role of clay in P sorption (Ryden and Pratt, 1980).

4-1.2.4 Crystalline and Non-Crystalline Iron and Aluminum Oxides

In many soils, P is adsorbed by Fe_2O_3 and oxyhydroxides that exist as both discrete components and as coatings on the other soil particles (Borggaard et al., 1990; Pena and Torrent, 1990). Hence, removal of Fe_2O_3 and Al_2O_3 drastically reduced P adsorption by soil (Udo and Uzu, 1972). Increasing Fe_2O_3 coatings by 1.6% on calcite surfaces was shown to increase P adsorption by 141 mg kg^{-1} (Hamad et al., 1992). Dithionite-citrate-bicarbonate (DCB) extractable Fe accounted for 22 - 37% of high energy sorption sites of the calcareous soils, which indicates the importance of metal oxides in P sorption (Holford and Mattingly, 1975b).

Ammonium oxalate extraction is known to dissolve non-crystalline and poorly crystalline Fe_2O_3 and Al_2O_3 (Pratt and Childs, 1988; Torrent, 1988). DCB extracts Fe and Al from non-crystalline as well as crystalline Fe and Al (hydr)oxides such as hematite and goethite and specially Al substituted for Fe (Boero and Schwertmann, 1989; Skjemstad et al., 1989; Wendt et al., 1993). Larger surface area of the non-crystalline and poorly crystalline Fe_2O_3 and Al_2O_3 extracted by NH_4^+ oxalate adsorbed large amounts of P (Adams et al., 1987; Buchter et al., 1989; Ryden and Pratt, 1980; Sanyal et al., 1993).

However, much P adsorption occurred in Mediterranean soils, after extraction of Fe and Al with DCB (Pena and Torrent, 1990).

The degree of crystallinity, and the amounts of surface area and (hydr)oxides of Al and Fe vary with by parent material and climate. Amounts of P sorption at high levels of phosphate addition are in the following order: hematite < goethite < ferrihydrite < allophane. These results are probably related to the specific surface area of the compound (Pratt, 1989). Furthermore, Torrent et al. (1994) showed that hematite has lower sorption and lesser affinity for P than goethite.

4-1.2.5 Effects of Fertilizer on P adsorption

The effect of fertilizer application on P adsorption depends on soil and mixture of N, P, and K carriers. Application of urea with CaCl_2 as the electrolyte increases P adsorption due to an increase of soil pH and, thereby increases precipitation of P as Ca-P. However, adding KCl to urea as a electrolyte does not change P adsorption (Fan et al., 1993). Therefore, P fertilizers can be combined with KCl (muriate of potash) in fertilizer mixtures without affecting P availability. Released OH^- and HCO_3^- from urea hydrolysis neutralizes soil acidity produced by the dissolution of acidic fertilizers, and thus, increases P availability (Kissel et al., 1988).

4-2 MATERIALS AND METHODS

4-2.1 Soil Description

This research was undertaken to study the change in P adsorption capacity and soil test P levels from long-term P fertilization and to investigate dynamic changes of P fractions from P fertilization. Two soil series that had long-term P fertilization, i.e., Davidson (clayey, kaolinitic, thermic, Rhodic Paleudults) and Tatum (clayey, mixed, thermic, Typic Hapludults), were selected for the study. These soils were derived from metamorphic rocks. The parent rock for the Davidson soil was Catocin greenstone and for the Tatum soil was Sericite schist.

Two long-term corn field experiment sites on the Davidson clay loam and Tatum silt loam were used for the experiment. The Davidson clay loam received annual broadcast superphosphate applications at the rates 0 and 30 kg P ha⁻¹ for the 34 year period from 1960 to date. The Tatum silt loam received applications of superphosphate at the rates of 0 and 25 kg P ha⁻¹ for a period of 39 years (Table 4-1). Soil samples for the study were taken in the spring of 1993.

4-2.2 Soil Analysis

The air dried soil samples were sieved to remove coarse fragments (>2mm) and thoroughly mixed. Textural analysis was carried out by the pipette method (Day, 1965).

Table 4-1. Description and fertilization history of the four soils from two soil series used in the investigation.

Soil Series	Taxonomic Classification	Treatments			Duration (yr)
		N*	P*	K*	
Davidson	clayey, kaolinitic, thermic Rhodic Kandiudults	170	0	112	34
		170	30	112	34
Tatum	clayey, mixed, thermic Typic Hapludults	200	0	25	39
		200	25	25	39

* Sources of fertilizer: N = Ammonium nitrate, P = Super phosphate, K = Muriate of potash.

Soil pH measurement were obtained from a 1:1 soil-to-deionized water mixture. Organic matter was determined by the Walkley-Black (1934) method, dithionite-citrate-bicarbonate (DCB) soluble Fe, Al, and Mn were extracted by the Mehra and Jackson (1960) procedure, and exchangeable (1 M KCl) Al by the Barnishel and Bertsch (1982) technique. Elemental concentrations from these extractions were determined by inductively-coupled argon plasma spectroscopy.

4-2.3 Adsorption Isotherms

Three-gram (3.0 g) sub-samples of air dried soil were weighed into nine 100-mL polypropylene centrifuge tubes. Fifty mL of 0.01 M CaCl_2 solutions with nine P concentrations between 0-200 $\mu\text{g ml}^{-1}$, i.e., 0, 1, 5, 10, 15, 25, 50, 100, and 200, were added to the tubes. The tubes were stoppered and shaken twice daily for 1 minute over a six-day period at laboratory temperature (22 °C) to achieve an equilibrium. Samples were then centrifuged (14,500 x g), and filtered through a Whatman number 42 filter paper. Phosphorus in the filtrate was determined by inductively-coupled argon plasma emission spectroscopy. All analyses were completed in duplicates.

Ideally, the adsorption should be determined in a system in which the surface would be free of the adsorbate ion. Usually, the ideal conditions are not feasible and a correction for initial surface phosphate is required. The correction was carried out by adding a amount of surface desorbed phosphorus to the adsorbed P (x/m $\mu\text{g/g}$) value. The need for a similar correction was identified and used by Olsen and Watanabe (1957).

The correction values were greater in the P fertilized than in the control treatments in the both soil groups. Average data from these P analyses, which were completed in duplicate, were plotted by the basic Langmuir model

$$\frac{x}{m} = \frac{V_m bc}{(1 + bc)} \quad 3.6$$

and by the two-site Langmuir model,

$$\frac{x}{m} = \frac{V_{m1} b_1 c}{1 + b_1 c} + \frac{V_{m2} b_2 c}{(1 + b_2 c)} \quad 3.7$$

Where, x/m is P sorbed at C , i.e., the concentration of P in solution,

b = the coefficient related to the free energy of transfer of P from solution to soil,

V_m = the adsorption maximum of volume of monolayer ($\mu\text{g P g soil}^{-1}$),

and the subscripts represent discrete energy sites and V_{m_n} represents the adsorption capacity due to sites of the n th discrete energy. Total maximum adsorption capacity of the soil is $= V_{m1} + V_{m2}$. The tangential buffering capacity (TBC) was calculated by substituting for C into the first derivative of x/m (Keramidas and Polyzopoulos, 1983):

$$TBC(C) = \frac{V_{m1} b_1}{(1 + b_1 C)^2} + \frac{V_{m2} b_2}{(1 + b_2 C)^2} \quad 3.8$$

where, Vm_1 , Vm_2 , b_1 and b_2 were estimated parameters. The maximum buffer capacity (MBC), the slope of the adsorption curve at solution P concentration (c)=0, is

$$MBC = Vm_1b_1 + Vm_2b_2.$$

4-2.4 Extractable P Analysis

Extractable P was determined by the Bray 1 (0.025 M HCl + 0.03 M NH_4F) method as described by The Council on Soil Testing and Plant Analysis (1980), the Mehlich 1 (0.05 M HCl, 0.0125 M H_2SO_4) method as described by Nelson and Mehlich (1953), the Mehlich 3 (0.015 M NH_4F + 0.25 M NH_4NO_3 + 0.2 M CH_3COOH + 0.013 M HNO_3 + 0.001 M EDTA) method as described by Mehlich (1984), and the Olsen P (0.05 M $NaHCO_3$ at pH 8.5) method as described by Olsen and Sommers (1982). Analyses were done in duplicate and, hence all values are averages of two replicates. In all methods, soil P was extracted in 100 mL polyethylene centrifuge tubes with a reciprocal shaker at recommended speeds for each procedure. After the centrifugation, supernatant was filtered through Whatman no. 42 filter paper. Extractable P contents by the four methods were determined colorimetrically by the molybdate blue-ascorbic acid method (Murphy and Riley, 1962) with a Hitachi Model 100-20 spectrophotometer.

4-2.5 Sequential Fractionation of Inorganic and Organic P

Sequential fractionation of inorganic soil P was carried out by the modified Chang and Jackson (1957) procedure of Peterson and Corey (1966). The procedure was further

modified as follows: to extract occluded P followed by reductant soluble P, residue soil sample was shaken for two hr with 0.2 M NaOH (50 mL). After each extraction, the suspensions were centrifuged 10 minutes at 14,500 x g in 100 mL tubes. The supernatant was filtered through Whatman no. 42 filter paper prior to P determinations, and the soil residue was washed twice with 25 mL of supersaturated NaCl solution to remove excess reagents.

Soil organic P (OP) was determined by the sequential extraction procedure described by Bowman (1989). The organic P contents were calculated as:

Acid extractable organic P (AEOP) = Total acid extractable P (TAEP) - Acid extractable Inorganic P (AEIP),

Base extractable organic P (BEOP) = Total base extractable P (TBEP) - Base extractable inorganic P (BEIP),

Total organic P (TOP) = AEOP + BEOP,

Total P (TP) = TAEP + TBEP, and

Residual P (RP) = TP - (sum of all inorganic fractions + TOP).

All inorganic and organic P fractions, except the reductant soluble P fraction, were determined by the Murphy and Riley (1962) procedure with the modifications given in Table 4-2. The reductant soluble P was determined as described by Olsen and Sommers (1982).

Table 4-2. Modified P determination procedures for NaOH and NH₄F fractions.

Fraction	Procedure
0.1 M NaOH - P 0.2 M NaOH - P	<p>1. <u>Decoloration</u> -</p> <p>Step I. Mix 5 mL supernatant with 0.5 mL NaOCl (4 - 6% NaOCl) and allow to stand for 1 hour.</p> <p>Step II. To eliminate extra oxidant (NaOCl), add 10 mL of 10% ascorbic acid and allow to stand for 10 min.</p> <p>Determine P in the decolorized 0.1 M NaOH and 0.2 M NaOH extracts.</p>
NH ₄ F - P	<p>1. <u>Decoloration</u> - (as above)</p> <p>2. <u>Elimination of F⁻ interference</u> -</p> <p>Add 10 mL of 1.5% H₂BO₃ solution and allow to stand for 30 min.</p> <p>Read NH₄F - P</p>

4-2.6 Clay Mineral Identification

Prior to mineralogical analysis, samples were pre-treated to remove organic matter (Kunze, and Dixon, 1986) and free iron oxide (Mehra and Jackson, 1960). The less than 0.002 mm (< 0.002 mm) fraction was prepared for clay separation according to the procedure by Jackson (1956). Oriented clay mounts were prepared by deposition of approximately 250 mg in suspension on an unglazed ceramic tile mounted on suction apparatus (Rich and Barnishel, 1977). Mineral identification was obtained through X-ray diffractograms (L.W. Zelazny, Personal communication). Kaolinite and gibbsite were quantified by mass-equivalent calibration of endothermic peak areas for poorly crystalline Georgia kaolinite and Reynolds synthetic gibbsite as standards. Other minerals were quantified using the following relationship:

$$I_x/I_k = C(M_x/M_k) \quad 3.9$$

Where,

I_x and I_k = integrated intensities of the unknown mineral and kaolinite,

C = a constant determined empirically as the slope of I_x/I_k vs M_x/M_k for known mixture of a standard mineral and kaolinite, and

M_x and M_k = masses of the unknown minerals and kaolinite, respectively.

The value M_k for the samples studied was taken as the mass percentage of kaolinite as determined from DSC calibration.

4-2.7 Greenhouse Procedure With Corn

Samples for the greenhouse study were obtained from the Ap horizon (0 - 15 cm) of the Davidson and Tatum soils which were used in the adsorption isotherm study (Table 4-1). Both fertilized and non-fertilized soils were again divided into two greenhouse P treatments, i.e., 0 and 70 P mg kg⁻¹ as Ca(H₂PO₄)₂. Samples from the Davidson clay loam (pH 5.4) were treated with CaCO₃ 1500 mg kg⁻¹ to neutralize soil acidity. The following quantities of soil amendments were mixed with each 3.33 kg soil: boron 0.5 mg B kg⁻¹ (H₃BO₃), manganese 15 mg Mn kg⁻¹ (MnCl₂ · 4H₂O), zinc 10 mg Zn kg⁻¹ (ZnSO₄ · 7H₂O), copper 10 mg Cu kg⁻¹ (CuSO₄ · 5H₂O), magnesium 40 mg Mg kg⁻¹ (MgSO₄ · 7H₂O), nitrogen 75 mg N kg⁻¹ (NH₄NO₃), and potassium 75 mg K kg⁻¹ (KCl). The amended soils were divided into three equal portions and placed into three plastic pots covered with polyethylene sealant for the three replicates. The pots were watered to field capacity and left for one week to equilibrate the soil before planting corn (*Zea mays* L).

The corn variety Pioneer 3163 seeds was planted at the rate five seeds per pot and thinned to 2 seedlings after five days. The experiment was arranged as a randomized complete design. Pots were irrigated daily to maintain the moisture level at the field capacity and rotated daily. Twenty mg N kg⁻¹ and 10 mg K kg⁻¹ per pot after thinning and weekly thereafter for 3 weeks. Seedlings were harvested after 3 weeks and dry weights obtained at 70 °C. The oven-dried plant samples were ground to pass through 20 mesh stainless steel sieve and used for tissue analysis.

4-2.8 Tissue Analysis

One gram of oven dried (70 °C) plant tissue samples were weighed into 100 mL Folin wu tubes and digested in a $\text{HNO}_3\text{-HClO}_4$ mixture (Gaines and Mitchell, 1979). After cooling, the samples were brought to a volume of 50 mL with 1.2 M HCl, mixed, and filtered through Whatman number 42 filter paper. Solution P contents were determined colorimetrically by a molybdate-vanadate yellow color method (Jackson, 1958) with a Hitachi Model 100-20 spectrophotometer.

4-2.9 Statistical Analysis

Plant tissue P contents, dry matter yields, and plant uptake data for the two soils and two P treatments were analyzed by analyses of variance. Mean separation was completed by the Tukey test. A nonlinear regression method was used to fit averaged values of the duplicated P sorption data to the original and two surface model Langmuir equations. The residual sums of square (RSS) values of the two models were calculated and compared for selection of the best fit of the equations.

4-3 RESULTS AND DISCUSSION

4-3.1 P Adsorption

Phosphorous adsorption isotherms for the long-term P fertilization and control (no P fertilizer) treatments in the Davidson clay loam and Tatum silt loam soils are illustrated in Figure 4-1. These isotherms show basic characteristics of a L-curve isotherm (Sposito, 1984). Phosphorus sorption by the four treatments had a strong initial phase with a relatively steep slope at low equilibrium concentrations, and then a weaker sorption phase at high concentrations with a decreasing slope which does not approach an asymptotic maximum within the P concentration range of the experiment. The strong adsorption phase is attributed to the existence of unoccupied high affinity sorption sites on the soil surfaces (Pratt et al., 1989; Agbenin and Tiessen, 1995). The weaker reaction phase is probably due to penetration of phosphate into Fe and Al (hydro)oxides-crystals or insertion between aggregates of microcrystals (Barrow, 1989).

The curvilinear form of the single site Langmuir model fitted to data is presented in Figure 4-2. Given the curvilinear nature of the data, it is evident that the original Langmuir model (monolayer model) tend to overestimate P adsorption at moderate levels of equilibrium P concentrations, and underestimate P adsorption at high concentrations. It can be seen that, when the original Langmuir model is used, a close fit to the equations

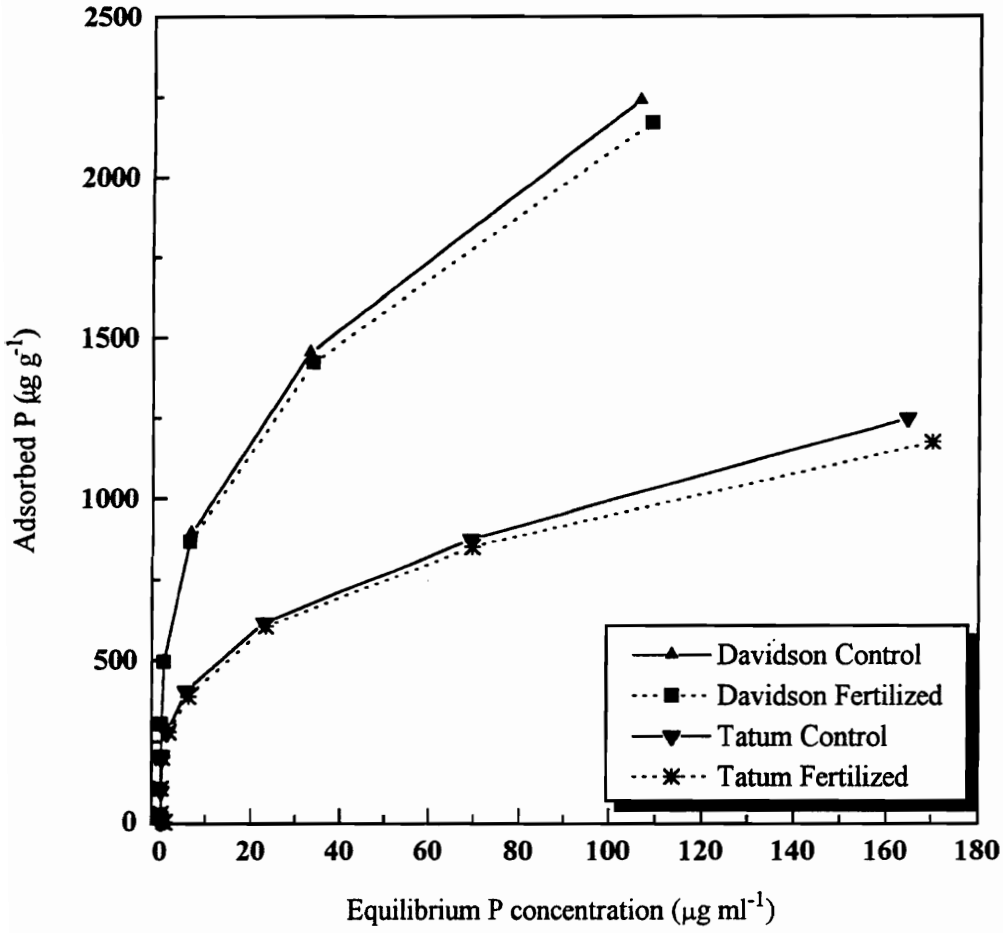


Fig. 4-1. Phosphate adsorption isotherms for four soils.

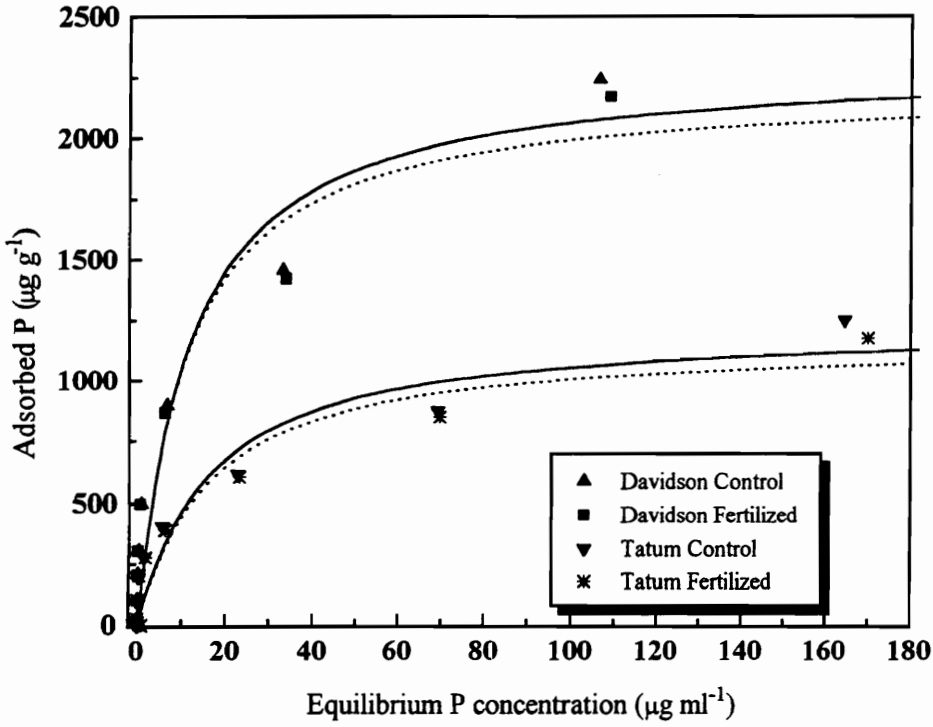


Fig. 4-2. Curvilinear Langmuir isotherms for phosphate adsorption by four soils.

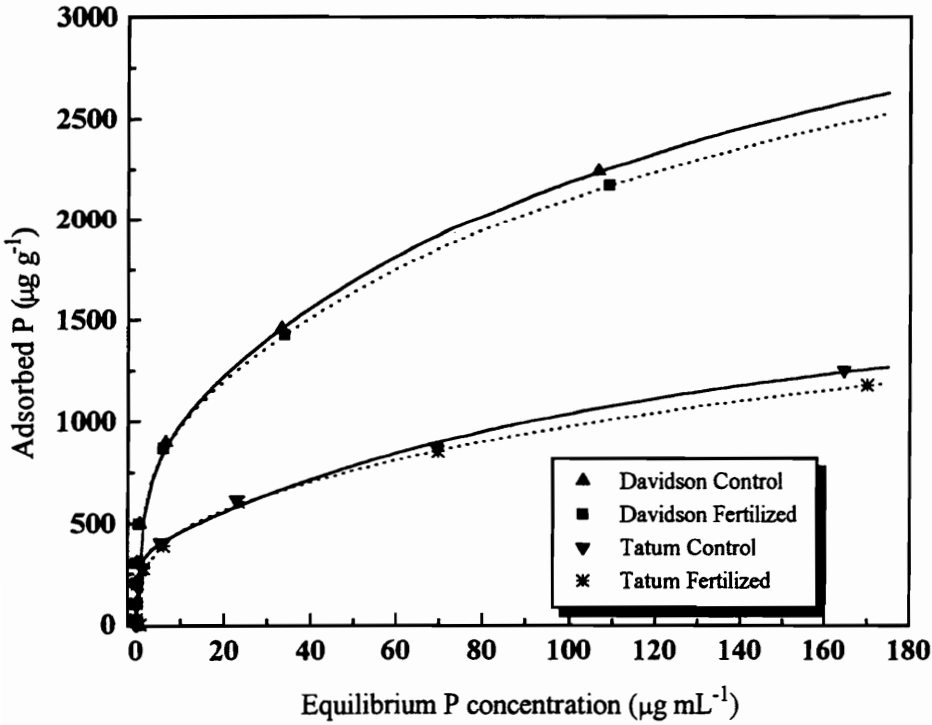


Fig. 4-3. Two site langmuir isotherms for phosphate adsorption by four soils.

can be obtained at lower concentration range, i.e., less than 15 mg L^{-1} (Sanyal and De Datta, 1991).

The two-site Langmuir model fitted to the data is shown in figure 4-3. It can be seen that the model fits the data closely and is free of the estimation problems observed in the original Langmuir model. The goodness of fit of the two models for the four treatments is examined by the residual sums of squares shown in Table 4-3. The statistical data show that, in all cases, the magnitude of the error for the two-site model is much smaller than for the one-site model. The lower error in the two site model implies the existence of multiple adsorption sites, or the involvement of adsorption sites which have widely different affinities for P (Muljadi et al., 1966a, 1966b, 1966c; Kuo, 1988). The soils used in the study are highly weathered and have been cultivated over a long duration. Thus, the observed behavior is compatible with such soils which tend to contain high amounts of clay and Fe_2O_3 .

The adsorption parameters estimated from the conventional and two-site Langmuir models are given in Table 4-4. The calculated adsorption maximum for the two-site model ($V_{m1} + V_{m2}$) shows an increase of about 42% over that of the original Langmuir model. This increase is lower than the increases of 48-140 percent reported in the literature (Holford et al., 1974; Gunary, 1970). The adsorption maxima for the non-fertilized control treatments were higher than for the fertilized treatments in the two soils.

Table 4-3. Residual sums of squares of the basic and two site Langmuir models.

Soil	Residual sums of square x 10 ³	
	Basic Langmuir model	Two site Lagmuir model
Davidson -Control	124.6	13.0
Davidson - Fertilized	106.3	51.0
Tatum - Control	341.6	185.8
Tatum - Fertilized	369.7	217.2

Table 4-4. Adsorption parameters obtained from the Langmuir models for four soils.

Soil	Adsorption Maxima ($\mu\text{g g}^{-1}$)				Binding Constant		
	Langmuir	Two site Langmuir		Langmuir	Two site Langmuir		
		Vm1	Vm2		Total	b1	b2
Davidson - Control	2308.9	898.5	3108.5	4007.0	0.086	0.665	0.007
Davidson-Fertilized	2211.9	875.5	2967.5	3843.0	0.092	0.765	0.007
Tatum - Control	1242.2	424.6	1754.3	2178.8	0.062	0.748	0.007
Tatum - Fertilized	1165.5	398.4	1635.5	2033.9	0.072	0.821	0.005

However, difference in P sorption maximum was not markedly different between the fertilized and non fertilized treatments. The small difference in P adsorption suggests that the fertilized and non-fertilized soils had similar numbers of unoccupied adsorption sites. Previously Kurtz and Quirk (1965) observed little or no reduction in adsorption maxima as a result of the past fertilization of a red brown earth from south Australia, but residual effects of P application were evident in brunizen and lateritic soils. Mullins (1991) reported that in southern United States, long-term P fertilization had a small influence on the adsorption capacity for recently added P.

Adsorption maxima (Table 4-4) show that the difference in P adsorbed to high affinity sites identified by V_{m1} was small between the fertilized and non-fertilized soils. These sites accounted for 23 percent of P adsorbed in the Davidson soil and 20 percent of P adsorbed in the Tatum soil. The difference in P adsorbed to low-affinity sites was greater both in absolute terms and relative terms. The rapid initial-phase P adsorption is caused by an inner-sphere complexation mechanism (McBride, 1994). In the high affinity phase, the adsorbed P is incorporated into the adsorbent structure with transfer of its charge to the surface (White and Zelazny, 1986). Thus, P adsorbed during this initial adsorption phase is transformed to crystalline forms. As the solution P concentrations in the soil increases, Al-P and Fe-P transformation occurs at a faster rate (Hsu, 1982a, 1982b). Juo and Ellis (1968) reported that Fe-P crystallization rate is faster than that of

Al. As soil undergoes weathering new adsorption sites are created and these sites enable the soils to adsorb P even after irreversibly reaction of P with original sites.

The low affinity adsorption phase P is not strongly held as initial phase P (Barrow, 1987). Therefore, P adsorbed in this phase replenishes the P removed from soil solution due to microbial and plant uptake. The rate of P crystallization from this loosely held P is lower than for the rapid initial-phase adsorbed P. In this study, the number of occupied adsorption sites in the fertilized soils do not appear to be considerably lower than those of the non-fertilized soils. This small difference in available P sorption sites may be related to the fact that the rates of P fertilization were only marginally higher than the P removal levels of corn. A crop of corn producing a grain yield of 9.5 tons/ha removes about 27 kg P/ha (Mengel and Kirkby, 1987). Thus, the net amount of retained fertilizer P content in the fertilized soil could have been relatively low.

The b_1 and b_2 coefficients of the two-site Langmuir model represent the free energy of transfer of PO_4^{3-} from solution to solid adsorbent surfaces of soil (Table 4-4). The b_1 coefficient represents free energy required for initial structural adsorption mechanisms. Structural adsorption of PO_4^{2-} by inner-sphere complexation reactions has high free energy requirements. The adsorption phase represented by b_2 is a low-energy consuming physisorption process that consists of both adsorption and precipitation reactions. In all cases binding energy values in the slower adsorption phase suggest that P is loosely held and quasi-equilibrated with soil solution P.

4-3.2 P Adsorption and Soil Properties

The rate of P adsorption in the Davidson soil is twice as large as that for the Tatum soil (Table 4-4). These differences in the adsorption rates can be associated with the various soil physical, chemical, and mineralogical properties below. The Davidson soil has a higher clay content (40 %) than the Tatum soil (30 %) (Table 4-5) and, hence, has a larger surface area for P adsorption. Significant correlation between the clay content and the P adsorption levels have been reported for many soils (Fox and Kamprath, 1970; Syers et al., 1973; Loganathan et al., 1987; Wada et al., 1989). Clay mineral surfaces in highly weathered soils consist of fine coatings of Al and Fe hydrous oxides. These coatings effectively increase the surface area available for P adsorption. The high levels of P adsorption in the Davidson soil reflected this property.

Kaolinite constitutes 60 percent of the clay mineral fraction in the Davidson soil and 62 percent in the Tatum soil (Table 4-6). The Davidson soil with a higher clay content has a larger kaolinite content than the Tatum soil. The large number exposed OH groups in the Al layer of kaolinite crystals are preferred sites of P fixation (Muljadi et al., 1966b). In addition, edge faces of kaolinite develops pH dependent charges that can adsorb P. Furthermore, it is suggested that phosphate reacts with kaolinite to form Al-P, thereby moving the adsorption process towards greater fixation (Low and Black, 1950). Therefore, the differences in the kaolinite content may partially

Table 4-5. The selected soil physical and chemical properties for two soils.

Parameter	Davidson soil	Tatum soil
pH (1:1, soil:water)	5.4	6.2
OM (%)	2.5	2.1
Texture - sand (%)	20.4	24.5
silt (%)	39.6	45.1
clay (%)	40.0	30.4
Exchangeable Al (mg kg ⁻¹)	3.9	4.0
DCB extractable - Fe ₂ O ₃ (%)	16.7	6.5
Al ₂ O ₃ (%)	1.5	0.8
Mn (mg kg ⁻¹)	3795.0	178.1

Table 4-6. Mineralogical composition of the clay (< 2 μm) fraction for the two soils.

Mineral	Davidson soil	Tatum soil
	(%)	
Kaolinite	60.0	62.0
Interstratified	-	22.0
Intergrade	27.0	-
Vermiculite	-	10.0
Mica	10.0	5.0
Gibbsite	0.2	-
Quartz	2.0	1.0

explain the higher P adsorption rate observed in the Davidson soil compared to the Tatum soil.

Dithionite-citrate-bicarbonate extractable Fe_2O_3 and Al_2O_3 contents are greater in the Davidson soil (16.7% and 1.5%) than in the Tatum soil (6.5% and 0.8%) which has a greater exchangeable Al content (Table 4-5). The DCB extractable Fe and Al contents in the Davidson soil (18%) and more than double that of the Tatum soil. The larger adsorption maxima in Davidson soil (Table 4-4) is probably due to the presence of higher Fe_2O_3 and Al_2O_3 , which increase the P adsorption capacity of soils. The specific adsorption of P on Al and Fe hydrous oxides has been attributed to replacement of OH_2 and OH groups by P in either monodentate (M- H_2PO_4 -M) or a bidentate (M-O-(POOH)-O-M) linkage (Hingston et al., 1974). Bingham et al. (1978) showed that dark red clay soils, which is very similar to the soils studied, were dominated by hematite (67%) and substantial amount of goethite (33%). These minerals are derived toward terminal stages of the weathering process, and are capable of fixing considerable amounts of P (Torrent et al., 1994). Removal of DCB extractable Fe and Al decreases P adsorption (Torrent, 1987; Weindt et al., 1993), i.e., eliminates the slow adsorption phase, which is probably associated with penetration of phosphate inside Fe and Al (hydro)oxides crystals or between aggregates. Overall, the large amount of Fe_2O_3 in the Davidson soil induces high P adsorption during both rapid phase and the slower phase, which explains the very high P adsorption by the Davidson soils.

Soil pH in the Davidson is lower than in the Tatum (Table 4-5). The charge and the electrostatic potential of positive pH dependent adsorption sites are increased at the lower pH. At low pH, the higher Al and Fe activities contribute to the higher adsorption capacity observed in the Davidson soil. The same relationship has been observed in previous studies by Bolan et al. (1988) and Adams and Odom (1985).

4-3.3 Dynamics of Soil P and Extractable P

The two soils in the study were annually planted to corn, and fertilized at two P rates for over three decades (Table 4-1). The high degree of weathering undergone by the Davidson soil, compared to Tatum soil which is in the same taxonomical order and physiographic region, is evident from its high clay content, DCB extractable Fe_2O_3 and Al_2O_3 contents, dark red color, and the presence of gibbsite (Table 4-5 and 4-6). These characteristics may influence P dynamics and fertility in the two soils. The fractionation scheme used in the study was designed to separate as many P fractions as possible.

The total P in the <2 mm soil fraction in control and fertilized treatments in the Davidson soil are 0.22 percent and 0.30 percent respectively (Table 4-7). In the Tatum soil, the P quantities are lower than that of Davidson soil, i.e., by 0.09 and 0.14 percent in the control and fertilized treatments, respectively. These P values are greater than the average total P content of 0.05 percent reported for a range of soils (Lindsay et al., 1989). The total native soil P content is a factor of the primary and secondary phosphate

Table 4-7. Acid and base extractable inorganic and organic P fractions and total P in the <2mm sized fraction of two soils.

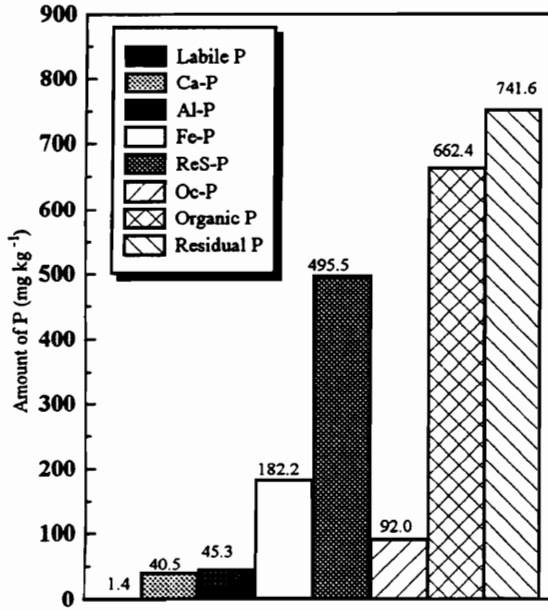
Soil	AEP	AEIP	AEOP	BEP	BEIP	BEOP	Total P
	(mg P kg ⁻¹)						
Davidson - Control	2031.3	1377.5	653.8	241.9	332.8	9.1	2273.2
Davidson -Fertilized	2609.4	1805.0	804.4	287.8	281.9	6.0	2997.3
Tatum - Control	837.5	487.5	350.0	87.8	80.9	4.9	923.3
Tatum - Fertilized	1275.0	800.0	475.0	98.0	95.6	2.4	1373.0

AEP = acid extractable P; AEIP = acid extractable inorganic P; AEOP = acid extractable organic P;
 BEP = base extractable P; BEIP = base extractable inorganic P; BEOP = base extractable organic P.

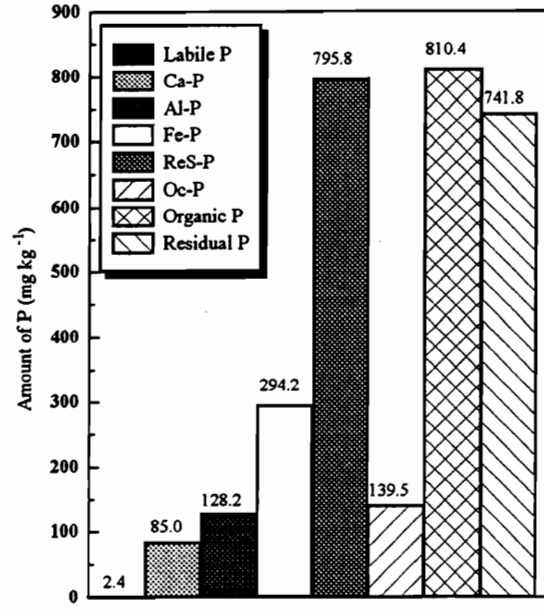
minerals in the soil. The type and composition of the P minerals are determined by the chemistry of the parent material and the degree of weathering (Nariagu, 1976; Lindsay, 1989). Additionally, the decomposition of plant and animal debris and fertilizer applications alter soil P levels. The addition of fertilizer increased the total P content in the Davidson soil by 32 percent and in the Tatum soil by 49 percent (Table 4-7). The Tatum soil has a low native P content, and is reported to give lower corn yields than the Davidson soil (Donohue and Heckendorn, 1994).

The distribution of eight different P forms in the fertilized soils and non-fertilized controls are shown in the Figure 4-4. In the Davidson soil, the order of non-labile P fractions from high to low concentrations is residual P > organic P > reductant soluble P > occluded P in the non-fertilized and organic P > reductant soluble P > residual P > occluded P in the non-fertilized soil. The order in the Tatum soil is organic P > residual P > reductant soluble P > occluded P in the non-fertilized soil and organic P > reductant soluble P > residual P > occluded P in the fertilized soil. The P fractions that are labile pool to moderately labile pools are distributed Fe-P > Al-P > Ca-P > labile P in both soils (Table 4-8). All P fractions are increased by the application of fertilizer.

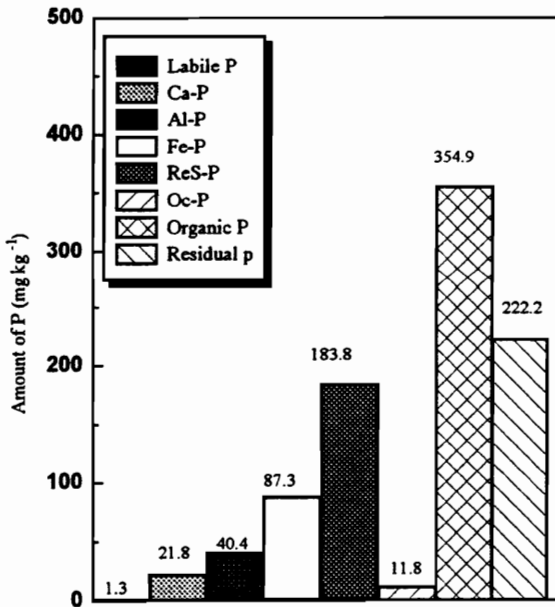
The residual P fraction which represents P held in primary and secondary silicate minerals accounts for the highest (33%) native P content in the Davidson soil (Table 4-8). This high residual P content in the Davidson soil can be attributed to the differences in



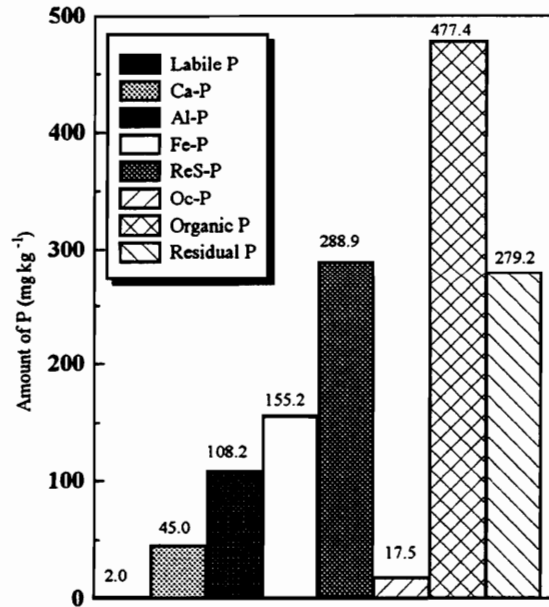
Davidson soil - Control



Davidson soil - Fertilized



Tatum soil - Control



Tatum soil - Fertilized

Fig. 4-4. Distribution of P forms in two soils by long term P fertilizer treatments.

Table 4-8. Percent change of P form due to fertilization and distribution of P forms as a percent of total P in two soils.

Forms of P	Davidson Soil				Tatum Soil			
	% Change*		% of Total P		% Change*		% of Total P	
	Control	Fertilized	Control	Fertilized	Control	Fertilized	Control	Fertilized
Labile P	71	0.1	0.1	0.1	50	0.1	0.1	0.2
Ca-P	110	1.8	2.8	2.8	107	2.3	2.3	3.3
Al-P	182	2.0	4.3	4.3	168	4.4	4.4	7.9
Fe-P	62	2.0	9.8	9.8	78	9.5	9.5	11.3
Reductant soluble P	61	21.8	26.6	26.6	57	19.9	19.9	21.0
Occluded P	52	4.1	4.7	4.7	49	1.3	1.3	1.3
Organic P	22	29.1	27.0	27.0	34	38.4	38.4	34.8
Residual P	-1	33.1	24.8	24.8	15	24.1	24.1	20.3

* Change due to P fertilization

the parent material and high kaolinite, and mica contents in its clay fraction. The residual P content in the Tatum soil is relatively low.

The reductant soluble P is the largest extractable P fraction in the two soils (Figure 4-3). The reductant soluble fraction accounts for 29 percent of the total P content in the control treatments in the Davidson soil, in which fertilizer applications increased this P content by 61 percent (Table 4-8). In the Tatum soil, the reductant soluble fraction accounts for 20 percent of the total P content, and this quantity was increased by 57 percent from fertilizer application.

The very high reductant soluble P contents in the native and fertilized Davidson and Tatum soils suggest that strongly bound P (inner sphere complexation) associated with the rapid-phase of adsorption isotherm is probably transformed into reductant soluble form (Table 4-5). Overall, the Davidson soil contains a larger portion of the total P content as occluded P than the Tatum soil. Smeck (1985) has suggested that occluded P is encapsulated by gibbsite of which the concentration is greater in the Davidson soil than in the Tatum soil.

Of the inorganic P fractions that are considered to be moderately labile to labile (Al-P, Ca-P, Fe-P, and $\text{NH}_4\text{Cl-P}$), the largest increases by P fertilization are in the Al-P and Ca-P fractions (Table 4-8). However, as a percent of total P content, Fe-P is greater than both Al-P and Ca-P. This relationship suggests the tendency for both native P and residual P to form Fe-P, because Fe-P formation is accelerated under conditions such as high soil Fe content and low pH (Hsu, 1982).

Organic P is the dominant native P form in both Davidson and Tatum soils and remains dominant even in the fertilized soils (Table 4-8 and Figure 4-4). The Davidson and Tatum soils have a high clay and Fe_2O_3 contents which are conducive for retaining organic P. The two soils had fairly similar organic matter contents. Organic matter has a favorable effect on P adsorption through formation of Fe and Al chelates (Saunders, 1965).

Bray 1, Mehlich 1, Mehlich 3, and Olsen extractable soil P contents are presented in Table 4-9. Olsen extractable P content is the largest in the Davidson soil followed by Bray 1 > M 3 > M 1 procedures. In the Tatum soil, the extractable P contents are in the order Bray 1 > M3 > Olsen > M 1. The high Olsen extractable P contents in the Davidson soil probably result from high Fe-P and organic-P contents in that soil. The Olsen method extracts more Fe-P from soil by forming strong chelated Fe complexes with organic matter thus reducing reprecipitation reactions (Ballard, 1974). Also Olsen procedure extracts P directly from organic P (Bowman and Cole, 1978; Headly, 1982b). The control treatments in the Davidson and Tatum soils have low levels of extractable P by the M 1 and Bray 1 methods compared with the reported standard yield calibration data for the procedures (Olsen and Simmers, 1982). The extractable P contents by all four methods were higher in the P fertilized soils applied with fertilizer (Table 4-9), and fell in the medium soil P category or high category based on the calibration data.

Table 4-9. Extractable P by four soil test methods, and estimated P buffering capacity and intensity values in two soils.

	Extractable P			Olsen (mg P kg ⁻¹)	Buffering capacity (mg kg ⁻¹)	Intensity values (mg P kg ⁻¹)			
	Mehlich 3 (mg P dm ⁻³)	Mehlich 1	Bray 1			Mehlich 3	Mehlich 1	Bray 1	Olsen
Davidson - Control	7.3	5.7	12.7	44.1	619.3	0.01	0.01	0.02	0.07
Davidson - Fertilized	28.2	21.7	38.6	49.4	690.6	0.04	0.03	0.06	0.07
Tatum - Control	6.9	6.2	7.9	5.9	329.9	0.02	0.02	0.02	0.02
Tatum - Fertilized	26.1	19.5	32.6	22.8	335.3	0.08	0.06	0.10	0.08

4-3.4 Relationship Between Soil P and Plant P

Table 4-10 shows dry matter yield, tissue P content, and plant uptake data from the greenhouse experiment with corn. Tissue P contents in corn grown in the previously fertilized soil are above the sufficiency range (0.2 %) with or without fertilizer application for the Davidson soil. For the Davidson soil that had not received fertilizer P, the tissue P content increased above the sufficiency range only with application of 70 mg P kg⁻¹ soil. Tissue P concentration in corn growing in both previously fertilized and non-fertilized Tatum soil were below the sufficiency range. With addition of P fertilizer, the tissue P concentration increases above the sufficiency level in the Tatum soil that received P application in the field. The results suggest that in the Davidson soil the residual effect is strong enough to supply adequate P quantities for a corn crop. In the Tatum soil, even though the extractable P contents were adequate according to soil test calibration, the availability of residual soil P was not adequate for growth of corn.

Phosphorous buffering capacities for the two soils calculated from adsorption isotherms are shown in Table 4-9. The Davidson soil has a buffering capacity twice as large as that of the Tatum soil. The higher buffering capacity of the Davidson soil compared to the Tatum soil can be attributed to the higher clay and kaolinite, and DCB extractable Fe₂O₃ and Al₂O₃ contents.

The solution P concentration of the soils known as the intensity factor was determined using the extractable P contents (quantity factor) and the buffering capacities of the two soils. These values ranged from 0.03 - 0.07 µg P mL⁻¹ in the Davidson soil

Table 4-10. Effect of P application on corn - greenhouse experiment.

	Davidson Soil			Tatum Soil		
	Control*	Fertilized**	Fertilized**	Control ⁺	Fertilized ⁺⁺	Fertilized ⁺⁺
Measurements	0	70	0	70	0	70
Dry matter weight (g)	1.3	3.2 ^{aa}	4.0	2.4	3.2 ^a	3.9 ^a
Tissue P (%)	0.15	0.21 ^{aa}	0.23	0.15	0.19 ^a	0.21 ^a
Plant uptake (mg / pot)	2.0	6.8	9.2	3.6	6.2	8.2

* No fertilizer P for 34 years

** Received fertilizer P for 34 years at the rate 30 kg P ha⁻¹

+ No fertilizer P for 39 years

++ Received fertilizer P for 39 years at the rate 25 kg P ha⁻¹^{aa} Treatment difference (0 and 70 mg P kg⁻¹) is significant at p = 0.01.^a Treatment difference (0 and 70 mg P kg⁻¹) is significant at p = 0.05.

and $0.08 - 0.10 \mu\text{g P mL}^{-1}$ in the Tatum soil (Table 4-9). These values are lower than the critical level of $0.2 \mu\text{g P mL}^{-1}$ reported in the literature (Fox and Kamprath, 1970; Juo and Fox, 1977). However, tissue P concentration data discussed above showed that the Davidson soil was able to provide sufficient P to corn plants while Tatum soil provided insufficient plant P contents. It has been shown that, at intensity factors as low as $0.03 \mu\text{g P mL}^{-1}$ grasses could absorb sufficient P contents (Christie and Moorby, 1975). These results are in agreement with the explanation by Singh et al. (1966) that under adequate moisture conditions the soils with higher clay contents have a greater capacity to replenish P into soil solution and have rapid rates of diffusion of P from soil surfaces to plant roots. The Davidson soil has a buffering capacity twice as large as that of the Tatum soil. Thus, even with an intensity factor consistently below that of the Tatum soil, the Davidson soil was able to supply plant P needs better.

4-4 CONCLUSIONS

Phosphorous adsorption behavior in the Davidson clay loam and Tatum silt loam soils was described very well by the two-site Langmuir model. phosphorus adsorption maxima in the non-fertilized treatments were $4,007 \mu\text{g P g}^{-1}$ in the Davidson soil and $2,179 \mu\text{g P g}^{-1}$ in the Tatum soil. In the Davidson soil, 23 percent of the total adsorption capacity was accounted by the high-affinity adsorption phase (V_{m1}). The high-affinity phase associated with P adsorption capacity in the Tatum soil was 20 percent. The maximum P sorption capacities of the soils were slightly (5%) decreased by the long term application of P.

The Davidson soil has a 83 percent higher P adsorption capacity and 88 percent higher buffering capacity than the Tatum soil. The differences in factors such as Fe_2O_3 , Al_2O_3 , kaolinite, gibbsite, clay content, and soil pH explained the higher P adsorption capacity of the Davidson soil. The influence of soil parent material and weathering intensity on the level of these factors caused the sharp difference in P adsorption, even though the two soils were in the same taxonomic order and physiographic region.

Fertilizer application increased all organic and inorganic P fractions in the Tatum soil and all except the residual P fraction in the Davidson soil. Of the P fractions considered to be non-labile, the largest increase is occurred in the reductant soluble P fraction in both soils. phosphorus structurally adsorbed by inner sphere complexation were transformed into non-labile forms, such as occluded and reductant soluble P in the

presence of structural forms of iron hydrous oxides such as hematite and goethite, which are commonly found in reddish color soils. A decline in the P adsorption capacity did not occur, even after irreversible reaction of applied P with the original sites, due to freeing of occupied sites with conversion of adsorbed P into non-labile forms and to creation of new adsorption sites with weathering. The largest increases by P fertilization in the labile pool P occurred in the Al-P and Ca-P fractions, but as a percent of total P content Fe-P is greater than both of these P fractions.

Bray 1, Mehlich 1, and Mehlich 3 extracted low levels of P in the non-fertilized soils as compared with standard yield calibration data for the procedures. Fertilizer application increased all extractable P contents in the two soils. Residual fertilizer P effects in the fertilized Davidson soil at 30 kg P ha^{-1} were adequate to maintain corn tissue P concentrations in the sufficiency range. Although extractable P contents in the Tatum soil were in the medium range of the standard calibration, the corn tissue P concentrations were below the adequate range.

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The performance of Bray 1, Mehlich 1, Mehlich 3, and Olsen extractants in the estimation of phosphorus (P) contents was evaluated for 43 soils with diverse physical and chemical properties. The relationships between extractable P content and soil physical and chemical properties, the contribution of various soil P forms to the extractable P content, and the effects of long-term P application on the phosphate adsorption, soil P transformation, and extractability by four soil test methods were investigated. The major conclusions from these investigations are summarized as follows:

1. The highest extractable P quantities were obtained by the Bray 1 (5 m) method followed in order by Mehlich 3, Bray 1 (1 m), Mehlich 1, and Olsen procedures. Mehlich 3 extractable P quantities were highly correlated with Bray 1 and Mehlich 1 extractable P, but not with Olsen extractable P.
2. Bray 1, Mehlich 1, and Mehlich 3 extractable P quantities were decreased by the soil clay content. Therefore, to improve reliability of these soil tests, calibration for P should be performed for soils grouped by the clay content. Since Mehlich 3

extractable P quantities are not affected by changes in soil pH, this extractant can be used for P determination in a wide range of soils after calibration grouped by soil clay content.

3. The tendencies of the Bray 1 procedure to extract more non-labile P relative to M 3 and of the Olsen procedure to extract organic P that may not be available to plants limit the usefulness of these extractants as good indicators of available P in highly weathered soils.
4. The degree of P solubilization by different extractions was satisfactorily explained by an acid-catalyzed nucleophilic substitution reaction mechanism. This approach provided a sound basis for evaluating the usefulness of various soil extractants to represent plant available P contents.
5. The labile to moderately labile P fraction which constituted 26 percent of the total soil P content was distributed in the following order: Fe-P > Al-P > Ca-P > NH₄Cl-P, whereas the non-labile P fraction with 49 percent of the total P was distributed Residual P > Reductant-Soluble P > Occluded P. Soil organic P fraction accounted for the remaining 25 percent of the total P content.

6. The Fe-P content in the labile pool was affected by contents of iron-oxide and clay, and soil pH, whereas other labile P (i.e., Al-P, Ca-p, $\text{NH}_4\text{Cl-P}$) fractions were not similarly affected. The levels of different fractions in the labile pool P are interrelated. These data indicate that increased formation of Fe-P initially as Al-P and Ca-P contents are increased, and then conversion from Fe-P to reductant soluble P.
7. Phosphorus adsorption capacity of the soils was slightly decreased by long term P application. The transformation of Fe-P to reductant soluble P and the creation of new adsorption sites by weathering enables soils to retain its P adsorption power even after long term P application.
8. Phosphorus accumulation in the reductant soluble fraction increase the potential eutrophication problem of an agricultural soil. Thus, erosion and movement of Piedmont and high clay soils with high reductant soluble P and Fe-P contents into water bodies has a high potential to cause eutrophication problems.
9. Long term P application increased extractable P content in the Davidson and Tatum soils. Residual fertilizer P from past applications was adequate to maintain tissue P concentrations of corn planted in the Davidson soil, but not in the Tatum soil.

Recommendations for Future Research

1. Soil test calibration for P fertilizer recommendation, especially in the highly weathered soils should be carried out according to soil groups based on clay content.
2. The Organic P fraction in the soil is quantitatively as important as the labile inorganic P fraction. Some extractants such as the Olsen procedure extract a portion of organic P. In order to assess the plant availability of organic P, investigations are needed to determine factors that affect the mineralization and the rate of mineralization of organic P should be investigated.

VITA

The author was born in Galle, Sri Lanka on September 10, 1950. She completed her primary education at the Museus College, Colombo, and the secondary education at the Southlands Girls School, Galle. After completion of high school in 1972, she became a teacher in mathematics and science, and left that in 1974 to enter University of Peradeniya to study for a degree in agriculture. In 1978, she finished the B.S. degree in Agriculture with second class honors, and became an Assistant Lecturer in the Department of Agricultural Chemistry and Soil Science in the Faculty of Agriculture. She joined the Department of Agriculture as a Research Officer in 1980, and served at the Angunakolpelessa Regional Agricultural Research Center until 1983 as a Research Officer in Soil Science.

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