

AN ABSTRACT OF THE THESIS OF

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Abstract approved:

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The effect of different rates of organic and inorganic amendments on phosphorus (P) sorption characteristics, P speciation, and P distribution in different P fractions was studied in soils (Ultisols and Andepts) from Oregon and Rwanda. Measurements were made on soil samples which had been amended with wheat straw (*Triticum estivum*), composted steer manure, alfalfa (*Medicago sativa*), CaCO_3 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and incubated for 28 days. Manure and alfalfa addition increased pH, available P, and P concentration of the equilibrium solution and reduced exchangeable Al, affinity constant, adsorption maxima, and P sorbed to attain 0.2 mg P L^{-1} ($\text{P}_{0.2}$). Although the addition of CaCO_3 followed similar trends as manure and alfalfa it had less effect on available P content and affinity constant. Soils amended with CaSO_4 only had a reduction in exchangeable Al. Previous research suggested that organic acids associated with organic amendments affected P sorption. This study shows that high P content residues reduced P sorption. Adding manure and alfalfa increased biologically available P, labile inorganic P, and chemically sorbed organic and inorganic P. The increase in chemically sorbed inorganic P and labile inorganic P provides strong evidence that PO_4 mineralized from organic residues complex P sorption sites.

Characterization of the soil solution showed that dissolved organic C (DOC), pH, ionic strength and basic cations increased in the soils amended with manure. The P speciation predicted by GEOCHEM indicated that in the absence of P addition ($1000 \text{ mg P kg}^{-1}$), Al and Fe solubility was controlled by gibbsite and goethite, respectively. However, when F was present, Al was preferentially complexed with this ligand. In the presence of added P, strengite controlled Fe and P solubility. Calcium- PO_4 controlled P solubility only in soil amended with manure. The ion activity product showed that PO_4 was in equilibrium with amorphous-like variscite. When the organic acids measured in soil solution (malic, maleic, malonic, citrate, succinic, formic, and acetic) or those calculated by the mixed model were used as input in GEOCHEM citrate was the only acid that had a significant affect on P sorption. It complexed Al and Fe and prevented precipitation of strengite and Ca-PO_4 .

EFFECTS OF ORGANIC AND INORGANIC
SOIL AMENDMENTS ON PHOSPHORUS SORPTION

by

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EFFECTS OF ORGANIC AND INORGANIC SOIL AMENDMENTS ON PHOSPHORUS SORPTION

INTRODUCTION

Phosphorus is often unavailable for plant uptake in highly weathered soils (Ultisols, Oxisols) and in volcanic soils with high amounts of amorphous compounds. In these soils high rates of chemical P fertilizers and other P sources are required to maintain crop yield. Phosphorus deficiency is common in these soils because soluble P reacts readily with soluble Al and Fe, Al and Fe oxides or hydrous oxides which are characteristic of acidic soils.

These sorption mechanisms have been extensively studied with pure minerals such as gibbsite or goethite. However, it has been difficult to extrapolate these results to agricultural soil because natural soil is a heterogeneous medium made up of the mineral and organic fractions. The presence of organic material (organic matter and biomass) may modify the surface properties of soil minerals, change the soil reactions, and therefore affect the P sorption capacity of the mineral compounds.

In some volcanic ash soils organic matter may increase P sorption capacity because Al bound to organic matter in these soils is more reactive than Al bound to allophanic materials. However, in non-volcanic ash soils, there is a general belief that P sorption capacity of many soils is negatively correlated with organic C. The plant availability of P is generally higher in the surface horizon than in the deeper soil horizons. This is related to the presence of organic acids such as oxalate, citrate, and others that are capable of complexing Al and Fe or of competing with P for the P sorption sites on the surfaces of

various clay colloidal minerals present in the soils. Another probable mechanism is the action on P sorption by SO_4 and PO_4 added by organic residues. Organic residues presence prevents any further sorption of added P by complexing exchangeable Al and Fe, lowering Al and Fe activity in the soil solution, or by reacting with P sorption sites. The addition of organic matter should change the factors affecting P sorption (pH, exchangeable Al), increase extractable P in solution (Bray 1 P), and decrease P sorption capacity as measured by affinity constants and sorption maxima. If P sorption capacity is decreased, then less P will be required for maximum crop production. P sorption characteristics and constants may be determined using classic models such as Langmuir, Freundlich or others.

The effect of inorganic amendments (lime) on P sorption has been studied extensively and is well known. But, most studies with organic amendments have been conducted without comparison to inorganic amendments. Such a comparison utilizing CaCO_3 , which removes Al and changes pH, or CaSO_4 , which removes Al while leaving pH unchanged, would provide insight into how organic amendments can affect P sorption.

Soluble P when added to acid soil forms Al- or Fe- PO_4 mineral solids (variscite or strengite) and when added to alkaline soil forms Ca- PO_4 (octacalcium and hydroxyapatite). It is also adsorbed by several mechanisms on the surface of Al or Fe oxides and hydrous oxides or calcium phosphates. Therefore, if the hypothesis that PO_4 originating from organic residues complexes P sorption sites is correct, the addition of organic residues should increase the inorganic P fractions of solution PO_4 and Al, Fe, or Ca-compounds, and biologically available P. Most studies of the changes in P fractions in soils have been conducted using cellulose as the organic amendment (Harrison, 1987, Hedley et al. 1982a, Hedley et al 1982b, Chauhan et al. 1984). However, cellulose is not a very labile C source and does not provide other nutrients that would be provided by more complex organic residues such as animal manure or plant residues. The chemical fixation of P dominates over microbial immobilization and causes the reduction of P sorption capacity (Ghoshal 1985). There is little information under controlled conditions on the role

of organic amendments and mineralization in decreasing P sorption. Measuring changes in soil P fractions such as labile P and Al- or Fe-bound P fractions after addition of organic residues offers a way to verify the hypothesis that P from organic residues complexes the sites of P sorption in soil.

Some studies have demonstrated that the addition of lime changes the distribution of Al species with a concurrent increase in pH (Pavan et al. 1982). In a similar way, organic residues can influence soil solution speciation indirectly by a "self-liming" effect (Hue 1992). Organic compounds, as well as cations and anions from organic residues, may affect the composition of soil solution species. Although isotherm diagrams of solubility are used extensively and are valuable in understanding changes in P solubility boundaries, they do not reveal which species are in the soil solution. Knowing which various species might be formed could improve our understanding of how different ions interact and influence P species in the soil solution. Various P species (free, complexes and solid), present in the soil solution, can be estimated using the computer program "GEOCHEM" (Sposito and Mattigod, 1980).

The overall goal of this work was to provide information on the mechanisms by which organic residues decrease P sorption capacity in high P sorbing soils.

The specific objectives were to evaluate the effects of organic and inorganic soil amendments on:

- (1) P sorption;
- (2) P fractions; and
- (3) the formation of soluble and solid complexes in the soil solution of different types of soils.

CHAPTER I

LITERATURE REVIEW

Phosphorus (P) retention, also known as fixation, is generally understood to be the transformation of soluble forms of P fertilizers into less soluble forms (Alveredo, 1982). This mechanism includes the adsorption of P on the solid phases or its precipitation in the form of insoluble compounds such as variscite, strengite, Ca-PO_4 , and Mn-PO_4 .

The general cycle of P is summarized in Fig. 1.1. The mineral phase and the biological pool are the main components of this cycle. The microbial immobilization of organic P is completely reversible through the process of mineralization. However, inorganic P, which has been adsorbed or precipitated, is only partially reversible through the process of desorption or dissolution.

Forms and Distribution of P in Soil

Phosphorus exists in soil either in organic (P_O) or inorganic (P_I) forms. Organic P constitutes 20 to 80% of total P (Brady, 1984). Nelson (1991), reported that most naturally occurring forms of soil P_O are esters of orthophosphoric acid, although phosphoric acid derivatives containing C-P bonds produced by rumen protozoa have been found in some soils as well (Anderson, 1980). The common esters are phytin (myo-inositol hexaphosphate), phospholipids, and glucose-phosphate. Esters of orthophosphoric acid are stable, particularly in acid conditions (Jackman, 1951). At very high pH inositol may become unstable, and be mineralized by microorganisms.

It seems that the mineralization of organic P is related to the ratio C:P. Dalal (1980) and Fuller and Nelson (1957) suggested that a C:P ratio higher than 300 caused immobilization of organic P, whereas a ratio less than 200 led to P mineralization. In acid soil, inorganic P exists either as soluble orthophosphate or can react with Al or Fe to form variscite or strengite. As shown in Fig. 1.1, solid P-compounds may dissolve and replenish the soil solution P when it has been depleted, e.g. plant uptake. The literature related to the formation and the properties of these minerals is presented in other sections of this chapter.

In acid conditions, $\text{PO}_4\text{-P}$ released in soil solution reacts quickly with soluble Al or Fe to form compounds that precipitate, with the remainder being immobilized by microorganisms. (Lee et al., 1990).

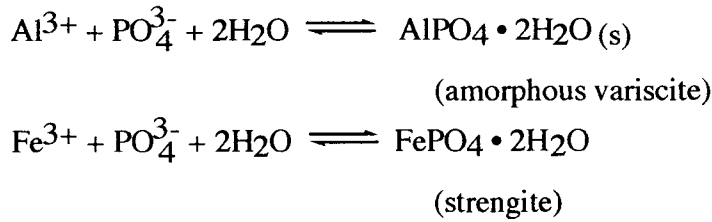
Attempts have been made to investigate the biological and chemical transformation of soluble P added to the soils as fertilizers (Hedley et al., 1982a; Chang and Jackson, 1957). The distribution of P in different fractions was carried out by a sequential extraction with alkaline and acid extractants (Hedley et al., 1982; Chauhan et al., 1979). The distribution of P among different fractions depends upon the chemical and biological environment prevailing in the treated soils. Ghoshal (1975) found that at an early stage soluble P added to soil is rapidly sorbed by chemical reactions. This suggests that at this stage, chemical fixation predominates over biological immobilization. However, all these P compartments are dynamic and reversible (Chauhan et al., 1979; Hedley et al., 1982; Tiessen et al., 1984). The biologically available P forms extracted by resin or sodium bicarbonate are important forms for plant nutrition. However, when these fractions are depleted from the soil solution they cause the dissolution of the P in Al or Fe minerals. Sodium hydroxide extractable P is presumably a measure of the slowly available P associated with these compounds.

Reactions and Kinetics of P in Soil

In acid soils, metal ions such as Al, Fe, and Mn commonly react with PO_4 ions to form soluble complexes or insoluble compounds. The most important reactions are precipitation and surface reactions. These two biogeochemical reactions of P in acid soils may be described by the following:

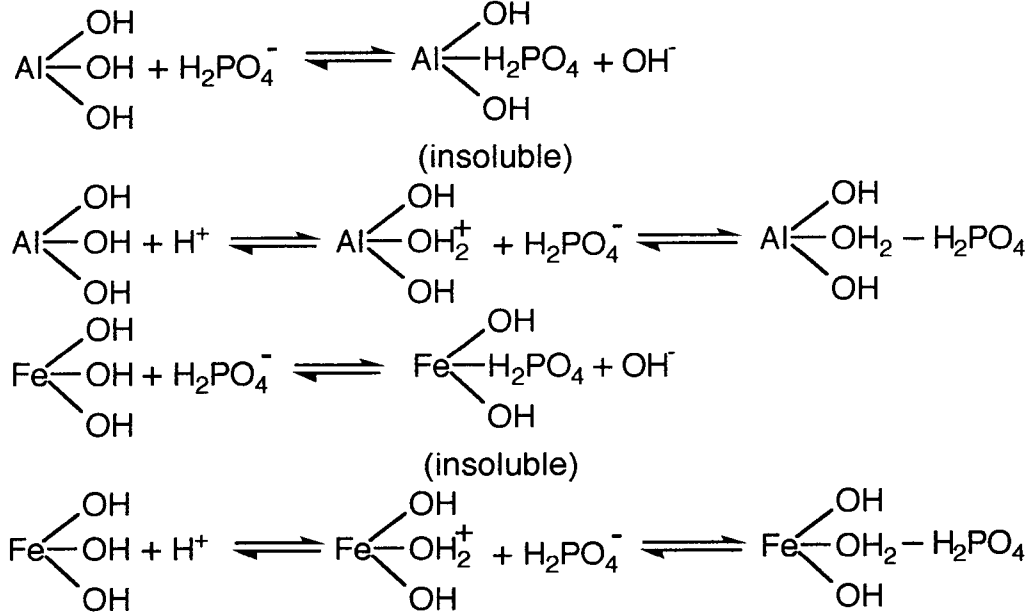
Precipitation/Dissolution

(1)

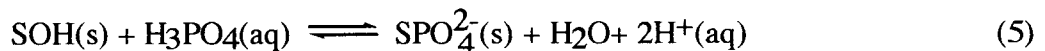
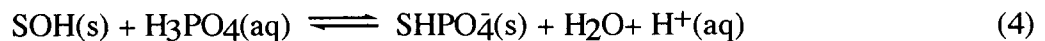
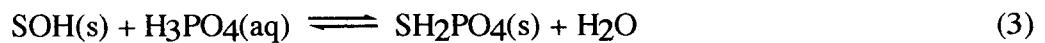


Surface adsorption reactions by hydrous oxide

(2)



The first set of equations (1) represent the precipitation/dissolution that occurs in acidic conditions in the presence of high concentrations of Al and/or Fe. These reactions lead to the formation of variscite, strengite or an amorphous analog to variscite. The second set of equations (2) corresponds to the reactions known as specific (ligand exchange) or non specific reactions. The mechanism of surface reaction by which PO₄ is sorb can be depicted as follows:



where SOH(s) represents one mole of reactive surface hydroxyls bound to a metal ion, and S is an oxide mineral (Goldberg and Sposito, 1984). Bohn et al. (1979) and Sposito (1990) have discussed the specific and nonspecific reactions. These mechanisms cannot be

evaluated separately because they occur simultaneously and the chemical bonds formed in both reactions can be very similar and described by the same sorption models such as the Langmuir equation. Sposito (1989) described the precipitation reaction as a tridimensional reaction whereas the adsorption reaction is bidimensional.

Attempts have been made to use kinetic data to distinguish between precipitation and adsorption of PO₄ ions. Rajan et al. (1974) suggested two steps:

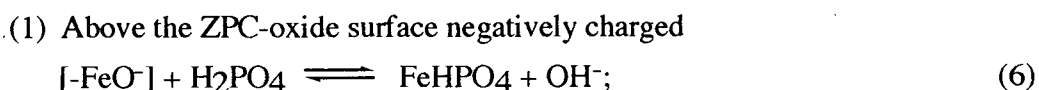
- (1) At low activities of P, ligand exchange mechanism dominates (specific adsorption);
- (2) At high activities, additional P is adsorbed by displacing the structural silica of soil clay minerals and there is formation of aluminous PO₄ compounds such as variscite.

Sposito (1984) distinguished rapid and slow stages of sorption. The rapid stage occurs when the PO₄ concentration in the soil solution is below saturation for any possible PO₄ solid. When the PO₄ concentration in soil solution is supersaturated with respect to some PO₄ solids, the slow stage, characterized by precipitation, is likely to dominate the sorption process.

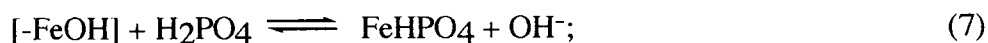
Bohn et al. (1979) suggested that "P-layer silicate adsorption reactions" consist of two stages:

- (1) The initial rapid stage corresponding to nonspecific adsorption and ligand exchange on mineral edges;
- (2) The slower reactions consist of complex combination of mineral dissolution and/or precipitation of added P with exchangeable or lattice cations.

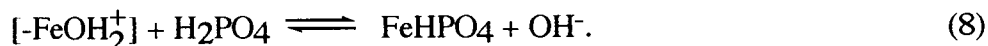
Other models of P adsorption reactions have been discussed by several investigators. Sanchez and Uehara (1980) proposed the following reactions with respect to surface charges of oxides such as Fe:



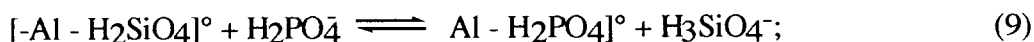
(2) At the ZPC-oxide surface with net zero charge



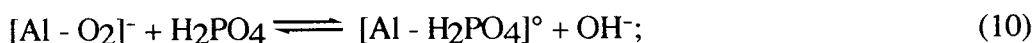
(3) Below the ZPC-oxide surface with net zero charge



Alveredo (1982) discussed these reactions and distinguished a fast adsorption reaction in which low concentrations of P are adsorbed to active sites of silicates as follows:P



to oxoalumino ligands (above the ZPC)



to hydroxyl alumino ligands (at the ZPC)



Other reactions are also suggested by Gebhardt and Coleman (1974) on allophanic materials such as: precipitation of variscite or strengite like compounds; specific (inner sphere) adsorption on protonated surfaces; and ligand exchange.

Solubility and Speciation of P

When the solubility of P is discussed, the first question that is addressed concerns which solid mineral controls P solubility. In acid soils, either strengite or variscite controls P solubility. Lindsay (1979) has summarized the conditions in which either one of them will control P solubility. When gibbsite controls Al solubility, then variscite is the most stable mineral. On the contrary, if kaolinite controls Al solubility, then strengite is likely to control P solubility. However, in many cases neither strengite nor variscite is the first mineral formed. Amorphous compounds seem to be the first formed when P reacts with Al or Fe. Veith and Sposito (1977) identified an amorphous like homologous of variscite in soil treated with P fertilizers. It is very often reported that in acidic conditions either Al or Fe PO₄ control P solubility, whereas in alkaline conditions Ca-PO₄ control P solubility.

Hetrick and Schwab (1992) reported a possible simultaneous coexistence between Al and Ca PO₄ when the P concentrations are high (>125 mg P kg⁻¹) and the pH is in the range of 5.5 to 6.5.

Lindsay and Moneno (1960) studied the stability of PO₄ solids. The solubility diagram expresses the stability of various solids containing P.

The general equations are:

$$\begin{aligned} \text{Variscite;} \quad & \text{pH}_2\text{PO}_4 = \text{pK} - \text{pH} \\ & \text{pK} = 10.7 \end{aligned} \quad (12)$$

$$\begin{aligned} \text{Strengite;} \quad & \text{pH}_2\text{PO}_4 = \text{pK} - \text{pH} \\ & \text{pK} = 10.9 \end{aligned} \quad (13)$$

where Al⁺³ and Fe⁺³ are considered to be controlled by gibbsite and goethite, respectively.

The diagram of solubility of H₂PO₄ solids is widely used by investigators. The main assumption is that the PO₄ is in equilibrium with respect to certain stable minerals which are likely to be present in soils (Lindsay and Moneno, 1960). These diagrams represent the thermodynamic relationship which can exist among the various PO₄ forms in soils.

Although the diagram of solubility can help to understand the minerals which are in equilibrium with P, it fails to predict all species of P present in the solution. The availability of P for plants is influenced by the species of P present in the soil solution and not by the total P as measured chemically.

The computer program GEOCHEM, attempted to solve this problem by calculating the activities of ion species present in the soil solution and enabling the prediction of the dominant P species in solution.

Since PO₄ ions react with Al⁺³ and Fe⁺³ to form different complexes in soil solution, the speciation of Al and Fe is of particular interest. The use of speciation models can provide information on underlying mechanisms of P sorption in relation to management of soils treated with organic or inorganic amendments.

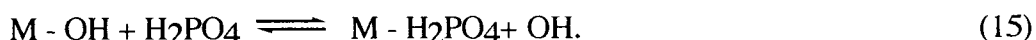
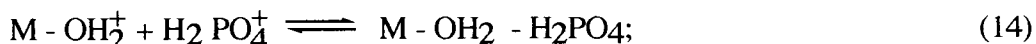
P Sorption in Soils

Mechanisms of P Sorption

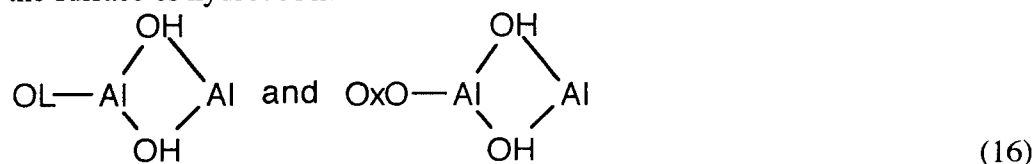
Stevenson (1986) has distinguished three mechanisms of P sorption:

1) chemisorption at protonated surfaces; 2) chemisorption by replacement of surface group OH^- (ligand exchange); and 3) physical sorption of P as a potential determination.

Mechanisms (1) and (2) are represented as follows:

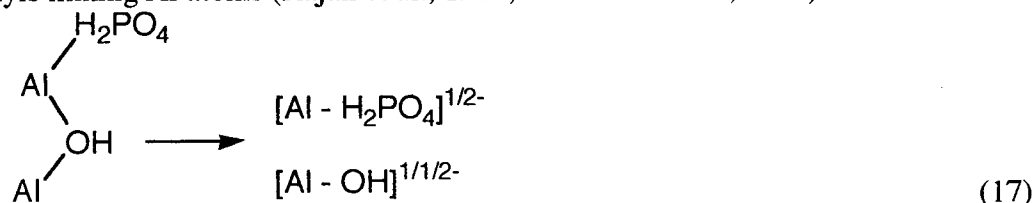


Rajan et al. (1974) proposed the following model to explain the ligand exchange of PO_4 at the surface of hydrous Al:



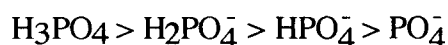
Hydrous Al oxide has a structure in which Al atoms are linked groups and the coordinate positions of the terminal atoms at the surface of polymeric structures are occupied by aquo $\text{Al}-\text{H}_2\text{O}$ or hydroxo $\text{Al}-\text{OH}$ groups which depend on pH. At low PO_4 concentrations the dominant group exchanged is the aquo group whereas at high PO_4 concentrations the hydroxo group is likely replaced.

At still higher concentrations of PO_4 the less reactive group OL becomes the dominant reactive group, by rupture of OH bridge induced by competition of PO_4 ions with hydroxyls linking Al atoms (Rajan et al., 1974; Hsu and Rennie, 1965) as shown below:

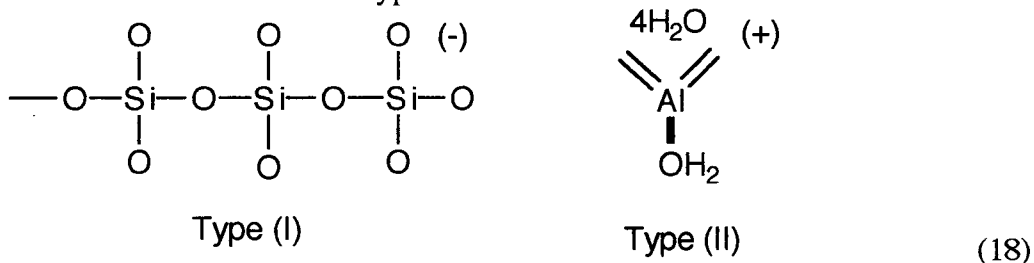


According to Hingston et al. (1972) it is unlikely that undissociated ($\text{H}_3\text{PO}_4^{-3}$) or fully dissociated PO_4 per se are the adsorbing species by ligand exchange, because adsorption would reach the same maximum at all pH values. This observation applies to

PO₄ adsorption. It is hypothesized that if HPO₄ forms, it rapidly reacts with protons in solution to form H₂PO₄⁻ which adsorbs at the surface of colloids (Rajan et al., 1974). This mechanism results from the fact that the specific adsorption of an ion by ligand exchange with OH⁻ is preceded by the conversion of hydroxo groups into aquo groups with the protons being supplied by the acid (Hingston et al., 1972). The ease of sorption of P species is in decreasing order (Cloos et al. 1968, 1969) as follows:

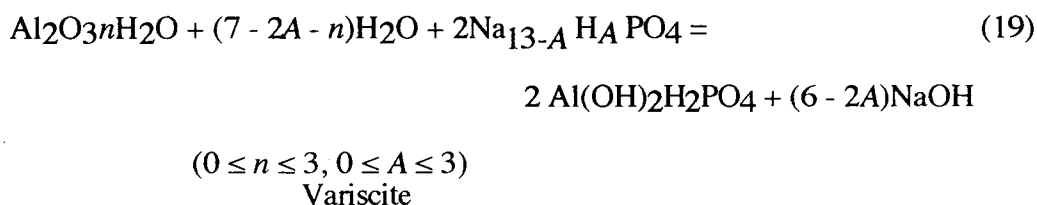


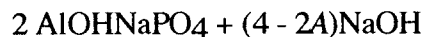
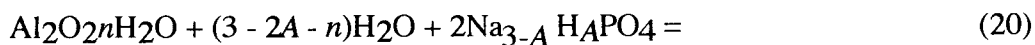
Alveredo (1982) proposed a structural model for amorphous silico-aluminos to explain P adsorption by silico-aluminos compounds. The assumption in this model is that silico-aluminos gels are made from a core in which tetrahedron silicon is partially substituted by Al (Type I) and from alumina coatings surrounding the core (Type II). The negative charges are balanced at least partly by mono- and polynuclear hydroxyalumina cations of increasing complexity, with decreasing net charge per Al atom as the Al/(Al + Si) atomic reaction increases. The two types are as follows:



The adsorption sites for PO₄ were assumed to consist mainly of the positively charged sites and OH groups of the Type II compounds (Alveredo, 1982).

Veith and Sposito (1977) have suggested that amorphous Al hydroxides react with PO₄ ions to form either variscite or montebasite by aging. These are represented as follows:





$$(0 \leq n \leq 3, 0 \leq A \leq 2).$$

Montebrasite

Phosphorus is found mainly in the soil Al, Fe, and Ca PO₄ compounds. Highly weathered soils with high content in hydrous oxides of Al and Fe, calcareous soils and volcanic soils have a particularly high P fixing capacity.

Amorphous hydrous oxides are very reactive and sorb a great amount of P. Several workers have shown high rates of fixation by Al and Fe hydrous oxides (gibbsite, goethite) and alumino silicates (kaolinite), in highly weathered soils (Oxisols, Ultisols) and in volcanic soils (Andepts) (Rajan, 1975; Rajan et al., 1974; Hsu and Rennie, 1965; Mizota and Chapelle, 1988; Gebhardt and Coleman, 1974; Fox, 1974; Sanchez and Uehara, 1980).

The magnitude and the nature of the reactions of P fixation depend upon several factors such as pH, nature and content of clay mineral as well as that of hydrous and anhydrous oxides, presence of alkaline earth carbonates, and metallic salts of soil and humic acids (Bumaya and Naylor, 1988). At pH 5 to 7, sorption of P on clay surface occurs. At pH greater than 7, P reaction with Mg or CaCO₃ (if present) dominates.

Also differences in PO₄ sorption between Al and Fe oxides have been observed (Jones et al., 1979). Aluminum oxides fix more P than equivalent amounts of Fe oxide (Bumaya and Naylor, 1988). The fixation capacity of Fe-compounds depends upon their nature. The amorphous forms of Al and Fe fix as much P as Al crystalline-oxides per unit-mass basis whereas the Fe-crystalline forms, which are common in soils, are nearly unreactive (Gebhardt and Coleman, 1974).

In soils with oxide mineralogy, most P will be sorbed as Fe-PO₄. In soils dominated by kaolinitic minerals, however, Al-PO₄ will be formed, and with time, the Al-PO₄ will be transformed into Fe-PO₄ (Sanchez and Uehara, 1980; Bumaya and Naylor,

1988). Iron compounds (strengite) are more stable than variscite (Bohn et al., 1979; Sposito, 1990). In soils high in kaolinitic minerals, the sorption of P results from the high amounts of hydrated oxides of Al associated with kaolinitic clays which have the ability to form pH-dependent charges due to OH groups at gibbsite layers. Besides the sorption of P in relation to soil mineralogy, the size distribution of particle fractions in soils also affects P sorption. As clay content increases, more P is sorbed.

The allophanic and allophanic-like compounds are responsible for P sorption in volcanic soils. Organic material combines with amorphous compounds and prevents Al and Fe hydroxides from crystallizing (Schwertmann et al., 1968). This mechanism keeps Al and Fe oxides in amorphous forms and then increases P sorption capacity of the soil. However, Saunders (1959) has found that the removal of organic matter from andepts of New Zealand increased the P adsorption capacity of the soils.

Appelt et al. (1975) found that P retention by volcanic soils was preferred over sorption of organic acids, and that neither fulvic nor humic acids affected adsorption of P. Instead, the same investigator observed an increase in P sorption by some soil samples that had been treated with HA or FA compounds.

From this discussion, it should be hypothesized that the extent to which P is sorbed depends greatly upon the nature and genesis of the soil. Agricultural soils often are limed with the goal to improve crop productivity by ameliorating acidity and toxicity of some elements and nutrient availability.

Management of Very High P-Fixing Soils

Liming and P Sorption

Liming acid soils to pH > 5.5 is the conventional method to improve P availability. Liming reduces P sorption by precipitating exchangeable Al ions by the following reactions:



Liming acid soils to a pH range of 5.5 to 6 decreases but does not eliminate P sorption (Sanchez and Uehara, 1980). At pH greater than 6, P sorption increases (Fox et al., 1968).

Bumaya and Naylor (1988) suggested that sorption of P by Fe and Al oxides is not eliminated by liming in some types of soils. For example, andepts that sorb large amounts of P have very low levels of exchangeable Al and the addition of lime leads only to the detrimental effects of over-liming.

Mendez and Kamprath (1978) report that applications of large amounts of P give no benefit from liming when the Al saturation is < 60% because of low concentration of Al in solution at these ranges.

Sims and Ellis (1983) found that the application of limestone to an acid soil optimized P uptake and minimized P adsorption. However, Reeve and Sumner (1970) observed in Natal soil that lime application eliminates Al toxicity but had little or no effect on P availability at pH 6.5.

Addition of CaSO_4 or CaCO_3 to soil dramatically decreased the concentration of Al^{3+} extracted with KCl (Pavan et al., 1982). Calcium sulfate treatment caused a significant amount of Al to form an ion-pair with $\text{SO}_4^{2-}(\text{aq})$ and $\text{AlSO}_4^+(\text{aq})$ species accounting for Al^{3+} in soil solution (36 to 43%) (Pavan et al., 1982) by the following proposed reaction:



Both lime and gypsum applications increase the Al^{3+} precipitation which augment P availability for plant uptake. Calcium sulfate is more mobile in the soil profile than CaCO_3 . Therefore, it will have some advantages in complexing Al ions in the subsoil. Sulfate could also act as a competitive anion for the sites of sorption. However, PO_4 ions are strongly adsorbed and are able to displace other ions (Parfitt and Smart, 1978) including SO_4 .

Organic Amendments and P Sorption

Some workers (Sibanda and Young, 1986; Struthers and Sieling, 1950) have shown that addition of organic compounds to the soil prevented P adsorption. Organic compounds can block exposed hydroxyls on the surface of Fe and Al oxides (Appelt et al., 1975) and decrease P fixation capacity of these oxides. Gaur (1969) and Stevenson (1986) suggested that organic compounds form stable complexes with Al and Fe and this results in increased P solubility.

Another study (Harter, 1969) showed that the addition of organic matter increased P adsorption either by microbial assimilation or exchange of P for some groups, such as hydroxyls at the surface of organic molecules. Appelt et al. (1975) did not observe any effects of organic acid on P fixation by volcanic soils.

Singh and Jones (1976) and Bumaya and Naylor (1988) found that the addition of organic residues to soils decreased P sorption but the incubation time and the nature of residues influenced the effects of the residues on P sorption.

Singh and Jones (1976) observed that various types of organic residues decreased P sorption up to 30 days. They also found that organic residues with more than 0.3% P decreased P sorption up to 150 days. High amounts of P were sorbed after 75 days of incubation when P contents in organic residue were less than 0.3% P. They concluded that P, initially fixed, started to reappear in the soil solution by the end of a 150 day incubation period. Bumaya and Naylor (1988) found that plant residues with P contents greater than 0.1% (wt/wt) at rates equivalent to or greater than 5% (wt/wt) increased the extractable P and decreased P sorption in the high P sorption soil.

Mnkeni and MacKenzie (1985) found a decrease in P sorption resulting from addition of plant residues and farm yard manure (FYM) to upland top soil and subsoil. They observed that the effects depended upon the nature of PO_4 added (orthophosphate, or polyphosphates).

Reddy et al. (1980) studying soil utilized for animal waste disposal reported that soil receiving high rates of manure sorbed less P and desorbed more P. They found that when the C/P ratio was higher than 130, the organic manure added did not decrease P sorption. From this it can be hypothesized that either organic acids or P released during the mineralization occupy the sites of adsorption or react with Al and Fe ions and prevent the sorption of further additions of inorganic P.

Isotherms of Adsorption

Langmuir (1918) established an equation to describe the adsorption of a monolayer gas by a solid. The Langmuir equation and others are presently used in soil science to predict the equilibrium state between the amount of P remaining in soil solution after an amount of P has been added to the soil and P adsorbed on solid phase.

The initial Langmuir equation has the form:

$$\frac{X}{m} = \frac{K X_m C}{1 + KC} \quad (24)$$

where X/m represents the amount of adsorbed element per unit of absorbent mass, C is the concentration of adsorbed element at equilibrium, X_m is the maximum capacity of adsorption by a monolayer of sites, and K is the binding energy between adsorbed element and absorbent.

Equation (17) can be rewritten as:

$$\frac{C}{X/m} = \frac{1}{KX_m} + \frac{C}{X_m} \quad (25)$$

The equation has the form of the regression equation $y = a + bx$. The constants can be calculated in the same way as the constant of a regression equation where b is the adsorption maxima and a is an affinity constant.

The Langmuir equation is valid only if two conditions are met:

- (1) the energy of adsorption is uniform;
- (2) and there is no interaction among adsorbed ions.

Although many researchers have used the Langmuir equation to describe sorption processes in soil, the two conditions are not satisfied in the natural environment (Olsen and Watanabe, 1957; Shapiro and Fried, 1959; Rennie and McKercher, 1959; Hsu and Rennie, 1965; Gunary, 1970; Syers and Cory, 1973; Fox and Kamprath, 1970).

The results obtained by the Langmuir equation are approximate because all components involved in adsorption do not have the same energy of adsorption and these results depend on the nature of the type of soil (Holford et al., 1974). The Langmuir equation has the ability to predict the maximum adsorption but it is not well suited to low concentrations.

Griffin and Jurnak (1973) point out that the Langmuir isotherm does not describe accurately P sorption data when the solution P concentration is low. The same observation applies when the concentration of P is high (Rennie and McKercher, 1959; Gunary, 1970; Syers and Cory, 1973).

Consequently, Gunary (1970) has developed a modified Langmuir equation which transforms the data to a convex curve and provides a better fit of the data at low concentrations. Gunary's equation is as follows:

$$\frac{C}{y} = A + BC + D(C)^{1/2} \quad (26)$$

where: C = equilibrium concentration of P in solution

y = quantity of P sorbed.

A, B, and D = constants

Gunary explained that the convex curve model fits the data because the soil strongly adsorbs only a small amount of added P. When the amount of P added increases, the soil adsorbs less until the sorption sites become saturated with P. The value $1/B$ in equation (26) represents the maximum adsorption value, since C tends to go to infinity, y approaches $1/B$.

The parameter $1/B$ in equation (26) is higher than that obtained by the original Langmuir equation. According to Gunary, the maximum adsorption determined from the Langmuir equation depends on the maximum concentration of P in the initial solution in contact with the soil.

Syers and Cory (1973) observed the existence of two types of adsorption which have different affinities for P. When the linearized sorption data were plotted according to the conventional Langmuir equation, two linear relationships were obtained indicating the presence of two types of sites. The sites in part I correspond to lower equilibrium P concentrations which have a much higher binding energy constant (k_1) than the sites of part II which correspond to higher equilibrium P concentrations. They proposed the following equation which reflects the presence of the two types of sites.

$$\frac{X}{m} = \frac{K_1 X_m C}{1 + K_1 C} + \frac{K_1 X_m C}{1 + K_1 C} \quad (27)$$

An additional advantage of equation (27) is that it allows calculation of the buffer capacity which is the product of X_m and k . A buffer capacity factor is important because it reflects the capacity of soil to replenish regularly the P in soil solution and the ability to make P available for the plant.

The theory for two types of sites is rejected by Halford (1978) who argued that the acceptance of two segments in the Langmuir equation implies the assumption that the adsorption of P on sites of lower energy starts only after the sites of high energy have been completely occupied. Halford concluded that the adsorption is a simultaneous process. Also a quadratic equation and a logarithmic form of Langmuir's equation are reported in the literature.

The advantage of the Langmuir two surface equation is that it is capable of representing any sorption curve, in contrast with the one surface model.

Although these opinions differ, applied research has been done successfully to study the use of isotherms in evaluating the P required for plant growth (Fox and Kamprath, 1970). The conclusion was that a soil containing 0.2 mg P L^{-1} in equilibrium solution would be sufficient to meet the needs of growing plants (Fox and Kamprath, 1970). However, the amount of P required to maintain 0.2 mg L^{-1} is affected by addition of organic matter (Singh and Jones, 1976).

The Freundlich equation is used as an alternative to the Langmuir equation. But the Freundlich equation is strongly criticized for its empirical characteristics (Holford et al., 1974), because it does not fit sorption data well when soils are high in native PO_4 .

The Freundlich equation and its logarithmic transformation are given as:

$$\frac{x}{m} = kb^n \quad (28)$$

$$\log \frac{x}{m} = \log k + n \log b \quad (29)$$

The advantage of this equation is that its parameters may be estimated from log plot. Its disadvantage is that it is unable to predict the maximum adsorption.

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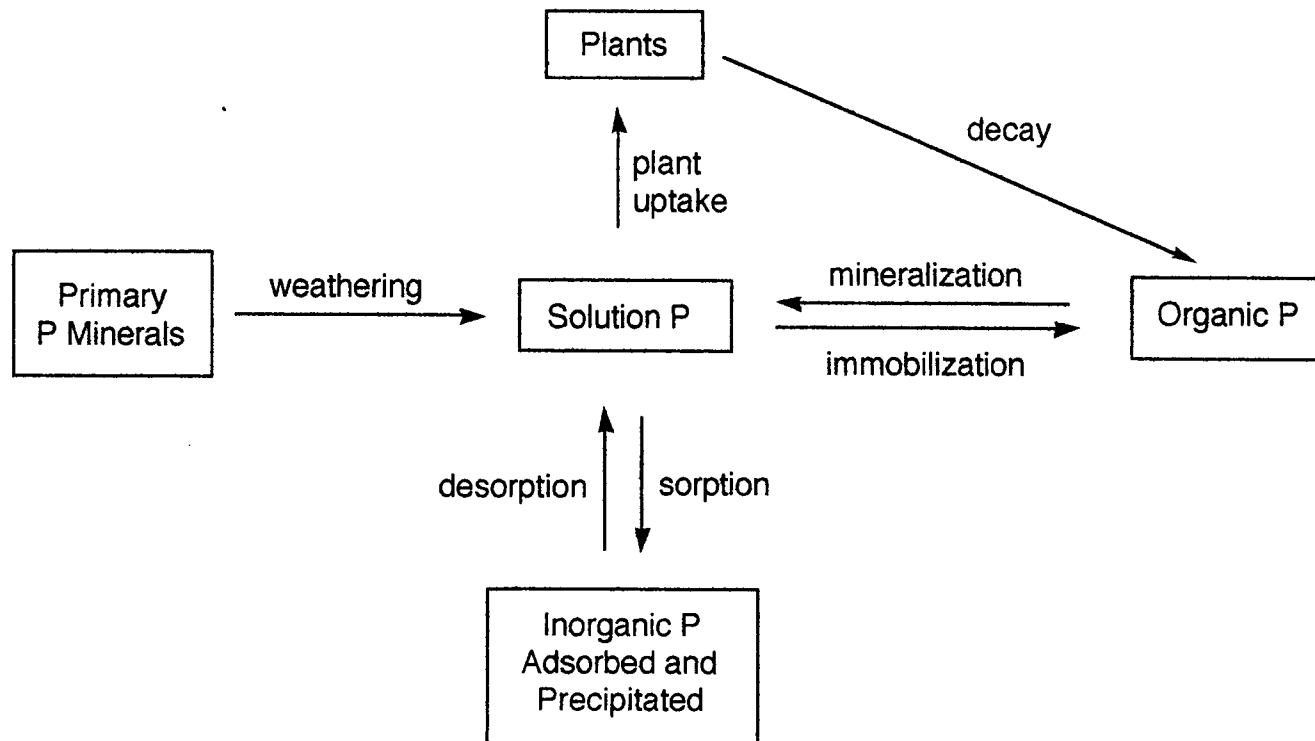


Figure 1.1. Phosphorus cycle in soil.

CHAPTER II

EFFECTS OF ORGANIC AND INORGANIC SOIL AMENDMENTS ON P CHEMISTRY AND P SORPTION IN SOILS

ABSTRACT

The influence of different rates and kinds of organic and inorganic amendments on phosphorus (P) sorption characteristics was determined on two soils from Oregon, Jory (xeric Haplohumult) and Tolo (Typic Vitrandept), and three soils from Rwanda, Mata (Sombrihumult), Kibeho (Paleudult) and Kinigi (Typic Placandept) in a laboratory incubation study. Steer manure (manure), alfalfa (*Medicago sativa*), and wheat straw (*Triticum estivum*) residues were added to Jory soil samples at the rates of 1, 2.5, and 5 % (wt/wt). The soil samples were also amended with CaCO_3 and CaSO_4 at rates of 1, 1.5 and 3 times the CaCO_3 equivalent required to neutralize exchangeable aluminum (Al). Other soils received only the highest rate of each soil amendment. After 28 days of incubation, the soil samples were air-dried and P sorption isotherms, pH, exchangeable Al, and extractable phosphorus were determined. Increasing the rate of manure or alfalfa increased pH, P in equilibrium solution, and extractable P, and decreased the exchangeable Al, affinity constant, adsorption maxima, and P sorbed at 0.2 mg P L^{-1} . Soils amended with CaCO_3 produced similar results as manure and alfalfa but did not markedly influence the extractable P or the affinity constant. The effect of wheat straw was variable and negligible in most of the soils. High rates of CaSO_4 decreased exchangeable Al, but did not affect the pH, extractable P, the affinity constant, and P sorbed at $0.2 \text{ mg P L}^{-1}(\text{P}_{0.2})$. Overall, organic amendments with high P content such as manure or alfalfa may substitute for CaCO_3 as a soil amendment to decrease P sorption capacity in soils. The magnitude of the response to amendments varied with the type of soil and amendment. However, all soils responded to the application of high rates of manure, alfalfa, and CaCO_3 . Tolo soil, with a trace of exchangeable Al and more available P, showed the greatest response to all amendments.

INTRODUCTION

Phosphorus (P) is often unavailable for plant uptake in highly weathered soils (Ultisols and Oxisols) and in volcanic soils with high amounts of amorphous compounds. Soluble P may be strongly adsorbed on the surface of Fe and Al oxides and hydrous oxides or may be precipitated out of the solution by soluble Al and Fe that are common characteristics of weathered soils.

Easterwood and Sartain (1990b) reported that present management techniques for reduction of P fixation involve either adding P as fertilizer or incorporating organic residues (Sanchez and Uehara, 1980). Treatment of high P sorbing soils with organic residues is particularly attractive in developing countries as a low cost alternative to conventional inorganic fertilizers and liming amendments. Furthermore, lime amendments such as CaCO_3 have given conflicting results on highly weathered or volcanic ash soils (Holford, 1983; Amarasi and Olsen, 1973; Smyth and Sanchez, 1980).

Hue (1990) reported that inorganic P fertilizers were more efficiently utilized by crops when applied in conjunction with organic inputs such as green manure and animal wastes, probably by reducing P sorption capacity and hence increasing P concentration in the equilibrium solution (Bhat and Bouyer, 1968; Singh and Jones, 1976; Bumaya and Naylor, 1988; Reddy et al., 1980). Conversely, Li et al. (1990) observed a decrease in P availability in soils with organic residues low in P content.

Organic amendments may react similarly to CaCO_3 by increasing the pH or precipitating Al and Fe (Hue, 1992; Hoyt and Turner, 1975). Calcium sulfate has also been used to decrease exchangeable Al in acidic subsoils by complexing with the exchangeable Al (Adams, 1976).

Studies to date have given conflicting results on the interaction of organic amendments and P sorption. Furthermore, most studies with organic amendments have been conducted on a single soil without comparison to inorganic amendments. Such a

comparison utilizing an amendment such as CaSO_4 , which removes Al but leaves pH unchanged, or to CaCO_3 , which removes Al and changes pH, would provide insight into how organic amendments can affect P sorption.

Therefore, the objective of our study was to evaluate the effects of organic amendments (manure, alfalfa, and wheat straw), and inorganic amendments (CaCO_3 , and CaSO_4) on P sorption characteristics (adsorption maxima, affinities), exchangeable Al, extractable P, and pH.

MATERIALS AND METHODS

Soil samples and amendment materials

Surface soil (0-20 cm) samples of three soils from Rwanda (Kinigi, Kibeho, and Mata), which are unclassified but are similar to Placandept, and Paleudult, and Sombrihumult, respectively, were collected. Kinigi is a poorly drained soil with high organic matter (16%). Mata is a high altitude soil and receives regular applications of organic residues from the homestead to maintain its fertility. Kibeho is a very weathered and eroded soil under a vegetation of *Eragrostis* spp. which is an index of soil degradation in the highlands of Rwanda. Some artifacts of the sombric horizon were visible in the sampled upper layers of the Kibeho soil. Two soils from Oregon, Tolo (Typic Vitrandept) and Jory (Xeric Haplohumult), were also collected. Tolo is formed on volcanic ash and Jory is a weathered soil; both are very well drained. Moist samples from the field were sieved through a 2.0 mm sieve and air-dried.

Wheat straw (*Triticum estivum*), composted steer manure and alfalfa (*Medicago sativum*) were obtained locally. Organic residues were air-dried, oven-dried at 60 °C, ground and sieved through a 1-mm sieve and stored in polyethylene bags at room temperature. Laboratory grade CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were used as inorganic amendments.

Laboratory analyses

Soil pH was determined with a glass electrode (soil:water ratio 1:2). Total C in the soils was determined by combustion in a C Analyzer (Dohrman, Santa Clara, CA) and total C in residues was measured by LECO WR-12 carbon autoanalyzer (LECO Corp., St. Joseph, MO). Total Kjeldahl N in soils and organic residues were measured. P availability indices were determined: Bray I (0.03 M NH_4F and 0.025 M HCl); or 0.01 M CaCl_2 extractable P. Total inorganic P was determined using 0.5 M H_2SO_4 (Olsen and

Sommers, 1982). Exchangeable Al was extracted with 1 M KCl solution (Olsen and Sommers, 1982). Dithionate-citrate extractable Fe and Al (Fe_d and Al_d), and NH_4 oxalate extractable Fe and Al (ox-Fe and ox-Al) were determined by the McKeague and Day method (1966) as modified by Mizota and Chapelle (1988) on soil fractions <2mm. Ortho-P was measured colorimetrically (Murphy and Riley, 1962). Calcium, Mg and K were extracted with ammonium acetate and measured by atomic absorption spectrophotometry (Thomas, 1982).

Incubation

Organic amendments (wheat straw, manure, or alfalfa) were added at rates of 0 (control), 1% (low), 2.5% (medium), or 5% (high) (wt/wt) to the Jory soil samples. Another set of Jory soil samples received inorganic amendments (CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at the rates of 1 (low), 1.5 (medium), and 3 (high) times the amount of CaCO_3 or CaSO_4 equivalents needed to neutralize exchangeable Al. The other soils (Mata, Tolo, Kinigi, and Kibeho) received only the highest rates of either organic or inorganic amendments. Double distilled water was added to the samples to bring the moisture to 66% of water holding capacity. All soil samples were incubated at 24 °C for 28 days in duplicate. The soil samples were aerated every other day and water content was maintained gravimetrically. After the period of incubation, the samples were air-dried for one week prior to their use for isotherms and for determination of pH, exchangeable Al, P soluble in 0.01 M CaCl_2 , Bray 1 P, and total inorganic P.

Isotherms

The P isotherms were done on duplicate incubated soil samples according to the method of Fox and Kamprath (1970). Three g soil samples were equilibrated, in 30 ml of 0.01 M CaCl_2 solution containing one of six concentrations of KH_2PO_4 (0.16, 0.32, 0.97, 1.62, 2.59, and 3.23 mM) for six days. A control sample to which no P was added

was included. Three drops of toluene were added to slow microbial activity. The samples were shaken twice a day for 30 min. After the period of equilibration the samples were centrifuged at 27,000x g for 10 min and a clear aliquot of the supernatant was analyzed colorimetrically for P concentration. The pH of the equilibrium solution was measured immediately. Phosphorus-sorbed was determined by the difference between P-added initially and P-remaining in the solution at the end of the equilibration period. After subtracting the control values, the data were fitted to a Langmuir equation using the SAS program (SAS, 1985) to determine sorption parameters as follows:

$$q = \frac{kbc}{1 + kc} \quad [\text{Eq. 1}]$$

where q = sorbed P (mg P kg^{-1} soil)
 k = adsorption affinity (L mg^{-1})
 b = adsorption maxima (mg P kg^{-1})
 c = P in solution of equilibrium (mg P L^{-1}).

RESULTS AND DISCUSSION

Soil characteristics

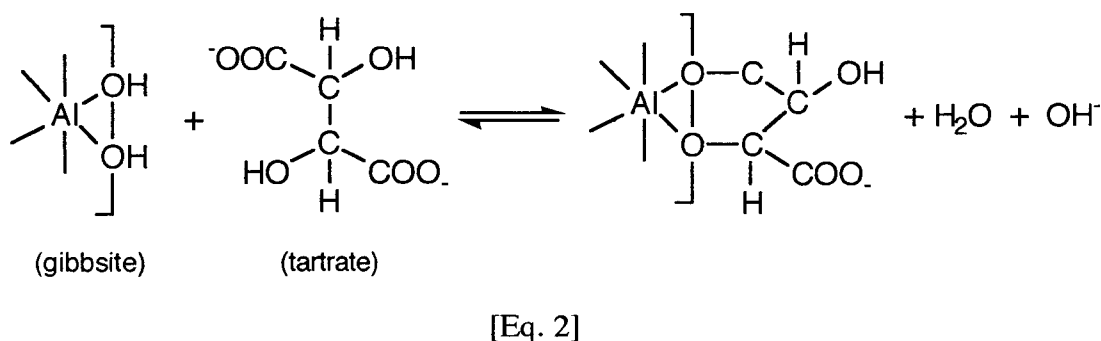
Initial chemical characteristics varied widely among the soils (Table 2.1). All soils are acidic and have a relatively high amount of exchangeable Al except for Tolo soil, which had only a trace amount of exchangeable Al. Phosphorus content in wheat straw, alfalfa, and manure was 0.09, 0.24 and 0.29 (wt/wt), respectively. Carbon content was 40, 40 and 10 % in wheat straw, alfalfa and manure, respectively.

Soil pH

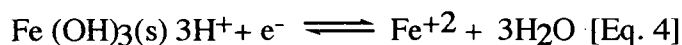
The highest rates of manure and alfalfa residues increased pH of Jory soil by more than one unit, whereas the highest rates of wheat straw produced an increase of only 0.2 pH units over the control sample (Table 2.2). The medium rates of manure and alfalfa and the highest rate of CaCO_3 were comparable in their effects and increased pH from 5.3 (control) to 5.0, 5.87, and 5.8 respectively. Slight increases were obtained with alfalfa and manure at the lowest rates. Low and medium rates of CaCO_3 increased the pH up to 5.58 and 5.61, respectively. Overall, wheat straw and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ did not significantly change pH values at any rate of application.

Table 2.3 shows the pH values for all 5 soils amended with the highest rate of organic or inorganic amendments. Wheat straw had little effect on soil pH, but manure and alfalfa caused the highest increases in pH, averaging more than 1 pH unit among the soils. Calcium carbonate added to Jory, Kibeho, and Mata soil samples also significantly increased the pH. The changes in pH caused by the addition of alfalfa residues were slightly higher than those brought about by manure in four out of five soils. The slight but constant decreases in pH observed with CaSO_4 could be attributed to the effect of Ca ions exchanging for Al ions on colloidal particles. It appeared that volcanic soils (Kinigi and Tolo) amended with manure or CaCO_3 experienced less change in pH than nonvolcanic

soils (Jory, Kibeho, and Mata). Calcium carbonate had effects comparable to organic amendments in four out of five soils. The increase in soil pH caused by the addition of manure is likely associated with the production of OH^- ions by ligand exchange mechanisms that occur between organic acids and hydroxyl Fe and Al in soils by the reaction of equation 2. An increase in soil pH caused by the mineralization of C and the release of "basic" cations ("self-liming" effect) was also reported by Hue (1992).



Hoyt and Turner (1975) obtained a significant reduction of acidity early in the incubation period when a large amount of organic residue (up to 10%) was added to a very acid soil. Hue (1992) obtained higher pH values in soil solutions treated with organic residues than in those amended with CaCO_3 . The pH changes were attributed to the high concentration of basic cations in the organic matter used and to the reduction of higher valence Mn oxides or Fe oxides and hydrous oxides in soils (Hue, 1992; Hoyt and Turner, 1975). The latter reaction leads to the "self-liming" effects observed in submerged soils caused by oxidation-reduction reactions:



Theoretically, these reactions should not have occurred in our experiment because these reactions are possible only if some reducing zones prevail in the soil samples. However, because of the heterogeneity of the bulk soils we can not exclude the presence of anaerobic zones in these samples.

Exchangeable Al

Increasing rates of organic residues added to the Jory soil reduced the concentration of exchangeable Al regardless of the type of residue (Table 2.4).

The order of amendments effectiveness was:

At the low rate: alfalfa > manure > wheat straw = CaCO_3 > CaSO_4

At the medium rate: alfalfa > manure > wheat straw > CaCO_3 > CaSO_4

At the high rate: alfalfa = manure = CaCO_3 > CaSO_4 > wheat straw

Alfalfa and manure at high and medium rates significantly decreased exchangeable Al by 100% to 91%. Wheat straw was less effective, ranging from 79% (high rate) to 22% (low rate). Pronounced reductions of exchangeable Al of 100% and 82% were observed in Jory samples treated with the highest rates of CaCO_3 and CaSO_4 , respectively.

Among the five soils, the effects of alfalfa, manure, and CaCO_3 were similar in all soils reducing the exchangeable Al up to 100% in all soils (Table 2.5). Again, wheat straw was less effective (58% to 78% reductions) than the other organic amendments in reducing exchangeable Al concentration, particularly in Mata, Kibeho, and Kinigi soils which had the highest initial amount of exchangeable Al. Among all amendments, Mata, Kibeho, and Kinigi showed relatively less decrease in exchangeable Al than Jory and Tolo soils. Calcium sulfate showed the smallest effect regardless of soil type.

The reduction of exchangeable Al in soils might be explained partly by the concomitant increases in pH observed in these soils when organic amendments and CaCO_3 were added (Table 2.3) and by the formation of Al complexes with some strong complexing agents such as F and SO_4 returned to the soil by organic amendments. These reductions may be due to the following mechanisms: precipitation of Al ions by OH ions released from the exchange of ligands between organic anions and terminal hydroxyls of Fe and Al oxides; and/or the complexation of Al by organic molecules (Hue, 1992). The "self-liming" of organic matter produces OH and therefore reduces the concentration of exchangeable Al (Hoyt and Turner, 1975). Hue (1992) estimated that the addition of 5 and

10 g of chicken manure per kg was equivalent to 3.39 and 6.74 cmol kg⁻¹ Ca(OH)₂. Organic acids such as oxalic, malic, malonic, and citric acid are believed to complex exchangeable Al (Hue et al., 1986). In a separate experiment that we conducted, malic, malonic, maleic, succinic, formic, and acetic acid were measured in the soil solution of Tolo and Jory samples. Although oxalic acid was not quantitatively determined in these soils, it also was qualitatively present on the ion chromatography diagram. It is interesting to note that citric acid, which is a powerful complexing agent included in some models describing organic acid-Al reactions, was not detected in our samples.

The decrease of Al ions by CaSO₄ results from the complexation of Al by SO₄ ions (Alva and Sumner, 1989; Noble et al., 1988). It is also possible that organic residues decreased exchangeable Al through the great amount of SO₄ added by these materials. High amounts of SO₄ ions averaging 200 to 500 mg SO₄ kg⁻¹ were measured in solution extractants of soil treated with organic residues.

Extractable Phosphorus

Calcium chloride extractable phosphate

Phosphorus extracted with 0.01M CaCl₂ was low in all treatments (< 0.16 mg P kg⁻¹) (data not shown). The highest average concentration of CaCl₂ extractable P was obtained with the addition of manure (0.062 mg P kg⁻¹) and the lowest average from the control (0.0048 mg P kg⁻¹).

Bray 1 extractable phosphate

Bray 1 P increased with increasing rates of organic amendments in Jory soils (Table 2.6). For example, manure had a net increase in Bray 1 P from 7.19 mg P kg⁻¹ soil (low rate) to 17.36 mg P kg⁻¹ soil (high rate). Among all soils, the order of effectiveness was manure > alfalfa > wheat straw with CaCO₃ and CaSO₄ having either no effect or decreased Bray 1 extractable P (Table 2.7). This observation agrees with the results

reported by Sims and Ellis (1983) who found that soil P (Bray 1 P) in the surface horizon showed little response to CaCO_3 after 30 d incubation, in contrast to a rapid increase of soil P in the samples treated with wheat straw and allowed to incubate for a longer period of time (30 to 240 d).

Inorganic P soluble in 1N H_2SO_4 extractant

Table 2.8 shows extractable inorganic P (P_i) (1N H_2SO_4 soluble P) measured in the five soils with the highest rates of organic and inorganic amendments. This fraction is thought to represent the more chemically labile P_i that was probably recently precipitated. Although there was some variation among soils, CaCO_3 and CaSO_4 had minimal effects on P_i levels compared to organic amendments. This suggests that during the incubation period CaCO_3 and CaSO_4 did not stimulate transformation of organic P to inorganic P.

Adding manure and alfalfa significantly increased inorganic P in all soil types except Mata. Whereas wheat straw tended to decrease inorganic P in most soils. Manure and alfalfa may have increased inorganic P after mineralizing organic P because of low C/P ratios (< 100), whereas wheat straw with a C/P ratio of 444 may have promoted P immobilization in microbial biomass. These ranges agree with those reported by Dalal (1977). Fuller and Nielson (1956) considered the soil amendment C/P ratio a probable index to predict mineralization or immobilization of P, and suggested that with a C/P ratio of 200 or less mineralization occurs, and with a ratio of 300 or more immobilization occurs.

These results are consistent with Li et al. (1990) who found that extractable P values in treated samples were highest with alfalfa residues and lowest with wheat straw residues. These researchers concluded that, in the short term, net immobilization of P may occur when a cereal straw is used because of its low P content. But, in the long run, there will be net mineralization.

Phosphorus isotherms

Equilibrium solution P

Phosphorus sorption isotherms of Jory soil samples treated with increasing rates of organic and inorganic materials are presented in Figs. 2.1- 2.5.

At the same level of P addition, manure and alfalfa residues resulted in the highest concentrations of P in equilibrium solution and wheat straw had the lowest concentration of P. Among inorganic amendments, CaCO_3 increased P concentration more than CaSO_4 . Increasing the rate of manure and alfalfa residues from the lowest (1%) to the highest (5%) increased the P in equilibrium solution from two to four times (Fig. 2.1 and 2.2).

Phosphorus concentrations in samples incubated with the high rate of wheat straw residues or CaCO_3 increased from 1.6 mg P L^{-1} soil (control) to 2.9 mg P L^{-1} of solution (Fig. 2.3 and 2.4). Samples amended with high rates of CaSO_4 increased P by less than 0.5 mg mL^{-1} (Fig. 2.5). Low and medium rates of manure and alfalfa, and medium rates of CaCO_3 increased P concentration in solution but to a lesser extent than the high rate. Low and medium rates of CaSO_4 and the low rate of CaCO_3 did not differ from the control.

The P concentration in the equilibrium solution increased in all soils regardless of amendment (Figs. 2.6, 2.7, 2.8, 2.9, and 2.10). At the low levels of P added, there were no significant differences among the treatments. At the highest levels of P added ($1000 \text{ mg P kg}^{-1}$ soil), Tolo soil samples responded the most to the addition of amendments in the order: manure > alfalfa = CaCO_3 > CaSO_4 > wheat straw; Kinigi soil responded the least (Fig. 2.9). However, at the low levels of P added to Tolo soil, CaCO_3 maintained less P in the equilibrium solution than alfalfa. The same observation applies to Jory soil treated with CaCO_3 and wheat straw at the highest level of added P. Calcium sulfate caused more increases in P concentration than wheat straw in Tolo soil samples at the highest levels of P added, and the two materials were comparable at the other levels.

Mata soil had a different isotherm response than the other soils. At low P additions P fixation was high, but at high P additions P fixation was lower than in the other soils.

The order of effectiveness of these amendments was manure > alfalfa > wheat straw > CaSO_4 .

The cross comparison among the soils within the same treatment showed that the average P concentration maintained in equilibrium solution increased in the order of Tolo > Mata > Jory \geq Kibeho > Kinigi. Other researchers reported similar increases of P concentration in the equilibrium solution of soils amended with animal waste (Reddy et al., 1980), or incubated with organic residues (Bumaya and Naylor, 1988).

Equilibrium P concentration

Equilibrium P concentration (EPC) represents the amount of P in the equilibrium solution at zero P sorbed (Reddy et al., 1980). EPC is the concentration at the intersection of the isotherm curve and the x-axis before subtracting the control concentration. These were less than 0.2 mg P L^{-1} regardless of the rate of the amendment (data not shown). Fox and Kamprath (1970) recommended the value of 0.2 mg P L^{-1} in the equilibrium solution was necessary to obtain an optimum yield in most crops. The highest EPC (0.09 mg L^{-1}) values were found in Tolo samples amended with the highest rate of manure. Therefore all treated and untreated soils must be considered economically as deficient in P and unable to obtain maximum crop yields without adding extra P.

P sorbed at 0.2 mg P L^{-1}

Phosphorus sorbed to provide 0.2 mg P L^{-1} ($\text{P}_{0.2}$) in the equilibrium soil solution was reported as the amount of soil P required to obtain 95 % of maximum millet production (Fox and Kamprath, 1970). The amount of P sorbed at 0.2 mg P L^{-1} in the equilibrium solution of Jory soil was decreased by increasing rates of organic amendments and CaCO_3 and markedly reduced by the highest rates of these amendments (Table 2.9). Manure and alfalfa $\text{P}_{0.2}$ reductions ranged from 41% to 50% in soils except for Kinigi soil (Table 2.10).

Kinigi soil required a high amount of added P to attain 0.2 mg P L^{-1} in equilibrium solution (more than 720 mg kg^{-1} soil) regardless of the type of amendment; even when amended with manure, the reduction averaged only 20% (Table 2.10). The values of $P_{0.2}$ calculated for Kinigi (untreated soil) were similar to the average ($450 \text{ mg to } 900 \text{ mg kg}^{-1}$ soil) reported for volcanic soils of Rwanda (Vander Zaag and Fox, 1981). The same authors reported that the sorbing capacity of volcanic soils of Rwanda was intermediate between Eutrandepts and Dystrandepts of Hawaii, depending on their different stage of weathering. Mizota and Chapelle (1988) reported that the fixing capacity of volcanic soils of Rwanda was related to the high amount of active Al bound to humus. Calcium carbonate was more efficient than CaSO_4 in decreasing P sorbed at 0.2 mg L^{-1} , and had $P_{0.2}$ values comparable to those of wheat straw which had the least effect among the organic amendments.

Affinity constant and adsorption maxima

The affinity constant of amended Jory samples decreased with increasing rates of organic materials particularly at the medium and the high rates (Table 2.9). These reductions were significantly influenced by the types and amounts of amendments with manure and alfalfa residues having the greatest effect. The reduction of affinities induced by manure ranged from 49.6% (low rate) to 69% (high rate). The changes of affinities in the samples treated with alfalfa were of about the same magnitude as those caused by manure. The reductions of affinities of samples treated with wheat straw ranged from 0% (low) to 40% (high) and were comparable to those induced by CaCO_3 . The reductions caused by CaSO_4 were the smallest and ranged from 0% to 20%.

All amendments reduced adsorption maxima only at the highest rate of applied amendments. The reductions were 60 (manure), 36 (alfalfa), 15 (wheat straw), 58 (CaCO_3), and 26 mg P kg^{-1} (CaSO_4). At the medium rate of manure, alfalfa, and wheat straw residues, the adsorption maxima was reduced by 23, 13, and 10 mg kg^{-1}

respectively. At the low rate only manure and CaCO_3 slightly decreased the adsorption maxima by 10 and 9 mg kg^{-1} respectively.

Overall, the magnitude of decreases of adsorption maxima induced by organic residues was relatively small but persistent in the five soils. In manure treated soil samples, which showed the greatest effect, the decreases ranged from 5% in Mata to 14% in Tolo. The adsorption maxima of Kinigi soil was only decreased by 4% after the addition of manure. The affinity constant of Kinigi soil still remained the highest and the P concentration in the equilibrium solution the lowest compared to the other soils. This may be explained partly by the great amount of native organic matter initially present in this soil that might have undergone rapid mineralization. Evidence for this is that air-dried or untreated (prior to incubation) Kinigi soil samples had a higher adsorption capacity (data not shown) than untreated incubated samples. Organic residues and inorganic amendments reduced adsorption maxima of Kibeho soil. This soil had the highest adsorption maxima of untreated soil samples and also the highest amount of exchangeable Al. The high adsorption maxima of untreated Kibeho soil samples might also have resulted from the particular characteristics of the Ap horizon which contained some subsoil material from the sombric horizon. One can infer that the mixture of surface and subsoil horizons drastically increased the sorption capacity of the soil. Other researchers (Mnkeni and MacKenzie 1985) have observed more decrease of P sorption capacity in the B horizon than in the upper horizon in the presence of CaCO_3 ; this may explain the effect of inorganic amendments in Kibeho soil samples which contains soil material from the deep horizons.

Addition of manure, alfalfa or CaCO_3 reduced adsorption maxima in most of the soils. However, the reductions of affinity caused by CaCO_3 were smaller in three out the five soils. Calcium sulfate markedly reduced adsorption maxima only in Kibeho and slightly in Tolo, Kinigi and Jory. However, CaSO_4 did not decrease the affinity constants of Mata and Kibeho. The reduction of adsorption maxima without subsequent reductions of affinity constants might be attributed to an increase in the rate of surface reactivity

without formation of new compounds capable of sorbing added P (Holford, 1983). In samples treated with a high amount of CaSO_4 , or CaCO_3 , Ca ions may increase positive charges that decrease the repulsion of PO_4 ions away from the surface of the adsorbent.

These results are consistent with other studies which have shown a reduction in adsorption maxima and affinity constants (Reddy et al., 1980), or a decrease of Freundlich K constant (Mnkeni and MacKenzie, 1985). Mechanisms for this effect proposed by these researchers and others (Hue, 1992; Bumaya and Naylor, 1988; Singh and Jones, 1976) include: (1) the competition of organic acids produced during mineralization for the same sites of fixation as P; and (2) the complexing of exchangeable Al by organic acids. The results of our study supports the hypothesis that P returned to the soil by organic residues reacts with the sites of sorption (Reddy et al. 1980). P sorption of soils amended with alfalfa and wheat straw, which had the same C content but different P content, reacted differently, whereas P sorption of soils amended with manure and alfalfa, which had a different C content but similar P content decreased similarly. Furthermore, there are indications that previous P applications can decrease P sorption (Smyth and Sanchez, 1980), so that inorganic P released from organic residues may complex with the sites of P sorption in surface reactions.

Organic amendments such as manure contain inorganic ligands such as SO_4 and/or F, and metals such as Ca and/or Mg which may be mineralized from organic amendments. Sulfate and fluorine can strongly complex exchangeable Al, and Ca may form soluble complexes with P in the soil solution, thus preventing P from being fixed by Al or Fe. The reduction in P sorption can also be attributed to the increased pH observed in the soil samples amended with organic residues. The high pH minimizes Al activity and the production of OH ions that compete with PO_4 for P adsorption sites. Another mechanism, rarely reported, is the physical retardation of P retention, in which organic residues absorb P from the soil solution, thus physically separating added P from the soil mineral fraction (Mnkeni and MacKenzie, 1985).

Although it is interesting to note that all organic and inorganic amendments were effective in reducing exchangeable Al, high P content organic residues cause an even greater reduction in P sorption. Previous researchers have attributed this to P complexation by organic acids and other organic compounds produced during organic matter mineralization. But there are other mechanisms to explain decreased P sorption. Soluble and mineralized PO_4 and SO_4 in organic residues also can decrease exchangeable Al and/or react with P sorption sites. The only parameter of interest to an agronomist, $\text{P}_{0.2}$, was markedly decreased in all soil types by all rates of manure and alfalfa, suggesting that, in the presence of organic residues, less P fertilizer will be required to satisfy crop production needs. The fact that organic residues with high P content (manure and alfalfa) were more effective in reducing P adsorption capacity and increasing P in equilibrium solution suggests that it is likely that enough P was added to the soil to prevent further P sorption. These amendments also had a potential lime effect in reducing exchangeable Al and adsorption maxima, and in increasing pH. Therefore as suggested by Hue (1992), organic manure may substitute efficiently for lime in soil management.

CONCLUSIONS

Adding increasing rates of organic residues to high P fixing soils increased pH, decreased exchangeable Al, sorption capacity, and the affinity constant. These results suggest that organic residues with high P_0 content may be used efficiently in very acid soils as a substitute for the conventional amendments like $CaCO_3$. This suggests that high P content residues partially offset P sorption by complexing the sites of sorption with P released by mineralization of organic P from these materials.

These effects, besides reduction of P sorption characteristics through organic acids or organic compounds of organic residues, may also be due to release of P from organic residue mineralization which could react with sorption sites. Evidence for this was shown by the fact that inorganic amendments ($CaCO_3$ or $CaSO_4$) did not significantly increase inorganic P whereas organic residues high in P (manure and alfalfa) did significantly increase this fraction.

The addition of these organic materials increased the amount of P in the equilibrium solution and soluble P in different extractants. No treatment provided enough equilibrium P concentration at the level of zero P added (EPC) to attain 0.2 mg P L^{-1} ; suggesting that all these soils are naturally deficient in P. High P content materials such as manure had the best effects regardless of the soil type. Low P content material such as wheat straw had minimal effects. High rates of $CaCO_3$ decreased exchangeable Al and increased pH in all soils, but to a lesser extent than manure and alfalfa. Calcium sulfate reduced exchangeable Al at the highest rates but did not increase the pH. Calcium carbonate and $CaSO_4$ did not increase Bray 1 P nor total inorganic P, as did organic amendments. However, $CaCO_3$ decreased P sorption in all soils.

Contradictory effects of lime on P sorption characteristics and availability were reported by Holford (1983), Haynes and Swift (1988), Amarasi and Olsen (1973), and Smyth and Sanchez (1980). Calcium sulfate substantially reduced adsorption maxima in

only three out of five soils and did not decrease the affinity constants of these soils. At the low rates CaSO_4 did not affect sorption characteristics. Wheat straw increased P in solution of equilibrium and decreased sorption capacity and affinity in most of the soils studied, although the effects were less than that of manure and alfalfa. That low P content of wheat residue decreased P sorption to some extent may indicate that other compounds or mineralization products in residues, such as organic acids, are involved in preventing P sorption.

Tolo soil (Vitrandept), with only traces of exchangeable Al, sorbed appreciable amounts of P, but responded more positively than most soils to the addition of organic residues. Surface reactions and other non-precipitation reactions may be actively taking place as evidenced by the large increases in pH of the equilibrium solution (data not shown). This soil seems to be very young and not yet at the ultimate stage of weathering that leads to the formation of very high P-fixing amorphous materials. Unlike other Andisols, this soil does not contain a great amount of organic material. Mizota and Wada (1980) reported that the fixing capacity of volcanic soil is related more to Al bound to organic matter than Al bound in allophanic material. The latter explanation may apply to Kinigi soil, a volcanic soil high in organic matter, that sorbed the greatest amount of P added in comparison to Tolo and the other soils studied. The non-volcanic Ultisols, Mata and Jory, were intermediate in P sorption capacity, although the higher P retention of Mata soil at low rates of added-P suggests that it reacted differently from Jory soil. The high P sorbing capacity of Kibeho soil may be attributed to the presence of some sombric horizon (deep layer) materials mixed in with the Ap horizon. The sombric material contained more exchangeable Al and less organic matter than the Ap horizon and reportedly had a pH measured in NaF solution greater than 9.4, the threshold pH for "andic" soils.

This study shows that organic residues, particularly those rich in P, increased P in the soil solution and decreased the P sorption capacity of these soils. The practical implication, as evidenced by a reduction of $\text{P}_{0.2}$ by almost 50% with organic amendments,

suggests that less fertilizer P should be required for a good crop yield when organic residues are utilized.

Calcium carbonate and CaSO_4 reduced exchangeable Al but had less effect on P sorption characteristics than manure or alfalfa. This suggests that a more complete amendment, with an organic constituent, induces additional reactions such as those involving PO_4 or organic acids. The salt effect produced by inorganic amendments like CaCO_3 and CaSO_4 applied at high rates may provide another explanation: the positive effect of their negative charges may be countered by positive charges resulting from the adsorption of Ca ions. The inability of inorganic amendments to greatly alter P sorption is also demonstrated by their lack of effect on Bray 1 P. As suggested in the discussion of the mineralization of organic residue, enough SO_4 is produced to complex exchangeable Al and minimize its activity in the soil solution. Organic residues may produce other ligands such as F that are very powerful Al- and Fe-complexing agents, even at low concentration.

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Table 2.1. Selected chemical characteristics of five soils used in the study.

	pH	Total C	N	Ca	Mg	K	Al	di-Fe [†]	di-Al [†]	ox-Fe [‡]	ox-Al [‡]
	cmol (+) kg ⁻¹										
Jory	5.45	3.34	0.009	1.13	0.54	0.65	0.396	110	11	4	19
Tolo	5.80	4.95	0.22	6.25	1.33	1.07	0.087	27	7	18	47
Kinigi	4.71	9.15	1.09	0.58	0.29	0.47	0.489	29	13	31	59
Mata	4.65	4.50	0.17	0.15	0.29	0.47	0.759	89	40	11	17
Kibeho	4.12	3.52	0.098	0.00	0.07	0.16	1.08	121	36	15	38

[†] Dithionite extractable Fe or Al

[‡] Oxalate extractable Fe or Al

Table 2.2. Effect of application rates of organic residues, CaCO₃, and CaSO₄ on pH of Jory soil.

Rates	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
Zero	5.3	—	—	—	—	—
Low	—	5.4	5.4	5.3	5.6	5.3
Medium	—	5.8	5.9	5.4	5.6	5.3
High	—	6.4	6.7	5.5	5.8	5.3

Table 2.3. The pH values of five soils treated at the high rate of organic or inorganic amendments.

Soil	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
Jory	5.4	6.4	6.7	5.5	5.8	5.3
Mata	4.7	6.0	6.2	5.3	5.9	4.5
Tolo	5.8	6.1	6.7	6.2	6.2	5.4
Kinigi	4.7	5.3	6.1	5.5	4.8	4.6
Kibeho	4.1	5.8	5.9	5.0	5.3	4.1

Table 2.4. Exchangeable Al in Jory soil samples treated with increasing rates of organic or inorganic amendments.

Rates	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
-----cmol (+) kg ⁻¹ -----						
Zero	0.426	—	—	—	—	—
Low	—	0.297	0.296	0.333	0.333	0.370
Medium	—	0.037	0.011	0.160	0.259	0.348
High	—	nd	nd	0.092	nd	0.074

nd-not detectable

Table 2.5. Exchangeable Al in five soils treated at the high rate of organic or inorganic amendments.

Soil	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
-----c mol (+) kg ⁻¹ -----						
Jory	0.426	nd	nd	0.093	0.004	0.074
Mata	0.704	0.009	0.004	0.296	0.009	0.467
Tolo	nd	nd	nd	0.004	nd	0.037
Kinigi	0.515	0.037	0.033	0.204	nd	0.370
Kibeho	1.080	nd	nd	0.321	nd	0.440

nd-not detectable

Table 2.6. Bray 1 extractable P in Jory soil samples treated with increasing rates of organic or inorganic amendments.

Rates	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
-----mg kg ⁻¹ soil-----						
Zero	10.9	—	—	—	—	—
Low	—	18.1	14.8	11.6	10.0	9.9
Medium	—	18.5	17.8	17.0	11.0	9.9
High	—	28.3	25.4	18.1	10.1	10.0

Table 2.7. Bray 1 extractable P in five soils treated with the highest rates of organic and inorganic amendments.

Soil	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
-----mg kg ⁻¹ soil-----						
Jory	10.9	28.3	25.4	18.1	10.0	10.0
Mata	2.5	18.9	14.5	11.6	3.1	3.4
Tolo	30.4	56.8	40.8	33.2	29.6	30.4
Kinigi	13.8	30.5	19.0	16.4	13.2	9.0
Kibeho	1.7	14.2	12.0	5.2	2.1	1.6

Table 2.8. Total 1 N H₂SO₄ soluble phosphorus in five soils treated at the high rate of organic or inorganic amendments.

Soil	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
	-----mg kg ⁻¹ soil-----					
Jory	1457	1590	1494	1421	1482	1421
Mata	413	582	543	467	429	418
Tolo	531	690	636	522	512	536
Kinigi	784	930	898	601	649	774
Kibeho	388	560	543	479	410	375

Table 2.9. Affinity constants (k), adsorption maxima (b), and P sorbed at 0.2 mg P L⁻¹ in Jory soil samples treated with increasing rates of organic or inorganic amendments.

Rates	Soil amendment						
	Parameters	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
Zero	k [†]	5					
	b [‡]	1089					
	P0.2 [§]	550					
High	k		2	1	3	3	4
	b		1029	1053	1074	1031	1063
	P0.2		244	200	392	410	501
Medium	k		2	2	3	3	4
	b		1066	1076	1083	1069	1088
	P0.2		312	338	414	431	515
Low	k		3	3	5	4	5
	b		1079	1085	1089	1080	1093
	P0.2		366	395	547	464	518

[†] k is expressed in L mg⁻¹,

[‡] b is expressed in mg kg⁻¹

[§] P0.2 is expressed in mg kg⁻¹

Table 2.10. Sorption parameters calculated by Langmuir equation in five soils treated with soil organic and inorganic amendments.

Soils	Soil amendment					
	Control	Manure	Alfalfa	Wheat Straw	CaCO ₃	CaSO ₄
Affinity (k) [†]						
Mata	9.580	3.190	3.990	5.770	7.120	8.810
Kibeho	7.970	3.430	3.350	4.790	7.200	7.800
Tolo	1.200	0.580	0.590	1.030	1.310	0.890
Kinigi	18.000	9.000	12.000	11.000	20.000	19.800
Jory	5.100	1.550	1.780	2.870	3.300	4.450
Adsorption maxima (b) [‡]						
Mata	1042	992	1007	1057	962	1048
Kibeho	1225	1060	1124	1132	1132	1138
Tolo	1035	891	946	1034	866	1011
Kinigi	1172	1120	1123	1123	1109	1150
Jory	1089	1029	1053	1074	1031	1063
P sorbed at 0.2 ppm P (P _{0.2}) [§]						
Mata	685	386	447	566	565	669
Kibeho	732	443	451	565	668	693
Tolo	200	93	100	177	170	152
Kinigi	917	720	793	772	867	918
Jory	550	244	200	392	410	501

[†] k is expressed in L mg⁻¹,

[‡] b is expressed in mg kg⁻¹

[§] P_{0.2} is expressed in mg kg⁻¹

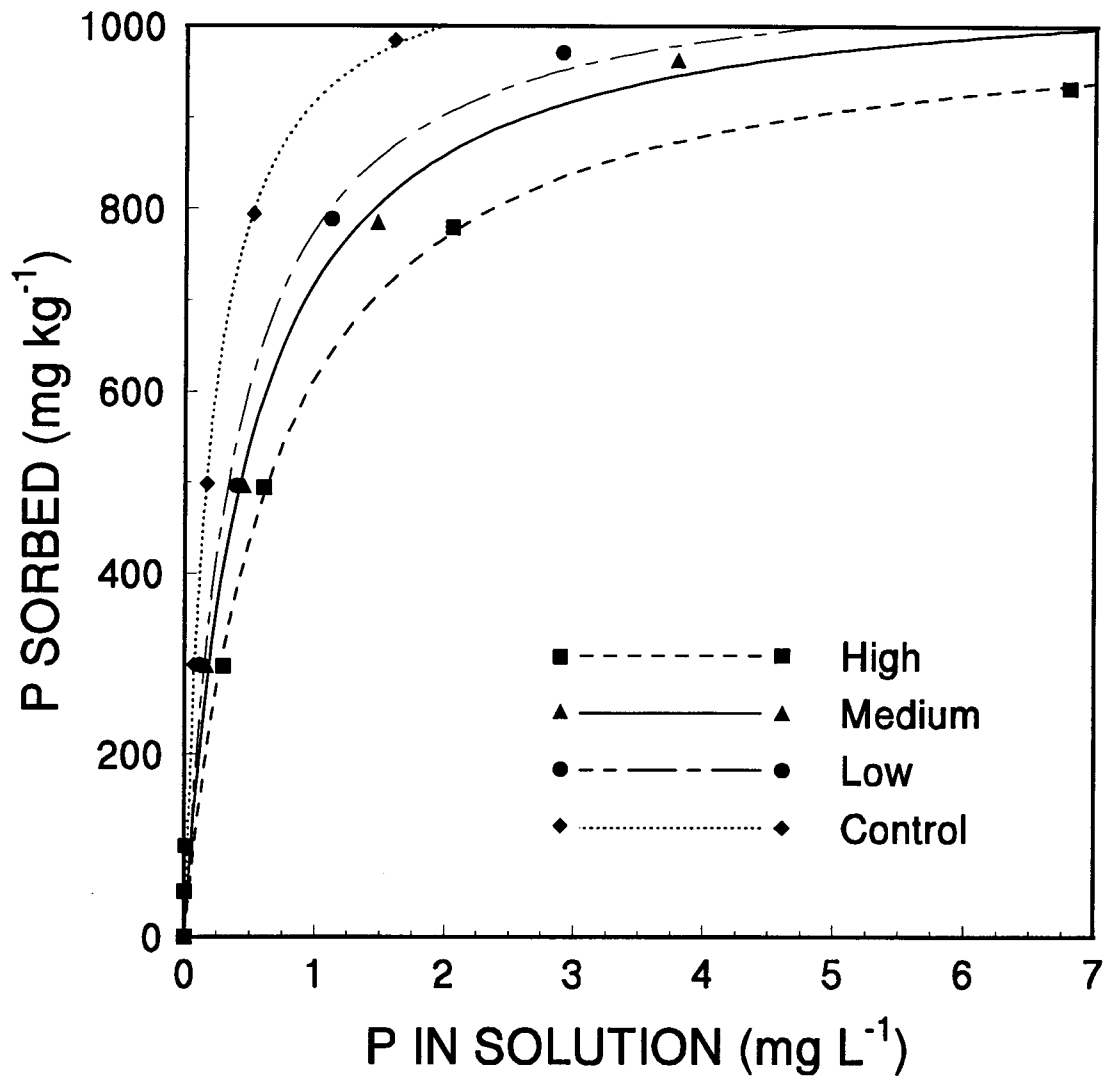


Fig. 2.1. Effect of rates of manure residues on P sorption of Jory soil.

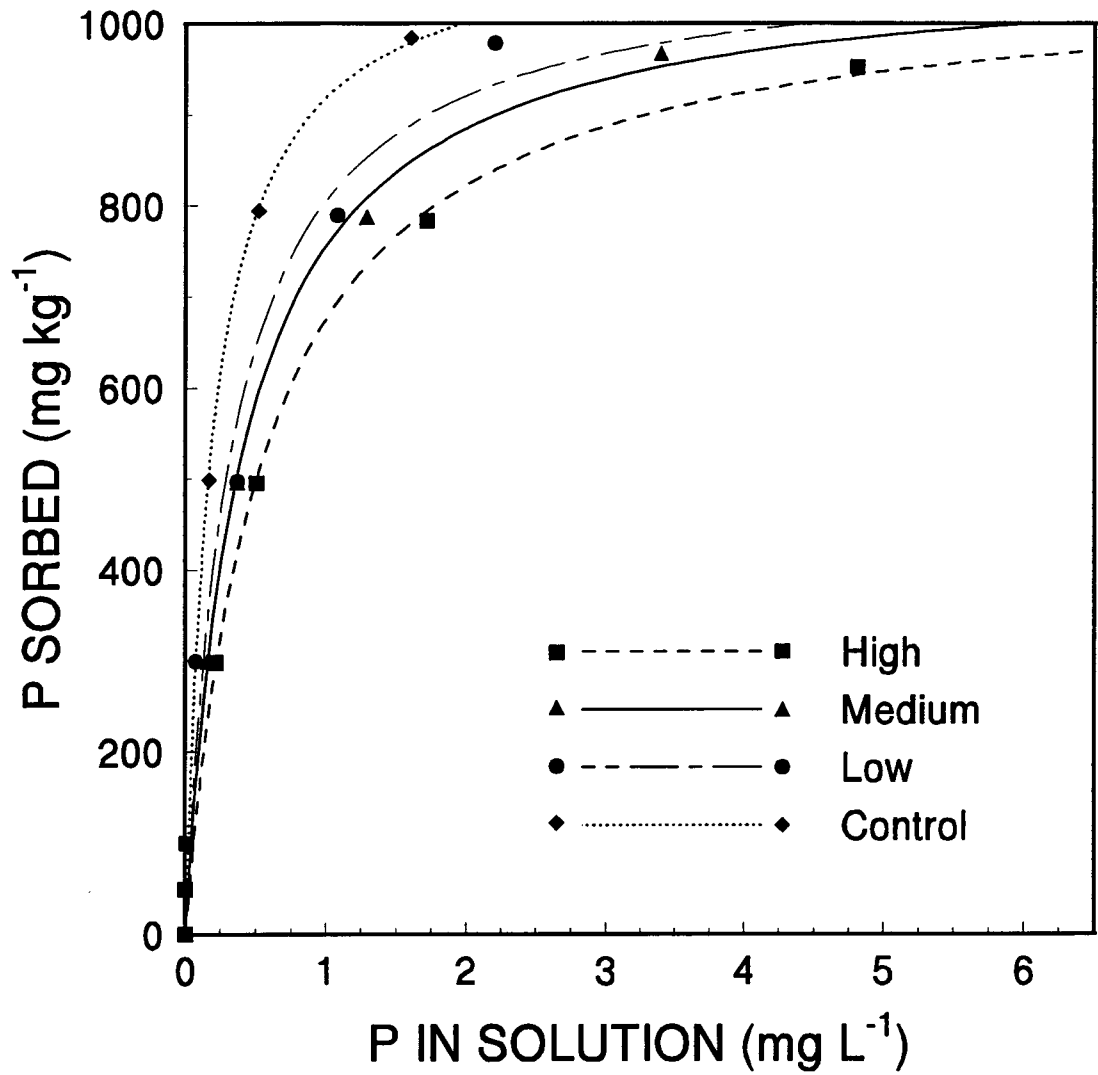


Fig. 2.2. Effect of rates of alfalfa residues on P sorption of Jory soil.

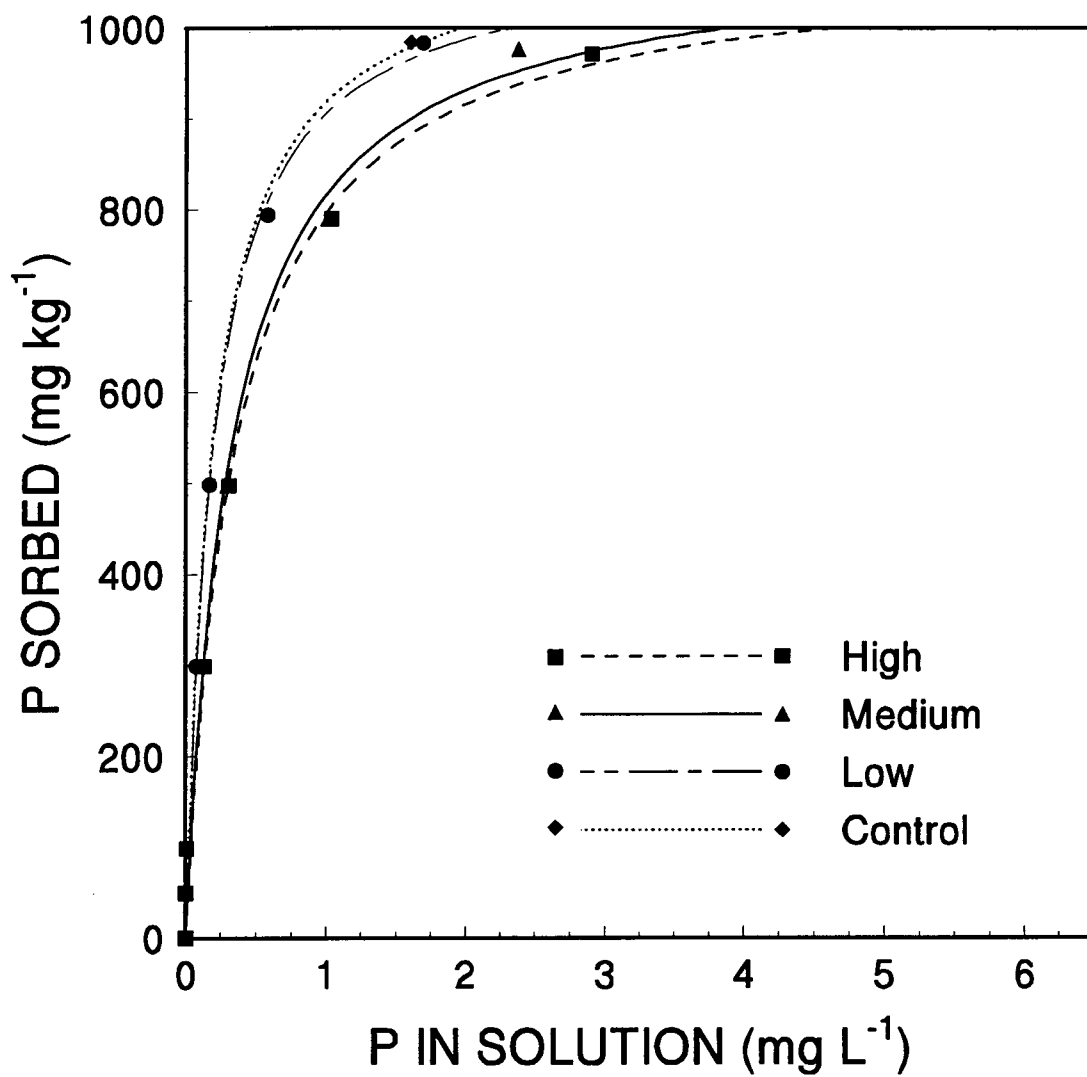


Fig. 2.3. Effect of rates of wheat straw residues on P sorption of Jory soil.

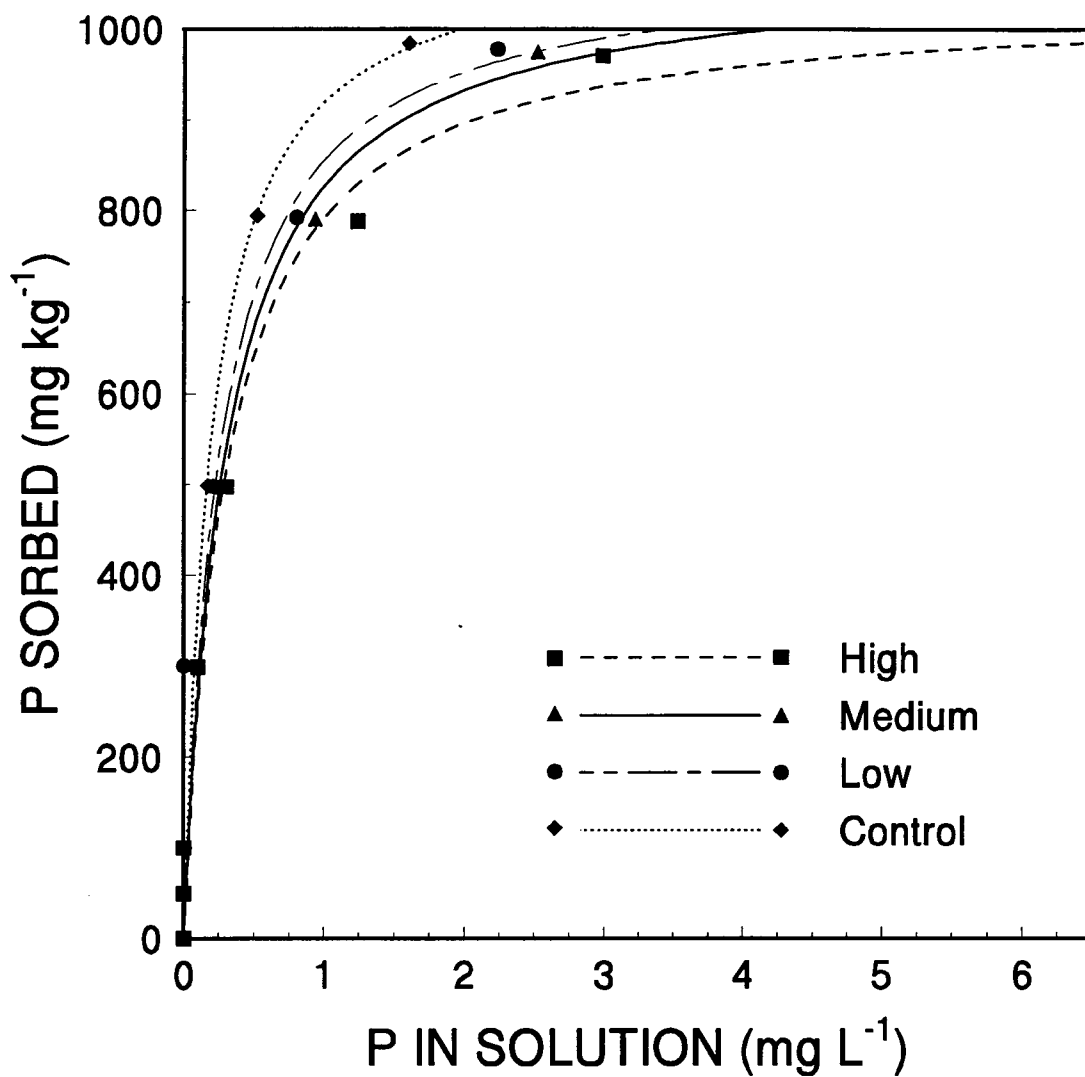


Fig. 2.4. Effect of rates of CaCO_3 on P sorption of Jory soil.

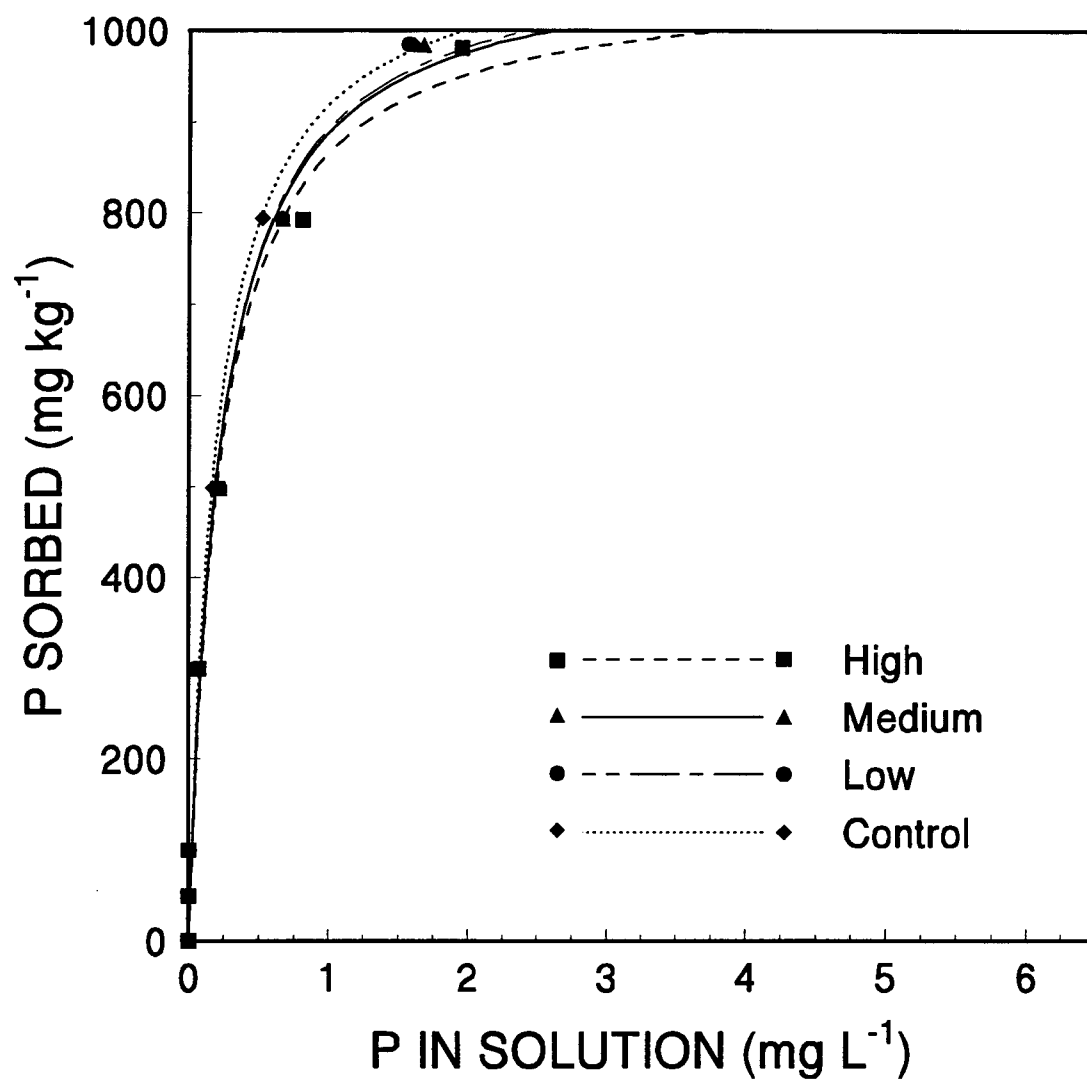


Fig. 2.5. Effect of rates of CaSO_4 on P sorption of Jory soil.

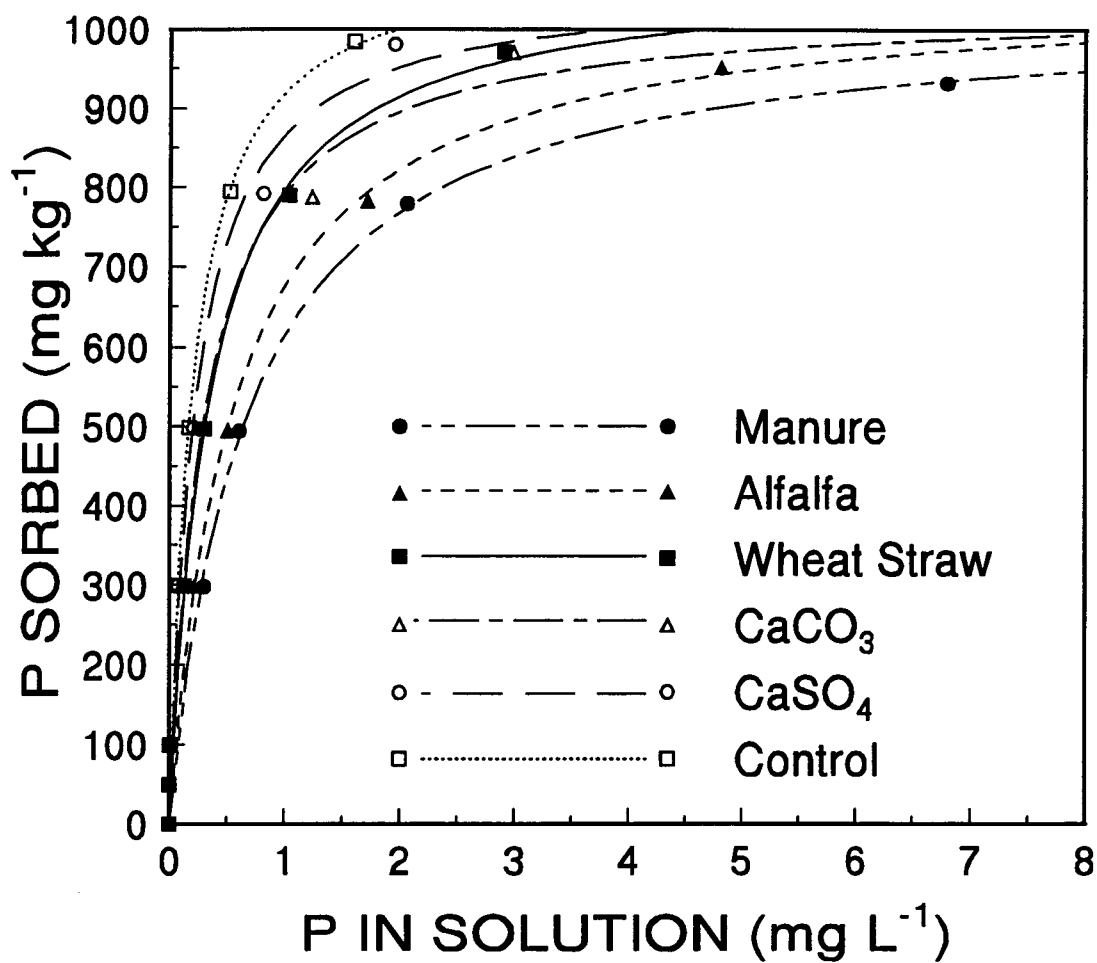


Fig. 2.6. Effect of soil organic and inorganic amendments on P sorption of Jory soil.

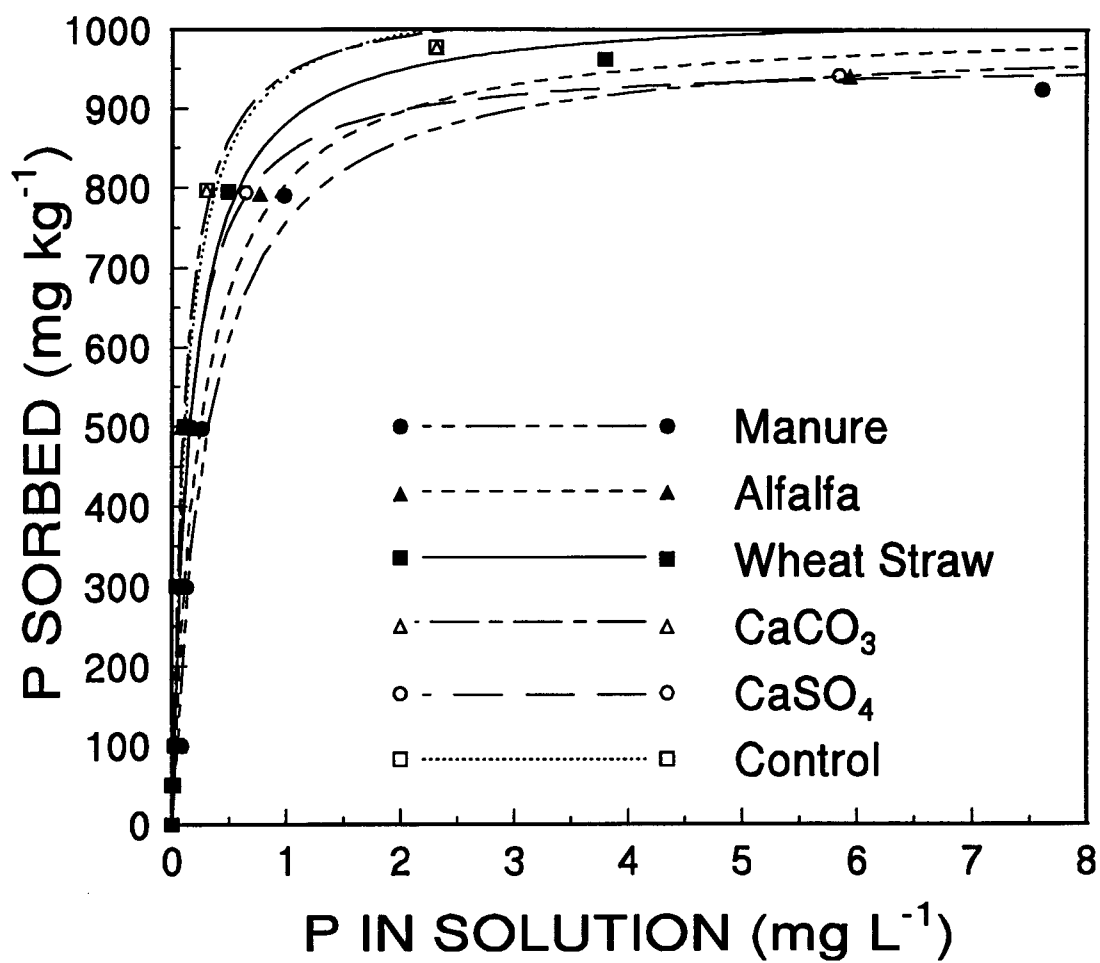


Fig. 2.7. Effect of soil organic and inorganic amendments on P sorption of Mata soil.

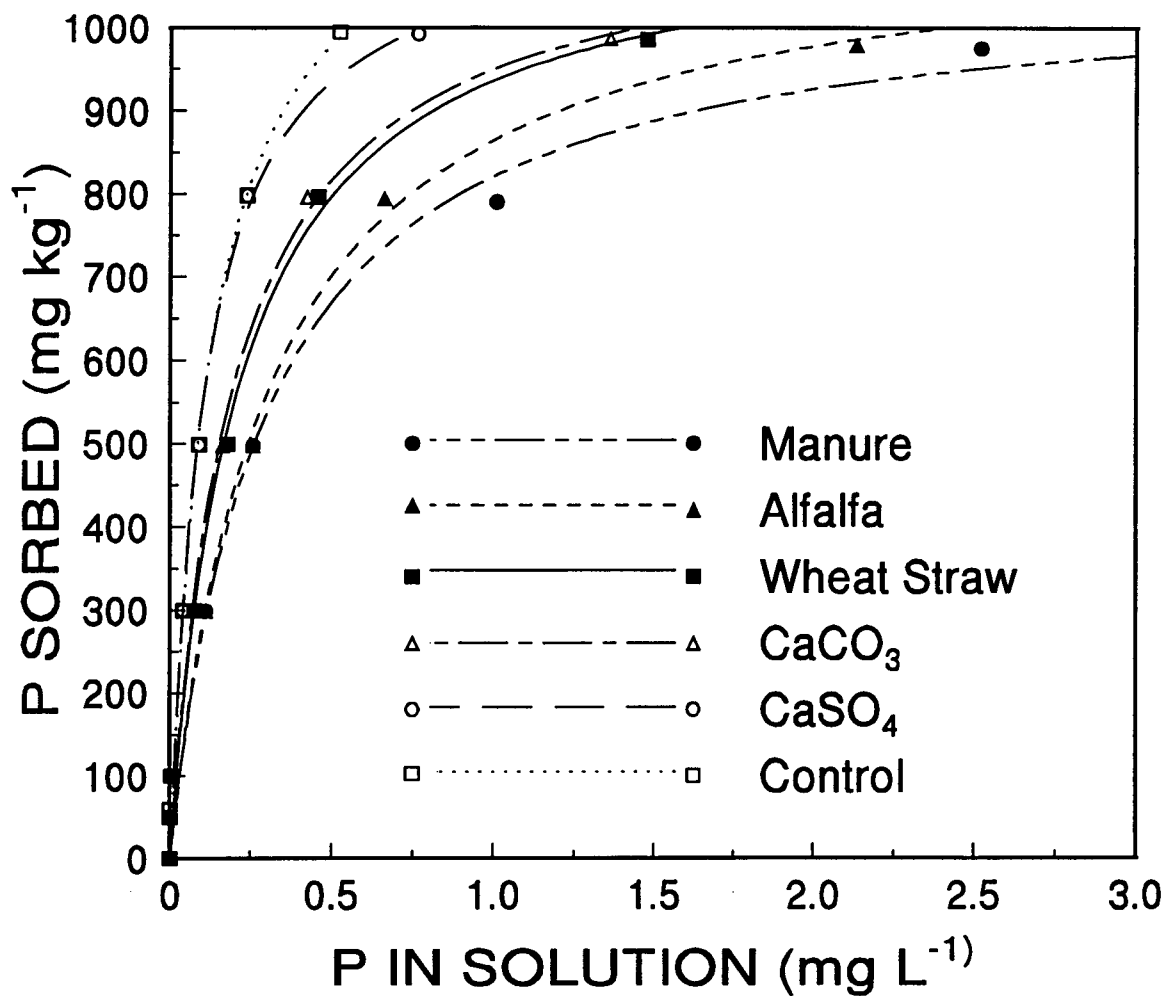


Fig. 2.8. Effect of soil organic and inorganic amendments on P sorption of Kibeho soil.

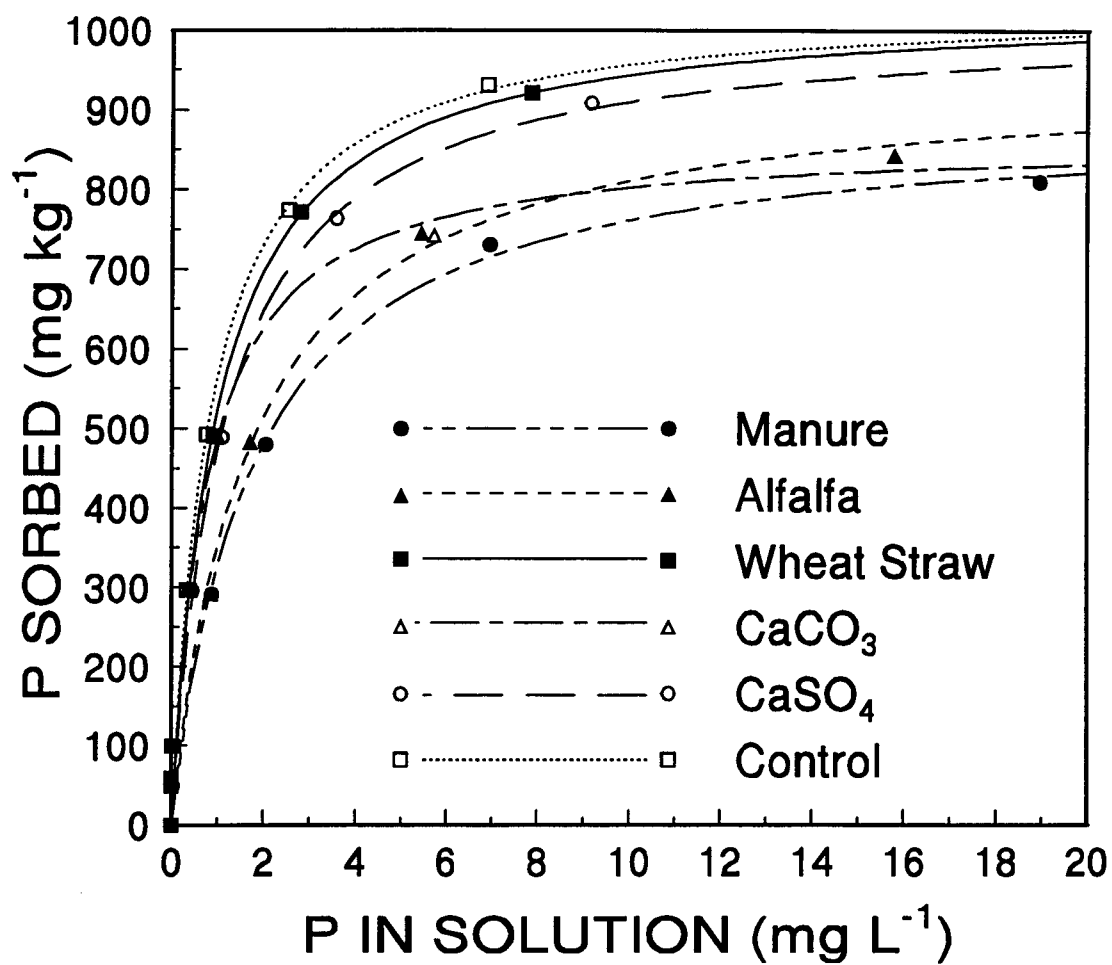


Fig. 2.9. Effect of soil organic and inorganic amendments on P sorption of Tolo soil.

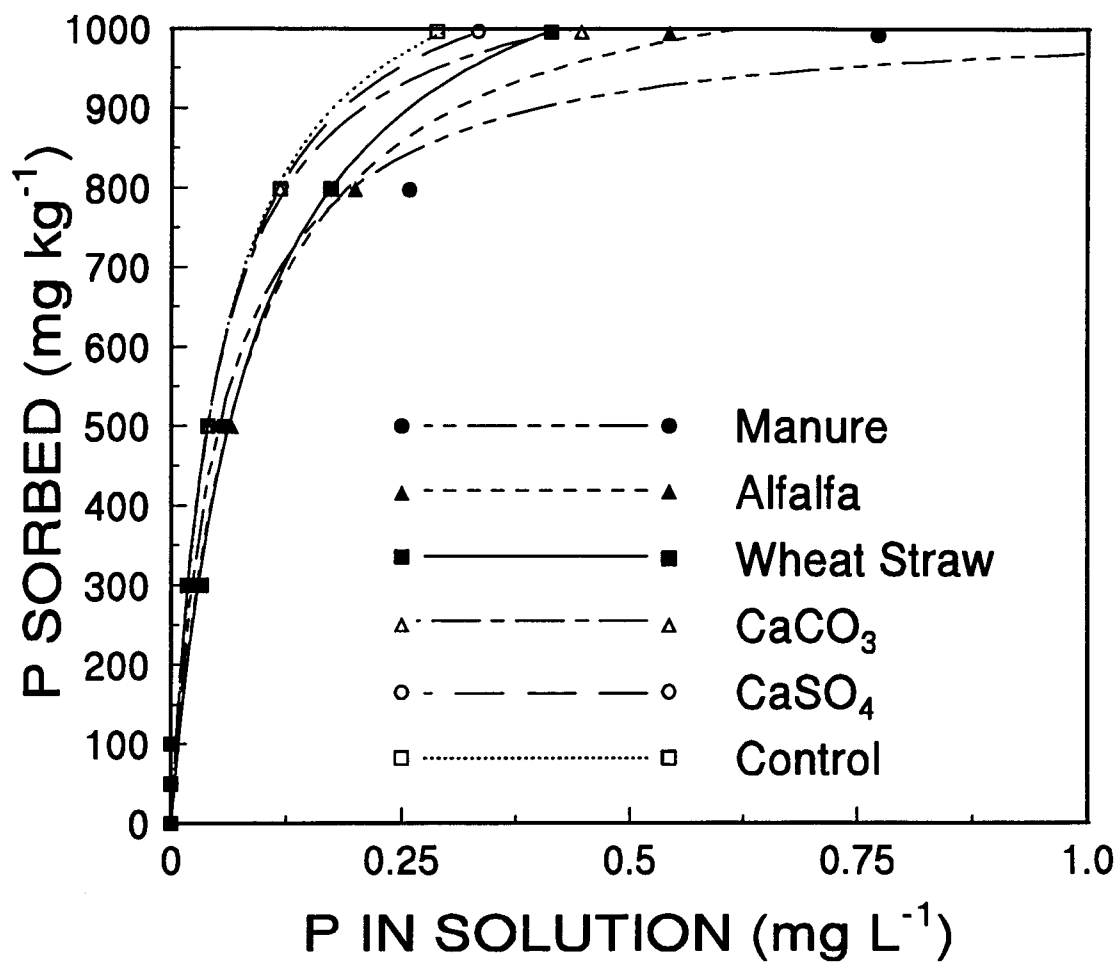


Fig. 2.10. Effect of soil organic and inorganic amendments on P sorption of Kinigi soil.

CHAPTER III

EFFECTS OF ORGANIC AND INORGANIC SOIL AMENDMENTS ON DISTRIBUTION OF SOIL PHOSPHORUS FRACTIONS

ABSTRACT

In a laboratory incubation experiment, different fractions of P soluble in acid or alkaline extracts were determined following the method of Hedley et al. (1982a) on five different soils amended with manure, alfalfa (*Medicago sativa*), wheat straw (*Triticum estivum*), CaCO_3 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The nine P fractions determined were: biologically available P; labile inorganic and organic P; chemisorbed inorganic and organic P; inorganically and organically sorbed P at the internal surface; occluded and residual P. The five soils were: Jory (clayey, mixed, mesic xeric Haplohumult) and Tolo (medial over loamy, mixed, frigid typic Vitrandept) from Oregon, and Mata (Sombrihumult), Kinigi (Placandept), and Kibeho (Paleudult) from Rwanda.

Manure and alfalfa residues increased biological available P, labile P_i , and chemisorbed P_i in all soils. Tolo soils showed the least increase of chemisorbed P_i , and the greatest increase of biologically available P and labile P_i . Chemisorbed P_i at the internal surface showed variations depending upon the type of soil and amendment, but was slightly increased in most samples treated with either manure or alfalfa. No changes were observed in 1.0 M HCl P fractions (apatite P) except for a slight increase observed in the Tolo samples treated with manure and CaCO_3 . The effects of wheat straw residues were variable and depended upon the types of soils: increasing biological P in Kinigi, and having almost no effect in Jory and Kibeho. Calcium carbonate and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ had little or no effect on inorganic P distribution.

The labile P_o was reduced in most soils by the addition of manure and alfalfa, whereas chemisorbed P_o was increased by the same organic residues.

For a given soil and treatment, chemisorbed P_i was greater than the chemisorbed P_o in all soils. Therefore in a high P-sorbing soil, inorganic P released from organic residues was largely chemically fixed rather than biologically immobilized by microorganisms.

This may partly explain reductions in the adsorption capacity observed in samples treated with high P-content organic residues (manure and alfalfa) in chapter 2.

INTRODUCTION

The results reported in chapter 2 demonstrated that the phosphorus (P) sorption capacity of five high P-fixing soils was reduced when amended with manure and alfalfa. As one possible mechanism for these results, it was suggested that newly released inorganic P (P_i) from organic residues complexed the sites of P sorption in these soils. When a soluble P is added to soil, it is chemically fixed or immobilized biologically in microbial biomass or organic P compounds (Ghoshal, 1974; Ghoshal, 1975a). Chemical fixation of P in soil is due to the ability of some soil compounds such as allophanic material, clay minerals and Al or Fe oxides and hydrous oxides to strongly sorb PO_4 ions (Parfitt, 1978). In acid conditions, P released into the soil solution reacts quickly with soluble Al or Fe to form compounds that precipitate out of solution (Lee et al., 1990). There is limited evidence that biological activity affects P availability from studies on the effect of cellulose or the fate of PO_4 added to soil (Chang and Jackson, 1957; Potter et al., 1991). All these P fractions exist in a dynamic equilibrium (Chauhan et al., 1979; Hedley et al., 1982a).

In the previous chapter we suggested, as have other researchers (Reddy et al., 1980), that a decrease in P sorption by soils treated with organic residues was due partly to a possible complexation of fixation sites by P originating from organic residues. In recent studies, Guertal et al. (1991) reported that successive extractions of P with resin in upper layer soil samples of a soil cropped under no tillage practices resulted in an increase of P sorption. This may be explained by the resin's removal of labile P from the surface of sorbing material, leaving the sites of P sorption uncovered. This is an indirect demonstration that P previously mineralized from organic matter reacted with the surface of sorbent material. Sharpley et al. (1984) observed that inorganic and organic fractions of P were increased in soils receiving feedlot manure.

There is little evidence under controlled conditions that mineralization of organic P plays a significant role in decreasing P sorption by residues reacting with the sites of P sorption. Measuring the changes in P content of different fractions such as labile P (resin P, $\text{NaHCO}_3\text{-P}_i$), and Al or Fe bound P fractions after addition of organic residues might be a way to verify the hypothesis that P from organic residue complexes the sites of P sorption in soil. Such complexing prevents any further sorption of added P since both pools of $\text{NaHCO}_3\text{-P}_i$ and NaOH-P_i represent either surface adsorbed P or precipitated P.

The objective of this study was to measure the changes in P fractions of different types of high P-fixing soils induced by various organic and inorganic amendments. The study also evaluated the extent to which labile P fractions and Al- and Fe-bound P fractions are affected by P originating from organic residues versus inorganic amendments. The results may explain partly the mechanism by which organic residues decrease P sorption capacity in very high P-fixing soils.

MATERIALS AND METHODS

Soil samples and amendment materials

Surface soil (0-20 cm) samples of three soils from Rwanda (Kinigi, Kibeho, and Mata) which are unclassified but are similar to Placandept, Paleudult, Palehumult, respectively, and two soils from Oregon (Jory and Tolo) which are classified as clayey, mixed, mesic, xeric Haplohumult and medial over loamy, mixed, frigid typic Vitrandept, respectively, were collected and used in this study. Kinigi is a poorly drained soil, high in organic matter (16%). Mata is a high altitude soil and receives regular applications of homestead residues to maintain its fertility. Kibeho is a very weathered and eroded soil under a vegetation of *Eragrostis* spp. which is an index of soil degradation in the highlands of Rwanda. Some artifacts of the sombric horizon were visible in the sampled upper layers of Kibeho soil. Tolo and Jory are very well drained soils. Moistened samples from the field were screened through 0.2-mm sieve and air-dried.

Wheat straw (*Triticum estivum*) residues were collected from the Hyslop Research Station, Oregon State University, Corvallis, OR. Steer manure and alfalfa (*Medicago sativum*) residues were obtained from a store in Corvallis, Oregon. These organic residues were air-dried prior to being oven-dried at 60 °C, ground and sieved through 1-mm sieve and stored in polyethylene bags at room temperature. Laboratory grade CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were used as inorganic amendments.

Laboratory analysis

Soil pH was determined with a glass electrode (soil:water ratio 1:2), total C of soil and organic residues was determined by combustion in a LECO C Analyzer. Carbon in organic residues was determined by an autoanalyzer, total N in organic residues by the Kjeldahl method. Total P was determined by the alkaline oxidation method (Dick and Tabatabai, 1977). Phosphorus availability indices were determined using the following

extractants: 0.03 M NH_4F^+ and 0.025 M HCl to measure Bray 1 P, 0.01 M $CaCl_2$ and 0.5 M H_2SO_4 to determine total inorganic P (Olsen and Sommers, 1982). Exchangeable Al was extracted by 1 M KCl solution (Olsen and Sommers, 1982). Phosphorus was measured colorimetrically (Murphy and Riley, 1962) and cations by atomic absorption spectrophotometry. All soil characteristics are presented in Table 2.1.

Incubation

Organic amendments (wheat straw, manure, and alfalfa) were added at increasing rates of 0 (control), 1% (low), 2.5% (medium), 5% (high) (wt/wt) to the Jory soil samples. Another set of Jory soil samples received inorganic amendments ($CaCO_3$ and $CaSO_4 \cdot 2H_2O$) at the rates of 1 (low), 1.5 (medium), and 3 (high) times the amount of exchangeable Al in these soils. The other soils (Mata, Tolo, Kinigi, and Kibeho) received only the highest rates of either organic or inorganic amendments. Double-distilled water was added to the samples to bring the soil moisture to 66% of water holding capacity. Duplicate samples were then incubated at 24 °C for 28 days. Every two days the incubation containers were aerated and water content maintained gravimetrically. After the period of incubation the samples were air dried prior to the determination of pH, exchangeable Al, soil P and the sequential fractionation of P.

Sequential fractionation of P

Fractionation of inorganic and organic P was performed on each soil treatment by the Hedley method (Hedley et al., 1982a). The analytical extractants and their associated soil P fractions are shown in Table 3.1. Biologically available P (resin P) was extracted by shaking (16 h) 0.5 g soil with 5 g resin oversaturated with bicarbonate in nylon bags in 30 ml deionized water. Phosphate ions adsorbed on resin were extracted by shaking the bag containing resin with 30 mL 0.1 M HCl for 16 h. The next steps of fractionation were performed by using the same samples and shaking 16 h with 30 mL of the appropriate

extractant. Total P was determined on fractions 2, 3, and 4 following EPA methods (1982). All P was determined colorimetrically (Murphy and Riley, 1962) after neutralization when necessary. Hedley et al. (1982b) summarized the rationale behind the P fractionation methodology as follows:

- a) Resin extractable P_i has been identified as the form of soil P from which plants normally draw their supply (Amer et al., 1955; Bowman and Cole, 1978)
- b) A resin pretreatment reduces the P_i concentration in the subsequent extractions and therefore reduces the risk of insoluble PO_4 precipitation under alkaline conditions.
- c) $NaHCO_3$ (0.5 M, pH 8.5) extracts additional P_i that is available to plants and also extracts the more labile forms of P_o (Bowman and Cole, 1978).
- d) The more strongly alkaline 0.1 M NaOH solution extracts some of the labile P_o (Anderson, 1964). It also partially dissolves Fe and Al- PO_4 (Chang and Jackson, 1957), and dissolves P_i from the surface of sesquioxides (McLaughlin et al., 1977; Parfitt, 1978).
- e) 1 M HCl dissolves acid soluble P_o in the form of Ca- PO_4 and some P_i which is occluded within sesquioxides and released on partial dissolution of these oxides.

RESULTS

Biologically available P

When the five control samples were compared, the biologically available P fraction ranged from 2.2 mg kg^{-1} soil (untreated Kibeho soil) to 33.94 mg kg^{-1} soil (Tolo soil). Manure and alfalfa residues increased the biologically available P, the labile P_i and the chemisorbed P_i in all soils (Fig. 3.1, 3.2, and 3.4). Both manure and alfalfa residues had comparable effects on the biologically available P fraction of Jory soil samples. Mata soil samples treated with manure residue had a greater amount of biologically available P (22 mg kg^{-1} soil) than alfalfa treated samples (14 mg kg^{-1} soil). The increases in Mata soil were 13.7 and 8.83 mg kg^{-1} soil in samples treated with manure and alfalfa, respectively. Wheat straw caused a slight decrease in the resin extracted biologically available P in Mata and Tolo but had no effect on Jory. Overall, Kibeho had the least amount of biologically available P, and Tolo soil had the greatest amount of biologically available P in the samples treated with manure or alfalfa. The highest increase of this fraction was found in Tolo samples amended with manure (17.98 mg kg^{-1}). In Kibeho soil, manure and alfalfa addition increased biologically available P by 4.33 mg kg^{-1} soil and 4.93 mg kg^{-1} respectively. These small increases are probably related to the small amount of initial biological available P and Bray I P in the control soil samples.

Manure and alfalfa caused comparable increases in Jory soil samples (8 mg kg^{-1} soil). The increases of resin P_i for manure and alfalfa treated samples of Kinigi soil were 6.9 and 9.3 mg kg^{-1} soil, respectively. Calcium carbonate and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ had no significant effect on the amount of biological P in all studied soils.

Labile organic and inorganic P

Adding manure and alfalfa residues caused a significant increase in the amount of labile P_i in all soils (Fig. 3.2). The greatest increase occurred in Tolo soil samples treated

with either manure (49.3 mg kg^{-1}) or alfalfa residues (49.38 mg kg^{-1}). After Tolo soil, Kinigi soil samples showed the highest increases caused by the addition of manure (30.39 mg kg^{-1} soil), or alfalfa (27.5 mg kg^{-1} soil). These high increases of labile P_i in Kinigi soil samples might have resulted from the mineralization of the native organic matter which is present in large amounts. Manure and alfalfa residues increased labile P_i in Jory soils by 23.8 and 17.5 mg kg^{-1} soil respectively and in Mata soil samples by 22 and 24 mg kg^{-1} soil, respectively. Adding manure and alfalfa to Kibeho soil samples increased labile P_i by 8.3 mg (manure) and 7 mg kg^{-1} soil (alfalfa). The samples treated with wheat straw had the lowest increases in P_i compared to other organic amendments regardless of soil type. Addition of either CaCO_3 or CaSO_4 resulted in little or no enhancement of the amount of labile P_i in all five soils except in the Kinigi soil where CaCO_3 increased labile P_i .

Labile P_o increased or decreased depending upon the type of soil and the type of residues (Fig. 3.3). The largest decreases in P_o were observed in Mata soil in the presence of manure (36 mg kg^{-1} soil) and alfalfa (34 mg kg^{-1} soil) with less of a decrease from the control. In Kinigi and Jory soils there was less of a decrease in P_o . In contrast, the labile P_o fractions of Tolo and Kibeho soil increased slightly. The differences among soils in P_o levels after treatment probably resulted from the mineralization or hydrolysis of sorbed organic P (inositol) (Trassar-Cepeda and Carballas 1991, Ghoshal 1975b) because of the instability of inositol at high pH. This fraction has been reported to be unstable by other researchers (Tiessen et al. 1983, Vazquez et al. 1991).

Chemisorbed P

It appeared that a great proportion of P returned to the soil by organic residues was recovered in $1M \text{ NaOH}$ extractant in all soils except the Tolo soil (Fig. 3.4). All samples amended with manure or alfalfa experienced a significant increase of the chemisorbed P_i fraction. The increases for soil samples incubated with manure were 12 , 78 , 93 , 115 and 169 mg kg^{-1} soil for Tolo, Kibeho, Jory, Mata, and Kinigi respectively. The changes in

samples that received alfalfa were as high as 78 (Jory), 71 (Mata), and 8 mg kg⁻¹ soil (Tolo). Wheat straw increased chemisorbed P_i only in Jory (40 mg kg⁻¹ soil) and Kinigi (46 mg kg⁻¹ soil). The very small increases of this fraction observed in Tolo may be due to it having small amounts of exchangeable Al and Fe. Tolo also has the lowest sorption capacity of the five soils studied. No changes were noted in the samples treated with inorganic amendments. The increases of chemisorbed P_i fractions observed in all soils were likely due to soluble inorganic P_i from the organic residues and from the mineralization of organic P.

Chemisorbed P_O fluctuated depending upon the type of amendments added and the nature of the soils (Fig. 3.5). Overall, manure or alfalfa amendments increased P_O in four out of five soils. The P gains in soil treated with manure were comparable and averaged 32 mg kg⁻¹ soil, except in Jory, where no increase was observed. The largest increase in the samples treated with alfalfa was found in Mata (57 mg kg⁻¹ soil) and the lowest in Jory soil (17 mg kg⁻¹ soil). Wheat straw caused increases ranging from 3 mg to 40 mg kg⁻¹ soil in Mata, Kibeho, Tolo, and Kinigi, and a significant decrease in Jory soil (30 mg kg⁻¹ soil). No effect of CaCO₃ or CaSO₄•2H₂O on P_O was observed in any of the soils.

Inorganic and organic P on internal aggregate surfaces

Increased inorganic P on the internal soil aggregate surface only occurred in Jory (manure and wheat straw) and Tolo (all organic amendments)(Fig 3.6). Tolo soil samples showed the greatest increases due to organic amendments; the magnitude of increase ranged from 18 (manure and alfalfa) to 35 mg P kg⁻¹ soil (wheat straw). The effects of organic amendments was relatively small in the other soils.

The P_O fraction on the aggregate surface increased with organic residue amendments (Fig. 3.7) probably because soluble inorganic P added through organic residues induced intense microbial activity. Except in Jory soil, these increases were

relatively small. Inorganic amendments of CaCO_3 and CaSO_4 did not show any effect on either P_i or P_o on the internal colloidal surface.

Residual and apatite P

No significant change occurred in apatite P_i content except in Tolo soils treated with manure or CaCO_3 , and Mata amended with manure (Fig. 3.8). The increases averaged 11 (manure) and 13 mg kg^{-1} soil (CaCO_3) in Tolo soil and only 6 mg kg^{-1} (manure) in Mata soil. Manure applied to Mata soil increased the pH above 6 and this may explain the increase of apatite P. The great amount of P extracted from Kinigi soil might result partly from a probable hydrolysis of P_o in the presence of HCl. The increases induced by CaCO_3 might have resulted from Ca ions sorbed at the surface of the adsorbent. The absence of changes in apatite P_i is understandable since most of the soils studied were very acid (Table 2.1) and therefore the only possible chemical reaction is the formation of Al and Fe compounds rather than Ca products. The amount of residual P in control soil samples depended upon the type of soil (Fig. 3.9). High amounts were extracted from Jory and low amounts from Tolo soil samples, reflecting the influence of native P in parent material. In general, organic or inorganic amendments had little effect on residual P.

DISCUSSION

The presence of wheat straw did not increase the inorganic fractions of P because the total amount of P and the portion of inorganic P added through wheat straw residue were very small compared with those of manure and alfalfa. Wheat straw residues also had a high C/P ratio (444) that would result in initial P immobilization (Li et al. 1990, Dalal 1977). Furthermore, wheat straw might have contributed to the depletion of soil P because of its high C/N ratio. The increases in biological available P, labile P_i , chemisorbed P_i and other inorganic P fractions due to manure or alfalfa are comparable with the results obtained by other researchers who reported increases of these fractions in samples incubated with cellulose and to which soluble P was added (Chauhan et al., 1979; Hedley et al., 1982a; Sharpley et al., 1984). This suggests that soluble inorganic P and mineralized organic P from organic residues contributed to the increases of these fractions.

It seems that in very high P-fixing soils, chemical fixation and biological immobilization control the distribution of P among the different P fractions. At the early stage of incubation of acid soils with organic residues rich in soluble P_i , the chemical fixation of P may be more important than the biological immobilization. Ghoshal (1975a) demonstrated that the rapid fixation of P at the beginning of incubation started with a non-biological process which depended upon the physico-chemical characteristics of the media.

The increases of labile P_i and chemisorbed P_i fractions observed in almost all soils suggest that a chemical fixation process was taking place, leading to the sorption of P at the surface of adsorbent material or to the formation of Al and/or Fe compounds through precipitation processes. Sharpley et al. (1984) reported that 54% of inorganic P added with feedlot wastes could be readily sorbed. In the same way we can suggest that a great portion of inorganic P added with manure or alfalfa was rapidly sorbed as labile P_i ($\text{NaHCO}_3 P_i$), or chemisorbed P_i ($\text{NaOH } P_i$), and therefore could have enhanced the size of these two P pools. Manure and alfalfa contained greater amounts of total inorganic P

than wheat straw, and this may explain the reason why manure and alfalfa residues tended to increase chemisorbed P_i and labile P_i in soils, whereas wheat straw did not. The largest increase among the soils was in Tolo soil where labile P_i was 6 to 7 times greater than chemisorbed P_i . This soil had only trace amounts of exchangeable Al and had low sorption capacity.

These results may be partially explained by a study of Sharpley and Smith (1985) who compared P distribution in virgin and cultivated soils. They concluded that mineralized organic P was immobilized in stable forms of inorganic P pools during cultivation. This implies that P_i in organic residues and mineralized P_o may be rapidly chemisorbed to the surface of Al and Fe oxides (or hydrous oxides), preventing the uptake of this portion of P by microorganisms. However, the conversion of one form to another may be reversed depending upon the environmental conditions. Soil samples incubated with organic residues and regularly mixed may behave like cultivated soils, increasing the pool of P complexed by Al and Fe and soluble in NaOH P_i . It appears that the manure P added to Tolo soil is not precipitated by Al or Fe ions but is instead loosely adsorbed by Al or Fe hydrous oxides, or by Al or Fe oxides in forms that are more soluble in 0.5 M NaHCO_3 (labile P_i) than in 1 M NaOH. In the sequential extraction, the labile P_i represent the fraction of P that is loosely sorbed, and these results may be related to the fact that Tolo soil contains only traces of exchangeable Al. It is also interesting to notice a slight increase of apatite P in Tolo samples amended with manure.

The labile P_o fraction showed no consistent pattern among the soils or organic amendments. This might be attributed to previous observations that this fraction is sensitive to microbial activity (Chauhan et al., 1979) and has a fast turnover rate (Tiessen et al., 1983; Trassar-Cepeda and Carballas, 1991; Haynes and Swift, 1988). This is because the major component of labile P_o is a diester PO_4 (Tiessen et al. 1984), which prevents it from binding strongly to soil minerals and making it susceptible to rapid mineralization during incubation (Trassar and Carballas, 1991; Ghoshal, 1975b). Variation of labile P_o

was low among treatment replicates, so the variation in P_O response among soils due to organic residues may be due to different stages of residue decomposition and microbial activity as a function of soil type after 8 d of incubation.

The increase in P_i from dispersed aggregates (sonicated P_i) in Jory, Tolo and Kinigi might be explained by the addition of an energy source which induced high microbial activity and subsequent mineralization of a portion of the immobilized P inside the aggregates. The differences observed among soils may be related to the nature of aggregates present in these soils. The dispersed aggregate P_O increased slightly in all soils. Lee et al. (1990) reported that the increases of P_O fractions in soil samples which received cellulose alone might have resulted from the uptake of soluble P by microbes in soil aggregates. Tiessen et al. (1984) reported that in many soils the highest proportion of total organic C was released by sonification.

Residual P content was related more to the nature of the soil than to the treatments. The slight but constant increases with organic residues resulted from some recalcitrant forms of P present in the organic residues.

In all soils, chemisorbed P_O values were smaller than chemisorbed P_i values in samples treated with manure or alfalfa. This implies that inorganic P from P rich residues complexed the sites of P sorption. This may explain why residues such as alfalfa and manure reduced P sorption capacity regardless of the type of soil.

CONCLUSIONS

Adding organic residues rich in total P (manure and alfalfa) affected the distribution of P in different P fractions of soils. Bioavailable P (biologically available P and labile P_i), and the fractions that reacted with Al and Fe (chemisorbed P_i) increased in all soils treated with manure and alfalfa. With few exceptions, wheat straw and inorganic amendments did not significantly affect P distribution. Chemisorbed P_i fractions of all soils amended with residues were greater than chemisorbed P_o fractions. This study tended to show that in very high P-fixing soils, the types of P fractions formed due to organic amendments are controlled by the magnitude of competition between chemical fixation and biological immobilization of P. In all cases, chemical fixation of P seemed to be preferential over biological immobilization in these very high P-fixing soils. This explains why chemisorbed P_i was greater than chemisorbed P_o . The latter observation may imply that most of the inorganic P released from organic residues saturated the sites of P sorption and therefore decreased sorption capacity and prevented further sorption of added soluble P.

Reductions in labile P_o were noticed mainly with manure and alfalfa. This is due to a possible mineralization of the P_o fraction such as inositol, which is described as non-stable at high pH. Inorganic and organic forms of P released from organic manure are able to complex the sites of P sorption in soils resulting in increased chemisorbed P_i and P_o . Anderson et al. (1974) reported that ester PO_4 were preferentially sorbed on the same sites that sorbed P_i . Morris et al. (1992) reported that chemisorbed P_o was the only fraction to correlate with estimated sorption parameters, and that the organic compounds available to block sorption sites were more abundant in soils with low buffer capacity.

The lack of visible effects of inorganic amendments on P dynamics suggests that a large portion of native organic P did not contribute to the P fraction changes brought about by the mineralization process. The changes observed were a result of P contributed by organic residues. In very high P-fixing soils all mineralized P is not necessarily recovered

in the labile fraction, but instead is found mostly in chemisorbed P fractions. Although several researchers have shown that P sorption capacity is depressed by organic acids competing for P sorption sites, we cannot rule out the importance of P added through manure or alfalfa as an additional competitor for adsorption sites.

Further studies of native soil P and organic residue P are required in order to quantify the contribution of each source to each fraction. This is possible if radioactively labeled organic material is used to distinguish the two P sources. A sequential extraction of samples treated with different organic residues containing the same amount of total P may give information on the real contribution of organic residue P in reducing the P sorption capacity of a soil. Such a study would facilitate calculating how much manure or alfalfa is needed to reduce a soil's P sorption capacity.

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Table 3. 1 Sequential Hedley fractionation procedure and phosphorus fractions.

<u>Extractant</u>	<u>Phosphorus fraction</u>
Anion exchange resin	Biologically available P
0.5 M NaHCO ₃ (oversaturated with bicarbonate)	Labile organic and inorganic P
0.1 M NaOH	Chemisorbed P (organic and 0.1M)
0.1 M NaOH/sonification	Inorganic and organic P on internal aggregate surfaces
1 M HCl	Apatite type mineral P
Oxidation (H ₂ O ₂) and acid digestion (conc. H ₂ SO ₄)	Residual P

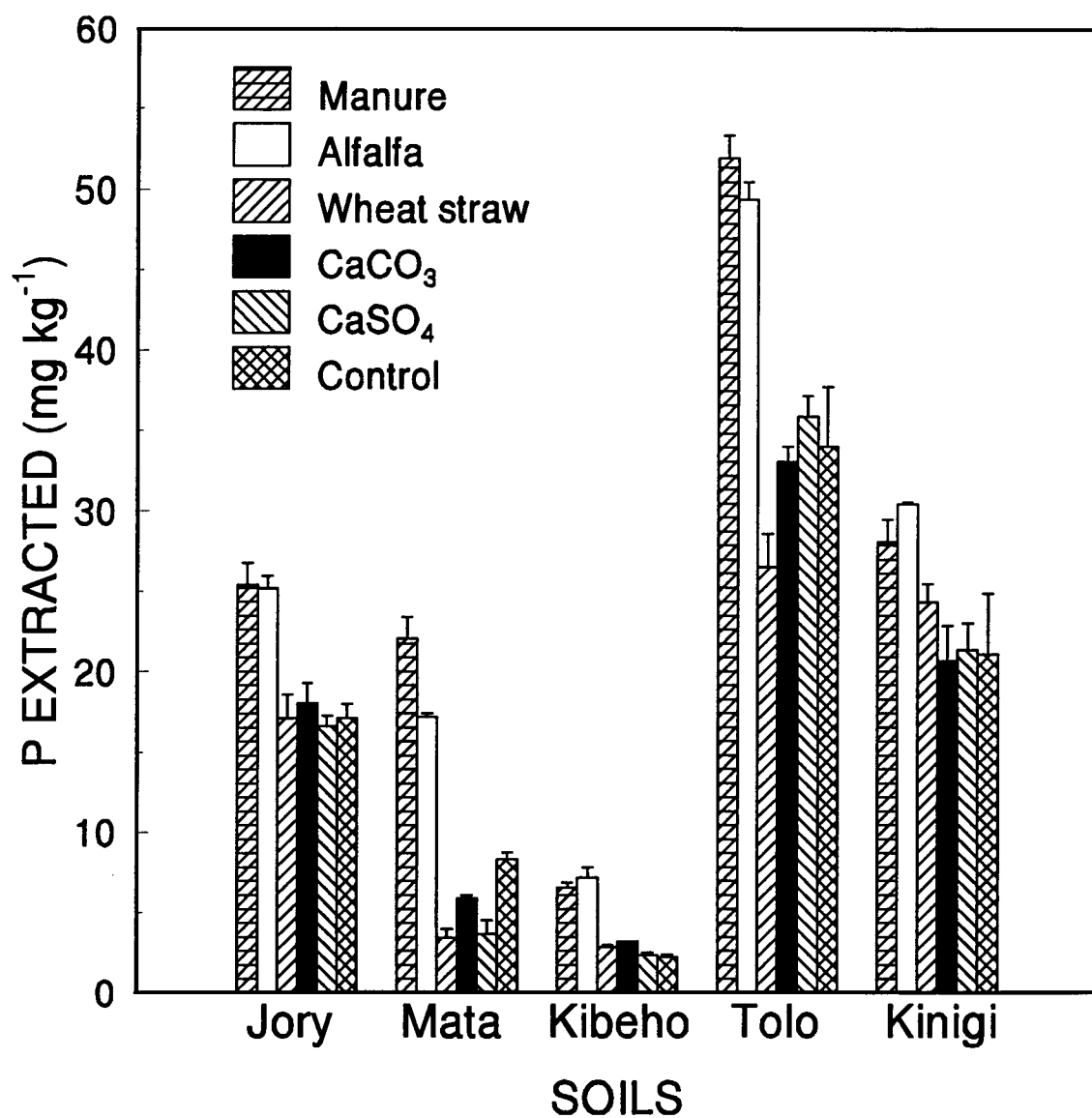


Fig. 3.1. Effect of soil organic and inorganic amendments on biologically available P fraction.

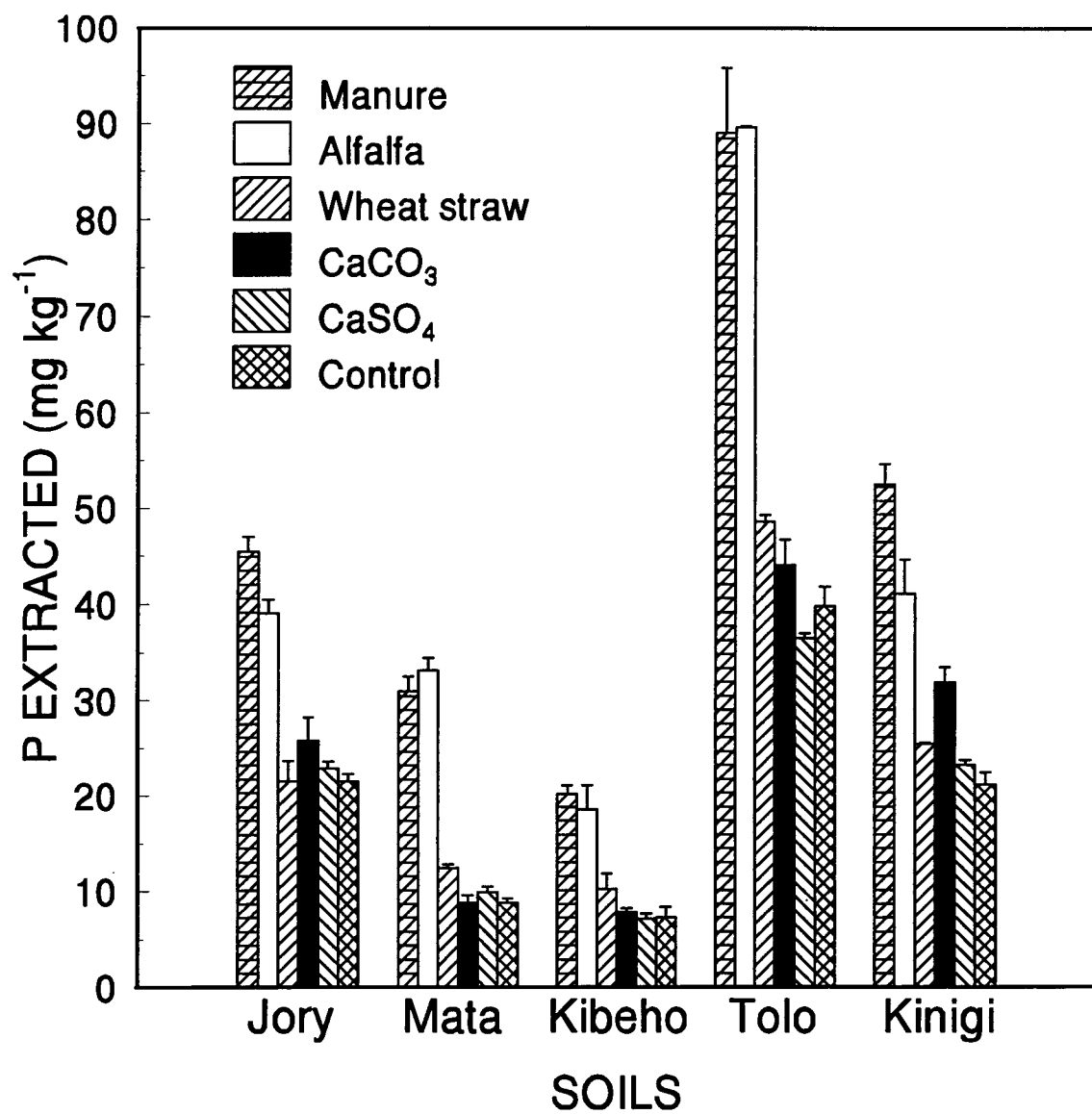


Fig. 3.2. Effect of soil organic and inorganic amendments on labile P_i fraction.

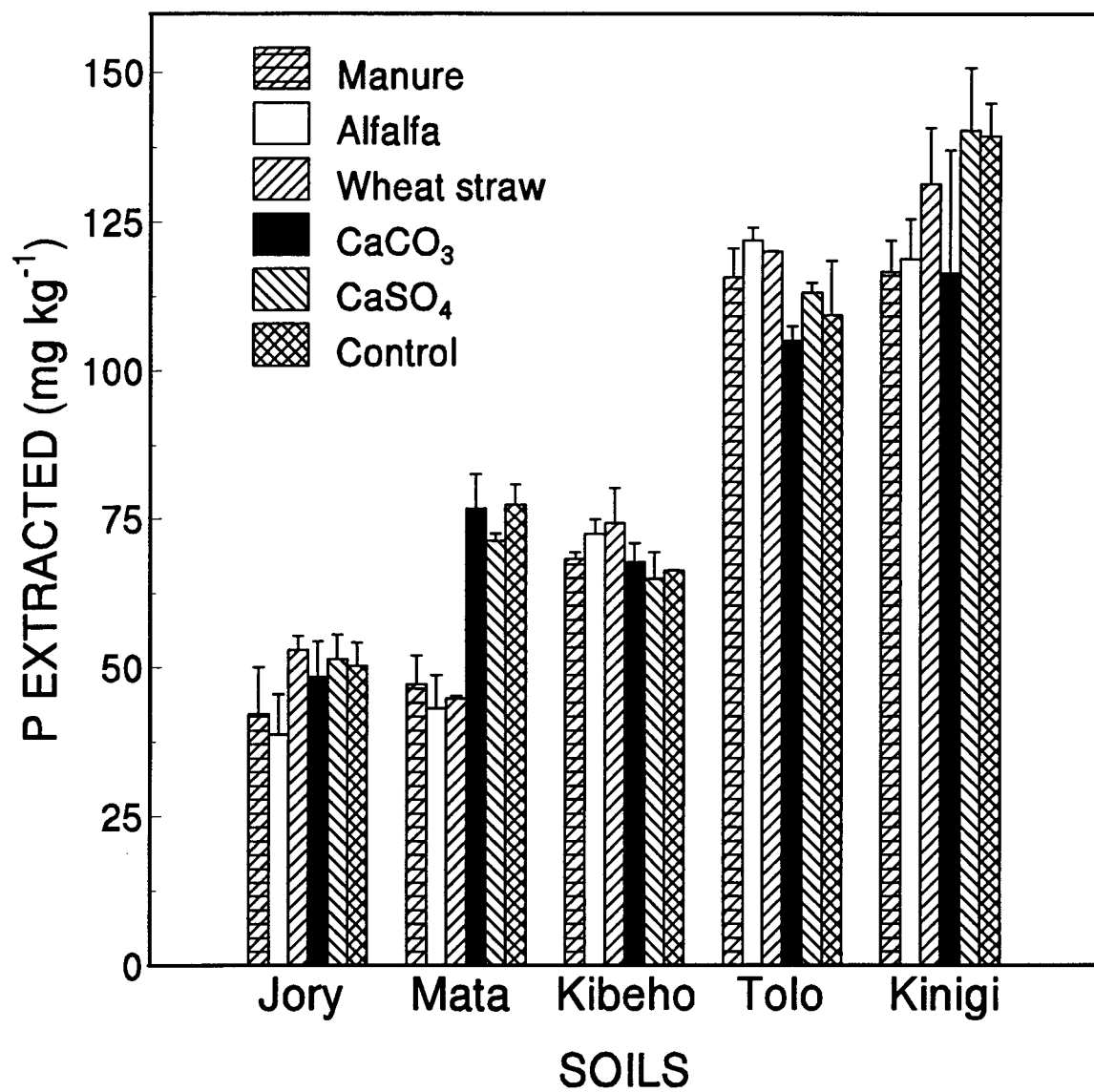


Fig. 3.3. Effect of organic and inorganic amendments on labile P_o fraction.

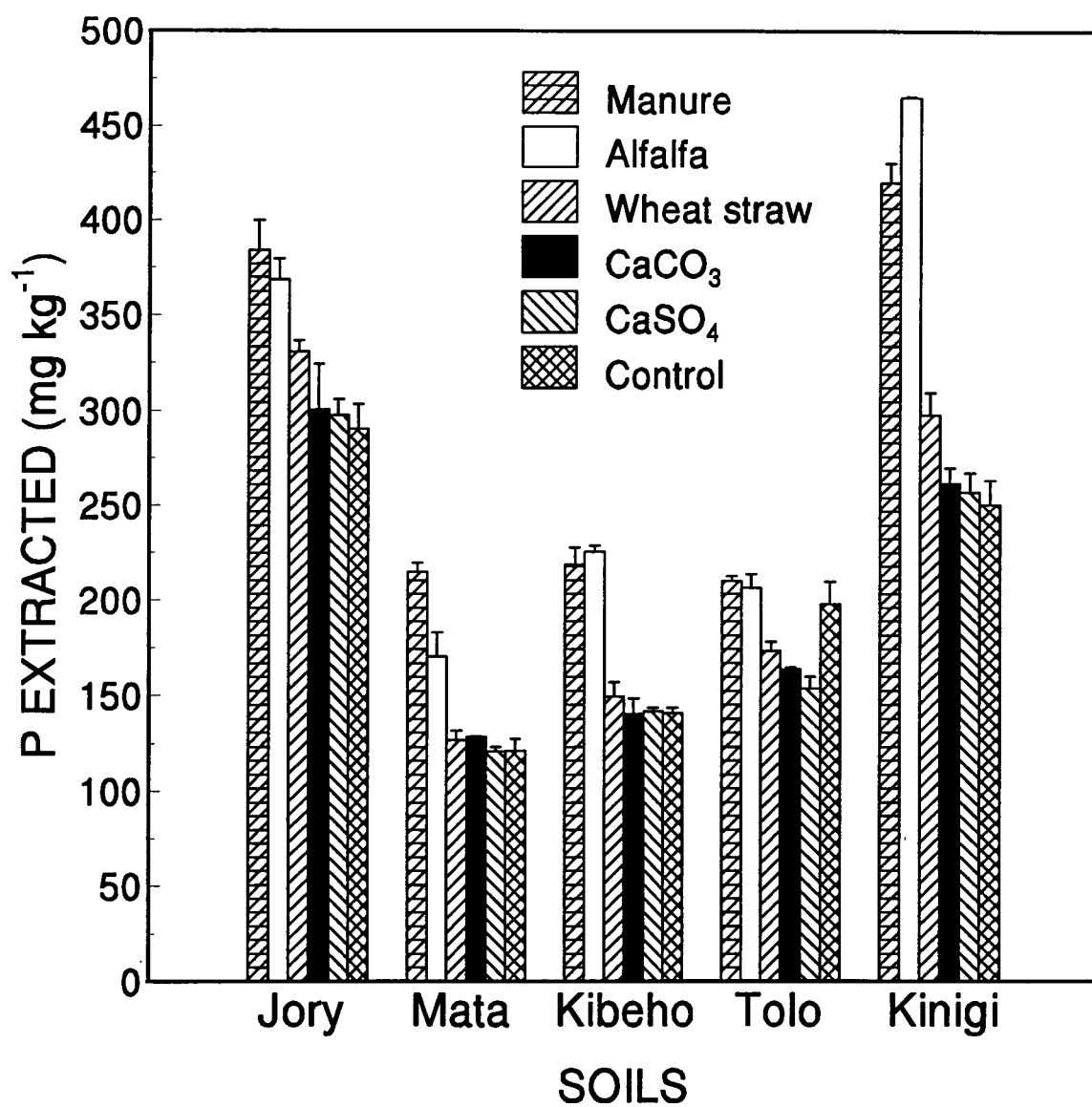


Fig. 3.4. Effect of soil organic and inorganic amendments on chemically sorbed P_i fraction.

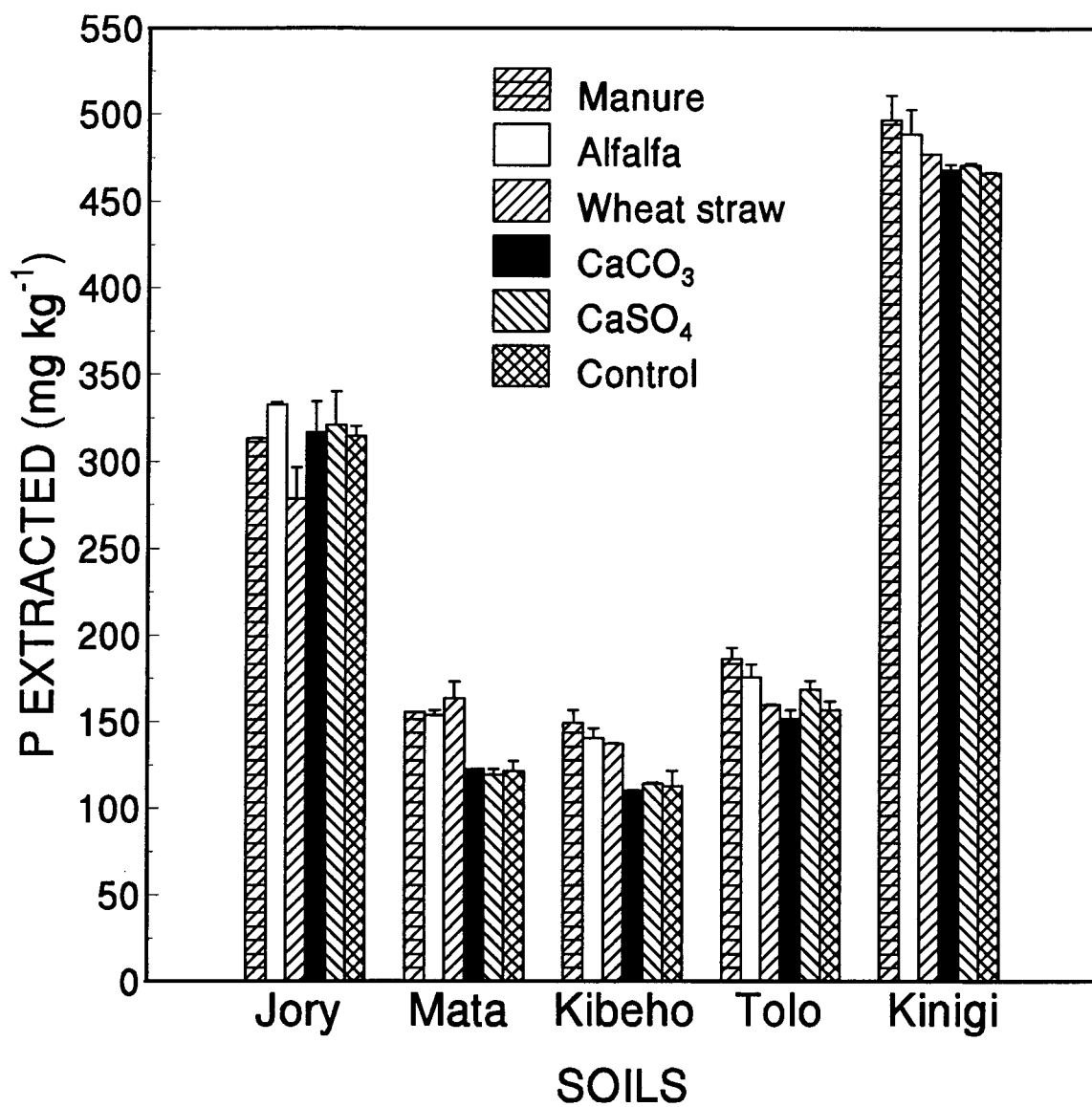


Fig. 3.5. Effect of soil organic and inorganic amendments on chemically sorbed P₀ fraction.

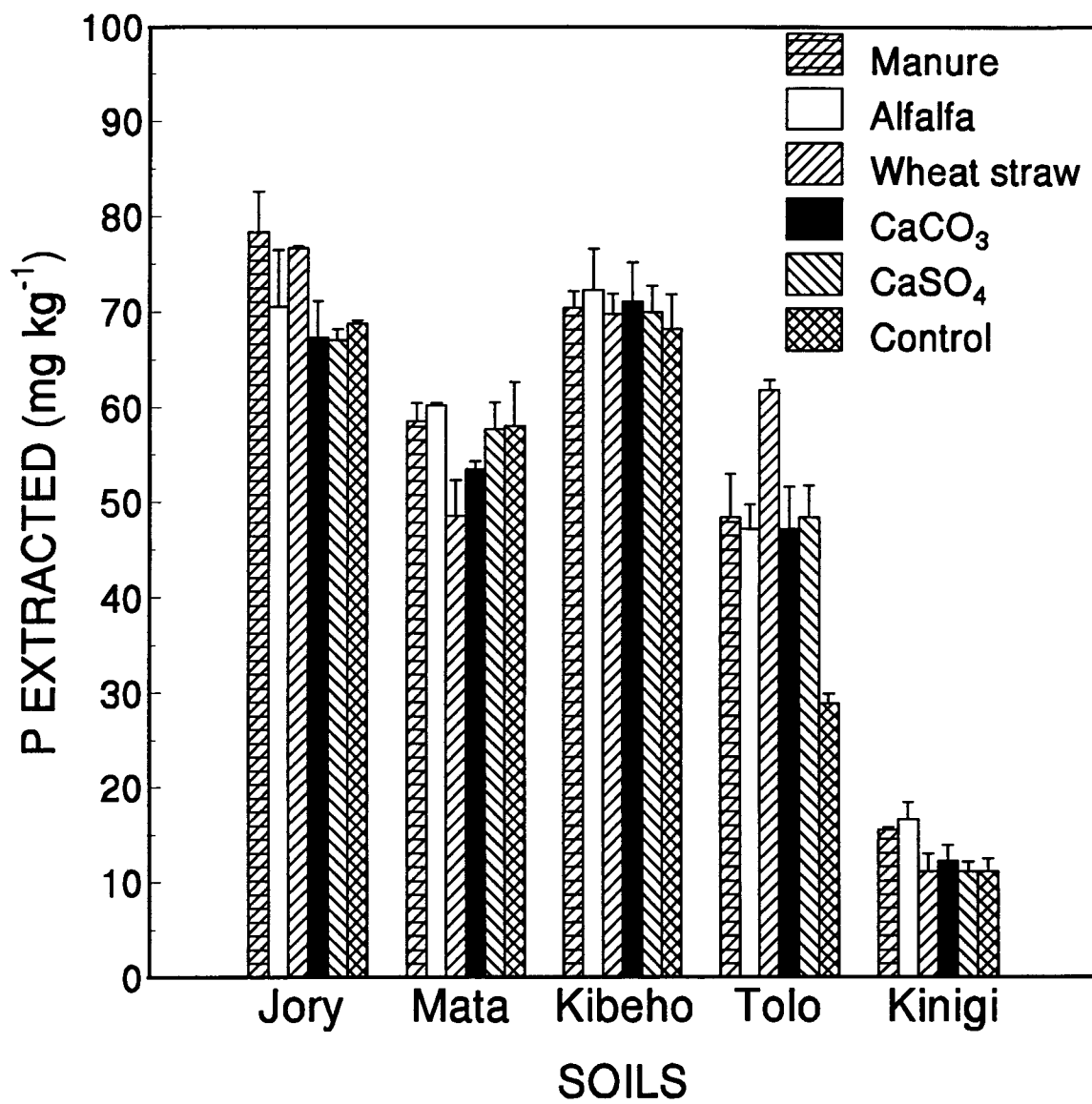


Fig. 3.6. Effect of soil organic and inorganic amendments on P_i fraction sorbed at the internal surface of aggregates.

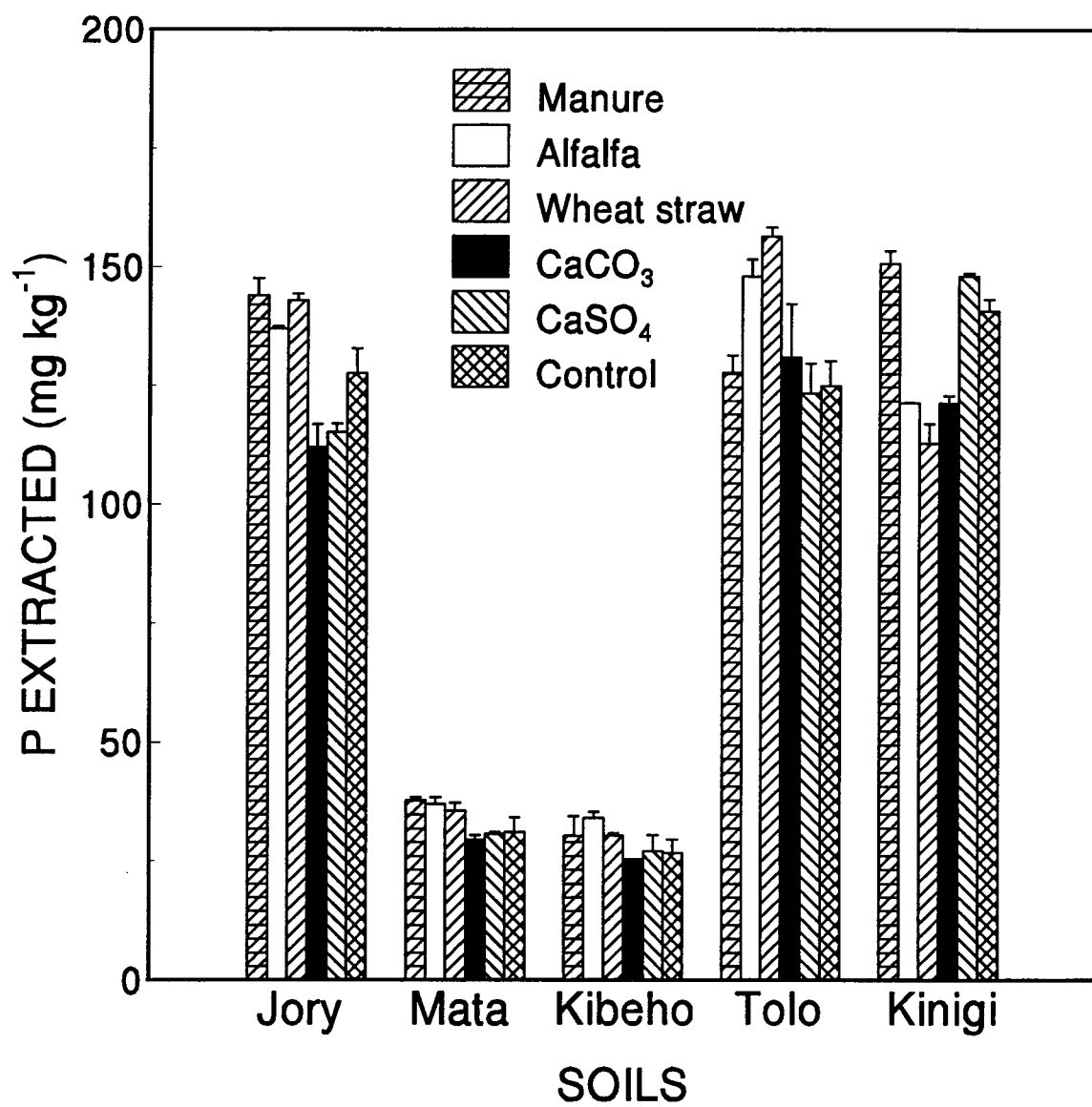


Fig. 3.7. Effect of soil organic and inorganic amendments on P_o fraction sorbed at the internal surface of aggregates.

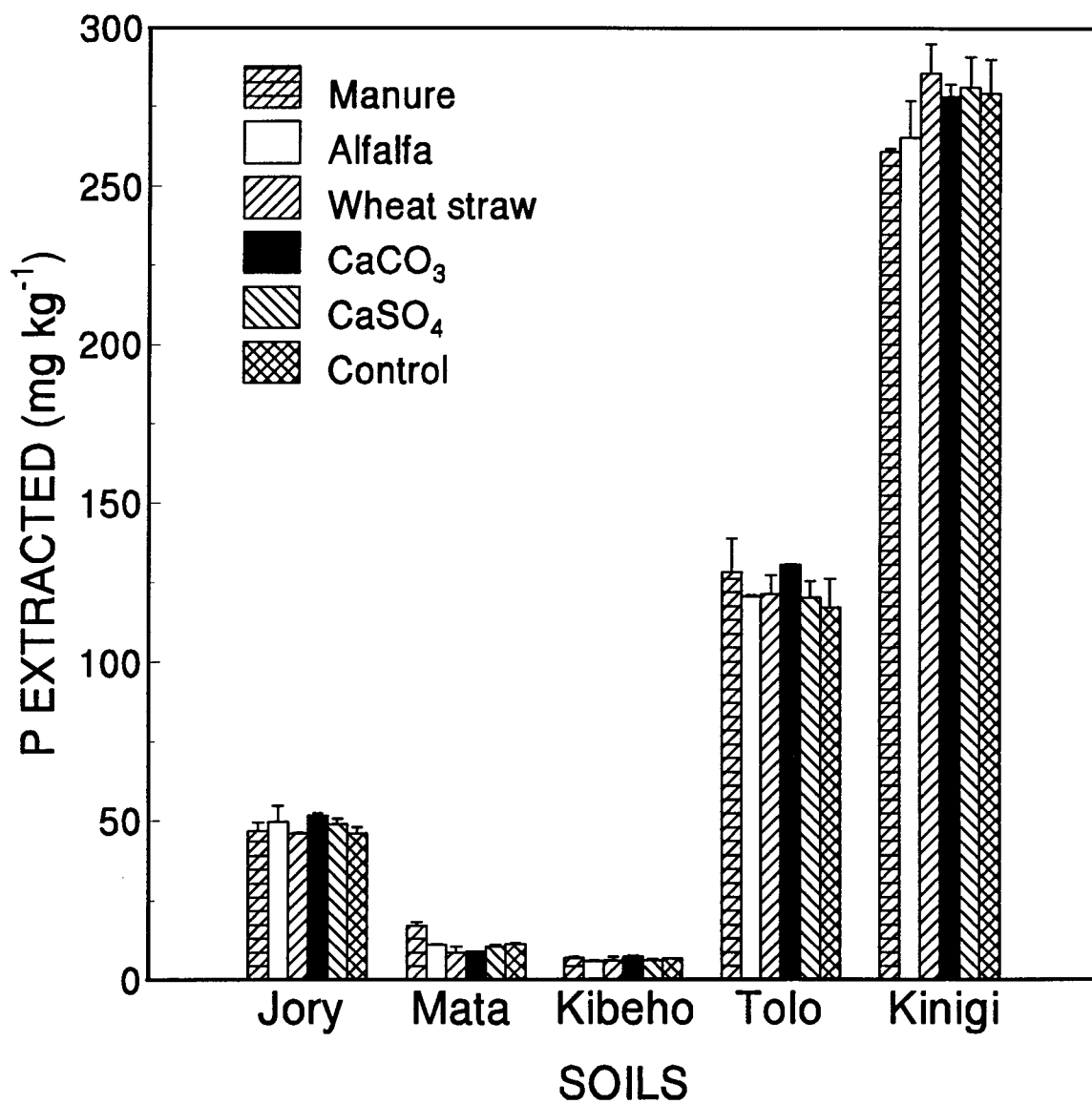


Fig. 3.8. Effect of soil organic and inorganic amendments on apatite P fraction.

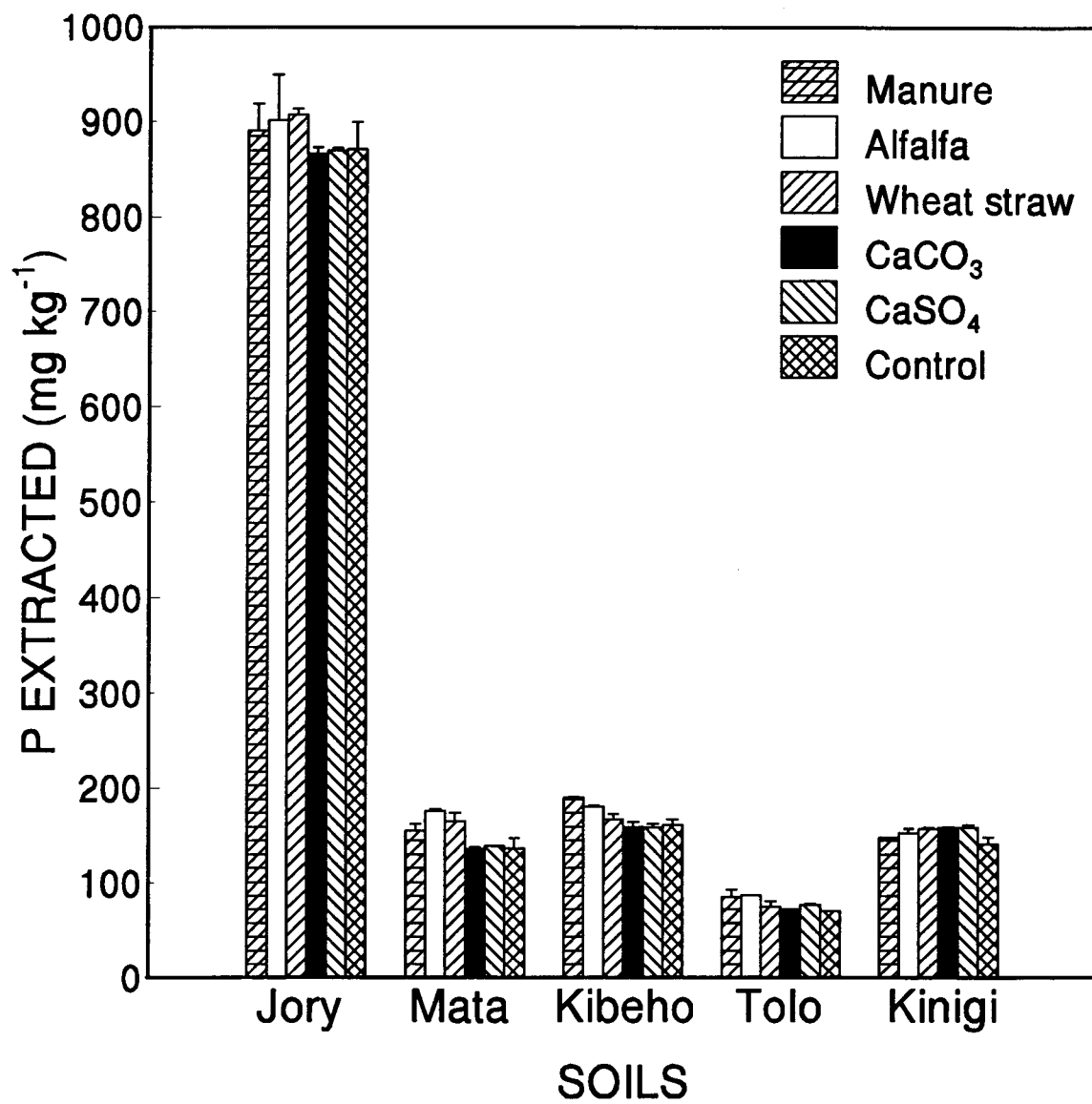


Fig. 3.9. Effect of soil organic and inorganic amendments on residual P fraction.

CHAPTER IV

EFFECTS OF ORGANIC AND INORGANIC SOIL AMENDMENTS ON SPECIATION OF PHOSPHORUS

ABSTRACT

The objective of this study was to determine the effects of different amendments on the soil solution and P speciation. Soil samples of Jory (xeric Haplohumult) and Tolo (typic Vitrandept) were treated with 5% manure and/or 3 times the CaCO_3 or CaSO_4 required to neutralize exchangeable Al and incubated for 28 d. The samples were brought to field capacity with 33 mmol P kg^{-1} soil with a solution of KH_2PO_4 (P solution) and allowed to equilibrate for 12 h. Soil solutions were extracted by centrifugation. Total concentrations of metals, inorganic ligands and DOC were measured in the solution extracted from the equilibrated soils. The computer program GEOCHEM was used to calculate the concentrations of the free metals, ligands and their complexes.

Adding manure decreased total Al and Fe and their activities in soil solution and increased basic cations and SO_4 and their activities. Total P solution increased in the samples that received manure and CaCO_3 . Calcium, Mg and K were mostly present as free ions. Calcium was also found in complexes with SO_4 or PO_4 . In the absence of metal complexing organic ligands (DOC), gibbsite and geotite controlled Al and Fe solubility, respectively, except in P treated samples where strengite controlled Fe and PO_4 solubility. In the presence of F, all Al was complexed by this ligand.

Phosphorus was over-saturated with respect to strengite and this solid phase tended to decrease in the presence of manure in the samples treated with P. Calculation of the ion activity product (IAP) showed that P was in equilibrium with an amorphous analog of variscite. This confirms the previous finding that when a soluble P fertilizer was added to the soil, the first Al PO_4 compound formed is not variscite but an amorphous analog of variscite. Calcium- PO_4 controlled P solubility in the Tolo samples treated with manure. However, the formation of this PO_4 mineral was depressed by citrate measured in this sample. When the organic acids measured in soil solution (malic, maleic, malonic, citrate, succinic, formic, and acetic) or those calculated by the mixed model were used as input in

GEOCHEM citrate was the only acid that had a significant affect on P sorption. It complexed Al and Fe and prevented precipitation of strengite and Ca-PO_4 .

INTRODUCTION

In acid soils, phosphorus (P) may be inadequate for plant nutrition even though total P levels are high. This is due to P precipitation or its adsorption by soil mineral colloidal fractions.

It is generally accepted that variscite or strengite controls P solubility in acid soils, and Ca-PO_4 in alkaline soils. However, other species of P such as soluble complexes of P or amorphous forms of P can also form (e.g. amorphous like variscite). Some of the soluble complexes (e.g. H_2PO_4) can be adsorbed onto the surface of soil mineral colloids. When a solution of fertilizer P is added to acid soils, the initial product that forms is an amorphous analog of variscite (Hetrick and Schwab, 1992; Veith and Sposito, 1977) but variscite formation at the low pH ranges prevailing in acid soils has been questioned by Hsu (1976). Hetrick and Schwab (1992) observed that in samples treated with P, activities of P were supersaturated with respect to variscite but under saturated with respect to the amorphous analog of variscite. Lindsay et al. (1962) identified approximately 30 crystalline PO_4 compounds of variable composition (in addition to colloidal precipitates) following the addition of fertilizer solutions to acid soils.

Schwab (1989) observed that in soils with $\text{pH} > 6$, P solubility apparently was controlled by hydroxyapatite or tricalcium PO_4 ; and for the more acidic soils receiving annual fertilizer PO_4 , the solubility appeared to be controlled by either Al or Fe- PO_4 . Bell and Black (1970) reported that some crystalline PO_4 of CaHPO_4 were found in soils after treatment with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. However, no evidence of Al or Fe- PO_4 was found even though a low pH of 2.8 was recorded close to the PO_4 source. Pierzynski et al. (1990) observed that samples that produced high supernatant pH (> 6.8) generally were more soluble than hydroxyapatite and less soluble than octacalcium PO_4 . Samples that produced low supernatant pH values (< 6.8) indicated an equilibrium with the amorphous analog of variscite.

Hetrick and Schwab (1992) observed simultaneous equilibrium between Al and Ca- PO_4 in soil samples treated with PO_4 when P concentrations were high and the pH was 5.5 to 6.5. Lopez-Hernandez et al. (1979), Nagrajah et al. (1977) and Traina et al. (1986) reported that the addition of organic acids to soil affects PO_4 sorption and therefore its solubility. Hue et al. (1986) demonstrated that different Al species were formed in the presence of organic acids, and that phosphorus availability was related to the types of species formed. Hetrick and Schwab (1992) reported that in some soils, P tended to be in equilibrium with Ca- PO_4 on the soil surface and with Al- PO_4 in deeper layers because of the high pH of the soil in surface layers probably resulting from high content of organic matter.

Although equilibrium isotherms and the ion activity product (IAP) parameter have been used to predict P solubility, they fail to predict the whole range of P species existing in the soil solution, the free ions and soluble complexes formed between P, and different cations (Lindsay and Moreno, 1960; Lindsay 1979; Pieryzinski et al., 1990; Hetrick and Schwab, 1992). The distribution and ion speciation of a given chemical element in the soil solution has several applications in many areas, besides agriculture. They can be used to test the solubility hypothesis and to determine the potential bioavailability of nutrient and toxic substances. During recent years many computer programs including GEOCHEM (Sposito and Mattigod, 1980) have successfully predicted the distribution and speciation of several compounds. The objective of this study was to characterize soil solution speciation and to determine different chemical species of P formed in the presence of organic or inorganic amendments.

MATERIALS AND METHODS

Samples of Jory soil (Haplohumult) or Tolo soil (typic Vitrandept) were screened through a 2-mm sieve, air-dried, and 200 gram subsamples were put in plastic containers in three replicates. The samples were mixed with either 5% (wt/wt) of manure, or three times the amount of CaCO_3 or CaSO_4 (laboratory grade) required to neutralize exchangeable Al in these soils, or a mixture of manure and each of these two inorganic amendments. The six treatments were: control; manure only; manure plus CaCO_3 ; manure plus CaSO_4 ; CaCO_3 alone; and CaSO_4 alone.

The samples were brought to water holding capacity with deionized water (DI) and incubated at 24° C for 28 days. Moisture was maintained gravimetrically and the samples were aerated every other day. After the incubation period, samples were air-dried at room temperature and 80 g subsamples were put into 250-cm³ plastic bottles. A volume of KH_2PO_4 solution (referred in to the text as P solution), enough to bring the soil moisture to the field capacity, was added to obtain 1mg P kg⁻¹ soil. The samples were then allowed to equilibrate for 12 h at 25° C. It was assumed that 12 hours was long enough for the soil solution to reach equilibrium and short enough to avoid the impact of microbial activity on the equilibrium. To homogenize distribution of the solution in the soil matrix, the sample bottles were attached to a slowly turning vertically positioned metal wheel. After the period of equilibration, the sample soil solutions were collected by centrifugation (Adams et al. 1980). One mL of solution was taken and pH measured immediately with a pH meter equipped with a microelectrode. The remainder of the solution was stored at -20° C until analysis.

Organic C in the soil solution was measured with a Carbon Analyzer (Dohman, Santa Clara, CA). Ammonium was measured with an Autoanalyzer ALPKEM RFA II. Total concentrations of F, Cl, NO_3 , PO_4 , SO_4 , malic, maleic, malonic, succinic, citric, acetic and formic acids were determined by ion chromatography (Dionex, Sunny Vale, CA)

using appropriate columns. Total concentrations of Ca, Mg, K, Cu, B, Zn, Mn, Al, Fe and Na ions were measured by inductively argon plasma spectrophotometer (ICAP). Electroconductivity (EC) of the solution was determined with an electroconductimeter in diluted soil solution (1:16). The EC of DI water measured less than one microsiemens and a curve of calibration showed a linear relationship. Ionic strength was calculated by the Marion-Bobcock equation (Sposito, 1990). The computer program GEOCHEM (Sposito and Mattigod, 1980) was used for speciation. The inputs consisted of the total concentration of each metal and ligand, pH, and ionic strength.

RESULTS AND DISCUSSION

Dissolved organic carbon, pH, and ionic strength

The values of pH, dissolved organic carbon (DOC) and ionic strength for Jory and Tolo soil samples are presented in the Tables 4.1 and 4.2 respectively.

Organic residues and CaCO_3 increased the pH in all samples of soils studied. Calcium sulfate alone, or in combination with manure, did not change the pH. The rise in pH of the soil solution in the presence of manure and CaCO_3 agrees with observations made in chapter 2 and by Hue (1992). The pH decreased in the samples when P solution was added. This reduction of pH is probably due to acidification of these samples by the P solution and the subsequent release of Al and Fe ions that hydrolysis water.

The concentration of DOC in the samples was increased by manure and P solution, unchanged by CaSO_4 , and reduced by CaCO_3 . The latter observation might indicate a rapid mineralization of the soil C in manure by the effect of CaCO_3 . Organic acids, malic, malonic, maleic, succinic, and acetic, were measured in appreciable amounts in the soil solution of treated and untreated samples of Jory and Tolo (Table 4.3). Oxalic acid was not determined but may also be present in an appreciable concentration as shown by its presence in the extract of the same samples with $\text{Ca}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. Ion strength increased in all treatments over the control probably because of the high concentration of basic cations present in the manure, or the high amount of Ca present in inorganic amendments.

Total concentration of metals and ligands

The total concentrations of Ca, Mg, and K increased in all soil solutions treated with manure which is probably due to their release from the manure during mineralization (Table 4.1 and 4.2). The increased K concentration in samples receiving P solution was expected and originated from K ions in the KH_2PO_4 solution. In samples treated with manure and/or CaSO_4 , and to which P solution was added, SO_4 ion concentration increased. In the first case, SO_4 ions came from mineralization of the manure; in the

second case, the displacement of SO_4 by PO_4 ions on the surface of the adsorbent material might have occurred (Hue 1992). Another possible explanation is the formation of soluble amorphous compounds of Al in the presence of SO_4 . Fluorine ions were found in some samples, and their concentration seemed to be positively influenced by the addition of manure or P solution.

As expected, manure, CaCO_3 , and CaSO_4 mixed with manure increased total P in the soil solution. Calcium sulfate by itself did not increase total P in the soil solution. In Jory soil solution, this may result from the low pH noticed in the soil samples treated with CaSO_4 . When no P solution was added, no P was detected in any of the samples.

The total concentrations of the soil solution Al and Fe decreased in all samples treated with manure (Tables 4.1 and 4.2). The addition of P caused an increase in these soil solution metals compared to the samples that did not receive P. The acidification and the high concentration of K in P solution might be responsible for the release of Al and Fe into the soil solution. Total Al and Fe increased in the samples treated with either CaCO_3 or CaSO_4 . This increase is probably a result of cation exchange in which Al and Fe are replaced by calcium ions, however, Al activity was decreased in these samples. This observation agrees with that of Sumner et al. (1985).

Metals and ligands activity

In Jory soil, the activities of Ca, Mg, and K were increased by all treatments (Table 4.4) except for CaCO_3 alone without addition of P, in which case Ca and Mg activities slightly decreased. The slight decreases of Ca and Mg may result from an increase in the negative charges of the adsorbent and subsequent adsorption of these cations. The fact that the addition of P solution to the samples treated with CaCO_3 alone slightly increased Ca and Mg suggests that adsorbed Ca and Mg are exchanged for K ions contained in the P solution. Most Fe activity in Jory samples was decreased except when treated with CaSO_4 and CaCO_3 plus manure and added P solution. Al activity was decreased in Jory soil

samples by manure and other treatments, except CaSO_4 alone or CaSO_4 plus manure.

Sulfate and Cl activities were increased by all treatments. Manure alone increased F activity. Free PO_4 activity was increased only in the samples treated with manure alone or in combination with CaCO_3 and CaSO_4 .

In Tolo soil (Table 4.5), the behavior of Ca, Mg, and K was highly variable. Without the addition of P solution, Ca activity was increased only in the samples treated with manure alone or manure in combination with CaCO_3 or CaSO_4 . With the addition of P solution, Ca activity was increased slightly by all treatments except manure plus CaCO_3 , which did not cause any change. The activity of Mg increased only in the samples treated with manure. Calcium carbonate and CaSO_4 alone did not increase Mg activity. Potassium activity increased in all samples treated with P solution and CaSO_4 alone. Iron activity was decreased by manure, but only slightly by CaCO_3 alone. The activity of Al was decreased only by manure and CaCO_3 plus manure, and increased slightly by the addition of P solution. Sulfate and Cl activities were increased by all treatments. In both Jory and Tolo soils, F activity occurred only in the samples to which P solution had been added, except in the sample amended with CaCO_3 plus manure where no F activity was measured. Phosphate activity was unchanged by all treatments except CaSO_4 plus manure, where it tended to decrease. The lack of increase of H_3PO_4 activities implies that most P exist in soil solution as either H_2PO_4^- or HPO_4^{2-} .

Speciation of basic cations, Al, Fe and Mn

In Jory soil, more than 99% of Ca and Mg were in the free ion form in the control and CaCO_3 treated samples (Table 4.6). These elements formed complexes with SO_4 in the remaining treatments. In Tolo soil, more than 99% of Ca and Mg were bound with SO_4 and SO_4 complexes (Table 4.7). The formation of CaSO_4 and MgSO_4 complexes is made possible by the high concentrations of either Ca, Mg or SO_4 provided by manure, or CaSO_4 .

In the control sample of Jory soil (Table 4.8), Al was over saturated in respect to $\text{Al}(\text{OH})_3$ (> 99.99%), identified as gibbsite. In the samples amended with manure alone or manure and CaSO_4 , no solid of Al was predicted by GEOCHEM. In these samples, 96% of Al was engaged in the formation of F complexes, Al had stronger affinity for F than OH ions. Addition of P to the control tended to decrease the percent of Al bound in the gibbsite and to increase the formation of Al-F complexes. This is because F concentration increases in the presence of P solution due to a probable exchange of ligands of F with PO_4 . Calcium carbonate did not change the percent of $\text{Al}(\text{OH})_3$, but when P was added, Al-bound in gibbsite was reduced to 51%, and the percentage of Al-fluoride complexes increased. Other complexes formed in the presence of P solution were AlPO_4 (3.09%), but the solution remained over saturated with respect to gibbsite. In the samples treated with CaSO_4 alone, Al was mostly in the free ion form (86%), with some Al-hydroxyl (7.4%) and SO_4 complexes (6.11%) also present. Addition of P solution to the samples treated with CaSO_4 reduced Al free ions and increased the formation of fluorine complexes (56.45%), SO_4 (2.22%), and PO_4 (10%). The precipitation of $\text{Al}(\text{OH})_3$ occurred in these samples in the presence of P solution.

Overall, it appeared that manure prevented the precipitation of Al and increased the formation of fluorine complexes. Both fluorine and dissolved organic compounds seem to be very important complexing agent in the presence of manure or added P solution. This suggests that adding PO_4 to Jory soil caused the displacement of F ions from the adsorbent surface resulting in the complexation of the remaining Al solution. Fluorine is thought to be specifically sorbed and its exchange for P implies that PO_4 was specifically sorbed.

The presence of Al in the form of $\text{Al}(\text{OH})_3$ in the control was not expected given the low pH in these samples. This might have resulted from the over estimation of Al in these samples as was proposed by Pierzynski et al. (1990). In Jory soils treated with manure, or CaCO_3 , or manure plus CaCO_3 , Fe was distributed predominantly in the solid $\text{Fe}(\text{OH})_3$ form (Table 4.9). The percent distribution of $\text{Fe}(\text{OH})_3$ was 99% or higher even

in the presence of P solution. In the CaSO_4 treated samples, the solid $\text{Fe}(\text{OH})_3$ form remained high but with 7.2 % in the $\text{Fe}(\text{OH})_3$ complex form, and 9% in the sample treated with CaSO_4 mixed with manure. In the presence of P, a small portion of Fe (< 1%) was in the solid FePO_4 form. Heavy metals such as Cu, Zn were mostly present in free ion forms in the control (Tables 4.10 and 4.11). In other treatments Cu and Zn also formed complexes with SO_4 and in some cases with PO_4 . Sulfate, Cl and F were present as free ions in the control samples. In the manured sample, however, SO_4 preferentially formed complexes with basic cations. Fluoride occurred also in the form of Al complexes in almost all treatments with P solution added.

The main difference between Jory and Tolo soil, was that in Tolo samples amended with manure, P solubility was controlled by Ca- PO_4 and Mn- PO_4 . Calcium PO_4 formation was expected because of the high pH or the treatment (Pierzynski, 1990). Conversely, in Jory soil, P solubility was controlled by Fe- PO_4 . In both soils Al-F, and in some case Al- PO_4 complexes occurred. Aluminum SO_4 complexes were also present but in small amounts (data not shown).

In Tolo soil, the formation of F complexes with Al (20.87% of total Al) decreased gibbsite formation in the control samples with added P (Table 4.12). In the Tolo samples treated with manure, $\text{Al}(\text{OH})_3$ dominated (98.64%) except in the presence of P where $\text{Al}(\text{OH})_3$ percent decreased (94.64 %), and Al or F- PO_4 complex occurred. In the Tolo samples treated with CaCO_3 , $\text{Al}(\text{OH})_3$ was the dominant fraction (99.9 %) but decreased down to (92.82%) when P solution was added, the remainder being fluoride complexes, Al F (3.8%) and Al- PO_4 (3%). Manure plus CaCO_3 did not change the distribution of Al except in the presence of P solution in which case $\text{Al}(\text{OH})_3$ disappeared and large amounts of F and PO_4 complexes formed. In CaSO_4 treated Tolo samples $\text{Al}(\text{OH})_3$ dominated again. However, in the samples treated with CaSO_4 plus manure and added P solution, $\text{Al}(\text{OH})_3$ disappeared and Al fluoride (45%) and Al- PO_4 (53.6%) dominated. Iron was

controlled by $\text{Fe}(\text{OH})_3$ and in the presence of P solution by precipitate FePO_4 regardless of the types of treatments (Table 4.13).

GEOCHEM predicted that Mn would exist in Tolo soil as free metal ions (> 90%) and Mn-SO_4 complexes (>9%). It predicted that Mn-PO_4 would form in the control sample of Tolo soil with added P (Table 4.13) and in manured samples of the same soil. The determination of Mn controlling phase can be difficult unless all appropriate parameters and the relative amounts of Mn and P in soils are determined (Boyle and Lindsay 1986); the most important parameter, not measured in our experiment, is the redox potential. However, Gotoh and Patrick (1976) showed little correspondence between predicted and measured Mn even when redox and pH were controlled. In the samples in which GEOCHEM predicted the precipitation of Al or Fe, Al was controlled by gibbsite and Fe was controlled by an amorphous $\text{Fe}(\text{OH})_3$. Strengite controlled Fe activity in most samples of the two soils in which P was added. Copper and Zn were mainly in free ions or complexed by SO_4 or PO_4 (Table 4.13). The presence of F in appreciable amounts depressed the formation of gibbsite, and all Al was involved in the formation of Al-F complexes. The role of F must be stressed because it seems to play an important role in complexing Al in the samples treated with manure and in those with added P solution.

Speciation of P

The distribution of P is illustrated in Tables 4.14 and 4.15. In the Jory and Tolo soil samples that received no P solution, GEOCHEM predicted no P because the concentration of P was below limits of detection. Overall, P was over saturated with respect to strengite in both Jory and Tolo soil samples. However, in the Tolo samples Mn-PO_4 was also predicted in the control and manured samples. In manured samples, solid Ca-PO_4 and Mn-PO_4 were predicted to control P solubility (Table 4.15). The formation of octacalcium PO_4 was expected because of the high pH in manured samples (Pierzynski, 1990). The formation of Mn(II)-PO_4 is more difficult to explain. Other researchers

(Collin and Buol, 1970) also were unsuccessful in explaining Mn solubility in their study. Although the choice of Mn(II) can be criticized there is evidence that both Mn(II)-PO₄ and Mn(III)-PO₄ can coexist in a range of $8 < pE + pH < 16$. Boyle and Lindsay (1985) reported that Mn(II)-PO₄ is more stable than strengite when $pE + pH < 16$, and Mn(III)-PO₄ more stable than strengite when $pE + pH > 8$. These researchers reported a possible formation of Mn(II)-PO₄ in soil of their study although Mn(III) was used as input. A great portion of P formed complexes with H ions to give H₂PO₄. This suggests that a surface adsorption mechanism involving H₂PO₄ ions probably occurred, and implies that adsorption reactions predominate over precipitation reactions. Calcium PO₄ complexes were also well represented in the samples treated with manure in both soils (1 to 3%), and in some cases Al-PO₄ complexes were predicted by GEOCHEM. The formation of Al-PO₄ complexes was reported in other studies (Pavan et al., 1982).

Tables 4.16 and 4.17 present the speciation of SO₄ and F. Calcium sulfate was the dominate SO₄ species and AlF₃ was the dominate F species in both soils.

In Jory soil samples, the highest percentage of solid Fe-PO₄ was found in the samples amended with CaCO₃ and P without manure (22.5%), in the remaining treatments this percentage was very small in comparison with that of H₂PO₄ or Ca-PO₄ complexes (Table 4.14). The percentage of solid Fe-PO₄ decreased in the samples treated with manure alone and with manure plus CaSO₄ in both Jory and Tolo soil, or CaCO₃ plus manure in Tolo soil. This decrease might result from the formation of Ca-PO₄ complexes observed in these samples. GEOCHEM did not predict formation of variscite. This was unexpected especially in Jory soil since variscite generally controls P solubility in acid soils. In some samples the lack of Al-PO₄ formation might be due to Al reaction with F, decreasing Al activity in pure solution. Hsu (1982) demonstrated that it is unlikely that variscite forms in the pH ranges prevailing in acid soils, and that the formation of FePO₄ solids in a condition of low Al and Fe concentration might be related more to Fe's greater

affinity for PO₄ in a pure solution (Hsu, 1976). In a laboratory study Juo and Ellis (1968) demonstrated that Fe-PO₄ crystallizes first, followed by Al-PO₄.

To explain why variscite was not predicted, an ion activity was calculated using the method of Pieryznski et al. (1990):

$$\log \text{IAP} = \log \text{Al}^{3+} + 2 \log \text{OH}^- + \log \text{H}_2\text{PO}_4$$

for both variscite and the amorphous analog of variscite. The two OH ions are included as a product of H₂O hydrolysis. The results (Table 4.18) show that in this study, the values fell in the range of the log of the solubility product, which is compressed between -27 and -28. These results suggest that P in solution was in equilibrium with respect to the amorphous analog of variscite described by Veith and Sposito (1977). This confirms the hypothesis that the amorphous analog of variscite is the first product formed when soluble P fertilizer is added to soil (Veith and Sposito, 1977). In such a context, variscite may form by the aging of amorphous analog of variscite. The same calculations were performed on the data obtained by GEOCHEM for Jory and Tolo samples and the results showed that P was in equilibrium with strengite although GEOCHEM predicted over saturation with respect to strengite. This is not a serious contradiction; this experiment was conducted 12 hours after P was added to soil and a steady state may not have been reached within this period.

The fact that GEOCHEM predicted an over-saturation of P with respect to strengite rather than variscite may be due to strengite being slightly more stable than variscite at the pH of these soils. Under such conditions, with Al and Fe at low concentration and PO₄ at high concentration, it is likely that strengite will form first.

Organic acids

In the previous discussion we did not take into account the effects of organic acids that are produced during the mineralization of organic matter and that are believed to play a role in reducing P sorption in soils, therefore these results predicted by GEOCHEM would be expected to overestimate P sorption. However when organic acids were actually measured in some of the treatments (Table 4.3), citric acid which is the most complexing acid of those studied was only detected in Tolo soil treated with manure. When the data from Table 4.3 was used as input for GEOCHEM, organic acids mainly formed complexes with the two heavy metals, Cu and Zn, as well as with basic cations, particularly Ca. Citric acid is the only organic acid which forms complexes with Al and Fe. Citric acid was only detected in the manure treated soil where it complexed all soluble Al, Fe, and Cu and 99% of Zn. It also markedly complexed Ca (45%), Mn (59%), and Mg (42%). By forming complexes with Ca, Mn and Cu, citric acid drastically reduced the precipitation of these species. Among the remaining organic acids, the most effective in complexing basic cations and heavy metals was maleic followed by malic acid. However, these organic acids seemed to be very weak in regard to Al and Fe complexation. This suggests that except for citric acid all other measured organic acids have a minimal effect on P sorption.

Since we did not measure organic acids in all samples, we used the mixed model to calculate organic acid concentration from dissolved organic carbon (DOC). In Jory soil, no precipitation of gypsite, geotite, or strengite occurred. Both Al and Fe formed complexes with citric acid (Table 4.19). In Tolo soil, no precipitation of gypsite, geotite, or strengite occurred except in the samples amended with CaSO₄ and manure where Fe and P solubility was controlled by strengite. Iron formed complexes with citric and salicylic acid and Al formed complexes with citric and benzenesulfonic acid (Table 4.20). All organic acids form complexes mostly with the earth metals Mn, Cu, and Zn (data not shown).

CONCLUSIONS

Dissolved organic C increased in all samples treated with manure. Ionic strength and basic cations increased in all treatments in Jory soil. In Tolo soil the effect of all treatments on the basic cations was not significant because this soil already had an appreciable amount of these elements. Total concentration of soluble Al and Fe was decreased by all treatments in the two soils, indicating that manure, CaCO_3 and CaSO_4 decreased soil solution Fe and Al in both Jory and Tolo soils. In Tolo soils F was found only in the samples to which P had been added whereas in Jory soils, regardless of amendments, F tended to increase when P was added. Possibly there were ligand exchanges between F and PO_4 ions. The pH of the soil samples would be favorable for this ligand exchange. The increase of soil solution P in Tolo samples was relatively more important than in those observed in Jory soil.

The speciation calculated by GEOCHEM showed that Ca and Mg were present as free metals or except in the samples treated with manure where the complexes with SO_4 were predicted. Conversely, Ca or Mg- SO_4 complexes were predicted in all samples of Tolo soil regardless of the treatments. In addition GEOCHEM predicted the formation of PO_4 complexes in Tolo soils.

Strengite controlled Fe and P solubility in all samples to which P solution had been added, and Fe bound in strengite tended to decrease in the presence of manure. Aluminum was controlled by gibbsite except in the presence of F where Al was totally complexed by this ligand. The calculation of IAP of Al and PO_4 showed that P was in equilibrium with the amorphous variscite like solid. In Tolo samples treated with manure, octacalcium PO_4 controlled P solubility and solid Cu or Mn- PO_4 were predicted to form in the same samples. Organic acids formed complexes with basic cations, Cu and Zn, except for citric acid that complexed most of the cations including Al and Fe. Citric acid also decreased the formation of the solid phase in the sample it was measured.

All treatments increased basic cations in Jory soil samples. The fact that these cations were increased in the presence of manure suggest that organic manure might be an important source of Ca and Mg for plant nutrition. In Tolo soils the effect of all treatments on these cations was not significant, probably due to the fact that this soil already contained an appreciable amount of these elements. Total Mn was slightly higher in Tolo soil than in Jory soil and seemed to be only slightly influenced by all the treatments in the two soils. The total concentration of soluble Al and Fe was decreased by all treatments in Tolo and Jory soils, indicating that manure, CaCO_3 and CaSO_4 were causing reactions that led to the decrease of Al and Fe. The slight but constant increase of total soluble Al and Fe in the presence of P solution might be attributed to the decrease of pH caused by the addition of P solution. In Tolo soil samples, F was only found in the samples to which P solution had been added whereas in Jory soil samples it was present regardless the type of amendment but tended to increase in the presence of P solution. This suggests that F ions, which are believed to be specifically sorbed, were competing for the sites of adsorption with PO_4 ions, or phosphate ions were replacing F ions from the adsorbent. The increases of total P in Tolo soil samples were relatively less than those observed in Jory soil except in Tolo samples treated with manure mixed with CaSO_4 where important increases were noticed. These small differences between treatments contrasted with the large differences observed between the control and the treated samples when these samples were shaken in a batch solution for six days to perform the isotherms of adsorption. One possible explanation is that surface precipitation of P in volcanic soil may occur and therefore, the period of 12 hours of equilibrium used in this experiment was not adequate to allow the surface precipitation which might be a slow process. Overall, the activities followed the same trends as the total concentrations of metals and ligands.

The speciation calculated by GEOCHEM showed that Ca and Mg were present as free metals except in the samples treated with manure where the complexes with SO_4 were predicted, whereas, Ca and Mg- SO_4 complexes were predicted in all samples of Tolo soils

regardless of treatment. In addition, PO_4 complexes were predicted by GEOCHEM in Tolo soil samples to which P solution had been added. However, all these complexes were small in comparison with free metals. Iron was controlled by goethite or strengite in the presence or absence of P solution, respectively. Aluminum was over-saturated in respect to gibbsite, or formed complexes with SO_4 , F, or PO_4 depending upon the type of treatments. In the presence of P solution Al-F complexes were formed suggesting that F is an important complexing agent with respect to Al. Total P concentration was increased in Jory soil samples amended with manure.

Phosphate was oversaturated with respect to strengite but the most important amount of P was predicted to be in form of H_2PO_4^- . This suggests that a large amount of P was susceptible to adsorption rather than precipitation. No variscite was predicted to form and this was unexpected particularly in Jory soil which is a very acid soil.

In Tolo soil, which had solution $\text{pH} > 6$, no Ca-PO_4 was predicted. This may result from the fact that the pH of the samples to which P solution had been added dropped below pH 5.8 which is considered to be the pH at which Ca-PO_4 cease to control P in solution and shifts to Al- PO_4 formation. Although variscite was not predicted by GEOCHEM, the calculation of the activity product showed that P was saturated with respect to the amorphous like variscite compound. This compound seemed to occur first and then to evolve by aging into variscite. This would confirm the hypothesis of variscite formation as the first product when P fertilizer is added to the soil.

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Table 4.1. Total concentration (-log c) of metals and ligands in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	Control	P	M	M/P	CaCO ₃	CaCO ₃ /P
Ca	3.65	3.52	2.08	2.32	3.57	3.24
Mg	4.08	4.02	2.79	2.92	4.10	3.85
K	4.14	2.66	2.45	1.86	3.93	2.39
Na	3.81	3.76	2.82	2.93	3.79	3.78
Fe ⁺³	4.89	4.90	5.64	5.08	4.39	3.51
Mn ⁺²	4.16	4.28	3.76	3.31	3.99	3.77
Cu ⁺²	6.82	6.09	6.87	6.09	5.90	5.52
Zn	4.88	5.15	5.49	5.30	5.46	5.46
Al	0.94	3.68	4.71	4.44	4.17	4.17
SO ₄	4.49	3.19	2.05	1.88	3.63	3.49
Cl	3.21	3.01	2.19	2.19	3.15	1.71
F	4.53	3.81	3.85	3.83		4.00
NH ₃	4.03	3.80	3.81		3.88	3.49
PO ₄		3.20		2.89		2.87
B(OH) ₄	4.96	4.93	4.54	4.82		2.87
NO ₃	3.28	3.34	2.15	2.22	3.69	4.35
pH	5.34	5.37	5.65	5.60	5.65	5.51
DOC	2.21	1.51	1.02	1.00	1.84	1.22
I(M)	0.46	0.78	1.62	1.75	0.84	1.10

Table 4.1. (continued) Total concentration (-log c) of metals and ligands in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	CaCO ₃ /M	CaCO ₃ /M/P	CaSO ₄	CaSO ₄ /P	CaSO ₄ /M	CaSO ₄ /M/P
Ca	2.08	2.09	2.96	2.77	1.89	1.95
Mg	2.80	2.78	3.44	3.22	1.63	2.64
K	2.50	1.86	3.59	2.13	2.43	1.66
Na	3.78	2.85	3.61	3.45	2.88	2.84
Fe ⁺³	5.57	5.45	5.53	4.93	5.31	5.30
Mn ⁺²	4.04	4.19	3.26	3.15	3.75	3.80
Cu ⁺²	7.01	6.40	6.44	5.97	6.29	5.83
Zn	5.38	5.23	5.22	5.36	5.11	5.21
Al	3.95	4.14	4.77	4.01	4.74	4.41
SO ₄	2.00	1.78	2.43	1.91	1.49	1.27
Cl	2.15	2.08	3.32	3.23	2.09	1.99
F				4.05		4.11
NH ₃	3.87	3.67	3.51	3.04	3.85	3.55
PO ₄		3.16		3.29		2.67
B(OH) ₄	5.45	5.24	4.97	5.65	5.14	5.27
NO ₃	2.15	2.07	3.89	4.55	1.94	1.85
pH	5.51	5.68	4.73	5.02	4.48	4.88
DOC	1.82	1.48	1.99	1.47	2.01	1.53
I(M)	1.67	1.86	1.80	1.43	1.80	1.97

Table 4.2. Total concentration (-log c) of metals and ligands in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	Control	P	M	M/P	CaCO ₃	CaCO ₃ /P
Ca	2.58	2.76	2.06	2.24	2.84	3.61
Mg	3.25	3.55	2.84	3.01	3.61	3.53
K	2.23	2.01	2.45	1.68	3.30	2.04
Na	3.43	3.99	3.05	3.14	3.91	3.88
Fe ⁺³	4.29	4.05	5.09	4.58	4.53	4.21
Mn ⁺²	3.61	3.33	3.53	3.66	3.69	3.56
Cu ⁺²	5.75	5.40	6.18	5.64	5.87	5.51
Zn	5.18	4.92	5.42	5.11	5.41	4.98
Al	4.63	4.25	5.55	4.77	4.79	4.32
SO ₄	2.51	2.50	1.73	1.86	2.36	2.32
Cl	3.15	3.09	2.23	2.44	2.46	3.00
F	4.46	3.94		4.00		4.33
NH ₃	3.09	3.22	2.99	3.61	3.01	2.84
PO ₄		2.20		1.54		2.25
B(OH) ₄	5.30	5.85	5.81	5.19	5.18	5.08
NO ₃	4.39	4.00	2.00	2.15	3.11	3.14
pH	6.55	5.87	6.91	6.40	6.50	5.92
DOC	1.34	1.03	1.10	0.93	2.21	1.17
I(M)	0.82	1.36	1.66	1.78	0.95	1.36

Table 4.2. (continued) Total concentration (-log c) of metals and ligands in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	CaCO ₃ /M	CaCO ₃ /M/P	CaSO ₄	CaSO ₄ /P	CaSO ₄ /M	CaSO ₄ /M/P
Ca	2.41	1.91	2.27	2.40	2.01	2.02
Mg	3.16	2.73	3.08	3.21	2.86	2.98
K	2.85	2.61	1.77	1.78	2.69	1.83
Na	3.42	3.24	3.27	3.70	3.30	3.32
Fe ⁺³	4.73	5.18	5.18	4.55	4.92	5.16
Mn ⁺²	3.42	3.70	4.28	3.55	3.87	4.18
Cu ⁺²	5.83	5.97	5.89	5.77	6.23	5.63
Zn	5.49	5.34	5.27	5.15	5.59	5.04
Al	4.97	4.96	4.90	4.59	4.95	4.90
SO ₄	1.89	1.70	1.68	1.65	1.66	1.47
Cl	2.31	2.24	3.00	2.90	2.53	2.28
F		4.02				4.44
NH ₃	3.04	3.31	2.83	2.87	2.99	3.03
PO ₄		2.06		2.05		1.96
B(OH) ₄	5.17	5.15	5.33	4.91	5.15	5.65
NO ₃	1.88	1.79	3.07	1.93	2.00	1.75
pH	6.75	5.67	5.93	5.48	6.20	5.36
DOC	1.36	1.35	1.30	1.24	1.32	4.30
I(M)	1.65	1.97	1.41	1.75	1.75	2.02

Table 4.3. Organic acid concentration (mM) in soil solution of Jory and Tolo soils as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Sample	Maleic	Citric	Malonic	Malic	Succinic	Formic	Acetic
<u>Jory soil</u>							
Control	480.82	nd	nd	2.91	7.76	8.20	nd
P	nm	nm	nm	nm	nm	nm	nm
M	nd	nd	nd	nd	13.42	21.48	2.33
M/P	nd	nd	12.60	nd	16.75	15.09	149.84
CaCO ₃	17.14	nd	nd	7.91	42.17	8.42	154.23
CaCO ₃ /P	707.58	nd	21.02	nd	34.25	7.05	37.90
CaCO ₃ /M	nd	nd	nd	nd	1806.88	193.41	338.61
CaCO ₃ /M/P	127.95	nd	nd	nd	26.74	21.85	134.68
CaSO ₄	73.82	nd	nd	33.03	8.17	15.94	33.56
CaSO ₄ /P	631.42	nd	nd	nd	26.30	14.11	46.26
CaSO ₄ /M	nm	nm	nm	nm	nm	nm	nm
CaSO ₄ /M/P	1264.66	nd	nd	nd	16.25	nd	nd
<u>Tolo soil</u>							
Control	nd	nd	2.80	nd	15.07	15.69	17.42
P	4973.25	nd	nd	nd	nd	nd	nd
M	nd	nd	nd	nd	6.66	22.70	34.35
M/P	3186.60	3547.5	4.67	nd	7.47	12.63	37.69
CaCO ₃	nd	nd	nd	nd	187.17	6.98	26.51
CaCO ₃ /P	3316.50	nd	23.79	8.17	11.37	1.75	nd
CaCO ₃ /M	nd	nd	nd	nd	18.73	24.66	56.51
CaCO ₃ /M/P	2132.20	nd	nd	20.95	3.60	nd	nd
CaSO ₄	nm	nm	nm	nm	nm	nm	nm
CaSO ₄ /P	1614.25	nd	5.02	2.93	4.46	4.80	nd
CaSO ₄ /M	nm	nm	nm	nm	nm	nm	nm
CaSO ₄ /M/P	nm	nm	nm	nm	nm	nm	nm

nm: not measured nd: not detectable

Table 4.4. Activities (-log a) of metals and ligands in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	Control	P	M	M/P	CaCO ₃	CaCO ₃ /P
Ca	4.19	4.23	2.87	3.12	4.28	3.98
Mg	4.63	4.73	3.58	3.72	4.82	4.59
K	4.28	2.83	2.63	2.04	4.10	2.57
Na	3.94	3.94	3.00	3.11	3.97	3.97
Fe ⁺³	12.52	12.44	13.45	14.93	13.45	11.85
Mn ⁺²	4.71	4.98	4.55	4.11	4.70	4.52
Cu ⁺²	7.36	6.77	7.67	6.91	6.62	6.27
Zn	5.43	5.86	6.28	6.11	6.17	6.21
Al	7.92	5.83	9.37	8.85	8.85	7.29
SO ₄	5.04	3.90	2.85	2.68	4.35	4.24
Cl	3.35	3.18	2.37	2.37	3.33	1.89
F	5.06	5.85	4.20	4.32		5.05
NH ₃	7.87	5.75	7.34		7.40	7.16
PO ₄		13.96		11.47		14.55
B(OH) ₄	8.78	9.77	7.92	8.24		6.45
NO ₃	3.41	3.51	2.32	2.39	3.87	4.53

Table 4.4. (continued) Activities (-log a) of metals and ligands in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	CaCO ₃ /M	CaCO ₃ /M /P	CaSO ₄	CaSO ₄ /P	CaSO ₄ /M	CaSO ₄ /M /P
Ca	2.87	2.90	3.75	3.56	2.72	2.81
Mg	3.59	3.58	4.23	4.00	3.44	3.48
K	2.68	2.04	3.76	2.31	2.62	1.86
Na	3.96	3.03	3.78	3.63	3.07	3.03
Fe ⁺³	13.03	14.81	10.69	13.39	9.94	13.74
Mn ⁺²	4.83	5.00	4.05	3.94	4.58	4.66
Cu ⁺²	7.81	7.22	7.23	6.76	7.13	6.71
Zn	6.18	6.04	6.01	6.15	5.94	6.08
Al	8.43	8.94	6.46	6.96	6.63	7.86
SO ₄	2.80	2.58	3.22	2.69	2.29	2.08
Cl	2.32	2.25	3.50	3.41	2.26	2.16
F				5.28		4.85
NH ₃	7.54	7.16	7.95	7.19	8.54	7.84
PO ₄		11.60		13.01		12.66
B(OH) ₄	8.97	8.58	9.26	9.69	9.68	9.39
NO ₃	2.33	2.24	4.07	4.73	2.11	2.02

Table 4.5. Activities (-log a) of metals and ligands in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	Control	P	M	M/P	CaCO ₃	CaCO ₃ /P
Ca	3.30	3.54	2.87	3.05	3.58	4.40
Mg	3.97	4.32	3.64	3.81	4.35	4.31
K	2.41	2.20	2.63	1.86	3.48	2.23
Na	3.61	4.17	3.23	3.32	4.09	4.07
Fe ⁺³	16.15	16.12	17.23	15.83	16.00	16.17
Mn ⁺²	4.33	4.11	4.33	4.47	4.43	4.33
Cu ⁺²	6.50	6.24	7.07	6.49	6.63	6.35
Zn	5.91	5.72	6.24	5.94	6.16	5.79
Al	11.55	9.51	12.63	9.22	11.40	9.66
SO ₄	3.23	3.27	2.52	2.66	3.09	3.09
Cl	3.33	3.27	2.41	2.61	2.64	3.17
F	4.65	4.24		4.33		4.55
NH ₃	5.72	6.54	5.26	7.08	5.68	6.10
PO ₄		10.28		8.65		10.22
B(OH) ₄	7.87	9.04	7.94	8.51	7.79	8.22
NO ₃	4.57	4.18	2.18	2.33	3.29	3.32

Table 4.5. (continued) Activities (-log a) of metals and ligands in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Elements	Treatments					
	CaCO ₃ /M	CaCO ₃ /M /P	CaSO ₄	CaSO ₄ /P	CaSO ₄ /M	CaSO ₄ /M /P
Ca	3.20	2.75	3.07	3.23	2.82	2.87
Mg	3.96	3.54	3.87	4.02	3.66	3.81
K	3.03	2.79	1.96	1.97	2.88	2.02
Na	3.60	3.42	3.46	3.88	3.48	3.51
Fe ⁺³	16.75	15.88	14.29	15.55	15.10	15.40
Mn ⁺²	4.22	4.52	5.09	4.36	4.69	5.02
Cu ⁺²	6.68	6.84	6.70	6.63	7.06	6.51
Zn	6.30	6.19	6.07	6.00	6.40	5.91
Al	12.15	9.47	9.69	8.34	10.50	8.78
SO ₄	2.68	2.50	2.47	2.45	2.46	2.28
Cl	2.49	2.41	3.17	3.07	2.71	2.45
F		4.30				4.77
NH ₃	5.47	6.81	6.07	6.56	5.97	6.84
PO ₄		10.52		10.86		11.00
B(OH) ₄	7.46	8.48	8.46	8.45	7.97	9.29
NO ₃	2.05	1.98	3.25	3.10	2.17	1.92

Table 4.6. Percent distribution of Ca, Mg, K and Na in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species							
	Ca	CaSO ₄	Mg	MgSO ₄	K	K ₂ SO ₄	Na	Na ₂ SO ₄
Control	99.9		99.9		99.9		99.9	
P	99.2		99.5		99.8		99.9	
M	96.8	3.12 ^c	97.3	2.49 ^c	98.8	1.10 ^c	99.1	
M /P	95.0	4.35 ^c	96.1	3.50 ^c	98.3	1.63 ^c	98.7	1.04 ^c
CaCO ₃	99.8		99.8		99.9		99.9	
CaCO ₃ /P	99.2		99.3		99.8		99.2	
CaCO ₃ /M	96.4	3.51 ^c	97.0	2.81 ^c	98.7	1.25 ^c	98.9	
CaCO ₃ /M /P	94.4	5.21 ^c	95.5	4.19 ^c	97.9	2.01 ^c	98.4	1.27 ^c
CaSO ₄	98.7	1.28 ^c	98.8	1.02 ^c	99.5		99.6	
CaSO ₄ /P	95.0	4.73 ^c	96.1	3.80 ^c	98.4	1.58 ^c	98.9	1.00 ^c
CaSO ₄ /M	90.1	9.87 ^c	91.8	8.00 ^c	96.0	3.91 ^c	97.2	2.50 ^c
CaSO ₄ /M /P	84.6	14.55 ^c	87.8	14.55 ^c	93.8	6.13 ^c	95.7	3.95 ^c

^c complex

^s solid

Table 4.7. Percent distribution of Ca, Mg, and K in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species							
	Ca	CaSO ₄	Ca-PO ₄	Mg	MgSO ₄	Mg-PO ₄	K	K ₂ SO ₄
Control	98.1	1.87 ^c		98.4	1.49 ^c			99.5
P	95.2	1.29 ^c	3.44 ^c	97.1	1.04 ^c	1.74 ^c	99.5	
M	93.5	6.42 ^c		94.7	5.16 ^c		97.6	2.32 ^c
M /P	92.4	4.43 ^c	3.12 ^c	95.1	3.62 ^c	1.11 ^c	98.2	1.71 ^c
CaCO ₃	97.6	2.36 ^c		98.0	1.89 ^c		99.3	
CaCO ₃ /P	94.8	1.96 ^c	3.21 ^c	96.6	1.59 ^c	1.75 ^c	99.3	
CaCO ₃ /M	95.4	4.57 ^c		92.2	3.66 ^c		98.3	1.63 ^c
CaCO ₃ /M /P	90.3	5.90 ^c	3.76 ^c	93.7	4.87 ^c	1.26 ^c	97.5	2.42 ^c
CaSO ₄	92.1	7.81 ^c		93.6	6.31 ^c		97.3	2.61 ^c
CaSO ₄ /P	89.0	6.98 ^c	3.95 ^c	93.2	5.81 ^c	0.94 ^c		97.2
CaSO ₄ /M	92.9	7.03 ^c		94.2	5.67 ^c		97.3	2.67 ^c
CaSO ₄ /M /P	86.2	9.30 ^c	4.41 ^c	91.2	7.81 ^c	0.81 ^c	95.9	4.02 ^c

^c complex

^s solid

Table 4.8. Percent distribution of aluminum in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species				
	Al ³⁺ _(aq)	Al(OH) ₃	AlF ₃	Al-PO ₄	Al-SO ₄
Control		99.9 ^s			
P		68.9 ^s	9.73 ^c	1.12 ^c	
M	0.09	0.11 ^c	99.7 ^c		
M /P	0.16		96.4 ^c	3.16 ^c	
CaCO ₃	0.06	99.8 ^s			
		0.1 ^c			
CaCO ₃ /P		51.1 ^s	44.4 ^c	3.09 ^c	
CaCO ₃ /M	0.13	99.7 ^s			
		0.11 ^c			
CaCO ₃ /M /P		99.0 ^s		0.8 ^c	
		0.09 ^c			
CaSO ₄	86.00	7.47 ^c			6.17 ^c
CaSO ₄ /P	4.25		58.4 ^c	10.0 ^c	
CaSO ₄ /M	53.8	2.52 ^c			43.5 ^c
CaSO ₄ /M /P			85.9 ^c	10.0 ^c	2.28 ^c
^c complex					
^s solid					

Table 4.9. Percent distribution of iron and manganese in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species						
	Fe	Fe ₂ (OH) ₃	Fe-PO ₄	Fe-SO ₄	Mn	Mn-SO ₄	Mn-Cl ₂
Control		99.6 ^s	0.32 ^c		99.8		
P		99.9 ^s	0.04 ^c				
M		99.0 ^s	0.97 ^c		96.4	3.11 ^c	
M /P		99.9 ^s	0.04 ^c		95.2	4.36 ^c	
CaCO ₃		99.9 ^s	0.05 ^c		99.8		
CaCO ₃ /P		100 ^s			98.4		1.41 ^c
CaCO ₃ /M		99.8 ^s	1.14 ^c		96.0	3.5 ^c	
CaCO ₃ /M /P		0.03 ^c	99.9 ^s	0.07 ^c	94.2	5.2 ^c	
CaSO ₄	0.03	92.5 ^s	7.42 ^c		98.6	1.28 ^c	
CaSO ₄ /P		0.01 ^c	99.8 ^s	0.1 ^c	95.2	4.74 ^c	
CaSO ₄ /M		90.5 ^s	9.03 ^c	0.3 ^c	89.6	9.83 ^c	
CaSO ₄ /M /P			99.6 ^s	0.31 ^c	84.8	14.59 ^c	

^c complex

^s solid

Table 4.10. Percent distribution of copper and zinc in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species					
	Cu ²⁺	CuSO ₄	Cu-PO ₄	Zn	ZnSO ₄	Zn-PO ₄
Control	99.6			99.6		
P	98.5			98.6		
M	95.2	3.68 ^c		96.1	3.10 ^c	
M /P	92.4	5.33 ^c	0.45 ^c	93.7	4.29 ^c	1.23 ^c
CaCO ₃	99.4			99.5		
CaCO ₃ /P	97.3		1.26 ^c	97.5		1.19 ^c
CaCO ₃ /M	94.8	4.35 ^c		95.7	3.49 ^c	
CaCO ₃ /M /P	91.7	6.37 ^c		93.3	5.15 ^c	
CaSO ₄	98.3	1.61 ^c		98.6	1.28 ^c	
CaSO ₄ /P	93.6	5.86 ^c		94.8	4.71 ^c	
CaSO ₄ /M	87.1	12.02 ^c		89.4	9.80 ^c	
CaSO ₄ /M /P	80.5	17.43 ^c	1.05 ^c	83.4	14.35 ^c	1.34 ^c

^c complex

^s solid

Table 4.11. Percent distribution of copper and zinc in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species							
	Cu	Cu(OH) ₂	CuSO ₄	Cu-PO ₄	Zn	Zn(OH) ₂	ZnSO ₄	Zn-PO ₄
Control	91.2	4.80 ^c	2.19 ^c		96.1	1.98 ^c	1.83 ^c	
P	84.8		1.44 ^c	12.96 ^c	90.6		1.22 ^c	7.76 ^c
M	76.3	12.25 ^c	6.59 ^c		89.5	3.69 ^c	6.15 ^c	
M/P	85.6		5.16 ^c	8.42 ^c	88.7		4.25 ^c	6.37 ^c
CaCO ₃	91.2	3.85 ^c	2.78 ^c		95.7	1.71 ^c	2.32 ^c	
CaCO ₃ /P	83.1		2.17 ^c	13.46 ^c	90.2		1.87 ^c	7.45 ^c
CaCO ₃ /M	84.0	7.21 ^c	5.07 ^c		92.2	2.62 ^c	4.42 ^c	
CaCO ₃ /M /P	82.4		6.79 ^c	9.48 ^c	85.9		5.62 ^c	7.48 ^c
CaSO ₄	89.1		9.51 ^c		91.7		7.78 ^c	
CaSO ₄ /P	82.8		8.26 ^c	7.52 ^c	85.7		6.72 ^c	7.36 ^c
CaSO ₄ /M	88.9	1.09 ^c	8.47 ^c		91.8		6.95 ^c	
CaSO ₄ /M /P	80.7		10.94 ^c	7.25 ^c	82.4		8.88 ^c	7.79 ^c

^c complex

^s solid

Table 4.12. Percent distribution of aluminum in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species			
	Al ³⁺ (aq)	Al(OH) ₃	AlF ₃	Al-PO ₄
Control		99.8 ^s 0.09 ^c	0.07 ^c	
P		75.3 ^s	20.87 ^c	3.66 ^c
M		98.8 ^s 1.21 ^c		
M /P		94.6 ^s	2.00 ^c	2.90 ^c
CaCO ₃		99.8 ^s 0.12 ^c		
CaCO ₃ /P		92.8 ^s	3.96 ^c	3.08 ^c
CaCO ₃ /M		99.7 ^s 0.24 ^c		
CaCO ₃ /M /P		0.17 ^c	81.0 ^c	18.64 ^c
CaSO ₄	0.06	99.6 ^s 0.26 ^c		
CaSO ₄ /P	0.74	79.0 ^c 19.24 ^s		
CaSO ₄ /M	0.01	99.8 ^s 0.18 ^c		
CaSO ₄ /M /P	0.57		45.1 ^c	53.6 ^c

^c complex

^s solid

Table 4.13. Percent distribution of sodium, iron and manganese in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species						
	Na ⁺	Na ₂ SO ₄	Fe(OH) ₃	Fe-PO ₄	Mn ²⁺	MnSO ₄ (aq)	Mn-PO ₄
Control	99.6		99.9 ^s		98.0	1.87 ^c	
P	99.7			100 ^s	97.3	1.32 ^c	1.32 ^s
M	98.3	1.48 ^c	99.9 ^s 0.02 ^c		93.2	6.4 ^c	
M /P	98.8	1.08 ^c		99.9 ^s	95.2	4.56 ^c	
CaCO ₃	99.4		99.9 ^s 0.01 ^c		97.2	2.36 ^c	
CaCO ₃ /P	99.5			100 ^s	97.9	2.03 ^c	
CaCO ₃ /M	98.8	1.04 ^c	99.9 ^s		95.1	4.56 ^c	
CaCO ₃ /M /P	98.2	1.54 ^c		99.9 ^s 0.04 ^c	93.5	6.11 ^c	
CaSO ₄	98.3	1.66 ^c	99.8 ^s 0.17 ^c		92.1	7.81 ^c	
CaSO ₄ /P	98.2	1.76 ^c		99.9 ^s 0.01 ^c	92.6	7.26 ^c	
CaSO ₄ /M	98.2	1.70 ^c	99.9 ^s 0.05 ^c		92.8	7.02 ^c	
CaSO ₄ /M /P	97.2	2.57 ^c		99.9 ^s 0.07 ^c	90	9.70 ^c	

^c complex

^s solid

Table 4.14. Percent distribution of phosphate in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species			
	H ₂ PO ₄	Fe-PO ₄	Al-PO ₄	Ca-PO ₄
Control				
P	97.4 ^c	1.99	0.37 ^c	
M				
M /P	96.7 ^c	0.64		2.30 ^c
CaCO ₃				
CaCO ₃ /P	77.0 ^c	22.5		0.26 ^c
CaCO ₃ /M				
CaCO ₃ /M /P	95.3 ^c	0.52		3.75 ^c
CaSO ₄				
CaSO ₄ /P	94.9 ^c	2.29 ^c	1.94 ^c	
CaSO ₄ /M				
CaSO ₄ /M /P	95.3 ^c	0.23		4.18 ^c
^c complex				
^s solid				

Table 4.15. Percent distribution of phosphate in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species			
	H ₂ PO ₄ ⁻	Fe-PO ₄	Mn-PO ₄	Ca-PO ₄
Control				
P	97.3 ^c	1.44 ^s	0.08 ^s	
M				
M /P	85.0 ^c	0.39 ^s		12.00 ^c
CaCO ₃				
CaCO ₃ /P	98.6 ^c	1.09 ^s		0.14 ^c
CaCO ₃ /M				
CaCO ₃ /M /P	94.3 ^c	0.08 ^s		5.32 ^c
CaSO ₄				
CaSO ₄ /P	97.6 ^c	0.32 ^s		1.74 ^c
CaSO ₄ /M				
CaSO ₄ /M /P	95.9 ^c	0.06 ^s		3.83 ^c

^ccomplex

^s solid

Table 4.16. Percent distribution of sulfate and fluorine in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species					
	SO ₄ ²⁻ (aq)	CaSO ₄	K ₂ SO ₄	F	AlF ₃	MgF ₂
Control	99.4			40.3	59.4 ^c	
P	99.3			23.3	76.5 ^c	
M	95.9	2.97 ^c		67.5	30.3 ^c	1.11 ^c
M /P	96.0	1.60 ^c	1.74 ^c	48.7	50.2 ^c	
CaCO ₃	99.6					
CaCO ₃ /P	98.9			41.1	58.7 ^c	
CaCO ₃ /M	96.1	2.93 ^c				
CaCO ₃ /M /P	95.2	2.52 ^c	1.67 ^c			
CaSO ₄	99.2					
CaSO ₄ /P	97.8			8.88	91.0 ^c	
CaSO ₄ /M	94.7	3.92 ^c				
CaSO ₄ /M /P	93.8	2.99 ^c	2.47 ^c	26.5	72.3 ^c	

^c complex

^s solid

Table 4.17. Percent distribution of sulfate and fluorine in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition.

Treatments	Species					
	SO ₄ ²⁻ (aq)	CaSO ₄	K ₂ SO ₄	F	AlF ₃	CaF ₂
Control	97.0	1.59 ^c		98.7		
P	97.6	1.30 ^c		77.0	22.42 ^c	
M	96.0	2.97 ^c				
M /P	91.8	0.90 ^c	6.00 ^c	97.8	0.98 ^c	0.10
CaCO ₃	98.9					
CaCO ₃ /P	98.4	1.22 ^c		91.7	7.92 ^c	
CaCO ₃ /M	98.0	1.40 ^c				
CaCO ₃ /M /P	95.9	3.57 ^c		77.5	19.60 ^c	1.39 ^c
CaSO ₄	95.5	2.01 ^c	2.13 ^c			
CaSO ₄ /P	96.4	1.23 ^c	2.06 ^c			
CaSO ₄ /M	96.1	3.19 ^c				
CaSO ₄ /M /P	95.3	2.60 ^c	1.74 ^c	70.4	27.75 ^c	

^c complex
^s solid

Table 4.18. The Ion Activity Product (IAP) of Al and P compared with those of veriscite and amorphous like veriscite.

Soil	Treatments	IAP
Jory	Control	28.69
	Manure	28.77
	CaCO ₃	28.56
	CaCO ₃ /Manure	28.98
	CaSO ₄	28.43
	CaSO ₄ /Manure	28.97
Tolo	Control	28.24
	Manure	28.24
	CaCO ₃	28.33
	CaCO ₃ /Manure	28.44
	CaSO ₄	29.04
	CaSO ₄ /Manure	28.24

Table 4.19. Percent distribution of aluminum, iron, and phosphorus in soil solution of Jory soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition as predicted by GEOCHEM using mixed model.

Treatments	Species						
	AlF ₃	Al-PO ₄	Al-citr [†]	Fe-citr [†]	Ca-PO ₄	Mg-PO ₄	H ₂ PO ₄
Control /P	0.56 ^c		99.44 ^c	100 ^c	0.14 ^c	0.02 ^c	99.84 ^c
Control /M /P	0.14 ^c		99.86 ^c	100 ^c	1.22 ^c	0.10 ^c	98.68 ^c
CaCO ₃ /P	0.09 ^c		99.91 ^c	100 ^c	0.18 ^c	0.01 ^c	99.81 ^c
CaCO ₃ /M /P			99.99 ^c	100 ^c	3.16 ^c	0.23 ^c	96.61 ^c
CaSO ₄ /P	0.89 ^c		99.10 ^c	100 ^c	0.66 ^c	0.02 ^c	99.31 ^c
CaSO ₄ /M /P	1.94 ^c	0.02 ^c	98.03 ^c	100 ^c	3.89 ^c	0.05 ^c	96.06 ^c

^c complex

^s solid

[†] citric acid

Table 4.20. Percent distribution of aluminum, iron, and phosphorus in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition as predicted by GEOCHEM using mixed model.

Treatments	Species						
	Al ³⁺ (aq)	AlF ₃	Al-PO ₄	Al(OH) ₃	AlSO ₄	Al-citr [†]	Al-bes [‡]
Control /P		0.03 ^c				99.97 ^c	
Control /M /P	63.19	25.62 ^c	7.34 ^c		2.80 ^c		1.05 ^c
CaCO ₃ /P						99.99 ^c	
CaCO ₃ /M /P		0.18 ^c	0.03 ^c			99.79 ^c	
CaSO ₄ /P			0.01 ^c			99.98 ^c	
CaSO ₄ /M /P	0.43	37.88 ^c	39.92 ^c	0.20 ^c	0.34 ^c	21.24 ^c	

^c complex

[†] citric acid

[‡] benzenesulfonic acid

Table 4.20. (continued) Percent distribution of aluminum, iron, and phosphorus in soil solution of Tolo soil as affected by phosphorus (P), manure (M), CaCO₃ and CaSO₄ addition as predicted by GEOCHEM using mixed model.

Treatments	Species								
	Fe ³⁺ _(aq)	Fe-PO ₄ [¶]	Fe-citr [†]	Fe-sali [§]	Al-PO ₄	Ca-PO ₄	Fe-PO ₄ [#]	H ₂ PO ₄ ⁻	Mg-PO ₄
Control /P			100 ^c			0.39 ^c		99.58 ^c	0.04 ^c
Control /M /P	3.73	87.43 ^c	0.02 ^c	7.68 ^c		0.08 ^c	0.08 ^c	99.83 ^c	
CaCO ₃ /P			100 ^c			0.06 ^c		99.89 ^c	0.04 ^c
CaCO ₃ /M /P			100 ^c			4.44 ^c		95.32 ^c	0.23 ^c
CaSO ₄ /P			100 ^c			1.21 ^c		98.74 ^c	0.05 ^c
CaSO ₄ /M /P		0.07 ^c			0.05 ^c	3.83 ^c	0.06 ^s	95.98 ^c	0.08 ^c
		99.86 ^s							

^c complex

^s solid

[†] citric acid

[‡] benzenesulfonic acid

[§] salicylic acid

[¶] Percent of Fe reacting with PO₄

[#] Percent of PO₄ reacting with Fe

APPENDIX

Appendix I Statistical analysis of sorption parameters calculated by Langmuir equation in five soils treated with soil organic and inorganic amendments.

Soil Amendments	Soils				
	Jory	Mata	Kibeho	Kinigi	Tolo
Affinity (k) [†]					
Manure	1.490 f	3.310 e	3.385 d	10.250 b	0.575 b
Alfalfa	1.785 e	4.090 de	3.295 d	13.500 b	0.590 b
Wheat straw	2.850 d	5.200 cd	4.760 c	9.625 b	0.970 ab
CaCO ₃	3.320 c	6.100 bc	5.170 c	26.500 a	1.350 a
CaSO ₄	4.520 b	7.650 ab	9.110 a	18.500 ab	1.040 ab
Control	5.110 a	8.000 a	7.535 a	19.050 ab	1.220 a
Adsorption maxima (b) [‡]					
Manure	1027 b	940 b	1063 d	1122 a	895 d
Alfalfa	1053 ab	1003 ab	1112 c	1122 a	947 c
Wheat straw	1046 b	1043 a	1132 bc	1122 a	1053 a
CaCO ₃	1034 b	1030 a	1136 b	1145 a	863 e
CaSO ₄	1057 ab	1046 a	1139 b	1158 a	1012 b
Control	1099 a	1048 a	1230 a	1174 a	1025 b

Means within a column followed by the same letter are not significantly different at P=0.05 LSD level

[†] k is expressed in L mg⁻¹,

[‡] b is expressed in mg kg⁻¹