THE PHOSPHORUS SORPTION POTENTIAL OF SELECTED HAWAIIAN SOILS IN RELATION TO THEIR MINERALOGY AND CHEMISTRY

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ABSTRACT

Eleven soils from Hawaii representing a wide range in properties that affect P sorption were used to quantify the effects of those factors on P sorption. The results were evaluated for a property's possible utility in predicting P sorption, which is important for improving P fertility management. Phosphorus buffering coefficients calculated from an incubation study and P sorbed at 0.2 mg P L^{-1} in solution from sorption isotherm data were correlated with soil properties.

A prediction of the number of sorption sites per gram of soil was the property that best predicted P sorption. The number of sorption sites per gram were predicted from analysis of X-ray diffraction patterns that indicated the quantity and average size of crystallites for each mineral in a soil. The results indicate a strong dependency of P sorption on soil mineral type and content with less influence of other soil properties. Data from a 180 day incubation study were fit with a negative exponential equation, the parameters of which indicate the proportions of P sorbed instantaneously and sorbed with time. The parameter estimate associated in instantaneous P sorption was most closely related with the number of sorption sites. The parameter estimates did not correlate with other properties, indicating that other unmeasured factors have an influence on the P sorption process.

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CHAPTER 1

INTRODUCTION

Phosphorus exists in numerous forms within the soil-plant system and transforms from one form to another at varying rates (Smeck, 1985). Labile and non-labile P refer to the rates at which transformations are likely to occur. For instance, labile organic P is that P in organic material that is readily decomposed to release the P into solution. This thesis is concerned with the inorganic P and its dynamics in changing from solution and labile P to non-labile P.

The transformation of solution P to labile and non-labile is a ligand exchange reaction of PO_4 species with hydroxyl functional groups on the surface of minerals (Sanyal and De Datta, 1991). The affinity for ligand exchange leads to the majority of P in a soil to be sorbed while a minute portion remains in solution. There is always some degree of equilibrium between sorbed P and solution concentration. This equilibrium is related to bond strength which is likely to be dynamic in that the bond can be mononuclear or binuclear and can conceivably be altered by neighboring sorbed ions (Barrow, 1980; Parfitt, 1989). The change in bond strength leads to a hysteresis between the adsorption and desorption of P in a soil, where the amount desorbed is less than that adsorbed. This indicates that sorbed P either desorbs at a much slower rate or that it is irreversibly sorbed.

The interest in the P sorption process lies in its effect on P fertility management. P sorption decreases plant available P, which in turn affects the proportion of P fertilizer applied to the soil. Soils that sorb more P require more fertilizer to supply the same amount of plant available P. The P sorbed may become available slowly as the available P is reduced due to plant uptake. This desorption can possibly provide a long term but very gradual supply of P, but is the desorption enough P to meet the growth demands of the plant? The dynamic nature of both the P supply in the soil and the P demand by the plant needs to be considered. Inefficiency of applied fertilizer results when most of the fertilizer remains in the soil while plants struggle to find available P.

An ability to predict the proportion of fertilizer that will be available is necessary for determining fertilizer requirements, and is valuable for evaluating the economic feasibility for growing crops on specific soils. If high sorption warrants large levels of fertilizer then the expense could prohibit profitable crop production. From an environmental viewpoint, high sorption causes P accumulation with each application, and poses environmental hazards if the soil were to erode into surface waters. An ability to predict the sorption potential from readily available data on soil properties would be a valuable tool for fertility management, agricultural planning and environmental considerations.

With these interests, research objectives were established regarding the sorption potential of soils in Hawaii.

1) To determine the sorption potential for a set of soils with a wide range in properties and determine which properties affect sorption potential. A significant property could be used to predict the sorption potential of a soil.

2) To characterize and establish a mathematical relationship for the change in extractable P with time. This would indicate the dynamic nature of P in a soil which is important for evaluating management options.

CHAPTER 2

LITERATURE REVIEW

Reactions with Soil Components

Several approaches have been taken in describing the phosphate sorption mechanism. The primary questions raised by the data that a mechanistic description needs to address are:

1) what is the chemical reaction that removes phosphate from solution?

2) why do some minerals or soils sorb more phosphorus than others on a μg P g^{-1} mineral basis?

3) why are there different rates of sorption?

4) why is there a continued slow reaction?

5) why does some of the phosphate desorb (remain labile) and some does not (become non-labile), or why is some plant available and some not?

To address these questions, researchers have attempted to correlate soil and mineral properties to the characteristics of a phosphate adsorption isotherm. There is normally an initial fast reaction that removes most of the P in solution within 24 hours. The adsorption continues to take place gradually to a constant concentration of phosphate in solution. This is the slow reaction (Fox & Kamprath, 1970).

The expressions fast reaction and slow reaction have been used for many different time scales in P sorption research. Fast reaction can refer to the amount of sorption that takes place within an hour up to a few days, and slow reaction can refer to the sorption that takes place from the end of the designated fast reaction period to any specified amount of time, days to years. Some of this difference in the time scales is due to the methods used to measure phosphate sorption. The various methods will be discussed later. Much of the following discussion will deal with the data from phosphate sorption isotherms for various minerals and soil types in order to determine the contribution of soil components to the soil-phosphorus interactions.

Soil Mineralogy

Soil minerals are the most dominant factor in controlling phosphate concentration in soil solution. As the substrate for P adsorption, the mineral's properties will determine the amount of phosphate to be adsorbed. The soil's physical and chemical environment will modify this sorption process and rate. The minerals, their crystallinity and particle size distribution indicate the reactive surface area for phosphate sorption, which is critical to determine phosphate sorption quantitatively.

A closer view at the P adsorption mechanisms will help to evaluate how each mineral contributes to the P sorption process. The mechanisms vary with differences in minerals, and several mechanisms have been described in the literature. A discussion follows for four types of soil minerals and poorly crystalline material that occur as major components in soils. These are the Fe and Al hydrous oxides, calcareous minerals, silicate clays and Fe and Al humus complexes. These are all secondary minerals that are involved in phosphate sorption. Soil primary minerals are not important to the sorption process, but they are often the original source of P to a soil system (Norrish and Rosser, 1983).

Iron and Aluminum Hydrous Oxides. The minerals with the highest sorption capacity for phosphate are the Fe and Al hydrous oxides. McLaughlin et al., (1981) demonstrated that the following minerals sorb phosphate in decreasing order: allophane > fresh Al gel > Fe gel > pseudoboehmite > aged Al gel > dried Fe gel > Fe-coated kaolinite > hematite > goethite > akaganeite > gibbsite. These sorption capacities are based on the maximum sorption parameter of the Langmuir equation for a sorption isotherm on synthetic minerals. Maximum sorption values correlated well with 1) surface area (r=0.85) and 2) hydroxyl buffering (r=0.98). Hydroxyl buffering, the amount of OH^- sorbed per unit increase in pH value, was believed to correlate better than surface area because the term provides an estimate of surface sites associated with P sorption, whereas specific surface area may measure portions of the surface not involved in P sorption.

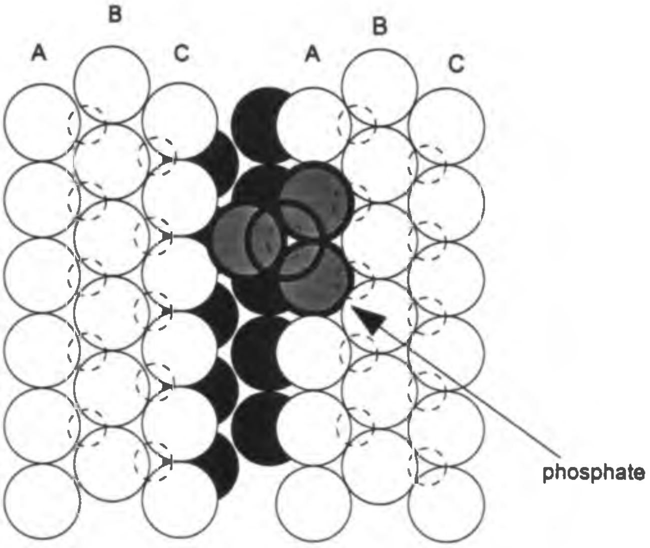
Parfitt (1989) measured the P sorption of some naturally occurring Fe and Al hydrous oxides and demonstrated the order for decreasing sorption capacity to be allophane > ferrihydrite > goethite > hematite. This series is similar to McLaughlin et al., except for the reversal of hematite and goethite, which maybe due to the surface area of the minerals in each of the studies (McLaughlin et. al. hematite=18.0 m^2 g^{-1} & goethite=17.0 m^2 g^{-1}; Parfitt, goethite=310m^2 g^{-1} calculated, and the hematite constituted approximately 10% of the sample). The sorption level of these minerals followed the order of their relative surface areas. A synthetic goethite had high crystallinity when compared with a natural goethite and showed no slow reaction, which was attributed to a diffusion controlled reaction at crystallin defect sites (Parfitt et al., 1989).

The two examples above indicate the importance of surface area and number of sorption sites in the amount of P sorbed. The mechanism is described as a ligand exchange with the surface hydroxyls of minerals. The reaction can be written in a generalized equation as follows:

$$aMOH_s + H_bSO_4{}^{(b-3)-}{}_{aq} + cH^+{}_{aq} \leftrightarrow M_aH_cPO_{4\ s} + bH_2O_{lq} + (a-b)OH^-{}_{aq}$$

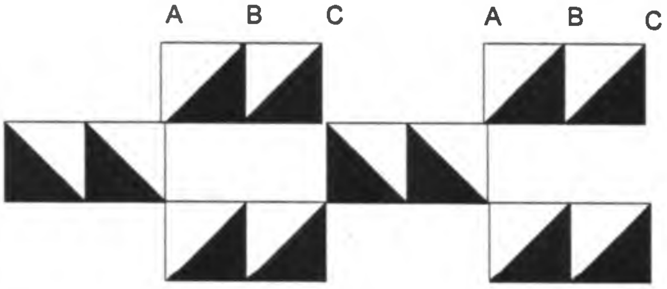
where M refers to a metal ion in a hydroxylated mineral, OH to a reactive surface hydroxyl (Goldberg and Sposito, 1985). Ligand exchange involves the removal of the hydroxyl and the bonding of the phosphate anion in its place to the Fe or Al in the mineral's structure (Figure 2.1). The initial fast reaction is commonly stated as a ligand exchange reaction that forms a monodentate bond of phosphate to Fe or Al (Olsen and Khasawneh, 1980).

Researchers generally agree that the initial reaction is a ligand exchange reaction (Sanyal and De Datta, 1991). The slow reaction has been difficult to characterize and several mechanisms have been suggested. Parfitt (1989) postulated different reactions based on the amounts of Si desorbed during the slow reaction of phosphate sorption, which was monitored from one to 30 days for the natural samples of allophane, ferrihydrite, and goethite, and a synthetic sample of goethite. For allophane the mechanism for the slow reaction, which follows the initial, rapid ligand exchange at defect sites, is sorption at less reactive defect sites, then if concentrations are high enough, alumino-phosphates precipitate and disrupt the allophane structure and create new defect sites. For goethite, phosphate is adsorbed initially at very reactive sites and silicic acid, silicate or hydroxide is desorbed by ligand exchange, then phosphate is sorbed at less reactive sites (Parfitt, 1989). With time phosphate may penetrate at defect sites or between microcrystals as part of the slow reaction. The extent of the slow reaction depends on the crystallinity and porosity of the mineral (Parfitt, 1989).



Goethite - planar view

A, B, C indicate 1,3, & 2 coordinated hydroxyls



Goethite - cross section

Figure 2.1 Ligand exchange of a phosphate anion with hydroxide anions on the surface of goethite (adapted from Schwertmann and Taylor, 1989).

A synthetic goethite had virtually no slow reaction, due to the well formed crystals with very few defect sites as indicated by electron micrographs. For ferrihydrite, the initial reaction is the same as goethite, but the slow reaction could be due to exposure of blocked surfaces, penetration at defect sites, and/or precipitation with weekly held Fe. Surfaces blocked by flocculated particles begin to disperse as adsorbed phosphate induces a negative surface charge on the particles (Parfitt, 1989). The data showed readsorption of the Si during the slow reaction after being initially desorbed in the fast reaction for ferrihydrite. This readsorption can be attributed to the exposure of new surfaces during the slow reaction.

It seems that reactive surface area controls the amount of phosphate that a soil will sorb. This property correlates well with phosphate sorption but not perfectly because there are other properties that have an effect. Inorganic and organic anions compete for sorption sites, and in this way block the site from reaction (Hue, 1991; Sanyal and De Datta, 1991). Goldberg and Sposito (1984a,b) used the constant compacitance model to describe quantitatively the adsorption of phosphate. This model is based on the ligand exchange mechanism and requires the determination of protonation-dissociation constants and surface complexation constants for the minerals and the phosphate anion in soil solution. Goldberg and Sposito's (1984a) test of this model showed that Al and Fe oxide minerals have similar phosphate adsorption behavior.

In native soils that have not been amended with P fertilizers, the inorganic P within the soil matrix, excluding any primary P containing minerals, is directly related to Fe hydrous oxides (Norrish and Rosser, 1983). Norrish and Rosser concluded this for Australian soils after doing a microprobe analysis. They found that the locations that contained P correlated well with the occurrence of Fe minerals. For every location in the soil matrix analyzed, if there was P present then there was also a proportional amount of Fe oxide present. The microprobe cannot analyze distinct mineral phases when the particles are less than 1μm in size, which is the case for much of the soil matrix. Thus the correlation between the occurrence of P with that of Fe indicates an association. Their data on native soil samples indicate that Al plays a minor role in retaining P in unamended soils, but sorption by Al hydrous oxides is equally comparable with that of the Fe hydrous oxides when soils are amended with P.

In addition to Fe and Al hydrous oxide minerals being the primary factor for phosphate sorption, there are also the amorphous coatings of Fe and Al hydroxide that form on the surfaces of soil particles. These particles also have a high capacity to sorb phosphate. Peinemann and Helmy (1992) demonstrated an increase in phosphate sorption from a low level for a montmorillinite sample to a much higher level of sorption when coated with a hydroxy Al material. The higher sorption level was comparable to that of Fe and Al hydrous oxides.

Carbonates. Calcareous soils also pose a problem to P fertility management as these soils sorb most of the P applied as fertilizer. Calcium carbonate adsorbs phosphate from the soil solution, and Ca in alkaline soils precipitates calcium phosphates from the soil solution. Sorption by calcite has been described as being chemical adsorption onto the surface of calcium carbonate particles when the concentration is less than 0.6mg L^{-1} P in the soil solution and then as precipitation/adsorption on the particle surfaces to form octacalcium phosphate when the concentration exceeds this amount (Norrish and Rosser, 1983). There is some discrepancy of the mineral formed upon precipitate of calcium with phosphate as some research has reported that dicalcium phosphate develops or physical adsorption takes place. With time and whatever the initial form of phosphate is, upon removal from solution, it should slowly convert to apatite (Berkheiser et al., 1980; Norrish and Rosser, 1983). The amount of phosphate sorbed in calcareous soils is controlled by the surface area of the carbonate material, which in some cases is inversely related to the content of calcium carbonate in the soil (Holford and Mattingly, 1975). Holford and Mattingly (1975) described phosphate sorption with a two-surface Langmuir adsorption model in which they delineate a high-energy adsorption surface and a low-energy adsorption surface (what is now referred to as an initial fast reaction followed by a continual slow reaction). The high-energy adsorption was correlated with the content of Fe hydrous oxides, and the presence of Fe with carbonates could control the high-energy adsorption in calcareous soils when they are present (Holford and Mattingly, 1975; Hamad et al., 1992).

Afif et al. (1993) found sorption in calcareous soils to correlate with silicate clay content and Fe oxides when the amount of P applied was relatively low. At high levels of applied P the sorption correlated with calcium carbonate content. They hypothesized that at low soil solution concentration adsorption at sites on Fe oxides and edge surfaces of clay minerals predominated than on $CaCO_3$ particles, and at high solution concentrations, near or above saturation for Ca-P compounds, precipitation predominates in controlling the sorption of phosphate.

Silicate Clays. In comparison to Fe and Al hydrous oxides and carbonates, the silicate clays sorb very little phosphorus. Adsorption on to minerals of illite, smectite and kaolinite has been measured to occur at low concentrations of P in solution, concentrations of less than 10mg L^{-1} P, above this range the surface dissolution of the clay minerals begins to occur and precipitation of alumino-phosphates results (Norrish and Rosser, 1983). Data on phosphate sorption isotherms for silicate clays indicate an initial fast reaction that is attributed to adsorption then a continual slow reaction that is attributed to the dissolution the clays and precipitate of alumino-phosphates. Sorption of phosphate onto these clays occurs at the edge sites of a terminal $Al(OH)_2^-$ and at defect regions in the crystalline structure (Muljadi et. al., 1966).

Iron and Aluminum Humus Complexes. For some soils, especially Andisols and Spodosols, there is a significant amount of Al and Fe complexed with organic matter. The complexes tend to stabilize the organic matter and promote its accumulation within the soil. The metallic ions in these complexes have demonstrated the ability to sorb phosphate. Norrish and Rosser (1983) conducted a microprobe analysis of organic fragments in soils that have received an application of P fertilizer. Their data show that the amount of phosphorus retained by the organic fragments, near the pockets of fertilizer, was correlated with the Al content of the organic matter. Also their data shows that the phosphate sorption occurred at a 1:1 ratio with the content of the Al in the organic matter. The positive correlation in some soils between the organic matter content and phosphate sorption has been attributed to the organically bound Al and Fe, and there is some indication that organic complexes can sorb more P than can the same amount of free Fe and Al oxides (Sanyal and De Datta, 1991).

Haynes and Swift (1989) studied the effect of pH changes and drying on the phosphate sorption by Al-peat and Al-humic samples. Their data indicates that Al-humic material sorbs phosphate in the range of 50 to 200 μmol P g^{-1} material, which is comparable to adsorption by Fe and Al hydrous oxides. Their data shows that both increasing pH and drying of the sample increased the amount of phosphate sorbed. An increase in pH promotes the formation of hydroxy-Al polymers, which provides sorption sites for phosphate. Drying the sample possibly caused the organic matter to detach at weak bonds from hydroxy-Al polymers allowing access to more sites at which sorption can take place. This possibility is indicated by the response at pH 3.5, in which the drying of the sample did not increase phosphate sorption because very few if any hydroxy-Al polymers exist at this pH, but at pH 7.0, the drying increased sorption, which can be explained by the formation of hydroxy Al polymers. The significant implications of this research is that for acid soils with a high amount of Al-humus complexes, phosphate sorption will likely increase upon liming the soil, and for soils with a significant amount of organic matter, which may block sorption sites on mineral surfaces (to be discussed in more detail later), the sorption capacity will increase upon drying. Haynes and

Swift (1989) also stated that Fe-organic matter complexes are likely to behave in a similar manner to Al-organic matter complexes because hydroxy-Fe polymers form similarly to Al-hydroxy polymers.

In summary, mineral components effect phosphate sorption in the following order, Fe and Al hydrous oxides, followed by calcareous minerals, then phyllosilicates. Humus complexes posses a great potential for phosphate sorption and must be considered carefully because it is greatly affected by soil management.

Soil Solution Chemistry

Soil solution chemistry controls the interaction of phosphate anions with the electrically charged mineral surfaces. The pH, ionic strength and valency of the predominant ionic species have a pronounced effect on the surface charge characteristics of the minerals. The phosphate anion's interaction with the minerals is greatly affected by changes in the diffuse double layer on mineral surfaces. Two characteristics of the diffuse double layer theory on colloid surfaces affect anion contact with sorption sites. One is the net surface charge of the particles with surface hydroxyls. For variable charge colloids, such as Fe and Al hydrous oxides, edges of phyllosilicates and organic compounds the pH of the soil solution will control whether there is a net negative or net positive surface charge. For anion adsorption, a net positive charge would promote contact between anions and sorption sites. Phosphate sorption will occur at all pH values with Fe and Al hydrous oxides, but the surface charge characteristics that allow the highest probability for phosphate anions to come into contact with the particle surface will promote the highest amount of phosphate sorption. The other characteristic is the thickness of the diffuse layer. A thinner diffuse layer is promoted by higher ionic strength which occurs with higher electrolyte concentration and/or higher valency species in the soil solution. A thinner layer allows closer proximity of anions in the diffuse second layer to the sorption sites which increases the probability of an adsorption reaction (Uehara and Gillman, 1981).

The effect of pH on phosphate sorption differs between soils. Barrow (1984) has demonstrated this effect and has described several factors that determine how pH effects phosphate sorption. One factor described is the relationship between the pH and the electrostatic potential at the particle surface. The electric charge and at the particle surface becomes more negative with an increase in pH. Thus phosphate sorption is reduced due to the electrostatic conditions. On the other hand, a rise in pH promotes a higher concentration of HPO_4^{2-}, which is more reactive with the sorption sites. Sometimes the effects of these two conditions offset each other.

Another factor which can alter the response to pH stated above is the electrolyte species and concentration in the soil solution. Higher ionic strengths induce a change in the surface potential of the minerals. If the net surface charge is negative, an increase in electrolyte concentration will decrease the negative surface potential as more cations move into the outer adsorption planes, and if the net surface charge is positive, an increase in electrolyte concentration will increase the negative surface potential as more anions move into the outer adsorption planes. A more negative surface potential will reduce phosphate sorption because it has a stronger force to repel anions. Thus, for a high electrolyte concentration the change in phosphate sorption will be greater as the surface charge changes with pH than when there is a low electrolyte concentration. Eze and Loganathan (1990) have demonstrated this relationship, but they also show that a high concentration (10^{-2} M) of Ca will reverse the effect of pH on phosphate sorption to increase phosphate sorption as pH increases above pH 5.0. Increasing concentrations of Ca can promote phosphate sorption by forming complexes with phosphate at negative charged surfaces and allow phosphate sorption to occur, and the presence of Ca will also promote precipitation of Ca-phosphates as soil solution pH increases (Helyar et al., 1976). Thus, with a significantly high concentration of Ca, an increase in pH will induce an increase in phosphate sorption.

The presence of extractable Al will also affect how a soil responds to increases in pH. As pH increase, Al hydroxides precipitate and provide new surfaces for phosphate sorption to occur. This relationship tends to occur when the extractable Al level is above 0.02 mole kg^{-1} soil (White, 1983).

Eze and Loganathan (1990) demonstrated that the amount of phosphate added to the soil also affects the response of phosphate sorption to pH changes. With a low level of 10 mgP L^{-1} of equilibrating solution the response to pH changes was very slight and the increase in sorption with pH in the presence of a Ca concentration did not occur. At low levels of added P the sorption will occur almost entirely at the high affinity sites, but with higher levels of added P the sorption that occurs following the initial fast reaction will be subject to the chemical environment of the soil solution. This relationship also suggests that the amount of phosphate already sorbed onto soil particles will affect the response the soil solution conditions in subsequent additions of P (Barrow, 1984).

Soil Organic Matter

Sanyal and De Datta (1991) suggest that both a positive and negative correlation between organic matter and phosphate sorption can exist. The positive correlation is related to the adsorption of phosphate by Fe and Al associated with organic matter (discussed above in Iron and Aluminum Humus Complexes), especially in soils in which Fe and Al in solution tend to have a stabilizing effect on the organic matter and promote organic matter accumulation. In addition, the presence of organic matter can inhibit the crystallization of Fe and Al hydrous oxides, thus resulting in poorly crystalline material with high surface area with a much larger sorption capacity (Haynes and Swift, 1989). This process, which is common to Andisols and Spodosols, promotes a positive correlation between organic matter and phosphate sorption, but it is an indirect relationship in that in the organic matter accumulates due to the presence of Fe and Al ions, and then promotes the formation of a very high phosphate sorbing material.

Organic matter can reduce phosphate sorption through competition for sorption sites on particle surfaces and also through aggregation promoted by clay-organic complexes, that limits the access of phosphate to particle surfaces. Organic anions can compete with phosphate for the sorption sites on mineral surfaces and thus block phosphate from being sorbed. Low molecular weight organic acids have been shown to decrease phosphate sorption of various minerals and soils when they were applied with the P or even more effectively when they were applied before P applications. These treatments allowed for more complete sorption of the organic anions before the phosphate could compete for the sites (Hue, 1991, Violante, 1991). The effect of humic and fulvic acids on phosphate sorption was studied by Sibanda and Young (1986). They found that organic materials strongly competed with phosphate for adsorption sites at low pH values. They hypothesize two mechanisms for the humic and fulvic acids to decrease phosphate sorption. One is that the electrostatic field generated around the adsorbed organic acid would tend to inhibit the phosphate anion from approaching the sorption site. The second is that the proton buffer power (change in degree of proton dissociation per change in pH) of the organic acids is greatest at pH 4-5 and for phosphoric acid it is greater at pH 7. This observation is significant because it is likely that proton-donation aids in the ligand exchange adsorption on to the hydroxylated sites of Fe and Al oxides. The proton released by the organic acid or phosphoric acid enhances ligand exchange with the hydroxyl. Thus, humic and fulvic acids have a higher sorption potential at lower pH values, that makes them more competitive in this pH range.

In addition to organic matter’s effect on phosphate sorption it can also be a major pool for P within the soil. The immobilization and mineralization of phosphorus is a sink and source, respectively, for available P. Tiessen et. al. (1984) studied the relationship between soil P pools, defined according to a sequence of extracting solutions, and statistically correlated the contents within the various pools for soils differing in pedogenesis. Their objective was to identify the pathways of P transformation between pools based on soil type. They found that for Mollisols 86% of the variation in available P is controlled by variations in the moderately labile inorganic P fractions. For highly weathered Ultisols they found available P largely controlled by the mineralization of organic P. The implication of these results is that the degree of phosphate sorption affects the transformations between the various P pools and especially these pools that buffer the available P pool. For soils which sorb a large amount of phosphate such as highly weathered Ultisols, the organic cycling through immobilization and mineralization becomes very important.

Soil organic matter is very complex, especially in terms of composition and interaction with soil minerals, thus its effects on phosphate sorption are difficult to determine. Research efforts attempt to examine specific organic compounds or a class of organic material, such as humic acids or fulvic acids, for their effects on phosphate sorption. Because of the complexity, caution must be exercised in piecing together information about experimentally isolated portions of the whole system. Organic matter affects many soil properties, such as its tendencies to promote higher microbial activity, which can lead some P to be immobilized and subsequently mineralized, and possibly become a major factor in the P availability, as well as promote better growth conditions which would allow roots to better disseminate for greater access to P dispersed throughout the soil.

Total P Content

The total P content in the soil affects how additional P will be sorbed. A comparison of two samples of the same soil with the only difference between them being the amount of total P will show the soil with a higher level of P to have more sorption sites already occupied by phosphate and a reduced amount of the additional phosphate sorbed. Barrow (1974) noted that prolonged contact of phosphate with soil makes the phosphate less available to plants and that this P in the soil would have an effect on the sorption of additional applied P. The data showed the amount of phosphate sorption was reduced as well as the buffer capacity, ie., the slope of the sorption isotherm. Thus, indicating the previous applied P to be occupying sorption sites and limiting further sorption and possibly buffering potential of the soil as well. These effects are attributed to the sorbed phosphate reducing the number of sites available for further sorption (Barrow, 1974, Parfitt et. al., 1989) and also due to change in surface charge properties of the minerals due to the previously sorbed phosphate, which increases the net negative charge (Barrow, 1978, Bolan and Barrow, 1984).

Summary

The process of phosphate sorption is primarily an adsorption reaction of phosphate anion in soil solution with the minerals that comprise the soil. The Fe and Al hydrous oxides have the strongest affinity for phosphate sorption. Calcareous minerals also sorb a significant amount of phosphate, and silicate clays make a slight contribution to the sorption process. Phosphate sorption is a continual dynamic process with most of the sorption occurring rapidly, but the remaining portion continues to sorb slowly and is strongly affected by the chemical and physical conditions of the soil. Soil solution pH and electrolyte concentration affect the surface chemistry of the minerals and thus the phosphate sorption process. Soil organic matter also affects the surface chemistry as well the physical conditions which affect access of phosphate to reactive surfaces. The amount of phosphate sorbed by minerals and in organic matter will affect the dynamics of phosphate in solution as more is added to the soil system or as it is removed by plant uptake. All of these factors involved with the phosphate sorption process must be recognized for their impact when measuring phosphate fertility conditions in the soil and when attempting to predict the phosphate status' impact on plant growth.

Measuring Responses to Applied Phosphorus

Soil Phosphorus Extractants

One of the most researched aspects for P fertility has been to find an extracting solution that will accurately determine the amount of available P. Because soil systems and their interaction with P vary widely, it is difficult to find a single extractant that is satisfactory for all soils. Instead several extractants have been developed for certain types of soils. The extractants work adequately for the soils and crops they were developed on, but when utilized outside of its research domain its results may be unrepresentative. Extractants remove phosphate in the soil solution as well as part of the sorbed phosphate, called labile P, which is the portion of the sorbed phosphate that will desorb into solution upon plant uptake. It is the removal of this portion of the sorbed phosphate that varies from soil to soil because differences in soil minerals and chemistry create different forms of sorbed phosphate that desorb at different rates.

A considerable amount of research has gone into the development of phosphorus extracting solutions in an attempt to find one that best meets the following three criteria (Bray, 1948);

1) all or a proportionate part of the plant available phosphorus should be extracted from many types of soils,

2) the extraction measurement should be made with reasonable speed and accuracy, and

3) there should be good correlation and sensitivity between the amount extracted and the growth response of each crop.

Meeting the first requirement has been very difficult because the chemistry of the soils can alter the effectiveness of the extractant. Kamprath and Watson (1980) classify the various extractants as

a) dilute concentrations of strong acids,

b) dilute concentrations of strong acids plus a complexing ion,

c) dilute concentrations of weak acids,

d) buffered alkaline solutions.

Given the different chemicals in each of the extractants, each one has a different mode of action for removing phosphorus and thus some are more suitable for certain types of soils. For example the dilute acid solutions were developed for acidic soils, but their use on calcareous soils may yield misleading results if the alkalinity of the soil changes the pH of the extractant so that it is less effective in extracting sorbed phosphate. The development of resin and Fe strips as an extractant provide a method that could potentially reflect P availability by minimizing the interaction with the soil chemistry (Sibbesen, 1978; Menon et al., 1989).

The importance of measuring the available P is to know if there is enough P available to allow plant growth. The extracting solutions give an instantaneous measurement and do not indicate any of the dynamics of the sorption and desorption processes within the soil. Ideally, in order to determine if enough P will be available for plant growth, one needs to know 1) how much phosphate is available in the soil at the start of plant growth, 2) the plant uptake rate of phosphate, and 3) how the amount available will change with time as phosphate is taken up by the plant. Soil P tests address the first factor and correlation of test levels with plant growth indirectly address the second and third factors, but the environmental dynamics and variability create difficulties in making this approach work consistently.

Research into the P sorption characteristics and its correlation with soil properties has also been the subject of much research into P fertility. This research is important in addressing the issue of how much P will be available from the P fertilizer. The use of soil tests to estimate available P requires support in determining how much fertilizer should be applied to raise the extractable P to the level needed for adequate plant growth. Studies on the soil's sorption characteristics are often done to determine how available P levels respond to P additions.

Phosphate Sorption Isotherms

The most commonly used method to assess the phosphate sorption characteristics of a soil is with the standard conditions for phosphate sorption isotherms proposed by Fox and Kamprath (1970). The "adsorption isotherm" term refers to an adsorption system in which temperature and an adsorbate concentration fully describe the system. This condition does not exist for the adsorption isotherm technique used for soils. Other factors include time, method of shaking, solution:soil ratio, species and concentration of supporting electrolyte, initial soil moisture, initial amounts of sorbed phosphate or other anions (Barrow, 1978). Standard conditions are needed in order to compare the sorption characteristics between soils. Isotherm plots include the "intensity", or concentration, of phosphate in solution plotted on the x-axis (mgP L^{-1}) and the "quantity", or mass, of the phosphate sorbed plotted on the y-axis (mgP kg^{-1} soil). P solutions are mixed with a soil sample and analyzed for phosphate concentration after being mixed. The amount of phosphorus removed from the original concentration is taken to be the amount of phosphate sorbed. The data, when plotted, show how the relationship of the quantity of P sorbed varies directly with the concentration of P in solution.

The isotherm is used to estimate an adsorption capacity and bonding energy. Both of these values are determined by fitting the data to model equations, such as the Langmuir equation. Comparisons can then be made between soils by correlating soil properties with the sorption capacity and bonding energy calculated from the sorption models.

Fox and Kamprath (1970) proposed a standard soil solution value of 0.2 mgP L^{-1} to be used in determining fertilizer requirement for soils. This soil solution concentration level generally provided at least 95% of maximum growth for the crops investigated. The phosphorus sorption isotherm would show the amount of phosphorus that would be sorbed in order to attain 0.2 mgP L^{-1} in solution, thus the amount of phosphorus sorbed would be the fertilizer requirement.

Desorption Isotherms. Of equal or greater importance to P fertility in soils is the desorption ability of the phosphate attached to soil colloids. As discussed earlier, the sorption with time shows an initial fast reaction which sorbs most of the P then a continual reaction that appears to reach an equilibrium, but never showing a distinct endpoint (Berkheiser et al., 1980; Barrow, 1983a; Sanyal and De Datta, 1991). The desorption of phosphate also shows a continual decrease in the amount of phosphate that will desorb with time, so not only is more and more phosphate being sorbed, but the amount that is sorbed will desorb to a lesser extent with time (Barrow, 1983b). The decrease in desorption with time is related to the mechanism for the slow reaction, which has been discussed previously for the various minerals. Kafkafi et al. (1967) hypothesized that the phosphate that desorbs is in an exchangeable state of a weak single bond, and that the phosphate which does not desorb is fixed with two of its oxygens each bonding to an Al or Fe atom on the mineral surface. Barrow (1983b) hypothesized the slow rate of sorption and the reverse, desorption, to be diffusion controlled, which is solid-state diffusion of phosphate into the adsorbing material.

Desorption has been measured through successive washings of the samples previously treated with phosphate to prepare a sorption isotherm. The amount of phosphate that moves into the wash solution, usually a weak electrolyte solution, is the amount that desorbs at the final concentration of phosphate in the wash solution. When this data is plotted it shows a hysteresis effect in that less phosphate is desorbed than was sorbed for each concentration in solution, i.e. the desorption curve does not follow the adsorption curve (Kafkafi et al., 1967; Fox and Kamprath, 1970) (Figure 2.2). These results indicate that phosphate desorption during plant uptake will supply less phosphate than indicated by the adsorption isotherm, because the sorbed phosphate must held strongly enough to not return to solution when the solution concentration changes as indicated by the adsorption isotherm.

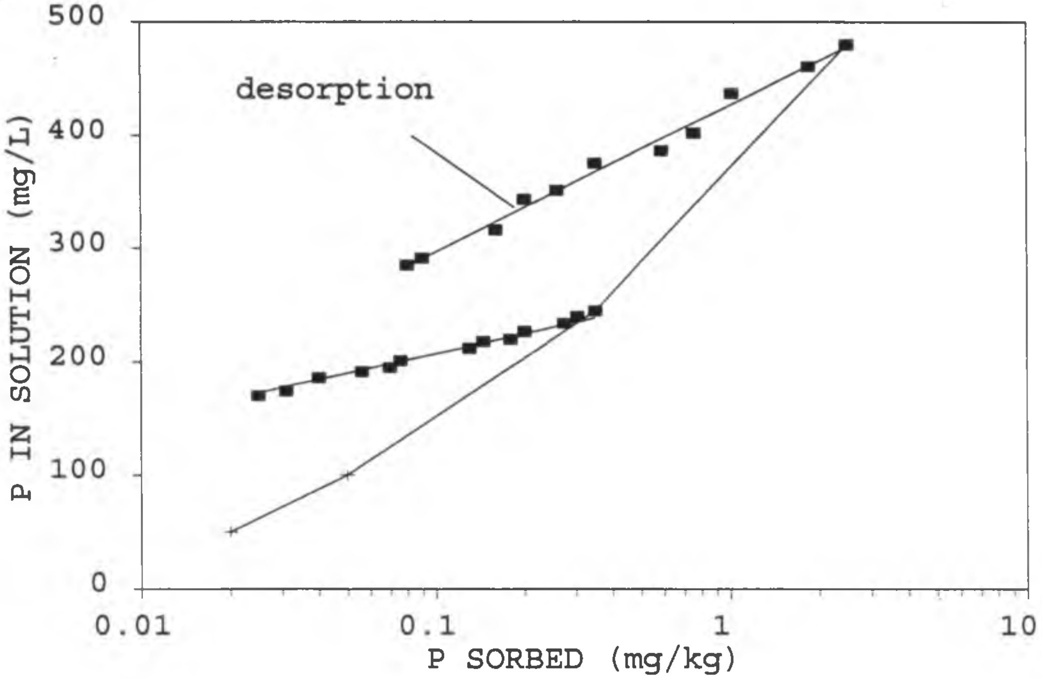


Figure 2.2 Adsorption isotherm followed with desorption by successive washings on two treatments (adapted from Fox and Kamprath, 1970).

Another measurement of desorption has also been made by mixing soils with increasing levels soil:solution ratios to allow phosphate to move into solution. The phosphate desorbed is found by the increase in phosphate concentration. Barrow (1983b) did this desorption as well as additional phosphate sorption onto the samples used to prepare a sorption curve and found the desorption curves to form a continuous line with the data points for the additional sorption (Figure 2.3). Barrow (1983b) hypothesizes that this relationship occurs due to solid state diffusion of phosphate into the adsorbing particles.

The P sorption isotherm approach to determining P needs may be inadequate because it does not indicate desorption rates nor does it reflect the adsorption that would take place under field conditions. The procedure calls for 1:10 mixture of soil:solution and an equilibration time of six days, which is believed to be sufficient time for sorption to take place (Fox and Kamprath, 1970). Where as in the field situation the soil moisture fluctuates from field capacity and the sorption process is different than for methods that use a high solution:soil ratio (Barrow, 1983a).

Incubation Studies

Incubation studies designed to better represent field conditions provide another method for determining how much P must be added to produce a desired level of available P in

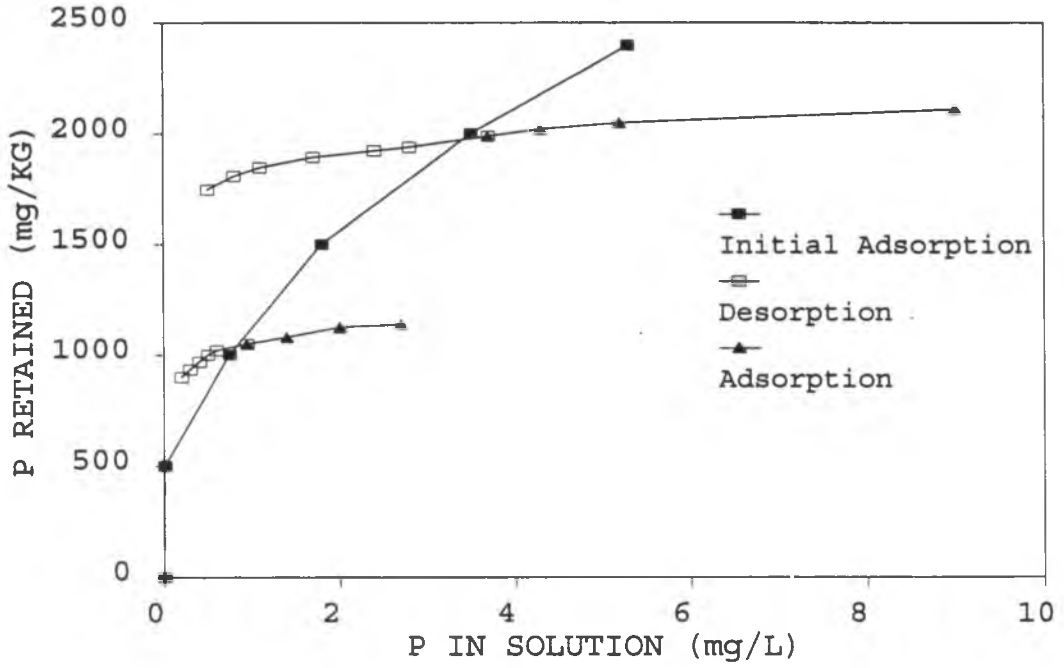


Figure 2.3 The desorption of phosphate following initial sorption (to the left of the isotherm) forms a smooth curve with subsequent adsorption (to the right of the isotherm) (Barrow, 1983b).

the soil. The approach of this method is to apply various rates of P to soil samples, add water to field capacity and incubate for a period of time. The moisture can be maintained at a constant level or allowed to be dried and rewetted to induce the effects of wetting and drying cycles.

Simulating field conditions involves more of the dynamics of the whole soil-phosphorus system because in addition to the sorption by mineral constituents there will also be interaction with the biological components of the soil. The conditions for incubation studies that must be set include incubation time, temperature, minimum and maximum water content, number of wetting and drying cycles, and the amount and form of phosphorus. The incubated samples are analyzed for changes in soil P by several methods, such as 1) extractants to determine available or labile phosphorus, 2) adsorption/desorption isotherms to determine soil solution content, 3) soil solution analysis, and 4) sequential extractions (Barrow, 1983a; Sharpley 1983; Bowman and Olsen, 1985b; Parfitt et al., 1989; Sharpley et al., 1989; Johnston et al., 1991). These measurements are commonly used to determine the relationship between the available phosphorus and the added P, and when measured over a period of time, it reflects the sorption rate of P by the soil. This relationship indicates the buffering ability of the soil to adjust to changes and maintain the concentration of phosphate in soil solution. The measurement of this ability has been given various names, such as phosphorus fertilizer factor, buffering coefficient or fertilizer requirement (Lins and Cox, 1989; Sharpley et al., 1989; Johnston et al., 1991). The use of incubation studies to measure soil response to applied phosphate will reflect most of the interactions that occur within the field, except those due to climatic effects and plant growth, and thus provide more applicable parameters to use for phosphorus management.

The two measurements of the buffering ability of phosphate in solution and the rate of change in buffering ability with time lead to characterizing the dynamics of P availability within the soil. Barrow (1980) concluded that the rate of reaction is an important component in characterizing a soil, and the rate can be established by analyzing an incubation study at 1 and 30 days. The rate determined for this time period was satisfactorily predictive of the soil solution concentration after 90 days. In another incubation study, Parfitt et al. (1989) noted that four soils varying in Fe and Al hydrous oxides exhibited a slow reaction with phosphate, and the rates of adsorption was similar for all soils, where as in a high solution:soil method the soil with allophane had a much higher sorption rate. They conclude this difference suggests other factors, such as the diffusion of phosphate into aggregates, are as important as the type of minerals. This conclusion points out that incubation studies may be important in providing the effects of physical properties of the soil on phosphorus sorption rates that are not considered when using suspensions with phosphate solutions.

In addition the effects of microbiological activity must be considered when investigating phosphorus sorption on whole soils (Parfitt et al., 1989; Sollins, 1991). P immobilization and mineralization through the soil organic matter is a major factor in maintaining available P in native ecosystems for some soils that have a high ability to sorb phosphate (Tiessen et al. 1984). To examine the changes in forms of P, sequential extractions of increasing strength are implemented to extract the phosphate held within the soil by different stages of reaction for both inorganic and organic materials. Hedley et al. (1982) utilized the following extracts in the order listed; anion exchange resin, sodium bicarbonate, sodium hydroxide, sonication/sodium hydroxide, hydrochloric acid, and a final digestion of residual soil material. The P pools that these extractants are intended to measure are both the organic and inorganic forms of labile P, moderately labile P and nonlabile P, which includes secondary minerals, occluded P and chemically and physically protected P. The amount of phosphate measured by this method is a result of the chemistry of the extractant, but presumably represent the forms of P stated above. When measured over time, the data will reflect more of the dynamics of the P interactions occurring within the soil.

Phosphate Buffering. The buffering ability of a soil refers to a soil's resistance to change phosphate concentration in soil solution through adsorption of phosphate when the concentration increases and desorption when the concentration decreases. This parameter would be helpful in predicting the supply of available P over a period of time and can be used in two ways. One, to determine the amount of fertilizer needed to provide a desired level of available P, and two, to predict how much will be available when the amount of sorbed P is known. The first parameter deals with sorption and the other with desorption, and both also involve a temporal rate component that is not often dealt with in the research literature. The measurement of a buffering coefficient is difficult because of the hysteresis between adsorption and desorption and the sensitivity of measurement to the methods employed.

Several approaches have been used to measure buffer coefficients. As mentioned previously, incubation studies are used to establish the relationship between extractable or soil solution phosphate and the amount of P added and/or time. Sharpley et al. (1989) measured what they termed a fertilizer factor, (P extracted)/(P applied), by using an anion exchange resin to extract P from samples incubated at five rates of P fertilizer after 30, 60, 90, 120, and 180 days. The fertilizer factor decreased with time, and $CaCO_3$ content or extractable Fe and Al content was the most closely related soil property to actual values of the factor and its change with incubation time. They hope to utilize the fertilizer factor, soil properties, and P applied to predict plant uptake of P in a soil-plant model. Bowman and Olsen (1985b) calculated a buffer capacity, (mgP kg^{-1} soil)/(mg P L^{-1} solution), based on the resin extractable P (quantity, Q) and the water-soluble P (intensity, I) following several harvests of crops in a greenhouse study. They suggest that the buffer capacities calculated from the Q/I relationship would be helpful to use with conventional soil P testing procedures to help evaluate P fertility status and predict crop response. The idea being that an extracted level of P used to measure the P fertility status can be enhanced with the buffer capacity to determine how much non-extracted P would be available as desorption takes place. Buffering abilities for the adsorption of added P and the desorption of sorbed P can provide essential information on the dynamics of P availability in soils.

There is no standard method for determining the buffering ability of a soil. Generally, it can be measured as the slope of sorption or desorption isotherms or the slope generated by incubation studies that analyze either sorption or desorption. Some research on buffer capacities attempt to find the simplest way to make the measurement.

The slope of adsorption isotherms seem to be the simplest way found thus far, as desorption measurements are sensitive to analytical errors and thus lack reproducibility (Bowman and Olsen, 1985a; Holford, 1988). The buffer capacity varies with the amount of P added so it is measured as the slope at one designated soil solution concentrations (with the derivative of an equation such as the Langmuir adsorption equation). The slope is sometimes calculated between two designated soil solution concentrations. The buffer capacity also varies with time following application of P to the soil. Due to the continued sorption of phosphate during the slow reaction, the buffer capacity will change with time (Sharpley et al. 1989).

Buffering capacity does not account for all of the factors that affect the dynamics of P availability. Bowman and Olsen (1985b) have listed several important considerations for plant uptake of P and P availability.

1) The water movement and soil pore size play a role in controlling the rate of P release into solution.
2) Mycorrhiza can contribute significantly to P uptake as well as other nutrients.
3) The mineralization of organic P is a major part of P cycling in some soils.
4) Plant root distribution and activity during the growth of the plant vary considerably between species

and environments and can not be considered to have a uniform interaction with all soil-P systems.

A comprehensive project to bring all important considerations into a model that predicts plant response to soil P conditions may have to be necessary, but thus far research has dealt with trying to find simplified approaches that will allow adequate prediction from the correlation of a few soil properties with the plant and soil response to added P.

Predicting Soil and Plant Response to Applied Phosphorus

The general approach to predict the amount of P fertilizer needed for sufficient crop growth has been to correlate extractable P levels with crop growth and then to calibrate how much P to apply to obtain the extractable P level needed. This approach is soil and crop specific and the data cannot readily be extrapolated to other soils or plants.

In an effort to overcome the costs and time of doing numerous correlation and calibration studies for many soils and crops, attempts to model soil P availability and needs are focusing on incorporating soil properties that indicate phosphate sorption ability. Models that have been generated thus far are essentially empirical models that establish constants for a given soil, and with information on the current level of P, the model attempts to predict fertilizer needs.

Cox et al. (1981) developed a descriptive model to represent the change in soil test P with time. The equation for this model equates the change in extractable P with time to the difference between the current level and an equilibrium level of P multiplied by a rate constant.

$$dP_{ext}/dT = -k(P_{ext}-P_{eq}) \quad (1)$$

They integrated this equation in order to calculate the extractable P level at any time.

$$P_{ext} = P_{eq} + (P_{init} - P_{eq})e^{-kT} \quad (2)$$

This relationship gives an exponential decrease in extractable P with time in which the constant k empirically represents the sorption ability of the soil and the effect of P uptake by plants. Thus a separate constant k value is needed for each soil and cropping system modeled by the equation. To remove the need to measure extractable P at T = 0 (P_{init}) it can be estimated from a quadratic relationship that predicts the extractable P level based on the amount of P fertilizer applied.

$$P_{init} = P_0 + b_1F + b_2F^2 \quad (3)$$

F is the amount of fertilizer applied, P_0 is the intercept and b_1 and b_2 are empirical constants that reflect the sorption ability of the soil. This regression was done on extractable P measurements from samples incubated with applied P for sufficient time to complete the initial fast reaction. When P_{init} is substituted out of equation (2) it becomes:

$$P_{ext} = P_{eq} + [(P_0 + b_1F + b_2F^2) - P_{eq}]e^{-kT} \qquad (4)$$

This model predicts the long-term residual affects of applied P during several cropping seasons. Without annual P applications the extractable P level gradually declines with continued sorption and crop removal. The effect of annual P fertilizer applications on the extractable P level can be modeled to reveal if application rates will maintain the extractable P level, cause it to increase or allow it to decrease over several cropping seasons.

Lins et al. (1985) modified the above equation to be able to account for fertilizer applications at various initial extractable P levels. They also extended the model to calculate the optimum fertilizer rate to provide the best economic return from the cost of the fertilizer applied. The calculation of fertilizer rate utilized the extractable P level and clay content as the independent variables. Inclusion of the clay content reflects the influence of reactive surface area on P sorption.

Matar (1988) modified equation (4) to include a P uptake term and a linear relationship for the extractable P level, P_0 following fertilizer application instead of a quadratic equation used in equation (3).

$$P_{ext} = P_{eq} + [(P_0 + bF) - P_{eq}]e^{-kT} - PU \qquad (5)$$

It is assumed that P uptake (PU) is proportional to the level of extractable P and that there is no replenishment of extractable P from the solid-phase P. Matar concluded that this descriptive model could predict the effect of residual P and thus reduce the need for frequent soil analysis to make fertilizer recommendations. To make the model much more effective, however, it would require incorporating aspects of the P buffer capacity of soils and the rate of P immobilization.

Jones et al. (1984) has developed a simplified soil and plant P model that attempts to estimate the levels of labile and organic P for a wide variety of soils on a long-term basis. This model includes various P pools such as plant uptake, soil organic matter and inorganic soil P. The flux of P between the pools of organic P and of inorganic P is modeled based on the fertilizer factor and initial measurements of the amount of labile P, which is defined as the amount extracted by an anion exchange resin. The fertilizer factor is determined as discussed earlier by the amount of extractable P following incubation with an amount of applied P. Rather than plan to make these measurements on all soils to be modelled, Sharpley et al. (1984) developed regression equations to estimate these values from routinely measured soil properties. The labile P can be estimated from either the Bray, Olsen or Double Acid extractant levels of P. Because sorption characteristics are determined by minerals, three sets of regression equations were established for the following three types of soils, calcareous, slightly weathered and highly weathered soils. The fertilizer factor can be estimated from the $CaCO_3$ content for calcareous soils, from base saturation, labile P level and pH for slightly weathered soils, and from the clay content, labile P level and organic carbon content for highly weathered soils. Thus, this approach utilizes some of the soil properties that determine the sorption ability of a soil.

The simplified plant and soil P model by Jones et al. utilizes the fertilizer factor to calculate the flux between the labile P and P sorbed in the fast reaction, and Cox et al.'s (1981) descriptive model of extractable P (discussed above) is utilized to determine the amount of slowly sorbed P. Immobilization and mineralization rates of organic P and plant uptake rates of P are included in this model. The incorporation of these aspects of soil P dynamics is a significant step to begin to accurately model long-term P fertility. The use of routinely measured soil properties in the model would allow it to be used much more widely than if special measurements have to be made, but regression of the soil properties with model parameters leads to uncertainty when extrapolated to soils outside of those included in the regression analysis. If, however, a more mechanistic understanding of the soil P dynamics could be included in the model, then the measured values from various soils may lead to increased accuracy.

In summary, the extent of understanding of the phosphate sorption process includes the aspect of ligand exchange with surface hydroxyls and the conditions that influence the interaction of phosphate anion with colloid surfaces. On the other hand, quantitatively predicting sorption from the combined affect of the soil conditions is not accurate. General levels of sorption ability can be estimated from the minerals present and texture, but accurately predicting the availability of P fertilizer for one or more growing seasons can not be estimated. This approach would involve estimating the rate of sorbed and desorbed phosphate and the effect of the buffering action, however, the factors that control these rates are not well understood. Due to interactions between the soil factors affecting phosphate sorption, it is very difficult to isolate and study directly how each one contributes to the dynamics of phosphate sorption and desorption. All explanations given for the slow reaction have yet to be thoroughly demonstrated by research results, nor is there a definitive explanation for why some of the sorbed phosphate will desorb but a portion will not. Accurately predicting the sorption rate and amount for applied P fertilizer allows more effective fertilizer management. This accuracy relies on knowing the factors and understanding the processes that determine the sorption rate with time. Efficient use of fertilizer requires understanding the desorption process which shows to be more than just simply the reversal of sorption.

Phosphate Sorption by Hawaiian Soils

The soils of the Hawaiian Islands are derived from basalt and volcanic ash. Many of the soils are highly weathered and contain predominantly secondary minerals such as kaolinite and Fe and Al hydrous oxides. The variation in soils is closely associated with the orographic weather patterns and the geomorphic position and age of the land surface. The island of Hawaii, which is the eastern most island, is the youngest with new surfaces formed by lava flows from its active volcanoes. The island of Kauai, furthest to the west, is the oldest with geomorphic surfaces of several million years old. The most highly weathered soils are those that are almost completely leached of silicon from its mineral matter and occur under warm tropical environments with high rainfall. Soils forming under moderate rainfall will contain kaolinite; the driest climates of the island will contain kaolinite and smectites. Younger soils with a considerable amount of volcanic ash as parent material will contain x-ray amorphous Fe, Al and Si hydrous oxides. The degree of crystallinity of these volcanic ash soils is closely related to the annual rainfall pattern that they formed under. The higher rainfall areas such as the northeastern facing coast on the island of

Hawaii promote the retention of x-ray amorphous hydrous oxides.

As discussed earlier, minerals determine the P sorption potential of the soils. Thus, the predominantly oxidic soils of Hawaii have high P sorption potentials. Table 2.1 shows the sorption levels to achieve 0.2 mg P L^{-1} in solution of soils of differing mineral composition as determined by P sorption isotherms. This table shows the very high sorption potential of volcanic ash soils which contain predominantly x-ray amorphous hydrous oxides. Highly weathered soils consisting of Fe and Al hydrous oxides and very little to no silicate clays have a high sorption potential. Soils with some 1:1 silicate clays and hydrous oxides have a moderate to low sorption potential

Table 2.1 Phosphorus sorption levels from different soil types on the Hawaiian islands.

Soil	Rainfall (mm)	Minerals	Parent Material	pH	P sorbed (mg/kg)
Lualualei	500	2:1 clays	Alluvium	7.4	40
Molokai	750	1:1 clays	Basalt	6.0	30
Wahiawa	1200	1:1 clays	Basalt	4.8	390
Kapaa	2300	Gibbsite Goethite	Basalt	5.8	660
Akaka	5000+	Amorphous	Volcanic Ash	3.8	1850

Table adapted from Fox et al., 1968

that is affected by the pH of the soil. Soils that developed from alluvial deposits within dryer climates contain predominantly silicate clays, have neutral pH values and exhibit low sorption potentials.

Sorption potentials of some Hawaiian soils have been shown to be reduced by amendments of agricultural lime, calcium silicate or previous P additions. Table 2.2 shows the effect of amendments on the sorption level at 0.05 mg P L^{-1} of solution of a Wahiawa soil as determined by P sorption isotherms (El-Tahir, 1976). This data indicates that the sorption level can be affected by the agricultural practices applied to a soil. The degree of decrease in the sorption level is proportionally higher for soils with moderate sorption potentials, and soils with high and very high sorption potentials will be affected by such amendments but the percent decrease in the P sorption will be much less.

Table 2.2 Amendment effects on the amount of P sorption to give 0.05 mg P L^{-1} solution in a Wahiawa soil (El-Tahir, 1976).

Amendment	pH	P sorbed (mg kg^{-1})
None	4.7	200
P (50 mg kg^{-1})	4.7	175
Calcium Carbonate	6.7	150
Calcium Silicate	6.6	100
Calcium Silicate & P (50 mg kg^{-1})	6.6	50

Phosphorus Sorption and Fertility Management

The present knowledge of Hawaiian soils and their P sorption potential extends to knowing the general amount ofP sorbed according to the sorption isotherms. Little is known about the dynamics of the sorption process for eachtype of soil and the specific amount each soil will sorb. Knowledge of the rate of sorption with time and the amount sorbed following P application is useful information for management of P fertility. The amount of P sorbed per unit applied P indicates the buffering ability of the soil, and is important for determining fertilizer needs and duration of fertilizer effect on plant growth. All P sorbed is not released, some is labile and some is irreversibly non-labile. Our ability to predict P fertility status over time is very poor. We can improve this ability by developing the quantitative relationships between soil components and P transformations in the soil.

The determination of P fertility requirements can be based on calculating the rates of three processes.

1) The demand rate for P by the plants in mgP m^{-2} d^{-1}.

2) The supply rate of P by the soil which includes the concentration of phosphate in soil solution (mgP L^{-1}) and rate of desorption of labile phosphate into soil solution in mgP kg^{-1} d^{-1}.

3) The increase in supply rate by P fertilizer addition.

These rates are necessary to calculate the demand and supply needs for the duration of a crop's growing season. If the data shows the supply rate to be inadequate for the crop's demands then the amount of fertilizer needed to increase the supply can be determined from the sorption relationship for the soil.

Standard soil P testing programs make recommendations based on correlations between soil P test values and crop growth. This relationship combines the first and second processes. The relationship does not provide accurate information for other crops or soils and thus must be established for each crop and soil of interest, which is expensive and time consuming research. Recommended fertilization rates are based on the correlation between fertilizer applied and soil P test values, which reflects the third process. This relationship also does not accurately transfer to other soils and must be established for each soil of interest.

If the rates for each process could be determined from the soil and plant components, then information could be determined from the components that make up the cropping system being managed. Various management practices and crop choices could be modeled to determine which system meets the resources and objectives of the grower. To model P fertility, data is needed on the components that determine the rates in each process; such as, plant growth and uptake values for the P uptake process, P content and soil properties for the supply process and increase process.

The focus of this thesis is on the third process and attempts to relate soil components and conditions to the sorption rate and change in extractable P following the application of P to the soil. The ability to determine sorption levels and rates from soil properties will help to accurately determine increases in available P from P fertilizer applications.

The information obtained from this study should be useful in calculating the amount of P fertilizer needed to raise the extractable P to a desired level based on soil property data. Once this information is established, it will not be necessary to do correlation studies between fertilizer rates and extractable P levels. The fertilizer needed to increase the P supply rate of a soil can be calculated directly. Further research on the plant demand for P and the soils supply rate of P can be joined with this research on increasing the supply rate to model P fertility in many types of cropping systems in any location.

This research will correlate many soil properties with P sorption to determine which properties or combination of properties are potentially useful for predicting P sorption. In addition, the dynamics of the sorption process will be monitored in an attempt to model the change in extractable P with time after application. The model parameters that best fit the data will be correlated with soil properties to determine the properties that control the sorption rate. The parameters for other soils could then be calculated from measured soil properties.

CHAPTER 3

MATERIALS AND METHODS

Soils

The eleven soils in this study were collected to represent a range in the properties affecting P sorption in Hawaiian soils. Most Hawaiian soils have high surface areas and contain Al and Fe hydrous oxides including some of the few loamy textured soils which are derived from volcanic ash and thus have high surface areas. Three Andisols (Kaiwiki Cultivated, Kaiwiki Uncultivated and Maile) were selected because of the amorphous characteristics of the Fe and Al hydrous oxides in these soils, to represent the high P sorption capacity of Hawaiian soils. Three Oxisols (Halii, Kapaa and Makapili) and one Ultisol (Haiku) were selected to give a range in mineral types from predominantly Fe hydrous oxides to predominantly Al hydrous oxides. Three soils were selected for relatively moderate sorption capability. Two of these (Molokai and Wahiawa) are Oxisols with kaolinitic minerals, and the third (Pulehu) is a Mollisol with a significant amount of $CaCO_3$. The other Mollisol (Waialua) was selected for a low sorption capability because of its predominance of silicate clays and relatively little Fe and Al hydrous oxides. A wide range of P sorption characteristics was desired as well as soils that are of significant agricultural importance to the state of Hawaii. The soils are listed in Table 3.1 along with their

Table 2.1 Soil series and classifications.

Soil Series	Classification
<u>Andisols</u>	
Kaiwiki	Typic Hydrandept, thixotropic, isothermic (Typic Hydrudand, hydrous,isothermic)
Maile	Hydric Dystrandept, thixotropic, isomesic (Acrudoxic Hydrudand, hydrous, isohyperthermic)
<u>Oxisols</u>	
Halii	Typic Gibbsihumox, clayey, ferritic, isothermic (Anionic Acrudox, fine, ferritic, isohyperthermic)
Kapaa	Typic Gibbsihumox, clayey, gibbsitic, isothermic (Anionic Acrudox, v.fine, sesquic, isohyperthermic)
Makapili	Typic Acrohumox, clayey, ferritic, isothermic (Anionic Acrudox, v.fine, sesquic, isohyperthermic)
Molokai	Typic Torrox, clayey, kaolinitc, isohyperthermic (Typic Eutrotorrox, fine, kaolinitic, isohyperthermic)
Wahiawa	Tropeptic Eutrustox, clayey, kaolinitic, isothermic (Rhodic Eutrustox, v.fine,kaolinitic, isohyperthermic)
<u>Ultisols</u>	
Haiku	Humoxic Tropohumult, clayey, ferritic, isothermic (Typic Palehumults, clayey, oxidic, isohyperthermic)
<u>Mollisols</u>	
Pulehu	Cumulic Haplustoll, fine-loamy, mixed, isohyperthermic
Waialua	Typic Haplustoll, v.fine, kaolinitic, isohyperthermic

The classifications are according to the State of Hawaii Soil Survey (Soil Survey Staff, 1972; Soil Survey Staff, 1973). Names in parentheses are the tentative classifications according to the 1992 revision of Soil Taxonomy (Dr. H. Ikawa, personal communication).

classification. The Kaiwiki and Maile soils were collected from the island of Hawaii. The Haiku, Molokai and Pulehu soils were collected from the island of Maui. The Wahiawa and Waialua soils were collected from the island of Oahu. The Halii, Kapaa, and Makapili soils were collected from the island of Kauai.

All soil samples were collected from the surface horizon, generally from 0 to 15 cm in depth. The Kaiwiki samples were allowed to dry slightly, only enough to allow the soil to crumble and pass through a 6.3 mm (1/4 inch) sieve without sticking to the sieve and re-adhering together to reform larger aggregates. The Maile soil was allowed to dry enough to pass through a 2-mm sieve without sticking. The remaining soils were air-dried and ground to pass through a 2-mm brass sieve.

Soil Characterization

Physical Properties

The characteristics of each soil were determined by the following methods. These properties were selected to reveal the characteristics that affect the P sorption process of soils.

Soil mineralogy was examined by x-ray diffraction analysis of the clay fraction for all soils except the Andisols. For the Andisols, the whole soil was analyzed following removal of organic matter with hydrogen peroxide (Kunze and Dixon, 1986). Following organic matter removal, the soils were wet sieved through a 45 μm sieve then dried and ground to pass through a 75 μm sieve. Due to the difficulty in dispersing these soil, the clay fraction was not separated for mineralogical analysis.

The samples were packed into bulk powder mounts and analyzed on a Philips Scientific Instruments XRG 3100 diffractometer with a Co X-ray tube operated at 40kV and 25mA. The samples were run with a 4-second integration time at 0.025 2-θ steps without a theta-compensating divergence slit for the range of 4 to 76 degrees 2-θ. Counts data were recorded on computer disks for plotting and processing.

Quantitative mineralogical analysis of the X-ray diffraction pattern was done using the SIROQUANT (Sietronics, Pty. Ltd. 1993; Taylor, 1991) computer program. This program utilizes the Rietveld method to simulate an observed X-ray diffraction pattern and quantify mineral compositions of the sample. The pattern is simulated from the structural factors of the mineral by calculating the position and intensity of each peak generated by the diffraction of X-rays. Rietveld refinement minimizes the squared differences between observed and calculated intensities by changing the parameters used to calculate the pattern. The resulting parameters then indicate the percentages of each mineral and the average "crystallite size", which is the dimension that contributes most to peak broadening, and unit cell dimensions of sample minerals.

Sorption sites per gram of soil was predicted for each soil based on the quantity and size of goethite, gibbsite and kaolin minerals in the soils. The quantity and size of these minerals were obtained from analysis of the X-ray diffraction pattern with the SIROQUANT program. Determination of sorption site surface density relies on calculating the surface area contribution of each mineral per gram of soil and the number of PO_4 sorption sites per square meter of mineral surface.

Surface area of goethite, gibbsite and kaolin in each soil was calculated from the assumption that each mineral has the shape of a cylinder. For goethite the length of the cylinder is much longer than the diameter to match its acicular morphology. Gibbsite has a disk like appearance which the cylinder simulates when the length is approximately equal to the diameter. Kaolin has a platy morphology which the cylinder assumes when its diameter is much greater than its length. From the geometry of the cylinder, the volume and surface area of particles can be calculated. The "crystallite size" from the SIROQUANT refinement provides only one of the two dimensions needed for determining the size of the cylinder. For goethite the "crystallite size" refers to the diameter of the needle, thus its length must be assumed, and for gibbsite and kaolin the "crystallite size" is the length of the cylinder and the diameter must be assumed in order to calculate surface area and volume. In the case of goethite, synthetic crystals are normally well defined needle-shaped crystals but in naturally occurring materials they come closer to being spherically shaped (Schwertmann and Taylor, 1989), thus the length of the goethite crystals in these soils was assumed to equal the diameter of the crystals. The same assumption was used for gibbsite as well because of its disk-like shape. For kaolin a diameter of 1000 Å was assumed, a size which was observed for several tropical soils in Puerto Rico (Jones et al., 1982).

Volume of cylinder = $\pi(D/2)^2L$

Surface area of cylinder = $2\pi(D/2)^2 + \pi DL$

where D is diameter and L is length in Å. The surface area of each mineral is calculated based on the size and unit cell volume obtained from the SIROQUANT refinement of each soil. The calculation is made from the following formula:

$$SA = \frac{AV_{No}}{MW_{uc}} x \frac{V_{cell}}{V_{cstl}} x \frac{SA_{cstl}}{10^{20}}$$

where SA is surface area in units of m^2 g^{-1}, AV_{No} is Avagadro's number of atoms in one mole, MW_{uc} is molecular weight of the unit cell for the mineral in grams, V_{cell} is the volume of the unit cell in $Å^3$, V_{cstl} is the volume of one crystal in $Å^3$, SA_{cstl} is the surface area of the crystal, and

10^{20} is the conversion factor for changing Å^2 to m^2 (R.C. Jones, personal communication). The logical steps embodied in this equation are 1) calculation of the number of unit cells in a crystal times 2) the weight of one unit cell in grams to give mass of one crystal. Then the reciprocal of this yields the number of crystals in one gram. The surface of one crystal times the number of crystals in one gram yields the surface area in one gram of mineral which is converted from Å^2 to m^2. The specific surface area of a mineral is multiplied by the proportion of that mineral in the soil to determine the surface area contribution of that mineral. The surface area of a mineral times the estimated sorption site surface density provides the number of sorption sites per gram of soil.

The sorption site surface density can be estimated from the amount of functional groups on the surface of a crystal as determined from the crystal structure and predominant crystal faces exposed (Sposito, 1984). Functional groups are exposed hydroxyls on the surface of the minerals. Goethite has the highest number of sorption sites per unit surface area because of the number of reactive OH groups that lie in the exposed plane parallel to the c-axis, which is the long axis of the acicular crystal. There are three types of hydroxyls in goethite, A-type hydroxyls are singly coordinated to Fe(III) in the crystal lattice, B-type hydroxyls are triply coordinated and C-type hydroxyls are doubly coordinated. The A hydroxyls are active in ligand exchange with PO_4 anions. Sposito (1984) estimates the following number of reactive hydroxyls and the proportion of the crystal surface with these exposed sites for the following minerals,

Goethite - one OH per 0.305 nm^2 on the plane perpendicular to the a axis (80% of crystal surface) and one OH_2 per 0.141 nm^2 on the plane perpendicular to the b axis (20% of crystal surface),

Gibbsite - one OH and one OH_2 per 0.245 nm^2 on the edge surfaces (41.9% of crystal surface),

Kaolinite - one Si-OH, one Al-OH and one OH_2 per 0.379 nm^2 on the edge surfaces (7.9% of crystal surface).

The above values are based on the position of functional groups and the number per unit area for a given crystal face. The area is determined from the unit cell dimensions. From these values goethite was estimated to have 6.7 $\mu mol_c m^{-2}$, gibbsite 5.6 $\mu mol_c m^{-2}$ and kaolinite 1.0 $\mu mol_c m^{-2}$ as maximum values. Due to the variable charge nature of the hydroxyls, the number of available sorption sites varies with pH. At higher pH values the OH_2 sites do not exist and thus the number of reactive sorption sites are reduced. The above values of sorption site surface density were multiplied by the surface area values to provide the number of sorption sites in μmol_c per gram of soil.

Calcium carbonate content was estimated by dissolution with known amount of HCl and back titrated with NaOH to determine amount of HCl consumed (Nelson, 1982). Only the Pulehu soil contained pedogenetic $CaCO_3$ and the Molokai and Waialua soils indicated the presence of agricultural lime by the pH and presence of visible white particles.

Soil texture was determined by the pipette method for all soils except the three Andisols (Soil Survey Laboratory Staff, 1991). Thirty gram samples of soils were dispersed with 50 mL of 10% sodium hexametaphosphate solution and sonicated for three ten-minute periods. Dispersed soil solution was sieved into a sedimentation cylinder to remove sand, and the total solution volume was brought to one liter. Silt and clay particles were thoroughly suspended throughout the cylinder and the suspension was sampled at a 10 cm depth by pipette after allowing enough time for all silt to settle below the 10 cm sampling depth. Twenty-five mL aliquots were drawn by pipette then dried to determine the amount of clay.

For the Oxisols and Ultisols 15 bar water was used as an alternative estimate of clay content. Because it is difficult to completely disperse clay particles of Fe and Al hydrous oxides, the clay content was estimated from moisture contents at 1.5 MPa tension determined by pressure plate and pressure membrane apparatus. Clay contents are estimated from the equation % Clay = 3 x (% MC - % OC) where MC is the moisture content at 1.5 MPa tension and OC is the organic C content (Soil Survey Staff, 1992).

For the Andisols, complete dispersion was difficult to attain because of the amorphous nature of the soil material. Thus, the clay content was not determined.

Oxalate extractable soil material estimates the amount of amorphous Fe and Al hydrous oxides in the soil. The method of Jackson et al. (1986) for acid ammonium oxalate reaction in the dark was used to determine extractable Fe, Al, Si and Mn and the soil mass loss by dissolution. An accurately weighed amount of approximately 0.2 g of oven-dried soil was mixed with 40 mL of 0.2M ammonium oxalate at pH 3.0 in a centrifuge tube wrapped in aluminum foil to prevent light from altering the reaction with hydrous oxides. The reaction was stopped by centrifuging and decanting off the oxalate solution. The treated soil was rinsed with ammonium carbonate three times then oven-dried and reweighed to determine the mass lost by dissolution in ammonium oxalate. The oxalate supernatant was analyzed for Al, Fe, Si and Mn concentration by ICAP analysis on a Perkin-Elmer Model 6500 Inductively Coupled Atomic Emission Spectrometer.

Surface area was calculated from the retention of glycerol according to the method of Kinter and Diamond (1958). Approximately 0.2 g of soil was accurately weighed and saturated with 5 mL of 2% glycerol solution then dried in an oven at 110° C in the presence of glycerol vapors. The amount of glycerol retained was weighed and converted to surface area based on the weight of a monolayer of glycerol at 566.6 mg m^{-2}.

Chemical Properties

Soil pH was measured on 1:1 soil:solution mixtures with two solutions, deionized water and 1M KCl solution. Suspensions were mixed and allowed to sit for 2 hours then the pH was measured with a Fisher Accumet pH meter with combination electrode immediately after stirring.

Exchangeable bases were determined by leaching soils with 1N ammonium acetate buffered at pH 7.0 to remove all exchangeable bases (Blakemore et al., 1987). The leachate was brought to 100 mL volume and analyzed for concentration of basic cations. Na and K were determined by atomic adsorption spectrometry, and Ca and Mg were mixed with lanthanum chloride solution and determined by atomic adsorption spectrometry.

Total acidity was determined by leaching soil with 1N KCl and titrating to neutrality with NaOH to determine acidity leached then the leachate was treated with KF and titrated to neutrality with HCl to determine amount of Al leached from the soil (Thomas, 1982).

Cation exchange capacity was determined by saturating the soil with 1 M ammonium acetate buffered at pH 7 and subsequent displacement of ammonium held at exchange sites with 1 M potassium chloride. The displaced ammonium in the leachate was analyzed by Kjeldahl distillation for determination of ammonium and calculation cation exchange capacity at pH 7.0 (Blakemore et al., 1987).

Effective cation exchange capacity was determined from the sum of exchangeable basic cations and exchangeable acidity (Blakemore et al., 1987).

Organic carbon was determined by dry combustion on a LECO Carbon Determinator, model WR-112. Samples were prepared by air drying and sieving all soils through a 120 mesh sieve. Soils were then oven dried, and an appropriate sample size was weighed and analyzed on the carbon analyzer (LECO Corp., 1985). All carbon measured was assumed to be organic carbon, except for soil that contained $CaCO_3$ which had the percent $CaCO_3$-C subtracted from the total C analyzed.

Total elemental analysis was done by x-ray fluorescence on a Siemens SRS303 Wavelength Dispersive X-ray Fluorescence Analyzer. Whole soil samples were analyzed for major element analysis on fused glass disks prepared by standard petrographic methods. Samples of 1.5 g were weighed and heated to 900° C for determination of loss on ignition. Two subsamples of 0.45000 g from the ignited sample were weighed and mixed with 2.95000 g of lithium tetraborate fusion mixture. The mixture was melted and swirled at 900° to

1000° C and formed into a glass disk for analysis (T. Huselbosch, personal communication).

P sorption isotherms were developed by mixing 3 g of soil with 30 mL of 0.001M $CaCl_2$ solution containing calcium phosphate (monobasic). This concentration of $CaCl_2$ solution was selected because higher concentrations promote more phosphate sorption and tropical soils generally have this order of magnitude of electrolyte concentration in soil solutions (Rajan and Fox, 1972). The 0.001M $CaCl_2$ solution matches the actual soil solution environment better than the normally used 0.01M $CaCl_2$ solution. The soils were allowed to equilibrate for six days with two 30-minute shaking periods each day. The concentration of P remaining in solution was measured to determine the amount of P sorbed. Five to ten levels of phosphate were used for each soil to provide a curve of the amount of P sorbed vs. the concentration of P in solution (Fox and Kamprath, 1970).

Incubation Study

For the incubation study, each soil was treated with five rates of phosphorus. Four sets of P levels were established for the incubation study: 0, 25, 50, 100, 200 mg P kg^{-1} soil; 0, 50, 100, 200, 400 mg P kg^{-1} soil; 0, 100, 200, 400, 800 mg P kg^{-1} soil; 0, 250, 500, 1000, 2000 mg P kg^{-1} soil. The set of P rates selected for a soil was based on the general sorption level expected for that soil.

Phosphorus was added as powdered calcium monobasic phosphate ($Ca(H_2PO_4)_2$). The appropriate amount of P was weighed for 350 g of sieved soil on an oven-dry basis (80 g for Kaiwiki series, and 130 g for Maile series was used because low bulk densities for these soils required less mass for the same volume). Soils were placed in plastic bags and the calcium phosphate was thoroughly mixed with the soil. The appropriate amount of water to bring the soil to field capacity (moisture content at 10 kPa) was added in 10 mL increments and thoroughly mixed upon each addition. The samples were incubated at 25° C ± 2° C for 180 days while the bags were kept open to allow the soils to dry. When soils had dried they were rewetted back to field capacity and allowed to go through wetting and drying cycles according to the rate at which the soil dried. The soil moisture content was monitored throughout the incubation period. The Kaiwiki and Maile soils were not allowed to dry out but always maintained with a moisture level that prevented a change in physical or chemical properties of the hydric materials (Lim, 1979).

Soils were sub-sampled for extractable phosphorus content at nine times: 2, 4, 8, 16, 32, 64, 96, 128, 180 days. These samples were analyzed for extractable phosphorus with the following three extracting solutions, modified Truog, Olsen, and Mehlich-3. The modified Truog extractant is 0.01M H_2SO_4 with 3% ammonium sulfate, and the extraction procedure utilizes a 1:100 soil:solution ratio with a shaking time of 30 minutes (Ayres and Hagihara, 1952; Truog, 1930). The Olsen extractant is 0.5M $NaHCO_3$ at pH 8.5, and it is used at a mixing ratio of 1:20 soil:solution and shaking time of 30 minutes (Olsen et al., 1954). The Mehlich-3 extractant is 0.2 N acetic acid, 0.25 N ammonium nitrate, 0.015 M ammonium fluoride, 0.013 M nitric acid and 0.001 M Ethylenediaminetetraacetic Acid (EDTA), and is used at a mixing ratio of 1:10 soil:solution and shaking time of 5 minutes (Mehlich, 1984). Sub-samples were measured by volume, 0.6 mL for modified-Truog, 2.5 mL for Olsen and Mehlich-3 extractions. The weight of each sub-sample was recorded to monitor soil removed and moisture content of incubation samples and for calculating the P extracted on a soil weight basis. Phosphate concentrations in all analyses were measured with ammonium molybdate reagent with ascorbic acid according to Murphy and Riley (1962) and Watanabe and Olsen (1965).

Statistical Analysis

Statistical analysis was utilized to 1) search for significant relationships between soil properties and measurements of P sorption potential, 2) examine the relationships between the various soil properties that were measured and 3) to fit a nonlinear equation with the data for the change in extractable P with time. All statistical analysis used the SAS software (SAS Institute Inc., 1985).

Linear regression was used to determine which soil properties had significant correlations with the P sorption measurements. PROC Stepwise of SAS was used to examine each of the soil properties and provide a probability value for testing the significance of the relationship. A correlation matrix was generated to examine the correlation coefficients between all combinations of soil properties in order to reveal dependencies between soil properties. PROC NLIN of SAS was used to fit the negative exponential model of change in extractable P with the data from the incubation study. PROC NLIN is a nonlinear regression routine that will search for the parameter values that provide the "best fit" of the model to the data points. "Best fit" is found by the set of parameters providing the least residual sum of squares.

CHAPTER 4

PHOSPHORUS SORPTION CHARACTERISTICS

Phosphorus Sorption Measurements

The soils' potential to sorb P was measured by two techniques. Sorption isotherms were utilized to determine the amount of P sorbed in order to increase the concentration in the equilibrium solution to 0.2 mg P L^{-1} ($PS_{0.2}$) and to determine the slope (b) of the isotherm at this concentration. The slope, b, represents the amount of P that will be sorbed for a unit increase in the P concentration of the equilibrating solution and is calculated as the slope of the tangent at 0.2 mg P L^{-1} on the isotherm curve plotted with P sorbed on the ordinate and P in solution on the abscissa. Because b changes with the P concentration, it must be measured at a given concentration value to compare with other soils. The second method utilized to measure the P sorption potential was to determine the P buffering coefficient (PBC) from the linear regression of the relationship between extractable P (P_{ext}) and the amount of P applied (P_{app}) in an incubation experiment. The slope of this regression is the PBC and represents the increase in P_{ext} per unit of P_{app} (Sharpley et al., 1984; Sharpley et al., 1989; Johnston et al., 1991; and Indiati et al., 1991).

P Sorption Isotherms

The Freundlich equation, $P_s=kP_l^n$, fit the P sorption isotherm values better than the Langmuir equation, $P_s=AkP_l/(1+kP_l)$. P_s is the P sorbed, P_l is the P in solution and k, n, and A are constants. Although the Freundlich equation is strictly empirical, its exponential constant represents a decrease in affinity for sorption as sites are filled, whereas, the Langmuir equation assumes a constant binding energy for all sorption sites (Sposito, 1980; Sanyal et al. 1993). The Freundlich equation has also provided a better fit of P sorption data by other researchers (Barrow, 1978; Kovar and Barber, 1988; Sanyal et al., 1993). Some of the low levels of P in the equilibrium solution were so variable that it was difficult to obtain reliable measurements of dilute P concentrations. Thus the higher equilibrium P concentrations have been used to fit the Freundlich equation (Sanyal et al., 1993).

The range in the $PS_{0.2}$ values for each soil can be divided into categories to represent very low, low, medium, high, and very high sorption. Juo and Fox (1977) designated these five categories of sorption values and the minerals usually encountered for each category (Table 4.1). The soils in this study generally agree with this relationship between mineral types and sorption categories.

Table 4.1 Categories of P sorption as measured by P sorption isotherms and the mineralogy typical of each category (Juo and Fox, 1977)

$PS_{0.2}$ (mg P kg^{-1} soil)	Scale	Usual Mineralogy
<10	very low	quartz, organic materials
10-100	low	2:1 clays, quartz, and 1:1 clays
100-500	medium	1:1 clays with oxides
500-1000	high	oxides, moderately weathered ash
>1000	very high	desilicated amorphous materials

Phosphorus Buffering Coefficients

The incubation method used to determine the PBC values incorporated the effects of wetting and drying cycles which are not a part of the P sorption isotherm method. This additional aspect is much more similar to field conditions than the high solution:soil ration used in the P sorption isotherm method. An example of the data obtained can be seen in Figure 4.1a, which depicts the change in P_{ext} with time for each level of P_{app}. The characteristics are a sharp drop in P_{ext} for the initial 32 d then a gradual decline or constant level to 180 d. Figure 4.1b depicts the linear relationship between P_{ext} and P_{app}, the slope of which represents the PBC for the soil. The slope will be lower with more. As the P_{ext} decreases with time so does the PBC as the soil continues to sorb P. Figure 4.2 shows the decrease in PBC to be rapid for approximately the first 32 d following the application of P then it gradually approaches a relatively constant value. For all soils only small

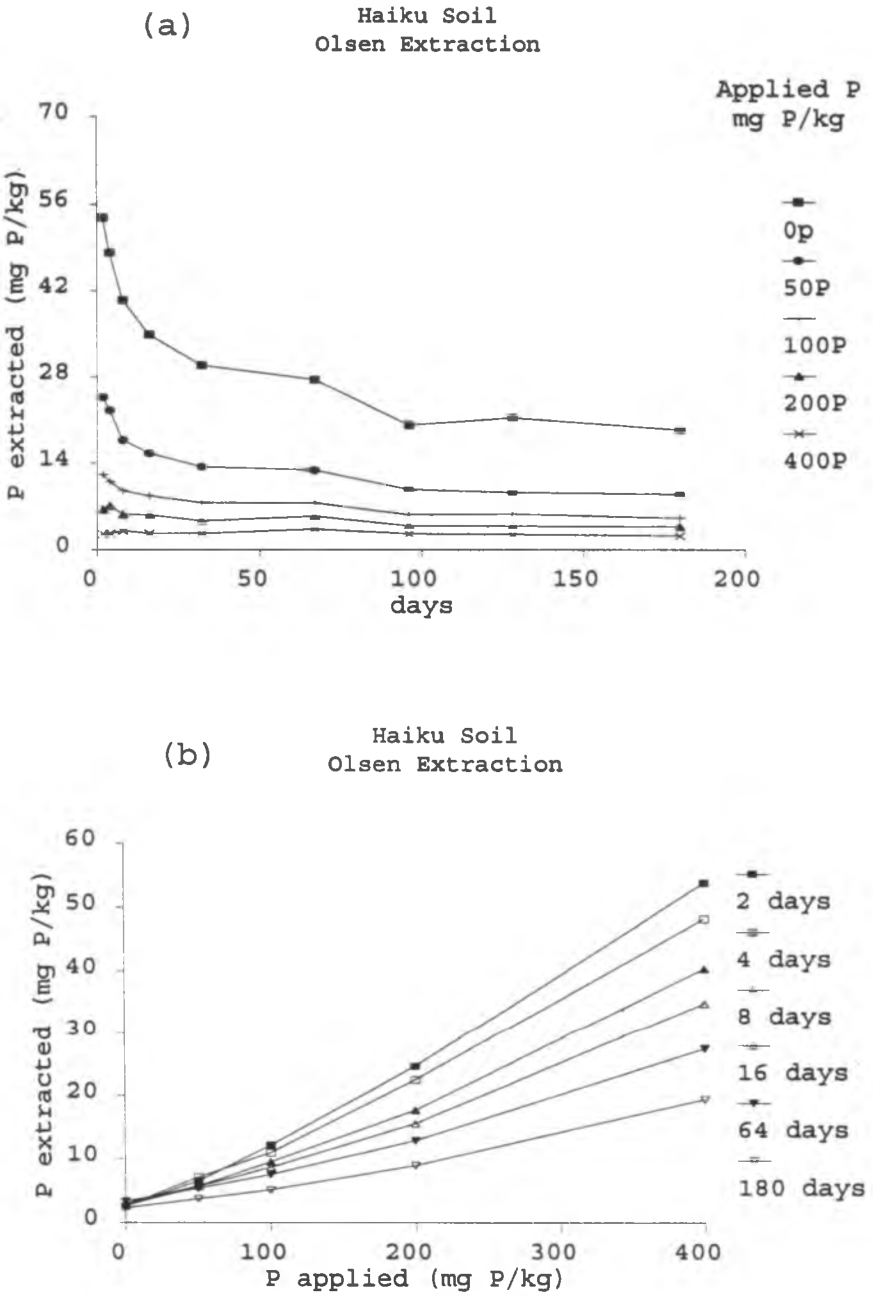


Figure 4.1 Changes in P_{ext} (a) with time (b) with levels of P applied.

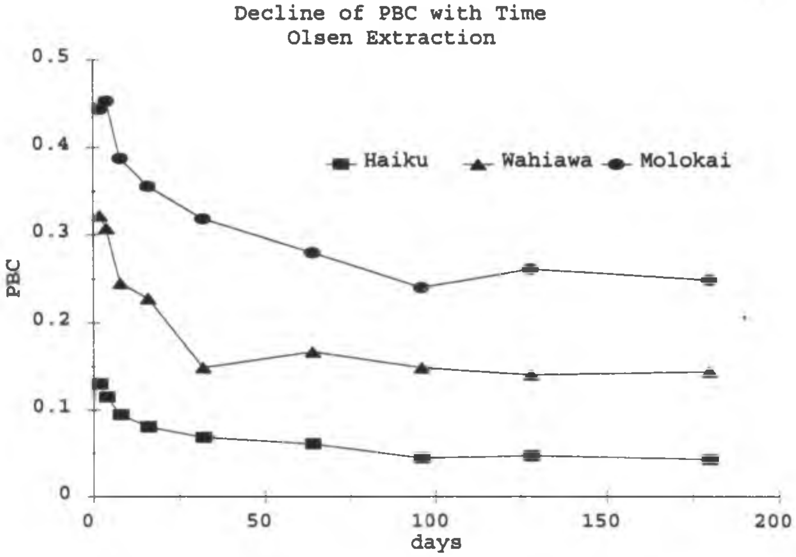


Figure 4.2 The decline of PBC values with time for the three soils. PBC values are determined from the Olsen Extraction.

changes in PBC occurred after 2 months of incubation, thus the PBC was averaged for the 64, 96, 128 and 180 d measurements to be used as a measure of relative P sorption potential of the different soils.

Soil Factors Influencing P Sorption

The set of soils used in this study contains a range of mineralogical and chemical properties. To determine which properties predict P sorption potential for Hawaiian soils, the measured properties were correlated with $PS_{0.2}$ values and PBC values (Table 4.2). Two properties, 1.5 MPa and surface area, had highly significant correlations, and the acid oxalate extractable soil had a significant correlation with the $PS_{0.2}$ values (Figure 4.3). These properties are closely

Table 4.2 Coefficients of determination (r^2) for soil properties correlated with $PS_{0.2}$ values and PBC values for each extractant.

Soil Property	$PS_{0.2}$:	Meh-3	M-Truog	Olsen
pH	0.16	0.29	0.36	0.35
Al	0.16	0.02	0.02	0.03
CEC	0.15	0.0032	0.01	0.004
ECEC	0.03	0.0001	0.03	0.01
OC	0.15	0.11	0.10	0.13
Clay[§]	0.38	0.12	0.10	0.18
1.5 MPa MC	0.75[**]	0.14	0.07	0.12
Surface Area	0.55[**]	0.12	0.03	0.06
Oxa. Extr.	0.36[*]	0.15	0.11	0.14
Total P	0.20	0.10	0.04	0.05

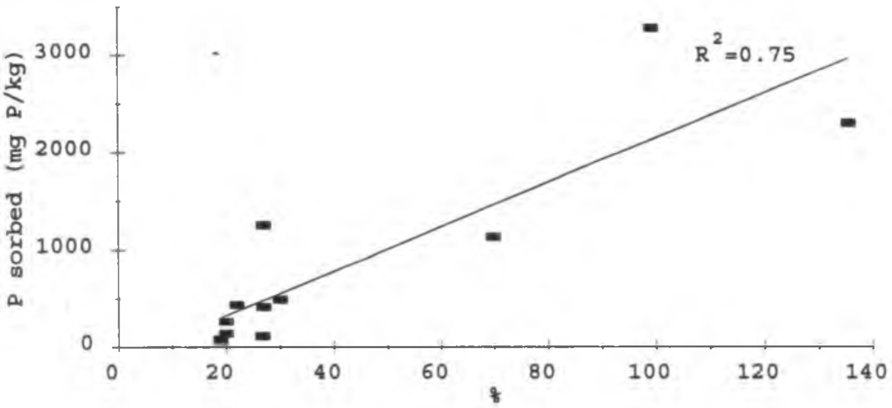
1.5 MPa MC - Moisture Content at 1.5 MPa tension
Oxa. Extr. - Oxalate Extractable soil material
[§] Only the eight soils for which clay content was determined were included in the correlation.
[**] highly significant; $P < 0.01$
[*] significant; $P < 0.05$

Table 4.3 Correlation matrix for soil properties.

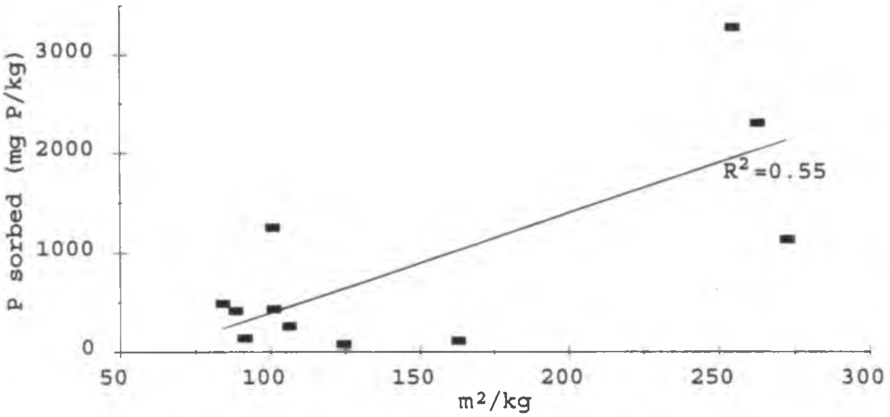
	TP	pH	CEC	ECEC	OC	OxEx	SA	ExAl
TP	1.0							
pH	.03	1.0						
CEC	.55	-.27	1.0					
ECEC	.63	.26	.48	1.0				
OC	.73	-.44	.75	.61	1.0			
OxEx	.80	-.45	.79	.50	.95	1.0		
SA	.69	-.43	.89	.32	.77	.88	1.0	
ExAl	-.18	-.57	.56	-.26	.30	.36	.43	1.0
1.5MC	.41	-.54	.73	-.30	.59	.76	.82	.72

TP - Total P, CEC - Cation Exchange Capacity,
ECEC - Effective Cation Exchange Capacity,
OC - Organic C content, OxEx - Oxalate Extractable Soil Material, SA - Surface Area,
ExAl - Exchangeable Al, 1.5MC - Moisture Content at 1.5 MPa of tension

(a) 1.5 MPa Moisture Content and P Sorbed



(b) Surface Area and P Sorbed



(c) Oxalate Extractable and P Sorbed

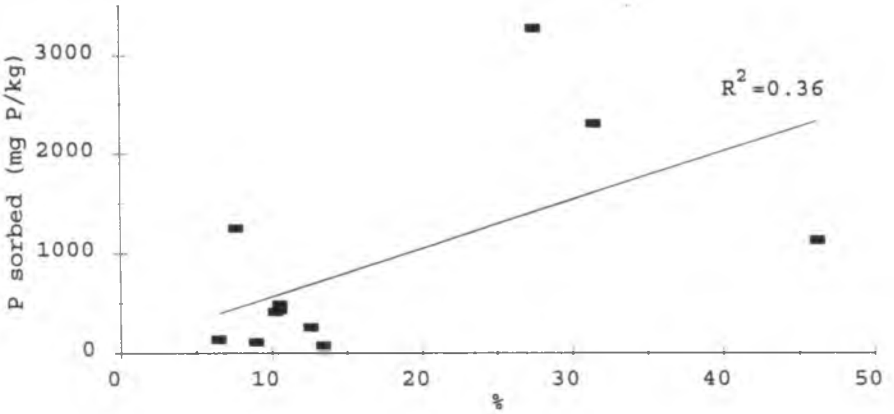


Figure 4.3 Relationships between $PS_{0.2}$ values and selected soil properties, (a) 1.5 MPa moisture content, (b) surface area, and (c) oxalate extractable soil material.

related to one another (Table 4.3) because the moisture content at 1.5 MPa tension reflects the surface area, and the oxalate extractable soil material is a measurement of amorphous soil material, which characteristically has high surface area and moisture content (Parfitt, 1989, Sanyal and De Datta, 1991). The surface area is a controlling factor for P sorption according to our understanding of the mechanism for P sorption. A definite number of sorption sites exists on the surfaces of mineral particles, thus their total surface area will determine the maximum amount of P sorption possible. Although research has shown each of the soil properties to have a direct effect on P sorption (Sanyal and De Datta, 1991; Berkheiser et al., 1980; Parfitt, 1989), for this set of soils only those that reflect surface area have the strongest relationship with $PS_{0.2}$ values. The interacting effects of soil properties are such that the resulting P reflects only surface area properties and the effects of the other properties appear confounded.

None of the properties showed a significant correlation with the PBC measurements, including no significant correlation between $PS_{0.2}$ and PBC values. The incubation method used to determine PBC values is a considerably different method than the P sorption isotherm method and thus reflects different properties that have a controlling effect on the P sorption measured. The use of the P sorption measurements from the two methods could have significantly different interpretations for practical purposes because they reflect different mechanisms in the P sorption process. A comparison of the results from these two methods will be discussed in a later section.

The relationships between soil properties and sorption measurements for our set of soils can be discussed within the three ranges of P sorption that are evident. $PS_{0.2}$ values range from 3277 to 79 mg P kg^{-1}. Four soils have values > 1000 mg P L^{-1}, the Kaiwiki Cultivated, Kaiwiki Uncultivated, Makapili and Maile soils. Four soils have medium range sorption between 150 to 500 mg P L^{-1}, the Haiku, Halii, Kapaa, and Wahiawa soils. The remaining three soils, Molokai, Pulehu, and Waialua, had $PS_{0.2}$ values < 150 mg P L^{-1}. Examination of the soils in these categories with respect to evidence in the literature elucidates some of the effects of mineral types and chemistry on the observed $PS_{0.2}$ values.

Very High Sorption

The soils in decreasing order of $PS_{0.2}$ values for the very high sorption range are the Kaiwiki cultivated, Kaiwiki uncultivated, Makapili and Maile (Table 4.4, Figure 4.4). Of the four soils in this range, three of them have greater than 25% oxalate extractable soil material, which is characteristic of andic soils. The Makapili, however, is not an andic soil and is composed primarily of kaolin and goethite (Table 4.5) with relatively little oxalate extractable soil material. The Makapili sample has a high clay content of 74.4 % clay (estimated from moisture content at 1.5 MPa tension) which would indicate the availability of a large surface area to react with P. The organic C content is relatively low, which could possibly mean little blockage of sorption sites due to the aggregating effects of organic matter and less competition from organic anions (Sanyal and De Datta, 1991). A soil pH of 7.10 and along with a high level of extractable Ca indicates that this soil had been limed. The pH for the surface of a Makapili soil is generally around 5.9 (Soil Conservation Service, 1976). Overliming of soils that sorb P strongly can increase P sorption in some cases (Kamprath, 1971: Sanyal and De Datta,

Table 4.4 Properties of soils with very high $PS_{0.2}$ values.

	Soil			
Property	KaiC	KaiU	Mak	Mai
$PS_{0.2}$ mg P/kg	3277	2304	1253	1134
$b_{0.2}$	6561	3834	1907	2816
Clay	ND	ND	74.4*	ND
pH	5.26	3.98	7.10	5.18
OC	7.93	12.5	2.21	24.0
Oxalate Ext %	27.5	31.5	7.6	46.3
Surface Area m^2/g	255	263	101	272
Total P mgP/kg	5700	2100	2100	7500
Extr. Al $cmol_+/kg$	0.00	2.98	0.00	0.12

ND not determined
*Clay content determined from 1.5 MPa tension moisture content.
KaiC - Kawiki Cultivated; KaiU - Kaiwiki Uncultivated
Mak - Makapili; Mai - Maile

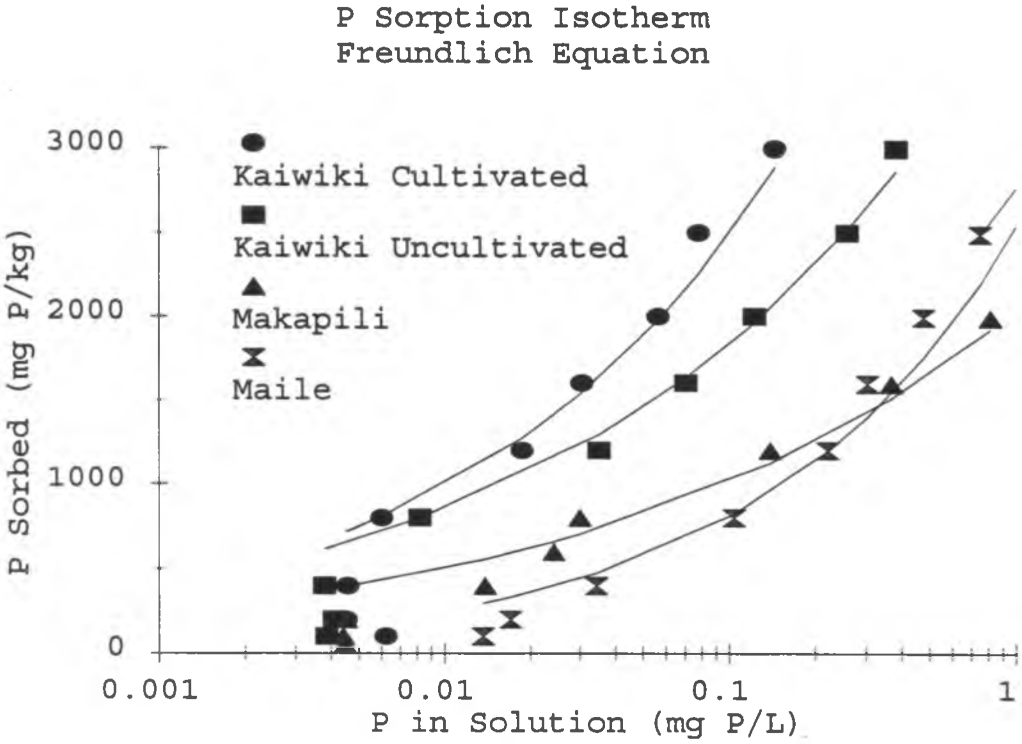


Figure 4.4 P sorption isotherms fit with the Freundlich equation, $P_s=kP_l^n$, for soils in the very high sorption range, $PS_{0.2} > 1000$ mg P kg^{-1}.

Table 4.5 Mineralogical composition of soils from Rietveld refinement of X-ray diffraction patterns (percent of clay fraction except where noted).

Soil	Gib	Goe	Hem	Rut	Ana	Mag	Kao	Ill	Mont	Quar	Amor*
Haiku	2.6	32.3	2.0	4.7	16.5	10.9	8.8			11.9	10
Halii	7.0	49.4	4.1	1.7	18.0					7.2	13
Kaiwiki*	11.4	19.7				8.1	19.5			11.3	30
Kapaa	11.1	25.5		2.4	10.5		34.3			2.1	10
Maile*			2.2			6.3	27.5			12.1	40
Makapili	1.8	33.8			8.4		47.5			0.6	8
Molokai	1.6		6.7	2.9			66.8	15.4			7
Pulehu			1.4				64.3	21.0			13
Wahiawa	7.9	1.2	5.7				46.2	27.9		0.7	11
Waialua			5.5				81.6		4.0		9

*Percent of whole soil

Gib - gibbsite; Goe - goethite; Hem - hematite; Rut - rutile;
Ana - anatase; Mag - magnetite; Kao - kaolin; Ill - illite;
Mont - montmorillinite; Quar - quartz; Amor - amorphous

1991). Although these factors may affect an increase in P sorption for soils with similar mineral content, the primary cause for the Makapili's high $PS_{0.2}$ is likely to be its reactive surface area of goethite. The content of goethite in this soil is slightly higher than the other soils (Table 4.6), and its particle size is smaller, except for that of the Kaiwiki's. Thus, goethite contributes a higher surface area in the Makapili than in the other Oxisols and Ultisol. The goethite in the Kaiwiki series contributes the most surface area because of its 75 Å "crystallite size". Jones (1981) demonstrated that $PS_{0.2}$ levels correlated well with the surface area of the goethite present in several Puerto Rican soils.

The Kaiwiki and Maile series are hydric volcanic ash soils which characteristically have a very high $PS_{0.2}$ level due to the high surface area of the amorphous Fe and Al hydrous oxides in these types of soil (McLaughlin et al., 1981; Parfitt, 1989; Sanyal and De Datta, 1991). The differences in sorption between the cultivated and

Table 4.6 Goethite crystallite size, content and surface area for the soils containing this mineral.

Soil	Size (Å)	% in soil	Surface Area $m^2\ g^{-1}$
Haiku	161	22.8	20.2
Halii	188	23.2	17.5
Kaiwiki	75	19.7	37.6
Kapaa	186	13.2	10.0
Makapili	129	25.1	27.4

uncultivated samples of the Kaiwiki soil can possibly be attributed to the organic C differences of 7.93% and 12.5% organic C, respectively. Through cultivation, organic matter is oxidized and its amount is lowered in the soil surface. These soils are deep tilled to as much as 40 inches for sugarcane production, which brings low organic matter soil material to the surface and reduces stable aggregates in the surface and promotes oxidation of the organic matter. This reduction in organic matter decreases the stability of aggregates during shaking and equilibration for measuring P sorption. Thus, stable aggregates that remain in the uncultivated Kaiwiki soil are likely to reduce short-term sorption due to the time required for P to diffuse into aggregates. The uncultivated sample contained 2.98 $cmol_+ kg^{-1}$ of extractable Al, and the cultivated sample contained no extractable Al. The corresponding soil pH was 3.98 and 5.26, respectively. For soils with greater than 6 cmol+ Al kg^{-1} an increase in pH is unlikely to contribute to additional P sorption (Eze and Loganathan, 1990; Sanyal and De Datta, 1991).

On the other hand, a factor that could have possibly induced lower P sorption in the cultivated Kaiwiki is its 5673 mg P kg^{-1} total P content, apparently due to fertilizer applications while the uncultivated Kaiwiki has 2138 mg P kg^{-1} total P. The presence of already sorbed P generally reduces the level of sorption for subsequent applications of

P (Barrow, 1974; Parfitt et al., 1989), however, for andic soils the potential for P sorption may be so high that previous applications have very little effect on subsequent P sorption (Espinosa, 1992).

The Maile soil has the lowest sorption level of the four soils in this range at 1134 mg P kg^{-1} soil. Based on having the highest values of surface area at 272 m^2 g^{-1} and an oxalate extractable soil content of 46.3%, we would expect this soil to sorb the most P. The Maile soil, however, does not have any goethite or gibbsite to contribute to P sorption and also it has 24% organic C, a very high amount that most likely reduces the P sorption level of the amorphous material through aggregation and anion competition of sorption sites. The high contents of amorphous Fe and Al hydrous oxides and the high surface area of the goethite in these soils cause the very high sorption of these soils. The organic matter appears to be a factor in reducing the amount of sorption below the potential indicated by the amount of amorphous material present. The Maile soil has no goethite and thus has sorption associated with the amorphous material and the Fe and Al humus complexes.

Medium Sorption

The soils in decreasing order of $PS_{0.2}$ values for the medium sorption range are the Wahiawa, Kapaa, Haiku and Halii (Table 4.7, Figure 4.5). These four soils vary considerably in mineral composition. Among the crystalline Al and Fe hydrous oxides, goethite has been shown to have higher sorption capacities than gibbsite and hematite, thus higher levels of goethite in a soil should result in higher levels of P sorption (Jones, 1981; Parfitt, 1989). The Wahiawa soil sorbed the most P among the soils in this range, but it contains the lowest goethite level. The predominant mineral for the Wahiawa soil is kaolin and illite with small amounts of gibbsite, goethite, and hematite. The mineral content of the Wahiawa is very similar to that of the Molokai, which has a low sorption level.

The chemical environment of the Wahiawa, however, is conducive to higher levels of P sorption. The pH is 4.78,

Table 4.7 Properties of soils with medium $PS_{0.2}$ values.

	Soil			
Property	Wahiawa	Kapaa	Haiku	Halii
$PS_{0.2}$ mg P/kg	490	434	416	260
$b_{0.2}$	567	663	654	596
Clay %	84.1*	51.9*	70.6*	47.0
pH	4.78	4.75	5.06	5.09
Organic C %	1.97	4.69	3.48	7.39
Oxalate Ext %	10.5	10.5	10.2	12.6
Surface Area m^2/g	84.2	101	88.6	107
Total P mgP/kg	570	1600	2000	1600
Extr. Al $cmol_+/kg$	0.35	0.51	0.02	0.31

*Clay content determined from 1.5 MPa tension moisture content.

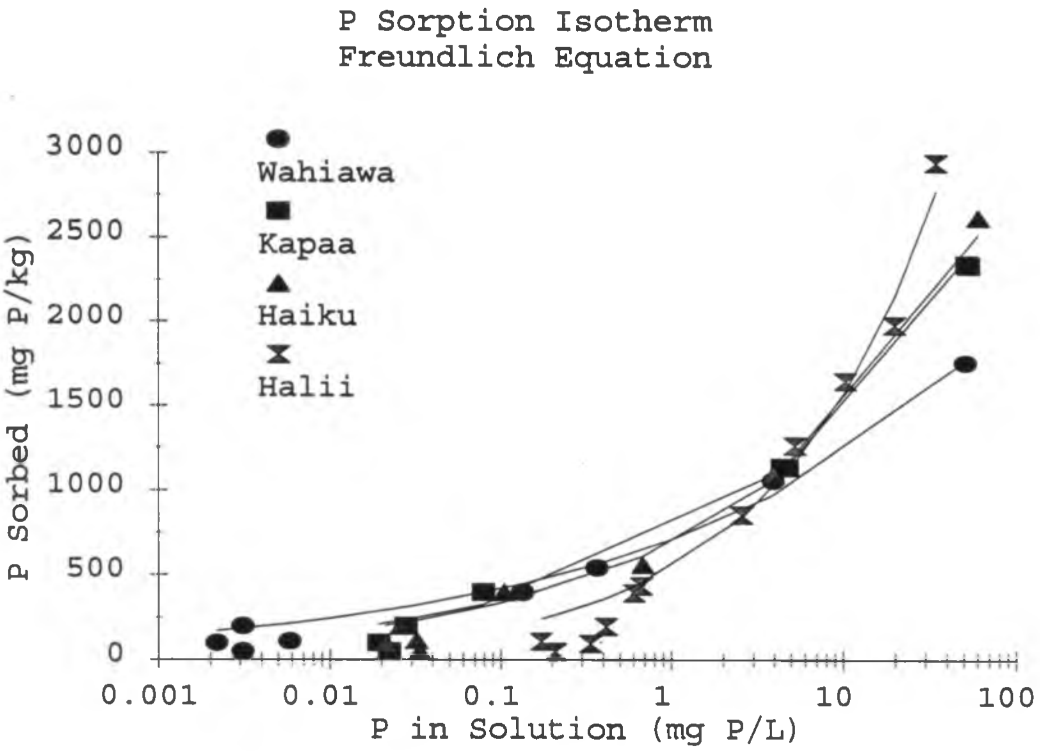


Figure 4.5 P sorption isotherms fit with the Freundlich equation, $P_s=kP_1^n$, for soils in the medium sorption range, 1000 mg P kg^{-1} > $PS_{0.2}$ > 150 mg P kg^{-1}.

there is a small amount of exchangeable Al, the organic C content is relatively low at 1.97% and the total P content is the lowest for the soils in this study at 567 mg P kg^{-1}, thus the pH and Al may enhance soil reactivity with P and the low organic matter and low total P suggests that fewer of the sorption sites will be blocked or occupied. It also has the highest clay content of the soils at 84.4% as determined by 1.5 MPa moisture content. Even though the sorption level of the Wahiawa was high among the soils in this range, the slope, or b value, of the sorption isotherm at 0.2 mg P g^{-1} concentration of P in the equilibrating solution, was lower than the other three soils, indicating that less sorption occurs per unit of increase in P concentration in the equilibrium solution. The low b value for the Wahiawa soil shows a different sorption characteristic than the other soils. This value is probably due to the kaolin minerals, which have less sorption per gram of mineral than the goethite or gibbsite predominant in the other soils (Sposito, 1984). The lower slope for the Wahiawa indicates that it will have less sorption than the other soils at higher P concentration in the equilibrating solution (Figure 4.5).

The other three soils of this sorption range have more oxidic minerals and less kaolinite. The Halii has the highest content of goethite and no kaolinite, but its sorption level is the lowest among the four soils in this sorption range. The exponent in the Freundlich equation of the Halii indicates the soil will sorb more P than the other soils with increasing concentrations of P in the equilibrating solution (Figure 4.5). Its pH is 5.09 and has a small amount of extractable Al, however its organic C content is relatively high at 7.39%. This level of organic C could have a significant effect on reducing the level of P sorption in this soil (Sibanda and Young, 1986; Hue, 1991; Violante, 1991). Another important aspect to consider is surface area of the goethite. As mentioned earlier, Jones (1981) demonstrated that the surface area of goethite correlated significantly with the P sorption levels of the soils. The crystallite size for the Halii is 188 Å, which is the largest among the goethite in these soils (Table 4.6). The large crystallite size indicates that the surface area of the goethite would be less for the Halii than the other soils with smaller goethite crystallite sizes.

The $PS_{0.2}$ values and the isotherm curves for the Kapaa and Haiku soils are essentially the same, 434 mg P kg^{-1} and 416 mg P kg^{-1}, respectively. The goethite content in the Haiku is twice as much and the crystallite size is 161 Å compared to 186 Å for the Kapaa. Thus, considering only the amount of probable goethite surface area, the Haiku should sorb much more than either the Kapaa or the Halii, because it has smaller sized crystallites and twice as much goethite. The Kapaa was more acidic than the Haiku soil.

The Kapaa soil pH was 4.75 with a small amount of extractable Al. The Haiku soil pH was 5.06 and no extractable Al. The organic C contents were similar as were the percentages of oxalate-extractable material. The measured surface area, however, was lower for the Haiku than for the Kapaa soil. There seems no apparent reason why the two soils sorbed similar amounts of P at 0.02 mg P L^{-1}. An added complication is that the determination of the percent clay in oxidic soils is approximate due to the difficulty in dispersing the clay particles (Soil Survey Staff, 1975).

The Makapili soil discussed earlier has similar soil minerals to those of the Haiku, Halii and Kapaa, but yet its P sorption level was more than twice as much. The primary reason for this was likely to be the higher surface area of the goethite present in the Makapili soil. This will be discussed in more detail in the section that discusses the influence of soil minerals.

The order of sorption potentials expected for these four soils as indicated by mineral types and contents was reversed. It is possible that organic matter contents and pH's could be a factor in the measured sorption potential of these soils. The sorption at higher levels of P concentration in the equilibrating solution, however, did reflect the sorption expected.

Low Sorption

The soils in decreasing order of $PS_{0.2}$ values for the low sorption range were the Molokai, Waialua and Pulehu soils (Table 4.8, Figure 4.6). These soils have low $PS_{0.2}$ because they are composed of predominantly kaolin and illite with only a small quantity of oxidic minerals. The Molokai has the highest content of oxides with 2% gibbsite, 7% hematite and 2% rutile, and this soil shows the highest sorption of these three soils. The Molokai soil is an Oxisol and has been shown to have a $PS_{0.2}$ sorption level of approximately 300 mg P kg^{-1} but for a sample that had a pH of 5.7. The similarity in minerals between these two Molokai samples is unknown (Munns and Fox, 1976). This sample of Molokai was apparently limed, soil pH was 7.56 and

Table 4.8 Properties of soils with low $PS_{0.2}$ values.

Property	Soils Molokai	 Pulehu	 Waialua
$PS_{0.2}$ mg P/kg	138	79	112
$b_{0.2}$	216	147	204
Clay %	52.8*	20.5	54.7
pH	7.56	7.70	6.52
Organic C %	2.40	2.80	3.21
Oxalate Ext %	6.5	13.4	8.9
Surface Area m^2/g.	91.6	125	163
Total P mgP/kg	1600	4200	2200
Extr. Al $cmol_+/kg$	0.00	0.00	0.00

*Clay content determined from 1.5 MPa tension moisture content.

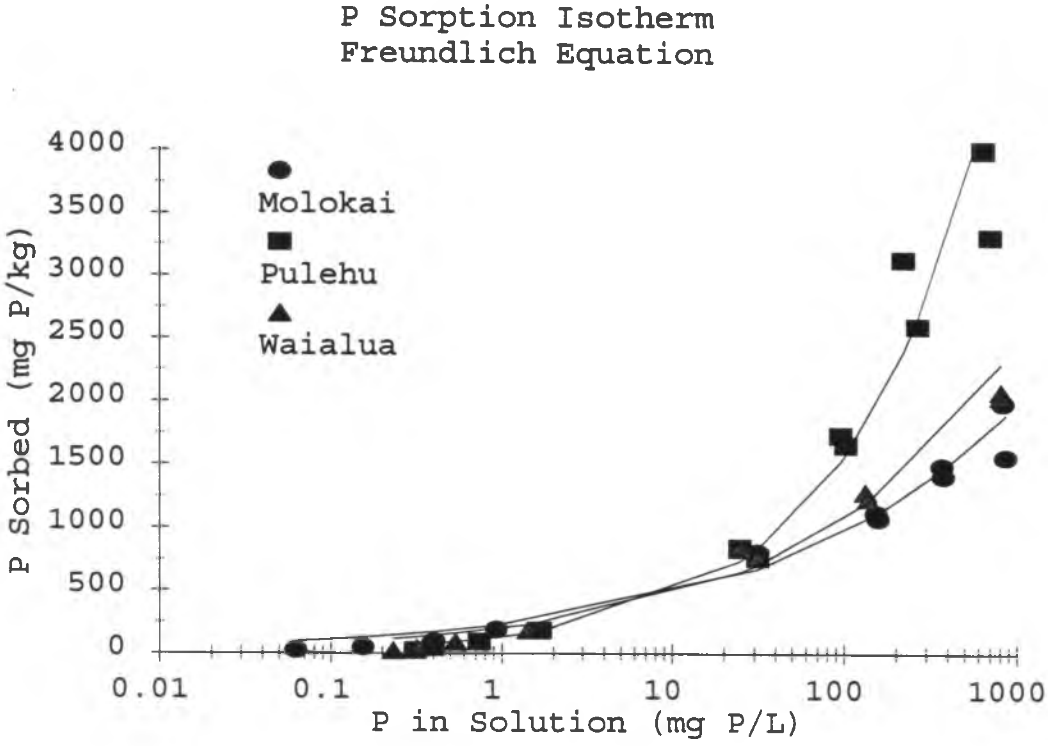


Figure 4.6 P sorption isotherms fit with the Freundlich equation, $P_s=kP_l^n$, for soils in the low sorption range, $PS_{0.2} < 150$ mg P kg^{-1}.

a high concentration of extractable Ca was measured. In comparison with the Wahiawa soil it has similar soil minerals, but the Wahiawa contains more gibbsite and a trace amount of goethite, and probably more importantly the pH of the Wahiawa soil is much lower, which is possibly an important factor for the high $PS_{0.2}$ in the Wahiawa soil. Kaolinite is the predominant mineral contributing to the sorption taking place, and the low pH promotes the maximum amount of sorption sites (Sposito, 1984). The Pulehu soil has a low clay content of 20% but has 5.8% $CaCO_3$ as coral sand in the soil and 13.4 % oxalate extractable soil material (determined after removal of the $CaCO_3$). Phosphorus sorption by the Pulehu soil is comparable to that of the Molokai and Waialua soils, which have clay contents just above 50%. The Waialua had 54.7% clay composed of mostly kaolin with a small amount of hematite and montmorillinite. The pH of the Waialua soil was 6.52 and has 8.9% oxalate extractable soil material. The $PS_{0.2}$ and b values were comparable among all three of these soils. Mineralogically and chemically they are similar, which is why they have similar sorption levels, however the Molokai is an Oxisol and the Pulehu and Waialua are Mollisols. The Wahiawa is mineralogically similar to the Molokai but has a 350% higher $PS_{0.2}$ value, which indicates that Oxisols with predominantly kaolin minerals can show a wide range in P sorption due to changes in chemical conditions of the soil.

Influence of Soil Minerals

Among the soils in this study, the soil mineral content varies from predominantly kaolinitic to oxidic to amorphous Fe and Al hydrous oxides. Soil properties related to surface area provided the only significant correlation with $PS_{0.2}$ values. The surface area shows a highly significant correlation with P sorption but the surface area of each mineral is likely to be more important because the number of sorption sites are determined by the mineral's composition and crystalline structure. To determine the relationship between soil minerals and $PS_{0.2}$ values the effect of mineral type and content must be quantified. As presented earlier the percentage of each mineral in the soil was determined as well as the crystallite size of goethite. These data were combined with the estimated sorption site surface density for three minerals, goethite, gibbsite and kaolinite (Table 4.9) (Sposito, 1984). The sum contribution of these three minerals to the number of sorption sites per gram of soil was calculated and plotted against the $PS_{0.2}$ values (Figure 4.7). The plot shows a curvilinear relationship that depicts the $PS_{0.2}$ values to increase rapidly with increasing number of sorption sites per gram of soil and was fit with a quadratic equation ($R^2 = 0.96$).

One crucial aspect of these estimates that was not included in total sorption site surface density was the contribution of sorption sites from the amorphous Fe and Al hydrous oxides in the soil. We had neither a method of determining the specific surface area of this material nor a method for calculating the number of sorption sites per unit area. Thus the contribution of sorption sites from amorphous material was not included. The Maile soil was not included in the correlation because it contained no goethite or gibbsite and had only a small amount of kaolin type mineral (from the X-ray diffraction pattern there was no 001 peak for kaolinite, only a 020 peak common to all phyllosilicates). The cultivated and uncultivated samples of Kaiwiki soil presented similar X-ray diffraction patterns so a mineralogical analysis was performed only on the cultivated sample. This soil contains up to 32% oxalate extractable material, which was not considered in predicting P sorption. The P sorption ability of amorphous material is the highest of any Fe and Al hydrous oxides and thus would contribute considerably to the number of sorption sites for all the soils and especially to the Kaiwiki and Maile soils (Ryden et al., 1977; Parfitt, 1989; Sanyal and De Datta, 1991).

The P sorption sites of these minerals occur at surface hydroxyls attached to the metal ion in the crystal lattice. Hydroxyl functional groups can absorb protons in low pH and release protons in high pH, thus making them variable charge. This charge characteristic of the sorption sites

Table 4.9 Surface area and corresponding number of sorption sites for goethite, gibbsite and kaolinite in each soil.

	Goethite		Gibbsite		Kaolinite		Total	
Soil	SA	SS	SA	SS	SA	SS	SA	SS
Haiku	20.2	89.0	0.6	1.8	3.0	1.0	23.8	91.8
Halii	17.5	76.8	1.1	3.2			18.6	80.0
Kaiwiki	37.6	165	4.5	12.7	12.5	4.4	54.6	183
Kapaa	10.0	44.0	1.9	5.4	19.5	6.8	31.5	56.3
Maile					43.8	15.4	43.9	15.4
Makapili	27.4	121	0.4	1.1	29.0	10.2	56.8	132
Molokai			0.3	0.7	33.9	11.9	34.2	12.6
Pulehu					13.4	4.7	13.4	4.7
Wahiawa	0.9	4.1	2.3	6.4	35.2	12.3	38.4	22.8
Waialua					48.4	16.9	48.4	16.9

SA is Surface Area (m^2 g^{-1}); SS is number of Sorption Sites ($cmol_c$ kg^{-1})
Sorption Sites calculated from multiplying Surface Area by 4.4 for goethite; by 2.8 for gibbsite; by 0.35 for kaolinite.

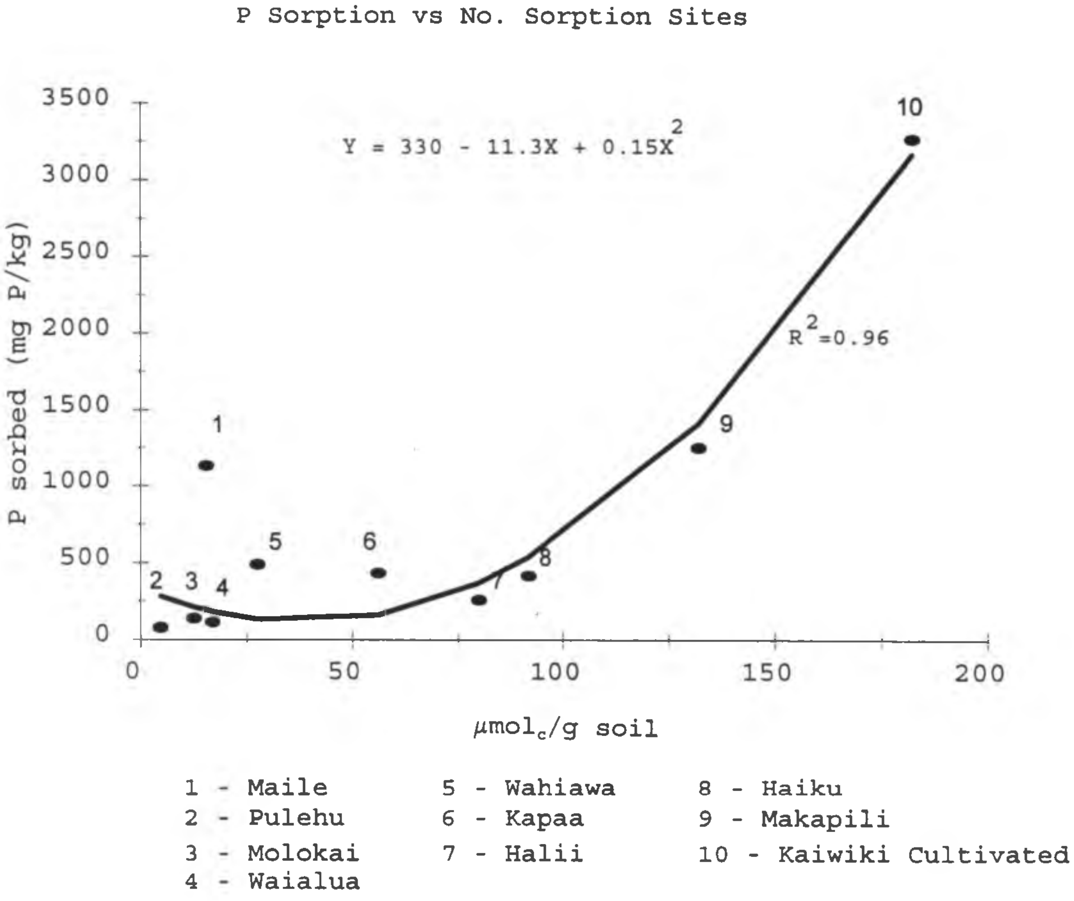


Figure 4.7 Relationship between total number of sorption sites per gram of soil and $PS_{0.2}$ values.

affects P sorption because the PO_4^{-3} anion is more reactive when the site is positively charged with protonated hydroxyls ($-OH_2^+$) and less reactive when it is negatively charged with deprotonated hydroxyls ($-O^-$) (Barrow, 1980; Sposito, 1984; Goldberg and Sposito, 1984a). The surface density estimates given here do not account for the affect of pH on the sorption site electrochemistry and is a source of error for these estimates. To account for pH the point of zero net charge would have to be measured for the soils and then related to the actual soil pH. Other sources of error for the relationship shown in Figure 4.7 are 1) the presence of sorption sites already occupied by phosphate, other inorganic anions such as HSO_4^-, or organic compounds, 2) estimation of crystallite size and surface area of each mineral, 3) determination of clay percentage for soils with difficulty in dispersing aggregated oxides.

According to the hydroxyl density estimates the two highest sorbing soils , Kaiwiki and Makapili, have approximately 90 to 95% of their sorption sites per gram of soil contributed by goethite. Goethite's small crystallite size adds to the surface area and thus sorption potential of the soil. The amorphous content also contributes greatly to the sorption of the Kaiwiki and the Maile soils. The soils with predominantly kaolinite have the lowest total sorption sites per gram of soil because the sorption sites are located only on the edges where the broken Al-OH bonds exist on the plate-like crystals. The soils with number of sorption sites less than 100 $cmol_+ kg^{-1}$ soil display some variation in their corresponding $PS_{0.2}$ values. At the lower number of sorption sites per kilogram of soil there is more susceptibility to the errors mentioned above, because a larger percentage of the sorption sites are affected by pH change and effects of organic matter. These interactions of soil properties add to the complexity of the P sorption system and thus the difficulty in trying to relate P sorption to measured soil properties.

The soils in this study represent three soil taxonomic orders that characteristically have different mineralogical systems. The Kaiwiki and Maile soils are Andisols, which are characteristically high in amorphous Al and Fe hydrous oxides. The Haiku, Halii, Kapaa, Makapili, Molokai and Wahiawa soils which are composed predominantly of clay size Al and Fe hydrous oxides and kaolinite. The Pulehu and Waialua soils are Mollisols with high base saturation and predominantly silicate clays. These soils represent extremes in the Soil Taxonomic system because of the three distinctly different mineralogical systems, and because of the role of minerals in P sorption, they represent different sorption ranges. The highly weathered Andisols are almost always high and very high in P sorption, the Mollisols and Vertisols are usually low in P sorption depending on the amount of $CaCO_3$ present, and the Oxisols and Ultisols range from very high to low, depending on the mineral contents and the surface as seen in this set of soils. Another group of soils not represented in this study would be soils high in quartz sand, which are usually very low in P sorption. The Oxisols tend to have the largest variation in P sorption because their mineral contents can vary from predominantly kaolinitic such as the Molokai and Wahiawa to mostly goethite or any mixture of Fe or Al hydrous oxide minerals such as the Halii.

The lack of correlation between clay content and P sorption values opposes the significant correlations reported by several researchers (Lins and Cox, 1989; Sharpley et al., 1989; Johnston et al., 1991). Juo and Fox (1977) studied a set of West African soils and found clay content, DCB extractable Fe and BET-surface area to significantly correlate with the amount of P sorbed to provide 0.2 mg P L^{-1} in the equilibrium solution. They segregated their set of soils into four groups based on soil order and parent material that is indicative of differences in types of soil minerals. The Alfisols and Ultisols derived from acidic rocks had significant correlations with clay content at the 1% level. Hydromorphic soils, however, were significant only at the 10% level and the Alfisols and Ultisols derived from basic rocks were not significantly correlated with clay content but the correlation with BET-surface area was significant at the 1% level. Their explanation for this observation was that BET-N_2 measured the external surface area of the soil particles which in this case indicates the extensiveness of the reactive surfaces. Their results indicate that for some high clay soils not all of the clay particles are participating in P sorption and thus do not reflect the clay content. Furthermore, differences in clay minerals could produce a poor correlation between $PS_{0.2}$ and clay content. Jones (1981) demonstrated that the surface area of goethite was the primary contributor to P sorption of 11 Puerto Rican soils while gibbsite contributed little to P sorption and hematite had essentially no contribution.

The percentage of a given mineral is often not as important as the mineral's total surface area. Crystal morphology and size can vary for a given mineral resulting in different amounts of specific surface area. Thus, a higher specific surface area for goethite in one soil, such as the Kaiwiki, will have a higher P sorption rate than a soil with the same amount of goethite but with a lower specific surface area, e.g., the Makapili soil.

Results from Incubation Experiment

The P buffering coefficient values were calculated for three extractants, Mehlich-3, M-Truog and Olsen, at nine intervals during the incubation period (Figures 4.8 to 4.10). The M-Truog extract consistently extracted more P

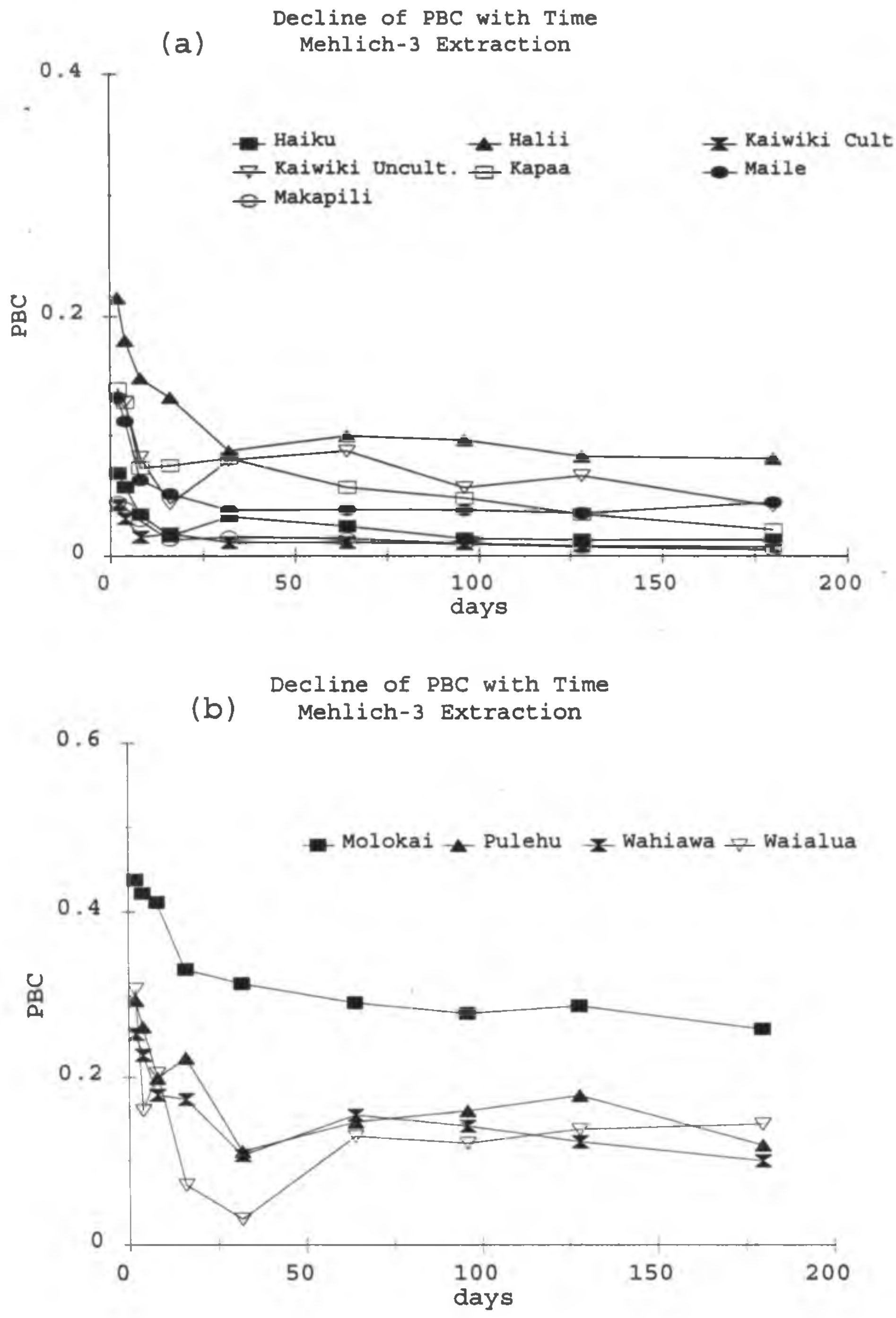


Figure 4.8 Change in PBC with incubation time by the Mehlich-3 extractant for (a) soils in the low range of PBC values and (b) soils in the high range of PBC values.

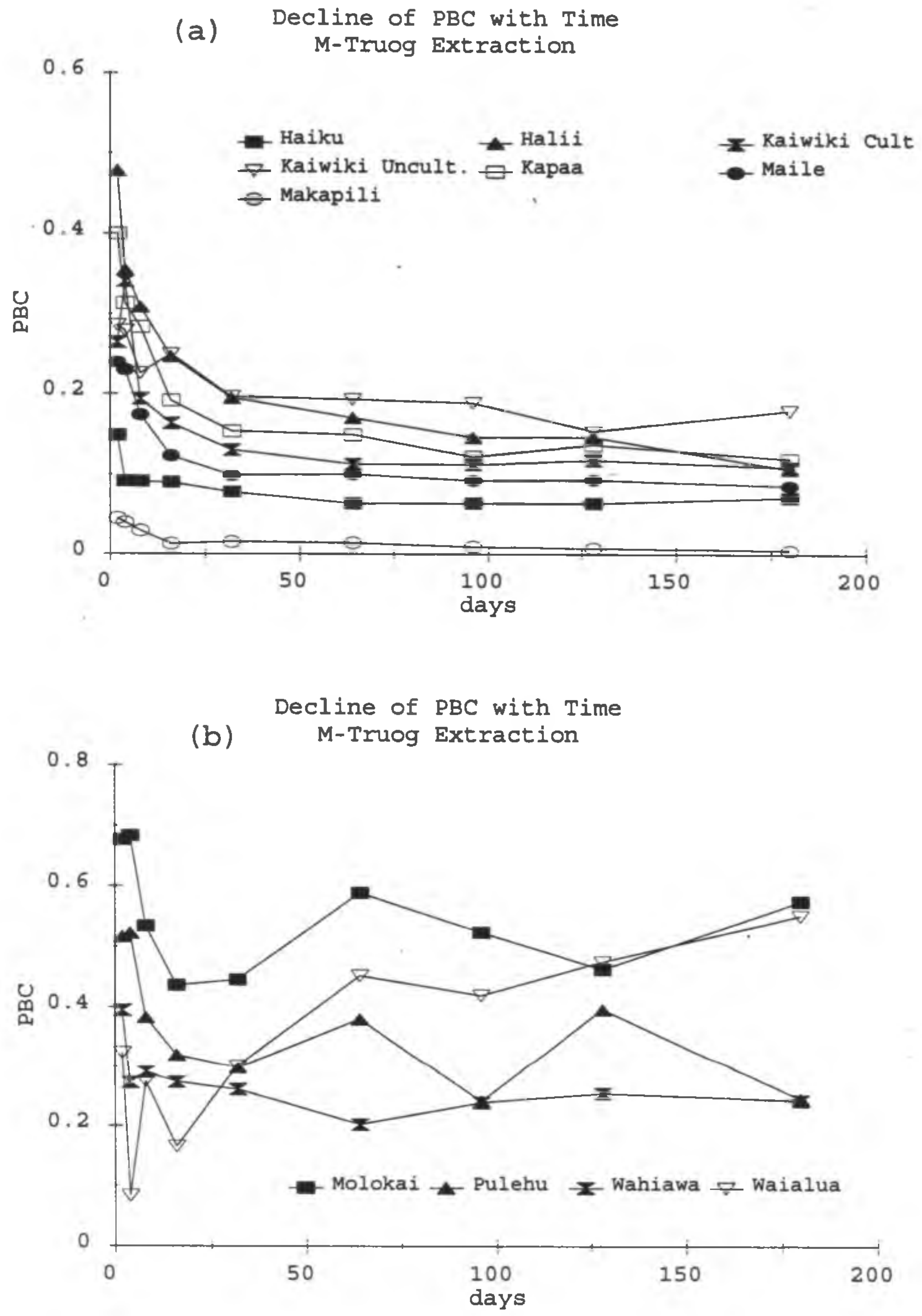


Figure 4.9 Change in PBC with incubation time by the M-Truog extractant for (a) soils in the low range of PBC values and (b) soils in the high range of PBC values.

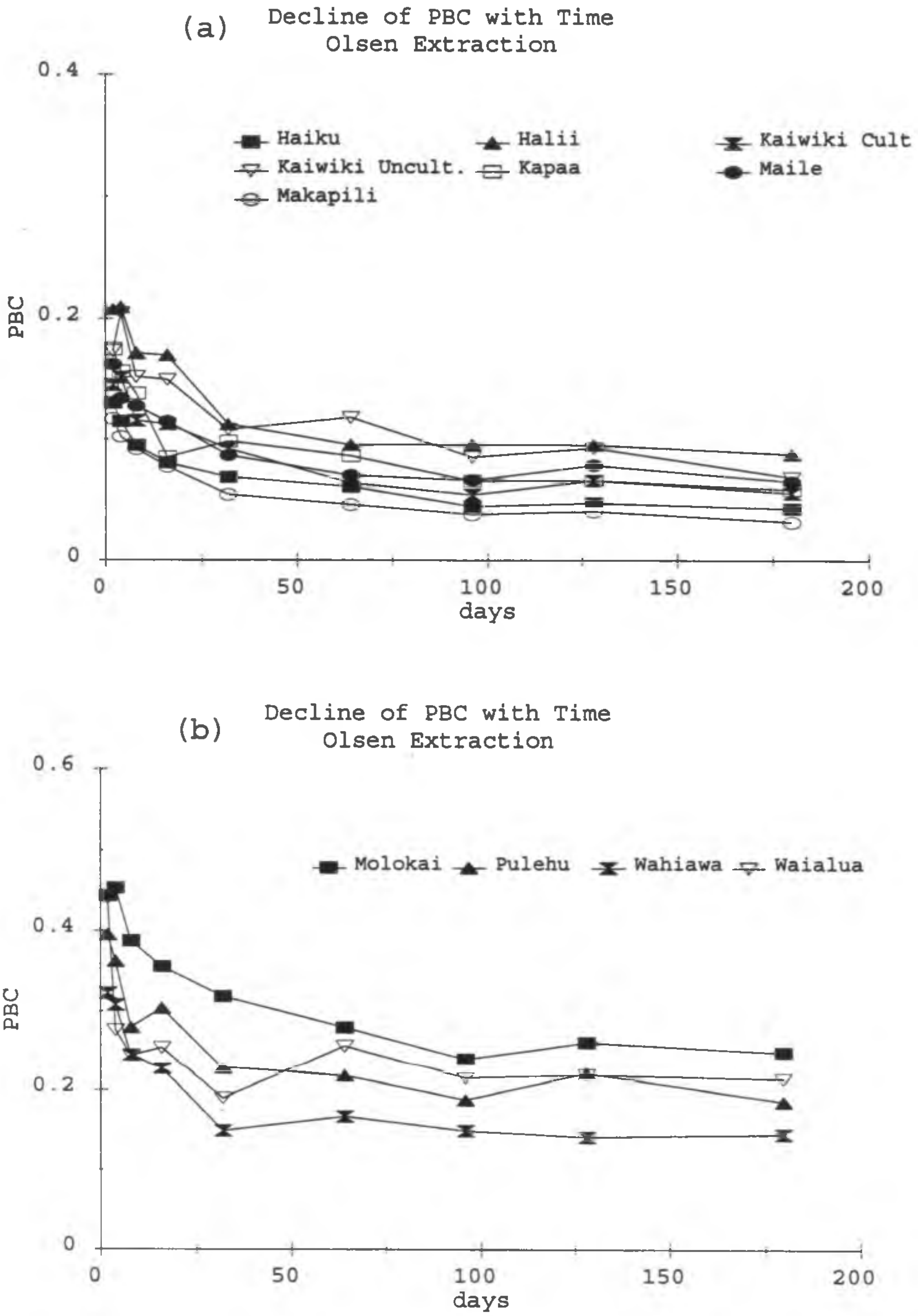


Figure 4.10 Change in PBC with incubation time by the Olsen extractant for (a) soils in the low range of PBC values and (b) soils in the high range of PBC values.

than the other two extractants and thus had higher PBC values, which ranged from 0.07 to 0.58 after 6 months of incubation. The Olsen extract, which ranged from 0.03 to 0.25, was higher or similar to the Mehlich-3 extract, which ranged from 0.01 to 0.26.

The PBC values decreased exponentially with time and approached a relatively stable value after 64 d of incubation. Smooth curves were produced for most of the soils, but for a few soils there was considerable variation, especially with the Waialua soil as the PBC decreased rapidly then increased with time. The decrease in extractable P with time varied for each soil and for each of the three extractants. Generally, the Olsen extractant produced a smooth decrease whereas, the Modified-Truog showed a rapid decline, levelling out to a constant value.

Probable sources of variation in the extractable P levels between samples are 1) volumetric measurement of soil under various moisture conditions that may lead to slight differences in soil:solution ratios and 2) inconsistencies in shaking and duration of soil in contact with extracting solution before centrifuging. Probable sources of variation in curve type between soils are 1) effects of microbial activity causing immobilization and mineralization of P, and 2) interaction of extract with chemical compounds of the soil to alter the effectiveness in extracting available P, eg., dissolution of $CaCO_3$ in the Pulehu soil to release sorbed P (Olsen and Khasawneh, 1980).

The soils can be categorized into two groups based on the PBC values resulting from 64-180 d of incubation (Figures 4.8 to 4.10). The Waialua, Pulehu, Molokai and Wahiawa soils had high PBC values; Halii, Maile and Kaiwiki uncultivated, Haiku, Kapaa, Kaiwiki cultivated and Makapili had low PBC values. The soils are categorized into groups because they tended to interchange their relative order within groups as the PBC values fluctuated with time. The same categories existed for each of the three extracts. Among the seven soils in the low PBC category, the Halii and Kaiwiki uncultivated PBC values were higher reflecting less P sorption while the Haiku, Makapili and Kaiwiki cultivated PBC values were lower reflecting high P sorption for all extractants. The Kapaa and Maile varied from the high to low depending on the extractants.

Relationship Between $PS_{0.2}$ and P Buffering Coefficients

In comparing the PBC values with the $PS_{0.2}$ values, the relative P sorption potentials among soils are not the same for the two methods. In some cases where there are large differences in $PS_{0.2}$ values there were only small differences or no distinct differences in PBC values. The Kaiwiki samples, Makapili and Maile soils have much larger $PS_{0.2}$ values than the Kapaa, Haiku, and Halii soils, but with the PBC values these soils suggest similar P sorption potentials. The Wahiawa soil shows a medium sorption potential by its $PS_{0.2}$ values, but a low sorption potential by its PBC value.

The differences in these two methods of measuring P sorption may be due to the effects of the physical conditions in the incubation experiment. Incubating the soils at field capacity moisture content adds the element of diffusion to the P sorption process. The P would have to diffuse into aggregates in order to reach additional sorption sites, whereas the isotherm method utilizes shaking the soils with a high solution:soil ratio which can break aggregates and expose more surface area. Thus, the isotherm method shows more sorption with increasing number of sorption sites whereas PBC values do not necessarily reflect this increase in sorption potential.

Soil Properties Influencing P Buffering Coefficients

Phosphorus buffering coefficient values change with time as sorption continues gradually. This gradual sorption has been attributed to diffusion of P into aggregates when the soil moisture level varies from field capacity to air dry conditions (Kovar and Barber, 1988; Staunton and Nye, 1989). Staunton and Nye, (1989) compared ^{32}P exchange with time under different methods for mixing the ^{32}P solution with soil and found a much higher proportion of the total ^{32}P exchanged to occur instantaneously for a suspension of soil in the solution than for when ^{32}P is added in enough solution to only moisten the soil. The less ^{32}P that exchanged instantaneously in the incubated soil indicates that under moist soil conditions ^{32}P must diffuse into the micropores of aggregates to gain access to exchange sites. This phenomenon indicates that for soils incubated with applied P, the initial PBC values would reflect the sorption that takes place at aggregate surfaces and subsequent decrease in PBC values with time occurs with diffusion of P into the aggregates. Shaking soil suspensions destroys aggregates and exposes surfaces and promotes rapid sorption. If this assumption is true, then soils with larger and more stable aggregates would have lower PBC values for longer periods of time and that may explain why the Maile and Kaiwiki uncultivated soils, which have high organic matter content and strong structure, show higher PBC values than some of the Oxisols, which have a much lower P sorption potential in the isotherm data.

The PBC values in the current study, however, did not correlate well with any measured soil properties. The poor correlation is possibly due to the compounding effects of soil minerals, chemistry and diffusion rates in the incubation method. A major influence of variation in any type of P sorption measurement is the minerals present, which are not reflected by routinely measured soil properties (Kovar and Barber, 1988). The soil mineral type and amount has two effects on P sorption in a moist soil.

One is the number of sorption sites contributed by each mineral determines the total P sorption potential. The second property is the physical characteristics of soils that affect diffusion through moisture retention and size and stability of aggregation. Sharpley et al. (1989) did not report details on the minerals of the soils in their study, so effects of varying mineral contents for their soils could not be investigated. Johnston et al. (1991) reported a significant relationship between PBC values and clay contents from a set of 76 soils representing a wide range in soil conditions. The PBC values where modeled with an exponential function dependant on clay content of the soils. This relationship seemed to predict PBC values well for soils with low clay content, but for soils with greater than 40% clay the variation in PBC values was too great to be predicted by a single curve. The wide variation at high clay contents is possibly due to differences in types of clay minerals in these soils.

Utilization of P Buffering Coefficients

In order to effectively utilize PBC values it is important to understand the soil properties that affect the value for a soil and the sensitivity of such changes in PBC values to fertilizer recommendations. Phosphorus buffering coefficients represent the proportion of P fertilizer that is still extractable after a given period of incubation (Sharpley et al., 1989; Indiata et al., 1991; Johnston et al., 1991). The practical application is to use the PBC to determine an amount of fertilizer needed to provide a given level of extractable P. It was the objective of this study to find properties that could be used to predict the PBC, and eliminate the need of testing each soil used in agriculture production. The data in this study provided no soil properties that could be used for this purpose. It should be noted that the majority of these soils had very low PBC values and within this range a PBC value that is two or three times another value will indicate two or three time the amount of fertilizer needed. That is to say, a difference from 0.030 to 0.060 or 0.090, which does not appear to be large, creates a two or three times difference in fertilizer recommendation. Accurate determination of PBC values in this range is very important because of the large scale differences that can be produced by a seemingly small difference in the PBC.

For practical purposes, the extremely high P requirements of the Andisols as indicated by the large $PS_{0.2}$ values was not confirmed by the incubation method. This discrepancy means that under the field conditions mimicked by the incubation method less P is sorbed leaving more available for plant use (Table 4.10). The Kaiwiki cultivated and uncultivated samples showed $PS_{0.2}$ values that were roughly two and three times higher, respectively, than the Makapili. The PBC values, however, were either approximately equal for the Mehlich-3 extract or showed half as much sorption (a PBC value two time greater) for the Olsen extract in comparing the cultivated Kaiwiki to the Makapili. The uncultivated Kaiwiki soil buffer coefficient was almost seven times larger than that of the Makapili soil for the Mehlich-3 extract and almost twice as much for the Modified-Truog extract. These are large differences when determining fertilizer recommendations. Research is still needed on the 1) effective use of PBC values for determining fertilizer requirements, 2) residual value of the P that is sorbed by the soils, and 3) effect of aggregation and other soil properties in determining PBC values.

Table 4.10 PBC values averaged from 64 to 180 days of incubation.

Soil	Mehlich-3	M-Truog	Olsen	$PS_{0.2}$
Haiku	0.016	0.065	0.049	416
Halii	0.090	0.14	0.094	260
Kaiwiki Cult.	0.0093	0.11	0.060	3277
Kaiwiki Uncult.	0.063	0.18	0.092	2305
Kapaa	0.040	0.098	0.070	434
Maile	0.0039	0.13	0.070	1134
Makapili	0.0092	0.090	0.039	1252
Molokai	0.28	0.54	0.26	139
Pulehu	0.15	0.32	0.20	79
Wahiawa	0.13	0.23	0.15	490
Waialua	0.13	0.48	0.23	112

CHAPTER 5

MODELING CHANGES IN P_{ext} DURING INCUBATION

Introduction

An extractable P level is the basis for determining the P fertility status of a soil. Levels of P_{ext} are correlated with plant growth in order to determine the response of plant growth to the measurement of P by a particular extractant (Dahnke and Olson, 1990). Due to the complexity of P-soil interactions, however, it is difficult to determine how much P must be added to provide the increase in P_{ext} needed. The uncertainty lies in the amount of sorption that takes place with time. Only a small proportion of added P becomes extractable. It is this proportion that can be utilized to calculate the amount of P needed to raise the P_{ext} level. This proportion, the PBC, is calculated from the slope of the linear relationship between P_{ext} and P_{app} as has been discussed previously. Caution must be exercised in determining and utilizing the PBC, because it changes with time as sorption continues. The mechanism of this continual sorption process and of the resulting equilibrium PBC value is poorly understood.

Upon calibration of plant response to the extractable P levels of a soil, a recommendation for the amount of fertilizer needed must be made. Recommendations are normally based on the yield response of a crop on a specific soil at a certain level of extractable P (Dahnke and Olson, 1990). One tactic to improve this process is to utilize models that predict the amount of fertilizer needed to increase the extractable P by a certain level from frequently measured soil properties (Yost et al., 1992). Effective models could be used to improve the P fertility management in many areas of the world where calibration tests are too expensive and time consuming to conduct. The controlling factors of P sorption for a soil are, however, complex, and the use of one or two frequently measured soil properties for determining the PBC for a soil seems remote for a wide range of soils based on the results discussed earlier. It may be possible to develop relationships between frequently measured soil properties and P sorption characteristics on soils with similar minerals, that seems to be the primary determining factor of soil-P interactions. Unfortunately, mineral types and contents are not easily and frequently determined.

P_{ext} Models

The P_{ext} data from the incubation study shows a decline in P_{ext} with time (Figure 5.1a). The P_{ext} drops rapidly for the first week of incubation then curves into a gradual decline probably approaching a constant value, which for the soils in the present study appear to reach in about two months. This drop in P_{ext} is an important consideration for agricultural practices because it suggests more P is

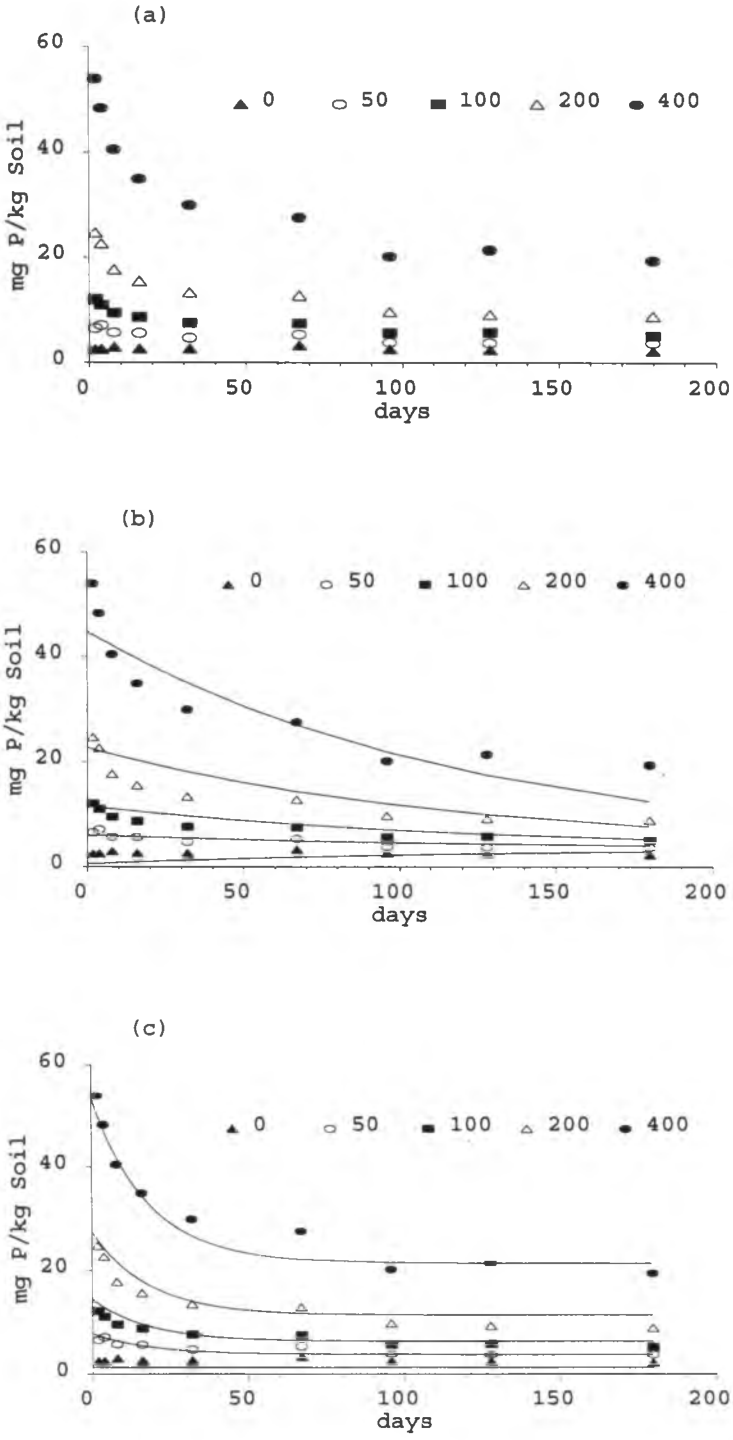


Figure 5.1 (a) Decline of P_{ext} with time, (b) data fit with equation (2), (c) data fit with equation (3).

available shortly after fertilizer application and is reduced significantly with time. Practices that aim to take advantage of the P while it is available can maximize the efficiency of applied P.

Negative Exponential Model

Extractable phosphorus values can be modeled well with a negative exponential curve that represents a decline in P_{ext} and approaches a constant equilibrium value after a period of a few years and covering several growing seasons (Cox et al., 1981). The equation used by Cox et al. (1981) is

$$P_{ext} = P_{eq} + (P_0 + b_1P_{app} + b_2P_{app}^2 - P_{eq})e^{-kT} \qquad (1)$$

The expression $P_0 + b_1P_{app} + b_2P_{app}^2$ represents the increase in P_{ext} per unit of P_{app}. In this case the relationship was fit with a quadratic equation and b_1 and b_2 are P buffering coefficients. A quadratic expression indicates that the PBC changes with the amount of P_{app}. For equation (1) at time T = 0, the exponential factor equals one and the starting level of extractable P is determined by this quadratic expression plus the initial equilibrium value in the soil. The term P_{eq} is the equilibrium value of P that the system started with and will ultimately reach. As T continues to infinity the exponential factor goes to zero and P_{ext} approaches P_{eq}. Cox et al., (1981) determined P_{eq} values based on experience and knowledge with 1) long term studies without fertilization, 2) exhaustive greenhouse studies or 3) virgin sites for the soils being considered. The constant k determines the curvature for the decline rate of P_{ext} and incorporates the effects of the soil's P sorption properties and also the effect of plant uptake.

Plant Uptake Component

Matar (1988) modified this model to include plant uptake as a separate component.

$$P_{ext} = P_{eq} + [(A + B*P_{app}) - P_{eq}]*e^{-kT} - TPU \qquad (2)$$

Where TPU is the total P uptake by plants. In this case the constant k embodies only the effects of the soil. The quadratic equation was also reduced to a linear expression for the relationship between P_{ext} and P_{app}. This approach separates the effect of plant uptake, which can be removed to fit the model with the incubation data. The effect of the single P_{eq} term, however, is to bring all levels of P_{app} to the same constant value, but from the data of the present study each level of P_{app} approaches its own constant value.

Equation (2), without the TPU term, was fit to the P_{ext} data from the incubation study (Figure 5.1b). Non-linear regression was used to find the best fit for the data and the corresponding model parameter, k. The fit shows the decline to drop below the observed values, especially for the higher rates of P as the model attempts to bring each level of P_{app} to the same constant value.

Effect of Applied Phosphorus

To improve the fit, the P_{eq} term in equation (2) was substituted with the expression $P_0 + PBC*P_{app}$ to provide a separate asymptotic constant for each level of applied P. PBC is the P buffering coefficient as mentioned above, and P_0 is a constant that represents the P_{ext} when no P is applied (the y-intercept for the linear relationship of P_{ext} and P_{app}). The linear regression term in Matar's equation is substituted with $A*P_{app}$ where A is a constant that represents the proportion of the P_{app} that sorbs slowly following the initial instantaneous sorption at time t=0 until the time equilibrium is achieved. The equation was thus modified to

$$P_{ext} = P_0 + PBC*P_{app} + A*P_{app}*e^{-kT} \qquad (3)$$

The term $A + B*P_{app} - P_{eq}$ is replaced with $A*P_{app}$ so that when the model determines P_{ext} at T=0 the coefficient A will represent the proportion of P_{app} that will be sorbed with time. Because we are interested in the change in P_{ext} from the time of application, it is necessary to start with the $A*P_{app}$ term. This model improves the fit with the data as it allows each level of P_{app} to asymptotically approach a separate constant value (Figure 5.1c). Non-linear regression was used to fit the model and find values for the regression was used to fit the model and find values for the parameters P_0, PBC, A and k for each soil (Table 5.1).

The proportion of P_{app} that is sorbed instantaneously can be calculated from 1 - (PBC + A). The PBC is the proportion of P_{app} that is extractable after a sufficiently long time to allow the sorption process to attain equilibrium, and A represents the proportion of P_{app} that is sorbed with time, as stated above. When t=0 then $e^{-kt}=1$ and the level of P_{ext} equals P_o + (PBC + A)P_{app}. Thus, PBC + A is the proportion of P_{app} that is extractable when t=0, and one minus this sum is the proportion that is instantaneously sorbed (IS).

The parameter k in equation (3) represents the curvature of the decline in P_{ext} from its initial level at t=0 to its equilibrium level. Thus, k represents the slow sorption process. The larger k is the more curvature there is as P_{ext} drops very rapidly and levels off to approach the equilibrium level in a short period of time. A smaller k value produces a much more gradual decline in P_{ext}, which requires more time to reach equilibrium.

Results from the P_{ext} Model

The PBC values from the nonlinear regression of equation (3) and the incubation data (PBC_2) correlated significantly with the PBC values averaged from the final four analysis times of the incubation (PBC_1) indicating that

Table 5.1 Parameter values for equation (3) fit by nonlinear regression to the P_{ext} incubation data.

Soil	Extract	P_0	PBC	A	k	IS[†]
Haiku	Mehlich-3	-0.116	0.019	0.073	0.190	0.908
	M-Truog	0.830	0.073	0.256	0.590	0.671
	Olsen	1.346	0.050	0.081	0.056	0.870
Halii	Mehlich-3	-1.431	0.091	0.143	0.107	0.766
	M-Truog	1.421	0.151	0.346	0.091	0.503
	Olsen	2.223	0.091	0.132	0.044	0.777
Kaiwiki-C	Mehlich-3	1.723	0.011	0.052	0.251	0.937
	M-Truog	47.17	0.114	0.228	0.193	0.658
	Olsen	8.015	0.055	0.097	0.033	0.848
Kaiwiki-U	Mehlich-3	-3.711	0.062	0.104	0.181	0.834
	M-Truog	-8.906	0.182	0.112	0.060	0.706
	Olsen	-3.642	0.089	0.102	0.037	0.809
Kapaa	Mehlich-3	-1.289	0.040	0.086	0.037	0.874
	M-Truog	-0.001	0.105	0.280	0.372	0.615
	Olsen	1.801	0.074	0.280	0.372	0.805
Maile	Mehlich-3	0.603	0.040	0.126	0.176	0.834
	M-Truog	9.175	0.134	0.322	0.108	0.544
	Olsen	0.434	0.071	0.092	0.057	0.837
Makapili	Mehlich-3	-0.307	0.011	0.040	0.110	0.949
	M-Truog	6.234	0.094	0.192	0.111	0.714
	Olsen	-0.515	0.040	0.079	0.050	0.881

[†] Calculated from 1-(PBC+A) as discussed in the text.

Table 5.1 (Continued) Parameter values for equation (3) fit by nonlinear regression to the P_{ext} incubation data.

Soil	Extract	P_0	PBC	A	k	IS[†]
Molokai	Mehlich-3	39.08	0.268	0.234	0.068	0.499
	M-Truog	146.9	0.481	0.484	0.225	0.035
	Olsen	25.74	0.248	0.222	0.041	0.529
Pulehu	Mehlich-3	61.20	0.104	0.340	0.095	0.556
	M-Truog	185.3	0.192	0.831	0.126	-.023
	Olsen	54.25	0.186	0.248	0.058	0.569
Wahiawa	Mehlich-3	-2.851	0.120	0.195	0.179	0.685
	M-Truog	0.067	0.250	0.301	0.441	0.449
	Olsen	-3.167	0.148	0.198	0.071	0.654
Waialua	Mehlich-3	19.19	0.098	0.299	0.192	0.603
	M-Truog	121.1	0.339	65.7	59.6	§
	Olsen	54.40	0.214	0.388	0.281	0.398

§ value not determined for this soil and extract due to the poor fit with the data and erroneous parameter values.

[†] Calculated from 1-(PBC+A) as discussed in the text.

the nonlinear regression was able to fit the exponential curves to asymptotes that represent the final levels of P_{ext} attained by the six-month incubation (Figure 5.1c). As discussed in chapter 4 the PBC_1 values did not correlate well with the $PS_{0.2}$ values and the same is true for the PBC_2 values. The PBC_2 values did not correlate with any of the measured soil properties, except, with the predicted number of sorption sites per gram of soil, which is based on soil mineral composition.

The P_{ext} model parameters PBC and A were significantly correlated with the predicted number of sorption sites per gram of soil, and the IS factor was highly significant

Table 5.2 Coefficients of determination between P_{ext} model parameters and number of sorption sites per gram of soil.

Parameter	Extract	r^2
PBC	Mehlich-3	0.41*
	M-Truog	0.32
	Olsen	0.57**
A	Mehlich-3	0.65**
	M-Truog	0.57*
	Olsen	0.52*
IS	Mehlich-3	0.63**
	M-Truog	0.62**
	Olsen	0.58**
k	Mehlich-3	0.28
	M-Truog	0.17
	Olsen	0.17

* significant; $P < 0.05$
** highly significant; $P < 0.01$

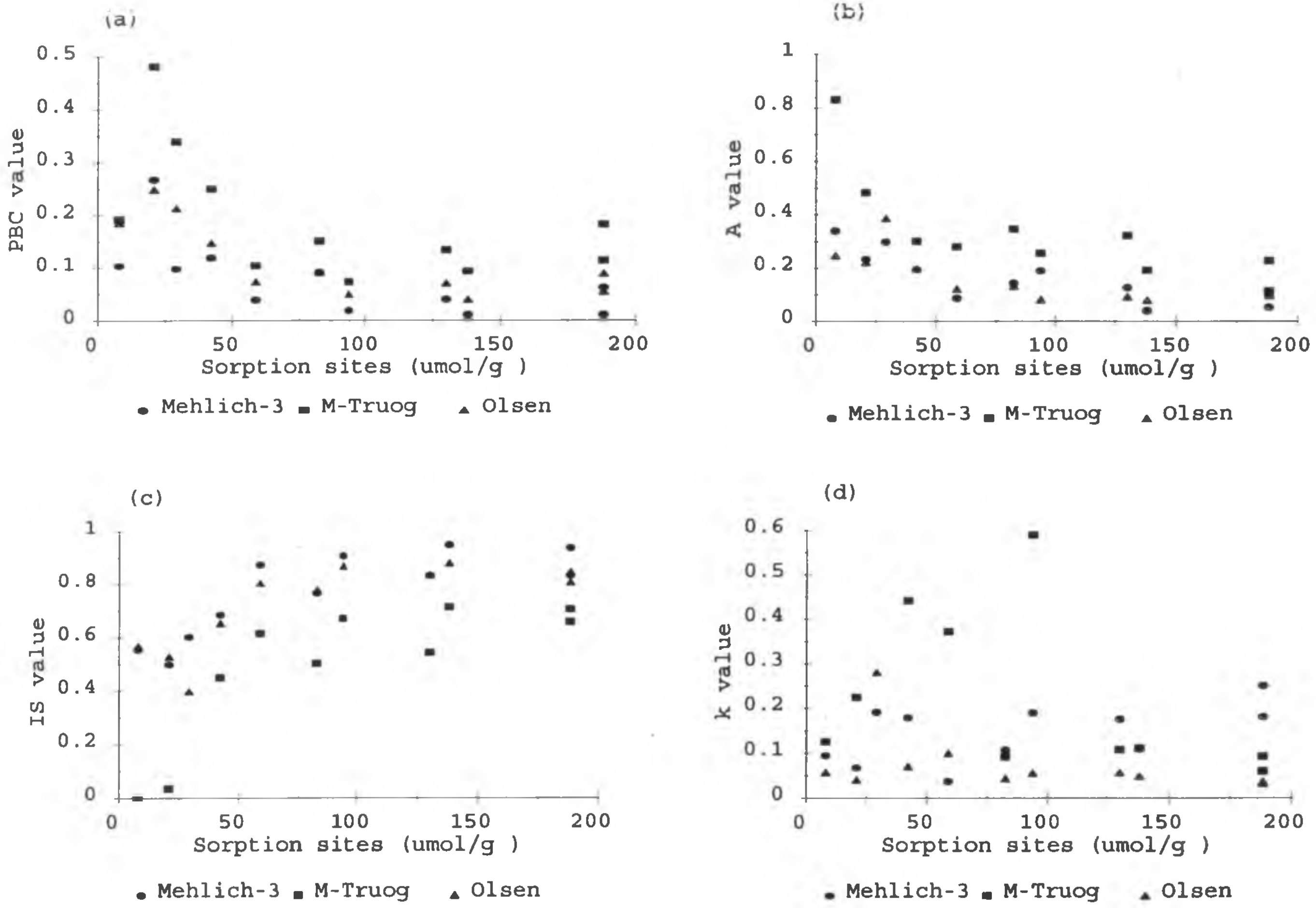
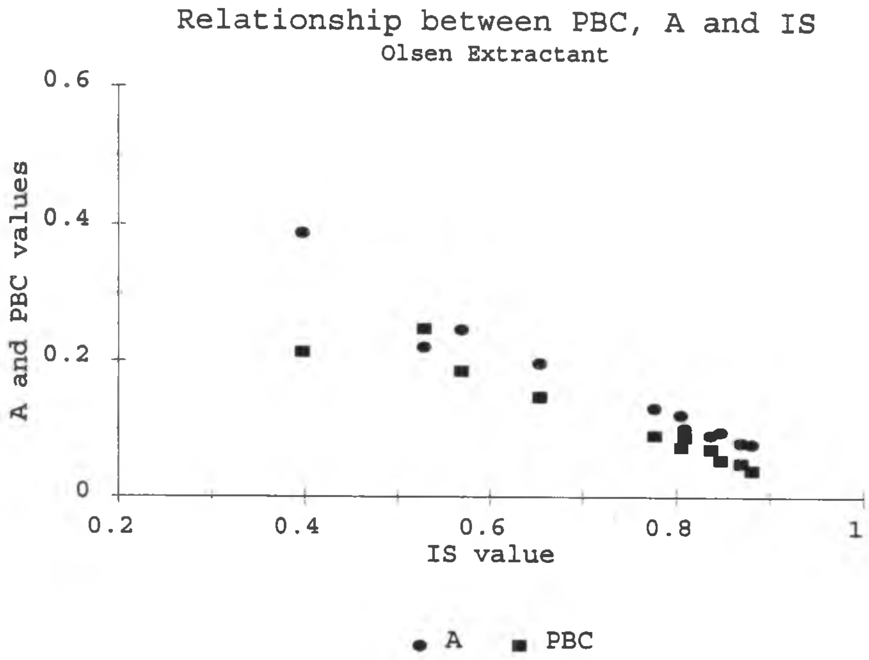


Figure 5.2 Relationships between model parameters and sorption sites per gram of soil (a) PBC, (b) A, (c) IS, and (d) k.

(Table 5.2). Significance is based on linear correlations, but visual examination of the relationships (Figure 5.2) shows that the relationship is curvilinear with the PBC taking on low values as the number of sorption sites increases. The A values show more of a linear relationship with A becoming smaller as the number of sorption sites increases. The IS values show an opposite relationship as they increase with number of sorption sites and gradually approach a level reading. The k values in the exponential term did not correlate with any soil property or with the number of sorption sites, which indicates factors controlling k were not clearly represented by any of the measured soil properties.

Values for PBC, A and IS were all linearly related with one another (Figure 5.3). When the instantaneous sorption is high, then the amount of subsequent, slow sorption is reduced considerably because there is little P remaining unsorbed. The fact that the correlation of the number of sorption sites with IS is more significant than either the PBC or A indicates that it is more directly controlled by this soil property than the other two. The number of sorption sites directly determines the proportion of P_{app} sorbed instantaneously, and other soil properties may have an effect if they alter the exposure of the sorption sites, for example aggregation and organic matter.



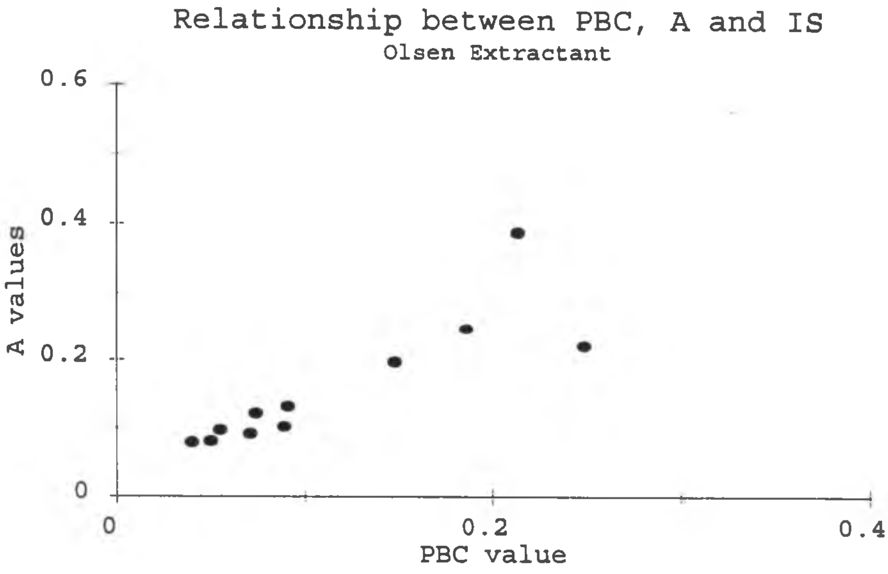


Figure 5.3 Relationships between the individual parameters of equation (3).

The value of A is controlled by the proportion of adsorbable P remaining and the factors that cause a slow sorption process. Slow sorption is likely to be one of or a combination of two general mechanisms: 1) Diffusion of P into aggregates where it becomes exposed to sorption sites as it diffuses (Stauton and Nye, 1989; Kovar and Barber, 1988). 2) Changes in chemical bonding at the sorption sites and occlusion of P in crystal defects (Torrent et al., 1992; Parfitt et al., 1989; Goldberg and Sposito, 1985; Ryden et al., 1977; Munns and Fox, 1976;). The PBC value is a result of the A and IS values and thus the soil properties that affect both of these values.

It should be noted that Figure 5.1 shows the PBC values to level to a somewhat constant range of values as number of sorption sites increase, but within this range the impact of PBC values on fertilizer requirement are very sensitive to change in the PBC values. The fertilizer requirement equals P_{ext}/PBC, where P_{ext} is the increase in P_{ext} desired. Because the numbers are small, there is little absolute difference between two values but the increase can be over 100% which translates to over 100% increase in fertilizer requirements to raise the P_{ext} to a desired level. For instance, the PBC values for the Haiku and the Halii are 0.019 and 0.091, respectively, for the Mehlich-3 extractant, and in order to increase the P_{ext} of each soil by 10 mg P L^{-1}, 526 and 110 kg P ha^{-1}, respectively, would have to be applied. These soils have similar sorption site numbers but the PBC values have a three fold difference between them and they both appear to fall within the range that PBC's reach when the sorption site numbers get large.

Summary and Conclusion

Two methods, P sorption isotherms and extractable P following incubation, were used to determine the P sorption potential for selected soils and the sorption measurements were correlated with measured soil properties. The conclusions made were:

1) the two methods are not equal in their measurement of P sorption potential in the sense that the soils were ordered differently according to their sorption potential,

2) the prediction of the number of sorption sites, which is a function of the surface area of each type of mineral in a soil, is the controlling factor for P sorption,

3) the measured soil properties do not predict the P sorption potential for a set of soils varying in types and contents of minerals,

4) extractable P decreases with time after application and reaches a stable value in one to two months of incubation,

5) the negative exponential equation depicts well the decrease in extractable P and can be used to determine the proportions of applied P that react instantaneously, with time, remains in extractable forms.

In order to improve our knowledge and ability to manage P fertility further research is needed on several topic related to or raised by data presented here.

1) The contribution of amorphous Fe and Al hydrous oxides to the number of P sorption sites per mass of soil needs to be investigated in order to improve prediction of P sorption potential.

2) The correlation of soil properties to sorption potential of soils with similar mineral composition would be helpful in developing management practices that will improve P fertility.

3) The properties that affect the slow sorption of P during incubation need to be determined, which would be helpful in developing management practices to improve P fertility.

4) The aspect of P desorption and its importance in P fertility needs to be quantified. The prediction of the number of sorption sites used in this study showed good correlation with P sorption potential. There may also be a relation with the number of sorption sites and desorption of P. This relationship needs to be investigated for the purpose of providing information on the supply rate of P for plant growth.

Appendix A

Incubation Experiment: Extractable Phosphorus Data

Meh-3, Mehlich-3; M-Tr, Modified-Truog; Olsen Extractants; P_{app}, mg/kg

Haiku Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	2.15	7.87	2.52
2	0	1.34	4.26	2.62
2	50	2.72	8.04	6.88
2	50	2.09	8.59	6.29
2	100	4.87	14.88	12.12
2	100	5.85	10.21	12.17
2	200	12.04	31.13	23.88
2	200	12.25	31.80	25.49
2	400	27.37	59.68	58.44
2	400	29.13	65.92	49.24
4	0	0.90	0.84	2.50
4	0	0.99	1.41	2.70
4	50	1.80	6.48	7.24
4	50	1.79	4.75	7.14
4	100	2.86	9.77	10.71
4	100	3.80	7.98	11.32
4	200	8.74	19.67	22.06
4	200	8.44	22.32	23.09
4	400	20.51	38.86	47.93
4	400	25.88	35.37	48.52
8	0	1.01	1.72	3.52
8	0	1.06	1.61	2.57
8	50	2.20	5.10	5.68
8	50	2.33	5.68	5.87
8	100	3.22	8.19	10.07
8	100	2.72	9.67	8.99
8	200	5.13	17.72	17.69
8	200	6.28	19.74	17.76
8	400	12.77	37.97	41.33
8	400	16.51	37.42	39.58
16	0	0.43	0.54	2.59
16	0	0.19	0.51	2.77
16	50	1.26	3.18	5.71
16	50	1.11	3.39	5.64
16	100	2.01	6.18	8.69
16	100	1.99	7.50	8.76
16	200	5.42	13.28	15.02
16	200	6.04	16.41	16.10
16	400	6.77	34.73	33.14
16	400	6.15	37.30	36.59
32	0	0.59	0.36	2.63
32	0	0.54	0.00	2.73
32	50	1.23	1.78	4.70
32	50	1.32	3.04	4.83
32	100	2.46	5.44	7.53

Haiku Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	100	2.27	5.23	7.74
32	200	5.28	13.65	13.36
32	200	5.99	13.29	13.52
32	400	12.84	29.40	31.48
32	400	13.54	31.80	28.34
67	0	0.53	2.42	3.32
67	0	0.68	2.18	3.42
67	50	1.37	5.22	5.49
67	50	1.70	4.52	5.32
67	100	1.83	7.94	7.46
67	100	2.57	6.88	7.63
67	200	4.23	13.75	12.51
67	200	4.30	13.45	13.26
67	400	9.84	27.81	27.04
67	400	10.98	26.95	28.05
96	0	0.44	3.68	2.57
96	0	0.28	2.21	2.72
96	50	0.75	4.76	3.80
96	50	0.84	5.51	4.06
96	100	0.92	8.54	6.05
96	100	0.85	7.70	5.37
96	200	2.04	16.69	10.15
96	200	2.07	13.14	9.42
96	400	6.12	28.23	21.18
96	400	5.90	27.45	19.23
128	0	0.33	2.02	2.49
128	0	0.38	2.32	2.57
128	50	0.78	4.98	4.03
128	50	0.68	4.46	3.66
128	100	1.55	6.87	5.90
128	100	1.24	7.37	5.72
128	200	2.19	13.30	9.21
128	200	2.06	12.83	9.34
128	400	5.53	26.95	21.13
128	400	5.77	27.92	21.67
180	0	0.16	2.88	2.22
180	0	0.18	2.45	2.38
180	50	0.36	4.24	4.01
180	50	0.44	4.18	3.52
180	100	0.79	6.83	5.04
180	100	0.88	7.80	5.31
180	200	1.69	13.21	8.81
180	200	1.74	13.67	9.12
180	400	5.61	30.86	19.18
180	400	5.46	30.13	19.66

Halii Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	1.06	8.45	4.22
2	0	1.48	6.72	3.44
2	50	8.07	21.48	12.15
2	50	8.14	21.97	12.40
2	100	17.99	40.71	23.69
2	100	19.21	42.31	22.47
2	200	35.37	97.33	42.92
2	200	38.10	90.46	43.07
2	400	82.40	191.93	88.85
2	400	90.77	196.25	84.05
4	0	1.49	5.26	4.24
4	0	1.52	4.79	4.16
4	50	6.77	18.85	11.48
4	50	6.30	17.45	10.94
4	100	13.93	35.26	21.81
4	100	13.70	35.01	21.35
4	200	29.27	66.13	40.00
4	200	31.03	69.39	40.63
4	400	75.33	147.65	83.84
4	400	69.15	143.62	90.67
8	0	1.02	4.47	4.39
8	0	0.94	4.11	4.41
8	50	4.99	14.80	10.90
8	50	5.78	16.74	11.31
8	100	11.35	27.64	17.76
8	100	10.83	30.00	17.56
8	200	24.67	57.64	36.11
8	200	22.51	59.12	35.11
8	400	60.60	123.99	70.96
8	400	58.45	129.17	73.38
16	0	1.41	4.64	4.63
16	0	0.93	5.08	4.05
16	50	3.88	14.09	10.16
16	50	4.13	13.60	9.87
16	100	9.53	18.76	16.89
16	100	8.46	22.51	20.13
16	200	20.04	49.84	35.06
16	200	21.78	52.43	35.71
16	400	56.12	95.80	74.10
16	400	49.05	106.38	68.41
32	0	0.88	4.99	3.57
32	0	0.66	4.18	3.65
32	50	3.20	9.92	8.54
32	50	3.75	9.86	8.01
32	100	7.78	20.37	13.31
32	100	8.49	19.29	13.33

Halii Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	200	17.03	38.24	27.47
32	200	14.85	35.07	22.29
32	400	34.86	84.56	47.44
32	400	35.36	78.39	49.03
64	0	1.13	4.29	3.88
64	0	1.32	4.40	3.74
64	50	3.50	9.67	7.36
64	50	4.07	10.58	7.00
64	100	7.46	16.25	10.67
64	100	7.36	15.21	12.01
64	200	15.91	31.05	20.09
64	200	16.91	31.79	21.03
64	400	39.79	69.80	41.56
64	400	40.95	73.96	41.68
95	0	1.36	3.53	2.97
95	0	1.37	4.15	3.05
95	50	4.47	9.23	6.51
95	50	4.23	10.24	6.44
95	100	7.65	16.07	10.21
95	100	8.11	14.95	10.03
95	200	14.79	34.10	17.66
95	200	15.88	27.90	19.45
95	400	39.79	65.76	40.92
95	400	39.41	57.78	41.21
129	0	0.65	5.42	4.17
129	0	0.77	4.97	3.69
129	50	3.21	8.06	7.39
129	50	3.24	9.55	7.94
129	100	5.66	15.00	11.49
129	100	5.42	13.45	12.04
129	200	12.61	29.04	19.80
129	200	11.98	31.13	11.24
129	400	33.50	63.29	43.26
129	400	33.31	61.30	42.64
180	0	1.11	4.18	3.50
180	0	1.15	3.96	3.83
180	50	3.36	10.08	6.66
180	50	3.32	10.62	7.15
180	100	6.44	11.50	10.56
180	100	6.40	12.11	10.36
180	200	12.77	23.55	18.95
180	200	13.35	22.77	18.99
180	400	33.81	44.47	38.99
180	400	32.32	49.93	38.08

Kaiwiki Cultivated Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	3.84	46.07	9.44
2	0	4.15	47.05	10.67
2	100	8.06	72.73	21.04
2	100	7.56	73.67	22.89
2	200	10.28	102.78	30.62
2	200	8.67	100.09	37.61
2	400	12.69	130.71	56.78
2	400	11.75	150.61	62.06
2	800	38.17	269.81	116.45
2	800	39.55	252.07	135.57
4	0	0.94	59.58	10.57
4	0	2.46	62.90	11.27
4	100	4.81	82.98	20.07
4	100	4.98	84.82	27.75
4	200	7.93	113.76	37.32
4	200	7.9	110.62	36.76
4	400	10.4	141.14	66.13
4	400	11.78	151.20	64.44
4	800	26.7	362.20	137.31
4	800	27.53	309.70	126.32
8	0	1.37	55.19	10.24
8	0	1.59	52.56	11.8
8	100	3.19	97.25	21.04
8	100	2.9	63.53	19.78
8	200	4.18	98.47	32.75
8	200	4.4	96.02	31.92
8	400	6.73	119.05	50.46
8	400	7.03	122.27	50.94
8	800	15.22	236.93	103.9
8	800	12.9	192.97	103.89
16	0	2.72	44.12	10.32
16	0	2.91	42.08	12.13
16	100	5.01	58.38	20.23
16	100	5.13	52.84	21.78
16	200	5.78	63.63	32.95
16	200	7.49	70.83	33.17
16	400	10.49	91.93	55.78
16	400	7.6	116.98	53.95
16	800	17.32	158.98	103.14
16	800	18.85	184.39	98.96
32	0	1.57	51.13	9.27
32	0	1.6	49.19	10.59
32	100	2.49	55.16	17.77
32	100	1.95	46.82	17.01
32	200	4.08	70.28	25.86
32	200	3.22	72.46	28.33

Kaiwiki Cultivated Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	400	6.87	93.65	41.77
32	400	6.11	95.29	42.85
32	800	11.48	155.8	82.05
32	800	8.74	145.5	85.41
64	0	1.79	48.62	9.85
64	0	1.92	51.29	7.6
64	100	2.56	65.71	13.11
64	100	3.57	65.28	15.2
64	200	3.39	71.5	18.95
64	200	4.23	67.72	18.31
64	400	5.59	96.85	32.24
64	400	5.24	87.15	35.09
64	800	10.41	142.14	59.87
64	800	11.62	142.75	58.61
95	0	2.05	49.88	6.59
95	0	2.09	58.61	7.13
95	100	3.38	60.29	13.14
95	100	3.33	51.14	11.62
95	200	5.83	67.08	22.38
95	200	4.76	69.05	24.42
95	400	7.02	86.55	29.59
95	400	5.24	100.03	31.83
95	800	9.48	140.97	51.03
95	800	11.61	138.91	51.34
129	0	1.42	58.78	8.58
129	0	1.53	48.24	8.71
129	100	2.25	60.98	11.87
129	100	2.13	65.11	15.27
129	200	3.74	67.15	19.1
129	200	3.03	73.3	20.93
129	400	5.07	93.41	31.13
129	400	5.05	97.75	32.4
129	800	8.1	142.71	62.99
129	800	8.13	151.09	59.62
180	0	2.03	48.24	7.25
180	0	1.41	44.38	7.3
180	100	2.21	52.83	11.34
180	100	2.14	55.04	12.07
180	200	2.59	65.6	16.38
180	200	2.44	70.32	17.31
180	400	3.74	94.74	26.5
180	400	3.96	96.69	27.24
180	800	7.77	118.36	49.84
180	800	7.42	145.08	53.78

Kaiwiki Uncultivated Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	3.35	3.58	3.03
2	0	3.07	6.08	2.37
2	250	19.25	55.41	34.13
2	250	21.92	59.90	39.41
2	500	53.33	118.30	77.74
2	500	62.23	145.30	63.33
2	1000	108.05	279.04	160.16
2	1000	133.46	263:94	166.04
2	2000	330.94	580.11	362.62
2	2000	182.04	560.81	327.08
4	0	5.69	4.62	1.97
4	0	2.03	7.20	0.90
4	250	30.30	44.46	52.62
4	250	20.20	47.54	34.87
4	500	46.98	105.95	73.43
4	500	41.46	113.44	72.71
4	1000	110.48	239.00	194.15
4	1000	89.96	251.24	184.15
4	2000	281.24	531.37	370.69
4	2000	234.24	574.62	439.67
8	0	7.64	5.08	2.22
8	0	7.54	6.20	2.58
8	250	20.76	53.87	33.75
8	250	24.82	40.82	29.53
8	500	42.93	95.40	60.05
8	500	39.71	109.24	60.86
8	1000	70.19	210.60	148.35
8	1000	85.77	222.94	135.54
8	2000	162.37	429.04	300.40
8	2000	178.45	473.00	304.11
16	0	4.07	1.00	3.53
16	0	3.43	1.25	2.25
16	250	24.47	38.44	32.05
16	250	15.39	40.47	33.27
16	500	47.81	101.40	65.55
16	500	38.59	103.57	71.88
16	1000	54.02	211.31	144.00
16	1000	48.89	208.48	146.25
16	2000	103.01	518.98	307.12
16	2000	87.17	471.26	291.62
32	0	3.09	-0.47	2.47
32	0	2.66	0.95	2.66
32	250	11.65	28.61	18.33
32	250	13.49	31.98	22.33
32	500	23.37	73.66	43.65
32	500	29.33	83.29	45.69

Kaiwiki Uncultivated Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	1000	59.36	162.94	103.46
32	1000	55.00	118.88	95.81
32	2000	156.68	380.11	216.85
32	2000	163.00	406.20	214.14
67	0	4.04	6.80	2.77
67	0	3.06	7.75	2.98
67	250	11.34	35.06	21.87
67	250	14.49	39.32	22.73
67	500	24.19	93.68	41.12
67	500	29.41	81.45	47.85
67	1000	59.82	177.36	101.92
67	1000	52.94	182.43	105.48
67	2000	159.42	418.72	244.75
67	2000	191.39	356.65	227.15
96	0	2.49	14.38	2.95
96	0	1.81	10.19	2.93
96	250	7.29	39.38	16.50
96	250	7.41	39.43	17.80
96	500	19.12	80.07	39.52
96	500	18.65	78.92	33.69
96	1000	37.79	169.50	76.42
96	1000	39.74	165.20	77.31
96	2000	118.65	373.27	174.96
96	2000	109.36	395.68	168.12
128	0	6.05	10.12	1.89
128	0	3.91	9.73	2.38
128	250	11.53	38.49	18.85
128	250	14.62	35.95	19.89
128	500	22.94	77.01	38.75
128	500	25.54	67.18	35.37
128	1000	55.16	138.44	85.21
128	1000	56.29	154.27	90.90
128	2000	138.22	298.47	190.44
128	2000	132.85	332.12	179.91
180	0	1.70	11.53	41.30
180	0	1.70	11.08	40.05
180	250	6.94	37.87	15.81
180	250	7.67	38.04	14.11
180	500	15.46	82.25	30.54
180	500	15.22	78.83	34.15
180	1000	31.03	155.55	76.51
180	1000	35.79	170.52	71.05
180	2000	82.21	374.21	162.92
180	2000	83.47	357.40	156.96

Kapaa Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	1.36	3.38	3.74
2	0	1.66	2.83	4.04
2	50	3.95	11.25	9.05
2	50	4.53	12.71	10.77
2	100	7.54	19.03	16.07
2	100	8.68	24.99	18.89
2	200	17.79	36.95	41.60
2	200	20.73	45.04	29.23
2	400	61.55	99.49	78.31
2	400	50.84	102.12	67.07
4	0	1.45	1.17	3.46
4	0	0.91	2.09	3.41
4	50	3.29	7.07	8.74
4	50	3.30	7.16	10.26
4	100	5.97	16.52	14.66
4	100	9.70	15.27	15.84
4	200	18.91	26.78	29.52
4	200	20.32	31.23	28.25
4	400	48.18	62.96	67.65
4	400	53.42	64.18	63.97
8	0	1.39	1.96	3.87
8	0	1.99	1.98	3.38
8	50	3.67	6.80	7.56
8	50	4.43	6.79	7.94
8	100	5.42	11.60	14.05
8	100	6.63	13.53	12.52
8	200	12.55	28.65	26.38
8	200	11.74	27.59	24.28
8	400	27.12	56.25	57.92
8	400	34.49	54.28	58.45
16	0	0.93	0.35	2.71
16	0	0.83	0.57	2.50
16	50	2.55	3.14	6.48
16	50	3.29	3.94	5.86
16	100	5.31	6.14	10.19
16	100	4.56	11.88	9.51
16	200	11.42	14.88	15.46
16	200	11.84	16.08	18.49
16	400	26.76	39.60	34.98
16	400	34.12	40.59	38.48
32	0	0.62	0.00	3.58
32	0	0.58	0.44	3.42
32	50	2.09	4.18	6.70
32	50	1.77	2.92	6.94
32	100	5.15	8.25	10.08
32	100	4.17	9.26	9.69

Kapaa Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	200	11.36	20.04	19.26
32	200	12.46	19.95	20.18
32	400	32.46	51.23	39.99
32	400	31.94	49.13	44.19
67	0	0.65	3.43	3.71
67	0	0.78	2.20	4.03
67	50	1.66	5.46	6.24
67	50	1.48	5.00	6.17
67	100	3.05	8.97	9.92
67	100	3.09	9.27	9.91
67	200	8.03	17.32	17.62
67	200	8.07	17.17	17.93
67	400	23.30	39.79	38.07
67	400	22.45	38.77	37.71
96	0	0.87	3.61	3.63
96	0	0.66	2.65	3.69
96	50	1.49	5.97	5.62
96	50	1.51	5.92	5.37
96	100	3.32	10.38	7.38
96	100	3.20	10.26	8.15
96	200	6.98	19.48	13.95
96	200	6.73	18.87	14.23
96	400	19.02	43.30	30.16
96	400	20.03	44.28	28.94
128	0	0.56	2.95	3.57
128	0	0.72	2.97	3.76
128	50	1.08	6.73	6.27
128	50	1.10	7.29	6.05
128	100	2.87	9.25	8.10
128	100	2.85	9.47	8.55
128	200	5.25	17.72	13.14
128	200	5.20	17.61	14.20
128	400	14.69	40.12	29.47
128	400	13.56	44.51	30.72
180	0	0.59	2.75	3.25
180	0	0.53	2.87	3.66
180	50	0.85	5.91	5.17
180	50	1.10	6.35	5.48
180	100	1.58	9.40	7.90
180	100	1.37	9.54	8.01
180	200	3.82	18.83	12.92
180	200	3.01	20.17	13.14
180	400	8.45	42.18	26.84
180	400	9.47	39.99	26.71

Maile Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	5.04	15.38	2.52
2	0	3.74	14.23	3.09
2	100	10.06	42.79	15.52
2	100	10.05	42.56	15.90
2	200	16.57	92.61	33.10
2	200	20.38	94.77	33.69
2	400	44.64	142.74	61.13
2	400	43.09	171.20	58.81
2	800	127.85	348.03	139.70
2	800	86.58	318.42	125.69
4	0	4.19	12.60	2.52
4	0	4.94	11.57	2.78
4	100	9.31	39.57	13.96
4	100	10.01	38.86	14.58
4	200	17.81	67.03	29.69
4	200	25.87	65.57	25.17
4	400	30.65	141.28	47.16
4	400	33.52	268.92	50.15
4	800	95.80	250.80	110.16
4	800	92.42	241.09	111.03
8	0	1.97	12.78	2.65
8	0	2.05	10.49	2.31
8	100	5.96	36.09	12.34
8	100	5.19	33.10	12.64
8	200	10.72	62.83	21.91
8	200	12.46	62.07	24.75
8	400	19.77	118.06	43.89
8	400	24.29	127.10	48.33
8	800	50.33	232.32	114.51
8	800	53.91	239.34	94.13
16	0	3.20	9.70	1.66
16	0	3.48	12.00	1.73
16	100	8.57	22.72	11.34
16	100	6.24	21.73	11.62
16	200	10.21	38.07	20.49
16	200	17.54	43.84	20.39
16	400	21.81	68.87	39.00
16	400	20.38	75.31	44.00
16	800	47.61	159.19	98.46
16	800	42.06	166.21	88.51
32	0	1.50	10.69	3.49
32	0	1.61	12.12	2.54
32	100	3.98	21.23	9.11
32	100	3.31	20.28	10.65
32	200	6.57	35.14	17.97
32	200	7.06	37.12	16.69

Maile Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	400	13.91	61.43	32.05
32	400	12.11	61.12	33.00
32	800	32.23	134.73	71.28
32	800	30.52	132.17	73.21
64	0	2.65	13.49	2.24
64	0	3.31	10.84	1.70
64	100	5.79	20.11	6.53
64	100	5.21	21.84	6.83
64	200	7.31	35.93	13.63
64	200	7.73	33.60	13.91
64	400	13.10	61.90	28.87
64	400	13.58	61.62	28.07
64	800	28.23	119.66	55.87
64	800	29.92	140.88	58.94
95	0	3.49	11.76	2.25
95	0	3.42	11.80	1.96
95	100	6.03	20.51	6.67
95	100	8.14	21.23	7.42
95	200	7.94	32.36	11.58
95	200	7.30	31.34	11.56
95	400	12.53	61.35	26.18
95	400	14.17	54.78	25.40
95	800	31.47	105.85	55.04
95	800	37.02	110.69	54.02
129	0	2.70	17.43	2.83
129	0	3.57	14.91	2.54
129	100	6.67	23.26	7.88
129	100	5.45	26.48	8.00
129	200	8.60	39.10	15.12
129	200	8.43	34.58	13.75
129	400	15.43	61.71	30.34
129	400	15.43	63.86	31.22
129	800	32.78	134.93	62.57
129	800	29.55	114.57	66.66
180	0	3.49	16.50	3.47
180	0	3.32	12.19	3.43
180	100	5.58	24.94	9.83
180	100	5.78	22.53	8.24
180	200	8.06	33.18	17.72
180	200	10.60	39.41	14.27
180	400	15.96	60.92	28.72
180	400	17.31	56.80	27.17
180	800	38.81	103.76	56.88
180	800	38.12	115.96	54.50

Makapili Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	0.23	8.17	0.89
2	0	0.23	7.54	0.92
2	50	1.84	19.35	4.58
2	50	0.72	18.59	4.88
2	100	2.03	28.35	9.22
2	100	1.77	31.34	9.35
2	200	7.50	54.49	20.55
2	200	8.53	51.19	19.55
2	400	16.55	99.47	48.85
2	400	18.23	107.40	45.60
4	0	0.25	7.32	0.69
4	0	0.30	8.23	1.09
4	50	1.23	18.40	4.13
4	50	1.39	16.71	4.43
4	100	2.20	29.52	7.94
4	100	2.62	25.81	8.24
4	200	4.74	44.42	16.32
4	200	4.74	48.42	16.65
4	400	16.30	103.16	41.36
4	400	15.88	97.04	41.69
8	0	0.67	8.48	1.11
8	0	0.35	7.04	1.19
8	50	0.73	16.80	4.29
8	50	0.86	14.54	3.92
8	100	1.59	20.96	7.58
8	100	1.46	21.89	7.58
8	200	3.90	37.16	15.17
8	200	4.81	38.54	16.15
8	400	12.51	73.94	37.53
8	400	10.94	80.69	37.64
16	0	0.38	6.56	0.54
16	0	0.50	6.31	0.61
16	50	0.69	11.34	2.79
16	50	0.60	13.75	2.93
16	100	1.05	15.82	5.58
16	100	1.11	16.23	5.49
16	200	2.67	29.17	12.56
16	200	2.85	28.32	11.85
16	400	5.07	57.83	30.93
16	400	5.81	53.57	31.49
32	0	0.15	6.93	0.53
32	0	0.24	5.93	0.75
32	50	0.54	11.27	2.23
32	50	0.47	9.55	2.42
32	100	1.03	16.31	4.81
32	100	1.17	15.62	4.71

Makapili Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	200	4.21	29.73	10.32
32	200	3.85	30.38	10.18
32	400	5.80	46.06	22.01
32	400	6.17	43.57	22.10
64	0	0.26	7.41	0.63
64	0	0.23	6.55	0.81
64	50	0.61	9.80	1.86
64	50	0.54	11.86	1.92
64	100	0.89	15.26	3.79
64	100	0.87	14.81	3.88
64	200	1.77	25.55	8.03
64	200	1.98	24.12	7.86
64	400	6.02	47.80	18.33
64	400	5.78	45.51	19.41
95	0	0.29	6.12	0.47
95	0	0.28	8.90	0.43
95	50	0.49	11.31	1.58
95	50	0.35	11.02	1.39
95	100	0.82	14.45	3.24
95	100	0.91	15.66	3.00
95	200	1.35	22.70	6.78
95	200	1.38	25.84	6.79
95	400	4.14	43.23	15.45
95	400	4.13	45.39	15.28
129	0	0.19	7.59	0.68
129	0	0.16	7.74	0.62
129	50	0.53	11.09	1.78
129	50	0.31	12.09	1.97
129	100	0.76	14.06	3.69
129	100	0.80	16.79	3.33
129	200	1.53	22.68	7.21
129	200	1.32	23.71	7.26
129	400	3.64	43.98	16.61
129	400	2.74	46.23	16.90
180	0	0.05	7.47	0.80
180	0	0.08	7.66	0.77
180	50	0.15	10.63	1.89
180	50	0.12	11.85	1.75
180	100	0.32	18.99	2.95
180	100	0.40	15.71	2.90
180	200	0.81	21.77	7.04
180	200	0.86	22.13	6.47
180	400	2.13	43.09	13.19
180	400	2.05	41.85	13.48

Molokai Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	45.65	152.18	27.45
2	0	47.56	160.26	28.03
2	25	58.41	181.05	37.77
2	25	56.92	164.63	38.08
2	50	60.92	251.37	47.55
2	50	57.87	180.26	47.80
2	100	77.61	223.01	69.71
2	100	83.36	222.11	70.88
2	200	135.45	294.63	118.58
2	200	133.29	299.15	113.29
4	0	44.44	145.96	26.43
4	0	45.32	148.38	26.10
4	25	53.80	172.64	37.60
4	25	53.61	157.36	37.67
4	50	60.91	173.98	45.74
4	50	60.96	186.72	46.75
4	100	86.86	211.15	70.16
4	100	86.11	204.34	69.92
4	200	126.89	272.32	119.24
4	200	128.60	298.88	113.99
8	0	43.27	179.51	28.57
8	0	42.72	143.98	27.29
8	25	50.13	175.60	36.57
8	25	51.27	179.83	36.29
8	50	58.20	177.53	44.70
8	50	60.59	171.54	46.31
8	100	72.14	204.59	64.41
8	100	73.79	198.18	65.06
8	200	130.53	269.64	105.77
8	200	120.72	269.67	104.26
16	0	43.75	153.77	26.97
16	0	42.74	133.44	26.83
16	25	43.64	157.37	34.79
16	25	43.67	151.80	36.22
16	50	60.52	170.23	44.83
16	50	57.39	157.15	43.86
16	100	76.50	178.25	62.09
16	100	68.63	163.39	62.37
16	200	107.22	243.43	98.62
16	200	106.77	224.27	97.18
32	0	35.06	125.76	27.02
32	0	39.22	140.36	26.64
32	25	47.62	140.79	33.14
32	25	45.73	151.72	33.18
32	50	50.33	163.87	44.03
32	50	52.39	161.37	42.42

Molokai Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	100	54.50	164.60	53.11
32	100	55.30	189.71	55.54
32	200	105.82	227.40	88.08
32	200	100.56	221.69	93.66
64	0	35.16	134.00	24.67
64	0	45.77	127.64	25.44
64	25	51.97	135.02	31.17
64	25	41.90	135.52	30.62
64	50	52.75	154.60	37.05
64	50	57.66	168.13	36.81
64	100	60.55	178.88	51.94
64	100	65.71	203.35	50.89
64	200	100.10	244.78	80.52
64	200	99.61	244.27	80.41
95	0	38.38	157.44	25.33
95	0	40.27	163.34	24.37
95	25	45.34	183.39	28.65
95	25	45.26	164.69	30.24
95	50	51.68	163.83	34.73
95	50	54.39	163.09	33.89
95	100	65.83	196.41	47.24
95	100	63.57	196.26	48.10
95	200	96.79	275.51	70.94
95	200	93.71	252.99	73.22
129	0	38.75	155.20	27.45
129	0	40.39	149.70	27.72
129	25	47.37	176.71	33.95
129	25	46.51	155.77	33.45
129	50	53.58	168.18	40.82
129	50	54.39	175.53	39.98
129	100	68.03	198.25	53.12
129	100	61.70	198.73	53.65
129	200	95.31	246.42	77.97
129	200	100.81	244.29	81.43
180	0	34.26	158.13	26.01
180	0	40.56	168.55	26.31
180	25	39.41	150.35	32.08
180	25	39.28	156.83	31.90
180	50	44.60	177.91	36.24
180	50	48.41	168.54	36.92
180	100	56.19	201.76	47.90
180	100	58.35	194.17	48.44
180	200	88.38	264.20	76.82
180	200	88.04	275.33	75.23

Pulehu Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	68.76	229.76	56.92
2	0	82.96	229.33	56.34
2	25	65.88	212.78	67.07
2	25	70.57	246.74	64.39
2	50	86.91	243.42	82.08
2	50	83.32	246.57	77.44
2	100	103.15	276.08	97.52
2	100	98.62	301.28	93.52
2	200	126.73	322.95	136.48
2	200	130.66	325.56	135.93
4	0	84.97	201.19	60.49
4	0	78.64	209.28	56.99
4	25	78.33	227.04	66.24
4	25	77.45	238.01	64.68
4	50	97.43	234.49	75.87
4	50	95.32	233.51	80.80
4	100	100.94	253.14	94.16
4	100	104.51	278.40	93.89
4	200	125.98	327.73	133.15
4	200	137.36	301.10	128.37
8	0	69.82	209.97	57.20
8	0	73.01	217.10	56.88
8	25	72.06	218.08	63.29
8	25	62.91	231.52	66.31
8	50	74.92	243.26	71.67
8	50	75.54	238.73	71.36
8	100	96.69	245.08	82.75
8	100	87.34	284.03	84.02
8	200	107.46	275.25	114.75
8	200	105.27	304.61	112.82
16	0	52.54	157.85	55.68
16	0	55.64	158.25	53.29
16	25	65.91	226.14	61.77
16	25	59.62	177.89	62.67
16	50	64.48	146.66	70.29
16	50	72.75	188.44	70.74
16	100	73.56	210.54	83.67
16	100	84.89	214.36	80.80
16	200	93.87	224.86	115.97
16	200	106.57	236.56	116.15
32	0	56.04	126.38	53.26
32	0	49.90	111.23	53.26
32	25	68.52	154.49	61.74
32	25	63.17	188.09	61.35
32	50	57.99	177.07	65.24
32	50	61.98	187.42	66.23

Pulehu Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	100	73.72	163.46	77.43
32	100	58.77	165.79	75.51
32	200	70.88	204.22	99.51
32	200	87.32	201.64	100.74
64	0	71.57	165.31	50.67
64	0	67.11	166.10	52.08
64	25	68.70	182.18	55.06
64	25	69.94	166.88	58.49
64	50	77.11	197.29	63.29
64	50	77.94	198.48	62.20
64	100	79.78	195.46	74.00
64	100	78.29	184.28	73.45
64	200	97.42	252.53	95.57
64	200	99.15	241.33	94.55
95	0	56.09	184.69	46.09
95	0	54.31	203.88	46.16
95	25	59.66	168.16	49.73
95	25	60.16	201.15	49.83
95	50	60.04	201.91	56.25
95	50	61.69	196.19	55.67
95	100	80.05	205.62	66.43
95	100	71.70	246.53	65.78
95	200	88.56	232.93	83.07
95	200	83.62	233.66	83.08
129	0	58.02	179.16	56.78
129	0	53.05	163.30	58.44
129	25	56.45	171.83	63.05
129	25	56.87	186.21	64.23
129	50	66.63	167.31	67.92
129	50	64.30	179.12	70.33
129	100	70.63	198.81	79.68
129	100	66.16	256.57	80.13
129	200	90.69	220.76	102.41
129	200	91.52	265.10	101.99
180	0	45.92	188.56	51.52
180	0	48.96	165.86	52.34
180	25	49.62	220.10	56.32
180	25	51.27	187.41	55.39
180	50	48.93	154.17	60.94
180	50	47.32	179.06	59.99
180	100	52.36	170.09	71.50
180	100	54.55	186.44	70.70
180	200	71.67	241.77	88.80
180	200	71.05	227.53	88.07

Wahiawa Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	0.49	4.78	1.53
2	0	0.79	5.42	1.33
2	50	6.24	19.85	11.57
2	50	7.19	14.24	12.50
2	100	13.84	24.93	23.43
2	100	14.79	27.93	24.62
2	200	45.63	69.66	55.86
2	200	43.44	61.68	56.26
2	400	102.03	154.36	137.96
2	400	95.88	165.29	118.47
4	0	0.82	5.41	0.97
4	0	0.47	6.93	1.21
4	50	7.89	15.75	10.07
4	50	9.08	17.18	10.58
4	100	14.58	30.53	22.45
4	100	14.97	28.77	21.69
4	200	40.44	53.58	51.59
4	200	40.84	53.04	51.06
4	400	83.55	117.31	122.45
4	400	95.41	111.72	121.77
8	0	1.58	4.06	1.03
8	0	1.17	4.35	1.51
8	50	6.12	12.63	9.28
8	50	6.34	16.04	8.83
8	100	12.67	27.97	19.80
8	100	11.62	25.69	18.32
8	200	28.18	48.23	44.07
8	200	33.03	65.01	45.13
8	400	67.26	115.09	99.68
8	400	75.22	121.71	95.30
16	0	0.93	2.20	0.94
16	0	0.91	3.11	0.89
16	50	5.19	11.47	7.23
16	50	5.38	10.10	7.94
16	100	10.63	22.34	18.67
16	100	10.32	19.77	17.62
16	200	17.10	45.53	43.12
16	200	12.45	46.33	40.43
16	400	28.15	106.45	89.48
16	400	40.31	114.06	90.66
32	0	0.24	1.85	0.69
32	0	0.39	2.27	0.85
32	50	3.54	11.39	4.97
32	50	2.96	10.63	5.06
32	100	7.26	23.95	9.49
32	100	4.87	20.82	10.35

Wahiawa Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	200	20.77	44.36	23.40
32	200	23.81	44.35	24.32
32	400	43.92	105.87	57.68
32	400	37.72	105.12	60.75
67	0	0.57	6.06	0.81
67	0	0.71	3.61	1.09
67	50	3.20	9.84	4.85
67	50	3.51	10.56	4.90
67	100	8.27	20.60	11.05
67	100	8.11	20.64	10.89
67	200	20.11	37.96	25.84
67	200	21.16	39.37	26.63
67	400	61.30	83.31	65.54
67	400	60.94	85.60	66.97
96	0	0.79	5.50	1.32
96	0	0.67	5.43	1.12
96	50	2.84	11.66	4.58
96	50	3.08	13.33	4.36
96	100	7.61	22.54	9.29
96	100	7.04	22.85	9.82
96	200	19.78	43.31	23.91
96	200	21.73	45.23	24.11
96	400	52.94	98.49	59.42
96	400	58.27	100.93	58.82
128	0	0.58	4.48	0.96
128	0	0.55	6.28	0.74
128	50	2.72	14.06	3.79
128	50	2.65	15.03	3.84
128	100	5.65	23.53	8.67
128	100	5.57	22.65	9.13
128	200	16.04	45.39	21.21
128	200	16.61	46.15	21.32
128	400	49.80	105.93	55.97
128	400	47.07	106.80	55.90
180	0	0.40	6.54	0.65
180	0	0.46	5.36	0.85
180	50	1.99	14.95	4.25
180	50	2.41	16.39	4.17
180	100	5.86	26.60	9.12
180	100	6.54	24.18	9.08
180	200	14.14	46.78	20.70
180	200	13.34	47.74	19.96
180	400	36.88	100.89	58.26
180	400	42.47	104.33	57.24

Waialua Soil

Day	P_{app}	Meh-3	M-Tr	Olsen
2	0	13.53	39.14	56.82
2	0	16.98	39.95	56.04
2	25	20.66	51.21	57.94
2	25	16.94	76.75	61.02
2	50	21.85	72.34	78.67
2	50	25.67	98.15	74.33
2	100	61.12	130.24	90.64
2	100	58.36	116.64	97.94
2	200	81.23	85.52	136.60
2	200	61.06	127.47	147.72
4	0	14.52	62.86	66.20
4	0	41.04	65.04	65.08
4	25	42.46	66.38	67.61
4	25	36.45	55.41	70.46
4	50	29.15	81.19	78.31
4	50	56.34	70.19	77.70
4	100	77.40	83.86	98.70
4	100	52.43	83.99	103.63
4	200	47.61	91.63	108.46
4	200	72.62	63.93	126.82
8	0	13.76	103.53	54.35
8	0	21.06	84.35	54.76
8	25	22.84	108.25	62.57
8	25	29.55	137.28	62.89
8	50	19.30	114.25	63.60
8	50	28.08	123.69	63.84
8	100	34.77	143.53	74.64
8	100	45.35	147.61	75.69
8	200	51.37	150.35	102.53
8	200	66.05	159.81	106.53
16	0	9.01	60.48	36.47
16	0	15.79	117.52	55.58
16	25	7.85	126.05	45.64
16	25	14.12	118.96	53.21
16	50	11.70	109.27	61.15
16	50	21.11	107.64	65.41
16	100	24.08	113.39	83.90
16	100	10.26	128.57	82.06
16	200	18.02	123.19	75.15
16	200	33.79	142.82	114.89
32	0	7.38	125.16	54.27
32	0	7.60	131.66	49.95
32	25	7.00	120.85	48.82
32	25	7.37	111.41	53.34
32	50	6.56	138.43	49.19
32	50	6.96	141.57	62.36

Waialua Soil (Continued)

Day	P_{app}	Meh-3	M-Tr	Olsen
32	100	9.21	121.32	70.41
32	100	10.80	164.31	71.44
32	200	11.83	182.87	88.51
32	200	13.68	183.72	84.69
67	0	16.80	156.43	57.64
67	0	18.07	155.57	58.91
67	25	20.56	163.34	64.02
67	25	19.82	158.73	65.07
67	50	22.65	169.60	69.26
67	50	21.58	163.46	71.33
67	100	29.98	186.89	80.26
67	100	30.31	196.52	80.84
67	200	43.87	244.55	110.45
67	200	41.81	242.40	109.76
96	0	28.00	163.04	56.75
96	0	26.85	168.57	54.59
96	25	28.47	161.60	58.84
96	25	27.87	167.40	58.79
96	50	30.05	174.58	61.63
96	50	27.63	175.31	62.52
96	100	38.85	192.70	76.95
96	100	39.40	197.13	75.63
96	200	48.01	242.70	96.13
96	200	51.77	248.08	98.25
128	0	22.84	175.66	54.45
128	0	23.35	173.87	52.78
128	25	21.47	175.26	56.99
128	25	21.70	173.43	57.61
128	50	30.58	186.71	62.09
128	50	31.67	187.75	62.94
128	100	35.60	204.66	73.62
128	100	36.05	211.81	73.83
128	200	50.18	265.58	96.71
128	200	47.94	265.72	96.77
180	0	23.47	170.42	58.15
180	0	26.21	173.48	57.58
180	25	28.60	168.67	61.57
180	25	28.21	174.95	62.42
180	50	29.14	182.88	65.90
180	50	27.54	180.48	68.40
180	100	36.15	209.12	77.88
180	100	34.23	218.71	76.54
180	200	54.21	278.34	98.87
180	200	53.35	273.78	101.97

Appendix B

Mineralogical Analysis

Introduction

Rietveld Refinement: Rietveld refinement of X-ray diffraction (XRD) patterns employs an *ab initio* approach to generating a synthetic pattern that is fit to an observed pattern by way of least-squares approximations. Starting with the crystal structure of each phase, the Miller indices (hkl) of all possible diffraction lines within a chosen angular range are calculated. Then on the bases of the scattering factors of the atoms defining each hkl line a structure factor (theoretical intensity) for each line is found. The resulting synthetic diffraction pattern for each phase is based on the initial (approximately correct) atomic coordinates, unit cell size and shape, occupancy of atoms, and the Debye-Weller temperature factors. The actual refinement process is, therefore, a repetitive adjustment of the starting parameters until the synthetic diffraction pattern fits the observed pattern to within a reasonably small error, expressed as a chi-square. At the conclusion of the refinement process, the new (refined) parameters accurately describe the crystal structure of the experimental phase.

In samples containing two or more phases, when possible, each phase is refined separately, at least to a satisfactory approximation if "standard" minerals are available. An example of a "standard" mineral might be a goethite that is highly substituted by aluminum. The refinement process also involves a scale factor for each phase in samples containing more than one phase. The scale factors not only control the intensities of the peaks for each phase but are also proportional to the quantity of each phase present. In summary, the Rietveld refinement process produces a new (refined) set of crystallographic parameters and quantitatively determines the percentages of each phase in a mixture.

Siroquant for Windows was used to quantify the mineral content for the soils used in this research (Sietronics Pty. Ltd., 1993). Siroquant is a computer program that utilizes the Rietveld method to calculate and then refine an X-ray pattern. The calculated pattern is refined untill a suitable reproduction of an observed X-ray diffraction pattern is obtained. The resulting parameters from the calculated pattern provide information about the quantity and crystal structure of each mineral (Taylor, 1991; Rietveld, 1969). The following is a description of the procedure used to refine the calculated pattern for each soil followed by plots of the observed and calculated patterns. Results of the percentage of each mineral found in the samples are in Table 4.5.

Refinement procedure using Siroquant for Windows

1. The computer files for the X-ray diffraction patterns were reformated to match the format required by Siroquant. A fortran program written by Dr. R. C. Jones was used to reformat the files generated from the X-ray diffractometer.

2. HKL files were generated in Siroquant for each of the minerals identified in the X-ray diffraction pattern. Unoriented files were made for each mineral, except for the minerals goethite and kaolin. The oriented plane choosen is usually a reflection which is enhanced (for plate-like crystals) or diminished (for rod-like crystals) by the preferred orientation of the crystal in the prepared sample.

    a) HKL files for goethite were oriented on the 001 face as recommended by Fazey et al. (1991) in order to obtain a better fit.

    b) For the Kaiwiki and Maile soils the kaolin HKL file was oriented on the 020 HKL reflection. These soils produced a 020 peak common to phyllosilicates but did not produce a 001 peak. The orientation would enhance the 020 peak and not produce a 001 peak. (see note 1).

3. A task file was created for each soils XRD pattern with HKL files for each mineral identified in the sample.

4. Prior to refinement, the background is removed from the observed XRD pattern. This was done by visually selecting points along the base of the peaks to yield a level pattern with approximately zero intensity along the base line.

5. The first refinement stage was an automatic pre-scale. This adjusts the relative scales for each of the minerals from their default value.

6. The second stage was a further refinement of the scale factors and the instrumental zero offset, usually at higher dampening values up to 0.8 and with 6 cycles.

7. The W parameter was refined seperately for the minerals with the largest peaks (generally peaks with 25 to 100% maximum intensity). Several alternating refinement stages between the scale factor and W parameter at 6 cycles and dampening value at 0.8 per stage were run till there was no longer improvement in the chi-squared value. Each stage was usually set to refine one parameter for one mineral unless two or more minerals had no overlapping peaks that would allow the refinement of one to interact with the another.

8. The unit-cell dimensions were refined to align the calculated peaks with the major peaks of the observed pattern (see note 2) ie., only the minerals which have had their scale and W parameters refined thus far.

9. The scale and W parameters were again refined for these minerals to adjust for the shift in peak positions.

10. Upon obtaining the best fit from refining the scale, W and unit cell dimensions, the scale, W and unit cell dimensions were then refined for the minerals with only minor peaks. Each parameter and mineral was usually refined individually due to overlapping of peaks.

11. Subsequent refinement focused on obtaining the best fit visually for the predominant and most isolated peak of each mineral. Again further refinement of scale, W and unit cell dimensions were sometimes necessary. At this point parameter values were adjusting manually to obtain the desired change in the calculated pattern. Once these parameter refinements showed no further improvement, refinement was done on the Pearson M shape factor if needed. Pearson M values near one represent Lorentzian (long tail) curves and values from two to ten represent Gaussian (sharp peak) curves.

12. For oriented mineral files, the Preferred Orientation factor was refined to adjust the relative intensities among the peaks for that mineral.

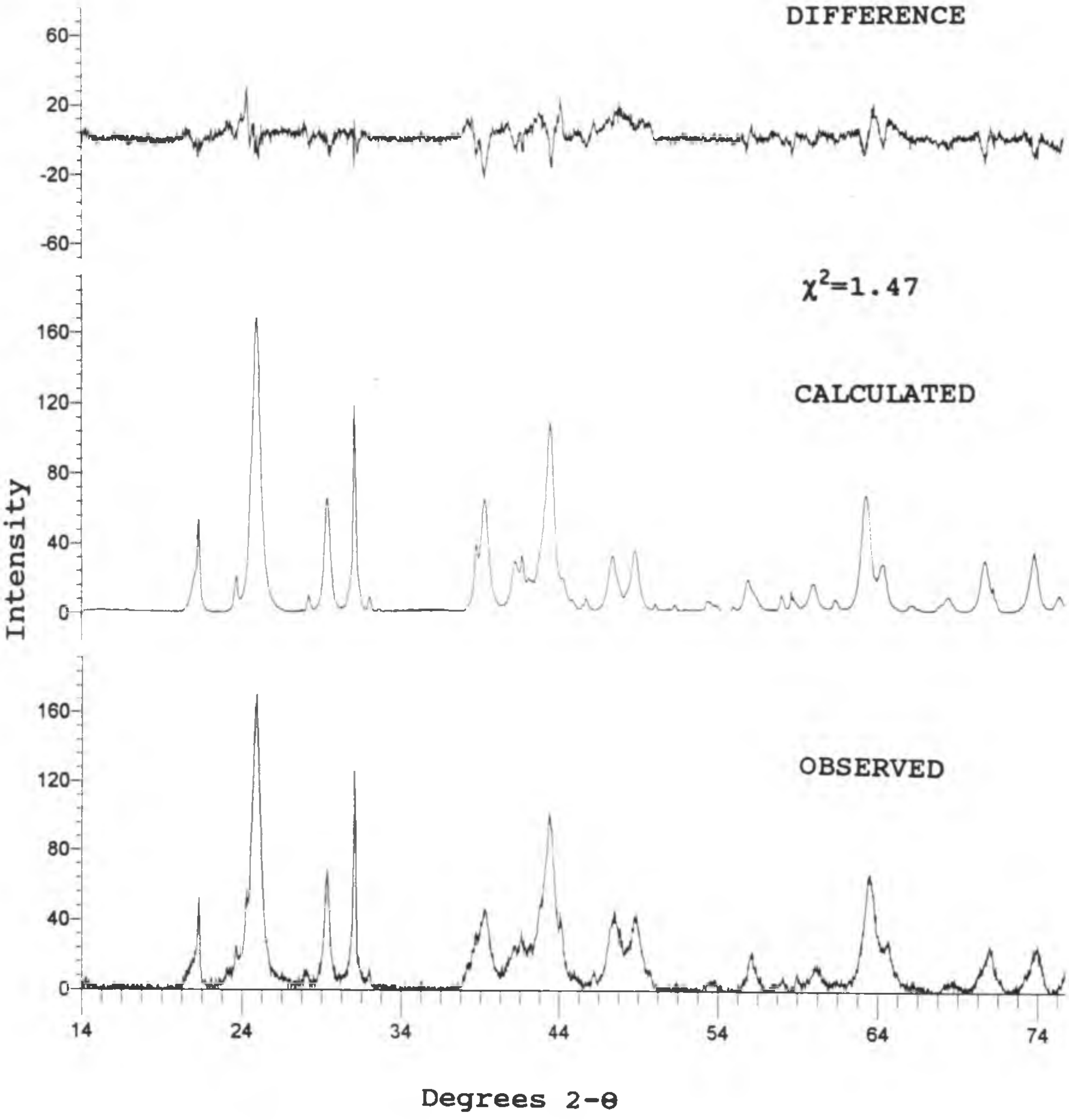
13. Upon achieving the best fit possible as indicated by visual examination of the important peaks for each mineral and by the χ^2 value for the whole curve (see note 3), the percentages and parameter values for each mineral can be obtained from the results file. To account for the amount of amorphous material in the sample, the laboratory data for oxalate extractable soil material was entered into the global parameters for the percentage of "non-diffracting material".

Note 1: Silicate clays pose a problem in that these minerals generate a strong 020 peak as a result of turbostacking, which is not represented in the HKL files generated from mineral structure data. Accurate determination of the layered silicate clays shows some difficulties due to the effects of this stacking disorder on the diffraction pattern (Bish, 1993). The Rietveld approach does not simulate these effects well and this must be taken into consideration when these minerals are present in the samples.

Note 2: The refinement works best when the peaks for each mineral in the pattern are well understood with respect to which hkl plane it represents and thus how changes in unit cell dimensions affect each peak. Refinement of the unit cell dimensions determines the size of the unit cells making up that particular mineral in the sample. These changes in dimensions from the reference size inidicate elemental substitution and structural differences for the mineral.

Note 3: The predominant concern to keep in mind during the refinement process is the affect overlapping peaks have on the parameter refinement. Refinement works best when focused on isolated peaks. Overlapping peaks can promote the parameters of one mineral to be adjusted for the intensities generated by another, thus causing erroneous results. The refinement averages out the differences in regions of overlapping peaks and may cause a less accurate representation of each mineral. This occurs primarily with the presence of goethite or kaolin minerals as they have many small peaks that the HKL files do not fit well to begin with. Thus, the parameters of other minerals overlapping with these peaks will be adjusted in an attempt to make up the difference between the calculated and observed patterns.

HALII SOIL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OBSERVED
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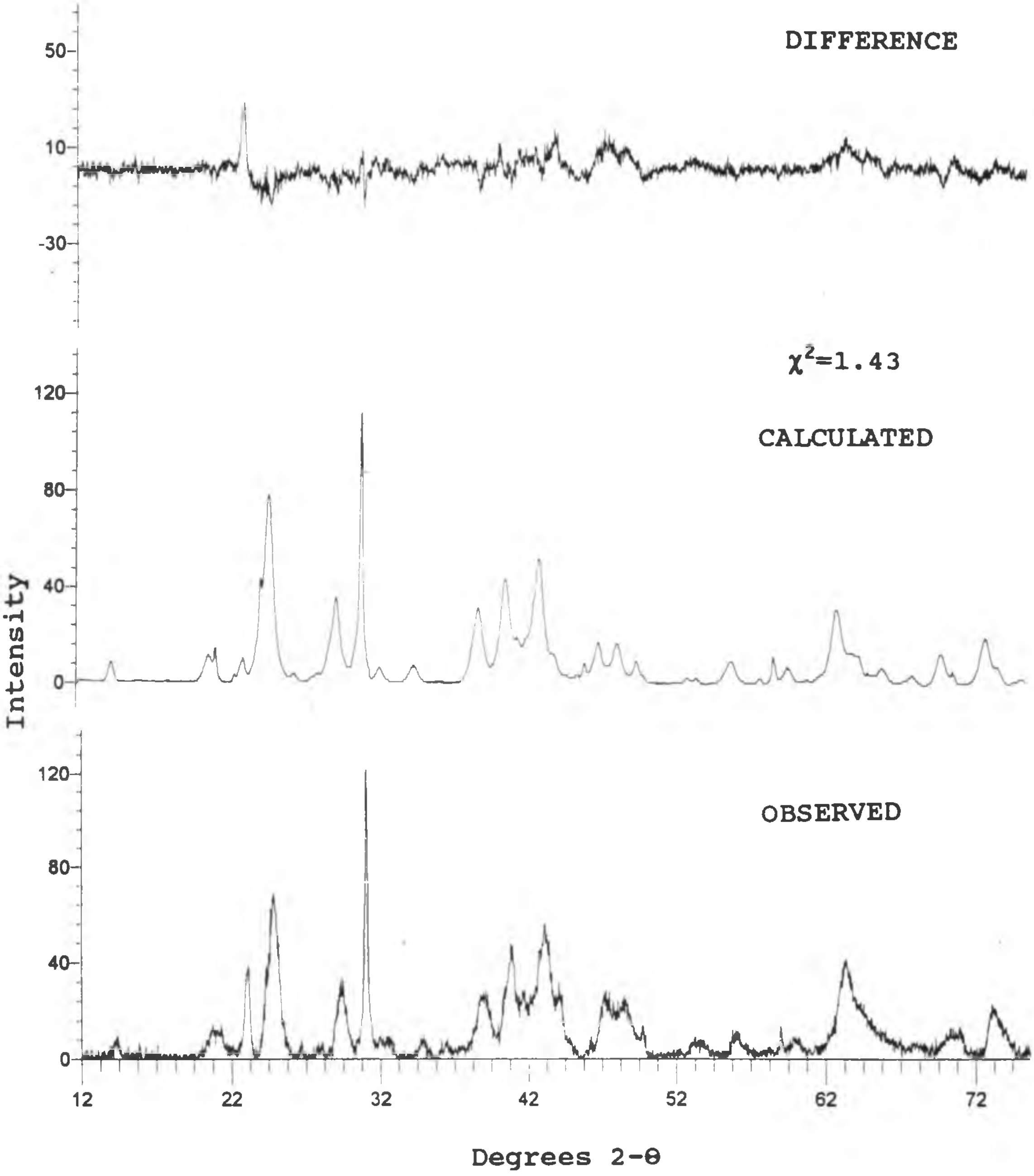
20
-20
-60
160
120
80
40
0
160
120
80
40
0
14
24
34
44
54
64
74
Degrees 2-θ

HAIKU SOIL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-30
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CALCULATED
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Intensity
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80
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52
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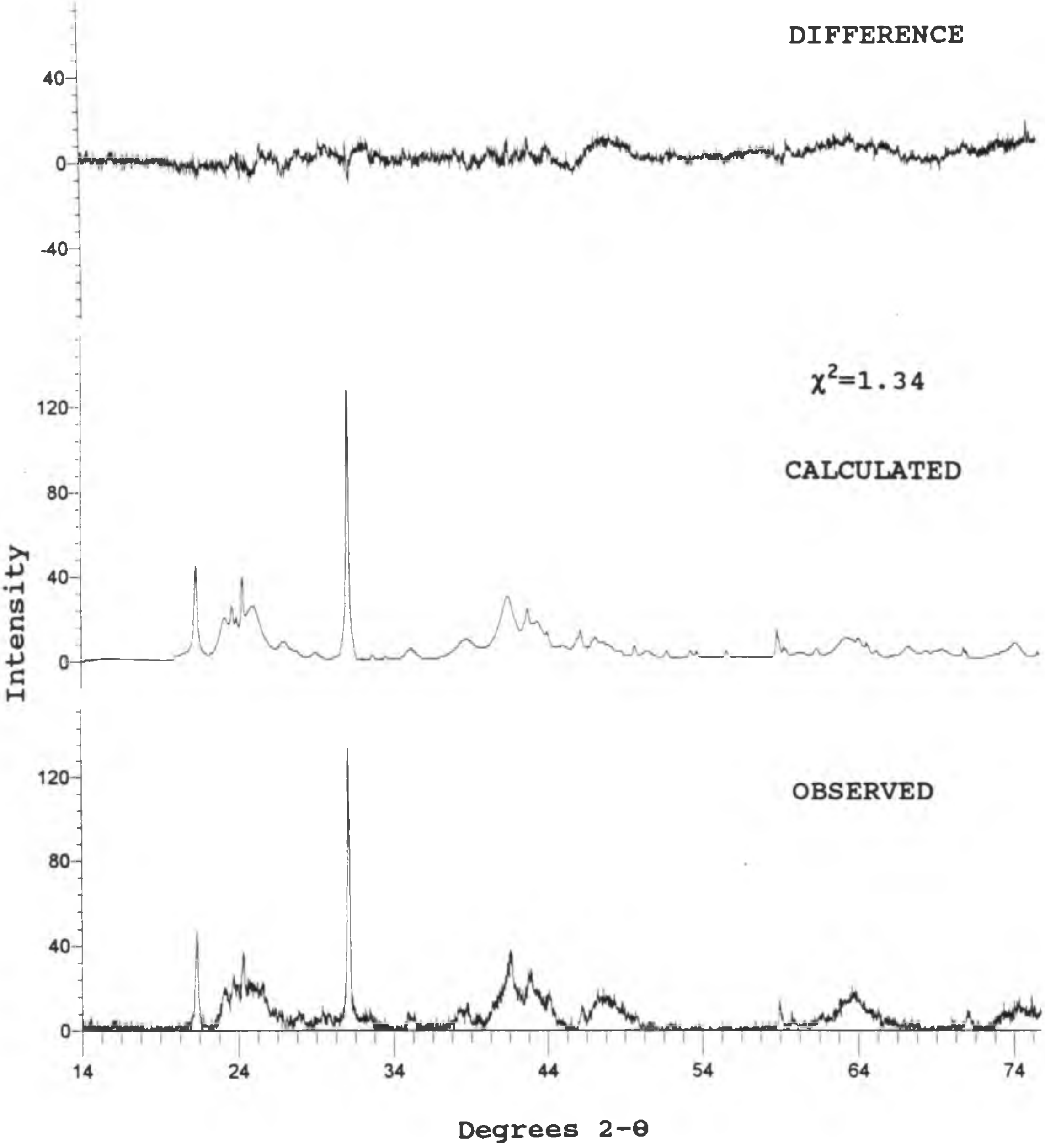
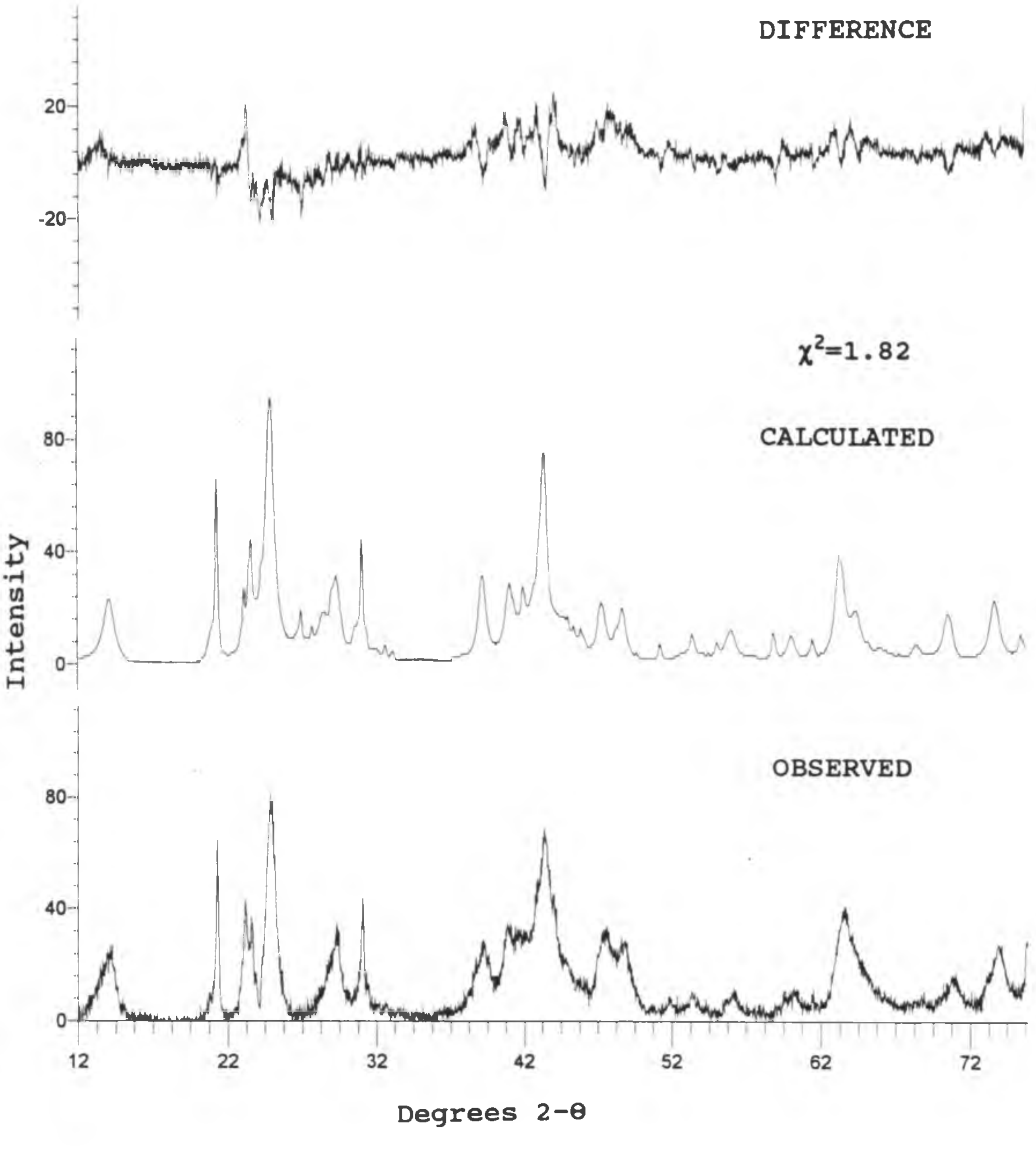
72
Degrees 2-θ

KAIWIKI SOIL



KAPAA SOIL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Intensity
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80
40
0
12
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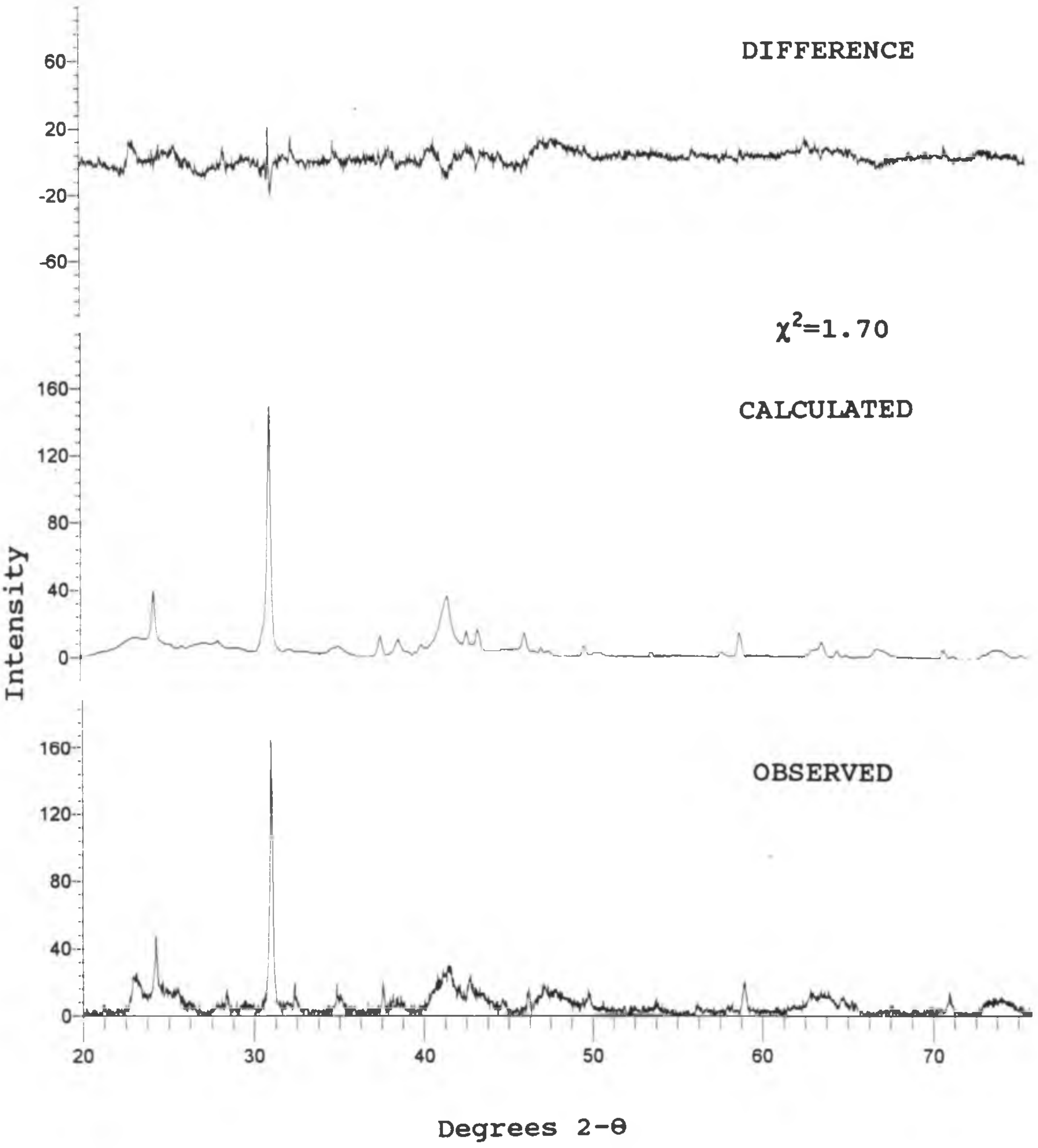
62
72
Degrees 2-θ

MAILE SOIL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120
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40
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Intensity
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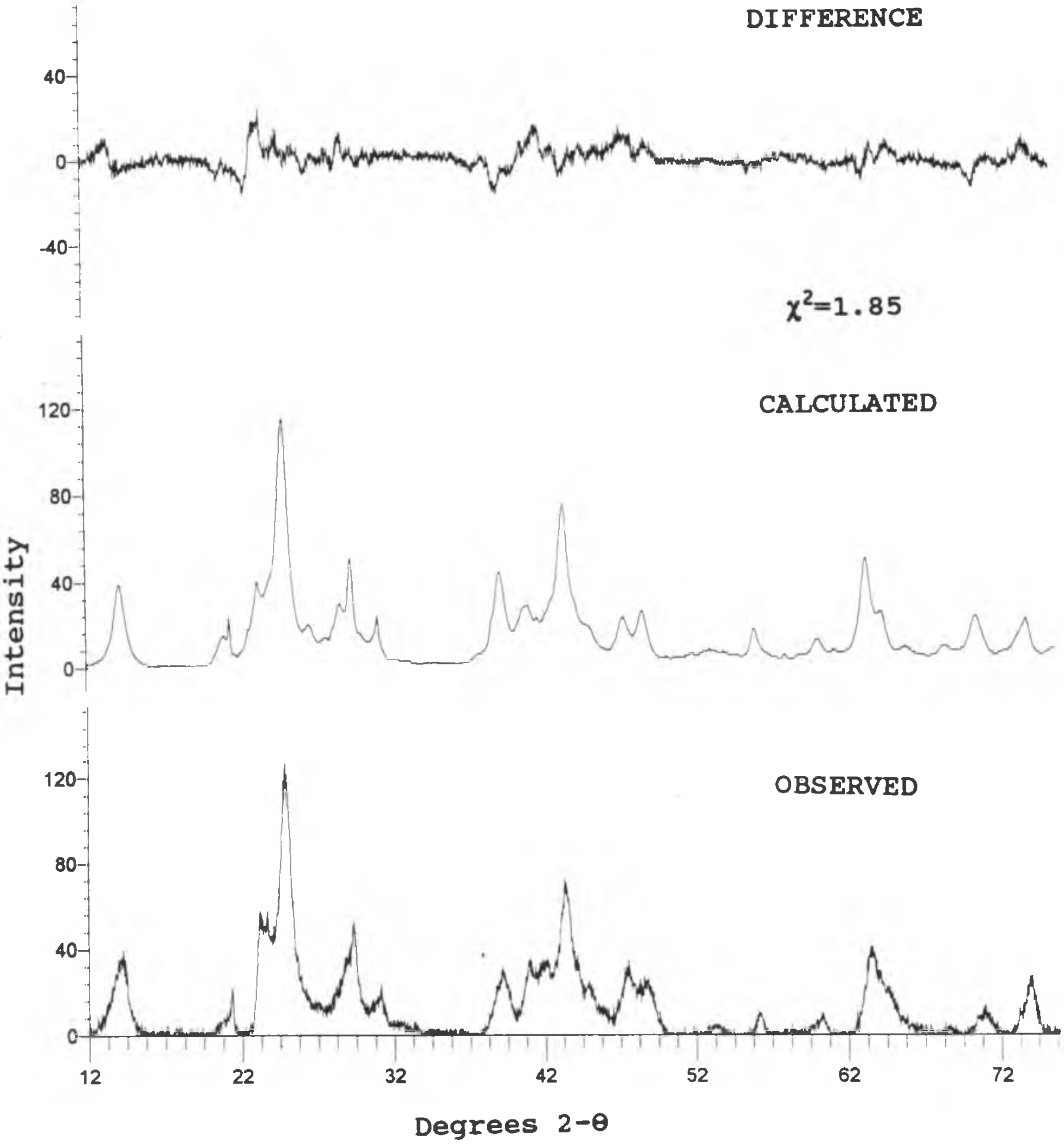
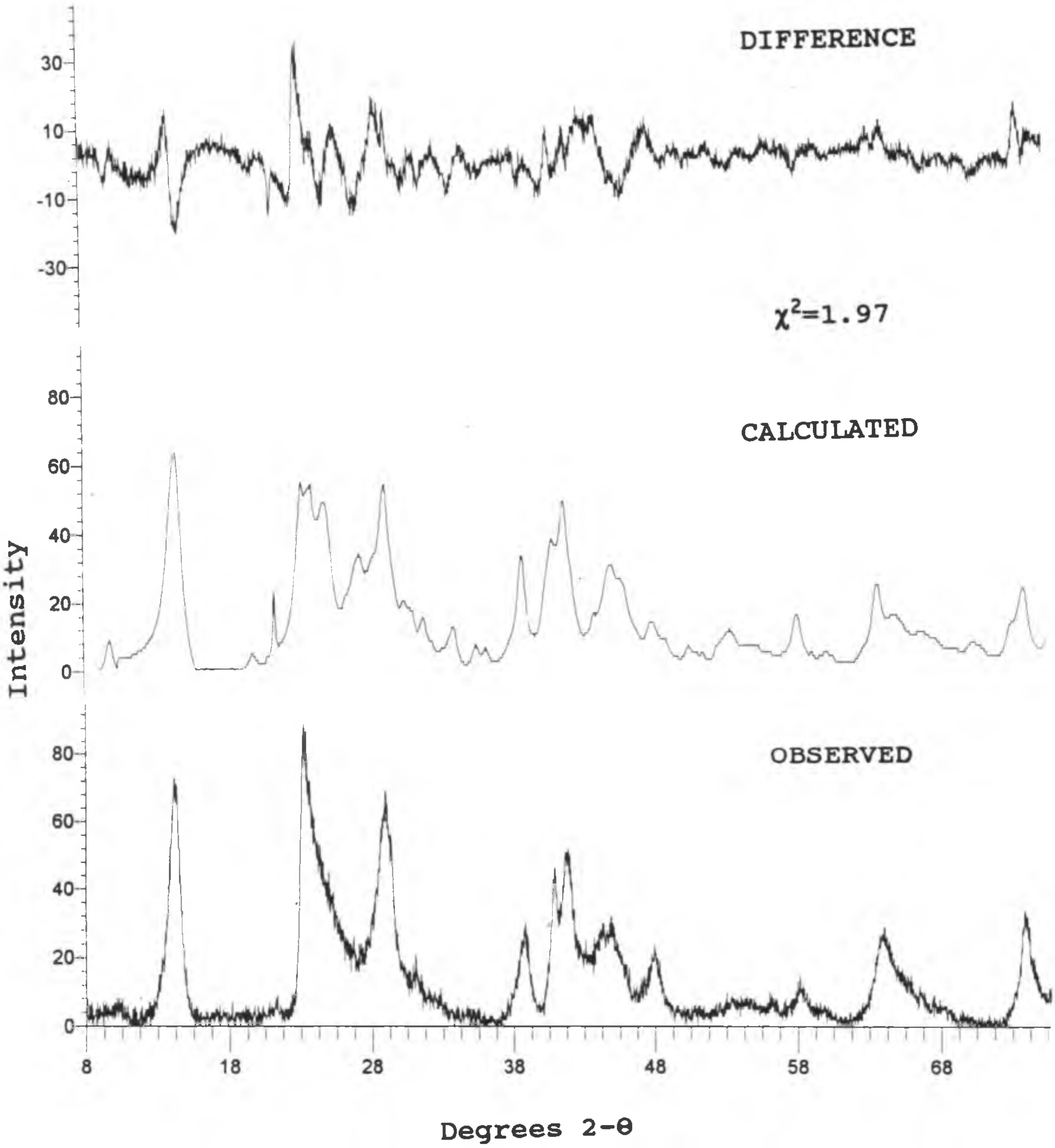
120
80
40
0
20
30
40
50
60
70
Degrees 2-θ

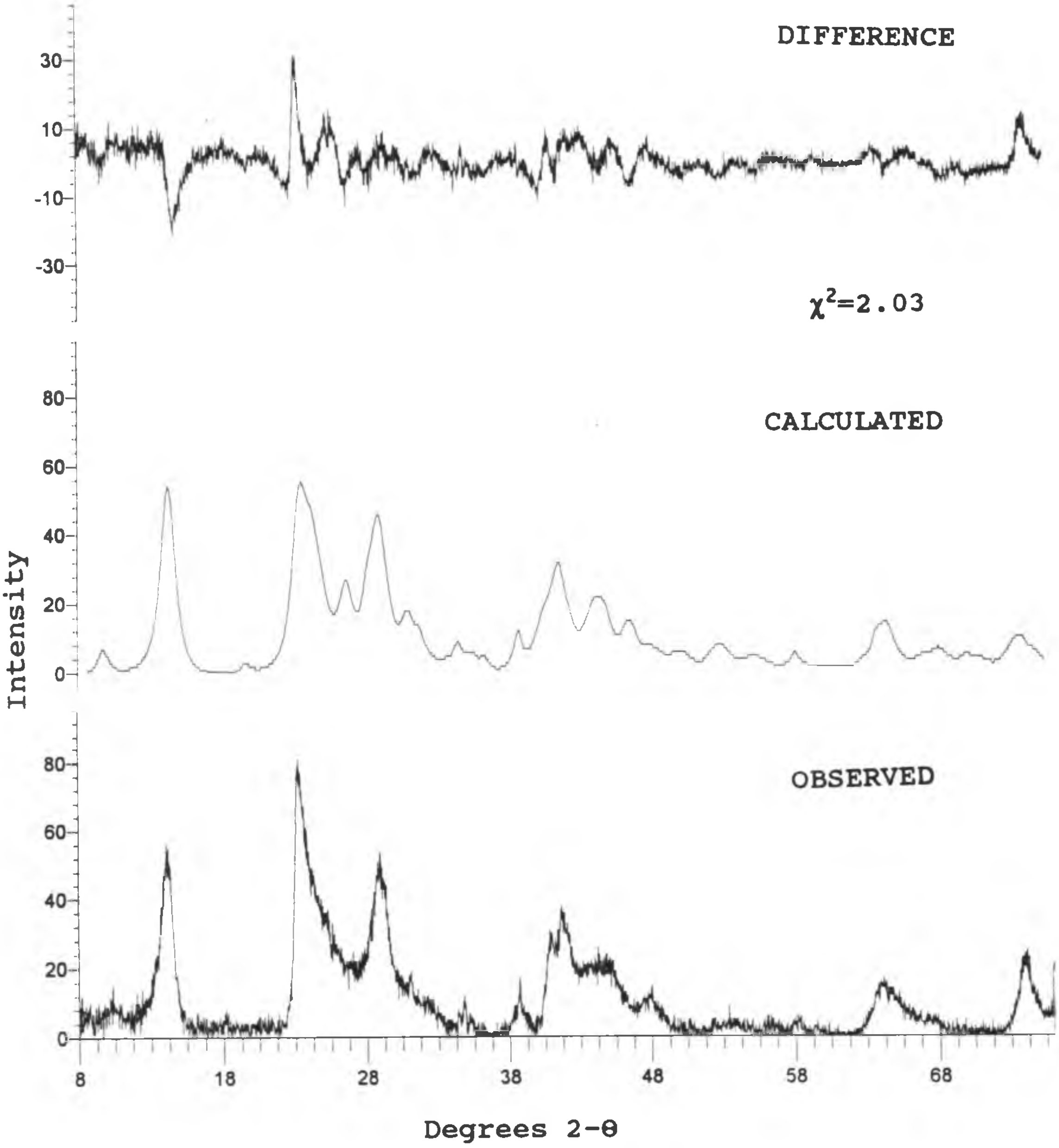
MAKAPILI SOIL



MOLOKAI SOIL



PULEHU SOIL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60
40
20
0
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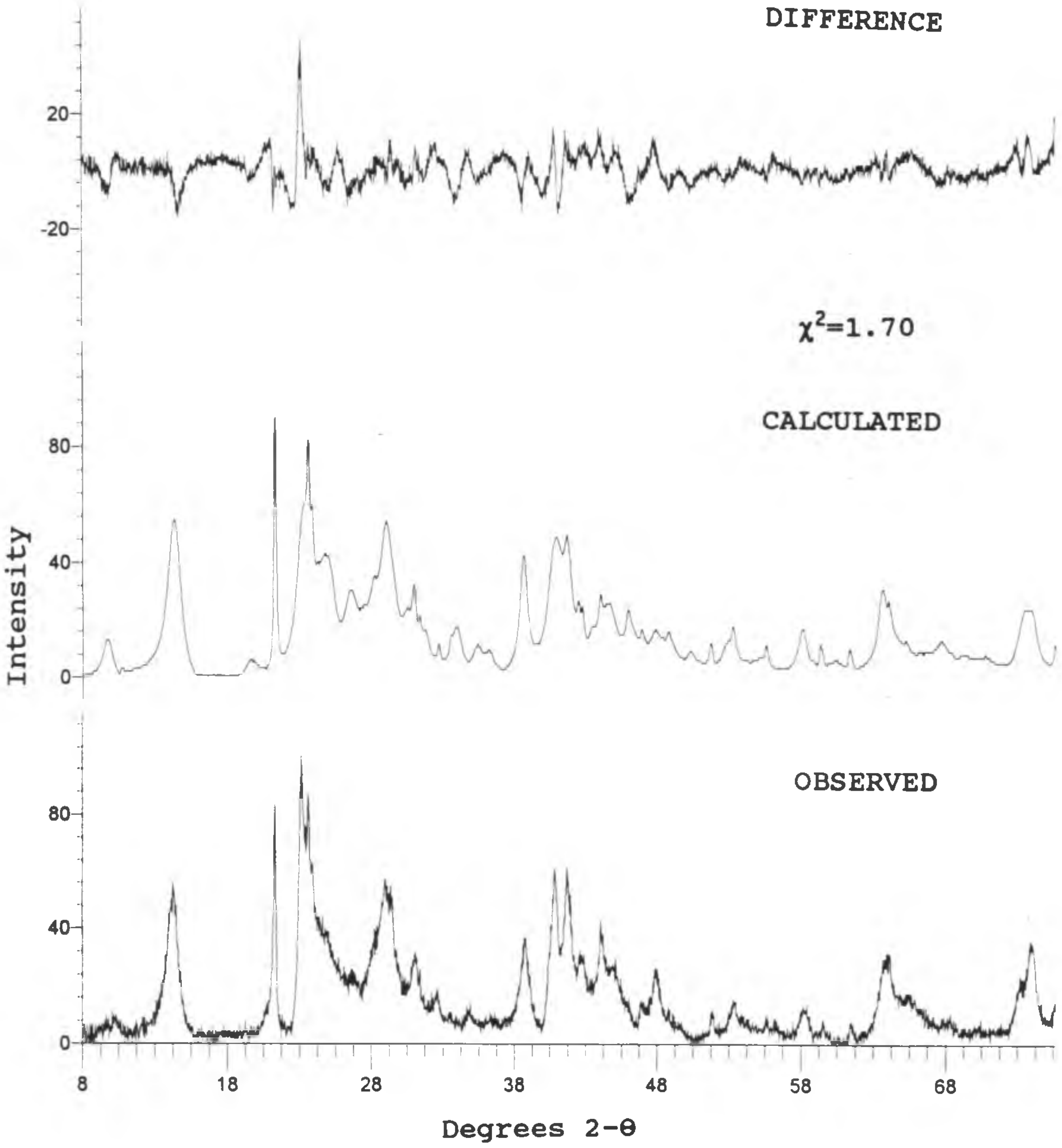
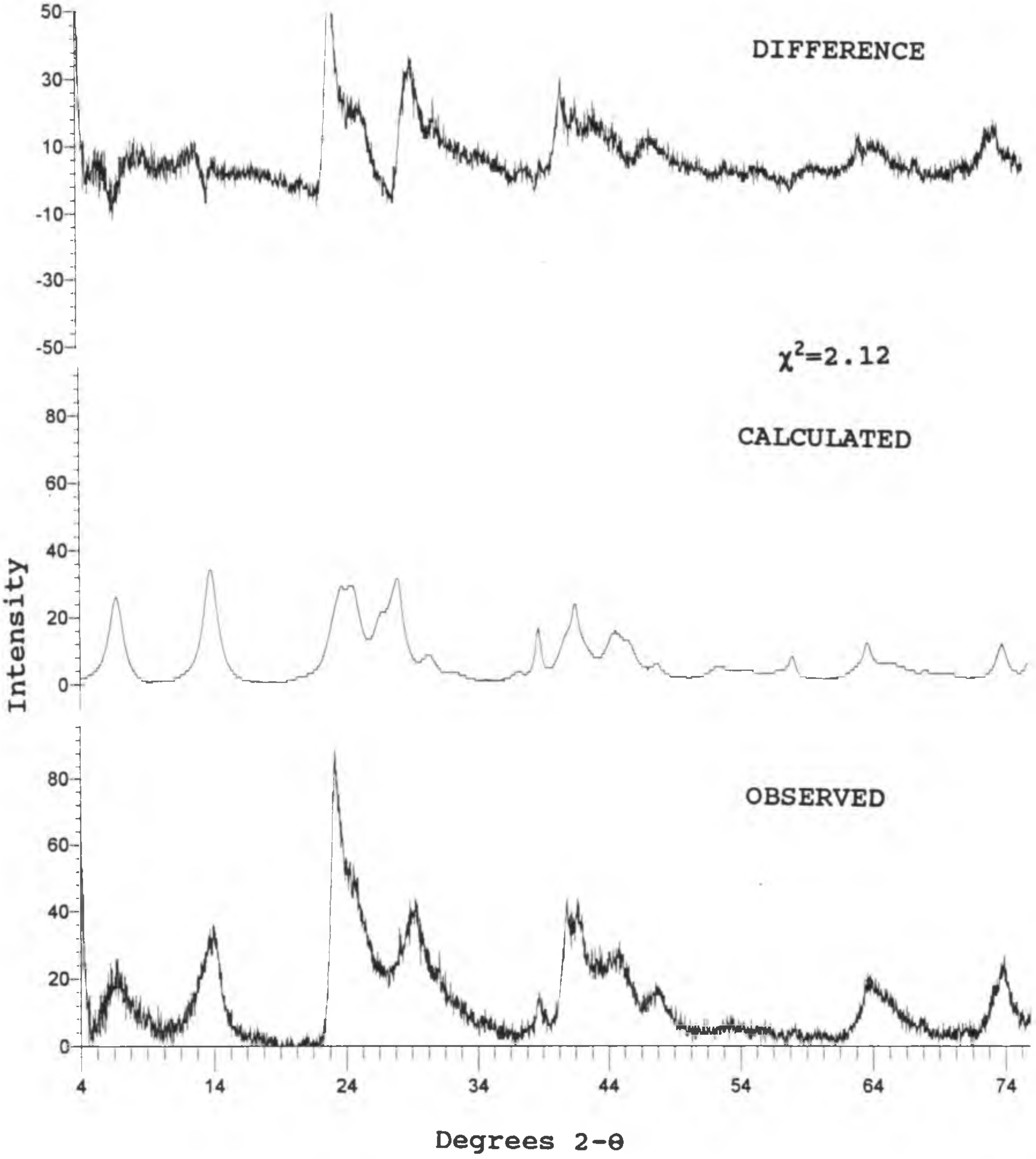
60
40
20
0
8
18
28
38
48
58
68
Degrees 2-θ

WAHIAWA SOIL



WAIALUA SOIL



Literature Cited

Afif, E., A. Matar and J. Torrent. 1993. Availability of phosphate applied to calcareous soils of West Asia and North Africa. Soil Sci. Soc. Amer. J. 57:756-760.

Ayres, A.S. and H.H. Hagihara. 1952. Available phosphorus in Hawaiian soil profiles. The Hawaiian Planters' Record. LIV:81-99.

Barrow, N.J. 1974. Effect of previous additions of phosphate on phosphate adsorption by soils. Soil Sci. 118:82-89.

Barrow, N.J. 1978. The description of phosphate adsorption curves. J. Soil Sci. 29:447-462.

Barrow, N.J. 1980. Differences amongst a wide-ranging collection of soils in the rate of reaction with phosphate. Aust. J. Soil Res. 18:215-224.

Barrow, N.J. 1983a. A discussion of the methods for measuring the rate of reaction between soil and phosphate. Fert. Res. 4:51-61.

Barrow, N.J. 1983b. On the reversibility of phosphate sorption by soils. J. Soil Sci. 34:751-758.

Barrow, N.J. 1984. Modelling the effects of pH on phosphate sorption by soils. J. Soil Sci. 35:283-297

Berkheiser, V.E., J.J. Street and T.L. Yuan. 1980. Partitioning of inorganic orthophosphate in soil-water systems. CRC Critical Reviews of Environmental Control. 10:179-224.

Bish, D.L. 1993. Studies of Clays and Clay Minerals Using X-Ray Powder Diffraction and The Rietveld Method. In Computer Applications to X-Ray Powder Diffraction Analysis of Clay Minerals, CMS Workshop Lectures, Vol. 5 eds. R.C. Reynolds, Jr. and J.R. Walker. The Clay Minerals Society.

Blakemore, L.C., P.L. Searle, and B.K. Daly. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil bureau Scientific Report 80. New Zealand Soil Bureau, Department of Scientific and Industrial Research, Lower Hutt, New Zealand.

Bollan, N.S. and N.J. Barrow. 1984. Modelling the effect of adsorption of phosphate and other anions on the surface charge of variable charge oxides. J. Soil Sci. 35:273-281.

Bowman, R.A. and S.R. Olsen. 1985a. Assessment of phosphate-buffering capacity: 1. Laboratory methods. Soil Sci. 140:287-291.

Bowman, R.A. and S.R. Olsen. 1985b. Assessment of phosphate-buffering capacity: 2. Greenhouse Methods. Soil Sci. 140:387-392.

Bray, R.H. 1948. Correlation of soil tests with crop response to added fertilizers and with fertilizer requirement. In Diagnostic techniques for soils and crops. (ed.) H.B. Kitchen. Amer. Potash Inst., Washington D.C.

Cox, F.R., E.J. Kamprath, and R.E. McCollum. 1981. A descriptive model of soil test nutrient levels following fertilization. Soil Sci. Soc. Amer. J. 45:529-532.

Dahnke, W.C., and R.A. Olson. 1990. Soil test correlation, calibration, and recommendation. In Soil Testing and Plant Analysis. 3rd ed.-SSSA Book Series, no. 3. Soil Sci. Soc. Amer. Madison, WI.

El-Tahir, A.E.M. 1976. Effect of soil pH, liming materials and phosphorus on growth and nutrient uptake of sugarcane. Ph.D. Dissertation, Department of Agronomy and Soil Science, University of Hawaii, Manoa.

Espinosa, J. 1992. Phosphorus diagnosis and recommendations in volcanic ash soils. In Tropsoils Bulletin No. 92-02. 1992 Proceedings of the Tropsoils Phosphorus Decision Support System Workshop, College Station, TX, March 11-12, 1992. Department of Agronomy and Soil Science, College of Tropical Agriculture and Human Resources, University of Hawaii, Honolulu, HI.

Eze, O.C. and P. Loganathan. 1990. Effects of pH on phosphate sorption of some paleudults of Southern Nigeria. Soil Sci. 150:613-621.

Fazey, P.G., B.H. O'Connor, and L.C. Hammond. 1991. X-ray powder diffraction Rietveld characterization of synthetic aluminum-substituted goethite. Clays and Clay MInerals. 39:248-253.

Fox, R.L. and E.J. Kamprath. 1970. Phosphate sorption isotherms for evaluating the phosphate requirements of soils. Soil Sci. Soc. Amer. Proc. 34:902-907.

Fox, R.L., D.L. Plucknett, and A.S. Whitney. 1968. Phosphorus requirements of Hawaiian latosols and residual effects of fertilizer phosphorus. 9th Int. Cong. of Soil Sci. Trans. 2:301-310.

Goldberg, S. and G. Sposito. 1984a. A chemical Model of Phosphate Adsorption by Soils: I. Reference Oxide Minerals. Soil Sci Soc. Amer. Proc. 48:772-778

Goldberg, S. and G. Sposito. 1984b. A chemical Model of Phosphate Adsorption by Soils: II. Noncalcareous Soils. Soil Sci Soc. Amer. Proc. 48:779-783.

Goldberg, S. and G. Sposito. 1985. On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces: a review. Commun. in Soil Sci. Plant Anal. 16:801-821.

Hamad, M.E., D.L. Rimmer, and J.K. Syers. 1992. Effect of iron oxide on phosphate sorption by calcite and calcareous soils. J. Soil Sci. 43:273-282.

Haynes, R.J. and R.S. Swift. 1989. The effects of pH and drying on adsorption of phosphate by aluminum-organic matter associations. J. Soil Sci. 40:773-781.

Hedley, M.J., R.E. White and P.H. Nye. 1982. Plant-induced changes in the rhizosphere of rape (*Brassica Napus* var. Emerald) seedlings. III. Changes in L value, soil phosphate fractions and phosphatase activity. New Phytol. 91:45-56.

Helyar, K.R., D.N. Munns, and R.G. Burau. 1976. Adsorption of phosphate by Gibbsite. II. Formation of surface complex involving divalent cations. J. Soil Sci. 27:315-323.

Holford, I.C.R. 1988. Buffering of phosphate in the soil solution during growth of ryegrass compared with buffering by sorption. Plant and Soil 111:3-9.

Holford, I.C.R. and G.E.G. Mattingly. 1975. The high- and low-energy phosphate adsorbing surfaces in calcareous soils. J. Soil Sci. 26:407-417.

Hue, N.V. 1991. Effects of organic acids/anions on P sorption and phytoavailability in soils with different mineralogies. Soil Sci. 152:463-471.

Indiati R., C. Izza, and A. Figliolia. 1991. Comparison of three short-period equilibration tests in predicting the P soil fertilizers requirements. Agrochimica 35:256-265.

Jackson, M.L., C.H. Lim, and L.W. Zelazny. 1986. Oxides, hydroxides, and aluminosilicates. In Method of Soil Analysis, Part 1. Physical and Mineralogical Methods - Agronomy Monograph no. 9 (2nd ed.). ASA-SSSA, Madison, Wi.

Johnston, M.A., N. Miles, G.R. Thibaud. 1991. Quantities of phosphorus fertilizer required to raise the soil test value. S. Afr. J. Plant Soil. 8:17-21.

Jones, C.A., C.V. Cole, A.N. Sharpley, and J.R. Williams. 1984. A simplified soil and plant phosphorus model: I. Documentation. Soil Sci. Soc. Amer. 48:800-804.

Jones, R.C. 1981. X-ray diffraction line profile analysis versus phosphorus sorption by eleven Puerto Rican soils. Soil Sci. Soc. Amer. J. 45:818-825.

Jones, R.C., W.H. Hudnall, and W.S. Sakai. 1982. Some highly weathered soils of Puerto Rico, 2. Mineralogy. Geoderma. 27:75-137.

Juo, A.S.R. and R.L. Fox. 1977. Phosphate sorption characteristics of some bench-mark soils of West Africa. Soil Sci. 124:370-376.

Kafkafi, U., A.M. Posner, J.M. Quirk. 1967. Desorption of phosphate from kaolinite. Soil Sci. Soc. Amer. Proc. 31:348-353.

Kamprath, E.J. 1971. Potential detrimental effects from liming highly weathered soils to neutrality. Soil Crop Sci. Soc. Florida 31:200-203.

Kamprath, E.J. and M.E. Watson. 1980. Conventional soil and tissue tests for assessing the phosphorus status of soils. In The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.) ASA, CSSA, SSSA, Madison, Wisconsin.

Kinter, E.B. and S. Diamond. 1958. Gravimetric determination of monolayer glycerol complexes of clay minerals. In Clays and Clay Minerals, Nat. Acad. Sci. - Nat. Res. Council. pub. 566:318-333.

Kovar, J.L. and S.A. Barber. 1988. Phosphorus supply characteristics of 33 soils as influenced by seven rates of phosphorus addition. Soil Sci. Soc. Amer. J. 52:160-165.

Kunze, G.W. and J.B. Dixon. 1986. Pretreatment for mineralogical analysis. In Method of Soil Analysis, Part 1. Physical and Mineralogical Methods - Agronomy Monograph no. 9 (2nd ed.) ed. A. Klute. ASA-SSSA, Madison, Wi.

LECO Corporation. 1985. WR-112 Wide Range Carbon Determinator, Model 788-600, Instruction Manual. St. Joseph, MI.

Lim, Howard Sookil. 1979. Effects of drying methods, extent, and inorganic cementing constituents on the structural properties of Typic Hydrandepts of Hawaii's forest land. Ph.D. Dissertation, Department of Agronomy and Soil Science, University of Hawaii, Manoa.

Lins, I.D.G. and F.R. Cox. 1989. Effect of extractant and selected soil properties on predicting the correct phosphorus fertilization of soybean. Soil Sci. Soc. Amer. J. 53:813-816.

Lins, I.D.G., F.R. Cox and J.J. Nicholaides, III. 1985. Optimizing phosphorus fertilization rates for soybeans grown on oxisols and associated Entisols. Soil Sci. Soc. Amer. J. 49:1457-1460.

Marschner, H. 1986. Mineral Nutrition of Higher Plants. Academic Press, San Diego.

Matar, A.E. 1988. A descriptive model for prediction of residual P in soil after phosphate fertilization. In Soil Test Calibration in West Asia and North Africa Proceeding of the Third Regional Workshop, Amman, Jordan; 3-9 September 1988. eds. J. Ryan and A. Matar. ICARDA.

McLaughlin, J.R., J.C. Ryden, and J.K. Syers. 1981. Sorption of inorganic phosphate by iron- and aluminium-containing components. J. Soil Sci. 32:365-377.

Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. in Soil Sci. Plant Anal. 15:1409-1416.

Menon, R.G., L.L. Hammond, and H.A. Sissingh. 1989. Determination of Plant-available Phosphorus by the iron hydroxide-impregnated filter paper (P_i) Soil Test. Soil Sci. Soc. Amer. J. 53:110-115.

Muljadi, D., A.M. Posner and J.P. Quirk. 1966. The mechanism of phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite. Part II. The location of the adsorption sites. J. Soil Sci. 17:230-237.

Munns, D.N. and R.L. Fox. 1976. The slow reaction which continues after phosphate adsorption: Kinetics and equilibrium in some tropical soils. Soil Sci. Soc. Amer. J. 40:46-51.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.

Nelson, R.E. 1982. Carbonate and Gypsum. In Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties - Agronomy Monograph no.9. (2nd ed.) eds. R.H. Miller and D.R. Keeney. ASA-SSSA Madison, WI

Norrish, K. and H. Rosser. 1983. Mineral Phosphate, chapter 24 In Soils: An Australian Viewpoint. CSIRO

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L.A. Dean. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939.

Olsen, S.R. and F.E. Khasawneh. 1980. Use and limitations of physical-chemical criteria for assessing the status of phosphorus in soils. In The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.) ASA, CSSA, SSSA, Madison, Wisconsin.

Parfitt, R.L. 1989. Phosphate reactions with natural allophane, ferrihydrite and goethite. J. of Soil Sci. 40:359-369.

Parfitt, R.L., L.J. Hume, and G.P. Sparling. 1989. Loss of availability of phosphate in New Zealand soils. J. Soil Sci. 40:371-382.

Peinemann, N. and A.K. Helmy. 1992. Phosphate sorption by hydroxy-aluminium and hydroxy-iron (III) treated montmorillonites. Applied Clay Sci. 6:419-428.

Rajan, S.S.S. and R.L. Fox. 1972. Phosphate adsorption by soils 1. Influence of time and ionic environment of phosphate adsorption. Comm in Soil Sci. and Plant Anal. 3:493-504.

Rietveld, H.M. 1969. A profile refinement method for nuclear and magnetic structures. J. Appl. Cryst. 2:65-71.

Ryden, J.C., J.R. Mclaughlin, and J.K. Syers. 1977. Time-dependent sorption of phosphate by soils and hydrous ferric oxides. J. Soil Sci. 28:585-595.

SAS Institute Inc. 1985. SAS® User's Guide: Statistics, Version 5 Edition. Cary, North Carolina.

Sanyal, S.K. and S.K. De Datta. 1991. Chemistry of phosphorus transformations in soil. Adv. in Soil Sci. 16:1-120.

Sanyal, S.K., S.K. De Datta and P.Y. Chan. 1993. Phosphate sorption-desorption behavior of some acidic soils of South and Southeast Asia. Soil Sci. Soc. Amer. J. 57:937-945.

Schwertmann, U. and R.M. Taylor. 1989. Iron oxides. In Minerals in Soil Environments (2nd edition) eds. J.B. Dixon and S.B. Weed. SSSA Book Series, no. 1. Soil Science Society of America, Madison Wisconsin.

Sharpley, A.N. 1983. Effect of soil properties on the kinetics of phosphorus desorption. Soil Sci. Soc. Amer. J. 47:462-467.

Sharpley, A.N., C.A. Jones, C. Gray, and C.V. Cole. 1984. A simplified soil and plant phosphorus model. II. Prediction of labile, organic and sorbed phosphorus. Soil Sci. Soc. Amer. J. 48:805-809.

Sharpley, A.N., U. Singh, G. Uehara, and J. Kimble. 1989. Modeling soil and plant phosphorus dynamics in calcareous and highly weathered soils. Soil Sci. Soc. Amer. J. 53:153-158.

Sibanda, H.M., and S.D. Young. 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. J. Soil Sci. 37:197-204.

Sibbesen, E. 1978. An investigation of the anion-exchange resin method for soil phosphate extraction. Plant and Soil 50:305-321.

Sietronics Pty. Limited. 1993. The new Siroquant for Windows Version 1. Canberra, Australia.

Soil Conservation Service. 1976. Soil Survey Laboratory Data and Descriptions for Some Soils of Hawaii. Soil Survey Investigations Report No. 29. Soil Conservation Service, US Department of Agriculture.

Soil Survey Laboratory Staff. 1991. Soil Survey Laboratory Methods Manual. Soil Survey Investigations Report No. 42. National Soil Survey Center, Soil Conservation Service, United States Department of Agriculture.

Soil Survey Staff. 1972. Soil Survey of the Islands of Kauai, Oahu, Maui, Molokai, and Lanai, State of Hawaii. USDA, Soil Conservation Service, Washinglton D.C.

Soil Survey Staff. 1973. Soil Survey of the Island of Hawaii, State of Hawaii. USDA, Soil Conservation Service, Washinglton D.C.

Soil Survey Staff. 1975. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. Agri. Handbook no. 436 USDA, Soil Conservation Service, Washinglton D.C.

Soil Survey Staff. 1992. Keys to Soil Taxonomy. SMSS Technical Monograph No. 19. 5th ed. Agency for International Development, USDA, Soil Conservation Service, Soil Management Support Services, Pocahontas Press, Inc., Blacksburg, VA.

Sollins, P. 1991. Effects of soil microstructure on phosphorus sorption in soils of the humid tropics. Unpublished.

Sposito, G. 1980. Derivation of the Freundlich equation for ion exchange reactions in soils. Soil Sci. Soc. Amer. J. 44:652-654.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, New York.

Staunton, S. and P.H. Nye. 1989. The effect of non-instantaneous exchange on the self-diffusion of phosphate in soil. J. Soil Sci. 40:751-760.

Taylor, J.C. 1991. Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. Powder Diffraction 6:1-9.

Thomas, G.W. 1982. Exchangeable Cations. In Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties - Agronomy Monograph no.9. (2nd ed.) eds. R.H. Miller and D.R. Keeney. ASA-SSSA Madison, WI

Tiessen, H., J.W.B. Stewart, C.V. Cole. 1984. Pathways of phosphorus transformations in soils of differing pedogenesis. Soil Sci. Soc. Amer. J. 48:853-858.

Torrent, J., U. Schwertmann and V. Barron. 1992. Fast and slow phosphate sorption by goethite-rich natural materials. Clays and Clay Min. 40:14-21.

Truog, E. 1930. The determination of the readily available phosphorus of soils. J. Amer. Soc. Agron. 22:874-882.

Uehara, G. and G. Gillman. 1981. The mineralogy, chemistry , and physics of tropical soils with variable charge clays. Westview Press, Boulder, Colorado.

Violante, A., C. Colombo and A. Buondonno. 1991. Competitive adsorption of phosphate and oxalate by aluminum oxides. Soil Sci. Soc. Amer. J. 55:65-70.

Watanabe, F.S. and S.R. Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Soil Sci. Soc Proc. 29:677-678.

White, R.E. 1983. The enigma of pH-P solubility relationships in soil. Third International Congress on Phosphorus Compounds. Brussels. pp. 53-64.

Yost, R., A.B. Onken, F. Cox, and S. Reid. 1992. The diagnosis of phosphorus deficiency and predicting phosphorus requirement. In Tropsoils Bulletin No. 92-02. 1992 Proceedings of the Tropsoils Phosphorus Decision Support System Workshop, College Station, TX, March 11-12, 1992. Department of Agronomy and Soil Science, College of Tropical Agriculture and Human Resources, University of Hawaii, Honolulu, HI.