

PHOSPHORUS SORPTION AND DESORPTION IN A BRAZILIAN ULTISOL:  
EFFECTS OF pH AND ORGANIC ANIONS ON PHOSPHORUS BIOAVAILABILITY

By

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Shinjiro Sato

This Ph.D. dissertation is dedicated to my life mentor,  
Dr. Daisaku Ikeda;  
and to  
all men, women, and children in the Amazon.

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Phosphorus bioavailability is a major limitation to plant productivity in weathered Brazilian soils. Soil pH change and organic anions such as oxalate and citrate produce known rhizosphere effects that influence P sorption and desorption. However, few data document their influence on P bioavailability. Quantitative measurement of bioavailable P pools is not well-defined. Our study focused on the surface soil developed under native Atlantic Forest in Bahia, Brazil. Objectives of our study were as follows:

- To investigate a method of developing P desorption isotherms using multiple strips of anion exchange membranes (AEMs)
- To evaluate the effect of pH on P sorption and desorption isotherms
- To separate ligand-desorbable P into ligand-exchangeable and ligand-dissolvable P
- To estimate the relative contributions of disequilibria- and ligand-desorbable P to the total desorbable P.

The Multiple AEM Method was suitable for developing well-defined isotherms and superior to sequential extraction methods over a range of solution concentrations in our

study. Increasing pH from 4.7 to 6 and 7 decreased P sorption (up to 21% and 34%, respectively) and increased P desorption for all P application rates. Using less than 1  $\mu\text{mol}$  oxalate or citrate  $\text{g}^{-1}$  soil and using 1 min contact time allowed us to desorb P solely by ligand exchange without surface dissolution. Nevertheless, dissolution played the major role in measuring ligand-desorbable P. Although most of P sorbed was found in the ligand-desorbable pool, P was preferentially found in the disequilibria-desorbable pool after P fertilization. The percentage of the total sorbed P that was desorbable was a function of time since fertilization; 13 to 22% on day 1 and 39 to 45% on day 14. This ageing process was due to a shaking artifact (30%), microbial immobilization (57%), and sorption of P onto the soil in a non-oxalate accessible form (13%). Liming and organic anion loading improved P bioavailability in this Brazilian soil. Long-term ageing and continuous exudation of organic anions also influence P bioavailability. Management options that recognize this will improve bioavailability of native and applied P sources in this important agricultural region of northeastern Brazil.

## CHAPTER 1 GENERAL INTRODUCTION

The management of tropical soils is crucial to addressing the issues of food security, soil degradation and environmental quality (Lal 2000). Low fertility; high soil acidity; and the role that land-use systems, fertilizers and liming play in mitigating these problems have been areas of interest for the past several decades. These problems have been addressed through the study of soil physical and chemical properties, which are of fundamental value when devising appropriate management approaches; and also through the social constraints that determine what management approaches are possible.

Because the soil is highly weathered, many humid, acid, tropical soils are phosphorus (P) deficient. Our study focused on the P chemistry of a particular tropical soil in northeastern Brazil as it relates to P bioavailability. This chapter will summarize some pertinent aspects of P bioavailability as an introduction to the objectives and hypotheses of this dissertation.

### **Forms of P in Soils**

#### **Soil Organic P – Solid Phase**

Organic soil phosphorus represents, on average, one-half of the total soil P and varies between 15 and 80% in most soils (Stevenson 1986). The amount of soil organic P depends on soil organic matter content; therefore, it tends to be high in the surface horizon and decreases with soil depth. Soil organic P compounds are synthesized by soil microorganisms as esters of orthophosphoric acid (Anderson 1980), with the most stable

and abundant compounds being inositol phosphates which make up 10 to 50% of the total soil organic P.

Phosphorus held in organic form must first be converted to inorganic form before plant uptake. The process is controlled by P mineralization and immobilization in a manner similar to processes described for release of organic nitrogen and sulfur from soil organic matter. Mineralization of organic P may be both biological and biochemical (Tate 1984). Biological mineralization releases P bound in organic matter as soil microorganisms mineralize soil organic matter.

Biochemical mineralization occurs when plant roots and microorganisms produce phosphatase enzymes that can catalyze the hydrolysis of ester bonds between P and C compounds. Phosphatases play a major role in mineralization of soil organic P. Phosphatase activity is generally enhanced in P-stressed soils (Clarholm 1993) and evidently have both spatial and temporal variability (Schneider et al. 2001). Since soil microbial activity is dependent on soil organic carbon content, the C:P ratio is critical in balancing P mineralization and immobilization processes. It has been proposed that critical C:P values for decomposing residues are  $< 200:1$  for net mineralization and  $> 300:1$  for net immobilization (Enwezor 1967, Sharpley 1985). The C:P ratio of the substrate being decomposed may be more important than that of soil organic matter or plant residues, with the critical C:P ratio calculated from microbial growth yield falling in the range of 50 to 70 (White 1981).

Besides P fertilization status, mineralization of organic P is influenced by many of the same soil properties that control decomposition of soil organic matter: namely, temperature, moisture, aeration, pH, and cultivation method and/or intensity. Therefore,

in soils of tropical regions where climatic conditions favor organic matter decomposition, P mineralization can supply a portion of the crop P requirement (Anderson 1980).

Inorganic P also can be immobilized in organic form as part of the microbial biomass. The quantity of P immobilized varies from 6 to 106  $\mu\text{g P g}^{-1}$  soil (Brookes et al. 1984, Joergensen et al. 1995), and from 38 to 46% of sorbed inorganic P for some variable charge minerals (He and Zhu 1998). The amount of P immobilized by microbes was estimated in one case to be 3 to 5 times greater than the amount of P absorbed by plants in semiarid grasslands (Cole et al. 1978).

### **Soil Organic P – Solution Phase**

Uptake of soluble organic P by plant roots is not well-documented. However, it has been shown that the presence of (endo- and ecto-) mycorrhizal fungi stimulates net mineralization of organic P because of phosphatase production (Condon et al. 1996, Joner et al. 2000). Red clover (*Trifolium pratense* L.) uptake of P increased as the plant and an associated arbuscular mycorrhizal fungus grew. Organic P sources (phytase, lecithin, and RNA) contributed (17 to 31%) to total plant P compatibly with an inorganic P source ( $\text{KH}_2\text{PO}_4$ , 23%) (Feng et al. 2003). Jayachandran et al. (1992) showed a similar effect of arbuscular mycorrhizal fungi associated with big bluestem (*Andropogon gerardii* Vit.), that promoted a significant increase in plant use of organic P (cytidine 3- and 5-phosphate) when added to a soil having low P fertility.

### **Soil Inorganic P – Solution Phase**

Phosphorus concentrations in the soil solution are low compared to other soil macronutrients, normally ranging from 0.001 to about 1  $\mu\text{g P mL}^{-1}$  with an average of about 0.05  $\mu\text{g P mL}^{-1}$  (Barber et al. 1962). Plant roots and mycorrhizal hyphae absorb soil solution P as orthophosphate ions in either the  $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$  form, depending on

soil pH. The dominant solution inorganic P species below pH 7.2 is the monovalent ion; while  $\text{HPO}_4^{2-}$  dominates at pH values between 7.2 and 12.1 (Fig. 1-1). Plant uptake of the divalent ion has been shown to be slower than the monovalent ion (Cresser et al. 1993).

### **Soil Inorganic P – Solid Phase**

If not absorbed by the plant or immobilized by microbes, inorganic P in the soil solution is subject to various chemical reactions. These include precipitation as and dissolution from inorganic P solids, and adsorption to and desorption from soil mineral surfaces.

Precipitation is a slow reaction in which phosphate ions react with dissolved  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mn}^{3+}$  in acid soils and  $\text{Ca}^{2+}$  in neutral to calcareous soils to form insoluble hydroxy phosphate precipitates (Sanchez and Uehara 1980). Variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ) and strengite ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ) are the most common stable minerals found in acid soils; while in alkaline soils, the most stable minerals are calcium phosphates such as octacalcium phosphate [ $\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ] and hydroxyapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ]. The solubilities of these Ca-P minerals decrease with increasing pH; whereas Al- and Fe-P minerals exhibit increasing solubility with increasing pH (Lindsay and Moreno 1960).

In contrast to precipitation, adsorption is a relatively fast initial reaction involving both anion and ligand exchange. Negatively charged phosphate ions in the soil solution are attracted to positively charged soil surfaces, via anion exchange. However, a significant quantity of positively charged surfaces will develop only at low soil pH in highly weathered soils that display variable-charge characteristics. Adsorption by ligand exchange results when an inner-sphere metal–O–P covalent bond is formed by replacement of hydroxyls on the edges of layer silicate clays and the surfaces of insoluble

oxides of Al, Fe, and/or Mn. This process is referred to as specific adsorption or chemisorption (Schindler and Sposito 1991).

Since it is difficult to distinguish adsorption and precipitation reactions from one another, they are usually referred to collectively as P sorption or fixation (Sposito 1984). Sorption of P seems to increase over time, apparently due to slow precipitation processes that are superimposed on the more rapid chemisorption (Van der Zee and Van Riemsdijk 1991). The amount of P in the soil solution appears to determine which reaction dominates. Chemisorption dominates at low solution P; while precipitation proceeds when the concentrations of P and associated cations in the soil solution exceed the solubility products ( $K_{sp}$ ) of the relevant P compounds. Therefore, for soils exhibiting low solution P concentrations such as many tropical soils, chemisorption should be a dominant mechanism.

Adsorbed or precipitated inorganic P undergoes desorption or dissolution reactions when moving from the solid to the solution phase. Desorption is of particular importance in bioavailability evaluations, because this process controls what the plant can eventually access. Desorption is used here to denote either the precise opposite of adsorption or the counterpart to sorption, which would include a combination of desorption and dissolution. Both soil and plant characteristics affect the extent and rate of desorption and dissolution for inorganic soil P. It is necessary, therefore, to understand these relationships in order to evaluate and predict P bioavailability and the fate of inorganic P.

### **Factors Affecting Inorganic P Sorption and Desorption**

The soil characteristics that influence P fixation include the amount and type of clay-fraction minerals, soil pH, soil organic matter content, soil temperature, time of reaction, exchangeable  $Al^{3+}$ , soil redox condition (Sanchez and Uehara 1980), and root

exudates. These factors are interactive rather than additive, which makes it difficult to predict inorganic P fixation under a wide range of soil conditions.

The higher the Al and Fe oxide contents of soil clay, and the less crystalline (more amorphous) the soil minerals, the greater an acid soil's P fixation capacity. This is largely attributed to the greater surface area which these conditions represent (Fernandes and Warren 1994, Gilkes and Hughes 1994, Quintero et al. 1999). Higher clay contents also result in greater P fixation (Sanchez and Uehara 1980, Harris et al. 1996, Voundi et al. 1997).

Soil pH, because of its influence on surface charge and the ease with which surface charge can be managed by liming, has been the focus of research on a variety of soils (Awan 1964, Parfitt 1977, Bar-Yosef et al. 1988, Naidu et al. 1990, Pardo et al. 1992, Rupa et al. 2001). In spite of this, results concerning P sorption or solution P concentrations as influenced by liming have been conflicting (Haynes 1982, Anjos and Rowell 1987). Given the P sorption patterns observed at different soil pH values, and the number of explanations used to account for these phenomena, it is clear that the influence of liming on P sorption is not well-understood.

In highly weathered and acid soils, existing data support the hypothesis that exchangeable  $\text{Al}^{3+}$  is the main factor determining the pattern of P sorption with changing pH (Lopes-Hernandez and Burnham 1974, Anjos and Rowell 1987, Chen and Barber 1990). Haynes (1984) said that one should expect liming to increase P sorption in soils that are initially high in exchangeable  $\text{Al}^{3+}$ , but to decrease P sorption in soils with low exchangeable  $\text{Al}^{3+}$  content. When soils with low exchangeable  $\text{Al}^{3+}$  are limed, the neutralization and precipitation of  $\text{Al}^{3+}$  ion and of hydroxy-Al species to form Al

hydroxide reduces the number of P-sorption sites. Where exchangeable  $\text{Al}^{3+}$  is initially high, the formation of amorphous hydroxyl Al with highly active sorbing surfaces may exceed any decrease in the sorption capacity of the original sorbing surfaces, resulting in increasing P sorption as pH increases.

Phosphorus desorption studies are rare compared to the frequency of P sorption studies. Some desorption studies determined bioavailable P by using agriculture-based extraction indices, and correlating them with plant P uptake (Parfitt 1979, Steffens 1994, Martin et al. 2002). Others described the kinetics of P desorption by extracting P using dilution methods or using anion-exchange resins. Such studies examined the suitability of relationships such as first-order, Elovich, and parabolic diffusion equations to describe kinetic P release from soil (Chien and Clayton 1980, Sharpley et al. 1981, Raven and Hossner 1994).

Several studies focused on the effect of soil pH on P desorption (Hingston et al. 1974, Rupa et al. 2001). However, the results have been inconsistent; with some workers finding increasing P desorption with increasing pH (Madrid and Posner 1979, Cabrera et al. 1981, De Smet et al. 1998) and others with decreasing pH (Barrow 2002). He et al. (1989) reported that P desorption decreased until pH was raised to about 4.8; and then increased with further pH increases for most of the acid soils from China which contained high Fe and Al oxide and/or kaolinite levels. In contrast, for three representative surface soils of India, both the amount and rate of P desorption initially increased with pH increase from 4.25 to 5.5; and then decreased at higher pH values of 6.75 and 8.0 (Rupa et al. 2001).

No relationship was found between P removal by various extractants and the affinity constant derived from the Langmuir equation for the original sorption of P (Kuo et al. 1988). It was found that the amount of P desorbed by all extractants was significantly related to the fraction of P saturation on soil surfaces, with higher P saturation of the surfaces yielding higher desorbed P values.

Kafkafi et al. (1967) found, for kaolinite, that a portion of applied P was non-exchangeable during simple washing using an indifferent electrolyte solution. They concluded that some of the applied P was incorporated into a fixed sink. In another study, Cabrera et al. (1981) postulated that the inability to desorb all P sorbed onto Fe-oxides using strongly alkaline solutions (e.g., 0.1 M NaOH) was due to the existence of micropores in the materials, where some of the applied P could remain occluded.

Plant roots are known to exude a range of organic acids including oxalate, malate, and citrate. Their positive effect on enhancing P desorption has been well-recognized (Jones 1998, Ryan et al. 2001). The mechanisms of P desorption by these compounds include ligand exchange and ligand dissolution; yet the evidence for which are active and in what proportion for a range of soils is not available. These processes and their relative contributions to changes in inorganic P bioavailability which can occur for the rhizosphere should vary with plant species, plant nutritional status, and ambient soil conditions (Hinsinger 2001).

### **Phosphorus Desorption Defines P Bioavailability**

Prior studies on P sorption have outlined trends and provided a foundation for understanding such sorption. However, bioavailability of P is a function of P desorption; not P sorption. Specific information for soils, where needed for agricultural development, is lacking for P desorption and its trends with soil characteristics. Humid,

weathered, tropical soils of Brazil represent one area where an understanding of P desorption dynamics is needed to better manage soils that are inherently P deficient.

Understanding and evaluating soil P bioavailability requires that one identify

- Form(s) of P absorbed by plants
- Form(s) of P that can be released from the solid to the adjacent and bioavailable solution phase
- Processes responsible for the release of P from the solid phase to the solution phase
- How soil/plant/mycorrhiza properties affect these processes
- Soil properties that affect movement of P in solution to the root/mycorrhiza
- Plant properties that are important in determining P absorption by the root/mycorrhiza when P arrives at its surface (Comerford 1998).

The P desorption process is poorly understood and virtually no such information exists for tropical soils. Phosphorus desorption must be studied separately from or in conjunction with P sorption, because there is a significant hysteresis between the two such that sorption data do not suitably relate to desorption behavior (Barrow 1983). To further confound the situation, the hysteresis that is commonly reported may be partially an artifact of the methodology used, since a recent study suggests that while sorption and desorption isotherms are strongly hysteretic; desorption and resorption isotherms (sorbing P after the desorption step) are not generally hysteretic (Barros et al. in press).

### **Classification of Desorbable Inorganic P**

For the purpose of this dissertation, the term desorption will be used in the same fashion as the counterpart term sorption. It does not distinguish desorption from adsorption; or distinguish dissolution from precipitation. To clarify the types of desorption that occur in soils, the following categorization is suggested. Two major mechanisms describe inorganic P desorption: disequilibria desorption and ligand

desorption. These can be subcategorized into exchange and dissolution types of desorption (Table 1-1). Disequilibria desorption is consistent with Le Châtelier's Principle; and requires that a disequilibrium exist between sorbed and solution P concentrations. Disequilibria can be created during uptake of solution P by plant roots; during leaching; during precipitation as secondary P minerals; during a change in rhizosphere pH that changes surface charge or solubilities; or during immobilization by soil microbes. As the solution P concentration is decreased, P is replenished through desorption from P adsorbed onto the soil surface in exchange with other anions in the solution (disequilibria exchange); or through dissolution of relatively soluble P compounds (disequilibria dissolution) (Wolf and London 1994).

Disequilibria-desorbable P can be measured in a specific time frame. It can be extracted by maintaining the solution P concentration at low levels through sequential extractions using anion-exchange resins (Sibbesen 1978, Saggar et al. 1990); anion-exchange membranes (Cooperband and Logan 1994); or iron oxide-impregnated paper strips (Menon et al. 1996/1997); or by shaking with water (Simard et al. 1994); or low-ionic-strength solutions (Rupa et al. 2001). This pool of desorbable P should be bioavailable to plants or soil microorganisms. The nature and pattern of this desorption, particularly when described as a desorption isotherm, is rare in the literature and non-existent for tropical soils.

Another desorbable pool of inorganic P can be released by ligands that have a higher affinity for the soil surface than does phosphate. Ligands in solution form inner-sphere complexes with the soil surface that exchange with P on the surface, because of their higher affinity for the soil surface (ligand exchange) (Cambier and Sposito 1991,

Hu et al. 2001). These ligands affect the stability of precipitates and contribute to dissolution of the solid, concomitantly releasing P from the surface (ligand dissolution) (Zinder et al. 1986, Ludwig et al. 1996). Plant roots and soil microbes produce a range of organic acids including acetate, oxalate, citrate, and malate. They are known to exude these acids into the soil solution at concentrations which can promote P desorption (Fox and Comerford 1990, Jones 1998).

The problem in defining the pool of ligand-desorbable P is that one does not know with certainty which ligands are in the soil solution; their loading rate onto the solid phase; the volume of soil affected by this loading; and how soil properties affect the effectiveness of P release by these ligands (Comerford 1998). Therefore, the best approach to quantifying this pool is to measure the total amount of P that is desorbable by ligand desorption.

### **Importance of Phosphorus Bioavailability in Tropical Soils**

Tropical soils are notorious for their low nutrient bioavailability (often related to low exchangeable base contents, high soil acidity, Al toxicity, and low P desorbability). Oxisols and Ultisols of humid, tropical Brazil are no exception. Low P bioavailability is the primary limiting factor for plant growth in many of these soils.

The origin of P deficiencies in these soils is threefold (Brady and Weil 1999). First, the total P level of the soils is low, ranging from 0.01 to 0.1% (Chen and Ma 2001). Second, the P compounds commonly found in these soils are highly insoluble. Third, when soluble sources of P, including those in fertilizers and manures, are added to soils they are sorbed to the soil, changed into unavailable forms and, over time, incorporated into highly insoluble compounds.

The high P fixing capacities of many tropical soils (Udo and Uzu 1972, Sanyal et al. 1993, Fontes and Weed 1996) are a function of their mineralogy and are a primary contributor to their P deficiencies. Therefore, it is critical to understand the physical and chemical properties of these soils that control the dynamics of inorganic P tie-up and supply. Better understanding should lead to better nutrient management and better maintenance of soil quality. This is particularly true for the acid, weathered soils of Brazil, where P chemistry is often poorly understood.

Based on the above discussion, it is obvious that P desorption is an important topic affecting the nutrient management of P in soils, and particularly many tropical soils. Phosphorus desorption determines P bioavailability; and its interaction with soil pH in the form of desorption isotherms remains poorly documented. Bioavailable inorganic P exists in two major pools, but quantitative estimates of these pools (and methods for deriving these estimates) remain poorly developed. Therefore, our study will address some of these gaps in knowledge, using a humid, highly weathered Ultisol from the Atlantic Forest in northeastern Brazil. The following is a brief description of each chapter.

Chapter 2 develops a method for constructing P desorption isotherms using anion exchange membranes (AEMs) in a way that minimizes time spent and experimental artifacts. This method is also compared to a more conventional method.

Chapter 3 investigates the effect of soil pH on both inorganic P sorption and desorption isotherms. The hypothesis is that P sorption and desorption isotherms are functions of soil pH, with increasing pH decreasing the amount of P that is sorbed and increasing the amount of P that is desorbed. In both cases, more P would be bioavailable.

Chapter 4 addresses the major types of P desorption (disequilibria desorption and ligand desorption); and attempts to differentiate between ligand-exchangeable desorption and ligand-dissolvable desorption for a Brazilian soil in its native and P-fertilized states. It also investigates the amount of P sorbed that cannot be accessed by the above two desorption mechanisms.

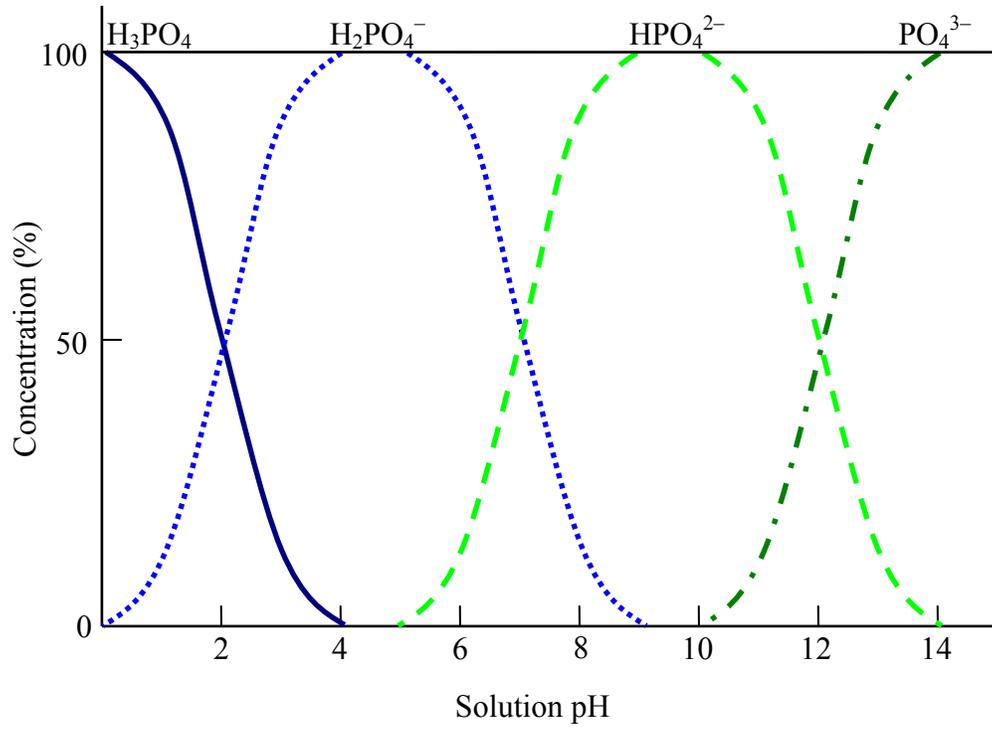


Figure 1-1 Influence of pH on the distribution of orthophosphate species in solution

Table 1-1 Types and mechanisms of inorganic P desorption

Major type	Reaction type	Mechanism
Disequilibria		Follows Le Châtelier's Principle. Requires P disequilibria between solution and solid phases, created by plant uptake, leaching, precipitation, rhizosphere pH change, and/or microbial immobilization.
	Exchange	Desorbs P from the soil surface in exchange with other anions in the soil solution.
	Dissolution	Desorbs P from relatively soluble P compounds.
Ligand		Influenced by anions of low-molecular-weight organic acids such as acetate, oxalate, citrate, and malate, which are exuded by plant roots and soil microbes. Ligands have higher affinity for the soil surface than phosphate and/or destabilize P minerals.
	Exchange	Desorbs P from the soil surface by forming inner-sphere complexes which exchange with P.
	Dissolution	Desorbs P from the soil surface by destabilizing and dissolving the solid itself.

CHAPTER 2  
ASSESSING A QUICK METHOD FOR DEVELOPING PHOSPHORUS  
DESORPTION ISOTHERMS USING ANION EXCHANGE MEMBRANES

**Introduction**

Inorganic phosphorus (P) bioavailability is defined by the combined processes of desorption and dissolution. These processes occur in response to disequilibria established in solution by removal of P from solution (disequilibria desorption); or in response to the action of ligands exchanging with phosphate or dissolving phosphate-bearing compounds (ligand desorption) (Table 1-1). Most commonly, bioavailable desorbable P is indexed by extracting a portion of the labile pool of P with chemical extractants such as Bray 1, Mehlich 1 or 3, or Olsen's Solution (Ziadi et al. 2001, Csatho et al. 2002). However, these soil P tests are interpretable only when combined with crop experimental data from the field or greenhouse (Kumar et al. 1992, Kleinman et al. 2001); and do not measure a pool of bioavailable P, but instead act simply as an index to P bioavailability. There is no absolute interpretation for the quantity of P extracted by any of these methods; nor do these methods define the pattern of P release, or the influence of P desorption on the soil solution concentration. Therefore, such techniques have limited utility in the mechanistic modeling of P bioavailability and uptake by plants.

Desorption can be described by a desorption isotherm, which is the relationship between P on the solid phase and P in the solution phase. This relationship has been referred to as a quantity (solid P)/intensity (solution P) relationship (Raven and Hossner 1993). The P desorption isotherm is a useful, descriptive characteristic of soil that

provides information on the ability of the soil to release P into solution as solution P is removed. This ability is represented by the slope of the desorption isotherm which is termed the partition coefficient ( $K_d$ ). Partition coefficients are directly related to the buffer power of the soil and are used to calculate soil diffusion coefficients (Van Rees et al. 1990b). Diffusion is important because, in many soils, it is the mechanism governing 90 to 98% of the P supply to roots (Barber 1980). Therefore,  $K_d$  is a useful parameter in computer-based nutrient uptake models. However, few comprehensive studies address P desorption; and fewer address development of P desorption isotherms.

Phosphorus is desorbed from soil, and thus P desorption isotherms can be developed by techniques that use dilution, sequential extraction, or anion exchange resin extraction (Brewster et al. 1975, Bhatti and Comerford 2002). For the dilution method, P is desorbed from the solid phase by shaking a soil sample over a range of soil:solution ratios for a specified equilibration time with single or successive extractions (Madrid and Posner 1979, Sharpley et al. 1981). In the sequential extraction, an extracting solution is added to the soil at a constant soil:solution ratio; and the sample is shaken for a constant equilibration time. This procedure is repeated until P desorption is exhausted or a pattern of P release is established (Fox and Kamprath 1970, Okajima et al. 1983, Bhatti and Comerford 2002). The anion exchange resin extraction is performed in the same manner as the sequential extraction except that bags filled with anion exchange resins (AERs) are used to enhance the removal of P from solution (Sibbesen 1977, Bache and Ireland 1980, Yang and Skogley 1992, Delgado and Torrent 1997). In place of AERs, resin-impregnated membranes such as anion exchange membranes (AEMs) have been used successfully in P desorption studies (Saunders 1965, Saggar et al. 1990, Nuernberg

et al. 1998). Both AERs and AEMs behave as a P sink, desorbing P from the solid phase by causing disequilibrium; and have proven to be useful indices of plant-available P when used as extractants in soil tests (Sibbesen 1978, Schoenau and Huang 1991, Ziadi et al. 2001). The AEM behavior in soil, including recyclability, P sorption kinetics, and adsorbability of solution P by AEMs, are well-documented (Cooperband and Logan 1994, Cooperband et al. 1999).

Anion exchange materials have been used to investigate the desorption kinetics of P (Raven and Hossner 1994); to measure P mineralization (Parfitt et al. 1994); and to measure total resin-desorbable P by sequential extraction (He et al. 1994). However, P desorption isotherms have rarely been developed. In one noteworthy case the validity of using AEMs for developing P desorption isotherms was confirmed for Brazilian Cerrado soils with varying clay and organic matter contents (Barros Filho et al. 2001, Barros Filho et al. in press).

Brewster et al. (1975) compared P desorption isotherms using AERs with those developed by dilution. Brewster and colleagues concluded that the use of the resins was a more desirable technique than dilution primarily because of the large dilution volumes required.

The sequential extraction method has some inherent problems. Since this method can require up to several weeks to develop a complete P desorption isotherm, continuous shaking of samples may increase the soil's surface area because of soil particles' abrasion (Barros Filho et al. in press). Another concern is that microbial P mineralization or immobilization that may be induced during the prolonged desorption process can influence P desorption patterns (Barros Filho et al. in press). The first objective of our

study was to evaluate the suitability of using multiple strips of AEMs (termed the Multiple AEM Method) to develop P desorption isotherms. Initial work showed that P desorption was sensitive to the amount of AEM surface area in contact with soil. This objective addressed whether the Multiple AEM Method could be used to more rapidly develop a desorption isotherm. The second objective was to compare the Multiple AEM Method with a sequential-extraction approach using AEMs (termed the Sequential AEM Method) to determine if the manner in which AEMs were used would influence the desorption isotherm.

## **Materials and Methods**

### **Soil Material**

The soil material used in our study was the surface horizon (0 to 30 cm depth) of a Kandiudult (Soil Survey Staff 1999), known as an Argissolo vermelho/vermelho-amarelo distrófico in the Brazilian system (Oliveira et al. 1992). It was taken from under a native Atlantic Forest cover type (Morellato and Haddad 2000) located near Una Ecoparque near the city of Una, Bahia, Brazil. Using a shovel, the material was collected from a 1 ha area. Approximately 20 sampling points were combined; and the soil was subsequently air-dried, passed through a 2-mm sieve, and stored in plastic bags. Selected chemical and physical properties of the soil material were determined by standard methods (Page et al. 1982), which are listed in greater detail in Chapter 3. Soil pH was 4.7 (1:2 soil:water), with 2.5% organic carbon and 25% clay content dominated by kaolinite. Mehlich 1-available P and total P were  $2.7 \mu\text{g g}^{-1}$  and  $98.3 \mu\text{g g}^{-1}$ , respectively. The iron content was greater than the aluminum content in both the amorphous and crystalline oxide forms.

### **Phosphorus Desorption Kinetics Using AEMs**

To maximize effectiveness of AEMs, the kinetics of P desorption in the presence of AEMs was first determined. Triplicate 2 g samples were weighed into 50 mL centrifuge tubes; and then 20 mL of 50 mM KCl containing 25  $\mu\text{g P mL}^{-1}$  as  $\text{KH}_2\text{PO}_4$  were added to each tube. Triplicate blanks of 20 mL of 50 mM KCl without soil and without P were included. The tubes were shaken horizontally for 20 h; and then centrifuged for 15 min at 2500 rpm. The supernatant was filtered through Whatman No. 5 filter paper and measured for soluble reactive P by the method of Murphy and Riley (1962), which was used for all P determinations in our study. Soluble reactive P as measured by this method is operationally defined as inorganic P. Sorbed P was calculated as the difference between the initial solution concentration added and the final concentration in the filtrate.

After decanting the supernatant, 50 mM KCl was added once more to each tube until it reached its original pre-shaking weight. The AEM strips (1.25 cm  $\times$  5.00 cm; Type AR204-SZRA-412, Ionics Inc., Watertown, MA) were prepared for use by soaking overnight in 1 M KCl of sufficient volume to provide an anion concentration at least 5 times greater than the total anion exchange capacity of the strips. After rinsing with double-deionized water, one strip was inserted into each centrifuge tube. The tubes then were shaken; and triplicate samples were removed from the shaker at 0.5, 1, 2, 4, 10, 24, and 48 h. Each AEM strip was carefully removed from the tube so as to not concomitantly remove soil particles; was rinsed with double-deionized water; and was placed in another centrifuge tube filled with 15 mL of 1 M KCl. This tube was then shaken for 30 min; and the solution was filtered through Whatman No. 5 filter paper. Phosphorus in this filtrate was determined.

### **Phosphorus Desorption as Affected by AEM Surface Area**

Ten sets of triplicate centrifuge tubes were prepared; and the P sorption process was performed in the same manner as described above. After decanting the supernatant, 50 mM KCl were added to the tube until it reached its original pre-shaking weight. After rinsing with double-deionized water, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 strips (1.25 cm × 5.00 cm) of AEMs that had been prepared as described above were inserted into each set of triplicate tubes. The tubes then were shaken for 2 h. The strips were removed from the tubes; were rinsed with double-deionized water; and were placed in another 10 sets of triplicate tubes filled with 15 mL of 3 M KCl for the 1-, 2-, and 3-strip tubes; 25 mL for the 4-, 5-, and 6-strip tubes; 30 mL for the 7- and 8-strip tubes; and 40 mL for the 9- and 10-strip tubes. These tubes were shaken for 30 min; and the solution was filtered through Whatman No. 5 filter paper. Phosphorus in the filtrate was determined.

### **Phosphorus Desorption Isotherms Using the Multiple AEM Method**

Phosphorus desorption isotherms then were developed using multiple AEM strips on soil samples with 3 levels of sorbed P. Phosphorus was sorbed onto the soil using initial loading levels of 40, 80 or 180  $\mu\text{g P g}^{-1}$  soil. These levels were chosen because they bounded normal fertilizer additions; and were equivalent to 16, 32, and 72 kg P ha<sup>-1</sup>, assuming the fertilizer to be broadcast and incorporated into the top 3 cm of soil.

Triplicate 2 g soil samples were weighed into 6 sets of triplicate centrifuge tubes; and the initial weight of each tube + soil was recorded. Twenty milliliters of 50 mM KCl containing 4, 8 or 18  $\mu\text{g P mL}^{-1}$  as  $\text{KH}_2\text{PO}_4$  were added to the tubes; and the total initial weight of tube + soil + solution was recorded. The tubes then were shaken for 20 h; and centrifuged for 15 min at 2500 rpm. The supernatant solution was filtered through Whatman No. 5 filter paper; and P in the filtrate was determined. Phosphorus sorbed

onto the solid phase was calculated as the difference between the initial or previous P concentration and the P concentration in the filtrate.

After decanting the supernatant, tube + soil weights were recorded; and each tube was filled with 50 mM KCl to its initial tube + soil + solution weight. The AEM strips prepared in KCl solution then were rinsed with double-deionized water; and 1, 2, 3, 4, 5, or 6 strips (1.88 cm × 7.50 cm) were inserted into each of 6 sets of triplicate tubes. The tubes were shaken for 2 h. The strips then were removed from the tubes; were rinsed with double-deionized water; and were placed in another 6 sets of triplicate tubes filled with 15 mL of 2 M KCl for 1-, 2-, and 3-strip tubes; and 30 mL for 4-, 5-, and 6-strip tubes. These KCl tubes were shaken for 30 min; and then filtered through Whatman No. 5 filter paper. Phosphorus in filtrate was measured. The original tubes with soil samples were shaken for 20 h; and then centrifuged for 15 min at 2500 rpm. The supernatant solution was filtered through Whatman No. 5 filter paper; and P in the filtrate was determined.

The first step of this procedure was designed to reduce desorbable P on the solid phase using AEMs. The equilibration step was required to develop a desorption isotherm, because the soil must come into an equilibrium or quasi-equilibrium to measure an equilibrium solution concentration. The entire procedure of the previous paragraph was repeated two more times, resulting in a total of 3 desorption steps and yielding 18 points for each desorption isotherm in 4 d.

### **Phosphorus Desorption Isotherms Using the Sequential AEM Method**

The Sequential AEM Method for P desorption isotherms was performed using a constant number of AEM strips and multiple extraction steps on soil samples having the same three P-addition levels as in the multiple AEMs study. The procedure was the same

as that using multiple AEM strips, except that only 4 strips were used in all extraction steps. The extraction steps were continued until the concentration of P desorbed by AEMs in the KCl filtrate solution reached the P detection limit ( $0.005 \mu\text{g P mL}^{-1}$ ;  $0.05 \mu\text{g P g}^{-1}$  soil). The Sequential AEM Method required 6, 9, and 13 desorption steps and took 7, 10, and 14 d to develop desorption isotherms for samples to which 40, 80, and  $180 \mu\text{g P g}^{-1}$  had been added, respectively.

### Statistical Analysis

Statistical differences in the pattern of P desorption using different methods and initial P loading levels were tested using the General Linear Models (GLM) procedure in the Statistical Analysis System framework (SAS Institute 1988). Observed P desorption was related to the amount of P initially added and the method by which P desorption isotherms were developed. The model used was:

$$C_s = \beta_0 + \beta_1 C_l + \beta_2 C_l^2 + \beta_3 (\text{Method} | \text{Padded}) + E \quad (2-1)$$

where  $C_s$  is the amount of P sorbed on the solid phase per unit mass of soil in  $\mu\text{g P g}^{-1}$  of soil;  $C_l$  is the equilibrium concentration of P in  $\mu\text{g P mL}^{-1}$ ;  $\beta_0$  is the intercept parameter, and  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are the slope parameters of the regression line; and  $E$  is the random error. The *Method* variable has two levels representing the Multiple and Sequential AEM Methods. The *Padded* variable has three levels of 40, 80,  $180 \mu\text{g P g}^{-1}$  initially added. Analysis of variance (ANOVA) was used to test differences among regression line parameters; and significance of the differences among means were determined by t-tests at the  $p = 0.05$  level. Means and standard deviations were used to summarize the data, where applicable.

### Equation for $K_d$ values

The tendency of the solid phase to buffer  $C_l$  can be described numerically using  $K_d$ . Since  $K_d$  is the rate of change of the ratio of sorbed P to solution P, it can be estimated from the first derivative of equation (2-1) with respect to the solution concentration, expressed as:

$$\frac{dC_s}{dC_l} = K_d = \beta_1 + 2\beta_2 C_l \quad (2-2)$$

## Results

### Phosphorus Desorption Isotherms: Kinetics and Effect of AEM Surface Area

The amount of P desorbed by the AEM strips increased with shaking time up to 2 h, after which it decreased once more (Fig. 2-1). Therefore, 2 h was chosen as the preferred shaking time. When the AEM surface area was increased, P desorption increased with increasing number of AEM strips (Fig. 2-2), with the relationship being linear between 1 and 6 strips ( $r^2 = 0.997$ ). When more than 6 strips were added, replicate variability increased dramatically; and the linear relationship weakened.

### Phosphorus Desorption Isotherms: Multiple Method vs. Sequential AEM Method

The amount of P initially sorbed at each P-addition level for the two extraction methods is provided in Table 2-1. There were significant differences in the amount of P sorbed between desorption methods for all 3 levels of P addition.

Both the Multiple and Sequential AEM Methods resulted in well-defined desorption isotherms for all 3 levels of sorbed P (Fig. 2-3). The P desorption GLM model well described the isotherms for both desorption methods for all three P-addition levels. As shown in Figure 2-4, 99.8% of the variability in observed  $C_s$  values were accounted for by the model. Type III model ANOVA table and parameter estimates for

the P desorption GLM model (Tables 2-2 and 2-3) confirmed that P desorption isotherms for each desorption method for each P-addition level were numerically different.

Statistical analysis also confirmed that the desorption methods and the P-addition levels affected the P desorption isotherms except for those isotherms at the lowest P-addition level ( $40 \mu\text{g P g}^{-1}$ ). There was no significant *Method\*Padded* interaction on  $C_s$  values at this P-addition level.

### **Phosphorus Desorption Isotherms: $K_d$ values**

Calculated  $K_d$  values derived from the P desorption GLM model were not a function of the desorption method or the amount of P initially sorbed. These  $K_d$  values were inversely and linearly related to equilibrium P concentration; and were expressed by the equation:

$$K_d = 48.1 - 60.862 C_l \quad (2-3)$$

The maximum  $K_d$  value was 48.1, which was the intercept of the above relationship.

### **Discussion**

In evaluating phosphorus bioavailability, it is P desorption rather than P sorption which determines the quantity of available P and subsequent ability of the soil to release P. Phosphorus flux through the soil to plant roots depends on the initial solution P concentration, the soil's buffer power, and the effective diffusion coefficient (Barber 1984). Buffer power and diffusion coefficients incorporate  $K_d$  values, which are calculated from P desorption isotherms. Therefore, a well-defined P desorption isotherm is critical, especially when evaluating P bioavailability using computer-based nutrient uptake models (Nye and Tinker 1977, Van Rees et al. 1990a, Smethurst and Comerford 1993, Macariola-See et al. 2003), since the output of the models is dependent on  $K_d$  values (Bhatti and Comerford 2002).

Our study showed that the Multiple AEM Method was suitable for developing desorption isotherms over a range of P sorption levels, thereby addressing our study's first objective. Regarding the second objective, it was shown that, for all P-addition levels, both methods provided well-defined P desorption isotherms, although they were numerically different. This difference was derived primarily from differences in the amount of P initially sorbed (Table 2-1). The fact that desorption isotherms by the different methods were not developed concurrently might also account for some of these differences.

However, since the ultimate goal of the desorption isotherms is to define  $K_d$  values with respect to solution P concentrations, both desorption methods gave the same result. Based on the GLM model used in our study, calculated  $K_d$  values were a function of simply the solution P concentration.

The most useful method for developing isotherms should be as rapid as possible in order to reduce the effects of shaking and microbial immobilization and mineralization (Barros Filho et al. in press). In this respect both the Multiple and Sequential AEM Methods are preferable to a dilution method, because the latter requires excessively high dilutions. The Multiple AEM Method may also be superior to sequential desorption methods, since it required about half the time to cover the same range of solution P concentration while providing more data points within that range. The Sequential AEM Method requires weeks to develop desorption isotherms; thus, this prolonged procedure may change the physio-chemical and biological status of P in both the solid and solution phases; and thereby influence the shape of the P desorption isotherm. In the case of highly aggregated soils, extended shaking may induce disaggregation, creating more

surface area. Reduced P desorption may result if more P is sorbed to newly created sorption sites.

Microbial P has been reported to reach its maximum level between 3 and 7 d after addition of 30 to 100 kg P ha<sup>-1</sup> as triple superphosphate to a Bh horizon from a Florida Spodosol (Bliss 2003). Therefore, the less time required to develop a desorption isotherm, the better the chance that the desorption method will not be influenced by outside factors. It can be concluded that the Multiple AEM Method is superior to the Sequential AEM Method because it requires less time to conclude.

Unfortunately, there is no standard methodology for developing desorption isotherms. The Multiple AEM Method gave more desorption data points with fewer extraction steps. This is encouraging enough to suggest that this method be tested on a range of soil types with an objective of evaluating its suitability in developing P desorption isotherms. These data from our study emphasize the need to standardized methodology for the development of desorption isotherms.

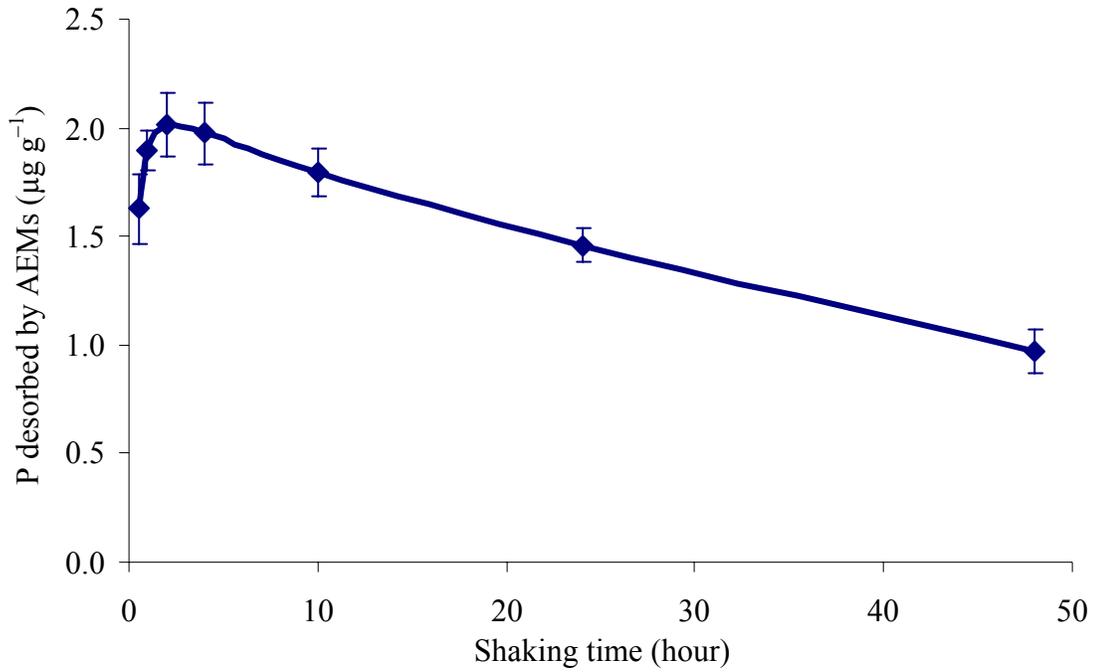


Figure 2-1 Kinetics of P desorption using AEMs

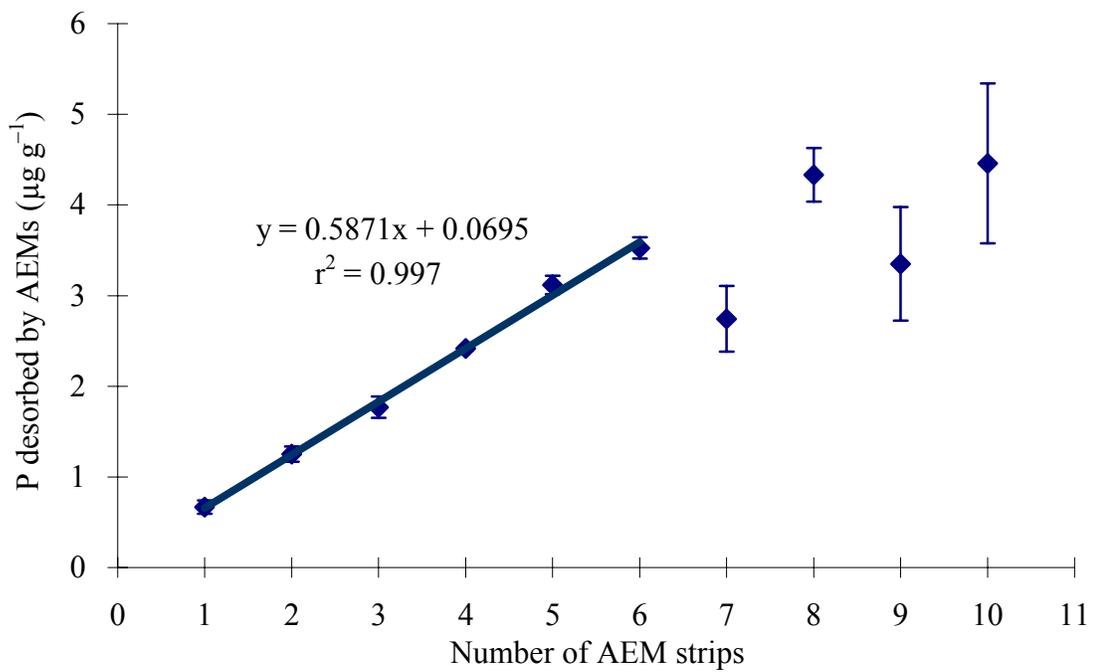


Figure 2-2 Phosphorus desorption with increasing number of AEM strips using a 2 h shaking time

Table 2-1 The amount of P sorbed for each desorption method at 3 different initial P-addition levels

P initially added ( $\mu\text{g g}^{-1}$ )	Desorption Method	P initially sorbed ( $\mu\text{g g}^{-1}$ )
180	Multiple AEM	152.04b <sup>†</sup>
	Sequential AEM	144.67a
80	Multiple AEM	74.91b
	Sequential AEM	72.12a
40	Multiple AEM	37.89a
	Sequential AEM	38.35b

<sup>†</sup> Different letters assigned in a column for each P-addition level denote significant differences between desorption methods at the 0.05 probability level, by Tukey's studentized range test

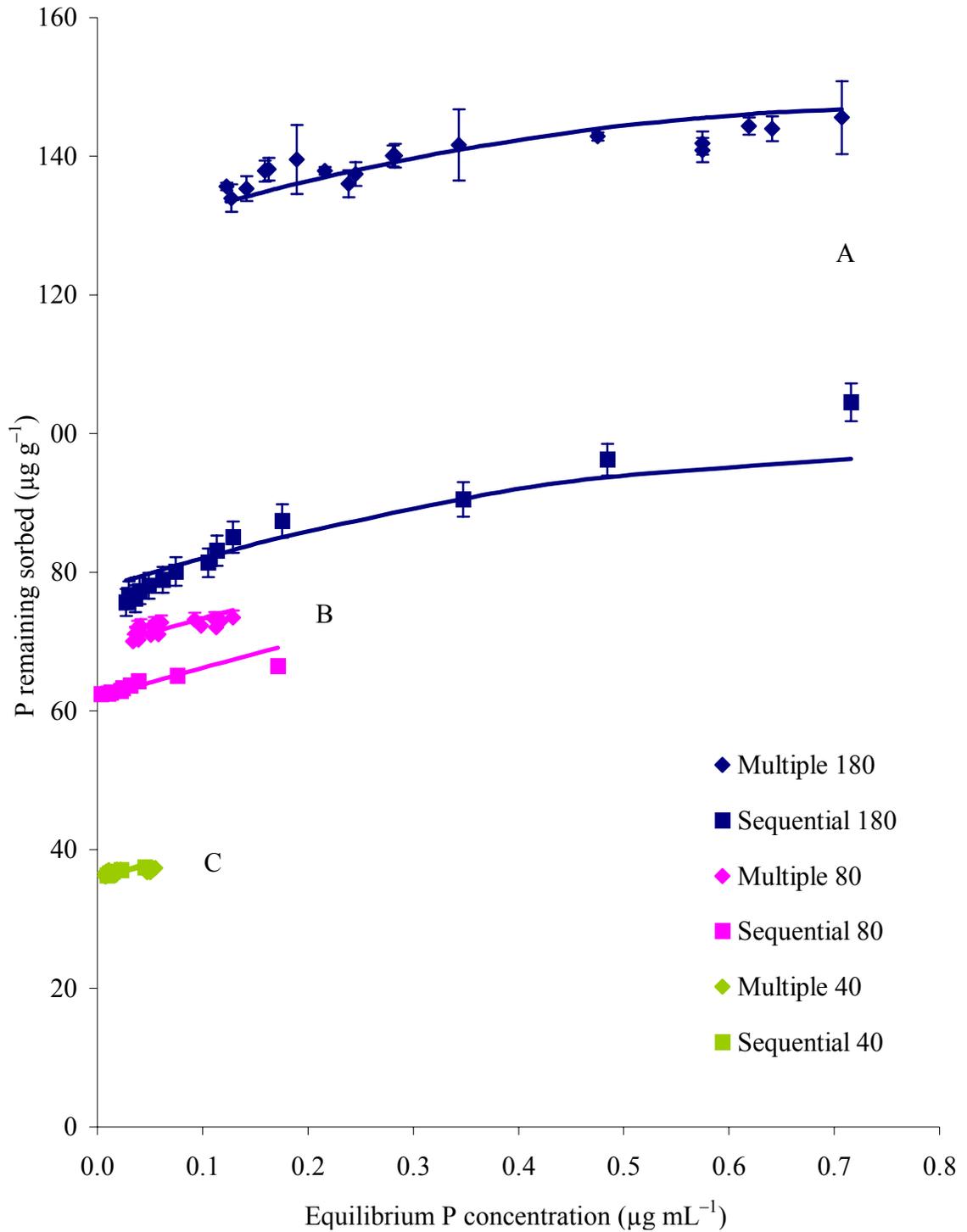


Figure 2-3 Phosphorus desorption isotherms using 2 desorption methods with 3 initial P-addition levels. A) 180  $\mu\text{g P g}^{-1}$ . B) 80  $\mu\text{g P g}^{-1}$ . C) 40  $\mu\text{g P g}^{-1}$

Table 2-2 ANOVA table for the GLM model evaluating the P desorption isotherms

Source	Type III Sum of Square	df	Mean Square	F value	Pr > F
Intercept	79692.83	1	79692.83	24832.61	< 0.0001
$C_l$	206.45	1	206.45	64.33	< 0.0001
$C_l^2$	46.39	1	46.39	14.46	< 0.0003
<i>Method</i>	5372.89	1	5372.89	1674.21	< 0.0001
<i>Padded</i>	22973.08	2	11486.54	3579.25	< 0.0001
<i>Method*Padded</i>	8640.22	2	4320.11	1346.16	< 0.0001
Error	240.69	75	3.21		

Table 2-3 Estimates for parameters of the GLM model used to test desorption isotherm differences

Parameter	Level of parameter	Estimate	Standard error	t value	Pr >  t
Intercept		128.00	1.00	127.99	< 0.0001
$C_i$		48.05	5.99	8.02	< 0.0001
$C_i^2$		-30.43	8.00	-3.80	< 0.0003
<i>Method</i> <sup>†</sup>	SEQ	-50.46	0.75	-67.23	< 0.0001
<i>Method</i>	MUL	0.00			
<i>Padded</i> <sup>‡</sup>	40	-92.41	0.97	-94.85	< 0.0001
<i>Padded</i>	80	-59.10	0.83	-71.27	< 0.0001
<i>Padded</i>	180	0.00			
<i>Method*Padded</i>	SEQ 40	50.72	1.12	45.34	< 0.0001
<i>Method*Padded</i>	SEQ 80	43.30	1.01	42.88	< 0.0001
<i>Method*Padded</i>	SEQ 180	0.00			
<i>Method*Padded</i>	MUL 40	0.00			
<i>Method*Padded</i>	MUL 80	0.00			
<i>Method*Padded</i>	MUL 180	0.00			

<sup>†</sup> SEQ and MUL represent Sequential AEM Method and Multiple AEM Method, respectively

<sup>‡</sup> Initial P-addition levels in  $\mu\text{g P g}^{-1}$

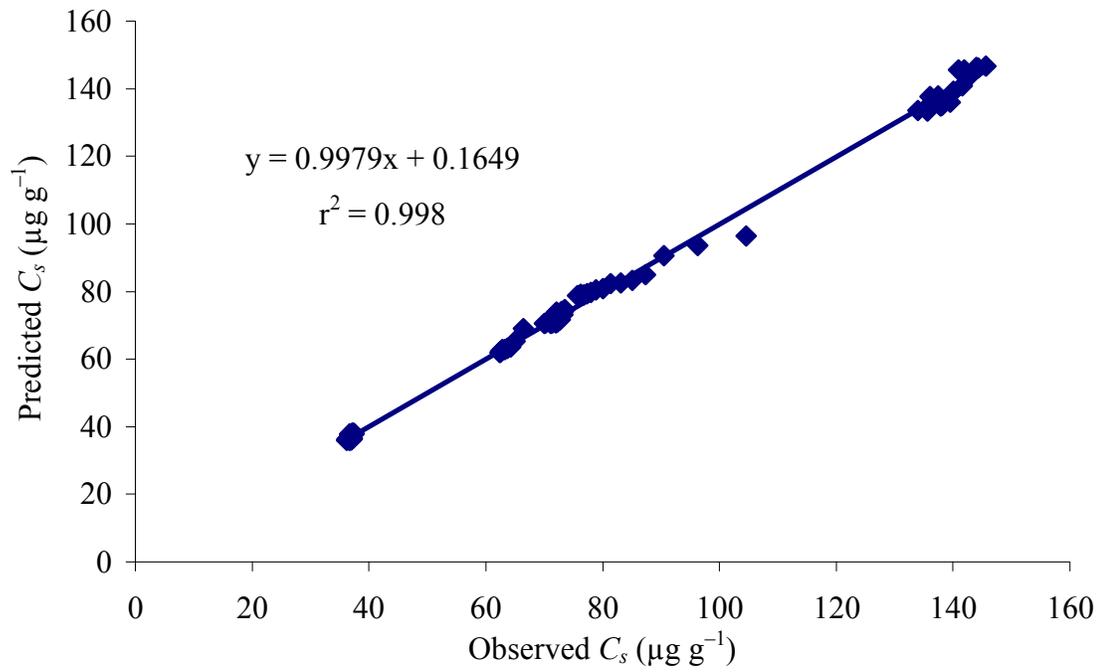


Figure 2-4 Relationship between observed  $C_s$  values and  $C_s$  values predicted from the P desorption GLM model

CHAPTER 3  
INFLUENCE OF SOIL pH ON INORGANIC PHOSPHORUS SORPTION AND  
DESORPTION IN A HUMID BRAZILIAN ULTISOL

**Introduction**

**Effect of Soil pH on P Sorption**

In tropical regions, liming is frequently used to raise soil pH and increase phosphorus bioavailability (Sanchez and Uehara 1980). However, published results regarding the effect of liming on P sorption and bioavailability are conflicting (Haynes 1982). Phosphorus sorption has been shown to both decrease (Naidu et al. 1990, Holford et al. 1994, Mora et al. 1999); and increase (Geelhoed et al. 1997, Pereira and De Faria 1998, Curtin and Syers 2001) with increasing pH. Still other reports have shown no significant influence of pH (Jones and Fox 1978, Arias and Fernandez 2001).

Liming 3 acid soils from southern Brazil increased the amount of P sorbed up to a pH of 5.0, at which point P sorption began to decrease (Anjos and Rowell 1987). Raising the pH of an Oxisol from the Cerrado region of Brazil with an initial pH of 4.5 also reduced P sorption by 18 to 24% (Smyth and Sanchez 1980). The authors attributed the reduced P sorption to increased hydroxyl concentration and increased competition between hydroxyl and phosphate ions for specific adsorption sites on mineral surfaces. Several authors thought that decreased P sorption could be due to the neutralization and precipitation of  $Al^{3+}$  and hydroxy-Al as Al hydroxide during liming; decreasing the number of P sorption sites (Smyth and Sanchez 1980, Anjos and Rowell 1987, Naidu et al. 1990). Bowden et al. (1980) and Haynes (1982) added that the mineral surface

became increasingly negative with increasing pH, which resulted in greater electrostatic repulsion and decreased P sorption.

Phosphate is preferentially sorbed by soil mineral surfaces as  $\text{HPO}_4^{2-}$  rather than as  $\text{H}_2\text{PO}_4^-$ ; and the concentration of the divalent ion ( $\text{HPO}_4^{2-}$ ) increases 10-fold for each unit increase in pH from 2 to 7 (Bowden et al. 1980). This change partially offsets any decrease in electrostatic potential (Haynes 1984). Thus, P sorption may decrease relatively slowly until pH 7; and then, above pH 7, the increase of  $\text{HPO}_4^{2-}$  concentration becomes progressively slower; whereas the decrease in surface potential continues, resulting in a more rapid decrease in P sorption (Haynes 1984).

In contrast to the studies above, Chen and Barber (1990) showed that for acid weathered soils of pH 4.2 to 4.6 when adjusted up to a pH of 8.3, sorbed P increased up to pH 6.0 to 6.2, and then decreased at higher pH values. The initial increase in P sorption was explained as the formation of amorphous hydroxyl Al with highly active sorbing surfaces. The subsequent decrease in P sorption was attributed to increased competition of hydroxyl with phosphate for sorption sites. Similar conclusions were drawn from liming studies involving Nigerian acid soils (Mokwunye 1975) and Al-organic matter complexes (e.g., Al-peat and Al-humate) (Haynes and Swift 1989).

### **Effect of Soil pH on P Desorption**

There are few investigations that focused on soil pH and P desorption; and the results have been inconsistent; increased P desorption with increasing pH in some cases (De Smet et al. 1998) and with decreasing pH in others (Barrow 2002). Studies of P desorption kinetics for synthetic goethite as a function of suspension pH from 4 to 10 (Madrid and Posner 1979, Cabrera et al. 1981) showed increased P desorption with increasing suspension pH. This trend could again be explained as above; as due to

competition from hydroxyl ions; and a lessened attraction or an enhanced repulsion caused by increased negative charge on the surface with increasing pH.

Rupa et al. (2001) also desorbed P from 3 surface soils using 6 consecutive dilution extractions at pH values varying from 4.2 to 8.0. The surface soils represented an Indian Vertisol, Alfisol, and Oxisol. Phosphorus desorption increased for all soils up to a pH of 5.5, and then decreased at pH values of 6.7 and 8.0. The soils had high levels of exchangeable  $\text{Ca}^{2+}$  plus  $\text{Mg}^{2+}$  (41.2, 8.7, and 4.3  $\text{cmol}_c \text{kg}^{-1}$  for Vertisol, Alfisol, and Oxisol, respectively). It was thought that decreased desorption at high pH values could be due to P precipitation as a Ca-phosphate.

Phosphorus desorption is a key process affecting inorganic P bioavailability; and desorption also can identify specific pools of bioavailable P. However, in order to use the desorption process in nutrient uptake models such as described by Smethurst and Comerford (1993), a P desorption isotherm is required. An isotherm describes the amount of P on the solid phase relative to the solution P concentration with the slope of this relationship being called the partition coefficient,  $K_d$ . The  $K_d$  is defined as the rate of change of the amount desorbed from the solid phase over the rate of change in solution concentration. The  $K_d$  values are directly related to soil buffer power as seen in the following equation:

$$b = \theta + \rho K_d \quad (3-1)$$

where  $b$  is the soil buffer power,  $\theta$  is volumetric water content in  $\text{cm}^3$  of water per  $\text{cm}^3$  of soil, and  $\rho$  is soil bulk density in units of  $\text{g cm}^{-3}$ . Both  $K_d$  and  $b$  are critical parameters for computer-based nutrient uptake models because of their role when calculating diffusion as a nutrient-supply mechanism. Diffusion is important because for many soils,

diffusion is the mechanism supplying 90 to 98% of P absorbed by roots (Barber 1980). Unfortunately, measuring P desorption isotherms is a time-consuming process; and there is no standardized method for their development (see Chapter 2).

The overall objective of our study was to investigate the influence of pH on P desorption from an Ultisol from the Atlantic Forest of Brazil. The Atlantic Forest is a major Brazilian ecosystem type, with only about 7.6% of the native forest remaining at present (Morellato and Haddad 2000). Much of the soil in this area has been degraded by deforestation and subsequent extensive management for pasture and row crops. Phosphorus management is a crucial component of rehabilitating these degraded soils. This soil also represents an area considered one of the most biodiverse on the planet (Oliveira and Fontes 2000).

Specific objectives of our study were to study this soil and its properties, as related to the effect of soil pH on P sorption and desorption. The first hypothesis was that P sorption is a function of pH, with decreasing sorption with increasing pH between 4.7 and 7.0. This soil is inherently low in exchangeable  $Al^{3+}$ , so the mechanism of amorphous Al-OH creating new surface for sorption was considered relatively unimportant. Understanding the influence of liming on P sorption for these soils should play a role in their management to enhance P bioavailability. A second hypothesis was that P desorption is a function of pH, with increasing desorption as pH increases. The degree to which liming influences P desorption is another important aspect of P management that is virtually unknown; and should also be critical to proper nutrient management.

## Materials and Methods

### Soil Material and Its Characterization

The soil material used in our study was the surface horizon (0 to 30 cm depth) of a Kandiudult (Soil Survey Staff 1999), known as an Argissolo vermelho/vermelho–amarelo distrófico in the Brazilian system (Oliveira et al. 1992). It was taken from under a native Atlantic Forest cover type located near Una Ecoparque near the city of Una, Bahia, Brazil. Using a shovel, the material was collected from a 1 ha area. Approximately 20 sampling points were combined; and the soil was air-dried, passed through a 2-mm sieve, and stored in plastic bags.

Soil characterization was performed as follows: pH (1:2 soil:deionized H<sub>2</sub>O; 1:2 soil:1 M KCl; and 1:2 soil:0.01 M CaCl<sub>2</sub>) using a glass-electrode pH meter, Orion Model 720A; organic carbon using a Walkley-Black method (Nelson and Sommers 1982); total N by flash combustion using a Carlo Erba Model NA 1500 apparatus (Dumas 1831); particle-size distribution using a pipette method (Gee and Bauder 1986); exchangeable cations using 1 M ammonium acetate (pH 4) as the displacing solution, with Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> measured by atomic absorption spectroscopy; 1 M KCl-exchangeable Al<sup>3+</sup> and 1 M ammonium acetate-exchangeable Fe<sup>3+</sup> measured by atomic absorption spectroscopy; acid ammonium-oxalate- and sodium citrate-dithionite-extractable Al<sup>3+</sup> and Fe<sup>3+</sup> determined by the method of McKeague and Day (1966); water-extractable P using 50 mM KCl; Mehlich 1-extractable P (Mehlich 1953); total P by digestion with H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> as described by Grierson et al. (1999); and clay mineralogy and its quantification determined by X-ray diffraction and thermogravimetric analysis, respectively.

### **Phosphorus Sorption Isotherms**

Two 100 g sub-samples were taken from the bulk soil sample and adjusted to pH 5.9 and 7.0 from the original pH of 4.7. Each sub-sample received the appropriate volume of NaOH solution to increase soil pH, based on an acid-base titration curve for the soil (appendix A). The sub-samples then were air-dried at room temperature.

Phosphorus sorption isotherms were produced for each of the 3 pH levels. Solution pH was not controlled during the sorption process. Triplicate 2 g soil samples were weighed into 50 mL centrifuge tubes; and 20 mL of 50 mM KCl containing 2, 4, 6, 8, 10, 12, 14, 16, 18, or 20  $\mu\text{g P mL}^{-1}$  as  $\text{KH}_2\text{PO}_4$  was added to each tube. Triplicate blanks of 20 mL of 50 mM KCl without soil and without P were included as well. The tubes were shaken horizontally for 20 h; and centrifuged for 15 min at 2500 rpm for the pH 4.7 and 5.9 samples, and for 15 min at 10,000 rpm for the pH 7.0 sample in order to clear the supernatant solution. The supernatant was filtered through Whatman No. 5 filter paper; and measured for soluble reactive P by the method of Murphy and Riley (1962), which was used for all P determinations in our study. Soluble reactive P as measured by this method is operationally defined as inorganic P. Sorbed P was calculated based on the difference between the initial solution concentration added and the final concentration in the filtrate.

### **Phosphorus Desorption Isotherms Using the Multiple AEM Method**

For the Multiple AEM Method, pH of the soil was adjusted as described for the P sorption-isotherms study. The pH adjustment was only at the beginning of the experiments and was not controlled throughout the study. The pH control during P desorption is not expected to have a significant effect on the P desorption process

(Bhatti and Comerford 2002); and pH is not controlled under field conditions following liming.

Phosphorus desorption isotherms were initiated from 3 different sorption points at each pH. Phosphorus was sorbed onto the soil using 40, 80, or 180  $\mu\text{g P g}^{-1}$  soil. These levels were chosen because they bounded normal fertilizer additions; and were equivalent to 16, 32, and 72  $\text{kg P ha}^{-1}$  (assuming fertilizer was broadcast and incorporated into the top 3 cm of soil).

Triplicate 2 g soil samples from each pH level were weighed into 6 sets of triplicate centrifuge tubes; and the initial weight of tube + soil was recorded. Twenty milliliters of 50 mM KCl containing 4, 8 or 18  $\mu\text{g P mL}^{-1}$  as  $\text{KH}_2\text{PO}_4$  were added to each tube; and the total initial weight of tube + soil + solution was recorded. Tubes were shaken for 20 h; and centrifuged for 15 min at 2500 rpm for the pH 4.7 and 6.0 samples, and for 15 min at 10,000 rpm for the pH 7.1 sample in order to clear the supernatant solution. The supernatant solution was filtered through Whatman No. 5 filter paper; and P in the filtrate was determined.

After decanting the supernatant, weights of tube + soil were recorded. Each tube then was filled with 50 mM KCl to its initial tube + soil + solution weight. Anion exchange membrane (AEM) strips (1.88 cm  $\times$  7.50 cm) prepared in KCl solution were rinsed with double-deionized water; and 1, 2, 3, 4, 5, or 6 strips were inserted into each of 6 sets of triplicate tubes. The tubes were shaken for 2 h; then the strips were removed from the tubes; were rinsed with double-deionized water; and were placed in another 6 sets of triplicate tubes filled with 15 mL of 2 M KCl for the 1-, 2-, and 3-strip tubes; and with 30 mL for the 4-, 5-, and 6-strip tubes. These tubes were shaken for 30 min; and

then filtered through Whatman No. 5 filter paper. Phosphorus in filtrate was measured. The original tubes with soil were shaken for 20 h; and then centrifuged for 15 min at 2500 rpm for the pH 4.7 and 6.0 samples, and for 15 min at 10,000 rpm for the pH 7.1 sample. The supernatant solution was filtered through Whatman No. 5 filter paper; and P in the filtrate was determined.

The first step of this procedure was to reduce desorbable P on the solid phase using AEMs. The equilibration step was required to develop a desorption isotherm because the soil must come into an equilibrium or quasi-equilibrium to measure an equilibrium solution concentration. The entire procedure of the previous paragraph was repeated two more times, resulting in a total of 3 desorption steps and yielding 18 points on a desorption isotherm for each pH in 4 d.

### **Equation for P Sorption and Desorption Isotherms**

The Langmuir equation was fitted to all data for both the sorption and desorption isotherms. The following form of the equation was used:

$$C_s = \frac{K b C_l}{1 + K C_l} \quad (3-2)$$

where  $C_s$  is the amount of P sorbed onto the solid phase per unit mass of soil in  $\mu\text{g P g}^{-1}$  of soil;  $C_l$  is the equilibrium concentration of P in  $\mu\text{g P mL}^{-1}$ ;  $K$  is the affinity index expressed in  $\text{mL } \mu\text{g}^{-1}$  of P; and  $b$  is the sorption maximum with unit of  $\mu\text{g P g}^{-1}$  of soil. Both  $K$  and  $b$  are empirical constants that can be calculated from a linear form of the equation plotted as  $C_l/C_s$  against  $C_l$ :

$$\frac{C_l}{C_s} = \frac{C_l}{b} + \frac{1}{K b} \quad (3-3)$$

where  $1/b$  and  $1/Kb$  are the slope and intercept of the linear regression, respectively.

Ability of the solid phase to buffer  $C_l$  can be described numerically using the partition coefficient,  $K_d$ . This reflects the rate of change of the ratio of sorbed P to solution P; and is the first derivative of equation (3-2) with respect to the solution concentration:

$$\frac{dC_s}{dC_l} = K_d = \frac{K b}{(1 + K C_l)^2} \quad (3-4)$$

### Statistical Analysis

Statistical differences among different linear regression lines were tested using the General Linear Models procedure in the Statistical Analysis System framework (SAS Institute 1988). Analysis of variance (ANOVA) was used to test differences among regression line parameters. Significance of the difference among means was determined by t-tests at the  $p = 0.05$  level. Means and standard deviations were used to summarize the data from P sorption and desorption isotherms, where applicable.

### Results

Selected physical and chemical properties of the soil are summarized in Table 3-1. The soil was acidic with low cation exchange capacity; and with low water-soluble and Mehlich 1-extractable P. Its 25% clay content was dominated by kaolinite. The iron content was greater than the aluminum content in both the amorphous and crystalline oxide forms.

### Phosphorus Sorption pH Envelope

Phosphorus sorption was a function of soil initial pH, with sorption decreasing with increasing pH when equilibrium solutions P concentrations were less than about  $3 \mu\text{g P mL}^{-1}$  (Fig. 3-1a). Phosphorus sorption decreased by up to 21% when pH was

increased from 4.7 to 5.9; and decreased by up to 34% when pH was increased from 4.7 to 7.0. Above  $3 \mu\text{g P mL}^{-1}$ , there were no sorption differences between pH treatments.

The Langmuir equation fit P sorption data for all 3 pH levels ( $r^2 = 0.970$  to  $0.993$ , Table 3-2), with Langmuir parameters such as  $K$  and  $b$  values being affected by pH levels. As pH increased,  $K$  values significantly decreased; while  $b$  values increased significantly only at the highest pH level (Table 3-2).

Changes in  $K_d$  values relative to equilibrium P concentration are provided in Figure 3-2. This relationship proved to be a function of soil pH. The  $K_d$  values at the higher pH levels were lower than that at the original pH, once the equilibrium concentration was reduced to about  $0.5 \mu\text{g P mL}^{-1}$ . The  $K_d$  values were as much as 22% and 34% lower at pH 5.9 and 7.0, respectively, than at pH 4.7.

### **Phosphorus Desorption pH Envelope**

Phosphorus desorption exhibited the expected hysteresis between sorption and desorption at all 3 pH levels for each level of P loading (Fig. 3-3). Since P sorption was a function of initial soil pH as mentioned above, P desorption isotherms began from different sorption points which depended on soil pH and the amount of P initially added (Table 3-4).

The Langmuir equation fit the majority of the desorption data well ( $r^2 = 0.338$  to  $0.867$ ) except for the low P-addition level; and soil pH significantly influenced the values of the Langmuir equation's parameters (Table 3-3). For the medium and high levels of added P,  $K$  values were significantly decreased only at pH 7.1. At the low level of added P, the  $K$  value significantly increased at pH 6.0 but significantly decreased at pH 7.1, compared to values at pH 4.7. The range of  $K$  values across pH levels for the medium

and low levels of P addition was approximately 6-fold and 40- to 127-fold higher than at the high P-addition level.

The  $b$  values were significantly lower at pH 6.0 and 7.1 than at pH 4.7, but were not significantly different from each other for the high level of P addition. For the medium P-addition level,  $b$  values for both elevated pH levels were significantly higher than at the original pH. For the low P-addition level,  $b$  value only at pH 6.0 was significantly higher than at pH levels of 4.7 and 7.1.

Phosphorus desorption was a function of soil pH when expressed in terms of either the amount of P desorbed or the ratio of P desorbed to P initially sorbed (Table 3-4). Higher pH levels resulted in more P desorbed and a higher ratio of P desorbed to P initially sorbed. This was true for both the medium and high levels of P addition. However, for the low level of P added, both P desorbed and the corresponding ratio were slightly decreased at pH 6.0 and significantly increased at pH 7.1, compared to values at pH 4.7.

The calculated  $K_d$  values, when plotted against equilibrium P concentrations, evidenced opposite trends to those documented in the sorption study (Fig. 3-4). For the high level of P addition,  $K_d$  values at pH 6.0 was lower than at pH 4.7 by up to 13%; while  $K_d$  values at pH 7.1 was up to 38% higher than at pH 4.7. For example,  $K_d$  values at pH 4.7, 6.0, and 7.1 were 32.9, 28.7, and 43.7 at an equilibrium concentration of  $0.2 \mu\text{g P mL}^{-1}$ , respectively.

For the medium level of P addition,  $K_d$  values at pH 6.0 and 7.1 were 13 to 14% and 76 to 85% greater than at pH 4.7, respectively. For the low level of P addition,  $K_d$

values were 52 to 53% lower at pH 6.0 and 120 to 126% greater at pH 7.1, respectively, compared to values at pH 4.8.

## Discussion

### Soil pH Effect on P Sorption

Results from the P sorption study supported the hypothesis that, in these soils, P sorption decreases with increasing pH. This is consistent with what has been shown for other weathered, acid soils with low levels of exchangeable  $Al^{3+}$  (Naidu et al. 1990). This result has been credited to an increased electrostatic repulsion due to the increased negative surface charge (Bowden et al. 1980, Haynes 1982) that accompanies increasing pH. A contributing factor is that higher hydroxyl concentrations, which can be 10 to 1000 times higher than at lower pH levels, compete effectively with phosphate ions for specific sorption sites on mineral surfaces (Smyth and Sanchez 1980). This result may also be assisted by a reduction in the number of P-sorption sites. At higher pH levels Al hydroxide polymers can neutralize sites where more reactive Al surfaces once were present (Sanchez and Uehara 1980). Soils dominated by kaolinite, goethite, and gibbsite, like the soil used in our study, are particularly susceptible to each of the above-named mechanisms.

Empirically, trends for the Langmuir  $K$  parameter and for  $K_d$  support these explanations. The reduced Langmuir  $K$  values with increasing pH suggest a reduced P affinity for the sorption surface. The  $K_d$  represents the rate of change in the amount of P sorbed relative to the amount of P in solution upon continued introduction of P to the solution phase. Therefore, decreasing  $K_d$  with increasing pH corresponds to decreasing rates of change in the amount of P sorbed, leaving more of the applied P in solution.

At higher equilibrium concentrations ( $\geq 3 \mu\text{g P mL}^{-1}$ ), there were no differences between isotherms at any pH. However, at a commonly practiced P-fertilization rate of  $50 \text{ kg P ha}^{-1}$ , which corresponds to  $125 \mu\text{g P g}^{-1}$  of soil using the above assumptions, maximum solution P concentration was only  $1.4 \mu\text{g P mL}^{-1}$ .

Soil solution P concentration is commonly around  $0.05 \mu\text{g P mL}^{-1}$  (Barber et al. 1962), and seldom higher than  $0.3 \mu\text{g P mL}^{-1}$  in most agricultural soils (Fried and Shapiro 1961). It is typically even lower in soils under native forests and forest plantations (Ballard 1980). Therefore, P sorption isotherms for the same 3 pH values were replotted focusing on a lower solution P-concentration range ( $0.0\text{--}1.0 \mu\text{g P mL}^{-1}$ , Fig. 3-1b).

These data show that P sorption decreases with pH increase under common P-fertilization practices. At a solution concentration of  $0.2 \mu\text{g P mL}^{-1}$ , sorbed P was 43, 36, and  $32 \mu\text{g P g}^{-1}$  of soil at pH 4.7, 5.9, and 7.0, respectively. These represent 16% and 26% reduction in sorption compared to a pH of 4.7 when the soil is limed to pH 5.9 and 7.0, respectively. These percentages represent 2.8 to  $4.5 \text{ kg ha}^{-1}$  of fertilizer P remaining in solution, ready for plant uptake.

### **Soil pH Effect on P Desorption**

Phosphorus desorption is a primary control on inorganic P bioavailability; yet virtually nothing is known about the nature of P desorption for acid, weathered tropical soils. Our study represents the first investigation of desorption isotherms for soils in this region of Brazil. The results endorse the hypothesis that P desorption increases with increasing soil pH. Both the decreased Langmuir  $K$  and the increased amounts of P desorbed at elevated pH levels support the positive relationship between pH and P desorption. These results are consistent with the findings of He et al. (1994). He and

associates determined P desorption from a variety of minerals and ranked the minerals according to their desorption capacity: goethite < kaolinite < amorphous Al-oxide < montmorillonite. Affinity constants also decreased in the same order.

The affinity constant,  $K$ , is related to the amount of P sorbed. Phosphate is held with its highest affinity to the soil surface when the surface coverage of sorbed P is low. The affinity then decreases with increasing surface coverage (Ryden et al. 1977).

The calculated  $K_d$  for desorption represents the rate of change in the amount of P desorbed relative to the solution P concentration. Therefore, increasing  $K_d$  is interpreted as increasing the rate of change in P desorption at a particular solution P concentration, as was observed for all levels of P loading when soil pH was raised to 7.1. Similar results can be found among the limited P desorption studies previously reported (Hingston et al. 1974, Madrid and Posner 1979, He et al. 1989, De Smet et al. 1998).

General consensus regarding the effect of soil pH on P desorption, drawn from the findings of these authors, is that increased P desorption with increased pH is due both to increased competition with hydroxyl ions and to the change in electrostatic potential of the surface. Although hydroxyl can be a good competitor with phosphate for metal coordination sites on the surface (McBride 1994), this theory is still untested because it has not been convincingly shown that electrostatic repulsion affects the specifically sorbed anions that are directly coordinated to discrete surface metal cations. Given the lack of prior work on P desorption mechanisms, it is suggested that this is a fruitful avenue for further studies.

Phosphorus desorption is potentially controlled by the type of P complexation with the surface: monodentate, bidentate mononuclear, and bidentate binuclear. These

complexes can be either non-protonated or protonated, depending on suspension pH (Tejedor-Tejedor and Anderson 1990). Bidentate complexes require more activation energy to break the bond than do monodentate complexes, so can be more difficult for P desorption to take place in environments where the bidentate complexes predominate between phosphate and the soil surface.

In spite of precise investigations using infrared spectroscopy (Parfitt and Atkinson 1976) and X-ray photoelectron spectroscopy (Martin and Smart 1987), assigning peaks among possible complexation types remains controversial (Persson et al. 1996, Arai and Sparks 2001, Kreller et al. 2002). Clarification of the effects of pH and P surface coverage on the formation of different surface-complex types may help to resolve these issues.

Environmental and socio-economic restrictions such as low pH, high P fixation capacity, and high costs of P fertilizer and liming materials make P management for humid, acid tropical soils problematic. Management strategies that make the most efficient use of P and lime are required. To this end, one objective should be to raise the soil solution P concentration, since it is directly related to plant P uptake. A small increment in solution P concentration increased through liming-induced P desorption can significantly influence plant growth. For example, Jones and Benson (1975) showed that P in sweet corn leaves and equilibrium solution P levels were correlated, with a critical solution P concentration of 0.12 to 0.13  $\mu\text{g P mL}^{-1}$ . The relationship between plant P and equilibrium P concentrations was curvilinear over the range of P concentrations from 0.01 to 1.8  $\mu\text{g P mL}^{-1}$  (Fox and Kamprath 1970).

Combining the results from both parts of our current study we conclude that liming has a twofold positive effect. It reduces the amount of P sorbed and increases the amount of P desorbed. Both these changes induce increased solution P concentration and P bioavailability. Translating these results, in combination with the use of non-conventional liming materials found in rural areas (Ohno and Erich 1990, Erich 1991, Chung and Wu 1997, Van den Berghe and Hue 1999, Nkana et al. 2002), should help rural farmers in tropical areas make the most efficient use of limited agricultural resources.

Table 3-1 Surface soil (0–30 cm) properties for the Atlantic Forest soil, Bahia, Brazil

Property	Value
Physical	
Soil texture, %	
Sand	66
Silt	9
Clay	25
Clay mineralogy, %	
Kaolinite	80
Goethite	7
Chemical	
pH	
1:2 water	4.7
1:2 KCl	3.6
1:2 CaCl <sub>2</sub>	3.6
Organic carbon, %	2.51
Total N, %	0.20
Exchangeable Ca <sup>2+</sup> , cmol <sub>c</sub> kg <sup>-1</sup>	0.53
Exchangeable Mg <sup>2+</sup> , cmol <sub>c</sub> kg <sup>-1</sup>	0.47
Exchangeable K <sup>+</sup> , cmol <sub>c</sub> kg <sup>-1</sup>	0.12
Exchangeable Na <sup>+</sup> , cmol <sub>c</sub> kg <sup>-1</sup>	0.06
Water-extractable (50 mM KCl) P, µg g <sup>-1</sup>	0.02
Mehlich 1-available P, µg g <sup>-1</sup>	2.68
Total P, µg g <sup>-1</sup>	98.29
KCl-exchangeable Al, µg g <sup>-1</sup>	60.52
NH <sub>4</sub> acetate-exchangeable Fe, µg g <sup>-1</sup>	2.85
AAO <sup>†</sup> extractable Al, %	0.16
AAO extractable Fe, %	0.45
SCD <sup>‡</sup> extractable Al, %	0.31
SCD extractable Fe, %	1.30

<sup>†</sup> Acid ammonium-oxalate

<sup>‡</sup> Sodium citrate-dithionite

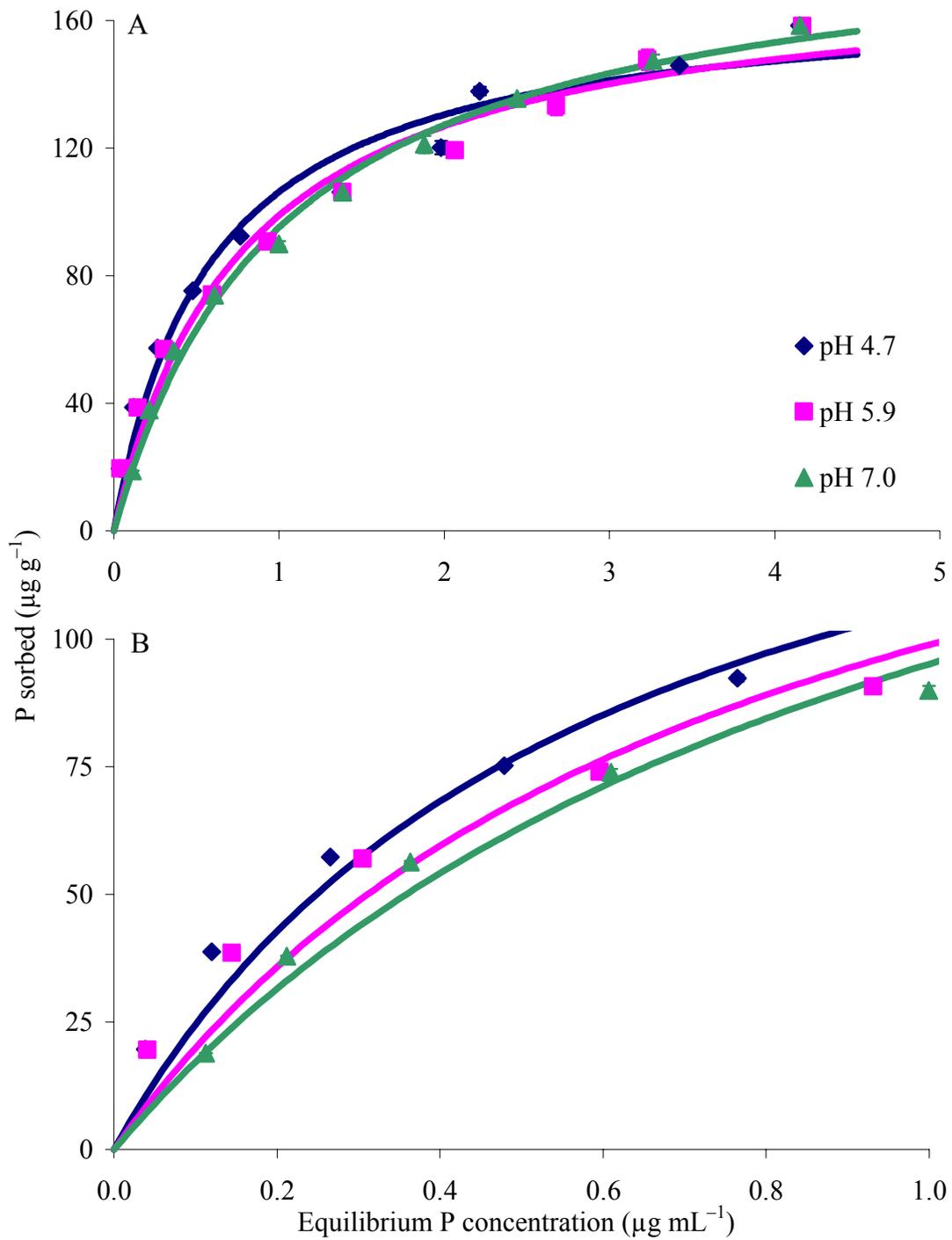


Figure 3-1 Phosphorus sorption isotherms at 3 different soil pH levels with equilibrium concentration of A) 0–5  $\mu\text{g P mL}^{-1}$  and B) 0.0–1.0  $\mu\text{g P mL}^{-1}$

Table 3-2 Langmuir parameters for P sorption isotherms at 3 different soil pH levels

Initial soil pH	Parameters of Langmuir equation		$r^2$
	$K$	$b$	
	mL $\mu\text{g}^{-1}$	$\mu\text{g g}^{-1}$	
4.7	1.69b <sup>†</sup>	169.04a	0.970
5.9	1.27ab	177.04ab	0.971
7.0	0.98a	192.12b	0.993

<sup>†</sup> Different letters assigned in a column for each parameter denote significant differences among pH levels at the 0.05 probability level, performed by Tukey's studentized range test.

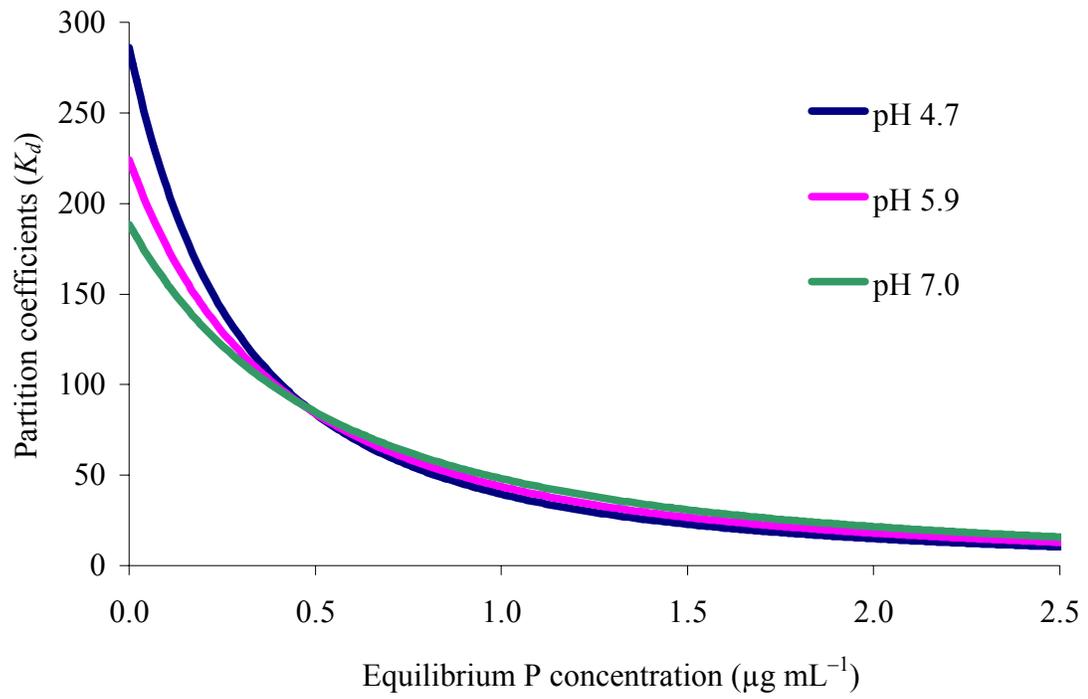


Figure 3-2 Partition coefficients relative to equilibrium P concentration for P sorption isotherms at 3 different soil pH levels

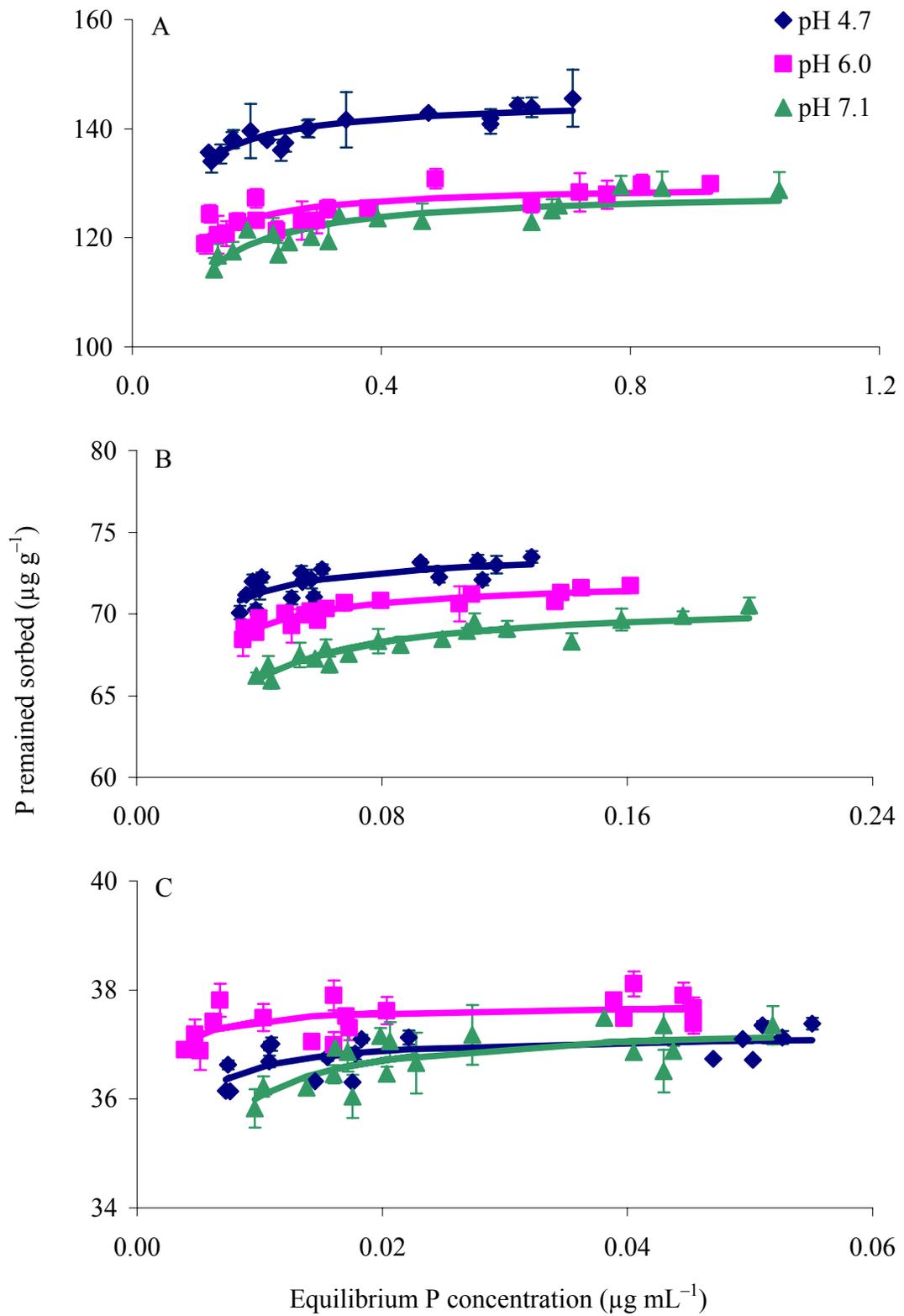


Figure 3-3 Phosphorus desorption isotherms at 3 different soil pH levels with 3 different initial P-addition levels. A)  $180 \mu\text{g P g}^{-1}$ . B)  $80 \mu\text{g P g}^{-1}$ . C)  $40 \mu\text{g P g}^{-1}$

Table 3-3 Langmuir parameters for P desorption isotherms at 3 different soil pH levels with 3 different initial P-addition levels

P added $\mu\text{g g}^{-1}$	Initial pH	Parameters of Langmuir isotherm		
		$K$ $\text{mL } \mu\text{g}^{-1}$	$b$ $\mu\text{g g}^{-1}$	$r^2$
180	4.7	100.05b <sup>†</sup>	145.28b	0.800
	6.0	102.88b	129.78a	0.651
	7.1	62.99a	128.34a	0.780
80	4.7	688.70b	73.86c	0.583
	6.0	586.92b	72.16b	0.867
	7.1	349.89a	70.73a	0.860
40	4.7	6046.62b	37.19a	0.430
	6.0	12999.13c	37.72b	0.338
	7.1	2668.71a	37.40a	0.524

<sup>†</sup> Different letters assigned in a column for each parameter at each P-addition level denote significant differences among pH levels at the 0.05 probability level, performed by Tukey's studentized range test.

Table 3-4 Total amount and ratio to P sorbed of P desorbed at 3 different soil pH levels with 3 different initial P-addition levels

P added	Initial pH	P sorbed	Total P desorbed	Ratio of P desorbed to P initially sorbed
$\mu\text{g g}^{-1}$		$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	%
180	4.7	152.04	18.94a <sup>†</sup>	12.5a
	6.0	139.47	21.52a	15.4b
	7.1	139.28	25.61b	18.4c
80	4.7	74.91	5.02a	6.7a
	6.0	73.65	5.59a	7.6a
	7.1	72.54	6.68b	9.2b
40	4.7	37.89	1.77ab	4.7ab
	6.0	38.44	1.68a	4.4a
	7.1	37.86	2.10b	5.5b

<sup>†</sup> Different letters assigned in a column at each P-addition level denote significant differences among pH levels at the 0.05 probability level, performed by Tukey's studentized range test.

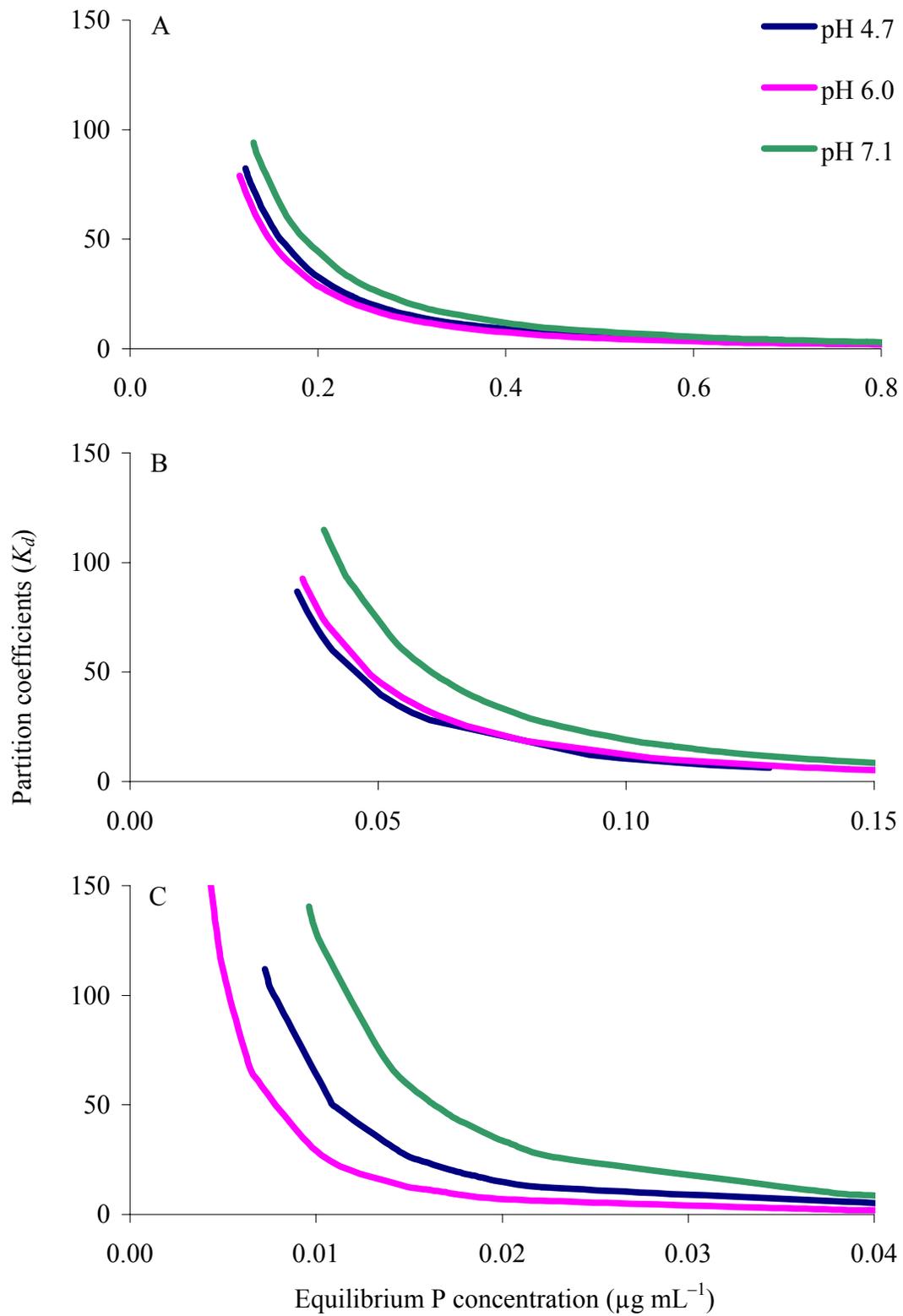


Figure 3-4 Partition coefficients relative to equilibrium P concentration for P desorption isotherms at 3 different soil pH levels with 3 different initial P-addition levels. A) 180  $\mu\text{g P g}^{-1}$ . B) 80  $\mu\text{g P g}^{-1}$ . C) 40  $\mu\text{g P g}^{-1}$

CHAPTER 4  
INFLUENCE OF LOW MOLECULAR WEIGHT ORGANIC ANIONS ON  
PHOSPHORUS DESORPTION AND BIOAVAILABILITY IN A HUMID  
BRAZILIAN ULTISOL

**Introduction**

Natural ecosystems and crops developing on humid, tropical soils often suffer from phosphorus (P) deficiency. Low levels of native bioavailable inorganic and organic P are common and P, when applied as fertilizer, can be sorbed by Al and Fe oxides. Sorbed P can also form a range of minerals in combination with Ca, Al and Fe; whereby little remains bioavailable (McLean 1976, Hsu 1982). However, some of the sorbed P is still bioavailable through the processes of desorption from the soil surface and dissolution of relatively soluble P mineral compounds. These adsorption/desorption and precipitation/dissolution equilibria control the concentration of P in the soil solution, its chemical mobility, and its bioavailability (Hinsinger 2001).

To alleviate P deficiency, soil management practices have been studied under field and laboratory conditions. Particularly important among them are liming and the use of organic and inorganic acids (e.g., from animal wastes) to enhance bioavailability of P in both native and applied forms. The effect of liming on inorganic P availability remains controversial (Haynes 1982) and was discussed in Chapter 3. The effect of organic acids on inorganic P bioavailability is discussed below.

The term desorption is used here in two ways. First, it is used as above to represent a process that is simply the reverse of adsorption. Second, it is used in the same fashion

as sorption, not distinguishing desorption from dissolution. This is considered necessary until proper terminology consistent with that for sorption is accepted.

To clarify the types of desorption that occur in soils, the following categorization is suggested. There are two major mechanisms that describe inorganic P desorption: disequilibria desorption and ligand desorption. These can be subcategorized into exchange and dissolution types of desorption (Table 1-1). Following Le Châtelier's Principle, disequilibria desorption requires a disequilibria between solid and solution phases. This disequilibria can be created by removal of solution P, mediated by various processes. As the solution P concentration decreases, P is replenished through desorption of P adsorbed onto the soil surface (disequilibria exchange) or dissolution of relatively insoluble P compounds (disequilibria dissolution) (Wolf and London 1994).

Ligand desorption is due to reaction of sorbed P with anions of organic acids such as oxalate, citrate, and malate, that are produced by plant roots and soil microorganisms. These ligands have a higher affinity for the soil surface than phosphate; and form inner-sphere complexes with the soil surface; therefore exchange with P, releasing P to the solution (ligand exchange) (Cambier and Sposito 1991, Hu et al. 2001). Ligands also reduce the stability of precipitates and promote dissolution of solids, releasing P (ligand dissolution) (Zinder et al. 1986, Ludwig et al. 1996).

Chemical extractants such as Bray 1, Mehlich 1 and 3, or Olsen's solution have been commonly used to extract a portion of the soil's bioavailable P; however, they have not been shown to quantify any of the pools described above. These soil P tests are useful only when combined with experimental data (Kumar et al. 1992, Kleinman et al. 2001). Phosphorus fractionation schemes, as represented by Hedley et al. (1982),

sequentially extract inorganic and organic P, that are presumably associated with different soil constituents. Bioavailable P defined by these schemes is usually taken as the sum of readily available (resin-extractable), labile, and microbial ( $\text{NaHCO}_3$  plus  $\text{CHCl}_3/\text{NaHCO}_3$  extractable) pools. These schemes provide an operational definition of bioavailable P, which does little, however, to either explain pools on a mechanistic basis, or indicate the manner by which the plant accesses bioavailable inorganic P. It also is not clear that they actually measure discrete bioavailable pools.

Recently anion exchange resins (AERs) and anion exchange membranes (AEMs) have successfully been used to extract a desorbable pool of inorganic P that has proven to be one of the better indices of plant-available P (Sibbesen 1978, Schoenau and Huang 1991, Ziadi et al. 2001). Since AERs and AEMs behave as a P sink and desorb P from the solid phase using disequilibria, P exhaustingly desorbed by AERs or AEMs should constitute the pool of disequilibria-desorbable P, categorized above, at least for the specific time frame of the extraction. This pool of desorbable P should be bioavailable to any plant root or soil microorganism. A description of the nature and pattern of disequilibria desorption, particularly when described by a desorption isotherm, is rare in the literature and non-existent for tropical soils.

On the other hand, quantitative measurements of ligand-desorbable P are not well-established for soils of any climatic region. The problem in defining this pool of desorbable P is that one is not certain which ligands are present in the soil solution; their loading rates onto the solid phase; the volume of soil affected by this loading; and how soil properties control the effectiveness of P release by ligand desorption (Comerford 1998).

Plant roots and soil microorganisms are known to exude a range of low molecular weight organic anions (LMWOAs) such as oxalate, malate, and citrate to the soil solution. The composition of these anions is variable and dependent on plant species, plant age, and physiochemical environment (Curl and Trueglove 1986). Exudation of organic anions from plant roots is enhanced by three environmental stimuli: nutrient deficiency (particularly that of P); exposure to toxic cations (particularly  $\text{Al}^{3+}$ ); and anoxia (Ryan et al. 2001).

Excretion of organic anions into the rhizosphere occurs essentially continuously for two reasons. First, the total organic anion concentration of roots ranges from 5 to 50 mM, depending on tissue type and nutrient status of the plant; while that in soil solution is about 1000-fold less. This creates a strong gradient for slow passive diffusion from roots to the soil solution. Second, a substantial electric gradient exists across the plasma membrane because of the operation of ATP-driven proton pumps ( $\text{H}^+$ -ATPases) and cytosolic  $\text{K}^+$  diffusion potential. While the  $\text{H}^+$  expelled into the apoplast by these  $\text{H}^+$ -ATPases creates a charge gradient to facilitate the uptake of cations from the soil, it also tends to draw anions (e.g., citrate<sup>3-</sup> and malate<sup>2-</sup>) out of the cells and into the external soil solution (Jones 1998).

Once exuded into the soil solution, LMWOAs have the capacity to complex metals both in solution and on the soil surface. The degree of complexation depends on the particular organic anion involved; the concentration and type of metal involved; and pH of the soil solution. Generally speaking, organic anions with a higher number of carboxyl groups (e.g., citrate<sup>3-</sup>) chelate the metals more strongly than do those with fewer carboxyl groups (e.g., oxalate<sup>2-</sup> and acetate<sup>-</sup>) (Ryan et al. 2001). The chemical equilibria

speciation program Geochem-PC (Parker et al. 1995) can predict the ability of organic anions to complex metals as a function of soil solution pH. An example of the complexation of malate, oxalate, and citrate with  $\text{Fe}^{3+}$  is diagramed in Fig. 4-1 (Jones 1998).

Organic anions in the soil solution have a positive effect on P bioavailability (Sagwal and Kumar 1995, Cajuste et al. 1996). Studies investigated interaction between organic anions and inorganic P sorption/desorption, and particularly the competitive interactions for surface sorption sites on synthetic goethite (Geelhoed et al. 1998); Al-oxides (Violante et al. 1991); kaolinite and montmorillonite (Kafkafi et al. 1988, He et al. 1992); and field soils (He et al. 1992). Organic anions are effective in decreasing P sorption and increasing P desorption, with their effectiveness being most pronounced between pH 3.0 to 7.0 (Violante and Gianfreda 1993, Liu et al. 1999); and when the ligand is sorbed to the soil surface before P (Violante et al. 1991). Violante et al. (1991) concluded that many mineral soil-surface sites were accessible to both P and organic anions during the sorption process; while other surfaces were specific to one or the other.

Ligand exchange of P is dependent on the concentration; sorption kinetics; degradation rate of specific anions involved in the reaction (Fox and Comerford 1992); as well as the type of P bonding complexes formed with the surface metals. Sorption of citrate onto the soil surface increases its resistance to microbial decay, positively affecting the mobilization of adsorbed P (Geelhoed et al. 1999). He et al. (1992) postulated that organic anions modify P-metal bonding complexes from bidentate to monodentate form, also making P more exchangeable with organic anions.

Ligand dissolution is based on the ability of organic anions to chelate metal cations both in solution and on the surface. For example, the stability constants of oxalate and citrate with  $\text{Fe}^{3+}$  (1:1:1 metal:ligand:proton stoichiometric ratio and zero ionic strength at 25 °C) are 7.74 and 11.50, respectively (Jones 1998). Lan et al. (1995) showed that inorganic P release from spodic horizons in Florida and Georgia was enhanced by organic anions when the Al stability constant with the anion was greater than about 4.4. When organic anions complex metals in solution, they prevent the precipitation of P by the metal and reduce the activity of P in the solution. By forming complexes with metals on soil surfaces, organic anions promote destabilization of the surface and dissolution of the metals, resulting in P release into the solution (Jones et al. 1996).

Given the discussion above, it is clear that there are no well-established techniques for quantitatively measuring the desorbable pools of soil inorganic P, with the possible exception of disequilibria-desorbable P. And yet, measuring these pools and understanding mechanisms involved in the release from each pool are fundamental to understanding and predicting P bioavailability to plants.

Our study addressed the above issues through 3 objectives. The first is to consider a method with which to measure ligand-desorbable P. The second objective is to attempt separation of the ligand-exchangeable and ligand-dissolvable pools. The hypothesis underlying this objective is that, since ligand exchange and ligand dissolution are thought to occur over different time scales, a kinetic approach might differentiate between them. The final objective is to use exhaustive desorption method with AEMs differentiate disequilibria-desorbable and ligand-desorbable pools, when fertilizer P is applied at

increasing rates. This tested the hypothesis that the majority of P added to a soil should be, in the short term, dominantly in the disequilibria-desorbable pool.

## **Materials and Methods**

### **Soil Material**

The soil material used in this study was the surface horizon (0 to 30 cm depth) of a Kandudult (Soil Survey Staff 1999), known as an Argissolo vermelho/vermelho-amarelo distrófico in the Brazilian system (Oliveira et al. 1992). It was taken from under a native Atlantic Forest cover type (Morellato and Haddad 2000) located near Una Ecoparque near the city of Una, Bahia, Brazil. Using a shovel, the material was collected from a 1 ha area. Approximately 20 sampling points were combined; and the soil was subsequently air-dried, passed through a 2-mm sieve, and stored in plastic bags. Selected chemical and physical properties of the soil material were determined by standard methods (Page et al. 1982), which are listed in greater detail in Chapter 3. Soil pH was 4.7 (1:2 soil:water), with 2.5% organic carbon and 25% clay content dominated by kaolinite. Water-extractable P performed using 50 mM KCl was 0.65 nmol g<sup>-1</sup> soil. Mehlich 1-available P and total P were 87.18 nmol g<sup>-1</sup> soil and 3.17 μmol g<sup>-1</sup> soil, respectively. The iron content was greater than the aluminum content in both the amorphous and crystalline oxide forms. Ammonium acetate-exchangeable Fe was 0.05 μmol g<sup>-1</sup> soil.

### **Standard P Fertilization and LMWOAs Extraction Methods**

The following series of studies used standard procedures for adding P at different rates and extracting P and/or Fe with LMWOAs of varying concentrations. To simplify procedure description, each procedure is described below and then referred to by name within the subsequent method descriptions.

The Sorption Procedure was accomplished by adding 2 g of soil sample to a 50 mL centrifuge tube along with 20 mL of a 50 mM KCl containing P as  $\text{KH}_2\text{PO}_4$  at varying concentrations. The P concentrations will be described later for each individual study. The centrifuge tubes were horizontally shaken for 20 h; centrifuged for 15 min at 2500 rpm; and the supernatant was filtered through Whatman No. 5 filter paper. Filtrate P was determined by the method of Murphy and Riley (1962), which was used for all P determinations in our studies. Sorbed P was calculated by difference between P initially added and P left in the filtrate.

When LMWOAs were added to the soil, oxalate or citrate solutions as potassium oxalate or potassium citrate of varying concentrations were adjusted to an initial pH of 4.0 with HCl. Twenty milliliters of a given anion solution and 2 g soil samples were used for each procedure. Anion Method 1 was performed in a 30 mL syringe tube that was shaken for varying time periods, as listed below for the specific studies. Each suspension then was filtered immediately through 0.22  $\mu\text{m}$  nylon membrane filters (MSI Inc.) without centrifugation.

Anion Method 2 was performed in 50 mL centrifuge tubes that were shaken for varying time periods on a horizontal shaker, and then centrifuged for 15 min at 2500 rpm. The supernatant was filtered through Whatman No. 5 filter paper.

Filtrate P and Fe for all methods were determined by the method of Murphy and Riley (1962) and by atomic absorption spectroscopy, respectively. When using the Murphy and Riley (1962) method in the presence of oxalate and citrate, care must be taken to maintain those anion concentrations below 2 mM, since concentrations above that may inhibit molybdenum blue color development (He et al. 1998, Appendix B).

## Experiments

### **Experiment 1. Optimum Time for Extraction of Ligand-Desorbable P (Objective 1)**

The Sorption Procedure was used by adding 0 or 5.81  $\mu\text{mol P g}^{-1}$  soil to triplicate samples. The Anion Method 2 was applied to these samples to extract P using oxalate and citrate solutions with 0.02  $\text{mmol g}^{-1}$  soil, at shaking times of 1, 2, 3, 4, 5, 10, 30, 60, 180, 360, or 600 min. The objective of this study was to identify the extraction time that released the most P.

### **Experiment 2. Optimum Anion Concentration for Extraction of Ligand-Desorbable P (Objective 1)**

The Sorption Procedure was used as for Experiment 1, to triplicate samples. The Anion Method 2 was used to extract P using oxalate and citrate solutions with 0.01, 0.05, 0.10, 0.25, 0.50, or 1.00  $\text{mmol g}^{-1}$  soil, except that 0.01  $\text{mmol g}^{-1}$  soil was not used for the fertilized soils; and a shaking time of 7 h. The objective of this study was to define the anion concentration that released the most P at the optimum shaking time.

### **Experiment 3. Short Kinetic Extraction of Native Soil with Oxalate (Objective 2)**

Triplicate samples of native soil were used with the Anion Method 1, where the oxalate solution was 0, 0.02, or 0.05  $\text{mmol g}^{-1}$  soil; and the shaking times were 1, 2, 3, 4, or 5 min. The objective of this study was to determine if using a low range of shaking times as in Experiment 1 would help differentiate ligand-exchangeable from ligand-dissolvable P.

### **Experiment 4. One-minute Extraction of Native and Fertilized Soils with Oxalate and Citrate at Lower Anion Concentrations (Objective 2)**

Soil samples at two P levels (0 and 5.81  $\mu\text{mol P g}^{-1}$  soil) were prepared using the Sorption Procedure. All samples were prepared in triplicate; and the Anion Method 1

was used with oxalate and citrate concentrations of 0.01, 0.10, 1.00, or 10.00  $\mu\text{mol g}^{-1}$  soil and with shaking time of 1 min. The objective of this study was to determine if, using a short shaking time, a range of low anion concentrations would help differentiate ligand-exchangeable from ligand-dissolvable P.

**Experiment 5. Seven-hour Extraction of Native Soil with Oxalate and Citrate at Lower Anion Concentrations (Objective 2)**

The Anion Method 2 was used to triplicate soil samples of native soil, using oxalate and citrate solutions of 0.01, 0.10, 1.00, or 10.00  $\mu\text{mol g}^{-1}$  soil and using a 7 h shaking time. The objective of this study was to determine if the results of Experiment 4 could be reproduced using a longer shaking time, thus demonstrating the importance of anion concentration versus shaking time in differentiating ligand exchange from ligand dissolution.

**Experiment 6. Differentiation of Desorbable P into Disequilibria- and Ligand-Desorbable P (Objective 3)**

Four soil levels of P were prepared in triplicate using the Sorption Procedure, at P rates of 0, 1.29, 2.58, and 5.81  $\mu\text{mol P g}^{-1}$  soil.

The first P extraction for these samples was accomplished using sequential extraction with AEMs, as described in Chapter 2. The desorption process was continued until incremental P removed by AEMs was lower than 2–5  $\text{ng P mL}^{-1}$  in the AEMs extracting solution, corresponding to 0.65–1.61  $\text{nmol P g}^{-1}$  soil. This is the detection limit of the Murphy and Riley (1962) method when using a 5 cm path length. The pool of disequilibria-desorbable P was defined as the difference between the amount of P initially sorbed and the amount of P remaining on the solid phase after the last AEMs extraction step. The objective of this step was to measure the total pool of disequilibria-desorbable P at different P-fertilization levels.

The samples were then extracted with the Anion Method 2 using a solution of 0.50 mmol oxalate  $\text{g}^{-1}$  soil and a 7 hr shaking time. The objective of this step was to measure what we defined above as the total ligand-desorbable pool of P, after disequilibria-desorbable P was extracted.

**Experiment 7. Mass Balance Verification for Ligand-Desorbable P (Objective 3)**

Triplicate soil samples of the four P levels of Experiment 6 were extracted using the Anion Method 2 of Experiment 6. The objective of this experiment was to confirm that total P extracted in Experiment 6 was equivalent to the amount extracted if only the Anion Method 2 was used.

**Experiment 8. Investigation of P Immobilization after Sorption**

Soil samples, in triplicate, had P applied at a rate of 2.58  $\mu\text{mol P g}^{-1}$  soil, using the Sorption Procedure. Enough samples were prepared to establish 3 treatments that could be destructively sampled over time. The treatments were: 1) P extraction by shaking without  $\text{HgCl}_2$  added (+S-H); 2) P extraction by shaking with  $\text{HgCl}_2$  added (+S+H); and 3) P extraction without shaking and with  $\text{HgCl}_2$  added (-S+H). Each treatment was extracted for 1, 3, 7, 10, or 14 d; and mercuric chloride was added to the appropriate samples (+H) at a rate of 1.84  $\mu\text{mol g}^{-1}$  soil. The shaking treatment (+S) was continuous shaking on a horizontal shaker; while the unshaken samples (-S) were kept in a test-tube rack next to the shaker. At each sampling time, P was extracted from each treatment in triplicate using the Anion Method 2 of Experiment 6.

It was shown in previous studies that part of the P sorbed by this soil was not extractable by the Anion Method 2. The objective of this experiment was to determine the role of microbial immobilization (+H vs. -H); shaking (+S vs. -S); and time of

interaction (short-term ageing of 1 to 14 d) on the non-extractability of P in previous experiments. Mercuric chloride was used because it is an effective soil sterilizant; and it reportedly causes minimal change to soil physio-chemical properties (Wolf et al. 1989).

### **Statistical Analysis**

Analysis of variance (ANOVA) using a One-Way ANOVA design was used to test differences among treatments using STATISTICA (StatSoft 1999). Significance of the difference among means was determined by t-tests of post hoc comparisons using Tukey's studentized range test at the  $p = 0.05$  level. Means and standard deviations were used to summarize the data from P sorption and desorption isotherms, where applicable.

## **Results and Discussion**

### **Ligand-Desorbable P**

In order to develop a method that measures ligand-desorbable P, an optimum extraction time (Experiment 1) and organic anion loading (Experiment 2) must be identified. Over 80% of the P released from both native and fertilized soils by oxalate and citrate was within the first hour and three hours, respectively (Fig. 4-2). For both anions, and for both native and fertilized soils, P desorption reached maximum levels and stabilized beyond 6 h. Seven hours was chosen as the extraction time for subsequent experiments.

Oxalate and citrate loading onto native and fertilized samples produced a diminishing return in desorbable P with respect to increasing anion loading (Fig. 4-3). Maximum P release coincided with a loading of 0.5 mmol of oxalate or citrate  $\text{g}^{-1}$  soil. Therefore, this loading was chosen for subsequent experiments.

### **Ligand-Exchangeable P vs. Ligand-Dissolvable P**

The premise used in evaluating these data was based on release of Fe from the soil. If only ligand-exchangeable P was being released, the amount of Fe released should not be greater than exchangeable Fe, which was  $0.05 \mu\text{mol Fe g}^{-1}$  soil. Once Fe in the extracting solution was greater than exchangeable Fe, dissolution must have occurred; and it would no longer be possible to differentiate ligand-exchangeable P from ligand-dissolvable P. Another background indicator was water-extractable P, which was  $0.65 \text{ nmol P g}^{-1}$  soil. Phosphorus levels higher than this suggested P desorption by the action of the organic ions.

Iron released from both native and fertilized soils by  $0.02 \text{ mmol oxalate g}^{-1}$  soil was up to 40-fold higher than exchangeable Fe, at a shaking time of 600 min (Fig. 4-2). When 1 to 5 min shaking times were tested, Fe release under the influence of no oxalate added ranged from  $0.01$  to  $0.03 \mu\text{mol Fe g}^{-1}$  soil (less than exchangeable) for all shaking times (Fig. 4-5). When  $0.02$  and  $0.05 \text{ mmol oxalate g}^{-1}$  soil were added, Fe release exceeded exchangeable Fe ( $0.20$  and  $0.35 \mu\text{mol Fe g}^{-1}$  soil, respectively) even for the 1 min shaking time.

The next step was to test if lower anion loadings and shorter contact times would distinguish exchangeable from dissolvable P. Figure 4-6 shows the effect of low anion loadings for a 1 min shaking time. Both oxalate and citrate were effective in desorbing P even at the lowest concentration ( $0.01 \mu\text{mol g}^{-1}$  soil). Phosphorus release with oxalate remained stable between  $0.01$  and  $1 \mu\text{mol anion g}^{-1}$  soil. Iron release at these concentrations was below exchangeable Fe, ranging from  $0$  to  $0.04 \mu\text{mol g}^{-1}$  soil. Beyond  $1 \mu\text{mol anion g}^{-1}$  soil both Fe and P release increased rapidly with increasing Fe far exceeding the exchangeable amount.

Figure 4-7 shows that the separation of ligand-exchangeable P from ligand-dissolvable P in the native sample is more a function of anion loading than of extraction time. When the same loadings were used with a 7 h shaking time, the same pattern and magnitude of P and Fe were released at anion loadings below  $1 \mu\text{mol g}^{-1}$  soil.

It was concluded from above studies as follows:

- Phosphorus was desorbed at all anion concentrations through the action of anions
- Phosphorus desorbed below  $1 \mu\text{mol anion g}^{-1}$  soil was dominated by ligand-exchangeable P because Fe release was below exchangeable Fe
- Phosphorus desorbed below  $1 \mu\text{mol anion g}^{-1}$  soil estimated the total amount of ligand-exchangeable P because
  - It was relatively stable over a 100-fold increase in anion loading
  - There was a close correspondence in P desorbed by either anion for both native and fertilized soil
  - Total P desorbed was the same after the 1 min and 7 h shaking times.

It was also concluded that additional P release above  $1 \mu\text{mol anion g}^{-1}$  soil involved ligand dissolution because of the high amount of Fe released with the P.

Therefore, the second objective of this study was met because it was shown that ligand-exchangeable and ligand-dissolvable P were analytically separable under specific conditions. It was also concluded that the ligand-exchange reaction was more dependent on anion concentration than on reaction kinetics.

A notable result was the increase in ligand-dissolvable Fe from the native to fertilized soils (Fig. 4-6). While citrate-extractable Fe increased from 0.16 to  $0.20 \mu\text{mol g}^{-1}$  soil (25%) with P fertilization; oxalate-extractable Fe increased from 0.15 to 0.34 (127%). Wang et al. (1991) previously noted that mineral dissolution by organic anions is influenced by the degree of P saturation of sorption sites. Such sorption

restricts goethite crystallization, leaving the mineral more oxalate-soluble. Conversely, P sorption reduced the solubility of Fe in  $\text{Fe}(\text{OH})_3$  in the presence of  $500 \mu\text{M}$  citrate (Jones et al. 1996). It is clear that oxalate and citrate differ in their interaction with this kaolinite-dominated soil. This is shown most clearly by the P:Fe molar ratio relative to each anion's concentration in the native soil (Fig. 4-4).

Flow calorimetry also showed that oxalate and citrate are sorbed differently onto soil surfaces. Flow calorimetry has been successfully used for measuring reactions at the liquid/solid interface (Rhue et al. 2002). Rhue et al. (2002) documented that phosphate sorption onto soil surfaces was exothermic; while precipitation of Al-phosphate was endothermic. In our study, phosphate and oxalate sorption were found to be exothermic; while citrate sorption was endothermic (Appendix C). Unfortunately, this study does not provide enough information to determine why this difference occurs.

### **Disequilibria-Desorbable P vs. Ligand-Desorbable P**

Disequilibria-desorbable P and ligand-desorbable P are presented in Table 4-1. The P in disequilibria- and ligand-desorbable pools were a function of the amount of P sorbed, with all desorbable pools increasing with increasing levels of sorbed P. However, the percentage of disequilibria-desorbable P to total desorbable P increased, while the ligand-desorbable P decreased. In the short term, P fertilization preferentially puts P in the disequilibria pool, which is a pool that all plants and soil-borne organisms can access.

Notably, it was shown that the percentages of total desorbable P to P initially sorbed remained constant, with only a 6% difference (55 to 61%) across all P-sorption levels. Total desorbable P was measured 7 to 14 d after the P application, which was the time required to exhaust the disequilibria-desorbable pool (Fig. 4-8). The shorter time frames represented less P sorbed, so less time was required for the extraction. When total

desorbable P was measured just 1 d after P addition, these percentages increased to 78 to 87% (Fig. 4-9).

It was concluded that the amount of desorbable P was a function of time, with decreasing P recovery rates over time. There also appeared to be a pool of sorbed P that oxalate could not access. This pool ranged between 13 and 22% of the P initially sorbed even after just 1 d of equilibration time.

### **Phosphorus Immobilization/Fixation after Sorption**

The cumulative P that was immobilized (i.e., inaccessible to Anion Method 2) over 14 d is represented in Figure 4-10. Phosphorus immobilized by the +S-H treatment is P immobilized by all factors studied under these laboratory conditions. The +S+H treatment eliminated microbial immobilization, therefore the difference between +S-H and +S+H was due to microbial immobilization. The treatments +S+H and -S+H should have removed the effect of microbes, so their difference would be the effect of shaking the soil.

All treatments were similar after 1d, with an average of  $0.23 \mu\text{mol P g}^{-1}$  soil immobilized (about 10% of the sorbed P). Phosphorus immobilization increased between 1 and 14 d. The P immobilized by microbes, expressed as a percentage of the total immobilized, was 19%, 52%, 56%, and 57% on days 3, 7, 10, and 14, respectively. The P immobilized due to shaking (expressed on the same scale) was 76%, 38%, 30%, and 30% of the total P immobilized. Therefore, P immobilized by what might be considered short-term ageing was 5%, 10%, 14%, and 13% for the time periods listed above. In the short run (1 to 3 d), microbes played less of a role than did shaking; but became the major factor at later dates.

Bliss (2003) showed that, for sandy soil material, microbial immobilization of fertilizer P reached its maximum approximately 3 d after fertilization. Khoshmanesh et al. (2002) reported that only a few hours were necessary for sediment bacteria under aerobic conditions to absorb applied P. Microbial P uptake rapidly contributes to P immobilization.

The ageing component of P immobilization was plotted against the square root of time to ascertain if a diffusion mechanism might be implicated (Fig. 4-11). The result was a positive linear relationship with high goodness of fit ( $r^2 = 0.985$ ). This suggests that P diffusion could be occurring along the clay surfaces or, less likely, into the clay structure itself. Assuming a crystal diffusion coefficient of  $10^{-23} \text{ cm}^2 \text{ s}^{-1}$ , it was calculated that diffusion could have moved P approximately 0.07 nm into the clay structure by 14 d.

Phosphate sorption in soil is known to occur rapidly and to precede a slow sorption process. The former is often thought to be controlled by ligand exchange and the latter by precipitation, penetration of the surface, or diffusion into dead-end pores (Parfitt 1978). Slow sorption is a time-dependent reaction and can account for a substantial portion of total P sorption in goethite-rich materials (Torrent et al. 1992). Duration and extent of the slow reaction apparently depend on the ratio between micropore surface area and total surface area (Torrent et al. 1992), and on the crystallinity of the materials (Strauss et al. 1997). Therefore, it is important to consider the effect of slow sorption as it reduces bioavailable P.

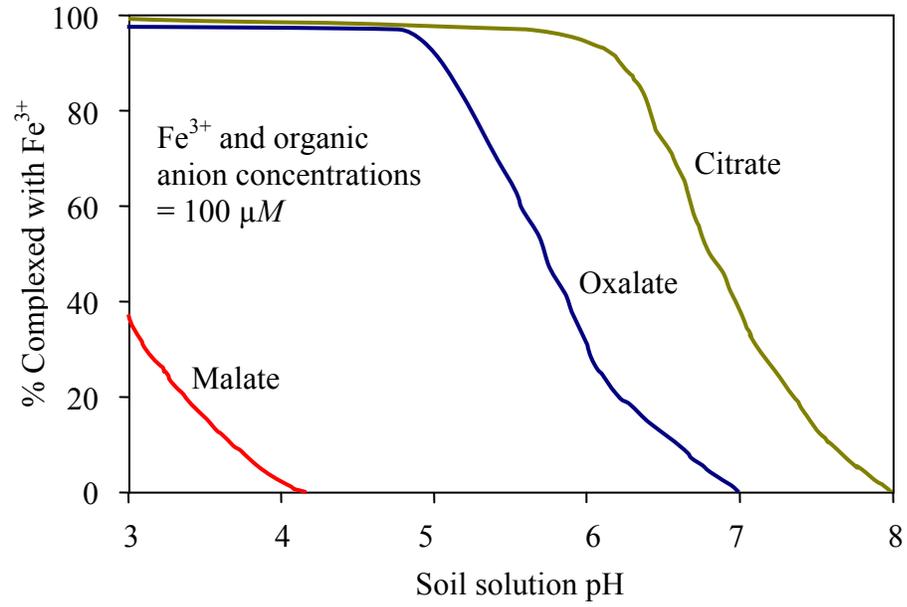


Figure 4-1 Ability of three organic anions to complex Fe as a function of pH as predicted using Geochem-PC (Parker et al. 1995)

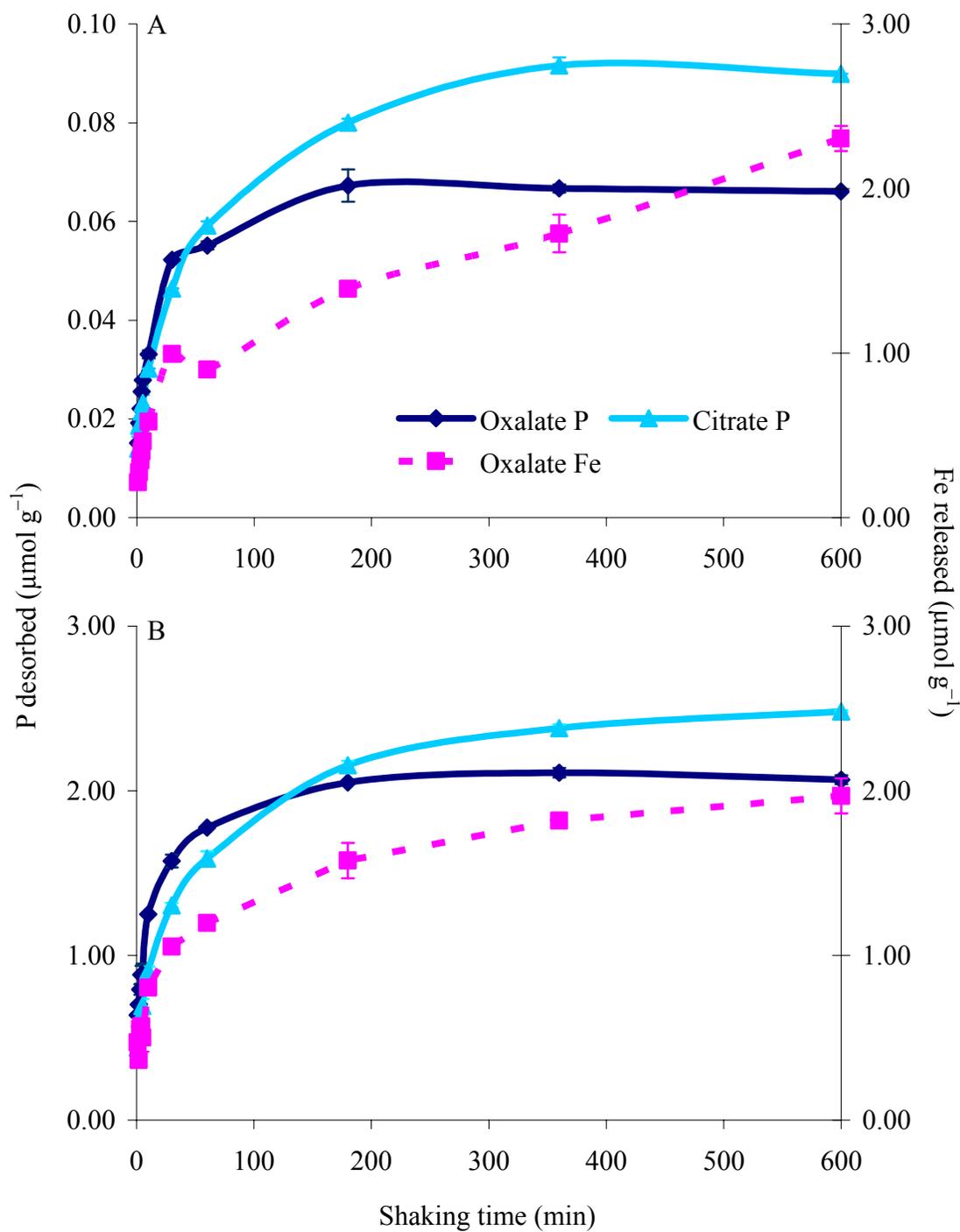


Figure 4-2 Phosphorus-desorption and Fe-release kinetics by organic anions when added at a loading of  $0.02 \text{ mmol g}^{-1}$  soil. A) native soil. B) P-fertilized soil

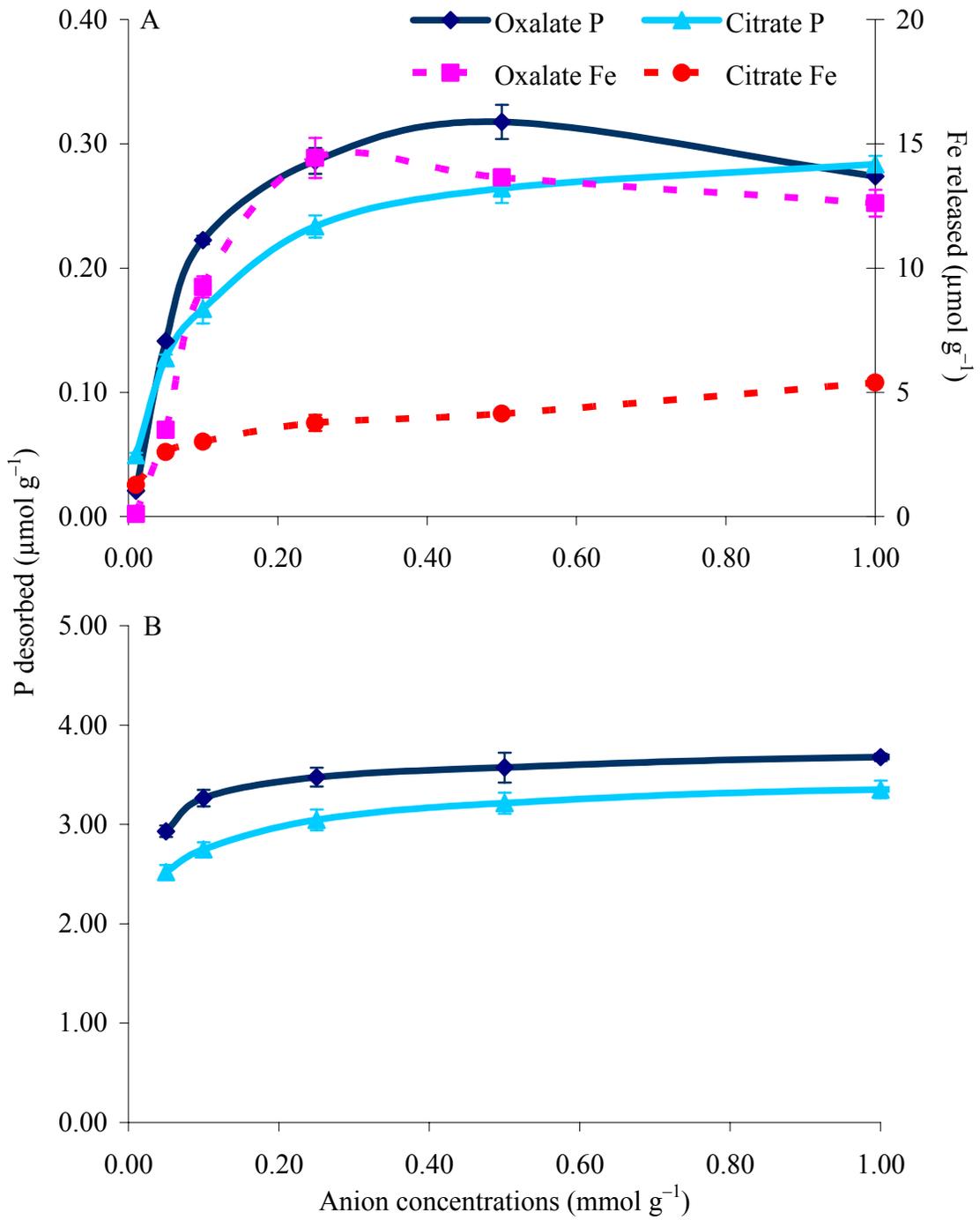


Figure 4-3 Effect of organic anion loadings for a 7 h interaction time on P desorption and Fe release. A) native soil. B) P-fertilized soil

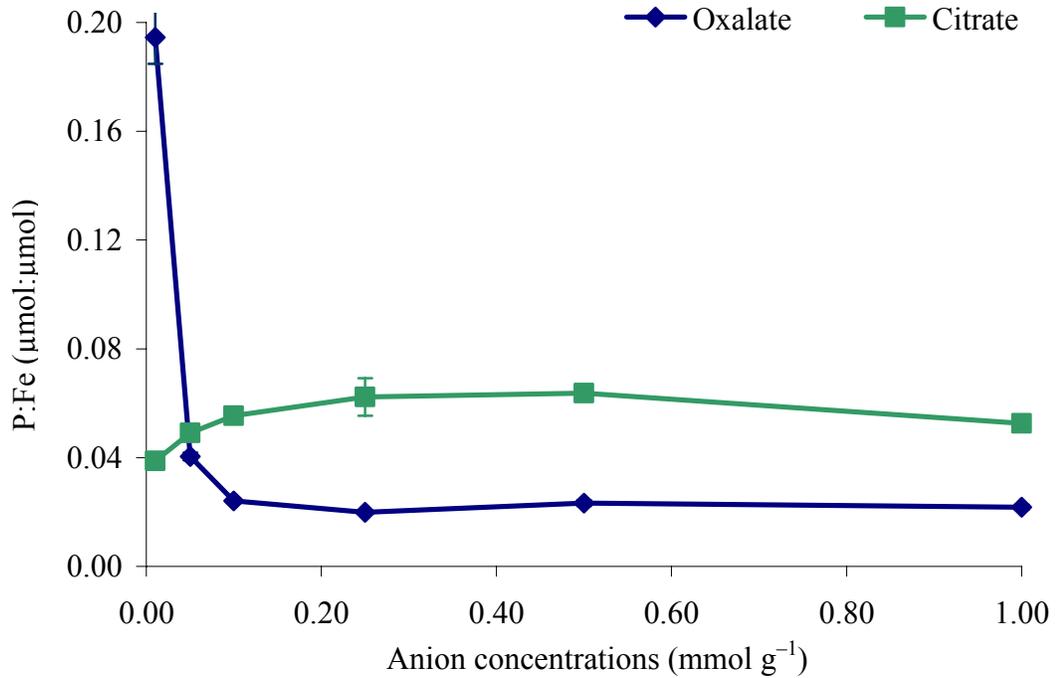


Figure 4-4 Effect of organic anion loading on the molar ratio of P desorption to Fe release from native soil

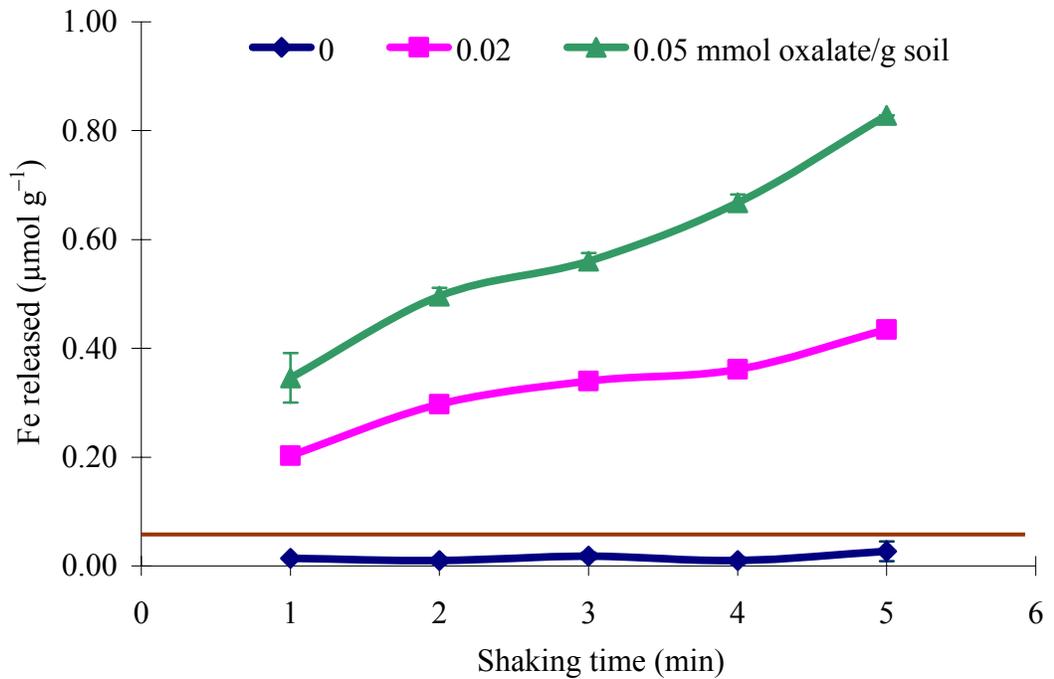


Figure 4-5 Iron release by 3 oxalate loadings as a function of shaking time. The horizontal line represents exchangeable Fe level (0.05 μmol Fe g<sup>-1</sup> soil)

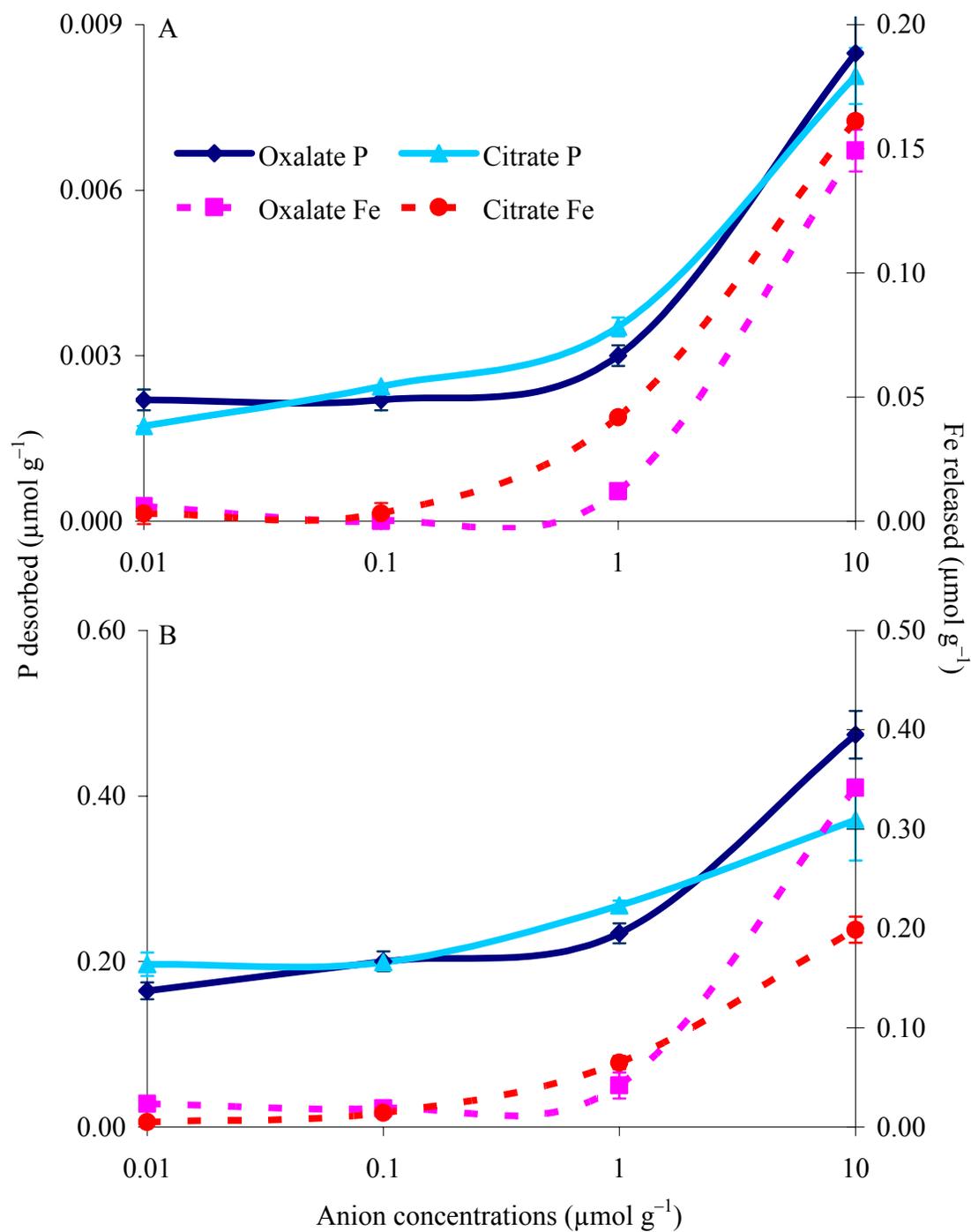


Figure 4-6 Effect of low anion loadings for a 1 min interaction time on P desorption and Fe release. A) native soil. B) P-fertilized soil

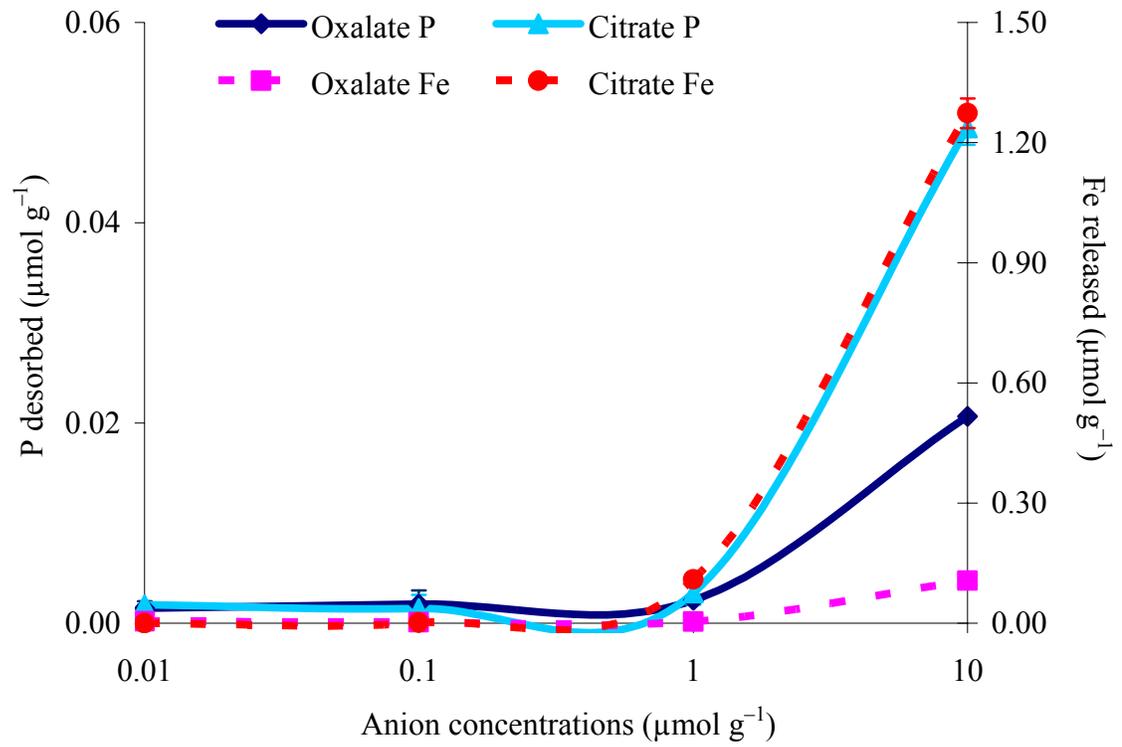


Figure 4-7 Effect of low anion loadings for a 7 h interaction time on P desorption and Fe release

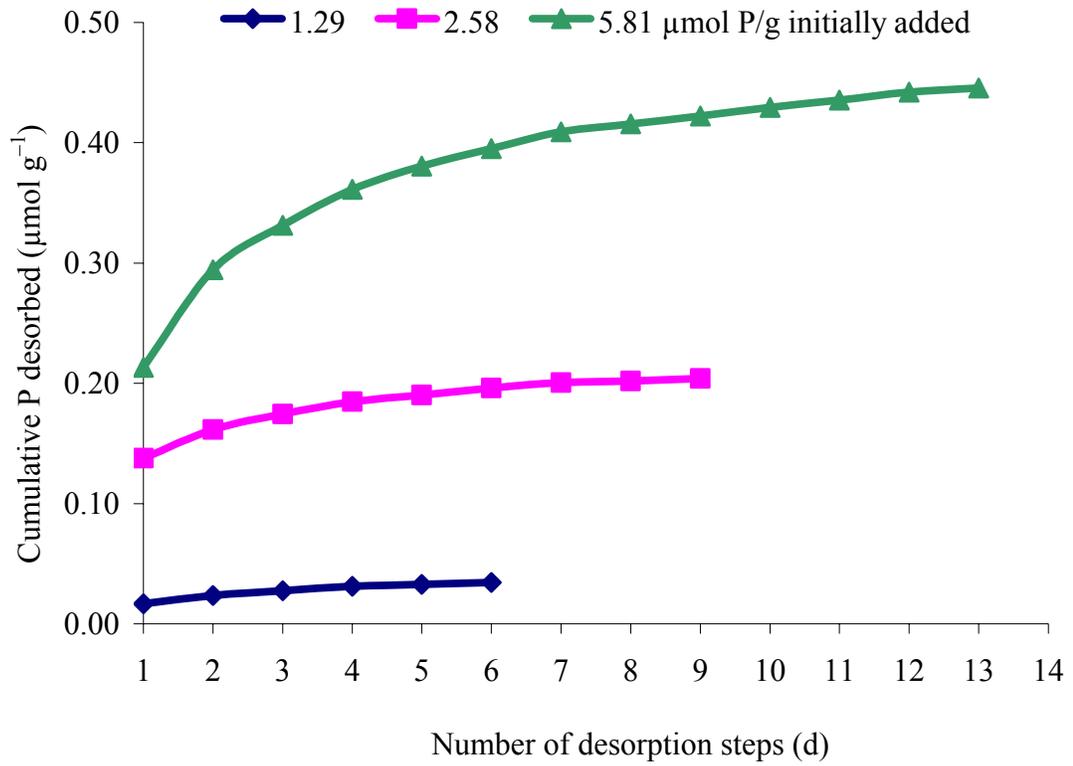


Figure 4-8 Cumulative P desorbed by AEMs from soil at 3 increasing levels of P. Each desorption step represents one day

Table 4-1 Disequilibria- and ligand-desorbable pools of P when 3 levels of P are sorbed to the soil

P initially added	P initially sorbed	Disequilibria-desorbable P		Ligand-desorbable P		Total desorbable P	
		$\mu\text{mol g}^{-1}$ ( $\times 10^{-2}$ )	% <sup>†</sup>	$\mu\text{mol g}^{-1}$	% <sup>†</sup>	$\mu\text{mol g}^{-1}$	% <sup>‡</sup>
1.29	1.24	6.4 <sup>§</sup> a <sup>¶</sup>	9a	0.63a	91a	0.69a	56a
2.58	2.33	31.0b	24b	0.98b	76b	1.29b	55a
5.81	4.04	83.8c	34c	1.61c	66c	2.44c	61b

<sup>†</sup> % of total desorbable P

<sup>‡</sup> Total desorbable P as a % of P sorbed

<sup>§</sup> Net P desorbed subtracting P desorbed at no P addition

<sup>¶</sup> Different letters assigned in a column denote significant differences among P-added levels at the 0.05 probability level, performed by Tukey's studentized range test

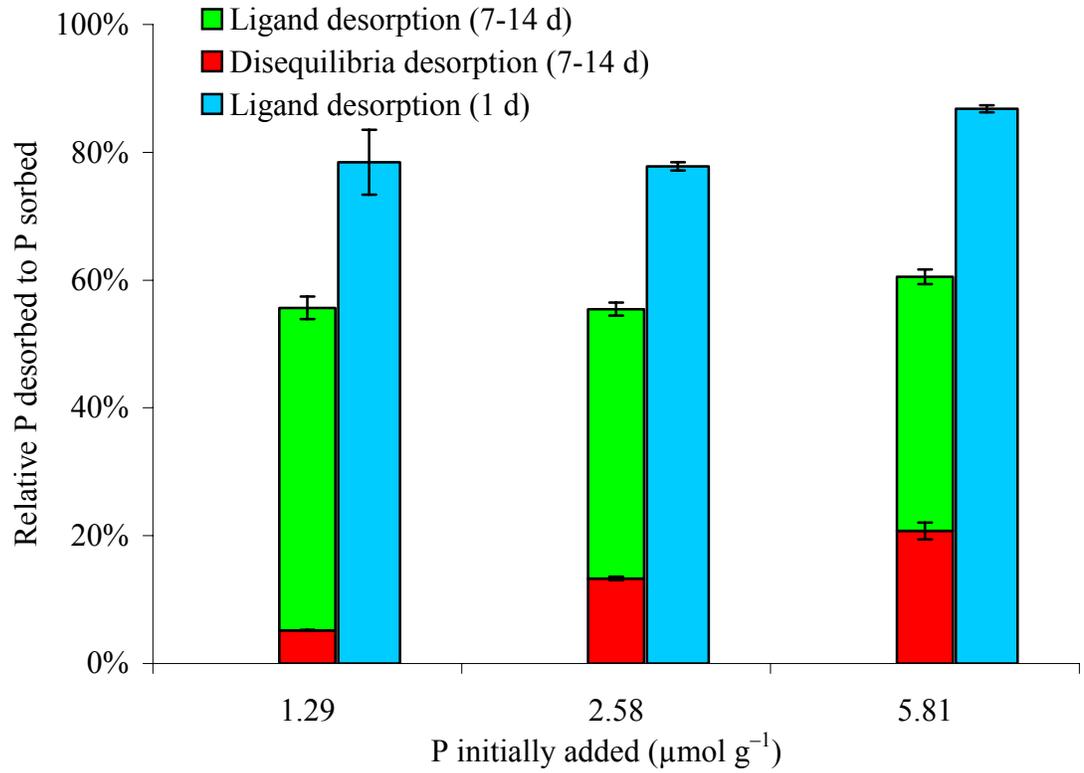


Figure 4-9 Distribution of sorbed P between the disequilibria- and ligand-desorbable pools. The first bar in each P-added level shows a combination of disequilibria- and ligand-desorbable pools; and the second bar shows total desorbable P 1 d after P sorption

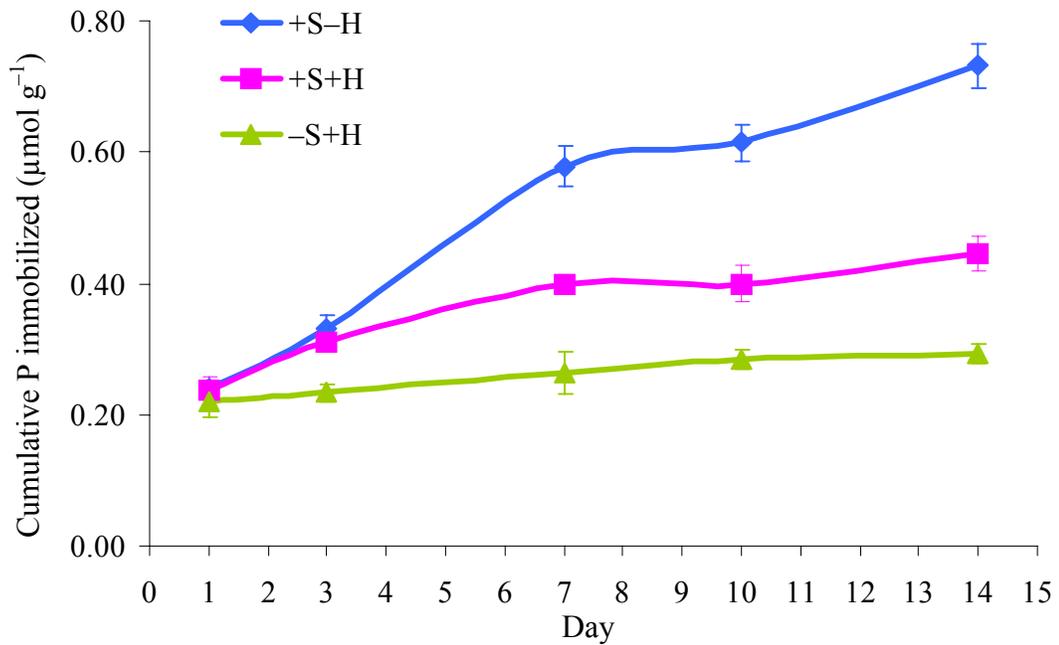


Figure 4-10 Cumulative P immobilization after P sorption. +S and -S are with and without shaking; and +H and -H are with and without mercuric chloride for microbial suppression

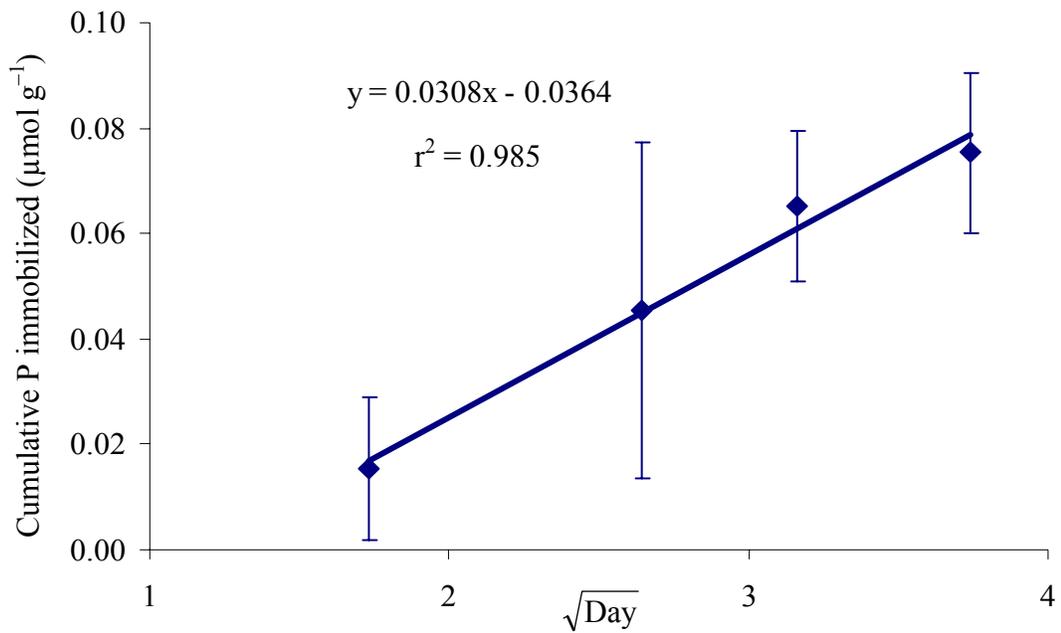


Figure 4-11 Cumulative P immobilization versus the square root of time. Immobilized P is that amount of P immobilized after the effects of microbes and shaking have been removed

## CHAPTER 5 SUMMARY, CONCLUSIONS, AND FUTURE RESEARCH

Tropical soils are notorious for their low nutrient bioavailability and low agricultural productivity caused by unfavorable soil properties and socio-economic constraints. Expert nutrient management is further complicated by difficulties in the extension of information. Many parts of tropical Brazil fit this scenario. In humid, acid soils of Brazil, phosphorus deficiency can control crop production, yet the soil dynamics of P are not well-understood at a process level. Because of low pH and Al toxicity, liming is a common soil management practice. However, effect of liming on P bioavailability is controversial and appears related to the amount of exchangeable Al present. Phosphorus sorption and, more importantly, P desorption are processes affecting P bioavailability. A more complete understanding of these processes, including the effect of pH change on P processes, is fundamental to establishing P management strategies. Unfortunately, quantitative measurement of bioavailable P pools is not well-defined. Standard methods are required to attain a meaningful database for P bioavailability.

Based on the above observations, this dissertation investigated specific aspects of P availability in soils from three points of view: method development; evaluation of the practical consequences of pH adjustment for soils; and fundamental investigations into the forms of inorganic bioavailable soil P.

Chapters 2 and 4 each addressed methodology questions. Desorption is a time-consuming and rarely investigated aspect of P dynamics. Chapter 2 investigated two techniques for measuring P desorption isotherms. Chapter 4 resulted in a method for

measuring inorganic P that is desorbable by some low molecular weight organic anions (ligand-desorbable P) that are characteristic of root and microbial exudates. This chapter also addressed whether there were experimental artifacts associated with in this method.

In Chapter 3, the effect of pH change on P sorption and desorption was investigated and interpreted with a view toward the degree to which this practice may help or hinder P-fertilizer availability. Chapter 4 further addressed potential pools of bioavailable inorganic P by trying to differentiate ligand-exchangeable from ligand-desorbable inorganic P. It also investigated how fertilizer P is partitioned between these two pools.

The combined studies of Chapters 2 to 4 provide detailed information for a specific soil type in Brazil; but also provide a path for continued research on P bioavailability in tropical soils. Each chapter was organized around a set of specific objectives, with a summary of results provided below.

### **Summary**

#### **Suitability of Using Multiple AEM Strips to Develop Desorption Isotherms**

The Multiple AEM Method was found suitable for developing well-defined P desorption isotherms. Isotherms were developed quickly and precisely over a range of P sorption levels. This method gave a high density of data points over a 3-day period.

#### **Comparison of Multiple AEM Method to Sequential AEM Method**

When the Multiple AEM Method was compared to the Sequential AEM Method, it was found that the desorption isotherms were numerically different. However, partition coefficients ( $K_d$  values) calculated from the isotherms were not a function of the desorption method or the amount of P initially sorbed; but were inversely and linearly related to equilibrium P concentration. If the intent of developing desorption isotherms was to derive  $K_d$  values, then either method was appropriate. It was concluded that over a

range of P solution concentration, the Multiple AEM Method was superior to the Sequential AEM Method because

- Isotherms were developed in less time, minimizing outside and time-related influences on isotherms
- It yielded more desorption points in a shorter time frame.

### **Effect of Soil pH on Phosphorus Sorption**

Phosphorus sorption decreased with increasing pH; and calculated  $K_d$  values decreased with pH increase at low solution P concentrations. At solution concentrations higher than  $3 \mu\text{g P mL}^{-1}$ , there was no effect of pH. Liming to pH values of 5.9 and 7.0 resulted in 2.8 to 4.5 kg P fertilizer  $\text{ha}^{-1}$  (calculated at  $0.2 \mu\text{g P mL}^{-1}$  solution concentration) that was not sorbed and remained in the soil solution ready for plant uptake.

### **Effect of Soil pH on Phosphorus Desorption**

P desorption increased as soil pH increased. Total P desorbed, the ratio of P desorbed to P sorbed, and  $K_d$  values increased as pH increased for all levels of P addition when soil pH was raised to 7. This resulted in an additional 0.2 to 1.0 and 0.7 to 2.7 kg P  $\text{ha}^{-1}$  that was desorbable at pH 6 and 7, respectively, which can be attributed to the effect of liming.

Combining the results of P sorption and desorption, liming had a twofold positive effect. It reduced the amount of P sorbed and increased the amount of P desorbed, which increased both solution concentration and P bioavailability.

### **Method for Measuring Ligand-Desorbable Phosphorus**

Oxalate and citrate were used in kinetic and loading studies to define a method that would remove the total amount of P accessible by these anions in the most efficient

manner. By 6 h the maximum P was removed from the soil, so 7 h was chosen as the shaking time. With a 7 h shake, the maximum amount of P was removed at 0.5 mmol anion g<sup>-1</sup> soil loading. This method was used for subsequent studies.

### **Separating Ligand-Desorbable P into Ligand-Exchangeable P and Ligand-Dissolvable P**

Ligand-desorbable P was successfully separated into ligand-exchangeable P and ligand-dissolvable P via an anion loading approach. Phosphorus release was a function of both anion loading and reaction time, with oxalate and citrate anions being used to release P from native and fertilized soil. Ligand-exchangeable P was released at anion loadings  $\leq 1$   $\mu\text{mol anion g}^{-1}$  soil. It was concluded that this represented the total pool of ligand-exchangeable P because

- The P desorbed was associated with quantities of Fe release that were less than exchangeable Fe
- The P desorbed was relatively stable over a 100-fold increase in anion loading
- There was a close agreement between the P desorbed by either anion under both native and fertilized conditions
- The same amount of P was desorbed after 1 min and 7 h reaction times.

Above 1  $\mu\text{mol anion g}^{-1}$  soil, desorbed P was a combination of ligand-exchangeable and ligand-dissolvable P. It is recommended that a separation of ligand-desorbable P in this soil be made by first extracting with 1  $\mu\text{mol}$  of oxalate or citrate g<sup>-1</sup> soil for 1 min, and then with the total ligand desorption procedure of Chapter 4, Objective 1.

Oxalate and citrate were different in the way they dissolved Fe, even though they removed similar amounts of ligand-desorbable P. This was evidenced by the P:Fe ratio with increasing anion loadings. While it is impossible to determine from this study the mechanisms causing this discrepancy; flow calorimetry showed that oxalate and citrate

have different surface reactions with this soil. Oxalate, like phosphate, sorption is an exothermic reaction; while the sorption of citrate is endothermic.

### **Differentiating Bioavailable Pools of Applied P into Disequilibria-Desorbable P and Ligand-Desorbable P**

The majority of P sorbed by the soil was found in the ligand-desorbable pool. As P was sorbed to the soil, it was preferentially found in the disequilibria-desorbable pool. The percentage of total desorbable P to sorbed P was independent of the amount of P added. Fifty-five to 61% of the sorbed P was desorbable by oxalate. Thirty-nine to 45% was fixed against oxalate desorption. The recovery of sorbed P was discovered to be a function of time over a 14 d period, with the P fixed in 1 d being 13 to 22% of the sorbed P and P fixed in 14 d represented by the numbers above.

This ageing process was demonstrated to be an artifact of shaking (30%), microbial immobilization (57%), and sorption of P onto the soil in non-oxalate-accessible form (13%). The amount fixed by ageing was linear with the square root of time, suggesting a diffusion mechanism.

### **Conclusions**

Soil pH effects on P sorption and desorption are still controversial for sorption and virtually unstudied for desorption. This is the first study to develop a multiple AEMs procedure for constructing a desorption isotherm, and is also the first study to use isotherms in evaluating the effect of pH on P desorption. The method developed here should promote greater progress in desorption studies; while the data relative to P sorption and desorption give order-of-magnitude effects for enhanced fertilizer availability due to liming.

This dissertation defines bioavailable pools of P via a categorization that is different than that found in the literature. While it is not the first time disequilibria and ligand desorption have been investigated, it is the first time that they have been investigated together, and is the first time that the influence of P fertilization on the distribution of P between forms has been investigated. This is also the first time that ligand-exchangeable P has been individually measured for a soil.

This dissertation has increased our database concerning measurement of P forms in soils and interactions of inorganic P with the soil surface. It has also advanced our methodology for measuring P in meaningful bioavailable pools, and has helped to better define bioavailable P and P dynamics under influences of soil pH and organic anions. Not all questions were adequately answered. However other research possibilities have been suggested by the results and problems associated with these experiments.

### **Future Research**

A variety of future research topics/directions were suggested by the results of the preceding experiments.

1. The Multiple AEM Method should be tested on a wider range of soils over a range of solution P concentrations in order to ensure its usefulness.
2. Since this dissertation did not address mechanisms of P desorption in relation to soil pH, clarification of the effects of pH and P surface coverage on the formation of different surface complexes should help to resolve these issues.
3. Although liming was shown to have positive effects on P bioavailability, high costs of liming materials and P fertilizers in tropical regions remains constraints. Investigations on the interactions of alternative liming materials such as wood ash and composts with soils and plants; and their effect on P bioavailability would be useful. Positive results of these studies would allow rural farmers to manage phosphorus and promote increased cropland productivity.
4. This dissertation showed that oxalate and citrate reacted differently with Fe and were sorbed differently to the soil surface. Although both were effective in desorbing P

from the surface, it would be fruitful to pursue an understanding of surface reaction mechanisms for these anions.

APPENDIX A  
ACID-BASE TITRATION CURVE FOR THE SOIL

An acid-base titration curve was developed for the Atlantic Forest soil using 10 g of soil in 20 mL of double-deionized water. Soil pH was measured at 2 h of continuous stirring of the suspension after each increment of 0.083 M NaOH added.

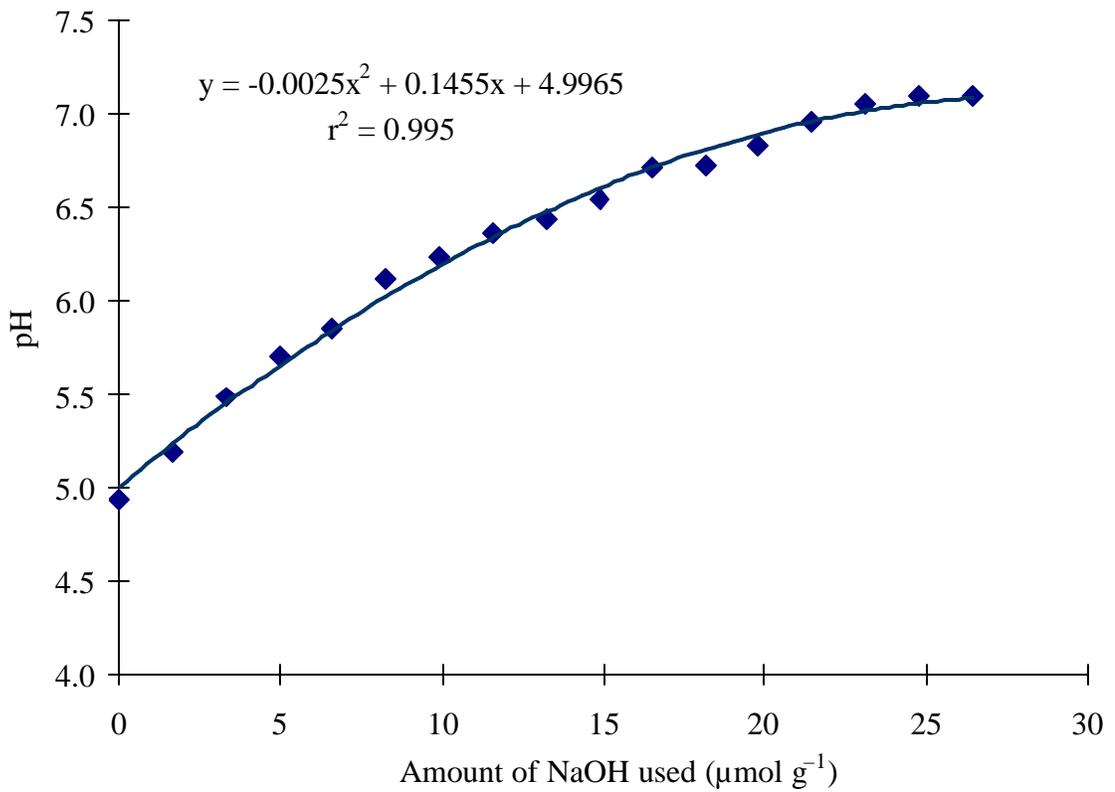


Figure A-1 Titration curve for the Atlantic Forest soil

APPENDIX B  
DETERMINATION OF SOLUBLE P IN THE PRESENCE OF ORGANIC ANIONS

Table B-1 Effect of varying concentrations of oxalate and citrate on absorbance over a range of standard P concentrations

Phosphorus				
Standard ( $\mu\text{g mL}^{-1}$ )	0.02	0.05	0.20	0.40
Absorbance <sup>†</sup>	0.014	0.036	0.148	0.265
Oxalate				
mM			% <sup>‡</sup>	
0.0	100.0	100.0	100.0	100.0
0.1	100.0	100.0	98.7	99.3
1.0	100.1	97.3	98.0	99.0
2.0	78.6	94.3	99.3	99.0
4.0	7.0	0.0	0.0	0.0
6.0	0.0	0.0	0.0	0.0
Citrate				
mM			%	
0.0	100.0	100.0	00.0	100.0
0.1	100.0	97.3	98.7	99.3
1.0	92.9	91.9	97.3	98.0
2.0	100.0	100.1	100.1	99.3
4.0	14.3	7.1	50.0	68.0
6.0	0.0	2.9	2.7	10.2

<sup>†</sup> Measured at 880 nm wavelength

<sup>‡</sup> Percentage of P absorbance in the presence of organic anions to P standard absorbance

APPENDIX C  
SURFACE REACTIONS OF PHOSPHATE, OXALATE, AND CITRATE  
MEASURED BY FLOW CALORIMETRY

Flow calorimetry was used to measure heats of reaction for the sorption of phosphate, oxalate and citrate onto the non-fertilized soil sample described in Chapter 2. The method was based on that described by Rhue et al. (2002).

A 67.4 mg soil sample was initially equilibrated with a solution of 50 mM KCl in a glass column under a flow rate of 0.39 mL min<sup>-1</sup>. Figure C-1 shows the heat of reaction of phosphate sorption with time when the solution was changed to 50 mM KCl containing 5 mM KH<sub>2</sub>PO<sub>4</sub> (KCl-P solution). Phosphate sorption onto the soil was exothermic.

The KCl-P solution was leached through the column to P-saturate the sample's sorption sites. Curve 1 in Figure C-2 shows subsequent oxalate sorption when the solution was changed to 50 mM KCl plus 10 mM oxalate as potassium oxalate. Oxalate sorption was exothermic. The solution was again changed back to the KCl-P solution; and P was resorbed onto the soil. Phosphate sorption gave the same exothermic reaction (Curve 2 in Fig. C-2).

The soil was again saturated with P as above; and the solution then was changed to sorb citrate onto the surface by passing a 50 mM KCl solution containing 10 mM citrate as potassium citrate through the column. Curve 1 in Figure C-3 indicates that the sorption of citrate was endothermic. Finally, the solution was changed back to the KCl-P solution; and P was resorbed again. Phosphate sorption continued to be exothermic (Curve 2 in Fig. C-3).

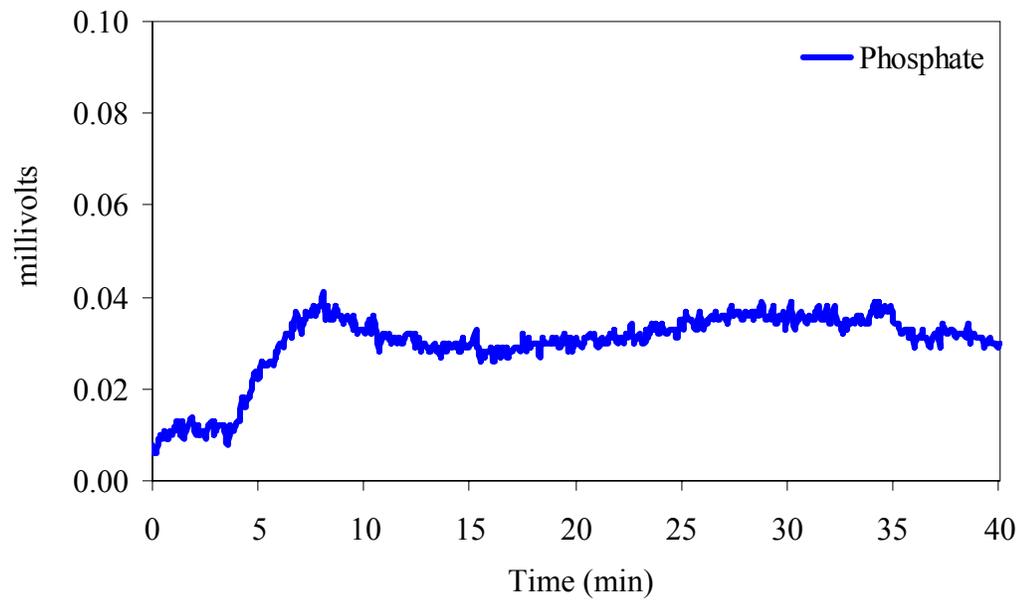


Figure C-1 Heats of reaction for phosphate sorption onto the study-site soil

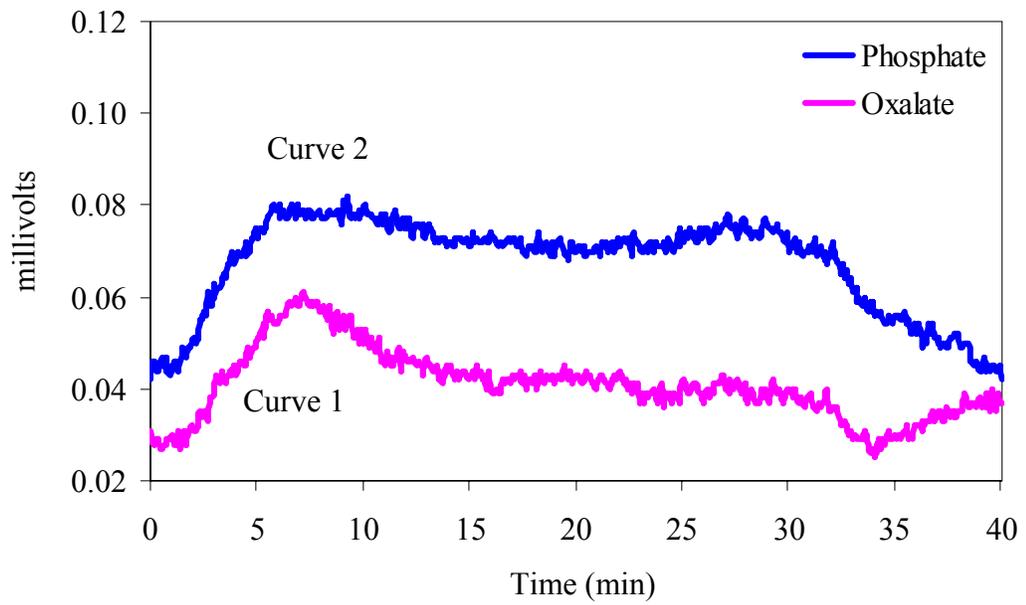


Figure C-2 Heats of reaction for oxalate sorption onto P-saturated soil preceding phosphate sorption onto oxalate-treated soil

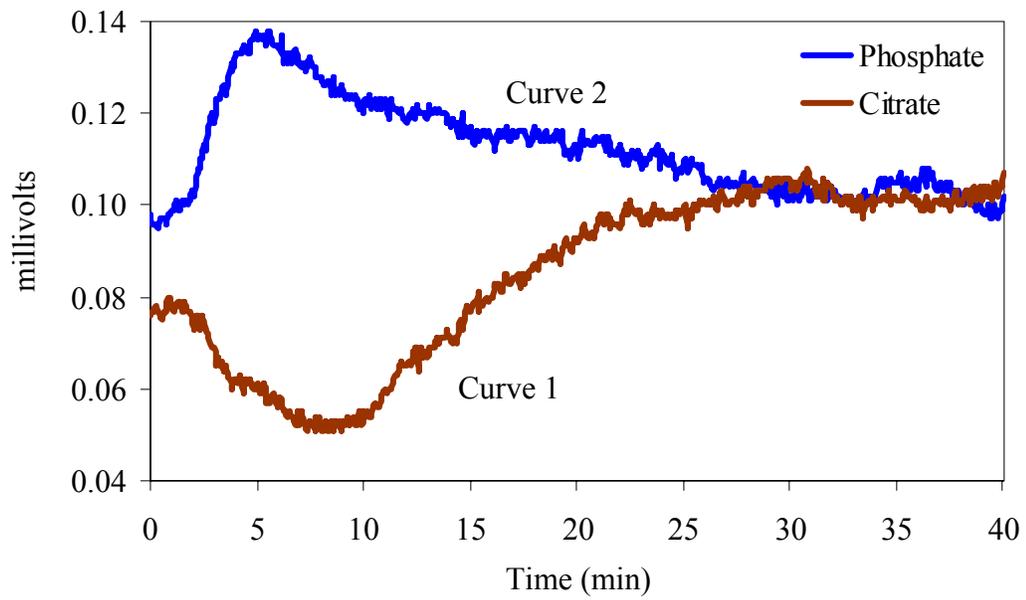


Figure C-3 Heats of reaction for citrate sorption onto P-saturated soil preceding phosphate sorption onto citrate-treated soil

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## BIOGRAPHICAL SKETCH

Shinjiro Sato was born to Nobuko and Kiyoshi Sato in Osaka-shi, Japan on February 1, 1970. He grew up in his hometown and graduated from Kansai Soka High School in 1988. He then attended Soka University and received a B.A. degree in English Literature in 1993. During his undergraduate work, Sato spent one year (1990–1991) as an exchange student of Portuguese language at the Federal University of Paraná in Curitiba, Brazil. He then attended the University of Tsukuba, Ibaraki-ken, Japan, where he earned an M.S. degree in Environmental Science in 1995. He then moved to Manaus, Brazil to work for NGOs as a project consultant (Japan–Brasil Network) and research assistant (Centro de Pesquisas Ecológicas da Amazônia) engaged in community-basis projects for 3 years. In the summer of 1998, Sato joined the University of Florida to pursue a Doctor of Philosophy in agroforestry in the School of Forest Resources and Conservation. As his research progressed, he felt that a more in-depth understanding of soil phosphorus chemistry was required; so he switched to the Soil and Water Science Department at the University of Florida in the spring of 2000. After receiving his doctorate in Soil Science, he plans continuous international research as a soil scientist including work in the Brazilian Amazon.