

QUANTITATIVE APPROACH FOR ASSESSMENT OF PHOSPHORUS LOSS RISK  
FROM ALAQUOD AND PALEUDULT SOIL PROFILES

By

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To my parents

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Abstract of Dissertation Presented to the Graduate School  
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Phosphorus (P) transported from agricultural fields can be a major contributor to eutrophication of aquatic systems. Sandy soils have higher risk of P loss because of limited P retention capacity. Vertical movement of P through the soil profile results in its contact with Bh horizons of Alaquods and Bt horizons of Paleudults which may act as P sinks. The purpose of this study was to evaluate a new tool, the “safe” soil P storage capacity (SPSC), based on a threshold P saturation ratio (PSR) value, to quantitatively assess P release potential from fertilizer-impacted Alaquod- and Paleudult- soil profiles which are of extensive occurrence in the SE United States coastal plain. Soil samples from Alaquod and Paleudult sites located within Florida were sampled by horizon. The SPSC calculated from P, Fe and Al using oxalate extractant was related to water-soluble P and equilibrium P concentrations ( $EPC_0$ ) obtained from traditional Langmuir isotherms. Plant P availability was determined using iron-oxide impregnated filter paper (FeO-P).

A different threshold PSR was obtained for Bh and Bt horizons compared to that of sandy surface horizons of Florida, reflecting the differences in soil components between

these horizons. Greater desorption potential of Bh in comparison to Bt likely relates to weaker bonding of P with organically-complexed Al. Environmental risk of P loss from Bt samples, may also be predicted from SPSC. The result indicates that although Bt soils have high P retentive capacity due to crystalline Fe oxides along with phyllosilicates, noncrystalline metal oxides extracted by oxalate are the components that bind P most tenaciously and that control sorption below PSR threshold. Plant P availability from fertilizer-impacted Alaquod and Paleudult subsurface horizons as inferred from FeO-P suggests deep-rooted plants can remove P from subsurface horizons in phytoremediation. Water soluble P,  $EPC_0$  and FeO-P are minimum when SPSC is positive and begin to increase when SPSC becomes zero. Results of this research support the validity of SPSC for quantitatively predicting the amount of P that can be safely added to a soil before a given horizon will likely constitute a P loss risk.

## CHAPTER 1 INTRODUCTION

Phosphorus (P) is essential for plant growth and development. However, continuous application of P and its subsequent loss to waterways accelerates eutrophication of surface waters (Sharpley et al., 2003; Withers and Haygarth, 2007; Filippelli, 2008). In Florida, the majority of surface horizon soils are sandy. In sandy soils the risk of P loss is higher because of limited P retention capacity of the soil (Nair et al., 2004). Due to excess P loading, P may move through the soil profile and can come in contact with subsurface horizons. Subsurface flow can also be a major pathway for P losses from agricultural soils (Sims et al., 1998; McDowell and Sharpley, 2001). Negative environmental changes such as algal blooms have been observed in Florida Bay during a 10-year observation period by the US Geological Survey evaluation of the South Florida National Water Quality Program (McPherson, 1999).

Alaquods of the SE U.S. are characterized by sandy textures, fluctuating water table and the presence of a subsurface spodic horizon (Bh) below an A-E horizon sequence (Soil Survey Staff, 1999). They represent the most extensive soil great group of Florida. The sandy A horizon usually has a depth of 15 to 20 cm with a small amount of organic matter. The thickness of the E horizon typically ranges from 20 to 140 cm, depending on the soil series. The Bh-horizon generally has low pH along with the accumulation of C and associated metals (mainly Al and Fe), which have relatively high affinity for P. The A and E horizons of these soils have negligible P retention capacity (Nair et al., 1998). When P loading is high, P may move through the soil profile coming in contact with the spodic horizon where it can be sorbed by spodic materials. Depth to the spodic horizon is important for evaluating P mobility; soils with a greater depth to

spodic horizons have greater susceptibility for P loss due to lower probability of interacting with the Bh-horizon before being laterally transported from the site.

Paleudults of the SE coastal Plain of U.S. have sandy epipedons overlying loamy or clayey Bt horizons. The E horizons of these Paleudults consist mainly of sand with coatings of silt and clay, as bound by relatively low amounts of metal oxides.

Phosphorus retention by Bt horizons is mainly influenced by inorganic metal oxides (Zhou et al., 1997). The P retention capacity of Bt horizons is significantly higher than that of overlying A and E horizons (Harris et al., 1996).

There is a need to study the chemical compositional differences between Alaquod and Paleudult subsurface horizons to evaluate implications for risk of P loss as P moves through a soil profile. Phosphorus sorption isotherms are used extensively to determine the P loss risk to runoff or drainage. Langmuir isotherms are widely used for describing P sorption by soils (Mehadi and Taylor, 1988; Taylor et al., 1996; Nair et al., 1998; Li et al., 2007). Factors such as clay content (Sanyal et al., 1993), extractable Fe and Al oxides (Li et al., 2007), organic matter (Sanyal and De Datta, 1991; Kang et al., 2009) and soil pH (Sato and Comerford, 2005) affect P sorption in soil. Experimentally the risk of P loss from soils can also be estimated from equilibrium P concentration ( $EPC_0$ ) as obtained from P sorption isotherms. The parameter  $EPC_0$  may be defined as the P concentration in solution at which neither adsorption nor desorption of P occurs in soil (Nair et al., 1998; Zhou et al., 2005).

Environmental risk of P loss from soil horizons can be easily evaluated from the phosphorus saturation ratio (PSR; Nair et al., 2004) and soil phosphorus storage capacity (SPSC; Nair and Harris, 2004). A threshold PSR (“change point”) above which

release of P from soil to solution abruptly increases can be determined for a given population of soils. Phosphorus saturation ratio may be calculated using extractants such as oxalate ( $PSR_{Ox}$ ), Mehlich 1 ( $PSR_{M1}$ ) or Mehlich 3 ( $PSR_{M3}$ ) as the molar ratio of P to [Fe + Al]. A PSR value of 0.10 (using oxalate -P, Fe and Al in the PSR calculation) has been determined as an environmental threshold for surface horizons of relatively-well drained sandy soils of Florida (Nair et al., 2004). Soil P storage capacity is a calculation of how much P can be added to a soil before reaching this critical PSR threshold. Phosphorus retention and release characteristics from Alaquod and Paleudult profiles still need to be studied thoroughly. There is no information available on a practical change-point related to P-release from subsurface horizons of Alaquods and Paleudults. The threshold value of Bh and Bt horizons will likely differ from each other and from surface horizons because of compositional differences.

The research hypotheses are as follows:

1. In comparison to A and E horizons of Alaquods, Bh horizons will release P differently because of compositional differences among the horizons.
2. Chemical compositional differences within and between Alaquod- and Paleudult profiles are responsible for differences in P retention and release from horizons that occur in these soils.
3. The  $EPC_0$  will be low when PSR values are below the change point threshold (i.e.,  $SPSC > 0$ ) because both measures relate closely to the point at which high-energy bonding sites for P are filled.
4. Bt horizons will have high P retention capacity but all the sorbed P may not be retained tenaciously beyond the threshold PSR which is controlled by noncrystalline metal oxides.
5. Deep-rooted plants can access P from subsurface horizons, particularly the spodic horizon of Alaquods, and may be successfully used to reduce the risk of P loss from these soils.

Based on the hypotheses, the specific objectives of this study were as follows:

1. Compare the P release characteristics of A- and E-, and subsurface (Bh) horizons of manure-impacted Alaquods to allow an evaluation of the soil P storage capacity of the Alaquod profile and to use this information for water table management strategies with respect to P transport.
2. Determine the compositional differences between subsurface horizons of Alaquods and Paleudults and to evaluate implications for risk of P loss via subsurface flow in these soils.
3. Compare P release behavior as assessed using PSR and SPSC and to relate it to the compositional differences between Alaquod and Paleudult subsurface horizons.
4. Evaluate the relation between  $EPC_0$  and SPSC which could serve as a more readily-determinable substitute for predicting P loss risk.
5. Evaluate the validity of SPSC in predicting the maximum safe loading of P for Bt samples (which contain appreciable crystalline Fe oxides and kaolinite clay) using known-P-additions approach.
6. Determine P availability for plant uptake from subsurface horizons of Alaquods and Paleudults and to evaluate the potential for phytoremediation for high P-loaded soils.



Figure 1-1. Alaquod soil profile (Source: [http://wgharris.ifas.ufl.edu/SEED/Htm.images/mya\\_p.htm](http://wgharris.ifas.ufl.edu/SEED/Htm.images/mya_p.htm))

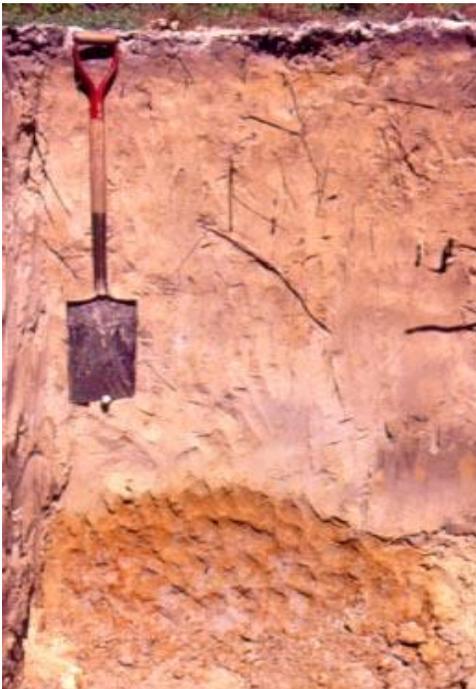


Figure 1-2. Paleudult soil profile (Source: <http://wgharris.ifas.ufl.edu/SEED/Htm.images/19.htm>)

## CHAPTER 2 REVIEW OF LITERATURE

### **Excess Application of P**

The United States Environmental Protection Agency (USEPA) identified agricultural non-point source pollution for the degradation of water quality (USEPA, 2002). One of the major causes of this pollution is P which moves from agricultural lands due to excessive application of fertilizers and manures. In manure application scenarios, nutrient loading is often based on crop N requirements, resulting in an excess of P in the soil due to high P/N ratio of manure (Robinson and Sharpley, 1996). Phosphorus moves from agricultural land both in soluble form and in association with particles and colloids (Haygarth et al., 1997). Particulate and colloid P transport is associated with soil erosion arising from raindrop impact and overland flow (McDowell et al., 2003; Owens and Walling, 2002) while soluble P is transferred to water bodies (Heckrath et al., 1995) via surface or subsurface flow. Phosphorus enrichment of surface water leads to eutrophication (Mansell et al., 1991; Sharpley and Halvorson, 1994; Sims et al., 1998; Logan, 2001). The concern about eutrophication of Lake Okeechobee, Florida has increased since 1970 due to increased water-column total P concentrations (Havens et al., 2003).

### **Surface and Subsurface Loss of P**

Hydrology is the driving force that controls the transfer of P from lands because water provides the energy and the carrier for P movement (Haygarth and Jarvis, 1999). Pathways for P movement can be broadly classified as surface or overland flow and subsurface flow. Loss of P in surface runoff from agricultural sources is one of the major non-point source pollution of P. In sandy soils the risk of P loss from surface-applied P

is higher than fine-textured soils because of limited P retention capacity of the soil (Nair et al., 2004).

Subsurface pathways include lateral flow through the soil, vertical drainage, and preferential flow through macropores and artificial drainage channels (Curley et al., 2010). Subsurface loss of P is substantial and it is well documented in different parts of the world, including the southeastern and Mid-Atlantic States of the United States (Sims et al., 1998), Canada (Simard et al., 1995); and Australia (Stevens et al., 1999; Melland et al., 2008). Subsurface P losses have often been ignored because of the greater probability of P retention by subsurface horizons. However, more recently subsurface P transfer has increasingly been addressed by the scientific community from an environmental perspective, since small P losses via subsurface flow may affect water quality (Tunney et al., 1997; Turner and Haygarth, 2000).

### **Soil P Distribution**

Soil P may exist in different pools including dissolved inorganic P, inorganic P sorbed on the soil particle surfaces, inorganic P sorbed by the slow time-dependent processes and the organic P pool which includes unbound precipitates (McGechan and Lewis, 2002). For the majority of the soils, 30 to 65% of the total P is organic P; however, high organic matter soils can contain up to 90% organic P (Harrisson, 1987). Organic P is repeatedly added to the soil in the form of animal, microbial and plant detritus (Condrón et al., 2005). Inorganic P exists mainly as adsorbed P and also as primary and secondary P solid phases. Soil inorganic P exists in different mineral forms. These minerals vary in solubility and ability to supply P to the soil solution depending on factors such as mineral P solubility, pH and concentration of metals like Al and Fe (Pierzynski et al., 2005). Organic P forms mainly constitute inositol phosphates,

phospholipids, and nucleic acids and their derivatives (Stevenson, 1982). Turnover of organic P in soils is determined by the rates of immobilization and mineralization.

Immobilization may be defined as the biological conversion of inorganic P to organic P in soil; whereas release of inorganic P from organic P is referred to as mineralization.

Phosphorus applied in the form of P fertilizers or crop residues, manures and sewage sludge will modify three major P pools in the soil-plant system: a) soil solution P, b) available soil P and c) unavailable soil P (Singh et al., 2005).

The quantity of P in soil solution is very low at any given time and it is in the order of  $<1 \text{ kg ha}^{-1}$  or  $<1\%$  of the total quantity of P in the soil (Pierzynski, 1991). Labile P may be defined as the soil or sediment P that equilibrates rapidly with an aqueous solution whereas; those P forms which do not readily equilibrate may be referred as the nonlabile P (Pierzynski et al., 2005). Available P (P quantity) and P availability (P intensity) are mainly used to describe the total plant available P pool and the P that may be used immediately by plants (Holford, 1997). These two factors are dependent on the buffer capacity or soil's sorptivity. Buffer capacity of the soil solution is the resistance of the solution concentration to change and is an indication of the quantity of P sorbed on surface sites which will be easily desorbed (Holford, 1997). Higher buffering capacity leads to slower P release to soil solution. Clayey soils have high buffering capacity because of high surface area (McGechan and Lewis, 2002) and also due to the high proportions of Fe or Al oxide minerals (Bowden et al., 1977).

### **Extractants Used for P Measurement**

Phosphorus release from P-impacted soils has been studied by several researchers using different extractants. Pote et al. (1996) observed water-soluble P (WSP) as the most appropriate environmental estimator of P concentrations in runoff

compared with other soil test methods developed for crop production. Several researchers (Graetz and Nair, 1995; Silveira et al., 2006) have also observed continuous releases of P from manure-impacted soils during sequential leaching. However, the small amount of soil P extracted by this method may not reflect all forms of labile P and thus has limited the use of water as an extractant (Elrashidi et al., 2001).

Many soil test extractants like Mehlich 1, Mehlich 3, Bray 1 and Bray 2 use strong acids like HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> to dissolve Fe, Al or Ca phosphates to determine the labile P. Mehlich (1953) introduced a double acid combination, the Mehlich 1 solution which constitutes 0.05 M HCl and 0.0125 M H<sub>2</sub>SO<sub>4</sub> for extracting P along with metals from acid soils in the southeastern part of the United States. Mehlich modified his initial soil test P (STP) by developing a multi-element extractant, the Mehlich 3 which may be used on a wider range of soils. Mehlich 3 is a more powerful extractant than Mehlich 1 and can be used in acid and neutral soils with much greater efficiency (Elrashidi et al., 2001). It contains ammonium fluoride, ammonium nitrate, acetic and nitric acids, and the chelating agent EDTA. Acetic acid acts as a buffer and maintains the pH of the solution at 2.5. Ammonium nitrate helps to extract basic cations such as calcium, magnesium, sodium and potassium. Nitric acid extracts a portion of calcium phosphates and its acid component helps in extraction of basic and micronutrient cations. Fluoride extracts Al and Fe phosphates, and EDTA mainly acts as a chelating agent (NCDACS, 2007). Fluoride ion is also used in Bray 1 (0.03 M NH<sub>4</sub>F + 0.025 M HCl) and Bray 2 (0.03 M NH<sub>4</sub>F + 0.1 M HCl) extractants to replace P sorbed at metal-hydroxide surfaces through ligand-exchange reactions and to initiate complex formation with metals in solution to prevent metal phosphate precipitation (Fox et al., 1990).

Oxalate extraction uses 0.1 M oxalic acid and 0.175 M ammonium oxalate solution. It was designed to remove P associated with amorphous oxides of Al and Fe in non-calcareous soils (Hooda et al., 2000). Protonation and complexation is the main mechanism for the dissolution of Fe and Al phosphate bonds (Cornell and Schwertmann, 1996). Oxalate anions replace P sorbed at metal-hydroxide surfaces through ligand-exchange reactions and prevent metal phosphate precipitation by complexing metals in solution (Fox et al., 1990).

Olsen extractant is a buffered alkaline solution of 0.5 M sodium bicarbonate solution at a pH of 8.5. Olsen extractant was developed mainly for calcareous soils but it works well on acid soils also (Smyth and Sanchez, 1982). Due to the high pH of the extractant, OH<sup>-</sup> ions react with Al and Fe and solubilize P from Al-P and Fe-P (Tyner and Davide, 1962). In calcareous soils it functions by replacing adsorbed P with HCO<sub>3</sub><sup>-</sup> which reacts with Ca as CaCO<sub>3</sub> and thus solubilizes Ca-P (Beegle, 2005).

### **Adsorption of P**

Transport of P with water in soils is dependent mainly on the extent of P sorbed by soil components. Adsorption is the process by which reactive chemicals (ionic P - H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>) are removed from solution and become attached to surfaces (McGechan and Lewis, 2002). Phosphorus sorption consists of a fast reversible true sorption process on soil particle surfaces and a slow almost irreversible process consisting of diffusion, precipitation and deposition which is described as the slow-sorption process. Iron and aluminum oxides and hydroxides in acidic soils and calcium in calcareous or alkaline soils have been identified as the principal soil constituents in phosphate adsorption (Hemwall, 1957). A small portion of the P which is sorbed can be desorbed easily. A major portion of the P added is rapidly fixed and thus not easily

desorbed. Hysteresis is mainly due to the differences in the rates of adsorption and desorption and does not necessarily constitute truly irreversible adsorption (Rhue and Harris, 1999). However, in sandy soils, with low concentrations of Fe and Al, little P will be held by the soils and P can be more easily lost from the soil. Hysteresis is a function of the P loading rate, solid-phase physicochemical characteristics, and residence time (Reddy and Delaune, 2008). Precipitation of P as insoluble compounds (van Riemsdijk et al., 1984), a change from monodentate to bidentate forms (less reversible) of sorbed P (Munns and Fox, 1976) and slow diffusion of P into soil solids (Ryden et al., 1977) are the possible mechanisms associated with hysteresis.

Phosphorus sorption isotherms (e.g. Langmuir and Freundlich) are widely used to determine potential risk of P loss to runoff or drainage (Sui and Thompson, 2000). Langmuir isotherms are widely used for describing phosphate sorption by soils (Mehadi and Taylor, 1988; Taylor et al., 1996; Nair et al., 1998; Li et al., 2007). Langmuir adsorption equation can be expressed as:

$$\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}} \quad (2-1)$$

where

S=S'+ S<sub>o</sub>, the total amount of P sorbed

S'= P sorbed by the solid phase

S<sub>o</sub>= originally sorbed P on the solid phase

C= concentration of P after 24 h equilibration

S<sub>max</sub> = P sorption maximum

k = a constant related to the bonding energy

The Freundlich equation can be represented as

$$S = KC^n \quad (2-2)$$

where,

K and n are constants for a given soil.

C is the equilibrium P concentration.

The Langmuir model has an advantage over the Freundlich model in environmental applications because the soils maximum sorption capacity and the bonding energy constant can be determined (Graetz and Nair, 2000). Phosphorus sorption isotherms are time consuming and complicated for routine use by soil test laboratories (Sharpley et al., 1994). However, Bache and Williams (1971) suggested a single equilibration using a high concentration of P (single-point isotherm) to determine the P sorption capacity of soils rapidly and easily with reasonable accuracy. This was also confirmed by Mozaffari and Sims (1994) for surface and subsurface horizons of four Atlantic Coastal Plain soils. For Florida soils a single point isotherm using a 100 mg L<sup>-1</sup> P solution gave a linear relationship with S<sub>max</sub> for both upland (Nair et al., 1998) and wetland (Reddy et al., 1998) soils providing a means of determining S<sub>max</sub> without isotherm development.

There are close positive relationships between P sorption and the abundance of crystalline and amorphous iron and aluminum oxides in many soils from different environments (Nair et al., 1998; Sanyal et al., 1993; Zhou et al., 1997; Agbenin, 2003; Wiriyaakitnateekul et al., 2005; Wisawapipat et al., 2009). Phosphorus sorption in Fe-humic substance mixture was six to seven times higher in comparison to amorphous Fe oxides which may be due to the ternary complex formation between Fe-humic substances and phosphate (Gerke and Hermann, 1992). Yuan and Lavkulich (1994)

observed significant correlations between P sorption and oxalate extractable Al and Fe in Spodosols from British Columbia. Positive relationship between C content of spodic horizons and P sorption had been observed by Nair et al. (1998). This relationship was due to the indirect effect of C through complex formation with cations such as Fe and Al associated with organic matter.

Various pools of Fe and Al associated with P retention are measured by selective dissolution with different extractants. Ammonium oxalate extracts both noncrystalline inorganic- and organically-complexed Fe and Al (McKeague and Day, 1966; Jackson et al., 1986). Citrate-bicarbonate-dithionite (CBD) primarily extracts free Fe oxides. The difference between CBD and oxalate-extractable Fe and Al is due to the dissolution of crystalline Fe oxides (McKeague et al., 1971). Sodium pyrophosphate extracts organically-complexed Fe and Al in soils (McKeague, 1967; Wada and Higashi, 1976) though it can extract some noncrystalline inorganically-complexed forms of these metals as well (Kaiser and Zech, 1996).

Several researchers have suggested  $\text{CuCl}_2$  or KCl as an alternative extractant for Al bound to soil organic matter (Oates and Kamprath, 1983a; Hargrove and Thomas, 1984). Juo and Kamprath (1979) found that 1.6 to 12 times more Al was extracted by 0.5 M  $\text{CuCl}_2$  than 1 M KCl. The affinity for the carboxylate sites is greater for Cu and it can easily replace Al bound to organic matter (Matus et al., 2008).  $\text{CuCl}_2$  is not efficient to remove Al significantly from aluminosilicate minerals, however, it is efficient in extracting some poorly ordered Al associated with soil mineral (Oates and Kamprath, 1983b).

Another very important soil property for P sorption is the soil clay content (Loganathan et al., 1987; Bennoah and Acquaye, 1989; Sanyal et al., 1993). Clayey soils with iron oxides have high P retention capacity in comparison to the sandy and loamy Ultisols and loamy Oxisols (Sanchez and Logan, 1992). Large surface area and presence of P sorbing minerals contribute for the greater P adsorption capacity for these soils compared to the coarse textured soils (Loganathan et al., 1987).

Soil pH has a role in P sorption; P sorption generally decreases with increasing pH. At higher pH, common mineral surfaces become negative resulting in electrostatic repulsion and decrease in P sorption (Haynes, 1982; Oh et al., 1999; Sato and Comerford, 2005). With increasing pH, hydroxyl ions compete with phosphate ions for specific sorption sites on mineral surfaces (Smyth and Sanchez, 1980). Also, at high pH, Al hydroxide polymers can neutralize sites where more reactive Al surfaces were present (Sanchez and Uehara, 1980).

### **Desorption of P**

Desorption is fundamental in controlling the soil solution P concentration and hence the bioavailability of soil P (Sato and Comerford, 2006). Phosphorus desorption can be determined by dilution, sequential extraction, or anion exchange resin extraction techniques (Brewster et al., 1975; Bhatti and Comerford, 2002). Dilution method is the process of P desorption from the solid phase by shaking the soil sample for a fixed equilibration time with a range of soil:solution ratios with single (Barrow, 1979) or successive (Sharpley et al., 1981) extractions. In sequential method an extracting solution is added to the soil at constant soil:solution ratio, and the sample is shaken at a fixed equilibration time. This procedure is repeated until P desorption is exhausted or a pattern of P release is recognized (Bhatti and Comerford, 2002). Anion exchange resin

(AER) extraction is performed in a similar manner as the sequential extraction where bags filled with AER are used to remove P from solution (Yang and Skogley, 1992; Delgado and Torrent, 1997). The difficulty of this method was to separate the soil from the resin after each desorption step. The use of nylon netting bags to hold the resin helped to retrieve and extract P from the resin (Saggar et al., 1990).

To overcome the difficulties with AER, Fe-oxide impregnated filter paper may be used to determine plant P availability, P desorption kinetics and P dynamics in the field (Chardon et al., 1996). In comparison to the common acid or base extractants used, P extracted by Fe oxide impregnated filter paper (FeO-P) may be successfully used to estimate the labile P pool as this method does not depend on the destructive dissolution of soil components or reaction products (Menon et al., 1989; Klatt et al., 2003). The FeO coating acts as a P sink and initiate adsorption mechanism similar to the one which occurs at the interface of soil and root surface (Myers et al., 1997).

### **Determination of Environmental P Risk**

Many point and nonpoint sources of P have the potential to induce eutrophication in surface water. Regulation for further P application and proper management of P in order to avoid water quality problems is essential. Soil test phosphorus (STP) measurements were mainly used for soil fertility and agricultural productivity; but later they were used to determine the risk of soil P to be transported to surface- and groundwater (Sharpley et al., 2003; Sotomayor-Ramirez et al., 2004). However, different soils have different critical STP values above which the release of P from soil increases significantly (Hesketh and Brookes, 2000).

Experimentally the risk of P loss from soils can be estimated from equilibrium P concentrations ( $EPC_0$ ) as obtained from P sorption isotherms. The parameter  $EPC_0$  may

be defined as the P concentration in solution at which neither adsorption nor desorption of P occurs in soil (Pierzynski et al., 1994; Nair et al., 1998). The potential for desorption of  $\text{PO}_4^{3-}$  from soils can be estimated from  $\text{EPC}_0$  (Fang et al., 2002; McDowell and Sharpley, 2003). Soils with high  $\text{EPC}_0$  values have a greater tendency to desorb dissolved P into runoff waters (Sharpley et al., 1994). Exchange of P between soils/sediments and the water column through the sorption process can also be defined by  $\text{EPC}_0$  (Kerr et al., 2011). Phosphate ( $\text{PO}_4^{3-}$ ) will sorb on solid surfaces to re-establish the equilibrium condition when the concentration of  $\text{PO}_4^{3-}$  in solution increases above equilibrium concentration. However,  $\text{PO}_4^{3-}$  would be desorbed from the solid sediment phase when the concentration in solution decreases (House and Denison 2000, 2002; Jarvie et al. 2005).

Phosphorus saturation ratio (PSR), which is the molar ratio of P to [Fe + Al], is often used as an environmental indicator of P loss from soils (Maguire and Sims, 2002; Nair and Harris, 2004). Phosphorus saturation ratio can be calculated from P, Fe and Al extracted with oxalate ( $\text{PSR}_{\text{Ox}}$ ), Mehlich 1 ( $\text{PSR}_{\text{M1}}$ ) or Mehlich 3 ( $\text{PSR}_{\text{M3}}$ ) solution (Nair et al., 2004). A “change point” at which water-soluble P (WSP) abruptly starts to increase with increasing PSR is evident from WSP-PSR relationships and can be used for management purposes to estimate the potential risk of P loss from soils. The change point refers to a threshold PSR value above which further P added may be lost easily through runoff or leaching (Casson et al., 2006). Above the change point PSR of 0.1 (using oxalate P, Fe and Al in the PSR calculations) there is a higher risk of P loss from Florida soils (Nair et al., 2004).

Neither STP nor PSR provides information on how much more P can be added to a certain volume or mass of soil before the soil begins to release P. The latter information is provided by the soil phosphorus storage capacity (SPSC) proposed by Nair and Harris (2004), calculated using P, Fe and Al extracted with oxalate solution. SPSC depends on a threshold PSR as determined for a specific range of soils and it is a function of Al and Fe concentrations. The relationship between SPSC and WSP indicated that when SPSC is positive, the soil is a P sink, and when it is negative the soil is a potential P source (Chrysostome et al., 2007).

### CHAPTER 3

## SOIL PHOSPHORUS STORAGE CAPACITY IN MANURE-IMPACTED ALAQUODS: IMPLICATIONS FOR WATER TABLE MANAGEMENT

With excessive use of fertilizers and manures soil phosphorus (P) in agricultural lands has increased, leading to eutrophication of surface water. In sandy soils the risk of P loss from surface-applied P is higher than from fine-textured soils because of limited P retention capacity of the soil (Nair et al., 2004). Phosphorus saturation ratio (PSR), which is the molar ratio of P to [Fe + Al], is often used as an environmental indicator of P loss from soils (Maguire and Sims, 2002; Nair and Harris, 2004). The change point refers to a threshold PSR value above which further P added may be lost easily through runoff or leaching (Casson et al., 2006). A PSR value of 0.10 has been determined (using either oxalate or Mehlich 1-P, Fe and Al in the PSR calculations), as an environmental threshold for surface horizons of relatively-well drained sandy soils of Florida (Nair et al., 2004). There is a need to determine the threshold PSR for Bh-horizon because of the inherent differences between the components of this horizon and those of surface horizons.

Soil test phosphorus (STP) and P saturation ratio (PSR) are often used as environmental risk assessments. However, neither STP nor PSR provide information about how much P can be added to a certain mass or volume of soil with minimal environmental risk. This information is provided by soil phosphorus storage capacity (SPSC) proposed by Nair and Harris (2004). Validity of the SPSC is contingent upon thorough extraction of the main forms of Al and Fe with which P is associated in the sample, as essentially accomplished by the oxalate extractant. Both M1 (Chrysostome et al., 2007) and M3 (Kang et al., 2009) do not extract Fe and Al with the same efficiency as does the oxalate solution. Differences in Fe and Al concentrations between

extractants in the calculation of SPSC require a conversion factor for calculating the true capacity of the soils to retain additional P when a soil test solution is used as the extractant. The value of the conversion factor is likely different for sandy A and E horizons, and for Bh horizons due to compositional differences among soil horizons. The conversion factor for SPSC calculated with M1 data is 1.3 for the A and E horizons of Alfisols, Entisols, Spodosols, and Ultisols (Nair et al., 2010); the conversion factor using M3 is 1.1 calculated from data of Chrysostome et al. (2007) using a threshold PSR of 0.08 (Nair et al., 2004). Based on SPSC, best management practices (BMPs) such as addition of Fe and Al amendments (to increase the P storage capacity of surface soils that have low P retention) or water table control (to utilize additional storage capacity of horizons for minimizing P loss) may be implemented.

The objective of this chapter was to compare the P release characteristics of A- and E-, and subsurface (Bh) horizons of Alaquod profile of dairy and beef manure-impacted soils. The specific objectives were to:

- determine the PSR “change point” for Bh horizons;
- determine a conversion factor enabling determination of SPSC for spodic horizons using practical soil tests (M1 and M3);
- evaluate the use of SPSC for water table management of dairy and beef manure-impacted soils.

## **Materials and Methods**

### **Soil Sampling**

Thirty Alaquod profiles from three beef (B1, B2 and B3) and three dairy (D1, D2 and D3) manure application sites (five profiles from each site) were sampled by horizon to a meter depth (Figure 3-1), for a total of 192 soil samples. Two of the sites (B1 and B3) are at the University of Florida’s Research and Education Centers located at

Alachua and Hardee County, FL, respectively. The third beef site (B2), located in Osceola County, FL, is a private ranch that has been in operation since the 1940s. All dairy sites were located in Okeechobee County, FL. The dairy sites comprised of pasture (grazing area) and forage (forage production area) components for D1, holding (area where cattle are held and fed overnight) and pasture components for D2 and intensive (small area closest to the barn) component for D3.

Forty-nine archived spodic horizon samples from six other locations - two beef (O1 and O2) and four dairy (O3, O4, O5 and O6) operations were also included in this study resulting in a total of 241 soil samples. The archived soils were from Okeechobee County, FL. Archived soils from four dairy components (intensive, holding, pasture and forage) differentially impacted by manure were used in this study. The archived beef sites were pasture locations at the beef ranches. Total P in the archived soils at dairy sites varied as intensive > holding > pasture > forage with mean values of 2330, 870, 255, and 45 mg kg<sup>-1</sup> for intensive, holding, pasture, and forage components, respectively; mean TP for the beef pastures of archived samples was 45 mg kg<sup>-1</sup> (Graetz et al., 1999).

### **Chemical Analyses**

Samples were thoroughly mixed and air-dried before analyses. Soil pH was determined using 1:2 soil and water suspension. Water-soluble P was determined using 1:10 soil to water ratio. The extraction was done by shaking 2 g soil with 20 mL of double deionized water in a reciprocating shaker at about 100 excursions min<sup>-1</sup> for 1 h and was filtered using a 0.45 µm filter paper. Total P of soil samples was determined using the ignition method (Andersen, 1976). Water-soluble P and total P concentrations were determined using an autoanalyzer (USEPA, 1983; Method 365-1) by the Murphy

and Riley (1962) procedure. Mehlich 1-extractable P (M1-P), Fe (M1-Fe), Al (M1-Al), Ca (M1-Ca) and Mg (M1-Mg) were obtained by extracting with a double acid solution (0.05 M HCl + 0.0125 M H<sub>2</sub>SO<sub>4</sub>) at a 1:4 soil to solution ratio for 5 min (Mehlich, 1953).

Mehlich 3-extractable P (M3-P), Fe (M3-Fe), and Al (M3-Al) were obtained by extracting soil with 0.2 M CH<sub>3</sub>COOH + 0.25 M NH<sub>4</sub>NO<sub>3</sub> + 0.015 M NH<sub>4</sub>F + 0.13 M HNO<sub>3</sub> + 0.001 M EDTA for 5 min at a 1:8 soil to solution ratio (Mehlich, 1984). Oxalate-extractable P (Ox-P), Fe (Ox-Fe), and Al (Ox-Al) were determined by extraction with 0.1 M oxalic acid + 0.175 M ammonium oxalate solution at a 1:50 soil to solution ratio, equilibrated for 4 h at a pH of 3.0 (McKeague and Day, 1966). All metals and P in M1, M3 and Ox solution were determined by inductively coupled argon plasma spectroscopy (Thermo Jarrel Ash ICAP 61E, Thermo Elemental, Franklin, MA).

### Calculations

Phosphorus saturation ratio was calculated for each sample using oxalate (PSR<sub>Ox</sub>), Mehlich 1 (PSR<sub>M1</sub>) or Mehlich 3 (PSR<sub>M3</sub>) solution as the molar ratio of P to [Fe + Al]. Soil P storage capacity was calculated based on oxalate extractions because oxalate extracts most of the reactive Al and Fe present in the soil and proportionately represents its P sorption capacity (Kleinman et al., 2003).

$$SPSC_{Ox} = (\text{Change point } PSR_{Ox} - \text{Soil } PSR_{Ox}) \times (Ox - Fe + Ox - Al) \times 31 \quad (\text{Nair and Harris, 2004}) \quad (3-1)$$

SPSC can also be determined using P, Fe and Al from a soil test solution such as M1 and M3.

$$SPSC_{M1} = (\text{Change point } PSR_{M1} - \text{Soil } PSR_{M1}) \times (M1 - Fe + M1 - Al) \times 31 \times X \quad (3-2)$$

$$SPSC_{M3} = (\text{Change point } PSR_{M3} - \text{Soil } PSR_{M3}) \times (M3 - Fe + M3 - Al) \times 31 \times Y \quad (3-3)$$

where X and Y are conversion factors needed when calculating SPSC using M1 and M3 parameters, respectively. The SPSC in equations (3-2) and (3-3) without the correction term is referred to as the “Capacity Factor”.

The Fe, Al and P (used in the calculation of PSR and SPSC) in equations (3-1) to (3-3) are expressed in moles. The SPSC in equations (3-1) to (3-3) are expressed in mg kg<sup>-1</sup>. Soil P storage capacity may be expressed on a per-mass basis (e.g., mmol kg<sup>-1</sup>, mg kg<sup>-1</sup>, kg ha<sup>-1</sup>) or on a per-volume basis (e.g., mg cm<sup>-3</sup>, mg m<sup>-3</sup>, kg ha<sup>-1</sup>) to a specified depth.

### **Statistical Analyses**

The data were analyzed using the General Linear Model procedure in the statistical package SAS (SAS Institute, 2001). Differences between means of soil parameters were compared using Fishers LSD. The relationship between PSR and WSP was modeled as a segmented line [equation (3-4)], with the parameters estimated using nonlinear least squares. The change point (d) in the fitted segmented-line model was directly estimated. The joining of the two line segments at the change point is ensured by estimating the slope of the left hand line as a function of the change point and other model parameters [equation (3-5)]. Standard errors were estimated from the Fisher information matrix and confidence intervals were constructed using these standard errors and an appropriate t distribution critical value. Computations for the change point or threshold PSR were determined using a NLIN procedure in SAS, similar to the one adopted in a previous study (Nair et al., 2004).

$$WSP = \begin{cases} a_0 + b_0PSR & PSR \leq d \\ a_1 + b_1PSR & PSR > d \end{cases} \quad (3-4)$$

$$b_0 = \frac{(a_1 - a_0) + b_1 d}{d} \quad (3-5)$$

where  $a_0$ ,  $b_0$ ,  $a_1$  and  $b_1$  are model parameters, and  $d$ , the change point as determined using the segmented line model.

## Results and Discussion

### Soil Characterization

The pH of the surface horizons ranged from 4.4 to 8.0 (Table 3-1). Manure application resulted in highest Ca and Mg concentrations in surface compared to subsurface horizons. Mean value of Ca and Mg in surface horizons were 1069 and 175 mg kg<sup>-1</sup>, respectively. However, Ca and Mg values were still elevated in subsurface horizons of sites D2 and D3 suggesting movement of manure constituents through the soil profile. Water-soluble P (WSP) was linearly related to TP for both surface- ( $R^2 = 0.77$ ) and spodic ( $R^2 = 0.78$ ) horizons. However, WSP values were <8% and < 5% of TP for most of the surface- and spodic horizons, respectively (data not shown). Low WSP of the spodic horizons suggests that the risk of P loss from these horizons was less than that of surface horizons. Higher concentration of Al in the spodic horizons in comparison to surface horizons (Tables 3-1 and 3-2) suggests that Al-associated P can be a major form of P association in the spodic horizons.

Many significant correlations have been observed between P sorption and oxalate-extractable Fe and Al in acid soils (Van der Zee and van Riemsdijk, 1986) including Spodosols (Yuan and Lavkulich, 1994; Villapando and Graetz, 2001). The oxalate solution extracts Fe and Al from amorphous inorganic substances as well as from horizons of accumulation of Fe and Al-organic matter complexes (McKeague, 1967). Thus this extractant is very effective for spodic horizons where most of the Fe and Al

are associated with organic matter. Oxalate-P represents over 80% of TP for most of the soils. Mehlich 1 and Mehlich 3 extracted less P in comparison to oxalate from most of the soils (Tables 3-1 and 3-2). The extraction efficiency of P along with the metals were oxalate > Mehlich 3 > Mehlich 1 for both surface and spodic horizons.

### **Phosphorus Saturation Ratio Change Points and SPSC for Soil Horizons**

For surface horizons a change point PSR of 0.10 using Ox- or M1- P, Fe and Al, and 0.08 using M3- P, Fe and Al were used for calculating the SPSC of the soils (Nair et al., 2004). Most of the surface horizons had PSR values in excess of the threshold PSR. These horizons have little P retention capacity due to low Fe and Al content (Tables 3-1 and 3-2) and thus have a high risk of P loss. Further land application of manure (high P/N ratio; Robinson and Sharpley, 1996), based on crop N requirements will aggravate the risk of P loss from the soil.

The threshold PSR for the spodic horizons was different from surface horizons in the case of all three extractants: Ox, M1 and M3 (Figures 3-2, 3-3 and 3-4). The change point was 0.05 (95% confidence limit: 0 to 0.10) for  $PSR_{Ox}$ ; 0.08 (95% confidence limit: 0 to 0.16) for  $PSR_{M1}$ ; and 0.09 (95% confidence limit: 0 to 0.19) for  $PSR_{M3}$ . Parameter estimates including standard errors and  $R^2$  values for the fitted nonlinear relationship models are given in Table 3-3. Discrete PSR thresholds for spodic horizons relative to other horizons of Florida soils documents that soil components influence change point behavior. The metals (dominantly Al) in the Alaquods of Florida are mainly organically complexed as a result of podzolization; which is consistent with findings of Zhou et al. (1997) showing that sorption of P by Bh horizon components is less tenacious than for the case of inorganically-complexed metal components (e.g., metal oxides) that are prevalent in most other horizons. We calculated the threshold PSRs for the spodic

horizons with and without the archived soils and no statistical differences were indicated.

Though spodic horizons have a higher P retentive capacity than surface horizons (Tables 3-1 and 3-2), once the P sorbing sites get saturated due to excess P loading, spodic horizons will release P and hence will be a P source. It has been shown that subsurface flow can be a major pathway for P losses from certain agricultural soils (Sims et al., 1998). In the rainy season when the water table is shallow, P from the Bh horizon can diffuse to the E horizons in these poorly drained soils and may flow laterally to the surface water body, further worsening the situation.

Although oxalate solution was chosen as the extractant to calculate the PSR and SPSC of these soils, it requires more time and resources than soil test procedures such as M1 and M3 that are routinely performed in most soil labs. It is possible to calculate the SPSC using data from a soil test extractant via a conversion factor developed from the population of soils that fall within a range for which a PSR threshold has been verified. The relationship between SPSC and the capacity factor (SPSC formula but using soil test data) for Bh horizon soils (Figures 3-5 and 3-6) suggests that SPSC can be calculated using M1- and M3- P, Fe and Al using a value of X=1.8 in equation (3-2), and Y=1.3 in equation (3-3).

Thus, considering the change point PSR and the conversion factor of spodic horizons, SPSC can be calculated from Ox, M1 and M3 extractant for Bh horizons from the following equations respectively:

$$SPSC_{Ox} = (0.05 - Soil\ PSR_{Ox}) \times (Ox - Fe + Ox - Al) \times 31 \quad (3-6)$$

$$SPSC_{M1} = (0.08 - Soil\ PSR_{M1}) \times (M1 - Fe + M1 - Al) \times 31 \times 1.8 \quad (3-7)$$

$$SPSC_{M3} = (0.09 - Soil\ PSR_{M3}) \times (M3 - Fe + M3 - Al) \times 31 \times 1.3 \quad (3-8)$$

Water-soluble P increases linearly when SPSC is negative for A and E,  $R^2 = 0.82$  (Figure 3-7) and Bh horizons,  $R^2 = 0.79$  (Figure 3-8). This observation confirms the relation of SPSC with WSP as noted by Chrysostome et al. (2007) in a laboratory study. In the current study, the majority of the surface horizon soils are P sources. Mean SPSC of Bh horizons ( $95\text{ mg kg}^{-1}$ ) was significantly higher than that of A horizons ( $-360\text{ mg kg}^{-1}$ ) due to much lower metal content and greater P loading. The majority of spodic horizons studied had a positive SPSC value indicating that a greater proportion of these horizons act as P sinks compared to surface horizons.

For both surface- and spodic horizons when SPSC values are negative, considerable amounts of P are released from the soils. Along with surface runoff, vertical leaching of P to shallow water table is a problem. By using the SPSC approach, the risk of a given soil horizon releasing excess P and hence contributing to P loss can be determined and this information can be used in making management decisions. As SPSC is additive, the overall P storage capacity of an entire soil profile can be calculated from the SPSC values of individual surface and subsurface horizons (Table 3-2).

### **Applications of the “Safe” Soil Phosphorus Storage Capacity**

Sandy eluvial horizons tend to have little P retention capacity because of a low abundance of P-retaining mineral components; this is especially true of the A and E horizons of Florida Alaquods (Harris et al., 1996). Lateral transport of P from sandy surface horizons to streams is enhanced by high water tables (Mansell et al., 1991). Spodic horizons tend to have a high initial SPSC compared to A and E horizons and

hence can serve as a significant P sink until they reach their PSR change point threshold. Thus, lowering the water table below the upper boundary of the spodic would tend to increase P retention in the soil by maximizing P contact with the spodic until SPSC becomes zero (Figure 3-9A). However, there could be little or no advantage of a lowered water table once the spodic reaches zero SPSC and negative SPSC would mean that the spodic would have potential to serve as a P source (Figure 3-9B). A management strategy that accounted for and utilized the positive SPSC of the spodic while not exceeding it would be environmentally optimal. Such a strategy would also require accounting for other factors such as diffusion rate, thickness of saturated zone above the spodic upper boundary, water flow dynamics, etc., as might be accommodated in a hydrologic model.

### **Summary**

Results confirm that Bh-horizons, dominated by organically-complexed metals, exhibit a discrete PSR change point threshold similar to that of other sandy coastal plain soil horizons. Soil P storage capacity can be calculated for Bh-horizons beyond which the continued loading of P would render the Bh a P source. This “soil capacity” assessment enables determination of the absolute amount of P that could be loaded prior to the Bh releasing P at an environmentally unacceptable level. This information is pertinent to water management in that maintaining a water table significantly above the Bh upper boundary would short circuit its potential for reducing off-site movement of agriculturally-applied P in cases where the Bh has significant P storage capacity.

Table 3-1. Mean and SD by site (D = dairy; B = beef) and horizon for selected chemical properties of soils studied.

Site	Horizon	Statistics	pH	WSP <sup>†</sup>	TP <sup>†</sup>	M1-P <sup>†</sup>	M1-Al <sup>†</sup>	M1-Fe <sup>†</sup>	M1-Ca <sup>†</sup>	M1-Mg <sup>†</sup>	M3-P <sup>†</sup>	M3-Al <sup>†</sup>	M3-Fe <sup>†</sup>
				-----mg kg <sup>-1</sup> -----									
D1	A	Mean	5.7	62	185	80	41	10	531	151	116	90	77
		SD	1.8	106	223	127	24	5	596	176	130	48	30
	E	Mean	5.8	8	27	10	9	4	62	18	11	34	16
		SD	1.6	15	28	17	7	2	77	22	21	13	10
	Bh/Bh1	Mean	5.5	6	186	35	566	6	198	35	69	1915	27
		SD	1.1	10	160	33	404	3	169	40	60	90	3
Lower Bh <sup>#</sup>	Mean	5.6	5	59	17	275	7	36	12	43	1220	32	
	SD	1.0	11	52	40	1740	3	52	25	69	309	8	
D2	A	Mean	6.9	7	69	33	44	18	522	81	43	74	80
		SD	1.4	10	42	35	6	6	211	104	36	10	16
	E	Mean	7.1	1	15	4	11	6	81	6	5	13	20
		SD	2.1	2	5	10	6	1.3	31	7	4	17	2
	Bh/Bh1	Mean	6.0	1	73	3	578	11	346	10	11	1886	33
		SD	0.5	1	12	1	244	7	191	4	1	206	21
Lower Bh	Mean	6.0	0	56	2	379	15	44	3	10	1314	56	
	SD	1.3	0	34	1	224	4	24	1	5.4	325	38	
D3	A	Mean	7.3	40	1610	558	40	11	3275	387	1233	90	134
		SD	0.5	13	202	967	31	9	2844	337	166	29	9
	E	Mean	8.0	11	94	42	10	2	202	37	70	12	8
		SD	0.3	3	56	32	4	1	130	19	45	6	8
	Bh/Bh1	Mean	7.6	27	499	271	448	2	787	347	387	646	9
		SD	1.0	5	93	78	130	1	211	42	57	272	10
Lower Bh	Mean	7.3	4	65	8	581	12	121	176	30	1169	25	
	SD	0.5	1	30	10	107	10	65	94	16	254	14	

Table 3-1. Continued

Site	Horizon	Statistics	pH	WSP <sup>†</sup>	TP <sup>†</sup>	M1-P <sup>†</sup>	M1-Al <sup>†</sup>	M1-Fe <sup>†</sup>	M1-Ca <sup>†</sup>	M1-Mg <sup>†</sup>	M3-P <sup>†</sup>	M3-Al <sup>†</sup>	M3-Fe <sup>†</sup>
				-----mg kg <sup>-1</sup> -----									
B1	A	Mean	4.9	15	94	24	78	14	732	104	29	103	126
		SD	0.3	10	130	19	38	9	323	64	20	91	34
	E	Mean	4.7	4	54	16	137	10	290	57	20	271	65
		SD	0.4	4	42	13	107	7	189	38	14	227	34
	Bh/Bh1	Mean	4.4	0	82	9	663	7	111	31	11	1017	25
		SD	0.3	0	66	14	476	5	64	14	15	588	19
Lower Bh	Mean	4.4	0	43	2	530	4	42	17	5	930	7	
	SD	0.3	0	33	2	282	2	28	7	4	380	8	
B2	A	Mean	5.5	20	198	97	75	16	704	85	106	109	130
		SD	0.8	17	374	123	32	11	542	87	143	79	77
	E	Mean	6.0	5	49	16	24	7	144	19	17	36	34
		SD	0.8	6	30	22	26	5	117	19	23	53	32
	Bh/Bh1	Mean	5.7	6	153	59	907	31	263	32	62	1116	126
		SD	0.7	9	78	77	545	41	262	39	70	534	103
Lower Bh	Mean	5.6	1	83	18	836	27	137	24	24	1140	83	
	SD	0.7	3	51	31	524	38	139	34	34	570	91	
B3	A	Mean	5.8	17	72	27	37	19	556	124	31	69	119
		SD	0.4	11	65	15	12	15	122	63	11	16	51
	E	Mean	6.2	1	4	1	10	4	50	6	2	14	9
		SD	0.4	2	5	3	8	2	53	8	3	14	6
	Bh/Bh1	Mean	5.1	5	88	46	672	19	136	26	56	802	110
		SD	0.4	4	22	33	643	20	53	12	34	580	119
Lower Bh	Mean	5.3	1	31	15	500	9	63	17	19	619	37	
	SD	0.2	1	26	14	535	4	20	11	13	439	21	

<sup>†</sup>WSP, water-soluble phosphorus; TP, total phosphorus; M1-P, Al, Fe, Ca and Mg, Mehlich 1-extractable phosphorus, aluminum, iron, calcium and magnesium, respectively; M3-P, Al and Fe, Mehlich 3-extractable phosphorus, aluminum and iron, respectively. <sup>#</sup>Horizons include Bh2 and other subjacent horizons to a depth of 1-m.

Table 3-2. Mean and SD by site (D = dairy; B = beef) and horizon for oxalate-extractable P and metals, data used in PSR and SPSC calculations for the soils studied.

Site	Horizon	Statistics	Ox-P <sup>†</sup>	Ox-Al <sup>†</sup>	Ox-Fe <sup>†</sup>	Ox Fe + Al	PSR <sub>ox</sub> <sup>††</sup>	SPSC <sup>††</sup>	SPSC <sub>total</sub> <sup>†††</sup>
			-----mg kg <sup>-1</sup> -----			Moles		-----kg ha <sup>-1</sup> -----	
D1	A	Mean	146 a <sup>‡</sup>	92 c	89 a	5 c	0.83 a	-297 b	
		SD	192	39	45	2	1.20	511	
	E	Mean	19 a	61 c	24 b	2 c	0.14 b	-42 ab	
		SD	34	32	34	1	0.21	84	
	Bh/Bh1	Mean	184 a	3568 a	66 ab	133 a	0.04 b	28 ab	
		SD	114	1048	20	39	0.02	200	
	Lower Bh <sup>#</sup>	Mean	49 a	1481 b	72 ab	56 b	0.02 b	286 a	
		SD	60	678	32	34	0.03	210	
D2	A	Mean	54 a	85 b	135 b	6 b	0.31 a	-61 b	-25
		SD	45	6	9	1	0.30	76	
	E	Mean	6 b	15 b	33 c	1 b	0.17 ab	-8 b	
		SD	4	18	31	1	0.13	14	
	Bh/Bh1	Mean	70 a	3985 a	245 a	152 a	0.01 b	350 ab	
		SD	12	905	260	38	0.01	9	
	Lower Bh	Mean	38 ab	3317 a	272 a	128 a	0.01 b	1053 a	
		SD	17	2631	166	100	0.02	1209	
D3	A	Mean	1300 a	248 bc	394 a	16 bc	2.50a <sup>††††</sup>	-6206 c	1334
		SD	424	134	19	5	0.50	4255	
	E	Mean	77 c	13 c	9 c	1 c	3.90 a	-234 b	
		SD	25	3	1	1	2.00	43	
	Bh/Bh1	Mean	488 b	1112 b	17 c	41 b	0.50 b	-974 b	
		SD	92	603	11	22	0.40	173	
	Lower Bh	Mean	56 c	2059 a	40 b	76 a	0.02 b	156 a	
		SD	35	609	15	23	0.01	93	
B1	A	Mean	66 a	255 b	245 a	14 b	0.15 a	-34 b	-7258
		SD	37	66	96	3	0.07	41	
	E	Mean	42 ab	329 b	84 b	14 b	0.10 b	9 ab	
		SD	29	210	45	7	0.08	93	
	Bh/Bh1	Mean	57 ab	1417 a	32 c	53 a	0.03 c	19 ab	
		SD	43	996	25	37	0.02	17	
	Lower Bh	Mean	28 b	1013 a	9 c	38 a	0.02 c	47 a	
		SD	24	531	12	20	0.01	44	

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Table 3-2. Continued

Site	Horizon	Statistics	Ox-P <sup>†</sup>	Ox-Al <sup>†</sup>	Ox-Fe <sup>†</sup>	Ox Fe + Al	PSR <sub>ox</sub> <sup>††</sup>	SPSC <sup>††</sup>	SPSC <sub>total</sub> <sup>†††</sup>
			-----mg kg <sup>-1</sup> -----			Moles		-----kg ha <sup>-1</sup> -----	
B2	A	Mean	155 a	212 b	223 a	12 b	0.39 a	-270 b	
		SD	136	79	137	5	0.27	304	
	E	Mean	41 b	68 b	38 b	3 b	0.52 a	-69 a	
		SD	26	56	37	3	0.26	48	
	Bh/Bh1	Mean	147 a	1935 a	256 a	76 a	0.12 b	-35 a	
		SD	79	1435	273	54	0.12	193	
	Lower Bh	Mean	76 b	1821 a	189 ab	71 a	0.07 b	85 a	
		SD	42	1435	272	54	0.11	279	
								-289	
B3	A	Mean	63 ab	118 b	167 a	7 b	0.24 a	-101 b	
		SD	68	33	122	3	0.20	151	
	E	Mean	2 c	53 b	2 c	2 b	0.03 b	15 a	
		SD	2	17	4	1	0.05	8	
	Bh/Bh1	Mean	80 a	1006 a	121 ab	39 a	0.09 b	-12 a	
		SD	27	902	146	32	0.06	43	
	Lower Bh	Mean	28 b	746 ab	36 b	28 ab	0.03 b	33 a	
		SD	22	707	30	26	0.03	42	-65

<sup>‡</sup>Mean values of soil characteristics within a column followed by the same letter are not significantly different ( $p < 0.05$ ), using the least significant difference procedure. <sup>†</sup>Ox-P, Al and Fe, oxalate-extractable phosphorus, aluminum and iron, respectively. <sup>††</sup>PSR<sub>ox</sub>, P saturation ratio using oxalate extract calculated as molar ratio of P to [Fe + Al]; SPSC, soil phosphorus storage capacity. SPSC for A-E and Bh horizons calculated using oxalate extraction according to equation (3-1) with change point PSR of 0.1 and 0.05 respectively. <sup>†††</sup>Total SPSC for A, E, Bh and Lower Bh horizon where the soil profile is of 1-m depth. <sup>††††</sup>High PSR value indicates that these soils have very low P retention capacity due to excess P loading or lack of metal oxides in the surface horizons. <sup>#</sup>Horizons include Bh2 and other subjacent horizons to a depth of 1-m.

Table 3-3. Estimated model parameters and statistics (with standard errors in parentheses).

Model	Fitted equations	Model R <sup>2</sup>
Oxalate	WSP = 0.089 <sub>(2.04)</sub> + 10.44 <sub>(86.85)</sub> PSR; PSR ≤ 0.05 <sub>(0.029)</sub> WSP = -4.23 <sub>(1.51)</sub> + 104.2 <sub>(4.33)</sub> PSR; PSR > 0.05 <sub>(0.029)</sub>	0.82***
Mehlich 1	WSP = -0.066 <sub>(0.877)</sub> + 24.21 <sub>(42.62)</sub> PSR; PSR ≤ 0.08 <sub>(0.054)</sub> WSP = -4.61 <sub>(1.55)</sub> + 83.82 <sub>(3.01)</sub> PSR; PSR > 0.08 <sub>(0.054)</sub>	0.88***
Mehlich 3	WSP = -0.329 <sub>(0.679)</sub> + 63.20 <sub>(24.90)</sub> PSR; PSR ≤ 0.09 <sub>(0.069)</sub> WSP = -3.41 <sub>(1.43)</sub> + 96.50 <sub>(2.86)</sub> PSR; PSR > 0.09 <sub>(0.069)</sub>	0.93***

\*\*\*Significant at the 0.001 probability level.

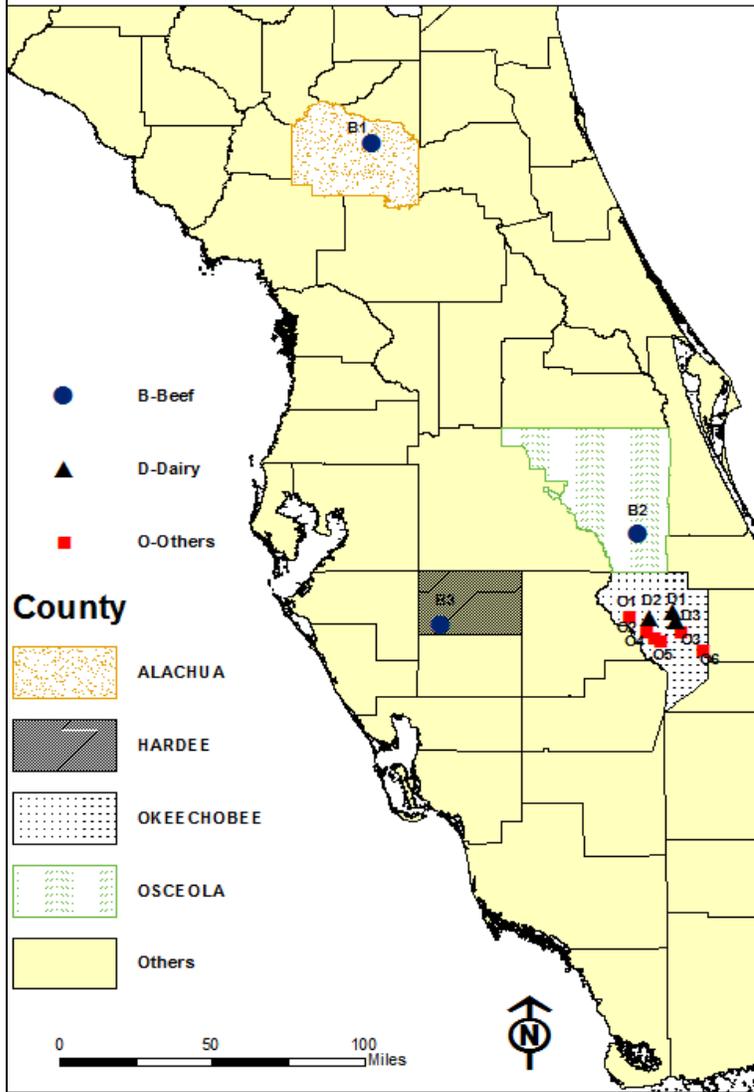


Figure 3-1. Location of the study sites.

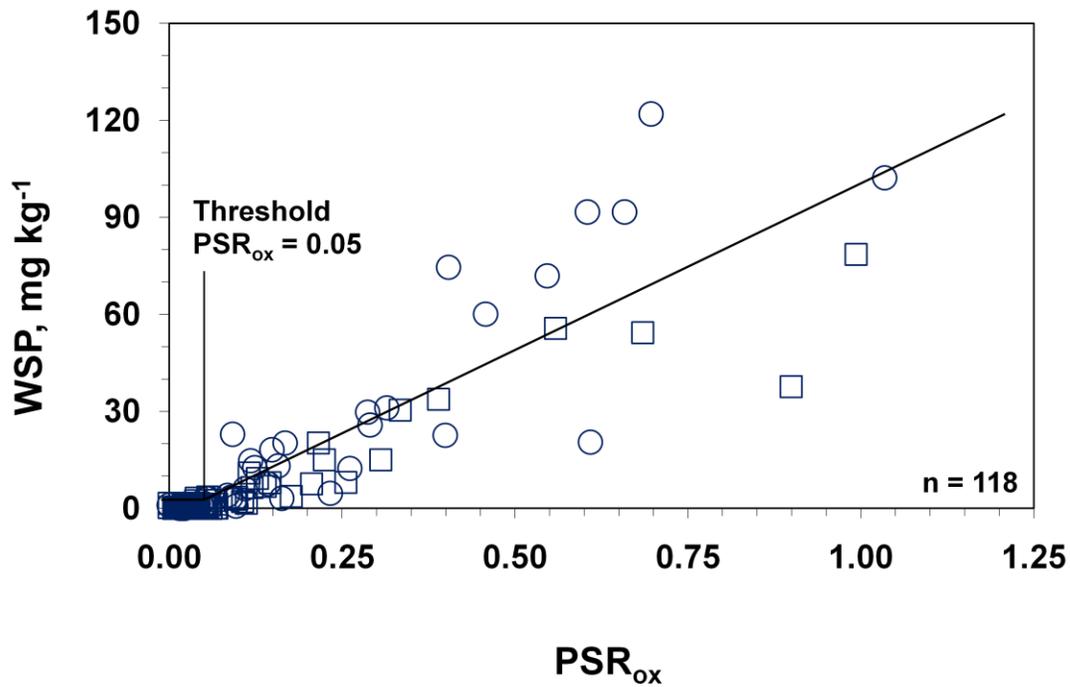


Figure 3-2. Relationship between water-soluble P (WSP) and P saturation ratio (PSR) calculated for the spodic horizon using P, Fe and Al in an oxalate extract (PSR<sub>ox</sub>). Threshold PSR<sub>ox</sub> value (0.05) is significant at the 0.001 probability level. Open squares are soils in the current study; open circles represent data from archived soils.

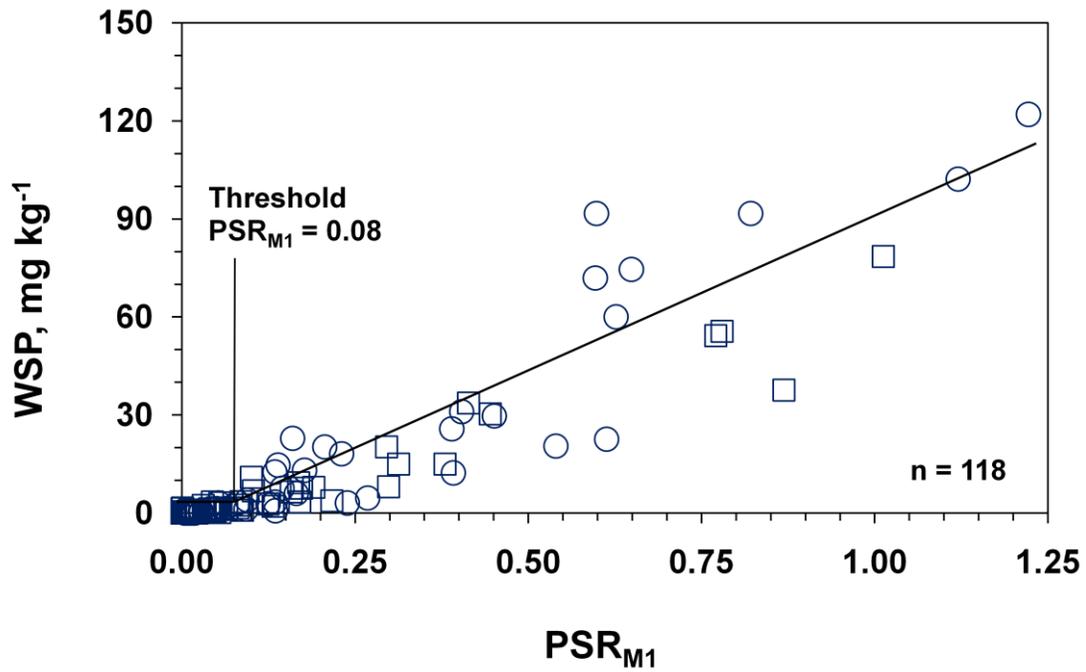


Figure 3-3. Relationship between water-soluble P (WSP) and P saturation ratio (PSR) calculated for the spodic horizon using P, Fe and Al in Mehlich 1 extract (PSR<sub>M1</sub>). Threshold PSR<sub>M1</sub> value (0.08) is significant at the 0.001 probability level. Open squares are soils in the current study; open circles represent data from archived soils.

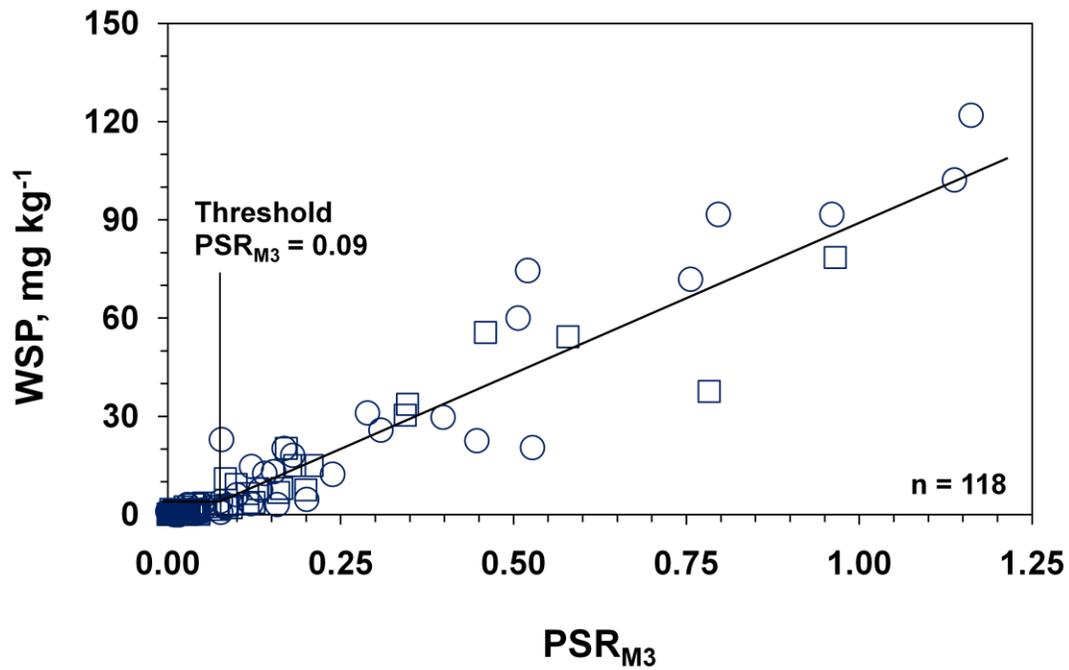


Figure 3-4. Relationship between water-soluble P (WSP) and P saturation ratio (PSR) calculated for the spodic horizon using P, Fe and Al in Mehlich 3 extract (PSR<sub>M3</sub>). Threshold PSR<sub>M3</sub> value (0.09) is significant at the 0.001 probability level. Open squares are soils in the current study; open circles represent data from archived soils.

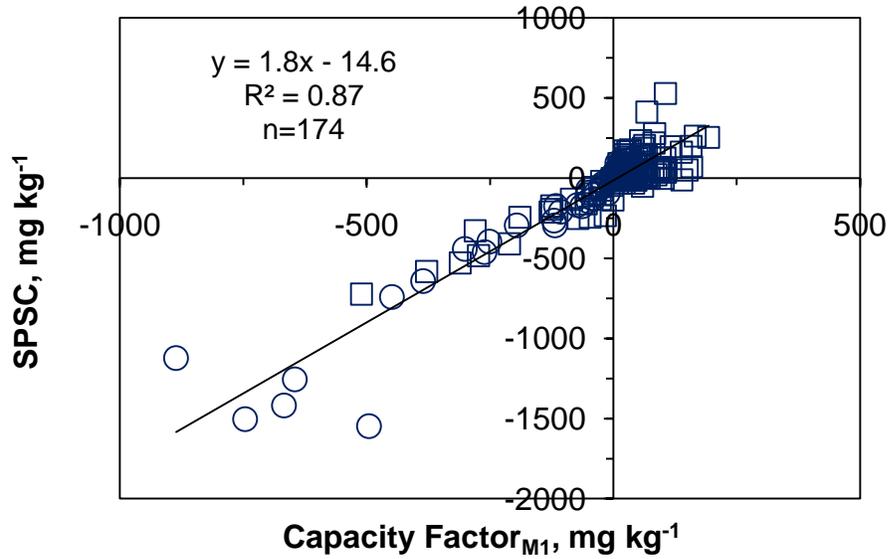


Figure 3-5. Relationship between soil phosphorus storage capacity (SPSC) and Capacity Factor for spodic horizons calculated using Mehlich 1-extractable P, Al and Fe. Open squares are soils in the current study; open circles represent data from archived soils.

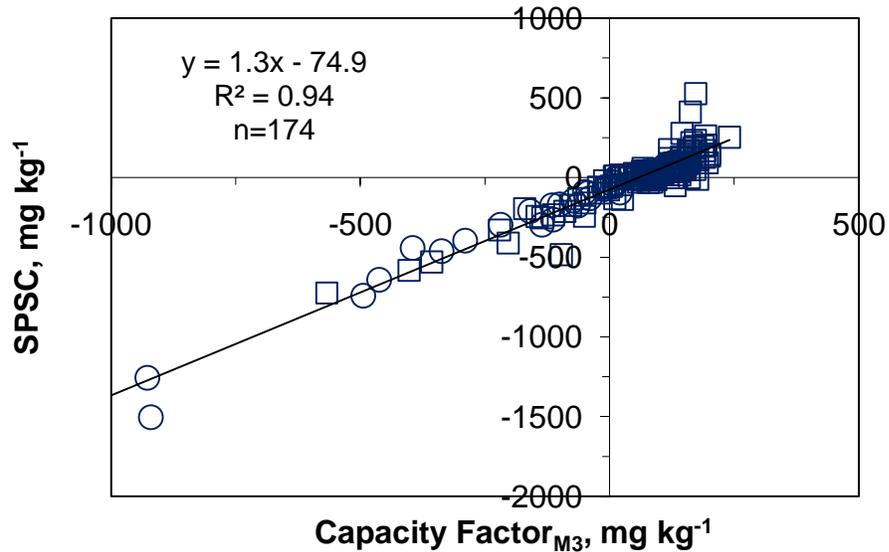


Figure 3-6. Relationship between soil phosphorus storage capacity (SPSC) and Capacity Factor for spodic horizons calculated using Mehlich 3-extractable P, Fe and Al. Open squares are soils in the current study; open circles represent data from archived soils.

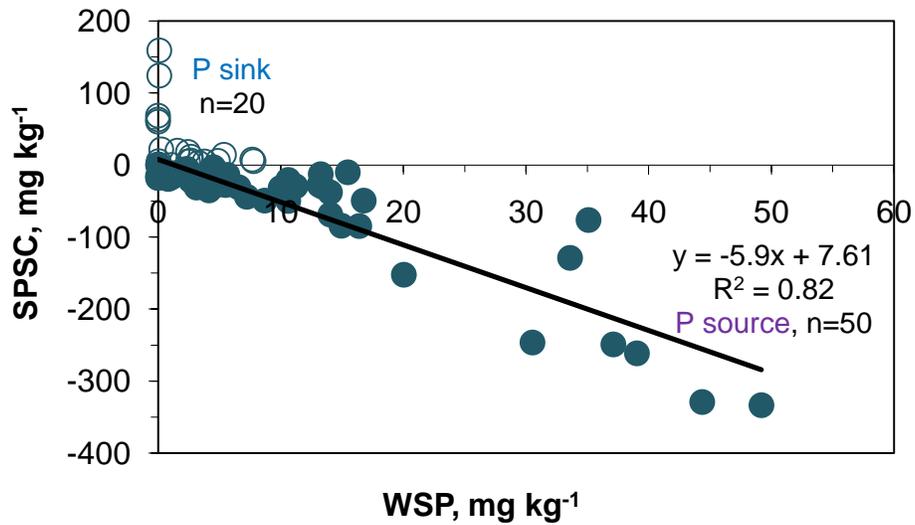


Figure 3-7. Soil phosphorus storage capacity (SPSC) vs. water-soluble P (WSP) of A and E horizons (using 0.10 as the change point P saturation ratio) of manure-impacted soils. Open and closed markers represent positive and negative SPSC respectively. The  $R^2$  value is for soils having negative SPSC.

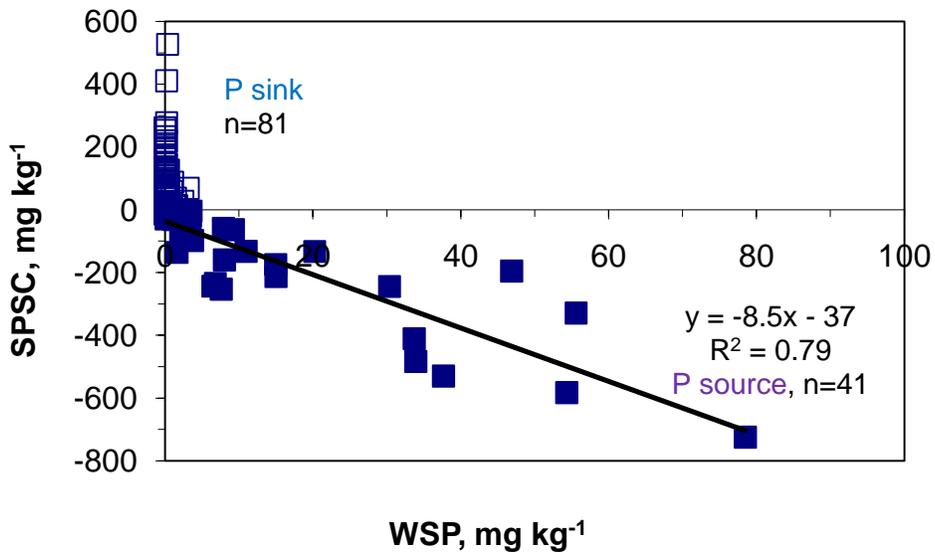


Figure 3-8. Soil phosphorus storage capacity (SPSC) vs. water-soluble P (WSP) of spodic horizons (using 0.05 as the change point P saturation ratio, Fig. 3.2). Open and closed markers represent positive and negative SPSC respectively. The  $R^2$  value is for soils having negative SPSC.

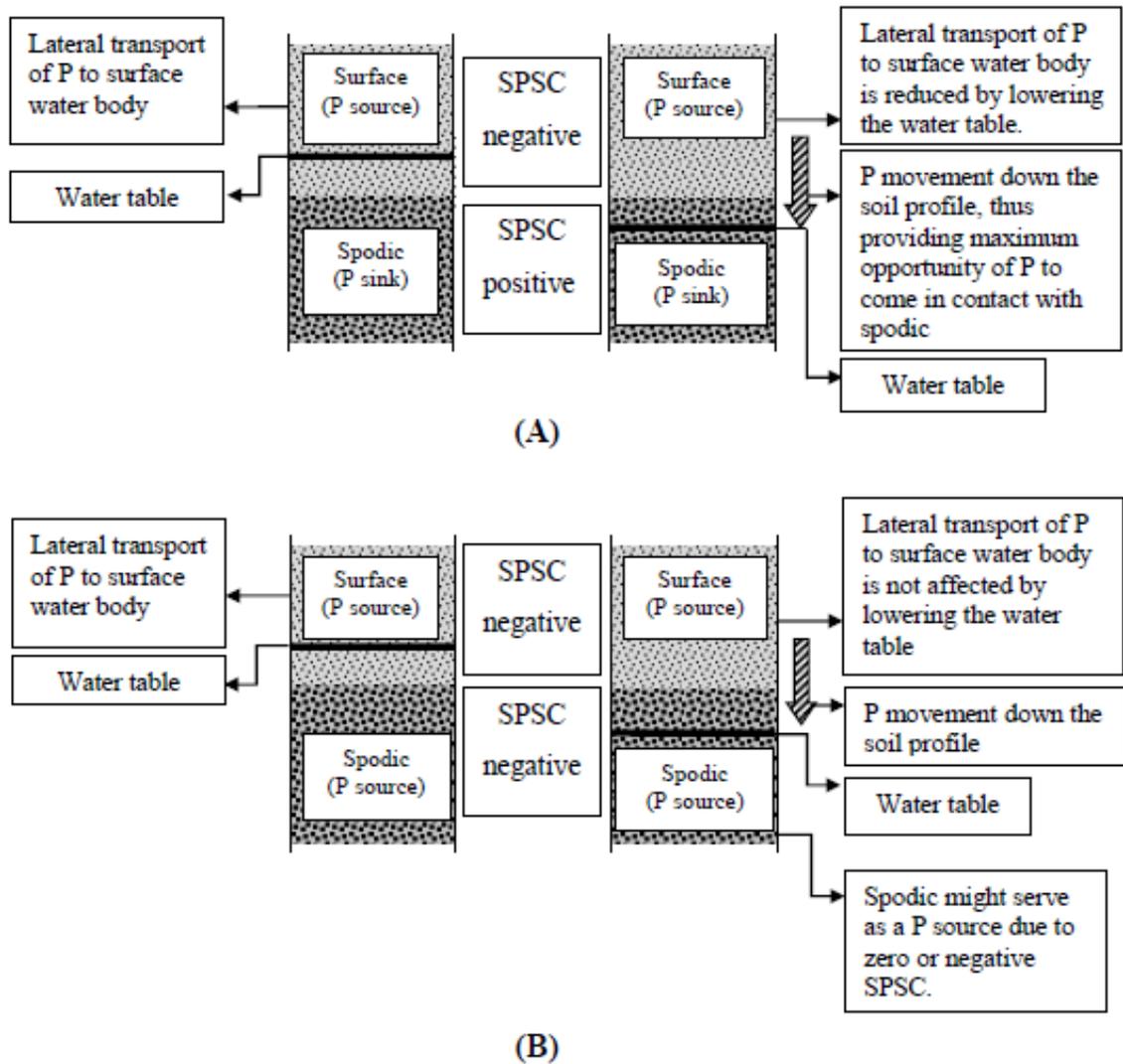


Figure 3-9. Schematic diagram of a soil profile illustrating the movement of P to surface and subsurface water bodies and the effect of water table manipulations when A) spodic is a P sink (SPSC > 0); B) spodic is a P source (SPSC < 0).

## CHAPTER 4

### COMPOSITIONAL DIFFERENCES BETWEEN ALAQUODS AND PALEUDULTS AFFECTING PHOSPHORUS SORPTION-DESORPTION BEHAVIOR

Alaquods and Paleudults with sandy A and E horizons occur extensively in the coastal plain of the SE United States. Compositional differences between Alaquod- E and Bh, and Paleudult- E and Bt horizons are factors affecting subsurface P transport in these soils. The risk of P loss from Alaquod and Paleudult subsurface horizons is related to the P retention characteristics of the horizons. Knowledge of the P retention characteristics between Alaquod and Paleudult subsurface horizons is still limited. Zhou et al. (1997) compared P sorption-desorption characteristics of Bh and Bt horizons using selective chelation to determine the effect of organo-metallic materials in Bh samples. This present study expands upon their work with a profile perspective considering paired subsurface E-Bh and E-Bt horizons of Alaquods and Paleudults, respectively.

The objective of this chapter was to relate P sorption characteristics to compositional differences in Alaquod and Paleudult subsurface horizons and to evaluate implications for risk of P loss via subsurface flow in these soils. The specific objectives were to:

- evaluate the differences in metal complexation (organic vs. inorganic) and crystallinity that are related to P retention of Alaquod- E and Bh, and Paleudult -E and Bt horizons using oxalate, pyrophosphate and CBD extractions and x-ray diffraction techniques;
- compare P sorption and release properties of Bh and Bt horizons and relate them to the equilibrium P concentrations and compositional differences;
- interpret implications for subsurface movement of P from Alaquod and Paleudult profiles due to excess P application.

## Materials and Methods

Alaquod profiles from three sites (S1, S2 and S3) and Paleudult profiles from three different sites (S4, S5 and S6) located within Florida (Figure 4-1) were sampled by horizon. Horizons greater than 25 cm thick were subdivided for sampling purposes. Surface horizons were not considered in this study since they constitute a relatively thin part of the soil profile and have minimal contribution for P loss from the soil profile. This study focused on subsurface horizons of Alaquod (E and Bh) and Paleudult (E and Bt) soil profiles. A total of 81 samples for Alaquod (E: 33 and Bh: 48) and 99 (E: 35 and Bt: 64) for Paleudult were analyzed for this study.

### Chemical Analyses

Samples were thoroughly mixed, air-dried and passed through a 2 mm sieve before analyses. Soil pH was determined using 1:2 soil to water suspension. Oxalate-extractable Fe (Ox-Fe) and Al (Ox-Al) for soils were determined using 0.1 *M* oxalic acid + 0.175 *M* ammonium oxalate solution, equilibrated at a pH of 3.0 (McKeague and Day, 1966). Citrate-bicarbonate-dithionite (CBD)-extractable Fe (CBD-Fe) and Al (CBD-Al) were determined following the procedure of Mehra and Jackson (1960). Pyrophosphate-extractable Fe (Pyro-Fe) and Al (Pyro-Al) for soils were determined using 0.1 *M* Na-pyrophosphate (McKeague, 1967). Iron and Al concentrations in oxalate, CBD and pyrophosphate extractions were determined using inductively coupled argon plasma spectroscopy (Thermo Jarrel Ash ICAP 61E, Thermo Elemental, Franklin, MA). Total carbon of the air-dried samples was determined by an automated combustion procedure using a CNS Analyzer (Carlo Erba, Milan, Italy).

## **Mineralogical Analysis**

Samples were saturated with Na to promote dispersion, washed free of salt, and sieved to remove material > 50 $\mu\text{m}$  in size. Clay (< 2 $\mu\text{m}$ ) was separated from silt by centrifugation (Soukup et al., 2008). Clay mounts were prepared for x-ray diffraction (XRD) via the “0.45- $\mu\text{m}$  membrane filter mount” technique (Harris and White, 2008) by which Mg- and K-saturated clay suspensions were collected on a filter under suction and transferred to glass slides. The Mg-saturated clay was solvated with glycerol prior to the XRD scan. Samples were scanned at  $2^\circ 2\theta$  with Cu K $\alpha$  radiation on a computer-controlled x-ray diffractometer equipped with stepping motor and graphite crystal monochromator.

## **Phosphorus Sorption**

Thirty-three Bh samples and 45 Bt samples were selected from the soils collected to give a wide range of Fe and Al contents for intensive P sorption characterization. Phosphorus sorption isotherms were determined using 2.0 g air-dried soil in a 50 mL equilibration tube to which 20 mL of 0.01 M KCl solutions containing 0, 0.1, 1, 5, 10, 25, 50 and 100 mg P L $^{-1}$  as KH $_2$ PO $_4$  were added (Nair et al., 1998). The equilibration was carried out in a reciprocating shaker at about 100 excursions min $^{-1}$  for 24 h at  $25 \pm 1^\circ\text{C}$ . The soil suspension was centrifuged and the supernatant was filtered through a 0.45  $\mu\text{m}$  membrane filter. Phosphorus in the solution was determined by the method of Murphy and Riley (1962). A single-point P sorption isotherm was also conducted accompanying the batch equilibrium sorption experiment with all the soil samples. Two gram of soil was equilibrated with 20 mL of KCl solution at saturated P conditions (1000 mg P kg $^{-1}$ ) for 24 h at  $25 \pm 1^\circ\text{C}$ . The soil suspension was similarly centrifuged, filtered and analyzed for soluble reactive P. The amount of P sorbed by the soils was calculated

from the difference between the P concentration in the equilibrium solution and the initial P added to the soil.

### Phosphorus Desorption

The amount of P sorbed by the soil after 24 h equilibrium represented the starting value for adsorbed P. After removing the supernatants, each tube containing a wet soil sample was weighed to estimate the volume of the residual solution and the P entrapped in it. These P saturated soils were then subjected to desorption with 20 mL of 0.01M KCl (that contained no P) equilibrated in a reciprocating shaker for 24 h (Dunne et al., 2006). Phosphorus in the extracts was analyzed as mentioned above.

### Calculations

Adsorption parameters were calculated using the Langmuir adsorption equation:

$$\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}} \quad (4-1)$$

where,

$S = S' + S_0$ , the total amount of P sorbed,  $\text{mg kg}^{-1}$

$S' =$  P sorbed by the solid phase,  $\text{mg kg}^{-1}$

$S_0 =$  originally sorbed P on the solid phase,  $\text{mg kg}^{-1}$

$C =$  concentration of P after 24 h equilibration,  $\text{mg L}^{-1}$

$S_{max} =$  P sorption maximum,  $\text{mg kg}^{-1}$

$k =$  a constant related to the bonding energy,  $\text{L mg}^{-1} \text{P}$ .

Initially sorbed P ( $S_0$ ) was estimated using the least square fit method which is based on the linear relationship between  $S'$  and  $C$  at low equilibrium P concentrations.

The relationship can be described by

$$S' = K'C - S_0 \quad (4-2)$$

where  $K'$  = the linear adsorption coefficient, and all other parameters are as defined earlier (Graetz and Nair, 1995). The “equilibrium P concentration” ( $EPC_0$ ) represents the concentration of P in solution where adsorption equals desorption and was the value of  $C$  when  $S' = 0$  (Nair et al., 1998). Maximum buffering capacity (MBC) of soils is the index of soil resistance to the change of P concentration in soil solution with the addition or removal of P (Sui and Thompson, 2000). From the sorption parameters  $S_{max}$  and  $k$ , MBC of soils were determined as  $MBC = S_{max}k$  (Holford, 1979). The value of MBC is the slope of the isotherm as  $C \rightarrow 0$  and dictates the steepness of isotherm at low concentrations (Zhang et al., 2009).

### **Statistical Analyses**

Empirical relationships between P sorption parameters and soil properties were assessed using correlation and regression analyses in Excel 2007. The data was analyzed using the General Linear Model procedure in the statistical package SAS (SAS Institute, 2001). Differences between means of soil parameters for soil groups were compared using Fishers LSD.

## **Results and Discussion**

### **Soil Characterization**

Soil pH values ranged from 4.4 to 6.5. Noncrystalline Al content was much higher in Bh than in other horizons as inferred from oxalate extraction (Table 4-1; Figure 4-2). Among all the horizons studied, E horizons of Alaquods had lowest Al concentration. The E and Bt horizons of Paleudults were intermediate in Al content, with Bt being significantly higher in Al than the E. The E horizons of Paleudults have significantly greater Fe- and Al- oxide content than Alaquod E horizons. For Paleudults, CBD-Fe was highly correlated to CBD-Al for E ( $R^2 = 0.698$ ,  $p < 0.001$ ) and Bt ( $R^2 = 0.719$ ,  $p < 0.001$ )

horizons. These results suggest that the source of CBD-Al in E and Bt horizons of Paleudults is mainly the Al which is substituted for Fe in the Fe oxides. Values for CBD-Al were generally lower than Ox-Al, but trends among horizons were essentially identical. For Paleudults, CBD-Fe is significantly higher than Ox-Fe ( $p < 0.0001$ ). The ratio of mean Ox-Fe and CBD-Fe for E and Bt horizons of Paleudults are 0.49 and 0.07 respectively. These ratios suggest the dominance of crystalline Fe oxides in Bt horizons.

Pyrophosphate has been shown to be most effective in extracting organically bound Al and Fe (McKeague et al., 1971), though it can extract some noncrystalline inorganically-complexed forms of these metals as well (Kaiser and Zech, 1996). Oxalate and pyrophosphate extractable Fe and Al, show a 1:1 relationship for Bh horizons where Fe and Al is predominantly complexed with organic matter (Figure 4-3). For Bt horizons, oxalate is more efficient as an extractant than pyrophosphate, which is consistent with low C content (Table 4-1) and predominance of inorganic Fe and Al oxides.

Carbon content is strongly related to oxalate-extractable Al for Bh horizons, but not for other horizons (Figure 4-4). No significant relation was obtained between C content and extractable Fe for any of the horizons. For Bh samples the metal/C ratios were  $<0.10$ , consistent with the conclusion of Higashi et al. (1981) that soil organic matter can bind Fe and Al at metal/C ratio up to 0.12.

### **Phosphorus Sorption and Desorption**

Phosphorus sorption capacity ( $P_{\text{sorp}}$ ) determined from single-point isotherms (1000 mg P kg<sup>-1</sup>) show that none of the E horizons of Alaquods has measurable P retentive capacity (Table 4-2). Harris et al. (1996) suggested that lack of aluminosilicate and

metal oxide clay in the albic E horizons which is mainly dominated by clean quartz grains accounts for its low P retention capacity. However, the E horizons of Paleudults sorb considerable amount of P which is consistent with the finding of Rhue et al. (2006). These horizons are expected to retain more P due to presence of sand-grain coatings (Harris et al., 1996). These coatings typically contain minerals (kaolinite, HIV, gibbsite, Fe oxyhydroxides, etc) with much greater surface area and P retention capacity than quartz sand (Harris et al., 1989). Quartz dominated the clay fraction of E horizons of Alaquods whereas E horizons of Paleudults have quartz and kaolinite in the clay fraction (Figures 4-5 and 4-6). Bh and Bt horizons have high P retention capacity as indicated by  $P_{\text{sorp}}$  (Table 4-2). The  $P_{\text{sorp}}$  values ranged from 137 to 846 mg kg<sup>-1</sup> for Bh horizons and from 119 to 897 mg kg<sup>-1</sup> for Bt horizons. These P sorption trends are consistent with those reported by Harris et al. (1996) and Zhou et al. (1997).

For Bh and Bt samples, P sorption behavior was further described by the Langmuir isotherm (Table 4-3). Mean values of Langmuir sorption maxima ( $S_{\text{max}}$ ) for the Bh and Bt horizons are 353 and 514 mg kg<sup>-1</sup> respectively. The clay fractions of Florida Alaquod Bh horizons are typically dominated by quartz, HIV and kaolinite (Harris and Carlisle, 1987), as was the case for the Bh of the representative Alaquod of this study (Figure 4-5). Particle size distribution was not determined for Bh horizons of this study but they were sands by field textural assessment. The clay fractions of Florida Paleudult Bt horizons are typically dominated by kaolinite (Harris et al., 1989), as was the case for the Bt of the representative Paleudult of this study (Figure 4-6). Phosphorus sorption capacity ( $P_{\text{sorp}}$ ) follows a 1:1 relationship with the  $S_{\text{max}}$  values for Bh ( $R^2= 0.978$ ,  $p<0.001$ ) and Bt ( $R^2=0.982$ ,  $p<0.001$ ) horizons. Total C content was related to  $S_{\text{max}}$

( $R^2=0.62$ ) for Bh but not for Bt ( $R^2=0.12$ ) samples. The equilibrium P concentration ( $EPC_0$ ) of Bh samples were higher than the Bt samples. Low  $EPC_0$  values for most of the Bt horizon in this study suggest that these horizons have not yet been significantly impacted by P enrichment and can act as sinks for P moving from overlying horizons.

The mean values of the initially sorbed P,  $S_0$ , for Bh and Bt horizons were 3.4 and 0.24 mg kg<sup>-1</sup> respectively. Langmuir constant  $k$ , was low for Bh samples in comparison to Bt (Table 4-3). Maximum buffering capacity (MBC) was high for high P sorbing samples. The soil's MBC values are environmentally significant since soils with larger MBC will have a greater tendency to maintain the original aqueous P concentration during the inflow of higher P concentrations (Zhang et al., 2009).

The proportion of P desorbed from Bh horizons were greater in comparison to Bt horizons (Table 4-3; Figure 4-7) corroborating results of Zhou et al. (1997). P desorbed expressed as a fraction of sorbed P (DEF) ranges from 2 to 57 % with a mean of 19 % for Bh horizons whereas for Bt horizons it ranges from 1 to 10 % with a mean of 5 %. Disparity in desorption is likely attributable to a) greater amounts of Fe oxides and other clay-sized minerals in Bt compared to Bh, as documented by Florida soil characterization data (<http://flsoils.ifas.ufl.edu/>); b) organic- vs. inorganic metal complexation in Bh vs. Bt as indicated by strong Al-C relation for Bh (Figure 4-4); c) weaker bonding of P with organically-complexed Al in Bh horizons as indicated by low Langmuir  $k$ . Only Bh samples with the highest oxalate-extractable Al showed high resistance to P desorption (Figure 4-8).

### **Correlation of Phosphorus Sorption Parameters with Soil Properties**

The P sorption maxima obtained from the Langmuir equation,  $S_{max}$ , correlated well with all forms of Al for Bh (Table 4-4) and Bt (Table 4-5) horizons. The positive

correlations of  $S_{\max}$  with all forms of Al (Ox-Al, CBD-Al and Pyro-Al) (Table 4-4) but not with Fe in Bh confirms the importance of Al for P retention in these horizons. For Bt horizons,  $S_{\max}$  was significantly correlated with CBD-Fe ( $r=0.474$ ,  $p<0.01$ ) but not with any other forms of Fe (Ox-Fe or Pyro-Fe) (Table 4-5). Clay content and  $S_{\max}$  were related for Bt samples ( $R^2= 0.70$ ). This implies that, for Bt samples inorganic metal oxides along with phyllosilicates, predominantly kaolinite contribute to P sorption. Langmuir sorption maxima  $S_{\max}$  negatively correlated with pH for both Bh and Bt horizons. This may be due to the fact that with increasing pH, mineral surfaces become increasingly negative resulting in greater electrostatic repulsion and decrease in P sorption (Haynes, 1982; Oh et al., 1999; Sato and Comerford, 2005). Total C correlated significantly with the Langmuir sorption parameters for Bh but not for Bt samples. Positive relationship between C content of spodic horizons and P sorption had also been observed by Nair et al. (1998). This relationship was due to the indirect effect of C through complex formation with cations such as Fe and Al associated with organic matter.

Phosphorus bonding constant ( $k$ ) and MBC were positively correlated with all forms of Al and Fe for Bh horizons and with all forms of Al, along with CBD-Fe for Bt horizons. Strong relationship between  $k$  and MBC was obtained for Bh ( $R^2= 0.87$ ) and Bt ( $R^2=0.94$ ) samples. A negative correlation of  $k$  with  $S_0$  for Bh horizons ( $r=-0.663$ ,  $p<0.001$ ) is consistent with the theory that the more saturated the sorption complex is, the lower the energy of subsequent sorption (Villapando and Graetz, 2001). Positive correlation between  $EPC_0$  and  $S_0$  was obtained for both Bh and Bt horizons. Equilibrium

P concentration  $EPC_0$  was negatively correlated with all forms of Al for Bh horizons and with Ox-Al for Bt horizons.

P desorbed expressed as a fraction of sorbed P (DEF) was negatively correlated to all forms of Al for Bh. For Bt, DEF was not correlated with any form of Al (Table 4-5) but was negatively correlated with oxalate Fe; we expected negative correlation with DEF for both Fe and Al and have no explanation for these results. Positive correlation of DEF with  $S_0$  for Bh horizons ( $r=0.432$ ,  $p<0.05$ ) suggests increased desorbability of newly sorbed P by the soils in the presence of P originally sorbed on the solid phase (Villapando and Graetz, 2001).

### **Environmental Implications**

The environmental risk of P loss is related to the compositional difference of horizons within the soil profile. Since E horizons of Alaquods have negligible P retentive capacity, they do not significantly retard the movement of agricultural P to Bh horizons or to streams and ditches via shallow subsurface flow (Figure 4-9A) as was suggested by Nair et al. (1995). Thus Bh horizons may easily get saturated with P during dry seasons when water tables are below their upper boundaries. These P-enriched Bh horizons can subsequently release P at environmentally hazardous rates when water tables reach seasonally high levels, further fostering lateral P movement to surface water (Figure 4-9B). On the other hand, in Paleudult soil profiles, the E horizons can retain relatively large amounts of P, retarding its vertical transport to the Bt horizon (Figure 4-9C). Lateral subsurface P transport would also be retarded by the retentive E horizons of Paleudults, though shallow subsurface water flow is less of a factor with Paleudults relative to Alaquods due to better drainage of the former. Also, the risk of P release is less for Bt than Bh due to greater resistance to P desorption. These

pedological, compositional, and hydrologic distinctions between Paleudults and Alaquods result in there being a greater risk of P loss for the latter under comparable P loadings.

### **Summary**

Sandy Bh horizons have high P adsorption capacity due to the predominance of organically-complexed metals, mainly Al. However, Bh horizons are more susceptible to P loss from excess P loading because of a greater tendency to desorb P relative to Bt horizons. The greater desorption potential of Bh horizons likely relates to weaker bonding of P with organically-complexed Al as inferred from low Langmuir  $k$ . Phosphorus sorption in Bt horizons is influenced by noncrystalline inorganic metal oxides along with crystalline Fe and phyllosilicates, predominantly kaolinite. Difference in crystalline and noncrystalline inorganic component between Bh and Bt horizons contributes significantly for the difference in P sorption-desorption behavior of these horizons. Compositional differences between Alaquod- and Paleudult subsurface horizons, in conjunction with pedological and hydrologic distinctions between these Great Groups, result in greater environmental risk of P loss for Alaquods under equal P loadings.

Table 4-1. Mean and SD by site and horizon for chemical properties of soils studied.

Great Group	Site	Horizon	n	Statistics	pH	Total C %	Ox-Fe <sup>†</sup>	Ox-Al <sup>†</sup>	CBD-Fe <sup>†</sup>	CBD-Al <sup>†</sup>	Pyro-Fe <sup>†</sup>	Pyro-Al <sup>†</sup>
-----mg kg <sup>-1</sup> -----												
Alaquod	S1	E	12	mean	5.8a	0.27 b	29 a	64 a	24 a	40 a	----	----
				SD	(0.7)	(0.29)	(37)	(60)	(28)	(43)	----	----
		Bh	16	mean	5.5a	1.6 a	217 b	2575 b	226 b	1597 b	204	2382
				SD	(0.6)	(1.0)	(364)	(1650)	(341)	(959)	(302)	(1372)
	S2	E	8	mean	5.9a	0.06 b	3 a	48 a	2 a	28 a	----	----
				SD	(0.4)	(0.08)	(5)	(24)	(4)	(5)	----	----
		Bh	11	mean	4.9a	0.54 a	112 b	930 b	101 b	733 b	99	888
				SD	(0.3)	(0.42)	(93)	(770)	(89)	(71)	(56)	(773)
	S3	E	13	mean	5.6a	0.01 b	3 a	46 a	4 a	20 a	----	----
				SD	(0.1)	(0.01)	(8)	(7)	(7)	(8)	----	----
		Bh	21	mean	5.7a	1.1 a	67 b	1095 b	72 b	847 b	61	1117
				SD	(0.1)	(0.38)	(113)	(437)	(106)	(243)	(110)	(533)
Paleudult	S4	E	8	mean	5.7a	0.12 a	241 a	446 a	437 a	325 a	----	----
				SD	(0.3)	(0.01)	(89)	(113)	(473)	(134)	----	----
		Bt	30	mean	4.7a	0.09 b	270 a	948 b	3641 b	615 b	95	533
				SD	(0.5)	(0.04)	(99)	(250)	(2991)	(244)	(134)	(147)
	S5	E	17	mean	4.9a	0.09 a	232 a	305 a	516 a	232 a	----	----
				SD	(0.5)	(0.05)	(88)	(169)	(1553)	(161)	----	----
		Bt	21	mean	4.5a	0.05 b	291 a	828 b	6759 b	737 b	194	600
				SD	(0.4)	(0.03)	(123)	(471)	(4785)	(372)	(208)	(405)
	S6	E	10	mean	6.4a	0.08 a	105 a	120 a	354 a	83 a	----	----
				SD	(0.7)	(0.06)	(54)	(75)	(236)	(41)	----	----
		Bt	13	mean	5.9a	0.05 a	223 b	447 b	1306 b	276 b	102	246
				SD	(0.6)	(0.02)	(162)	(102)	(491)	(71)	(94)	(31)

<sup>†</sup>Ox- Fe and Al, oxalate-extractable iron and aluminum, respectively; CBD-Fe and Al, citrate bicarbonate dithionite-extractable iron and aluminum respectively; Pyro-Fe and Al, pyrophosphate-extractable iron and aluminum respectively. Mean values of soil characteristics within a column followed by the same letter are not significantly different (p < 0.05), using LSD. <sup>#</sup>Pyrophosphate extraction was not performed for the E horizons of Alquod and Paleudult, since pyrophosphate extracts organically complexed Fe and Al which is expected to be negligible for these horizons.

Table 4-2. Mean and standard deviation (SD) by sites and horizons of P sorption capacity ( $P_{sorp}$ ), determined using single-point ( $1000 \text{ mg P kg}^{-1}$ ) isotherm.

Great Group	Site	Horizon	n	$P_{sorp}$	SD
				$\text{mg kg}^{-1}$	
Alaquod	S1	E	12	----	#
		Bh	16	570	235
	S2	E	8	----	----
		Bh	11	116	13
	S3	E	13	----	----
		Bh	21	260	109
Paleudult	S4	E	8	53	39
		Bt	30	675	186
	S5	E	17	124	108
		Bt	21	569	227
	S6	E	10	58	54
		Bt	13	276	60

# No P sorption values could be obtained for the E horizons of Alaquod since they have no P retentive capacity, thus these values were either zero or negative for these soils.

Table 4-3. Phosphorus sorption and desorption parameters for Bh and Bt horizons.

Site	n	Horizon	Statistics	$S_{max}^{\dagger}$ -----mg kg <sup>-1</sup> -----	$S_o^{\dagger}$ -----	$EPC_o^{\dagger}$ mg L <sup>-1</sup>	$k^{\dagger}$ L mg <sup>-1</sup>	$MBC^{\dagger}$ L kg <sup>-1</sup>	$DEF^{\dagger}$ %
S1	10	Bh	Mean	603	2.33	0.66	0.41	247	10
			SD	277	5.16	1.80	0.24	219	6
S2	8	Bh	Mean	151	2.08	2.09	0.04	6	16
			SD	8	4.61	2.01	0.03	4	1
S3	15	Bh	Mean	306	5.60	0.98	0.10	31	30
			SD	141	3.11	0.62	0.07	16	16
S4	25	Bt	Mean	688	0.58	0.22	1.04	716	6
			SD	177	1.26	0.38	0.88	835	2
S5	10	Bt	Mean	562	0.01	0.15	1.30	734	5
			SD	264	0.02	0.21	0.77	688	2
S6	10	Bt	Mean	295	0.12	0.40	0.92	270	3
			SD	90	0.04	0.18	0.51	127	2

<sup>†</sup> $S_{max}$ , P sorption maximum;  $S_o$ , P originally present in the solid phase;  $EPC_o$ , equilibrium phosphorus concentration;  $k$ , P bonding constant;  $MBC$ , maximum buffering capacity;  $DEF$ , P desorbed expressed as a fraction of sorbed P.

Table 4-4. Correlation of sorption parameters with selected soil variables for Bh samples studied (n=33)<sup>†</sup>.

	$S_{max}$	$EPC_0$	MBC	k	DEF
CBD-Fe + Al	0.912***	-0.525**	0.872***	0.764***	-0.568***
CBD-Fe	0.13	-0.093	0.411*	0.537**	-0.105
CBD-Al	0.947***	-0.543***	0.862***	0.730***	-0.591***
Ox-Fe+Al	0.936***	-0.534**	0.870***	0.746***	-0.573***
Ox-Fe	0.091	-0.059	0.394*	0.518**	-0.069
Ox-Al	0.955***	-0.544***	0.858***	0.718***	-0.586***
Pyro-Fe+Al	0.935***	-0.573***	0.852***	0.741***	-0.637***
Pyro-Fe	0.21	-0.163	0.495**	0.611***	-0.178
Pyro-Al	0.952***	-0.579***	0.837***	0.711***	-0.645***
pH	-0.481**	0.374*	-0.482**	-0.470**	0.390*
$S_0$	-0.619***	0.895***	-0.611***	-0.658***	0.432*
Total C	0.743***	-0.480**	0.778***	0.655***	-0.354*

\*Significant at the 0.05 probability level. \*\*Significant at the 0.01 probability level. \*\*\*Significant at the 0.001 probability level. <sup>†</sup>CBD is citrate bicarbonate dithionite; Ox is oxalate; Pyro is pyrophosphate;  $S_{max}$ , P sorption maximum;  $S_0$ , P originally present in the solid phase;  $EPC_0$ , equilibrium phosphorus concentration; k, P bonding constant; MBC, maximum buffering capacity; DEF, P desorbed expressed as a fraction of sorbed P.

Table 4-5. Correlation of sorption parameters with selected soil variables for Bt samples studied (n=45)<sup>†</sup>.

	$S_{max}$	$EPC_0$	MBC	k	DEF
CBD-Fe + Al	0.492***	-0.236	0.404**	0.358*	-0.127
CBD-Fe	0.474**	-0.222	0.371*	0.328*	-0.126
CBD-Al	0.557***	-0.302	0.576***	0.516***	-0.12
Ox-Fe+Al	0.822***	-0.482***	0.725***	0.604***	-0.059
Ox-Fe	-0.211	-0.073	-0.12	-0.05	-0.456**
Ox-Al	0.835***	-0.455**	0.725***	0.595***	0.037
Pyro-Fe+Al	0.441**	-0.28	0.419**	0.383*	-0.051
Pyro-Fe	-0.203	-0.018	-0.231	-0.14	-0.234
Pyro-Al	0.551***	-0.295	0.540***	0.466 **	0.031
pH	-0.500***	0.19	-0.323*	-0.328*	-0.115
So	-0.408**	0.453**	-0.218	-0.267	0.267
Total C	0.246	-0.115	0.127	0.016	0.112

\*Significant at the 0.05 probability level. \*\*Significant at the 0.01 probability level. \*\*\*Significant at the 0.001 probability level. <sup>†</sup>CBD is citrate bicarbonate dithionite; Ox is oxalate; Pyro is pyrophosphate;  $S_{max}$ , P sorption maximum;  $S_o$ , P originally present in the solid phase;  $EPC_0$ , equilibrium phosphorus concentration; k, P bonding constant; MBC, maximum buffering capacity; DEF, P desorbed expressed as a fraction of sorbed P.

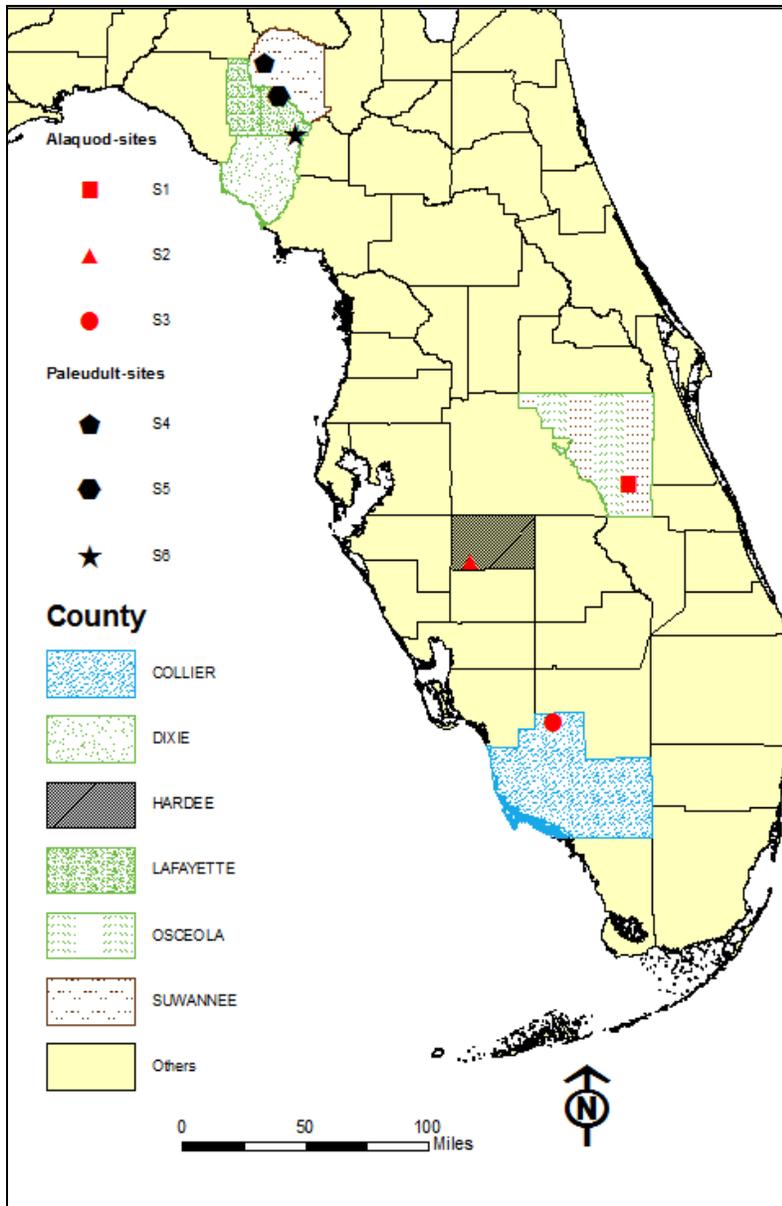
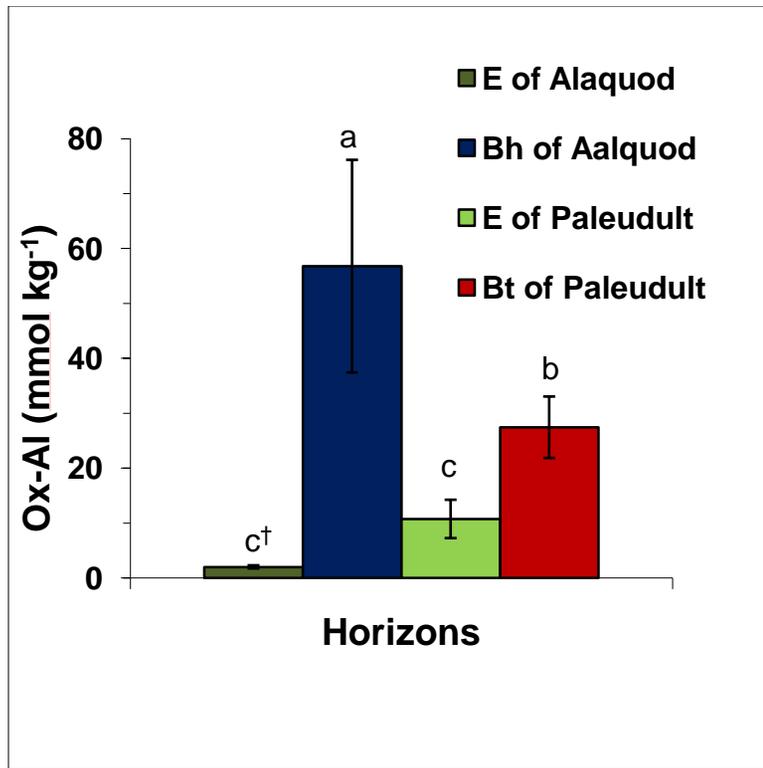
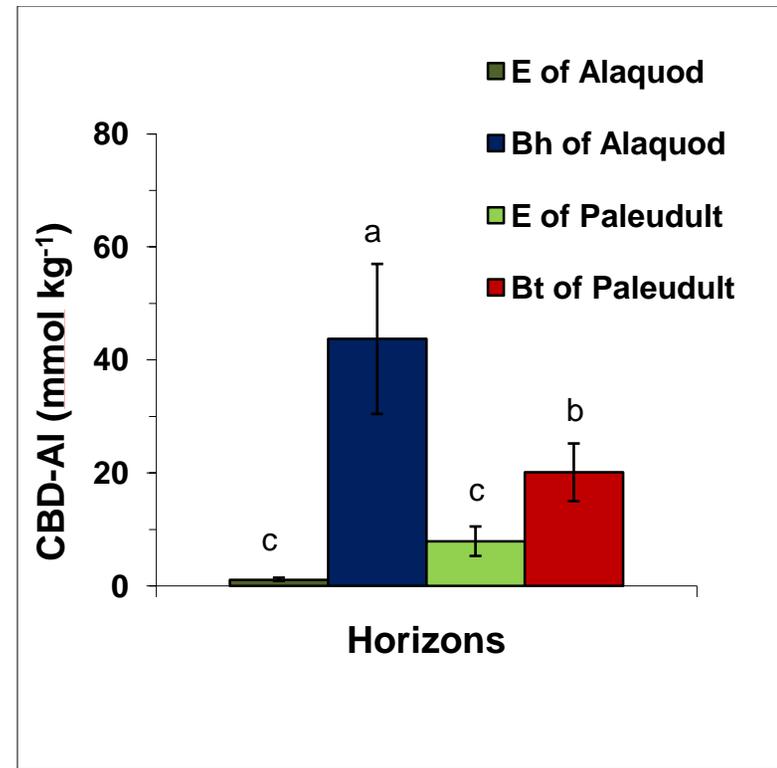


Figure 4-1. Location of the study sites.



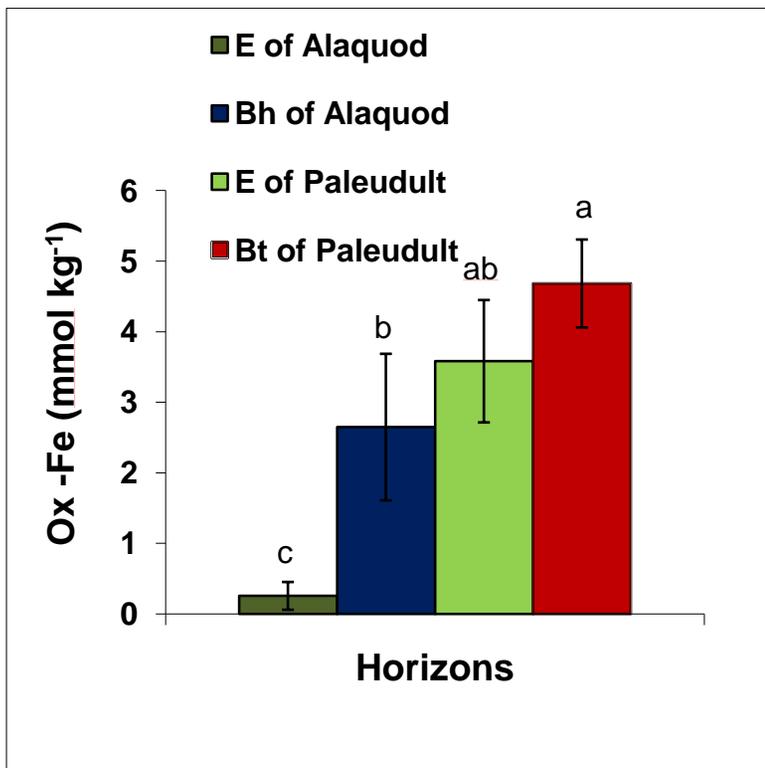
(A)



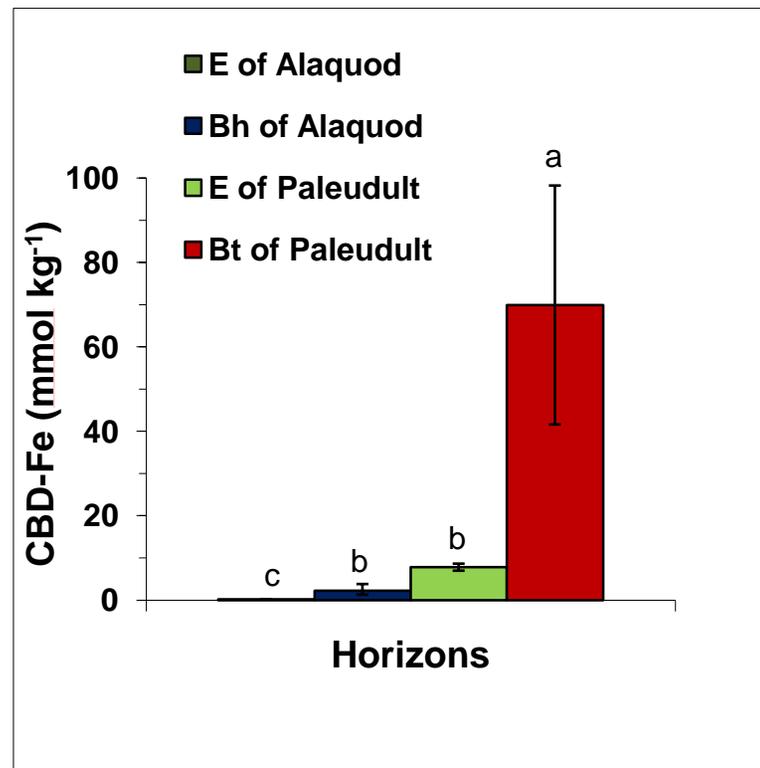
(B)

†Mean values for a given component within the horizons with the same letter are not significantly different ( $p < 0.05$ ), using the least significant difference procedure.

Figure 4-2. Comparison of A) oxalate-extractable Al; B) CBD-extractable Al; C) oxalate-extractable Fe; D) CBD-extractable Fe for E and Bh horizons of Alaquods and E and Bt horizons of Paleudults.



(C)



(D)

Figure 4-2. Continued.

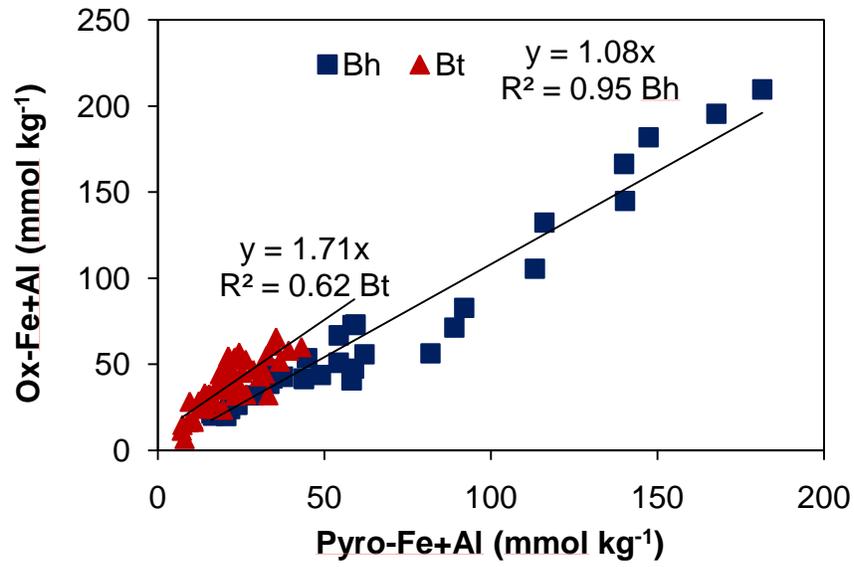
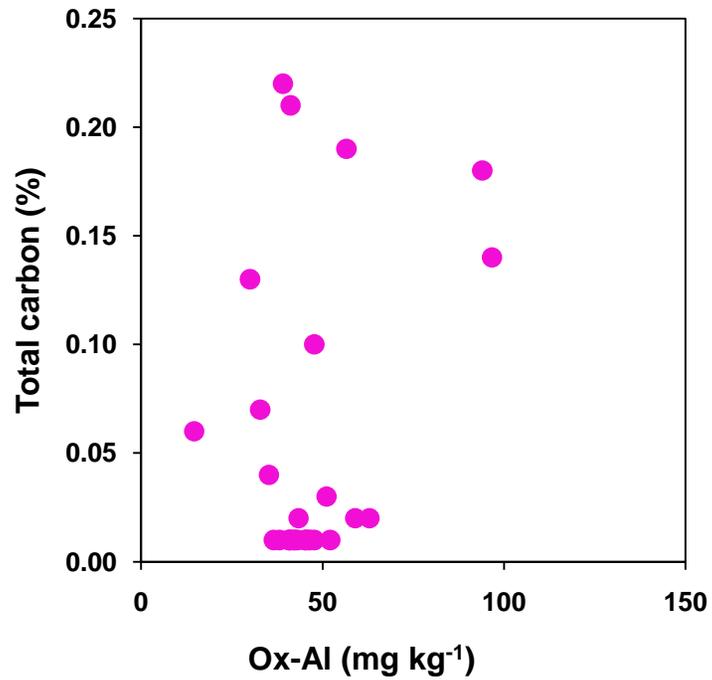
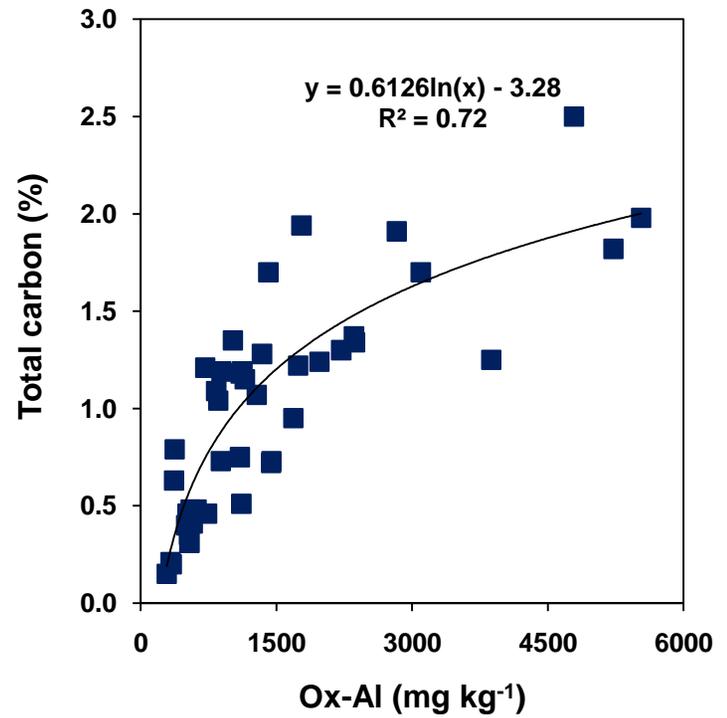


Figure 4-3. Relationship between oxalate-extractable Fe and Al, Ox-Fe+Al and pyrophosphate-extractable Fe and Al, Pyro-Fe+Al for Bh and Bt horizons.

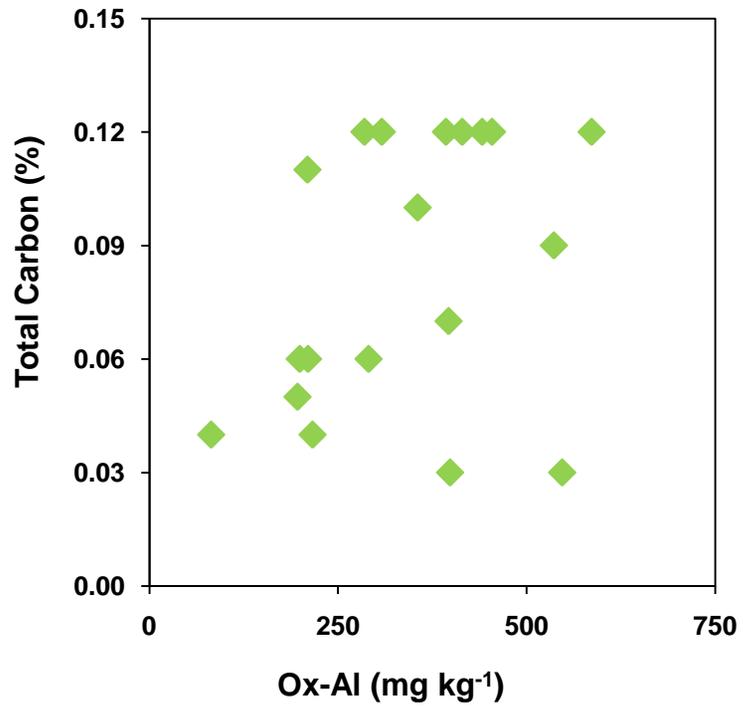


(A)

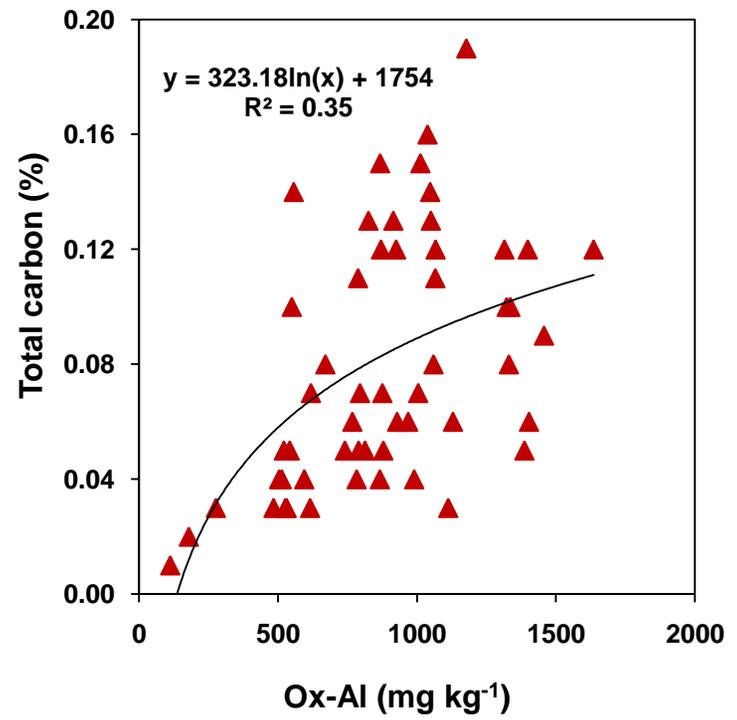


(B)

Figure 4-4. Relationship between total carbon and oxalate-extractable Al for A) E of Alaquods B) Bh of Alaquods C) E of Paleudults and D) Bt of Paleudults.



(C)



(D)

Figure 4-4. Continued.

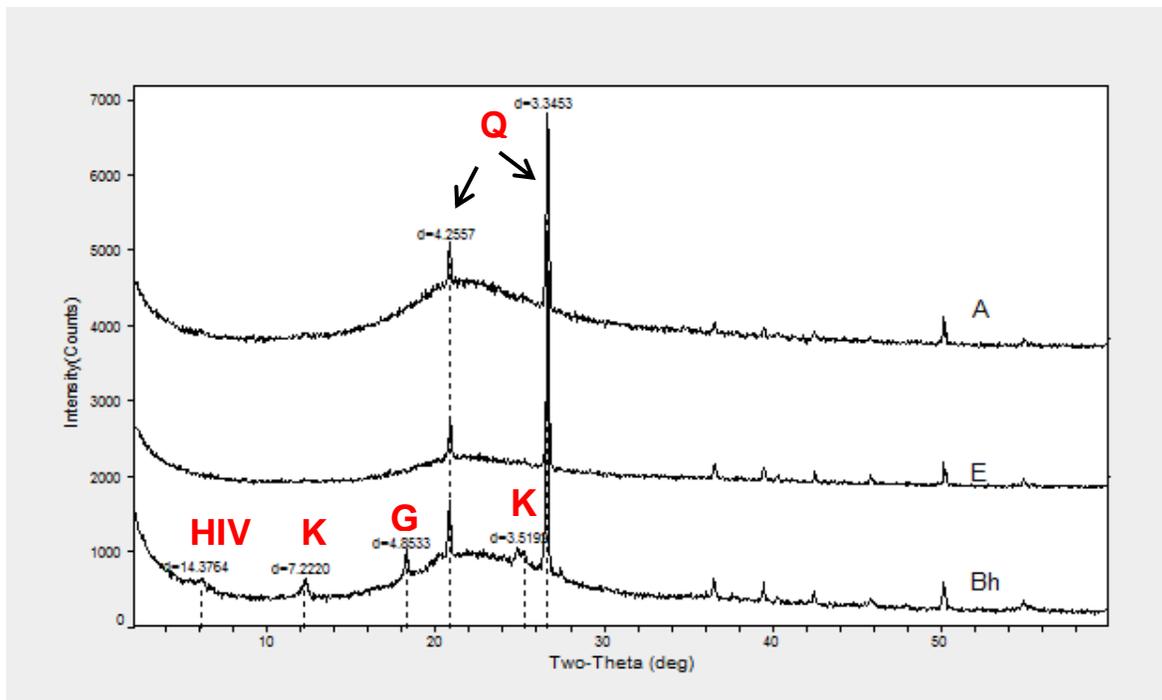


Figure 4-5. X-ray diffraction analysis of clay fraction for the Alaquod profile. The minerals identified are as follows: G: Gibbsite; HIV: hydroxy- interlayered vermiculite; K: kaolinite and Q: quartz.

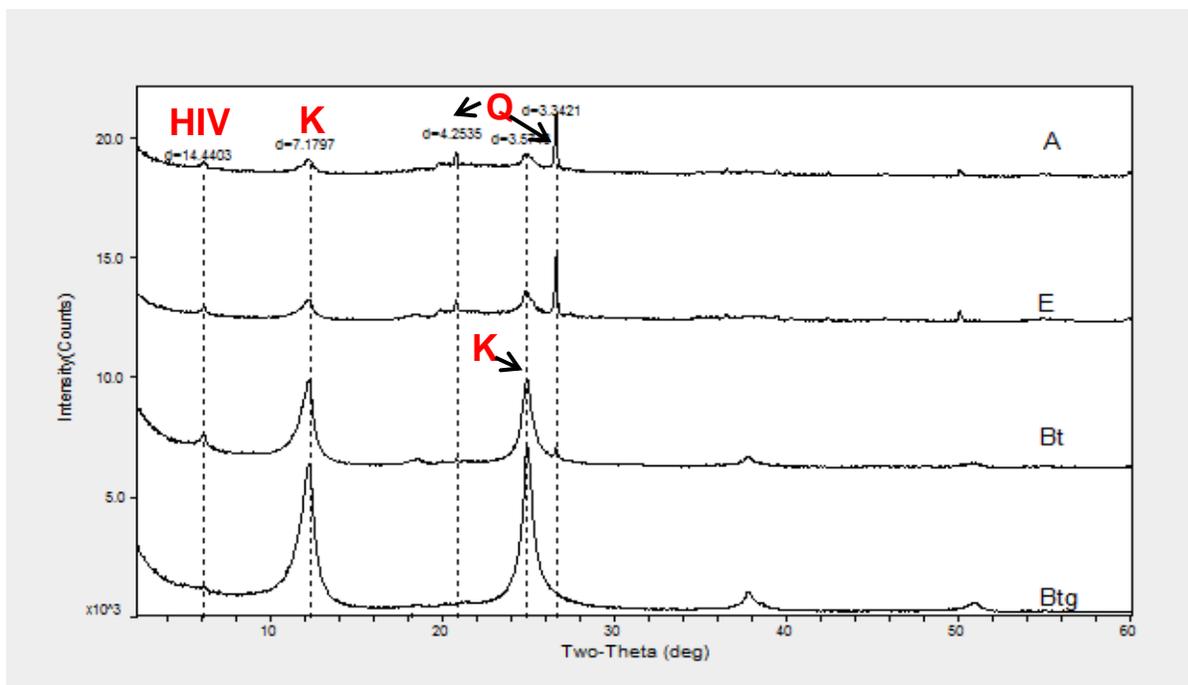


Figure 4-6. X-ray diffraction analysis of clay fraction for the Paleudult profile. The minerals identified are as follows: HIV: hydroxy- interlayered vermiculite; K: kaolinite and Q: quartz.

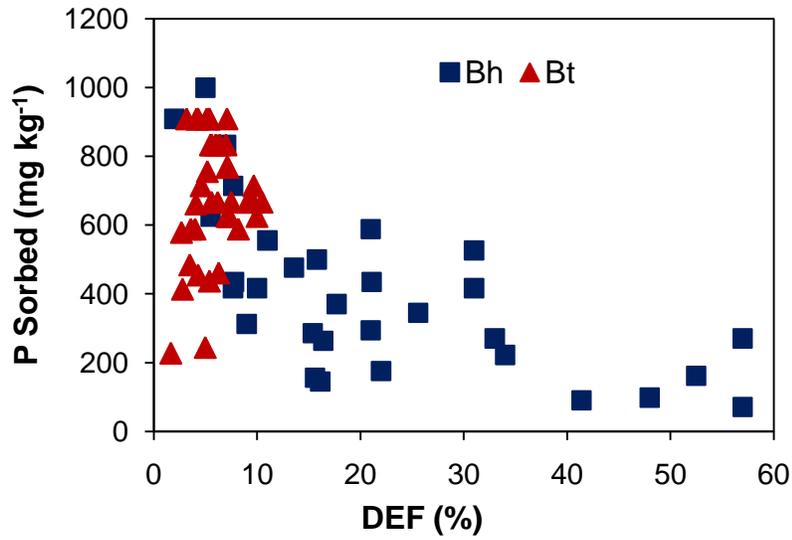


Figure 4-7. Relationship between P sorbed (mg kg<sup>-1</sup>) versus P desorbed expressed as a fraction of sorbed P, DEF (%) for Bh and Bt horizons.

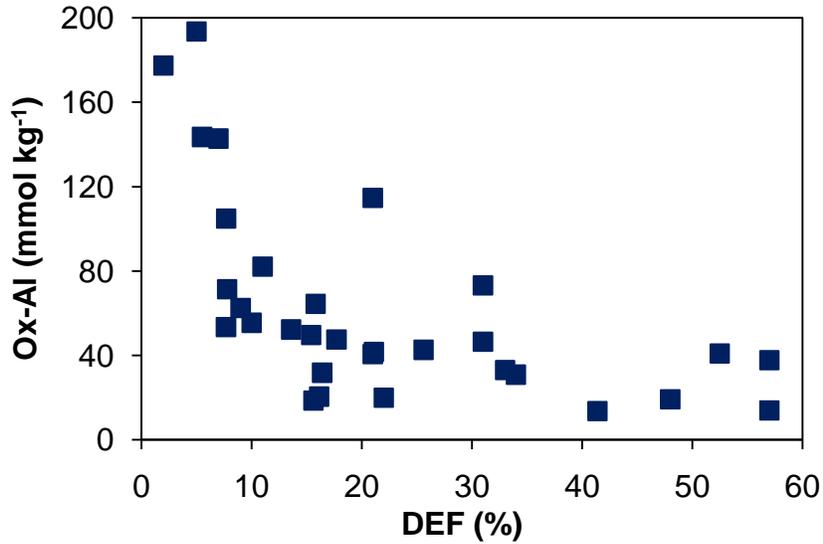


Figure 4-8. Relationship between oxalate-extractable Al, Ox-Al (mmol kg<sup>-1</sup>) and P desorbed expressed as a fraction of sorbed P, DEF (%) for Bh horizons.

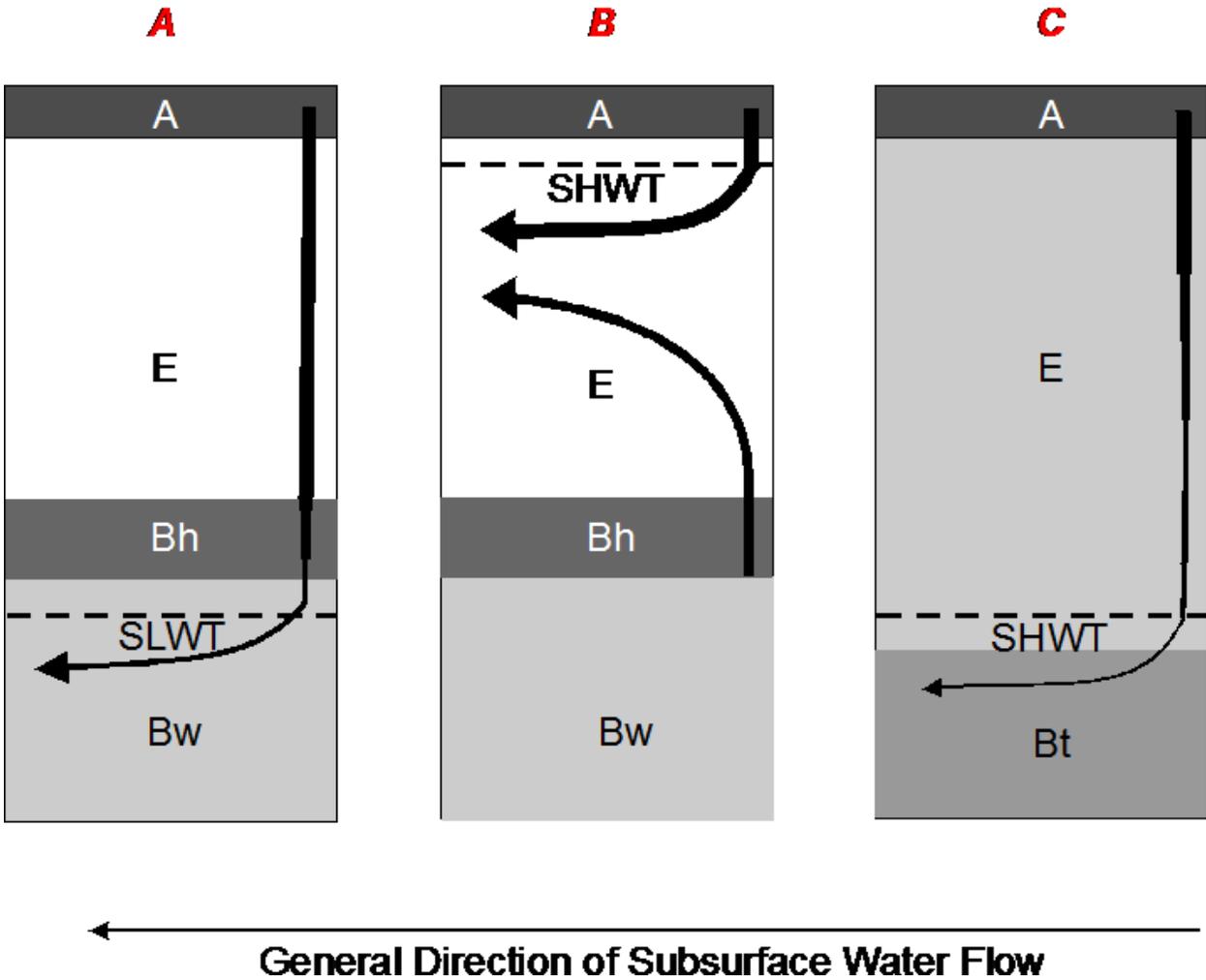


Figure 4-9. Schematic diagram depicting seasonal scenarios of water- and P-movement trends in Alaquod (A and B) and Paleudult (C) soil profiles under comparable P loadings based on horizon and soil compositional differences documented in this study. Relative P concentrations are depicted by thickness of the line with arrow (higher for thicker line). Thickness of line depicting concentration is arbitrary. A) Alaquod profile with water table at a seasonal low level (SLWT); B) Alaquod profile with water table at a seasonally high level (SHWT); C) Paleudult profile with water table at a seasonally high level (SHWT). These trends depict differences in P loss potential between Alaquods and Paleudults as well as seasonally for Alaquods.

## CHAPTER 5

### A COMPARISON OF P DYNAMICS BETWEEN ALAQUODS AND PALEUDULTS: IMPLICATIONS FOR ENVIRONMENTAL RISKS AND PHYTOREMEDIATION.

Chapter 4 dealt with the compositional difference between Alaquods and Paleudults subsurface horizons. Compositional differences between subsurface horizons of Alaquods and Paleudults result in different P sorption behavior and P loss risks with excess P application. Understanding the ease with which P is released from different soils might help better assess the soils that are potentially vulnerable to P loss to nearby water body. The PSR and SPSC concepts which were used to determine environmental risk of P loss have mainly been applied to sandy soils; there was a need to verify its applicability to finer textured horizons (Bt) in coastal plain soils. Plant P availability as determined from iron-oxide impregnated filter paper (FeO-P) may be used as an implication of plant-based clean-up strategy (phytoremediation) for high P loaded soils.

The objective of this chapter was to relate environmental P loss risk assessed by PSR and SPSC to the compositional difference between Alaquod and Paleudult subsurface horizons. The specific objectives were to:

- compare P release behavior of Alaquod and Paleudult subsurface horizons using PSR and SPSC;
- determine the effectiveness of SPSC as an alternative of  $EPC_0$  for predicting the risk of P loss;
- test the applicability of SPSC in clayey or loamy (Bt) horizons;
- evaluate the potential for phytoremediation to remove subsurface P.

## Materials and Methods

### Soil Sampling

Alaquod profiles from three sites (S1, S2 and S3) and Paleudult profiles from three different sites (S4, S5 and S6) located within Florida presented in Figure 4-1 were used for this study. As stated before, surface horizons were not considered in this study since they constitute a relatively thin part of the soil profile and have minimal contribution for P loss from the soil profile. The total numbers of soil samples analyzed in this study were 90 (E: 34 and Bh: 56) for Alaquods and 101 (E: 34 and Bt: 67) for Paleudults.

### Soil Characterization

Samples were thoroughly mixed, air-dried and passed through a 2 mm sieve before analyses. Soil pH was determined using 1:2 soil and water suspension. Mehlich 1-extractable P (M1-P), Fe (M1-Fe) and Al (M1-Al) were obtained by extracting soil with a double acid solution ( $0.05\text{ M HCl} + 0.0125\text{ M H}_2\text{SO}_4$ ) at a 1:4 soil to solution ratio (Mehlich, 1953). Mehlich 3 extractions for determination of P (M3-P), Fe (M3-Fe), and Al (M3-Al) were obtained by extracting with  $0.2\text{ M CH}_3\text{COOH} + 0.25\text{ M NH}_4\text{NO}_3 + 0.015\text{ M NH}_4\text{F} + 0.13\text{ M HNO}_3 + 0.001\text{ M EDTA}$  at a 1:8 soil to solution ratio (Mehlich, 1984). Oxalate-extractable P (Ox-P), Fe (Ox-Fe), and Al (Ox-Al) were determined for soils using a  $0.1\text{ M}$  oxalic acid +  $0.175\text{ M}$  ammonium oxalate solution, equilibrated at a pH of 3.0 (McKeague and Day, 1966). All metals and P in M1, M3 and Ox solution were determined by inductively coupled argon plasma spectroscopy (Thermo Jarrel Ash ICAP 61E, Thermo Elemental, Franklin, MA).

Plant available P: Whatman 50 filter papers were immersed in  $0.65\text{ M FeCl}_3$  solution overnight. They were then air dried and immersed in  $2.7\text{ M NH}_4\text{OH}$  for 30 s; rinsed and kept in DDI water for 1 h (Myers et al., 1997). The filter paper can then be

used immediately or dried and stored for future use. The filter paper is then placed into mesh screen and sealed with a plastic clamp. In 4 oz glass bottle 5g of soil and 30 mL of DI water was added. The mesh screen was inserted with enclosed filter paper so that it does not move during shaking (Figure 5-1). The bottle was then capped. It was then shaken for 16 h. At the end of the shaking, each paper was removed from the screens. It was then rinsed with DI water. Phosphorus extracted from iron-oxide impregnated filter paper (FeO-P) by adding 50 mL of 0.2 M H<sub>2</sub>SO<sub>4</sub> in 125 mL Erlenmeyer flasks and shaking for 1 h.

Water-soluble P (WSP) was determined using 1:10 soil to water ratio. The extraction was done by shaking 2 g soil with 20 mL of double deionized water for 1 h and filtering through a 0.45 µm filter paper. Total P (TP) was determined using the ignition method (Anderson, 1976). Water soluble P, FeO-P and TP concentrations were determined using an autoanalyzer (USEPA, 1983; Method 365-1) by the Murphy and Riley (1962) procedure. Sorption and desorption parameters for 33 Bh and 45 Bt samples (selected based on Fe and Al content) were obtained from the results as presented in chapter 4 (Table 4-3).

### **Determination of Observed and Predicted SPSC**

Predicted soil P storage capacity (SPSC<sub>predicted</sub>) was determined using 2 g of air dry soil in 50 mL centrifuge tubes to which 30 mL of P having different concentrations (0, 5, 10, 15, 20, 30, 40 and 60 mg P L<sup>-1</sup> as KH<sub>2</sub>PO<sub>4</sub>) were added. The tubes were then placed on a reciprocating shaker for a 24 h equilibration period. At the end of the period, the soil samples were allowed to settle for 1 h, the supernatant filtered through a 450-nm membrane filter, and the filtrate analyzed for soluble reactive P. Difference between

the P concentration in the equilibrium solution and the initial P added to the soil is the amount of P sorbed by the soils.

After removing the supernatants, each tube containing a wet soil sample was weighed to estimate the volume of the residual solution and the P entrapped in it. Twenty mL DI water was then added to the centrifuge tubes, shaken for 1 h, filtered and analyzed for WSP. From the relationship between WSP and the amount of P sorbed,  $SPSC_{\text{predicted}}$  is determined corresponding to the point at which WSP increases significantly with increase in P sorption. The observed SPSC ( $SPSC_{\text{observed}}$ ) for the soils were obtained using equation (5-3).

### Calculations

PSR and SPSC of the soils were calculated based on oxalate extractions because oxalate extracts most of the reactive Al and Fe present in the soil and represents its P sorption capacity (Kleinman et al., 2003).

$$PSR = \frac{\text{Oxalate - extractable P}}{\text{Oxalate - extractable [Fe + Al]}} \quad (5-1)$$

Soil P storage capacity for E horizons of Alaquods were calculated based on threshold PSR of 0.1 as obtained from Nair et al. (2004).

$$SPSC = (0.1 - \text{Soil } PSR_{Ox}) \times \text{Extractable (Fe + Al)} \times 31 \quad (5-2)$$

where Soil  $PSR_{Ox}$  is for the specific soil based on which SPSC is calculated.

Soil P storage capacity for Bh horizons of Alaquods and E and Bt horizons of Paleudults were calculated as:

$$SPSC = (\text{Threshold } PSR_{Ox} - \text{Soil } PSR_{Ox}) \times \text{Extractable (Fe + Al)} \times 31 \quad (5-3)$$

where Threshold  $PSR_{Ox}$  for Bh horizons of Alaquods and E and Bt horizons of Paleudults were determined statistically using NLIN procedure.

The P, Fe and Al in equations (5-1) to (5-3) are expressed in moles. The SPSC in equations (5-2) and (5-3) are expressed in  $\text{mg kg}^{-1}$ .

### **Statistical Analyses**

Empirical relationships between soil parameters were performed using correlation and regression analyses in Excel 2007. Computations for the change point or threshold PSR were done using the Statistical Analysis System (SAS Institute, 2001) using a NLIN procedure, similar to the one adopted in a previous study (Nair et al., 2004).

## **Results and Discussion**

### **Soil Characterization**

Soil pH values were acidic for both Alaquod and Paleudult subsurface horizons (Table 5-1). Extraction efficiency of P follows the order: Oxalate-P > M3-P > M1-P > FeO-P > WSP (Tables 5-1 and 5-2). There is an increasing concern that the use of agronomic soil P tests such as, M1 and M3 for environmental purposes may not be appropriate. For instance, Sharpley et al. (2004) observed at high soil P levels, M3-P extracts some P which may not be immediately released from manured surface soil to overland flow. Potential release of P in runoff may be better estimated by extracting soil with water than other traditional soil tests (Hooda et al., 2000). Water-soluble P measures the amount of P that will be released from the soil when it is in contact with water from sources like rain or irrigation. Water-soluble P in this study ranged from 0.10 to 35  $\text{mg kg}^{-1}$  for Alaquods and from 0 to 39  $\text{mg kg}^{-1}$  for Paleudults subsurface horizons. Phosphorus extracted by iron-oxide impregnated filter paper (FeO-P) was strongly related to WSP as obtained using a 1:10 soil:water ratio, for both E and Bh horizons of Alaquods ( $R^2 = 0.74$ ) and E and Bt horizons of Paleudults ( $R^2 = 0.93$ ) and is almost twice in magnitude to that of WSP (Figures 5-2 and 5-3). However FeO-P provides a

better estimate of plant P availability in comparison to WSP since the quantity of P extracted by water is too low and it does not simulate the adsorption mechanism prevalent in natural soil system (Menon et al., 1989; Myers et al., 1997).

### **Environmental Risk of P Release**

Environmental risk of P loss from Alaquods and Paleudults subsurface horizons can be evaluated from PSR and SPSC. The lower threshold PSR for Bh (0.05) relative to Bt (0.12) (Figures 5-4 and 5-5) likely relates to differences in soil components that affect P sorption. As observed in the previous chapter, P sorption in Bt horizons is largely controlled by noncrystalline metal oxides, crystalline Fe oxides and phyllosilicates (mainly kaolinite) which have more tenacious binding with P in comparison to organo-metallic complexes that dominate Bh horizons. E horizons of Paleudult, which have appreciable P retentive capacity due to the presence of metal oxides, have a threshold value similar to the Bt horizons. Relationship of WSP with PSR indicates that WSP is minimal below the threshold PSR and increases rapidly once the threshold PSR is crossed for both Alaquod and Paleudult profile and thus may be of environmental concern. Considerable numbers of E samples and majority of the Bt samples of Paleudult profiles studied have PSR below the threshold value. In contrast, an appreciable number of Bh samples had PSR greater than the threshold and thus would act as a potential source of P. Low WSP of the E horizons of Alaquods is due to the low P retentive capacity associated with the horizon as observed in the previous chapter. Phosphorus extracted from iron-oxide impregnated filter paper, FeO-P, increases considerably when PSR is greater than the threshold value for Alaquod and Paleudult subsurface horizons and follows the same trend as WSP/PSR relationship (Figures 5-4 and 5-5).

Relationships between SPSC and WSP for Alaquod and Paleudult subsurface horizons show that as long as SPSC is positive, WSP is at a minimum; but when SPSC is negative, the release of P from the soil increases linearly (Figures 5-6 and 5-7). Majority of the Bt samples have positive SPSC and hence they likely would act as P sink. Also, the appreciable P retention capacity of Paleudult E horizons further reduces the susceptibility of underlying Bt horizons to become loaded above the PSR threshold. On the other hand, the negligible P retentive capacity of Alaquod E horizons results in minimal retardation of P transport to underlying Bh horizons. Thus Bh horizons are susceptible to excess P loading and may act as a P source.

Plant P availability as inferred from FeO-P was proportional to negative SPSC (Figures 5-8, 5-9 and 5-10) but was consistently minimal as long as SPSC was positive. The relationship between SPSC and FeO-P suggests that considerable amount of P is available for plant uptake from subsurface horizons of Alaquods and E horizons of Paleudults. The value of the slope of the equations describing plant P availability in figures 5-8 and 5-9 are same indicating that irrespective of the compositional differences between subsurface horizons of Alaquods and Paleudults, plant P availability from both the profiles will be identical.

For Bh and Bt horizons P loss risk was also evaluated from  $EPC_0$ . The mean values of  $EPC_0$  for Bh and Bt samples were 1.3 and 0.3 mg L<sup>-1</sup> respectively. Soils exhibit their maximum buffer capacity (MBC) up to the P concentration corresponding to  $EPC_0$  (Bridgham et al., 2001). The MBC value ranges from 3 to 625 L kg<sup>-1</sup> for Bh and from 59 to 1667 L kg<sup>-1</sup> for Bt. MBC of soils may be defined as the measurement of soil resistance to the change of P concentration in soil solution with the addition or removal

of P (Sui and Thompson, 2000). Most of the Bt samples have high MBC as shown in Table 4-3. Relationship between  $EPC_0$  with SPSC (Figure 5-11) showed that as long as SPSC is positive (PSR is below the change point) the  $EPC_0$  value is low; whereas the value increases considerably when SPSC is negative. This indicates the effectiveness of SPSC for predicting the risk of P loss from soils. High  $EPC_0$  values are mainly associated with samples with low Ox-Al and high P loading. When the relationship between SPSC and  $EPC_0$  is verified,  $EPC_0$  values may be predicted from P, Fe and Al data. Determination of SPSC of any soil is much easier than determination of  $EPC_0$ . Thus the environmental risk of P loss from any soil horizon may be easily calculated using the concept of SPSC.

### **Effectiveness of SPSC in Loamy to Clayey Soil Horizons**

Phosphorus storage capacity for 9 Bt samples were thoroughly studied by determining experimentally the actual SPSC ( $SPSC_{\text{predicted}}$ ) for each sample. A 1:1 relationship between  $SPSC_{\text{observed}}$  and  $SPSC_{\text{predicted}}$  was observed with a strong  $R^2$  of 0.86 (Figure 5-12). Thus the environmental risk of P loss may be predicted from SPSC for loamy to clayey Bt horizons as well as for sandy eluvial horizons of coastal plain soils. These results indicate that although crystalline Fe oxides along with phyllosilicates play a dominant role for P retention in Bt samples, the noncrystalline metal oxides extracted by oxalate are the components that bind P most tenaciously and that control sorption below the PSR threshold.

Relationship of PSR and P fraction-desorbed indicates two different slopes below and above the threshold PSR for Bh horizons (Figure 5-13). This may be due to the fact that in Bh samples P retention is predominantly controlled by organo-metallic

complexes with weaker P binding strength. As a result, once the threshold PSR is crossed P is released much easily in Bh.

No relationship between PSR and P fraction-desorbed was obtained for Bt where P is retained more tenaciously by the inorganically-complexed metals along with other factors influencing P retention. It implies that even if threshold PSR is crossed for Bt soils it still has relatively high P retentive capacity and degree of hysteresis.

### **Implications of Phytoremediation of Subsurface P**

Availability of P to plants from fertilizer-impacted Alaquod and Paleudult subsurface horizons (as well as plant uptake capacity) is pertinent to potential efficacy of phytoremediation. Phytoremediation involves removal of elements from soil by plants (Salt et al., 1995). It has potential to be a safe and economical method for reducing excess P in soils and thus helps to minimize P loss through surface or subsurface flow. Since deep-rooted plants can access P from subsurface horizons of Alaquods and Paleudults, soils under trees will be less susceptible to P loss in comparison to treeless pastures. Removal of P from subsurface horizons is of considerable importance particularly in sandy soils where leaching is often a major mode of transport.

Nair et al. ( 2007) reported that the mean SPSC of a soil profile in a pasture with trees vs. treeless pastures up to a meter depth were 1494 and 370 kg P ha<sup>-1</sup>. Although the SPSC was positive for both the profiles, it was less positive for the treeless pasture in comparison to pasture with trees. This indicates P removal by deep rooted plants in pasture with trees which also in turn increases the capacity of these soils to retain more P in comparison to pasture without trees.

## Summary

Environmental risk of P loss from soils may be more conveniently predicted by SPSC than by EPC<sub>0</sub>. Loamy and clayey Bt horizons have higher P retentive capacity than overlying sandy eluvial horizons due to greater abundance of inorganic metal oxides along with crystalline Fe and phyllosilicates. However, the components responsible for tenaciously binding P and maintaining low P solution concentrations are noncrystalline metal oxides. Alaquod subsurface horizons have higher risk of P loss in comparison to Paleudult subsurface horizons. Phytoremediation is a potential approach to remove P from subsurface horizons, thereby reducing P loss risk. Since deep-rooted plants can access P from subsurface horizons of Alaquods it may be successfully used to reduce the risk of P loss from these soils.

Table 5-1. Mean and SD by site and horizon for chemical properties of soils studied.

Site	Horizon	n	Statistics	pH	WSP <sup>†</sup>	FeO-P <sup>†</sup>	M1-P <sup>†</sup>	M1-Fe <sup>†</sup>	M1-Al <sup>†</sup>	M3-P <sup>†</sup>	M3-Fe <sup>†</sup>	M3-Al <sup>†</sup>
					----- mg kg <sup>-1</sup> -----							
S1	E	15	Mean	5.95	4.91	7.55	16	7	24	17	34	36
			SD	0.79	5.60	8.55	22	5	26	23	32	53
	Bh	20	Mean	5.56	2.67	5.47	35	27	961	41	94	1200
			SD	0.62	6.54	11.2	56	41	516	52	101	524
S2	E	8	Mean	6.01	2.57	3.52	3	4	10	3	5	14
			SD	0.43	2.02	1.44	2	2	8	3	6	14
	Bh	11	Mean	4.94	2.55	8.21	27	13	583	29	64	705
			SD	0.25	3.24	7.12	26	12	569	25	77	486
S3	E	11	Mean	5.55	0.13	0.66	1	2	4	3	4	8
			SD	0.12	0.16	1.1	2	3	3	3	3	9
	Bh	25	Mean	5.57	5.50	18.88	88	12	551	102	70	850
			SD	0.33	4.80	13.87	68	19	195	76	109	328
S4	E	8	Mean	5.68	18.17	40.03	125	28	202	196	110	646
			SD	0.33	4.14	11.28	35	18	43	24	40	94
	Bt	36	Mean	4.69	2.62	5.76	22	8	207	23	31	1221
			SD	0.56	8.11	17.63	54	4	40	40	21	572
S5	E	15	Mean	5.14	0.20	0.26	3	31	144	8	104	424
			SD	0.55	0.40	0.34	2	23	76	4	47	170
	Bt	21	Mean	4.46	0.02	0.11	1	9	221	2	31	1331
			SD	0.36	0.06	0.17	1	6	107	2	17	1092
S6	E	11	Mean	6.42	0.41	2.41	5	5	31	13	98	194
			SD	0.66	0.39	1.84	2	2	15	7	136	223
	Bt	10	Mean	5.97	0.14	3.32	7	5	61	20	39	825
			SD	0.59	0.22	4.68	8	3	35	20	7	149

<sup>†</sup>WSP, water-soluble phosphorus; FeO-P,P extracted from iron-oxide impregnated filter paper; M1-P, Al, Fe, Mehlich 1-extractable phosphorus, aluminum and iron respectively; M3-P, Al and Fe, Mehlich 3-extractable phosphorus, aluminum and iron, respectively.

Table 5-2. Mean and SD by site and horizon for oxalate-extractable P and metals, data used in PSR and SPSC calculations and total P for the soils studied.

Site	Horizon	n	Statistics	TP <sup>†</sup>	Ox-P <sup>†</sup>	Ox-Fe <sup>†</sup>	Ox-Al <sup>†</sup>	PSR <sup>†</sup>	SPSC <sup>†</sup>
				-----mg kg <sup>-1</sup> -----					mg kg <sup>-1</sup>
S1	E	15	Mean	49	41	38	68	0.52	-31
			SD	30	26	37	56	0.27	24
	Bh	20	Mean	117	113	214	2070	0.08	12
			SD	64	68	294	1483	0.09	125
S2	E	8	Mean	5	4	6	23	0.13	-1
			SD	4	2	7	17	0.09	6
	Bh	11	Mean	54	48	69	870	0.06	4
			SD	36	34	93	770	0.05	40
S3	E	11	Mean	6	4	5	15	0.2	-2
			SD	2	4	8	8	0.08	1
	Bh	25	Mean	128	115	85	1035	0.09	-53
			SD	100	89	146	397	0.07	81
S4	E	8	Mean	230	256	262	454	0.4	-176
			SD	75	93	89	111	0.12	83
	Bt	36	Mean	263	51	270	949	0.05	134
			SD	71	86	100	250	0.09	106
S5	E	15	Mean	19	20	232	309	0.04	38
			SD	10	9	72	154	0.01	19
	Bt	21	Mean	75	10	291	828	0.01	157
			SD	43	4	123	471	0.01	79
S6	E	11	Mean	30	22	104	120	0.12	1
			SD	42	9	54	75	0.03	9
	Bt	10	Mean	371	41	223	447	0.06	55
			SD	339	33	162	102	0.04	22

<sup>†</sup>TP, total phosphorus; Ox-P, Al and Fe, oxalate-extractable phosphorus, aluminum and iron, respectively; PSR, P saturation ratio using oxalate extract calculated as molar ratio of P to [Fe + Al]; SPSC, safe phosphorus storage capacity. SPSC for Bh and Bt horizon soils calculated using oxalate extraction according to equation (5-3).



Figure 5-1. Setup of Iron-oxide impregnated filter paper.

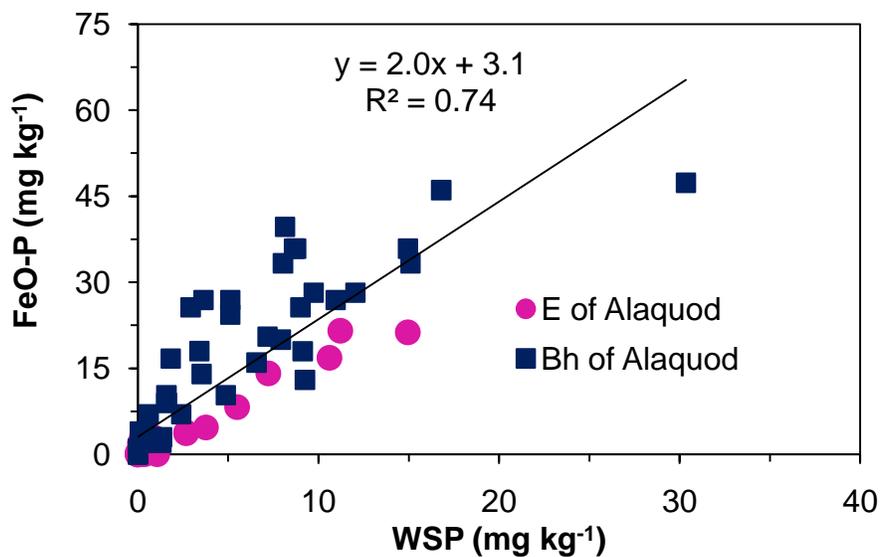


Figure 5-2. Relationship between P extracted from iron-oxide impregnated filter paper (FeO-P) and water soluble P (WSP) for E and Bh horizons of Alaquods.

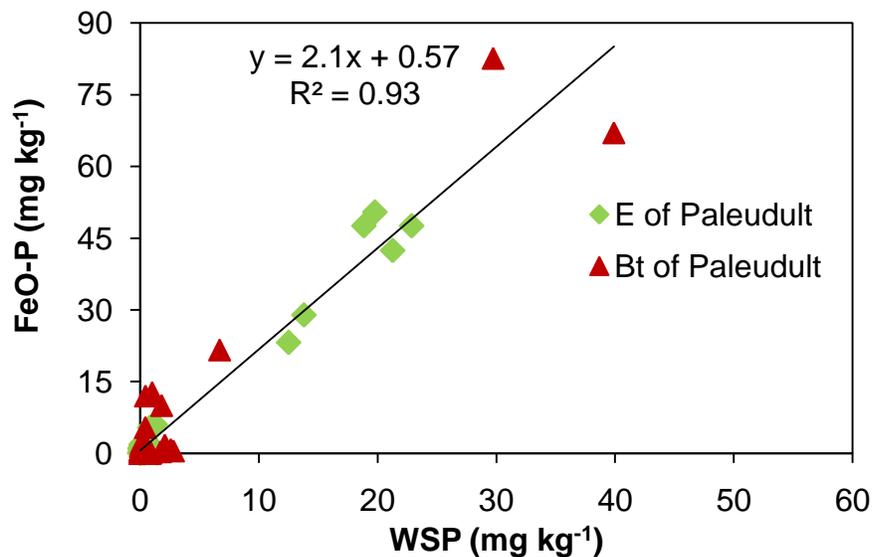


Figure 5-3. Relationship between P extracted from iron-oxide impregnated filter paper (FeO-P) and water soluble P (WSP) for E and Bt horizons of Paleudults.

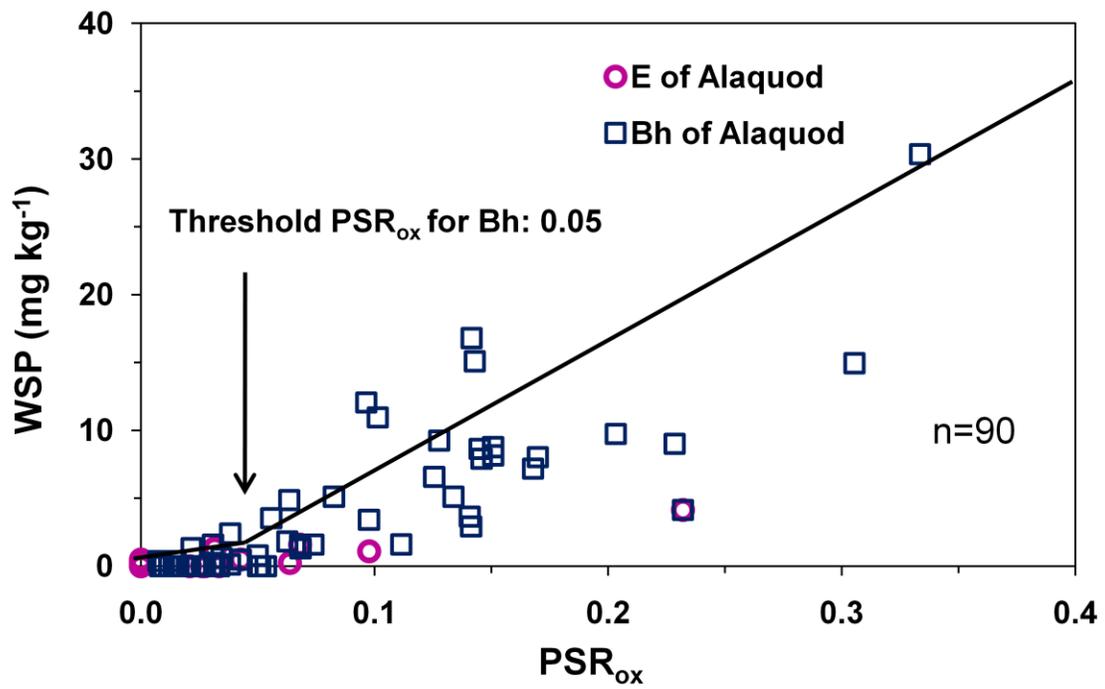


Figure 5-4. Relationship between water soluble P (WSP) and P saturation ratio calculated for subsurface E and Bh horizons of Alaquods using P, Fe and Al in an oxalate extract (PSR<sub>ox</sub>).

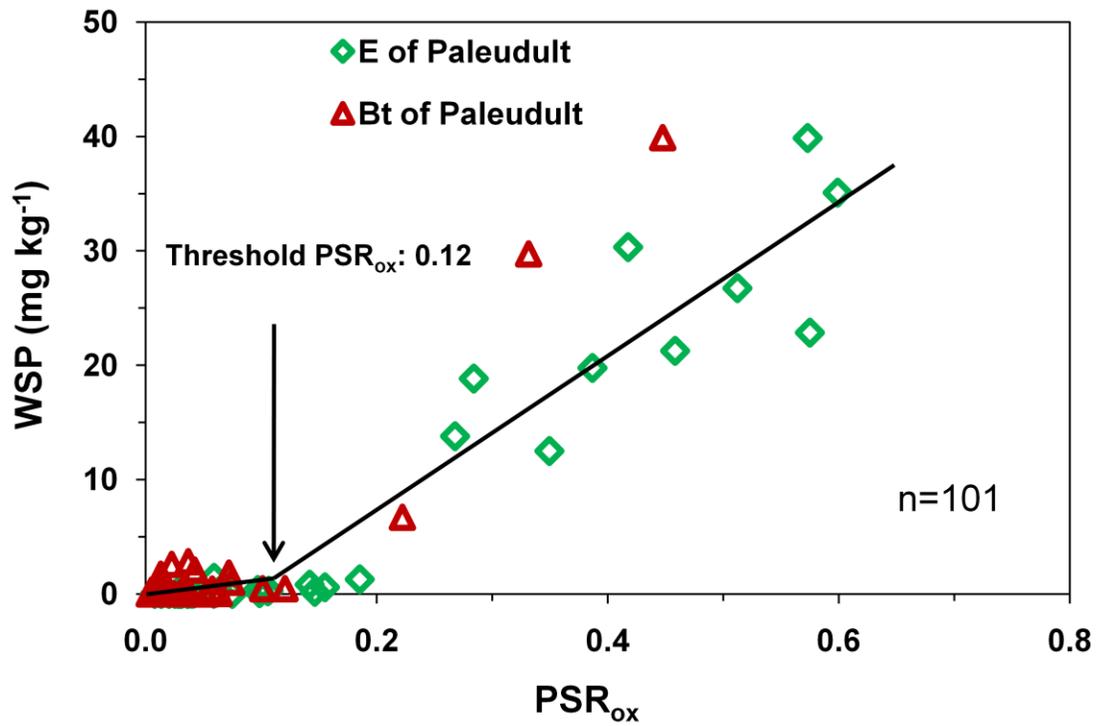


Figure 5-5. Relationship between water soluble P (WSP) and P saturation ratio calculated for the subsurface E and Bt horizons of Paleudults using P, Fe and Al in an oxalate extract (PSR<sub>ox</sub>).

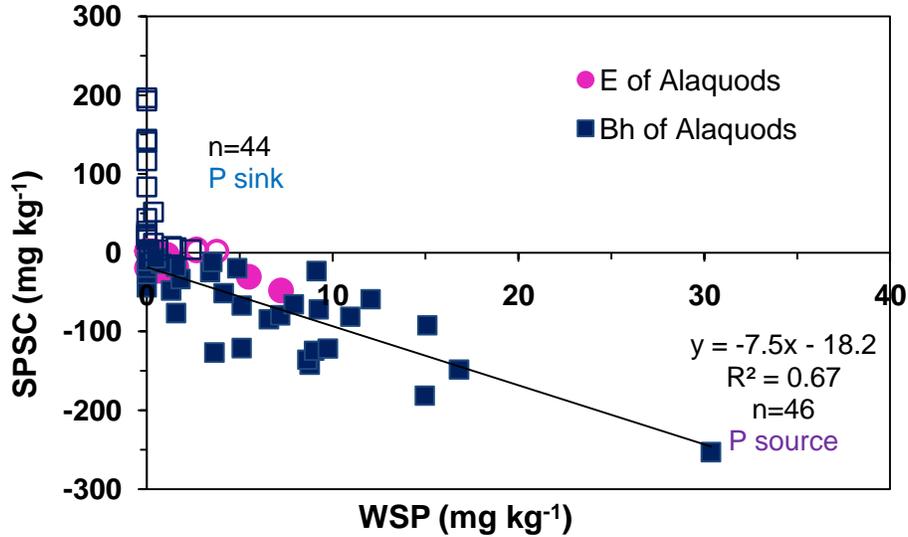


Figure 5-6. Relationship between soil P storage capacity (SPSC) and water soluble P (WSP) for E and Bh horizons of Alaquods. Open and closed markers represent positive and negative SPSC respectively. The R<sup>2</sup>-value is for soils with negative SPSC.

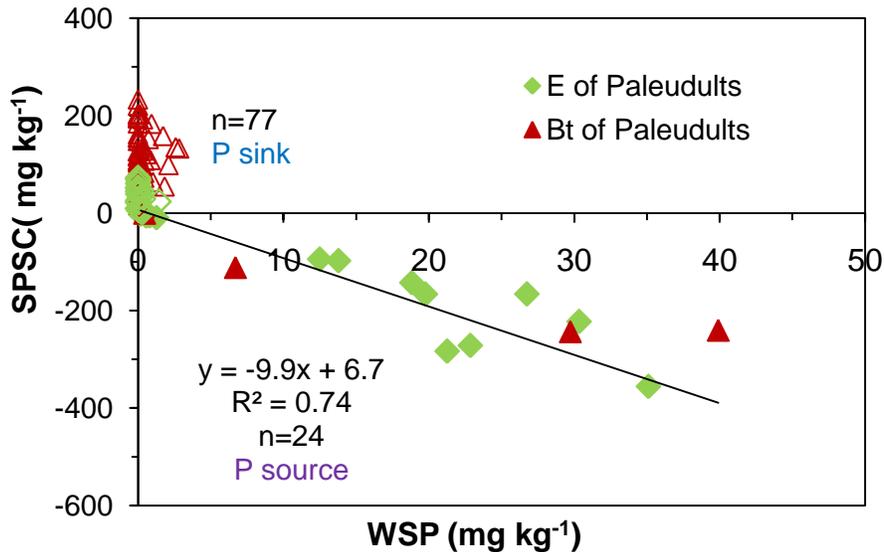


Figure 5-7. Relationship between soil P storage capacity (SPSC) and water soluble P (WSP) for E and Bt horizons of Paleudults. Open and closed markers represent positive and negative SPSC respectively. The R<sup>2</sup>-value is for soils with negative SPSC.

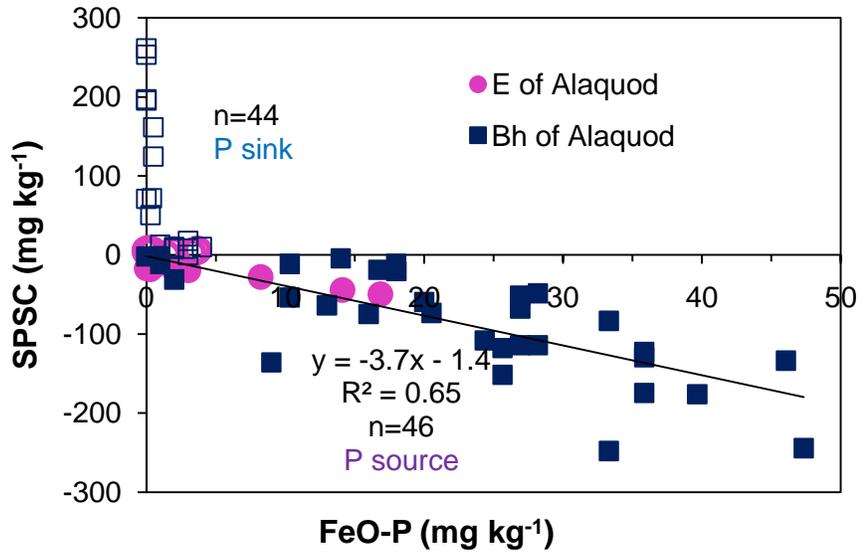


Figure 5-8. Relationship between soil P storage capacity (SPSC) and P extracted from iron-oxide impregnated filter paper (FeO-P) for E and Bh horizons of Alaquods. Open and closed markers represent positive and negative SPSC respectively. The  $R^2$ -value is for soils with negative SPSC.

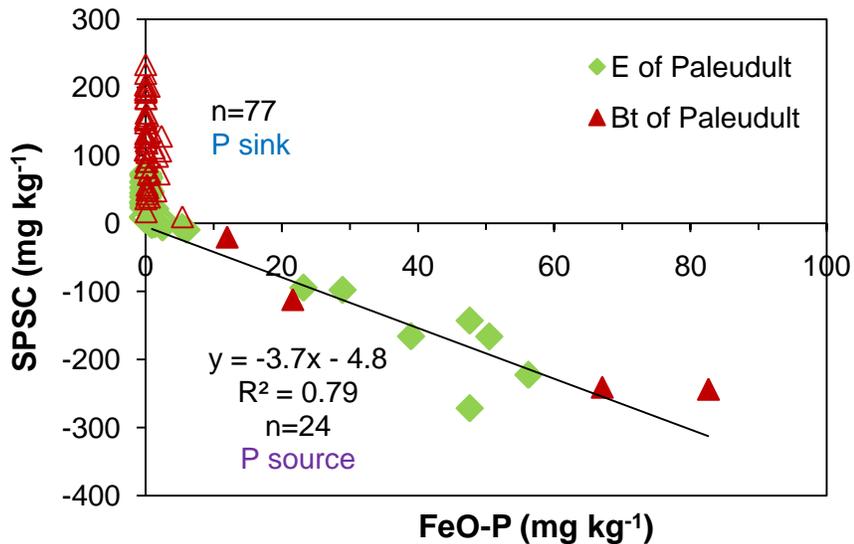


Figure 5-9. Relationship between soil P storage capacity (SPSC) and P extracted from iron-oxide impregnated filter paper (FeO-P) for E and Bt horizons of Paleudults. Open and closed markers represent positive and negative SPSC respectively. The  $R^2$ -value is for soils with negative SPSC.

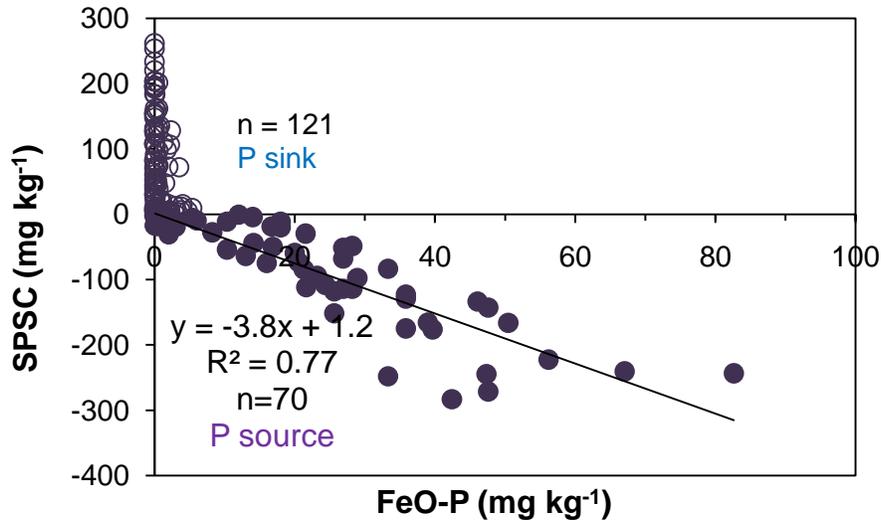


Figure 5-10. Relationship between soil P storage capacity (SPSC) and P extracted from iron-oxide impregnated filter paper (FeO-P) for Alaquod and Paleudult subsurface horizons (combined data). Open and closed markers represent positive and negative SPSC respectively. The  $R^2$ -value is for soils with negative SPSC.

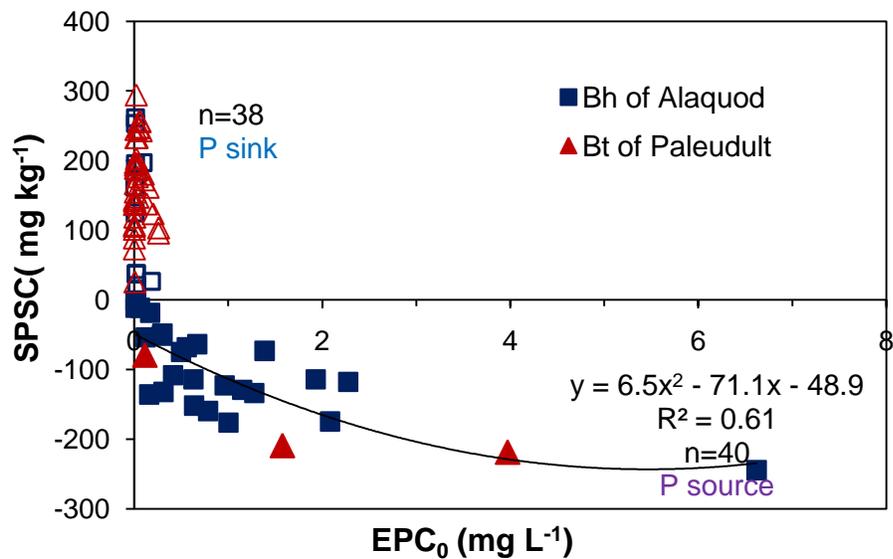


Figure 5-11. Relationship between soil P storage capacity (SPSC) and equilibrium phosphorus concentration (EPC<sub>0</sub>) for Bh and Bt horizons.

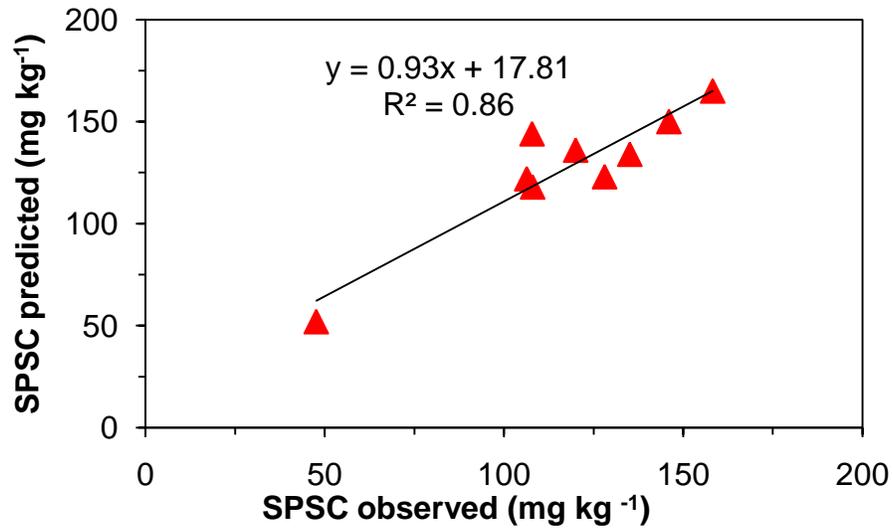


Figure 5-12. Relationship between soil P storage capacity (SPSC) predicted vs. SPSC observed for Bt samples.

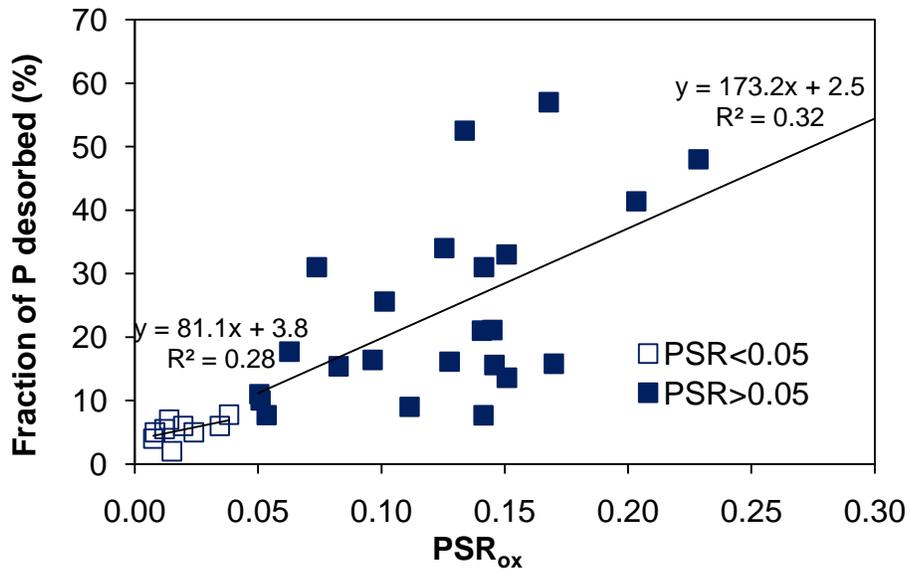


Figure 5-13. Relationship between Fraction of P desorbed and P saturation ratio calculated for the Bh horizons of Alaquods using P, Fe and Al in an oxalate extract (PSR<sub>ox</sub>).

## CHAPTER 6 CONCLUSIONS

Continuous application of P fertilizers in excess of plant requirements causes P loss to waterways resulting in accelerated eutrophication of surface waters. Sandy soils have higher risk of P loss because of limited P retention capacity, with Fe and Al often used as a surrogate for P retention. Vertical movement of P through the soil profile results in its contact with Bh horizons of Alaquods and Bt horizons of Paleudults which may act as P sinks. Loss of P via surface and subsurface movement is an environmental concern. Alaquods and Paleudults with sandy A and E horizons occur extensively in the coastal plain of the SE United States. It is critical to relate P sorption characteristics to compositional differences in Alaquod and Paleudult horizons and to evaluate implications for risk of P loss via subsurface flow in these soils. This study evaluated the P release potential from fertilizer-impacted Alaquods and Paleudults of coastal plain soils.

Alaquods of the SE U.S. are characterized by sandy textures, fluctuating water table and the presence of a subsurface Bh horizons below sandy surface horizons. In this study, the threshold PSR for Bh horizons was evaluated using oxalate ( $PSR_{Ox}$ ), Mehlich 1 ( $PSR_{M1}$ ) and Mehlich 3 ( $PSR_{M3}$ ) extractants. The change point was 0.05 for  $PSR_{Ox}$ ; 0.08 for  $PSR_{M1}$ ; and 0.09 for  $PSR_{M3}$ . Different threshold PSR for Bh horizons in comparison to surface horizons of Florida soils suggests that change point is influenced by the soil components. For most practical purposes, a PSR of 0.1 may be used when M1 or M3 is used as the extractant; the value falls well within the confidence intervals of 0 to 0.16 for M1 and 0 to 0.19 for M3.

Phosphorus release characteristics of surface and subsurface horizons of Alaquods were evaluated using SPSC. Validity of SPSC requires thorough extraction of the forms of Al and Fe with which P is associated in the sample as accomplished by oxalate extractant. Conversion factors of 1.8 and 1.3 were derived for SPSC calculated with M1 and M3 data for Bh horizons to compensate for the underestimation of the remaining capacity of the soil to adsorb additional P using these extractants. SPSC of Bh horizons was significantly higher than that of surface horizons due to much lower metal content and greater P loading of the later. The SPSC status of any horizon may be used to predict the consequences of water table management regimes with respect to P transport. For example, maintaining the water table below a positive Bh horizon could favor P retention and minimize risk of P loss from the soil.

Eluvial horizons of Alaquods have negligible P retentive capacity whereas E horizons of Paleudults can retain P due to the presence of metal oxides as indicated by oxalate-, pyrophosphate- and CBD extractions. Higher resistance to P desorption for Bt horizons of Paleudults relative to Bh horizons of Alaquods likely relates to the greater abundance of Fe oxides and kaolinite clay in Bt and the predominance of organically- over inorganically-complexed Al in the Bh. Differences in P sorption-desorption behavior between Bh and Bt relate to the difference in crystalline and noncrystalline inorganic components between these horizons. The threshold PSR (using oxalate P, Fe and Al in the PSR calculation) for Bt was found to be higher (0.12) relative to Bh (0.05). The lower PSR threshold for Bh horizons suggests that the proportion of metals serving as a high-energy binding site for P is lower for organically-complexed forms relative to inorganically-complexed noncrystalline forms.

The environmental risk of P loss is related to the compositional differences among horizons within the soil profile. Eluvial horizons of Alaquods have negligible P retentive capacity which accounts for the minimal retardation of P transport to underlying Bh horizons or to streams and ditches via shallow subsurface flow. On the other hand, in Paleudult soil profiles, the E horizons can retain relatively large amounts of P which in turn reduces the susceptibility of underlying Bt horizons to become loaded above the threshold PSR. Thus, it can be inferred that pedological, compositional, and hydrologic distinctions between Paleudults and Alaquods result in greater risk of P loss from Alaquods under comparable P loadings.

Since SPSC concepts have mainly been applied to sandy soils; there was a need to verify their applicability to finer-textured horizons (Bt) in coastal plain soils. The predictive validity of SPSC for Bt-horizon samples was tested by a method of known P additions. SPSC predictions of P “safe” sorption capacity ( $SPSC_{\text{predicted}}$ , determined experimentally) corresponded closely to the observed values ( $SPSC_{\text{observed}}$ , calculated based on oxalate extractant) with a  $R^2$  of 0.86 and a slope of 0.93. The above findings indicate that reduction in SPSC with P application can be predicted for loamy-to-clayey soil horizons as well. These results also indicate that although crystalline Fe oxides along with phyllosilicates play a dominant role for P retention in Bt samples, the noncrystalline metal oxides extracted by oxalate are the components that bind P most tenaciously and that control sorption below the threshold PSR.

Relationship between SPSC and equilibrium P concentration ( $EPC_0$ ) for Bh and Bt samples show that as long as SPSC is positive (PSR is below the change point) the  $EPC_0$  value is low; whereas the value increases considerably when SPSC is negative.

When the relationship between negative SPSC and  $EPC_0$  is verified,  $EPC_0$  values may be predicted from P, Fe and Al data that can be easily obtained from any soil testing laboratory. Environmental risk of P loss from soils may be more conveniently predicted by SPSC than by  $EPC_0$ .

This study also emphasized the need to develop management strategies to remove subsurface P from Alaquods and Paleudults to minimize degradation of water quality. Iron-oxide (FeO) impregnated filter paper has been successfully used as an indicator of plant P availability. It was observed that plant P availability is minimal when SPSC is zero or positive and increased with negative SPSC. Plant P availability as inferred from FeO-paper suggests that the P availability remains the same irrespective of compositional differences between subsurface horizons of Alaquods and Paleudults. Availability of P to plants from fertilizer-impacted Alaquod and Paleudult subsurface horizons is pertinent so that P can be removed from deeper horizons via phytoremediation to reduce risk of subsurface P loss through leaching.

Environmental risk of P loss along with plant P availability can be predicted using the SPSC concept for sandy and loamy-to-clayey soil horizons. Since SPSC is additive, it is possible to predict P storage and release across soil profiles to a depth of hydrological relevance for P transport, to include Bh or Bt horizons when present.

Further study is needed on calcareous soils for applicability of the SPSC concept when P retention is not regulated by Fe and Al in the soil. The SPSC approach is more rigorous than the use of STP and therefore can be possibly be used to develop an agronomic-environmental SPSC-based protocol. Research to date on SPSC has been on Florida soils. It will be beneficial to test the validity of this approach for acidic soils of

other regions. Soil P storage capacity can serve as a more readily-determinable alternative for  $EPC_0$  since the latter is consistently low when SPSC is positive. When SPSC is positive,  $EPC_0$  is minimal suggesting that up to the threshold PSR, P release is regulated only by Fe and Al, and other factors such as the clay content do not play a role in P retention. However, further research is needed to establish the relationship between SPSC and  $EPC_0$  when SPSC is negative.

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## BIOGRAPHICAL SKETCH

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