

ENHANCED RETENTION OF PHOSPHORUS APPLIED AS FLUSHED DAIRY MANURE

By

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To my Mom

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Abstract of Thesis Presented to the Graduate School
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Leaching of phosphorus (P) is a major concern in many areas of the world, especially in environments with karst topography that contain sensitive and valuable aquifers and springs. In one such area, North Florida of the SE United States, dairy farming is prevalent, and in such operations it is common to spray crop fields with flushed dairy manure (FDM) as a means of nutrient recycling. We investigated the fate of P in three sandy soils that typify and encompass large areas of the region. At the University of Florida Dairy Research Center, anaerobic digestion of FDM is currently practiced and provides many benefits including reduction of organic matter (OM) and mineralization of nutrients, including P. Three different P amendments were applied to soil columns in a randomized complete block design: raw FDM, digested FDM, and inorganic P. Since OM is known to form complexes and compete for sorption sites with P, thereby reducing P sorption, it was hypothesized that retardation of P would be least in soils receiving P as raw FDM and most in soils receiving inorganic P. Soil columns were kept under 20 cm of suction to promote unsaturated flow and amendments were applied at one half of the soil pore volume. Leachate was collected per pore volume and analyzed colorimetrically for total P (TP) and dissolved reactive P (DRP). Little evidence of OM transport of P was found in columns receiving

both raw and digested FDM, and through 30 pore volumes, very little leaching of P at all. The soils receiving inorganic P retarded leaching the least, and the extent of retardation was related to the soils inherent P sorbing capacity through Al and Fe oxide content. ANOVA output revealed significant differences in P accumulation in the soils among P amendments and soils, as well as a P amendment * soil interaction. Duncan's Multiple Range Test showed the P accumulated in soils receiving inorganic P to be significantly less than those receiving raw or digested FDM. Precipitation with Ca and Mg contained in the FDM, entrapment of particulate P, and immobility of OM due to soil chemistry are the suspected explanations for the lack of P breakthrough in FDM amended columns. The precipitated P is not expected to be stable and will leach into the deeper soil horizons. This study highlights the differences in P behavior in soils when delivered through different mediums and the complexity of the soil chemistry regarding P when FDM is amended to soils. It also demands further research in this area to better understand the processes and consequences of P leaching where similar practices are employed.

CHAPTER 1 INTRODUCTION

Background

Phosphorus (P) is an economically important input in both crop and livestock production systems (Hansen et al. 2002). It also poses an environmental risk if it migrates elsewhere in the environment. Increased concentrations of P in inland and coastal waters can lead to problems associated with eutrophication. Therefore, great importance has been given to determine the behavior and movement of P in the environment. Phosphorus is transported from agricultural fields via surface runoff and leaching. Leaching of P is especially important in sandy soils and even more important in soils overlying sensitive and valuable aquifers. As part of nutrient management strategies, it is common practice on many dairy farms to spray fields with flushed manure in order to improve crop production and pasture land. However, many times high P levels occur in soils as a result of N:P imbalance in the wastewater.

Studies by Iyamuremye et al. (1996) and others highlight the importance of the interaction of P with organic matter. Dissolved organic matter may compete with P for sorption sites in soil, displace sorbed P, and mediate movement by sorption with P itself. Particulate organic matter may physically block sorption sites, also promoting leaching of P. It follows that the application of inorganic phosphate may lead to less leaching of P than when applied in the presence of organics. Flushed dairy manure (FDM) wastewater has substantial amounts of suspended particulate and dissolved organic matter. However, innovative techniques in treating FDM are increasingly used to improve farm operations in various ways. Fixed-film anaerobic digestion of FDM is one such technique, and it significantly lowers and alters the organic matter content which may decrease leaching of P (Wilkie, 2004). Some of the benefits of anaerobic digesters include decreasing potential adverse effects the FDM may have on animal and plant life

in associated water bodies by lowering biological oxygen demand (BOD), decreasing fecal coliforms, and production of methane. It is possible the digested effluent could also be used to minimize P leaching. This study seeks to determine if there is less retardation of P when it is applied with organics compared to inorganic application, and if so, whether there is a difference in retardation between anaerobically digested FDM and raw FDM. The results of this study will highlight differences, if any, between the movement of inorganic and organic P, and contribute to the understanding of the role of organic matter in P mobility.

Hypotheses

The main hypothesis at the outset of this research was that organic matter in the FDM wastewater would compete with P for sorption sites in the soil, displace P on sorption sites, and mediate movement by sorption with P. Thus, soils applied with inorganic phosphate would retard P mobility the greatest. Because the digested FDM wastewater has less organic matter and organic P than the raw FDM wastewater, it should have greater retardation of P movement. The actual results of this study, however, documented behavior that directly contrasted with these initial expectations.

Objectives

- Determine P leaching potential inorganic and total P when soil is amended with raw FDM wastewater, anaerobically digested FDM wastewater, and inorganic phosphate.
- Determine the relative P sorption capacity of sandy soil materials used in the experiment.

Literature Review

The movement of P through soils has been examined in many studies (Sharpley et al. 2003). The interactions and transformations of P within the soil profile are important in understanding the leaching risk of P. Studies examining different forms of P and P sources have also highlighted important differences in reactivity and leaching potential. Research has shown

that P movement varies from soil to soil (Dodjic et al., 2004; Elrashidi et al., 2001; van Es et al., 2004) Many properties of soils have been shown to have an impact on P behavior. The complexity resulting from the multiple factors determining P behavior in soils has made it the subject of many studies. This review will examine literature concerning P movement when delivered in different forms, such as organic or inorganic fertilizers, the characteristics of different forms of P and its sources, especially raw and digested FDM, and the interactions of P in the soil that relates to its retention and leaching potential.

As the delivery and specific characteristics of P sources are important for understanding P fate, attention must be given to how it is derived, especially when considering organic amendments. The production of FDM is one option used by dairy operations to properly deal with livestock manure. Wilkie et al. (2004) describe a system utilized at the Dairy Research Unit at the University of Florida in which the FDM is anaerobically digested in a fixed-film digester. Dairy facilities are kept sanitary by flushing the manure down narrow alleys into a series of storage ponds where separation of bedding sand and very fibrous materials occurs mechanically and by sedimentation (Figure 1-1). The fixed-film digester contains media on which microbes colonize. The microbes include a symbiotic group of anaerobic bacteria which convert complex organic matter into smaller molecules including methane and carbon dioxide (Wilkie 2005). The benefits of anaerobic digestion include production of energy-yielding methane, mineralization of nutrients, including P, reduction of odors, inactivation of weed seeds, and lower pathogen levels. The reduction and change of the organic matter and mineralization of nutrients may have an effect on P mobilization when applied to the soil.

Dissolved P interacts with Fe, Al, Mn, and Ca in soils (Brady and Weil, 2002; Pardo et al., 2003). Many authors have found the amount of Fe and Al in soils to be important in

determining adsorption of P. Novak and Watts (2004) increased the sorption capacity of a sandy soil several fold by incorporating water treatment residuals that were flocculated with liquid alum ($\text{Al}_2(\text{SO}_4)_3$). Freese et al. (1992) found phosphate adsorption in German soils to be predominantly related to the amount of amorphous Fe and Al oxides. Also, Phillips (2002) found leaching to be related to the availability of Fe oxides on soil colloids. Al-bound P was the main form of P when Elrashidi et al. (2001) studied accumulation of P in Florida sandy soils (Myakka, Zolfo, and Adamsville). The P moved through the soil profile, but the low solubility of Al-phosphates (Al-P) in the acidic saturated zone of these soils prevented infiltration into groundwater. Ca-bound P (Ca-P) is also pH sensitive but in some forms they are extremely insoluble and considered largely as unavailable (Brady and Weil, 2002; Pardo et al., 2003). Zhou et al. (1997) found the high adsorption capacity of the Spodosol Bh horizon a result of aluminum-organic matter complexes. These complexes can form in the soil profile and affect the P leaching potential as they release P more readily than inorganic metal oxides.

Many studies have examined the interactions of P and other soil constituents, especially comparing these interactions when the P form is inorganic or organic. Most have found adsorption of inorganic P greater than organic P, but not all. In fact, Leytem et al. (2002) found organic P forms to be preferentially adsorbed over inorganic, ortho-P. They studied the behavior of four organic P compounds: three nucleotides, ATP, ADP, AMP, and IHP (inositol hexaphosphate) while KH_2PO_4 was used as an inorganic reference. All the organic P compounds had greater adsorption than KH_2PO_4 on Blanton Sand and Cecil sandy clay loam. In the Belhaven sandy loam, IHP had the greatest adsorption followed by KH_2PO_4 and the nucleotides. When Lilienfein et al. (2004) studied preferential adsorption of organic and inorganic P, the organic P already present in the soil was examined, not specific organic P compounds. They

found preferential adsorption of PO_4 over dissolved organic P. Because the number of phosphate groups on a molecule increases its sorption, and the number and density of phosphate groups in soil organic matter is variable, the adsorption characteristics vary as well, which explains differing results when the P source and form changes (Qualls and Haines, 1991; Leytem et al., 2002).

Leaching of P when using organic and inorganic fertilizers is often studied. Siddique et al. (2000) conducted leaching trials using five loam soils with P from anaerobically digested sewage, processed into dry biosolids, or inorganic Ca-P. Both sources of P were amended into the different soils and placed in soil columns (6.5 cm diameter and length of 30 cm) to a depth of 20cm. Although the biosolids contain organic P, after the digestion process, up to 80% of P is inorganic, and up to 97% of the P leached was inorganic. The columns were leached with a total of 5 L of deionized water. In most cases more P was released from the inorganic fertilized soils. This was attributed to slower P saturation in the biosolid treated soils caused by less soluble P in the biosolid amendments compared with the Ca-P fertilizer. Jiao et al. (2004) compared loads of P from soils receiving either organic or inorganic fertilizer. The soil was a fine-silty, mixed, frigid Typic Endoaquent. The composition of the soil was 300 g kg^{-1} sand, 540 g kg^{-1} silt, and 160 g kg^{-1} clay with $15.4 \text{ g total C kg}^{-1}$ and pH 6.1 in the 0- to 15-cm layer. Soil columns (10 cm diameter and 20 cm depth) were leached with synthetic rainwater and nutrient loads were calculated. Soils receiving inorganic fertilizer had 48% less dissolved reactive P load than soils receiving organic fertilizer. They stated that the soil had less sorption capacity for dissolved organic P than for inorganic P. The dissolved reactive load was positively related to the soil Mehlich-3 P concentration ($R^2 = 0.50$). Carefoot and Whalen (2003) studied leaching of P from a silt-loam Gleysol fertilized with inorganic (triple superphosphate) and organic (composted cattle

manure) P sources by measuring P in the subsurface water at a 60cm depth. It contained 0.3 to 1.7 mg P L⁻¹. Particulate P was the dominant P form at most sampling dates. Also, Phillips (2002) studied leaching of P from piggery wastewater using a Vertisol and a Spodosol in undisturbed soil cores (diameter of 30 cm and depth of 60 cm). Both molybdate reactive P and unreactive P were leached. The author lists unreactive P as dissolved organic P, particulate P, and non-reactive P. The Spodosol leached mostly molybdate reactive P (approximately 70%) because the wastewater contained about 70% of this form, and the soil had little adsorption capacity. The P leached from the Vertisol was mostly (approximately 80%) unreactive P because the molybdate reactive P was adsorbed by the soil colloids. These studies highlight differences in leaching potential of P from soils when different forms of inorganic and organic P are applied to different soils.

The interactions of organic matter with P and P adsorption sites are a critical area of research concerning P mobility. Organic colloids have been shown to transport metal contaminants in subsurface soils. Karathanasis and Johnson (2006) reported higher metal elutions up to four orders of magnitudes greater than the controls. Biosolids, derived from municipal wastes, and poultry manure were applied to an Alfisol, a Mollisol, and an Entisol. The metals, Cd, Mo, and Cr, were present in both the particulate and soluble fractions, and the significant increase was attributed to increased organic-metal complexation and exclusion facilitators. Iyamuremye et al. (1996) found that organic amendments to soil decreased P sorption sites and sorption that was related to changes in pH and exchangeable Al. Chardon et al. (1997) conducted a set of experiments examining the leaching potential of dissolved organic P (DOP) in cattle slurry applied on sandy soil. The DOP in the slurry consisted mainly of high molecular weight compounds. Leaching of P was examined using laboratory soil columns

(diameter of 15.3 cm and length of 100 cm) and outdoor lysimeters. The soil columns contained a quartzitic sand, with a total P of 6.5 mg kg^{-1} , up to 70 cm with a 16 cm layer of a sandy loam, containing 530 mg kg^{-1} , total P placed on top. The columns were leached with 100 mL of water twice a week for four months. Of the total P leached, more than 90% from the soil columns and more than 70% from the lysimeters leached as DOP, indicating its high mobility. Also, DOP in the soil pore water increased from about 10% of total P in the topsoil to more than 70% at 70 to 80 cm depth. Because the leaching of total P mainly occurred in periods of low Cl and NO_3 concentrations, indicative of high leaching rates, the authors suggested that the P transport was mediated by dissolved organic carbon and other colloidal particles. Eghball et al. (1996) also found deeper movement of P in soils receiving manure application than soils receiving equal amounts of inorganic P. They, too, suggested that the P moved in organic forms or chemically reacted with compounds in manure, enhancing solubility. This was examined further by Motoshita et al. (2003). They studied leaching of colloidal and dissolved P in soil column experiments using a surface loam soil with a high Olsen-P content (93 mg-P/kg). The columns were leached with artificial irrigation solution. Colloidal P leaching showed a minor increase with time, and dissolved P leaching was nearly constant. Dissolved P consisted of 81-86% of total P leached. There was a high correlation between dissolved P leaching and dissolved organic matter leaching ($R^2 = 0.82$). The P sorption was investigated and showed that the P was sorbed to or formed complexes with the dissolved organic matter. These studies show the importance of organic forms of P and dissolved organic matter relating to P mobility in the soil.

In addition to the interactions affecting P mobility, many have investigated the physical pathway and flow that P takes within the soil. This is especially important for finer textured soils. Djodjic et al. (2004) sought to establish a relationship between soil P levels and actual P

leaching in structured clay soils. Leaching of total P and dissolved reactive P were measured over three years in undisturbed soil columns. There was no general correlation between P concentrations and soil test P or P sorption indices of the topsoil. In one soil, where preferential flow was the dominant water transport pathway, water and P bypassed the high sorption capacity of the soil, resulting in high P losses. A comparison of two soil textural extremes, a clay loam and loamy sand, was conducted by van Es et al. (2004). The study took place on farm land with artificial drainage and liquid manure application. High P leaching losses were measured in the clay loam as soon as drain lines initiated flow after manure application. Flow weighted mean P leaching losses on clay loam plots averaged 39 times higher than those on loamy sand plots. Preferential flow was determined to be the main transport mechanism in the clay loam, but the authors stated P leaching from manure applications on loamy sand soils do not pose environmental concerns as long as soil P levels remain below saturation levels. This is further supported by Akhtar et al. (2003) where five soils of differing textures were leached with synthetic acid rainwater enriched with inorganic and organic P. At low flow rates, P appeared in the drainage water soon after application of either inorganic or organic P for the silt loam soil. Soils in which matrix type flow dominated had little or no increase in drainage water P. Elevated P concentrations in the drainage water could not be explained by the P adsorption strength of the soils with the possible exception of the sandy loam soil, where the outflow P concentration was consistently low.

Agricultural practices, such as plowing, affect the porosity of the soil. Geohring et al. (2001) found that plowing in liquid manure applications before irrigation greatly reduced P leaching. Column studies using pack soil and artificial macropores were designed to examine the role of macropore size on P sorption to pore walls. They found that soluble P may be transported

through macropores 1mm or greater with negligible P sorption to pore walls. When macropores were absent, no measurable P was transported through the soil column. The macropores were disrupted from plowing which promoted matrix flow and reduced P leaching.

The literature, to date, explains many of the factors concerning the potential for P mobility in soils. With regards to sandy soils, studies have shown variable ability to uptake P. Some of the sandy soils had little capacity while others almost completely prevented leaching. This is due, in part, to the inherent P sorbing compounds present in the soil, such as Fe and Al oxides. When organic amendments are added to the soil, complexes that mediate transfer of P can form. The extent that this occurs varies among soils and also depends on the P source. Organic sources of P, such as raw and digested FDM, can have different effects on P mobility than other organic sources. The consequences of excessive P leaching, such as eutrophication, require an understanding of all the contributing factors. Further research of P movement in various soils and application methods will aid in the development of management practices that both aid in agricultural production and prevent water pollution.

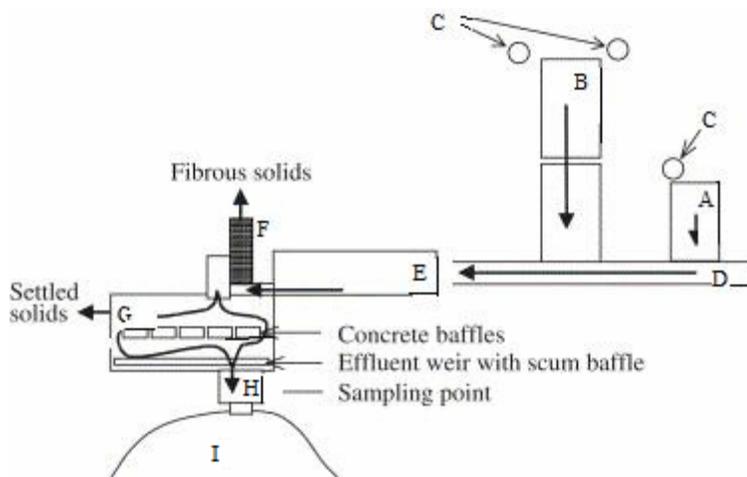


Figure 1-1. Schematic layout of University of Florida Dairy Research Unit manure-handling system. Heavy arrows indicate flow of flushwater and manure solids. A) Milking parlor. B) Freestall barns. C) Flushwater holding tanks. D) Wastewater collection channel. E) Sand-trap. F) Mechanical separator. G) Sedimentation basin. H) sampling Pit. I) Primary storage pond. (Wilkie, 2004)

CHAPTER 2 MATERIALS AND METHODS

Soil Selection and Sampling

Sandy horizons were sampled from soils of three series that occur in the coastal plain of the southeastern USA: Tavares (sandy, hyperthermic, Typic Quartzipsamment), Millhopper (loamy, siliceous, hyperthermic, Grossarenic Paleudult), and Orsino (sandy, hyperthermic, Spodic Quartzipsamment). Tavares and Millhopper soils are extensive in Florida across a range of moderately-well-drained landscapes, as are the taxonomic families they represent. Orsino soils are commonly associated with old dunes or other landforms underlain by deep sandy parent materials and occupied by oak scrub or sand pine plant communities. These three soils encompass a wide range of sandy soil horizons and environments in Florida, and were selected on this basis. Other research criteria satisfied by these soils is that they (i) prospectively provide an intermediate and representative range of P retardation and (ii) they occur on some leaching-prone landscapes which are the types of soil/landscapes to which results of this study should apply. The E2 horizons of the Millhopper and Tavares and the Bw horizon of the Orsino were chosen for the column experiment described below. All soils were air dried and sieved through a 2 mm sieve prior to experimental use.

Soil Analyses

Oxalate-Extractable Iron (Fe) and Aluminum (Al)

The Fe and Al content of the soils was determined by extraction with acid ammonium oxalate in the dark (Baril and Bitton, 1967; McKeague and Day 1966). This method extracts both amorphous inorganic Fe and Al and organic complexed Fe and Al in soils. The acid oxalate extracting solution was made by mixing 700 mL of 0.2 M ammonium oxalate and 535 mL of 0.2 M oxalic acid together and adjusting pH to 3.0 by using either of the base solutions. For each

sample, 2 g of soil was placed in 50 mL centrifuge tubes that were wrapped in aluminum foil to exclude light. A 50-mL aliquot of acid oxalate extraction solution was added to the soil in tubes, which were then capped tightly and placed in a reciprocal shaker at low speed for 4 hours. Tubes were centrifuged for 20 min at 2000 rpm, and supernatant solutions filtered through Whatman 42 filters and stored cold (4°C) until analysis within a few days.

An atomic absorption spectrophotometer was used to determine Fe and Al content. The standard solutions were prepared so that the matrix contained the same concentration of acid oxalate as the extracting solutions.

Total P (TP) of Soils

The TP of the three soils was determined by using an ashing and acid digestion procedure (Anderson, 1976). A 50 mL beaker containing 1 g of soil was placed into a muffle furnace at 350°C for one hour and at 550°C for two more hours. After cooling, 20 mL of 6M HCl was added, and it was allowed to slowly evaporate on a hotplate. After the sample dried, the temperature was raised briefly and then allowed to cool. Then 2.2 mL of 6M HCl was added, and the beakers were heated so that the residue was easily dislodged. The mixture was then transferred to a funnel with a Whatman #42 filter paper, and the solution filtered into 50 mL volumetric flask. The beakers and the filters were rinsed repeatedly with deionized water, and the volume of the flasks was brought up to 50 mL.

Analysis of P in extracts was done colorimetrically (Murphy and Riley, 1962), with P standards ranging from 0 to 35 mg L⁻¹. 0.5 mL of each standard and unknown solution was placed in a test tube. Reagent A_s was prepared by dissolving 12 g of ammonium molybdate in 100 mL of H₂O and 0.2908 g of antimony potassium tartrate in another 100 mL of H₂O; both of these solutions were added to 1 L of 2.5M H₂SO₄ and diluted to 2 L. This was kept stored in a

dark, cool place. Reagent B_s was made fresh from a stock solution of Reagent A_s for each analysis. To make Reagent B_s, 1.056 g of ascorbic acid was dissolved in 200 mL of Reagent A_s.

Reagent B_s was added in 4 mL aliquots to test tubes containing soil extractant solutions or standards. Then, 10 mL of deionized H₂O was added while turning the tube to rinse the sides. Blue color developed in the test tubes commensurate with the amount of P they contained. The absorbance readings were taken on a spectrophotometer at 880 nm wavelength after color developed for thirty minutes. The standard curve was accepted if the R² was at least 0.997. The absorbance readings of the soil samples were interpolated on the standard curve to determine P mg L⁻¹.

Relative Phosphorus Retention Capacity (RPA)

The RPA is a procedure developed to provide a quick practical measure of the P sorption capacity of sandy soils (Rhue et al, 1994). This analysis used Reagent A and Reagent B that differs somewhat from the Reagent A and Reagent B that was used in determining TP of the soils. For convenience, the reagents used in the TP of soil procedure will be referred to as Reagent A_s and Reagent B_s, and the reagents used in this and other analyses will be referred to as Reagent A_w and Reagent B_w. Reagent A_w was prepared by combining three different solutions: 12 g of ammonium molybdate dissolved in 200 mL of distilled water, 0.2908 g of antimony potassium tartrate dissolved in 50 mL of distilled water, and 144 mL concentrated sulfuric acid (18M) in 1500 mL of distilled water that was allowed to cool. The solution mixture was then diluted to 2 L, mixed, and stored in a cool, dark place. Prior to each analysis, Reagent B_w was made by adding 0.75 g of ascorbic acid to 50 mL of Reagent A_w and diluting to 500 mL.

The RPA was determined by placing 10 g of soil in 20 mL scintillation vials and adding 2 mL of 2000 mg L⁻¹ P solution. The vials were capped and vigorously shaken. This was allowed to equilibrate for 24 hours. Whatman #1 filters were cut to fill the bottom of 50 mL polyethylene

centrifuge tubes that had 6 to 8 small holes in the bottom. The filter was also wetted with 50 mM KCl and centrifuged by itself at 1500 g for 5 min to drain excess KCl solution. The wet soil was transferred to the centrifuge tubes and collection cups were taped to the bottom. The tubes were then centrifuged at 1500 g for 5 min in order to extract the soil solution. The solution was then filtered through 0.45 μm filters, and 0.1 mL aliquots were put in glass centrifuge tubes. A set of P standards were made by transferring 0.1 mL of 0, 50, 100, 200, 400, 600, 800, 1000, 1500, and 2000 mg L^{-1} P standards in glass centrifuge tubes. All were placed in a drying oven at 70°C overnight. After drying, 20 mL of 0.1M HNO_3 was added to all tubes. The tubes were mixed vigorously and 0.5 mL aliquots were added to 5 mL Reagent B_w . Color development proceeded for two hours, at which time absorbance readings were taken at 880 nm.

The amount of P adsorbed (S) was calculated using the formula:

$$S = [(2000 - C_{ps}) \times 2] / 10,$$

where S is the amount of P adsorbed ($\mu\text{g/g}$ of soil), C_{ps} is the P concentration in pore solution after 24 hour equilibration with soil ($\mu\text{g/mL}$). With S, the RPA was calculated thusly:

$$\text{RPA} = S/400,$$

where 400 $\mu\text{g/g}$ represents the maximum adsorption possible under the experimental conditions.

Particle Size Distribution Analysis (PSDA) of Soils

The particle size distribution for each soil was determined (Soil Survey Staff, 1992). To begin, 100 mL of Calgon (5% solution of sodium hexametaphosphate) was added to 250 mL Erlenmeyer flasks containing 50 g of dried soil. The flasks were stoppered and placed on a shaker for 16 hours. The contents were transferred into cylinders and were diluted to 1000 mL with deionized water while thoroughly rinsing the flasks. The cylinders were shaken and inverted 6 times. They were then placed in a bath at 3 min intervals. After the allotted time, a glass pipette was lowered into the cylinder at the allotted depth to withdraw the clay fraction. The clay

aliquots were placed in weighed, metal cups, dried in an oven, and weighed again the following day. The contents of the cylinders were then rinsed through a No. 325 sieve (48- μm mesh) to remove the clay and silt. The remaining sand was collected and after drying, it was fractionated into very coarse (2000-1000 μm), coarse (100-500 μm), medium (500-250 μm), fine (250-100 μm), and very fine (100-48 μm particles using sieve Nos. 18, 35, 60, 140, and 325. Sand fractions were weighed and the distribution was calculated using the formulas:

$$\% \text{Sand} = (\text{sand weight}) (100) / (\text{sample weight}),$$

$$\% \text{Clay} = \{[(\text{metal cup} + \text{clay weight} + \text{Calgon}) - \text{metal cup} - \text{blank weight}](40)\}(100) / (\text{sample weight}),$$
$$\% \text{Silt} = 100\% - \% \text{Clay} - \% \text{Sand}.$$

Flushed Dairy Manure Analyses

Flushed dairy manure samples were collected at the Dairy Research Unit in Hague, Florida. The raw FDM was collected from the pump sump that feeds into the digester. The digested FDM was obtained directly from the effluent line. All samples were stored in a cold room at 4°C. The FDM samples were primarily analyzed for TP, DRP, pH, and chemical oxygen demand (COD). The samples from September 14, 2005 were chosen as treatments for this study out of all samples taken because the digested and raw FDM showed typical differences in DRP and COD, i.e., DRP was greater, and COD less, for digested FDM. It was important for the purposes of this study that digested and raw FDM show these differences because the hypothesized differences in potential P leaching relates to the proportion of DRP to TP. The pH was measured with a standard, portable pH meter. The TP was determined by taking a 5 mL aliquot of wastewater and diluting to 10 mL with deionized water. From this mixture, 0.1 mL was taken and placed in a Hach COD reactor test tube. This was done so no more than 2.5 μg of P would be contained in each test tube. The samples were dried and then ashed in a muffle furnace at 300°C for 1 hour and at 550°C for two more hours. Aliquots of 0.1 mL P standard

solutions of 0, 5, 10, 15, 20, 25, and 30 mg L⁻¹ P were transferred into test tubes and were evaporated. Then, 5 mL of Reagent B_w was added to each sample and standard, and blue color developed for two hours at which time absorbance readings were taken at 880 nm.

Total P (TP) Method Investigation - HCl Digestion vs Only Ashing

Five mL of FDM was diluted to 10 mL with deionized water. After mixing, 0.1 mL aliquots, totaling 12, were transferred to Hach COD reactor test tubes. All test tubes were dried using the COD reactor at 120°C. After drying, all test tubes were placed in a muffle furnace at 300°C for 1 hour and 550°C for two hours. After cooling, 6 of the wastewater samples, two of the 30 mg L⁻¹ P standards, and one of the 0 mg L⁻¹ P standard received 5 mL 6 M HCl. These were heated in the COD reactor for several hours at 120°C, just above refluxing temperature but, no visible signs of boiling, until all liquid had evaporated. After cooling, 5 mL of Reagent B_w was added to each sample and a set of standards, and blue color developed for 2 hours at which time absorbance readings were taken at 880 nm. The P concentrations of the samples that were HCl digested with 6 M HCl were compared with those that were not. It was determined that this modified procedure was satisfactory for the purposes of this study, enabling rapid assessment of TP in small volumes of column effluent (described below). The mean TP of the FDM that had HCl digestion was 46.5 ± 0.6 mg L⁻¹ and the mean TP of the FDM with no HCl digestion was 48.6 ± 0.8 mg L⁻¹.

Dissolved Reactive Phosphorus (DRP)

In order to determine if any constituent of the wastewater interfered with analysis reagents and skewed results, a spike recovery test was performed. The raw and digested FDM was filtered through 0.45 µm filter, and 0.5 mL was diluted to 15 mL with distilled water. From this, 1 mL aliquots were transferred into test tubes. In duplicate, samples were spiked with 0.1 mL of 0, 5, 10, and 15 mg L⁻¹ P standards. A set of standards was made: 0.1 mL of 0, 5, 10, 15,

20, 25, and 30 mg L⁻¹ P. Five mL of Reagent B_w was added to each sample and standard, and blue color developed for two hours at which time absorbance readings were taken at 880 nm. The increasing spike was checked to be linear ($r^2 > 0.998$).

Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) of the raw and digested FDM was determined as an indication of digestion. The mg L⁻¹ COD results are defined as the mg of O₂ consumed per liter of sample used in the procedure. The anaerobic digestion process eliminates a significant amount of the COD from the raw FDM. COD analyses were performed as described in Wilkie (2004). First, 500 mL of each FDM was homogenized in a blender for 2 minutes, and a 2 mL aliquot was added to the COD Digestion Reagent Vial provided by Hach. Also, a subsample of the homogenized FDM was centrifuged at 12,000 min⁻¹ for 30 min, and the supernatant was sampled to determine the soluble COD. Vials were heated in the Hach COD reactor for 2 hours at 150°C. The reagent contains dichromate (Cr₂O₇⁻²), which oxidizes organic compounds and is reduced to the green chromic ion (Cr⁺³). The amount of Cr⁺³ produced is determined colorimetrically from which the COD is calculated.

Soil Column Experimental Procedures

Column Construction

Twenty seven cylindrical soil columns were used in this experiment. They have an inside diameter of 1.6 cm and stand 20 cm tall. The columns have a bushing-like fitting that contains a glass frit at the bottom. A nipple at the bottom and a piece of glass tubing are made continuous by a piece of clear plastic tubing. The collection vial encompasses the glass tubing so that suction can be applied to the vial, pulling the soil leachate under unsaturated flow. The continuous suction is supplied by an elevated Erlenmeyer flask that has a siphon held to it. Air leaks anywhere on the column are mediated by tape and petroleum sealant. The elevation of the

Erlenmeyer flask controls the amount of suction. For this experiment the flasks were held at an elevation that results in 20 cm of suction (Figure 2-1).

Pore Volume Determination

The mass of soil used in each column for this experiment was 20 g. The pore volume for each soil was determined by placing 20 g of soil in weighed columns, wetting with 50 mM KCl, and applying 20 cm of suction. When excess KCl finished passing through the column and any addition of KCl resulted in immediate elution, the column was weighed again to determine the pore volume.

Background P

The background P of the soils was determined by elution with 50 mM KCl. The first background value was collected from leachate from the initial wetting of the soil. The subsequent background values were taken from leachate obtained by the addition of 0.5 pore volumes of KCl to the columns at least one day apart. A total of 6 KCl pore volumes were collected to get steady background P values. Then, 2.5 mL aliquots of the soil leachates were filtered through 0.45 μm filter, placed in test tubes, and dried in an oven overnight at 70 C. A set of standards: 0.1 mL of 0, 1, 2, 3, 4, and 5 mg L^{-1} P was made. Each sample and standard received 5 mL of Reagent B_w, and color developed for two hours at which time absorbance readings were taken at 880 nm.

Flushed Dairy Manure (FDM) Storage and Sampling

Approximately 11.5 liters of both raw FDM and digested FDM were collected for the experiment. They were collected and stored in 3.8 L jugs at 4°C. A procedure was devised to minimize anticipated clogging of soil columns and to provide a regular consistency of the FDM amendments when applied to soil columns and when sampled for analytical purposes. The largest suspended particles were allowed to settle at the bottom of the jugs. The smaller particles

remained suspended. At the time of each addition, the jugs were slightly shaken, in a similar way, to mix the suspended particles and then a small portion was transferred to a separate beaker. Each jug was not used once it had become halfway empty. This ensured an approximately equal consistency of the FDM added to the soil columns that was evident by observation.

Leaching Procedure

Each soil received three treatments: raw FDM, digested FDM, and a solution of KH_2PO_4 . Based on TP analyses the solution of KH_2PO_4 was prepared at $48 \text{ mg L}^{-1} \text{ P}$ with a 50 mmol KCl background electrolyte concentration. This ensured roughly equal TP values for all amendments. Treatments were done in triplicate per soil in a randomized complete block design. To allow for adequate sorption of P, the rate of addition was 0.5 pore volume of the amendment per addition. The leachate was collected per whole pore volume.

The rate of the additions was limited by clogging of some columns receiving FDM amendments. In some cases more than 48 hours elapsed for complete infiltration. The clogging occurred in the top portion of the columns as the larger particulates settled there and slowed infiltration. The columns were kept in dark as much as possible to discourage algal growth.

Leachate Analyses

The soil leachates were analyzed for TP and DRP. Total P determination was performed by the ashing procedure without HCl digestion, as described in the “Total P method investigation” section. Dissolved reactive P analysis included filtration, dilution if needed, and the addition of Reagent B_w . Absorbance was taken at 880nm after 2 hours.

Statistical Analyses

An ANOVA was run evaluating the statistical significance of the randomized complete block design experiment, and Duncan’s Multiple Range Test was used to determine significant differences in the P accumulated in the columns among the three treatments. Both of the

preceding tests utilized SAS software. A regression analysis was used to demonstrate the significance of the relationship of P accumulated in the columns receiving P as PO_4 and the RPA value of the soil.



Figure 2-1. Columns containing 20g of soil were kept under 20 cm of suction utilizing Erlenmeyer flasks to ensure unsaturated flow of leachate, which was collected in glass vials.

CHAPTER 3 RESULTS

Soil Descriptions

The Tavares sand was collected on May 18, 2005 in Alachua County, FL 604m south of Lake Mize in the Austin Cary Memorial Forest. The soil was collected by boring three holes, 20 cm apart, with an auger. Tavares sand is derived of sandy marine deposits and is moderately well drained. It occurs in a forested environment on a <2% slope dominated by oak and long-leaf pine. The Tavares soil horizons are described in Table 3-1.

The Millhopper soil was collected on May 18, 2005 in Alachua County, FL. University of Florida, 126 m WNW (307°) from the NW corner of Museum Rd and Newell Dr. The soil was similarly collected by boring three holes, 20 cm apart, with an auger. It is a moderately well drained soil derived from sandy marine deposits. It occurs in a small forested area on a <5% slope dominated by sweetgum, hickory, oak, and other small trees and shrubs. Table 3-2 shows the descriptions of the Millhopper soil horizons.

The Orsino soil Bw horizon was obtained from the Soil Mineralogy lab at the University of Florida. It was collected by Willie Harris from a vertical exposure of an old sand dune near Cedar Key (Levy County), FL, during a professional field trip. It occurred in an Orsino fine sand map unit and the profile conformed to the Orsino series (personal communication, Willie Harris). Orsino soils typically occur on elevated ridges and knolls. They have low available water capacity and fertility, but still support natural vegetation including slash pine, sand pine and scrub oak. A description of this soil taken from the Levy County Soil Survey (Slabaugh et al., 1996) is included in Table 3-3. The typical pedon is listed as being located 3,300 feet (approximately 1000 m) north and 250 feet east (approximately 76 m) of the southwest corner of sec. 11, T. 14 S., R. 16E. The Bw horizon used in this study was morphologically similar to the

Bw1 of the Levy County typical pedon, with the exception that the matrix color was 10YR 5/6 instead of 10YR 6/4.

Soil Characterization

The results of the analyses characterizing the soils in Table 3-4 show some important properties for P adsorption and mobility in sandy soils. The TP of the three soils were typical and indicated little or no impact from anthropogenic activities regarding P loads. The RPA varied considerably among the soils with the Tavares soil having an unexpectedly high value, but there was a commensurate increase in the amount of Fe and Al oxide present, and there was high correlation ($r^2 = 0.90$) between the RPA and the total amount of oxalate extracted Fe and Al (Figure3-1) . The Orsino Bw horizon had the highest percentage of fine sand (Table 3-5), consistent with its formation in dunal parent material which characteristically is well sorted and dominated by fine sand. Note that the Tavares E1 and Millhopper E1 were not used in the column experiment.

Flushed Dairy Manure (FDM) Characterization

Mean TP values of the raw and digested FDM are similar whereas the mean amount of DRP in the digested FDM is about 25% more than in the raw FDM (Table 3-6). The spike recovery test results showed no interference in the DRP testing procedure. The digestion process removed over half the COD present in the wastewater, but did not appear to significantly change the pH.

Analyses of P in Leachate

Background P values (Figure 3-2) stabilized after 6 pore volumes. Less than 0.1 mg L^{-1} P was detected in any horizon with the Millhopper E2 horizon having slightly higher values. Soil differed with respect to retardation of P applied as inorganic P (Figure 3-3). The Millhopper soil started to have breakthroughs of P on the second pore volume. The Orsino and Tavares soils

adsorbed virtually all P until the 9th and 19th pore volume, respectively. This order of P adsorption capacity is in agreement with the RPA values of the soil horizons.

In all soils, there were higher values of TP in the leachate for the first few pore volumes. These values decreased until the 5th pore volume. The largest difference of TP between raw and digested FDM amended soils was in the Millhopper soil where leachate from the digested FDM was slightly higher than those derived from the raw FDM. The leachate of the Tavares soil derived from the raw and digested FDM showed little differences in TP values. There were also little differences from the Orsino soil, except for the leachate from the raw FDM having higher values initially and the digested FDM leachate being higher at the last pore volumes. In all cases, after the breakthrough of P derived from the inorganic P treatment occurred, the level of TP in the leachate derived from the raw and digested FDM was lower than those derived from inorganic P.

The DRP in the leachate roughly follows the same trends as the TP (Figures 3-3, 3-4, and 3-5). Leachates derived from the raw and digested FDM had low levels of DRP for the Tavares and Orsino soils, except for an increase in the last pore volumes derived from the digested FDM in the Orsino soil. The DRP in the leachate from the raw and digested FDM from the Millhopper soil is higher than other soils. There is an increase in the last pore volumes as well as a spike in concentration at the 20th pore volume. The largest differences between TP and DRP values occur during the initial pore volumes (Figure 3-5). Afterwards the levels of P are more closely aligned, especially for Tavares and Orsino.

Soils and P Accumulation: FDM vs Phosphate

Calculated P accumulation in the soils (Figure 3-6) shows that the raw and digested FDM accumulate similarly in each soil and among all soils, and to a significantly greater extent than for the inorganic P treatment (Tables 3-7 and 3-8). These values were derived by subtraction of P

in leachate from that which was added to the columns. The P delivered as inorganic P accumulated differently and relates to the RPA (Figure 3-7), which was found to be well correlated with the amount of oxalate extractable Fe and Al oxides (Figure 3-1). Table 3-7 shows the accumulation of P in the soil columns only differ significantly between the inorganic P amendments and the FDM amendments. Differences between soils were not tested statistically due to the soil x amendment interaction (Tables 3-7 and 3-8).

Table 3-1. Tavares soil description

Horizon	Depth (cm)	Description
A	0-15	Dark grayish brown (10YR 4/2) sand, clear boundary.
AE	15-50	Brown (10YR 5/3) sand, gradual boundary.
E ₁	50-75	Brown (10YR 5/3) sand, gradual boundary.
E ₂	75-95	Light yellowish brown (10YR 6/4) sand, gradual boundary.
E ₃	95-120	Pale brown (10YR 6/3) sand, redox concentrations and depletions, gradual boundary.
E ₄	120-200	Very pale brown (10YR 7/3) sand, redox concentrations and depletions, gradual boundary.

Table 3-2. Millhopper soil description

Horizon	Depth (cm)	Description
A	0-14	Very dark grayish brown (10YR 3/2) sand, clear boundary.
AE	14-29	Brown (10YR 4/3) sand, clear boundary.
E ₁	29-52	Yellowish brown (10YR 5/4) sand, gradual boundary.
E ₂	52-83	Brown (10YR 5/3) sand, gradual boundary.
E ₃	83-105	Pale brown (10YR 6/3) sand, gradual boundary.
E ₄	105-118	Light gray (10YR 7/2) sand, redox concentrations and depletions, red matrix, clear boundary.
Bt	118-140	Brown (7.5YR 5/4) sandy loam, redox concentrations and depletions, clear boundary.
Btg1	140-175	Light gray (10YR 7/1) sandy clay loam, redox concentrations and depletions, gradual boundary.
Btg2	175-189	Light gray (10YR 7/1) sandy clay, redox concentrations and depletions.

Table 3-3. Orsino typical pedon description, taken from the Levy County Soil Survey Report (Slabaugh et al., 1996). The Orsino Bw horizon used in this study was collected from a similar Orsino soil in Levy County.

Horizon	Depth (cm)	Description
A	0-10	Gray (10YR 5/1) fine sand; weak fine granular structure; very friable; many fine roots, strongly acid; clear wavy boundary.
E1	10-20	Very pale brown (10YR 7/2) fine sand; single grained; loose; strongly acid; clear wavy boundary.
E2	20-32	White (10YR 8/1) fine sand; single grained; loose; strongly acid; abrupt irregular boundary.
Bw and Bh	32-122	Brownish yellow (10YR 6/6) fine sand (Bw); single grained; loose; common fine roots; discontinuous lenses of weakly-cemented dark yellowish brown (10YR 4/4) fine sand (Bh) that are 1 to 5 cm thick at the upper contact of the horizon; strongly acid; gradual wavy boundary.
Bw1	122-147	Light yellowish brown (10YR 6/4) fine sand; few fine faint brownish yellow (10YR 6/6) mottles; single grained; loose; few fine roots; strongly acid, gradual wavy boundary.
Bw2	147-175	Brownish yellow (10YR 6/8) fine sand; single grained; common fine distinct strong brown (7.5YR 5/8) mottles; loose; few fine roots; strongly acid; gradual wavy boundary.
C	175-200	White (10YR 8/1) fine sand; few medium distinct yellow (10YR 7/8 mottles; single grained; loose; moderately acid.

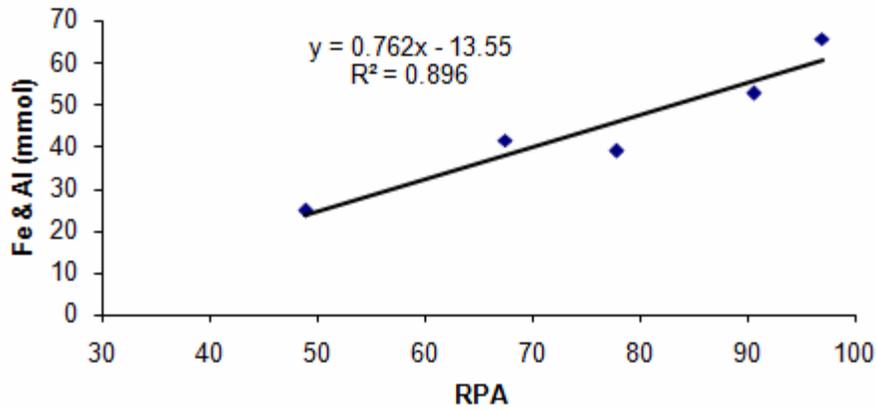


Figure 3-1. Correlation between total oxalate extracted Fe and Al in molar concentrations and RPA values of the soils. Data points include soils Millhopper E2, Orsino, Millhopper E1, Tavares E2, and Tavares E1 in order of ascending RPA (Table 3-4).

Table 3-4. Characterization of soils collected. (n = 3)

Soil	TP mg kg ⁻¹	RPA (%)	Fe † mg kg ⁻¹	Al † mg kg ⁻¹	Total Fe & Al mmol kg ⁻¹	Sand g kg ⁻¹	Silt g kg ⁻¹	Clay g kg ⁻¹	pH
Orsino Bw	177	67	544	857	41.5	980	10	10	4.0
Tavares E1	208	97	811	1380	65.7	950	††	††	5.8
Tavares E2	200	91	856	1008	52.7	950	30	20	5.7
Millhopper E1	231	78	279	919	39.0	940	40	20	6.3
Millhopper E2	169	49	324	511	24.7	950	30	20	6.0

† oxalate extracted

†† clay was lost, so only sand is reported

Table 3-5. Sand size distribution among soils collected and pore volume of soil horizons used in the experiment.

Soil	% Very Coarse	% Coarse	% Medium	% Fine	% Very Fine	Pore volume at 20 cm suction (mL)
Orsino	.2	3.0	22.6	66.7	5.3	5.0
Tavares E1	.3	7.0	44.5	36.2	6.9	
Tavares E2	.3	6.1	42.4	37.7	8.5	4.2
Millhopper E1	.3	5.8	43.9	40.3	3.5	
Millhopper E2	.3	5.7	45.9	39.3	4.1	4.7

Table 3-6. Selected characteristics of raw and digested flushed dairy manure (FDM). (n = 3)

	Total P mg L ⁻¹	Dissolved Reactive P mg L ⁻¹	Dissolved Organic P mg L ⁻¹	% DRP	Total COD† mg L ⁻¹	Soluble COD mg L ⁻¹	pH
Raw FDM	45.8	29.5	1.0	64	3360	1770	7.4
Digested FDM	48.9	39.1	1.0	80	1595	696	7.3

† COD = Chemical oxygen demand

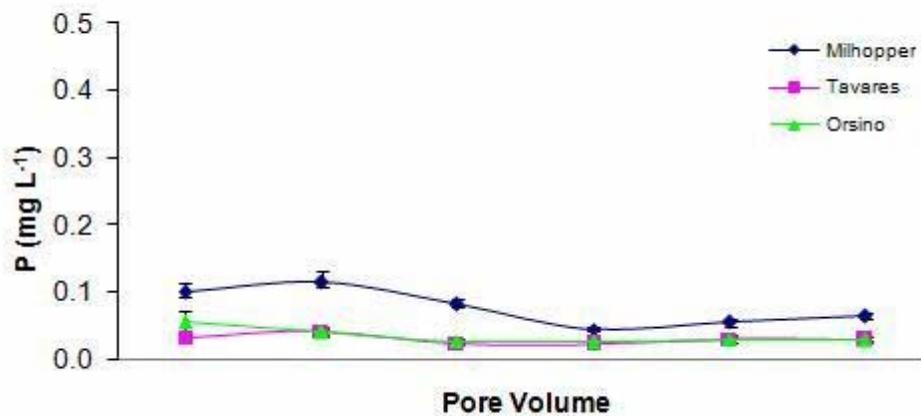


Figure 3-2. Background P of leachate obtained from addition of 50mM KCl solution to soil columns.

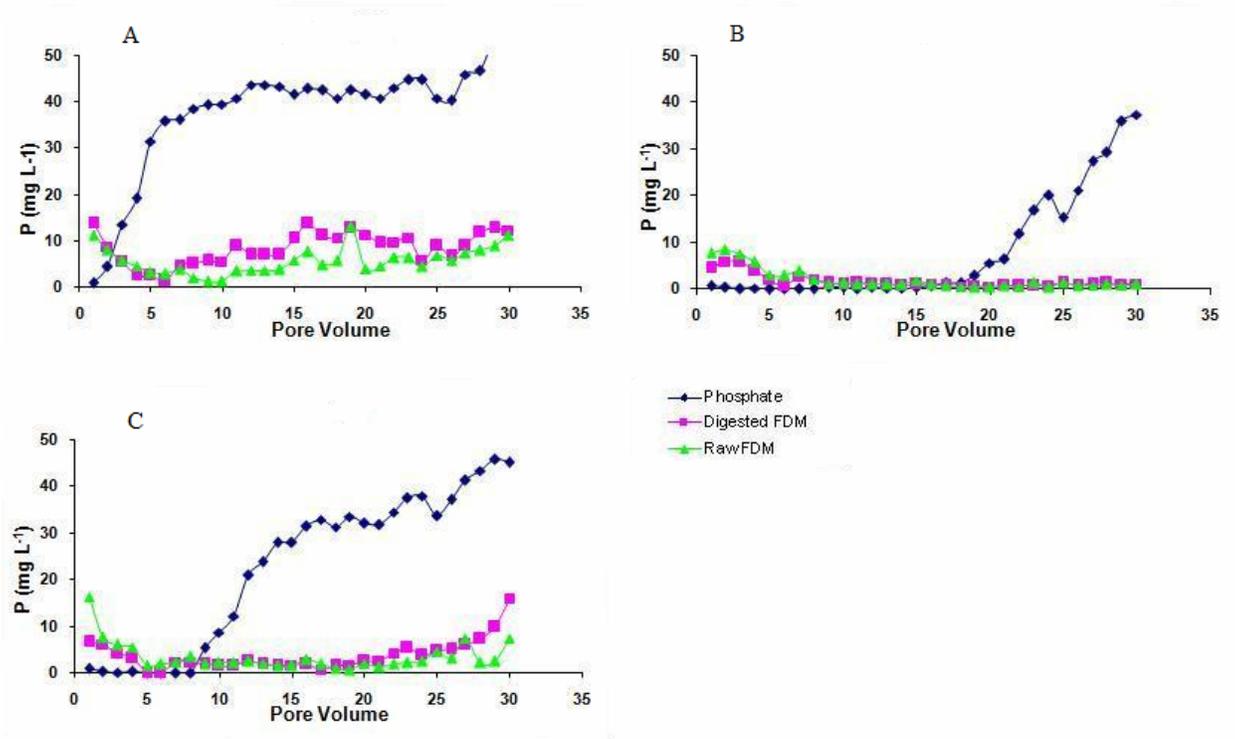


Figure 3-3. Total P (TP) in leachate for each pore volume. Definite breakthroughs can be seen in the columns receiving the inorganic P amendments contrasted with the lack of breakthroughs in the columns receiving the flushed dairy manure (FDM) amendments. A) Millhopper TP. B) Tavares TP. C) Orsino TP.

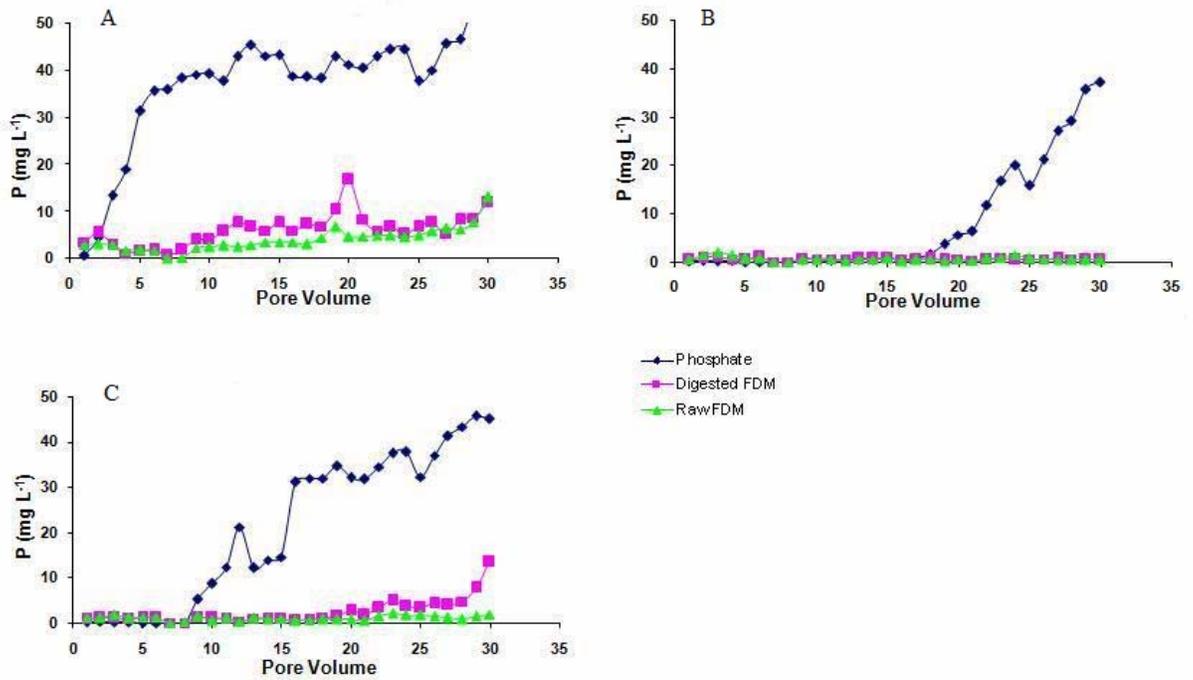


Figure 3-4. Dissolved reactive P (DRP) concentrations in leachate for each pore volume. With regards to flushed dairy manure (FDM) amended columns, concentrations DRP and total P are similar which suggests that nearly all total P leaching through the columns is DRP. A) Millhopper DRP. B) Tavares DRP. C) Orsino DRP.

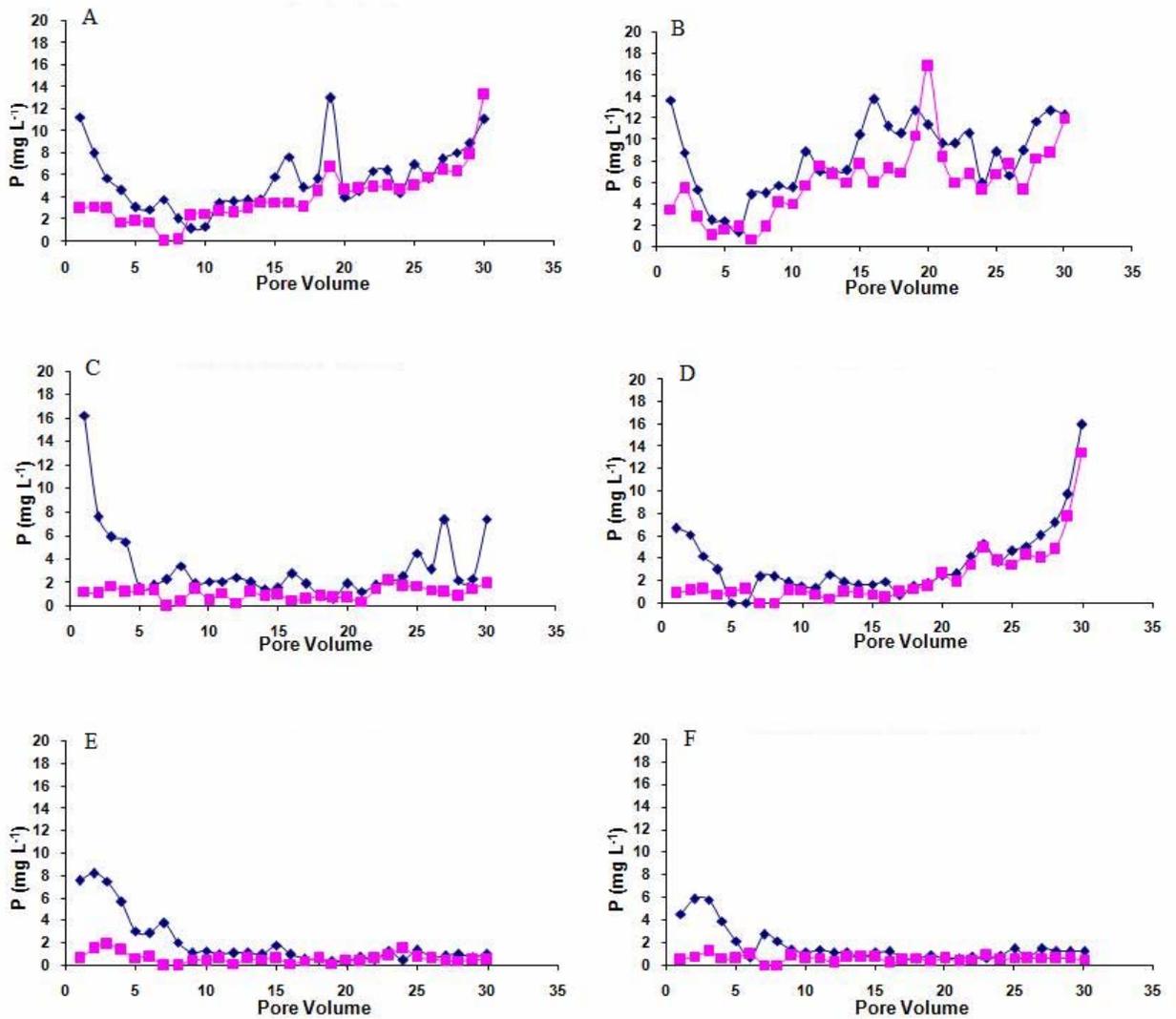


Figure 3-5. P in leachates for flushed dairy manure (FDM) treatments, shown as both total P (TP) and dissolved reactive P (DRP). With the exception of the beginning pore volumes, this illustrates that P in the leachate is largely comprised of DRP. A) Millhopper raw FDM: TP vs. DRP. B) Millhopper digested FDM: TP vs. DRP. C) Orsino raw FDM: TP vs. DRP. D) Orsino digested FDM: TP vs. DRP. E) Tavares raw FDM: TP vs. DRP. F) Tavares digested FDM: TP vs. DRP.

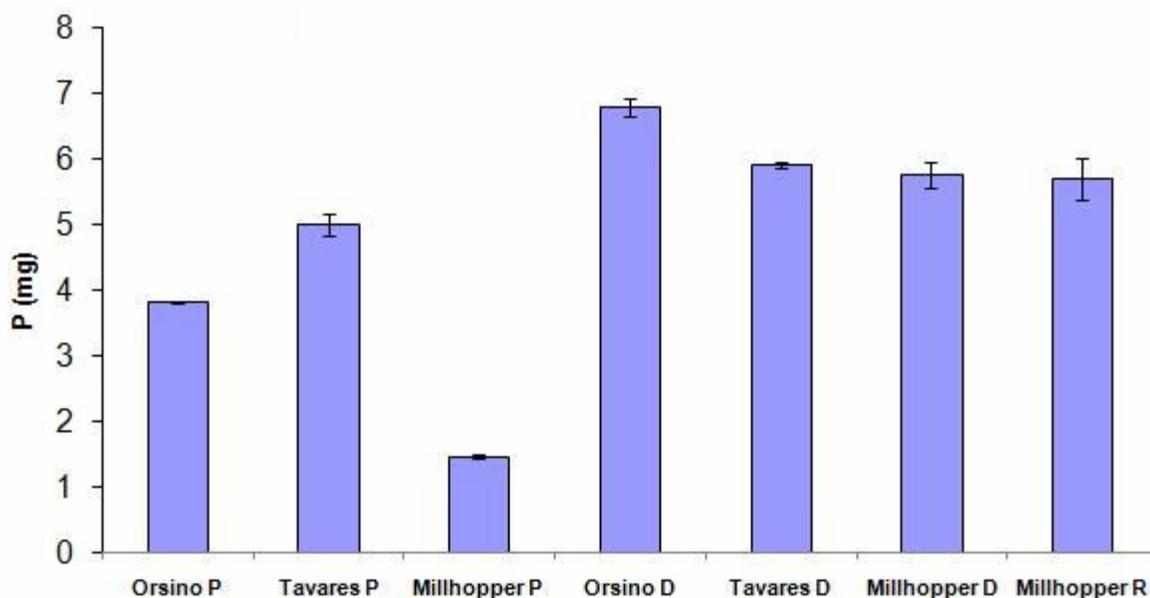


Figure 3-6. P accumulated in soils receiving different P amendments. “P”, “D”, and “R” indicate inorganic P, digested flushed dairy manure (FDM), and raw FDM amendments, respectively. Orsino R and Tavares R values are absent due to column clogging resulting in discontinued P additions. Error bars represent standard deviation.

Table 3-7. ANOVA output

	Df	Type III SS	Mean Square	F value	Pr > F
P source	2	35.34007	17.67003	747.60	< 0.0001
Soil	2	8.57565	4.28782	181.41	< 0.0001
P source * soil	4	10.88270	2.72067	115.11	< 0.0001
Rep	2	0.04502	0.02250	0.95	0.4095

Table 3- 8. Duncan’s Multiple Range Test for Accumulated P. The mean accumulated inorganic P was significantly different than the mean accumulated digested flushed dairy manure (FDM) and raw FDM. The mean accumulated P in the FDM treatments were not significantly different. Clogging of soil columns receiving raw FDM resulted in missing data for two soil columns.

Duncan grouping	Mean (mg P)	N	P form
A	6.0	9	Digested FDM
A	5.5	7	Raw FDM
B	3.3	9	KH ₂ PO ₄

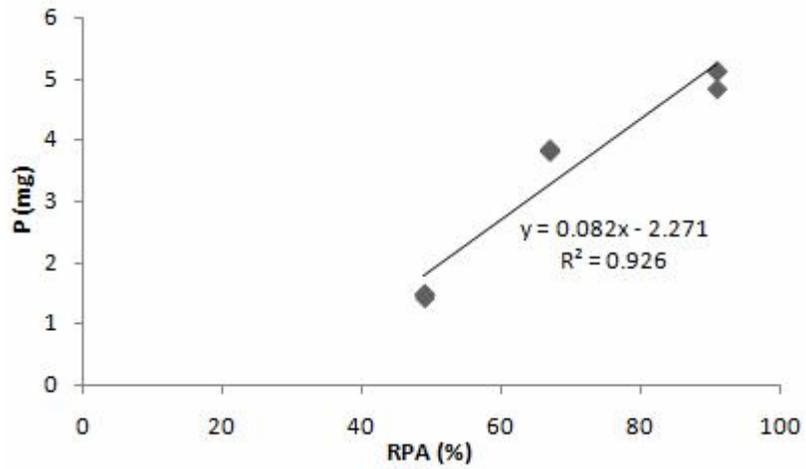


Figure 3-7. Correlation between P accumulated in soil columns, delivered as inorganic P at 48 mg L⁻¹ P solution, and soil RPA values. In ascending RPA values, data points include the soils Millhopper E2, Orsino Bw, and Tavares E2. (p < 0.0001)

CHAPTER 4 DISCUSSION

Organic matter has been known to promote the leaching of P by competing with or blocking of sorption sites, displacing P that is sorbed, and mediating transport of P (Agbenin and Igbokwe, 2006; Andrade et al., 2003; von Wandruszka, 2006; Hens and Merckx, 2001). However, as evident in the lack of P breakthrough in this study among the FDM treated columns (Figures 3-3 and 3-4), other processes must play a major role in the fate and transport of P as applied as FDM on sandy soils in the southeastern United States. Sorption to Fe and Al oxide coatings is a dominant process by which P is fixed in soils similar to these in Florida. Indeed, there was a strong correlation of the RPA values of the soils used in this experiment and the amount of oxalate extracted Fe and Al they contained (Figure 3-1). However, other mechanisms affecting retention of P applied as FDM likely involve components delivered to the soil by the FDM itself, since retention of P applied as FDM did not vary with the soil relative P adsorption capacity as it did for the inorganic P treatment. It is unlikely that the lower DRP concentrations in the FDM could have caused the delayed breakthroughs shown in Figures 3-3 and 3-4, as the concentrations are not low enough based on an RPA-retardation relation determined for sandy soils by Rhue et al. (2006). Prospective mechanisms explaining the retention of P added as FDM are (i) precipitation of P with Ca and Mg and (ii) entrapment of particulate P in the soil column.

The role of Ca in P fixation in soils is well documented in semi-arid and arid regions where calcareous soils are prevalent (Delgado et al., 2002). This is a major problem concerning farmers, whose fertilizer P becomes unavailable for crops. Many authors have written on the subject and have highlighted the role of organic amendments to increase P availability in the soil (Agbenin and Igbokwe, 2006; Bennani et al., 2005; Fernandez-Perez et al., 2005; Delgado et al., 2002; Cong and Merckx, 2005). This would seem to discourage the use of organic amendments,

such as FDM, in areas sensitive to P leaching, but if precipitation of P minerals occurs in the surface horizon, another dynamic process must be considered. Studies have shown that the concentration of Ca in manure is sufficient to induce precipitation of calcium phosphates (Ca-P), but the minerals are in non-crystalline form, which makes them more soluble. (Wang et al., 1995; Hansen and Strawn, 2003). Harris et al. (1994) and Wang et al. (1995), using x-ray diffraction, were unable to detect any crystalline P minerals in soils that received manure from dairy operations for many years. Organic acids, Mg, and Si have all been suggested as preventing crystallization of P minerals (Cooperband and Good, 2002; Harris et al., 1994). Sharpley et al. (2004) determined ion activity products of manured soils using MINTEQA2 chemical speciation model and ion concentrations in solutions. They reported tricalcium P and octacalcium P as the dominant Ca-P forms in manured soils, and hydroxyapatite as the dominant mineral in non-manured soils. These minerals are not stable in the manured soil and are subject to leaching (Hansen and Strawn, 2003; Graetz and Nair, 1995.) However, apatite minerals seem to pose relatively little risk of P leaching in soils affected by manure as long as soil pH remains in the neutral to alkaline range. Wang et al. (1995) did not find any higher levels of P in leachates derived from soils spiked with apatite than non-spiked soils. If, as suspected, Ca-P phases are precipitating, then knowing the specific form will indicate solubility and release potential.

Hansen and Strawn (2003) indicated Ca-P minerals such as octacalcium P and tricalcium P controlled the P concentration of the soil solution in manure amended alkaline soils. Desorption experiments they performed showed a rapid release of P followed by a slow, steady release. This was done using 1g of soil extracted with 20 mL of 0.005 M NaCl. After 12 replenishments of such extractions, 29% of the total P was desorbed from the surface horizon and 8% was desorbed from the subsurface horizon. Wang et al. (1995) used simulated rainfall to

leach dairy manure impacted soil samples in soil columns. After 17 weeks of simulated rainfall: each week receiving synthetic rain 80% of the soil pore volume, 13% to 26% of the total P was leached from the most impacted areas. Graetz and Nair (1995), after 10 sequential extractions on A and Bh horizons of soils from active dairies found 2% to 18% of the total TP was extracted. The soils, however, kept releasing P at diminished levels in the concluding extractions. They also found higher SRP concentrations in Bh horizons of abandoned dairy sites compared to active sites (43 mg kg⁻¹ to 14 mg kg⁻¹, respectively), supporting the notion that P, over time, will continue to be released and leach. It should also be noted, however, that these sandy soils had little to no P retention capacity, especially the A and E horizons, unlike the Tavares soil used in this experiment.

The change that manure amendments, such as FDM, have on soils is remarkable with regards to P fate and transport. As demonstrated in this experiment, P delivered as KH₂PO₄ solution behaved very differently than P delivered as either digested or undigested FDM in the same soils. The leaching and accumulation of P from inorganic P additions could seemingly be predicted from the RPA values of the soils (Figure 3-7). The reported change manure amendments bring about in acid soils, such as these, is a shift from Al and Fe reaction products to Ca/Mg reaction products, due largely to the great influx of manure-derived bases increasing soil pH (Harris et al. 1994; Sharpley et al. 2004). This change is largely confined to the surface horizons as Graetz and Nair (1995) show the shift from Ca/Mg-P predominance in the surface horizon to Al/Fe-P predominance in the deeper horizons and similar nonimpacted soils have Al/Fe-P predominance throughout the profile. This is a significant phenomenon because the factors controlling P mobility change as P leaches through the soil. For example, the most important factor organic matter may play in the surface horizon is the inhibition of stable Ca-P

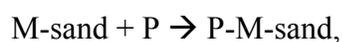
minerals, whereas in the deeper horizons its role of preventing stable Al/Fe-P sorption may be most important. Also, the role of changing pH is important. In the surface horizon the increased pH allows the precipitation of Ca-P minerals leading to their, at least transient, accumulation. In the more acidic subsurface layers, precipitation is not favored. However Harris et al. (1994) found an apatite-like mineral in stream sediments associated with, but not in, soils that received the manure directly. This may indicate that, in some cases, elements near the P source may inhibit crystallization of apatite, but elsewhere precipitation of this stable Ca-P may occur.

The lack P breakthrough when delivered as FDM shows that, contrary to the original hypotheses, retardation of P movement was not reduced by competition of FDM organic components for P adsorption sites and that mediated transfer of P by dissolved organic matter (OM) in the FDM does not play an immediate role in P leaching. Most of the organic P in the FDM is predominant in a particulate form, which is prone to entrapment, which would minimize leaching in the short-term, rather than in dissolved form, which could favor reduced adsorption to soil components and greater leaching. The microbes filtered out of the FDM by the sand in the columns would almost certainly flourish in the column environment. Their growth could retain P and trap it in cellular material. The extent, capacity, and short and long term significance of this activity, given the large concentration of P being added, is unknown, but as evident in the difference in COD between raw and digested FDM shown in Table 3-6, the food to microorganism ratio would be higher for the raw FDM. This may also play a factor concerning leaching when FDM is used as fertilizer for crops.

The role of organic matter (OM) colloids has been reported as a dominant process in P mobility in high P soils (Motoshita et al., 2003). Hens and Merckx (2001) and others have shown that organic matter-metal-orthophosphate (OM-M-P) complexes form in soils. The OM

may be mobile depending on pH, ionic strength, and the ratio of monovalent to divalent cations. They state low ionic strengths and high ratios of monovalent to divalent cations promote organic matter mobility. Also, when they added Al and Fe to soils, the amount of these complexes (defined as high molecular mass molybdate reactive P), increased, but when they just added inorganic P, no increase was observed. This indicates that the metal must bond to the OM prior to the P. The soils in their experiment had low ionic strengths, low Ca concentrations, and high Na/Ca ratios, whereas the soils in this experiment certainly have the opposite conditions. This may explain why there was little difference in the TP and DRP concentrations in the leachates of this experiment. Hesketh et al. (2001) also investigated colloid transport of P using lysimeters with soils amended with pig slurry and found very little evidence of it; 1% of P applied was leached. The combination of precipitation and the maintenance of high divalent cation concentration in the soil may contribute to the prevention of immediate leaching of P. If FDM amendments are suspended, the pH and amount of divalent cations would decrease with rainfall, perhaps increasing the mobility of P sorbed to OM and precipitated as Ca-P.

An interesting factor in this scenario is the bond strength of the OM-M versus the M-P bond. If OM-M-P complexes leach into E horizons with significant amounts of Al/Fe oxide sand coatings, they could sorb as a solid phase. Hens and Merckx (2001) state that metastable OM-M-P complexes will destabilize with decreasing pH, a condition that would be found in the lower horizons of acidic soils. If the OM-M bond hydrolyzes more easily than the M-P bond, in some instances, P may be occluded without decreasing the sorption capacity (assuming high concentrations of available P bonding metals). A series of reactions may occur where P and metals may build upon each other when OM-M bonds destabilize:



P-M-sand + OM-M → OM-M-P-M-sand,

OM-M-P-M-sand → OM + M-P-M-sand,

M-P-M-sand + P → P-M-P-M-sand,

and so on. The significance of this hypothetical P sink may not be great, but perhaps a study is warranted.

This experiment indicates that P entering the soil from FDM application may be in several “pools” that each has its own release constant. About ¼ to ½ of the P, from the digested or raw FDM, respectively, is contained in the particulate fraction, which is subject to varying rates of decomposition as soil humus. The remainder may precipitate with Ca, sorb with Fe and Al oxides or become complexed with OM along with metal ions. In the soils used in this experiment, the FDM immediately creates conditions that result in less P leaching than occurs with inorganic P amendments, which effectively rejects the original hypothesis. Indeed, any organic transport is overridden by the accumulation caused by precipitation and entrapment of P in OM. The rate of FDM addition and the rate of rainfall will be important factors concerning future P leaching. Based on this study and others, P, as delivered by FDM, will likely accumulate to high levels in these soils (Lehmann et al., 2005; Graetz and Nair, 1995). Most of the P will likely be metastable Ca-P along with P associated with mineralizable organic particulates, both of which are ultimately subject to leaching under rainfall, particularly when FDM (and hence Ca) additions cease. The complexation of inorganic P with the OM will affect its mobility depending on soil properties down the profile, which can be very different in originally acidic soils. Eventually these soils may leach P at slow, steady rate.

The relatively small amount of P leached when using digested or raw FDM was very similar between these two treatments. However, less P was removed as DRP for the digested

FDM than for the raw FDM, considering that DRP comprised a higher proportion of TP for the former. The benefit of digested FDM over raw FDM in spray field applications may be more linked with factors other than leaching of P, such as more plant available P and odor and pathogen reduction. The higher proportion of plant available P in the digested FDM would be preferable because more of the P would be available for immediate uptake through the crops when the FDM is applied.

These soils have a predictable sorption capacity when P is delivered as KH_2PO_4 and is largely a function of the RPA (Fig 3-7). The soils can quickly reach their sorption capacity and then offer little resistance to P leaching and leachate P concentrations could be very high. However, the Al/Fe-P is more stable than the Ca-P minerals formed under the influence of manure (Hansen and Strawn, 2003; Makris et al. 2005). Depending on the environmental, agricultural, and practical conditions, one method of P fertilization may be favored over another. Concerning leaching of P in these soils, when at similar P concentrations, the largest apparent difference between P delivered as FDM and P delivered as KH_2PO_4 is that when irrigating with FDM, the surface horizon acts as an expanding, but leaky bucket with regards to containing P; that is, the P is accumulated in the surface horizon but steadily leaches at a slow rate. However, the soil acts as a “fixed” bucket when using an inorganic P fertilizer. P progressively travels down the soil profile becoming more permanently fixed than metastable Ca-P, but reaches its inherent P capacity as Al/Fe-P, and then the soil offers no more resistance to P leaching. As stated above, more analyses of these experimental soils could provide useful information concerning P fate and environmental risk.

Future Studies

Further study of the soil columns could evaluate the evidence of Ca-P precipitation, the extent to which it occurs, and its relevant properties. An analysis, such as x-ray diffraction, could

determine if any crystalline precipitant formed, and leaching of the soil columns would be very useful in determining the stability of the accumulated P. Also, another column study involving soils, with a range of P sorption capacity (such as those used in this experiment), overlaid with a highly impacted soil of similar soil type with large amounts of accumulated P may show how P in the leachate is affected by changes in the soil chemistry and if OM leaches into the subsurface layer and prevents sorption at Al/Fe sorption sites.

Summary and Conclusions

Three different sandy soils in a column experiment showed processes related to P leaching differ when delivered as inorganic P as opposed to when delivered by both raw and digested FDM. The capacity of the soils to retard the movement of P when amended with inorganic P is related to the amount of Fe and Al oxide present in the soil. In contrast, the soils amended with FDM accumulated P and very little leached through the columns. After the addition of 30 pore volumes, the amount of P leached from the columns amended with inorganic P was significantly greater than those that received both raw and digested FDM. It is apparent that FDM creates conditions in the soil that promote accumulation of P. This is likely due to an increase in pH, from the addition of base cations present in the FDM, notably Ca, and a shift from Al/Fe-P to Ca/Mg-P reaction products. Also, any transport of P via OM is minimal compared to the factors promoting P accumulation, and the immobility of OM may also be caused by the changes FDM creates in the soil. The formation of meta-stable Ca-P should be verified by analytical means, and leaching of the columns would provide data on the stability of the P accumulated in all of the soil columns. Also, as there is a shift back to the original soil chemistry in deeper horizons, leaching of FDM amended soils over the same or similar nonimpacted soils in a column experiment could help determine what factors are important with relation to P leaching as the soil chemistry changes.

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BIOGRAPHICAL SKETCH

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