Phosphorus Losses in Runoff from Virginia Soils

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Abstract

Previous research shows that dissolved P losses in runoff are well related to soil test P (STP), thus, various P loss prediction models incorporate the use of a STP vs. runoff DRP relationship. However, the relationship between STP and runoff DRP will vary based on soil type due to differences in soil properties. The purposes of the first two studies were to (i) investigate the effect of soil mineralogy on P sorption behavior and dissolved P in runoff and (ii) determine if any simple soil test extractions could indirectly take into account this effect of mineralogy.

Nine soil types from the Virginia Piedmont, Coastal Plain, and Ridge and Valley were collected and used in a rainfall simulation study. Phosphorus retention among separated clay fractions and whole soils were related to Al bearing minerals such as hydroxy-interlayered vermiculite (HIV), gibbsite, and amorphous Al. Samples dominated by kaolinite retained very little P. Application of these results to runoff data showed that soil types with a HIV:kaolinite ratio > 0.5 caused significantly less DRP in runoff for a given soil WSP level compared to soils with a ratio < 0.5.

The second study showed that the soil P vs runoff DRP relationships varied between physiographic provinces. Generally, the Coastal Plain soils resulted in a higher runoff DRP concentration for a given soil P level compared to Piedmont and Ridge and Valley soils. However, soil M3-P/Al resulted in one relationship with DRP for all three groups of soils. Results from the incubation study suggested that Al related P is more easily desorbed into solution compared to Fe related P.

The final study demonstrated that phytase enzyme and high available P corn supplements in poultry diets can reduce manure WSP and total P. Results from the runoff study showed that DRP losses were related to sediment losses which consisted of > 90% manure particles. Manure particles were directly deposited into the collection container followed by desorption of P based upon the WSP content of that manure type. The results emphasized best management practices that prevent direct loss of manure particles from soil into surface waters.

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Chapter One: Introduction

Nature of the Problem

Phosphorus (P) is an essential element for the growth and development of living organisms and its presence in terrestrial systems greatly improves biological productivity. Phosphorus is applied to cultivated fields as fertilizers, biosolids (treated municipal sewage), and animal manures to achieve optimum crop yields or to establish vegetation that will hinder runoff losses of water, nutrients and sediment. Although P is not known to be detrimental to terrestrial life, its excessive presence in aquatic environments presents a major problem to water quality, specifically by eutrophication, defined as a process of nutrient enrichment of water bodies leading to dense growth of biomass (plant matter). The decomposition of this excess plant matter results in decreased levels of dissolved oxygen in the water column. Water quality problems caused by eutrophication are damaging to the economy as well as the ecosystem. For example, eutrophication can increase the costs of maintaining surface waters that are used for recreational and navigational purposes.

Past research has shown that runoff, leaching, and subsurface flow from agricultural land containing particulate and/or dissolved P is a significant non-point source of P pollution to surface waters (Sharpley, 1995, 1997). The loss of P to surface waters is dependent upon many factors, however, in order to fully comprehend those factors, which contribute to P losses from agricultural land, one must first establish a general basis of P behavior in soils.

Phosphorus Behavior

Sufficient levels of soil P are necessary for the production of agronomic crops. Because crop production depletes available soil P, P fertilization is often necessary in agriculture. Naturally occurring plant available soil P originates from the weathering of primary minerals. After P is released from these pools and becomes available in the soil to plants and microorganisms, it begins to accumulate and stabilize within the landscape. If P is not immobilized in the biological pool by organisms, it may erode from soil and be deposited with the sediment in surface waters. Animal operations and human populations convert immobilized P in biologically accumulated forms (feed or food) to more available (labile) forms in manure and biosolids. This form of P is recycled back into the environment (soil and water). The P cycle is explained in more detail in the following paragraphs.

Plants take up P mostly as orthophosphate ($H_2PO_4^-$ and HPO_4^{2-}), that is found in the soil solution. As the soil solution is depleted by plant uptake, it is replenished by mineralization of organic P and dissolution of precipitated P; this is a function of the solubility of secondary P minerals, desorption from clays and oxides, and the mineralization rate of soil organic matter. Organic P typically represents 50% of the total P in soil and is mainly found in the topsoil.

Inorganic P in solution not absorbed by plant roots or immobilized by microbes can be adsorbed to mineral surfaces or precipitated as secondary P compounds. Inorganic P precipitates in low pH soils as secondary Fe and Al minerals. In neutral to alkaline soils, P precipitates with secondary Ca minerals and/or is adsorbed to surfaces of clay minerals and calcium carbonate. The release of P from these secondary minerals is a function of the solubility product of the minerals. Also, desorption of P adsorbed to clays, OM, and metal oxides supply P to the soil solution. As solution P decreases, secondary minerals dissolve and P adsorbed on clays, metal oxides, and OM is released into solution through desorption.

Phosphorus added as Fertilizer

Phosphorus is added to the soil as inorganic or organic fertilizer. Organic forms include any animal or municipal waste, composts and plant residues and sometimes-industrial wastes. Inorganic P fertilizers include rock phosphate, phosphoric acid, calcium orthophosphates, ammonium phosphates and polyphosphates, nitric phosphates, and potassium phosphates. The goal of these fertilizers is to increase the amount of P in solution (which is immediately available to the plant) as well as to supply P to plants for an entire growing season.

When P fertilizers or organic wastes are added to soils, the concentration of P in the soil solution increases due to the dissolution of inorganic forms and mineralization of organic forms of P (organic wastes also contain inorganic P). Since the equilibrium between solid P and solution P is now altered, solution P will begin to convert to solid forms by immobilization, precipitation, and adsorption reactions.

These newly formed solid forms of P can be converted back into solution relatively quickly when the equilibrium of solid/solution P is disturbed in the other direction (i.e. solution P concentrations are much less than the solid phase). Thus, when plants take up P from the soil solution, the equilibrium is shifted, and more P is converted from solid phase to solution P. However, solid phase P becomes more stable or more strongly adsorbed with time. When this occurs, solid phase P forms cannot replenish the soil solution rapidly enough to satisfy plant needs; at this point, P fertilizer needs to be added to optimize plant growth. If fertilizer or organic P is added consistently in a manner that exceeds plant needs, the residual portion of P in the soil will increase, as well as the potential for P losses in runoff.

Since P loss in runoff is affected by the buildup of residual P in a soil, a knowledge of soil P dynamics is necessary when managing to minimize runoff P losses. These different pools and forms of soil P have differing potentials for releasing P in surface runoff.

Phosphorus Loss in Runoff

All forms of P have been shown to be susceptible to transport from land to water bodies. Phosphorus is always “naturally” moving from terrestrial sources to surface waters. This is supported by the fact that the ocean’s sediments are the largest global P sinks. However, the process of P transport to surface waters has been hastened by human activity. This movement of P mostly occurs as loss via surface flow, but small amounts can move in soluble forms by subsurface flow. The desorption and dissolution of P from the thin zone of surface soil and organic material produces dissolved P. Almost all soluble P that is transported by surface runoff is biologically available. However, particulate P moving from soil to surface water via erosion may not be immediately available to aquatic life; the P must first be dissolved or desorbed in order to contribute to eutrophication. With the potential problem related to soil P losses through runoff, nutrient management programs use strategies to minimize P losses in runoff by addressing fertilizer application strategies (inorganic and organic), conservation tillage practices, and erosion control mechanisms such as terraces and grassed waterways. Traditionally, P loss has commonly thought to be controlled by reducing the amount of sediment lost by erosion, but recent research has shown that a substantial amount of dissolved P can occur in runoff from high P soils even when erosion is minimal (Sharpley et al., 1977, 1978; Daniel et al., 1994).

Previous research has shown that the P content of surface soil directly influences the amount of dissolved reactive phosphorus (DRP) in runoff from that soil (Sharpley et. al., 1977, 1978, 1994; Daniel et al., 1994). For example, a study by Sharpley (1995) that involved measuring runoff P from soils amended with poultry litter showed that when Mehlich-3 soil P levels were 50, 100, and 150 mg kg^{-1} soil, DRP in runoff was 400, 600, and 1500 µg L^{-1}. The loss of particulate P in runoff is a function of erosion; and this can be decreased by soil conservation measures. However, dissolved P is more difficult to reduce and control; the measure used in controlling it has been limited to preventing soil P accumulation to environmentally damaging levels (Sharpley, 1995).

Soils considered "excessive" in agronomic soil test P (STP) are often considered to be at risk for causing non-point DRP losses in runoff (Daniel et al., 1994). Soils become "excessive" in P by continuous application of P in the form of chemical fertilizers, animal manures, or municipal biosolids beyond plant needs. Typically, animal manures and biosolids are applied to the soil at the plant available nitrogen rate (PAN), however this often results in the over application of P in regard to plant uptake. More specifically, the low N:P ratio found in many organic wastes cause soil P to become excessive over time (Pote et al., 1996). For example, a poultry litter application that is based on the rate of N (9000-kg ha^{-1}) will add about 135 kg P ha^{-1}. If this is applied to a corn crop (removes about 23 – 28 kg P ha-1), an annual excess of about 107 kg of P will occur. As a result, continuous N-based applications cause a slow build up of soil P that can potentially be lost in runoff, causing non-point nutrient pollution of surface waters (Sims et al., 1998).

Soil P Levels in Virginia

Recent research in the state of Virginia has shown that many of the soils found in counties dominated by intensive animal and row crop agriculture are high or very high in STP. In a study by Brosius et al. (1999) a total of 62 fields were sampled on various farms in Accomack, Amelia, and Rockingham County and tested for agronomic STP (Mehlich-1 P, M1-P). These counties were chosen to represent Coastal Plain, Piedmont, and Valley and Ridge soils of the state, that have been impacted by intense animal and row crop agriculture. According to Virginia Tech's agronomic soil test categories (0 - 6 ppm is low, 6 – 18 is medium, 18 – 55 is high, and > 55 is very high), they found that 84%, 93%, and 100% of samples collected from Rockingham, Amelia, and Accomack County, respectively, were high to very high in M1-P. This large percentage of soils considered high to very high in STP indicates that many agricultural soils in Virginia posses the potential to release high levels of P in surface runoff.

Nutrient management legislation in several states have taken similar approaches in attempting to reduce the input of non-point P to surface waters. Laws and regulations in Virginia (1999), Maryland (1998), and Delaware (1999) will use “high” STP levels in some manner to identify sites where P application must be limited or restricted. Specifically, Virginia has targeted the state’s poultry industry and mandates that P application rates shall not exceed the greater of crop nutrient needs or crop nutrient removal.

As a result of increased awareness and interest in reducing P losses from agricultural soils to surface waters, a large amount of research has been conducted in regard to understanding P loss mechanisms and determining possible solutions for reducing non-point source P losses. Such research has focused on determining how certain soil properties affect P losses, the development of a P index tool for simple evaluation of sites for risk of P loss, the use of certain soil tests as “predictors” of P loss, and various types of farm management. The use of farm management as a tool for reducing P losses includes crop management, runoff management (for example, buffer strips), manure management (timing and methods of application, amendments such as aluminum, iron, and calcium compounds (Miller and Moore, 1994), and diet manipulation (phytase and high available P corn (HAP)).

This study intends to focus on (i) the influence of soil type and various soil properties on runoff P losses, (ii) evaluation of various soil P tests as “predictors” of runoff P losses, and (iii) the effectiveness of a phytase supplemented diet in reducing runoff P losses when the resulting manure is land applied.

Chapter 2: Soil Mineralogy in relation to Phosphorus Sorption Behavior and Losses in Runoff from Virginia Soils

ABSTRACT

The relationship between soil test phosphorus (STP) and dissolved reactive P (DRP) in runoff has been shown to vary with soil type due to differences in soil properties. This study was conducted in order to determine the effect of mineralogy on P sorption behavior and DRP losses in runoff using simulated rainfall. Nine different soil types were sampled from four different fields in order to provide a range in STP. Un-amended soils were packed into runoff boxes for use in a rainfall simulation study. One representative sample from each soil type was used in a mineralogical analysis and adsorption/desorption isotherm. Results indicated that P retention for adsorption and desorption in separated clay fractions and whole soils was well correlated to Al bearing minerals such as hydroxy-interlayered-vermiculite (HIV), gibbsite, and amorphous Al. However, P retention was negatively related to kaolinite content, which was also confirmed by isotherms conducted on pure clay minerals. Based on the isotherm results, all soils were split into two groups based on the ratio of HIV:kaolinite. Soils with a HIV:kaolinite ratio > 0.5 had a significantly lower concentration of DRP in runoff for a given soil water soluble P level compared to soils with a ratio < 0.5.

Abbreviations: DRP, dissolved reactive phosphorus; STP, soil test phosphorus; WSP, water soluble phosphorus; M1-P, Mehlich-1 phosphorus; Fe_{ox} and Al_{ox}, ammonium oxalate extractable Fe and Al, respectively; HIV, hydroxy-interlayered vermiculite;

INTRODUCTION

Phosphorus losses from agricultural soils to surface waters has been of recent public concern due to the negative effects of increased P concentrations on surface water quality (Sharpley et al., 2000). Agricultural soils considered high in P can cause significant movement of P into waterways (Sims, 1998) in the form of dissolved P and particulate P. Although erosion control has been shown to decrease total P and particulate P losses (Quinton et al., 2001), significant concentrations of dissolved P can occur in runoff from soils where erosion is kept at a minimum, particularly from soils that are high in soil test P or having received recent P applications (Sharpley et al., 1977, 1978; Daniel et al., 1994). Dissolved P concentrations in surface runoff from soils are typically much less relative to P losses from recently applied amendments (Moore et al., 2000), although significant dissolved P losses can occur from high P soils that have not received recent P amendments (Pote et al., 1996). With the established link between soil test P concentrations and dissolved P losses in runoff (Sims et al., 2002), many P loss models have incorporated the relationship between some measure of soil P and runoff dissolved P (Gburek et al., 2000; Coale et al., 2002; Vadas et al., 2002). However, recent research has shown that this relationship will vary based on soil type (Sharpley, 1995; Sharpley et al., 1996; Pote et al., 1999). Therefore, an understanding of how different soil properties affect P concentrations in solution, leachate, and runoff is necessary in determining the effect of soil type on the relationship between soil test P (STP) and runoff P losses.

One of the most influential soil properties in regard to P sorption is soil clay content, which has often been correlated to P sorption parameters (Fox and Kamprath, 1970; Loganathan et al., 1987; Solis and Torrent, 1989; Bennoah and Acquaye, 1989). However, it is the high surface area and presence of various P sorbing minerals that results in the common observation that high clay soils often adsorb more P compared to coarse textured soils (Loganathan et al., 1987). Phosphate sorption is attributed primarily to ligand exchange reactions between hydroxyls exposed on surfaces of minerals and the phosphate molecule in soil solution. The mineralogy of a soil will take into account both surface area (due to the fact that most phyllosilicates and oxides/hydroxides each have a specific range in surface area) and the Fe/Al content of a soil. Therefore, analysis of mineral types and content should provide an estimate of potential P-sorption sites (Jones, 1981; Sposito, 1984; Parfitt, 1989) and the potential for a soil to release P into runoff. Variation in surface area and differences in the ability of different minerals to retain P should be responsible for the observed differences in the relationship between soil P levels and runoff dissolved P concentrations among soil types.

Although there has been significant work conducted on P adsorption in regard to soil mineralogy, few mineralogical studies have been performed in conjunction with P desorption isotherms or runoff studies. The objectives of this study were to (i) investigate the role of soil mineralogy on P adsorption / desorption behavior in Virginia soils, and (ii) relate soil mineralogy and adsorption / desorption behavior to potential dissolved P losses in surface runoff from Virginia soils.

MATERIALS AND METHODS

Nine soil types were chosen to represent the major agricultural soils of the Piedmont, Coastal Plain, and Ridge and Valley physiographic provinces of Virginia. Among each soil type, four different soils (i.e. locations) were collected to provide a range in Mehlich-1 extractable P from below moderate (< 18 mg kg-1) to very high (> 55 mg kg-1) agronomic P levels (Virginia DCR, 1995). One exception to this was the Bojac soil type (only three different M1-P levels were located for this soil). Bulk samples were collected from cooperating farmer's fields that had not received any organic amendments or P additions within one year prior to collection.

The Piedmont soils used in this study consisted of Cecil (Fine, kaolinitic, thermic Typic Kanhapludults), Tatum (Fine, mixed, semiactive, thermic Typic Hapludults), and Davidson (Fine, kaolinitic, thermic Rhodic Kandiudults) series. Coastal plain soils used consisted of Emporia (Fine-loamy, siliceous, subactive, thermic Typic Hapludults), Slagle (Fine-loamy, siliceous, subactive, thermic Aquic Hapludults), and Bojac (Coarse-loamy, mixed, semiactive, thermic Typic Hapludults) series. The Ridge and Valley soils chosen for this experiment were Frederick (Fine, mixed, semiactive, mesic Typic Paleudults), Groseclose (Fine, mixed, semiactive, mesic Typic Hapludults), and Sequoia (Fine, mixed, semiactive, mesic Typic Hapludults) series.

Each sample was collected by removing soil from the surface 0-5 cm layer and sieving through a 19 mm sieve before being air-dried for use in the rainfall simulation study. Composite soil samples were taken from each soil and sieved to 2-mm for the following characterization: pH (1:1 soil:water ratio), sand, silt, and clay analysis by the hydrometer method (Day, 1965), and water soluble P (WSP 1:10 soil:deionized water, 1 h reaction time, filtration with 0.45 μm Millipore membrane [Kuo, 1996]). Soil test P was analyzed by Mehlich-1 (M1-P: 1:4 soil: 0.05 *M* HCl + 0.0125*M* H_2SO_4, 5 min reaction time, filtration with Whatman #2 paper [Kuo, 1996]). Mehlich 1-P and WSP solutions were analyzed for P by inductively coupled plasma emission spectroscopy (SpectroFlame Modula Tabletop ICP; Spectro Analytical Instruments, Inc., Fitchburg, MA).

Phosphorous adsorption and desorption experiments

Among each of the nine soil types, one sample was chosen for use in a P adsorption and desorption experiment that was conducted on both whole soils and the separated clay fraction from each soil. Clay fractions were separated from whole soils as described in the "Mineralogical Analysis" section. Individual samples within each soil type were chosen based on their measured WSP concentrations (Table 1). In addition to the whole soils and clay fractions, the sorption experiments were conducted on several mineral source materials; (i) synthetic goethite (yellow 920Z, Bayer Corporation; Krefelt, Germany), (ii) synthetic hematite (red 1120Z, Bayer Corporation; Krefelt, Germany) (iii) synthetic gibbsite (RH-31F, Reynolds metals company, Bauxite, AK), (iv) well crystalline kaolinite from Washington County, GA (Source Clay Minerals Repository, Clay Minerals Society), and (v) poorly crystalline kaolinite from Warren County, GA (Source Clay Minerals Repository, Clay Minerals Society). A single point P adsorption isotherm was conducted by adding 34 mL of 0.01 *M* $CaCl_2$ and 6 mL of 100 mg P L^{-1} solution (KH_2PO_4) to 50 mL centrifuge tubes containing 0.4 g of sample (1.5 mg P added per 1 g of sample). Samples were duplicated and placed on a reciprocating shaker for 24 h. Solutions were centrifuged at 2000 rpm for 10 min and then filtered through a 0.45 µm Millipore membrane and analyzed for P by the Murphy-Riley method (Murphy and Riley, 1962). The percent of P adsorbed was then calculated from the difference between P added and P left in solution (% of added P that was adsorbed). The P saturated samples from the single point adsorption isotherms were then used in the desorption isotherm by sequentially desorbing the samples four consecutive times with 40 mL of 0.01 *M* $CaCl_2$ and shaking for one h. After each successive desorption, samples were centrifuged, filtered, and analyzed for P as previously described for the single point P adsorption. The total amount of P desorbed was calculated as the sum of the mass of solution P from each desorption and the percentage of P retained after four desorptions was calculated as follows:

$$\frac{\text{Adsorbed P after 4 desorptions}}{\text{P adsorbed from single point isotherm}} \text{ X } 100$$

Soil Mineralogical Analysis

Mineralogical analysis was conducted on the same nine samples used in the adsorption and desorption experiment. Pretreatments for mineralogical analysis included removal of organic matter with 30% H_2O_2 buffered at pH 5 with 1 M NaOAc (Kunze, 1965). Sand was separated by wet sieving through a 300 mesh sieve and silt and clay fractions were separated by centrifugation and decantation using 0.1 *M* Na_2CO_3 (pH 9.5) as a dispersant. X-ray diffraction was used to determine clay mineral suites present by analyzing oriented K saturated samples with no heat treatment and after heating for 4 h at 110, 300, and 550ºC. Samples were scanned at a fixed counting time of 4s at a 0.075º 2θ with a Scintag XDS 2000 x-ray diffractometer (Scintag, Madison, WI) using CuKα radiation (40mA, 45 kV). Subsamples of the K saturated clay fractions were also analyzed for weight loss by thermogravimetric analysis (TGA) from 25 to 1000ºC using a TGA 2950 (TA instruments, NewCastle, DE). Amorphous Al and Fe (Al_{ox} and Fe_{ox}, respectively) for both clay fractions and whole soils were determined by ammonium oxalate extraction (1:40 ratio of soil to 0.2 M ammonium oxalate [pH 3], 2 h reaction time in the dark and filtration with Whatman #42 paper [McKeague et al., 1966]). Resulting extracts were analyzed for Al and Fe by ICP-AES. Total surface area of Ca saturated whole soils was determined using ethylene glycol monoethyl ether (EGME) as described by Carter et al. (1965).

Rainfall Simulation Study

Dried and sieved soils were poured into wooden runoff boxes approximately 100 cm x 20 cm x 5 cm in size (SERA-17, 2004), replicated three times, leveled, and pre-saturated 24 h before being placed under a rainfall simulator to ensure that runoff would occur during the rainfall event. The amount of water necessary to pre-saturate each soil type was determined by adding water to one box for each soil until ponding on the soil surface occurred. That same volume of water was then applied to all boxes containing the respective soil type.

The rainfall simulator consisted of a single "Tee Jet" HH-SS-50WSQ nozzle attached to a 3m x 3m x 3m metal frame, and calibrated to achieve an intensity of 7.5 cm hr^{-1} at 90% uniformity (SERA-17, 2004). The runoff boxes were placed randomly under the rainfall simulator on steel racks adjusted to a 5% slope. Rainfall events were 30 min long and all runoff was collected in 9-L plastic containers. Runoff sub-samples were pipetted in 10-mL aliquots from bulk runoff samples that were mixed on a stir plate to keep all sediment in suspension. These sub-samples were analyzed for DRP (40 mL runoff filtered through 0.45 µM Millipore filter papers and analyzed by the Murphy and Riley colorimetric method [Murphy and Riley, 1962]).

Statistical Analyses

The distribution of data was tested for normality by the Shapiro-Wilkes statistic conducted by the "Univariate" procedure of the Statistical Analysis System, Version 8.0 (SAS Institute, 1999). All correlation, and analysis of variance procedures were conducted by standard procedures of SAS. Multiple linear regression was conducted using the "stepwise" procedure of SAS

RESULTS AND DISCUSSION

Soil Properties

The general properties of the soils used in the P adsorption and desorption experiment are listed in Table 1. These individual soils were chosen within each soil type based upon their measured WSP with the intent of obtaining a set of samples that are relatively uniform to prevent soil WSP from being a confounding factor in the adsorption and desorption experiments. As a result the range of WSP for these soils was 5.62 to 11.85 mg kg^{-1} with an average of 7.75 mg kg^{-1}. Although WSP was relatively uniform for the soils used in the experiment, M1-P was more varied (11 to 85 mg kg^{-1}) (Table 1). With the exception of the Cecil and Emporia soils, the natural pH ranged from 6.11 to 7.07 (Table 1). This point is important since pH can have a strong effect on the charge properties of soils as well as the solubility of Al and Fe which can in turn influence P behavior. The variation in clay content among the soils indicates that the Coastal Plain soils (Emporia, Slagle, and Bojac) possessed the lowest clay content, Piedmont soils (Cecil, Tatum, and Davidson) had the highest, while Ridge and Valley soils (Frederick, Groseclose, and Sequoia) had a clay content intermediate to the Coastal Plain and Piedmont soils (Table 1). One exception to this was the Sequoia soil which had a much higher percent clay (40%) compared to all other soils. This may be due to the fact that this sample was collected on a steep slope and much of the topsoil may have been eroded leaving the subsoil exposed. Support for this conclusion lies in that the Sequoia sample contained much higher amounts of mica (which often occurs in the subsoil) compared to the other soils (Fig. 1a).

X-ray diffraction patterns conducted on the K saturated clay fraction at 25ºC (Fig. 1a) indicated that the Cecil and Tatum soils contained the highest amounts of kaolinite compared to the other soils. Quartz appeared in every soil except Slagle (Fig. 1a). Because chlorite and HIV share the same peak at 25ºC, the samples were heated to 550ºC in order to partially collapse HIV to approximately 12 angstroms. At this temperature chlorite maintains a 14 angstroms peak and it is then possible to distinguish between the two minerals. Significant amounts of HIV occurred in every sample while it was a minor component of Cecil, Tatum, and Sequoia. Tatum was the only soil containing any appreciable amount of chlorite (Fig. 1b). Thus the 14 angstrom peaks at 25ºC for all soils except for Tatum are primarily attributed to HIV (Fig. 1a). The presence of mica was pronounced only in the Sequoia soil, and significantly present in Groseclose, and Tatum soils. In addition the data in Table 1 indicates that all soils contained a greater amount of Fe_{ox} than Al_{ox} except for the Cecil, Emporia, and Slagle. Overall, the mineralogical makeup of these samples in regard to P chemistry was dominated by kaolinite, HIV, amorphous Al, amorphous and crystalline Fe, and is considered typical for Virginia soils. Of these minerals, amorphous Fe and Al are considered the most important in regard to P sorption followed by goethite, kaolinite and 2:1 clay minerals such as HIV (Jackman et al., 1997; Juo and Fox, 1977).

Phosphorus Adsorption and Desorption

The greatest amount of P per unit weight of clay was absorbed by the separated clay fraction of the Davidson, Emporia, and Bojac soils as indicated by the single point isotherm (Fig. 2). Data presented in Fig. 2 also shows that the Cecil, Tatum and Frederick soils adsorbed the lowest amount of added P while the Slagle, Groseclose, and Sequoia soils were intermediate between the two groups. Not only were the Davidson, Emporia, and Bojac clay fractions able to adsorb the most P, these samples also retained the highest percentages of the adsorbed P after four sequential desorptions (Fig 2). Clay fractions of soils that adsorbed less P also desorbed more P when compared to the other soils (i.e. Cecil, Tatum, and Frederick). In an attempt to relate mineral type and quantity to P sorption, we correlated the mineral content as quantified by TGA to the amounts of P retained after the single point P addition and four sequential desorptions (Table 2). Pearson correlation coefficients indicated that HIV and amorphous Al as determined by ammonium oxalate extraction were the only significant variables related to P adsorption (Table 2). Retention of P after four sequential desorptions was also significantly related to HIV and amorphous Al, and gibbsite. In addition, kaolinite possessed a significant and negative relationship with P desorption (Table 2). These results suggest that HIV and amorphous Al can adsorb high amounts of P as well as retain the adsorbed P throughout sequential desorptions while in comparison kaolinite is not able to retain P as strongly.

As expected the results of the single point P adsorption isotherm and sequential desorption isotherm conducted on the whole soils was different from that of the clay fractions (Fig. 3). In this case we observed that the Emporia soil adsorbed the lowest amount of P compared to the other soils since this soil contained the least amount of clay and next to the lowest amount of Al_{ox} and Fe_{ox} (Table 1). Adsorption of P was clearly the highest among the Davidson, Bojack, Frederick and Sequoia soils, while surprisingly the Cecil and Tatum adsorbed lower amounts of P relative to the other soils as was also observed with the clay sized fractions (Figs. 2 and 3). Unlike P sorption by the separated clay fractions, soils that adsorbed high amounts of P were not necessarily able to retain the adsorbed P following four sequential desorptions in the whole soil samples (Fig. 3). For example, although the Emporia and Slagle soils adsorbed very little P, these two soils retained nearly 70% of the P adsorbed after four sequential desorptions. Again, P retained after four desorptions from the whole soils indicated that the Cecil and Tatum retained the least amount of adsorbed P per unit weight compared to the other samples.

The Cecil and Tatum were among the highest in clay content, suggesting that clay content for these soils was not a significant variable in explaining P adsorption and desorption. Evidence for this is shown in Table 2 in that clay content of the soils was not significantly correlated with P adsorption or P retained after four sequential desorptions. This result is in contrast to previous studies (Fox and Kamprath, 1970; Loganathan et al., 1987) which showed that clay content was well related to the amount of P required to reach 0.2 mg P L^{-1} in solution. For example, Mozzaffari and Sims (1994) reported that P single point isotherm values were significantly correlated with clay content ($r = 0.90^{***}$). In our case the lack of correlation between clay content and P retention suggests that mineral type and quantity may be more important than the total amount of clay sized particles present in the soil. Evidence for this is shown in Table 2 in that gibbsite, HIV, and amorphous Al were significantly related to P adsorbed, similar to results of the clay sized fraction (Table 2).

Surface area per g of clay was also well related to P adsorption. The significant relationship of P adsorption with surface area per g clay and not with clay content occurred because different minerals vary in surface area (Van Olphen and Fripiat, 1979).

As a result, soils with similar clay contents can possess very different surface areas and thus different P adsorption capacities. The data in Table 2 indicates that the only mineral related to P retention after four sequential desorptions was kaolinite (negative relationship), thus soils with higher levels of kaolinite were not able to retain P as tightly compared to the other soils. Note also that the soil WSP content did not appear to be a confounding factor as indicated by the lack of a significant relationship between P sorption and soil WSP concentration (Table 2).

Differences in P sorption between mineral types

Overall observation of the Pearson correlation coefficients for the separated clay fractions and whole soils (Table 2) suggests that HIV, gibbsite, and amorphous Al are the most important P sorbing minerals in these samples in regard to P adsorption and P retention after four sequential desorptions. It also appears that kaolinite was not able to retain as much P as the other soil minerals following four sequential desorptions. Surprisingly, total Fe oxides and amorphous Fe were not significantly related to P sorption for either the separated clay fractions or whole soils. This was unexpected since Fe minerals have been shown to adsorb large amounts of P (Hingston et al., 1974; Dao et al., 2001).

In addition to simple correlation we also conducted multiple linear regressions (MLR) on each data set using the "STEPWISE" procedure in SAS to determine the best fitting model. Results from the MLR in Table 3 agree with the results of the simple single correlations in that gibbsite, HIV, and amorphous Al were the best parameters used in predicting P retained from both adsorption and desorption. Kaolinite content was identified as the only significant variable in explaining P retention after four sequential desorptions from the whole soils (negative relationship). SAS also identified total Fe oxides as an important model component in explaining P adsorption by the separated clay fractions. However this was unexpectedly a negative relationship (Table 3).

In order to confirm these results we repeated the adsorption and desorption experiment on pure clay minerals (goethite, hematite, gibbsite, poorly crystalline kaolinite, and well crystalline kaolinite). These minerals had a pH range of 5.5 to 6.0 and a WSP content less than 0.30 mg P kg^{-1}. Data presented in Fig. 4 shows that the two Fe oxides (goethite and hematite) adsorbed the highest amounts of P from the single point addition and retained a greater percentage of P after four sequential desorptions from the same samples when compared to gibbsite and kaolinite. This was expected since Fe oxides have a higher surface area (14 - 177 m^2 g^{-1}) compared to gibbsite (0.4 - 7.5 m^2 g^{-1}) and kaolinite (5 – 30 m^2 g^{-1}). The high P retention (both adsorption and desorption) by the Fe oxides is in contrast to the lack of a significant, positive relationship between P sorption and total Fe oxides or amorphous Fe among the soils used in this experiment. The results in Fig. 4 also confirm that kaolinite was not able to adsorb as much P relative to other P sorbing minerals and also was not able to retain as much of the adsorbed P after undergoing four sequential desorptions.

Previous studies have generally shown that Fe and Al oxides such as goethite, gibbsite, and amorphous materials possess a higher P adsorption capacity compared to 1:1 and 2:1 clay minerals. Jackman et al. (1997) conducted a P sorption study on ten mineralogically diverse Hawaiian soils and found that the highest degree of P sorption was exhibited by Andisols that predominantly contained amorphous Fe and Al hydrous oxides, very fine-grained goethite, and no kaolinite. Medium sorption soils included the Oxisols that contained mostly illite, some goethite and gibbsite. The low P sorbing soils were Mollisols mostly rich in kaolinite containing very low amounts of Fe and Al hydrous oxides. Juo and Fox (1977) suggested that soils with very high P sorption capacities usually contain desilicated amorphous material, those with medium P sorption capacities contain 1:1 clay minerals and oxides, and those soils with low P sorption capacities contain 2:1 and 1:1 clay size minerals with quartz. One similarity between these and other past studies is the conclusion that 1:1 clay minerals such as kaolinite tend to adsorb more P compared to 2:1 minerals. Our results somewhat contradict that notion since HIV (2:1) was better related to P retention (both adsorption and desorption) compared to kaolinite (Tables 2 and 3). In relation, Wijesundara (1996) found that the P adsorption maximum for both fertilized and non-fertilized Davidson soils were greater than for Tatum soils. In that study the two soils had nearly the same percentage of kaolinite (Davidson = 60% and Tatum = 62%) while the Davidson contained 27% HIV and the Tatum had none.

One possibility for this discrepancy (a 2:1 mineral adsorbing more P than a 1:1) may be that previous studies on P sorption in relation to soil mineralogy usually did not include soils that contained HIV since HIV occurs predominantly in the Southeastern US (Rich, 1968). HIV is a unique 2:1 mineral in that its interlayer is intermediate to that of vermiculite (K, Mg, or Ca) and chlorite (Al or Mg hydroxy sheet). Although most 2:1 minerals possess little capacity to adsorb P because of few exposed terminal hydroxyls, HIV may be an exception to this rule of thumb due to its unique structure. The interlayer of HIV contains both K, Ca, or Mg (which holds the layers together) and disconnected sheets of amorphous Al hydroxides. Together they form "wedge zones" in the minerals and result in a highly exposed Al hydroxide with an increased surface area. The exposed Al hydroxide can potentially adsorb and retain P. As observed in this study, there was a significant and positive correlation between amorphous Al and HIV in the separated clay fraction (r =0.77). Therefore this data set is unable to document that there is truly something unique about the structure of HIV that would make it a greater P sink compared to amorphous Al hydroxides in the soil (such as P being trapped in the interlayer), or if P adsorption by HIV is simply due to the Al hydroxide comprising the mineral (i.e., the ammonium oxalate extraction could simply be removing amorphous Al from the edges of the HIV).

P adsorption and Fe

As previously discussed, it was unexpected that there were no significant and positive correlations between P retention and total Fe oxides or amorphous Fe among whole soils and clay fractions (Tables 2 and 3). Again, this is in direct contrast to the literature and results from the P adsorption and desorption isotherms conducted on pure minerals in this study (Fig. 4a and b). This suggests several possibilities: (i) P has a preference for adsorption sites in regard to Al and Fe (ii) the different minerals are interacting with each other, and (iii) some co-correlations exist between Fe and some other minerals. The poor correlation between Fe minerals and P sorption can be somewhat explained by the results from the soil incubation (Fig 5). Data presented in Fig. 5 shows that for each of the soils used in the incubation (original WSP ranged from 2.3 to 5.6 mg kg^{-1}), the dominant P fraction was Fe related P for the non P amended soils (83 to 92% Fe related P).

However, as P was added to the soils, the percentage of Fe related P decreased while the percentage of Al related P and "loosely soluble" P increased. This suggests that for soils that contain P but not at high levels (such as the ones used in this incubation), added P may be preferred onto Al instead of Fe. However, because the unamended incubation soils were initially dominated by Fe related P, this also suggests that the soils originally had adsorbed P onto Fe instead of Al mineral surfaces, or perhaps with time P equilibrated onto Fe mineral surfaces (Fig 5). For example, Hartikainen (1982) conducted a P study on 104 different Finnish soils in order to relate WSP parameters to other soil properties such as soil carbon and specific inorganic forms of P. She found that P associated with Fe compounds was greater than the amount of P associated with Al compounds in almost all soils. In addition, Wijesundara (1996) found that 24% of total P extracted from 43 Virginia soils was in the form of Fe related P compared to only 10% Al related P.

Application of the results of the incubation study to the mineralogy experiments suggest that the reason we may not have observed a significant and positive correlation between P retention and Fe minerals (Tables 2 and 3) is because added P from the adsorption isotherms adsorbed onto Al rather than Fe for unknown reasons. This could be due to a preference of P for Al because the soil Fe was more saturated in P relative to Al among soils with P contents similar to those used in this study. In a recent study Khare et al. (2004) used X-absorption near edge spectroscopy (XANES) to identify P adsorbed onto mixtures of ferrihydrite (amorphous Fe mineral) and boehmite (amorphous Al mineral). The authors found that on the clean samples P was initially preferred onto Fe, but with increasing P the Al mineral appeared to have an equal or greater affinity for P compared to the Fe mineral. Cabrera et al. (1977) concluded in a study of P adsorption onto various Al (gibbsite, boehmite, and corundum) and Fe (goethite, lipidocrocite, and hematite) oxides, that "Al oxides are more reactive than Fe oxides of similar specific surface areas".

Mineralogy and runoff DRP

The retention of P during the sequential desorption experiments may be a good indicator of the potential for dissolved P release from soils not having received recent P amendments. Based on these results (Tables 2 and 3), soils not having received a recent P amendment (P is in a steady state condition with the soil) and contain a low proportion of HIV to kaolinite (< 0.5) would readily release DRP into runoff more easily compared to soils with a high proportion of HIV to kaolinite (> 0.5). We were able to test this hypothesis by grouping soil types into "high" or "low" HIV:kaolinite and plotting their WSP values with runoff DRP concentrations from the simulated rainfall study. Data presented in Fig. 6a shows that for a given soil WSP value, soils with low HIV:kaolinite yield more DRP in runoff compared to soils with high HIV:kaolinite. Also, in an attempt to normalize the soils based on clay content we repeated the same procedure and expressed soil WSP as soil WSP/clay (Fig. 6b). This normalized data (Fig. 6b) indicates the same trend as previously described in Fig. 6a, at any given value of WSP/clay the low HIV:kaolinite soils resulted in more runoff DRP compared to high HIV:kaolinite soils.

However, caution should be exercised in application of these results since this rainfall study was conducted on soils that did not receive P amendments for over one year. The observation that high HIV:kaolinite soils were able to retain P more tightly during a simulated rainfall may not hold true for soils receiving recent P amendments. Therefore the best application of this data would be for soils that are no longer receiving P amendments in which the P is at steady state with the soil. For example, in Virginia permitted poultry operations with soils possessing M1-P values greater than 55 mg kg^{-1} can only receive a maximum single P application equivalent to the 3 year crop removal rate. Thus, the low HIV:kaolinite soils among these would be expected to release more P in runoff compared to high HIV:kaolinite soils at similar soil P concentrations.

One problem in application of this research to field situations is that mineralogical analysis of soils may not be practical and the existing database of soil mineralogy (i.e. the soil survey) is based on subsoil mineralogy rather than the topsoil where runoff interacts with soil P. Therefore it might be worthwhile to conduct mineralogical analysis on an extensive collection of representative topsoils in order to assess the amount of various clay minerals such as HIV and kaolinite in the topsoil of important agricultural soils. Studies on the effects of other clay mineral types (i.e. monmorillinite, chlorite, vermiculite) on DRP losses in runoff might also be necessary. Potentially, this would be easier and less expensive compared to conducting simulated rainfall on many different soil types having a range in soil test P in order to construct soil P vs runoff DRP relationships for each soil type. The information could then be applied directly to a P index that utilizes the relationship between soil test P and WSP in assessing DRP losses in runoff from soil P pools.

CONCLUSIONS

Losses of P from soils not having recently received P amendments can still be significant in regard to surface waters considered to be P limited (Vadas et al., 2004). Although soil P concentrations as determined by various extractions have proven to be well related to dissolved P losses in surface runoff, use of these relationships in predicting dissolved P losses is complicated due to differences among soil types. This study attempted to indicate that these different relationships may be due in part to differences in soil mineralogy, since ligand exchange of phosphate molecules in solution is mainly a function of mineralogy.

For the soils used in this study, clay content was not an important factor in regard to P sorption behavior, rather, the mineralogy of the soils better explained variation in P adsorption and desorption. Phosphorus retained from P additions and sequential desorption expermiments using separated clay fractions and whole soil samples was mainly correlated with HIV, amorphous Al, gibbsite, and kaolinite. However, the correlation of kaolinite with P sorption was a negative relationship, indicating that kaolinite was not able to retain P throughout the sequential desorptions as strongly in comparison to the other minerals. This observation was confirmed by adsorption and desorption studies conducted on pure clay minerals. The significant and positive correlations of HIV with P retention was somewhat unexpected since 2:1 minerals are considered to have the least potential to adsorb P. This trend could be a result of P adsorbing onto Al hydroxides in the interlayer of HIV since amorphous Al was well related to HIV. Future studies using selective dissolution techniques could possibly answer this question.

Also unexpected was the result that Fe oxides and amorphous Fe were not significantly related to P retention. This could be due to co-correlations between Fe and other minerals, interaction between different minerals, or a preference of P adsorption onto certain Al minerals. Previous literature suggests that initially P may be preferentially adsorbed on Fe, but with further P additions Al may be preferred as an adsorption site.

Soils considered high in the proportion of HIV:kaolinite yielded less DRP in runoff for a given WSP and WSP/clay level when compared to the low HIV:kaolinite soil types. However, there are limits in the application of these results since the soils used in the rainfall study had not received P amendments for at least one year prior to collection. This approach in using soil mineralogy to broadly group soils into categories for potential DRP losses could be easier and less expensive compared to determining the relationship between soil test P and runoff DRP for many different soil types using rainfall simulation studies.

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Table 2.1. General properties of soils used for the P sorption and mineralogy study.

Soil type	WSP	Mehlich 1 P	pH	Clay	Al_{ox}	Fe_{ox}
	mg kg^{-1}			%	mg kg^{-1}	
Cecil	7.56	57	5.14	29.9	547	453
Tatum	6.89	41	6.57	27.9	555	1511
Davidson	7.68	19	6.29	29.4	840	1659
Emporia	7.71	33	5.35	10.9	331	152
Slagle	8.4	37	6.11	14.9	240	110
Bojac	7.73	45	6.57	16.9	739	772
Frederick	11.85	85	7.07	24.2	628	712
Groseclose	5.62	11	6.25	17.9	809	1162
Sequoia	6.35	23	6.30	40.0	705	1816

Table 2.2. Pearson correlation coefficients between the percentage of P retained from a single point isotherm, 4 sequential desorptions and soil mineral quantity among both clay fractions and whole soils. *, **, indicates significance at the 0.05 and 0.01 probability level, respectively.

Soil Parameter	% P retained from single point P addition	% P retained after 4 sequential desorptions	% P retained from single point P addition	% P retained after 4 sequential desorptions
	Clay fraction		Whole soil	
gibbsite	0.5	0.67*	0.63*	0.26
Fe oxides	0.22	0.21	0.24	0.28
kaolinite	-0.41	-0.63*	0.21	-0.76*
HIV	0.76*	0.79**	0.92**	0.32
am ox Al	0.81*	0.75*	0.67*	0.05
am ox Fe	0.44	0.51	0.60	0.18
WSP	na	na	0.28	0.45
% Clay	na	na	0.44	0.45
Surface area/g clay	na	na	0.66*	0.47

Table 2.3. Results of the "STEPWISE" mulitiple linear regression analysis conducted by SAS on the relationship between mineral quantities and percentage of P retained from a single point isotherm (“adsorption”) and 4 sequential desorptions (“desorption”) performed on both whole soils and clay fractions. Analysis based on p value of 0.05

Significant Model Parameters	Partial Slope	Partial R-Square	Model R-Square	C(p)
	Clay Fraction P retention: adsorption			
Al_{ox}	0.004	0.65	0.65	98.8
Fe oxides	-5.592	0.17	0.83	48.6
gibbsite	5.078	0.11	0.94	16.6
	Clay Fraction P retention: desorption			
HIV	8.187	0.66	0.66	8.1
	Whole Soil P retention: adsorption			
HIV	19.555	0.86	0.86	1.9
	Whole Soil P retention: desorption			
Kaolinite	-8.012	0.58	0.58	8.5

Fig. 2.1. X-ray patterns for the nine soils used in the P sorption study conducted on (a) room temperature samples and (b) samples heated to 550ºC.

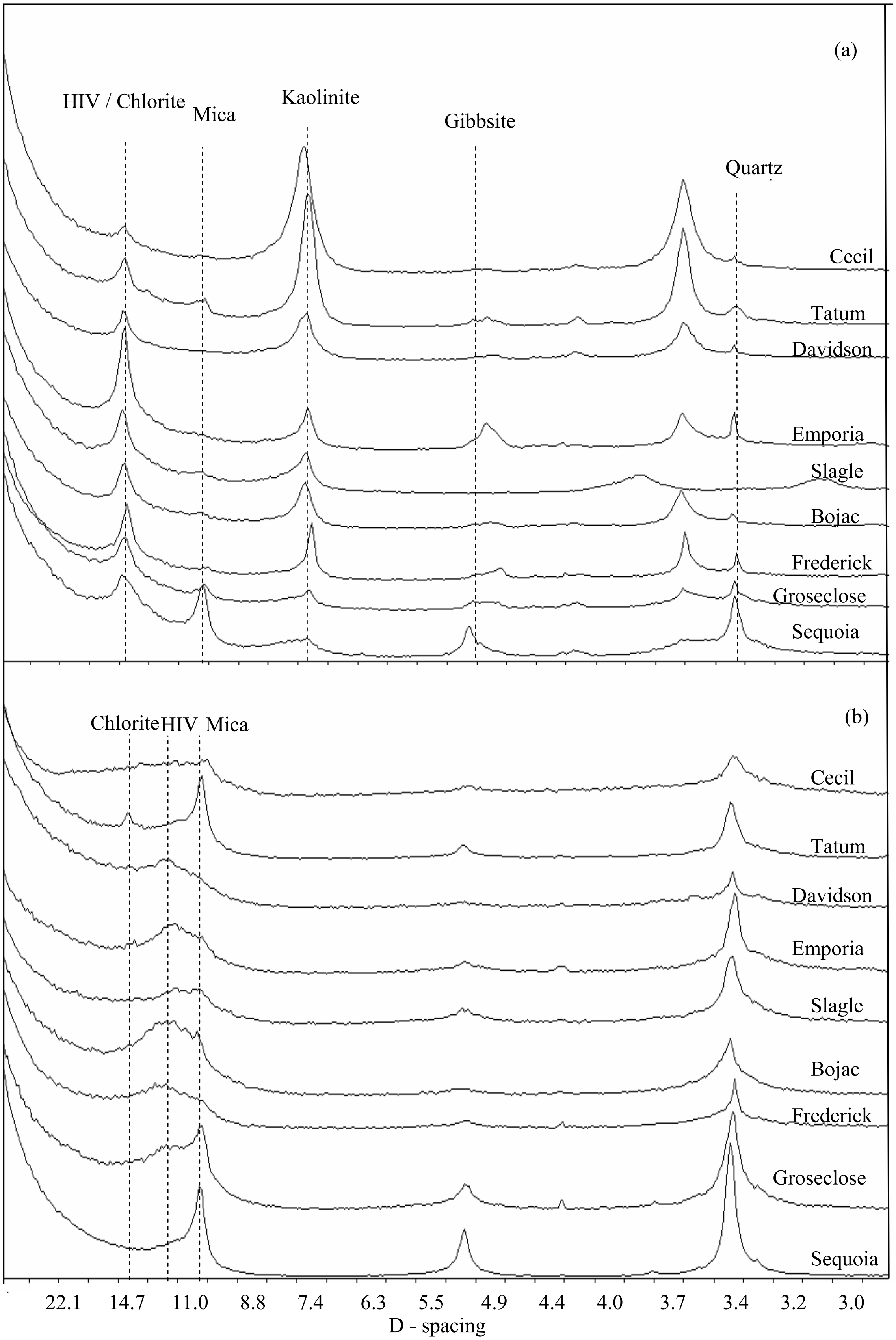


Fig. 2.2. Phosphorus retention by the separated clay fractions of each soil type expressed as the percentage of added P that was absorbed during a single point isotherm (adsorption) and the percentage of P retained on samples after four sequential desorptions with 0.01 *M* CaCl$_2$ (desorption). Error bars indicate standard deviation.

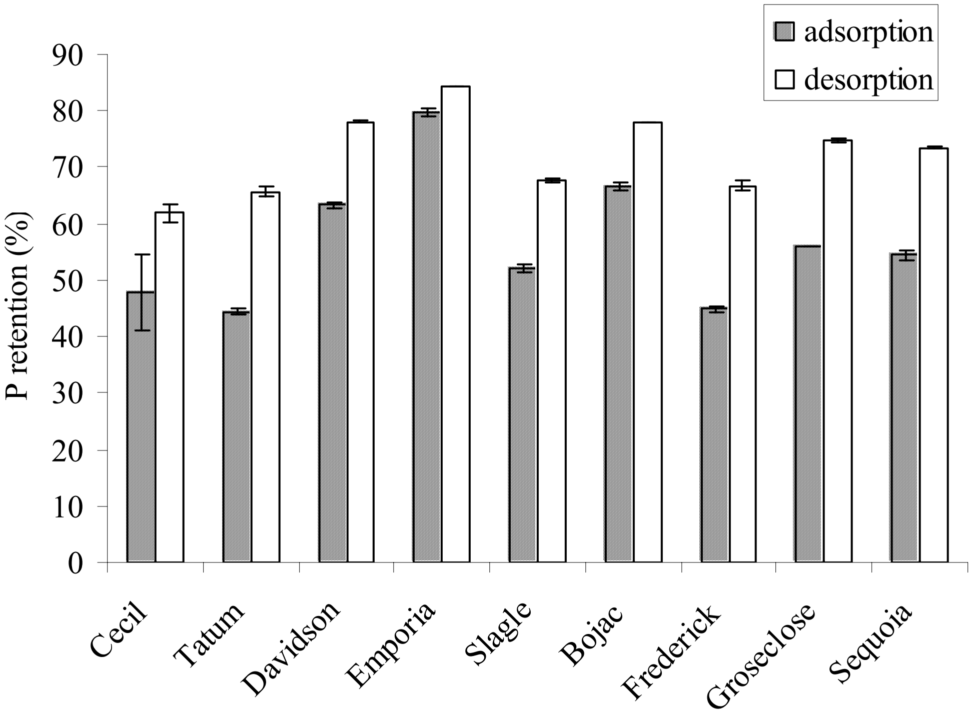


Fig 2.3. Phosphorus retention by whole soils expressed as the percentage of added P that was absorbed during a single point isotherm (adsorption) and the percentage of P retained on samples after four sequential desorptions with 0.01 *M* $CaCl_2$ (desorption). Error bars indicate standard deviation.

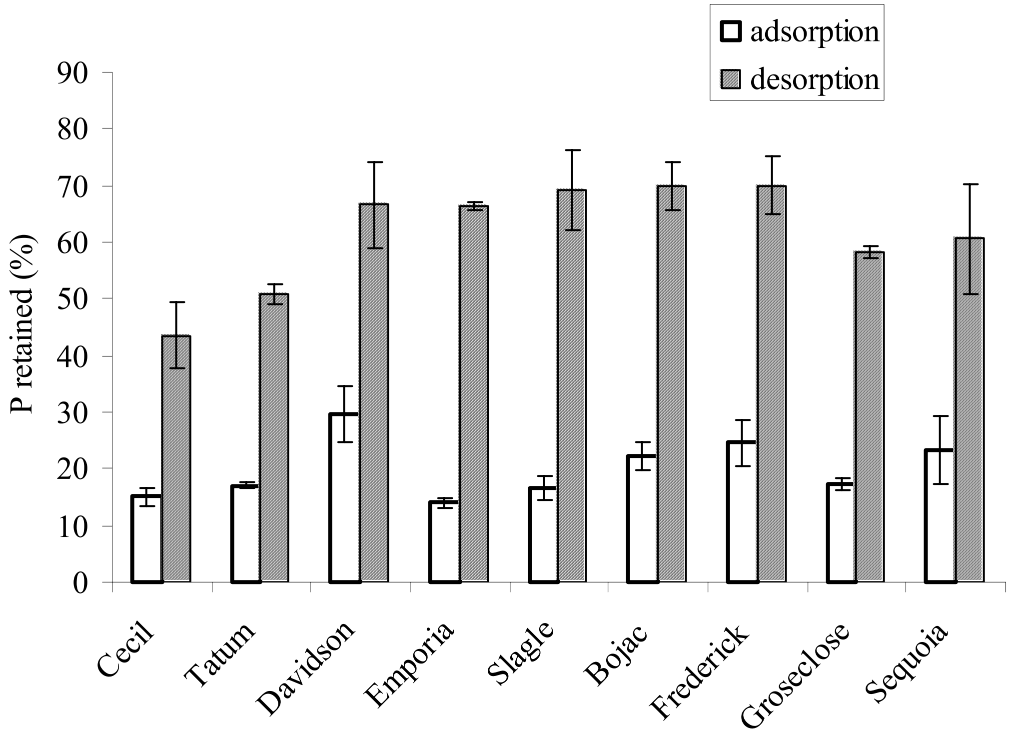


Fig 2.4. **Phosphorus retention by the pure minerals expressed as the percentage of added P that was absorbed during a single point isotherm (adsorption) and the percentage of P retained on samples after four sequential desorptions with 0.01 M CaCl2 (desorption). Error bars indicate standard deviation.**

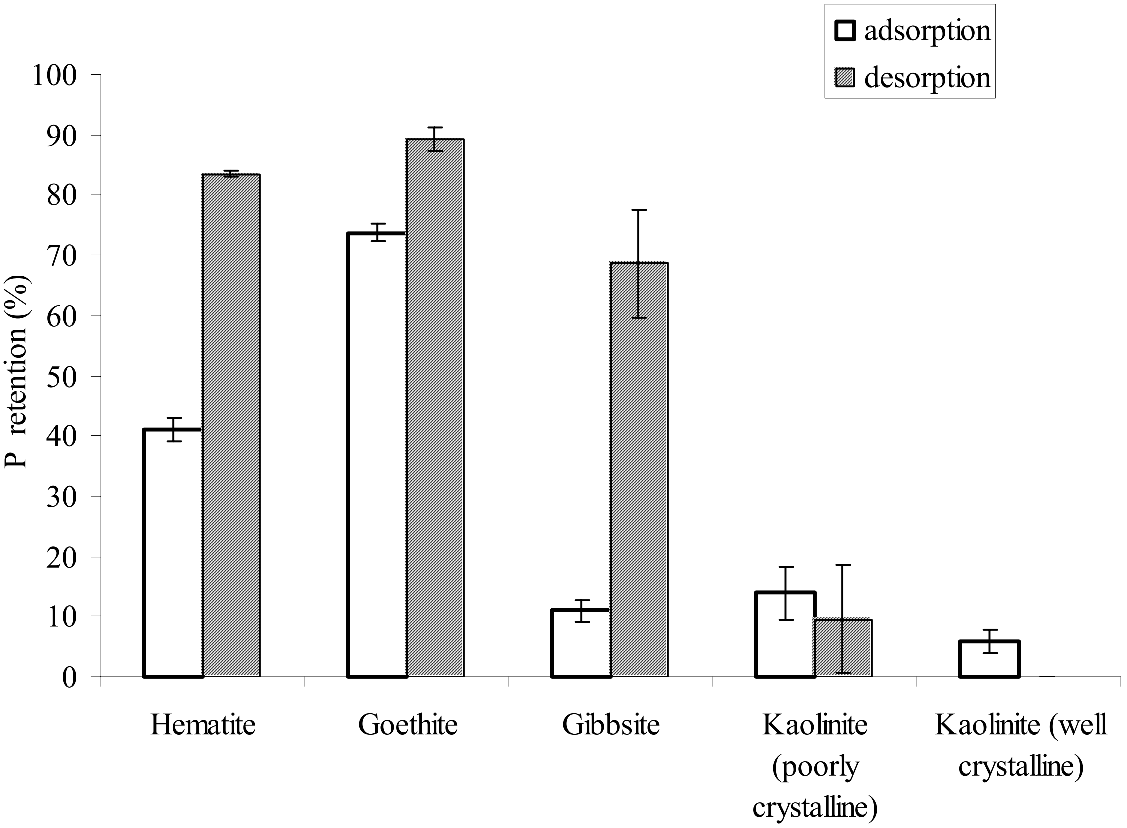


Fig 2.5. Changes in the P fractions of (a) Frederick, (b) Groseclose, (c) Tatum, and (d) Davidson soils amended with 13 different rates of P in the form of KH_2PO_4.

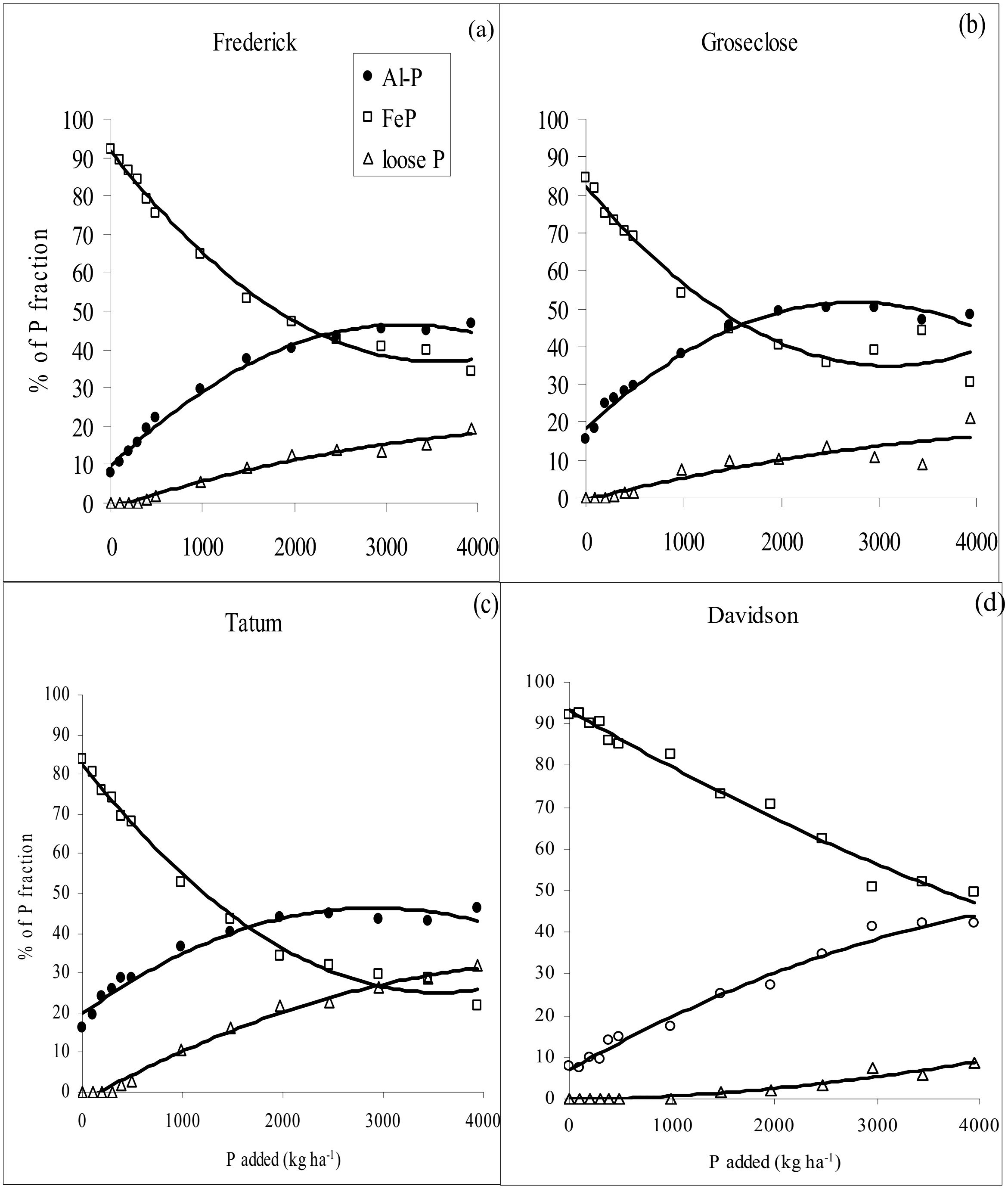
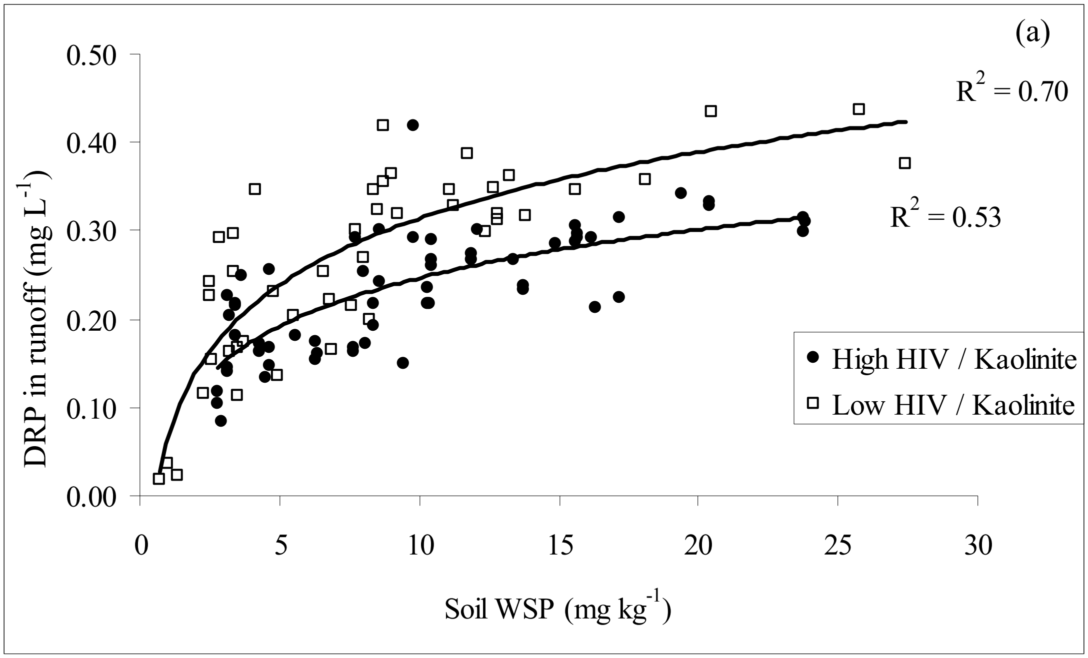
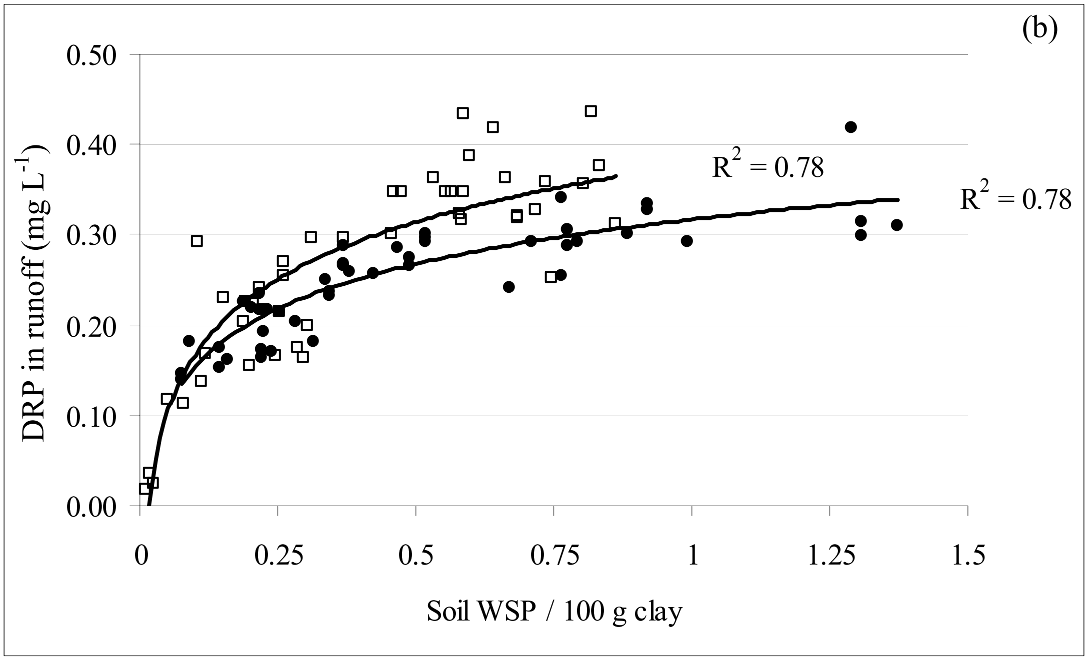


Fig 2.6. Relationship between (a) soil WSP, (b) soil WSP/100 g clay and runoff DRP for soils considered "high" (>0.50) and "low" (<0.50)in the ratio of HIV to kaolinite based upon soil mineralogical analysis of the nine different soil types. For each figure, correlation lines of "high" and "low" HIV to kaolinite were significantly different from each other at p = 0.05.





Chapter 3: Relationship of Soil Test Phosphorus to Runoff Dissolved Phosphorus in Piedmont, Coastal Plain, and Ridge and Valley Soils of Virginia

ABSTRACT

The relationship between soil test phosphorus (STP) and dissolved reactive P (DRP) in runoff has been shown to vary with soil type due to differences in soil properties such as mineralogy. The purpose of this study was to determine if soil tests could indirectly take into account mineralogy and thus provide one relationship with STP and runoff DRP among a variety of soil types. Nine different soil types were sampled from four different fields in order to provide a range in STP. Un-amended soils were packed into runoff boxes for use in a rainfall simulation study. Four soil types were also used in an incubation study intended to examine the solubility of soil Al and Fe related P. All soils were analyzed for P, aluminum (Al), and Iron (Fe) using various extractions and correlated to runoff DRP losses from all soils grouped based on physiographic province. Coastal Plain soils resulted in higher DRP concentrations at a given STP level, possibly because the Coastal Plain soils are dominated by Al related P. However, soil Mehlich 3 P/(Al+Fe) and P/Al were the only parameters that resulted in one relationship with runoff DRP for all three physiographic provinces. The results of this and previous studies suggest that P desorption is mostly a function of soil Al bearing minerals among acidic, non-calcareous soils. Since Mehlich 3 extracts mostly Al related P compared to Fe, the Mehlich 3 P/Al parameter may serve as a universal approximation of DRP losses in runoff from un-amended soils.

INTRODUCTION

Increased P concentrations to surface waters typically stimulate algal production and eutrophication (Kenney et al., 2002). The degradation of water quality in the Chesapeake Bay and other surface waters in the Mid-Atlantic region is attributed in part to increased loading of P (Coale, et al., 2002). In addition, agriculture is considered an important nonpoint P source for both particulate (erosion) and dissolved forms to surface waters. Although erosion control can significantly reduce bioavailable P (Uusitalo et al., 2003) and total P (Sharpley and Kleinman, 2003) losses, significant losses of dissolved P can still occur when erosion is kept to a minimum (Sharpley, 1995; Daniel et al., 1994). Dissolved P losses in runoff have been shown to be well related to soil P concentrations and the degree of P saturation onto soil Fe and Al (Sims et al., 2002; Pote et al., 1996; Sharpley et al., 1977). Thus, soils with high concentrations of extractable P are considered to be at a greater risk of causing nonpoint dissolved P losses compared to low P soils.

Because of the increased awareness in regard to P losses from agricultural soils to surface waters, various P loss prediction models and P index tools have been developed (Karpinets et al., 2004; Vadas and Sims 2002; Lemunyon and Gilbert, 1993) and often incorporate the relationship between extractable soil P and runoff dissolved P concentrations. The closeness of the relationship between P in solution, P leaching, and P in runoff with STP depends on the range of soils studied as well as the extractants used. These correlations are usually strong when the studied soils are fairly homogeneous in soil properties such as texture and pH (Sims et al., 1998; Yuan and Lavkulich, 1995; Lookman et al., 1996; Pote et al., 1996). As a result, recent studies have concluded that the relationship between extractable soil P and runoff dissolved P will vary with soil type (Torbert et al., 2002; Pote et al., 1999; Sharpley, 1995).

Penn et al. (2005) suggested that among non P amended soils, variability in the soil P vs dissolved P relationship could be due to differences in clay mineral type and quantity since phosphate sorption is primarily attributed to ligand exchange reactions between hydroxyls exposed on the surfaces of minerals and the phosphate molecule in soil solution. Although the authors showed that the relationship between soil water soluble P (WSP) and runoff dissolved reactive P (DRP) among nine soil types could be reduced to two regression equations based upon soil hydroxy-interlayered vermiculite (HIV) and kaolinite content, analysis of soil mineralogy for this purpose would not be practical.

Thus a “universal” soil extractant capable of creating one relationship between soil P and runoff dissolved P regardless of soil type would be useful as a component in P prediction models. In theory, a universal soil extractant would indirectly take into account soil mineralogy and different P forms by primarily removing P from soil minerals that retain P with the least strength during a runoff event. The objective of this study was to evaluate the use of various soil P extractants in predicting runoff P losses from selected agricultural soils of the Piedmont, Coastal Plain, and Ridge and Valley of Virginia.

MATERIALS AND METHODS

Soil Collection and Characterization

Nine soil types were chosen to represent the major agricultural soils of the Piedmont, Coastal plain, and Ridge and Valley physiographic provinces of Virginia. Four soil samples (four different fields) were collected within each soil type in order to provide a range in Mehlich-1 extracable P (M1-P) of < 18 to > 55 mg P kg^{-1}. Only soils which had not received any sort of P fertilization within one year prior to collection were used in this study. A summary of relevant soil properties are shown in Table 1. These soils are the same as those described by Penn et al. (2005) and consist of the Piedmont soils Cecil, Tatum, and Davidson; Coastal Plain soils Emporia, Slagle, and Bojack; and Ridge and Valley soils Frederick, Groseclose, and Sequoia.

Soils were collected by sampling the top 0 - 5 cm of the topsoil, air dried and sieved to 19 mm for later use in the rainfall simulation study. Composite samples of each soil type were further sieved to 2 mm for characterization. Soil characterization consisted of (i) pH (1:1 soil:solution ratio); (ii) sand, silt, and clay by the hydrometer method (Day, 1965) (ii) Mehlich-1 P, Al, and Fe (M1-P, M1-Al, and M1-Fe: 1:4 soil: 0.05 *M* HCl + 0.0125*M* H_2SO_4, 5 min reaction time, filtration with Whatman #2 paper [Kuo, 1996]); (iii) water soluble P (WSP: 1:10 soil:deionized water, 1 h reaction time, filtration with 0.45 μm Millipore membrane [Kuo, 1996]); (iv) oxalate extractable P, Al, and Fe (P_{ox}, Al_{ox}, Fe_{ox}; 1:40 soil: 0.2*M* acid ammonium oxalate (pH 3), 2 h reaction time in the dark; McKeague and Day, 1966); (v) Mehlich-3 P, Al, and Fe (M3-P, M3-Al, and M3-Fe: 1:10 soil:0.2 *M* CH_3COOH + 0.25 *M* NH_4NO_3 + 0.015 *M* NH_4F + 0.13 *M* HNO_3 + 0.001 *M* EDTA, 5 min reaction time, filtration with Whatman #42 paper [Kuo, 1996]); and (vi) Fe strip P (1:40 soil to 0.01 *M* $CaCl_2$ + Fe-oxide coated filter paper strip, 16 h reaction time, followed by dissolving P from the filter paper strip for 1 h in 0.1 *M* H_2SO_4 [Chardon et al., 1996]). Extracted P, Al, and Fe were analyzed by ICP-AES. The ratio of ammonium oxalate extractable P to (Al + Fe) (all values in mmol kg^{-1}) was expressed as:

$$(P_{ox} \div [Al_{ox} + Fe_{ox}]) \times 100$$

and will be referred to as $Pox/(Al_{ox}+Fe_{ox})$. Note that this is exactly the same as soil degree of phosphorus saturation (DPS) calculation except without the empirical constant α, which is used to relate soil P sorption capacity to Al_{ox} and Fe_{ox} and acts to express the effective total soil P sorption maximum. Because our experiment consisted of a broad range of soil types in which the α value was unknown, no α value was used. Beauchemin and Simard (1999) noted that various studies have applied an α value of 0.5 to all soils, regardless of soil properties. The authors noted that the α value is empiric and needs to be determined for each soil type and experimental conditions. In addition, Beck et al. (2004) recommended that the α alpha value be omitted from the DPS calculation. Similarly, we also calculated the ratio of M1 and M3 P to (Al+Fe), simply referred to as M1-P/(Al+Fe) and M3-P/(Al+Fe).

In addition to the WSP method, P desorption by water was also estimated by the "ponded" P method (Beck, personal communication). Soil samples were placed into saturated-paste cups to a depth of 1.3 cm (80 cm^3), to which 25 mL of deionized water was added and allowed to equilibriate overnight. Fifty five mL of deionized water was then added to yield a 1:1 soil:solution ratio by volume resulting in ponded conditions. After 30 minutes, 15 mL of ponded solution was removed from the surface. The collected ponded solutions were filtered through a 0.45 μm filter and analyzed for P using ICP-AES.

Simulated Rainfall Study

Dried and sieved soils were poured into wooden runoff boxes approximately 100 cm x 20 cm x 5 cm in size, replicated three times, leveled, and pre-saturated 24 h before being placed under a rainfall simulator to ensure that runoff would occur during the rainfall event (SERA-17, 2004). The amount of water necessary to pre-saturate each soil type was determined by adding water to the box until ponding on the soil surface occurred. That same volume of water was then applied to all boxes containing the respective soil type.

The rainfall simulator consisted of a single "Tee Jet" HH-SS-50WSQ nozzle attached to a 3m x 3m x 3m metal frame, and calibrated to achieve an intensity of 7.5 cm hr^{-1} at 90% uniformity. The runoff boxes were placed randomly under the rainfall simulator on steel racks adjusted to a 5% slope. Rainfall events were 30 min long and all runoff was collected in 9-L plastic containers. Runoff sub-samples were pipetted in 10-mL aliquots from bulk runoff samples that were being mixed on a stir plate to keep all sediment in suspension. These sub-samples were analyzed for DRP (40 mL runoff filtered through 0.45 μM Millipore filter papers and analyzed by the Murphy and Riley colorimetric method [Murphy and Riley, 1962]).

Soil Incubation

Subsamples from the lowest M1-P extractable samples of the Frederick, Groseclose, Tatum, and Davidson soils (10, 11, 10, and 6 mg M1-P kg^{-1}, respectively) were sieved to 2 mm and adjusted to pH 6.0 using 0.01 *M* HC1 and NaOH for an incubation study intended to determine P adsorption and desorption patterns in regard to Al and Fe. Each soil type was split into thirteen 200 g samples placed in plastic cups with lids having aeration holes to ensure that anaerobic conditions would not occur. A P solution (KH_2PO_4) was added to each soil type at rates of 0, 98, 197, 296, 394, 493, 985, 1478, 1971, 2463, 2956, 3449, and 3942 kg P ha^{-1} and incubated at 25ºC (Precision low temperature incubator, model 815, Winchester, VA) for 60 d at 13% moisture. At the end of the incubation, a sequential chemical extraction for inorganic P was conducted on the soils: (a) 1 *M* NH_4Cl, 30 min reaction time for loosely soluble P; (b) 0.5 *M* NH_4F, 1 h reaction time for Al related P (Al-P); and (c) 0.1 *M* NaOH, 17 h reaction time for Fe related P (Fe-P). In addition, each soil sample was analyzed for ponded P concentrations as previously described.

Statistical Analysis

The distribution of data was tested for normality by the Shapiro-Wilkes statistic conducted by the "Univariate" procedure of the Statistical Analysis System, Version 8.0 (SAS Institute, 1998). All correlation, and analysis of variance procedures were conducted by standard procedures using SAS.

RESULTS AND DISCUSSION

Soil Properties

The range for selected background properties of the soils used in the runoff study are listed in Table 1. Although most of the soils exhibited a wide range in WSP, some soil types were limited in the range of M1-P. For example, although the Davidson had a wide range in WSP, the M1-P values were limited relative to the other soil types. This highlights the differences between the two P extracting solutions, specifically that Mehlich 1 can vary in P extracting efficiency as a function of soil type. Presumably, this variation in P extraction efficiency is a result of the differences in P forms among the soils types.

Based on the Virginia Tech Soil Testing Lab guidelines, most of these soils are considered to range from "medium" (6 – 18) to "very high" (> 55) in M1-P, although some of the soils are considered "low" (0 – 6) and only range up to "high" (18 – 55) in M1-P. It is important to keep in mind that these ratings are based on agronomic crop P needs, and do not necessarily reflect potential P loss risk. Ranges in soil pH were typical for agricultural soils with the exception of a Tatum and Emporia soil sample which had a pH > 7.5 (Table 1). As expected, soil clay content was the highest among the three Piedmont soils (Cecil, Tatum, and Davidson), lowest among Coastal Plain soils (Emporia, Slagle, and Bojak), and intermediate among Ridge and Valley soils (Frederick, Groseclose, and Sequoia) (Table 1). Further, the lower WSP content of the Coastal Plain soils may be related to the lower clay content of those soils compared to the Piedmont and Ridge and Valley soils (Table 1) since soils with clayey textures tend to adsorb more P than sandy textured soils (Fox and Kamprath, 1970; Loganathan et al., 1987).

Predicting Runoff Dissolved Reactive Phosphorus Losses using Soil Phosphorus Extractions

Runoff volumes were not significantly different among soil types. In addition, since there was no significant relationship between clay content and runoff volume ($R^2 = 0.01$), correlation procedures were conducted on runoff concentrations and will be referred to as "P losses". Runoff DRP losses were well related to soil P (Table 2, Figs. 1 and 2). Various authors have also shown that soil Fe-strip P, M1-P, M3-P, WSP, M3 DPS, and Ox DPS can be fairly good predictors of runoff DRP (Torbert et al., 2002; Penn and Sims, 2001; Pote et al., 1996). Although the relationships between various soil P measurements and runoff DRP were statistically significant when grouped based on soil type, it is more practical to group soil types together into physiographic provinces. This is warranted due to the fact that soil types within a certain physiographic province are more similar compared to soils outside that physiographic province. The relationship between soil P and runoff DRP varied based upon physiographic province (Table 2, Figs. 1 and 2) just as several other studies have shown that the relationship will vary between soil types (Sharpley, 1995; Pote et al., 1999, Penn et al., 2005).

Since the Mehlich 1 and 3 solutions were designed to extract a variety of soil P pools, it is not surprising that these soil tests resulted in varying relationships depending on physiographic province (Table 2). However, within physiographic provinces, M1-P was better related to runoff DRP compared to M3-P (Table 2). Although R^2 values for the two extractants were nearly the same for Piedmont and Ridge and Valley soils, M1-P was better related to DRP losses among Coastal Plain soils (Table 2).

As expected, the soil P tests based on DI water (WSP and ponded P) showed less variation between physiographic provinces in regard to the relationship with runoff DRP (Fig. 1). This is likely due to the fact that the extracting solution for WSP and ponded P (DI water) is more similar to the simulated rainfall water (tap water) compared to the Mehlich 1 and 3 solutions. However, Fig. 1 shows that for a given amount of WSP and ponded P, the Coastal Plain soils caused significantly higher concentrations of runoff DRP compared to the Piedmont and Ridge and Valley soils, which were not significantly different from each other. Initially it appeared as though the low clay content of Coastal Plain soils (Table 1) may have been the cause for the observation that the Coastal Plain soils possessed a significantly different ponded P and WSP vs DRP relationship compared to the Piedmont and Ridge and Valley soils. However, soil clay content is merely indicative of the P sorption capacity of soils (Mozzaffari and Sims, 1994), not the strength in which P is held onto the soil (Penn et al., 2005; Vadas et al., 2004). In this case since Coastal Plain soils possess a greater percentage of measured ponded P and WSP that is lost in runoff as DRP (Fig. 1), this suggests that the Coastal Plain soils may contain different P forms or different P saturation levels compared to the Piedmont and Ridge and Valley soils. Although it is useful to minimize specific relationships between soil P and runoff DRP based upon physiographic province, a “universal” extractant capable of providing one relationship for soil P and runoff DRP would be useful and practical.

According to Figs. 2a, 2c, and Table 2, normalization of extractable soil P content based on soil Al and Fe ($P_{ox}/[Al_{ox}+Fe_{ox}]$ and M1 P/[Al+Fe]) did not correct for the varying runoff DRP relationships among the physiographic provinces. In addition, P_{ox}/Al_{ox} resulted in higher R^2 values ($R^2 = 0.41^*$, 0.80^{**}, and 0.58^{**} for Coastal Plain, Piedmont, and Ridge and Valley soils, respectively) compared to $P_{ox}/(Al_{ox}+Fe_{ox})$, while M1 P/Al was approximately equal to M1 P/(Al+Fe) (Table 2). Interestingly, M3 P/(Al+Fe) was the only soil parameter that resulted in one relationship with runoff DRP for all physiographic provinces (Fig. 2b). This suggests that Mehlich 3 may be extracting forms of P that are most soluble during a rainfall event as well as forms of Fe and Al that the extracted P are adsorbed to. In the case of ammonium oxalate, the loosely held P and more recalcitrant P associated with amorphous Fe and Al is extracted from the soil and analysis of solution Al and Fe does not indicate how much P was associated with each fraction. In contrast, Mehlich 3 extracts both crystalline and amorphous Al (59% of all samples had more Al extracted by Mehlich 3 compared to ammonium oxalate) and removes much less Fe relative to Al compared to ammonium oxalate. For example, 18% of M3 (Al+Fe) was Fe. This trend was also noted by Sims et al. (2002) who found that M3-Fe represented about 7% of M3 (Al+Fe). As a result, the M3 P/(Fe+Al) values may represent the saturation of soil Al with P for acidic, non calcareous soils with very little calcium phosphate. For this reason, we found that the M3 P/Al parameter also resulted in one significant relationship with runoff DRP among the three physiographic provinces (Table 2). Maguire and Sims (2002) also found that M3 P/(Al+Fe) was very well related to M3 P/Al ($R^2 = 0.99$) for five soil types from Delaware. Similarly, in a literature review conducted by Vadas et al. (2004) among 16 independent runoff studies, 24 of the 30 soils did not significantly differ in soil M3-P and Bray-1 P extraction coefficients (slope). The authors concluded that “the agronomic Mehlich-3 and Bray-1 soil tests are equally, if not more, effective for evaluating the potential for soils to release dissolved P to runoff as the environmentally oriented water extraction test”.

Other studies have also noted the superiority in using M3 P/Al for predicting DRP concentrations in runoff and leaching (Sims et al., 2002; Maguire and Sims, 2002; Beauchemin and Simard, 1999; Beauchemin et al., 1996). For example, the Quebec, Canada guidelines for assessing risk of P loss includes Mehlich 3 P/Al, rather than the more common $P_{ox}/(Al_{ox}+Fe_{ox})$ with the use of an alpha factor (Beauchemin and Simard, 1999). Their use of the Mehlich 3 P/Al parameter is based in part on the results of a study conducted on 58 Quebec soils that found that M3-Al was significantly correlated with Xm (P sorption maximum) (Giroux and Tran, 1996). Penn et al. (2005) also found that the amount of P adsorbed from a single point isotherm (whole soils and clay fractions) was mostly related to Al minerals with no significant positive correlations between Fe mineral quantity and P adsorbed. These and other studies suggest that P adsorbed onto Al may be more easily desorbed compared to P adsorbed onto Fe. This could possibly explain why the Coastal Plain soils possessed a greater percentage of WSP and ponded P that was lost as DRP in runoff (Fig. 1).

Coastal Plain soils in Virginia typically contain more Al related P compared to Fe related P. Wijesundara (1996) conducted a sequential P fractionation, various soil test P extractions, and physical/chemical property analyses on 43 Virginia soils (19 Coastal Plain, 17 Piedmont, and 7 Ridge and Valley). In this study all soils except for the Coastal Plain, Fe related P was greater than Al related P. The study also showed that M3-P and Bray P were well correlated to the Al related P fraction, but not the Fe related P fraction. For the soils used in our study, all of the Coastal Plain soils had more Al_{ox} than Fe_{ox} compared to only 30% of the Piedmont and Ridge and Valley soils. The results of Wijesundara's (1996) study suggests the Coastal Plain soils used in this study consisted mostly of Al related P rather than Fe related P. This could explain why the M3 P/(Al+Fe) and P/Al was able to normalize the runoff DRP relationships into one regression line (Fig. 2) because the extracting solution mostly removed Al related P from the soil compared to other forms of P.

Phosphorus Desorption from Al and Fe

The incubation study was designed to examine the solubility of Al related P compared to Fe related P. In order to minimize variability due to differences in soil texture and initial P content, only Piedmont and Ridge and Valley soils were used, and only samples < 12 mg kg-1 in M1-P. Data presented in Fig. 3a shows that three (Groseclose, Frederick, and Davidson) of the four soils contained equal sums of fractionated P (loosely soluble P + Al related P + Fe related P). Thus, a comparison of the ponded P concentrations among these three soils is warranted since each soil is different in its distribution of soil P forms, but equal in the sum of P fractionated (Fig 3b). Note that this fractionation scheme did not include reductant soluble P and Ca related P. These were not included since the former fraction is only soluble under reduced conditions and we expected very little Ca related P in these soils due to the acidic pH and low WSP concentrations. Although the sum of P fractions were equal for the three soils (Fig. 3a), the strength of P retention varied significantly as shown by differences in ponded P concentrations (Groseclose > Frederick, > Davidson) (Fig. 3b). The data in Fig. 3c suggests that the differences in ponded P concentrations may be a result of the differences in P forms among the three soils. Specifically, the soil Al related P content mimicked that of the ponded P concentrations (Fig. 3c) and was opposite of Fe related P (Fig. 4) suggesting that Al related P desorbs P into solution more readily compared to Fe related P. As further evidence, the Tatum soil contained a lower sum of fractionated P than the Davidson (Fig. 3a), but the two soils were not significantly different in ponded P concentrations (Fig. 3b), presumably because the Tatum consisted of more Al related P and less Fe related P compared to the Davidson (Fig. 3c). In addition, Fig. 4 shows that among all four soils, those dominated by a greater percentage (percentage of the sum of fractionated P) of Al related P compared to Fe related P possessed higher concentrations of ponded P.

Several researchers have reported differences between soil Fe and Al compounds in regard to P desorption (Beauchemin and Simard, 1999; Beauchemin et al., 1996; Penn and Sims, 2002). These studies have pointed toward the idea that P saturated Al components are able to release (desorb) P more easily than P saturated Fe components, most likely because phosphate forms a stronger bond with Fe than with Al (Aura, 1978). For example, Hartikainen (1982) conducted a study on 104 Finnish soils to relate WSP parameters to other soil properties. Soil WSP was most closely connected with loosely bound P and Al related P. The correlation of WSP with Fe-P was very poor and non-existent with the reductant soluble fraction. In addition, WSP was well correlated to the ratio of Al related P to Al. The author noted that "The results imply that WSP is primarily controlled by the ratio of Al related P to Al. This explained 77% of the variation in the loosely bound P and also illustrates the role of the Al related P fraction in determining the concentration of phosphate in the soil solution". The ratio of Al related P to Al can be thought of as the P saturation of the Al component of the soil.

Beauchemin et al. (1996) also examined the role of soil Fe and Al in regard to P desorption. Soil columns consisting of a Mawcook soil were leached with a P rich solution in order to adsorb P onto the soil followed by leaching with water. There was a significant relationship between the number of pore volumes of water necessary to reach a concentration of 1 mg P L^{-1} in the effluent and the Al_{ox} content of the samples. This suggests that the reversibility of the sorption process is related, among others, to the Al_{ox} content. Also, there was no statistically significant relationship between the number of pore volumes at 1 mg P L^{-1} and the content of Fe_{ox}, Al_{ox}+Fe_{ox}, or the P sorption index. In a related study, Lemare (1982) also showed that the exchangeability of P was positively correlated with the soil Al_{ox} content.

The results of these studies suggests that because Al has a lower bonding strength with P compared to Fe, Al related P soil components may control P desorption. This would explain why the Coastal Plain soils tended to release more DRP in runoff compared to Piedmont and Ridge and Valley soils for a given amount of WSP and ponded P, and why the M3 P/Al parameter appears to normalize this trend. Similarly, using the same set of soils Penn et al. (2005) found that for a given WSP level, soils possessing higher proportions of hydroxy-interlayered vermiculite (HIV) to kaolinite in the clay sized fraction yielded lower concentrations of DRP in runoff compared to soils with low HIV to kaolinite. The authors attributed this trend to the fact that in sorption studies kaolinite was negatively related to P desorption while HIV was positively related. Presumably, since the P sorption component of HIV is a broken Al hydroxy chain, soils containing greater amounts of HIV would possess less P saturated Al components and thus result in less runoff DRP for a given level of WSP. Also in the previous study soil Fe was not found to be significantly related to P sorption parameters, not because soil Fe is not an important P sink, but because low P soils tend to have more P saturated onto the Fe components compared to the Al components (Hartikainen,1982; Khare et al., 2004). Thus as P was added to the soils more Al was available for P adsorption compared to Fe resulting in P mostly adsorbing onto Al than Fe. This would explain why Penn et al. (2005) found that P sorption parameters were significantly correlated with soil Al minerals.

CONCLUSIONS

Although various soil extractions for P have been shown to be well related to runoff DRP, the relationship typically varies based upon soil type (Sharpley, 1995; Pote et al., 1999). Presumably, this variation occurs because of differences in P forms among soils. As expected in this study, when soil types were grouped based on physiographic province the relationship between soil P and runoff DRP varied among groups. Specifically we found that for a given level of WSP and ponded P, Coastal Plain soils yielded higher concentrations of DRP in runoff compared to Piedmont and Ridge and Valley soils which were not significantly different from each other. However, M3 P/(Al+Fe) and M3 P/Al were the only parameters that resulted in one relationship with DRP for the three physiographic provinces.

Since Mehlich 3 extracts mostly Al related P (Sims et.al, 2002; Maguire and Sims, 2002; Wijesundara, 1996) and since the Coastal Plain soils of Virginia tend to contain more Al related P compared to Fe related P (Wijesundara, 1996), we hypothesized that higher DRP losses in simulated runoff from Coastal Plain soils were due to a P system mostly dominated by Al rather than Fe. Results from the incubation study showed that among soils containing equal amounts of the sum of fractionated P (loosely bound P + Al related P + Fe related P), the amount of P easily desorbed from the soils (ponded P) varied as a function of the soil P distribution. More specifically, soils with a higher proportion of Al related P and less Fe related P desorbed more P into solution compared to soils dominated with Fe related P.

Based on the results of this study and as noted by others (Hartikainen 1982; Beauchemin et al. 1996) it appears that Al controls P desorption in many acidic soils containing little Ca phosphates. This would explain why M3 P/Al normalized the observed differences in the relationship between soil P and runoff DRP for the three physiographic provinces. In theory, P adsorbed onto Al is held with less strength compared to P onto Fe, and as the Al component becomes more saturated with P, P is readily released into runoff. Based on the results of this and other studies (Sims et al., 2002; Maguire and Sims, 2002; Giroux and Tran, 1996), M3 P/Al could be used as a "universal extractant" for predicting DRP losses from acidic, non calcareous soils. This is not however, meant to take the place of a more comprehensive P loss assessment tool such as the P index, only to refine the component of P loss models that incorporate the use of a soil P vs runoff DRP relationship. Because many soil testing labs already routinely conduct Mehlich 3 extractions, this would be both practical and cost effective.

On the other hand, application of this study to the Virginia P index confirms the use of M1-P as the best soil test extractant for predicting DRP concentrations in runoff when the soils can be classified into one of the three physiographic provinces. However, for areas outside of Virginia (acidic, non-calcareous soils) in which the specific relationship for STP with runoff DRP is not known, the M3-P/Al would serve as the best variable in relating STP to DRP losses.

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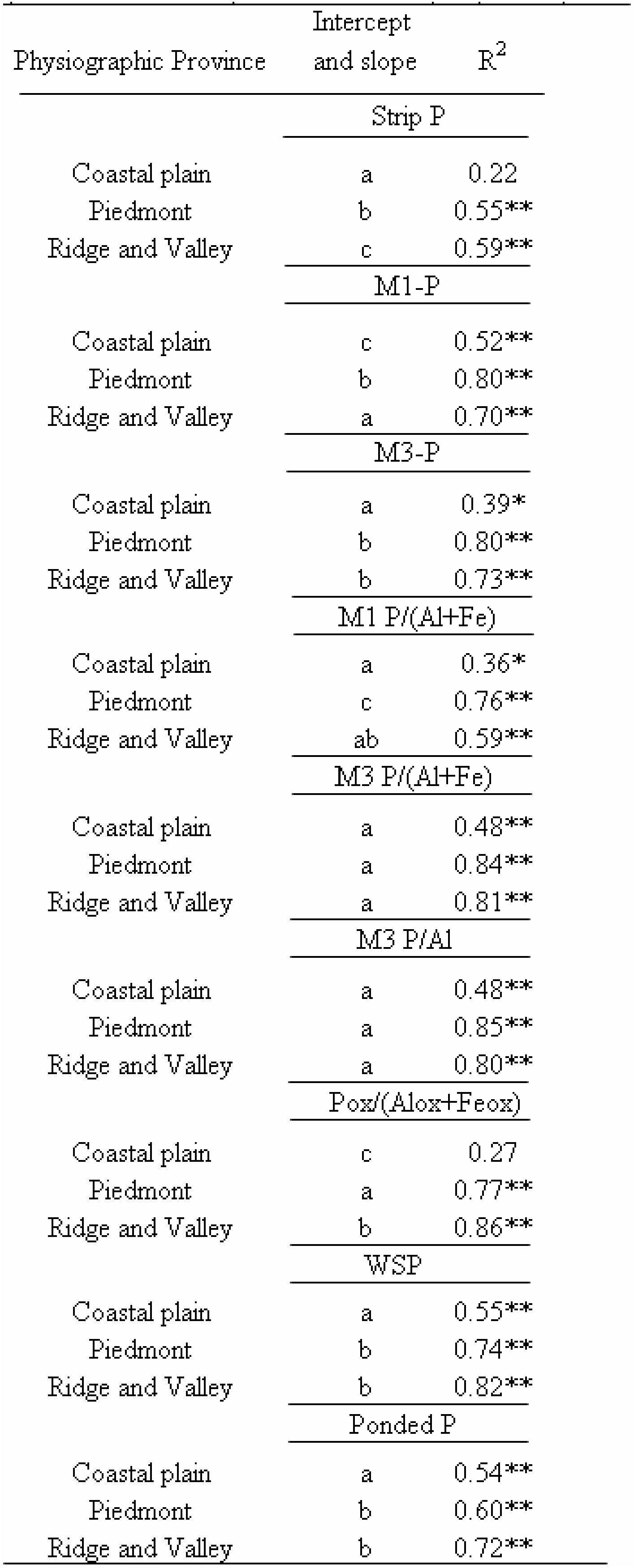
Table 3.1 General properties of soils used for in the simulated rainfall study.Values are presented as a range. Numbers in parentheses are means.

Soil type	WSP	Mehlich 1 P	pH	Clay	Classification
	mg kg^{-1}			%	
Cecil	0.7 - 27.4 (11.7)	4 - 134 (69)	5.1 - 6.8 (5.9)	30 - 56 (38)	Fine, kaolinitic, thermic Typic Kanhapludults
Tatum	2.2 - 18.1 (7.1)	10 - 94 (40)	5.1 - 7.7 (6.7)	23 - 44 (32)	Fine, mixed, semiactive, thermic Typic Hapludults
Davidson	2.9 - 17.1 (8.1)	5 - 28 (19)	5.6 - 6.9 (6.1)	30 - 55 (41)	Fine, kaolinitic, thermic Rhodic Kandiudults
Emporia	3.1 - 9.7 (6.1)	19 - 38 (27)	5.3 - 7.7 (6.0)	7 - 16 (12)	Fine-loamy, siliceous, subactive, thermic Typic Hapludults
Slagle	2.5 - 12.8 (6.3)	10 - 69 (31)	5.8 - 6.9 (6.0)	10 - 16 (13)	Fine-loamy, siliceous, subactive, thermic Aquic Hapludults
Bojac	3.3 - 12.8 (8.1)	13 - 112 (59)	5.6 - 7.1 (6.7)	7 - 18 (14)	Coarse-loamy, mixed, semiactive, thermic Typic Hapludults
Frederick	3.1 - 15.6 (11.6)	10 - 111 (64)	5.5 - 7.1 (6.1)	18 - 40 (29)	Fine, mixed, semiactive, mesic Typic Paleudults
Groseclose	5.6 - 23.7 (14.7)	11 - 91 (59)	6.3 - 7.1 (6.5)	17 - 28 (22)	Fine, mixed, semiactive, mesic Typic Hapludults
Sequoia	6.3 - 13.7 (9.6)	23 - 75 (43)	5.6 - 6.3 (6.1)	34 - 47 (41)	Fine, mixed, semiactive, mesic Typic Hapludults

Table 3.2. Relationship between extractable soil P and runoff DRP for Coastal Plain, Piedmont, and Ridge and Valley soils. Letters indicate significance at p = 0.05 based upon differences between intercept and slope for each group. *, ** indicates significant R2 values at p = 0.05 and 0.01, respectively.



Physiographic Province	Intercept and slope	R^2
	Strip P	
Coastal plain	a	0.22
Piedmont	b	0.55**
Ridge and Valley	c	0.59**
	M1-P	
Coastal plain	c	0.52**
Piedmont	b	0.80**
Ridge and Valley	a	0.70**
	M3-P	
Coastal plain	a	0.39*
Piedmont	b	0.80**
Ridge and Valley	b	0.73**
	M1 P/(Al+Fe)	
Coastal plain	a	0.36*
Piedmont	c	0.76**
Ridge and Valley	ab	0.59**
	M3 P/(Al+Fe)	
Coastal plain	a	0.48**
Piedmont	a	0.84**
Ridge and Valley	a	0.81**
	M3 P/Al	
Coastal plain	a	0.48**
Piedmont	a	0.85**
Ridge and Valley	a	0.80**
	Pox/(Alox+Feox)	
Coastal plain	c	0.27
Piedmont	a	0.77**
Ridge and Valley	b	0.86**
	WSP	
Coastal plain	a	0.55**
Piedmont	b	0.74**
Ridge and Valley	b	0.82**
	Ponded P	
Coastal plain	a	0.54**
Piedmont	b	0.60**
Ridge and Valley	b	0.72**

Fig. 3.1 Relationship between (a) soil WSP and (b) ponded P with runoff DRP for Coastal Plain, Piedmont, and Ridge and Valley soils. Letters indicate significant differences between regression lines at $p = 0.05$. *, ** indicates significant R^2 values at $p = 0.05$ and 0.01, respectively.

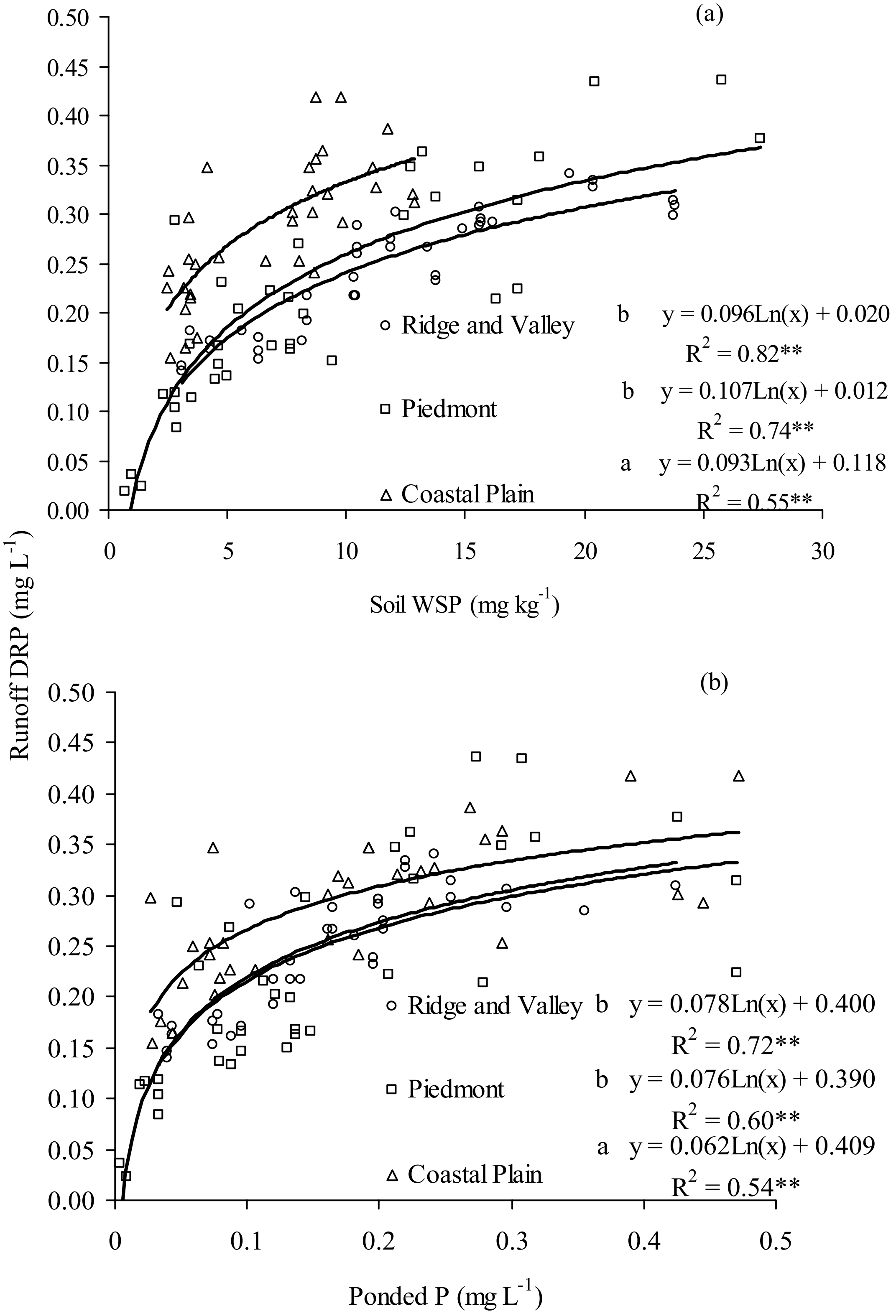


Fig. 3.2. Relationship between (a) soil Pox/(Alox+Feox), (b) M3 P/(Fe+Al), and (c) M1 P/(Fe+Al) with runoff DRP for Coastal Plain, Piedmont, and Ridge and Valley soils. Letters indicate significant differences between regression lines at p = 0.05. *, ** indicates significant R2 values at p = 0.05 and 0.01, respectively.

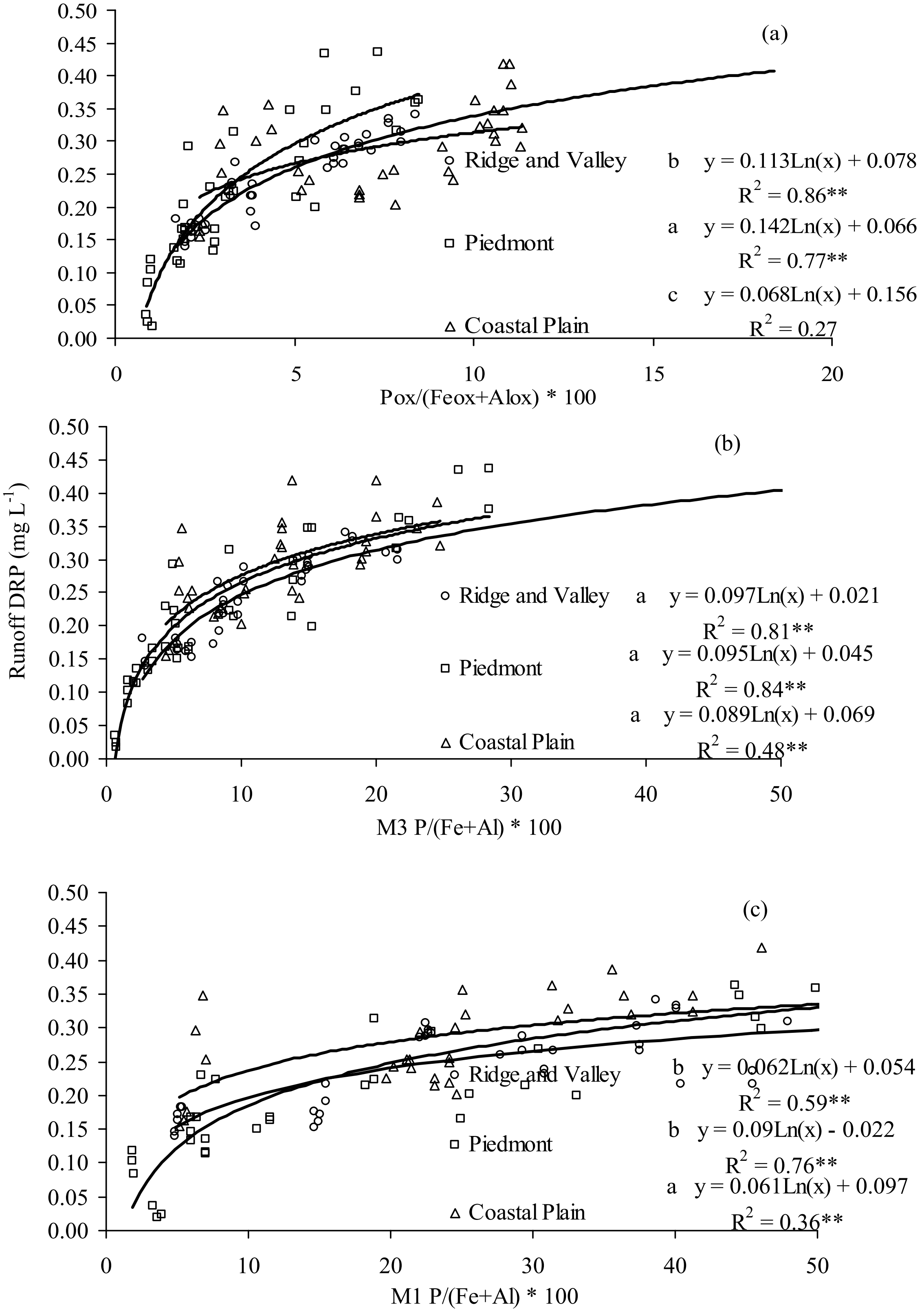


Fig. 3.3. Concentrations of (a) sum of fractionated P (loosely bound P + Al related P + Fe related P), (b) ponded P, and (c) Al related P for Groseclose, Frederick, Davidson, and Tatum soils with P additions. Letters indicate significant differences between regression lines at p = 0.05. *, ** indicates significant R2 values at p = 0.05 and 0.01, respectively.

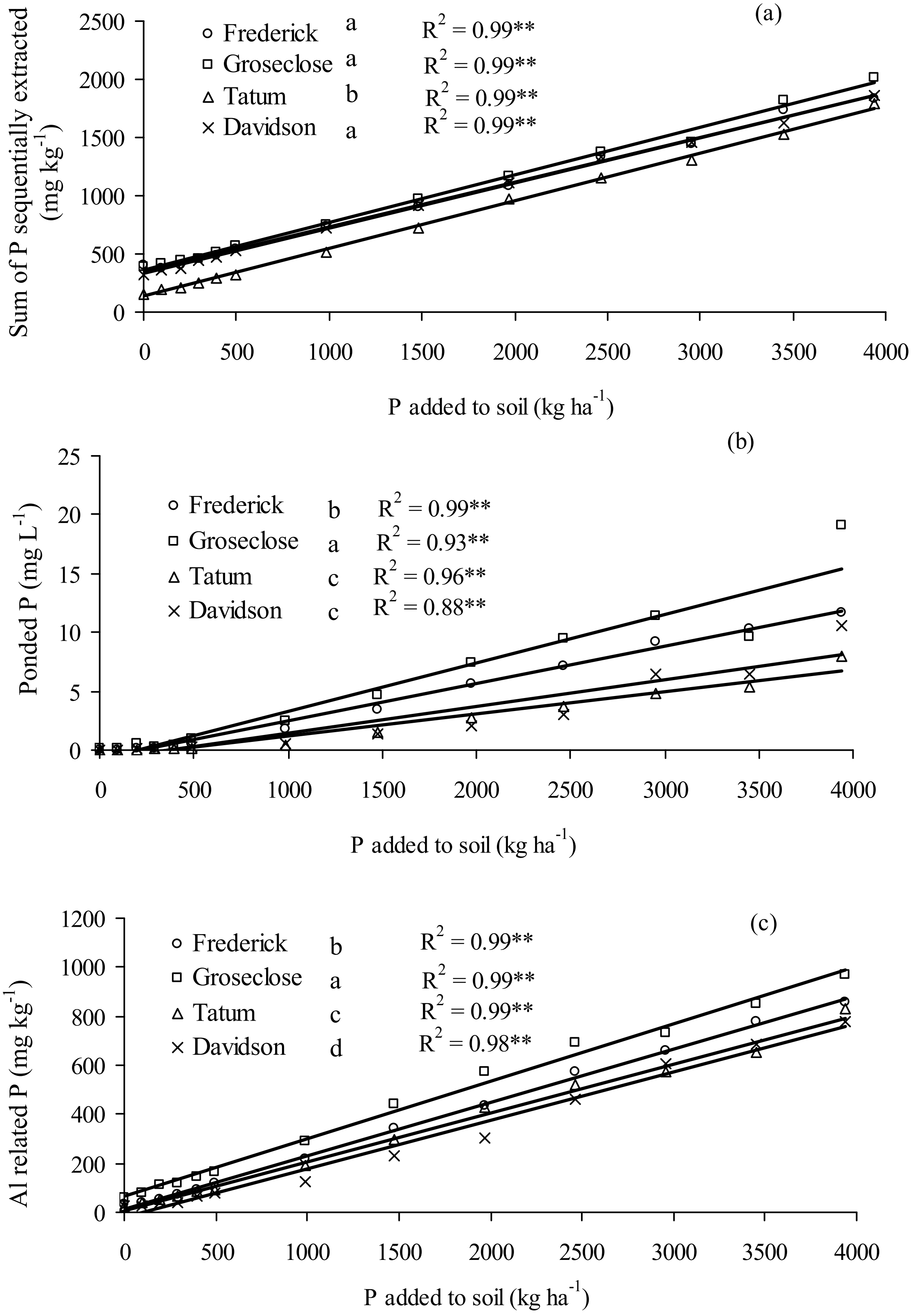
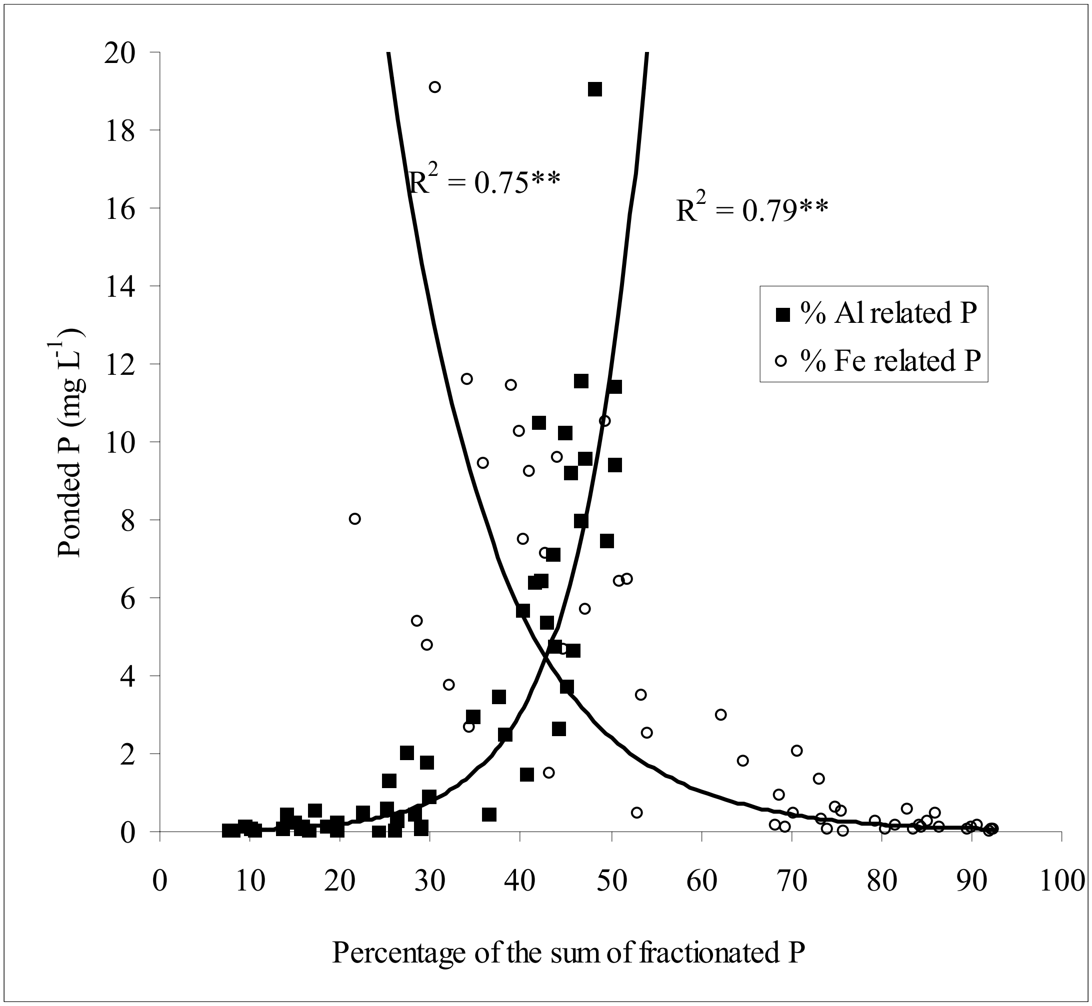


Fig. 3.4. Changes in soil ponded P concentrations with soil P distribution among all soils used in the incubation study. Percent Al and Fe related P presented as a percentage of the sum of fractionated P (Al related P + Fe related P + loosely soluble P). ** indicates significant R^2 values at p = 0.01.



Chapter 4: Surface Runoff Losses of Phosphorus from Virginia Soils Amended with Turkey Manure Using Phytase and High Available Phosphorus Corn Diets

ABSTRACT

Many states have passed legislation that regulates agricultural P applications based upon soil P levels and crop P uptake in an attempt to protect surface waters from nonpoint P inputs. Phytase enzyme and high available phosphorus (HAP) corn supplements to poultry feed are considered potential remedies to this problem because they can reduce total P concentrations in manure. However, less is known about their water solubility of P and potential nonpoint source P losses when land applied. This study was conducted to determine the effects of phytase enzyme and HAP corn supplemented diets on runoff P concentrations from pasture soils receiving surface applications of turkey manure. Manure from five poultry diets consisting of various combinations of phytase enzyme, HAP corn, and normal phytic acid (NPA) corn were surface applied at 60 kg P ha^{-1} to runoff boxes containing tall fescue (*Festuca arundinacea*) and placed under a rainfall simulator for runoff collection. The alternative diets caused a decrease in manure total P and water soluble P (WSP) compared to the standard diet. Runoff dissolved reactive P (DRP) concentrations were significantly higher from HAP manure amended soils while DRP losses from other manure treatments were not significantly different from each other. DRP concentrations in runoff were not directly related to manure WSP. Instead, because the mass of manure applied varied for each treatment causing different amounts of manure particles lost in runoff, the runoff DRP concentrations were influenced by a combination of runoff sediment concentrations and manure WSP.

INTRODUCTION

The transport of P in runoff from agricultural land to surface waters has been reported to contribute to accelerated eutrophication of receiving surface waters (Schindler, 1977; Edwards and Daniel, 1992; Heathman et al., 1995). This nonpoint source of transported agricultural P is typically either from surface soils with P concentrations considered in excess of agronomic needs (Reddy et al., 1980; Pautler and Sims, 2000; Breeuswma et al., 1995), or directly from animal manure that has been recently land applied (Sauer et al., 2000; Edwards and Daniel, 1993). In either situation, a reduction in the amount of total P applied to soils could benefit water quality. In addition, the application of a P source that is less soluble in water could reduce P losses that are occurring directly from land applied manure that has not had sufficient time to react with soil and convert to more stable forms (Sharpley and Syers, 1979; Edwards and Daniel, 1993; Kleinman et al., 2002). Therefore, the buildup of soil test P (STP) and the loss of P directly from applied manures could be reduced by either applying less manure or reducing the total P content of manure applied.

In Virginia, the legislative response to water quality problems associated with nonpoint losses of P was the Virginia Poultry Waste Management Act of 1999 targeting the state's poultry industry and mandates that P application rates shall not exceed crop nutrient needs based on soil test recommendations or crop nutrient removal. As a result of this limitation on the amount of poultry manure land applied, many farms no longer possess sufficient land area to dispose of all their poultry manure and also lack in the capacity to store the waste. Therefore, the ability to decrease manure total P could allow farmers to utilize a greater proportion of their poultry manure in a manner that would also help reduce nonpoint source P losses to surface waters compared to previous management.

Since naturally occurring organic phytate P found in grain is mostly unavailable for utilization by poultry, supplemental P from inorganic sources (usually Ca phosphate) is often added to conventional corn (*Zea mays*) and soybean (*Glycine max*) diets in order to meet the nutrient requirements of poultry. Inorganic as well as plant derived forms of nonphytate P are therefore considered the most digestible forms of P in conventional poultry diets. Although inorganic forms of P are much more digestible than phytate P, they are not 100% available to the bird. As a result, all of the phytate P and a portion of the supplemental inorganic P ingested passes directly through the birds into the manure.

The principal method for increasing digestibility, and thus the efficiency of phytate P uptake is the addition of the phytase enzyme to the birds diet. This enzyme cleaves phosphate groups from the phytic acid molecule, thereby making P available to the bird. Phytase supplemented diets result in greater availability of plant derived P, less inorganic P needed as a supplement, and therefore less total P content in the manure. The use of phytase supplements along with reduced inorganic P supplements has also been shown to reduce the manure total P content by 25 to 30% (Duval, 1996).

A second method for enhancing the digestibility of phytate P in poultry diets involves feeding grains that contain a high amount of digestible P. One example is low phytic acid corn, also known as HAP corn (high available P). This corn hybrid produces grain that is similar in total P content to normal corn, but contains about 60% less phytate P

(Raboy et al., 1994). Several researchers have shown that more P is available to poultry from diets containing HAP corn than diets containing normal corn (Kersey et al., 1998; Li et al., 1998; Yan et al., 1998). Therefore, the net result of HAP corn use is similar to the effect achieved with the phytase enzyme: since a greater proportion of P is ingested in an available form, the total amount of P in the diet and manure can be reduced without sacrificing animal performance.

Although previous research has shown that the use of HAP corn and phytase enzyme in poultry diets can reduce the amount of total P in manure, a study by Lawrence (2000) showed that an observed decrease in manure total P was coupled with an increase in the percentage of total P that is water soluble. As a result, the authors hypothesized that when applied to soil on an equal total P basis, phytase and HAP corn poultry manure would cause increased concentrations of dissolved P in runoff compared to manure from conventional poultry diets.

Therefore our objective was to determine the effects of phytase enzyme and HAP corn supplemented diets on dissolved and total P losses in runoff under a simulated rainfall when the resulting manure is surface applied to tall fescue in runoff boxes.

MATERIALS AND METHODS

Manure Collection and Characterization

The manure for this experiment was generated from a study conducted at Virginia Tech by the Department of Animal and Poultry Science which focused on the effect of diet on turkey nutrition, health, and manure properties. Twelve different diets were replicated eight times with nine turkeys per cage (96 cages) ranging in age from one to five weeks. Birds had access to unlimited feed. The pens containing the birds were housed in environmentally controlled rooms with steel mesh acting as the floor of the pens that were further underlain with its own manure tray. These manure trays were removed daily, scraped clean and the manure discarded except for three manure collection days during the fourth week of the feeding trial (Lawrence, 2000). No bedding was used in the production of this manure, therefore we were working with raw turkey manure rather than poultry litter. The manure samples were mixed mechanically to ensure uniformity before being frozen in storage prior to use in this simulated rainfall study. Dietary treatments used in the study were (i) normal phytic acid corn and 0.135% inorganic P (NPA); (ii) normal phytic acid corn, 600 units phytase enzyme, and 0.135% inorganic P (NPA + 600); (iii) high available P corn and 0.135% inorganic P (HAP); (iv) high available P corn, 600 units phytase, and 0.135% inorganic P (HAP + 600); and (v) normal phytic acid corn and 0.345% inorganic P (NPA + P). Note that the NPA + P diet is the current industry standard.

Manure was characterized as follows:(i) total P by wet digestion using nitric and perchloric acid (Jones and Case, 1990); (ii) WSP (1:10 wet manure:deionized [DI] water, conducted on a dry weight basis, 1 h reaction time, filtration with 0.45 µm Millipore [Bedford, MA] membrane [Kuo, 1996]); (iii) "sediment WSP" extraction on the wet manures using an extraction ratio of manure to DI water equal to the mass of sediment lost in runoff to the volume of runoff water collected, therefore each replication had a unique manure to solution ratio. Solutions were then treated the same as previously described for the standard manure WSP tests; (iv) pH (1:1 manure:deionized water); (v) organic matter (OM; by loss on ignition at 360°C [Nelson and Sommers, 1982]); and (vi) moisture content (based on mass of manure before and after drying for 24 h at 65°C). Analysis of P in solution was determined by inductively coupled plasma emission spectroscopy (ICP-AES).

Soil Collection, Preparation, and Characterization

Blocks of sod approximately 20 cm x 100 cm in size were removed from a Braddock loam (Clayey, mixed, mesic Typic Hapludult) at a depth of 5 cm from the Virginia Tech agronomy research farm (Kentland Farm). The sod consisted of established tall fescue (*Festuca arundinacea*), which had not received any organic amendments or P fertilizer for at least five years prior to sod removal.

The sod was placed into wooden runoff boxes approximately 20 cm x 5 cm x 100 cm with nine drilled holes 3 mm in diameter at the bottom to allow for free drainage. Sod was allowed to equilibrate and establish while being kept moist for four weeks prior to use in the rainfall simulation experiment (SERA-17, 2002). One week after the sod was placed in runoff boxes, we applied 17 kg N ha^{-1} onto the tall fescue in the form of liquid urea-ammonium-nitrate. After two additional weeks of growth, the tall fescue was cut to a height of 10 cm; after an additional week of growth, (24 h before the first rainfall event) the sod was cut to a height of 5 cm. For all trimming, the cuttings were removed from the runoff boxes.

Rainfall Simulation Experiment

Immediately after the tall fescue was trimmed to 5 cm, each turkey manure treatment was uniformly surface applied to the tall fescue at 60 kg total P ha^{-1} (dry weight basis). It is important to note that the manure was applied at its original moisture content and non-incorporated, also the reason for our choice of experimental conditions is because they are representative of agricultural practices found in the Shenandoah Valley of Virginia. In this area, poultry manure although almost always mixed with bedding is surface applied onto pastures often with slopes greater than 10%.

Three simulated rainfall events were then conducted on the amended soils plus a control (tall fescue receiving no manure amendment) at 24 h (Event 1), one week (Event 2), and three weeks (Event 3) after manure application. Soil boxes were kept indoors between rainfall events in order to prevent runoff from naturally occurring rainfall. Each treatment was replicated three times for a total of eighteen runoff samples per event.

Tall fescue was trimmed to a height of 5 cm and runoff boxes were pre-wetted 24 h before each simulated rainfall event to ensure that runoff would occur immediately after rainfall began, however, in regard to Event 1 pre-wetting was done before the manure treatments were surface applied. Simulated rainfall events were conducted at an intensity of 7.5 cm h^{-1} for thirty minutes with uniformity greater than 95% and all runoff collected into a single container. Soil runoff boxes were placed at a slope of 5 % during rainfall events. The simulator was based on the design of Shelton et al. (1985), with one TeeJet 1/2HH-SS50WSQ nozzle (Spraying Systems, Wheaton, IL) placed in the center of the simulator, three meters above the surface of the runoff boxes.

Immediately after a rainfall event, total runoff volume was determined by weight. Collected runoff was then sub-sampled with a pipet while all runoff was constantly mixed on a magnetic stir plate to ensure that all sediment was in suspension. Runoff sub-samples were subjected to the following analysis; (i) dissolved reactive P (DRP, 20 mL of runoff filtered through a 0.45µm filter and analyzed for P by the molybdate blue method (Murphy and Riley, 1962); (ii) total P (100 mL of non-filtered runoff digested by the EPA 3050 total digestion method [USEPA, 1986] with the resulting extract analyzed for P by ICP-AES); and (iii) sediment concentration (40 mL of non-filtered runoff evaporated at 70 ^{o}C).

Statistical Analysis

All data were tested for normality by the Shapiro-Wilkes statistic conducted by the PROC UNIVARIATE procedure of the Statistical Analysis System (Version 8.0) and found to be normally distributed (SAS Institute, 1999). All correlation, regression and analysis of variance procedures were conducted by standard procedures of SAS.

RESULTS AND DISCUSSION

Manure Properties

The addition of phytase enzyme (NPA + 600) and the use of HAP corn (HAP and HAP + 600) in turkey diets decreased the amount of total P and WSP in the resulting manure relative to the standard poultry diet (NPA + P) (Table 1). We observed a 40, 41, and 42 % decrease in manure total P for NPA + 600, HAP, and HAP + 600 diet treatments, respectively (relative to NPA +P). Even greater decreases were observed in WSP concentrations in manure from the alternative poultry diets. For example, there was a 52, 47, and 48 % decrease in manure WSP for NPA + 600, HAP, and HAP + 600 diet treatments, respectively (relative to NPA +P). Note that there were also decreases in manure total P and WSP for the NPA treatment simply due to the fact that this diet did not receive supplemental P. However, this treatment also resulted in poor bird health whereas the other three diets that decreased manure total P and WSP did not adversely affect bird health and productivity (Lawrence, 2000). One consideration to the manure WSP numbers is that the analysis was done in triplicate on each composited manure sample rather than an analysis conducted on each individual pen replication. Therefore, any measure of variability between replications would be meaningless.

In addition to a reduction in manure total P and WSP from the use of phytase enzyme and HAP corn, there was a decrease in the percentage of total P that was water soluble (Table 1, "% WSP"). The percent WSP is greatest for the standard poultry diet (NPA + P) (Table 1) which is in contrast to those found by Lawrence (2000) and Sims et al. (2000), although both of those studies did show a reduction in manure total P content from the use of phytase and HAP corn. A potential explanation for the differences in %WSP among the alternative diets in comparison to results from Lawrence (2000) is the fact that their WSP extractions were conducted over a 15 h period (extracted for 15 h using an automatic extractor, not a 15 h shaking period) using 0.01 *M* $CaCl_2$ as the extracting solution, whereas our study used a one hour shake period followed by an immediate extraction period. Due to the methods being very different, our results cannot be readily compared to those of Lawrence (2000). In support of our results, McGrath et al. (2002) did find that the use of phytase enzyme supplements to poultry diets caused a 5 % decrease in the amount of manure total P that was water soluble. Maguire et al. (2004) also found that the addition of phytase enzyme to turkey diets receiving decreased inorganic P resulted in lowered total P concentrations in manure, but showed no differences in WSP compared to standard diets.

According to our results, land application based on an equal total P basis of these manures would result in a greater mass of phytase and HAP corn manure amended to the soil (Table 1). With many states limiting P applications based on total P contents of the manure and soil extractable P concentrations, more phytase and HAP corn manure (NPA + 600, HAP + 600, and HAP) could be applied per unit area compared to regular turkey manure (NPA + P), thus helping to prevent potential point source P pollution (stored manure) and manure storage/disposal problems. In addition, because the percentage of manure total P that is water soluble is lower in the alternative diets compared to the standard diet, (Table 1) land application of the phytase and HAP corn manure on a total P basis will also result in a smaller amount of manure WSP applied compared to the standard manure. This is important because previous research has shown that increased additions of WSP applied to soils will cause a corresponding increase in the amount of WSP measured in the soil, which will ultimately result in greater concentrations of DRP in runoff during a rainfall event either from the soil WSP reservoir or directly from the amendment itself (Moore et al., 2000a and 2000b; Withers et al., 2001; Kleinman et al., 2002). Penn and Sims (2002) conducted a simulated rainfall study involving the application of biosolids and poultry litter amendments and found a significant correlation between the amount of WSP applied with the amendment and the corresponding increase (relative to a non-amended soil) in soil WSP and runoff DRP concentrations.

Furthermore, in situations where manure is applied on an equal mass basis instead of an equal total P basis, the phytase and HAP corn treatments would again result in the application of less WSP, but also less total P compared to the standard poultry diet. For example, a hypothetical application rate of 15 Mg dry manure ha^{-1} (based on an average plant available nitrogen (N) application rate among the five manure types) would result in the addition of 219, 129, 129, and 127 kg total P ha^{-1} and 122, 58, 63, and 65 kg WSP ha^{-1} for the NPA+P, NPA+600, HAP, and HAP+600 treatments, respectively. In addition to decreased additions of WSP to the soil, the decrease in the amount (relative to the standard diet) of total P applied is equally important since this could help to slow down the buildup of extractable P in the soil. It has been well documented that increasing concentrations of extractable soil P will cause elevated concentrations of DRP in runoff (Sharpley et al., 1978, 1994; Sharpley, 1995; Daniel et al., 1994; Sims et al., 2002).

Phosphorus Losses in Runoff

Runoff volumes were not significantly different among treatments resulting in that runoff loads (mg) are simply 5.3 times runoff concentrations (mg L^{-1}). For the remainder of this paper runoff P "losses" will be expressed as and meant to be taken as concentrations rather than loads. Phosphorus losses from manure amended soils were significantly greater than losses from the non-amended (control) soil for Event 1 (Fig. 1). For Events 2 and 3, P loss in runoff from manure amended soils decreased dramatically, so that 80 to 95% of cumulative P loss occurred during the first rainfall. Similarly, 70 to 95% of cumulative sediment loss occurred in the first rainfall event. High loss of P in the first runoff event following manure application is typical (McLeod and Hegg, 1984; Sharpley, 1997). These results show the enormous potential for surface applied, non-incorporated manures on pasture to contribute to nonpoint source P pollution. In contrast, Sharpley (1997) showed that DRP concentrations in runoff from soils where poultry litter had been incorporated at a rate of 160 kg P ha^{-1} ranged from 0.17 to 1.34 mg L^{-1}. In our study the lowest DRP concentration in runoff from manured soils was 61 mg P L^{-1}. Incorporated manures or manures applied to bare soil have a much greater contact with soil than manure applied to pasture. This greater contact increases soil adsorption of the water soluble P in manure, thus decreasing P availability to loss in runoff.

Effect of Manure Type on P Losses in Runoff

For all simulated rainfall events, total P and DRP concentrations in surface runoff were significantly lowest from the non-amended soils (control) (Fig. 1). Among manure amended soils, there were no significant differences in total P losses in runoff during Event 1. However, Event 1 DRP concentrations from the HAP manure treatment were significantly higher than all other treatments, while the remaining manure treatments were not significantly different from each other (Fig. 1). For rainfall Events 2 and 3, DRP and total P concentrations among manure amended soils were not significantly different from each other, with the exception of HAP manure in Event 2 being significantly higher and NPA+P significantly lower in total P compared to the other treatments.

In an attempt to explain why the HAP manure caused the largest concentrations of DRP in runoff from Event 1, various water extractions were conducted on the manures and correlated to P losses in runoff. There was no relationship between the WSP concentration in the manure and DRP concentration in runoff. This was not expected since many previous studies have shown that WSP contents of P amendments are usually well related to DRP losses in runoff (McDowell and Sharpley, 2001; Penn and Sims, 2002; Kleinman et al., 2002). In addition, the percentage of manure total P that is water soluble (% WSP) and the mass of WSP applied with each treatment was also poorly related to runoff DRP concentrations and loads.

Instead, we found that sediment losses from the manure-amended soils appeared to be related to DRP losses with the result being a good relationship between the percentage of manure lost in runoff and runoff DRP concentrations (Fig. 2). Although it is considered typical for sediment losses to be related to total P losses in runoff (Yli-Halla et al., 1995; Sharpley, 1997; Withers et al., 2001), it was unexpected to observe the correlation between the percentage of manure lost and DRP. The calculation of percent manure lost in runoff was based on the fact that sediment losses from non-amended soils (control) represent erosion of only non-manure particles, one can subtract this amount from the sediment losses of manure amended soils and estimate how much of the runoff sediment concentration was manure particles. This calculation revealed that 93 to 97% of the sediment load in rainfall Event 1 from manure-amended soils was manure particles. In this case we hypothesize that the manure particles are desorbing high amounts of P into solution both during transport and after being deposited into the runoff collection container with very few soil particles to act as a P sink resulting from the conditions of the study (wet manure surface applied to pasture).

Effect of Sediment Losses on P Losses in Runoff

Due to the fact that each manure was amended on an equal total P basis, the total mass of manure applied to each box also varied between treatments (Table 1). The large variation in the mass of wet manure applied to the tall fescue was well related to the amount of sediment (manure particles) collected in runoff during each rainfall event (Fig. 3). Thus, the higher the rates of manure surface applied onto the boxes, the greater the concentration of manure particles found in the resulting runoff. The increased loss of manure particles then resulted in a corresponding increase of runoff total P and DRP (Fig. 2).

We hypothesized that under these conditions (wet manure surface applied onto pasture, without incorporation), the runoff DRP concentration is strongly influenced by manure particles lost in runoff that desorb high amounts of P in solution both during and after transport into the water body (collection container). However, because the WSP content of each manure is different from one another (Table 1) and since each manure type had a different concentration of sediment in runoff (Fig. 3), it seems logical that each manure would have a unique “sediment WSP concentration”, where sediment WSP concentration is defined as the concentration of dissolved P in runoff resulting from the desorption of P from sediment (manure particles in runoff). This is based on the knowledge that over 90% of sediment lost in this study was actually particles of manure. This hypothesis was tested by correlating measured “sediment WSP” concentrations (WSP extraction on the wet manures using an extraction ratio of manure to DI water equal to the mass of sediment lost in runoff to the volume of runoff water collected) to runoff DRP concentrations. It has been shown that soil and manure particles may be preferentially eroded due to their physical and chemical characteristics (Sharpley and Kleinman, 2003; Sharpley, 1980), therefore an extraction of the entire manure would not exactly represent the eroded particles. Additionally, the chemical composition of the runoff water was likely quite different from the DI water used to extract the manure. Nonetheless, we hypothesized such an extraction would provide a good index of how the manure properties and sediment concentrations in runoff interacted to produce the DRP concentrations determined in this study. Figure 4 shows that both the sediment concentration in runoff (i.e. eroded manure particles) and the WSP concentration of the manure controlled runoff DRP concentrations from each manure amended soil.

Figure 5 shows that DRP in runoff is a likely a function of sediment loss and P solubility in manure. In Fig. 5 sediment and manure WSP concentrations are calculated on a relative 1 to 10 scale (i.e. for manure WSP, the treatment with the highest manure WSP concentration is assigned a level of 10, and all other treatments are calculated relative to this) and added to each other (20 is the highest possible level for any treatment). One can see that the sum of relative sediment and manure WSP levels is well related to actual DRP concentrations measured in runoff. As previously discussed, eroded manure particles comprised most of the sediment lost in runoff from pastures receiving surface applied manure and manure application rate determines the amount of manure eroded in runoff (Fig. 3). Therefore, because losses of manure particles were well related to runoff DRP (Fig. 2) and runoff DRP under these conditions was shown to be a function of both manure lost and manure WSP (Fig. 4), we can illustrate the extent of which each of the two controlling factors influenced runoff DRP concentrations for each treatment in Fig. 5. The relationship observed in Fig. 5 clearly demonstrates that DRP concentrations in runoff from pastures receiving surface applications of poultry manures can be dominated by high manure application rates (thus, high concentrations of manure particles in runoff; i.e. HAP), high P solubility in manure (NPA+P), or a combination of both (NPA+600, HAP+600, and NPA).

Under these conditions where manure was surface applied onto pasture, the amount of manure particles lost in runoff (which was a function of manure application rate) appeared to have at least as much influence on DRP concentrations in runoff compared to the manure WSP content (Figs. 3 and 4). Therefore when manure application rates are based on total P, manures with lower total P contents resulting from alternative poultry diets such as NPA+600 and HAP (Table 1) can result in a greater mass of poultry litter land applied (Table 1) and thus higher concentrations of DRP and total P in runoff even though these manures contain the lowest amounts of WSP and %WSP compared to the other treatments (Table 1). However, we speculate that if the tall fescue was amended at equivalent rates of manure it is likely that we would have observed that manure types such as NPA+P containing high concentrations of total P and WSP would cause the greatest concentrations of DRP and total P in runoff. Another consideration is that if the tall fescue was amended in a manner that left a short length of non-amended buffer area at the end of the runoff box we may have found that the concentration of WSP in the manure would have a greater effect on runoff DRP than sediment losses since this would prevent much of the eroded manure particles from entering the water body (collection container). Finally, because the simulated rainfall intensity (7.5 cm h^{-1}) is much higher than most natural rainfall events, the loss of particulate manure in runoff would probably be less under normal circumstances. This would likely cause DRP and total P concentrations to be significantly lower than what we observed and may also result in manure WSP concentrations to be the dominating factor controlling DRP losses in runoff.

Nussbaum-Wagler et al. (2002) conducted a rainfall simulation study on Cecil (Fine, kaolinitic, thermic Typic Kanhapludults), Sleeth (Fine-loamy, mixed, active, mesic Aeric Endoaqualfs), and Creldon (Fine, mixed, active, mesic Oxyaquic Fragiudalfs) soils, in which swine and poultry manure from standard diets and a low phytic acid corn plus phytase enzyme diet were surface applied at equivalent N rates. The authors found that there was less DRP, bioavailable P, and total P in runoff from the alternative diet compared to the standard diet for both animal species.

Lastly in regard to P loss assessment tools such as the P index (Lemunyon and Gilbert, 1993), our results suggest that there lies a need to account for P losses from actual manure particles that are lost in runoff. For example, Kleinman and Sharpley (2003) found that the influence of manure WSP on runoff P grows with application rate in a study that involved surface applications of poultry, swine, and dairy manure to soil at six different rates. Many P loss models include soil erosion as a transport factor, but do not directly account for manure losses (Weld et al., 2000).

CONCLUSIONS

With the Virginia Poultry Waste Management Act in effect October 2001, the maximum amount of P that poultry producers can apply onto "high" P soils (> 55 mg kg^{-1} Mehlich 1 P) is equal to a three year P crop removal rate. As a result, there lies a need to reduce the total P content of poultry manure and litters so that producers can continue to utilize their manure by land application in a manner that will not adversely affect water quality. Results from this study show that the addition of phytase and HAP corn to poultry diets can reduce the amount of total P and WSP in manure compared to standard poultry diets. In addition, the percent of manure total P that is water soluble was also reduced by using phytase and HAP corn supplemented poultry diets. Therefore when applied on an equal total P basis, a greater rate of HAP corn and phytase manure could be land applied compared to manure from standard diets without applying greater amounts of WSP that can potentially be lost in runoff. When applied on an equal mass basis, manure from phytase and HAP corn diets will add less total P and WSP to the soil compared to manure from standard poultry diets which will help to prevent soils from becoming "very high" in soil test P (assuming that the amount of total P applied is not in excess of crop requirements).

With the exception of HAP manure, the alternative diets caused no significant increases in Event 1 runoff DRP and total P concentrations compared to the standard diet (NPA+P). Under the conditions in this study which consisted of surface applied wet manure applied at an equivalent total P basis onto tall fescue, we found that runoff DRP and total P concentrations were poorly related to the WSP contents of the manures alone, instead P losses were also influenced by the sediment concentrations in the resulting runoff due to the fact that > 90% of the eroded sediment was made up of manure particles. As a result when applied on a total P basis, manure types that contained lower concentrations of total P (i.e. HAP) had higher application rates of manure resulting in higher sediment concentrations which translated into higher total P and DRP losses. We showed that eroded manure particles were strongly contributing to the observed runoff DRP concentrations by conducting manure WSP extractions using a manure to solution ratio equal to the measured sediment concentration in runoff and correlating the resulting WSP concentrations to DRP losses in runoff.

Overall, runoff DRP concentrations were influenced by the combination of application rates and manure WSP concentrations. As the total amount of manure surface applied increased (i.e. manure from the alternative diets), manure particles were more easily lost in runoff. These eroded manure particles desorbed P into solution based on the WSP concentration of the manure itself. In determining what manure types posses the greatest potential for causing P losses in runoff, the conditions of the application will greatly affect the outcome (type of surface, incorporation vs non-incorporation, type of application rate), not just the WSP content of the manure itself. Although the alternative diets can reduce the WSP contents of the manure, potentially resulting in a decrease in runoff DRP losses, the management of the manures is equally influential on DRP runoff losses.

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Table 4.1. General manure properties as a function of turkey diet.

Diet	Total P	WSP[†]	% WSP[‡]	Wet manure applied[§]	pH	OM[¶]
	—g kg^{-1}—	—mg kg^{-1}—		—— Mg ha^{-1}——		—g kg^{-1}—
NPA+P	14.6	8120	55.6	17.2	5.10	750
NPA	9.2	4383	47.6	27.7	5.16	770
NPA+600	8.6	3872	44.9	32.3	4.84	710
HAP	8.6	4220	49.2	36.2	5.24	790
HAP+600	8.4	4315	51.1	27.9	5.38	770

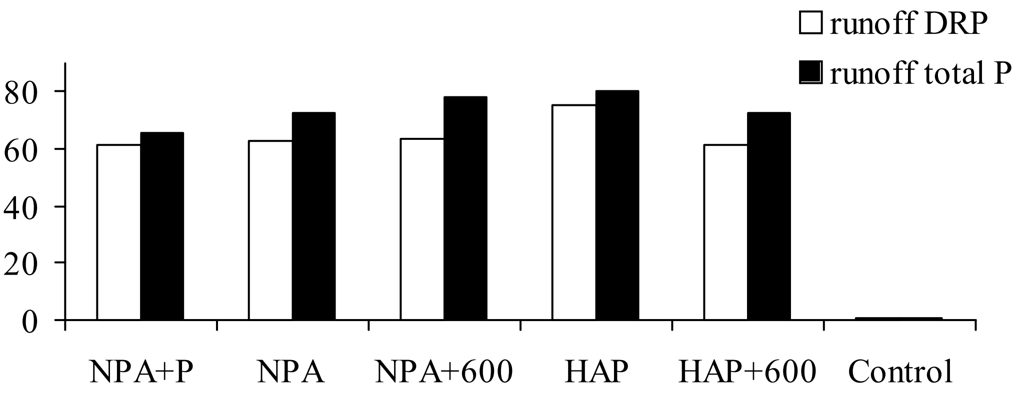
† Water soluble P, determined from 1:10 wet manure:de-ionized water

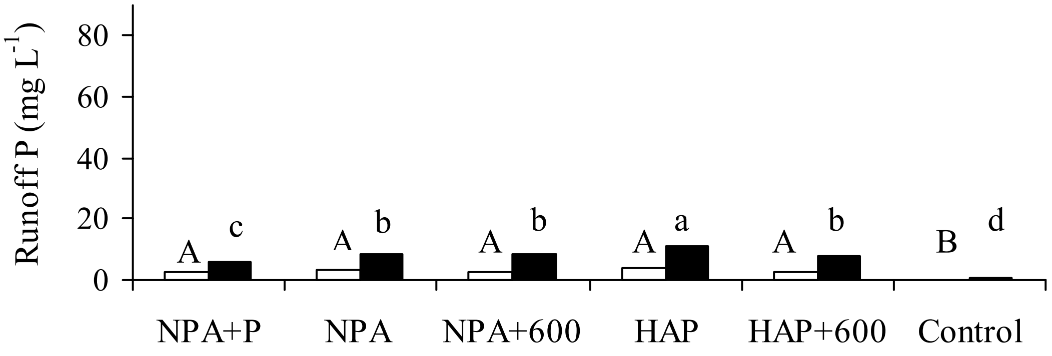
‡ Percent of total P that is water soluble

§ Total mass of wet manure applied to runoff boxes based on 60 kg total P ha^{-1} (dry weight basis)

¶ OM, organic matter

Fig. 4.1. Mean runoff dissolved reactive phosphorus (DRP) and total phosphorus (total P) concentrations following surface applications of different poultry manures to tall fescue during (a) rainfall Event 1, (b) rainfall Event 2, and (c) rainfall Event 3. Letters above bars columns identify groupings of means that are not significant at p = 0.05, with capitals denoting DRP and lowercase denoting total P.


(a) Event 1


(b) Event 2

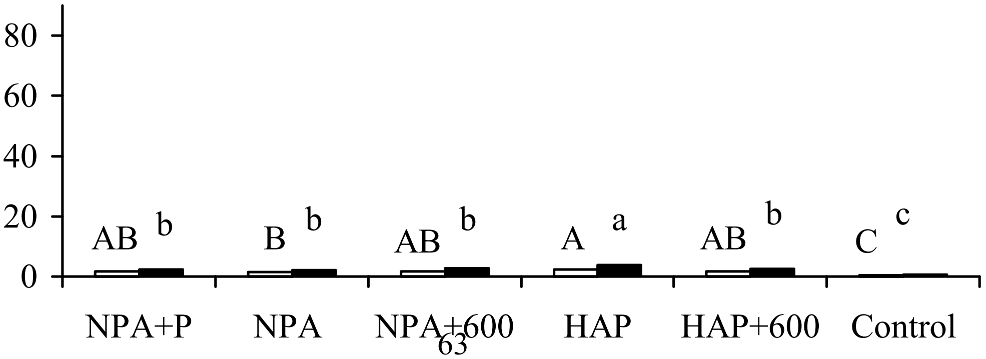

(c) Event 3

Fig. 4.2. Effect of particulate manure lost in runoff on Event 1 runoff dissolved reactive phosphorus (DRP) and total phosphorus (total P) concentrations.

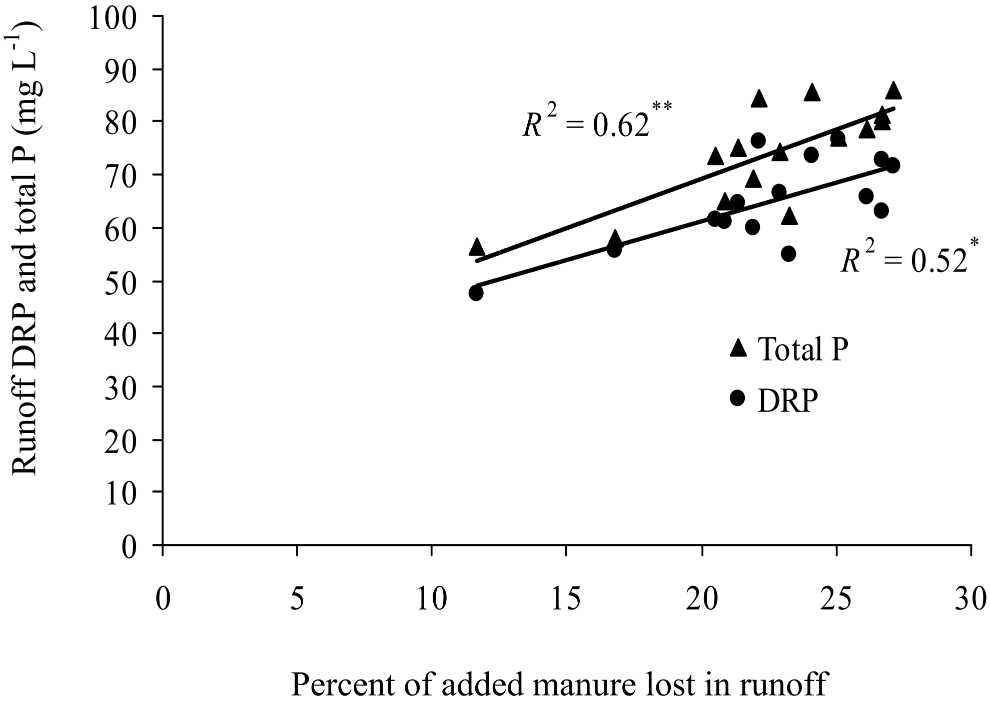


Fig. 4.3. Effect of manure application rates on sediment concentrations in runoff from manure amended soils during each rainfall event.

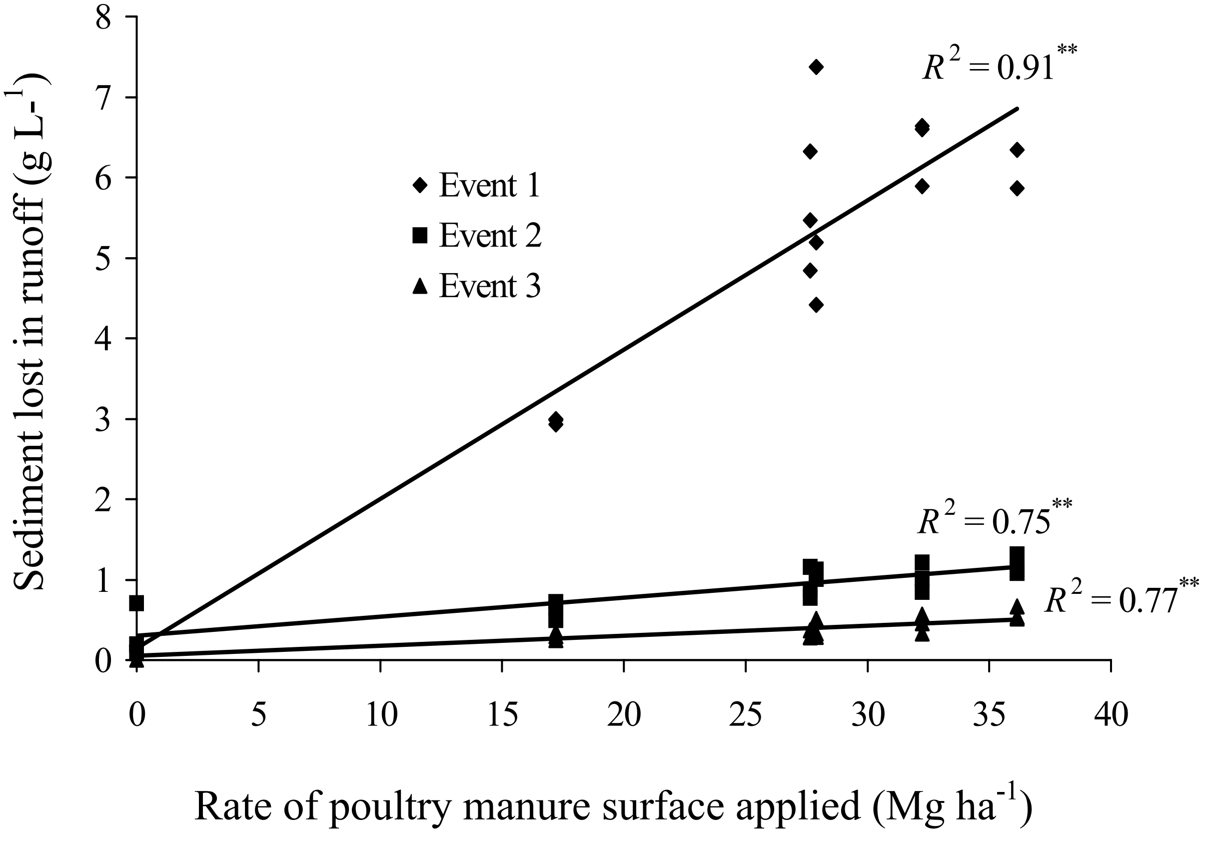


Fig. 4.4. Relationship between measured sediment waster soluble phosphorus (WSP) and dissolved reactive phosphorus (DRP) concentrations in runoff from manure amended soils. Measured sediment WSP concentration determined from WSP extracted from manure using a manure:solution ratio equal to measured sediment concentration : measured runoff volume.

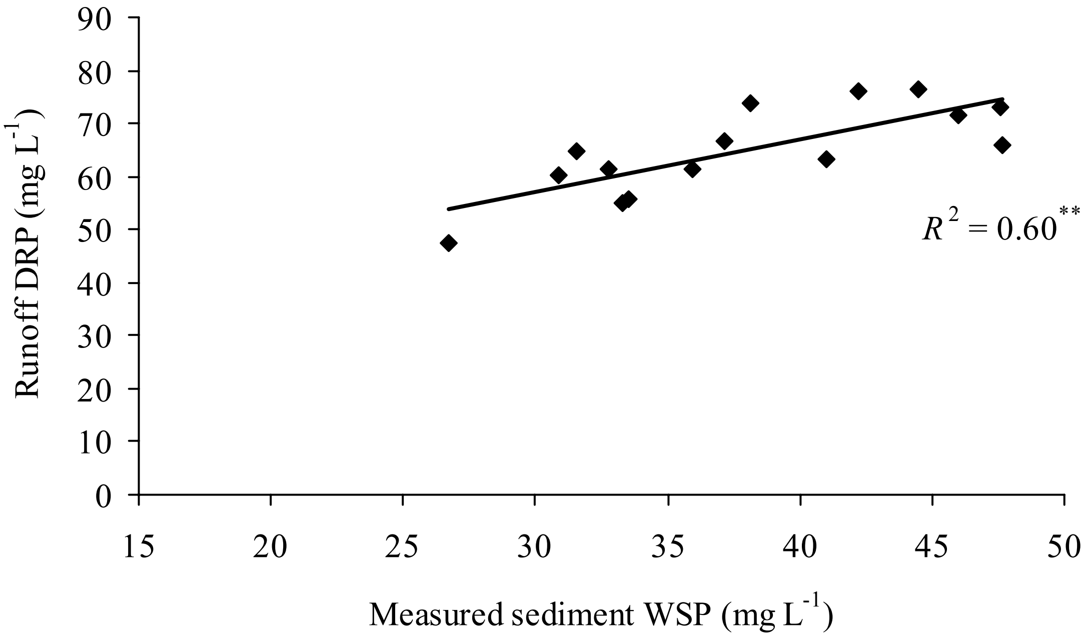
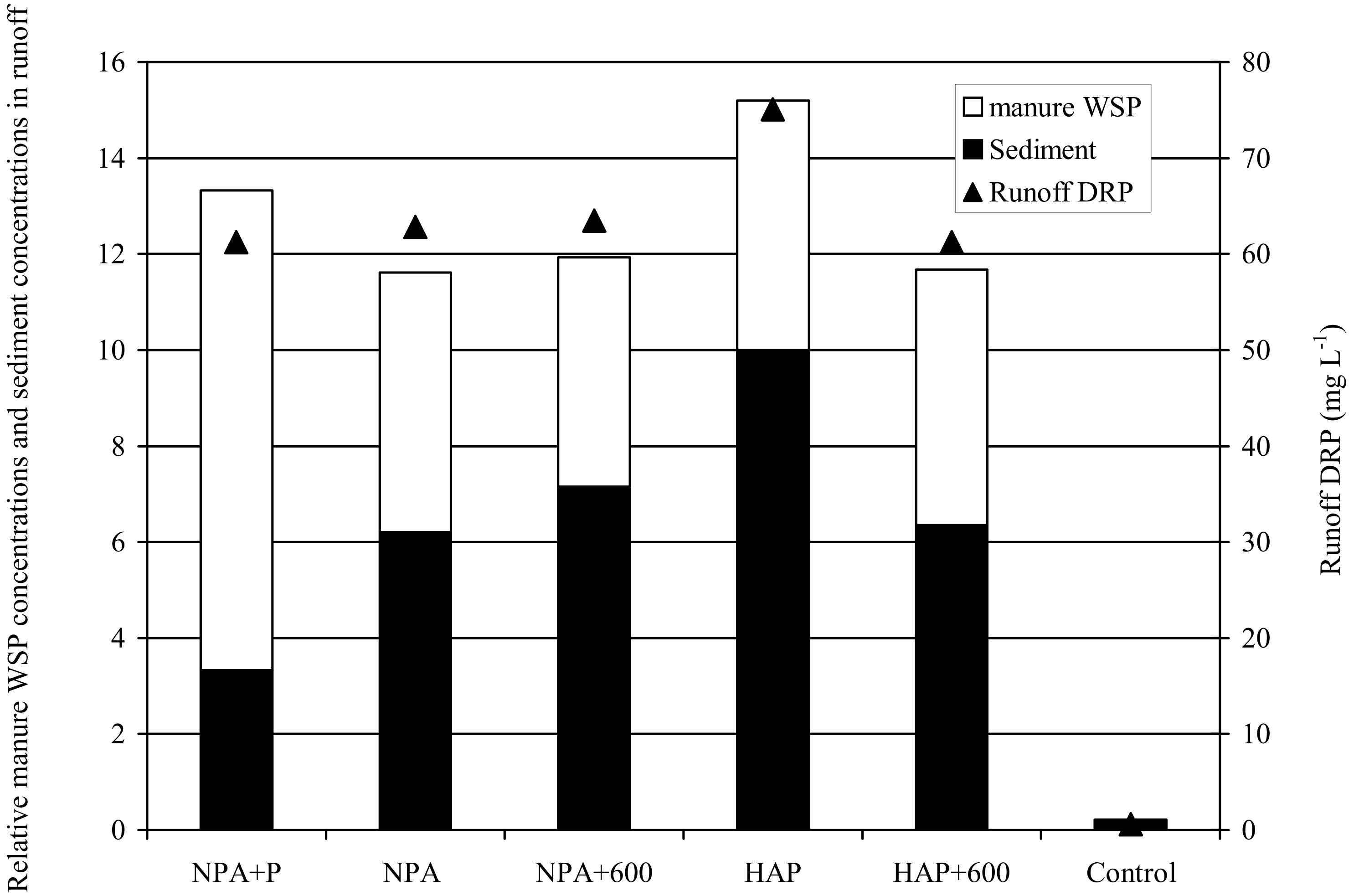


Fig. 4.5. Relative contribution of manure sediment losses and manure water soluble phosphorus (WSP) concentrations to measured Event 1 runoff dissolved reactive phosphorus (DRP) concentrations. Relative manure WSP and sediment levels calculated on a 1 to 10 scale with the highest sediment and manure WSP concentration set equal to 10 and all others calculated relative to it.



Chapter 5: Overall Conclusions

Previous runoff studies involving unamended soils indicated that different soil types vary in the relationship between soil P and runoff DRP. This variation further complicates P loss prediction models and assessment tools and implies the need for determining the soil P vs runoff DRP relationship for every major soil type. Since this would be time consuming, impractical, and expensive, an alternative solution is necessary. Because P adsorption and desorption is truly a function of mineralogy, then mineralogical analysis of a soil could indicate its potential to release P in runoff.

We found that soil Al minerals (HIV, amorphous Al, and gibbsite) were well related to P retention in whole soils and clay fractions during both adsorption and desorption isotherms, while kaolinite content was negatively related to P retention. Surprisingly, soil Fe minerals were not significantly related to P retention in whole soils or clay fractions. This may have occurred due to a preference of P for Al over Fe, possibly because Fe minerals were already more saturated with P compared to Al minerals. Adsorption and desorption isotherms conducted on pure minerals indicated that Fe minerals (goethite and hematite) adsorbed and retained the most P after four sequential desorptions compared to gibbsite, which was followed by kaolinite.

When soils were split into groups based upon mineralogy using the ratio of "HIV/kaolinite" as an indicator of "high" vs "low" risk for runoff P losses, those soils with high HIV/kaolinite caused significantly less DRP in runoff for a given soil WSP content compared to low HIV/kaolinite soils. These differences were also observed when soil WSP was normalized for clay content.

Although it is useful to know that soils high in Al minerals such as HIV and low in kaolinite are at less risk for releasing DRP into runoff, the use of such knowledge may not be very practical in application. For example, application of this to P models implies that the mineralogical make-up of each soil type be known, and although the soil survey contains soil mineralogical data, this data is based on the subsoil instead of the topsoil where rainfall interacts with soils. On the other hand, a mineralogical analysis of major agricultural topsoils would still be more practical and less expensive compared to conducting simulated rainfall experiments on the same soils for a variety of soil P levels.

Next, an attempt was made at grouping soils based on physiographic province, since soils within each province are considered more similar to each other compared to soils not in the same province. Again, almost all soil tests (M1-P, strip P, M1-P/[Al+Fe], Ox P/[Al+Fe]) resulted in significantly different relationships with DRP. Somewhat better was WSP, ponded P, and M3-P, which resulted in the same relationship for the Piedmont and Ridge and Valley soils, but significantly different from the Coastal Plain soils. In each case, for a given amount of soil WSP, ponded P, and M3-P, the Coastal Plain soils had more DRP lost in runoff. However, the M3-P/(Al+Fe) parameter resulted in one relationship with runoff DRP in which each physiographic province was not significantly different from each other.

This was likely due to the fact that Mehlich 3 solution dominantly removes Al from the soil compared to Fe, thus the M3-P/(Al+Fe) parameter is truly a measure of the P saturation onto Al. In addition, M3-P/Al was not significantly different from M3-P/(Al+Fe). M3-P/(Al+Fe) may have acted as a "universal extractant" because Al related

P is held with less strength compared to Fe related P as suggested by previous studies, and because Mehlich 3 extracts mostly Al related P. This also implies that the reason the Coastal Plain soils in this study possessed a greater percentage of soil WSP and ponded P lost as DRP in runoff compared to the other soils was because Virginia Coastal Plain soils typically contain more Al related P than Fe related P.

These results are not to suggest that soil Fe is not an important P sink, but that P desorption is mainly a function of soil Al and its saturation with P. This idea was supported by previous studies and the incubation study which showed that soils with equal amounts of total P (sum of fractionated P) varied in ponded P concentration as a function of Al related P and Fe related P. Specifically, soils containing more Al related P and less Fe related P had lower ponded P concentrations compared to soils dominated with Fe related P. These results are supported by the mineralogy study and also help explain why soils dominated with Al minerals such as HIV tended to retain P better during sorption isotherms and under rainfall simulation.

Combining results from this and previous studies may be useful in creating a qualitative, theoretical model for P adsorption and desorption in acidic, non-calcareous soils dominated with Al and Fe. (i) Initially on clean mineral surfaces which have no P, added P is preferred onto Fe; (ii) the resulting Fe related P is held very tightly and does not readily desorb into solution; (iii) as Fe surfaces become more saturated with P, the continued addition of P results in that newly added P is now preferred onto Al surfaces; (iv) Al related P is held with much less strength compared to the Fe related P; (v) as a result, it is Al related P that mainly desorbs P into solution while Fe related P contributes less, comparatively; (vi) thus, the degree of P desorption into solution is mainly a function of P saturation onto Al.

Regardless of mechanisms, the M3-P/Al and M3-P/(Al+Fe) can be used as a universal extractant in P loss prediction models that incorporate the relationship between soil P and runoff DRP. Since Mehlich 3 is considered a routine agronomic soil test by many soil testing labs, this would prove to be both practical and cost effective.

The final study involved P losses from pasture soils receiving poultry manure which resulted from various diets. In regard to the different broiler diets, the use of phytase enzyme and HAP corn reduced WSP and total P in the manure compared to conventional broiler diets. Therefore, land application on an equal total P basis would result in that a greater mass of phytase and HAP manures could be applied. This is particularly important since current legislation in Virginia restricts poultry manure applications based on soil test P concentrations and crop uptake. In addition, land application of the phytase and HAP corn diet manures on an equal mass basis would result in less total P and WSP applied to the soil. This would decrease the rate in which soil test P increased, thus resulting in less potential for runoff losses to occur compared to manure from conventional diets.

When the manures were surface applied at equal total P rates to runoff boxes containing tall fescue, there were few significant differences in runoff DRP and total P among the different manure types. In addition, manure WSP was not related to runoff DRP losses. Instead, DRP losses were more of a function of sediment losses, which consisted of > 90% manure particles. Knowing the sediment concentration in runoff and the volume of runoff lost from every soil box, the “sediment WSP” concentration was determined. This measurement was made by conducting a WSP analysis on each treatment and replication at the ratio of manure:water equal to the ratio of sediment lost:runoff volume. The resulting P concentration in solution was well related to runoff DRP and confirmed that the observed DRP concentrations in runoff were a function of both sediment (manure particles) lost in runoff and the WSP concentration of the manure itself. In this case because manure was applied on an equal total P basis, manures with more total P resulted in a lower mass of manure applied compared to manures with lower total P concentrations. Thus, the treatments that had a greater mass of manure applied (HAP corn, phytase) resulted in DRP concentrations that were mostly attributed to greater sediment (manure particle) losses, while DRP losses from the conventional manure (more total P, less manure applied) was mostly attributed to increased manure WSP content.

The results from this study emphasize the importance of best management practices that prevent manure particles from leaving the site of application and particularly from directly entering surface bodies of water.

Chapter 6: Summary

Although problematic losses of P from agricultural land results primarily due to the application of P beyond the needs of plants and poor management practices in high transport areas, the root of the problem is a result of a geographic nutrient imbalance. Since much of the animal feed consumed in the Eastern U.S. is produced in the Mid-West, the net result is an overall accumulation of nutrients such as P among high animal density farms in the East. In order to truly remedy the problem, excess nutrients (animal waste) produced in the East would have to be transported back to the soils of the Mid-West where the animal feed was originally grown. Since this option is not currently considered to be economically viable, alternatives such as diet manipulation to increase animal P use efficiency (phytase and HAP corn), chemical treatment of wastes (alum, for example), and BMPs designed to prevent P from entering surface waters are currently receiving attention. As a result, greater emphasis has been placed on the ability to accurately predict P losses in runoff or index P loss risk using readily available or accessible information.

The results from the first two studies (influence of soil type on P losses) of this project could be very useful in determining the risk of DRP loss from soils not having received a recent P amendment, while information from the final study (diet modifications) could be useful in estimating the differences in potential P losses from different types of poultry manure. Although these studies were scientifically sound, several limitations of the experimental conditions should be considered when these results are applied to field situations.

The concentrations of P in simulated runoff from the runoff boxes may not be exactly the same as what is measured in the field. The purpose of the runoff boxes is to simply compare treatments and to determine differences between treatments, not to make an estimate of P concentrations that are actually delivered from agricultural fields and entering surface waters. At best, the measured runoff P concentrations are an estimate of edge of field P losses. For example, from the first study one could conclude that for Virginia soils not having recently received a P amendment, Coastal Plain soils will have higher DRP concentrations in runoff compared to Piedmont soils for a given soil WSP level. However, these results cannot be used to estimate exactly what concentrations of DRP one could expect in runoff from Coastal Plain soils.

Phosphorus concentrations from runoff boxes may vary from field situations for several reasons. Because the soils used in the boxes are dried and sieved, the soil no longer has the same structure as prior to collection in the field. Due to the shallow depth of the boxes, the hydraulic head is different from that which occurs in the field, and the drainage may not be representative of field conditions. Next, runoff as it occurs over the landscape may encounter many different fields, soil types, and cover types before it ever reaches surface water (if it reaches surface water). These effects are not accounted for when using runoff boxes. That is why the runoff boxes are an edge of field estimate. The next issue concerns the rainfall intensity used in all three studies. For Blacksburg, Virginia, 7.5 cm h^{-1} is considered to have a return period of 25 to 30 years. This is a very high intensity and is not representative of typical local conditions in Virginia. However, this intensity is considered to be a national standard with the intent of comparing data throughout the country and was chosen to provide the worst case scenario since most P is lost during high intensity storms. Similarly, saturating the soil prior to a runoff event creates a situation that may be different from what typically occurs in the field. As a result of this practice there may be more runoff produced using the runoff boxes than would have probably occurred in the field under natural rainfall conditions. It is important to consider that this and the other manipulated experimental conditions of indoor rainfall simulation were chosen in order to obtain better uniformity among replications and to better determine differences between different treatments.

Although there is much data available in regard to P adsorption on many soils (including Virginia soils), few studies have included runoff P loss data without the influence of P additions. Therefore, the results from the unamended soil runoff study can be directly applied to the SERA-17 benchmark soil database. This database consists of P concentrations in runoff from various soil types considered to be "benchmark" agricultural soils for each state.

The most accurate runoff data for use in a P loss prediction model would be results from field studies; however, the advantage of runoff box data as presented in this study is that these experimental conditions allowed for the ability to attribute differences in runoff P concentrations to soil type only (all other factors were kept constant). In addition, the runoff DRP concentrations would be more realistic compared to soil WSP values. One direct application of this data is to the Virginia P index which currently utilizes ponded P values as an estimate of runoff DRP concentrations. This ponded P value is calculated from a linear equation that relates M1-P to ponded P values for each physiographic province. Therefore, the data from this study could be applied to the P index and used to directly predict runoff DRP from M1-P rather than using ponded P as an estimate of runoff DRP.

Because this project also showed that the soil M3 P/Al parameter could be used as a "universal" (regardless of physiographic province) runoff DRP predictor, this data could be readily used by other states. As a result, other states with P indices could utilize the relationship between soil M3 P/Al and runoff DRP without having to conduct rainfall simulation studies on various soil types of interest. As an alternative, soils with high amounts of kaolinite could be considered at greater risk of causing runoff DRP losses while soils dominated by HIV could be considered to pose a lower risk in regard to DRP losses (based upon the mineralogy study).

In regard to future studies stemming from this research, there are several possibilities. In regard to P adsorption by HIV, more work is needed in order to confirm this hypothesis. Various selective dissolution techniques could be employed in achieving this objective including P sorption studies before and after removing the interlayer component (Al hydroxy polymer) of HIV. An alternative or supplement to this study could be a solid state technique that could identify P in the interlayer of HIV. One problem with these approaches is that there is no natural, pure sample of HIV that exists. HIV does not occur in mines as does kaolinite and montmorillonite. Synthetic production of HIV is possible, but synthetic HIV is very difficult to make and does not display the same selectivity as natural HIV.

Solid state techniques could also be used in determining if a preference for P onto Al and Fe exists, and also in determining the relative solubility of P adsorbed onto Al compared to Fe. This information could become very important in choosing chemicals that could be used as soil amendments with the purpose of making soil P less soluble.

Several possible studies result from the runoff experiments conducted on the "unamended" (not having received P additions within 1 year prior to collection) soils. Since we observed that no unamended soil resulted in more than 0.5 mg DRP L^{-1} in runoff, it would be interesting to learn if there is some type of an upper limit to P losses in runoff from unamended soils. This "ceiling" in runoff DRP concentration could be a function of the kinetics of P desorption from soils during a runoff event. For both amended and unamended soils, the effect of rainfall intensity on runoff DRP losses and the balance between runoff DRP and total P would also be useful information. As previously stated, since the rainfall intensity used in this study was relatively high and represented a rare storm event, P losses in runoff from less intense storms would be of interest.

Chapter 7: Appendix

Fig. A.1. Net change in DRP concentration after movement through a soil cup (Ponded P – leached P) as related to soil $P_{ox}/(Fe_{ox}+Al_{ox})$.

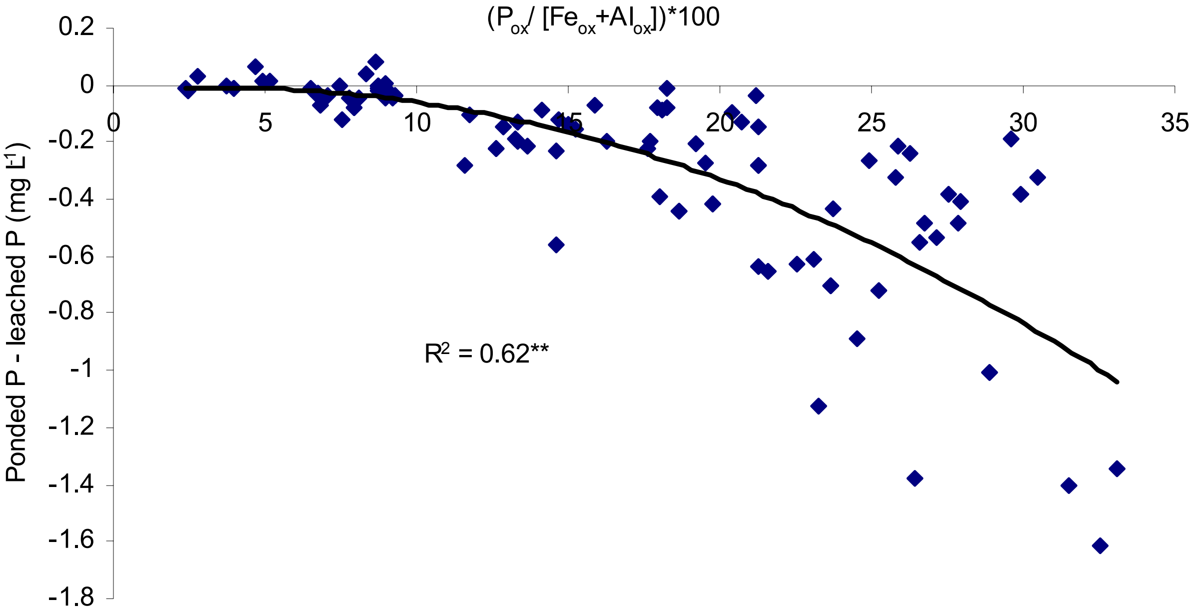


Fig. A.2. Natural log of enrichment ratio (ER) as related to the natural log of runoff sediment concentration. ER = runoff Fe strip P (mg P kg^{-1} sediment) / soil Fe strip P (mg P kg^{-1} soil).

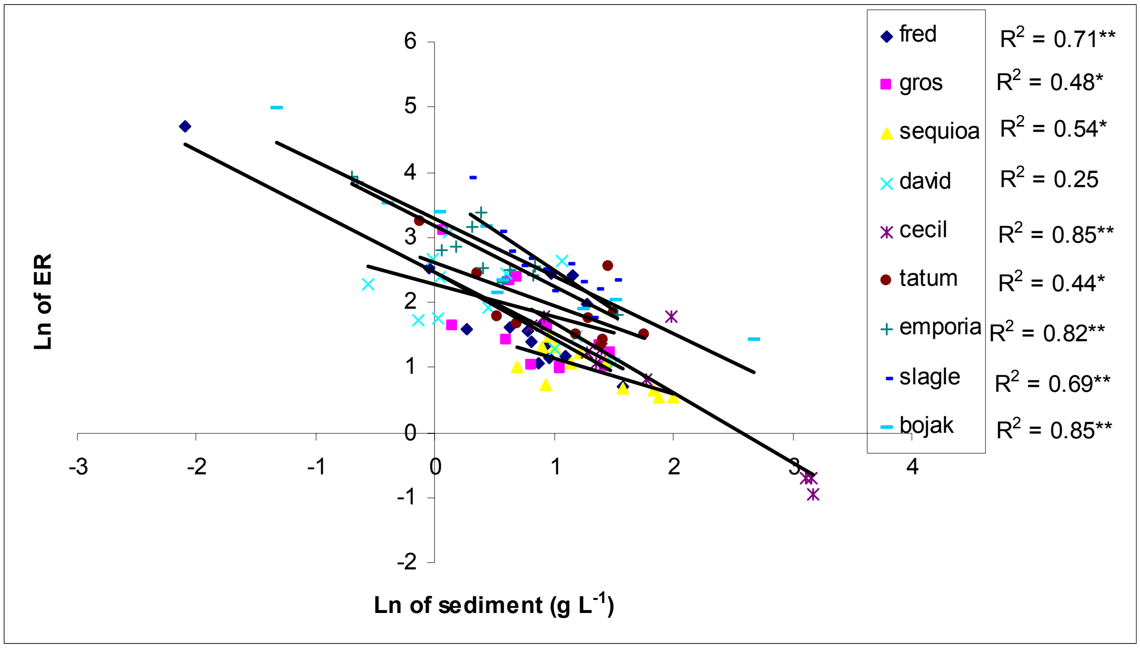


Fig. A.3. Effect of soil clay content on runoff P availability and variablility in the relationship based upon soil kaolinite content. Runoff P availability = (runoff Fe strip P / runoff total P) * 100.

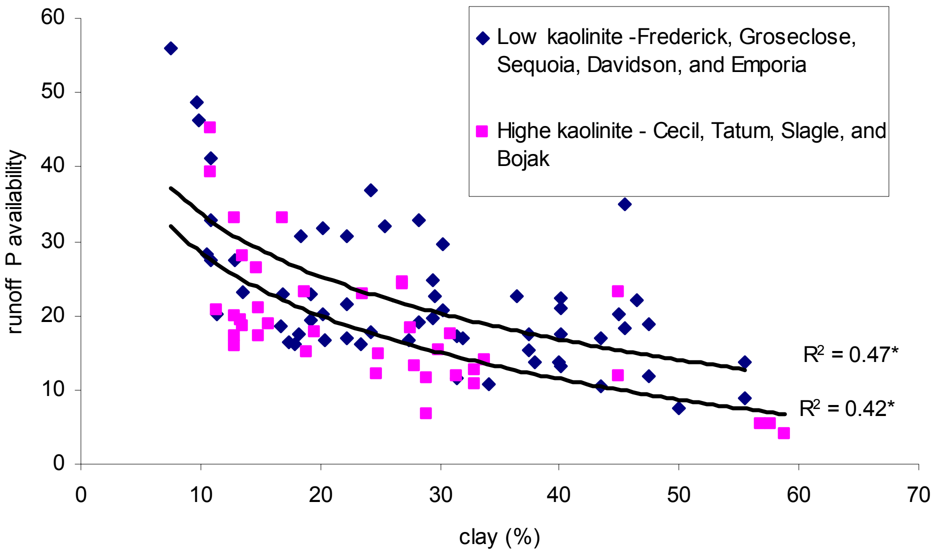


Fig. A.4. Effect of soil clay content on runoff enrichment ratio (runoff Fe strip P / soil Fe strip P).

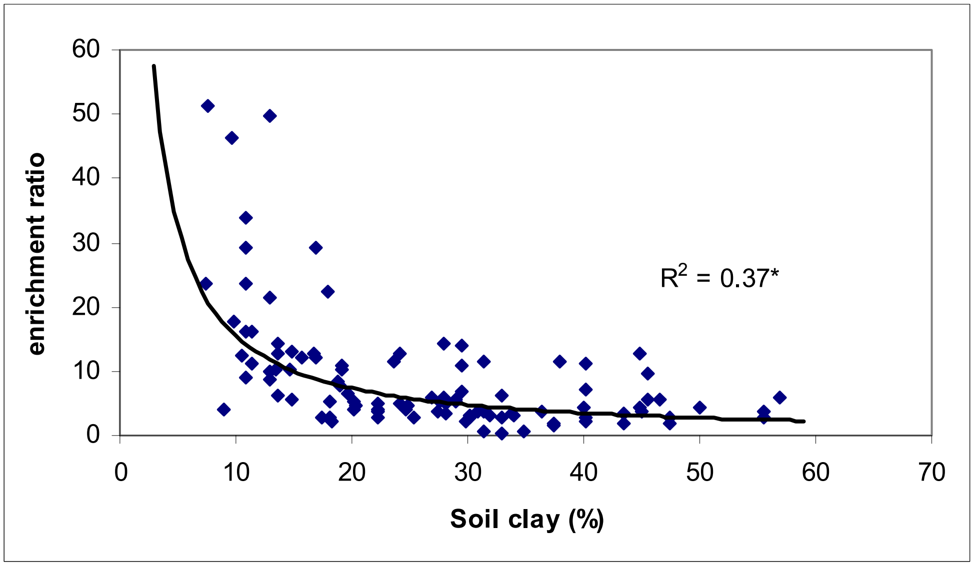


Fig. A.5. Correlation between runoff volume and soil clay content.

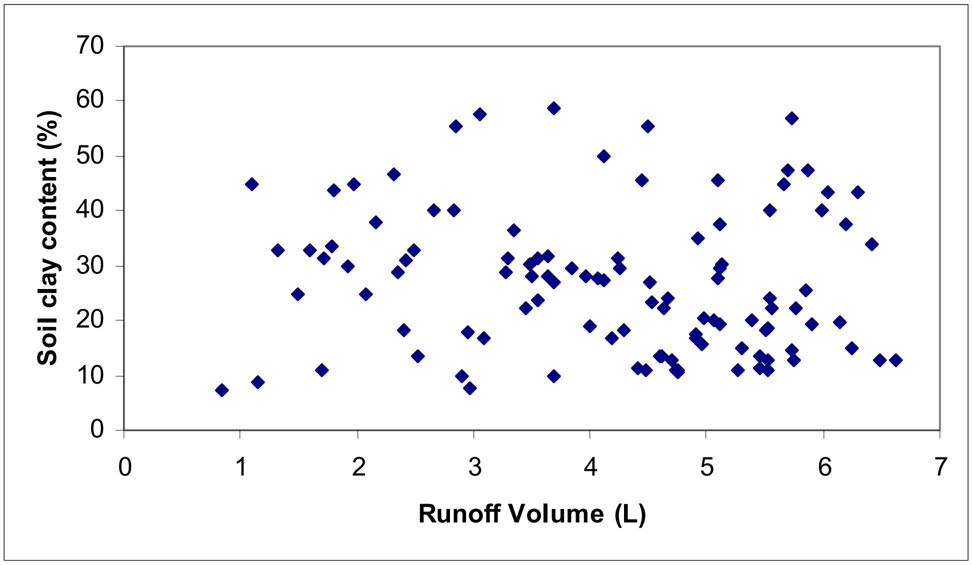


Fig. A.6. Relationship between Soil M3-P and M3-Al and Fe.

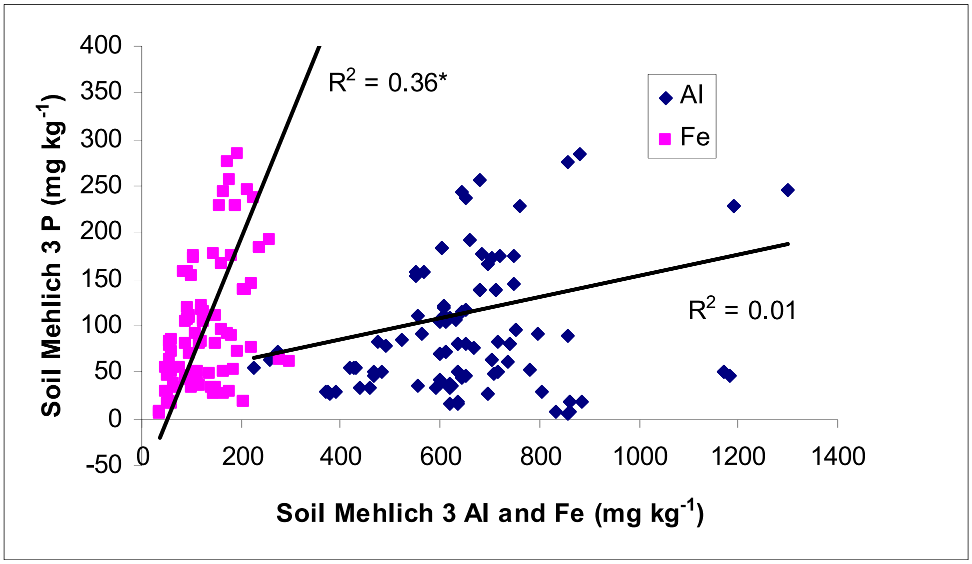


Fig. A.7. Effect of soil M3 Al/Fe ratio on the relationship between soil WSP and runoff DRP.

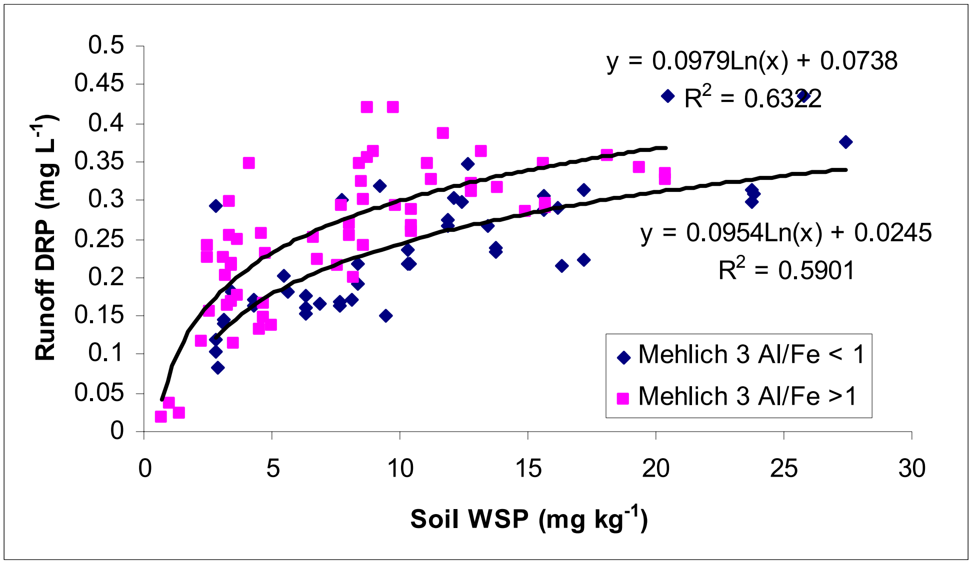


Fig. A.8. Changes in P forms among four soil types with P addition.

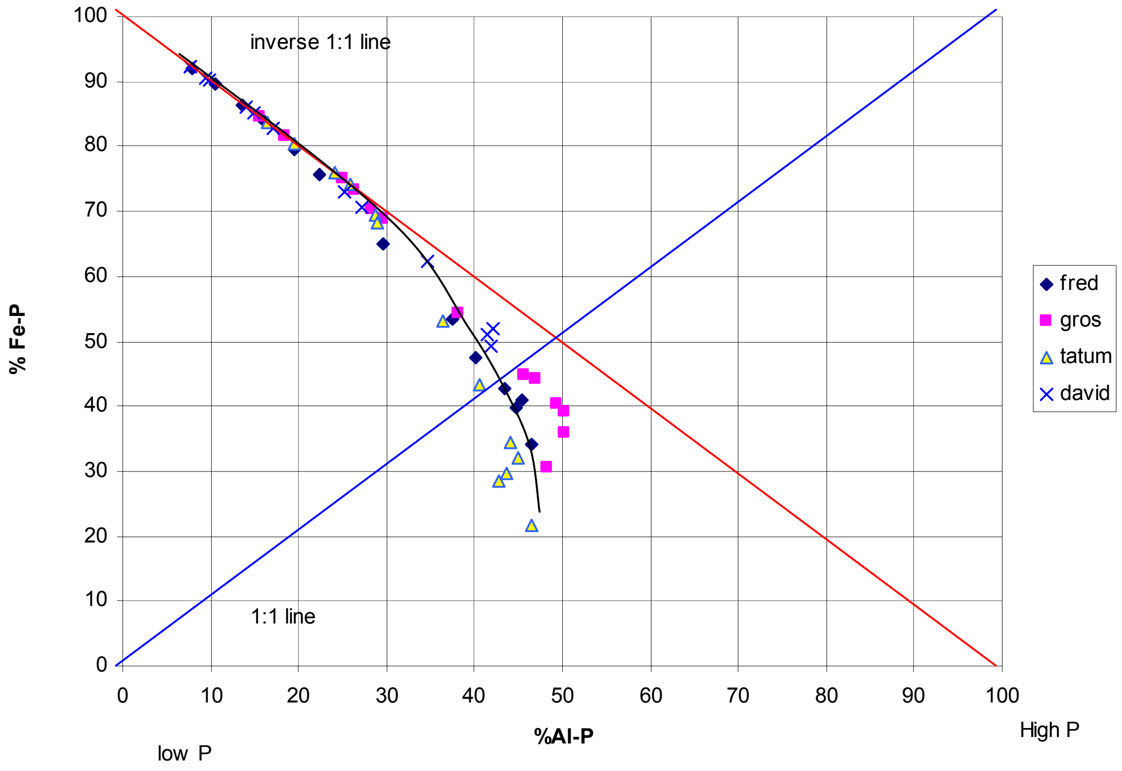


Fig. A.9. Changes in Fe related P (Fe-P) with P additions among four different soil types.

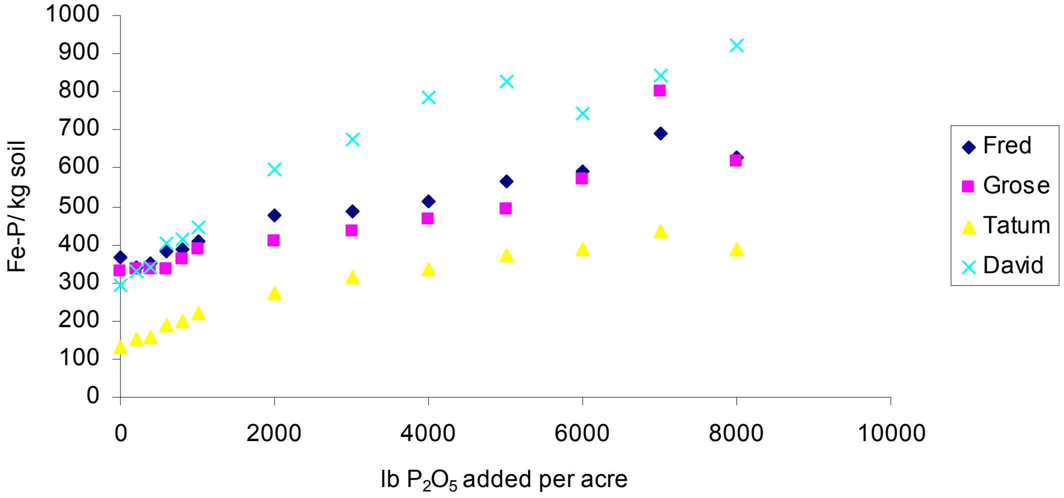


Fig. A.10. Changes in soil WSP with decreasing pH in comparison to a non pH adjusted soil amended with poultry litter (PL). Soil taken from Harold Ritchie's farm and had a history of high loading with layer litter.

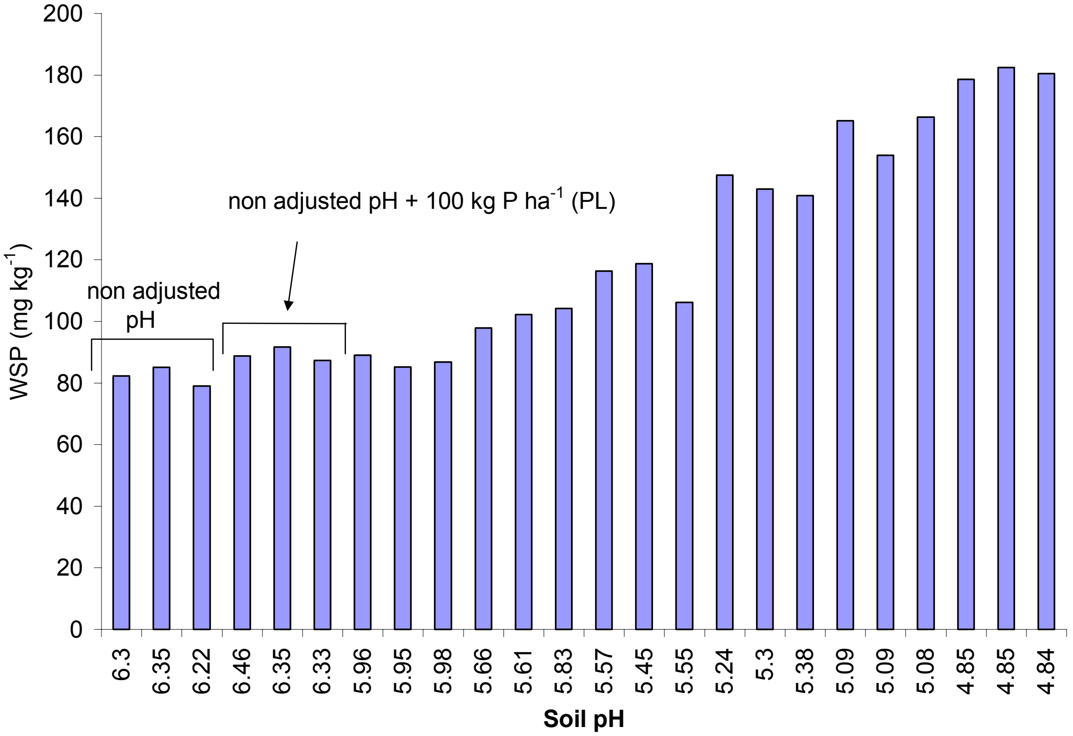


Fig. A.11. Relationship between soil WSP and soil pH among the incubated soils from Harold Ritchie's farm.

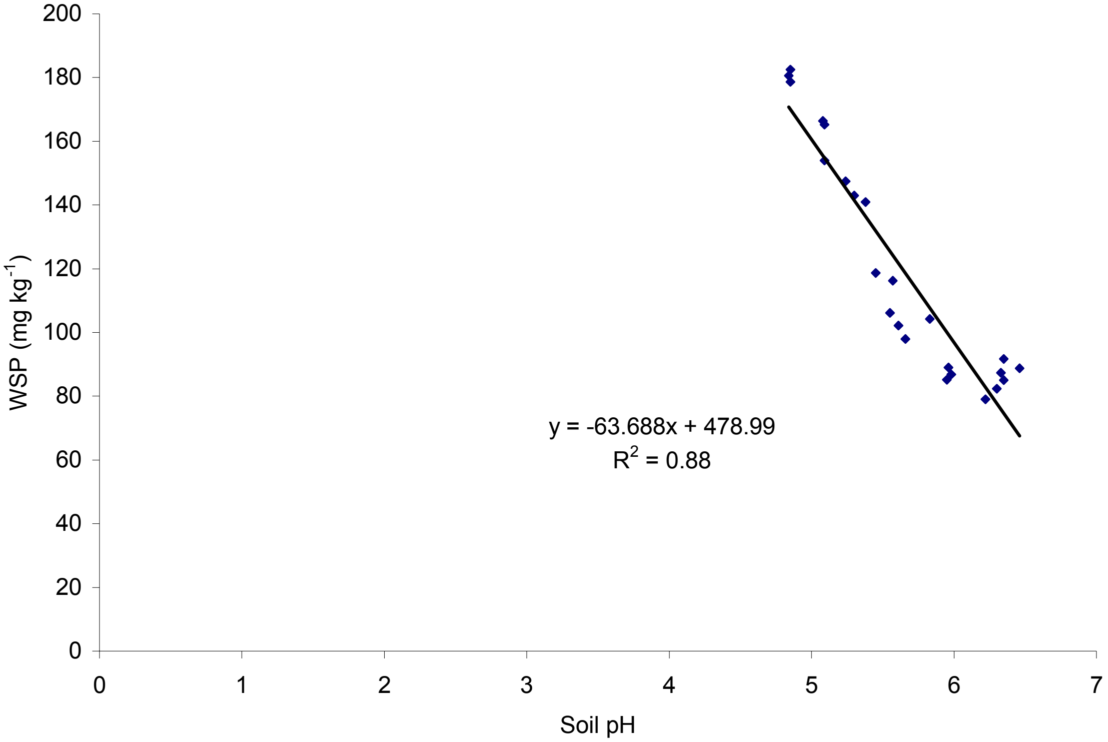


Fig A.12. Log stability diagram of incubated soil samples (blue diamond) in comparison to pure mineral solubility of various phosphate minerals.

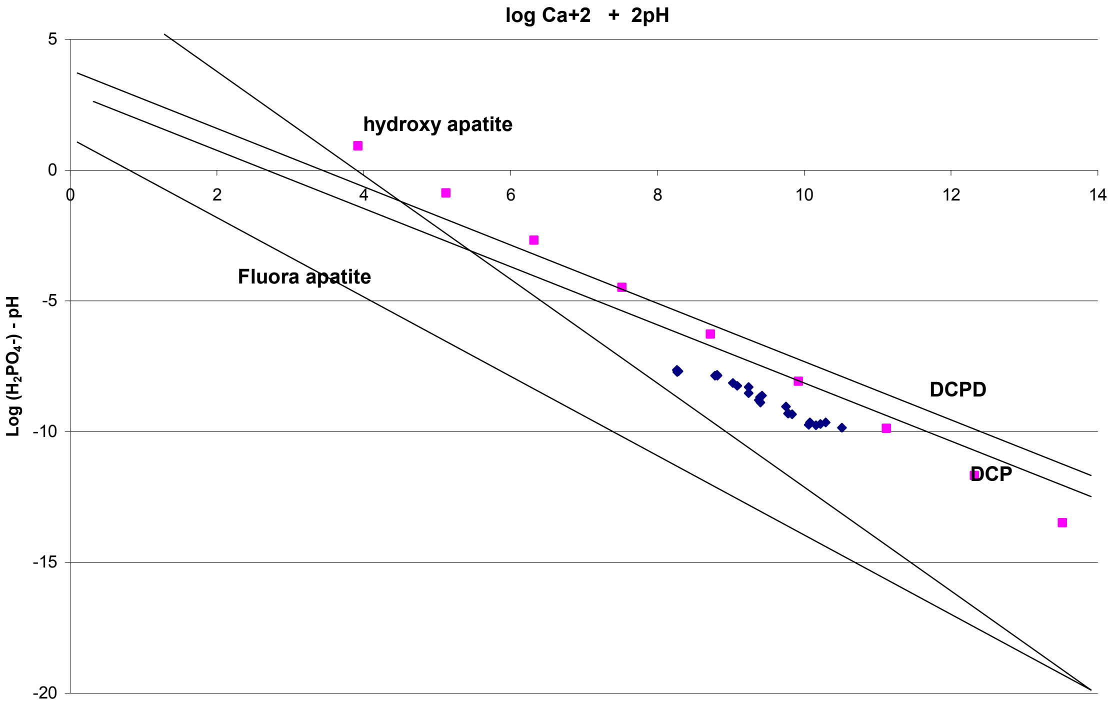


Fig. A.13. Cumulative losses of total P and DRP in runoff from manure amended soils after three rainfall events.

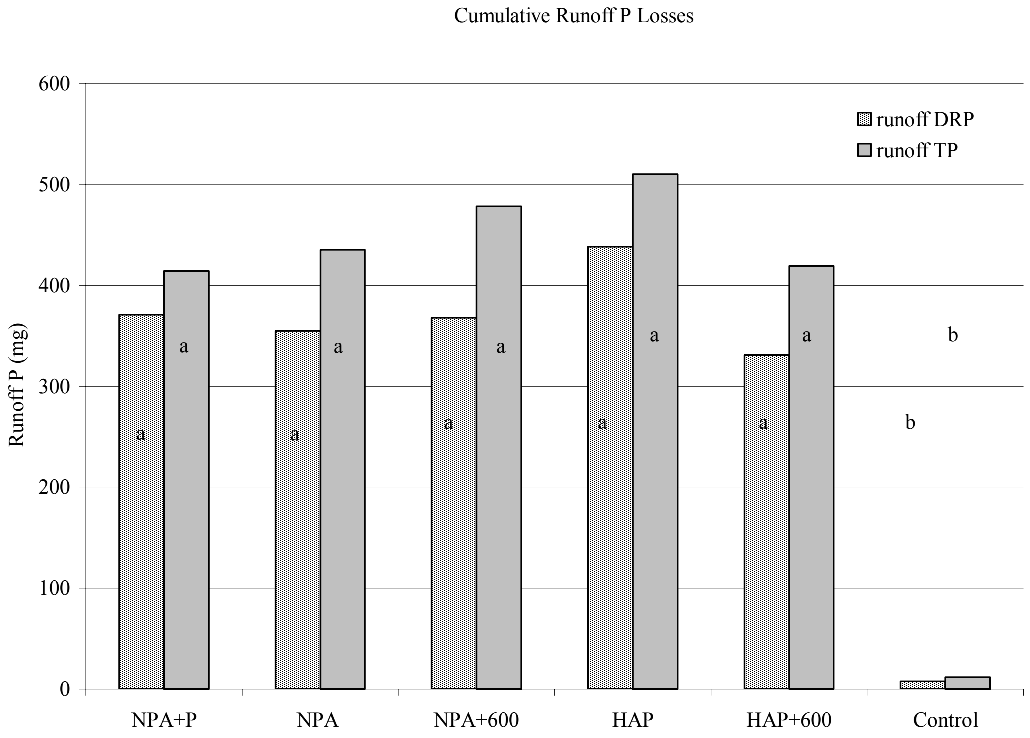


Table A.1. Results of WSP extractions conducted with various solutions and manure:solution ratios on dry and wet manure. DI = distilled/deionized water; RFW = rainfall water

moisture status of manure	wet	wet	wet	wet	dry	dry	dry	dry	wet	wet
manure:solution ratio	1:10	1:10	manure:RF vol	manure:RF vol	1:10	1:10	sed:runoff vol	sed:runoff vol	sed:runoff vol	sed:runoff vol
extracting solution	DI	RFW	DI	RFW	DI	RFW	DI	RFW	DI	RFW
Manure			mg kg^{-1}					mg L^{-1}		
NPA+P	8120	6853	4606	4674	11986	9662	34.6	35.7	32.6	34.5
NPA	4383	3970	3697	3685	6566	5775	41.5	39.2	32.2	34.1
NPA+600	3872	3759	4201	4163	7012	6207	42.2	40.8	42.6	41.5
HAP	4220	4115	4951	4918	7992	5854	46.5	44.3	45.1	44.8
HAP+600	4315	4364	4264	4539	8136	7254	47.2	42.7	34.5	41.5
coef Var	**4.79**	**5.99**	**4.47**	**5.29**	**18.77**	**4.24**	**18.16**	**16.23**	**16.54**	**16.55**

Table A.2. Soil WSP concentrations in the runoff boxes at two different depths after three rainfall events.

		WSP (0-2.5 cm)	WSP (2.5-5 cm)
Treatment	Replication	------- mg kg^{-1}	------------
NPA+600	1	3.652	1.109
NPA+600	2	3.301	1.021
NPA+600	3	2.239	0.626
HAP+600	1	2.49	1.011
HAP+600	2	4.231	0.771
HAP+600	3	3.015	2.285
control	1	1.681	0.651
control	2	1.238	0.693
control	3	1.855	0.66
NPA	1	1.84	0.65
NPA	2	2.75	0.612
NPA	3	2.764	0.783
NPA+P	1	2.031	0.572
NPA+P	2	2.716	0.551
NPA+P	3	2.84	0.75
HAP	1	2.304	0.4686
HAP	2	1.898	0.4318
HAP	3	2.584	0.546

Vita

Chad John Penn was born in Waterford, PA. He received his B.S. in soil science from the Department of Agronomy at Penn State University. He also received a M.S. in soil science from the Department of Plant and Soil Science at the University of Delaware. He is married to Stephanie Ann Penn (Hazle)