Phosphate Reactivity in Long-Term Manure Amended Soils in the Ridge and Valley of Virginia

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ABSTRACT

Phosphorus (P) released in overland flow is related to P form, soil solution P concentration and the release rate of P from soil. Models relating soil test P (STP) to water soluble P (WSP) and the degree of P saturation (DPS) to STP are used in Virginia to estimate P loss potential. Typically the reservoir of biologically available P in eastern soils has been attributed to P sorbed onto surface sites of non-crystalline aluminum (Al) and iron (Fe) oxides, extractable in ammonium oxalate. More recently, soils with a longterm history of manure application have exhibited properties that indicate calcium (Ca) may also be limiting P, especially in soils impacted by poultry manure. Accurate estimation of P loss potential is critical for justification of long-term management approaches. To evaluate the accuracy of model estimation of P loss potential and P source, we evaluated the (i) soil chemical properties, (ii) soil solution equilibria, (iii) inorganic speciation, and (iv) P desorption capacity of soils impacted over a long period of time by poultry litter (broiler and layer), dairy manure and commercial fertilizer applications. Soil chemical properties were measured with various extractions, while soil solution was measured in samples equilibrated at field capacity. Inorganic material was analyzed using scanning electron microscopy with electron dispersive capacities. Phosphorus desorption capacity was determined by calculating the rate of P release into a 0.01 M NaCl batch reactor. Out of the said analysis, we found that Al and Ca were the primary soil chemical elements limiting soil test P extractability and release. Soils with a high P sorbing capacity (PSC), that were not yet saturated, retained the most total soil P over a 60 hr. batch release experiment. Phase diagrams show that all soils were supersaturated with respect to common Al-, and Fe-P minerals. Saturation indices calculated with Visual Minteg were correlated with the degree of P saturation, and suggested that as the DPS increased, formation of less soluble Ca -P minerals occurs. The soils found to be supersaturated with respect to tri-calcium phosphate (TCP) and octacalcium (OCP) had the highest P release rate coefficients for both the first (k_1) and second (k_2) phases of release. Scanning electron microscopy with electron dispersive analysis (SEM-EDS) found that for some manure impacted soils, Al formed associations with P that are stable over a large soil to solution ratio. Additionally, it appears that as non-crystalline Al becomes saturated with P, Ca-P forms may act as an additional reservoir of P in soils with a long-term history of poultry manure application.

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INTRODUCTION

Phosphorus (P) has received great attention in recent years due to eutrophication of freshwater and saline ecosystems, which is detrimental to ecosystem health and threatens economies (Sharpley and Moyer, 2001). Phosphorus is considered to be the primary nutrient contributing to eutrophication of freshwater systems, because it is the limiting nutrient for algal growth. The Chesapeake Bay is one of the aquatic communities that has suffered from eutrophication, and its health is critical to the economic livelihood of many communities in Virginia, Maryland and Delaware. The Shenandoah Valley in Virginia is one of the contributing watersheds, whose tributaries drain into the Bay, and has been cited as a critical area to manage if the water quality of the Bay is to be improved.

The Virginia Department of Conservation and Recreation (VADCR) has determined that 60% of non-point source P (NPS-P) is linked to regional agricultural land uses (VGA-JLARC, 2005). This finding, as well as federal regulations, has led to a concerted effort to mitigate agricultural contributions to eutrophication. Nutrient Management Plans (NMPs) are the primary methods for P management from agricultural land uses. Nutrient Management Plans seek to "minimize adverse environmental effects, primarily on water quality, and avoid unnecessary nutrient applications above the point where long-term farm financial returns are optimized" (VADCR, 2002). The NMP is a balance between nutrient inputs, crop/livestock production, and regional water quality goals. Nutrient Management Plans encompass a whole farm operation, but focus on the management of individual fields within the acreage of the farm (VGA-JLARC, 2002).

Manure is typically applied to a field based on crop nitrogen (N) needs, and the P:N ratio in manure is high as compared to actual crop needs, thus the extra P applied above crop needs remains in the soil. In Virginia, nutrient applications are based on soil test values (Mehlich 1 extractable (Mehlich, 1984)) that indicate the level of nutrients available for crop uptake and available for export off the farm following a rainfall event. Excess P can be a water quality risk, and could lead to regulatory action if not properly managed. Risk assessment of P is included in NMPs and is based on soil test P (STP) values. Phosphorus field recommendations are made with the use of a threshold soil P level alone, or a threshold index derived from a computation framework known as the "P-Index" (Sharpley et al., 1996). The threshold P level is determined by the modeled relationship between biologically available P, represented by soil test P (STP), and dissolved reactive P in simulated runoff (DRP) or water soluble P (WSP) (Sharpley et al., 1996; Vadas et al., 2004).

The P Index uses the STP/WSP relationship as the basis of its recommendations; however, it also considers field characteristics such as closeness to stream, and conservation practices such as buffer strips when evaluating risk (Wolfe et al., 2005). The P index is an interface based on analytically derived values and relationships for soils in each physiographic region (Wolfe et al., 2005). It configures field characteristics into a management matrix integrating environmental, anthropogenic management, and hydrologic characteristics into a final calculation to determine P risk for both surface and subsurface export pathways (Wolfe et al., 2005; USDA-NRCS, 1994).

Virginia soils are diverse and have a large array of P storage capacity, ranging from very low (coastal soils) to very high (ridge and valley soils) (Beck et al., 2004; Penn et al., 2005). Routine STP procedures were not originally intended to be used as an environmental risk assessment, and for this reason the STP value does not test for differences between soils in this capacity. Thus, in the Virginia P Index, STP is used in conjunction with the degree of P saturation (DPS), calculated by the following equation:

$$DPS = [P_{ox} (mmol kg^{-1})] / [Al_{ox} + Fe_{ox} (mmol kg^{-1})] *100 Eq. 1$$

where P_{ox} , Al_{ox} , and Fe_{ox} are the total P, Al, and Fe extracted by ammonium oxalate (Schoumans, 2000). The DPS value represents P that is associated with amorphous Al and Fe found in a soil, which represents the capacity of a soil to sorb P (Sharpley and Smith, 1995). The P Index is site specific and is a useful tool for identifying fields at risk for P loading, without the bias of a standardized STP threshold value (USDA-NRCS, 1994).

Clay mineralogy in the Shenandoah Valley is determined in part by weathering rates, where increased temperatures and precipitation will support weathering of parent material and formation of phyllosilicate clay minerals. The Frederick soil series is a dominant soil series of the Ridge and Valley physiographic province of Virginia and has a clay mineralogy dominated by kaolinite, and hydroxyl-interlayer vermiculites (HIV), with lesser quantities of mica, quartz, gibbsite, goethite, chlorite, and amorphous material (Penn et al., 2005). Phosphorus adsorption to clay material occurs when P undergoes ligand exchange reactions with the singly coordinated hydroxyl groups on edge sites of oxy-hydroxides, gibbsite, and geothite (Kuo and Lotse, 1973). Phosphorus adsorption and retention capacity is also well correlated to HIV, gibbsite, and amorphous materials (Penn et al., 2005). Solubility of P is typically thought to be determined by the mineralogical composition of soils of the Mid-Atlantic states (Penn et al., 2005; Beck et al., 2004). The capacity for soil minerals to sorb P is determined by amorphous Fe and Al, followed by goethite, kaolinite, and 2:1 clay minerals such as HIV (Jackman et al., 1997; Juo and Fox, 1977). Repeated application of manure can cause total soil P to build up, eventually exceeding the capacity for the mineralogical matrix to act as a P sink, causing significant risk to regional fresh and salt-water systems (Penn et al., 2005; Sharpley et al., 1999; Sato et al., 2005; Toor et al., 2004).

While soil mineralogy is thought to dominate P solubility, the chemical impact of manure applications can accumulate over time. Soils that have a history of manure application have exhibited a relative increase in soil pH compared to unamended soils (Kingery et al., 1994; Eghball et al., 2002; Whalen, 2000). Soluble salts may dominate P solubility in some manures (CaCO₃ and Ca-P) (Cooperband and Good, 2002; Toor et al., 2005), which can buffer the soil pH at near neutral values (Whalen, 2000). Manure salts that would otherwise leach through the soil profile, can reside in the soil due to lack of vertical or lateral flow in a field with a semi-impermeable plow layer, or a pasture with a significant clay bulge in the B horizon of the soil profile (Vadas et al., 2003).

The fate of salts applied with manure treatments after application, is highly dependent on soil pH. According to equilibria relationships between P, Al, Fe, and Ca; in soils with a pH < 6.5 Ca-P forms would dissolve and P would be available for plant uptake or be retained on the sorption/exchange complex (Lindsay, 1979). Whereas soils with a pH > 6.5, Ca-P forms may be stable and excess P may even be adsorbed onto edge sites of CaCO₃ (Griffin and Jurinak, 1980; McDowell et al., 2001). In whole soils,

researchers have found that Ca-P can be the dominant form of P even in some acid soils (Beauchemin et al., 2003; Sato et al., 2005). Control of P by both Al and Ca is feasible and has been found in soils sampled from a long-term research experiment (Park Grass) in Rothamsted England (McDowell and Sharpley, 2003). These soils exhibited supersaturation with respect to both hydroxyl-apatite (HA) and variscite at a pH > 5.8, (McDowell and Sharpley, 2003). In summation, mineralogy determines the fate of soil solution P in the initial years of manure application. Yet, with consecutive manure applications the state of a soil environment moves further from an equilibrium dominated by mineralogy, towards an equilibrium defined by both mineralogy and manure history.

The Frederick soil series exhibited a unique chemistry when the STP/WSP relationship was being calibrated for use in the Virginia P Index (VPI). During calibrations, when Frederick soils were compared with other Ridge and Valley soil types; Frederick soils with a high STP did not fit the linear model used to predict WSP. All the outlying soils had lower WSP than predicted by the model as well as a long-term history of manure application and high Mehlich 1 extractable Ca values when compared with other soils (Mullins et al., 2003). The exact significance of the Ca, P, and manure application history combination is unclear but may be similar to that found by Sharpley et al. (2004). They found that lower than expected water soluble P values may be due to Ca-P associations soluble in the Mehlich 3 extract that are not soluble in water. They stated that a shift in the soil component controlling P solubility in eastern soils may occur after long-term manure application. Whereas, amorphous and mineral oxy-hydroxides would normally limit P solubility, the application of manure may have increased the pH and Ca in fields enough to temporarily sustain a Ca dominated P solubility.

Phosphorus Chemistry – Defining Phases and Forms

In the scientific literature, a plethora of terms describe P in soils. Phosphorus is thought to exist in crystalline, sorbed, meta-stable, and soluble forms (Lookman et al., 1995; Lookman et al., 1997; Cooperband and Good, 2002; Beauchemin et al., 2003; Arai et al., 2005; and Sato et al., 2005). Total P in a whole soil is a combination of several or all of these forms, and identifying what forms exist in soils can serve to predict P loss potential.

Three pools of P have been identified in non-calcareous agronomic soils (Lookman et al., 1997). The first pool consists of P dominated by the inherent clay mineralogy of a soil and is typically evaluated with the use of Fe, Al, and P extractable in ammonium oxalate. This pool is considered to be stable, yet not irreversibly sorbed (Lookman et al., 1997). The second pool consists of stable Ca-P, extractable in ammonium oxalate, this phase of P is thought to arise when amorphous calcium phosphate hydrolyzes to eventually develop into more stable species such as hydroxyapatite (HAP) (Sato et al., 2005). Direct identification of this pool of P is complicated by low relative concentration, but proportions relative to total P can be estimated with the use of P K-edge x-ray adsorption near edge spectroscopy (XANES) (Beauchemin et al., 2003).

The third pool consists of an available P pool, consisting of meta-stable –P compounds, where meta-stable refers to a compound(s) whose crystallinity is kinetically limited and exists somewhere between solution and solid crystalline phases. Meta-stable material may include micro-crystalline or short range order material. This pool of P is

water and dilute salt extractable (Lookman et al., 1997; McDowell and Sharpley, 2003).

The application of manure also includes the addition of significant amounts of organic matter (OM), and OM can play a major role in the soil chemistry of a field system. Organic acids can impede the crystallization of Ca-P compounds. Grossl and Inskeep (2002) found that tri-calcium phosphate (TCP, β -Ca₃(PO₄)₆) and octa-calcium phosphate (OCP, Ca₈H₂(PO₄)₆·5H₂O) were favored to form over the less soluble more stable hydroxyapaptite (HA, Ca₅(PO₄)₃OH), when Ca-P chemistry was observed in an environment influenced by organic acids. Organic matter can also impede P adsorption, as both P and organic acids are ligands and organic acids can compete with P for sorption sites (Turner et al., 2004). Although organic acids added in manure may compete with P for sorption sites, the formation of organo-metallic solids may significantly increase phosphate sorption, especially in acid systems. Here repetitive application of manure is accompanied with an increase in organic matter which may lead to an increase or decrease in P solubility further complicating the predictability of P solubility.

Predicting Soil P – Stability Diagrams

"The solid phase of the soil, rather than being a pure homogeneous material, is often a mixture of a large number of discrete solid phases which are out of equilibrium with each other as well as out of equilibrium with the solution phase."

(Sparks, 1999)

Phase diagrams provide a means of representing the potential soil solid phases by calculating activities from the chemical composition of the extracted soil solution (Sparks, 1999). Phase diagrams have been frequently used to deduce the forms of P

dominating P solubility in soils that have a long-term history (10+ years) of manure application (Hansen and Strawn, 2003; Hetrick and Schwab, 1992; McDowell and Sharpley, 2003; Pierzynski et al., 1990a; Sharpley et al., 2004). It is typical for such soils to exhibit equilibria supersaturated with respect to several Ca, Al, and Fe –P phases.

While soil equilibria studies are relatively inexpensive; there are several limitations one must be conscious of in such data. For example, calculating and plotting thermodynamic equilibria requires the researcher to define each system based on parameters of temperature, partial pressure, soil pH, ionic strength, equilibrium redox potential, and suspended colloidal materials (Sparks, 1999; Wolt, 1994). These parameters are either assumed to be fixed or are measured and included in calculations (Sparks, 1999). Regardless, CO₂ degassing and exposure of redox species to atmospheric conditions can confound these assumptions (Wolt, 1994; Sparks, 1999).

Additionally, solubility equilibria are calculated based on constants found in pure systems. Yet in whole soils, manifestation of the most stable forms of Al-P, Fe-P and Ca-P may be inhibited by the adsorption of ligands onto amorphous surfaces of hydroxides or Ca-P compounds (Grossel and Inskeep, 2002). Delgado and Torrent (2000) found that hydroxyapatite (HA) precipitation is kinetically limited and meta-stable tri-calcium phosphate (TCP) and octa-calcium phosphate (OCP) phases form first, slowly evolving to more stable phases. While phase diagrams pose some limitations, they remain the most cost effective method for predicting solid and solution phases. By plotting the solubility of inorganic phosphate minerals as a function of pH, one can observe the relative state of saturation of soil solution with respect to phosphate bearing phases (Hsu and Jackson, 1960).

The soil solution parameters that have controlling influence over chemical concentration, speciation, and activity of ions in solution include soil pH, and ionic strength, suspended colloidal material and redox potential (Wolt, 1994). In this study we concentrate on the effect of soil pH, as this soil factor has a marked effect on P solubility equilibria (Lindsay, 1979). McDowell et al. (2003) combined solubility data with magnetic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) and found that in soils with a pH below 5.8, Ca-P would play an insignificant role in determining soil solution P in a continuous root cropping experiment in England. Silicon and Ca, as well as Al and Fe, affect the availability of P in neutral to mildly acidic soils impacted by long-term applications of manure (Delgado and Torrent, 2001; McDowell and Sharpley, 2003; Sharpley et al., 2004). Meta-stable Ca-P compounds are thought to exist in some fields in the Netherlands impacted by animal manure (Koopmans et al., 2003). Control of P solubility may be simultaneously dominated by Al and Ca, and has been observed following high loading of rock-phosphate on a Samolan silt loam between pH 5.5 and 6.5 (Hetrick and Schwab, 1992). Extended and recurrent application of animal manure tends to increase the relative soil pH, and could potentially change the solubility dynamics of an acid soil (Whalen, 2002). It is evident that manure has the capacity to be one of the factors that can alter the soil chemical components, namely Al, Fe, and/or Ca that control the solution phase of soil P.

Identifying Soil P - Spectroscopy

Nutrient management is based on models which calibrate soil test P (STP) to dissolved reactive P (DRP) in runoff and apply theoretical relationships based on soil P forms and P sorption reactions. However, the form of soil P cannot be conclusively

explained with phase diagrams, because of their largely theoretical nature (Sharpley et al., 2005; Shenker and Bloom, 2005). Exact forms of stable solid state soil P can only be ascertained with the use of direct spectroscopic and microscopic techniques.

Phosphorus forms are present in low concentrations and are usually below detection limits for x-ray diffraction units (< 5% by weight) (Arai et al., 2005). Other direct methods such as liquid and solid state nuclear magnetic resonance spectroscopy (NMR), X-ray absorption near-edge structure spectroscopy (XANES), scanning electron microscopy (SEM) with electron dispersive capabilities (EDS) or electron microprobe analysis (EMA) have been utilized because they each allow for analysis of a whole soil with relatively little alteration of the solid state (Arai et al., 2005; Beauchemin et al., 2003; Lookman et al., 1997; Pierzynski et al., 1990b). Lookman et al. (1997) used MAS-NMR to study acid sandy soils amended with large amounts of animal manure, and found that inorganic P was associated with Al and Ca; with one of the Ca-P compounds being more soluble or less condensed than loosely adsorbed P. Beauchemin et al. (2003) used X-ray adsorption near edge spectroscopy (XANES) to identify P forms in three acid soils (pH 5.5-6.2) and two slightly alkaline soils (pH 7.4-7.6). XANES results showed that phosphate was adsorbed on Fe and Al oxy-hydroxides, and Ca-phosphate was present in all soils. Pierzynski et al. (1990) used SEM with electron microprobe capabilities to examine the elemental composition of P-rich particles in a Plainfield loamy sand (pH 5.6) and found that P was associated with both Al and Ca in some P-rich particles.

Combining solubility equilibria with direct spectroscopic methods allows a researcher to understand the soil solution as well as solid phase chemistry, allowing for a better grasp on the current and future management needs of a system. This understanding

allows for more adaptive nutrient management strategies, and more precise management (Sato et al., 2005).

P Release and Availability

Soil kinetics are often based on relatively short experiments (0-180 days) compared to processes that occur in the field. These experiments are based on the assumption that a soil system perturbed farther into disequilibrium will demonstrate qualities and characteristics similar to that which would happen over a longer time period in natural systems. There is inherent error in this approach as short term kinetic studies often overestimate the reaction rates that the resulting data represents (Sparks, 1989). Yet, such experimentation remains the most consistent and effective way of predicting a soil's response to changing soil solution concentrations of agronomic and environmental variables.

Phosphorus released from soil is usually described using biphasic or multi-phase models, indicating an initial rapid release phase that is followed by a plateau (Chien and Clayton, 1980; McDowell and Sharpley, 2003; Hansen and Strawn, 2003). The initial rapid release has been associated with the release of P from edge-sites on clay minerals, meta-stable salts, and P associated with organo-metal complexes (Gerke, 1992; Gerke and Hermann, 1992; Lookman et al., 1996; Lookman, 1995). The second phase has been associated with a slower transport limited diffusion of P from sorption sites that P occupies on interior clay aggregate complexes or from micropores (McDowell and Sharpley, 2003; Tomar, 1997). Lookman et al. (1995) found that the slower or secondary P desorption coefficient was related to Al-P and that this P appeared to be released in the

second phase of the bi-phasic release over a period of 180 days. Despite significant correlations, mechanistic kinetics are very difficult to quantify. Mechanistic kinetics can only be ascertained with the use of flow methods such as miscible displacement or relaxation techniques such as Pressure-Jump relaxation (Sparks et al., 1996). Yet, such methods are costly and time consuming compared to more routine analysis.

Objectives

This study was designed to quantify how long-term amendment application can affect the solubility of P; specifically among Frederick soils receiving application of broiler litter (BL), layer litter (LL), dairy manure (DM), and commercial fertilizer (CF) applications. Our objectives were to 1) evaluate the relationship between WSP, Mehlich extractable P and total soil P (TP), 2) determine the soil solution solubility equilibria for soils with such amendment histories, 3) identify meta-stable solid forms in a representative soil impacted over a long period of time by manure application using SEM-EDS, and 4) identify the soil components that are controlling P release, and suggest a method of controlling this component to mitigate dissolved P losses from these fields. Meeting these objectives will allow for better understanding and management of soils with a long-term history of manure application and will allow one to develop a method for controlling P release and mitigate dissolved P losses from agricultural fields.

MATERIALS AND METHODS

The soils in this study represent a small subset of soils impacted by manure in the Ridge and Valley physiographic region in Virginia within the Frederick soil series. The manured soils had no reported history of liming or inorganic fertilizer application (other than supplemental N). The soils selected for study represent a highly weathered acid soil with a long term history of broiler litter (BL), layer litter (LL), dairy manure (DM), or commercial fertilizer (CF) applications. All fields were located within the Frederick Soil Series delineation which is formed in residuum derived from dolomitic limestone and classified as fine, mixed, semiactive, thermic, and in the typic Paleudult regime. The Frederick Soil Series is of particular importance to agriculture and is referred to as a benchmark soil that can represent other soils with similar chemical characteristics (USDA-NRCS, 2005). All fields are located in the Shenandoah Valley in Virginia and are representative of soils in the physiographic region known as the Ridge and Valley (USDA-NRCS, 2005). The nine fields were sampled in the spring of 2004 to a depth of 0 - 15 cm. All fields were sampled prior to the yearly fertilizer amendment application for spring crops. The fields represent row crop systems and pasture/hay rotations. Typical cropping rotations included maize (Zea Mays L.) harvested for silage, wheat (Triticum *aestiuum L.*) and soybean (*Glycine max L.*). Soils were collected in bulk fashion with a shovel and placed into a 5-gallon bucket. The collected soil was then air dried and passed through a 2 mm sieve.

Sub samples of soil collected from each field were sent to the Virginia Tech Soil Testing Laboratory for determination of Mehlich 1 extractable P (M1-P), Ca (M1-Ca), Fe, Zn, Mn, Cu, B, and K (Mehlich, 1972). Mehlich III P (M3-P) was determined by shaking 2-g soil with a 20 mL mixture of 0.2 M CH₃COOH, 0.25 M NH₄NO₃, 0.015 M NH₄F, 0.013 M HNO₃, and 0.001 M EDTA end over end for 5 min (Mehlich, 1984). Native soil pH was determined using a 1:1 soil to distilled water ratio. A sub-sample of soil was ground to pass a 0.85 mm sieve, and analyzed for total Kjeldahl P (EPA 365.4;

USEPA, 1979). Water extractable P (WSP) was determined by shaking soil using a 2:20 soil:water ratio for 1 hr at room temperature (Self-Davis, 2000). The mixture was filtered through a Whatman No. 42 filter membrane. The extract was analyzed for total P (WSP) and for ortho-P (P_i) by the molybdate blue method (Riley, 1962). Ammonium-oxalate extractable P (P_{ox}), Al (Al_{ox}), and Fe (Fe_{ox}) was determined using the procedure described by Schoumans (2000). The degree of P saturation (DPS) was calculated under the assumption that the bulk density of the tillage layer was identical and uniformly sampled. Degree of P saturation was calculated by Eq. 1, using 0.2 M NH₄-Oxalate extractable P (P_{ox}), Fe (Fe_{ox}) and Al (Al_{ox}) values (Beck et al., 2000).

DPS = [Pox (mmol kg-1)]/[Alox + Feox (mmol kg-1)] *100 Eq. 1

Extracts were analyzed for Al, Fe, Ca, and/or P using a spectro flame FTMOA85D, inductively coupled plasma emission spectroscopy (ICPES) (Spectro Analytical Instruments, Inc. Kleve Germany), unless otherwise indicated.

Phase Diagrams

Preliminary calculations of P phases were determined from a soil solution extraction at field capacity. Sampling all soils at field moisture conditions reduces variation in soil solution extraction across a broad range of mineralogical and soil chemical compositions (Khasawneh and Adams, 1967). One hundred and fifty grams of each soil was weighed into a 250 mL centrifuge bottle. Each sample was brought to field capacity, which was measured according to Tan (1996) and equilibrated for 24 hrs at 24°C (Precision low temperature incubator, model 815, Winchester, VA). No preliminary experimentation was performed to evaluate the time needed to obtain steady state conditions (Hetrick and Schwab, 1990). The equilibrated soil was centrifuged at 27,642 *g* for 2 hr at a temperature of 22°C (Sorvall SUPER T 21 Refrigerated Superspeed Centrifuge, Asheville, NC). Supernatant "soil solutions" were filtered through 0.2 μ m filter paper and measured for electrical conductivity (E_c) and pH. Care was taken to measure E_c prior to determining pH. Ionic strength (μ) was calculated from E_c at 25°C (Griffin and Jurinak, 1973).

IAP and K_{sp}

Total dissolved soil solution concentrations of Al, P, Ca, and Fe, solution pH and ionic strength (μ) were entered into Visual MINTEQ Version 2.30. A default option was used that did not allow oversaturated species to precipitate, and the extended Debye-Huckel equation was used to calculate activities. Saturation indices (SI) were calculated in MINTEQ and signify the relative solubility for common phosphate (H₂PO₄⁻), iron (Fe³⁺), aluminum (Al³⁺), and calcium (Ca²⁺) minerals (Zhang et al., 2001). Saturation indices were calculated from the solubility product (K_{*sp*}) and the solution ion activity product (IAP). Solubility products (K_{*sp*}) are the equilibrium constants relating free energy of the solid phase to the dissolved products in solution. An example of such a relationship is shown in the following equation:

$$\frac{\{\mathbf{M}^{+}\}\{\mathbf{L}^{-}\}}{\{\mathbf{ML}\}} = \mathbf{K}_{sp} \qquad \text{Eq. 2}$$

Where $\{ \}$ denotes ion or species activity as calculated with the Debye-Huckel equation, M⁺ represents a free cation in solution, and L⁻ denotes the concentration of free anion (or ligand) species dissolved and measurable in solution (Sparks, 1999). The ion activity product (IAP) is a product of the activities in solution corresponding to the equilibrium expression considered for a given solid phase (K_{sp}) (Sparks, 1999). A saturation index (SI) is a value used to denote the saturation status of a solution with respect to a particular mineral phase:

$$\frac{\log IAP}{\log K_{sp}} = SI \qquad Eq. 3$$

A positive SI value indicates that the soil solution is supersaturated with respect to a given phase according to standard equilibria values for that mineral and the properties of the solution.

Phase diagrams graphically show the location of the stability field of a given solid phase relative to the equilibria state of the extracted soil solution and provide reference for a researcher as to the saturation of the soil solution (Sparks, 1999). All double function plots for this study were created manually using calculated activities of free $\{Al^{3+}\}, \{Fe^{3+}\}, \{H_2PO_4^-\}, \text{ and } \{Ca^{2+}\} \text{ from Visual MINTEQ}. The negative logarithm (p)$ $of <math>\{Al^{3+}\}, \{Fe^{3+}\}, \{H_2PO_4^-\}, \text{ and } \{Ca^{2+}\} \text{ (pAl, pFe, pH}_2PO_4^-, \text{ and pCa, respectively) were$ calculated in Microsoft excel and used to plot the data. All stability fields for Al-P, Fe-Pand Ca-P minerals were calculated using K_{sp} values derived from Lindsay (1979) exceptfor wavellite and crandellite which were obtained from Naigu (1976).

Scanning Electron Microscopy

It was necessary to isolate the clay and silt fractions. Since these fractions often act as P sorption sinks in soils due to high surface area and mineralogy (Penn et al., 2005). General estimates of clay, silt, and sand were obtained by typical wet sieving and sedimentation procedures *without* pretreatment (Day, 1965). Twenty gram sub-samples of all soils were separated into sand, silt and clay fractions.

The separated clay and silt fractions were dried, weighted and a sub-sample was diluted followed by ultrasonic dispersion. A 10 mL sample was then taken and diluted and dispersed again until a suspension of 0.9 mg/L⁻¹ was obtained. One drop of this suspension was added to an Al-stub covered with carbon tape. The samples were covered and air dried overnight. Prior to image analysis, the entire stub was sputter coated with Au-Pd. The "clay" fraction is not uniform and does contain organic material and non-crystalline Fe- and Al- oxides. Organic matter and non-crystalline Al and Fe can act as cementing agents, therefore in addition to the natural cementation that occurred in the field, wetting and drying during dispersion, separation, and then drying on the stub may have further concentrated the clay particles making them difficult to disperse fully. We observed with SEM that many of the clusters of particles in the clay fraction were larger than 2.2 μ m after drying on the stub.

Clay and silt samples were analyzed by scanning electron microscopy (SEM) using a JEOL JSM-5800LV SEM (JEOL U.S.A., Peabody, MA). Imaging was performed at a voltage of 5 kV. The unit was equipped with IXRF Iridium Microanalysis System energy dispersive (EDS) x-ray analyzer that operated at a voltage of 20 kV quantifying the percent chemical makeup of selected particles (Tracor Northern, Middleton, WI). The scanning resolution of the SEM-EDS electron beam is 1 μ m by 1 μ m, scanning 1 μ m in depth. A count of 100 counts per minute represents an approximate P concentration of 5 g kg⁻¹ (Joy et al., 1986). All particles were selected manually. Integrated x-ray counts were obtained for selected regions of interest on individual stubs and monitored with each EDS

spectra collected with the K- α lines for Al from 1.30 to 1.60 keV, Si from 1.6 to 1.92 keV, P from 1.92 to 2.16 keV, K from 3.16 to 3.52 keV, Fe from 6.20 to 6.64 keV, and Ti from 4.32 to 4.66 keV. Particles were classified as P rich if they gave 100 or more x-ray cpm from the region of interest. Relative concentrations of detectable elements in an area irradiated by the electron beam were estimated by the software package (IXRF Iridium Microanalysis System), and gave cation composition of the area irradiated by the electron beam (Pierzynski et al., 1990).

Clay material has been observed by SEM analysis in colloid form larger than $2\mu m^2$ and was thought to be cemented with organic matter (Laird, 2001). Gravity separated clay fractions from LL1, BL1, DM1, DM2, and CF1 and a gravity separated silt fraction were imaged from LL1, yet the majority of our efforts were spent on LL1 and BL2. Phosphorus rich particles were difficult to isolate and locate, therefore a selection criteria was applied. For example, after multiple selection and analysis of particles with a high visual reflectance on the SEM imaging screen, electron dispersive analysis showed that those particles typically were silica-oxide or titanium oxide, and therefore particles with such reflectance were avoided for sampling. No pretreatment of the solids was used to avoid the loss of easily dissolvable mineral forms.

Phosphorus Release Kinetics: Batch System

The batch reaction methods used to study the short term release of P is very similar to those described in Hansen and Strawn (2003). The only exception is that Hansen and Strawn used $CaCl_2$ as the background electrolyte for the batch reactor, in this study 0.01 M NaCl was used as a background electrolyte. We chose to accept some given level of re-adsorption that was related to the conditions of the experiment.

Duplicate 1.175-g sub samples of each soil were added to 50 mL polyethylene centrifuge tubes along with 35 mL of electrolyte solution (0.01 M NaCl). The capped tubes were placed on a rotating shaker at a rate of 45 rpm, for a period of 60 hrs. Following shaking at various times, the batch reactors (test tubes) were removed from the rotating shaker and centrifuged at 25,000 g for 25 min. The pH of the suspension was measured with an electrode and an 18 mL aliquot of supernatant was removed from suspension. Care was taken not to disturb the settled soil. The solution aliquot was filtered through a 0.2 µm filter, and 18 mL of replacement solution (0.01 M NaCl) was added back to each tube. The tubes were then placed on a vortex to remix the sample and returned to the rotating shaker, repeating the procedure until the final sampling interval was reached. Filtered solutions were analyzed for total P and Ca by ICP-AES. Rate constants were determined based on the principle that all aliquots removed from the batch reactor were taken at a state of disequilibrium.

Kinetic Modeling

The following equations were applied to the kinetic desorption data: the modified Freudlich equation (power function equation release = αt^{β}), and two first order equations that were optimized at visually determined rate changes. All models successfully fit the data; however two first-order equations resulted in the best fit based on coefficients of determination (R²) and are presented in this paper. The first order rate equation adapted from Sparks et al. (1980) was used to model the data as two first-order reactions:

$$\ln (L_t^2/L_0^2) = -kd(t)$$
 Eq. 4

where L_t^{-} was the amount of ligand sorbed at desorption time t (mmol kg⁻¹), L_0 was the

amount of ligand sorbed at time 0 (mmol kg⁻¹), *t* is time (s), and *k*d is the apparent desorption coefficient (s⁻¹). If the reaction is first order a graph of ln (L_t/L_0) vs. *t* should yield a straight line of slope -*k*d. The data was divided into two sections resulting in two first order equations. These two equations were then used to describe a biphasic trend of P release over the 60 hr period. Optimized time ranges were 0 to 5 hr and 6 to 60 hr.

Complex models are often developed with the use of several soil characteristics to define desorption parameters. Our goal was to understand how release was affected by soil characteristics. Thus, the use of such models would be, for our purposes, excessive and would divert attention from the individual characteristics that each soil brings to the study. These coefficients did not discriminate between soils but allowed for comparisons.

Statistical Analysis

Correlation analysis was performed for all soils combined using PROC CORR (SAS Institute, 1999). PROC REG with STEPWISE selection was used to calculate best fit regression equations to predict WSP (SAS Institute, 1999). Statistical analysis between treatments for soil chemical characteristics (WSP, WS-Ca, M-3P, M-3Ca, M-1P, P_{ox}, Al_{ox}, Fe_{ox}, TP) were performed using Proc CORR and Tukey's LSD in PROC GLM (SAS Institute, 1999).

RESULTS AND DISCUSSION

A summary of relevant surface properties is shown in Table 1. Soils with a history of poultry manure application (layer or broiler litter) had the highest WSP, M-1P, M-3P, and TP of the nine soils analyzed. The only exception to this was LL2, which released

significantly less P in water than all other poultry manured soils (11 mg WSP kg⁻¹). Poultry manured soils exhibited Mehlich (1 & 3) and water extractable values similar to other soils with a long-term history of poultry manure application (Beck et al., 2004; Sharpley et al., 2004).

WSP, STP, and TP

The relationship of STP to WSP is the foundation of many nutrient management decisions in Virginia. Water soluble P is representative of dissolved reactive P (DRP) in simulated runoff events (Pote et al., 1999; Sims et al., 2001). Virginia Tech soil testing lab (VSTL) currently uses M-1 as a standard soil test extract but is considering switching to M-3. Mehlich 3 is not as easily neutralized by CaCO₃, a residue commonly found in agronomic soils. Our results show that WSP is predicted well with the general linear model by M-1P ($r^2 = 0.83$) and M-3P ($r^2 = 0.89$) (Figs. 1 -2). M-1P is also well correlated with M-3P (r = 0.98), soil solution P extracted at field capacity (SSP) (r = 0.89), and P_{ox} (r = 0.80), while M-3P was similarly correlated to SSP (r = 0.82), and P_{ox} (r = 0.86), establishing that either M-1 or M-3 can provide reasonable predictions of the many extractable forms of soil P.

The Virginia P Index allows for use of either or both soil test data (Mehlich 1 extractable) and DPS calculated from values obtained from an ammonium oxalate extract (Wolfe et al., 2005). A DPS value of < 20% would indicate that manure applications based on nitrogen (N) are acceptable (Wolfe et al., 2005). While for a DPS value of > 65% it is suggested that no P be applied to that field. For DPS values between 20% and 65% it is recommended that the P application should be based on the calculated P index

value (Wolfe et al., 2005), these values were in part developed through a curvilinear model determined by Beck et al. (2004).

Similar to Beck et al. (2004), we found that the relationship between Mehlich 1 extractable STP and DPS was described well using both the general linear model ($r^2 =$ 0.91) or a curvilinear equation (power function; $r^2 = 0.89$) (Fig. 3). Whereas the relationship between M-3P and DPS was best described with a curvilinear model, indicating that saturation capacity decreases at an increasing rate as M-3P increases ($r^2 =$ 0.86, linear $r^2 = 0.75$) (Fig. 3). These soils appear to reach a saturation plateau at a DPS of 60%, similar to the 65% value used for Ridge and Valley soils as assessed with the Virginia P Index (Wolfe et al., 2005).

The Virginia P index (VPI) uses the relationship between total P and M-1P to predict an estimate of sediment total P (ppm), this estimate is then combined with runoff estimated using the runoff curve number approach that includes management, slope and soil type to estimate the runoff sediment P contribution potential of a given field (Wolfe, et al., 2005). The model found for the soils in this study is similar to that in the VPI. Total P was well correlated with both M-1P and M-3P (Fig. 5). Similar to results found by Beck et al. (2005), a power function model was a better descriptor of the relationship between TP and M-1P than with M-3P. This is most likely due to the fact that M-3P has chelating agents such as EDTA and is less neutralized by soil carbonates, allowing for more P to be released in M-3 than M-1 (Kuo, 1996).
able 1.	Selected ah Valle	properti y of Virgi	es of surfa nia.	ace soils	(0-15 cm)	from	nine fields	located w	vithin the	Frederick	soil ser	ies in the
History	₩SP†	MIP‡	M-3P§	Pox	WSCa†	DPS#	TP††	M -3Ca§	Alox	Feox	pH‡‡	QMQ
			mg kg ⁻¹			%	B	kg-1	Inmol	kg-1		%
LL1	48	798	1671	53	108	100	2040	5530	34	20	6.8	6
LL2	11	308	667	27	63	28	1153	4235	70	28	7.0	9
BL1	41	583	1244	54	59	54	1745	3954	65	34	6.9	5
BL2	NA	NA	1511	30	NA	44	NA	3726	38	29	6.7	9
BL3	30	630	1034	31	39	99	948	1802	37	10	6.4	4
DM1	18	102	323	16	31	29	619	1085	40	14	5.9	9
DM2	9	107	302	14	48	22	567	1654	50	17	6.4	3
CF1	16	125	353	25	58	20	655	2704	88	38	6.7	7
CF2	1	15	55	5	39	10	223	876	35	13	6.4	4
(WSP)	Water ex	tractable F	and Ca 1:	l soil: sol	ution ratio							
‡ (M-1P)	Mehlich	1 extracta	ble P									
§ (M-3P)	Mehlich	3 extracta	ble P, and (Ca								
(P_{ox}, A)	_{ox} , and Fe	3 _{0x}) 0.2 Ac	id-NH ₄ -ox	alate P, A	l, and Fe							
# (DPS) I	Degree of	f P saturati	on $DPS = [$	P _{ox} (mmo	Ikg ⁻¹)]/[Al	$_{ox} + Fe_{ox}$	(mmol kg	$^{1}] *100$				
†† (TP) Tc	ital P wa	s determin	ed using the	e Kjeldahl	method fo	r total di	igestion					
‡‡ Native	soil pH w	ras determ	ined using a	a 1:1 soil	to distilled	water ra	tio					
Q (OM) C)rganic N	fatter = [P	ercent Orga	unic Carbo	on ((ml FeS	O4 blank	x – sample)	*NFeSO4)/	g sample)*	0.395]* 2		



Fig. 1. The relationship of water soluble phosphorus (WSP), and Mehlich 1 extractable P (M-1P) for all soils (excluding BL2). The solid line shows WSP as estimated by M-1P modeled with a linear function, and the dashed line is the relationship modeled with a power function.



Fig. 2. The relationship of water extractable soil P (WSP) and Mehlich-3 extractable soil P (M3-P) for all soils (excluding BL2). The solid line represents WSP as estimated by M-3P modeled with a linear function, and the dashed line is the relationship modeled with a power function.



Fig. 3. The relationship of degree of P saturation (DPS), and Mehlich 3 extractable P (M-3P) for all soils. The solid line shows DPS as estimated by M-3P modeled with a linear function, and the dashed line is the relationship modeled with a power function.



(excluding BL2). The solid line shows DPS as estimated by M-1P modeled with a linear function, and the Fig. 4. The relationship of degree of P saturation (DPS), and Mehlich 1 extractable P (M-1P) for all soils dashed line is the relationship modeled with a power function.



extractable P. Relationships are estimated using both linear (black lines) and power functions (dashed curve). The equations and correlation coefficients for linear and power models are Fig. 5. The relationship between total soil P (TP) and Mehlich 1 (triangles) and Mehlich 3 (circles) presented near their respective lines.

Selected Soil Properties

Phosphorus solubility in soil is initially dominated by sorption mechanisms (noncrystalline Al and Fe associations). As P in solution continues to build up, P specific adsorption sites are satisfied (DPS approaches 100%). The concentration of P on and near the surface eventually becomes saturated, with forms of near surface P including specific P sorption onto edge sites, and multi-nuclear complexes that have varied chemical compositions (Rietra et al., 2001). Phosphorus then forms associations with partner ions in solution until the solution reaches saturation with regard to the solid phase of these associations. After saturation solid P phases will precipitate, or nucleate on a surface (McDowell et al., 2001).

The mechanism dominating P solubility in acid soils is adsorption to amorphous oxides of Fe and Al which can be estimated with ammonium oxalate (Al_{ox}, Fe_{ox}, and P_{ox}). Ammonium oxalate extractable P has been found to be directly related to the presence of amorphous Al-Fe oxides for acid clayey and acid sandy soils (Lookman et al., 1996; Vadas and Sims, 2002; Arai et al., 2005), however this was not the case for these soils. Ammonium oxalate extractable P was not well correlated with Al_{ox} (r = 0.11; p = 0.57) and Fe_{ox} (r = 0.42; p=0.03). Rather, P_{ox} was best correlated with TP (r = 0.97), and it was also well correlated with M-1P (r = 0.89), M-3P (r = 0.86), WSP (r = 0.94), WSCa (r = 0.72), and M-3Ca (r = 0.82). It is apparent that P_{ox} in these soils is related to other soil chemical factors such as Ca, in addition to amorphous forms of Al and Fe. It is possible that some P affiliated with Ca is being released in the acidic M-3 and ammonium oxalate extractions; since Ca-P solids are soluble at low pH values (Lindsay, 1979). The pH

values of these soils ranged from 5.9 to 7.0 (Table 3). Based on the research of McDowell et al. (2003), the P in these soils may be dominated by Al and Ca chemistry, as all of the soils have a pH above 5.8.

Results for the degree of P saturation, calculated with Eq. 1 shows that LL1 is the soil most saturated with P (100%), followed by BL3 (66%), and BL1 (54%). These soils also have the highest water extractable values 48 mg kg⁻¹, 30 mg kg⁻¹, and 41 mg kg⁻¹, supporting the concept that, as soils become "saturated" with respect to P, additional P added to the soil will not be sorbed but will be available for release in water. Soils with a history of layer litter application had the highest pH (6.9), Mehlich 3 extractable Ca (M-3Ca) (4883 mg kg⁻¹), and water extractable Ca (85 mg kg⁻¹). Soils with a history of broiler litter application had a high M-3Ca of 3161 mg Ca kg⁻¹, and mean soil pH of 6.7 (Table 1). The higher Ca values and elevated pH levels of surface soils impacted by poultry manure can be attributed to the nature of poultry manure and residual CaCO₃ from the manure applications.

Mehlich-3 extractable calcium was correlated with TP (r = 0.88), M-3P (r = 0.81) and P_{ox} (r = 0.81), and poorly correlated with all other surface properties presented in Table 1. Total P digestions, M-3, and ammonium oxalate are each acidic extraction procedures, and it appears that the form of P related to M-3Ca is more extractable in acidic procedures and less extractable in more mild procedures such as a water extraction (r = 0.67), suggesting that the more stable pool of Ca-P may exist in the soils with high TP, M-3P, and P_{ox}, when complimented by high extractable Ca. Water soluble Ca (WSCa) was measured (data not shown in Table 1) however, it did not correlate as well with P extracted in digestions, Mehlich-3, or ammonium oxalate extractions. These results suggest that there may be two pools of Ca-P dominating P solubility, a more stable Ca-P pool, and a meta-stable or relatively soluble Ca-P pool.

The distribution of non-crystalline sesquioxides varied greatly among all soils. BL1, LL2, and CF1 have notably more non-crystalline Al and Fe than all other soils (Table 1). These three soils also exhibited the lowest P release rates (Table 7), indicating that fractions of P associated with amorphous Al and Fe are less mobile compared to other P fractions. The remaining soils have a significantly lower total non-crystalline fraction or P adsorption capacity (PSC) ($Al_{ox}+Fe_{ox}$). There is no single property that can explain the high amorphous fractions found for BL1, LL2, and CF1; however the occurrence of such P sorbing capacity may be related to location of the soil on the soil forming landscape or catena. Areas of high slope and elevation would be more susceptible to surface erosion. This may result in an eroded Ap horizon, an exposed B horizon, or a mixture of both.

Organic matter (%) content was consistently higher for soils impacted by poultry manure, with the highest value being for LL1 (18% OM), and the lowest values observed for DM2 and CF2 (6% OM) (Table 1). It was interesting that CF1, a soil that had no previous history of impact by organic amendments would have an OM% higher than some of the manure affected soils, perhaps this is due to the high amorphous Al content in this soil. Many studies have found correlation between Al_{ox} and OM, indicating non-crystalline organic-metallic solids may form in soils that have significant quantities of both amorphous Al and OM reducing the turnover of organic matter and this may have occurred in CF1 (Lookman et al., 1996; De Cristofaro et al., 2000; Schulten and Leinweber, 2000).

The nine soils vary in the amount of extractable Al, Ca, and pH. The combination of relatively high pH, Al and Ca exists for two soils only, BL1 and LL2. LL2 has a significantly lower Mehlich extractable P than all the other poultry manure amended soils, and it is expected that this was accompanied by a lower WSP value (Table 1). Additional retention capacity may be caused by a combination of high pH (7.01), high extractable Al (Al_{ox}) and high extractable Ca (M-3Ca). The combined factors of Al, Ca, and $pH \ge 5.8$ may enable the interaction between Al, Ca and P to inhibit P solubility in water. Reitra et al. (2001) evaluated the interaction between goethite, PO₄, and Ca in under saturated (Ca-P) conditions, showing that both Ca and PO₄ can sorb onto goethite at pH values ranging from 6 to 9. They also found that the lower the goethite concentration, more Ca was adsorbed for conditions where PO₄ was also present. They conjectured that higher adsorption of Ca at lower goethite levels could be explained by higher surface coverage of goethite, and decreased surface repulsion of Ca. Aluminumphosphorus-calcium may form multi-nuclear complexes, similar to those found with Fe-P-Ca that play an additional role in P retention for some of the soils here. There is a lack of information regarding Al-P-Ca surface complexes, and investigation of Al-P-Ca ternary surface complexes should be prioritized in the future.

Soil Solution Activity

Results in Table 2 show that $H_2PO_4^-$ activity (p{ $H_2PO_4^-$ }) in the soil solution generally increased in the order of layer litter > broiler litter > dairy manure > and commercial fertilized soils, with the exception of LL2, which had a significantly lower P activity than all other manured soils. Layer litter 2 (LL2) also had a lower E_c than most other manured soils, and a high sand content indicating that the overall ion activity may be lower due to the lack of reactive clay in the mineralogical matrix. Layer litter 1 (LL1), BL1, and BL2 had the highest E_c of all the soils studied.

Proc CORR was used to calculate correlation coefficients between extractable P and the *log* activity of Al, Ca, Fe, and P as determined by Visual Minteq (ver. 2.30), and soil solution pH at time of filtering. Results show that as the activity of P increased the extractability of P in various solutions also increased. M-3P was the best predictor of P activity (r = 0.80), followed closely by WSP (r = 0.72) and M-1P (r = 0.74) (Table 3). WSP was well correlated to the activity of Al, Ca, Fe, and H⁺ (Table 3). The *log* {Ca} and *log* {H₂PO₄⁻} were directly related to extractable P indicating that as the activity of Ca or P increased, the extractability of P increased as the extractability of P increased, suggesting that a soil solution with high activity of Al or Fe retained P more effectively than most Ca active in soil solution. Mehlich-1P was also well correlated to all elements. The activity of Ca in soil solution was best correlated with M-1P (r = 0.71), while M-3P was not correlated to *log* {Ca}, indicating that different P sources were extracted in Mehlich 1 than in Mehlich 3. The *log* {Al} was the only solution element measured that correlated to

M-3P. The degree of P saturation appears to be related to the activity of Ca and Al in solution, more so than Fe. In summary, the activity of Al again appears to be important in determining the accumulation of P sources extractable in the Mehlich 1 and 3 extracts, and ammonium oxalate, while the activity of Ca is most important for accumulation of P sources extractable by Mehlich 1.

	$log{Al}$	log{Ca}	log{Fe}	$log\{H_2PO_4^-\}$	SSpH†	E _c §
LL1	- 10.8	- 2.6	- 14.2	- 4.1	7.0	3.0
LL2	- 9.4	- 2.8	- 13.3	- 4.7	6.7	1.9
BL1	- 10.2	- 2.8	- 13.8	- 4.2	7.0	3.1
BL2	- 8.1	- 3.1	- 12.3	- 3.7	6.4	4.1
BL3	- 9.2	- 2.3	- 13.3	- 4.1	6.6	0.9
DM1	- 8.4	- 2.8	- 12.9	- 4.7	6.6	2.3
DM2	- 6.8	- 3.0	- 11.4	- 4.5	6.1	1.5
CF1	- 10.2	- 2.8	- 13.9	- 4.8	7.1	1.9
CF2	- 8.2	- 2.9	- 12.8	- 5.0	6.3	1.6

Table 2. The *log* activity of Al, Ca, Fe, and diprotic ortho-phosphate in soil solution extracts.[†]

 \dagger All values were obtained from an extraction of soil solution of soil at field capacity after 24 hour equilibration, centrifugation, and filtering (0.22 μ m).

‡ (SSpH) pH of soil solution directly after filtering.

§ (E_c) Electrical conductivity of soil solution.

specialio	n program.				
	$log{Al}$	log{Ca}	log{Fe}	$log{H_2PO_4^-}$	SSpH
WSP	-0.66**	0.56**	-0.61**	0.72***	0.61**
M-1P	-0.60**	0.71***	-0.54**	0.74***	0.50*
M-3P	-0.42*	0.25†	-0.33†	0.80***	0.38†
Pox	-0.66***	0.37†	-0.58**	0.58**	0.63***
DPS	-0.52**	0.57**	-0.46*	0.62**	0.44*
ТР	-0.69**	0.34†	-0.59*	0.69**	0.63

Table 3. PROC CORR *r* values for the *log* activity (where $\{M^+\}$ or $\{L^-\}$ denotes activity of Al, Fe, Ca, and P as calculated by Minteq (ver. 2.30) speciation program.

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

 \dagger NS, non-significant at the < 0.05 probability level.

Stepwise Selection Analysis for the Prediction of WSP

In order to evaluate the effect of soil extractable Fe, Al, and Ca on P solubility in soils with a long term history of amendment application, stepwise regression analyses were conducted. Water soluble elements (Ca, Al, and Fe), pH measured in a 1:1 soil to solution matrix, Mehlich 3 extractable elements (P and Ca), ammonium oxalate extractable Al and Fe; and P, Al, Fe, Ca, and pH in soil solution were each used as dependent variables to model WSP using stepwise regression. The models tested and corresponding results are presented in Table 4. Soil solution Ca did play a significant role in controlling WSP in this subset of soils, and served as the best predictor of WSP of all measured soil solution elements. Furthermore, WSP was best predicted by WSCa with a compatibility index (Cp) ratio of 1.75 and a model $r^2 = 0.40$ (Table 4). Where a Cp ratio is a measure of the ability of a soil chemical characteristic to predict consistent results in this case the results refer to the ability of water to extract P. Mehlich-3 extractable P predicted WSP well, describing 90% of the variance, and adding M-3Ca to the model reduced the variance error by an additional 2%. Water soluble P was well predicted by P_{ox} ($r^2 = 0.88$) and 6% of additional variability was explained by including Al_{ox} in the

model, also significantly reducing the Cp ratio. These findings indicate that many of the soil chemical properties evaluated here affect P solubility in water. However, the most consistent players appear to be Ca and Al, where P associated with Ca appears to be relatively meta-stable when compared with that associated with Al.

Frederick soils as a function of pH and	d the con	centrations of P, Ca, Al, and Fe in water ^T , Mehlich-3, a	ammonium	n-oxalate ar	ld
soil solution extracts.					
Before Stepwise	Eq.	After Stepwise	\mathbb{R}^2	C(p)	$P_{T} > F$
WSP = WSAI WSCa WSFe pH [*]	5	WSP = -3.83 + 0.45 (WSCa)	0.40	1.75	0.0007
WSP = M-3P M-3Ca ^{$\\$}	9	WSP = 1.28 + 0.029 (M-3P)	0.90	5.36	<.0001
	L	WSP = -1.0 + 0.034 (M-3P) - 0.002 (M-3Ca)	0.92	3.00	0.0497
$WSP = P_{ox} Al_{ox} Fe_{ox}^{\#}$	8	$WSP = -3.11 + 0.87 (P_{ox})$	0.88	22.00	<.0001
	6	$WSP = 6.7 + 0.91 (P_{ox}) - 0.21 (Al_{ox})$	0.94	2.18	<.0001
WSP = SSP SSCa SSAl SSFe SSpH ^{$\uparrow\uparrow$}	10	WSP = 4.0 + 3.9 (SSP)	0.80	37.72	<.0001
	11	WSP = -6.9 + 3.62 (SSP) + 0.11 (SSCa)	0.91	6.57	<.0001
	12	WSP =-52.6 + 3.58 (SSP)+ 0.07 (SSCa) + 7.5 (SSpH)	0.93	2.80	0.0200
† (WSP, WSAI, WSCa, WSFe) Water e:	xtractable	P, Al, Ca, and Fe 1:1 soil: solution ratio			
‡ (pH) the native soil pH determined usi	ing a 1:1 s	soil to distilled water ratio.			

Table 4. Results of STEPWISE multiple regression analysis in PROC REG. Results predict water soluble P (WSP) in the nine

M-3P, M-3Ca)) Mehlich 3 extractable P, and Ca
(P_{ox}, Al_{ox}, and Fe_{ox}) 0.2 Acid-NH₄-oxalate P, Al, and Fe
(SSP, SSCa, SSAl, SSFe SSpH) Soil solution concentrations of P, Ca, Al, Fe, and pH after extraction at field capacity

Thermodynamic Stability

Thermodynamic solubility plots were constructed to evaluate ion activity and equilibria in the nine soils. We found that several soils had soil solution properties conducive to the formation of Ca-P phases. Results from Visual Minteg speciation program indicate that as STP increases, soils with a history of poultry manure or commercial fertilizer application can become supersaturated with respect to various Ca-P phases while maintaining equilibrium with Al-P phases. The solution equilibria of CF1 was near equilibrium with respect to semi-soluble tri-calcium phosphate (TCP, β- $Ca_3(PO_4)_6$ (Fig. 6). BL1 and BL3 were in equilibrium or slightly under-saturated with respect to octacalcium phosphate (OCP, Ca₄H₂(PO₄)₃• 5H₂O), while LL1 was in equilibrium with dicalcium phosphate (DCP, Ca₂(PO₄)₄). BL2, DM1, DM2, and CF2 were under-saturated with respect to all Ca/P solid phases except for hydroxyapatite (HA), where CF2 and DM2 were in equilibrium with HA (Fig. 6). Soil solution of poultry manure amended soils was more saturated with respect to Ca-P phases than other soils. Solid forming reactions are kinetically limited, and it appears that the less stable Ca-P phases become more thermodynamically feasible as DPS increases. High values of DPS were complimented by saturation index values that indicated super-saturation with respect to several meta-stable (kinetically limited) Ca-P phases (Table 5).

Saturation indices (SI) determined by Minteq using Eq. 3, indicate the saturation of the soil solution with respect to a particular solid phase and are shown in Table 5. Soils with a history of litter layer application, CF2, and BL2 were under-saturated (negative SI) with respect to amorphous Al (Al(OH)₃ amorphous). All soils were supersaturated with respect to soil (crystalline) Al(OH)₃ (Table 5). The SI values showed that most of the soil solutions were strongly supersaturated with respect to amorphous and crystalline strengite and variscite (Table 5 and Figs. 7 & 8). Furthermore, all soils were supersaturated with respect to crandallite, a Al-P-Ca phase based on the activity of Al for each soil and that soil's Ca and P activity (Fig. 6).

Sharpley et al. (2004) suggested that for 20 soils with a long-term history of dairy, and poultry manure application, Ca-P forms dominated P solubility. They found that these forms were not soluble in water but are soluble in acidic soil test extracts (Mehlich 3). Calcium and P forms are feasible in these nine soils according to Minteq saturation indices, and these associations are further supported by correlations in the previous section. For these Frederick soils it is unclear what fraction of meta-stable Ca-P is released in Mehlich 1 or 3 extracts. Ca-P minerals are most likely meta-stable, and over time their presence would decrease as weathering conditions leach Ca and reduce soil pH especially under the influence of acid rainfall and/or ammonium containing fertilizers.

LL1 LL2 BL1 BL2 BL2 BL3 DM1 CF1 CF1 CF1 CF2 CF2 Significa	Hydroxide‡ (0.5) (0.1) 0.1 0.5 0.5 0.3 0.3 0.2 0.2 0.0 0.0	Hydroxide				Hwdrons	Hudrovy.	
LL1 LL2 BL1 BL1 BL2 BL2 DM1 DM2 CF1 CF1 CF2 DPS ⁴	(0.5) (0.1) 0.1 0.5 0.5 0.3 0.5 0.3 0.2 0.0 0.0	2.0	TCP§	OCP#	DCP††	DCP [‡] ‡	apatite⊊	Strengiteð
LL2 BL1 BL2 BL2 BL3 DM1 DM2 CF1 CF1 CF2 DPS [©] * Significa	(0.1) 0.1 0.3 0.5 0.3 0.3 0.3 0.2 0.0 -0.77*	y C	2.1	1.1	0.1	(0.2)	9.6	2.6
BL1 BL2 BL3 DM1 DM1 DM2 CF1 CF1 CF2 Significa	0.1 (0.3) 0.5 0.5 0.3 0.2 0.0 -0.77*	C.7	(1.1)	(3.2)	(1.0)	(1.3)	4.7	2.2
BL2 BL3 DM1 DM2 CF1 CF1 CF2 <u>DPS⁰</u>	(0.3) 0.5 0.5 0.3 0.2 0.0 -0.77*	2.6	<u>1.1</u>	(0.2)	(0.2)	(0.5)	8.3	2.9
BL3 DM1 DM2 CF1 CF1 CF2 DPS [©]	0.5 0.5 0.3 0.2 0.0	2.2	2.0	1.1	0.3	0.0	9.4	3.1
DMI DM2 CF1 CF2 DPS ⁵ * Significa	0.5 0.3 0.2 0.0 -0.77*	3.0	(1.2)	(2.9)	(0.7)	(0.0)	4.1	3.7
DM2 CF1 CF2 DPS [©] * Significa	0.3 0.2 -0.77*	3.0	(1.8)	(4.2)	(1.2)	(1.5)	3.4	2.4
CF1 CF2 DPS ⁴ * Significa	0.2 0.0 -0.77*	2.9	(3.3)	(5.7)	(1.4)	(1.6)	0.6	3.4
CF2 DPS ^{\$\$} * Significa	0.0 -0.77*	2.7	0.1	(1.9)	(0.8)	(1.1)	6.7	2.3
DPS [®] * Significa	-0.77*	2.5	(3.6)	(0.6)	(1.9)	(2.2)	0.4	1.7
* Significa		-0.76*	0.83**	0.83**	0.78*	0.77*	0.84^{**}	0.03^{+}
** Signific *** Signific * NS, nor * NS, nor # Alumin & Tri-calc # Octa-ca # Octa-ca # Di-calc # Hydroxy & Strengite \$ aturatio	ant at the 0.05 I ccant at the 0.01 ficant at the 0.01 n-significant at hous Hydroxid num Hydroxide cium Phosphate alcium Phosphate ium Phosphate ium Phosphate rium Phosphate rium Phosphate rium Phosphate of P Saturatic of P Saturatic on indices for v	probability leve probability leve 01 probability lev 01 probability lev 01 probability and e - Al(OH) ₃ (at e - Al(OH) ₃ (at e - Al(OH) ₃ (at e Beta (TCP- β) ate (OCP) - Ca ₈ (Hyrdrous-DC - Ca ₁₀ (PO4) ₆ (O PO4)·2(H ₂ O)) on correlation arious common	el. /el. level. bability le mophous) il) il) il) il) il) il) ca3(PO 3(HO4)3 O4 3(HO4)3 O4 3(H)) H) il) il) il) il) il) il) il) il) il) il	vel. 4) ₂ (β) 3H ₂ O PO ₄ :2H ₂ O it <i>r</i> when t <i>r</i> when s in soils.	PROC C	ORR was co	orrelated wit	the the

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Characterization of P-rich Particles

SEM-EDS analysis allowed for observation of the many components of the whole soil, including organic material, non-crystalline material, metallic-organic particles, and mineralogical fractions. No pretreatment of the material was performed to keep cementing agents and meta-stable minerals intact, and lack of pretreatment necessitated analysis of both the clay and silt fractions. The original objective of the SEM analysis was to identify Ca-P forms. The Ca, P and pH values of LL1 and BL2 were originally thought to be sufficient for Ca-P solid phase growth. Soil solution data show that P is strongly correlated with Ca for this set of soils. However, no Ca-P forms were observed using SEM for any size fraction of any soil. These forms may exist as meta-stable species which may dissolve during fractionation procedures or may be masked by coatings of other mineral phases (Cooperband and Good, 2002; Pierzynski, 1990b).

Only the silt of LL1 and the clay fraction of BL2 exhibited any significant P. Typically each image is a conglomerate of material, yet the actual EDS scan represents only a 1 μ m³ volume of the particle and material adhered onto the particle surface. The specimen in Fig. 9 is from the silt fraction of LL1. The chemical composition and image of the specimen are suggestive of a silicaceous mineral (i.e. quartz) with several phyllosilicate or plate-like particles adhered to the surface. The particle on the left side of the image was a silica-oxygen specimen with a relatively smooth surface (spectra not shown), and the more porous and platy particle on the right side of the image contains detectable concentrations of Na, Al, Si, P, K, and Fe (Fig. 10. The percent make up of the particle discussed is shown in Table 6. The specimen in Fig. 11 was found in the silt

fraction of LL1 and also has a porous surface. This specimen can be considered an example of a Si-Al-P phase (Fig. 12 and Table 6).

These findings demonstrate that the stable forms of P in soils with a long-term history of layer litter application can be associated with Al, and that relationship between P and Al is not susceptible to high dilutions, indicating that it is relatively insoluble in water for these short time periods. These findings agree with the double function plots of free Al and free diprotic P plotted which showed that soil solution was supersaturated with respect to several Al-P phases (Fig. 8). While approximately 50 particles were sampled and chemical analyses performed, there were no particles present that were strictly associated with either Fe or Ca, indicating that these forms may be meta-stable or not as easily detectable as Al forms.



Fig. 9. Phosphorus rich particles found in the gravity separated silt fraction from LL1 (taken at 5 kV).



Fig. 10. Electron dispersive scanning spectra (20 kV) of Fig. 9.



Fig. 11. Phosphorus rich particles found in the gravity separated silt fraction from LL1 (taken at 5 kV).



Fig. 12. Electron dispersive scanning spectra (20 kV) of Fig. 11.

Table	6. T	he s	stoic	hiom	etr	y of
the sp	ectra	for	the	two	P	rich
partic	les des	scrib	ed.†			
		Stoi	chio	metry	y	

	Stoichiom	netry
Element	Fig. 10	Fig. 12
С	NA	NA
Ο	7.3	7.0
Al	0.9	2.2
Si	0.7	0.2
Р	0.8	0.6
Ca	NA	NA
Fe	0.1	0.01
Na	0.2	NA
K	NA	NA
Mg	NA	NA
Ti	NA	NA
Cl	NA	NA

† NA Not Applicable

Phosphorus Release

Two first order equations were used to describe P and Ca release data. These equations enabled calculation of rate coefficients k_1 , (rate coefficient for t = 0 to t = 5 hr) and k_2 (rate coefficient for t = 5 hr to t = 60 hr) (Fig. 13 and 14). The total P released over a 60 hr period is shown in Table 7. The rate of release increased as total P increased for all soils. The rate of P release for LL1, BL2, and BL3 was the highest of all soils. These three soils were expected to have the greatest P release because they had the highest TP values (2040 – 948 mg kg⁻¹). Calcium release showed that soils amended with layer litter had a rate of Ca release significantly higher than all the other soils. This is expected because of the high concentration of Ca found in soils impacted by layer litter (Table 1).

At low concentrations of P the fate of P is regulated by optimal sorption sites. In acid soils these sites are predicted with the use of phosphorus sorption capacity (PSC), however as TP increases over time and manure application, these sites become saturated and the DPS increases approaching 100%. In this study, as DPS approached 100%, P appeared to participate in less optimal associations. The thermodynamic saturation indices for meta-stable calcium phosphate phases directly reflected the results of the kinetic data, suggesting that as DPS approached 100%, the soil solution exhibited supersaturation with respect to meta-stable Ca-P compounds such as OCP, DCP, and TCP (Table 5). Soils supersaturated with respect to these Ca-P phases (LL1 and BL2) had significantly higher rates of P release, signifying such phases are indeed meta-stable. However, while LL2 and BL1 had similar STP values as LL1 and BL2, these soils exhibited a significantly lower coefficient of P release (Fig. 15). Similarly, LL2 (98 mmol kg⁻¹) and BL1 (97 mmol kg⁻¹) had very high PSC (98 mmol kg⁻¹ and 97 mmol kg⁻¹ respectively) that was not yet near saturation (DPS = 27% for LL2, and 54% for BL1) (Table 1). Calcium appears to be a contributing factor in retaining P in these soils as P sorption capacity nears saturation.

P History	P Release	P Release	Ca Release	Ca Release	$\sum P$	% TP
1 1110001 9	k_1	k_2	k_1	k_2	Released	released
		mmol I	$r^{-1} \mathrm{hr}^{-1} - \cdots - r$		mg Kg ⁻¹	%
LL1	65	6	280	28	221	11
LL2	23	3	226	18	86	8
BL1	28	6	205	15	117	7
BL2	65	6	92	17	226	NA†
BL3	41	4	111	8	147	16
DM1	36	6	119	18	133	22
DM2	45	7	220	31	170	30
CF1	28	3	196	14	92	14
CF2	4	0	94	7	12	6

Table 7. The first (k_1) and second (k_2) release rates for P and Ca, and the sum of total P released $(\sum P)$ over a three day (60 hrs) batch desorption experiment using a 1:4 ratio of soil to 0.01 M NaCl.

† NA Not Available



Fig. 13. The rate of P released over time in a three day (60 hrs) batch desorption experiment. Soils are representative of fields impacted by long-term history of receiving layer litter, broiler litter, dairy manure, and commercial fertilizer.



Fig. 14. The rate of Ca released over time in a three day (60 hrs) batch desorption experiment. Soils are representative of fields impacted by long-term history of receiving layer litter, broiler litter, dairy manure, and commercial fertilizer.



Fig. 15. The first (k_1) and second (k_2) rate coefficients of P release over a 60 hour batch release experiment. Letters represent Tukey's HSD group, where samples with the same letter are not significantly different.



Fig. 16. The first (k_1) and second (k_2) rate coefficients of Ca release over a 60 hour batch release experiment. Letters represent Tukey's HSD group, where samples with the same letter are not significantly different.

PROC CORR was run to identify correlations between P and Ca release and soil surface properties for the whole dataset. Total soil P (TP) correlated well with P release rate, thus soils with a history of poultry manure application had the highest TP and P release rates (Table 7 and 8). Interestingly, although the Frederick series contains a significant amount of Fe and Al oxides, neither Alox nor Feox correlated well with P release rate, and was found to be more significant when evaluated on a soil by soil basis (Table 8). It may be that Al_{ox} and Fe_{ox} are not the primary surfaces for P adsorption when soils have been impacted by poultry manure and exhibit high STP values. Water soluble Al (WSAl) and Fe (WSFe) was negatively correlated with the rate coefficients obtained for the first phase of release (k_1) . These results correspond to other research that shows that the presence of Al and Fe will retard release due to the strength of the bonds formed between P and solids containing Al and Fe (McDowell, 2003). When Al and Fe are present in soil solution the formation of Al-, and Fe- P ion-complexes and specific adsorption or co-precipitation activity is favored, resulting in a reduced rate of initial P release. Other studies have shown slow desorption behavior when P is dominated by inorganic soil components such as ferrihydrite, goethite, and gibbsite (Arai et al., 2005; Lookman et al., 1995; Ryden and Syers, 1977).

Calcium was somewhat correlated with both periods of release (Table 8). Similar to Lookman et al. (1997) we found that Ca-P phases were the phases that dominated P release, though while Lookman was able to distinguish between first (meta-stable) and secondary (strongly held) sources of P with the use of correlation analysis, we found that Ca dominated P release for both periods of release. OM did not appear to significantly affect the release of P under the conditions of this study.

	k_1	k_2		k_2
	Phosphorus	Phosphorus	k ₁ Calcium	Calcium
WSP	0.66**	0.54*	0.24†	0.39†
M1P	0.61*	0.41†	0.27†	0.28†
M3P	0.74***	0.55*	0.44†	0.33†
Pox	0.48*	0.45†	0.35†	0.44^{+}
DPS	0.67**	0.48*	0.39†	0.41†
ТР	0.58*	0.26†	0.45†	0.56*
WSCa	0.57*	0.32†	0.81***	0.67**
M3 _{Ca}	0.48*	0.32†	0.72***	0.56*
WSAI	-0.47*	-0.23†	-0.47†	-0.24†
Alox	-0.36†	-0.23†	-0.12†	0.06†
WSFe	-0.55*	-0.13	-0.45†	0.22†

Table 8. Correlation coefficients (r) for first (k1) and second (k2) rates of P and Ca release as related to soil chemical characteristics shown in Table 1.

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

 \dagger NS, nonsignificant at the < 0.05 probability level.

‡ pH measured in a 1:1 soil:water ratio after equilibration for 1 hr.

CONCLUSION

Models relating soil test P (STP) to water soluble P (WSP) and the degree of P saturation (DPS) to STP are used in Virginia to estimate P loss potential in nutrient management planning. These models, while useful for most soils, may not accurately predict P release for soils with a long-term history of manure application. The data presented here indicates that very high STP levels do not always correspond to high rates of P release. This data set suggests that the use of a singular P threshold as the sole means of managing P is not appropriate for all high P soils.

Similar to several other studies, we found that sparingly soluble Ca-P compounds were possible in Virginia soils that have been impacted by layer litter and broiler manure application. Soil solution saturation with respect to Ca-P compounds increased as TP and DPS increased. The saturation of sorption sites with P leaves Ca to serve as an additional reservoir for biologically available, semi-soluble P. Our results show that these forms are meta-stable and as saturation indices show increased supersaturation with respect to meta-stable forms the rate of P release increases.

While no Ca-P minerals were found with scanning electron microscopy (SEM-EDS), our results show that crystalline Al-P forms do exist in these soils. Release results show that phosphorus sorption capacity (PSC ($Al_{ox} + Fe_{ox}$)) plays a significant role in reducing P release. The strength of the relationship between P and Al/Fe in these soils, and the instability of the second Ca-P pool described by Lookman et al (1997), supports the theory that this Ca-P pool may have dissolved during sample preparation for SEM-EDS analysis, and that the other pool is at too low a concentration and went undetected.

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Together Al-P and Ca-P fractions act to limit the solubility of P in systems with a long-term history of manure application. In order to maintain this association, encourage meta-stable Ca-P to hydrolyze into more stable Ca-P such as hydroxyl-apatite, and limit excessive P loss in surface runoff, Ca must be managed in fields that have a long term history of poultry manure application. Calcium is readily taken up by plants or leached through the soil profile with frequent rainfall events with a slightly acid pH over time (Josan et al., 2005; Palmer et al., 2004). However, solution levels of Ca can be maintained by periodic liming.

Based on current P management for these manure impacted soils, a very high STP would be managed by reducing manure application. This method of management may be detrimental to efforts that seek to limit P solubility long-term. Not only does poultry manure provide needed calcium carbonate equivalence to maintain the Ca-P reservoir and buffering soil pH. It also provides significant organic material whose role is not yet understood in reducing P availability. Neglecting to maintain soil pH by applying additional Ca in the form of lime or additional manure may result in significant risk to water bodies since a decrease in soil pH could result in increased P solubility

In summary, it is recommended that further field work be performed to evaluate over a multi-year period how different treatments (cessation of manure application, liming, and maintaining manure application) will affect WSP in these soils. Regardless, more work needs to be performed before specific management applications to mitigate the risk P availability in runoff can be determined.
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APPENDIX

Figure A1 shows the results found in this study for Mehlich 3 extractable P as a function of water soluble P (WSP). The data shows that there was no increase in predictability of WSP when the model was split based on the threshold value found in Sharpley et al. (2004) for soils with a long-term history of manure application



Fig. A1. Plot of WSP and M3P with samples separated and linear and logarithmic (poultry) relationships for data above and below suggested threshold level from Sharpley et al. (2004). Pink data is for dairy and commercial fertilized soils, and blue data is from soils that have a history of broiler or layer litter application.

Particle size analysis data for the nine soils is shown in Table A1. Clay, silt and sand content were estimated based on sieving results found prior to analysis with the scanning electron microscope (SEM). The soil with the highest clay content was LL2. BL3 had a significantly higher sand content than all other poultry manure impacted soils, which may explain some of the inability of this soil to retain P.. The soils with the lowest silt content (which is a combination of silt and clay due to separation procedures) were BL3, DM1, and DM2. Although these soils had a history of manure application they exhibited lower STP than all other manure impacted soils, most likely due to lower active mineralogical surfaces.

Clay perior meu	without pro	eneatmen	11.
P History	Sand	Silt	Clay
		%	
LL1	16	80	5
LL2	19	68	13
BL1	20	72	8
BL3	54	44	3
DM1	29	65	6
DM2	25	68	8
CF1	24	71	5
CF2	16	80	5

Table A1. Gravity Separated Sand, Silt andClay performed without pretreatment.

Data presented in Figure A2 shows the effective values where the soils studied here become supersaturated with respect to several meta-stable Ca-P forms. Note where the various lines representing OCP, DCP, TCP, and hydroxyl-apatite cross the x-axis, beyond this point (DPS level) the soils are supersaturated with respect to these forms.



Fig. A2. Saturation indices (SI) as a function of degree of P saturation % (DPS). The dotted black line represents tri-calcium phosphate (TCP) regressed on DPS, the solid black line represents octa-calcium phosphate (OCP) regressed on DPS, the grey dashed line represents di-calcium phosphate (DCP) regressed on DPS and the solid grey line represents hydrous di-calcium phosphate (DCP) regressed on DPS.

This section described the modified freundlich equation, the second method used to describe P desorption. The models developed in this section were not as statistically accurate as those developed with two first order equations.

Modified Freudlich equation

Two methods of modeling were used to describe P and Ca release data, the modified Freundlich equation (release = αt^{β} where t = time), and two first order equations (discussed in bulk of thesis). The modified Freundlich equation resulted in two coefficients, 1) release rate (α), and 2) the rate at which release declines (β) (McDowell and Sharpley, 2002). The results reflect the method of modeling using two first order equations; with the exception of β . Beta (β) did not show a relationship to any of the soil properties obtained in the characterization section of the experiment. Data presented in Table A2 illustrate P and Ca release as modeled by the power function or modified freundlich equation. However, note that the model fits rather poorly for the entire dataset of DM2, and for all of the data points in the first (0-5 hours) phase of observation (Fig. A3 – A6). For this reason we felt that including this data in the bulk of the thesis would divert attention from the more clear models.

Alpha P (α P), alpha Ca (α Ca) and the rate at which release declined for P and Ca (β P, and β Ca) are shown in Table A2. The rate of P release (α P) for LL1, BL2, and BL3 was the highest of all soils, yet they were statistically different. We expected these to have the greatest P release because they had the highest TP values (2040 – 948 mg kg⁻¹). However, BL1 and LL2 exhibited significantly lower rates of P release (α P) than all other poultry waste amended soils (Table A2). This was not expected, because while TP

was significantly lower than all other soils for LL2 (1153 mg kg⁻¹); BL1 has the second highest TP value (1745 mg kg⁻¹) and M-3P (1244 mg kg⁻¹) value respectively. The low rate of release for both may be due to the high M-3Ca (4236 and 3955 mg kg⁻¹) respectively. This cannot however entirely account for the lower rate, because LL1 has both a high M-3P (1671 mg kg⁻¹) and M-3Ca (5531 mg kg⁻¹), but has the highest observable rate of P release for all the soils. The rate of P release for soils with a long term history of dairy manure application (DM1 & DM2) did not significantly differ in their rate of P release from CF2. The rate of Ca release was highest for LL1 and LL2, with no significant difference between the two soils.

Correlation coefficients (r) for the rate of release coefficients were calculated by PROC CORR in SAS. The results are very similar to those found for the two first order models. The rate of initial P release (k_1) related significantly to the amount of water and Mehlich 3 extractable Ca, WSAI, and WSFe. WSAI and WSFe correlations revealed that as the concentration of Al and Fe increases in water extractions the rate of release decreases (Table A3). As expected the release of Ca was well correlated with Ca extracted in either the Mehlich 3 extract or deionized water.



Fig. A3. Phosphorus (P) release from soils with a history of poultry waste amendment application (LL1, LL2, BL1, BL2, and BL3). Each curvilinear line represents the power function fit to represent P release.



Fig. A4. Phosphorus (P) release from soils with a long term history of dairy manure and inorganic fertilizer application (DM1, DM2, CF1, and CF2). Each curvilinear line represents the power function fit to represent P release.



Fig. A5. Calcium (Ca) release from soils with a history of poultry waste amendment application (LL1, LL2, BL1, BL2, and BL3). Each curvilinear line represents the power function fit to represent Ca release.



fertilizer application (DM1, DM2, CF1, and CF2). Each curvilinear line represents the power Fig. A6. Calcium (Ca) release from soils with a long term history of dairy manure or inorganic function fit to represent Ca release.

Table A2. Release rate (α) and the rate at which release declines (β) for solution P and Ca for a 60 hour batch desorption experiment. The letters in parenthesis represent Tukey's HSD mean groupings for the coefficients as calculated in SAS.

Soil	F)	С	a
	α	β	α	В
		mmo	1 L ⁻¹	
LL1	36.1 (a)	0.366 (de)	194 (a)	0.349 (ab)
LL2	8.9 (e)	0.421 (c)	176 (ab)	0.321 (ab)
BL1	1.7 (g)	0.684 (a)	17 (e)	0.537 (ab)
BL2	28.0 (b)	0.402 (cd)	205 (a)	0.287 (b)
BL3	23.3 (c)	0.369 (de)	98 (cd)	0.303 (ab)
DM1	2.8 (fg)	0.638 (b)	25 (e)	0.512 (a)
DM2	3.5 (f)	0.646 (ab)	75 (de)	0.450 (ab)
CF1	10.9 (d)	0.404 (c)	164 (abc)	0.302 (ab)
CF2	2.8 (f)	0.327 (e)	108 (bcd)	0.274 (b)

Table A3.	. Correlat	ion coeffi nd increase	cients (r) nic fertiliz	for Ca an	id P relea	se rates a	and signi	ficant soil physiogra	propertie	s for soil ince in Vi	s with a] rainia	long term	
	WSP	MIP MIP	M3P	Pox	DPS	TP	WSCa	M3Ca	WSAI	Alox	WSFe	Feox	Hd
a P	0.93	0.95	0.97	0.89	0.89	0.87	0.78	0.72	-0.61	-0.28	-0.67	0.18	0.46
p value	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.001	0.002	0.022	0.288	0.009	0.516	0.072
a Ca	0.36	0.46	0.63	0.60	0.35	0.61	0.76	0.82	-0.19	0.26	-0.09	0.68	0.89
p value	0.202	0.102	0.009	0.014	0.182	0.020	0.002	<.0001	0.509	0.324	0.750	0.004	<.0001
4													

Incubation Experiment: Effect of Previous Manure Management and Soil pH on P Solubility

This section describes the methods and unfinished results for an incubation experiment performed for all soils with the exception of BL2. The reactivity of Ca-P compounds in soils with an acidic mineralogy is not well understood. It may be that these compounds can become more soluble as soil pH decreases with time as weathering occurs, resulting in a significant water quality risk. The goal of the experiment was to evaluate the response of these soils to a change in pH. However, the results are unclear and need to be more thoroughly examined by the authors before conclusions can be derived.

METHODS

Incubation

Sub samples of soils were obtained from all soils except BL2 and sieved to 2 mm. Each sub-sample was split into four containers, representing soils to be altered to pH 4, 5, 6, and 7. When desired pH was obtained within 0.5 pH units with 0.01 *M* HC1 and NaOH (Penn, 2004), the contents of the containers were air-dried and subsequently separated into three 250 g samples and one 150 g sample, with no replication. These samples were placed in covered cups with aeration holes to ensure that anaerobic conditions would not occur. The cups were incubated at 25 °C in a Precision low temperature incubator (model 815, Winchester, VA) and selectively removed at day 5, 41 and 74 and the 150 g subsample was removed at 91 d. The samples were brought to field capacity every 3 d. The incubation study was designed as a 4*3*8 factorial experiment (four sampling times, three pH levels, and eight types of amendment (6 manures and 2 inorganic fertilizer controls)). Soil removed from the incubator was air dried, weighed and subjected to selected extractions. Mehlich 3 extractable Ca (M3Ca) and P (M3P) were determined after shaking 2 g soil with a 20 mL mixture of 0.2 *M* CH₃COOH, 0.25 *M* NH₄NO₃, 0.015 *M* NH₄F, 0.013 *M* HNO₃, and 0.001 *M* EDTA end over end for 5 min (Mehlich, 1984). Native soil pH was determined using a 1:1 soil to distilled water ratio. Water extractable P (WSP), and Ca (WSCa) were determined by shaking soil using a 2:20 soil:water ratio for 1 hr at room temperature (Self-Davis, 2000). The mixture was filtered through a Whatman No. 42 filter membrane. Ammonium-oxalate extractable P (P_{ox}), AI (Al_{ox}), and Fe (Fe_{ox}) was determined using the procedure described by Schoumans (2000). The degree of P saturation (DPS) was calculated under the assumption that the bulk density of the tillage layer was identical and uniformly sampled. Degree of P saturation was calculated by Eq. 2, using 0.2 M NH₄-Oxalate extractable P (P_{ox}), Fe (Fe_{ox}) and AI (Al_{ox}) values (Beck et al., 2000).

DPS = [Pox (mmol kg-1)]/[Alox + Feox (mmol kg-1)] *100

Eq. 1

Extracts were analyzed for Al, Fe, Ca, and/or P using a spectro flame FTMOA85D, ICPES (Spectro Analytical Instruments, Inc. Kleve Germany), unless otherwise indicated.

Surface Properties - Incubation

Soil solutions were analyzed for E_c , pH, Al, Ca, P, and Fe for three target pH levels including 7, 6, and 5.5. Soil solutions were collected in duplicate at 5, 41 and 79 days. Preliminary calculations of P phases were determined from a soil solution

extraction at field capacity. For soil solution collection, 150-grams of each soil was weighted into a 250 mL centrifuge bottle. Each sample was brought to field capacity, which was measured according to Tan (1996) on unaltered soil. The sample was then equilibrated for 24 hrs at 24°C (Precision low temperature incubator, model 815, Winchester, VA). No preliminary experimentation was performed to evaluate the time needed to obtain steady state (Hetrick and Schwab, 1990). The equilibrated soil was centrifuged at 27,642 g for 2 hr at a temperature of 22°C (Sorvall SUPER T 21 Refrigerated Superspeed Centrifuge, Asheville, NC). Supernatant "soil solutions" were filtered through 0.2 μ m filter paper and measured for electrical conductivity (E_c) and pH. Care was taken to measure E_c prior to determining pH. Ionic strength (μ) was calculated from E_C at 25°C (Griffin and Jurinak, 1973).

Phase Diagrams - Incubations

Phase diagrams graphically show the location of the stability field of a given solid phase relative to the equilibria state of soil solution extracted to provide reference for a researcher as to the saturation of the soil solution (Sparks, 1999). All double function plots for this study were created manually using calculated activities of free {Al³⁺}, {Fe³⁺}, {H₂PO₄⁻}, and {Ca²⁺} from Visual MINTEQ. The negative logarithm (p) of {Al³⁺}, {Fe³⁺}, {H₂PO₄⁻}, and {Ca²⁺}(pAl, pFe, pH₂PO₄⁻, and pCa, respectively) were calculated in excel and used to plot the data. Stability fields for Ca-P minerals were calculated using K_{sp} values derived from Lindsay (1979).

Soil Surface Properties – Incubation

The STEPWISE selection process for the best fit model to describe WSP was performed in PROC REG (SAS Institute, 1999). Water soluble elements (Ca, Al, and Fe), pH measured in a 1:1 soil to solution matrix, Mehlich 3 extractable elements (P and Ca), ammonium oxalate extractable Al and Fe; and P, Al, Fe, Ca, and pH in soil solution were each used as dependent variables to model WSP using stepwise regression to predict WSP. The models tested and corresponding results are presented in Table A-12. Calcium did play a significant role in controlling WSP in the incubated soils, and as Mehlich-3 extractable Ca increased the WSP in the incubated soils decreased. Furthermore, soil solution pH (SSpH) also impacted the soils significantly, and soils showed that as SSpH increased along with soil solution P, WSP increased as well and served as the best predictor of WSP of all measured soil solution elements. These findings further indicate that Ca has a direct significant relationship to WSP in these soils, while Al reduces WSP. Aluminum and Ca influence the solubility of P in the soil solution and ultimately the risk of P loading from soil erosion.

Table A4. Results of STEPWISE mu	ultiple regression	analysis used to predict water solu	ble P (WSP) in the n	nine Frederick	soils
as a function of pill and the concel extracts.		a, Al, anu re III watel, Menur-	, aшшишиш-ихагач	to alla sull'sull	11011
Before Stepwise	Eq.	After Stepwise	\mathbb{R}^2	C(p)	$P_{T} >$
			0000	(T 1	

Before Stepwise	Eq.	After Stepwise	R⁺	C(p)	$\Pr > F$
WSP = WSAI, WSCa, WSFe, $pH^{\$}$	13	WSP = intercept + (WSCa)	0.08	5.12	0.0030
$MSB - M 3D M 3C_2$	14	WSP = -1.39 + 0.23 (M-3P)	0.61	9.88	<.0001
WJF – M-JF, M-JCa	15	WSP = 2.02 + 0.29 (M-3P) - 0.021 (M-3Ca)	0.64	3.00	0.0036
115 C $-$ D \wedge I $-$ C	16	$WSP = 3.07 + 0.16 (Fe_{ox})$	0.55	54.29	<.0001
$WSF = F_{0x}$, AI_{0x} , Fe_{0x}	17	WSP = $12.83 + -0.64$ (P _{ox}) 2.23 (Fe _{ox})	0.70	3.43	<.0001
$MCD = CCD CCC^2 CC + 1 CCC^2$	18	WSP = 1.44 + 0.50 (SSP)	0.72	9.45	<.0001
wər – ээг, ээса, ээлі, ээге, рп	19	WSP = -17.95 + 8.45 (SSP) + 5.04 (SSpH)	0.91	6.57	<.0001
$WSP = M-3P$, $M-1P$, P_{ox} , DPS , TP	20	WSP = $6.64 + 0.23$ (M-3P) - 0.22 (P _{ox})	0.62	2.21	0.0178
\ddagger (WSP, WSAI, WSCa, WSFe) Water ϵ	extracta	ble P, Al, Ca, and Fe 1:1 soil: solution ratio			
* (aII) the matire as il all determined	.1.	1 apil to distilled wrother action			

(pH) the native soil pH determined using a 1:1 soil to distilled water ratio.
(M-3P, M-3Ca)) Mehlich 3 extractable P, and Ca
(P_{ox}, Al_{ox}, and Fe_{ox}) 0.2 Acid-NH₄-oxalate P, Al, and Fe
(SSP, SSCa, SSAI, SSFe SSpH) Soil solution concentrations of P, Ca, Al, Fe, and pH after extraction at field capacity

The data shown below (Data=LongtermInc) includes the soil "code", soil pH as changed with the use of HCl and NaOH (PrepH), the removal time in days (Time), and the subsample (Rep) for each analysis taken during the incubation experiment. "Tag" is a label that combines soil "code" and "prepH" allowing for grouping of all removal intervals and subsamples for that soil at the altered pH. Mehlich 3 P and Ca (M3P and M3Ca) were measured for each subsample and removal time. "Alox", "Pox", and "Feox" represent ammonium oxalate extractable elements. "AloxFeox" represents P sorption capacity, and "DPS" represents degree of P saturation. Soil solution elements are represented by "SSAI", "SSCa", "SSFe", "SSP", and soil solution pH at time of filtration is represented by "SSPH". "pH11" represents soil pH taken after removal from the incubation chamber, a after air drying, in a 1:1 soil to water ratio. Water soluble P and Ca are noted by "WSP" and "WSCa", while the percent Mehlich 3 extractable P and Ca extractable in water is represented by "%H2OCa" and "%H2OP". Finally, "pHlovel" represents the an altered pH category.

Data=LongtermInc

	33.88	33.66	32.48	32.41	31.87	33.34	34.38	32.20	34.81	34.06	33.59	33.41	32.88	33.63	32.16	33.06	31.52	30.23	14.90	15.40	30.19	29.90	30.69	29.73	21.85	21.88	21.20	20.99	21.77	21.60	21.34	20.95	18.24
Feox	62.38	59.73	58.63	58.11	57.73	62.05	65.86	63.54	64.57	64.57	65.22	65.22	63.54	66.51	59.47	60.69	63.02	57.79	44.55	45.65	62.63	60.63	61.67	61.02	22.60	23.05	22.34	21.63	22.86	22.21	22.79	22.08	17.35
Pox	64.41	63.45	62.12	61.97	60.41	63.52	65.75	63.30	67.38	66.12	66.12	66.34	64.64	66.49	63.01	67.08	53.22	51.15	53.37	53.89	52.93	51.96	53.07	52.70	42.25	42.99	42.03	41.14	42.77	42.10	42.33	40.62	29.67
X	799.60	808.60	812.40	786.60	684.25	682.87	700.91	684.74	716.40	773.60	781.00	742.20	799.20	789.60	781.40	747.20	748.20	710.20	757.60	811.80	794.00	761.60	707.20	785.40	350.80	341.00	352.40	350.40	361.20	353.20	354.60	372.40	318.80
Ald	219.2	221.0	222.2	220.6	214.6	215.2	218.3	214.7	202.4	206.6	206.4	197.6	205.6	205.4	217.2	213.4	206.0	200.6	103.8	105.0	204.2	205.2	199.4	206.2	180.8	175.0	174.8	177.2	187.8	185.8	183.6	193.6	172.8
M3P M3Ca	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	HRBLH02	WBPLL01								
Blank\$	1	2	1	2	1	2 I	1	2 I	1	2	1	2	1	2 I	1	2	1	2	1	2	1	2	1	2	1	2	1	5	1	2	1	5	1
Time Rep	5	5	41	41	<i>6L</i>	<i>6L</i>	91	91	5	5	41	41	<i>6L</i>	<i>6L</i>	91	91	5	5	41	41	<i>1</i> 9	<i>6L</i>	91	91	5	5	41	41	79	79	91	91	5
PrepH	5.48	5.48	5.48	5.48	5.48	5.48	5.48	5.48	6.07	6.07	6.07	6.07	6.07	6.07	6.07	6.07	7.18	7.18	7.18	7.18	7.18	7.18	7.18	7.18	5.33	5.33	5.33	5.33	5.33	5.33	5.33	5.33	6.01
Code \$	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL3								
Tag \$	BL1-5.48	BL1-5.48	BL1-5.48	BL1-5.48	BL1-5.48	BL1-5.48	BL1-5.48	BL1-5.48	BL1-6.07	BL1-6.07	BL1-6.07	BL1-6.07	BL1-6.07	BL1-6.07	BL1-6.07	BL1-6.07	BL1-7.18	BL1-7.18	BL1-7.18	BL1-7.18	BL1-7.18	BL1-7.18	BL1-7.18	BL1-7.18	BL3-5.33	BL3-6.01							

BL3-6.01	BL3	6.01	5	2	WBPLL01	170.4	311.00	29.57	17.39	17.47
BL3-6.01	BL3	6.01	41	1	WBPLL01	182.0	321.45	38.62	21.37	19.12
BL3-6.01	BL3	6.01	41	0	WBPLL01	181.1	314.71	40.47	22.66	20.95
BL3-6.01	BL3	6.01	79	1	WBPLL01	181.2	315.80	30.42	19.36	18.11
BL3-6.01	BL3	6.01	79	0	WBPLL01	180.9	320.14	29.30	18.72	17.75
BL3-6.01	BL3	6.01	91	1	WBPLL01	178.8	320.68	29.74	18.72	18.16
BL3-6.01	BL3	6.01	91	7	WBPLL01	181.0	323.52	29.32	18.34	17.90
BL3-7	BL3	7.08	5	1	WBPLL01	169.6	317.60	0.02	23.25	20.49
BL3-7	BL3	7.08	5	0	WBPLL01	172.8	324.20	35.21	21.63	19.84
BL3-7	BL3	7.08	41	1	WBPLL01	169.7	297.53	36.77	22.73	21.20
BL3-7	BL3	7.08	41	0	WBPLL01	175.1	309.07	37.28	22.73	21.49
BL3-7	BL3	7.08	79	-	WBPLL01	178.8	333.80	36.62	23.31	21.27
BL3-7	BL3	7.08	79	0	WBPLL01	183.2	345.20	33.50	20.86	19.88
BL3-7	BL3	7.08	91	-	WBPLL01	172.2	316.20	32.76	20.28	18.41
BL3-7	BL3	7.08	91	7	WBPLL01	168.8	314.60	32.91	20.47	18.52
CF1-4.83	CF1	4.83	5	-	TFCFH03	55.70	569.00	82.28	66.51	14.90
CF1-4.83	CF1	4.83	5	0	TFCFH03	55.06	532.20	83.76	67.80	15.18
CF1-4.83	CF1	4.83	41	-	TFCFH03	54.98	540.00	83.02	68.45	15.22
CF1-4.83	CF1	4.83	41	0	TFCFH03	54.66	476.80	83.76	67.15	15.33
CF1-4.83	CF1	4.83	79	-	TFCFH03	58.34	466.70	81.54	65.86	15.01
CF1-4.83	CF1	4.83	79	7	TFCFH03	57.81	475.14	79.31	64.25	14.72
CF1-4.83	CF1	4.83	91	1	TFCFH03	58.57	488.98	81.54	66.51	15.04
CF1-4.83	CF1	4.83	91	0	TFCFH03	58.38	479.59	81.54	67.15	15.15
CF1-5.87	CF1	5.87	5	-	TFCFH03	53.86	489.80	85.24	71.03	15.26
CF1-5.87	CF1	5.87	5	7	TFCFH03	53.20	481.40	83.76	60.69	15.33
CF1-5.87	CF1	5.87	41	-	TFCFH03	52.02	488.80	83.76	68.45	15.08
CF1-5.87	CF1	5.87	41	0	TFCFH03	52.26	503.60	84.50	72.96	14.93
CF1-5.87	CF1	5.87	79	-	TFCFH03	54.30	529.80	85.24	71.67	15.11
CF1-5.87	CF1	5.87	79	7	TFCFH03	54.40	529.20	88.21	75.55	15.51
CF1-5.87	CF1	5.87	91	-	TFCFH03	55.44	531.20	83.76	71.03	14.83
CF1-5.87	CF1	5.87	91	7	TFCFH03	55.04	535.80	85.98	73.61	15.36
CF1-6.99	CF1	6.99	5	-	TFCFH03	9.41	156.20	32.76	26.41	2.76
CF1-6.99	CF1	6.99	5	7	TFCFH03	9.38	155.00	31.65	24.80	2.67
CF1-6.99	CF1	6.99	41	-	TFCFH03	54.42	488.60	74.12	71.67	15.15
CF1-6.99	CF1	6.99	41	7	TFCFH03	53.72	488.20	74.87	73.61	15.33
CF1-6.99	CF1	6.99	79	1	TFCFH03	54.04	465.80	72.86	69.74	14.76
CF1-6.99	CF1	6.99	79	7	TFCFH03	54.78	485.80	74.12	73.61	15.26

CF1-6.99	CF1	6.99	91	-	TFCFH03	54.46	493.80	71.60	66.51	14.79
CF1-6.99	CF1	6.99	91	2	TFCFH03	54.10	518.00	70.64	65.22	14.54
CF2-5.26	CF2	5.26	5		SWCL04	9.45	157.40	38.54	27.31	3.02
CF2-5.26	CF2	5.26	5	0	SWCL04	9.64	159.40	40.18	28.48	3.11
CF2-5.26	CF2	5.26	41		SWCL04	9.72	157.80	37.88	26.47	2.92
CF2-5.26	CF2	5.26	41	0	SWCL04	9.83	159.00	34.91	22.92	2.78
CF2-5.26	CF2	5.26	62		SWCL04	10.57	167.14	36.69	25.96	2.88
CF2-5.26	CF2	5.26	79	0	SWCL04	10.32	165.22	37.80	27.25	2.99
CF2-5.26	CF2	5.26	91	1	SWCL04	11.03	172.33	37.73	26.99	3.00
CF2-5.26	CF2	5.26	91	2	SWCL04	10.35	160.09	37.88	26.80	2.97
CF2-6.16	CF2	6.16	S		SWCL04	52.80	516.60	85.98	72.96	15.18
CF2-6.16	CF2	6.16	5	7	SWCL04	53.44	454.20	88.21	75.55	15.51
CF2-6.16	CF2	6.16	41		SWCL04	9.47	159.00	39.36	27.38	3.02
CF2-6.16	CF2	6.16	41	7	SWCL04	9.39	157.20	38.47	27.06	2.92
CF2-6.16	CF2	6.16	79		SWCL04	9.49	158.40	40.47	27.89	3.03
CF2-6.16	CF2	6.16	79	0	SWCL04	9.27	164.20	39.81	27.64	2.97
CF2-6.16	CF2	6.16	91	-	SWCL04	9.51	161.80	38.99	27.89	2.96
CF2-6.16	CF2	6.16	91	2	SWCL04	9.48	161.00	39.66	28.09	2.94
CF2-6.6 CF2	6.60	5		SWCL04	9.28	162.20	35.21	29.38	2.92	
CF2-6.6 CF2	6.60	5	7	SWCL04	9.37	160.00	34.54	28.41	2.93	
CF2-6.6 CF2	6.60	41	1	SWCL04	9.12	157.40	33.36	25.70	2.87	
CF2-6.6 CF2	6.60	41	7	SWCL04	9.01	155.80	33.43	26.34	2.87	
CF2-6.6 CF2	6.60	79	1	SWCL04	9.13	156.00	34.84	28.22	2.94	
CF2-6.6 CF2	6.60	79	7	SWCL04	9.11	162.60	34.76	29.12	2.98	
CF2-6.6 CF2	6.60	91	1	SWCL04	8.87	160.00	27.74	19.99	2.40	
CF2-6.6 CF2	6.60	91	0	SWCL04	8.96	158.40	26.55	18.27	2.66	
DM1-4.95	DMI	4.95	5	, ,	YDLH06	63.64	234.20	47.00	30.67	8.09
DM1-4.95	DM1	4.95	5	5	YDLH06	61.44	225.20	44.18	31.77	10.74
DM1-4.95	DMI	4.95	41	, ,	YDLH06	61.84	225.20	42.03	30.03	10.35
DM1-4.95	DMI	4.95	41	5	YDLH06	63.18	228.80	43.59	30.80	10.64
DM1-4.95	DMI	4.95	79	, ,	YDLH06	64.94	236.20	42.40	31.32	10.35
DM1-4.95	DMI	4.95	79	5	YDLH06	63.40	222.20	43.21	31.32	10.64
DM1-4.95	DMI	4.95	91	-	YDLH06	66.28	225.60	42.18	31.12	10.46
DM1-4.95	DMI	4.95	91	2	YDLH06	65.06	219.00	40.92	29.90	10.21
DM1-6.07	DMI	6.07	5	-	YDLH06	58.66	209.80	44.99	31.19	10.60
DM1-6.07	DMI	6.07	5	6	YDLH06	59.54	218.20	42.92	30.41	10.35
DM1-6.07	DMI	6.07	41	-	VDLH06	61.56	224.40	42.33	29.70	10.46

																									3.06											
10.03	10.24	10.56	10.46	10.46	10.85	10.10	10.82	10.28	10.42	10.24	10.82	10.39	8.42	8.34	8.42	8.17	8.42	8.17	8.09	10.24	7.95	7.95		7.84	30.80	7.95	7.91	10.17	7.95	8.31	6.88	7.17	7.91	8.09	7.99	8.24
29.19	31.51	33.00	30.48	30.74	31.32	30.15	31.90	30.28	30.86	30.99	43.33	41.58	30.03	29.90	30.22	30.61	31.32	31.06	30.67	29.96	30.22	29.77		29.57	4	30.28	30.74	40.23	28.54	29.70	21.42	23.06	30.22	30.74	29.25	30.35
41.14	42.84	44.40	42.77	42.92	38.62	36.62	38.25	36.99	37.28	36.54	36.84	35.80	48.26	47.88	48.18	47.07	48.77	47.66	47.29	41.88	45.81	45.59		45.07	45.4	44.99	45.22	56.33	39.29	41.21	33.07	34.81	39.95	40.62	40.10	41.07
224.20	214.60	216.00	212.40	214.00	224.20	209.20	220.20	214.80	218.20	217.80	203.20	202.20	296.60	290.40	315.40	302.60	305.80	322.40	315.60	332.00	277.40	274.00	1262.00	1250.00		294.77	293.27	298.17	288.60	287.80	298.20	293.00	305.40	298.80	291.20	293.60
59.20	58.66	58.94	63.46	62.86	60.90	59.66	61.52	59.80	61.66	61.74	54.12	54.32	48.10	46.24	47.34	47.64	48.40	50.90	50.56	51.12	47.86	47.22	281.8	275.8		49.78	50.05	50.37	48.78	48.42	48.80	48.60	49.06	49.12	48.84	48.60
ADLH06	VDLH06	VDLH06	YDLH06	YDLH06	VDLH06	YDLH06	VDLH06	VDLH06	YDLH06	YDLH06	VDLH06	VDLH06	YDLL10																							
7	1	7	-	0	1	0	1	0	1	0	-	0	1	7	1	7	-	0	1	0	1	0	1	0	1	0		0	-	0	-	7	-	7		7
41	79	79	91	91	5	5	41	41	79	79	91	91	5	S	41	41	79	79	91	91	5	5	41	41	79	79	91	91	5	5	41	41	79	79	91	91
6.07	6.07	6.07	6.07	6.07	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	4.99	4.99	4.99	4.99	4.99	4.99	4.99	4.99	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	7.26	7.26	7.26	7.26	7.26	7.26	7.26	7.26
DMI	DMI	DM1	DM1	DM1	DM1	DM1	DM1	DM1	DM1	DM1	DM1	DM1	DM2																							
DM1-6.07	DM1-6.07	DM1-6.07	DM1-6.07	DM1-6.07	DM1-7.17	DM1-7.17	DM1-7.17	DM1-7.17	DM1-7.17	DM1-7.17	DM1-7.17	DM1-7.17	DM2-4.99	DM2-6.23	DM2-7.26																					

5.5 5 5.5 5 5.5 41	4 v v 4	- (1 -		JRLL05 JRLL05 JRLL05	285.81 285.01 47.48	308.00 320.00 285.20	38.62 39.14 41.44	40.94 40.81 43.78	36.17 36.89 37.96		
-	5.5	41	0	JRLL05	47.66	279.20	38.69	40.03	35.17		
	5.5	62 02	(JRLL05	285.81	245.02	37.51	38.74	34.56		
	0. V 0. V	6 I	- v	IRLI 05	C.162 (1241./2 1240.26	37 88	40.68	33.81 33.81		
	5.5	91	- 7	JRLL05	292.7	1285.51	37.95	39.84	33.92		
	LL1	6.05	5	1	JRLL05	275.0	1178.00	0 39.73	41.00	35.42	
	LL1	6.05	5	0	JRLL05	272.0	1174.00	0 38.40	41.00	33.77	
	LL1	6.05	41	1	JRLL05	290.0	1344.00	39.66	40.16	34.92	
	LL1	6.05	41	2	JRLL05	257.2	1166.0	39.36	40.42	34.52	
	LL1	6.05	79	1	JRLL05	270.8	1222.00	37.14	38.36	31.80	
	LL1	6.05	79	7	JRLL05	277.2	1248.00	37.88	38.29	33.09	
	LL1	6.05	91	1	JRLL05	262.4	1134.00	37.66	39.32	32.52	
	LL1	6.05	91	7	JRLL05	281.4	1226.00	0 38.54	39.00	33.92	
	LL1	7.10	S	1	JRLL05	279.0	1172.00	0 34.84	44.68	34.63	
	LL1	7.10	S	6	JRLL05	261.2	1074.00	0 34.54	43.59	34.74	
	LL1	7.10	41	1	JRLL05	267.2	1158.00	0 34.02	42.42	34.63	
	LL1	7.10	41	7	JRLL05	274.4	1206.0	0 32.76	39.84	33.38	
	LL1	7.10	79	1	JRLL05	271.4	1192.00	0 33.50	40.16	34.74	
	LL1	7.10	79	0	JRLL05	268.2	1214.00	0 32.99	40.94	33.49	
	LL1	7.10	91	1	JRLL05	260.0	1138.00	0 33.13	41.20	33.45	
	LL1	7.10	91	2	JRLL05	260.2	1120.00	0 32.76	41.13	33.13	
	LL2	5.13	5	1	WCLL0	8	108.68	64.80	67.38	47.72	17.30
	LL2	5.13	5	0	WCLL0	8	108.88	76.80	67.90	49.40	17.41
	LL2	5.13	41	1	WCLL0	×	107.0	835.20	69.75	49.27	18.12
	LL2	5.13	41	7	WCLL0	8	107.8	857.20	69.01	49.53	17.91
	LL2	5.13	62	1	WCLL0	8	112.3	786.22	66.19	47.78	17.15
	LL2	5.13	79	7	WCLL0	8	117.08	20.96	67.31	48.82	17.12
	LL2	5.13	91	1	WCLL0	8	115.08	20.00	66.71	47.39	17.08
	LL2	5.13	91	6	WCLL0	8	114.58	10.96	66.56	47.39	17.19
	LL2	6.17	S	1	WCLL0	8	101.2	787.60	67.23	47.46	16.51
	LL2	6.17	5	7	WCLL0	8	98.7	758.40	67.68	47.85	16.55
	LL2	6.17	41	1	WCLL0	×	101.2	775.60	66.93	47.59	16.22
	LL2	6.17	41	7	WCLL0	8	100.2	802.40	66.56	46.75	16.08
	LL2	6.17	79	1	WCLLO	8	100.8	839.80	67.53	47.98	16.15

												pHII	5.57	5.74	5.88	5.94	5.96	5.98	5.94	5.95	5.83	6.02	6.07	6.13	6.13	6.10	6.09	6.09	6.93	6.97	7.06	7.09	6.97	6.92	6.94	6.97
	15.69	15.83	14.68	14.97	30.73	30.51	16.15	18.05	16.30	15.54	,											-	-	-	-	-	Ĩ	-	-	-			-	-	Ĩ	
	47.65	47.46	45.65	48.69	60.12	58.18	47.78	47.07	48.04	46.04	2	SSpF	5.60	5.73	5.24	5.45					5.94	6.02	5.93	6.00	5.99	6.03			7.14	7.26	6.58	6.84	6.92	7.24		
	65.97	66.27	54.33	56.04	52.78	52.18	58.56	57.67	58.71	56.48		SSP	2.26	2.32	1.74		0.16				1.48	1.33	1.20	1.48	1.45	1.47			1.32	1.18	0.18	0.16	0.89	0.83		
801.60	810.60	807.20	731.40	384.80	717.00	742.20	690.41	686.68	838.20	786.60		SSFe	0.04	0.04	0.02		0.01				0.02	0.02	0.03	0.03	0.02	0.02			0.01	0.01	0.01	0.00	0.00	0.00		
102.0	106.4	104.8	102.8	66.08	197.6	198.6	108.5	110.9	108.8	108.0		SSCa	775.00	694.83	560.92		12.48				503.78	500.08	837.83	609.82	524.53	812.53			96.04	88.22	158.36	132.26	103.31	77.39		
CLL08	CLL08	CLL08	CLL08	CLL08	CLL08	CLL08	CLL08	CLL08	CLL08	CLL08		SSAI	0.01	0.01	0.01		0.01				0.00	0.00	0.00	0.00	0.00	0.00			0.01	0.00	0.00	0.00	0.00	0.00		
MC	M	M	MC	M	MC	M	M	M	M	MC MC		DPS	63.46	61.50	61.98	61.57	62.55	64.06	65.78	66.53	63.19	64.46	65.40	65.38	65.16	66.43	62.49	69.00	74.37	71.02	65.26	65.89	75.36	74.06	73.62	74.03
9 2	1	1 2		6	:1	:1 2	9 1	9 2	1 1	1 2	1	AloxFeox	98.29	97.12	94.60	94.38	32.29	96.87	100.13	95.50	102.19	100.18	17.96	97.66	7.51	100.12	95.17	100.14	34.74	31.37	58.27	59.29	33.12	81.87	83.77	82.43
5.17 7	5.17 5	5.17 9	7.29 5	7.29 5	7.29 4	7.29 4	7.29 7	7 29 7	7.29 9	7.29 9	ţ	Kep	-	0	1	0	1	2		5	-	2	1	7	1	7	1	2	1	2	1	5	1	5	-	2
LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	i	lime	5	5	41	41	62	62	91	91	5	5	41	41	79	62	91	91	5	S	41	41	62	62	91	91
7	-	2	6	6	6	6	¢	6	6	6	;	PrepH	5.48	5.48	5.48	5.48	5.48	5.48	5.48	5.48	6.07	6.07	6.07	6.07	6.07	6.07	6.07	6.07	7.18	7.18	7.18	7.18	7.18	7.18	7.18	7.18
LL2-6.1	LL2-6.1	LL2-6.17	LL2-7.29	LL2-7.29	LL2-7.29	LL2-7.29	LL2-7.29	LL2-7_26	LL2-7.29	LL2-7.29	•	Codes	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1

33 5 1 64.10 35.26	1 64.10 35.26	64.10 35.26	35.26		0.02	322.39	0.04	4.64	4.82	5.51
33 5 2 64.87	2 64.87	64.87		35.53	0.03	279.47	0.04	4.20	4.85	5.3
33 41 1 63.23	1 63.23	63.23		35.33	0.02	332.32	0.04	3.66	5.16	5.50
33 41 2 62.13	2 62.13	62.13		34.82	0.01	209.77	0.04	3.45	5.13	5.52
33 79 1 64.54	1 64.54	64.54		35.41	0.01	270.47	0.03	3.48	5.41	5.54
33 79 2 63.70	2 63.70	63.70		34.87	0.01	219.93	0.03	2.62	5.61	5.56
33 91 1 63.67	1 63.67	63.67		35.80						5.56
33 91 2 61.57	2 61.57	61.57		35.87						5.56
01 5 1 47.92	1 47.92	47.92		36.20	0.01	60.69	0.01	1.95	6.14	6.26
01 5 2 47.04	2 47.04	47.04		36.96	0.01	70.06	0.01	1.93	5.77	6.14
01 41 1 57.74	1 57.74	57.74		37.01						6.05
01 41 2 61.42	2 61.42	61.42		36.90						5.96
01 79 1 48.53	1 48.53	48.53		39.90	0.01	67.16	0.01	1.01		5.88
01 79 2 47.04	2 47.04	47.04		39.80	0.01	59.31	0.00	0.96		5.85
01 91 1 47.90	1 47.90	47.90		39.09						5.83
01 91 2 47.22	2 47.22	47.22		38.85						5.86
18 5 1 20.51	1 20.51	20.51		40.45	0.24	7.46	0.13	2.13	7.39	6.69
18 5 2 55.05	2 55.05	55.05		39.29	0.26	8.49	0.14	1.97	7.49	6.71
08 41 1 57.97	1 57.97	57.97		39.21	0.00	0.69	0.00	0.09	6.81	6.50
08 41 2 58.77	2 58.77	58.77		38.67	0.06	11.40	0.05	1.75	6.95	6.46
08 79 1 57.89	1 57.89	57.89		40.27	0.03	27.32	0.02	1.37	6.86	6.51
18 79 2 53.38	2 53.38	53.38		39.07	0.02	26.03	0.02	1.54	7.17	6.50
08 91 1 51.17	1 51.17	51.17		39.62						6.38
18 91 2 51.43	2 51.43	51.43		39.80						6.36
33 5 1 97.18	1 97.18	97.18		68.44	0.17	979.10	0.19	0.39	4.82	5.16
33 5 2 98.95	2 98.95	98.95		68.52	0.17	1058.35	0.19	0.39	4.90	5.14
33 41 1 98.24	1 98.24	98.24		69.67						5.28
33 41 2 99.09	2 99.09	<u>90.66</u>		67.77						5.31
33 79 1 96.54	1 96.54	96.54		68.22	0.01	339.36	0.01	7.52		5.32
33 79 2 94.03	2 94.03	94.03		68.33						5.38
33 91 1 96.58	1 96.58	96.58		68.86						5.40
33 91 2 96.69	2 96.69	96.69		69.46						5.34
37 5 1 100.50	1 100.50	100.50		70.67	0.00	433.42	0.03	0.25	6.40	6.13
37 5 2 99.09	2 99.09	60.66		69.73	0.00	416.27	0.03	0.27	5.95	6.08
87 41 1 98.84	1 98.84	98.84		69.25	0.00	670.40	0.04	0.23	5.79	6.04
87 41 2 99.44	2 99.44	99.44		73.38	0.00	583.87	0.04	0.22	5.88	6.00
37 79 1 100.36	1 100.36	100.36		71.42	0.00	803.96	0.02	0.22	5.94	5.76

5.78	5.77	5.78	6.80	6.54	6.65	6.77	6.78	6.84	6.84	6.87	5.56	5.06	5.07	5.17	5.20	5.24	5.28	5.29	6.86	6.89	6.46	6.22	6.03	5.98	5.94	5.90	6.35	6.26	6.22	6.20	6.15	6.14	6.09	6.08	5.15	
6.08			6.60	6.05	6.54	6.55	6.28	6.31			4.68	4.74	5.56	5.56	5.56				6.66	6.73	5.98	5.87	6.10	6.13			7.19	7.29	6.14	6.14	6.22	60.9			4.90	
0.21			0.07	0.06	0.18	0.18	0.70	1.07			0.06	0.08	0.12	0.12	0.13	0.14			0.20	0.21	0.05	0.06	0.05	0.04			0.09	0.07	0.06	0.08	0.05	0.05			0.46	0
0.01			0.01	0.01	0.01	0.00	0.01	0.01			0.05	0.06	0.03	0.03	0.05	0.03			0.01	0.01	0.00	0.00	0.00	0.00			0.03	0.04	0.00	0.01	0.00	0.00			0.05	
457.07			70.39	70.52	129.92	108.17	68.60	63.14			156.32	220.32	205.53	189.21	181.31	242.00			98.97	108.50	70.92	87.69	135.92	88.84			23.00	15.15	48.17	45.39	98.07	54.14			116.05	
0.00			0.01	0.01	0.00	0.00	0.01	0.01			0.10	0.12	0.03	0.03	0.02	0.02			0.00	0.00	0.00	0.00	0.00	0.00			0.05	0.07	0.00	0.01	0.00	0.00			0.07	
72.84	72.05	72.63	74.33	72.25	80.29	81.61	79.59	82.36	76.98	76.56	65.72	65.78	64.89	60.81	65.60	66.80	66.27	65.61	72.12	72.84	64.60	65.37	64.12	64.62	66.50	65.93	77.06	75.83	70.94	72.58	74.68	77.16	66.31	62.58	55.68	
103.72	98.59	101.35	35.53	34.32	89.27	90.19	87.62	89.38	86.40	85.18	41.56	43.29	40.80	37.70	39.57	40.79	40.73	40.84	101.17	103.72	42.38	41.39	43.51	42.77	41.95	42.60	38.12	37.47	36.22	36.30	37.78	37.74	30.14	29.20	55.09	
7		2	-	7	-	0	-	2	-	0		0	-	0		0		0		7	-	0		0		0	-	0		0		0		7	-	•
<u>79</u>	91	91	S	S	41	41	62	62	91	91	5	5	41	41	79	<i>6L</i>	91	91	5	5	41	41	79	79	91	91	5	5	41	41	<i>6L</i>	<i>6L</i>	91	91	5	ı
5.87	5.87	5.87	6.99	6.99	6.99	6.99	6.99	6.99	6.99	6.99	5.26	5.26	5.26	5.26	5.26	5.26	5.26	5.26	6.16	6.16	6.16	6.16	6.16	6.16	6.16	6.16	6.60	6.60	6.60	6.60	6.60	6.60	6.60	6.60	4.95	
CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	DMI	

5.23	5.24	5.56	5.41	5.31	5.28	5.78	5.54	5.48	5.34	5.31	5.30	5.30	5.30	7.08	6.93	7.07	7.10	6.49	6.38	7.47	6.85	5.30	5.26	5.39	5.47	5.50	5.55	5.54	5.52	6.33	6.26	0.18	6.19	6.20	6.23	6.23
	4.90					5.81	5.48	5.58	5.49	5.57	5.29			6.96	7.06	7.30	6.86	6.48	6.41			4.91	4.80	5.26	5.23	6.19	5.74			6.48	6.42	0.01	5.81			
0.65	0.63					0.55	0.59	0.77	0.76	0.62	0.60			1.21	1.40	1.68	1.81	0.68	0.82			0.23	0.22	0.18	0.15	0.11	0.11			0.14	0.14		0.18	0.17	0.17	
0.09	0.09					0.03	0.03	0.04	0.03	0.03	0.03			0.39	0.54	0.63	0.62	0.05	0.08			0.07	0.06	0.07	0.06	0.05	0.06			0.00	0.00	0.00	0.02	0.00	0.00	
235.21	215.29					117.22	115.70	68.45	70.71	181.90	147.33			20.21	17.84	17.60	21.27	75.19	40.04			596.64	565.71	640.49	445.20	401.35	518.63			106.36	146.61		238.87	138.80	158.44	
0.09	0.10					0.05	0.05	0.06	0.05	0.04	0.04			0.56	0.75	0.86	0.82	0.06	0.10			0.07	0.07	0.04	0.04	0.01	0.01			0.00	0.00		0.00	0.01	0.00	
57.32	56.80	59.37	58.15	59.13	58.48	56.10	57.09	56.27	57.04	59.36	60.03	57.26	57.58	63.30	64.55	65.01	64.07	64.70	66.25	90.92	90.03	52.98	53.17	53.39	55.41	54.76	55.63	55.38	57.48	56.21	55.60		55.89	57.57	57.20	57.85
52.38	54.22	52.75	53.85	52.63	51.12	55.59	53.27	52.78	51.17	53.09	54.97	53.23	53.38	49.47	46.72	49.06	47.27	47.71	46.79	47.66	46.19	56.67	56.23	56.60	55.23	57.19	55.83	55.39	52.12	53.76	53.54		52.91	53.50	52.94	53.13
-	0	-	7	1	0	1	7	1	7	-	0	1	0	1	0	1	7	1	0	1	7	-	7	1	0	-	7		0	-	0	-	0	-	0	1
41	41	79	79	91	91	5	5	41	41	79	79	91	91	5	5	41	41	79	79	91	91	5	5	41	41	79	79	91	91	5	5	41	41	79	79	91
4.95	4.95	4.95	4.95	4.95	4.95	6.07	6.07	6.07	6.07	6.07	6.07	6.07	6.07	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	4.99	4.99	4.99	4.99	4.99	4.99	4.99	4.99	6.23	6.23	6.23	6.23	6.23	6.23	6.23
DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2

	0.22	0.48	6.62	6.72	6.76	6.82	6.81	6.80	6.78	5.43	5.58	5.64	5.67	5.72	5.70	5.75	5.81	6.11	6.14	6.18	6.18	6.17	6.18	6.19	5.95	7.26	7.26	7.15	7.07	7.01	7.00	7.01	6.99	5.72	5.67	5.68	5.70
				7.66	7.59	7.55	7.63			4.99	5.15									5.93	6.10	6.20	6.22					6.97	6.93	6.99	7.06			5.19	5.06	5.29	5.32
				0.22	0.22	0.18	0.17			18.54	16.83			0.50	0.53			6.13		5.21	5.24	4.08	4.74			1.10	1.13	1.37	1.63	1.48	1.19			0.86	0.97	0.91	0.85
				0.01	0.01	0.01	0.01			0.04	0.03			0.07	0.08			0.07		0.02	0.02	0.01	0.01			0.01	0.01	0.01	0.02	0.01	0.01			0.11	0.16	0.06	0.05
				48.96	61.74	92.11	75.27			771.32	711.48			659.53	804.85			352.45		516.84	361.99	283.74	359.69			107.61	89.46	52.08	66.74	93.11	98.83			1322.59	2124.40	1627.44	1408.61
				0.01	0.00	0.00	0.00			0.03	0.03			0.03	0.03			0.01		0.01	0.01	0.01	0.01			0.01	0.01	0.01	0.02	0.01	0.00			0.02	0.05	0.02	0.05
01 07	60.49 60.49	00.42	59.98	53.61	54.94	63.13	63.09	60.83	61.56	54.74	53.68	55.14	54.20	53.76	54.39	56.75	55.44	54.56	56.81	53.86	54.71	55.64	53.95	56.04	53.82	64.32	62.91	61.79	60.23	58.85	61.59	61.87	62.42	56.35	57.91	56.07	56.98
11 64	10.00	47.74	49.52	39.96	41.97	47.87	48.71	48.09	49.30	74.79	76.03	79.40	73.86	72.07	71.59	71.69	71.87	75.15	72.17	74.57	73.88	68.94	70.97	70.17	72.46	69.47	69.28	68.65	66.14	68.24	66.47	66.58	65.89	84.68	85.30	87.87	86.92
c	7 -	-	0	1	0	-	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	-	0	1	0	-	0	-	0	-	0	1	7
01	91 2	n	S	41	41	79	79	91	91	5	5	41	41	79	79	91	91	5	5	41	41	79	79	91	91	S	S	41	41	79	79	91	91	S	5	41	41
()	0.23	07.1	7.26	7.26	7.26	7.26	7.26	7.26	7.26	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	7.10	7.10	7.10	7.10	7.10	7.10	7.10	7.10	5.13	5.13	5.13	5.13
	DMZ	DM/2	DM2	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL1	LL2	LL2	LL2	LL2						

5.77	5.83			6.18	6.24	5.99	6.05	6.61	11.26			6.99	6.95	6.65	6.82	7.14	7.24			pHlovel	1	1	1	1	1	1	1	1	<mark>7</mark>	2	2	2	2	<mark>7</mark>	2
0.77	0.78			0.48	0.45	0.43	0.43	0.32	6.28			0.22	0.21	0.95	0.69	0.17	0.16			6H2OP	1.37	1.27	7.07	4.75	5.78	7.17	6.29	7.80	2.26	0.84	9.53	0.47	9.84	9.96	7.25
0.04	0.04			0.03	0.03	0.04	0.04	0.02	6.75			0.01	0.00	0.01	0.01	0.01	0.00			Ca %	0	0	1	÷	1	1	-	1	0	0	1	0	1	1	-
1268.83	1197.04			961.06	898.29	1174.67	1081.67	565.83	0.31			97.27	125.28	144.46	128.34	223.19	158.09			%H2O	150.67	136.64	133.43	138.18	156.09	154.85	164.29	176.76	113.60	96.18	100.36	104.86	101.46	103.52	98.32
0.02	0.05			0.00	0.00	0.01	0.01	0.00	0.02			0.00	0.00	0.01	0.00	0.00	0.00			WSCa	1204.78	1104.87	1084.02	1086.92	1068.03	1057.41	1151.51	1210.32	813.81	744.08	783.81	778.24	810.90	817.40	768.29
57.33	57.82	56.56	56.59	56.67	56.81	57.23	56.57	57.33	573.67	58.36	57.81	66.15	68.56	71.99	70.35	63.96	62.17	64.05	63.92	WSP	46.85	47.01	37.92	32.53	33.86	36.95	35.56	38.23	45.06	43.06	40.31	40.45	40.80	41.00	37.46
83.35	84.42	83.80	83.75	83.74	84.22	83.16	82.64	83.68		81.66	82.10	69.02	71.01	83.50	82.70	74.71	75.72	75.00	72.03	Rep	-	0	1	0		0	-	7	-	7	-	0	1	7	
(7		0	1	7	1	7	1	7	-	2	1	7	1	2		2	1	2	Time	5	5	41	41	62	79	91	91	5	5	41	41	79	79	91
6 <u>7</u>	67	91	91	S	S	41	41	79	79	91	91	5	S	41	41	79	79	91	91	H															
5.13	5.13	5.13	5.13	6.17	6.17	6.17	6.17	6.17	6.17	6.17	6.17	7.29	7.29	7.29	7.29	7.29	7.29	7.29	7.29	Prep	5.48	5.48	5.48	5.48	5.48	5.48	5.48	5.48	6.07	6.07	6.07	6.07	6.07	6.07	6.07
LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	Code\$	BL1	BL1	BL1	BL1	BL1	BL1	BL1								

 5.71

 5.73

 5.73

 5.74

 5.75

 5.75

 6.17

 6.17

 6.16

 6.26

 6.28

 999.82

 6.28

 7.04

 7.11

 7.05

 7.05

 7.28

 7.24

20.36		23.97	16.88	13.59		24.21			35.69	35.90	30.02	29.11	26.49	26.99	26.96	26.31	20.03	19.72	18.17	19.75	15.77	16.41	18.45	18.87	24.09	23.94	29.18	1.00	25.85	24.24	22.54	25.57	3.38	10.95	4.02	2.31
116.07		18.21	28.85	24.69		23.24			167.72	164.16	131.02	133.24	133.15	140.66	143.06	138.14	46.12	46.08	54.70	56.63	48.51	43.73	66.79	65.02	12.17	20.57	22.16	24.60	20.74	15.74	21.02	29.08	252.63	257.47	252.84	269.25
867.27		129.35	218.59	200.41		176.97			588.35	559.79	461.71	466.87	480.94	496.81	507.28	514.45	147.02	143.31	175.82	178.22	153.19	139.99	214.18	210.35	38.64	69.99	65.93	76.02	69.22	54.32	66.48	91.47	1437.48	1370.24	1365.34	1283.77
43.44		48.09	17.52	14.27		49.68			64.52	62.82	52.48	51.59	49.74	50.14	49.49	50.94	34.61	33.60	33.07	35.76	28.57	29.69	32.99	34.15	40.86	41.37	49.53	1.76	46.22	44.41	38.81	43.16	1.88	6.03	2.21	1.26
0	1	0	1	0	1	0	1	7	1	7	1	7	1	0	1	0	1	0	1	7	1	0	1	0	1	0	-	0	1	0	1	0	1	7	-	2
91	5	5	41	41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41
6.07	7.18	7.18	7.18	7.18	7.18	7.18	7.18	7.18	5.33	5.33	5.33	5.33	5.33	5.33	5.33	5.33	6.01	6.01	6.01	6.01	6.01	6.01	6.01	6.01	7.08	7.08	7.08	7.08	7.08	7.08	7.08	7.08	4.83	4.83	4.83	4.83
BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL1	BL3	BL3	BL3	BL3	BL3	BL3	BL3	BL3	BL3	CF1	CF1	CF1	CF1															
1.82	1.30	2.44	3.00	13.87	4.98	13.00	6.39	16.30	11.12	15.84	8.54	19.13	18.66		4.52		28.90	30.92	25.38	10.79		7.61	0.00	0.00	0.00		10.91	22.27	28.93	26.60	10.22	0.00	9.92	9.88	21.20	16.27
---------	---------	---------	---------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	------	--------	------	--------	--------	--------	--------	--------	--------	--------	--------	--------	------	--------	--------	--------	--------	--------	--------	--------	--------	--------	-------
283.32	265.09	278.98	291.61	156.59	156.26	141.06	141.96	145.93	142.27	146.01	159.58	75.77	75.41		78.20		38.61	41.98	34.82	239.71	220.78	211.83	211.36	193.84	201.09		235.68	30.81	34.09	81.69	88.52	92.83	90.83	88.25	104.56	47.78
1322.27	1259.56	1364.15	1398.56	766.98	752.23	689.51	714.89	773.12	752.88	775.63	855.01	118.35	116.89		381.75		187.58	207.31	180.39	377.31	351.92	334.27	336.06	323.99	332.24		377.31	159.17	154.84	129.89	139.16	147.05	149.14	142.79	168.34	77.50
1.06	0.75	1.43	1.75	7.47	2.65	6.76	3.34	8.85	6.05	8.78	4.70	1.80	1.75		2.43		15.83	16.84	13.73	1.02	0.00	0.74	0.00	0.00	0.00		1.13	11.76	15.46	2.52	0.96	0.00	0.92	0.94	2.01	1.51
1	7	1	7	1	0	1	0	1	0	1	0	1	0	1	7	1	0		0	1	0	1	7	1	0	1	7	-	7	1	7		7		7	1
79	62	91	91	S	5	41	41	79	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41	62	79	91	91	S	S	41	41	79	79	91	91	S
4.83	4.83	4.83	4.83	5.87	5.87	5.87	5.87	5.87	5.87	5.87	5.87	6.99	6.99	6.99	6.99	6.99	6.99	6.99	6.99	5.26	5.26	5.26	5.26	5.26	5.26	5.26	5.26	6.16	6.16	6.16	6.16	6.16	6.16	6.16	6.16	6.60
CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF1	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2	CF2

-----<u>000000000000000000-----</u>000000000

15.69	10.75	484.80		14.83	13.08	83.46	28.66	28.65		22.33	19.91	22.81	19.01	19.00	39.91	33.24	28.88	33.85	26.99	31.30	31.28	27.97	56.29	56.52	53.12	44.68	43.24	35.05		10.86	11.93	7.44	9.95	- 0.7	1.95
50.67	45.53	34.58		57.84	62.03	18.74	170.92	170.55		154.76	135.99	145.59	148.06	157.21	65.51	57.80	79.46	81.04	103.30	99.81	98.43	86.98	13.53	14.70	10.71	8.39	26.41	21.78		13.26	259.74	248.78	213.42		235.14
81.07	71.67	53.88		94.04	99.25	29.68	400.29	384.08		354.09	321.22	323.51	334.02	344.29	137.43	126.13	178.30	181.70	221.69	215.60	209.07	186.13	30.34	30.76	23.59	18.03	57.62	47.44		26.82	770.39	722.45	673.12		/11.52
1.47	0.98	43.69		1.35	1.16	7.48	18.24	17.60		14.11	12.93	14.46	12.60	12.36	23.41	19.79	17.78	20.04	15.83	18.45	19.85	17.58	34.28	33.72	32.68	26.72	26.66	21.64		5.90	5.74	3.44	4.71	000	0.92
7	-	7	-	7	1	7	1	7	1	7	-	7	1	2	1	0	1	7	1	6	1	2	1	7	1	0	-	0	1	7	1	6	1	¢	7
S	41	41	62	62	91	91	5	S	41	41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	11	41
6.60	6.60	6.60	6.60	6.60	6.60	6.60	4.95	4.95	4.95	4.95	4.95	4.95	4.95	4.95	6.07	6.07	6.07	6.07	6.07	6.07	6.07	6.07	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	4.99	4.99	4.99	001	4.99
CF2	CF2	CF2	CF2	CF2	CF2	CF2	DMI	DM1	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DMI	DM1	DMI	DMI	DMI	DM2	DM2	DM2		7MI7

10.76	9.29	8.04	10.59	260.28	1.44		5.12	9.33	4.27	14.25		27.13	20.58	22.34		23.96	28.54	47.76	44.27	214.53	209.69	31.13	29.65	29.64	30.15	28.94	29.07	23.50	26.36	23.05	22.98	22.00	23.74	16.73	19.49	17.84
221.20	229.17	91.16	82.20	3.80	20.27		92.39	105.79	109.68	21.05		19.58	24.49	23.17		29.03	32.91	181.49	169.82	707.17	713.72	161.80	165.23	173.45	177.82	97.57	92.71	78.96	91.26	87.53	87.89	92.48	94.20	18.68	20.83	18.31
698.10	760.86	252.88	225.22	6.26	253.38	278.01	272.33	310.24	327.04	60.74		58.39	71.77	70.75		84.53	96.62	2373.84	2241.62	2016.84	1992.70	2014.47	2051.69	2151.19	2285.89	1149.32	1088.45	1061.20	1064.12	1069.65	1096.82	1048.77	1154.84	218.95	223.75	211.98
5.44	4.75	3.85	5.00	5.41	3.97	3.79	2.55	4.67	2.15	6.95		13.24	10.00	10.96		11.70	13.87	136.49	126.18	101.86	99.94	88.97	86.36	83.79	88.25	79.59	79.06	68.16	67.81	62.41	63.71	57.73	66.81	46.67	50.90	47.67
	7	-	7	1	7	1	7	1	7	1	7	1	7	1	7	-	7	1	7	1	7	1	7	1	0	1	7	-	0	-	0	-	0	1	7	-
91	91	5	5	41	41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41	6L	62	91	91	5	5	41	41	62	62	91	91	5	5	41
4.99	4.99	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	7.26	7.26	7.26	7.26	7.26	7.26	7.26	7.26	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	7.10	7.10	7.10
DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	DM2	LL1	LL1	LL1	LL1																								

15.49	15.69	16.26	16.35	16.85	10.28	8.73	8.51	7.34	4.10	7.99	5.88	6.86	13.01	11.14	10.56	11.52	10.31	1	10.17	12.20	15.71	16.87		6.42		7.89		12.16
17.33	20.33	20.25	20.81	23.71	222.83	202.15	201.42	197.86	220.52	208.02	224.74	234.99	139.55	132.05	126.31	122.58	119.02	2	118.81	139.79	20.99	55.21		36.61		41.52		37.72
209.00	242.38	245.84	236.83	265.52	1927.00	1772.49	1682.22	1696.08	1733.79	1707.77	1842.89	1905.67	1099.08	1001.50	979.66	983.62	999.54	11.04	963.07	1128.39	153.52	212.43		271.72		285.09		296.72
42.50	42.57	43.62	42.52	43.85	11.16	9.50	9.11	7.91	4.60	9.34	6.76	7.86	13.17	11.00	10.69	11.54	10.39	124.73	10.82	12.79	16.15	11.15		12.75		8.75		13.13
7	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	7	1	0	1	0	1	0	1	0	1	0
41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41	62	62	91	91	5	5	41	41	62	62	91	91
7.10	7.10	7.10	7.10	7.10	5.13	5.13	5.13	5.13	5.13	5.13	5.13	5.13	6.17	6.17	6.17	6.17	6.17	6.17	6.17	6.17	7.29	7.29	7.29	7.29	7.29	7.29	7.29	7.29
LL1	LL1	LL1	LL1	LL1	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2	LL2									

Phase Diagrams – Incubation Study

The solubility diagrams were unclear and calculations in Minteq (based on thermodynamic constants), were clearly affected by the alteration of pH which these soils had endured. Thus, we found that the data would not add to the bulk of the thesis and have been included it for viewing here (Figs. A7 – A10). All of the soils were supersaturated with regards to variscite and strengite. Phase diagrams for Al and Fe are not included.



Fig. A7.Thermodynamic Stability for LL1 and LL2 using soil solution extraction of 1:0.3 w/v ratio. \ddagger \ddagger pKsp (TCP - tricalcium phosphate) = $3Ca^{2+} + 2pH_2PO_4^-$ - 4pH; (3) pKsp (OCP - octocalcium phosphate) = $4pCa^{2+} + 3pH_2PO_4^-$ -5pH; (4) pKsp (HA - hydroxyapatite) = $5pCa^{2+} + 3pH_2PO_4^-$ -7 pH.



Fig. A8. Thermodynamic Stability for BL1 and BL3 using soil solution extraction of 1:0.3 w/v ratio. \ddagger \ddagger pKsp (TCP - tricalcium phosphate) = $3Ca^{2+} + 2pH_2PO_4^-$ - 4pH; (3) pKsp (OCP - octocalcium phosphate) = $4pCa^{2+} + 3pH_2PO_4^-$ -5pH; (4) pKsp (HA - hydroxyapatite) = $5pCa^{2+} + 3pH_2PO_4^-$ 7 pH.



Fig. 17. Thermodynamic Stability for DM1 and DM2 using soil solution extraction of 1:0.3 w/v ratio. \ddagger \uparrow pKsp (TCP - tricalcium phosphate) = $3Ca^{2+} + _2pH_2PO_4^-$ - 4pH; (3) pKsp (OCP - octocalcium phosphate) = $4pCa^{2+} + 3pH_2PO_4^-$ -5pH; (4) pKsp (HA - hydroxyapatite) = $5pCa^{2+} + 3pH_2PO_4^-$ -7 pH.



Fig. A10. Thermodynamic Stability for CF1 and CF2 using soil solution extraction of 1:0.3 w/v ratio. \ddagger \ddagger pKsp (TCP - tricalcium phosphate) = $3Ca^{2+} + _2pH_2PO_4^-$ - 4pH; (3) pKsp (OCP - octocalcium phosphate) = $4pCa^{2+} + 3pH_2PO_4^-$ -5pH; (4) pKsp (HA - hydroxyapatite) = $5pCa^{2+} + 3pH_2PO_4^-$ -7 pH.

Defining soil solution

Soil solution is "the aqueous phase of the soil, which is linked to the gaseous and numerous solid phases via the transport of energy and matter" (Sparks, 1999). The method of separating *ex situ* soil solution from the solid phase differs from researcher to researcher, and usually involves a relatively low soil:solution ratio for extraction. Hetrick and Schwab (1992), for example, used a 1:2 soil: 0.01 M CaCl₂ solution to provide an equilibration matrix with a fixed ionic strength. While Sharpley et al. (2004) used a 1:5 soil: 0.01 M CaCl₂ solution ratio. These ratios overlook disequilibrium between phases because they are not taken at field capacity (Sparks, 1999). Sampling all soils at field moisture conditions reduces variation in soil solution extraction across a broad range of mineralogical and soil chemical compositions (Khasawneh and Adams, 1967).

Organic Matter Determination

Organic Carbon content was determined by Walkley-Black and oxidizable organic matter was determined by titrating excess Cr_2O^{-2} with a standardized solution of FeSO₄ using a ferron indicator. Percent organic carbon (%OC) and organic matter (%OM) was determined using the following equations:

% OC = $(mL \text{ FeSO}_4 \text{ required for blank} - mL \text{ required for sample}) \times N \text{ FeSO}_4 \times 0.395$ Dry sample weight in grams

%OM = %OC * 1.724 (Walkley and Black, 1934)

%OM = %OC * 2 (Zelazny Laboratory Methods)