ABSTRACT

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Agricultural drainage ditches can provide a direct connection between fields and surface waters, and some have been shown to deliver high loads of phosphorus (P) to sensitive water bodies. A potential way to reduce nutrient loads in drainage ditches is to install filter structures containing P sorbing materials (PSMs) including gypsum to remove P from ditch flow. One projected advantage would be the potential application of spent PSMs to agricultural fields to provide nutrients for crop production after the filter has lost its effectiveness. The study evaluated the feasibility of this strategy. Gypsum was saturated at two levels on mass basis of P, and applied to two soil types, a silt loam and a sandy loam and applied at both a high and low rate. The treated soils were incubated at 25° C, and samples were collected at 0, 1, 7, 28, 63, 91, 119, and 183 days after saturation.

UTILIZATION OF GYPSUM AS A FILTER MATERIAL IN AGRICULTURAL DRAINAGE DITCHES: IMPACTS OF LAND APPLICATION ON SOIL FERTILITY CONDITIONS

By

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Chapter 1: Introduction

Justification

Accelerated eutrophication of the Chesapeake Bay has become a large concern over the past few decades. Nitrogen and phosphorus sources from agriculture and residential areas are a large contributor to water quality degradation of the bay and its tributaries. The Delmarva Peninsula (comprising the nine counties of the eastern shore of Maryland, Accomack and Northampton counties in Virginia, and the state of Delaware) contains four major poultry companies. According to the Delmarva Poultry Industry, in 2009 there were nearly 2000 growers that produced more than 568 million birds weighing nearly 3.5 billion pounds. The EPA estimated in 2005 approximately half of the nitrogen and phosphorus loads going into the Chesapeake Bay are a result of agriculture industries on the peninsula (EPA, 2005). In the past, manure has been land applied and application rates were based on N needs of the crop. However, because the P:N ratio found in manure is much higher than the P:N ratio required by plants, excessive P application has occurred (Pote et al., 1996). The lower eastern shore of Maryland and the Delmarva Peninsula have unique hydrology that results in a great amount of subsurface flow. Phosphorus leaching to groundwater is greatly increased in sandy soils with limited capacity to retain P, in soils with high P saturation, and in ditch drained soils containing preferential flow pathways (Sims et al., 1998). These combinations result in excess P movement and environmental quality issues.

According to Leader et. al (2006), phosphorus loss from soil to water can potentially be improved by using by-product materials that have the capacity to sorb phosphorus. When using by-products, costs can be reduced and can be more likely implemented on farms across the Delmarva Peninsula. For example, gypsum is produced as a by-product of the coal combustion process, and has potential to sorb phosphorus.

The United States and other developed nations are large producers and consumers of power, using coal and other resources as energy sources. Flue gas desulfurization (FGD) technologies have been successful at removing sulfur dioxide and other materials produced as a result of coal combustion. With increasing environmental standards, there is increased pressure to find beneficial reuses of coal combustion and FGD by-products. Gypsum is currently used in the drywall and building industry. In 2000, about 23 Mt of FGD materials were produced, and about 4.5 Mt (20%) was used in the wallboard manufacturing process (Kalyoncu, 2001). The excess means there is great potential to reuse gypsum and other by-products for alternative purposes, including as agricultural amendments. Increasing yields, improving soil fertility and nutrient efficiency, and reducing the negative impacts of agricultural practices are some top priorities of the agriculture industry. These products can provide some of these important ecosystem services. Although there may be some impurities and potential environmental hazards associated with the reuse of FGDs, the by-products can provide essential soil and plant nutrients, improve soil physical and chemical properties, as well as provide a beneficial economic and environmental alternative to landfilling coal combustion byproducts.

Chapter 2: Current Knowledge

Nitrogen and Phosphorus use in Crop Production

Nitrogen (N) is a naturally occurring element and is one of the most important mineral nutrients used in crop production and crop uptake. Nitrogen fertilizer sources include organic sources such as manure and legume crops, as well as synthetic fertilizers. In the past, many agricultural fields have applied nutrients on an N basis, meaning the application rates have been based on the N crop needs. Nitrogen undergoes a number of processes above and within soil, and is converted between different forms to serve crop needs. One form, nitrate (NO_3^-) can be leached from soils (especially sandy soils or low organic matter soils). Agricultural leaching losses not only represent economic losses to the farmer, but may also have toxicological implications for animals and humans (Camargo and Alonso, 2006). Excess NO_3^- may also result in eutrophication, hypoxia, and denitrification, especially in coastal waterways. However, little nitrate-N is lost from the landscape via surface runoff; most is lost through subsurface drainage (including tile lines) or base flow (Jackson et al., 1973).

Another form of nitrogen commonly found in soil is ammonium (NH_4^+). Ammonium-N is a mineralized form of N that can be taken up by plants, nitrified, immobilized by soil microorganisms, lost as a gas by volatilization, held as an exchangeable ion in clays or other colloids, or fixed in the interlayers of certain minerals. Ammonium tends to be taken up more easily by plants, but plants tend to take up more total nitrate, because it is present in larger concentrations than NH_4^+.

Phosphorus (P) is another essential nutrient for crop production. Soils deficient in P cannot support proper plant productivity which reduces yields and crop outputs. In the soil, phosphorus typically exists as organic P, inorganic P, or P as part of the soil solution. Organic P can be mineralized to become soluble or immobilized to form stable compounds of inorganic phosphorus. This conversion of inorganic P to a more stable form is known as fixation or sorption (Sharpley and Beegle, 1999). Typically organic phosphorus accounts for less than 50% of the phosphorus found in soils. Organic P is deposited by plants and other living matter. Unlike nitrogen, phosphorus does not typically leach through the soil, and therefore is found in greater concentrations near the surface. The movement of phosphorus is important when considering management strategies to reduce phosphorus concentrations in aquatic ecosystems. Phosphorus and phosphate ions are found in different forms in soil largely dependent on the pH of the soil solution. At lower pHs, more hydrogen ions are present, so species containing more hydrogen dominate. At higher pHs, less hydrogen ions are present, and the species contain less hydrogen ions.

Soil phosphorus exists in many forms within the soil. Soil P can be found in inorganic and organic forms ranging from ions to compounds. In most soils, the amount of phosphorus available to plants from the soil solution is only about 0.01% of the total P in soil. Inorganic P compounds mainly form bonds with amorphous and crystalline forms of Al, Fe, and Ca (Negassa and Leinweber, 2009). Organic compounds are associated with organic molecules such as nucleic acids phospholipids, sugar phosphates, inositol phosphates, and humic substances (Hedley et al., 1982). Phosphorus can be applied in many forms, but is generally applied

through inorganic sources (such as KH_2PO_4 fertilizer) or through organic sources (such as manures or compost).

Challenges result from using manures to provide crop nutrients. In areas with intensive animal agriculture, manure and litter are typically land applied to field surfaces. Manures are not uniform in their composition and are difficult to apply at uniform rates. In addition, intensive animal agriculture produces a continuous flow of manure and nutrients, even when fields are fallow or are not taking up nutrients. This results in the necessity to sometimes apply manure nutrients at less than optimal times relative to crop needs. Finally, manure application rates in the past have been based upon the nitrogen needs of crops. However, because the N:P ratio is usually smaller than the N:P uptake ratio of the crop, P can accumulate in the soil (Eghball, 1999). In areas with high moisture, humidity, and rainfall the runoff from these soils enters waterways, and the nutrients contribute to water pollution. In unique soil situations (including high phosphorus soils, sandy soils, and soils with a high water table) P can also travel through subsurface flow and through groundwater and result in water quality issues. The resulting excess nutrient concentrations from agriculture and residential landscapes can result in eutrophication, or the over-fertilization and addition of excess nutrients to aquatic ecosystems. Phosphorus is the limiting nutrient in most freshwaters, and therefore these increases in nutrients result in an increase in plant and algae growth (Sharpley and Beegle, 1999).

Nitrogen and Phosphorus as Water Quality Concerns

Phosphorus can enter the streams from non-point and point sources. Point sources, such as sewage treatment plant outflow pipes, businesses, and industries, are

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usually easy to identify and have been the focus of past phosphorus cleanup efforts. Nonpoint sources, including agriculture, are harder to identify and control. There has been more focus in recent years to identify and control sources of eutrophication from agricultural processes.

Most salt and brackish waters are limited by nitrogen, and therefore their growth is not altered by additions of phosphorus. Freshwater lakes and streams are limited by phosphorus because P levels are typically low. Cyanobacteria in these waterways are also able to fix their own nitrogen, so it is not the limiting factor. When phosphorus is added to these systems, algal blooms form and cover the surface. Other plant species also benefit from the nutrient additions and continue to grow. The plants can provide beneficial habitats to a number of aquatic species, but when they die, microorganisms work to decompose the plant material and use up the oxygen in the ecosystem. The process of decomposition reduces dissolved oxygen levels within the water, resulting in poor water quality. Poor water quality can jeopardize drinking water supplies, decrease the recreational use of waterways, impact fisheries, and reduce the water ability for industrial uses. Eutrophication is triggered by levels of approximately 0.03 mg L^{-1} of dissolved phosphorus and 0.1 mg L^{-1} total phosphorus.

Phosphorus loss from a watershed can be increased by a variety of human activities including timber harvest, livestock grazing, soil tillage, and application of manures and fertilizers. Because phosphorus has typically been applied in excess amounts, management practices have resulted in increases in the phosphorus content of surface soils. Phosphorus can be lost in runoff when sediment is eroded. It can also be lost in the runoff water through unincorporated surface additions (as dissolved P).

Many natural filters such as forests, oysters, wetlands, and underwater grasses have also been depleted due to human activities. Maryland alone has been estimated to lose more than 75 percent of its wetlands (Chesapeake Bay Foundation, 2010). With decreased natural systems to remove phosphorus, more has been able to enter local waterways and eventually the Chesapeake Bay.

Agricultural Drainage Ditches

The Delmarva Peninsula (especially the southern portion) is very flat and is dominated by sandy, poorly drained soils. The water table in this area is very close to the surface and surface or sub-surface drainage systems are typically installed to remove water to allow for agriculture, residential buildings, and other land use in the area. Therefore, much of the area is drained by a series of ditches. The eastern shore contains approximately 1321 kilometers (821 miles) of ditches in 101 public drainage associations (PDAs; Maryland Department of Agriculture, 2010). The ditches drain approximately 74,060 hectares (183,000 acres) of mixed-use land. The PDAs are governed by managers who are elected to three year terms who are responsible for the decision making of the ditches. The landowners who are benefited by the PDAs are taxed annually by the counties to cover the operation and maintenance costs of the ditches.

The PDA ditches offer many potential benefits to surrounding landowners. The most obvious is they increase drainage of frequently saturated soils and help to lower the water table in the area. This can in turn create more productive farmland, increase the grazing and growing season, and reduce flooding in the area. Reduced flooding can help protect public health by removing standing water from the surface.

They can also improve the transportation infrastructure and support local economies. Artificial drainage can significantly improve the structural stability of the soil by reducing waterlogging of soil (Dils and Heathwaite, 1999).

Although the PDA ditches offer some benefits, they also have some drawbacks. The ditches are connected hydrologically to local streams and rivers. They can serve as a direct pathway for sediment and nutrients from agricultural ecosystems (Vadas and Sims, 1998). Drainage ditches are unique ecosystems due to their hydrology because they integrate characteristics of streams and wetlands (Needelman et al., 2007). Ditches can also divert the water around critical storage areas such as buffer zones prohibiting natural processes to remove P from the ecosystem (Dils and Heathwaite, 1999). The southern part of the Delmarva Peninsula is characterized by a high density of agricultural drainage ditches that often have soluble phosphorus concentrations greater than 5 mg L^{-1} (Needelman and Wills, 2006). The ditches can also break up natural ecosystems and disturb wildlife habitat.

BMPs Available to Alleviate Water Quality Concerns- (PSMs)

Best management practices (BMPs) are agricultural or environmental practices that have been identified to control or reduce nutrient loads entering waterways. Some of these practices can potentially be addressed through the beneficial use and reuse of PSMs and other waste materials. Some BMPs already in use on the Delmarva Peninsula include: Implementation of nutrient management plans, controlling pollution from manure, planting cover crops, installing and maintaining buffer strips along farm fields, and setting and implementing forested buffer goals. Although these BMPs are effective at treating surface runoff and

drainage, they are ineffective in a ditch drained system. Recent studies have found that overland flow from eastern shore fields (located at the UMES farm) to two ditches accounted for $\leq 8\%$ of annual ditch P export, emphasizing groundwater as a key pathway for P transport to ditches (Kleinman et al., 2007). The drainage ditches can also serve as a treatment point for the large amount of subsurface drainage that occurs as a result of the unique hydrology.

Use of Phosphorus Sorbing Materials to Reduce Non-point Phosphorus Losses

One possible way to reduce phosphorus loss from soil to water is to use by-product materials that can sorb phosphorus (also known as phosphorus sorbing materials, PSMs) (Leader et. al., 2008). Phosphorus sorption is the process of adsorption and precipitation of P from dissolved to solid forms (Penn et al., 2007). The goal of PSMs is to provide a substrate for which chemical fixation can occur (through precipitation with metals and/or adsorption onto metal oxides or hydroxides) (Moore and Miller, 1994). Phosphorus sorbing materials usually contain Al, Ca, Fe, or Mg. Examples of some phosphorus sorbing materials include alum (aluminum sulfate), gypsum (calcium sulfate), Al and Fe oxides, and industrial byproducts (Penn et al., 2007). The main reactions that occur are chemisorption, anion exchange, and precipitation. Similar technology has been in use for decades in wastewater treatment plants. Possible precipitation reactions are shown below:

Alum: $\qquad Al_2(SO_4)_3 \cdot 14\ H_2O + 2PO_4^{3-} \rightarrow 2AlPO_4 + 3\ SO_4^{2-} + 14\ H_2O$

Ferric Sulfate: $\qquad Fe_2(SO_4)_3 \cdot 2\ H_2O + 2PO_4^{3-} \rightarrow 2FePO_4 + 3\ SO_4^{2-} + 2\ H_2O$

Lime: $\qquad 5Ca(OH)_2 + 3H_2PO^- + 3H^+ \rightarrow Ca_5(PO_4)_3OH + 9\ H_2O$
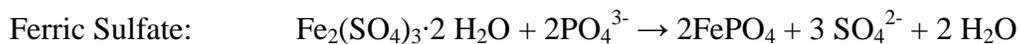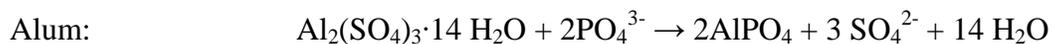
Phosphorus sorbing materials can be used in a number of ways to remove phosphorus from agricultural runoff and drainage. They can be applied directly to soil or manure, broadcast into ditches, or used in flow-through structures. Each system has advantages and disadvantages. Applying to soil and manure is usually a cost effective and efficient solution. However, the amendment rate and long term P solubility are often unknown. Applying PSMs in ditches is also generally cost effective and low maintenance, but is not effective during high flow or large rainfall events. Using flow-through structures has a great ability to "capture" and remove P from water/system, remove particulate and dissolved P, and allows for good contact time in ditches. However, these structures may not be able to handle large flow events, and are more expensive than simple application of PSMs to the ditches. Moore and Miller (1994) found that soluble P levels in poultry litter could be reduced using Al, Ca, and/or Fe amendments in a laboratory incubation setting. Field research by Penn and Bryant (2006) concluded the effectiveness of P sorbing materials is likely to be dependent on quantity, solubility, and reactivity of Al, Ca, and Fe.

Utilization of industrial byproducts as PSMs may present special challenges. These products are relatively cost efficient because they are inexpensive and are usually locally available (reducing storage and transportation costs). They may contain some heavy metals, toxins, or other materials that may have detrimental environmental impacts. These impurities must be considered before being applied to the landscape and any potential for environmental hazard must be reduced. Also, the P minerals formed through the processes may not be stable in all geochemical environments, and may vary from one soil type to another.

Public Drainage Association ditches concentrate the runoff carried to local

waterways. They can also offer opportunities for capturing P in runoff from large

areas of land (Penn et. al., 2007). Ditch filter systems are likely to be more efficient in

treating high P runoff water than to treat the soils themselves. They are also more

efficient than treating only riparian buffers because the P in drainage ditch flow is

more likely to be transported downstream (Penn et al., 2007). Phosphorus sorbing

materials can be applied to the agricultural drainage ditches to reduce phosphorus

loads from an entire watershed. Ditch trials by Penn et al. (2007) found that 75-95%

of total phosphorus in ditch flow was in the dissolved form, and a total of 99% of the

dissolved P that flowed through the filter structure was able to be removed from the

ditch water (equivalent to 0.54 kg of P).

Use of Gypsum as a Phosphorus Sorbing Material

Land application of gypsum

Flue Gas Desulfurization (FGD) gypsum application has the potential to

improve some soil physical and chemical properties. Gypsum, like lime, contains

calcium, but because it contains SO_4 instead of CO_3 (found in lime), it does not alter

the pH of the soil. Lime ($CaCO_3$) and other FGDs have the potential to alter the pH

providing benefits, especially to acid soils as shown in the equation:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$$
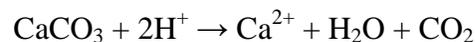
Some FGDs contain alkalizing agents (including CaO, $Ca(OH)_2$, and $CaCO_3$)

that have the potential to increase the soil pH (Clark et al., 2001). However, gypsum

additions do not permanently alter soil pH. In some soils, gypsum can neutralize

some acidity, but only on a short-term basis. In these soils, the SO_4^{2-} displaces OH^-

(from iron and aluminum hydrated oxides on soil surfaces) creating a partial neutralization of acidity. Gypsum additions, therefore, do not permanently alter the soil pH.

Gypsum can help to reduce the symptoms of low pH (mainly seen on plants) by reducing the toxicity of some elements, especially those toxic at low pH ranges, specifically aluminum. Gypsum ($CaSO_4$) breaks into its component parts (Ca^{2+} and SO_4^{2-}) and Ca^{2+} ions replace Al^{3+} on soil exchange sites. The sulfate ions react with metal ions, therefore the sulfate does not go into solution with H^+. Gypsum does not directly raise the pH, but it can help relieve the symptoms of pH by lowering aluminum concentrations in solution (by creating the insoluble $Al(OH)_3$) and increasing calcium concentrations.

FGD gypsum application has the potential to improve soil physical properties by alleviating surface crusting and compaction, increasing water infiltration and holding capacity, improving aggregate stability, and reducing water runoff and erosion (Clark et al., 2001). Salts can promote dispersion. Calcium can increase flocculation and aggregation of the soil particles. When surface applied, gypsum can help improve root growth and increase water and nutrient uptake in plants (Sumner et al., 1986). Pure gypsum, which can be mined, has been applied on sodic soils to alleviate dispersion of soil particles caused by excess sodium. Sodic soils contain an excess of exchangeable Na^+ on soil colloids and have soluble carbonates in the form of Na_2CO_3 and $NaHCO_3$ (Chun et al., 2001). The presence of Na_2CO_3 and $NaHCO_3$ increase the soil pH by increasing the activity of carbonate and bicarbonate which bind to H^+ ions (Chun et al., 2001).

Although pure gypsum is useful at promoting flocculation, some of the materials used in the production of by-product gypsum contain high levels of sodium, when amending the soil with this material, could cause more dispersion of clay particles which reduces water infiltration over time (Clark et al., 2001). Many detrimental effects of high soil pH on plants are caused by B, K, Mg, Na, and Cl (Clark et al., 2001). The high content of soluble salts can increase the electrical conductivity (EC) of the soil, and negatively affect the osmotic potential of plant roots decreasing the nutrient uptake by plants. Pure gypsum contains many beneficial compounds to improve soil structure, but impurities in by-product gypsum (including salts) must be considered before land application.

Gypsum from FGD has the potential to provide plant nutrients, especially calcium, sulfur, and magnesium. Exchangeable K^+ content has not been influenced by gypsum application, but could potentially be added through other sources (Caries et al., 2006). Additional elements provided through FGD application (including macronutrients) are displayed in table 1.

The main elemental addition from gypsum is calcium. Calcium is used in large amounts by plants, behind only nitrogen and potassium. Calcium is mainly taken up by young plant roots, and therefore, the timing of gypsum application is important to plant uptake and calcium concentrations in plant tissues. The main roles of calcium as a plant nutrient are to provide structural support and enzyme signal activation, perception, and transduction (Schaberg et al., 2006). Calcium deficiencies appear in the growing points of the plant including buds, fruits, and root tips. Deficiencies in Ca can also reduce the photosynthetic carbon fixation (McLaughlin

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and Wimmer, 1999). Many plants exhibiting calcium deficiencies also show other stresses including the inability to cope with high or low temperatures, oxidative stress, mechanical injury, salinity, and drought (Schabert et al., 2006).

Gypsum also provides large amounts of sulfur to soils and plant tissues. As an essential macronutrient sulfur must be available in relatively large amounts for good crop growth. Sulfur concentrations in soils have declined over the past decades due to cleaner industry practices and reductions in sulfur emissions. Many concentrated fertilizers contain little or no sulfur, and sulfur levels have also been decreasing due to intensive cropping systems, increased crop yields, less S deposition from the atmosphere, and less use of S-containing pesticides (Chen et al., 2005). Sulfur deficiencies result in decreased yields and may also decrease the feed value of some cereal crops. Sulfur deficiencies may also result in decreased nitrogen fixation rates in some legumes. Additional sulfur from gypsum additions may alleviate hidden S deficiencies and also improve the nitrogen uptake by plants (Zheljazkov et al., 2006).

Magnesium is required in smaller quantities than other plant macronutrients. However, magnesium is an essential component of chlorophyll, and therefore is involved in plant photosynthesis. Magnesium is also involved in energetic metabolism and acts as an enzyme cofactor (Shaul, 2002). Magnesium deficiency is much more common than calcium deficiencies in plants and affects plant growth and biomass partitioning between root and shoot (Hermans et al., 2004). Gypsum application and the addition of high amounts of calcium promote the downward movement of magnesium (Mg^{2+}) through the soil (Caires et al., 2006). The application of large amounts of gypsum (and Ca^{2+}) create the potential for decreases

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in plant available Mg. Therefore, when gypsum is applied at high rates, strategies must be developed to minimize the loss of exchangeable Mg^{2+} and keep it available for plant uptake.

Other elements that may be added in large quantities due to the impurities found in gypsum and other FGD products include iron and aluminum. Iron is an essential micronutrient that can act as an electron carrier in plants. Aluminum plays a central role in soil acidity. The influx of additional aluminum ions displaces calcium ions on soil faces. The displaced calcium ions are then able to leach out of the soil solution, and are no longer available for plant uptake. At low pH levels soluble Al^{3+} ions react with water to form $AlOH^{2+}$ and H^+ ions. Aluminum can also attach to the soil surface, decreasing the cation exchange capacity (CEC) available for plant nutrients the soil.

Toxic Components of By-Product Materials

PSMs have many possible benefits when used for the removal of phosphorus. There are some concerns, however, of possible environmental hazards that they present. For example, Penn and Bryant (2006) noted in a PSM field study that alum was most effective in reducing soil water soluble P levels, but it also destroyed the grass stand when directly applied to soil. The loss of grass was likely due to acidity or Al toxicity. A possible solution is to regulate the pH with lime or another pH buffer.

Materials contained in the PSMs can also damage or destroy plants through other mechanisms. Coal-combustion waste materials tend to contain high concentrations of soluble salts, including borates, which can lead to plant toxicity

problems (Gray and Schwab, 1993). Figure 1 displays the elemental composition of different coal combustion byproducts.

Another concern associated with the land application of gypsum and FGD materials is the addition of mercury. Oxidized mercury is often released from the combustion gasses during coal burning. Depending on the FGD process, a large portion of the Hg may be incorporated into the FGD slurry and the byproducts, including synthetic gypsum (Kairies et al., 2006). The toxicity and bioaccumulation becomes a concern when there is potential for its release into the environment (Kairies et al., 2006). Studies by Kairies et al. (2006) show a large range of magnitude of Hg in the by-product gypsum (from 140 to 1500 μg kg^{-1} dry basis), varying largely from origin of gypsum, nature of processing, or both, and are weakly correlated with the iron content of the material. It is important to determine the environmental implications of these mercury additions to soil and its potential transport into plant systems, groundwater, or surface water systems. Figure 2 shows the concentrations of mercury from the original FGD-gypsum (before processing) and the wallboard manufactured from it (after processing). Each shows the potential to present some environmental hazards with the addition of mercury into the environment.

Research Objectives

Given the above background information, the following objectives were developed to characterize land application of ditch filter materials. The objectives of this study were to determine (i) the influence of adding gypsum and phosphorus to soil on the mineralization and phosphorus forms within soil over time (ii) the

distribution of inorganic and organic P forms within simulated field conditions

through an incubation study and (iii) the connection between soil factors and

properties that effect phosphorus forms within soil.

Chapter 3: Materials and Methods

Soil Incubation Study

A soil incubation study was initiated to determine and compare the effect of adding phosphorus saturated flue gas desulfurization gypsum ($CaSO_4 \cdot 2H_2O$) on soil chemical properties. Treatments consisted of two soil types (silt loam and sandy loam), two gypsum rates (high rate and low rate), and two P rates (determined at 25% and 75% of the gypsum sorption maximum; see below for details), and sampled at seven dates. The treatments were assigned in a two (soil type) by two (gypsum rate) by two (P rate) by seven (sampling date) factorial design, resulting in 56 treatment combinations. Each treatment combination was randomly assigned within four incubators, with each incubator serving as one block. The incubators used were VWR Scientific Model 2020 low temperature incubators set at $25^{o}C$.

Sandy loam and silt loam soil samples were collected from the top 12 inches of soil from Maryland's eastern shore. The sites had a history of manure application, but were chosen due to relatively low levels of background P concentration. The sandy loam is a Galestown siliceous, mesic Psammentic Hapludult and was collected from the edge of a cultivated field (was planted in corn when collected) in Quantico, MD. The silt loam is a Mattapex fine-silty, mixed, active, mesic Aquic Hapludult and was collected from the edge of a cultivated field (in soybeans when collected) in Chestertown, MD.

The soils were air-dried at room temperature, ground to pass through a 20-mm wire screen, and then 200g (dry weight) of soil was added to 288 plastic cups. Each cup had a snap cap with four 3.97 mm (5/32 inch) holes drilled in the lid to allow for

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minimal air exchange. Prior to amendment addition, a pre-incubation was conducted where each cup was brought to a moisture content equivalent to 70% of field capacity (determined by the method of Tan, 1996) and incubated at 25°C for 14 days. In addition to the treatment combinations described above, there was one cup in each block for each soil (eight total cups) placed in the pre-incubation that was analyzed at day 0 prior to amendment addition to establish baseline conditions. Baseline conditions (soils receiving no treatment) are displayed in Table 2.

In order to determine the amount of P to add to the gypsum for the incubation study, P sorption isotherms were conducted. Gypsum was air-dried and sieved (2 mm) and 2 g of sample was weighed into 50 mL centrifuge tubes. Phosphorus solutions were made at 12 concentrations (0, 1, 5, 10, 50, 100, 800, 1600, 2400, 3200, 6400, 10000 mg P L^{-1}) using KH_2PO_4 and deionized water. Four tubes with gypsum were amended with 30 mL of solution at each concentration for a total of 48 tubes. The tubes were placed in an end over end shaker and shaken for 24 hours. Samples were then centrifuged at 1163 x G and filtered through 0.45μm filters using the Millipore filtration apparatus. The supernatant was then analyzed for total dissolved P using inductively coupled plasma-optical emission spectroscopy (ICP-OES). This process was repeated three more times. A sorption curve was created by plotting the sum of P adsorbed during the four sequential sorption experiments versus the initial P concentration in solution (Figs. 3-4). The point at which the cumulative curve (Fig. 3) leveled off was assumed to represent the potential sorption maximum. The initial P concentrations that represented 25% and 75% of the initial P concentration required to achieve this sorption maximum. At the sorption maximum, approximately 24.7 mg

g^{-1} of P was sorbed with an initial P concentration of 2400 mg L^{-1}. The amount of P adsorbed at 25 and 75% of this maximum was approximated at 6.25 and 18.75 mg g^{-1}, requiring initial P concentrations of 550 and 1550 mg L^{-1}.

The FGD gypsum was collected from US Gypsum Company in Baltimore, MD and split into 8 batches into 5 gallon buckets. Using the data from the sorption isotherm, the material was saturated with P to reach the desired 25 and 75% levels. Phosphorus solutions at initial P concentrations of 550 and 1550 mg L^{-1} were prepared using deionized water and KH_2PO_4. In order to saturate the gypsum with P, 200 g of gypsum and 2.27 L of 550 mg P L^{-1} solution was mixed in a Nalgene® carboy, and placed on the reciprocating shaker and allowed to react for 1 hour. An additional 200 g of gypsum and 2.42 L of 1550 mg P L^{-1} solution was mixed in a Nalgene® carboy and mixed for the same amount of time. After the reactions were complete, the excess solution was poured off and the gypsum was allowed to air dry. The resulting P saturated gypsums had P concentrations of 6.25 and 18.75 mg kg^{-1}.

After completion of the pre-incubation, soils were amended with the high and low P gypsum sources at two rates each, 5.6 and 22.4 Mg ha^{-1}, assuming 2244 Mg ha^{-1} of soil. The two levels of P saturation and two rates of gypsum resulted in four treatment combinations: low P and low gypsum (LP-LG), high P and low gypsum (HP-LG), low P and high gypsum (LP-HG), and high P and high gypsum (HP-HG). The resulting P and Ca application rates associated with each treatment combination are presented in Table 3. After amendment the cups were returned to the incubators (25 ^{o}C). During the incubation study, samples were weighed every 7 days, and sufficient deionized water was added to maintain the moisture content at 70% of field

capacity. Cups were destructively sampled 1, 7, 28, 63, 91, 119, and 183 days after

amendment addition. When removed, samples were oven dried at 60°C for 24 hours

and sieved using a 2-mm sieve prior to sample analysis. All samples were then

analyzed for total carbon (C), hydrogen (H), and N; WEP, M-3P, nitrate-N (NO$_3$-N),

ammonium-N (NH$_4$-N), pH, and EC. Total P was determined in samples collected on

days 7 and 119 and chemically defined P fractions were determined for samples

collected on days 1, 7, and 119. Methods for each analysis are presented in more

detail below.

Analysis of Samples

Water-extractable P was determined by weighing 2 g of dried and sieved soil

into 50 mL centrifuge tubes and adding 20 mL of deionized water. The tubes were

then placed on their side in a reciprocating shaker and shaken on low speed for one

hour. The tubes were then centrifuged at 1163 x G for 15 minutes then immediately

filtered through 0.45μm filters using the Millipore filtration apparatus. Phosphate-P

was determined using the molybdate blue method on a Lachat QuikChem 8500 Flow

Injection Analysis System (Hach Company, Loveland, CO) by the methods of

Murphy and Riley (1962). Mehlich 3 P was determined by shaking 2.5 g of soil with

25 mL of Mehlich 3 solution (0.2 *M* CH$_3$COOH, 0.25 *M* NH$_4$NO$_3$, 0.015 *M* HNO$_3$,

and 0.001 *M* EDTA) in a 50 mL centrifuge tube for five minutes on a reciprocating

shaker (Mehlich, 1984). Inorganic N (NO$_3$-N and NH$_4$-N) concentrations were

determined using an automated ascorbic acid colorimetric method (Keeny and

Nelson, 1982) on a Lachat QuikChem 8500 Flow Injection Analysis System (Hach

Company, Loveland, CO). To determine pH and electrical conductivity, 10 g of dried

and sieved soil was weighed into sample cups with 10 mL of deionized water to achieve a 1:1 volume:volume ratio. The mixture was stirred with a glass rod to achieve a homogeneous slurry and then allowed to sit for 15 minutes, and then stirred again. The glass stirring rod was rinsed with distilled water and dried in between each sample. They sat another 15 minutes, and were measured for pH and EC using a Mettler Toledo InLab® Expert Pro pH and Mettler Toledo InLab® 731 EC probe and meter. Finally, all samples were analyzed for total C and N using a LECO® Corporation 2000 Elemental Analyzer by the method of Campbell (1992).

In addition to the methods described above, samples from day 1, 7, and 119 were also extracted using the phosphorus fractionation method modified from Hedley et al. (1982). See Fig. 5 for overview of extraction procedure. Samples were extracted sequentially by deionized H_2O, 05 M $NaHCO_3$, 0.1 M NaOH, and 1.0 M HCl at a solid to solution ratio of 1:60 (0.5 g to 30 mL). Samples (0.5 g) were weighed into 50 mL centrifuge tubes and shook for 24 h with 30 mL of the respective extractant at low speed on a reciprocating shaker. After shaking, samples were centrifuged for 15 minutes at 1538 x G. The supernatant was passed through a 0.45 µm Millipore filter, diluted ten fold with deionized H_2O, and analyzed for P using ICP-OES. Solids remaining in the centrifuge tube were then extracted with the next solution following the same procedure until they had been extracted by each of the four solutions.

Total P was determined in soil samples from days 7 and 119 using EPA method 200.2 (Martin et al., 1994). Soil (0.5 g) was digested using an Environmental Express hot block model SC154 with 2 mL of 1:1 HNO_3 and 5 mL of 1:4 HCl at

95°C. The samples were removed from the hot block after 30 minutes, cooled, and diluted to 50 mL total volume using deionized H_2O and analyzed using the ICP-OES.

Statistical Treatment of Results

Statistics were conducted using SAS version 9.1. Although the experimental design was a randomized incomplete block design, the results were analyzed as a randomized complete block design (background samples were not considered in statistical analysis, but were indicated as comparisons) in order to avoid using contrast statements. Incubators served as blocks, and the blocks were treated as a random factor. Due to large differences in background soil types (differences between sandy loam and silt loam), for some analyses data was sorted by soil type and soils were considered separately. Proc mixed was used as the data analysis model. Tukey's Multiple Mean Comparison Test was used to make pair wise comparisons. Significant differences in means was determined at $\alpha<0.05$. Results are displayed using letters indicating significant differences among treatment results.

Chapter 4: Results and Discussion

Effect of Gypsum and Phosphorus Rate on Soil P Concentrations

      Water Extractable Phosphorus (WEP) and Mehlich-3 Phosphorus (M3P) both indicated that there was an interaction between P saturation rate and gypsum rate as well as an interaction between soil type and time. Soil WEP ranged from 4.5 to 20.8 mg kg^{-1} over all dates and treatments. The background soil WEP (no treatment added to soils) was 6.5 mg kg^{-1}. The LP-LG, HP-LG, and LP-HG treatment combinations all produced statistically similar soil WEP concentrations with means over time and soil type of 4.5, 7.1, and 6.6 mg kg^{-1} respectively (Fig. 6). The HP-HG treatment resulted in significantly higher WEP concentrations than the other three treatment combinations.

      Trends seen in the effect of P saturation level and gypsum rate on M3-P concentration were similar to WEP concentrations (Fig. 7). Soil M3-P ranged from 61.9 mg kg^{-1} to 117.3 mg kg^{-1} averaged over all dates and treatments. As seen with WEP, the HP-HG treatment combination resulted in significantly higher soil M3P concentrations than the other three treatments. The HP-LG, and LP-HG treatment combinations produced statistically similar soil M3-P concentrations with means over time and soil type of 70.4 mg kg^{-1} and 76.2 mg kg^{-1} respectively. However, these treatments were statistically higher than the LP-LG treatment combination. The background soil M3P for both soil types was 46.5 mg kg^{-1}, which was lower than any of the soils amended with gypsum.

The combination of P saturation rate and gypsum rate also had a statistically significant effect on the concentrations of P extracted through sequential extraction. The main effects of gypsum rate and P saturation level are discussed, averaged across time and soil type. Cumulative P extracted through the sequential procedure was calculated by summing the P extracted in each fraction. The HP-HG treatment combination resulted in significantly higher P concentrations than the other three treatment combinations within H_2O, $NaHCO_3$, NaOH, and cumulative P fractions (Table 6). The $NaHCO_3$ fraction differed from the H_2O and NaOH fractions in that the LP-LG treatment combination resulted in P concentrations that were significantly less than the LP-HP treatment. The HCl fraction differed from the other fractions in that no significant differences were detected between any of the four treatment combinations.

Total P applied through the four treatment combinations had an overriding effect on soil WEP, M3-P, and chemically defined P fractions (Figs.6-8; Table 4). Total P rates added to the soil were 35, 105, 140, and 420 kg ha^{-1} with the LP-LG, HP-LG, LP-HG, and HP-HG treatments, respectively (Table 3). Substantially more P was added with the HP-HG treatment, which was evidenced by significantly higher soil M-3P and water-extractable P concentrations. In addition, this treatment combination resulted in significantly higher soil P concentrations extracted in all of the fractions except for the HCl. The three lower P application rates resulted in statistically similar soil WEP concentrations. While no statistical comparisons could be made, these concentrations were similar to the background soil water-extractable P concentrations before amendment. These results indicate that addition of gypsum at

the lower P concentrations or at the high gypsum rate and low P saturation did not add enough P to substantially increase water-extractable P. In fact, application of the low P saturation gypsum at the lowest rate actually decreased soil water-extractable P relative to the control.

The results of the water-extraction were mirrored by the M3-P results with the exception that M3-P concentrations were mostly a function of the amount of P added with each treatment combination (Table 3 and Fig. 7). As seen in Table 3 the HP-LG (105 kg ha^{-1}) and LP-HG (140 kg ha^{-1}) treatments added very similar amounts of P, while the HP-HG (420 kg ha^{-1}) treatment added substantially more P and the LP-LG (35 kg ha^{-1}) add substantially less than the other three treatments. Finally, the M3-P extraction showed an increase in soil P concentrations relative to the background soils upon P application among all treatment combinations. Therefore, one can conclude the M3 extraction apparently was more efficient at extracting the P held by the gypsum when compared to the water extraction where the three lower P rates did not show an increase in water-extractable P or a slight decrease compared to background levels.

Effect of Soil Type and Time on Soil P Concentrations

Water Extractable Phosphorus (WEP) and Mehlich-3 Phosphorus (M3P) both had interactions between soil type and time therefore the main effects of these two factors can be discussed averaged across gypsum rate and P saturation. The sandy loam samples ranged from 17.8 mg kg^{-1} WEP for day 1 samples compared to 9.1 mg kg^{-1} WEP for the day 183 samples. The silt loam samples ranged from 12.8 mg kg^{-1} WEP for the day 1 samples to 4.6 mg kg^{-1} WEP for the day 183 samples (Fig. 9). For

both soil types, there was significantly higher water soluble P initially (day 1 samples) versus the end of the incubation study (day 183). Soil M3-P ranged from 73.2 mg kg^{-1} for the day 1 sandy loam samples to 83.5 mg kg^{-1} for the day 183 samples. For the silt loam samples, the M3P ranged from 64.2 mg kg^{-1} for the day 1 samples to 50.0 mg kg^{-1} for the day 183 samples. Fig. 9 shows that P extractability gradually decreases with time.

Fig. 10 exhibits a slightly different trend where M3-P increased and peaked between days 63 and 91 followed by decreasing back to near initial levels. The main difference to note in Figs. 9 and 10 are those exhibited between soil types. The silt loam has a higher buffer capacity and therefore exhibits less of an impact of the P application on water-extractable P concentrations. This can be attributed to the higher clay and silt content and therefore greater surface area for P retention found in the silt loam compared to the sandy loam. In addition, the higher P buffer capacity and lower P saturation of the silt loam allowed P concentrations to return to near background levels for both water-extractable P and M3-P compared to the sandy loam. The difference in the shape of the lines in Figs. 9 and 10 indicate that P was moving between different organic and inorganic P pools. This is evidenced by the fact that the M3-P concentrations (Fig. 10) peaked later in the study than the water-extractable P concentrations. Fig. 9 shows that the initial application of inorganic P was quickly removed either by sorption processes in the soil or microbial immobilization. The M3-P took longer to react to the P application, but apparently responded to what may have been a shift to microbial pools of P around day 63. Fundamentally, this data shows that with time soils can fix (through chemical or microbial processes) most of

the P added with saturated gypsum regardless of the P application rate. However, the finer textured soils, with higher P buffering capacity are better able to sorb this added P.

Soil type and time were also important factors when conducting a sequential fractionation of the samples; however, they did not have an interaction with one another. The soils had different levels of background phosphorus, and therefore, soil type had a large effect on the amount of extractable phosphorus. Figure 11 displays the simple effect of soil type on the chemically defined P fractions within all soils averaged across all sampling dates, P saturation levels, and gypsum rates. Statistical significance is displayed within each extraction type, not between extractants. For all fractions except H_2O the silt loam had higher P concentrations, resulting in higher cumulative P extracted. In addition to having statistically significant effect of soil type, the water extractant also had interactions between gypsum rate*P saturation, soil type*gypsum rate, and soil type*P saturation. Therefore, statistics are not displayed for that fraction. The NaOH extractant had a three-way interaction between soil type*gypsum rate*sampling date so statistical significance is also not shown for this fraction. For the $NaHCO_3$, HCl, and cumulative P fractions, the amount of phosphorus extracted from the silt loam samples is significantly higher than the sandy loam samples. The silt loam samples contained more background phosphorus; therefore, more was extracted with the stronger extractants. It is interesting to note, that although statistical significance cannot be shown, the water portion is the only portion where more P was extracted from the sandy loam sample than the silt loam sample. Although this fraction cannot be analyzed statistically due to interactions, its

trend is different from the other fractions, and demonstrates the differences among the soil type and their ability to retain P. The sandy loam contains less clay and less surface area, and therefore cannot hold on to P and other ions as tightly. However, as stronger extractants are used, more P is able to be able to be extracted from the silt loam, likely because it has a larger pool of P prior to P additions.

The sampling date was also a significant factor when comparing chemically defined P fractions for some extractants used in the sequential fractionation. Therefore, the simple effects of time are displayed averaged across the two soil types, P saturations, and gypsum application rates (Fig. 12). The NaOH extractant had a three-way interaction between soil type*gypsum rate*sampling date, and therefore, statistical significance was not shown for this fraction. Although there is not a clear trend in data, in general there is a shift in P from more labile P to more insoluble forms over time. Also, for the H_2O and HCl fractions, there was no significant difference between days 1 and 7, but both had more extractable phosphorus in the day 1 fraction versus the day 119 fraction. For example, the water extractable portion resulted in 24.7, 24.9, and 16.5 mg P kg^{-1} for day 1, day 7, and day 119 respectfully. These values follow the same trends discussed in the water soluble P results, meaning over time, the phosphorus fraction becomes less water soluble, indicating the phosphorus becomes tied up in other, less soluble forms.

Samples were also extracted to determine total P concentrations. Unlike the other extractions, there was no interaction between gypsum rate and P saturation when considering total soil phosphorus. Therefore, the main effects of soil type and time are discussed. Samples were only analyzed for total P on sampling days 1 and

119. These sampling dates were chosen so values could be compared to those in the sequential phosphorus fractionation. There were some differences between soil types. The sandy loam samples had values of 213 mg kg^{-1} and 187 mg kg^{-1} for day 1 and day 119 respectively, however these means were not determined to be significantly different. Significant differences were detected between total P concentrations in the silt loam samples on day 1 compared to day 119, which were 434 mg kg^{-1} and 470 mg kg^{-1}, respectively. The background soil level for the sandy loam (averaged across both dates) was 185 mg kg^{-1} compared to 418 mg kg^{-1} for the silt loam sample (Fig. 13). The increase in soil P concentration of the silt loam samples could partially be attributed to decrease in the amount of soil present in the incubation cup after 119 days. Microbial activity could consume and respire C as CO_2, decreasing the total amount of soil present and thereby increasing the total P concentration. This effect would be magnified in the silt loam compared to the sandy loam because of its higher organic matter and C content.

The fractionation procedure has identified some differences in P fractions between soil types, time of incubation, and the overall P rate (combination of gypsum and P saturation). Although statistical significance cannot be shown for all P fractions, in general the silt loam sample tended to have higher extractable P than the sandy loam. The cumulative P extracted from the silt loam soil was more than double of the cumulative P extracted from the sandy loam soil. However, when comparing the amount or percentage of phosphorus extracted of cumulative by means of the sequential fractionation to the total P extracted by EPA 200.2, there is no statistically significant difference between the extraction procedures. Figure 14 displays the

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relationship and correlation between total phosphorus extracted using the EPA 200.2

method and the cumulative P extracted using the sequential fraction procedure. The

R^2 value of 0.79 shows a relationship between the two extraction techniques, but does

not explain the variation in amounts extracted. Because there is no interaction

between any of the factors (gypsum rate, soil type, P saturation, or sampling date),

there is no relationship in the amount of P extracted comparing the two extraction

procedures among the different treatment combinations and soil types.

Chapter 5: Conclusions

The purpose of the laboratory incubation study was to model possible field conditions that would occur through the application of spent gypsum from a ditch filter. The two soils chosen are typical soils found on the Eastern Shore of Maryland, and were chosen because they are relatively low in P (ideal soils to receive gypsum application). The two P saturation rates represent a range of P concentrations, a low concentration of P (25% saturation) and a higher concentration of P (75% saturation), and exceed typical ditch soil P concentrations. Finally, the two gypsum rates represent a typical field application rate and an over-application rate, which would likely result in other soil problems.

The main focus was to determine the role and transport of phosphorus through the system, when applied as a soil amendment. Water extractable phosphorus (WEP) is an effective indicator of environmental P loss (Kleinman et al., 2002). Water dissolves less P then other soil test P extractants, but is likely the most appropriate method to measure runoff dissolved P (Pote et al., 1996).

This study showed that as more P is added more P is extracted using the WEP method, regardless of soil type. However, when applied at typical field application rates (LG- 2.5 tons acre^{-1}), there were no significant differences in the amount of phosphorus extracted. Therefore, applying "spent" gypsum at typical amendment rates would not appear to result in any detrimental water quality impacts. Kleinman et al. (2007) evaluated ditches on Maryland's eastern shore and found that ditches draining high P areas transported 4.3 to 25.3 kg total P ha^{-1} year^{-1}. In comparison, ditches receiving runoff from more typical fields exported 2.6 to 4.8 kg total P ha^{-1}.

Kleinman et al. (2007) found ditch water P concentrations ranged from 0.51 to 6.17 mg L^{-1} total P. By comparison P solution concentrations used to spike the gypsum in this study were 550 and 1550 mg P L^{-1} for the low and high P saturation levels, respectively. Therefore, the materials used in this study were reacted with solutions containing substantially higher P concentrations. Nonetheless, addition of gypsum spiked with these solutions to the soil resulted in little change of water-extractable P or M3-P concentrations at all but the highest total P application rate (HP-HG) relative to background soil P concentrations. Therefore, if spent materials from actual ditch treatment structures were land applied they would not contribute enough P to increase soil P concentrations to levels of environmental concern.

When considering the effect of time on field application of spent gypsum, the amount of WEP extracted decreases. Therefore, as long as the P held in the gypsum was not over-applied (applied at higher than recommended field application rates) it would not be expected to build up and cause impaired water quality over time. In fact, under typical field conditions where spent gypsum would have much lower P concentrations, one would expect that there would be additional P sorbing capacity due to the gypsum application, and gypsum may tie up additional P from the soils once land applied, depending on the rate of application. From an environmental standpoint, the phosphorus is tied up and would not be leached downstream, but it also appears that the P-saturated gypsum would not be able to be a long term fertilizer source for crops and plants as evidenced by increases in M3-P.

The Mehlich-3 P extraction is commonly used for soil test P in soil testing laboratories. However, like other common soil testing methods, these methods were

developed to assess the fertility status of soil for crop production, not to predict runoff water quality (Pote et al., 1996). Therefore, the Mehlich-3 extraction is a better indicator of P availability for crop needs. Similar to the WEP method, the M3-P rate increased as more P is added to the soil (Fig. 7). The results from the incubation study showed the highest concentrations of M3-P 63 and 91 days after amendment. In a field setting, this would mean that the P would not be as immediately available for plant uptake. However, soil microbial communities, moisture, and temperature would be expected to have a large effect on P availability under real-world conditions. Nonetheless, the current laboratory study showed that there may be some potential to increase soil M3-P concentrations, although timing of application to allow for the P to enter the M3-P pool would need to be accounted for. For example, corn crops in the Mid-Atlantic region require the nutrients a few days after germination. If a farmer applied the gypsum in March, and the crop is planted in Mid-April, this would coincide with the maximum M3-P rate, and likely be plant available as a plant nutrient source.

The total P and sequential P procedures are used to estimate P forms within soil. Results for total P extraction were higher than the cumulative P extracted using the sequential fractionation procedure. The sequential fractionation procedure used HCl as its strongest extractant. The total P extraction procedure is a measurement of all soil P. Therefore, the total P procedure accounts for the pool of P that is most strongly bound, or is in mineral form that cannot be extracted using HCl. The sequential extraction method recovered 35 – 106% of the total P extracted using the EPA 200.2 method. Evaluation of the portion of total P extracted through all four

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sequential extractants (cumulative P) did not reveal any interaction between the two extraction methods and the treatment factors. Therefore, it is not clear why the percentage of total P extracted through the sequential fractionation did not exhibit a consistent trend across all samples. Hedley et al. found that approximately one quarter of bacterial cell P is non-extractable from soil (1982) using the sequential fractionation procedure. Therefore, it is important to consider soil characteristics and P additions when considering P forms over time.

Although the main focus of the study was the role of P, other nutrients are also important for soil fertility and plant nutrition. In the incubation study, the temperature was kept relatively constant. However, this is not the case in a temperate climate field. Microorganisms play an important role in the mineralization, volatilization, and cycling of nutrients within soil. For example, Hedley et al. (1982) found that it is possible that monthly stimulation of a bacterial population by mixing would result in the slow accumulation of residual P in soil. Although the incubation soils were not mixed, spikes in nutrient values (including nitrogen- in the form of ammonia and through CHN analysis) indicate the role of microbes within the soils. Therefore, if temperatures or microbial populations were different, the P and other nutrients and the results would be altered.

Although a great deal of insight could be gathered from the above analyses, additional research could be conducted to better explain the fate and transport of P after land application of spent ditch filter material. One factor that was not considered, but should be included in future research is the fate and transport of mercury through the system. If mercury is found to build up or be easily transported

through the ditch or soil systems, then the ditch systems may not be a viable option to remove P.

In conclusion, the application of spent gypsum from a ditch filter at field application rates does not appear to increase soil WEP or M3-P values. Therefore, it would not be a particularly good source of plant available P, especially directly after application. At higher application rates and higher phosphorus levels, it may be able to serve as a plant nutrient source some days after application (as shown by the M3-P data), but at these application rates, other problems may result from Ca displacement of Mg. From an environmental standpoint, typical application rates do not result in water quality impairment due to additional P application. In some cases, it may also actually reduce P present in the solution, which would be beneficial in high P soils. Consideration of soil type and time of application are important in determining the environmental and agronomic impacts of applying the spent materials. The research concluded that P saturated gypsum typically found within filter systems can be land applied at recommended rates to improve soil fertility conditions without adversely affecting the environment or water quality.

Tables

Table 1- Elemental composition of various flue gas desulfurization byproducts found in literature.

Element	FGD† Crews and Dick, 1998	Vermiculite FGD Chen et al., 2005	Perlite FGD Chen et al., 2005	Gypsum Chen et al., 2005	ANT (fly-ash) Dou et al., 2003	FBC (fly-ash) Dou et al., 2003	FGD Dou et al., 2003
	--- g kg⁻¹ ---						
Al	5.22	19.6	7.4	2.4	2.2	4.7	nd‡
Ca	132	260	191	245	503	161	272
Fe	20.9	16.5	29.6	3.8	0.9	9.8	0.4
K	1.5	nd	nd	nd	338	1.7	6.5
Mg	75.3	27.1	11.9	26.9	0.4	13.7	0.9
S	22.6	67.1	66.4	161	nd	nd	nd
	--- mg kg⁻¹ ---						
As	nd	118	363	462	83.4	48.1	48.2
B	369	194	289	98.9	46	691	61
Ba	nd	122	90.7	76.4	nd	nd	nd
Cd	nd	< 0.12	< 0.12	< 0.12	7.5	7.5	nd
Cr	nd	123	29.3	10.4	nd	nd	nd
Cu	37.4	1.57	7.04	< 0.60	13.3	47.3	22.4
Mn	71	302	128	225	nd	nd	nd
Mo	nd	13.2	< 0.6	< 0.6	70.1	58.1	41.5
Na	410	nd	nd	nd	nd	nd	nd
Ni	52.3	72.4	< 0.6	< 0.6	115.9	126.2	108
P	312	nd	nd	nd	510	660	540
Pb	29.3	139	101	99.7	nd	nd	13.2
Se	nd	nd	nd	nd	80.9	177.6	218.4
Zn	46.4	33.2	93.4	8.7	1200	1800	1300

†FGD = Flue Gas Desulfurization

‡nd = no data available

Table 2- Baseline water extractable phosphorus, Mehlich-3 phosphorus, pH and electrical conductivity for each soil after 14-day pre-incubation at 25°C, but prior to amendment addition.

Soil	WEP (mg kg^{-1})	M3-P (mg kg^{-1})	pH	EC (S m^{-1})
Sandy Loam	6.00	54.45	4.56	18.03
Silt Loam	4.70	38.01	6.17	42.48

Table 3- Phosphorus (P) and calcium (Ca) application rates associated with each P saturation and gypsum treatment combination.

Low P: LP = 25% saturation
High P: HP = 75% saturation
Low Gypsum: LG = 5.6 Mg gypsum ha^{-1}
High Gypsum: HG = 22.4 Mg gypsum ha^{-1}

P and Ca application rate

	(kg-P ha^{-1})	(kg-Ca ha^{-1})	P:Ca Ratio
LP-LG	35	1232	1:35.20
HP-LG	105	1232	1:11.73
LP-HG	140	4928	1:35.20
HP-HG	420	4928	1:11.73

Table 4- Effect of gypsum rate and phosphorus saturation level on chemically defined phosphorus fractions averaged across soil type and sampling date.

Treatment Combination	Chemically Defined Phosphorus Fraction								Cumulative P	
	H$_2$O		NaHCO$_3$		NaOH		HCl			
	------------------------mg kg^{-1}------------------------									
LP-LG	13.77	b	36.53	c	90.23	b	25.18	a	165.72	b
HP-LG	14.50	b	40.80	bc	92.81	b	26.64	a	174.76	b
LP-HG	14.77	b	45.60	bc	94.27	b	23.96	a	179.28	b
HP-HG	45.02	a	63.70	a	104.68	a	26.33	a	239.72	a

Figures

Figure 1- Elemental composition of coal combustion by-products (selected minor nutrient additions).
Adapted from Crews and Dick, 1998, Chen et al., 2005, and Dou et al., 2003.
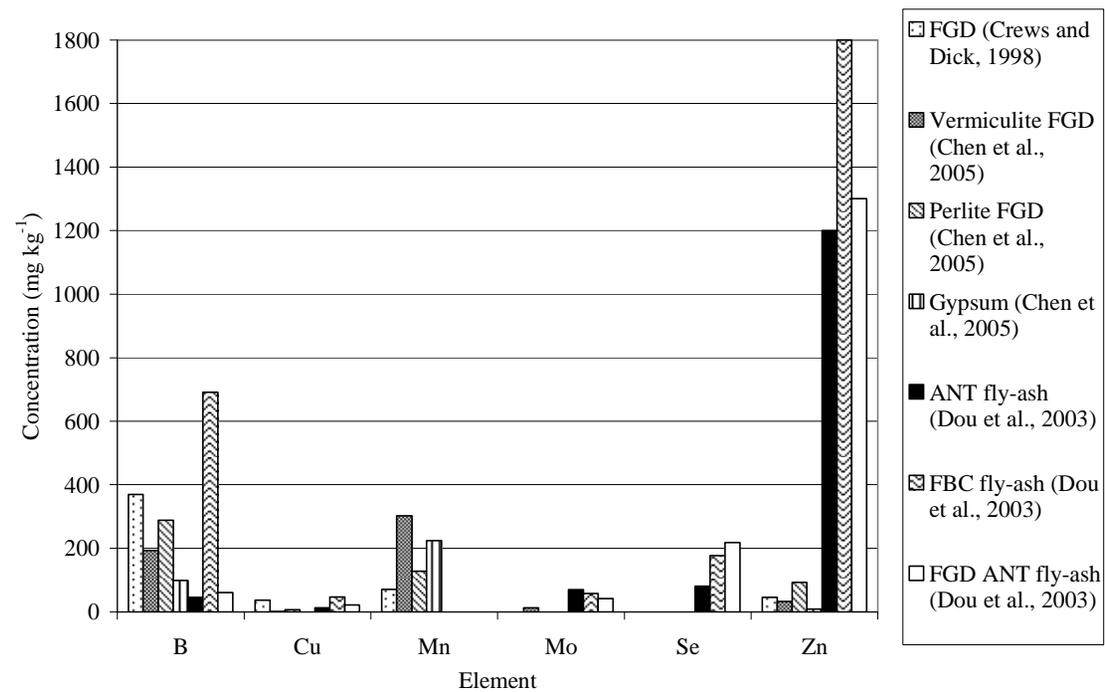
Figure 2- Mercury retention during the manufacturing of wallboard from synthetic gypsum.
Adapted from Kairies et al., 2006. Standard error bars indicated.
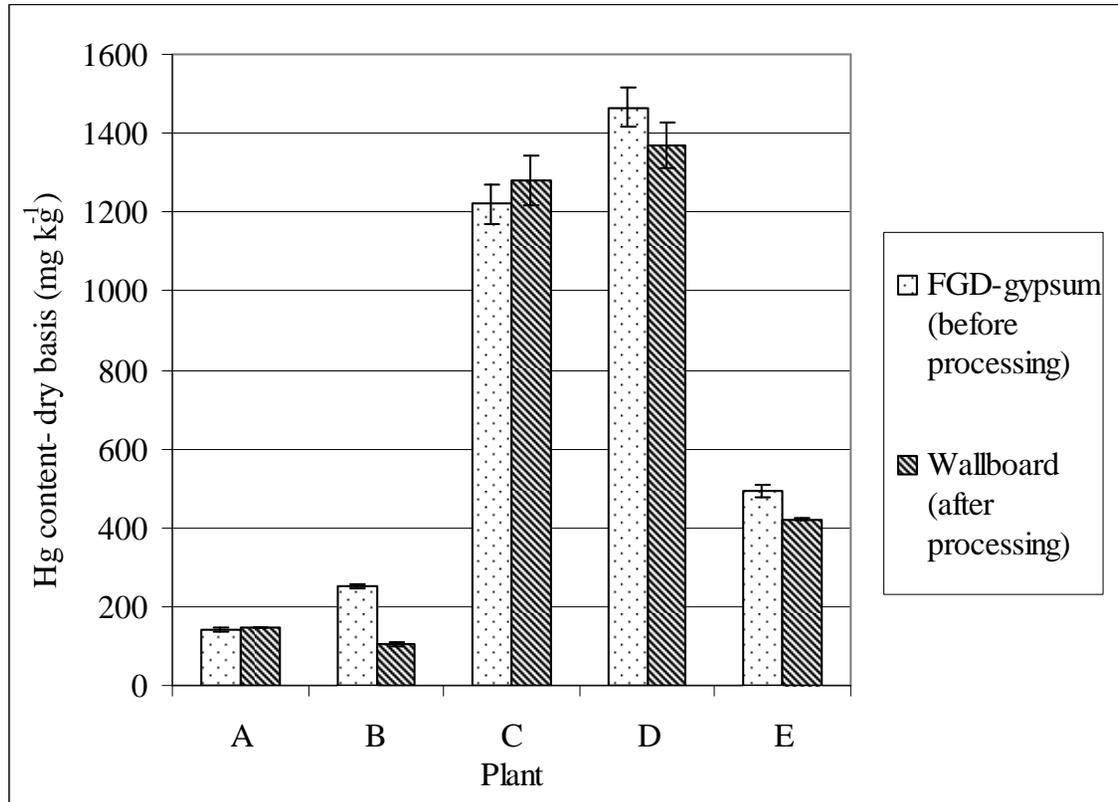
Figure 3- Phosphorus sorption curve used for calculation of phosphorus saturation levels. Sum of days 1-4, measured on Lachat using Murphy-Riley molybdate blue colorimetric method.
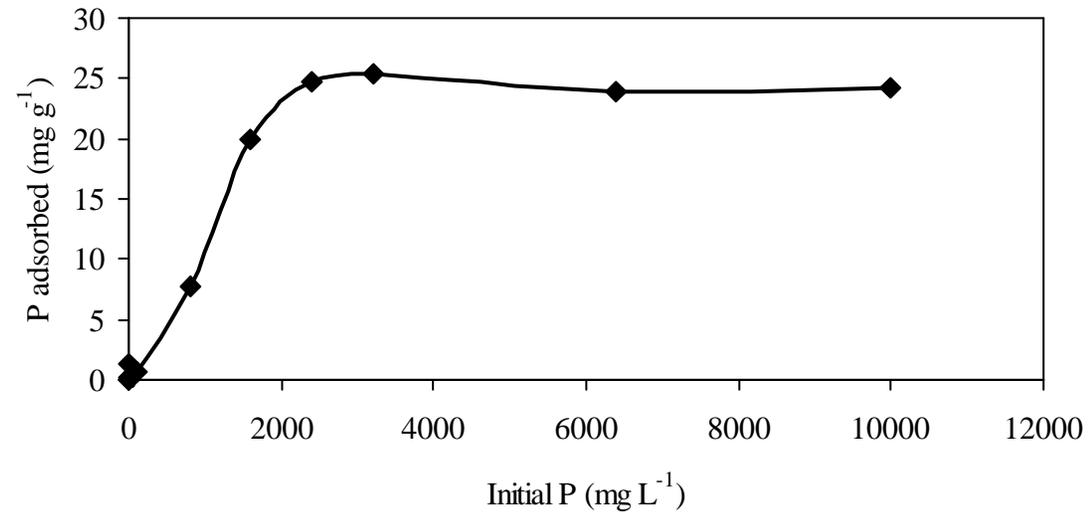
Figure 4- Phosphorus sorption curves for each day measured on Lachat using Murphy-Riley molybdate blue colorimetric method.
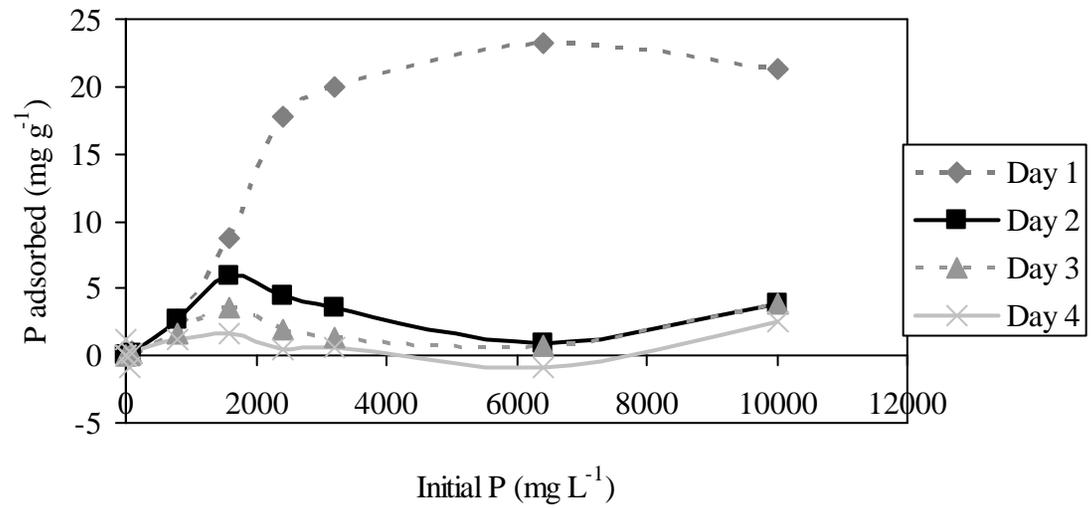
Figure 5- Flow chart of the fractionation of soil phosphate into various P fractions.

0.5g of Sample
(Soil + Gypsum/P)

P Pool Extracted

diH$_2$O

- Labile P- Easily extractable, most available to plants and algae, P in solution

0.5 M NaHCO$_3$

- Plant available P – loosely held Fe/Al and organic P

0.1 M NaOH

- Fe- and Al-Bound P and associated with humic compounds

1.0 M HCl

- Strongly held P – phytate P, mineral P, held in internal structures
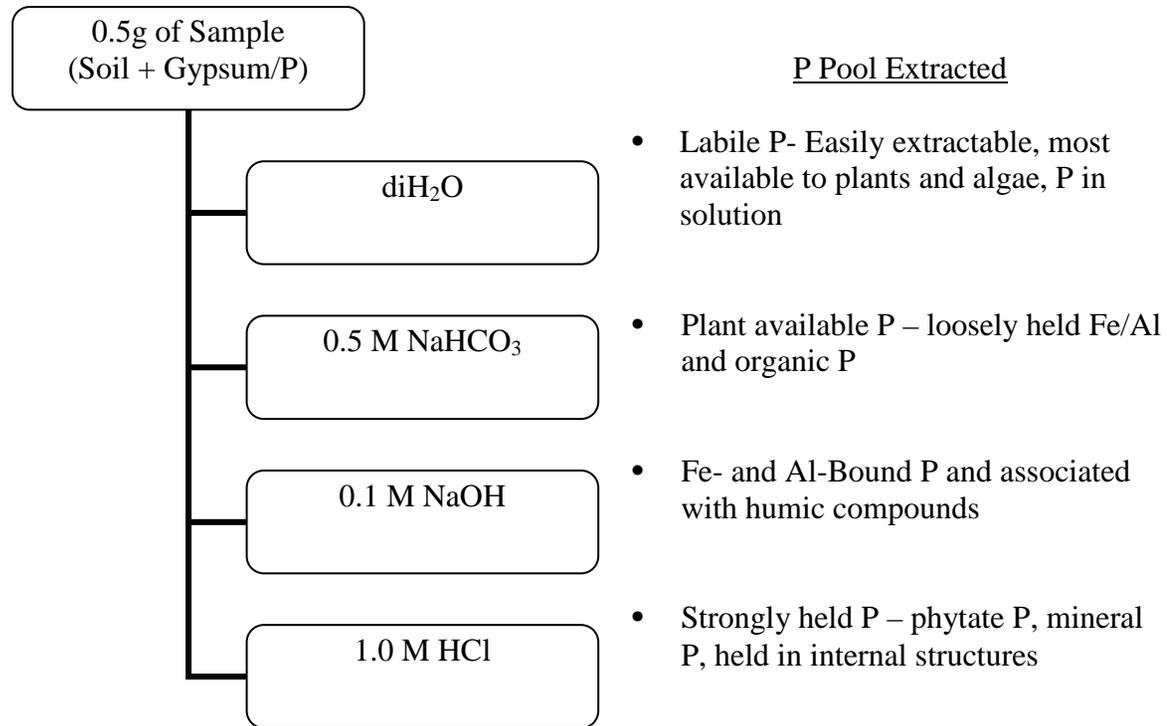
Figure 6- Effect of phosphorus saturation and gypsum rate on water extractable phosphorus averaged across sampling date and soil type with the background concentration shown by the dashed line.
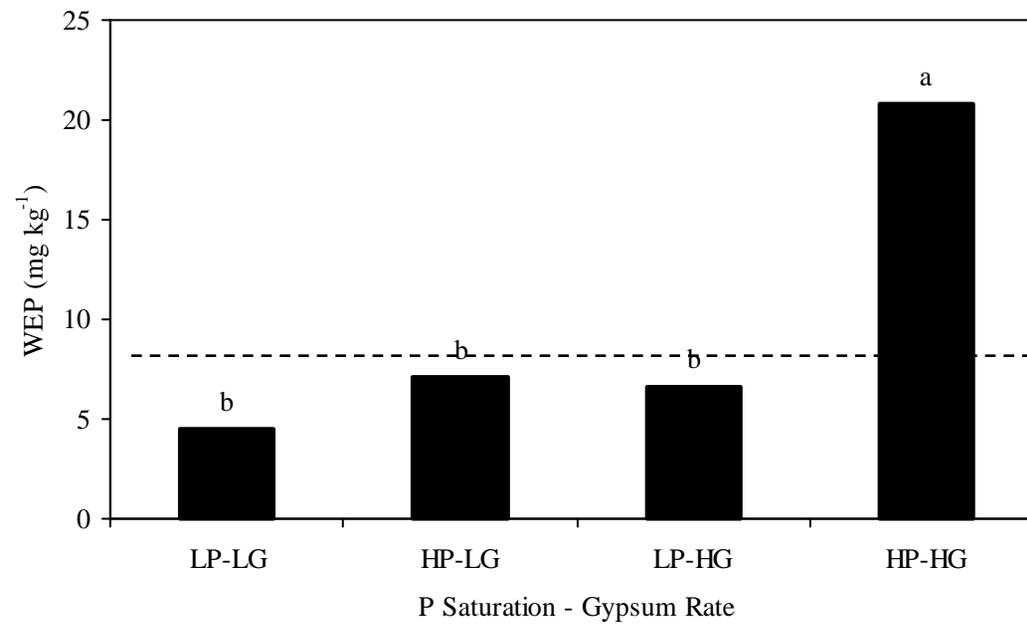
Figure 7- Effect of phosphorus saturation and gypsum rate on Mehlich 3-P averaged across sampling date and soil type with the background concentration shown by the dashed line.
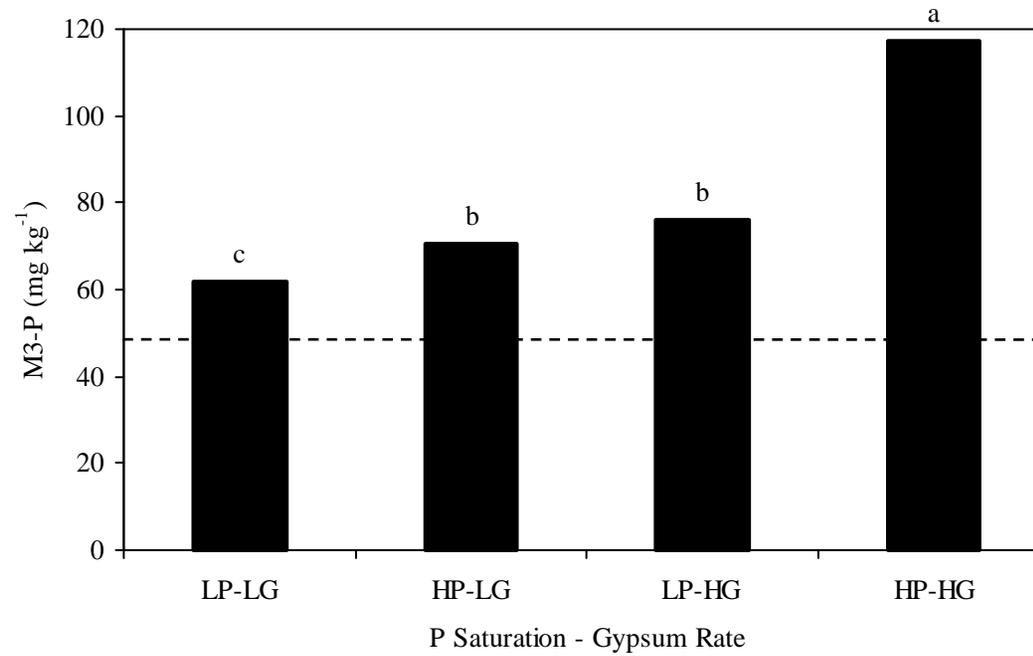
Figure 8- Combined effect of gypsum and phosphorus rate on chemically defined P fractions averaged across soil type and time.
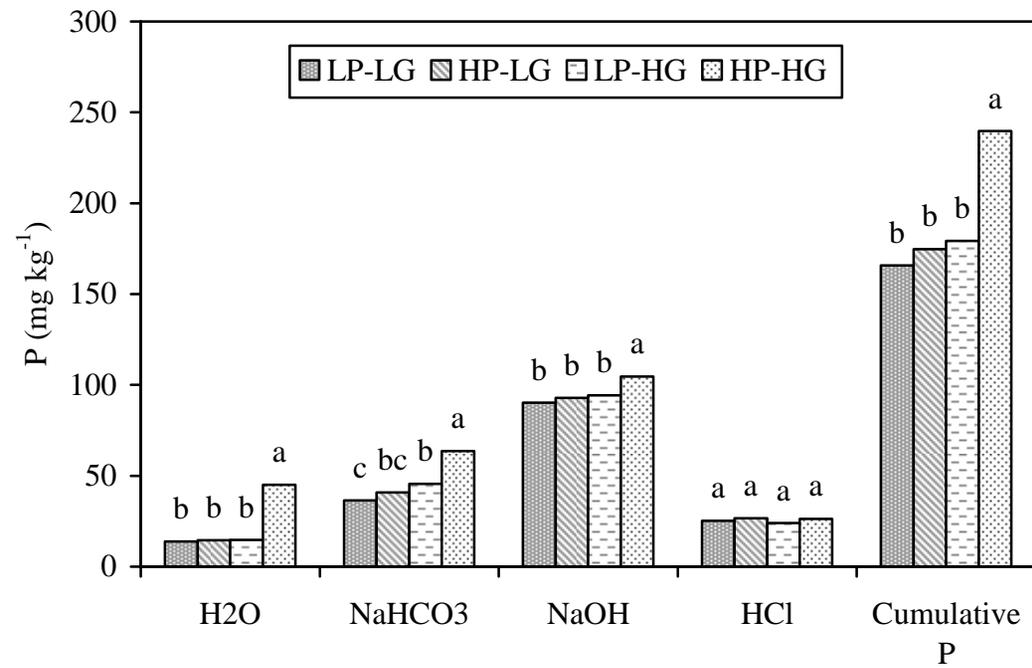
*Statistical significance can only be shown within each extraction type, not between extractants

Figure 9- Effect of soil type and time on water extractable phosphorus (WEP) averaged across P saturation and gypsum rate.
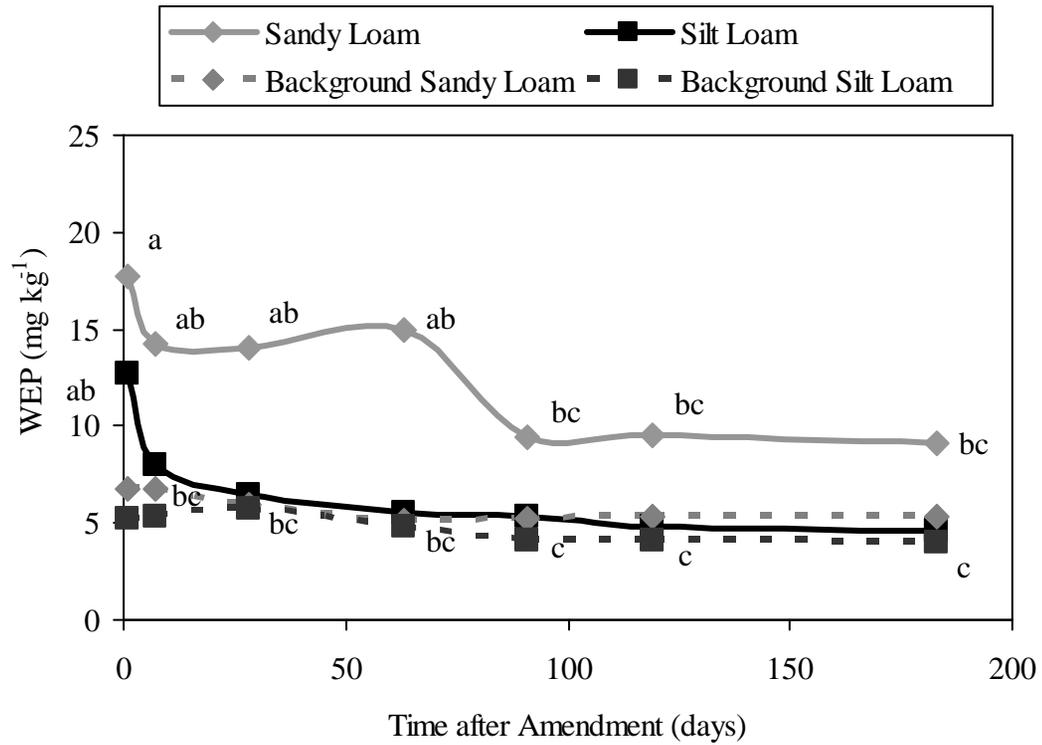
**Figure 10- Effect of soil type and time on Mehlich-3 extractable P (M3-P) averaged across P saturation and gypsum rate.**
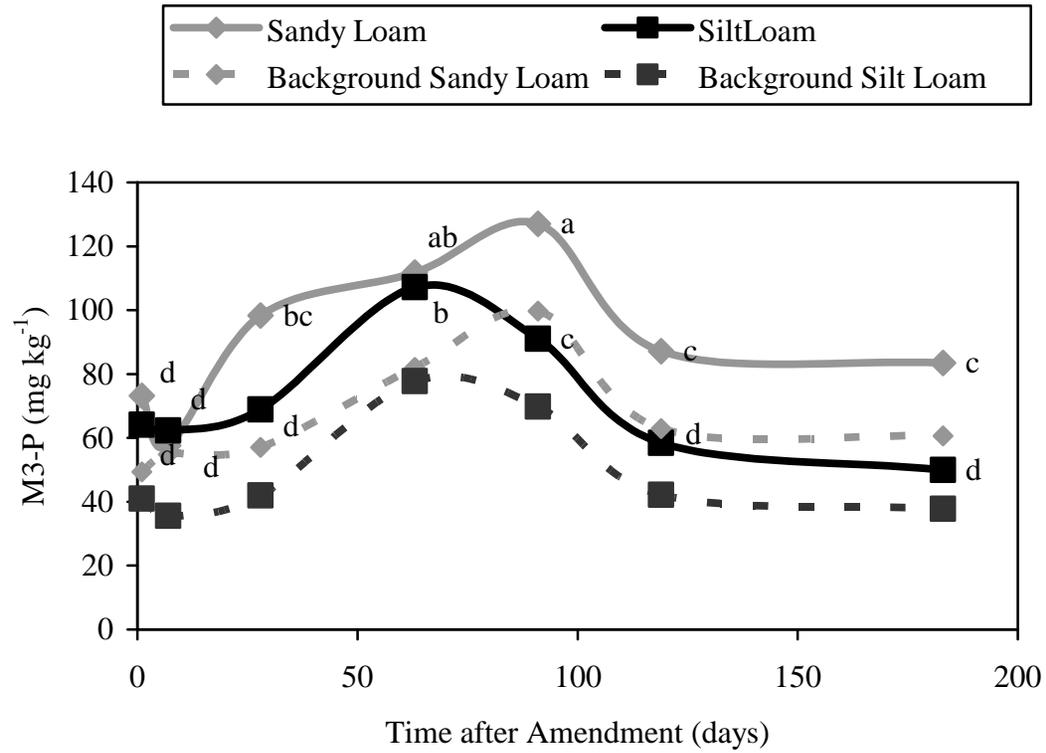
Figure 11- Effect of soil type on chemically defined P fractions in soil averaged over all dates.
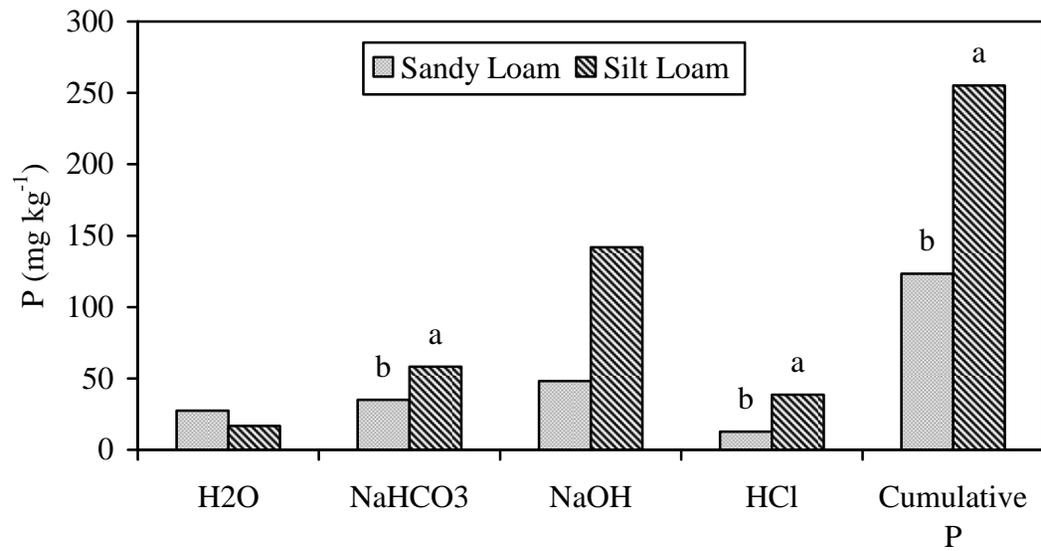
*Statistical significance can only be shown within each extraction type, not between extractants

Figure 12- Effect of sampling date on chemically defined phosphorus fractions averaged across soil type, gypsum rate, and P saturation.
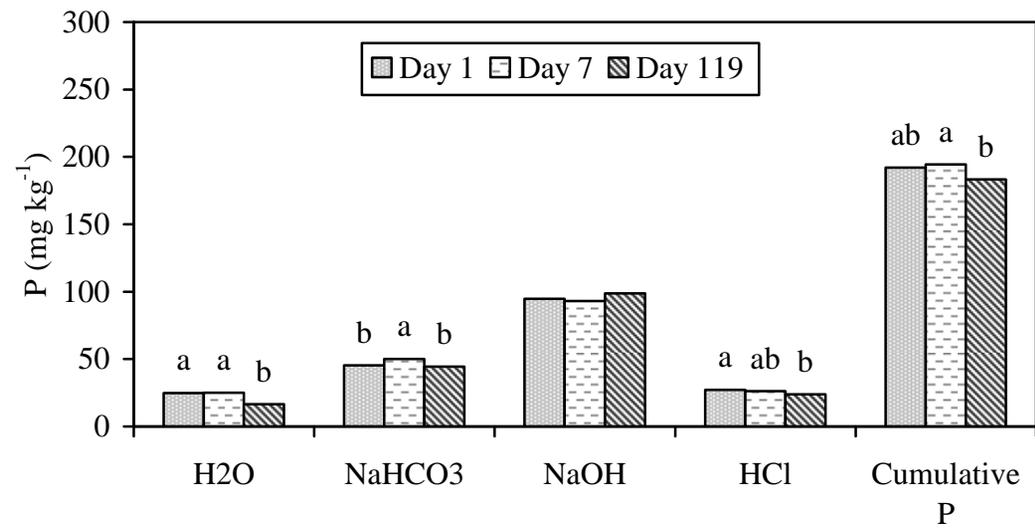
*Statistical significance can only be shown within each extraction type, not between extractants

**Figure 13- Effect of soil type and time on total soil P averaged across P saturation and gypsum rate.**
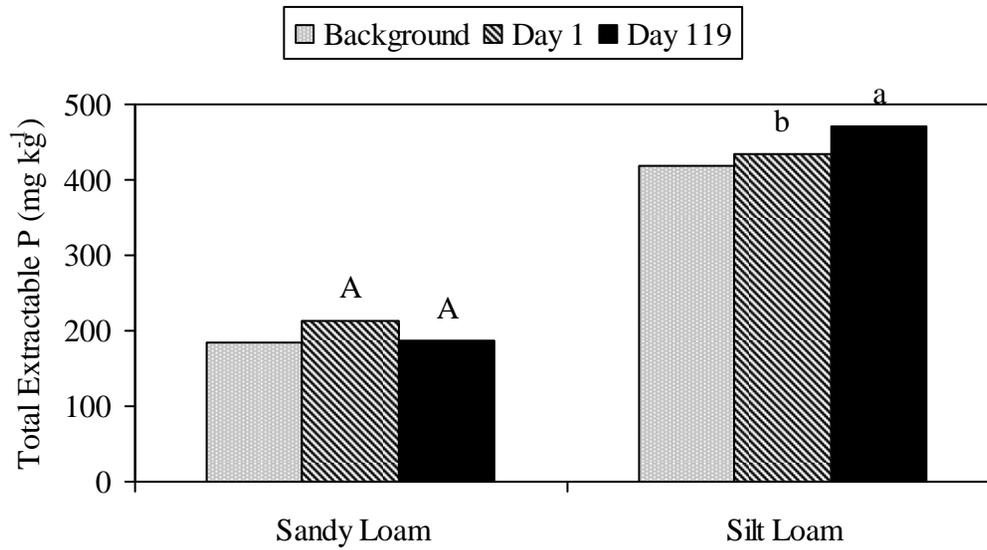
Figure 14- Relationship of EPA 200.2 vs. cumulative P results determined through sequential fractionation procedure.
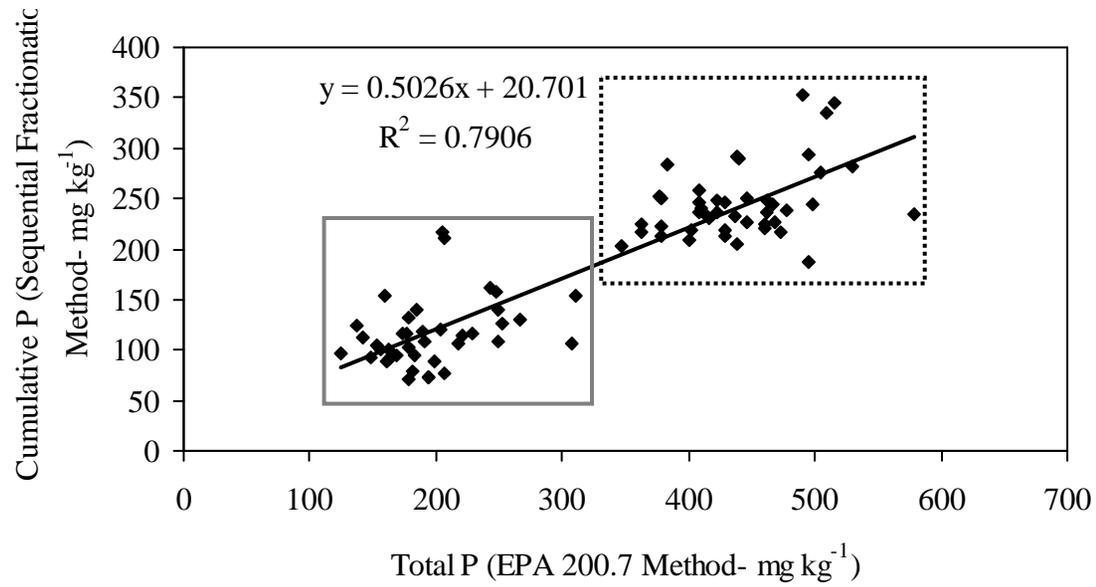
*Solid box indicates Sandy Loam samples; dashed box indicates Silt Loam samples

Appendix A

Inorganic Nitrogen

Nitrate and ammonia are other important soil fertility considerations. Due to large background differences in the soils, soils were considered separately when conducting statistical analysis. Within the silt loam samples, there was an interaction between gypsum rate and P saturation rate therefore the main effects are discussed averaged across day (Fig. A-1). Day was not included in any interactions, and day was found to be a significant factor in both soil types, therefore day is averaged across gypsum rate, p saturation, and soil type (Table A-1).

Table A-1 shows a relatively steady increase in soil nitrate for both soil types. Within columns, means followed by the same letter are not significantly different. Background soil nitrate levels are included for comparisons, but are not included in the statistical analysis. The sandy loam sample had a relatively steady increase, with the day 91, 119, and 183 samples not being significantly different from one another. The silt loam shows a similar trend, with slightly higher day 1 samples, than day 28 and 63, but day 183 is higher than all other samples. The silt loam soils also have an interaction between gypsum rate and level of P saturation (Fig. A-1). The LP-HG combination (131.13 mg L^{-1}) is higher than the LP-LG combination (118.68 mg L^{-1}). The HP-LG and HP-HG combinations are not significantly different from all other combinations (128.35 mg L^{-1} and 126.31 mg L^{-1} respectively). The background soils (receiving no treatment and not incubated) had a nitrate value of 153.50 mg L^{-1}.

Ammonia measurements can indicate changes in microbial activity, mineralization, or temperature within soils and other ecosystems. Once again, due to large background differences in soils, soils were considered separately. The combination of gypsum rate and sampling rate was found to be statistically significant, and therefore values are considered across all P saturation rates. Values are displayed in table A-2, and statistical significance can only be shown within each soil type, but not across soil types. Background soil values are also included for comparison, but are not included in the statistical analysis.

The ammonia data shows an interesting trend with a spike in the ammonia amount at day 91. This indicates a spike in microbial activity. Although the temperature was to remain constant over time, the temperature was not logged or recorded on a constant basis, and there could have been a spike in temperature within the soils or incubators which caused a large increase in microbial activity, and resulting in the spike in amount of ammonia produced. This mimics actual field conditions, and is similar to what happens within temperate soils during spring and summer as they warm up and mineralization and volatilization increases.

pH and EC

pH has been identified as a critical parameter in the regulation of micronutrient ability (Sims, 1986). Due to large background differences in soil pH, for statistical analysis and display purposes, soil types are presented separately. Figs. A-2 and A-3 show the pH trends for each soil type for each treatment combination (P saturation*gypsum rate). The sandy loam soil has a lower background pH and is more acidic than the silt loam soil. The background pH for the sandy loam soil averaged

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across all dates is 4.55 compared to a background pH of 6.17 for the silt loam samples (with no treatment applied).

Electrical conductivity (EC) is a measurement of the soluble salts within a soil solution. EC was taken on the samples to determine if differences existed with varying phosphorus saturations and gypsum levels. Both soil types showed a slight spike in the EC (in S m^{-1}) at day 63, and also had a steady increase over time (disregarding day 63 samples). Statistics were not run on the results, and graphs are displayed only to show the trends in soil EC (see figures A-4 and A-5).

CHN Analysis

Carbon

All samples were tested for the carbon content through CHN analysis. The sandy loam soils had a statistically significant interaction between P saturation and day, and the results are displayed in figure A-6. The day 91 high phosphorus sample and day 119 low phosphorus samples are significantly higher than the carbon contents of the day 119 high phosphorus samples and both day 183 samples. All other sample dates (1-63, and low phosphorus day 91) are not significantly different from the other carbon contents.

The silt loam soils had statistically significant carbon contents across different days and gypsum rates, but had no significant interactions. Figure A-7 displays the effect of day on carbon content for the silt loam samples. Day 7 has the highest carbon content and is higher than the day 63 and day 91 carbon contents. The day 183

samples are significantly lower than all other samples, indicating a potential decrease in carbon over time. The carbon content generally decreases over time.

The silt loam also shows differences in carbon content due to differences in gypsum rate. The higher gypsum rate obtains a higher amount of carbon than the low gypsum rate (fig. A-8). One potential explanation is that the addition of calcium can potentially complex with organic matter. This would cause the carbon in the form of organic matter to be more sable, and therefore it would have less of a chance to be oxidized by microbes. The higher gypsum content would have more organic matter and therefore more carbon present. This could also serve as an explanation for the decrease in carbon over time, because microbes would be working to break down the carbon and release it as carbon dioxide, which would no longer be measured within the soil.

Nitrogen

The nitrogen data from the CHN analysis was similar to the nitrate and ammonia data extracted using the KCl method and analyzed using the molybdate blue method. As shown in figs. A-9 and A-10 both soil types show a general decrease in the amount of nitrogen present and then a spike in the day 91 and 119 samples. This spike in the nitrogen is likely due to an incubator issue. The incubator temperatures were not logged, but were expected to remain at $25^oC \pm 1^oC$. However, if a power outage, or temperature fluctuation were to occur within all the incubators, then there would likely be a spike in nitrogen due to increased microbial activity or increased or decreased volatilization. Without this data, no conclusions can be drawn, except for

the spike in nitrogen at days 91 and 119. The CHN data does support the nitrate and

ammonia data discussed earlier.

Table A-1- Nitrate data for incubation soils.

| Day after Start | Nitrate | |
	Sandy Loam	Silt Loam
	------------- mg N L^{-1} -------------	
Background	23.60	153.50
Day 1	23.33 c	125.88 BC
Day 7	22.05 c	115.12 CD
Day 28	34.23 b	98.46 D
Day 63	38.38 b	97.12 D
Day 91	60.19 a	143.94 B
Day 119	59.90 a	144.19 B
Day 183	63.81 a	158.13 A

*Statistical significance can only be shown within each soil type, background values not included in comparison

Table A-2- Ammonia data for incubation soils- Results for gypsum rate and sampling date for each soil type.

Day after Start	Sandy Loam		Silt Loam	
	Low Gypsum	High Gypsum	Low Gypsum	High Gypsum
	------------------------------ mg N L^{-1} ------------------------------			
Background	10.54		4.49	
Day 1	13.28 b	11.37 b	7.26 C	7.38 C
Day 7	9.23 bc	7.75 bc	3.49 D	3.18 D
Day 28	8.36 bc	6.35 c	7.40 C	5.80 C
Day 63	5.58 c	4.33 c	4.30 CD	3.71 C
Day 91	12.5 b	28.93 a	14.67 B	28.79 A
Day 119	5.50 c	3.86 c	3.78 CD	5.09 CD
Day 183	5.47 c	5.55 c	7.43 C	7.52 C

*Statistical significance can only be shown within each soil type, background values not included in comparison

Figure A-1. Nitrate data for silt loam soil- Combination of gypsum rate and P saturation averaged across sampling date (time).
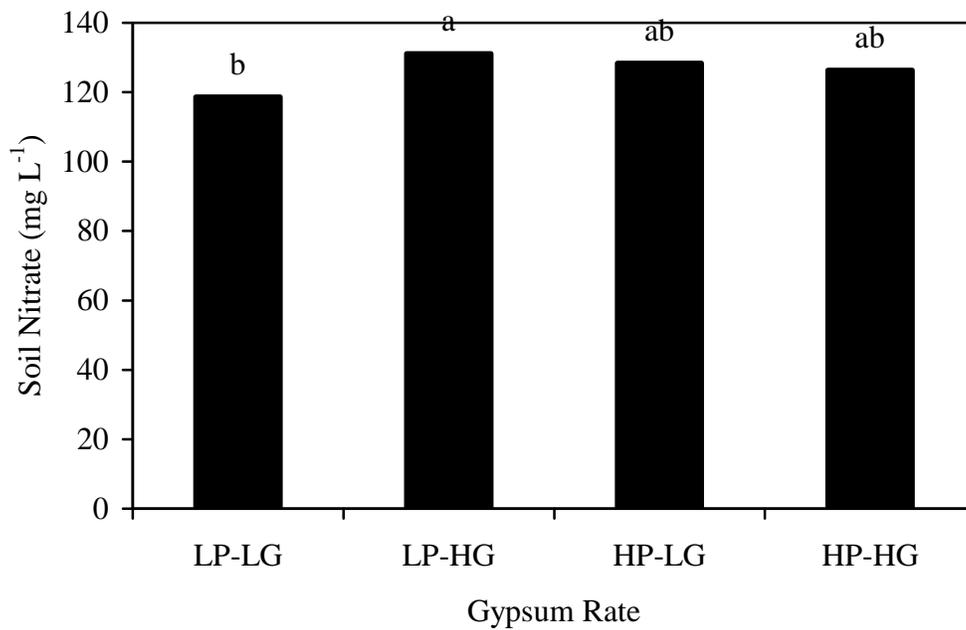
**Figure A-2. Changes in soil pH over time for the sandy loam soil.**
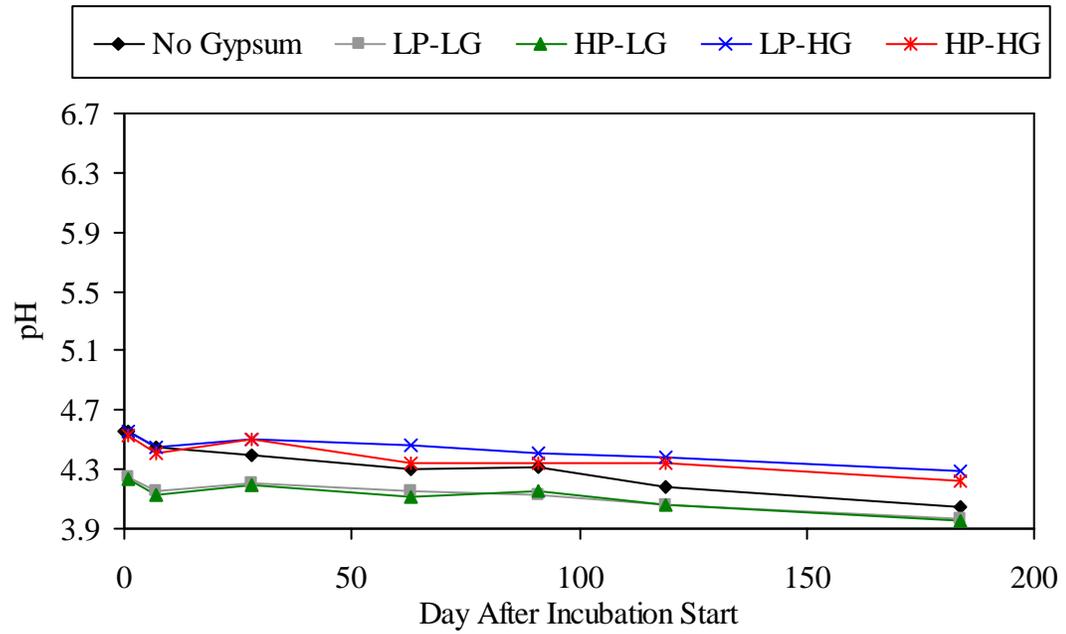
**Figure A-3- Changes in soil pH over time for the silt loam soil.**
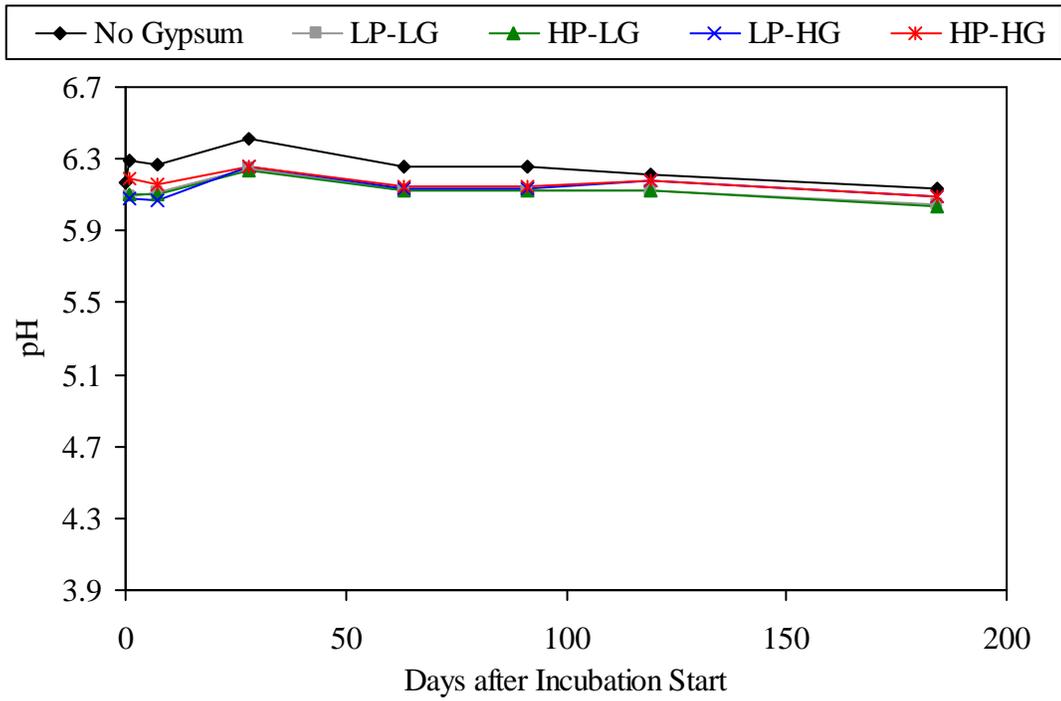
**Figure A-4- Changes in soil EC over time for the sandy loam soil.**
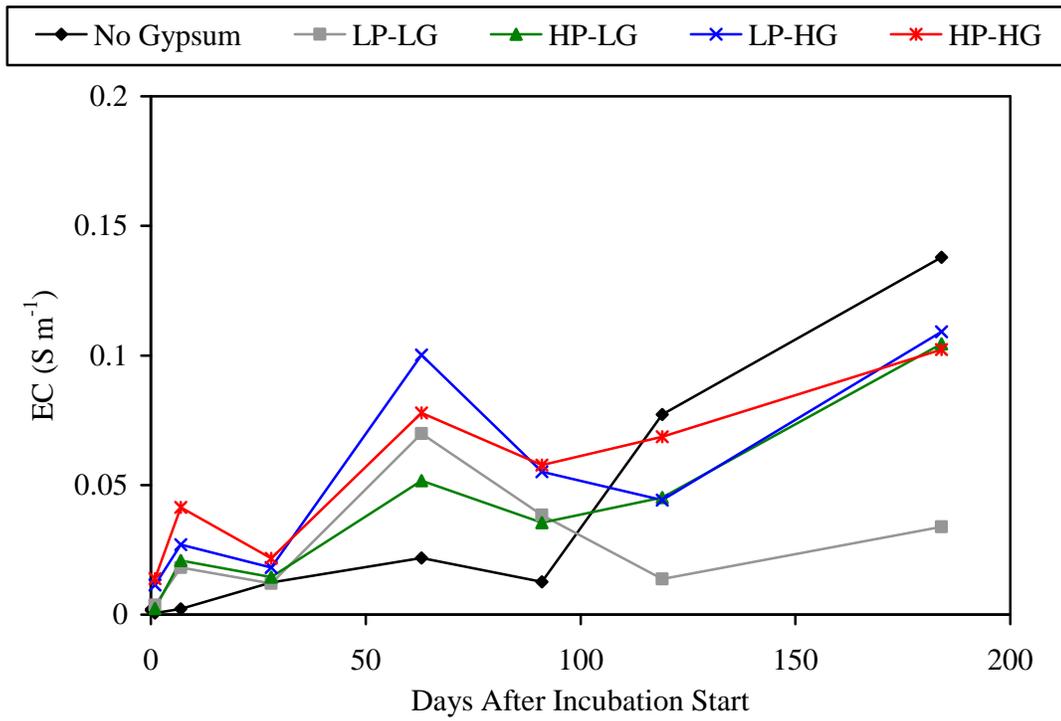
**Figure A-5- Changes in soil EC over time for the silt loam soil.**
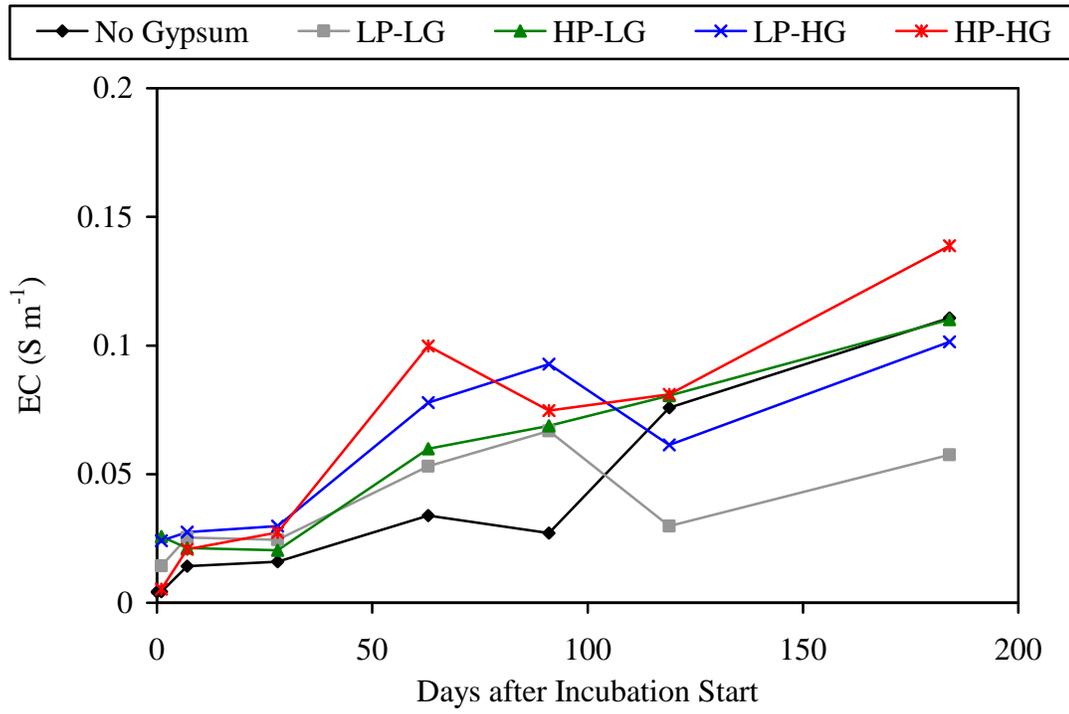
Figure A-6- Effect of P Saturation and sampling date on carbon content for the sandy loam soil.
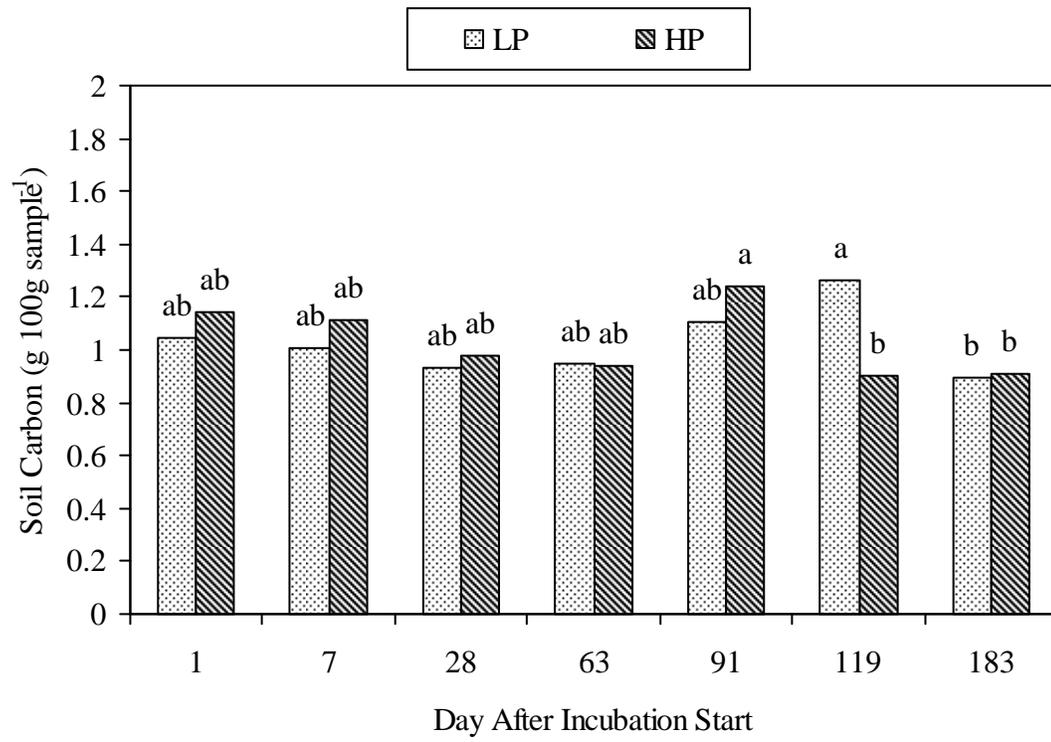
Figure A-7- Effect of day on carbon content averaged across gypsum rate and P saturation for the silt loam soil.
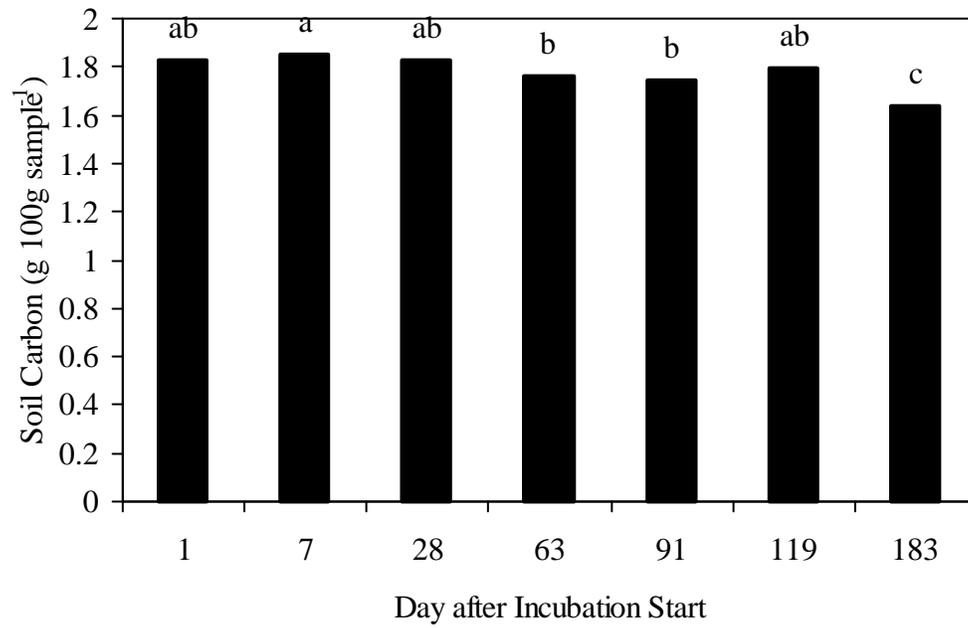
Figure A-8- Effect of gypsum rate on carbon content averaged across P saturation and sampling date for the silt loam soil.
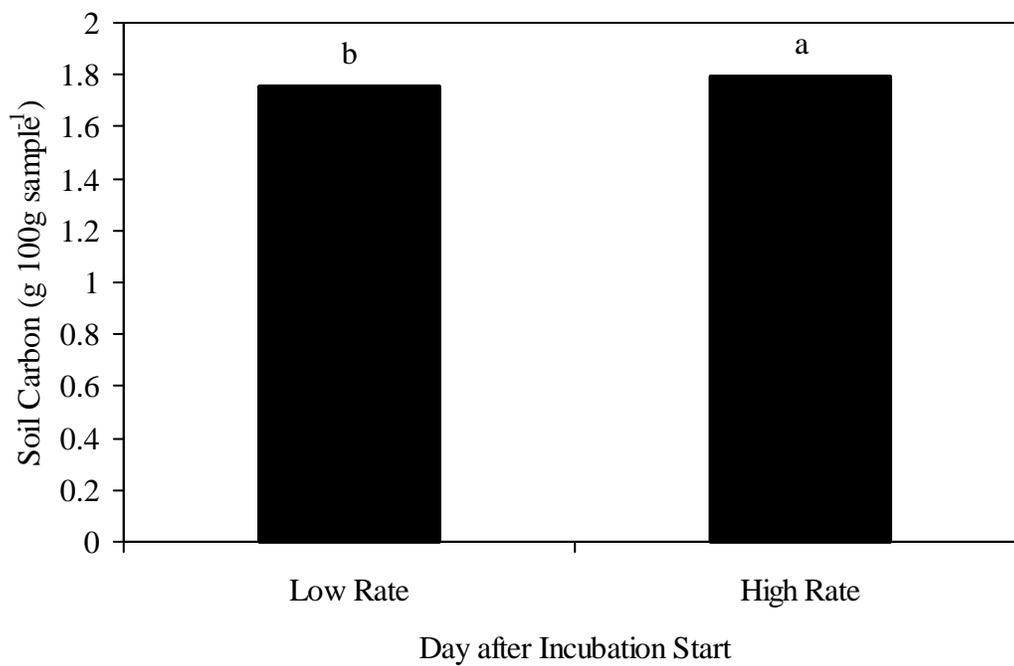
Figure A-9- Effect of day on nitrogen content averaged across P saturation and gypsum rate for the sandy loam soil.
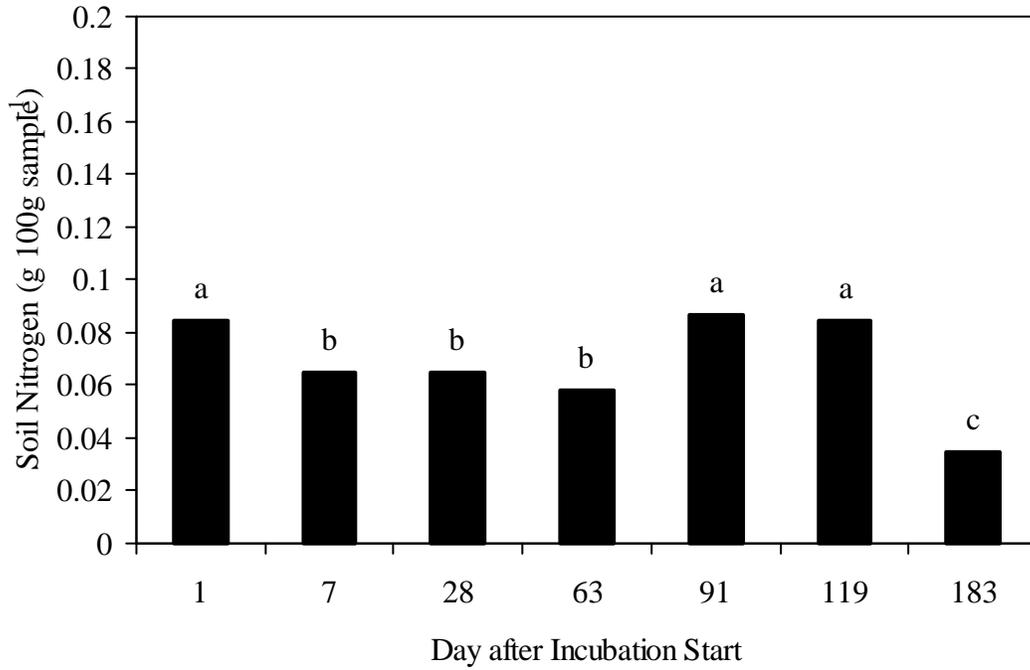
Figure A-10- Effect of day on nitrogen content averaged across P saturation and gypsum rate for the silt loam soil.
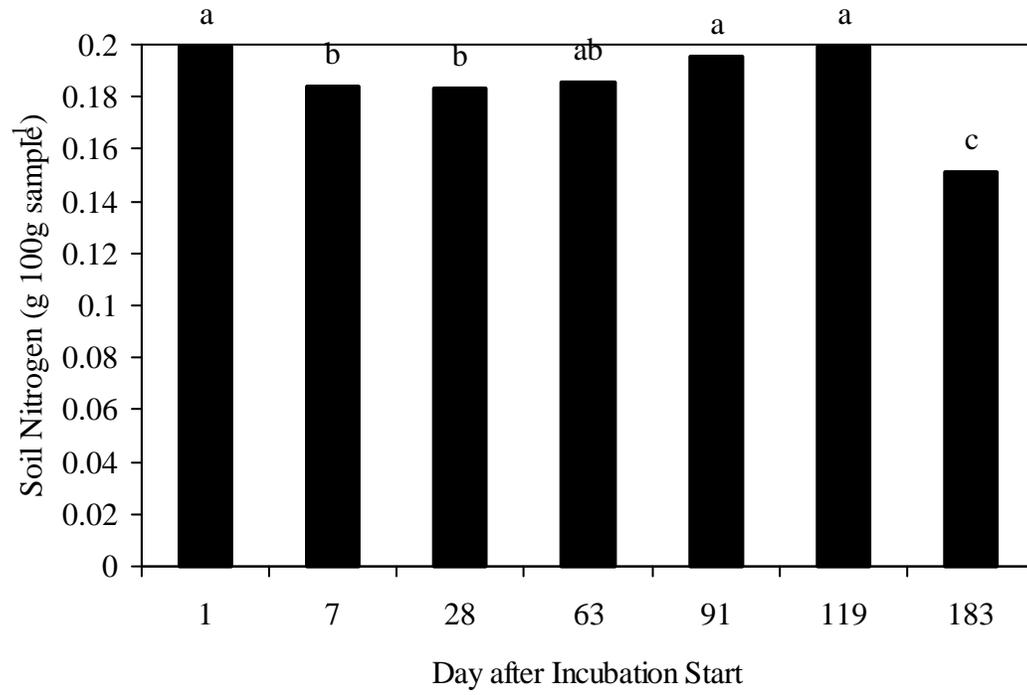
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