

**STRATEGIES FOR MANAGEMENT OF HIGH PHOSPHORUS  
AGRICULTURAL SOILS ON THE DELMARVA PENINSULA**

by

Zhixuan Qin

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Plant and Soil Sciences

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## ABSTRACT

Historical application of poultry litter to Delmarva agricultural soils at nitrogen (N)-based rates resulted in build-up of soil test phosphorus (P) above agronomic optimum levels. These high P “legacy” soils have an increased risk of dissolved P losses in runoff or leachate. Phosphorus losses from these legacy P soils are a concern for water quality in sensitive water bodies. Unfortunately, most of traditional best management practices (BMPs) focus only on controlling particulate P losses or dissolved P losses related to current P applications and are not effective at controlling dissolved P losses from the soil itself. New and innovative BMPs are urgently needed to specifically address the issue of dissolved P losses from legacy soils. The objectives of this paper are to: 1) evaluate changes in P distribution among soil P fractions and P sorption characteristics of agricultural soils following long-term applications of poultry litter and commercial fertilizers; 2) determine the mechanisms of P removal by P sorbing materials (PSMs) used in stormwater P filtrations structures; and 3) evaluate fall silicon (Si) fertilization to enhance soil P availability and uptake by winter wheat from legacy P soils.

We found that long-term application of poultry litter or inorganic fertilizer at above crop removal rates can significantly increase soil test P levels, and build up P concentrations in both labile (extracted by  $\text{H}_2\text{O}$  and  $\text{NaHCO}_3$ ) and recalcitrant soil P pools (extracted by  $\text{NaOH}$  and  $\text{HCl}$ ; Objective 1). The increase in labile soil P will immediately increase the dissolved P losses from legacy sites while the increase in

recalcitrant soil P pool will act as a long-term P source to slowly release P over the time.

Stormwater filtration structures are one of a few existing BMPs that can effectively reduce dissolved P in runoff water. Using synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy technique, we identified various calcium-, iron-, and/or aluminum-associated phosphate in reacted PSMs (Objective 2). Knowing the P speciation of different PSMs enable us to select appropriate materials for efficient P removal in stormwater filtration structures, as well as determine the potential disposal options for spent materials.

We also found that Si fertilization is a promising BMP that can improve early-season soil P availability and reduce the use of starter fertilizer for the growth of winter wheat on high P legacy soils in Delmarva Peninsula (Objective 3). Specifically, the applied Si can compete with phosphate for soil sorption sites and thus increase the solubility of bonded P. However, more research is needed to identify commercially-available Si sources that can be easily accessible by farmers

## **Chapter 1**

### **LITERATURE REVIEW**

#### **1.1 Phosphorus Dynamics in Manured and Fertilized Soils**

##### **1.1.1 Adsorption and Desorption Characteristics of Soil P**

The adsorption and desorption of P by soils are important factors affecting the plant availability of soil P supplies (Borling et al., 2004; Singh et al., 2006) and recommended fertilizer rates (Dhillon et al., 2004). Soils with a high natural P sorption capacity may have reduced P availability, requiring additional fertilizer inputs to maintain adequate crop production. Phosphorus binds to aluminosilicate clays and soil organic matter on edge hydroxyls and/or through bridging cations (e.g., iron [Fe<sup>3+</sup>], aluminum [Al<sup>3+</sup>], and calcium [Ca<sup>2+</sup>]) (Sample et al., 1980). Soluble P is mainly adsorbed by oxides of Fe and Al in acid soils (Ryden et al., 1977) and by Ca carbonate in alkaline soils (Bertrand et al., 2003). Ligand exchange and precipitation are the two major mechanisms by which dissolved P is removed from soil solution by hydrous metal oxides (e.g., Fe and Al oxides) in soils (Sample et al., 1980). Soil P adsorption/desorption varies with soil pH, ionic strength, and concentration of competitive ions (Polyzopoulos et al., 1985).

Isotherm experiments are commonly used to study P adsorption and desorption in soils (Zhang et al., 2009). It is typically conducted through batch experiments where soils are equilibrating with a series of P standards with varying concentrations (e.g., 0–50 mg P L<sup>-1</sup>) (Dou et al., 2009). The amount of P sorbed or desorbed can then be

estimated as the difference between the concentration of P standards and equilibrium P concentration in soil solution, from which the P adsorption and desorption characteristics can be modeled (Dou et al., 2009). Several models have been proposed to evaluate the P adsorption and desorption dynamics. Langmuir and Freundlich are the two main models used to fit batch sorption data and describe P adsorption to soils (Graetz and Nair, 2000; Villapando and Graetz, 2001; Barrow, 2008). The Langmuir model is most commonly used in environment-related P adsorption studies because it can estimate the soil maximum capacity to sorb P ( $S_{\max}$ ) and the P bonding energy constant ( $k$ ) (Graetz and Nair, 2000; Villapando and Graetz, 2001, Zhang et al., 2009). The Langmuir model can be presented as:

$$S = \frac{S_{\max} \times k \times C}{1 + (k \times C)}$$

where  $S$  ( $\text{mg kg}^{-1}$ ) is the total amount of P sorbed in soils per unit mass of soil,  $S_{\max}$  ( $\text{mg kg}^{-1}$ ) is maximum soil capacity,  $k$  ( $\text{L mg}^{-1}$ ) is bonding energy constant,  $C$  ( $\text{mg L}^{-1}$ ) is the equilibrium P concentration in solution (Zhang et al., 2009). The fitting of  $S_{\max}$  and  $k$  allows estimation of soil buffering capacity and the potential for soil P loss (Zhang et al., 2009). In comparison, Freundlich model can be presented as:

$$\log S = \log K_f + \frac{1}{n} \times \log C$$

where  $S$  ( $\text{mg kg}^{-1}$ ) is the total amount of P sorbed in soils per unit mass of soil,  $K_f$  ( $\text{L kg}^{-1}$ ) is the rate of P sorption,  $n$  is the slope parameter,  $C$  ( $\text{mg L}^{-1}$ ) is the equilibrium P (Toor and Sims, 2015). The  $K_f$  parameter is mostly used to provide an estimation of the rate of soil P sorption.

Phosphorus desorption kinetics is first estimated using anion exchange resin and/or anionic extractant to understand the availability of soil P to plant roots

(Sharpley et al., 1981). With increasing environmental concern on P release from agricultural soils to overland flow and runoff waters, recent P desorption characteristics are typically estimated by reacting soils with no P solution (e.g., water, 0.01 M CaCl<sub>2</sub>) and then measuring equilibrium P concentration (Sharpley et al., 1981; Vadas and Sims, 2002; Dou et al., 2009). The quantity of P desorption is largely affected by the time allowed for desorption and the water (solution)/soil ratio during desorption (Barrow, 1979). In most cases, soil P desorption pattern is best described by exponential or logarithmic equations (Vadas and Sims, 2002). It is also commonly observed that P desorption reactions occur very fast at first and then decrease when approaching equilibrium (Vadas and Sims et al., 2002). Sharpley et al. (1981) evaluated P desorption from five major soil types (Paleudalfs, Pellusterts, Udertic and Torrertic, Paleustolls, and Ustochrepts) in Oklahoma and Texas reported by reacting soils with different water/soil ratios (10:1–1000:1) at 25°C for 5 to 180 min, and proposed a simplified P desorption model:

$$P_d = K \times P_o \times t^\alpha \times W^\beta$$

where  $P_d$  (mg kg<sup>-1</sup>) is the amount of P desorbed in time  $t$  (min), at a water/soil ratio  $W$  (mL g<sup>-1</sup>),  $P_o$  (mg kg<sup>-1</sup>) is the initial amount of desorbable P in soil, and  $K$ ,  $\alpha$ ,  $\beta$  are empirical constants for a specific soil (Sharpley et al., 1981). Phosphorus desorption can also be fitted by linearized Freundlich equilibrium model (Sparks, 1995) after reacting soil successively with certain amount of water (e.g., 3g soil with 30 ml distilled water) for several times (Hooda et al., 2000):

$$\log X_d = \log K + \frac{1}{n} \times \log C$$

where  $X_d$  (mg kg<sup>-1</sup>) is the amount of P desorbed,  $\log K$  is indicative of the number of sorption sites,  $1/n$  is related to the bonding energy of specific soil,  $C$  (mg L<sup>-1</sup>) is

equilibrium concentration in solution (Hooda et al., 2000). Other studies evaluated P adsorption-desorption characteristics together and used soils from adsorption experiments to react with no P solution, from which the relationship between adsorbed and desorbed P can be developed (Reddy et al., 1980; Li et al., 2007).

Repeated applications of manure or fertilizers at P rates that exceed crop removal may decrease the availability of sorption sites, which leads to decreased soil P adsorption capacity and increased soil P desorption capacity (Borling et al., 2004; Singh et al., 2006; Jiao et al., 2007; Dou et al., 2009). Singh et al. (2006) evaluated the adsorption-desorption behavior of a Typic Ustochrept soil (maize-wheat-cowpea rotation) with continuous farm yard manure application over 32 years at a manure rate of  $10 \text{ t ha}^{-1} \text{ yr}^{-1}$  in Ludhiana, India. The authors indicated that unfertilized soils exhibited a  $S_{\text{max}}$  of  $182 \mu\text{g g}^{-1}$ , while soils receiving farm yard manure exhibited  $S_{\text{max}}$  of approximately  $88 \mu\text{g g}^{-1}$  when fitted with Langmuir model (Singh et al., 2006). In addition, 71–82% less P was desorbed from the unfertilized control soil compared to soils receiving long-term application of manure. This reduction in P sorption capacity was mainly attributed to fewer available P exchange sites (e.g., Fe and Al oxides) after 32 years of continuous P application.

Similarly, Dou et al. (2009) showed that two Pennsylvania soils (Bucks and Chester series; both described as mesic Typic Hapludults) that received manure (dairy, poultry, swine manure or spent mushroom compost) at P rate of  $120 \text{ kg ha}^{-1} \text{ yr}^{-1}$  for 10 years had desorbed 3- to 30-fold greater P than unamended soils. The desorbed P concentrations after equilibrating manured soils with  $0.01 \text{ M CaCl}_2$  containing  $0 \text{ mg L}^{-1}$  P for 24 h were mostly more than 10 times of the critical environmental concentration thresholds ( $0.01\text{--}0.076 \text{ mg P L}^{-1}$ ) for flowing waters (Dou et al., 2009).

The authors attributed the enhanced P desorption from manured soils to the elevated soil P concentrations and availability following repeated manure applications.

However, manure amended soil exhibited higher P sorption capacity ( $S_{\max}$  of 1404 and 1420 mg kg<sup>-1</sup> for Bucks and Chester when fitted with Langmuir model, respectively) than unamended soils ( $S_{\max}$  of 503 and 625 mg kg<sup>-1</sup> for Bucks and Chester, respectively), which did not fit the conventional expectation. The authors suggested that other models may be needed to better describe P sorption dynamics for high P soils (e.g., manure treated soils) due to the potential P precipitation that influences P retention in addition to traditional Al and Fe sorption mechanism (Dou et al., 2009).

Moreover, long-term application of manures can further decrease soil P adsorption capacity and increase soil P desorption when compared with application of inorganic fertilizers (Singh et al., 2006; Jiao et al., 2007). For example, Jiao et al. (2007) observed a 25–31 % reduction of P adsorption in a sandy loam soil (frigid Typic Endoaquent) receiving composted cattle manure compared with soils receiving inorganic fertilizer (triple superphosphate) at an annual equivalent plant-available P rate of 45 kg ha<sup>-1</sup> for four years. One possible explanation for reduced P sorption capacity is increased accumulation of negatively charged organic acids in manure amended soils, which may compete with orthophosphates and occupy available P sorption sites (e.g., Fe and Al oxides) (Singh et al., 2006; Jiao et al., 2007). As a result, manure application will decrease P adsorption capacity more than commercial fertilizers (Singh et al., 2006; Jiao et al., 2007). Similarly, soils receiving manure had a higher potential to release adsorbed P when compared with soils receiving commercial fertilizer due to the competition for sorption site with organic acids in manure amended soils (Jiao et al., 2007).

### **1.1.2 Phosphorus Distribution among Operational Soil Pools**

Soil P is generally categorized into three types: solution P, labile (or active) P, and stable (or fixed) P (Busman et al., 2002). Solution P is a very small soil P pool, but is the P fraction that is directly available for plant uptake and lost during runoff or leaching events. Soluble P transfers from soils to sensitive water bodies during runoff and leaching events may result in immediate stimulation of the growth of aquatic species (Busman et al., 2002). Labile P is P that is loosely bound to soil mineral surfaces; labile P can quickly replenish the solution P pool as it is depleted (Busman et al., 2002). Solution and labile P together constitute the major source of plant available P (Busman et al., 2002). Lastly, stable P represents the majority of soil P species (e.g., insoluble organic P) that are generally insoluble or slowly soluble and considered unavailable to plants in the near term (Busman et al., 2002).

#### **1.1.2.1 Soil Test P (STP)**

Various extraction methods are now available to operationally define soil P pools and estimate soil P content. Typically, these methods involve reacting soils with a specific reagent for a given period of time and subsequently analyzing the P content of the extract. Agronomic soil tests (e.g., Bray-1, Mehlich-1 and-3, Olsen) are historically developed to identify soils with a potential P deficiency (with respect to plant growth or crop yield) and extract soil P from “pools” that are available for plant uptake over a growing season (Kumaragamage et al., 2006; Sims et al., 2000). Those agronomic tests were developed regionally to account for variable soil conditions (e.g., soil pH, organic matter, etc.). For example, Olsen P test was developed to extract P from calcareous, alkaline, and neutral soils using 0.5 M sodium bicarbonate ( $\text{NaHCO}_3$ ) at a pH of 8.5 (Olsen et al., 1954). Mehlich first introduced a combination

of HCl and H<sub>2</sub>SO<sub>4</sub> acids (Mehlich-1) to extract soil P for north-central region of U.S. (Mehlich et al., 1953), and later developed a multi-element extractant (Mehlich-3) to remove P and other elements in acid and neutral soils using a combination of acids (acetic and nitric acids), salts (ammonium fluoride and ammonium nitrate), and the chelating agent ethylenediaminetetraacetic acid (Mehlich-3, 1984). Bray-1 soil test was introduced to remove easily acid-soluble P forms (largely Al- and Fe- phosphates) using a combination of HCl and NH<sub>4</sub>F (Bray and Kurtz, 1945). Those agronomic soil tests haven been extensively used to determine whether soil P is enough for crop growth and make recommendations for proper fertilization rates based on years of multi-site, multi-year field studies that correlate STP with crop yields (Sims, 1998b). However, management practices based on agronomic soil tests today can no longer exclusively focus on soil fertility and productivity with increasing concerns for the role of agricultural P losses in the eutrophication of surface waters (Sims, 1998b). As a result, agronomic soil P testing has been used, either alone or as a component of multi-parameter field indexes (e.g., degree of P saturation) and watershed-scale nutrient-transport models (e.g., P index), to estimate the potential environmental risk of agricultural P to water quality (Breeuwsma et al., 1995; Pote et al., 1996; Sims, 1998a; Sims et al., 2000). For example, McDowell and Sharpley (2001) investigated P release from soils to surface runoff (collected from runoff box placed at 5% slope; artificial rainfall at 50 mm h<sup>-1</sup> for 30 min) and subsurface drainage (collected from lysimeters in response to artificial rainfall of 10 mm h<sup>-1</sup> for 30 min) on a Denbigh silt loam (Dystrudept) from Devon, U.K. and Alvin (Fragiaquult), Berkds (Dystrochrept), Calvin (Dystrochrept), and Watson (Fragiudult) soils series from Pennsylvania. The results indicated that the concentration of dissolved reactive P (DRP) in drainage

water from lysimeters were significantly correlated with STP (Olsen-P and Mehlich-3 P for U.K. and Pennsylvania soil respectively) for Denbigh, Calvin, and Watson soil ( $r^2=0.42-0.93$ ). A changing point of 193 mg kg<sup>-1</sup> Mehlich-3 P was observed for Alvira and Berks, above which DRP in drainage water increased significantly. Similarly, DRP in surface runoff was significantly correlated with STP (Olsen-P and Mehlich-3 P for U.K. and Pennsylvania soil respectively) for Denbigh, Calvin, and Watson soil ( $r^2=0.62-0.95$ ). A changing point of 185 mg kg<sup>-1</sup> Mehlich-3 P was also observed for Alvira and Berks (McDowell and Sharpley, 2001).

Other soil tests that have been used majorly for environmental purposes were developed to either measure a specific pool of soil P that is environmentally-important or to predict the capacity of soil to retain added P (Gartley and Sims, 1994). Iron oxide-impregnated filter paper strip (Fe-oxide strip) was developed as an innovative approach to estimate plant available P pool (or labile P) in soils (Menon et al., 1990; Gartley and Sims, 1994). Unlike traditional soil P tests that use extracting solutions, the Fe-oxide strip paper does not react with soil. Instead, it acts only as an infinite sink and sorbs/retains the P entering the soil solution (Menon et al., 1990). As a result, the Fe-oxide strip test are less sensitive to soil type than other P tests, and can be used in acid, alkaline, or calcareous soils (Menon et al., 1990). Deionized water or weak salt solutions are commonly used to extract the most soluble and labile “forms” of soil P (i.e., solution P) (McCray et al., 2012). This test was developed to address the concern of the potential nonpoint soil P pollution since rainstorms and subsequent runoff events can transport dissolved reactive P and particulate P in soil to nearby waterways (Pote et al., 1996; Fuhrman et al., 2005). Soil test on solution P is probably the most appropriate environmental estimator of P contents in runoff compared with other

agronomic soil tests that developed for crop production (Pote et al., 1996). Although solution P test can help estimate the soluble P that is directly available to alga and other aquatic plants and thus likely to cause accelerated eutrophication, the P in eroded soil particles may not be uniformly bioavailable to algae and other aquatic plants (Sims, 1998b). As a result, researchers also developed soil tests (e.g., algal-available P) to quantify the relative bioavailability of soil and/or sediment P (Dorich et al., 1985; Sharpley, 1993). But those soil tests on P bioavailability will take much longer time than solution P test or other soil tests due to a higher solution/soil ratio and longer shaking period (e.g., 0.1 M NaOH, 500:1, 16h) (Sims, 1998b). Acid ammonium oxalate extraction (oxalate extraction; e.g., 0.1 M oxalic acid+0.175 M ammonium oxalate) was first developed to dissolve Fe and Al in soil to assist soil horizon identification on Fe-enriched soils (McKeague and Day, 1966), based on which, other researchers developed a concept of degree of P saturation to estimate a soil's potential to release P (Hooda et al., 2000; Nair et al., 2004).

Repeated application of manure to soils at rates that exceed crop P uptake can increase the concentration of water- and weak-acid extractable P and agronomic soil test P concentrations (Buda et al., 2010; Sharpley et al., 2004; 2013). Motavalli and Miles (2002) showed significant accumulation (25–75 mg kg<sup>-1</sup>) of Bray 1-extractable P in a silt loam in Columbia, Missouri following 111 years of dairy/horse manure application to soils at rate of 13.4 Mg ha<sup>-1</sup> y<sup>-1</sup> (dairy manure had about 3.9 g kg<sup>-1</sup> total P; no information for horse manure). In another study, Penn and Sims (2002) reported forms of P in two Delaware soils (Elsinboro silt loam and Woodstown sandy loam) after receiving poultry litter at a rate of EPA3050 P 200 kg ha<sup>-1</sup>. The results showed that manure amended soils had significantly higher water extractable P (WEP; 1.04–

26 mg kg<sup>-1</sup>) and Mehlich-3 P (67–311 mg kg<sup>-1</sup>) for those two soils when compared with unamended controls (0.38–14 and 42–237 mg kg<sup>-1</sup> for WEP and Mehlich-3 P, respectively) (Penn and Sims, 2002). Similarly, Sharpley et al. (2004) reported that manure-amended soils had significantly higher WEP (11–74 mg kg<sup>-1</sup>) and Mehlich-3 P concentrations (82–2840 mg kg<sup>-1</sup>) in soils from New York (6 sites), Oklahoma (8 sites), and Pennsylvania (6 sites) following long-term (10–25 years) manure (dairy, poultry, or swine) addition at annual P rate of 40–200 kg ha<sup>-1</sup> when compared to unamended control soils (0.6–6.0 and 4.0–64 mg kg<sup>-1</sup> for WEP and Mehlich-3 P, respectively). Maguire et al. (2000) also found that biosolids (municipal sewage sludge) addition at average total P rate of 108–249 kg ha<sup>-1</sup> per application (application years and numbers of application varied with sites) significantly increased oxalate-extractable P in topsoils (0–20 cm) of amended areas (589 mg kg<sup>-1</sup>) compared with adjacent unamended areas (296 mg kg<sup>-1</sup>) on 11 farms in Delaware (2), Maryland (5), and Virginia (4).

#### 1.1.2.2 Degree of P Saturation

Degree of P saturation (DPS) is a calculated relationship between soil test extractable P, Fe, and Al (Nair et al., 2004). Soil DPS was first calculated using oxalate extractable P, Fe and Al (Shoumans and Groenendijk, 2000) by the following equation:

$$DPS_{ox} = \frac{P_{ox}}{\alpha \times [Al_{ox} + Fe_{ox}]} \times 100$$

where  $P_{ox}$ ,  $Al_{ox}$ , and  $Fe_{ox}$  are the concentration of oxalate-extractable P, Al, and Fe, respectively in units of mmol kg<sup>-1</sup>, and  $\alpha$  is an empirical factor that compares different soils in relation to P saturation (Nair et al., 2004). Degree of P saturation is commonly

used as an indicator of a soil's potential to release soluble P (Hooda et al., 2000; Nair et al., 2004). The concept is based on the knowledge that soil P sorption is related to the active sorption sites of Al and Fe and thus soil P desorption is affected by how many sorption sites has been occupied by P (Breeuwsma et al., 1995). Several researchers determined the environmental threshold for  $DPS_{ox}$  (specific to region and/or soil type), above which potential soluble P release from soil in leaching and/or runoff events would increase significantly (Breeuwsma et al., 1995; De Smet et al., 1996; Nair et al., 2004). For example, Maguire and Sims (2002) evaluated five Delaware soil series (Fragiudults, Quartzipsamments, Umbraquults, and two Hapludults) and found that P concentration in leachate increased rapidly when  $DPS_{ox}$  reached a changing point of 56%. Similarly, McDowell and Sharpley (2001) also reported change points of 36–56% for the relationship between  $DPS_{ox}$  and leachate P for four silt loams from Pennsylvania. In another study, Pote et al. (1999) showed that DRP concentrations in runoff (estimated from water extractable P) from three Ultisols in Arkansas increased at DPS values  $> \approx 20\text{--}30\%$ . Pautler and Sims (2000) also determined the relationship between  $DPS_{ox}$  and other STP that proposed to measure the potential for P loss by erosion, runoff, and leaching (e.g., soluble P, Fe oxide strip-P) for 127 soils (122 from Delaware and five from Netherlands). The results indicated that soluble and Fe oxide strip-P tended to increase significantly around a  $DPS_{ox}$  value about 30%.

The definition of DPS was later expanded to include other soil tests such as Mehlich-1 and Mehlich-3 extractions due to limited adoption of oxalate extraction by soil test laboratories (Nair and Graetz, 2002; Sims et al., 2002) and non-ideal application of oxalate extraction in calcareous soils (Beauchemin and Simard, 1999).

While several equations are available to calculate DPS, a commonly used equation can be summarized as:

$$\text{DPS} = \frac{\text{ST-P}}{\alpha \times [\text{ST-Al} + \text{ST-Fe}]} \times 100$$

where ST-P, ST-Fe, and ST-Al is soil test extractable P, Fe, and Al respectively in units of mmol kg<sup>-1</sup>;  $\alpha$  is an empirical factor. For example, Maguire and Sims (2002) found that DPS based on Mehlich-3 test correlated closely with DPS based on oxalate test ( $r^2=0.94$ ) in five Delaware soil series (Fragiudults, Quartzipsamments, Umbraquults, and two Hapludults) and the DPS<sub>M3</sub> threshold value for P in leachate is around 23%. Nair (et al., 2004) studied the relationship between WEP and different DPS parameters in Suwanne River basin (dominant soils are Entisols) in Florida. The results indicated that WEP increased significantly when DPS<sub>ox</sub>, DPS<sub>M1</sub>, and DPS<sub>M3</sub> were above 20, 20, and 16% respectively (Nair et al., 2004). In another study, Sims et al. (2002) evaluated the relationship between DPS<sub>M3</sub> and runoff P using a rainfall simulation runoff box method (5% slope, rainfall applied at 7.5 cm h<sup>-1</sup>), and relationship between DPS<sub>M3</sub> and leachate P using undisturbed soil columns (15-cm i.d., 20-cm depth; leached with deionized water for equivalent of 5-mm rainfall) on five Delaware soil (Fragiudults, Quartzipsamments, Umbraquults, and two Hapludults). The results showed that the concentration of DRP in runoff and leachate increased significantly once DPS<sub>M3</sub> values were above 14 and 21% respectively (Sims et al., 2002). Other studies also successfully incorporated soil P sorption index (PSI; determined in one-point isotherm experiment and calculated as P sorbed divided by P concentration at equilibrium in solution) into the equation of DPS (Zheng et al., 2014). Zheng et al. (2014) collected organic (muck) soils from a total of 44 sites with varying chemical and physical properties in Ontario, Canada to test whether different DPS

equations (e.g.,  $STP/(STP+PSI)$  or  $STP/PSI$ ) can be used to predict DRP loss in surface runoff. All soils were analyzed for a series of soil test P (e.g., Olsen P, Bray-1 P, Fe-oxide strip P (FeO-P etc.) and equilibrated with  $75 \text{ mg P L}^{-1}$  solution to determine PSI. Surface runoff box study was conducted to artificially generate surface runoff (box was placed at a 5% slope below a rainfall simulator, which applied rainfall at  $75 \text{ mm h}^{-1}$ ) from those soils and runoff water was analyzed for DRP (Zheng et al., 2014). The result indicated that the flow-weighted mean runoff DRP concentration (collected during 30 min period) was significantly correlated with a lot of DPS equations ( $r^2=0.78-0.88$ ). But DPS expressed as  $Bray1-P/(Bray1-P + PSI)$  and  $FeO-P/(FeO-P + PSI)$  showed the highest correlation ( $r^2=0.86$  and  $0.88$  respectively) and thus can be recommended as good environmental risk predictor for surface runoff DRP from organic soils (Zheng et al., 2014).

Similar to trends in STP, soil DPS tends to increase following repeated applications of manure beyond plant needs, indicating an increase in the potential for soils to release P to the environment (Nair and Graetz, 2002; Butler and Coale, 2005; Dou et al., 2009). Nair and Graetz (2002) evaluated the effects of manure addition on P saturation in South Florida Spodosols. Soils that were heavily impacted by manure (i.e., used as the feeding and holding areas for cattle) had higher DPS (expressed as the percentage of Mehlich-1 extractable P to the sum of oxalate-extractable Fe and Al; average = 44.7%) than native pasture soils (average = 2.08%) (Nair and Graetz, 2002). Correspondingly, WEP extracted from these Spodosols increased with increasing DPS, suggesting that soils heavily impacted by manure also had a higher potential to release solution P during runoff or leaching events (Nair and Graetz, 2002). Similarly, Dou et al. (2009) compared  $DPS_{ox}$  in soils collected from 10 agricultural fields in PA

that received manure (dairy, poultry, swine manure) or spent mushroom compost for more than eight years with  $DPS_{ox}$  in unamended field soils. The authors found that manure amended soils had much higher  $DPS_{ox}$  values (80–90%) than untreated soils (11–30%). The application of manure significantly increased the concentration of inorganic orthophosphate in soil (79–93% of total P by microwave-assisted acid digestion) compared with unamended soils (33–71% of total P). With data from four locations in Mid-Atlantic Coastal Plain in Maryland, Butler and Coale (2005) also indicated that repeated application of manure (dairy or broiler manure; total P application of 400–1,600 kg ha<sup>-1</sup>) over four years at four locations in MD led to an increase in  $DPS_{ox}$  in the surface soils (0–15 cm) to levels above 25%, which was reported to be the local environmental threshold. The authors concluded that repeated applications of P in manure could overwhelm the soil P sorption capacity, which could increase the potential of P solubilization and P loss during runoff or leachate events (Butler and Coale, 2005).

### **1.1.2.3 Sequential Fractionation**

Sequential fractionation methods (Chang and Jackson, 1957; Hedley et al., 1982; Kuo, 1996; Sui et al., 1999) are commonly used to separate total soil P into different soil pools (e.g., solution, Al/Fe-P, Ca-P) by sequentially reacting soils with a series of reagents with increasing extracting capacity (Levy and Schilesinger, 1999; Shafqat and Pierzynski, 2010). Each of these fractions can then be analyzed individually for inorganic and organic forms of P (Levy and Schlesinger, 1999). For example, Hedley fraction is one of the most commonly used methods, in which, soils are reacted sequentially with anion-exchange resin, 0.5 M sodium bicarbonate (NaHCO<sub>3</sub>), 1 M sodium hydroxide (NaOH), and 1 M hydrogen chloride (HCl) to

estimate P in the most bioavailable and labile P (highly plant available), P associated with Fe and Al, and P associated with Ca, respectively (Hedley et al., 1982; Qian et al., 2004). Sequential fractionation methods can only provide a general idea about P distribution in various “operational” soil pools because chemical extractants do not target specific chemical forms or species of P. Direct methods, such as synchrotron based X-ray absorption near edge structure (XANES), X-ray powder diffraction (XRD), P-31 nuclear magnetic resonance (P-NMR) etc., are required to identify specific chemical forms of P in soils or other environmental samples; these methods are expensive and have limited access. However, sequential fractionation offers an inexpensive method to estimate P speciation in soils, and, as such these methods are prolific in the literature.

Previous researchers have employed sequential fractionation methods to show that long-term manure application can increase soil P in labile (Qian et al., 2004; Shafqat and Pierzynski, 2010), stable (Shafqat and Pierzynski, 2010), and total soil P (Qian et al., 2004) pools. Shafqat and Pierzynski (2010) reported significant increases in P concentrations in all soil fractions using a modified Hedley method (used FeO-impregnated filter paper instead of anion-exchange resin) in a Kennebec silt loam after eight years of beef manure application at a P rate of 40 kg ha<sup>-1</sup> when compared with an unamended soil. The readily bioavailable P pools (extracted by FeO-impregnated filter paper and NaHCO<sub>3</sub>) had the greatest relative increases in P concentration compared to the control soils (approximately 60, 40, and 10 mg kg<sup>-1</sup> at 0–5, 5–15, 15–30 cm, respectively). In the meantime, the stable P pool (extracted by HCl) also increased significantly by approximately 50 and 20 mg kg<sup>-1</sup> at 0–5 and 5–15 cm, respectively compared with the unamended soil (Shafqat and Pierzynski, 2010). Similarly, Qian et

al. (2004) evaluated P distribution in Saskatchewan soils (loamy textured black chernozem) after five years of swine or cattle manure application at an N rate of 0, 100 (low), 200 (medium), or 400 (high) kg ha<sup>-1</sup> yr<sup>-1</sup>. The authors indicated that total P concentration (hot acid digestible P) in surface soils (0–15 cm) was significantly higher following medium (673 mg kg<sup>-1</sup>) and high (698 mg kg<sup>-1</sup>) rates of cattle manure compared to unamended soils (610 mg kg<sup>-1</sup>). Labile P fractions (resin-P and NaHCO<sub>3</sub>-P) also increased significantly with increasing rate of cattle manure addition. However, the authors reported no significant effect of application of swine manure (at any rate) on soil total or labile P fractions in amended soils; the lack of P increase was attributed to the lower amount of total P added with the swine manure (23–92 kg ha<sup>-1</sup>) compared with cattle manure (155–622 kg ha<sup>-1</sup>) when application rates were based on the same N rate (Qian et al., 2004).

Zhang et al. (2004) suggested that continuous application of P fertilizers can potentially enhance the transformation of plant available P to more recalcitrant P pools. The authors measured STP and completed soil P fractionation of a Ste. Rosalie clay soil in Canada that received commercial P fertilization (both mono-ammonium phosphate and triple super phosphate; hand broadcasted and incorporated to soil shortly before planting each year) to continuous corn for more than 10 years. The results indicated that the increase of total extractable P (the sum of NaHCO<sub>3</sub>-P, NaOH-P, and HCl-P) in plots receiving normal (44 kg P ha<sup>-1</sup> y<sup>-1</sup>) and high (132 kg P ha<sup>-1</sup> y<sup>-1</sup>) fertilizer rates represented 57 and 64% of the added fertilizer P. Among the increases in total extractable P, 75 and 49% increase were found in NaHCO<sub>3</sub>-P in normal and high rates plot respectively. In contrast, of increase in total extractable P, 25 and 53% were found in NaOH-P in plots receiving normal and high rates,

respectively (Zhang et al., 2004). The authors suggested that the P addition at high rate elevated the transformation of more available P pool ( $\text{NaHCO}_3\text{-P}$ ) to relatively more stable P pool ( $\text{NaOH-P}$ ) (Zhang et al., 2004). Similarly, Vu et al. (2008) evaluated P fractionation following 65 years P application (granular single superphosphate applied at 0, 3, 6, 9, or 12 kg P  $\text{ha}^{-1}$   $\text{yr}^{-1}$ ) to a calcareous sandy soil in a Mediterranean climate. The authors showed that residual P (most stable P pool, extracted by hot acid digestion on residue of sequential extraction) increased significantly as P rate increased. The author suspected that the applied P was increasingly precipitated at higher rates of P fertilization and converted to more recalcitrant P pools since other studies showed that applied P was mainly precipitated in highly calcareous soils (Lombi et al., 2004; Vu et al., 2008).

## **1.2 Legacy Phosphorus Dynamics in Phosphorus Drawdown Scenario**

Previous studies have suggested that decades or even longer may take to draw down STP concentrations in “legacy P” soils to concentrations that are more in-line with unfertilized soils (McCollum, 1991; Scharer et al., 2007; Sharpley et al., 2009). For example, McCollum (1991) evaluated changes in STP and crop yields during 8 yrs of active P buildup (1956–1963; broadcast  $\text{P}_2\text{O}_5$  at 0, 10, 20, 40, or 60 kg P  $\text{ha}^{-1}$   $\text{yr}^{-1}$ ) and 26 yr of residual decline (1964–1989; except for P, soil fertility was maintained at near-optimum levels) of a Portsmouth fine sandy loam under a corn-soybean rotation in North Carolina. For each of the P treatments, four levels of initial P (22, 56, 99, or 121  $\text{g m}^{-3}$  Mehlich-1 extractable P) were established by broadcasting different rates of P fertilizers in 1955. The results indicated that, at the lowest initial P level, P application caused a highly significant yearly increase in Mehlich-1 extractable P (1.2–7.4  $\text{g m}^{-3}$   $\text{yr}^{-1}$ ). However, at the highest initial P level, P application caused no

measurable change in Mehlich-1 P. The author believed this is due to analytical anomaly that the acid concentration in the extracting solution was too diluted to extract such large amounts of P from a soil with high organic matter (3.5%; McCollum, 1991). The results also showed that the relationship between extractable P ( $P_s$  ( $\text{g m}^{-3}$ )) with time ( $t$  (yr)) during the residual decline phase was best described by an exponential equation ( $\ln P_s = 4.54474 - 0.09668t$ ), based on which, the author predicted that the same soil with 100–120  $\text{g P m}^{-3}$  will drop to yield-limiting STP levels (Mehlich-1 P  $\leq 20 \text{ g m}^{-3}$ ) in about 14 years (McCollum, 1991). Similarly, Zhang et al. (2004) found a Mehlich-3 P decline at a rate of 3.96  $\text{mg P kg}^{-1} \text{ yr}^{-1}$  following cessation of P fertilization on a Ste. Rosalie clay in Canada. The authors predicted that it would take about 28 years to deplete the 110  $\text{mg P kg}^{-1}$  of soil (built up during a 6 year of high-rate P addition) to base-line levels (Zhang et al., 2004).

In another study, Liu et al. (2014) evaluated legacy P dynamics in a Semiarid Prairie in Saskatchewan, Canada, with P fertilization from 1967–1995 (10  $\text{kg P ha}^{-1} \text{ yr}^{-1}$  as ammonium phosphate) followed by either P fertilization or P cessation (1995–2000). Before the begin of P draw down (1995), average Mehlich-3 extractable P was 70.6 and 20.7  $\text{mg kg}^{-1}$  in surface (0–7.5 cm) and subsurface (7.5–15 cm) soils respectively. From 1995–2000, P cessation significantly reduced Mehlich-3 extractable P in surface soil (from 70.6–48.6  $\text{mg kg}^{-1}$ ; no significant difference in subsurface soil), suggesting crop P uptake depleted plant available P in surface soil when no external P was applied. In contrast, further P application did not significantly increase surface and subsurface soil P from 1995–2000; the applied P was likely removed by crop or sorbed by minerals (Liu et al., 2014). Legacy P in the soil was able to sustain the growth of spring wheat without P addition for 15 years, as

evidenced by the lack of statistical difference in crop yields were found between fertilized and un-fertilized soils. The authors also indicated that wheat depleted the Al- and Ca-phosphate pools preferentially (as measured by Chang and Jackson (1957) sequential fractionation and XANES) compared with the Fe-phosphate pool, which was possibly due to the low solubility of Fe-phosphates (Liu et al., 2014).

The STP concentrations and P transformation that occur under a P draw-down scenario (no or reduced P application) is dependent on factors such as soil type, initial soil P status, and previous fertilization, and cropping history (Zhang et al., 2004; MacDonald et al., 2012). The reduction in STP levels during draw-down may due to reduced P inputs (MacDonald et al., 2012) and conversion of labile P into more recalcitrant forms (Richter et al., 2006). MacDonald et al. (2012) conducted a global meta-analysis to explore the possible factors that affect total (based on differing forms of acid digestion) and labile (mostly based on typical STP extractants that target inorganic readily exchangeable P in soils) P concentrations by analyzing data from 94 studies conducted in areas with a history of croplands, pasture, or forage grasslands following agricultural abandonment (i.e., any change to non-agricultural use, whether permanent or temporary) relative to pre-agricultural or current agriculture levels. The analyses were based on comparison of abandoned agricultural areas to nearby reference sites with no known history of agricultural uses and nearby sites that remained under agricultural use. The land-use legacy effect on soil P was estimated using the natural logarithm of the response ratio at each site ( $X_{ab}/X_{ref}$  and  $X_{ab}/X_{ag}$ , where  $X_{ab}$ ,  $X_{ref}$ , and  $X_{ag}$  is the mean soil P concentration of abandoned agricultural, reference, and current agricultural site respectively; MacDonald et al., 2012). The results showed that soil P content was commonly elevated after agricultural

abandonment compared to reference levels, but reduced compared to soils that still remained under agriculture. Between the abandoned agriculture and reference sites, time since transition, change in pH compared with the reference site, whether or not the site was afforested, clay content, and former land use are five variables that significantly explained differences in labile P; while time since transition, length of the agricultural period, region (e.g., Africa, Europe, North America etc.), maximum sampling depth, former land use, and mean annual temperature were six variables that significantly explained the differences in total P (MacDonald et al., 2012). For example, draw down of labile P pools in soils with a history of cropland typically took a longer period of time than soils with a history of pasture when fertilization ceased; the authors attributed this delay in drawdown to higher P inputs associated with the cropping land use (Fraterrigo et al., 2005; MacDonald et al., 2012). In contrast, reduction in labile P was faster in clayey soils with relatively high P-fixation capacity because applied P potentially precipitated as less available forms in those soils (McCollum, 1991).

Some researchers indicated that the decline of labile soil P pool may due to the soil P transformation from labile pool to more recalcitrant forms (Shelton and Coleman, 1968; Yost et al., 1981). For example, Yost et al. (1981) evaluated soil P dynamics on an Oxisol (Dark Red Latosol) with high P sorbing capacity fertilized at different P application rates (total 140, 280, and 560 kg P ha<sup>-1</sup> in the form of superphosphate during four growing seasons; P applied initially as one broadcast application, or in equal increments as banded application) under corn production in Central Brazil. Application of P was ceased starting from the fifth growing season and soil samples were collected at multiple times thereafter (3, 6, 12, 18, and 30 months

after last P application). The results indicated that the concentration of extractable soil P (by 0.5 M NaHCO<sub>3</sub> and 1 M HCl+0.025 N H<sub>2</sub>SO<sub>4</sub>) declined over time in all treatments ( $r^2 = 0.29-0.66$ ) (Yost et al., 1981). The authors attributed the decrease in extractable P to both plant P uptake and conversion of more soluble Al phosphates to less soluble Fe phosphates, as evidenced by the faster decline of NH<sub>4</sub>F-P (P associated with Al) than the decline of NaOH-P (P associated with Fe) over time (Shelton and Coleman, 1968; Yost et al., 1981). However, Linquist et al. (1997a) evaluated P dynamics using a modified Hedley fractionation to monitor available P in a Kaiku clay soil in Hawaii over four-years in a soybean and maize rotation where P treatments was only applied in the first two years (accumulatively total P at 0, 155, 310, or 930 kg ha<sup>-1</sup> in the form of triple super phosphate). The authors showed that the proportion of applied P that was recovered from each operational soil P (calculated as the difference between each P pool in P added treatments and no P treatment related to total fertilizer P) changed very little throughout the study, suggesting that fertilizer P equilibrated quickly among different operational soil P pools. As a result, the authors suggested that the decline in plant available P in drawdown stage cannot be explained by the conversion of labile P to more recalcitrant forms as suggested by other researchers (Linquist et al., 1997a). Further, Linquist et al. (1997b) also proposed that the decline of labile P during drawdown may result from a diffusion related mechanism, where applied P is first adsorbed on the outside of soil aggregates and then subsequently diffuses into the interior of soil aggregates over time.

In areas of intensive animal production, it is likely not feasible to completely eliminate manure applications, and hence P additions due to reasons like higher price of P fertilizers, benefit of applying organic source of nutrients, and difficulties to

translocate manure to other areas etc. As a result, soil P draw-down is expected to take much longer when P additions are reduced to rates that are at or below crop removal. Zhang et al. (2006) evaluated changes in soil P fractions (modified Hedley fractionation) in a calcareous paddy soil under four-years of rice cropping with different fertilization treatments in China. Decline of P in the unamended soil (P mass balance of -6 to -8 kg ha<sup>-1</sup>) occurred at a rate of 1.0–1.5, 2.3–2.5, and 3.6–3.8 mg kg<sup>-1</sup> yr<sup>-1</sup> for resin-P, NaHCO<sub>3</sub>-P, and NaOH-P fraction, respectively. In contrast, decline of soil P in P amended soils (P mass balance of +8 to +10 kg ha<sup>-1</sup>) occurred at a rate of 0.5–0.7, 0.9–1.2, and 0.6–0.7 mg kg<sup>-1</sup> yr<sup>-1</sup> for resin-P, NaHCO<sub>3</sub>-P, and NaOH-P fraction, respectively (Zhang et al., 2006).

### **1.3 Possible Management Practices to Manage or Mitigate P Level in Legacy Sites**

#### **1.3.1 Failure of Traditional BMPs**

Soils and applied P fertilizers/manures are regarded as two major non-point sources P pollution from agriculture (Lemunyon and Gilbert, 1993). Implementation of BMPs (e.g., managing fertilizer/manure applications) has significantly reduced non-point P pollution from the use of fertilizers/manures and soil P losses as particulate P (Sharpley, 1999; Mulla et al., 2008; Meals et al., 2010; Sharpley et al., 2011).

However, dissolved P can still be released into water bodies from P-enriched soils.

Soils are used regarded as a sink that can accept labile P; but with high P accumulation, soils may instead act as P sources to nearby water bodies (Kleinman et al., 2000; Vadas et al., 2005). For example, Sims et al (2000) compiled STP data and animal production information for 26 counties in Delaware and Maryland; the authors suggested that the enrichment of STP to concentrations that exceed agronomic

optimum (Mhelich-3 P = 50–100 mg kg<sup>-1</sup>) will significantly increase the dissolved P concentrations in runoff. In another study, Vadas et al. (2005) compiled data of STP and dissolved P in runoff from 17 published studies that covered 31 soils with a variety of management conditions; the authors reported a strong positive correlation ( $r^2 = 0.74\text{--}0.97$ ) between STP and dissolved P in runoff. Both studies illustrated the potential role of high-P soils in releasing dissolved reactive P into runoff water.

Unfortunately, traditional BMPs, such as fertilizer management to halt P addition (McCollum, 1991), tillage management to mix surface high-P soils with subsurface soils (Kleinman et al., 2011), conservation tillage to reduce soil erosion (Sharpley et al., 2011) are not effective at controlling dissolved P released from P-enriched soils. For example, conservation tillage can reduce soil erosion and particulate P losses from high P soils, but it may lead to buildup of STP in surface soils (top 5 cm) (Sharpley et al., 2011). Periodic tillage to mix surface high-P soils with subsurface soils reduces the risk of P losses in runoff from long-term no till sites, where P accumulation in the near surface (top 5 cm) is an environmental issue; however, it is only a short-term solution (Kleinman et al., 2011). Some entities recommend banning application of manures and P based commercial fertilizers to high P soils to allow draw-down of STP by crop removal. However, in the Delmarva region, banning manure applications would result in serious waste disposal issues for the region and burden growers by requiring a shift to purchased commercial fertilizers to supply N, K, and other essential plant nutrients. Moreover, researchers suggest that drawdown of STP from “legacy P” soils receiving no further P application to agronomically optimum levels under traditional grain or forage crop rotations would take decades even if manure or fertilizer P applications were P fertilization was to stop

(McCollum, 1991; Coale and Krachtovil, unpublished data). As a result, more research is needed to help develop more effective BMPs that target at managing and controlling dissolved P released from P-enriched legacy soils.

### **1.3.2 Phosphorus Removal with P Sorbing Materials (PSMs)**

#### **1.3.2.1 Concept of PSMs**

A wide range of industrial byproducts, such as steel electric power production, drinking water treatment, metal foundries, mining operations, and fertilizer production have been identified as PSMs (Penn et al., 2007b; Leader et al., 2008). These materials commonly contain a significant amount of Al, Fe, Ca, or magnesium (Mg) that can bind with P (Penn et al., 2007a). Materials like Al sulfate, gypsum (Ca sulfate) and natural or synthetic Al and Fe oxides can also be used as PSMs (Penn et al., 2007a). The literature includes several studies that describe how application of PSMs can reduce soluble P concentrations in soils (Stout et al., 1998) and manures (Staats et al., 2004) and reduce P losses in leachate (Elliot et al., 2002) and runoff from manure-amended soils (DeLaune et al., 2004; Penn and Bryant, 2006). Stout et al. (1998) showed that application of two types of PSM (fluidized bed combustion fly-ash and flue gas desulfurization byproducts) at a rate of 10 g kg<sup>-1</sup> reduced Mehlich-3 P and WEP by 8–13 and 48–71%, respectively when applied to eight soils that were collected from across the United States, representing a wide range of soil P, texture, and organic matter content. The reduction in soil P was likely due to the conversion of readily desorbable soil P to less soluble Ca-, Al-, and/or Fe-associated pools (Stout et al., 1998). In another study, Elliot et al. (2002) monitored P in leachate from greenhouse columns where Bahiagrass (*Paspalum notatum* Flueggé) was planted on

Immokalee soils (sandy, siliceous, hyperthermic arenic Alaquods) amended with triple superphosphate at rate of 224 kg P ha<sup>-1</sup> and Fe-, Al-, and/or Ca-water treatment residuals (WTR) at 56 Mg ha<sup>-1</sup>. The authors showed that leaching of applied P was decreased from 21% of added triplesuperphosphate to 3.5 (Fe-WTR), 2.5 (Ca-WTR), and <1% (Al-WTR) of applied P, respectively, within four months of amendment. Similarly, Penn and Bryant (2006) broadcast different types of PSMs (e.g., gypsum, fly-ash, alum, and water treatment residual) to cattle loafing areas (silt loam) in Pennsylvania where soil Mehlich-3 P concentrations were 400–800 mg kg<sup>-1</sup>. The authors indicated that dissolved P concentrations in runoff were lower (3–98% reduction) from soils amended with PSMs than from unamended soils within one week after application.

Generally, there are three major types of PSMs based on the mechanism for P sorption: 1) sorbed based on Fe/Al mechanism, 2) sorbed based on Ca/Mg mechanism, and 3) sorbed based on both mechanisms (Penn et al., 2011). The sorption capacity of PSMs is affected by the chemical and physical properties of the materials, such as sorbing elements (e.g., Fe, Al, and Ca) and their concentration, specific surface area, porosity, and particle distribution (Richardson and Craft, 1993; Drizo et al., 1999; Lyngsie et al., 2014). Oxides of Fe/Al normally bind P more strongly than Ca-based sorbents; the latter normally have a high desorption (Lyngsie et al., 2014). The sorption capacity of PSMs is also related to the physical structure (i.e., crystalline or amorphous) of bonding element (Leader et al., 2008; Penn et al., 2011). For example, adsorption of P to Fe- or Al-rich materials is greater for materials with amorphous structure when compare with materials having crystalline minerals (Penn et al., 2007a). Moreover, environmental conditions such as pH, buffer capacity, ionic

strength, and common ion effects also play an important role in determining the P sorption capacity of PSMs (Penn and Bryant, 2006; Penn et al., 2011). For example, PSMs that sorb based on Fe/Al mechanism may have reduced sorbing capacity at elevated pH levels (Hieltjes and Lijklema, 1980), while PSMs that based on Ca/Mg mechanism may have reduced sorbing capacity under low pH conditions (Leader et al., 2008). Penn et al. (2011) evaluated the capacity of 6 potential industrially sourced PSMs (e.g., acid mine drainage treatment residuals, water treatment residual, fly ash, bauxite mining residual, and flue gas desulfurization product) to sorb inorganic P from solution. The authors indicated that the Ca/Mg-rich PSMs (e.g., flue gas desulfurization product) were most effective to precipitate P when the metal elements were highly soluble (i.e., not coated or shielded by other minerals from solution) and pH of the materials was maintained around 6.5–7.5; Fe/Al-rich PSMs were more effective to sorb P when the materials are not coated with other minerals and in a low-pH environment and a greater amorphous nature. On the other hand, bauxite mining residual may not be appropriated for use in the environment due to the high soluble sodium, electrical conductivity, and pH that prohibit the sorption of P.

Phosphorus sorbing materials can be surface applied or incorporated into high-P agricultural soils to reduce P solubility (Dayton and Basta, 2005; Silveira et al., 2006) or applied to ditch soils or at the edge-of-stream to bind P before it enters nearby waters (Dayton and Basta, 2005; Penn and Bryant, 2006). In addition, manures can be amended with PSMs to reduce P solubility prior to land application (Staats et al., 2004). Although direct amendment of soils and/or manures with PSMs can significantly reduce dissolved P losses (Stout et al., 1998; DeLaune et al., 2004; Staats et al., 2004), such reductions may be temporary, since P is not actually removed from

the system (Penn and Bryant, 2006). Therefore, researchers have proposed construction of “P removal structures” using PSMs, where P enriched agricultural runoff can be treated before being discharged to surface water bodies; P saturated (spent) PSMs can be recovered and disposed of (Penn et al., 2010). The P removal structure can act as an effective tool to mitigate the release of legacy P in runoff (Penn and Bryant, 2006). For example, Penn et al. (2007b) constructed a P removal structure containing a Fe-rich PSM byproduct in a surface water drainage ditch on Maryland’s Eastern Shore. The authors showed that the ditch filtration structure removed 99% of dissolved P that entered the structure during a single rainfall event lasting nearly 18 h (Penn et al., 2007b). However, the amount of runoff water that can be treated with the P removal structure may be limited since PSMs generally have relatively low hydraulic conductivity (Penn and McGrath, 2011). The selection of proper PSMs is crucial to ensure effective function of P removal structures. To be an efficient sorbent for use in a P removal structure, PSMs need to possess high P bonding affinity, high P sorption capacity, fast bonding kinetics, and low desorption potential (Lyngsie et al., 2014) and must have adequate hydraulic conductivity (Penn and McGrath, 2011).

#### **1.3.2.2 Methodologies to Evaluate PSMs Sorption Capacity and Mechanism**

Generally, batch isotherms and flow-through system are two major ways to evaluate the sorption capacity of PSMs. Traditional batch isotherms are conducted by reacting PSMs with different P concentrations in a gradient to develop the relationship between equilibrium P concentrations and P sorption (Leader et al., 2008). Normally, P sorption will increase with increasing equilibrium P concentration at the beginning, and gradually level off (Leader et al., 2008). By developing this relationship, we can estimate the adsorbing rate of PSMs and the maximum amount of P sorption (Leader

et al., 2008; Penn et al., 2011). To date, a number of researchers have evaluated P sorbing capacity of PSMs using traditional batch isotherms (Penn and Bryant, 2006; Leader et al., 2008; Penn et al., 2011). However, one problem with traditional batch isotherms is that the use of unrealistic high equilibrium P concentrations promotes precipitation of solid P minerals on the surface of PSMs.

The use of a flow-through system more closely mimics field conditions and is more suitable for estimating potential P removal by PSMs used in P removal structures (Stoner et al., 2012). The flow-through system is an improvement over the batch technique because it allows for constant application and replenishment of a fixed, low P concentration solution with fixed with simultaneous removal the soluble reaction products (Stoner et al., 2012). Also, PSMs will remain intact in a flow-through setting while they may be broken up due to excessive shaking in traditional batch isotherm (Drizo et al., 2002). As a result, the batch method may overestimate the P sorbing capacity by increasing the surface area of PSMs (Drizo et al., 2002). Additionally, using flow-through system, we can control the retention time (i.e., the time in which PSMs are in contact with P solutions) to mimic storm conditions, allowing evaluation of the effect of retention time on the performance of P removal structures (Penn and McGrath, 2011; Stoner et al., 2012). Penn and McGrath (2011) used a flow-through approach to predict P sorption into steel slag in a pilot scale system under different retention times (0.5, 3, 6, and 8 min) and P concentrations (0.5, 1, 5, 10, and 15 mg L<sup>-1</sup>). The authors indicated that increasing retention time can increase P removal efficiency, but will reduce the total amount of runoff that can be treated especially under high flow conditions (Penn and McGrath, 2011).

Although batch and flow-through methods have been extensively used in literature to evaluate PSMs, there is still imitation on these methods. The batch and flow-through methods only allow you to evaluate kinetics of P removal by PSMs and also the capacity of PSMs to sorb P. What you can't determine with these methods is the chemical speciation of P on PSMs, which would also suggest the mechanism of P removal (e.g., sorption or precipitation). Instead, synchrotron based X-ray absorption spectroscopy (XAS) can be used to determining P species in mixed environmental samples (Shober et al., 2006), like PSMs. X-ray absorption spectroscopy measures how X-rays are absorbed by the interested element (e.g., P) at energy level near and above the transition of element from core electronic states to the excited electronic states (Yano and Yachandra, 2009). There are two main types of analyses available with XAS: 1) X-ray absorption near-edge structure (XANES; structure in the absorption at energy around the threshold for electron release), and 2) extended X-ray absorption fine structure (EXAFS; structure in the absorption at energies greater than the threshold for electron release). These two analyses provide different structural information about the element of interest. The XANES spectra determine electronic structure and symmetry of element, while the EXAFS spectra determine numbers, types, and bond distances to ligands and neighboring atoms from the absorbing element (Yano and Yachandra, 2009).

X-ray absorption near-edge structure is an effective tool to characterize P forms and species in soils (Beauchemin et al., 2003), biosolids (Shober et al., 2006), and poultry manures and litters (Toor et al., 2005). By comparing XANES spectra of representative standards with the spectrum of unknown samples, we are able to characterize poorly crystalline, amorphous materials, and organic species (Shober et

al., 2006). For example, Beauchemin et al. (2003) was able to identify the different species and relative contribution of P components in three types of soils (loamy Mawcook, clayey Providence, and loamy St-Aimé) using XANES. The authors identified species to include P related to Fe ( $\text{PO}_4^{3-}$  on ferrihydrite and goethite, non-crystalline  $\text{FePO}_4$ , and strengite), P related to Ca (monetite, octa-Ca phosphate, and hydroxyapatite) and other P species (inositol hexametaphosphate, P on Al hydroxide and alumina, and variscite; Beauchemin et al., 2003). Similarly, XANES analysis can be used to identify chemical species of P associated with PSMs after reaction with P solution.

Phosphorus sorbing materials vary in their ability to remove P and will eventually become saturated with P when used as filtering materials. The information on forms of P binding with PSMs can help identify appropriate materials for use in P removal structures in a specific environmental setting (Penn et al., 2011) and evaluate the disposal alternatives of spent PSMs (e.g., recycled P fertilizer). Evehorn et al. (2009) used XANES to identify P speciation of six filter media (Filtralite P, Filtra P, Polonite, Absol, blast furnace slag, and wollastonite) used in on-site wastewater treatment. The authors reported the formation of crystalline calcium phosphates, and to a lesser extent, amorphous calcium phosphate and P associated with Fe or Al, depending on the filter media collected from on-site wastewater treatment systems or reacted in the laboratory. The authors suggested that filter media binding P in an amorphous phosphate would act as a suitable fertilizer due to higher solubility and plant availability of P (Evehorn et al., 2009). While these PSMs were evaluated for use in on-site wastewater treatment, they may also be suitable for use in stormwater filtration structures. Yet, there are many additional types of PSMs available and

information about the P removal mechanisms of these materials is lacking. As a result, more research is needed on molecular level information about P speciation and sorption mechanism when reacted with PSMs so that we can target more effective and locally available PSMs in filtration structures, determine the ability to regenerate PSM sorption capacity (remove or wash off P), or ensure proper disposal of the spent PSMs if they cannot be regenerated.

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## Chapter 2

### SOIL PHOSPHORUS DYNAMICS FOLLOWING LONG-TERM APPLICATION OF FERTILIZER OR MANURES: SOIL PHOSPHORUS SORPTION AND CHEMICAL FRACTIONATION

#### 2.1 Introduction

High intensity poultry production and historical application of poultry litter (PL) at nitrogen (N)-based rates on the Delmarva Peninsula has led to the build-up of soil test phosphorus (P) to concentrations that far exceed agronomic optimum. The risk for dissolved and particulate P losses from “legacy P” soils (i.e., soils with excessive soil test P concentrations as a result of past practices) is well documented due to high concentrations of soluble and desorbable P (Sims et al., 2000). This accumulated or “legacy” P acts as a slow source of dissolved P from agricultural soils during runoff and/or leaching events (McDowell et al., 2002). Runoff and leachate P losses have been implicated in the deterioration of water quality (Sims et al., 1998) in many water bodies, including the Chesapeake Bay. As a result of legacy P, farmers on Delmarva Peninsula are facing increasing pressure to reduce future applications of PL on many agricultural fields due to the need to decrease the risk of P losses from soils.

Researchers have shown that repeated application of manure or P fertilizers to soils at rates that exceed crop P removal can increase the concentration of soil test P (Penn and Sims, 2002; Buda et al., 2010; Sharpley et al., 2004; 2013). For example, Sharpley et al. (2004) found that long-term (10–25 years) application of dairy, poultry, or swine manure significantly increased water extractable P (WEP) and Mehlich-3

extractable P concentrations (M3P) of amended soils compared with unamended controls at 20 field sites across New York (6), Oklahoma (8), and Pennsylvania (6). Long-term manure or P fertilizer additions may also alter soil P dynamics by decreasing the availability of sorption sites, which leads to decreased soil P adsorption capacity and increased soil P desorption capacity (Borling et al., 2004; Singh et al., 2006; Jiao et al., 2007; Dou et al., 2009). For example, Singh et al. (2006) indicated that unfertilized soils exhibited a higher maximum sorption capacity ( $S_{\max}$ ) ( $182 \mu\text{g g}^{-1}$ ) than soils receiving farm yard manure for more than 32 years ( $88 \mu\text{g g}^{-1}$ ); 71–82% less P was desorbed from the unfertilized control soil compared to manured soils. Similarly, Dou et al. (2009) showed that two manure amended Pennsylvania soils had greater potential to release P than unamended soils.

There is evidence to suggest that the equilibrium among soil P pools may shift as soil test P concentrations increase, leading to a redistribution of P among the more labile (i.e., plant available) and more recalcitrant chemical pools (Zhang et al., 2004; Vu et al., 2008). For example, Zhang et al. (2004) reported that continuous application of commercial P fertilizer for 10 years increased the total extractable P of amended soils. Among the increases in total extractable P, a higher percentage was found in the relatively more recalcitrant (extracted by NaOH) soil P pool, and a lower percentage was found in the relatively more labile (extracted by  $\text{NaHCO}_3$ ) soil P pool in soils receiving high rate of P compared with soils receiving moderate P rate. The authors suggested that the repeated P addition at high rate enhanced the transformation of relatively more labile P to relatively more recalcitrant P (Zhang et al., 2004). Similarly, Vu et al. (2008) showed that residual P (most stable P pool) increased significantly with increasing P application rates when commercial P fertilizer was

applied to a calcareous sandy soil in a Mediterranean climate for 65 years. The conversion of labile P into more recalcitrant P pools may affect P availability in soils and require additional P inputs to ensure good crop yield in the long-term, which may potentially sustain P losses in runoff and/or leaching from high P legacy soils. As such, tracking trends in soil test P (STP) alone may not provide the information needed to properly manage fields with significant stores of legacy P. The objective of our study was to evaluate changes in P dynamics such as P distribution among soil P fractions and P sorption characteristics of agricultural soils following long-term applications of poultry litter or commercial fertilizers.

## **2.2 Materials and Methods**

### **2.2.1 Study Design and Site History**

For this study, we selected soil samples from two “long-term” field sites on the Delmarva Peninsula, where soil P was monitored on plots receiving various fertilizer and manure applications for over 14 years (starting in the spring of 2000). The first field site is located at the University of Delaware Carvel Research and Education Center in Georgetown, DE. The dominant soil series at the Georgetown field site was Pepperbox loamy sand (Loamy, mixed, semiactive, mesic Aquic Arenic Paleudults). The second site is located at Chesapeake Farms near Chestertown, MD, where the dominant soil series was Mattapex silt loam (Fine-silty, mixed, active, mesic aquic Hapludults). Initial soil properties for both sites are shown in Table 2.1. The cropping rotation in each field was continuous corn (*Zea Mays* L.) from 2000–2004, followed by a corn-full season soybean (*Glycine Max* L.) rotation from 2005–2013. Specifically, corn was planted in 2005, 2007, 2011, 2012 (Pepperbox Loamy sand

only) and 2013, and soybean was planted in 2006, 2008, 2010, and 2012 (Mattapex silt loam only).

Each field site was split into  $4.57 \times 12.2$  m plots to evaluate long-term application of PL and commercial P fertilizers (in the form of triple superphosphate [TSP]) at various rates. A total of 10 fertilization treatments were applied in a randomized complete block design with six replications; a detailed description about all 10 fertilization treatments and other management practices (e.g. fertility management, lime history, pest control, etc.) on each field can be found in Shoher et al. (2017). We selected five of the fertilization treatments for evaluation in this study: no P control (C), application of PL only from 2000–2002 (PL-20), application of moderate (PL-43) and high rate of PL (PL-65), and application of TSP. All the PL treatments received the same total P rate from 2000–2003 as part of a poultry diet study to evaluate the effects of phytase and low-phytate corn varieties on P concentrations and solubility in manure; the average annual PL rate was approximately  $6.73 \text{ Mg ha}^{-1}$  during this period (Shoher et al., 2017). No PL was applied in 2003 and 2004 due to the suspension of the previous diet study. From 2005–2013, soils assigned the PL-20, PL-43, and PL-65 treatments received PL at 0, 4.48, and  $8.97 \text{ Mg ha}^{-1}$ , respectively, to corn in odd years. Poultry litter was sourced locally with one PL collected from a local broiler farm and four PLs from a feeding trial from 2000–2002; PL was collected from one single local source annually from 2005–2013. Poultry litter subsamples were submitted to the Delaware Department of Agriculture, Agriculture Compliance Laboratory for chemical analysis with the exception that samples from 2000–2002 were submitted to the University of Delaware Soil Testing Laboratory. The chemical properties of litter samples were used to

determine the annual total P application rate and the cumulative total P load over the project duration for each plot (Table 2.2). The TSP treatment received concentrated TSP (0-46-0) at a P rate of 75.9 kg ha<sup>-1</sup> in 2000 and 2001, 64.6 kg ha<sup>-1</sup> in 2002, and 58.7 kg ha<sup>-1</sup> in 2005, 2007, 2009, 2011, and 2013; no TSP was applied in 2003, 2004, 2008, 2010, or 2012. All P sources were broadcast by hand in the spring prior to sowing corn and incorporated with a disk immediately following application. The annual grain yield in each plot were evaluated as described in Shober et al. (2017). The grain samples were analyzed for total digestible P concentrations using inductively coupled plasma optical emission spectroscopy (ICP-OES) following digestion in nitric acid using a CEM MARS5 microwave digestion system (CEM Corporation, Matthews, NC). Grain total digestible P was used to determine the annual and total P removed by crop removal for the project duration for each plot.

### **2.2.2 Soil Testing and Analysis**

Composite soil samples were collected from each plot (8–12 cores per plot) to a depth of 20 cm using a soil probe (1.3-cm diameter) in the spring of 2000 prior to any form of P application (initial conditions), and in the Fall following crop harvest from 2000–2013. Collected soil samples were composited, air-dried, ground, sieved through 2-mm screen, and stored in a cloth soil bag until analysis. Soils from all five treatments from the year of 2000–2013 were submitted to the University of Delaware Soil Testing Laboratory annually for analysis of pH (1:10 soil/deionized water), Adams-Evans buffer pH, and organic matter (loss on ignition), using standard soil testing procedures (NECC-1312, 2011); initial soil samples were also analyzed for soil particle size using hydrometer method (Bouyoucos. 1962). Soil test P, aluminum (Al), iron (Fe), and calcium (Ca) concentrations were determined by ICP-OES following

Mehlich-3 extraction (1:10 ratio of soil to solutions of 0.2 M CH<sub>3</sub>COOH + 0.25 M NH<sub>4</sub>NO<sub>3</sub> + 0.015 M NH<sub>4</sub>F + 0.13 M HNO<sub>3</sub> + 0.001 M EDTA, 5-min reaction time, filtered through Whatman #42 paper; NECC-1312, 2011). The degree of P saturation (DPS<sub>M3</sub>) was calculated as the molar ratio of M3P in mmol kg<sup>-1</sup> divided by the sum of Mehlich-3 extractable Al and Fe in mmol kg<sup>-1</sup>, and converted to percentage by multiplying with 100.

To examine the P dynamics in long term build-up plots, archived samples from the selected five fertilization treatments (C, PL-20, PL-43, PL-65, TSP) were evaluated. Specifically, archived samples from all five treatments in 2000 (Spring), 2002, 2005, 2007, 2011, and 2013 were analyzed for WEP (Self Davis et al., 2009). In brief, 20 mL of deionized water was added to 2 g of soil and shaken for 1 h on a rotary shaker. Solution was then centrifuged (at 2000 rpm for 13 min), filtered through a 0.45-μm filter, and analyzed for P using the molybdate blue method (Murphy and Riley, 1962). The drawdown or buildup of M3P and WEP in plots receiving each fertilizer treatment at each field site was fit to a first-order decay equation:

$$y = Ae^{Bt} \quad [1]$$

where y is P concentration, t is time in years, and A and B are constants (Fiorellino et al., 2017; McCollum, 1991). The constant B represents the rate of P drawdown or buildup over the time period of t (e.g. B= -0.030 and 0.030 means soil P concentration decreased and increased by an average of 3% each year over the time period t respectively; Fiorellino et al., 2017).

Phosphorus sorption isotherms were constructed for archived soil samples collected from plots receiving C, PL-43, PL-65, and TSP treatments in 2013. We reacted 2 g of air-dried soil with 30 mL of 0.01 M CaCl<sub>2</sub> using P solutions containing

the following P concentrations (as  $\text{KH}_2\text{PO}_4$ ): 0, 1, 5, 10, 20, 35, 50, and 100  $\text{mg L}^{-1}$  (Reddy et al., 1980; Nair et al., 1984). Samples were placed on an end-over shaker for 24 h. All reacted samples were centrifuged (at 2000 rpm for 12 min), filtered through a 0.45- $\mu\text{m}$  filter, and analyzed for P using ICP-OES. Adsorption analysis was fit with the Langmuir model to determine the soil maximum sorption ( $S_{\text{max}}$ ; Bolster and Hornberger, 2007). A modified Hedley sequential chemical fractionation was performed on archived soils collected from plots receiving C, PL-20, PL-43, PL-65, and TSP treatments prior to application of P sources in spring 2000 (2002 for unamended control plots) and after 14 years of fertilization treatment in Fall 2013 to evaluate the effect of long-term P applications on the operational “forms” of P in the soils (Sui et al., 1999). In brief, 0.5 g of each soil was sequentially extracted with: (1) 30 mL of deionized water, shake for 16 hours, ( $\text{H}_2\text{O}$ -extractable P); (2) 30 mL of 0.5  $M$   $\text{NaHCO}_3$ , shake for 16 hours, ( $\text{NaHCO}_3$  extractable-P); (3) 30 mL of 0.1  $M$   $\text{NaOH}$ , shake for 16 hours, ( $\text{NaOH}$  extractable-P); and (4) 30 mL of 0.1  $M$   $\text{HCl}$ , shake for 16 hours, ( $\text{HCl}$  extractable-P). All extracts from the fractionation were centrifuged (at 2000 rpm for 12 min), filtered through a 0.45- $\mu\text{m}$  filter, and analyzed for P by ICP-OES. The total extractable inorganic P was calculated as the sum of all four extractable P for each treatment at each site.

### **2.2.3 Data Analysis**

This study was designed as a randomized complete block with five fertilization treatments and six replications. Missing WEP data were estimated randomly based on the sample mean using the rannor function in PROC SQL (SAS version 9.4; SAS Institute, Cary, NC; Zhang et al., 2008). The effect of fertilization treatments on the rate of M3P and WEP build up or drawdown over the course of the study was

evaluated using an exponential rise or decay function in SAS using PROC NLIN. Treatment effects on the build-up or drawdown constants were evaluated using PROC MIXED with treatment as a fixed effect and replicate as a random effect to determine the effect of fertilization treatment on the changing rate of M3P and WEP. Mehlich-3 P, WEP, operationally-defined soil inorganic P fractionation pools,  $DPS_{M3}$ , and  $S_{max}$  were analyzed by year using a mixed model analysis of variance (ANOVA) procedure (PROC MIXED in SAS) with treatment as a fixed effect and replicate as a random effect (SAS Institute, 2008) for each soil type to determine the effects of P treatments on soil P dynamics. The concentrations of extractable P or the fractions of extractable P in total extractable P were evaluated using PROC MIXED with year as a fixed effect and replicate as a random effect for each soil type and each extracting step to determine their changes over time. Normality assumptions were confirmed by examining histogram and normality plots of the conditional residuals. All pairwise comparisons were completed using the Tukey's honestly significant difference test with a significance level of  $\alpha=0.05$ .

## **2.3 Results and Discussions**

### **2.3.1 Initial Soil Properties**

The soils at each location had moderately acidic pH (<6) prior to P applications and similar concentrations of organic matter (Table 2.1). The Mattapex soils had a silt loam surface texture and an initial M3P concentration close to two times the Delaware agronomic critical level of  $50 \text{ mg kg}^{-1}$  (Shober et al., 2013). In comparison, the Pepperbox soils had a loamy sand surface texture and an initial M3P concentration closer to the agronomic critical level (Table 2.1). The concentrations of

total P and Mehlich-3 extractable Ca and Al appeared to be higher in Mattapex silt loam than Pepperbox loamy sand, while their concentrations of Mehlich-3 extractable Fe were similar. However, both soils had similar levels of P saturation prior to the application of PL or TSP (Table 2.1). The  $DPS_{M3}$  values indicated levels below the environmental threshold for increased risk of P loss and thus still had the capacity to sorb applied P prior to the application of PL or TSP. For example, Maguire and Sims (2002) summarized that the threshold of  $DPS_{M3}$  was around 23% for five Delaware soil series (Butlerstown, Evesboro, Matapeake, Pocomoke, and Sassafra), above which, the concentrations of dissolved P in leachate increased dramatically. Similarly, Sims et al. (2002) showed that the  $DPS_{M3}$  threshold was around 14% for dramatic increase in dissolved P concentrations in runoff based on the same five Delaware soils.

### **2.3.2 Fertilization Treatments**

In terms of fertilization, the PL-65 or TSP treatments supplied the highest cumulative total P over the course of the study, followed by the PL-43 and PL-20 treatments. Application of the PL-65 treatment to the Mattapex silt loam supplied significantly higher cumulative total P than the TSP treatment, while there was no statistical difference between the cumulative total P applied with these two treatments to the Pepperbox loamy sand (Table 2.2). Total P removed in grain from Mattapex silt loam soils receiving PL-43 was significantly higher than soils receiving no P, while total P removed in grain from the Pepperbox loamy sand soils receiving no P was significantly lower than the total P removal from plots receiving all other P treatments (Table 2.2). Over the entire study period (2000–2013), the cumulative total P rate supplied by the C or PL-20 was below total crop P removal (P insufficiency or drawdown). The plots receiving TSP or PL-65 received P at rate in excess of crop P

removal (P surplus or buildup) over the entire study period. Application of the PL-43 treatment supplied total P at a rate that was slightly lower than crop P removal for both soils; but the total P budget was the closest to a balance when compared with the other treatments (Table 2.2).

### **2.3.3 Mehlich-3 and Water Extractable P**

We report a significant fertilization treatment effect on the annual rate constants (decay or growth) of M3P (Figure 2.1) and WEP (Figure 2.2) for both soils. Treatments receiving C and PL-20 had statistically similar annual decay rate constants for M3P and WEP in both soils. Based on this relationship, drawdown of M3P to agronomic critical level ( $50 \text{ mg kg}^{-1}$ ) would take approximately 16 and 17 years for the unamended Mattapex silt loam and Pepperbox sandy loam soils, respectively; soils receiving the PL-20 would reach agronomic critical level within 23 and 28 years (for the Mattapex and Pepperbox, respectively) if no additional P was applied. The annual decline of -1.88 to -5.34% of measured M3P for soils receiving C or PL-20 was similar with the decay rates presented by other researchers (-2.86 to -9.70% of measured M3P) when grain crops (corn, wheat, soybean) were the main crops planted to remove soil P after P inputs ceased (Fiorellino et al., 2017; McCollum, 1991).

Mattapex silt loam receiving PL-43 experienced a drawdown of M3P (Figure 2.1) and WEP (Figure 2.2), which was consistent with the fact that this treatment resulted in an overall P insufficiency throughout the study period (Table 2.2). However, Pepperbox loamy sand receiving PL-43 resulted in a slight buildup of M3P (Figure 2.1) despite an overall P insufficiency over the course of the study, which might be related to the release of P from more recalcitrant soil P pool. Pepperbox

loamy sand receiving PL-43 still resulted in a drawdown of WEP over the time (Figure 2.2).

For both soils, we reported no significant difference in the M3P build up rate for plots receiving the PL-65 and TSP treatments (Figure 2.1). Yet, the M3P rate constant for the Mattapex silt loam soils receiving TSP (-0.089%) suggested that the M3P concentrations remained almost unchanged over the 14-year study period. Similar trends were reported for soil WEP when these same treatments were applied to the Mattapex silt loam soils (Figure 2.2) since both of these treatments resulted in a similar cumulative P surplus (Table 2.2). However, application of PL-65 to the Pepperbox loamy sand increased WEP at a significantly faster rate than soils receiving TSP (Figure 2.2).

We found no significant differences in M3P and WEP concentrations prior to applying fertilizer treatments in 2000 (Table 2.3). But after 14-years of fertilization, both soils receiving the PL-65 or TSP had significantly higher M3P and WEP concentrations than unamended controls. Soils receiving the PL-65 also resulted in higher WEP concentrations compared with soils receiving TSP, while concentrations of M3P were similar in plots receiving these two treatments for both soil types (Table 2.3). Application of PL-20 did not significantly impact M3P and WEP concentrations for either soil type. However, soils receiving PL-43 had significantly higher M3P concentrations than the unamended controls (Table 2.3).

Our findings echo those of previous researchers, who reported a significant increase in soil WEP and/or M3P after repeated manure and/or inorganic P applications (Penn and Sims, 2002; Sharpley et al., 2004). Penn and Sims (2002) also reported that manure amended agricultural soils from Delaware (Elsinboro silt loam

and Woodstown loamy sand) had significantly higher WEP (1.04–26 mg kg<sup>-1</sup>) and M3P (67–311 mg kg<sup>-1</sup>) concentrations after receiving poultry litter at a rate of 200 kg ha<sup>-1</sup> (based on EPA3050 P digestion) compared with unamended soils (0.38–14 and 42–237 mg kg<sup>-1</sup> for WEP and M3P, respectively). Similarly, Sharpley et al. (2004) reported significantly higher WEP (11–85 mg kg<sup>-1</sup>) and M3P concentrations (82–2840 mg kg<sup>-1</sup>) in 20 agricultural soils from New York (6 sites), Oklahoma (8 sites), and Pennsylvania (6 sites) after long-term (10–25 years) manure (dairy, poultry, or swine) addition at annual P rate of 40–200 kg ha<sup>-1</sup> compared to unamended controls (0.6–6.0 and 4.0–64 mg kg<sup>-1</sup> for WEP and M3P, respectively). In another study, Zhang et al. (2004) reported higher M3P concentrations (71–190 mg kg<sup>-1</sup>) in a Ste. Rosalie clay soil in Canada compared with no P control plots (46 mg kg<sup>-1</sup>) following ten-years of commercial fertilizer application in the form of monoammonium phosphate and TSP at an annual P rate of 44 or 132 kg ha<sup>-1</sup>.

#### **2.3.4 Degree of P Saturation**

Before application of P in any form, we found no significant difference in  $DPS_{M3}$  for either soil type. However, after 14-years fertilization treatments, application of TSP or PL-65 increased the soil  $DPS_{M3}$  compared with unamended controls in both soil types. Application of PL-43 also significantly increased the soil  $DPS_{M3}$  compared with the controls in the Mattapex silt loam soils only (Table 2.3), which might be related to the finer soil texture of Mattapex silt loam soils compared with Pepperbox loamy sand that led to potentially higher sorption of applied P. Several studies have reported a threshold  $DPS_{M3}$  value (above which significant increase of P losses will be noted in leachate and/or runoff water) for our region. For example, Maguire and Sims (2002) summarized that the threshold of  $DPS_{M3}$  was

around 23% for five Delaware soil series (Butlerstown, Evesboro, Matapeake, Pocomoke, and Sassafra). The concentrations of dissolved P in leachate increased by 0.0098 and 28.44 mg L<sup>-1</sup> for each 1% increase in DPS<sub>M3</sub> when soil DPS<sub>M3</sub> values were below and above the threshold, respectively (Maguire and Sims, 2002). In another study, Sims et al. (2002) evaluated the relationship between DPS<sub>M3</sub> and runoff P using a rainfall simulation runoff box method (5% slope, rainfall applied at 7.5 cm h<sup>-1</sup>) for the same five Delaware soils. The researchers showed a significant increase in the concentration of dissolved reactive P in runoff DPS<sub>M3</sub> exceeded 14% (Sims et al., 2002). Specifically, the concentrations of dissolved P in runoff increased by 0.024 and 4.33 mg L<sup>-1</sup> for each 1% increase in DPS<sub>M3</sub> when soil DPS<sub>M3</sub> values were below and above the threshold respectively (Sims et al., 2002). Generally, the DPS<sub>M3</sub> of our soils remained below the reported thresholds for our region after 14 years of PL or TSP treatment. However, we can expect that if P were continually applied above crop removal, the DPS<sub>M3</sub> levels would continue to increase and eventually approach or exceed identified critical levels, at which point, the non-point P losses from the evaluated sites could potentially represent an environmental concern.

Our results were consistent with previous studies that showed increased DPS levels after repeated manure applications (Butler and Coale; 2005; Dou et al., 2009). For example, Dou et al. (2009) compared DPS<sub>ox</sub> (calculated based on oxalate-extractable P, Al, and Fe) in soils collected from 10 agricultural fields in PA that received manure (dairy, poultry, swine manure) or spent mushroom compost for more than eight years (annual P rate ranged from 29–120 kg ha<sup>-1</sup>) with DPS<sub>ox</sub> in unamended field soils. The authors found that manure amended soils had much higher DPS<sub>ox</sub> values (80–90%) than untreated soils (11–30%). Similarly, Butler and Coale (2005)

also indicated that repeated application of manure (dairy or broiler manure; total P application of 400–1,600 kg ha<sup>-1</sup>) over four years at four locations in MD led to an increase in DPS<sub>ox</sub> in the surface soils (0–15 cm) to levels above 25%, which was reported to be the local environmental threshold. The authors concluded that repeated applications of P in manure could overwhelm the soil P sorption capacity, which could increase the potential of P solubilization and P loss during runoff or leachate events.

### **2.3.5 P Sorption Isotherms**

We found no significant fertilizer treatment effect on the S<sub>max</sub> values for either soil after 14 years fertilization treatments (data not shown). The lack of significant fertilizer treatment effect on S<sub>max</sub> in our study is inconsistent with other studies, where researchers reported a significant reduction in P sorption capacity after long-term manure and/or inorganic P addition (Borling et al., 2004; Singh et al., 2006; Jiao et al., 2007). For example, Singh et al. (2006) evaluated the adsorption-desorption properties of a Typic Ustochrept soil (maize-wheat-cowpea rotation) that received single superphosphate or diammonium phosphate at four levels of P application (no P, optimal [120–150 and 20 kg ha<sup>-1</sup> yr<sup>-1</sup> for maize and wheat, and cowpea respectively], sub-optimal [half the rate as optimal], and super-optimal [1.5 times the rate as optimal]) over 32 years in Ludhiana, India. One of the optimal P rate treatment also received farmyard manure at a manure rate of 10 Mg ha<sup>-1</sup> yr<sup>-1</sup> before the sow of maize. The authors indicated that soils receiving farmyard manure (S<sub>max</sub> at approximately 88 mg kg<sup>-1</sup>) had significantly lower P sorption capacity than the unfertilized soils (S<sub>max</sub> at 182 mg kg<sup>-1</sup>) when fitted with Langmuir model. The S<sub>max</sub> value of manure amended soils was even lower than the S<sub>max</sub> value of soils received super-optimal P rates (107 mg kg<sup>-1</sup>) (Singh et al., 2006). Laboski and Lamb (2004) also found that manure

application reduced P sorption capacity in five soil series (Port Byron, Sanburn, Verndale, Ves, and Barnes soils) in Minnesota compared with unamended soils ( $S_{\max}=163\text{--}447\text{ mg kg}^{-1}$ ) collected adjacent to the manure-amended soils ( $S_{\max}=102\text{--}338\text{ mg kg}^{-1}$ ) when fitted with Langmuir model. But manure application did not significantly impact the P sorption capacity on Waukegan soil series, which the authors attributed to the fact that this soil series only received a one-time manure application (swine) prior to sampling instead of repeated manure application over several years, and P supplied from the swine manure may not enough to cause a change in sorption capacity ( $168\text{ kg ha}^{-1}$ ; Laboski and Lamb, 2004). Laboski and Lamb (2004) and Singh et al. (2006) believed that the reduction in P sorption capacity in amended soils was mainly attributed to fewer available P exchange sites (e.g., Fe and Al oxides) due to the competition between orthophosphates with organic acid anions released during manure decomposition.

The discrepancy between our results and those reported from other studies may be attributed to the difference in the manure sources and application rate. Specifically, the total manure applied was about  $320\text{ Mg ha}^{-1}$  in Singh et al. (2006), which was much higher than the total PL application rate in our study ( $20.2\text{--}65.0\text{ Mg ha}^{-1}$ ). The higher rates of manure in the Singh et al. (2006) study could potentially generate more organic acids during decomposition to compete for P sorption sites. On the other hand, soils evaluated in Laboski and Lamb (2004) that showed significant reduction in maximum P sorption capacity mainly received dairy manure ( $298,800\text{--}429,400\text{ L ha}^{-1}$ ), and to a lesser extent, swine ( $0\text{--}140,000\text{ L ha}^{-1}$ ) and/or turkey litter ( $0\text{--}13.5\text{ Mg ha}^{-1}$ ). Dairy manure contained a much greater proportion of water soluble P compared with PL (Sharpley and Moyer, 2000), which may have a more immediate impact on

soil P sorption capacity. As a result, it is possible that an even longer P application and/or higher P application rate may be needed to impact on the P sorption capacity for our soils.

We did, however, find that the average  $S_{\max}$  values of the Mattapex silt loam soils (312 mg kg<sup>-1</sup>) were significantly higher than the  $S_{\max}$  values of the Pepperbox loamy sand (241 mg kg<sup>-1</sup>), which is related to the finer soil texture, higher clay, and relatively high Fe and Al content in Mattapex soils when compared with Pepperbox soils (Table 2.1); these soil properties affect overall soil P sorption capacity (Sample et al., 1980).

### **2.3.6 Concentrations of Operationally-defined Soil P Pools**

Based on the concentrations of extractable P (Table 2.4), our results indicated that NaOH-extractable P (Fe/Al associated P) is the dominant inorganic P pool in both soil types before and after applications of PL or TSP to corn over the 14-year study period. We found no significant treatment effect on P concentrations in all extracts or total extractable inorganic P prior to TSP or PL application in spring 2000 for Mattapex silt loam soils (Table 2.4). Slight variation in extractable P concentrations was noted for Pepperbox loamy sand in spring 2000 prior to P application. However, there was no difference in control soils with P-amended soils except soils designated to receive PL-20 or PL-43, and TSP had higher NaHCO<sub>3</sub>-extractable P concentrations than soils designated as control prior to any P application (Table 2.4).

Significant fertilizer treatment effects were noted on the concentrations of operationally-defined soil P pools in 2013 after 14-years of PL or TSP treatments. Specifically, soils at both sites receiving PL-65 or TSP had significantly higher labile soil P pools (extracted by H<sub>2</sub>O or NaHCO<sub>3</sub>) than the unamended controls (Table 2.4),

which was consistent with the fact that these treatments received P at a rate that resulted in overall P surplus (Table 2.2). Soils receiving PL-65 also resulted in higher H<sub>2</sub>O-extractable P concentrations than soils receiving TSP. Although the application of PL-43 resulted in an overall P deficit over the entire study period (Table 2.2), this treatment still significantly increased the concentrations of H<sub>2</sub>O-extractable P when compared with the unamended controls for both soil types; the concentrations of NaHCO<sub>3</sub>-extractable P were also higher than controls in Mattapex silt loam soils receiving the PL-43 treatment (Table 2.4). Application of PL-65 or TSP to the Mattapex silt loam led to a significant increase in more recalcitrant soil P pools (i.e., those extracted by NaOH and HCl) when compared with the unamended control; application of PL-43 to the Mattapex soils also resulted in significantly higher HCl extractable P compared with the control (Table 2.4). However, only the application of PL-65 led to a significant increase in NaOH- and HCl-extractable P over the unamended control in the Pepperbox loamy sand. As a result, when applied at roughly the same total P rate, PL application generally resulted in a more significant increase in operationally-defined soil P pools (especially the H<sub>2</sub>O-extractable P) compared with the application of TSP. The stronger impact of PL over TSP may relate to the increased accumulation of negatively charged organic acids in manure amended soils, which may compete with orthophosphates and occupy available P sorption sites (e.g., Fe and Al oxides) (Jiao et al., 2007; Singh et al., 2006). Consequently, manure application will decrease P adsorption capacity more than commercial fertilizers (Singh et al., 2006; Jiao et al., 2007), which in turn increases the concentrations of extractable P (e.g., H<sub>2</sub>O-extractable P).

In terms of the total extractable P, soils receiving P above crop removal (PL-65 or TSP) had significant higher total extractable inorganic P compared with soils receiving C at both sites. The application of PL at lower rates did not significantly impact on total extractable inorganic P pools compared with unamended controls in any of the soil; the only exception was PL-43 had higher total extractable inorganic P compared with controls in Mattapex silt loam (Table 2.4).

Our results are consistent with other studies that showed increased P concentrations in different operationally-defined soil P pools ranging from the relatively labile (i.e., extracted by water, anion exchange resin, FeO-impregnated strips, or diluted salt) to the recalcitrant pools (e.g., extracted by NaOH and/or acid) after repeated manure addition (Qian et al., 2004; Sharpley et al., 2004; Shafqat and Pierzynski, 2010). For example, when compared with unamended soils, Shafqat and Pierzynski (2010) reported a 60 and 80 mg kg<sup>-1</sup> increase for soil P concentrations extracted by FeO-impregnated filter paper and NaHCO<sub>3</sub>, respectively, and a 20 and 60 mg kg<sup>-1</sup> increased in NaOH- and HCl-extractable P, respectively in the surface layer (0–5 cm) of a Kennebec silt loam after eight years of beef manure application at an annual P rate of 40 kg ha<sup>-1</sup>. Similarly, Qian et al. (2004) reported a significant increase in resin- and NaHCO<sub>3</sub>-extractable P concentrations (labile P) with increasing rate of manure addition in Saskatchewan soils (loamy textured black chernozem) after five years of swine (total P rate of 23, 46, or 92 kg ha<sup>-1</sup>) or cattle manure (total P rate of 155, 311, or 622 kg ha<sup>-1</sup>) application. Concentrations of total digestible P in surface soils (0 to 15 cm) also increased significantly following the addition of cattle manure at a total P rate of 311 or 622 kg ha<sup>-1</sup> (673 and 698 mg kg<sup>-1</sup> respectively) compared with no P control (610 mg kg<sup>-1</sup>; Qian et al., 2004).

When compared with extractable soil P conditions early in the study, we found that the concentrations of relatively labile soil P pools (extracted by H<sub>2</sub>O and/or NaHCO<sub>3</sub>) were generally more temporally impacted by fertilization treatments compared with the concentrations NaOH- and/or HCl-extractable P. Specifically, the drawdown and buildup of soil P concentrations was mostly reflected in the H<sub>2</sub>O- and/or NaHCO<sub>3</sub>-extractable P pools compared with the NaOH- and HCl-extractable pools (especially in Pepperbox loamy sand soils; Table 2.4). The labile soil P pools were mainly affected because PL and TSP supply a soluble form of inorganic P (Edwards and Daniel, 1992; Leikam et al., 2000; Seiter et al., 2008) that directly increases H<sub>2</sub>O- and/or NaHCO<sub>3</sub>-extractable P under a buildup scenario. For example, using synchrotron based X-ray absorption near edge structure (XANES) analysis, Seiter et al. (2008) found that two normal PLs (i.e., not treated with aluminum sulfate to reduce soluble P) contained about 60 to 80% inorganic P species (N-, potassium (K)-, Al-, and/or Ca-phosphate), among which, about 40–80% was N- and/or K-phosphate that can be easily extracted by H<sub>2</sub>O and NaHCO<sub>3</sub>. Under the drawdown scenario, the labile soil P pools were mainly affected because the preferential uptake of H<sub>2</sub>O- and/or NaHCO<sub>3</sub>-extractable P by crops. Our buildup and drawdown of soil P also significantly impacted on the total extractable inorganic P. Specifically, no P addition in Mattapex silt loam soils resulted in a significant reduction in total extractable inorganic P over the time. Application of PL-65 (highest P surplus among all treatments) resulted in a significant increase in total extractable inorganic P concentrations in both soils while application of TSP resulted in a significant increase in Mattapex silt loam soils only (Table 2.4).

### 2.3.7 Distribution of P among Operational Soil P Pools

For the most part, we reported no significant difference in the distribution of inorganic P pools for either site in 2000. However, prior to any P application in 2000, Pepperbox loamy sand soils designated to receive P had significantly higher proportion of  $\text{NaHCO}_3$ -extractable P compared with soils designated as no P control; unamended controls also had higher proportion of NaOH-extractable P compared with soils designated to receive PL-43 (Fig. 2.3).

However, long-term application of PL and/or TSP significantly impacted the distribution of inorganic P among the operational soil P pools. In 2013, soils receiving PL-43, PL-65, or TSP (Mattapex silt loam only) had significantly higher proportion of total extractable P in the  $\text{H}_2\text{O}$ -extractable pools compared with unamended controls; application of PL-65 also resulted in significantly higher proportion of  $\text{H}_2\text{O}$ -extractable P than PL-43 and TSP in Mattapex silt loam soils (Figure 2.3). Soils receiving PL-20 (Mattapex silt loam only), PL-65, or TSP (Mattapex silt loam) had significantly higher proportion of total extractable P in the  $\text{NaHCO}_3$ -extractable pools compared with unamended controls; Mattapex silt loam receiving PL-65 or TSP also had higher proportion of  $\text{NaHCO}_3$ -extractable P than soils receiving PL-20 (Figure 2.3). Soils receiving PL-43, PL-65, or TSP had significantly lower proportion of total extractable P in the NaOH-extractable pools than soils receiving C or PL-20; Mattapex silt loam receiving PL-65 also had lower proportion of NaOH-extractable P than soils receiving PL-43 or TSP while soils receiving TSP also had lower proportion of NaOH-extractable P than soils receiving PL-43 (Figure 2.3). Mattapex silt loam soils receiving PL-43 or TSP had significantly higher proportion of total extractable P in the HCl-extractable pools compared with soils receiving PL-20; no significant treatment effect was noted for Pepperbox loamy sand soils at the HCl fraction (Figure 2.3).

Sharpley et al. (2004) also reported that the ratio of NaOH-extractable P to total extractable P was lower in soils (14–31%) receiving long-term manure application (10–25 yrs in the form of dairy, poultry or swine manure) compared with adjacent un-amended background soils (18–65%) at 20 selected sites in New York (6 sites), Oklahoma (8 sites), and Pennsylvania (6 sites). However, the authors reported a significant increase in the proportion of total extractable P in the HCl-extractable pool after manure addition (35–64%) as compared with control soils (12–53%). Sharpley et al. (2004) suggested that the increase in the proportion of HCl-extractable P resulted from a general shift in soil P chemistry from NaOH-extractable P (Fe- and Al-associated P) to HCl-extractable P (Ca-associated P), which were related to the high total Ca content in amended manures (21.9–108 g kg<sup>-1</sup>). Similarly, Graetz and Nair (1995) also found that manure application (dairy manure for 8–32 yrs) decreased the ratio of NaOH-extractable and increased the ratio of HCl-extractable P to total extractable P in surface soils (0–20 cm) of three Spodosols (Myakka, Immokalee, and Pomello fine sands) compared with untreated soils; this shift was attributed to the Ca- or magnesium (Mg)-associated P in the applied dairy manure. In another study, Lehmann et al. (2005) found that repeated poultry manure additions (6–25 yr) increased the proportion of total extractable P extracted by HCl from 10 to 62% in a naturally acidic soil (Wellsboro channery silt loam) in southern New York state due to the increased stability of Ca-phosphate as soil pH increased from acidic (4.1) to near neutral (6.0–7.2).

The relative decrease in the fraction of NaOH-extractable P in our amended soils compared with unamended controls is consistent with the pattern reported by others in the literature (Graetz and Nair, 1995; Sharpley et al., 2004), and can be

largely attributed to the increased contributions from other extractable P pools (especially the labile P) to total inorganic P after the long-term application of PL and/or TSP (Figure 2.3). The lack of treatment effect on the proportion of total inorganic P extracted by HCl in our study is inconsistent with previous studies, which showed a significantly higher proportion of HCl-extractable P of manure-amended soils than the unamended controls (Sharpley et al., 2004; Lehmann et al., 2005). However, our amended soils had lower M3P concentrations (61.1–138 mg kg<sup>-1</sup>) compared with those reported in literature (200–2800 mg kg<sup>-1</sup>), which reflects the more intensive manure application history of sites evaluated by Sharpley et al. (2004) and Lehmann et al. (2005). Total P inputs reported by Sharpley et al. (2004) and Lehmann et al. (2005) ranged from 180–8000 kg ha<sup>-1</sup> with most soils received total P higher than 700 kg ha<sup>-1</sup>; our soils received total P inputs ranged from 175–542 kg ha<sup>-1</sup>. As a result, the more intensive manure application history led to an accumulation of HCl-extractable P for sites evaluated by Sharpley et al. (2004) and Lehmann et al. (2005). Moreover, our amended soils appeared to have slightly lower soil pH (5.5–6.1) compared with pH of the amended soils evaluated in the above studies (5.7–7.6). As a result, Ca-associated P extracted by HCl might be more stable in the previous studies, which may also explain the difference with our results.

Previously, researchers identified the Ca-associated P minerals (e.g., calcium phosphate, hydroxyapatite) in poultry litter (Shober et al., 2006; Seiter et al., 2008) using X-ray absorption near edge structure spectroscopy (XANES). As a result, we suspect that the addition of PL or TSP (which is derived mainly from calcium dihydrogen phosphate and monocalcium phosphate) at rates that exceed crop P removal may directly increase the pools of Ca-associated P extracted by HCl, or

indirectly enhance the formation of Ca-associated P by increasing the Ca concentrations in soils. We did find that PL and TSP amended soils had higher concentrations of Mehlich-3 extractable Ca (665–858, and 463–576 mg kg<sup>-1</sup> for the Mattapex and Pepperbox soils, respectively) compared with unamended controls (660 and 394 mg kg<sup>-1</sup> for the Mattapex and Pepperbox soils, respectively). Recently, Gamble et al. (2017) identified P species in four soil series collected in DE, MD, and PA (Mullica-Berryland, Davidson, Hagerstown, and Berks) using a combination of X-ray fluorescence and XANES analysis. These soils properties were typical of agricultural in the Mid-Atlantic region, with extremely acid to slightly acid soil pH (4.2–6.4) and a wide range of M3P concentrations (27.4–668 mg kg<sup>-1</sup>). The authors confirmed the presence of discrete Ca-phosphate minerals (e.g., apatite, monetite, and/or fluorapatite), supporting the idea that Ca-associated P species can remain stable and accumulated in acidic soils. As a result, we believe that continued application of PL or TSP to our soils at rates exceeding crop removal could eventually result in a higher proportion of total inorganic P extracted by HCl compared with the unamended soil. The hypothesis is supported when one compares the changes in P distribution conditions when PL-43 (both soils), PL-65 (Pepperbox loamy sand only), or TSP (Pepperbox loamy sand only) were applied over a period of 14 years (Figure 2.3).

## **2.4 Conclusions**

We recognize that the soil test P concentrations in our soils (47.0 to 138 mg kg<sup>-1</sup> M3P) were below the concentrations in many legacy soils in the Delmarva region. Yet, the results of our 14-year study evaluating the effect of PL and/or TSP fertilization on soil P dynamics on two Delmarva Peninsula soils still provide valuable insights on the behavior of soil P. Repeated applications of P at rates above crop P

removal result in the build-up in the relatively labile P pools, and can increase the risk of non-point P losses that lead to immediate water quality concerns (especially in areas with high P transport potential). However, the concomitant build-up of the more recalcitrant P pools, especially Ca-associated P, should not immediately affect water quality, but could limit the ability to effectively drawdown high soil test P by plant removal. Liming can potentially promote the solubilization of Fe- and/or Al-associated P from high P soils and increase plant uptake. However, this practice is limited to times when pH management is necessary. In contrast, application at or slightly below crop removal rates is a trusted and environmentally-responsible agronomic practice that should be followed to provide adequate fertility for cropping and protect environmental quality. As a result, estimation of P balance at farm scale will be beneficial for adoption of appropriate P application rates and effective nutrient management strategies.

Table 2.1: Selected soil properties (0–20 cm) at the Chestertown, MD and Georgetown, DE sites in 2000 prior to the initiation of a long-term field study to evaluate the effects of repeated poultry litter and commercial P fertilizer on soil P dynamics.

Soil Properties	Chestertown, MD	Georgetown, DE
Soil Series	Mattapex	Pepperbox
Subgroup	Aquic Hapludults	Aquic Hapludults
pH	5.8	5.6
OM, g kg <sup>-1</sup>	20	15
Sand, g kg <sup>-1</sup>	140	810
Silt, g kg <sup>-1</sup>	620	100
Clay, g kg <sup>-1</sup>	240	90
Total P, mg kg <sup>-1</sup>	626	198
Mehlich3-P, mg kg <sup>-1</sup>	92	67
Water extractable P, mg kg <sup>-1</sup>	2.4	1.4
Mehlich3-Ca, mg kg <sup>-1</sup>	663	269
Mehlich3-Al, mg kg <sup>-1</sup>	1037	698
Mehlich3-Fe, mg kg <sup>-1</sup>	175	153
DPS <sub>M3</sub> , %	7.1	7.5

Table 2.2: Summary of total P applied in the form of poultry litter (PL) or triple superphosphate (TSP), total P removed in grain at harvest, cumulative P balance, and annual P balance at the Chestertown, MD (Mattapex silt loam) and Georgetown, DE (Pepperbox loamy sand) sites from 2000 to 2013. Fertilization treatments were only applied to corn in 2000-2002, 2005, 2007, 2009, 2011 and 2013.

Treatment	Total Materials Applied	Total P Applied	Total Grain Harvested	Total P Removed by Harvest	P Balance	Annual P Balance
	Mg ha <sup>-1</sup>	kg ha <sup>-1</sup>	Mg ha <sup>-1</sup>	kg ha <sup>-1</sup>		
<u>Mattapex silt loam</u>						
C	0	0 e <sup>†</sup>	99.2 ab	362 b	-362 d	-25.9 d
PL-20	20.2	175 d	100 a	374 ab	-199 c	-14.2 c
PL-43	42.6	306 c	99.1 ab	384 a	-78 b	-5.54 b
PL-65	65.0	542 a	100 a	376 ab	166 a	11.9 a
TSP	2.54	510 b	95.6 b	371 ab	139 a	9.94 a
<u>Pepperbox loamy sand</u>						
C	0	0 d	89.0 b	281 b	-281 d	-20.1 d
PL-20	20.2	187 c	94.9 b	321 a	-134 c	-9.58 c
PL-43	42.6	329 b	104 a	351 a	-22 b	-1.60 b
PL-65	65.0	522 a	96.8 ab	341 a	181 a	12.9 a
TSP	2.54	510 a	96.8 ab	332 a	178 a	12.7 a

<sup>†</sup>Values within each location with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

Table 2.3: Effect of long-term poultry litter (PL) or inorganic triple superphosphate (TSP) applications on Mehlich-3 and water extractable P concentrations, and degree of P saturation for the Mattapex silt loam (Chestertown, MD) and Pepperbox loamy sand (Georgetown, DE) in 2000 and 2013.

Treatment	Mehlich-3 P		Water Extractable P		Degree of P saturation	
	2000	2013	2000	2013	2000	2013
mg kg <sup>-1</sup>						
<u>Mattapex silt loam</u>						
C	93.2 a <sup>†</sup>	47.8 d	1.35 a	0.63 c	7.3 a	3.9 c
PL-20	81.5 a	61.1 cd	2.00 a	0.89 c	6.3 a	4.8 c
PL-43	92.7 a	91.2 bc	2.22 a	2.01 bc	7.2 a	7.5 b
PL-65	95.7 a	138 a	2.66 a	5.32 a	7.6 a	11.1 a
TSP	94.6 a	120 ab	2.32 a	3.33 b	7.3 a	9.1 ab
<u>Pepperbox loamy sand</u>						
C	64.8 a	47.0 d	1.63 a	0.57 c	7.8 a	4.8 c
PL-20	77.9 a	63.5 cd	1.59 a	0.74 c	8.2 a	5.8 bc
PL-43	69.2 a	85.3 bc	1.32 a	1.58 bc	7.3 a	7.8 bc
PL-65	56.6 a	128 a	1.25 a	4.83 a	7.0 a	12.2 a
TSP	66.8 a	98.5 ab	1.43 a	2.31 b	7.2 a	9.0 ab

<sup>†</sup>Values within each year and location with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

Table 2.4: Effect of long-term poultry litter (PL) or inorganic triple superphosphate (TSP) applications on operationally-defined soil P pools for the Mattapex silt loam (Chestertown, MD) and Pepperbox loamy sand (Georgetown, DE) in 2000 and 2013.

Treatment	H <sub>2</sub> O-extractable P		NaHCO <sub>3</sub> -extractable P		NaOH-extractable P		HCl-extractable P		Total inorganic P	
	2000	2013	2000	2013	2000	2013	2000	2013	2000	2013
mg kg <sup>-1</sup>										
<u>Mattapex silt loam</u>										
C	11.9 a <sup>†</sup>	5.40 c - <sup>††</sup>	40.0 a	22.6 c -	324 a	297 c -	48.7 a	44.0 b	425 a	370 c-
PL-20	7.62 a	5.98 c	36.1 a	31.7 bc	306 a	304 bc	44.0 a	44.3 b	394 a	386 bc
PL-43	9.90 a	12.8 b	37.2 a	36.6 b	320 a	349 abc	44.8 a	61.1 a +	412 a	460 ab
PL-65	9.87 a	24.9 a +	40.4 a	62.5 a	327 a	372 a	55.4 a	69.9 a	425 a	529 a+
TSP	9.77 a	16.5 b +	37.5 a	56.3 a +	313 a	357 ab +	49.4 a	61.1 a +	410 a	491 ab+
<u>Pepperbox loamy sand</u>										
C	5.48 a	4.54 c	23.9 c	13.3 c -	117 a	111 b	7.3 ab	7.1 b	153 a	135 c
PL-20	6.06 a	2.87 c -	33.9 a	21.0 bc -	140 a	134 ab	9.0 ab	9.7 ab	189 a	167 bc
PL-43	6.56 a	9.86 b +	33.3 ab	20.4 bc -	137 a	134 ab	10.2 a	12.8 ab	187 a	177 bc
PL-65	5.76 a	16.9 a +	27.6 bc	32.7 a +	111 a	168 a +	6.1 b	14.6 a +	150 a	233 a +
TSP	6.64 a	10.3 b +	32.3 ab	24.4 ab	138 a	144 ab	7.8 ab	11.8 ab +	185 a	191 ab

<sup>†</sup>Values within each year and location with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

<sup>††</sup> Values designated with "-" and "+" indicates values within each treatment, location, and extraction that decreased or increased significantly from 2000 to 2013.

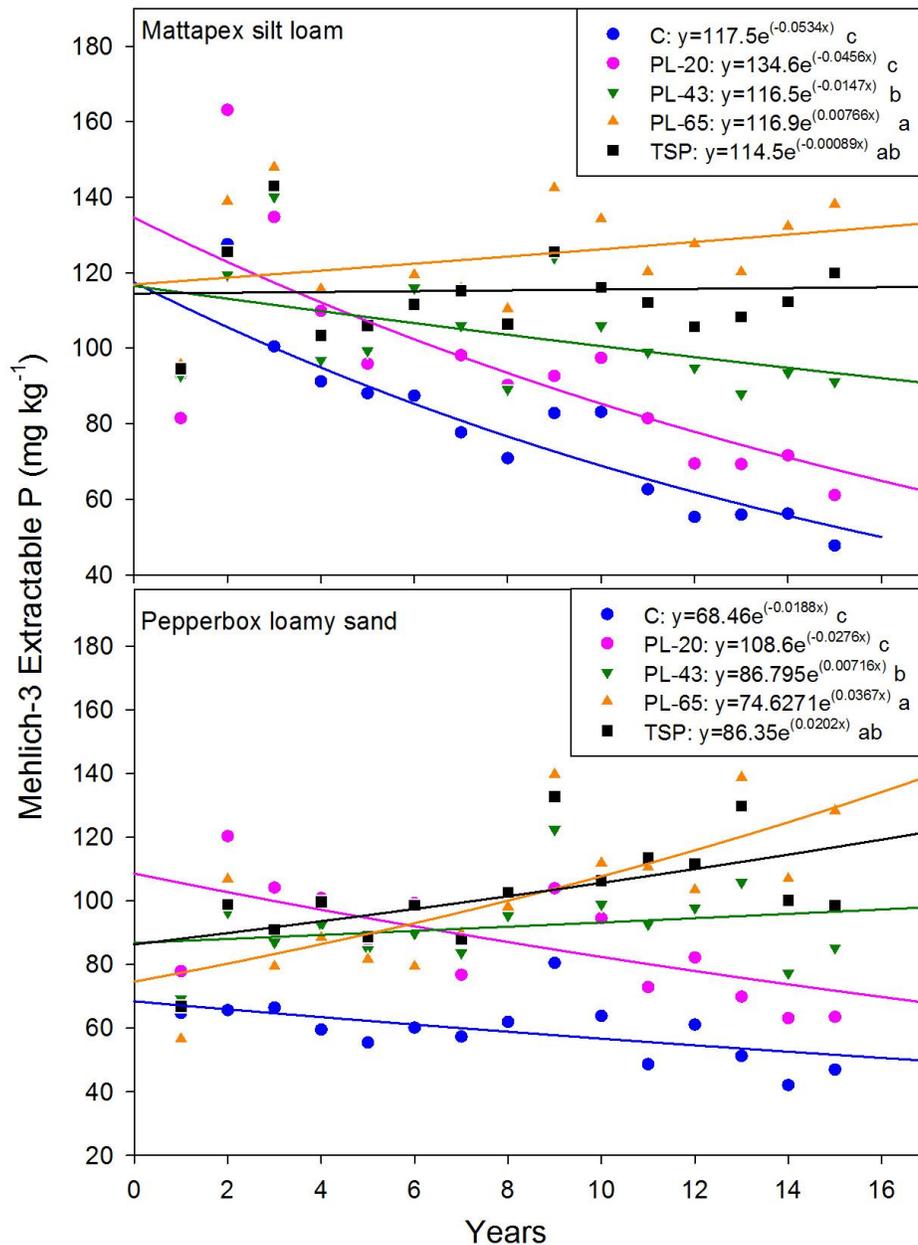


Figure 2.1: Trends in average Mehlich-3 extractable P concentration from 2000 (year 1) to 2013 for a Mattapex silt loam (Chestertown, MD) and a Pepperbox loamy sand (Georgetown, DE) receiving no P (C), poultry litter (PL), or triple superphosphate (TSP) to corn in 2000-2002, 2005, 2007, 2009, 2011, and 2013. Rate constants within each location with different letters were statistically different using Tukey's honestly significant difference test at  $P < 0.05$ .

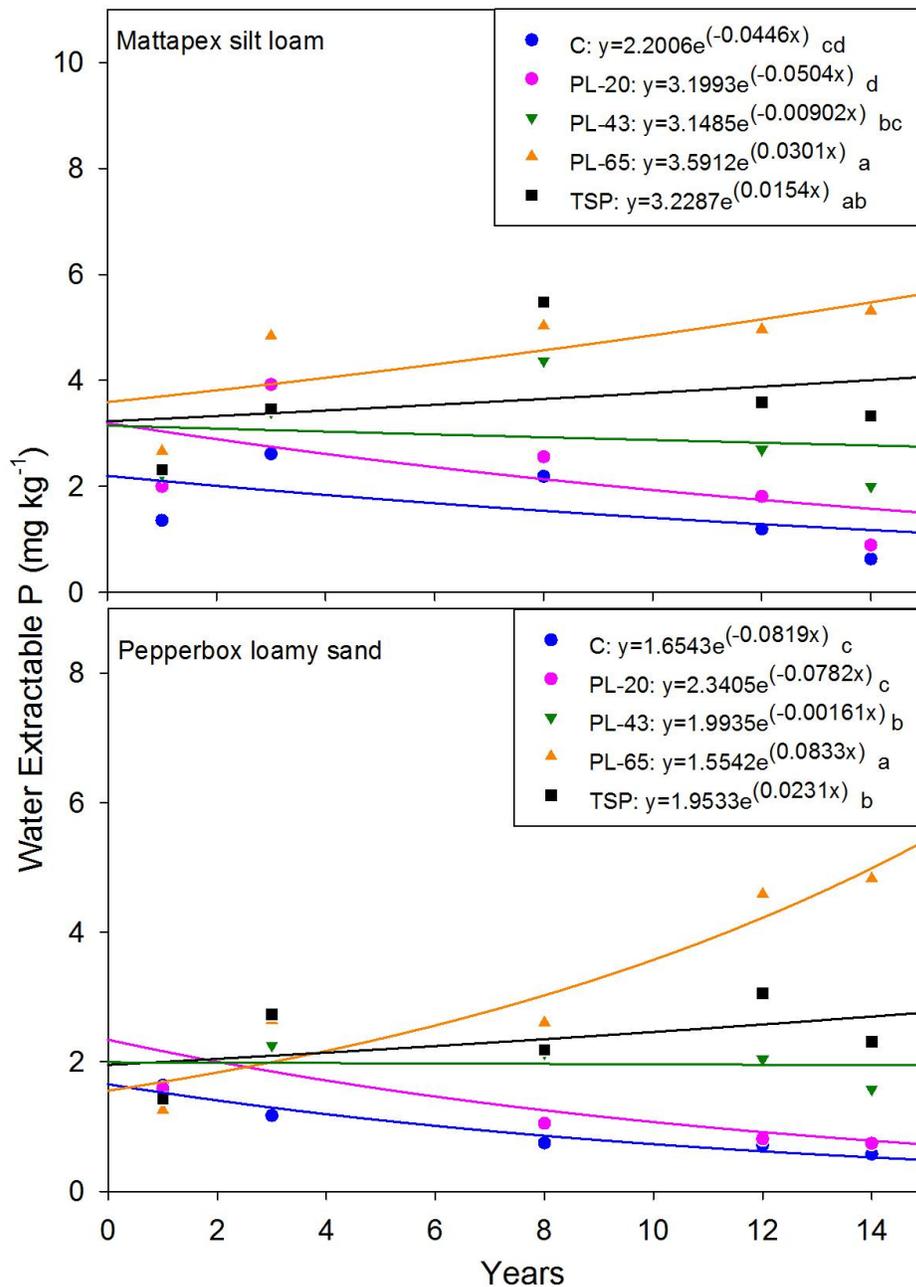


Figure 2.2: Trends in average water extractable P concentration from 2000 (year 1) to 2013 for a Mattapex silt loam (Chestertown, MD) and a Pepperbox loamy sand (Georgetown, DE) receiving no P (C), poultry litter (PL), or triple superphosphate (TSP) to corn in 2000-2002, 2005, 2007, 2009, 2011, and 2013. Rate constants within each location with different letters were statistically different using Tukey's honestly significant difference test at  $P < 0.05$ .

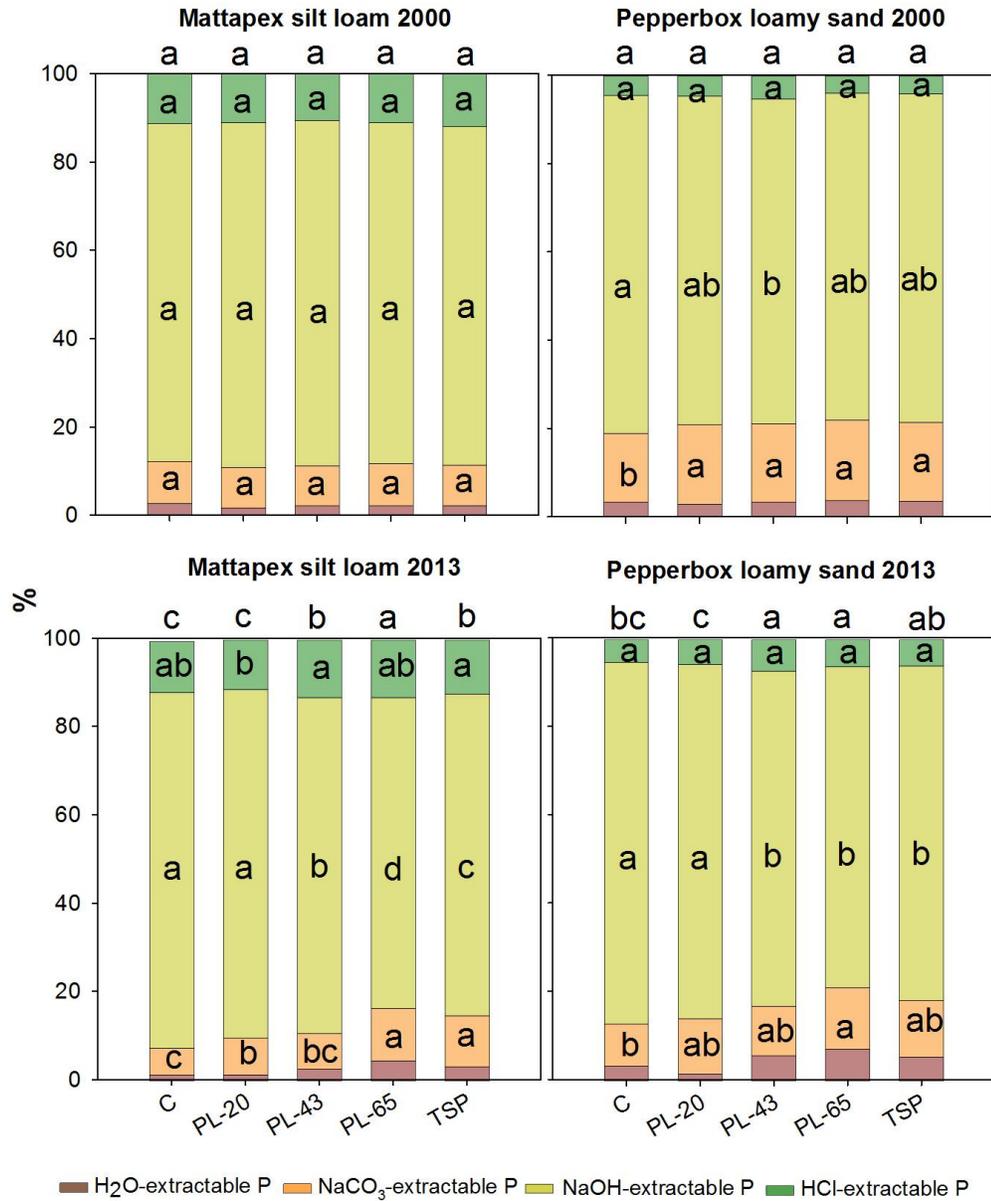


Figure 2.3: The percentage of total extractable inorganic P solubilize by H<sub>2</sub>O, NaHCO<sub>3</sub>, NaOH, and HCl for a Mattapex silt loam (Chestertown, MD) and a Pepperbox loamy sand (Georgetown, DE) before (2000) and after (2013) long-term poultry litter (PL) or triple superphosphate (TSP) applications. Values within each extraction with different letters were statistically different using Tukey's honestly significant difference test at P<0.05 (Letters showing statistical differences for H<sub>2</sub>O-extractable P are located above the bars.).

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## Chapter 3

### MECHANISMS OF PHOSPHORUS REMOVAL BY PHOSPHORUS SORBING MATERIALS

#### 3.1 Introduction

Widespread implementation of best management practices (BMPs) has significantly reduced agricultural dissolved and particulate non-point phosphorus (P) pollution over the past few decades (Sharpley, 1999; Mulla et al., 2008; Meals et al., 2010; Sharpley et al., 2011). However, traditional BMPs, such as fertilizer management (Fiorellino et al., 2017), conventional tillage to mix P-enriched surface soils with subsurface soils (Kleinman et al., 2011), and conservation tillage to reduce soil erosion (Sharpley et al., 2011) are not particularly effective at controlling dissolved P released from P-enriched soils. For example, conservation tillage can reduce soil erosion and particulate P losses from soils, but it may lead to buildup of soil test P (STP) in surface soils (0–5 cm depth) to concentrations that exceed agronomic optimum and increase the risk for dissolved P losses (Sharpley et al., 2011). Periodic tillage to mix surface P-enriched soils with subsurface soils reduces the risk of P losses in runoff from long-term no till sites, where P accumulation in the near surface is an environmental issue; however, it is only a short-term solution (Kleinman et al., 2011) and can potentially reduce crop yield by destroying soil structure and introducing low fertility subsurface soils to the surface. Some entities recommend banning application of manures and commercial P fertilizers to “high P” soils to allow draw-down of STP by crop removal. For example, Maryland state law

prohibits application of P to soils that exceed  $512 \text{ mg kg}^{-1}$  Mehlich-3 P, which is estimated to impact roughly 3,525 ha (or 11%) of crop land on Maryland's lower eastern shore (Maryland Department of Agriculture, 2016). However, implementing manure bans of this nature in areas with intensive animal production, such as the Delmarva Peninsula, could result in serious waste disposal issues and burden growers economically by requiring a shift to commercial fertilizers to supply nitrogen (N), potassium (K), and other essential plant nutrients.

By-products generated from a variety of industries, such as steel manufacturing, electrical power production, drinking water treatment, metal foundries, mining operations, and fertilizer production, can act as low-cost P sorbing materials (PSMs) that can be applied to soils to reduce P solubility (Leader et al., 2008) or used in filtration structures to remove P from drainage water (Penn et al., 2007b). These PSMs commonly contain a significant concentrations of aluminum (Al), iron (Fe), calcium (Ca), or magnesium (Mg) that can bind with P (Penn et al., 2007a). Several researchers have described how PSMs can reduce soluble P concentrations in soils (Stout et al., 1998) and manures (Staats et al., 2004) and reduce P losses in leachate (Elliot et al., 2002) and runoff from manure-amended soils (DeLaune et al., 2004; Penn and Bryant, 2006). For example, Stout et al. (1998) showed that application of two types of PSMs (e.g., fluidized bed combustion fly-ash and flue gas desulfurization by-products) at four different rates (10, 20, 40, or  $80 \text{ g kg}^{-1}$ ) reduced soil Mehlich-3 P by about  $20\text{--}110 \text{ mg kg}^{-1}$  and water extractable P (WEP) concentrations by about  $7\text{--}9 \text{ mg kg}^{-1}$  in eight soils representing a wide range of soil P, texture, and organic matter content from locations across the United States. The reduction in soil P was likely due to the conversion of readily desorbable forms of soil P to less soluble Ca-, Al-, and/or

Fe-associated pools (Stout et al., 1998). In another study, Elliot et al. (2002) monitored P in leachate from greenhouse columns where Bahiagrass (*Paspalum notatum* Flueggé) was planted on sandy Florida soils receiving triple superphosphate at a P rate of 224 kg ha<sup>-1</sup> following amendment with Fe-, Al-, and/or Ca-water treatment residuals at 56 Mg ha<sup>-1</sup>. The authors showed that addition of water treatment residuals significantly reduced total cumulative P loads in leachate within four months of amendment (0.04–1.81 kg ha<sup>-1</sup>) when compared with leachate P loads from an unamended soil (10.7 kg ha<sup>-1</sup>).

Industrial PSMs also serve as effective media for use in storm water filtration structures. A storm water filtration is a structural BMP that removes soluble P from agricultural drainage water by forcing water through a sorbent material. Filters are one of the only BMPs that are specifically designed to mitigate soluble P losses from “legacy P” soils (i.e., soils with excessive STP levels as a result of past practices) (Penn and Bryant, 2006). However, the P sorption capacity of specific PSMs varies when they are used as filtration media, and ultimately, all PSM-based filter media will eventually become saturated with P thereby reducing their efficacy. Most of the previous literature evaluates the P sorption capacity of unreacted and reacted PSMs based only on results of bulk chemical analysis (Penn and Bryant, 2006). As such, comprehensive information about the P speciation and removal mechanisms of PSMs materials is lacking. This information is vital to determine 1) the efficacy of various PSMs as filter media and 2) appropriate disposal options for PSMs once their P sorption capacity is reached.

Synchrotron based X-ray absorption near-edge structure (XANES) is an effective, in-situ tool to characterize P species (including poorly crystalline,

amorphous materials, and organic species) in mixed environmental samples, such as soils (Beauchemin et al., 2003), biosolids (Shober et al., 2006), manures (Toor et al., 2005; Shober et al., 2006), and on-site wastewater treatment media (Eveborn et al., 2009). The objective of this research is to determine the mechanisms of P removal by PSMs used in stormwater P filtrations structures using XANES.

## **3.2 Materials and Methods**

### **3.2.1 Preparation and Chemical Characterization of PSMs**

A total of 12 PSMs, including three acid mine drainage residuals (AMDR), two drinking water treatment residuals (WTR), Excell Minerals, two fly-ashes, and four electric arc furnace steel slags of varying textures were evaluated in this study (Table 3.1). The elemental composition and chemical properties of these unreacted PSMs (with the exception of slag2) were reported previously in the literature. Specifically, AMDR1 and AMDR3 were naturally formed at mining sites in Pennsylvania when acid mine drainage water flowed out of an old well to the surface where Fe became oxidized and precipitated. These materials were strongly to moderately acidic, contained the highest concentrations of digestible and oxalate extractable Fe (when compared to other PSMs), and were dominated by goethite mineral (Table 3.1; Stoner et al., 2012). The AMDR4 was collected from an engineered facility in Pennsylvania that was designed to remove acidity and precipitate Fe from acid mine drainage water. The AMDR4 had higher pH and concentrations of digestible Ca when compared with AMDR1 and AMDR3, and was dominated by calcite mineral (Table 3.1) due to the use of Ca carbonate during the acid mine drainage treatment process (Stoner et al., 2012). The Al-WTR1 and Al-

WTR2 were collected from the Tulsa, OK AB-Jewell and Mohawk drinking water treatment plants, respectively, where aluminum sulfate was used as the flocculating agent (Stoner et al., 2012). These two WTRs were materials had neutral pH, the highest total digestible and oxalate Al concentration when compared to other PSMs, and were mainly composed of quartz (Table 3.1; Stoner et al., 2012). The Excell Minerals (Harsco Corp., Camp Hill, PA) is a Ca- and Mg-silicate derived soil amendment used to supply silicon (Si) to growing plants (Stoner et al., 2012). Fly-ash1 and fly-ash2 were byproducts of a fluidized bed combustion process at coal-fired power plants located in Muskogee, OK and Red Rock, OK, respectively (Stoner et al., 2012). Four electric arc furnace steel slags with varying textures were collected periodically from a steel production facility (TMS International, Ft. Smith, AR). Specifically, slag1 was sieved to achieve particle size from 6.35 to 11 mm for use in filtration structures. The slag fines consisted of only particles < 0.5 mm diameter while slag2 consisted of particles excluding <0.5 mm diameter. The coated slag was a rejuvenated slag that was generated by treating spent (i.e., P saturated in a filtration structure) slag with Al sulfate and sieving to achieve particle size of 6.35 to 11.00 mm to increase the hydraulic conductivity when used in filtration structure; aluminum sulfate treatment resulted in the precipitation of amorphous Al hydroxide on the slag surface (Penn and McGrath, 2011). Excell Minerals, fly-ash, and all un-coated slag materials exhibited alkaline pH, while the coated slag had near neutral pH. With the exception of the AMDR4, the Excell Minerals, fly ashes, and slag material had the highest total digestible Ca concentrations; slags also contained relatively high concentrations of total digestible Fe (Table 3.1; Stoner et al., 2012). Some Fe-, Ca-,

and/or Si- associated crystalline minerals were detected in unreacted Excell Minerals, fly-ashes, and slags (Table 3.1).

All PSMs were reacted with P either in the laboratory or in the field inside a filtration structures. Specifically, the slag1 and slag2 were spent materials from filter structures that are currently deployed to remove P from stormwater runoff at field sites in Stillwater, OK. Coated slag was also evaluated as spent field material that was removed from a pond-filter structure at Oklahoma State University turfgrass research farm. The remaining PSMs (including a fresh coated slag material) were reacted with P in the laboratory under batch or flow-through conditions (Table 3.1). For batch reactions, fresh PSMs were ground into a fine powder and reacted with 5 mg L<sup>-1</sup> P solution (as KH<sub>2</sub>PO<sub>4</sub>) at a 1:15 w/v ratio for 30 min. After shaking, samples were centrifuged at 2000 rpm for 13 min and then passed through a 0.45 μm filter. The residual PSMs were then reacted with a fresh 5 mg L<sup>-1</sup> P solution again. After each reaction, filtrate was analyzed for dissolved reactive P on a spectrophotometer by the molybdate blue method (Murphy and Riley, 1962). This process was repeated sequentially for each PSM until the calculated sorbed P reached 30 mmol kg<sup>-1</sup>. In addition to the batch reaction, AMDR1 and Al-WTR2 were also reacted with P solution in a flow-through cell, which was constructed as described in DeSutter et al. (2006) and Penn and McGrath (2011). In the flow-through cell, PSMs were reacted with P solution as described in Stoner et al. (2012). Briefly, materials were reacted with 5 mg L<sup>-1</sup> inflow P concentrations at a constant rate for a period of 5 hours. Outflow solution was sampled and analyzed for dissolved P every 30 min (Stoner et al. 2012). All lab and field reacted PSMs were air-dried at room temperature and stored until analysis. After reaction, the laboratory reacted PSMs were analyzed for

elemental composition by X-ray fluorescence (XRF) (Supermini200, Rigaku Americas, Inc., The Woodlands, TX) to determine the elemental composition, and by X-ray diffraction (D8 XRD, Bruker AXS, Madison, WI) to identify crystalline mineral components.

### **3.2.2 Phosphorus Standard Preparation and Synthesis**

Reference materials included monetite ( $\text{CaHPO}_4$ ), brushite ( $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ ), hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ), fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), beta-tricalcium phosphate ( $\beta\text{-Ca}_3(\text{PO}_4)_2$ ), octacalcium phosphate ( $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ), monocalcium phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ), phytic acid, phosphate sorbed to alumina hydroxide ( $\text{Al}(\text{OH})_3\text{PO}_4$ ), Al-phosphates of varying crystallinity, variscite ( $\text{AlPO}_4 \cdot \text{H}_2\text{O}$ ), wavellite ( $\text{Al}_3(\text{PO}_4)_2(\text{OH}, \text{F})_3 \cdot 5\text{H}_2\text{O}$ ), non-crystalline Fe-phosphate, phosphate sorbed to ferrihydrite, Fe-phosphates of varying crystallinity and strengite ( $\text{FePO}_4 \cdot \text{H}_2\text{O}$ ). Monetite was purchased from J.T. Baker (Mallinckrodt Baker, Phillipsburge, NJ), brushite and hydroxylapatite were purchased from Fisher Scientific (Hampton, NH), monocalcium phosphate and phytic acid (Ca and sodium salts) were purchased from Sigma-Aldrich (St. Louis, MO), variscite was purchased from Ward's Natural Science (Rochester, NY), and fluorapatite and wavellite were purchased from Excalibur Mineral (Charlottesville, VA). The remaining standards were synthesized in the laboratory as described in Shoher et al. (2006).

### **3.2.3 Phosphorus K-edge XANES Spectra Collection**

Collection of all P K-edge XANES spectra was conducted at the bending magnet beamline 9-BM at Advanced Photon Source (APS), Argonne National Laboratory. The photon energy range used in the experiments was from 2099–2309

eV, using a Si (111) and (220) double crystal monochromator. The samples were placed in a He atmosphere to mitigate air absorption. Samples and standards were ground into fine powder using an agate mortar and pestle and pressed into a small pellet (7 mm diameter). Each pellet was attached to a double-sided carbon tape and mounted to sample holders prior to spectra collection.

Sample spectra were collected along the energy range from 2115–2266 eV while the standard spectra were collected along the energy range from 2099–2309 eV. Phosphorus K-edge XANES spectra of reacted PSM samples were collected in fluorescence mode using a 4-element Vortex silica drift detector with a step size of 1.0, 0.125, and 1.0 eV for the energy ranges of 2115–2139, 2139–2174, and 2174–2266 eV, respectively. We collected spectra of P standards in total electron yield (TEY) mode using an electron yield detector to minimize the effects of self-absorbance (which causes attenuation of the white line peak in fluorescence mode; Hesterberg et al., 1999; Shober et al., 2006), with a step size of 2.0, 0.125, and 1.0 eV for the energy ranges of 2099–2134, 2134–2179, and 2179–2309 eV, respectively. Multiple scans (2–5) were collected for each sample and averaged. The monochromator was calibrated to the maximum peak energy of the first derivative ( $E_0 = 2149$  eV) using a standard ( $P_2O_4$  in this study) at the beginning of every run and subsequently every four samples.

Data processing was performed using Athena software (Ravel and Newville, 2005). Obvious artifacts in the spectra pattern were deglitched before normalization and calibration. The raw spectrum was normalized with a normalization order of two from a pre-edge range of -50 to -10 and -33 to -10 for standards and samples respectively, and a normalization range of 15–150 and 15–115 for standards and

samples respectively. The  $E_0$  of all the spectrum was assigned to the maximum peak of its first derivative resulting in no energy shift in the spectrum. Phosphorus XANES spectra of reacted PSM samples were compared with spectra of P standards using the linear combination fitting (LCF) tool in Athena to identify the P forms and respective contributions in each PSM that provide the best fitting. The linear fitting range was -5 to 50 eV relative to the peak edge. A total of 19 P K-XANES standard spectra that were used in LCF are shown in Figure 3.1. The diagnostic features of P K-edge XANES spectra of Al-, Fe-, and Ca-associated P species were described in detail in Hesterberg et al. (1999) and Beauchemin et al. (2003). While these studies found that the spectrum of adsorbed phosphate species (e.g., P sorbed to goethite) exhibited a stronger white-line peak compared with those of the Fe- and/or Al- phosphate minerals (e.g., strengite; Hesterberg et al., 1999; Beauchemin et al., 2003), our adsorbed phosphate species generally had a less significant white-line peak compared with the more crystalline phosphate minerals (Figure 3.1). This inconsistency might be due to the fact that our standards were collected in TEY mode instead of fluorescence mode as used in Hesterberg et al. (1999) and Beauchemin et al. (2003). All standards were initially selected for LCF; samples that contributed to less than 10% of fitted spectra were systematically eliminated until all remaining fitted standards contributed to at least 10% of fitting spectra.  $E_0$  was allowed to float up to  $\pm 1$  eV during the fitting. Residual factor (R-factor) and  $\chi^2$  values were generated by the LCF tool in Athena to evaluate the goodness of fit with smaller values indicating a better fit. However, fluorapatite standard was not used for LCF eventually because we did not detect the presence of fluorine in any of our PSMs using XRF. We also did not use phytic acid in the fitting of laboratory-reacted PSMs since those materials were not

likely to contain organic form of P after reacting with inorganic P standard (as  $\text{KH}_2\text{PO}_4$ ).

### **3.3 Results and Discussions**

#### **3.3.1 Characterization of Elemental and Mineral Compositions of Reacted PSMs**

The overall composition of Al, Fe, and Ca of the laboratory-reacted PSMs (as determined by XRF; Table 3.2) was similar to the chemical compositions of raw PSMs as evaluated in previous studies using chemical digestion (Table 3.1). We also found that most of the reacted PSMs contained relatively high Si concentrations ( $>100 \text{ g kg}^{-1}$ ; Table 3.2). Materials that were rich in Ca (Excell Minerals, fly-ashes, slags, and AMDR4) also contained relatively high concentrations of Mg (Table 3.2). We did not detect crystalline P species in any of the laboratory-reacted PSMs using XRD. Our inability to identify crystalline P species using XRD was likely due to the relatively low concentration of P in the evaluated materials as determined by XRF. In fact, the P concentration of all laboratory-reacted PSMs ranged from  $3.4\text{--}24 \text{ g kg}^{-1}$  (Table 3.2), which was much lower than the concentrations of Al ( $21\text{--}520 \text{ g kg}^{-1}$ ), Fe ( $58\text{--}900 \text{ g kg}^{-1}$ ), and Si ( $44\text{--}400 \text{ g kg}^{-1}$ ). As a result, any crystalline P mineral that was formed during reaction of PSMs with P solution was likely below the detection limit of XRD.

The main crystalline minerals identified in our laboratory reacted PSM samples were calcite, goethite, and quartz (Table 3.2), which was generally consistent with those detected in fresh PSMs evaluated in previous studies (Table 3.1). However, we did not detect gypsum, tricalcium magnesium orthosilicate, and portlandite in the laboratory-reacted coated slag, Excell Minerals, and slag fines, respectively; these crystalline minerals were all identified in fresh materials from the same sources by

Stoner et al. (2012). Our inability to detect these minerals in the laboratory reacted samples might be because those minerals are somewhat water-soluble (Anthony, 1990; Stoner et al., 2012; Lebedev and Kosorukov, 2017), and thus they may have gradually dissolved during the P loading reactions to the point where they were below the detection limit of XRD. Instead, we detected quartz in laboratory-reacted AMDR3, merwinite in laboratory-reacted Excell Minerals, and calcite and periclase in the laboratory-reacted slag fines; these minerals were not identified in the fresh material by Stoner et al. (2012). The calcite in reacted slag fines could be formed from portlandite ( $\text{Ca}(\text{OH})_2$ ) being reacted with carbon dioxide-bearing solution. However, it is not likely that other minerals were formed during reacting process since minerals like merwinite and periclase are formed under relatively high temperature (Anthony, 1990). As a result, the inconsistency of XRD results may be attributed to the heterogeneity of the evaluated samples.

### **3.3.2 Characterization of P Species on PSMs**

#### **3.3.2.1 AMDRs and WTRs**

Based on the results of LCF of the XANES spectra, we identified various Fe- and/or Al-associated phosphate species in AMDR materials following reaction with P. Reaction of AMDR1 resulted in the formation of Fe-phosphate minerals (Figure 3.2 and Table 3.3), with formation of non-crystalline Fe-phosphates under batch conditions and semi-crystalline Fe-phosphates under flow conditions (Figure 3.2 and Table 3.3). Under both batch and flow conditions, a small amount (16–17%) of total P precipitated as strengite in AMDR1, a crystalline Fe-phosphate mineral. Reaction of AMDR3 with P solution resulted in sorption of  $\text{PO}_4$  to Al hydroxides and to

ferrihydrate (to a lesser extent), as well as precipitation of semi-crystalline Fe-phosphates (Figure 3.2 and Table 3.3). Reaction of AMDR4 with P solution resulted mainly in precipitation of strengite, with a smaller fraction of total P precipitated as monetite or sorbed to ferrihydrate (Figure 3.2 and Table 3.3).

The XANES fitting results for WTR materials (Al-WTR1 and Al-WTR2) revealed that reaction with P solution predominantly resulted in the formation of Al-phosphate species, namely wavellite and other Al-phosphates of varying crystallinity (Figure 3.2 and Table 3.3). To a lesser extent, reaction of the Al-WTR1 with P solution also resulted in sorption of PO<sub>4</sub> to Al hydroxide. However, semi-crystalline Al-phosphates did not form when Al-WTR2 was reacted with P under flow conditions, instead, a similar amount of strengite was formed (Table 3.3).

The predominant formation of Fe- and/or Al- phosphates when the AMDRs and WTRs were reacted with P solution is consistent with the high total and oxalate-extractable (amorphous) Al and/or Fe content of these materials (Table 3.1 and Table 3.2). Most of the AMDRs and WTRs materials (except AMDR4) also had a material pH lower than 7.5, which favors the reaction of phosphate with Al and/or Fe oxides (Penn et al., 2007a). Removal of dissolved P by Al and/or Fe will be less effective when the pH is higher than 7.5 due to a significant reduction of positive charged sites on the mineral surfaces (Rhoton and Bighan, 2005). The AMDR4 also formed a small fraction of Ca-associated phosphate (monetite) due to the higher total Ca concentration and material pH compared with other AMDRs and WTRs (Table 3.1 and Table 3.2).

Similar to our results, Ippolito et al. (2003) also found that the sorbed P on WTRs was mainly in an amorphous Al-P phase using wavelength dispersive spectroscopy. In another study, Penn et al. (2011) found that ammonium fluoride

(NH<sub>4</sub>F)- extractable P (i.e., Al-associated P) accounted for 56 and 69% of the total P removed by a AMDR and WTR material, respectively. However, Penn et al. (2011) also noted that sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)- extractable P (i.e., Ca-associated P) accounted for 58% of the total influent P removed by another AMDR material, which was largely due to the coating of calcite on the Fe and Al oxides/hydroxides that formed during the use of lime to increase pH and precipitate Fe in the acid mine drainage treatment systems (Penn et al., 2011).

### **3.3.2.2 Excell Minerals, Fly-ash, and Slags**

The two fly-ash materials evaluated in this study had very similar elemental concentrations and material pH (Table 3.1 and Table 3.2). Consequently, reaction of both fly-ash materials with soluble P resulted in the formation of Ca-phosphates, either in the form of octacalcium phosphate or hydroxyapatite (Figure 3.3 and Table 3.4). Similar to fly-ash, the Ca-rich, alkaline Excell Minerals also formed Ca-phosphate minerals (i.e., hydroxyapatite and monetite) when reacted with P (Figure 3.3 and Table 3.4).

Reaction of P (either in the laboratory or in the field) with all evaluated slag materials resulted in the formation of hydroxyapatite (36.7–87% of total P; Figure 3.3 and Table 3.4). In addition, the slag materials (with the exception of field-reacted slag1) also precipitated Fe- and/or Al- associated phosphates (non-crystalline and/or semi-crystalline) (Figure 3.3 and Table 3.4). However, the batch-reacted coated slag only formed 14.8% Al-associated phosphate, which is lower than our expectation considering the coating of Al sulfate at the surface of this slag material. We believe that the grinding of samples before reacting with P destroyed the Al coating. As a

result, the batch-reacted coated slag was similar to normal Ca-rich slag materials in the end.

The predominant formation of Ca-phosphate when P was reacted with Ca-rich alkaline materials (i.e., Excell Minerals and fly-ashes) and most of the slag materials is consistent with the fact that those materials had among the highest total and/or water-soluble Ca and relatively high material pH (>9 except the coated slag; Table 3.1 and Table 3.2). Others also reported the formation of Ca-phosphate dominated over other chemical forms when slags and/or Ca-rich alkaline materials were reacted with P (Eveborn et al., 2009; Hussain et al., 2014; Zuo et al., 2015). For example, Zuo et al (2015) evaluated the P speciation in argon oxygen decarburization slag that was designed for use in wastewater treatment using a combined Visual MINTEQ and XANES analysis. The authors indicated that dissolved phosphate mainly precipitated with Ca when reacted with slag materials, with apatite and brushite being the dominant precipitates formed under highly alkaline and neutral solution conditions, respectively (Zuo et al., 2015). Hussain et al. (2014) characterized the P species of basic oxygen furnace slag that was used to treat P-rich lake water through a series of spectroscopic tools. The results showed that dissolved phosphate either sorbed to calcite or precipitated as calcium phosphate dibasic dehydrate when reacted with the slag materials (Hussain et al., 2014). In another study, Eveborn et al. (2009) used XANES to identify P speciation of six Ca-rich alkaline filter media (Filtralite P, Filtra P, Polonite, Absol, blast furnace slag, and wollastonite) that were used for on-site wastewater treatment. The authors reported that reaction of wastewater with all six materials formed a significant amount (>30%) of crystalline Ca-phosphate (e.g., octacalcium phosphate, hydroxyapatite, and/or monetite). Some amorphous Ca-

phosphate (14–63%) also formed when wastewater was reacted with Filtralite P, Filtra P, Polonite, or Absol. More than 35% of the P sorbed by Filtralite P and blast furnace slag was also associated with Fe and/or Al (hydrated Al-phosphate, phosphate adsorbed to Al oxide or ferrihydrite; Eveborn et al., 2009). Contrary to our findings, Penn et al. (2011) reported that the formation of Al-bound P ( $\text{NH}_4\text{F}$ -extractable P) dominated when P solution was reacted with fly-ash using a sequential fractionation analysis. However, the fly-ash evaluated by Penn et al. (2011) had a lower total Ca concentration ( $38.6 \text{ g kg}^{-1}$ ) and pH (8.2) than the untreated fly-ash materials evaluated in our study (Table 3.1 and Table 3.2), which explains the variation in P speciation with our study.

Other researchers also reported the presence of amorphous calcium phosphates (Eveborn et al., 2009; Zuo et al., 2015) or phosphate sorbed to calcite (Hussain et al., 2014) when slag and/or Ca-rich alkaline materials were used as PSMs. However, we only identified crystalline Ca-phosphate (mainly hydroxyapatite) in our evaluated PSMs. This was likely because we did not have any non-crystalline Ca-phosphates or sorbed phases of Ca in our standards library. Therefore, we suggest that amorphous Ca-phosphate could be present in our reacted slags and/or Ca-rich alkaline PSMs, especially when the material pH was lower or near 9.3 (e.g., coated slag and slag1). The XRD analysis on the reacted coated slag indicated the presence of calcite (Table 3.2) and when combined with a pH close to 7, could result in the sorption of phosphate to calcite when reacted with P. Drizo et al. (2002) also suggested that amorphous Ca-phosphates would be converted to octacalcium phosphate at pH of 7 to 9; the latter would quickly hydrolyze to hydroxyapatite under more alkaline conditions ( $\text{pH} > 9.3$ ).

### 3.3.3 Phosphorus Removal Mechanism of PSMs

Based on the characterization of P species on the reacted PSMs, we can generally divide our evaluated materials into three categories in terms of the dominant P removal mechanisms. Removal of P from solution by most slag materials, the fly-ashes, and the Excell Minerals was driven by Ca sorption or precipitation. The P removal by AMDRs and WTRs was driven by sorption to Al- or Fe-(hydr-)oxides or precipitation of Al- or Fe-phosphates. In contrast, P removal from stormwater by slag materials (coated slag and slag<sub>2</sub>) used in field scale filtration structures occurred by both mechanisms (Ca and Al/Fe).

To some degree, the dominant P removal mechanism was identifiable by evaluating the total concentration of P sorbing elements Ca, Fe, and Al (either using XRF or chemical digestion), where PSMs with higher total Al/Fe or Ca concentrations generally had a dominant P removal mechanism of Al/Fe or Ca sorption, respectively. Amorphous Fe or Al, and water-soluble Ca pools were also important in estimating the major P removal mechanism of PSMs, since they represent the most reactive types of the sorbing elements (Penn et al., 2007a). However, P removal mechanism was also affected by the chemical and physical environment (e.g., pH, buffer capacity, ionic strength, ion composition, and P concentration in the influent solution, etc.) in which the P sorption takes place (Penn et al., 2011). For example, we found that the AMDR1 and Al-WTR2 reacted with P solution under flow-through conditions formed more semi-crystalline and/or highly crystalline Fe- and/or Al-phosphate compared with those reacted through batch experiment (Table 3.3). This may be related to the more constant and stable P concentration in the flow-through system compared with batch reaction (P concentration will gradually decrease as dissolved P sorb to PSMs in batch reaction). In comparison, coated slag removed P predominantly by Ca precipitation

when batch-reacted in the lab with pure phosphate solution while. However, when the same material was used as field PSMs in filtration structure, a significant amount of the P removed from stormwater was associated with Al (Table 3.4). This was largely due to the loss of Al-coating of lab-reacted coated slag because of the grinding of samples before P sorption. Overall, PSMs reacted in the field were exposed to a more complex and dynamic solution environment (more solutes) compared with the lab-controlled batch or flow-through reaction environment (reacting with P only).

We also recognize that P removal is not a static process (especially under field conditions). As a result, it is possible that the major P removal mechanism will shift as the properties of PSMs and/or solution environment changes in the filtration structure. For example, Eveborn et al. (2009) found the presence of Fe- and/or Al-associated P (9–48% of total sorbed P) in some alkaline filter media (Filtralite P, Filtralite P, and Polonite) used for wastewater treatment. The authors proposed that those materials removed dissolved P from solution initially by Ca-phosphate precipitation. As Ca stores gradually become exhausted, the solution pH drops, causing the dissolution of some Ca-phosphates and formation of Fe- and/or Al- associated phosphate species (Eveborn et al., 2009). This shift in the chemical properties of the reaction environment may explain the equally important role of Al/Fe and Ca based mechanism in P removal by field-reacted coated slag and slag<sub>2</sub> materials as predicted by our XANES analysis. It is also possible that Fe and/or Al played a more important role in removing dissolved P once the stored Ca is used up in field-reacted coated slag and slag<sub>2</sub>. However, we noticed that Fe- and/or Al-associated P did not form in field-reacted slag<sub>1</sub> material, which might due to the variability in reacting environment.

Moreover, even if PSMs exhibit the same dominant P removal mechanism, there can still be significant differences in the chemical forms of accumulated P species. For example, AMDR1 and AMDR3 both removed P by Fe and/or Al sorption; but AMDR1 mainly formed Fe-phosphate precipitates. In contrast, P removed by AMDR3 was mainly adsorbed to Fe and/or Al (hydr-)oxides (Table 3.3). As a result, bulk chemical analysis alone cannot provide a full prediction of the P speciation and P removal mechanisms on different PSMs.

Magnesium and manganese (Mn) can also play an important role in some of the evaluated PSMs; however, we did not include any Mg- or Mn-associated phosphate species in our evaluated XANES standards. Specifically, Mg is a P sorbing element that behaves like Ca and tends to precipitate P at relatively high solution pH (Penn et al., 2011). As a result, it is likely that our slags and Ca-rich alkaline PSMs also removed dissolved P by precipitating as Mg-phosphate since those reacted PSMs also contained notable amounts of Mg (Table 3.2). Phosphate precipitation with Mn is another important mechanism that removes dissolved P in solution (Leader et al., 2008), which happens mostly at the pH of 6.5–9 (Heintze, 1968). Considering the material pH (Table 3.1) and the amount of Mn in the reacted PSMs (Table 3.2), it is plausible that Mn-phosphate precipitates formed when P was reacted with WTRs, AMDR4, and coated slag.

### **3.3.4 Selection of PSMs for Stormwater Filtration and Recycling Options**

The determination of P removal mechanism and P speciation can shed light on the selection of PSMs in use for stormwater filtration structure and the recycling of spent (P-saturated) materials. From the perspective of effective P removal, P removal via adsorption to the surface of Fe and/or Al minerals is more rapid compared with the

P removal via Ca precipitation (Penn et al., 2007a). Oxides of Fe and/or Al also potentially bind P more strongly than Ca-based sorbents; the latter normally have higher likelihood of desorption (Lyngsie et al., 2014). As a result, PSMs that remove P via the Fe/Al mechanism are generally more efficient filtration media compared with PSMs that rely on Ca-based removal mechanisms (Dou et al., 2003; Moore and Miller et al., 1994), and therefore, are preferred for use in stormwater filtration structures due to the short contact time of stormwater with PSMs in the filtration structure. Materials that remove P majorly by adsorbing to the surface of Fe and/or Al (hydr-)oxides (e.g., AMDR3) are especially preferred for structures with relatively high flow rates since this process is even faster than Fe and/or Al phosphate precipitation (McGechan and Lewis, 2002). However, other physical and chemical properties of PSMs (e.g., specific surface area, porosity, and particle distribution etc.) and the reacting environment (e.g., solution pH, redox condition, etc.) are also important when selecting appropriate materials for different filtration structure (Richardson and Craft, 1993; Drizo et al., 1999; Lyngsie et al., 2014). For example, PSMs that sorb based on the Fe or Al mechanism may have reduced sorbing capacity at elevated pH levels (Hieltjes and Lijklema, 1980), while PSMs that remove P by the Ca or Mg mechanism may have reduced sorbing capacity under low pH conditions (Leader et al., 2008). Also, sorption of P to Fe- or Al-rich materials is greater for materials with amorphous structure, such as ferrihydrite, when compared with PSMs that are dominated with crystalline minerals like goethite or gibbsite (Penn et al., 2007a).

On the other hand, PSMs that capture soluble P in adsorbed or amorphous form are more desirable from a P recycling perspective compared with PSMs that precipitate P in crystalline form (Eveborn et al., 2009). When spent PSMs are surface

applied to soils as a source of P, these materials that contain sorbed or non-crystalline P phases will likely be more plant available when compared to PSMs containing crystalline P minerals with lower solubility. Also, PSMs that sorb P based on Al and/or Fe mechanism are likely to be less soluble than PSMs that sorb P based on Ca mechanism under acidic conditions. As a result, AMDRs and WTRs are less suitable for application to acidic soils as a P fertilizer in terms of plant P availability when compared to slags and Ca-rich alkaline materials. However, other material properties, such as pH, electrical conductivity, sodium content, heavy metal content, etc., need also be considered to ensure the safety of ecosystem function and crop consumption when spent PSMs are applied to soils (Penn et al., 2011). For example, our XRF results indicated the presence of trace elements in some of the evaluated PSMs (Table 3.5). The coated slag and Excell Minerals in particular contained about 20 g kg<sup>-1</sup> chromium. Although the concentrations of most trace elements were generally low (<10 g kg<sup>-1</sup>) in the evaluated PSMs, the elemental analysis by XRF does not provide any information on the bioavailability and the transport potential of the hazardous elements once the PSMs are applied to soils. As a result, special caution should be taken and additional risk assessments should be exercised before using those PSMs for land application.

Table 3.1: Selected chemical properties of P sorbing materials prior to reaction with phosphate solution in the laboratory or stormwater in the field.

Material ID	Reaction type	Total Ca	Total Al	Total Fe	Oxalate Al	Oxalate Fe	Water-soluble Ca	pH	Crystalline minerals	Reference
<u>g kg<sup>-1</sup></u>										
<u>Laboratory Reacted Materials</u>										
AMDR1	Batch and flow- through	0.2	2.0	455	0.1	26	0.1	3.2	Goethite	Stoner et al. (2012)
AMDR3	Batch	8.3	9.3	338	0.4	40	3.7	6.4	Goethite	Stoner et al. (2012)
AMDR4	Batch	204	17	118	5.4	33	0.7	8.4	Calcite	Stoner et al. (2012)
Al-WTR1	Batch	3.3	157	17	58	2.5	0.4	7.3	Quartz	Stoner et al. (2012)
Al-WTR2	Batch and flow-through	19	81	15	37	2.1	2.2	7.3	Quartz	Stoner et al. (2012)
Coated slag	Batch	270	41	152	- <sup>†</sup>	-	5.8	7.1	Calcite, Gypsum, Tri-calcium magnesium orthosilicate	Penn and McGrath (2011)
Excell Minerals	Batch	268	20	71	2.3	19	0.2	10.9	orthosilicate	Stoner et al. (2012)
Fly-ash1	Batch	151	87	42	27	8.6	1.1	11.4	Quartz	Stoner et al. (2012)
Fly-ash2	Batch	153	65	37	29	10	1.0	11.4	Quartz	Stoner et al. (2012)
Slag fines	Batch	272	37	155	0.9	4.4	0.6	11.3	Portlandite	Stoner et al. (2012)
<u>Field Reacted Materials</u>										
Slag1		195	20	164	-	-	0.2	9.4	-	Penn et al. (2012)
Coated slag		270	41	152	-	-	5.8	7.1	Calcite, gypsum	Penn and McGrath (2011)
Slag2 <sup>††</sup>		245	28	112	0.3	2.2	-	11.6	-	Penn (2017), unpublished data

<sup>†</sup>Data not available.

<sup>††</sup>pH was determined using a 1:1 w/v ratio instead of 1:5 w/v; Total element concentrations were determined by EPA3050 digestion instead of EPA3051 digestion.

Table 3.2: X-ray fluorescence analysis of selected elemental composition and X-ray diffraction analysis of crystalline minerals on laboratory reacted PSMs after reacting with P under batch (not specified) or flow-through condition (specified in parenthesis).

Material ID	P	Fe	Al	Ca	Mg	Mn	Si	Crystalline minerals
	g kg <sup>-1</sup>							
AMDR1	6.5	840	29	nd <sup>†</sup>	9.5	0.9	100	Goethite
AMDR1 (Flow-through)	12	900	21	nd	nd	1.0	50	Goethite
AMDR3	4.2	640	86	4.6	nd	1.1	250	Goethite, quartz
AMDR4	3.4	270	55	440	130	28	44	Calcite
Al-WTR1	19	77	520	11	6.7	11	310	Quartz
Al-WTR2	24	77	350	38	7.6	59	400	Quartz
Al-WTR2 (Flow-through)	16	82	300	92	8.9	75	360	Quartz
Coated slag	18	190	150	300	120	54	140	Calcite
Excell Minerals	12	98	67	410	160	16	210	Merwinite
Fly-ash1	21	76	220	240	77	nd	330	Quartz
Fly-ash2	21	58	200	240	88	nd	290	Quartz
Slag fines	24	89	130	350	280	22	94	Calcite, periclase

<sup>†</sup>nd – Concentration was below the instrument detection limit.

Table 3.3: X-ray absorption near-edge structure spectroscopy linear combination fitting results showing the relative proportion of phosphate (PO<sub>4</sub>) standards giving the best fit to spectra from acid mining drainage residual (AMDR) and drinking water treatment residual (WTR) samples. The fitting range is from -5 to 50 eV. The materials are reacted under batch (not specified) or flow-through condition (specified in parenthesis).

Material ID	PO <sub>4</sub> sorbed to				PO <sub>4</sub> sorbed to					R-factor
	Al hydroxide	Al-PO <sub>4</sub> (10d) <sup>††</sup>	Al-PO <sub>4</sub> (30d)	Wavellite	ferrihydrite	Amorphous Fe-PO <sub>4</sub>	Fe-PO <sub>4</sub> (3d)	Strengite	Monetite	
% of total P										
AMDR1	- <sup>†</sup>	-	-	-	-	83.2	-	16.0	-	0.0026
AMDR1 (Flow-through)	-	-	-	-	-	-	81.6	16.8	-	0.0007
AMDR3	66.5	-	-	-	19.6	-	14.6	-	-	0.0016
AMDR4	-	-	-	-	17.1	-	-	70.5	12.0	0.0011
Al-WTR1	12.4	23.4	36.6	24.6	-	-	-	-	-	0.0003
Al-WTR2	-	11.2	47.1	39.5	-	-	-	-	-	0.0003
Al-WTR2 (Flow-through)	-	-	-	36.5	-	-	-	59.9	-	0.0084

<sup>†</sup>Species not identified using linear combination fitting.

<sup>††</sup>Semi-crystalline P species. The reaction days are specified in the parenthesis.

Table 3.4: X-ray absorption near-edge structure spectroscopy linear combination fitting results showing the relative proportion of phosphate (PO<sub>4</sub>) standards giving the best fit to spectra from Excell Minerals, fly-ashes, and a variety of slag samples. The fitting range is from -5 to 50 eV.

Material ID	PO <sub>4</sub> sorbed								R-factor
	to Al hydroxide	Amorphous Al-PO <sub>4</sub>	Al-PO <sub>4</sub> (10d) <sup>††</sup>	Al-PO <sub>4</sub> (30d)	Amorphous Fe-PO <sub>4</sub>	Monetite	Octacalcium -PO <sub>4</sub>	Hydroxyapatite	
% of total P									
Laboratory Batch Reacted Materials									
Coated slag	14.8	- <sup>†</sup>	-	-	-	-	-	87.0	0.0045
Excell Minerals	-	-	-	-	-	16.4	-	81.2	0.0024
Flyash1	-	-	-	-	-	-	59.1	39.3	0.0032
Flyash2	-	-	-	-	-	-	19.8	78.8	0.0028
Slag fines	-	-	-	-	11.4	-	-	86.9	0.0025
Field Reacted Materials									
Slag1	-	-	-	-	-	24.7	-	72.5	0.0407
Coated slag	20.8	-	13.4	26.9	-	-	-	36.7	0.0008
Slag2	-	40.4	-	-	14.2	-	-	44.4	0.0048

<sup>†</sup>Species not identified using linear combination fitting

<sup>††</sup>Semi-crystalline P species. The reaction days are specified in the parenthesis

Table 3.5: X-ray fluorescence analysis of heavy metals and other potential contaminants on laboratory reacted PSMs after reacting with P under batch (not specified) or flow-through condition (specified in parenthesis).

Material ID	Ag	As	Br	Cr	Cu	Nb	Ni	Sr	Ti	Zn	Zr
	g kg <sup>-1</sup>										
AMDR3	- <sup>†</sup>	-	-	-	-	-	-	-	3.9	-	-
AMDR4	-	-	-	-	-	-	1.3	2.4	-	2.0	-
Al-WTR1	-	0.4	-	-	-	-	-	0.4	-	-	0.3
Al-WTR2	-	0.4	0.5	-	0.8	-	-	-	-	-	0.3
Al-WTR2 (Flow-through)	1.8	-	1.3	-	1.6	-	0.5	0.4	10	-	0.2
Coated slag	-	-	-	17	0.3	0.2	-	0.3	4.2	0.4	0.6
Excell Minerals	-	-	-	23	-	1.0	0.8	0.4	6.1	-	0.6
Flyash1	-	-	-	-	-	-	-	4.6	13	0.4	-
Flyash2	-	-	-	-	0.2	-	-	3.4	10	-	-
Slag fines	-	-	-	4.9	0.3	-	-	0.1	1.8	1.3	0.6

<sup>†</sup> Concentration was below the instrument detection limit

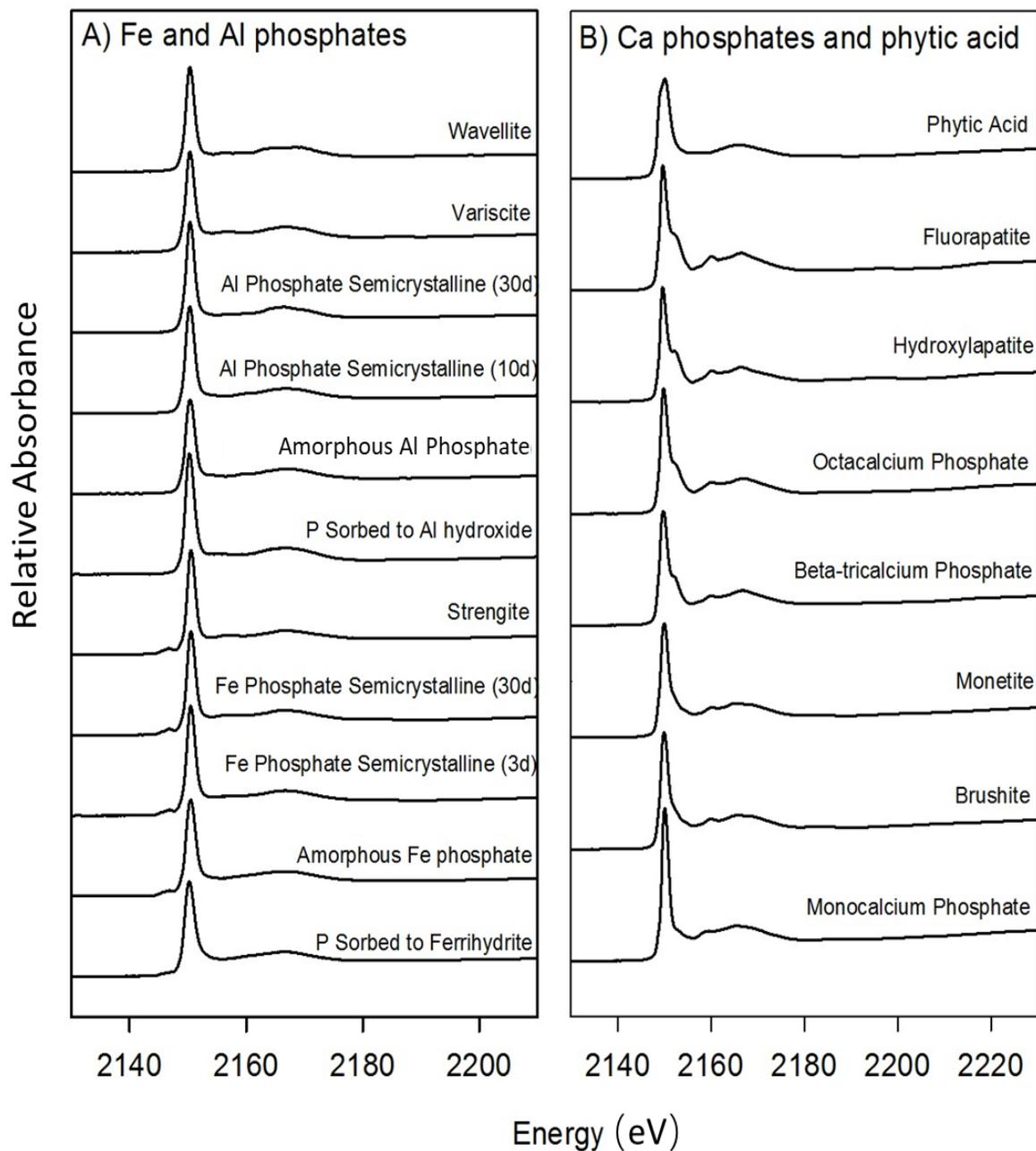


Figure 3.1: Phosphorus K-XANES spectra of phosphate standards used in linear combination fitting.

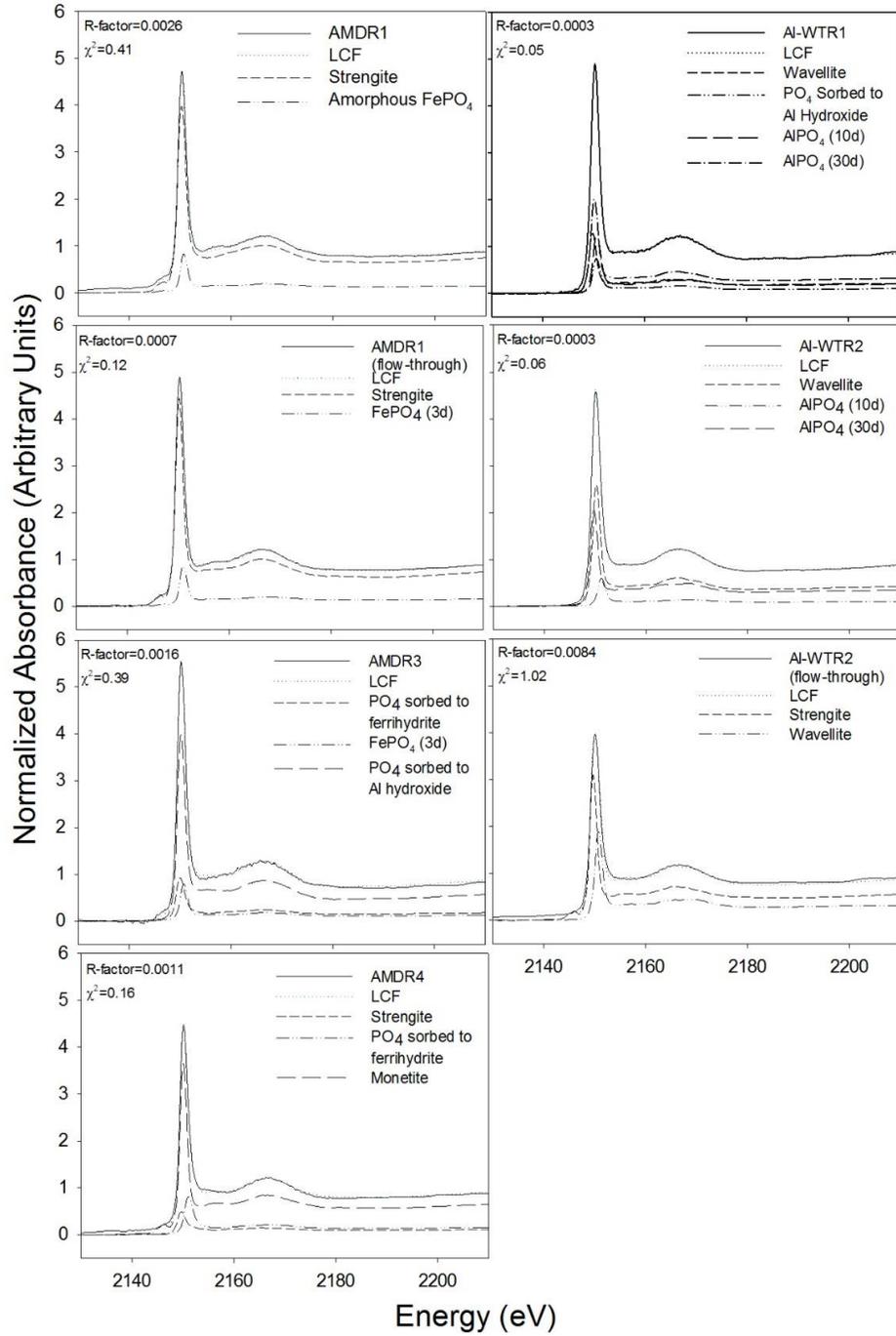


Figure 3.2: Linear combination fitting (LCF) results for acid mining drainage residuals (AMDR) and drinking water treatment residuals (WTR) materials reacted under batch or flow-through condition (specified in the parenthesis).

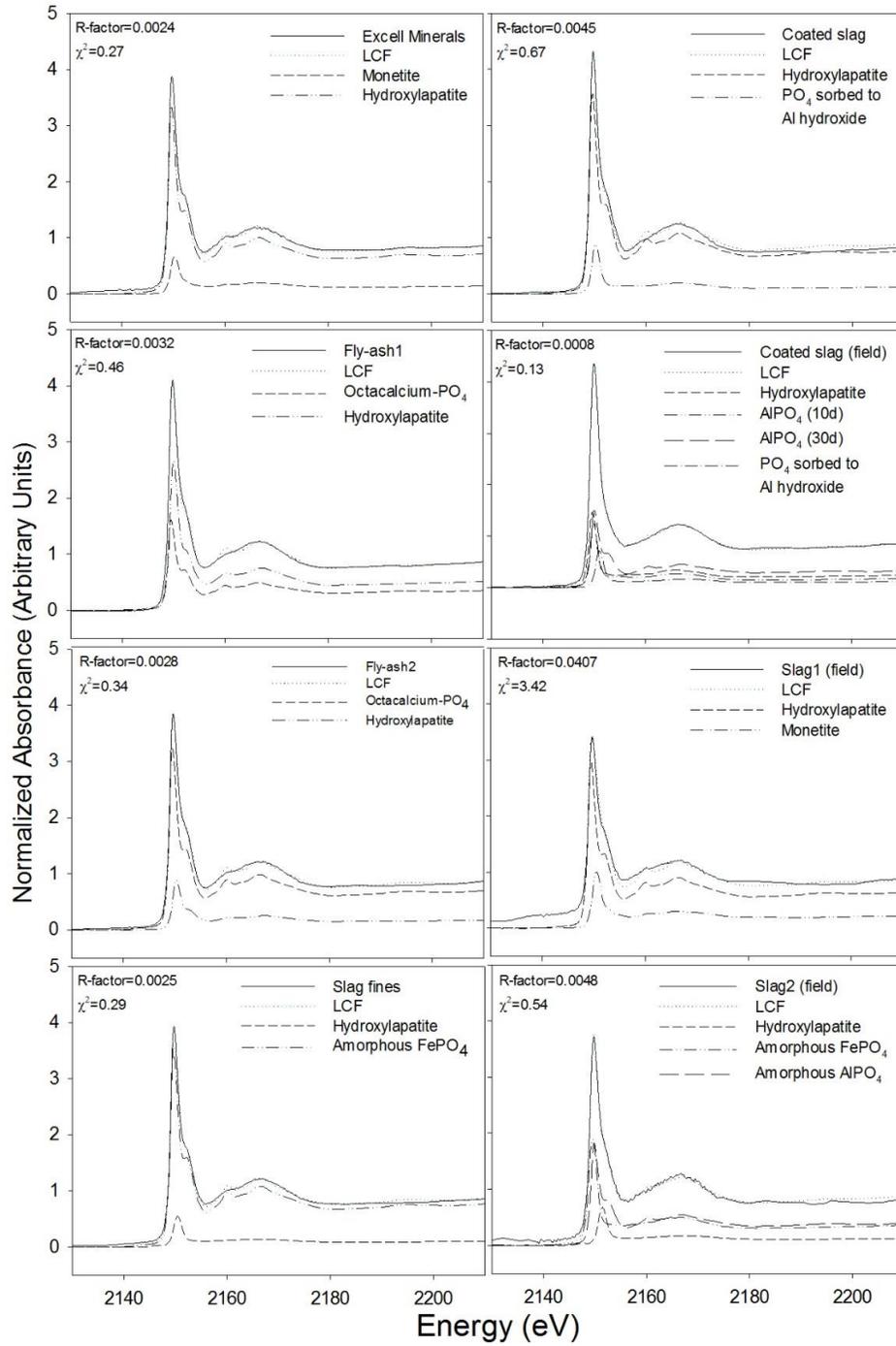


Figure 3.3: Linear combination fitting (LCF) results for Excell Minerals, fly-ashes, and slag materials reacted under laboratory batch condition or in the field (specified in the parenthesis).

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## Chapter 4

### SILICON FERTILIZERS ENHANCE SOIL P AVAILABILITY AND UPTAKE FROM LEGACY P SOILS BY WINTER WHEAT

#### 4.1 Introduction

Grain farmers in areas of intensive animal production like the Delmarva Peninsula, face significant nutrient management issues related to phosphorus (P) build-up in soils from historical application of manure to agricultural lands at rates that exceeded crop P removal. This accumulated or “legacy” P acts as a slow source of dissolved P from agricultural soils during runoff and/or leaching events (McDowell et al., 2002; Kleinman et al., 2011) and can negatively impact water quality in sensitive water bodies, like the Chesapeake and Delaware Inland Bays. As a result, it is important for farmers to carefully manage legacy P soils to reduce the risk of P losses.

Despite the prevalence of legacy P soils on Delmarva, farmers often indicate issues with P uptake by crops, particularly with small grains like winter wheat [*Triticum aestivum* L.]. Many farmers tout the benefits of starter P fertilizers on winter wheat to combat early season P deficiency and ensure the good fall tillering that is vital for achieving maximum yields (Grant et al., 2001; Stewart et al., 2003). Early season P deficiency is related to cool soil temperatures at the time winter wheat is planted (Grant et al., 2001) and the fact that P bound strongly to iron (Fe) and aluminum (Al) in acid soils may not be immediately available to growing crops. However, application of P fertilizer to legacy P soils is often considered taboo because supplemental P applications may further enrich soils with P, thereby exacerbating

regional water quality issues. As a result, it is important to identify effective best management practices (BMPs) that can improve early season P availability to winter wheat and enhance the crop removal of soil P.

Silicon (Si) is the second most abundant element in the earth's crust and is a non-essential nutrient for plant growth; Si is taken up by plants as silicic acid ( $\text{H}_4\text{SiO}_4$ ; Lewin, 1969; Seyfferth and Fendorf, 2012). Typically, the soil solution contains about 0.1 to 0.6 *mM* Si, mainly in the form of  $\text{H}_4\text{SiO}_4$  (Epstein, 1994). Researchers have shown that monocot plant species, such as winter wheat, barley and rice, accumulate Si in plant tissue (Ma and Takahashi, 1991; Tubaña and Heckman, 2015). While Si is often not considered an essential nutrient, several researchers showed that application of supplemental Si can increase plant resistance to diseases (Heckman et al., 2003; Provance-Bowley et al., 2010) and abiotic stressors (Owino-Gerroh and Gascho, 2005; Tubaña and Heckman, 2015). Application of supplemental Si has also been shown to increase concentrations of P in the plant tissue of corn (Owino-Gerroh and Gascho, 2005), barley (Brenchley et al., 1927; Fisher, 1929), and grass species (i.e., rhodes grass, timothy grass, sudangrass, and tall fescue; Eneji et al., 2008); application of Si can also increase crop yields (Fisher, 1929; Provance-Bowley et al., 2010). As such, the effects of Si on soil P dynamics, plant uptake of P, and crop yield are of interest because Si fertilization may help to enhance crop P uptake, eliminate the need for fall starter-P applications for small grains, and improve small grain yields.

Researchers attribute an increase in crop P uptake to increased soil P solubility (Smyth and Sanchez, 1980) due to substitution of Si for P on the soil matrix (Koski-Vahala et al., 2001), increased soil pH in acid soils after Si fertilization (Owino-Gerroh and Gascho, 2005), and inhibition of metal toxicities (e.g., Fe, Al, and

manganese (Mn); Ma and Takahashi, 1991). For example, Koski-Vahala et al (2001) surmised that addition of high concentrations of soluble Si will compete with P for sediment sorption sites, and thus increase P desorption from sediment and soluble P concentrations in interstitial water, especially under elevated pH. Lee et al. (2004) also reported an increase in the amount of P desorbed from a silt loam and loam soil (covered with plastic film) with increasing Si concentration and temperature. However, some researchers report a decrease in plant P uptake following Si fertilization (Ma and Takahashi, 1989; 1990; Gao et al., 2005). For example, Ma and Takahashi (1990) found that addition of Si can reduce P uptake of cultured rice compared with unamended controls when P concentrations of Kimura B nutrient solution are very high. The authors suspected this was a beneficial effect of Si addition to reduce the high osmotic pressure in plant cell due to excess P uptake (Ma and Takahashi, 1990).

In light of contradicting reports of the effects of Si on crop P uptake, we evaluated the effects of Si addition on soil P dynamics and crop P uptake, especially for acid soils with excessive soil test P concentrations where P is bound to soil Fe and Al minerals. We hypothesize that applied soluble Si will replace adsorbed P on the soil exchange complex and increase soil P solubility, thereby enhancing P uptake by small grains (such as winter wheat). The objectives of our research are 1) to evaluate the ability of Si fertilization (at different sources and rates) to enhance soil P availability from legacy P soils in a soil-only incubation trial, and 2) to determine the effects of Si fertilizer sources (especially available agronomic Si sources that would be accessible to and easily applied by farmers) and Si rate on soil P dynamics and winter wheat response (e.g., yield, P uptake) in a pot trial.

## 4.2 Materials and Methods

### 4.2.1 Soil Selection and Characterization

Soil samples were collected from three legacy P impacted agricultural fields near Millsboro, DE. The major soil complexes for the fields were Ft. Mott (Loamy, siliceous, semiactive, mesic Arenic Hapludults)-Henlopen (Sandy, siliceous, mesic Lamellic Paleudults), Ingleside (Coarse-loamy, siliceous, semiactive, mesic Typic Hapludults)-Hammonton (Coarse-loamy, siliceous, semiactive, mesic Aquic Hapludults), and Mullica (Coarse-loamy, siliceous, semiactive, acid, mesic Typic Humaquepts)-Berryland (Sandy, siliceous, mesic Typic Alaquods), respectively. Composite soil samples were randomly collected to a depth of 15 cm from each field using a shovel to obtain several kilograms (equivalent to 0.21 m<sup>3</sup> soil) of soil for use in incubation and pot studies. Soils used for incubation study were collected from the same field eight-months later than soils used for pot study. The soils were air-dried following removal of large pieces of plant detritus and soil clods (larger than fist size).

Prior to initial chemical analysis, soil samples were ground and sieved through 2-mm screen. Soil samples were analyzed, in duplicate, using NECC (2011) standard soil testing procedures for pH (1:10 soil/deionized water), Adams-Evans buffer pH, and organic matter by loss on ignition, as well as for soil particle size using hydrometer method (Bouyoucos, 1962). Soil test P, Al, Fe, potassium (K), magnesium (Mg), manganese (Mn) and calcium (Ca) concentrations were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) following Mehlich-3 extraction (1:10 ratio of soil to 0.2 M CH<sub>3</sub>COOH + 0.025 M NH<sub>4</sub>NO<sub>3</sub> + 0.015 M NH<sub>4</sub>F + 0.13 M HNO<sub>3</sub> + 0.001 M EDTA; 5-min reaction time; NECC, 2011). The degree of P saturation (DPS<sub>M3</sub>) was calculated as the molar ratio of Mehlich-3

extractable P (M3P) divided by the sum of the molar ratios of Mehlich-3 extractable Al and Fe, and converted to percentage by multiplying with 100 (Maguire and Sims, 2002). Initial soils were also analyzed for water extractable P (WEP; Self Davis et al., 2009) by spectrophotometer (Murphy and Riley, 1962) following reaction of 2 g of soil with 20 mL of deionized water for 1 h (centrifuged, filtered through 0.45- $\mu$ m filter), and 0.5 M acetic acid extractable Si (AA-Si; Heckman and Wolf, 2011) by ICP-OES.

#### **4.2.2 Laboratory Soil Incubation**

Approximately 230 g of air-dried soils from each field was added to 240-mL polyethylene snap top cups with holes drilled in the caps to allow gas exchange. Switchgrass residue ash (burned in broiler to generate heat in University of Maryland Wye Research and Education Center), commercially available calcium silicate ( $\text{CaSiO}_3$ ) lime alternative (Agrowsil; Harsco Corp., Sarver, PA), and silicic acid (80 mesh, Sigma-Aldrich, Co. St. Louis, MO) were applied to soils as Si fertilizer materials. All Si sources were analyzed for total Si content by X-ray fluorescence (XRF; Supermini200, Rigaku Americas, Inc., The Woodlands, TX) prior to incorporation into each of the selected legacy P soils (in triplicate) at 0, 0.25, 0.50, 1.0, and 2.0  $\text{Mg ha}^{-1}$  total Si rates. Soils and Si sources in each cup were mixed thoroughly by hand. All soils were then wetted to 80% field capacity (Tan, 1996) and mixed again to ensure homogeneous wetting. Soil moisture content was maintained at 80% field capacity by adding deionized water weekly. Soils were sampled from each incubation cup at eight intervals (e.g., 2, 7, 14, 28, 56, 91, 119, and 150 d) and analyzed for WEP and AA-Si (except soils sampled at 2 d), as described previously. Soils receiving  $\text{CaSiO}_3$  lime alternative or silicic acid at total Si rate of 2  $\text{Mg ha}^{-1}$  sampled at 150 d

were also evaluated for CaCl<sub>2</sub>-extractable Si (0.01 M CaCl<sub>2</sub>; 1h shaking; Korndörfer et al., 1999) because the CaSiO<sub>3</sub> treatments appeared to inflate the AA-Si concentrations. Soil samples collected from each cup at 56 and 150 days were also analyzed for pH, organic matter, Mehlich-3 extractable P, Al, Fe, K, Ca, and Mg, and DPS<sub>M3</sub> as described previously. The ratio of WEP to M3P was calculated to evaluate the solubility of soil P for each cup (i.e., higher ratio suggesting higher P solubility).

#### **4.2.3 Winter Wheat Pot Experiment**

Fifty-four pots were arranged outdoors at the University of Delaware (UD) research farm located in Newark, DE in a completely randomized design with three replicates. Air-dried soil from each of the three “legacy P” fields was added to 11.4-L plastic pots to a depth of 20 cm. Silicon fertilizers were mixed thoroughly into each of the soils as follows: 1) locally available CaSiO<sub>3</sub> lime alternative (Agrowsil; Harsco Corp., Sarver, PA) at the rate required to raise pH to optimum growth of winter wheat based on results of the initial soil test; 2) silicic acid (80 mesh, Sigma-Aldrich, Co. St. Louis, MO) at the same total Si rate as in treatment 1; 3) silicic acid at two times the total Si rate as in treatment 1; 4) silicic acid at a total Si rate of 2 Mg ha<sup>-1</sup> and 5) Si gel (70-230 mesh, Sigma-Aldrich, Co. St. Louis, MO) at a total Si rate of 2 Mg ha<sup>-1</sup>. Based on the pH and buffer pH of initial soils (Table 4.1), commercial lime rates of 2.2, 2.2, and 4.5 Mg ha<sup>-1</sup> were suggested for Ft. Mott-Henlopen and Ingleside-Hammonton, and Mullica-Berryland soil series respectively to provide optimum growth of winter wheat (pH = 6.0; Shober et al., 2017). However, we were concerned that Si treatments based on application of CaSiO<sub>3</sub> lime alternative (100% calcium carbonate equivalent) suggested rate may not provide enough Si (only about 0.27 to 0.54 Mg ha<sup>-1</sup> based on XRF analysis) to affect plant growth and P solubility. As a

result, we increased the liming rate slightly to achieve a pH of 6.5 by applying 3.4, 3.4, and 5.6 Mg ha<sup>-1</sup> of CaSiO<sub>3</sub>, which resulted in approximately a Si application rate of 0.41, 0.41 and 0.68 Mg ha<sup>-1</sup> for the Ft. Mott-Henlopen, Ingleside-Hammonton, and Mullica-Berryland soil series, respectively. Additionally, an unamended control (no Si) treatment was included for each soil type. Calcitic lime (CaCO<sub>3</sub>) was applied to all pots, except those receiving the agronomic CaSiO<sub>3</sub> treatment, to achieve a pH of 6.5 for winter wheat at rates based on the initial soil test.

Before potting, ammonium sulfate (21-0-0-24S) was applied to soils at a nitrogen (N) rate of 34 kg ha<sup>-1</sup> (Alley et al., 2009). Potassium (in the form of K<sub>2</sub>SO<sub>4</sub>, 0-0-52-18S) and manganese (Mn, in the form of MnSO<sub>4</sub>) was applied based on the initial Mehlich-3 K and Mn concentrations (Table 4.1) following UD fertility recommendation (Sims and Gartley, 1996). Lime, nutrient, and Si sources were thoroughly mixed into all three soils using a mixer and transferred to pots. Each pot was then thoroughly wetted on 16 Nov. 2015 and left fallow for a week to allow equilibrium of applied fertilizers and lime. Soils were sampled using a hand probe on 20 Nov. 2015 to evaluate Si and P dynamics soon after the application of Si. Soil subsamples were collected from three random locations in each pot using a hand probe and mixed to create a composite sample for each pot. Soil samples were then air-dried and sieved through 2-mm filter and analyzed for WEP and AA-Si, as described previously. Winter wheat was planted to achieve a seeding rate of 400 seeds m<sup>-2</sup> (equal to 25 seeds per pot) in a greenhouse (to achieve rapid and uniform germination) on 24 Nov. 2015. Potted wheat was then transferred to an outdoor pot-in-pot facility at the UD Newark research farm on 1 Dec. 2015 to be grown under ambient conditions through 24 June 2016 (approximately 31 weeks). Additional N fertilizer was applied at

green-up (on 1 Apr. 2016; approximately Zadocks' growth stage 25) at a N rate of 67 kg ha<sup>-1</sup> (Alley et al., 2009), and again on 2 May 2016 at a N rate of 34 kg ha<sup>-1</sup> to correct visual N deficiency.

Soil samples were randomly collected from each pot using a tip-removed 10-mL syringe (5 to 10 samples from each pot) every month until post-grain harvest (12 July 2016); soil samples were analyzed for WEP and AA-Si as described previously. Additional soil samples collected from each pot at 40 d (early growth) and 209 d (post-harvest) after Si incorporation were analyzed for pH, organic matter, Mehlich-3 extractable P, Al, Fe, K, Ca, and Mg, DPS<sub>M3</sub> and WEP to M3P ratio as described previously. Soil samples collected at harvest were also analyzed for P sorption characteristics to evaluate changes in P sorption capacity of soils following Si addition. Briefly, 2 g of air-dried soils were equilibrated with 30 mL of P solution (as KH<sub>2</sub>PO<sub>4</sub> dissolved in 0.01 M CaCl<sub>2</sub>, CaCl<sub>2</sub> being used to maintain a constant ionic environment) at P concentrations of 0, 0.1, 1, 5, 10, 35, and 50 mg L<sup>-1</sup>. Samples were shaken for 24 h, centrifuged for 10 min, and filtered through 0.45- $\mu$ m filters and the extracts were analyzed for P using ICP-OES. Phosphorus sorption data was used to construct Langmuir isotherms (Bolster and Hornberger, 2007) to estimate soil maximum sorption capacity of P ( $S_{\max}$ ).

At harvest, all aboveground biomass was removed at the soil surface, oven dried at 65 °C and weighed. Wheat berries were then hand harvested and weighed separately, and the straw weight was calculated by subtracting the weight of the grain from the weight of the total above ground biomass for each pot. All oven-dried wheat berries and straw were ground separately using a Wiley mill. Sub-samples of straw and grain berries were analyzed separately for Si and P after microwave-assisted nitric

acid digestion following the method described in Seyfferth et al. (2016). Straw weights, grain weights, and corresponding total digestible P concentrations were used to estimate the P uptake by winter wheat following application of Si treatments.

#### **4.2.4 Data Analysis**

All parameters were analyzed by soil type using a mixed model ANOVA using the PROC MIXED procedure in SAS (version 9.4) with Si treatment (source and rate combination) as fixed effect and replicate as a random effect (SAS Institute, 2008). Soil WEP and AA-Si concentrations were analyzed using a repeated measures mixed model ANOVA with ar(1) covariance structure. We reported a significant Si treatment  $\times$  sampling date effect on soil WEP and AA-Si. Therefore, all pairwise comparisons of least squares means of the interaction were completed using the Tukey's honestly significant difference test with a significance level of  $\alpha=0.05$ . Soil pH, Mehlich-3 nutrients,  $DPS_{M3}$ , WEP to M3P ratio, and  $S_{max}$  were analyzed using a mixed model ANOVA by soil type and sampling date with treatment as the fixed effect and replication as a random effect. All pairwise comparisons of least squares means of the main effect were completed using the Tukey's honestly significant difference test with a significance level of  $\alpha=0.05$ . In addition, regression analysis was used to evaluate the relationship between soil WEP and AA-Si concentrations for the incubation study by Si source and soil series using JMP Pro 13. Normality was checked by examining histogram and normality plots of the conditional residuals.

### **4.3 Results and Discussions**

#### **4.3.1 Initial Soil Characterization**

All three legacy P impacted agricultural soils had a loamy sand soil texture (Table 4.1). The Mullica-Berryland was classified as a “black soil”, with a relatively high organic matter content (Table 4.1). Soil pH was strongly acidic (<5.1) for all three soils when samples were collected in October 2015 for the pot study. Although the same fields were sampled for the incubation study, the initial soil pH was higher (moderately acidic to near neutral) when soils were collected eight-months later. Specifically, the soil pH of the Ft. Mott-Henlopen and Ingleside- Hammonton soils collected for incubation studies were higher due to fall lime applications by the land managers (Table 4.1). The Mehlich-3 extractable Ca and AA-Si concentration were also higher in the Ft. Mott-Henlopen soils when sampled in October 2015 for the pot study compared with samples collected eight-month later for incubation study, which might also be related to the liming effect as well as the plant nutrient uptake in the field. The soil test P concentrations of the Ft. Mott-Henlopen, Ingleside-Hammonton, and Mullica-Berryland soils was approximately three, seven, and ten times Delaware’s 50 mg kg<sup>-1</sup> agronomic critical value of Mehlich-3 extractable P (Shober et al., 2013), respectively. The Mullica-Berryland soils had the highest Mehlich-3 extractable K, Al, and Ca concentrations of all the selected soils, while the Ingleside-Hammonton soils had the highest Mehlich-3 extractable manganese (Mn) concentrations (Table 4.1). The DPS<sub>M3</sub> values indicated that all three soils were highly saturated with P, and were above the environmental thresholds of 23 and 14% for increased P losses in leachate and runoff, respectively reported for Delaware by Maguire and Sims (2002) and Sims et al. (2002).

### **4.3.2 Laboratory Soil Incubation**

#### **4.3.2.1 Switchgrass Ash**

Soil WEP concentrations of all three soils decreased with increasing switchgrass ash application rate (Figure A.1). In fact, application of switchgrass ash consistently led to a significant reduction in soil WEP concentrations compared with unamended control (Figure A.1) despite supplying of Si to soils (especially applied at total Si rate of 2 Mg ha<sup>-1</sup>). Specifically, switchgrass ash supplied similar levels of AA-Si when applied at the same total Si rate as silicic acid in all three evaluated soils (Table A.1). We suspect that the fine texture and porous surface nature of the ash materials resulted in a material with significant surface area for binding soluble P, which in turn masked the effect of Si addition in improving soil P availability. The burning of plant residues like switchgrass in furnace under high temperature is similar to the pyrolysis process for plant-based biochar production, which results in materials with high binding capacity for chemicals (Chen et al., 2011; Park et al., 2015). As a result, we removed the switchgrass ash from our evaluation because it did not improve soil P solubility when applied to legacy P soils and would not be a viable amendment for farmers seeking to improve P uptake by winter small grains.

#### **4.3.2.2 Silicic Acid**

Application of silicic acid at total Si rate of 1 or 2 Mg ha<sup>-1</sup> increased WEP concentrations compared with un-amended controls in both Ft. Mott-Henlopen and Ingleside-Hammonton soils (Figure 4.1). The Ingleside-Hammonton soils generally showed a quicker response to Si addition (i.e., soil WEP increases noted as early as 7 d) than the Ft. Mott-Henlopen soils (i.e., soil WEP increases noted by 56 d). The silicic acid applied to the Ingleside-Hammonton soils at a total Si rate of 0.5 Mg ha<sup>-1</sup>

also periodically (14, 28, and 119 d of incubation) resulted in higher soil WEP concentrations compared with the unamended control (Figure 4.1). In both soils, soil WEP concentrations tended to increase with increasing application of silicic acid (Figure 4.1). However, there was no significant effect of silicic acid on soil WEP concentrations when applied to the Mullica-Berryland soils, regardless of total Si application rate (Figure 4.1).

Our routine soil analysis conducted at 56 (early stage) and 154 d (end of the study) of the incubation showed that the silicic acid applied at total Si rate of 1 or 2 Mg ha<sup>-1</sup> significantly increased the ratio of WEP to M3P (i.e., increased soil P solubility) relative to the unamended Ft. Mott-Henlopen soils (Table 4.2). In comparison, application of silicic acid to the Ingleside-Hammonton soils at total Si rate of 0.5 Mg ha<sup>-1</sup> resulted in lower M3P concentrations than the unamended control at day 56 of the incubation; this trend did not persist through 154 d. But application of silicic acid at total Si rates higher than 0.25 Mg ha<sup>-1</sup> increased the ratios of WEP to M3P relative to unamended Ingleside-Hammonton soils at 56 d; this effect persisted to the end of the study only when silicic acid was applied at total Si rate of 2 Mg ha<sup>-1</sup> (Table 4.2). For Mullica-Berryland soils, application of silicic acid at 2 Mg ha<sup>-1</sup> significantly increased M3P concentrations when compared with the unamended control by the end of the incubation (154d), and increased the ratios of WEP to M3P at the early stage of the incubation only (Table 4.2).

Overall, the application of silicic acid tended to improve soil P solubility by increasing soil WEP concentrations and the WEP to M3P ratio, which was driven by the competition between dissolved Si with P for soil sorption sites. In fact, we found that soil WEP concentrations increased with increasing AA-Si concentrations when

silicic acid was applied to all three evaluated soils ( $P$  value < 0.0001 for all three soils; Figure 4.2); the relationship between soil WEP and AA-Si was stronger for Ft. Mott-Henlopen soils ( $r^2 = 0.60$ ) compared with the other two soil series ( $r^2 = 0.34$  and  $0.21$  for Ingleside-Hammonton and Mullica-Berryland soils, respectively). Similarly, Lee et al. (2004) also found a positive linear relationship between the amount of desorbed phosphate and adsorbed silicate when high P film-house soils were equilibrated with different concentrations of silicate solutions, supporting that silicate anions can enhance phosphate desorption from soil surface (Lee et al., 2004).

The lack of Si treatment effects on the WEP concentrations for the Mullica-Berryland soils specifically may be related to the low soil pH (mostly lower than 5), which reduced competition of Si for soil sorption sites (Lee et al., 2004). Application of silicic acid tended to further decrease soil pH at the early stage of the incubation (56 d) (Table 4.2), which could further reduce Si efficacy. In fact, Obihara and Russell (1972) showed that Si adsorption by two soils (a silty clay loam and a clay loam) from pure silicic acid solution was the highest at a pH of 9.2 and decreased with decreasing solution pH; soil Si adsorption was almost zero at pH lower than 5. Ma and Takahashi (1991) also found that Si application (sodium silicate [ $\text{Na}_2\text{SiO}_3$ ]) did not significantly impact soil P adsorption when compared with an unamended very acidic Yakuno soil (pH ranged from 4.5–5.5).

#### **4.3.2.3 Calcium Silicate Liming Alternative**

Application of  $\text{CaSiO}_3$  lime alternative to the Ft. Mott-Henlopen soil at a total Si rate of  $2 \text{ Mg ha}^{-1}$  significantly increased soil WEP concentrations compared with the unamended control during the entire 156 d incubation study (Figure 4.3). Similarly, application of  $\text{CaSiO}_3$  to the Ft. Mott-Henlopen soils at the  $1 \text{ Mg ha}^{-1}$  total

Si rate also significantly increased soil WEP concentrations compared with the unamended control from 91 through 156 d of the incubation (Figure 4.3).

Concentrations of soil WEP tended to increase with increasing application of  $\text{CaSiO}_3$  in Ft. Mott-Henlopen soils (Figure 4.3). In contrast, application of  $\text{CaSiO}_3$  at rates exceeding  $0.5 \text{ Mg ha}^{-1}$  total Si often significantly reduced soil WEP concentrations compared with unamended controls when applied to the Ingleside-Hammonton and the Mullica-Berryland soils (Figure 4.3). In fact, application of  $\text{CaSiO}_3$  to the Ingleside-Hammonton soils at a total Si rate as low as  $0.25 \text{ Mg ha}^{-1}$  also resulted in lower soil WEP concentrations than the unamended control throughout much of the study.

Routine soil analysis on incubated soils at 56 (early stage) and 154 d (end of the study) showed that application of  $\text{CaSiO}_3$  at total Si rate of  $1 \text{ Mg ha}^{-1}$  significantly decreased soil M3P concentrations compared with the unamended Ft. Mott-Henlopen soils at the end of the incubation (Table 4.2). However,  $\text{CaSiO}_3$  applied at total Si rate of 1 or  $2 \text{ Mg ha}^{-1}$  significantly increased the  $\text{DPS}_{\text{M3}}$  values of Ft. Mott-Henlopen soils compared with the control when soils were incubated for 56 d; this effect disappeared by the end of the incubation. These two rates of  $\text{CaSiO}_3$  application also significantly increased the ratios of WEP to M3P (i.e., increased soil P solubility) at 56 and 154 d compared with the controls when soils were incubated (Table 4.2). In comparison, application of  $\text{CaSiO}_3$  at total Si rate of 1 or  $2 \text{ Mg ha}^{-1}$  significantly reduced M3P concentrations, increased  $\text{DPS}_{\text{M3}}$ , and decreased the ratios of WEP to M3P at 56 d relative to the unamended Ingleside-Hammonton soils. Application of  $\text{CaSiO}_3$  at lower rates also significantly reduced the ratios of WEP to M3P at 56 d compared with the unamended Ingleside-Hammonton soils. However, all these effects disappeared when

Ingleside-Hammonton soils were incubated for 154 d (Table 4.2). For Mullica-Berryland soils, application of  $\text{CaSiO}_3$  at total Si rate of  $2 \text{ Mg ha}^{-1}$  only significantly decreased M3P concentrations relative to the unamended control when soils were incubated for 56 d. Application of  $\text{CaSiO}_3$  at total Si rate higher than  $0.25 \text{ Mg ha}^{-1}$  also resulted in lower ratios of WEP to M3P than the unamended Mullica-Berryland soils at 56 and 154 d (Table 4.2).

We found that application of  $\text{CaSiO}_3$  lime alternative resulted in much higher soil AA-Si concentrations when compared with other Si sources. For example, when applied at a total Si rate of  $2 \text{ Mg ha}^{-1}$ , the average AA-Si concentration of  $\text{CaSiO}_3$  amended soils was about 24 times the average AA-Si concentration of the silicic acid amended soils ( $296$  vs.  $12.1 \text{ mg kg}^{-1}$ ). We suspect that the high concentrations of AA-Si in the  $\text{CaSiO}_3$  amended soils was due to an overestimation of plant-available Si using acetic acid extraction (Nonaka and Takahashi, 1990; Sauer et al., 2006). For example, Nonaka and Takahashi (1990) found that acetic acid extraction can overestimate the Si concentrations of soils previously amended with  $\text{CaSiO}_3$  by dissolving plant-unavailable Si from  $\text{CaSiO}_3$ . Snyder (2001) also suggested that acetic acid was too strong for soils amended with  $\text{CaSiO}_3$  fertilizer and could dissolve residual fertilizer in soils. As a result, we reanalyzed some soils (incubated after 154 d) receiving  $\text{CaSiO}_3$  lime alternative or silicic acid at total Si rate of  $2 \text{ Mg ha}^{-1}$  using a milder  $\text{CaCl}_2$  extraction (Korndörfer et al., 1999). The average  $\text{CaCl}_2$ -extractable Si concentrations in the  $\text{CaSiO}_3$  amended soils was within the same magnitude as the  $\text{CaCl}_2$ -extractable Si concentrations of the silicic acid amended soils ( $7.89$  vs.  $5.64 \text{ mg kg}^{-1}$ ). Thus, we confirmed that acetic acid extraction was not an ideal method to evaluate plant-available Si in soils previously amended with  $\text{CaSiO}_3$ . As a result,

comparisons of AA-Si concentrations between soils receiving CaSiO<sub>3</sub> and other Si treatments were avoided.

When relating WEP with AA-Si concentrations, we found that soil WEP concentrations increased with increasing AA-Si concentrations when CaSiO<sub>3</sub> was applied as the Si source to the Ft. Mott-Henlopen soils ( $r^2 = 0.72$ ;  $P$ -value  $< 0.0001$ ); this pattern was also noted for Ingleside-Hammonton soils ( $r^2 = 0.05$ ;  $P$ -value = 0.037) but with a much weaker relationship (Figure 4.4). However, soil WEP concentrations decreased with increasing AA-Si concentrations when CaSiO<sub>3</sub> was applied to the Mullica-Berryland soils ( $r^2 = 0.58$ ;  $P$ -value  $< 0.0001$ ; Figure 4.4). The effect of CaSiO<sub>3</sub> application on soil P dynamics is likely controlled by a variety of factors including soil pH and the presence of Ca and Mn in soils; many of these parameters were directly affected when CaSiO<sub>3</sub> was introduced to the soil system (Table A.2). Specifically, application of CaSiO<sub>3</sub> increased soil pH (Table 4.2) and the concentrations of AA-Si, and Mehlich-3 extractable Ca, Mg, and Mn (Table 4.3). While the increase in Si concentrations can enhance P desorption and soil P solubility (as in the case of silicic acid), the increase in P binding elements (i.e., Ca, Mg, and Mn) with the application of CaSiO<sub>3</sub> can lead to the adsorption or precipitation of P, thereby reducing soil P availability. The Ingleside-Hammonton and Mullica-Berryland soils had M3P concentrations that were about seven and ten times the agronomic optimum and were much higher than the Ft. Mott-Henlopen soils (Table 4.1). It is possible that the high P concentrations in Ingleside-Hammonton and Mullica-Berryland soils further drove the precipitations or sorption of solubilized P with Ca, Mg, or Mn, thereby masking the effects of the Si application in improving soil P availability. In comparison, this effect may be lower in Ft. Mott-Henlopen soils

because of the lower P concentrations. As a result, we were still able to see a net positive effect of  $\text{CaSiO}_3$  addition on soil P availability when applied to the Ft. Mott-Henlopen soils. Moreover, the Mullica-Berryland soils also had relatively higher organic matter content compared with the other two soils (Table 4.1). Organic matter-Al soil complexes play an important role in P adsorption in acid soils (Bloom, 1981) and could potentially influence the effects of Si application on soil P availability for the Mullica-Berryland “black” soils.

### **4.3.3 Winter Wheat Pot Experiment**

#### **4.3.3.1 Effect of Si Fertilization on Soil P Dynamics**

We found that application of silicic acid to the Ft. Mott-Henlopen and Mullica-Berryland soils at the  $2 \text{ Mg ha}^{-1}$  total Si rate significantly increased soil WEP concentrations compared with the unamended soils throughout the study. The Ingleside-Hammonton soils amended with  $2 \text{ Mg ha}^{-1}$  silicic acid also periodically showed increased soil WEP concentrations, which persisted for at least 40 d after Si incorporation (Table 4.4). Application of silicic acid to the Ft. Mott-Henlopen soils at the total Si rates lower than  $2 \text{ Mg ha}^{-1}$  periodically increased the soil WEP concentrations compared with the unamended control, especially early in the study (at least through 40 d after Si incorporation). Application of silicic acid at two times total Si rate provided by  $\text{CaSiO}_3$  lime to the Mullica-Berryland soils also increased the soil WEP concentrations compared with the unamended control (4, 40, 80, and 129 d after Si incorporation; Table 4.4). However, silicic acid applied at total Si rates lower than  $2 \text{ Mg ha}^{-1}$  did not increase soil WEP concentrations compared with unamended control for the Ingleside-Hammonton soil (Table 4.4). Silica gel applied at total Si rate of 2

Mg ha<sup>-1</sup> also periodically increased soil WEP concentrations when applied to the Ft. Mott-Henlopen (4, 40, 98, 189, and 209 d after Si incorporation) and the Mullica-Berryland soils (80 and 129 d after Si incorporation) compared with the unamended control; this treatment did not increase soil WEP concentrations when applied to the Ingleside-Hammonton soils (Table 4.4).

Application of CaSiO<sub>3</sub> to Ft. Mott-Henlopen and Ingleside-Hammonton soils resulted in significantly higher soil WEP concentrations compared with the unamended controls only at 4 d after Si incorporation, which was 4 d before winter wheat was planted (24 Nov. 2015). In contrast, CaSiO<sub>3</sub> application to the Mullica-Berryland soils increased soil WEP compared with the control through the first three sampling dates (until 80 d after Si incorporation; Table 4.4). It is possible that the Si amount provided by the CaSiO<sub>3</sub> application at the liming rate was not enough to sustain the P solubilization for a long period for Ft. Mott-Henlopen and Ingleside-Hammonton soils especially with the active nutrient uptake by growing wheat (approximate total Si rate is 0.41 Mg ha<sup>-1</sup> for Ft. Mott-Henlopen and Ingleside-Hammonton soils compared with 0.68 Mg ha<sup>-1</sup> for Mullica-Berryland soils).

When applied at the same total Si rate (2 Mg ha<sup>-1</sup>), silicic acid and silica gel typically had a similar effect on soil WEP concentrations for all three evaluated soils. Similarly, when applied at the same total Si rate, CaSiO<sub>3</sub> often resulted in similar soil WEP concentrations as silica acid regardless of soil type (Table 4.4).

There was little to no Si treatment effect on soil M3P concentrations or DPS<sub>M3</sub>. Specifically, the unamended Ft. Mott-Henlopen soils had significantly higher M3P concentrations than soils receiving silicic acid at total Si rate of 2 Mg ha<sup>-1</sup> only at 209 d after Si application. In addition, the Ft. Mott-Henlopen soils receiving silica gel at

total Si rate of 2 Mg ha<sup>-1</sup> had significantly higher DPS<sub>M3</sub> compared with soils receiving CaSiO<sub>3</sub> or the unamended control only at 40 d after Si incorporation (one month after planting; Table 4.5). However, we did find that Si fertilization tended to increase the WEP to M3P ratio in all three evaluated soils. Specifically, application of silicic acid to Ft. Mott-Henlopen soils at a total Si rate of 2 Mg ha<sup>-1</sup> resulted in significantly higher ratios of WEP to M3P than the unamended control throughout the study; this treatment effect was also noted for Mullica-Berryland and Ingleside-Hammonton soils at 40 and 209 d after Si application, respectively (Table 4.5). Application of silica gel at the 2 Mg ha<sup>-1</sup> Si rate and/or silicic acid at lower rates to the Ft. Mott-Henlopen soils also resulted in significantly higher ratios of WEP to M3P when compared with the unamended control throughout the study. Silicic acid applied to the Mullica-Berryland soils at two times the CaSiO<sub>3</sub> rate also resulted in significantly higher WEP to M3P ratios than unamended controls at 40 d after Si incorporation. Application of CaSiO<sub>3</sub> only significantly increased the ratio of WEP to M3P in Mullica-Berryland soils when soils were sampled on 40 d after Si incorporation (Table 4.5).

Analysis on the maximum soil P sorption capacity ( $S_{\max}$ ) at the end of the study indicated that there was no Si treatment effect on  $S_{\max}$  for the Mullica-Berryland soils, while significant treatment effect was noted in Ft. Mott-Henlopen and Ingleside-Hammonton soils (Table 4.6). For Ft. Mott-Henlopen soils, silicic acid applied at 2 Mg Si ha<sup>-1</sup> significantly reduced  $S_{\max}$  values compared with the no P control; but silicic acid applied at CaSiO<sub>3</sub> Si rate significantly increased soil  $S_{\max}$  compared with the control. For Ingleside-Hammonton soils, Si amendments significantly reduced  $S_{\max}$

when compared with the control, except that soils receiving silicic acid at 2 Mg Si ha<sup>-1</sup> was not significantly different with the control (Table 4.6).

#### **4.3.3.2 Effect of Si Treatments on the Yield and P and Si Uptake of Winter Wheat**

While Si treatments tended to improve soil P availability, Si addition did not significant increase winter wheat grain or straw yield relative to the unamended control when treatments were applied to the Ft. Mott-Henlopen or Ingleside-Hammonton soils (Table 4.7). There was also no significant Si treatment effect on the grain yield of winter wheat grown in Mullica-Berryland soil; but Mullica-Berryland soils receiving Si gel at 2 Mg ha<sup>-1</sup> total Si had significantly higher straw yield than wheat grown in the unamended soil (Table 4.7). Similarly, Provance-Bowley et al (2010) reported no significant difference in winter wheat yield (grain and/or straw) between Si-amended plots and no Si control (CaCO<sub>3</sub> was used as the liming agent instead) in the first two years of a three-year (2006–2008) field trial (Quakertown silt loam) where CaSiO<sub>3</sub> was added annually as a liming agent to winter wheat. However, Si amendment significantly increased the winter wheat grain yield by 12% in the third year of the study when AA-Si concentrations in amended soils increased from 40.2 to 83.2 mg kg<sup>-1</sup> (Provance-Bowley et al., 2010). In comparison, our soil AA-Si concentrations were typically lower than 83.2 mg kg<sup>-1</sup> (Figure 4.5). Other researchers have suggested a soil AA-Si concentration of 21.4 mg kg<sup>-1</sup> for Florida Histosols (Kondörfer et al., 2001) and 77.4 mg kg<sup>-1</sup> for Ultisoils in India (Narayanaswamy and Prakash. 2009), below which a yield response to Si fertilizer is expected for rice. However, rice tends to absorb more Si and has a different absorption mechanism than the wheat evaluated in this study (Tamai and Ma, 2003). Therefore, it is likely that a

higher Si application rate and/or longer Si application history may be needed to significantly impact on the yield of winter wheat (especially grain yield) when grown on our soils.

In terms of plant nutrition, we found increased Si concentrations in plant tissues (especially in the straw) for Si amended soils when compared with plants grown in the unamended soils (Table 4.7). However, there was no significant Si treatment effect on straw or grain tissue P concentration for any of the soils when compared with wheat grown in the unamended soil. Cumulatively, there was also no significant Si treatment effect on total crop P removal for any of the soils (Table 4.7), suggesting that Si amendment did not help to accelerate the drawdown of soil P stored in evaluated legacy soils through crop removal. However, we only evaluated P concentrations in aboveground plant tissues. It is possible that enhanced P uptake is reflected in the root biomass. Similarly, Provance-Bowley et al (2010) also found that winter wheat grown in Si-amended soil had similar flag-leaf P concentrations compared with plants grown in unamended soils. While the effect of Si application on wheat P uptake has not been widely evaluated, the Si amendment has been shown to increase plant tissue P concentrations of corn (Owino-Gerroh and Gascho, 2005), barley (Brenchley et al., 1927; Fisher, 1929), and several grass species (Eneji et al., 2008). For example, Eneji et al. (2008) found a strong positive correlation between the uptake of Si and P ( $r^2 > 0.82$ ) when Si amendments (potassium silicate,  $\text{CaSiO}_3$ , or silica gel) were applied to four grass species (rhodes grass, timothy grass, sudangrass, and tall fescue) on a Sandune Regosol at Si rates ranging from approximately 0.14–23  $\text{g kg}^{-1}$ . In another study, Schaller et al. (2011) evaluated P uptake by common reed (*Phragmites australis*) growing in a peat soil chamber in the presence of Si (in the

form of low acidic, amorphous Si). The authors showed increased P uptake at medium Si addition ( $4.66 \text{ g kg}^{-1}$  soil), but decreased P uptake at high Si addition ( $46.6 \text{ g kg}^{-1}$  soil) due to stress from excessive Si uptake. Our Si application rate was equivalent to  $0.15\text{--}0.74 \text{ g kg}^{-1}$  depending on treatment, which was within the lower range of Si rate in Enej et al. (2008), but was much lower than the Si application rate evaluated in Schaller et al. (2011). As a result, it is possible that a higher Si application rate is needed to significantly enhance the P uptake of winter wheat in our study especially under high soil P levels with most of P being bounded with Al and/or Fe (hydro)-oxides. However, Ma and Takahashi (1990) found that the addition of Si (as silicic acid) reduced rice total P uptake (rice was cultured in Kimura B nutrient solution) by 27–30 % compared with unamended control when P concentrations in nutrient solution were high ( $6.51$  and  $21.7 \text{ mg L}^{-1}$ ). The authors attributed the decrease in P uptake to a mechanism by the plant to reduce high osmotic pressure within the plant cells due to excessive P uptake. However, our soil WEP concentrations ranged from  $4.86\text{--}28.0 \text{ mg kg}^{-1}$  (equivalent to approximately  $0.49\text{--}2.80 \text{ mg L}^{-1}$ ), which were much lower than the P concentrations in nutrient solution evaluated by Ma and Takahashi (1990). As a result, it is not likely that our wheat was suffering from excessive P uptake as suggested by Ma and Takahashi (1990).

#### **4.3.4 Potential of Replacing Early Season Starter P with Si Fertilization**

Silicon fertilization must improve the soil P availability in order to reduce or eliminate the use of starter P fertilizer for small grains (like winter wheat) on high P legacy soils. Increases in P solubility following Si application are preferred early in the season (i.e., from planting through the forming of tillers) so that the seedlings can access enough P when soil temperatures are cold to produce a vigorous root system

and more fertile tillers (Grant et al., 2001). Both the soil only incubation and winter wheat pot experiment showed the possibility of replacing starter P fertilizers with Si fertilizers to correct the early-season P deficiency of growing winter wheat on Delmarva Peninsula. Although the application of  $\text{CaSiO}_3$  was not effective at improving soil P availability when applied to Ingleside-Hammonton and Mullica-Berryland soils in the soil only incubation study, it tended to increase soil P availability for these two soils when evaluated in the pot study with active growth of winter wheat. In the latter case, plants were available to absorb nutrients from soils, including soil P and P binding elements (i.e., Ca, Mg, and Mn) supplied by  $\text{CaSiO}_3$  liming alternative. As a result, the P sorption or precipitation reactions may be largely suppressed in the pot study, thereby leading to a more significant effect of  $\text{CaSiO}_3$  application in improving soil P availability.

We also found that Ft. Mott-Henlopen soils was generally more responsive to Si fertilization in improving soil P availability compared with the other two soils (Figure 4.1, Figure 4.3, and Table 4.4). This responsiveness might be related to the fact that Ft. Mott-Henlopen soils had much lower initial P concentrations (especially WEP) compared with the other two soils (Table 4.1). As a result, when applied at the same total Si rate, the soluble Si will compete more effectively with P for sorption sites with a lower level of soluble P.

Previous investigations also resulted in increased soil P availability following Si application (Koski-Vahala et al., 2001; Lee et al., 2004; Owino-Gerroh and Gascho, 2005). The prevailing thought is that P desorption is enhanced due to competition between silicate and phosphate anions for sorption sites (Koski-Vahala et al., 2001; Lee et al., 2004). For example, Koski-Vahala et al (2001) evaluated the effect of Si

addition ( $\text{Na}_2\text{SiO}_3$ ) on P mobility by incubating the surface layer of sediments (0–2 cm) collected from the Enonselkä basin of Lake Vesijärvi in southern Finland (where the water depth was 9 m) using a sequential fractionation analysis and an isotope-labelling technique. The authors showed that high Si addition ( $47 \text{ mg L}^{-1}$  sediment) resulted in an increased dissolved P concentration in the interstitial water ( $6.92\text{--}16.16 \text{ mg L}^{-1}$ ), and an increased Si concentrations extracted by NaOH ( $6.72\text{--}6.81 \text{ g kg}^{-1}$ ; Fe associated sorption) and  $\text{NH}_4\text{F}$  ( $1.93\text{--}2.04 \text{ g kg}^{-1}$ ; Al associated sorption) compared with the unamended control ( $0.06\text{--}1.53 \text{ mg L}^{-1}$ ,  $6.04\text{--}6.13 \text{ g kg}^{-1}$ , and  $1.67\text{--}1.86 \text{ g kg}^{-1}$  for P concentrations in interstitial water, Si concentrations extracted by NaOH and  $\text{NH}_4\text{F}$  fractions, respectively). The authors surmised that the added Si can compete with P for sediment sorption sites that were associated with Al and Fe, thereby increasing the soluble P concentrations in interstitial water. However, this competition will only be triggered with a specific threshold Si level since the low Si addition ( $0.35 \text{ mg L}^{-1}$  sediment) did not enhance P desorption. Similarly, Lee et al. (2004) also reported increased P desorption from high P film-house soils with salt accumulation due to intensive fertilizer application collected from Chojeon-li, Chinju, Korea (0–15 cm) following increasing Si concentration (applied as  $\text{Na}_2\text{SiO}_3$ ) and temperature, regardless of the soil texture (i.e., silt loam vs. loam), but only when soil pH ranged from 6–10. The authors suspected that Si adsorption to soils can potentially increase the net negative charges in soils, which further promoted soil P desorption (Lee et al., 2004). However, Owino-Gerroh and Gascho (2005) attributed the decreased soil P sorption in a Greenville sandy clay (Rhodic Paleudult) through isotherm analysis to the increase in soil pH from the addition of  $\text{Na}_2\text{SiO}_3$  that promotes P availability. However, results from our pot study (where unamended control was also limed to the

same target pH) supported that application of Si can go beyond liming effect and further improve soil P availability (Table 4.4).

#### **4.4 Conclusions**

Based on our results, we suggested that Si fertilization is a promising BMP that can improve early-season soil P availability and reduce the use of starter fertilizer for the growth of winter wheat on high P legacy soils in Delmarva Peninsula. But a specific Si application rate is needed to trigger the positive effect depending on soil properties; total Si rate of 2 Mg ha<sup>-1</sup> seemed efficient for all three evaluated high P soils. Silicic acid and silica gel were the most effective Si sources in improving P availability in our study; however, they are not commercially-available and would be cost-prohibitive for farmers to purchase. Locally-available CaSiO<sub>3</sub> liming alternative can simultaneously adjust the soil pH and supply Si. However, CaSiO<sub>3</sub> may only be a sufficient Si source for low pH soils with relatively high buffer capacity and may not be providing enough Si for other soils due to its liming effect. Future research should evaluate other Si alternatives (e.g., wheat residues) that can be easily used by farmers. Future investigation should also repeat the pot study for more growing seasons to determine any lag time effect of Si fertilization on the yield and P uptake of winter wheat (we did not see a response during one growing season). Nutrient analysis on root samples is also needed to evaluate the P uptake in the belowground biomass following Si fertilization. Moreover, on-farm field trials will be needed to test the interaction between Si and P (both in soils and plants) at larger scale.

Table 4.1: Selected initial soil properties (0-20 cm) for three agricultural legacy P impacted agricultural soils that were used for pot and incubation studies to evaluate Si application effects on P solubility. Soils used for incubation study were collected about nine months later than soils used for pot study from the same three fields.

Soil Series	Texture	pH	Buffer pH	Organic Matter	Water extractable P	Mehlich -3 P	Mehlich -3 K	Mehlich -3 Al	Mehlich -3 Fe	Mehlich -3 Mn	Mehlich -3 Ca	Acetic acid extractable Si	DPS <sub>M3</sub>
				g kg <sup>-1</sup>		mg kg <sup>-1</sup>						%	
<u>Pot Study</u>													
Ft. Mott-Henlopen	Loamy sand	5.0	7.7	20	6.01	171	67.0	508	82.1	8.54	520	7.96	27
Ingleside-Hammonton	Loamy sand	5.0	7.7	21	14.1	349	94.0	580	104	13.1	540	4.17	48
Mullica-Berryland	Loamy sand	5.1	7.4	42	17.8	492	135	1037	115	3.84	751	6.18	39
<u>Incubation Study</u>													
Ft. Mott-Henlopen	Loamy sand	6.6	7.9	17	4.54	189	33.6	714	137	10.1	225	4.03	21
Ingleside-Hammonton	Loamy sand	6.2	8.0	20	14.1	361	113	650	123	12.1	584	6.09	44
Mullica-Berryland	Loamy sand	5.7	7.3	55	15.7	684	258	1487	180	3.75	697	5.04	38

Table 4.2: Effect of Si fertilization on soil pH, Mehlich-3 extractable P (M3P), degree of P saturation (DPS<sub>M3</sub>), and the ratio of water extractable P (WEP) to M3P when three legacy P impacted agricultural soils were incubated with Si amendments for 56 and 154 d.

Source	Total Si rate Mg ha <sup>-1</sup>	pH		M3P		DPS <sub>M3</sub>		WEP/M3P		
		56 d	154 d	56 d	154 d	56 d	154 d	56 d	154 d	
		mg kg <sup>-1</sup>				%				
<u>Ft. Mott-Henlopen</u>										
Control	0	5.87	5.97	220	238	23.2	23.4	1.72	1.94	
CaSiO <sub>3</sub>	0.25	6.07	6.23 *	213	209	23.6	23.2	1.76	2.10	
	0.5	6.27	6.33 *	219	212	24.5	25.1	1.77	2.36	
Silicic acid	1	6.67 *	6.70 *	195	191 *	25.1*	24.1	2.24 *	2.96 *	
	2	7.03 *	7.27 *	194	205	25.5 *	25.4	3.58 *	3.85 *	
	0.25	5.73	5.73 *	221	201	23.6	22.2	1.75	2.40	
	0.5	5.80	5.67 *	199	222	23.6	23.3	2.00	2.17	
Silicic acid	1	5.73	5.80	197	191	23.8	22.1	2.18 *	2.82 *	
	2	5.47 *	5.83	201	197	23.6	25.4	2.35 *	3.02 *	
	<u>Ingleside-Hammonton</u>									
Control	0	5.53	5.90	557	542	48.9	51.0	2.76	3.33	
CaSiO <sub>3</sub>	0.25	6.03	6.23 *	553	516	49.3	52.7	2.25 *	3.06	
	0.5	6.40 *	6.47 *	538	518	49.8	51.9	2.18 *	2.84	
Silicic acid	1	6.87 *	6.80 *	511 *	523	51.9 *	52.3	2.32 *	2.71	
	2	7.27 *	7.40 *	507 *	509	51.9 *	56.1	2.47 *	2.89	
	0.25	5.70	5.80	553	526	48.9	51.4	3.01	3.85	
	0.5	5.73	5.60 *	475 *	534	49.3	51.9	3.71 *	3.82	
Silicic acid	1	6.07 *	5.67 *	522	535	48.9	48.9	3.35 *	3.81	
	2	6.00	5.57 *	532	529	50.2	55.6	3.71 *	4.56 *	
<u>Mullica-Berryland</u>										
Control	0	5.63	4.77	791	752	38.4	43.0	2.44	3.38	

CaSiO <sub>3</sub>	0.25	5.83	5.00 *	775	755	38.6	44.7	2.23	3.02
	0.5	5.23 *	5.03 *	785	774	38.5	43.5	2.11 *	2.80 *
	1	5.43	5.40 *	769	772	38.0	44.7	1.85 *	2.46 *
	2	5.73	5.73 *	746 *	787	38.4	48.1	1.74 *	1.91 *
Silicic acid	0.25	5.47	4.63	783	819	38.8	46.4	2.56	3.16
	0.5	5.03 *	4.67	810	777	38.5	46.0	2.38	3.30
	1	4.90 *	4.77	812	799	38.6	47.2	2.48	3.29
	2	4.90 *	5.07	788	847 *	39.6	45.1	2.83 *	3.07

\* values within each soil were statistically different than the control using Tukey's honestly significant difference test at P<0.05; pairwise comparisons were made by the Si source and by soil series.

Table 4.3: Effect of CaSiO<sub>3</sub> application on Mehlich-3 extractable Ca, Mg, and Mn when three legacy P impacted agricultural soils were incubated for 56 and 154 d.

Source	Total Si rate	Mehlich-3 Ca		Mehlich-3 Mg		Mehlich-3 Mn	
		56 d	154 d	56 d	154 d	56 d	154 d
mg kg <sup>-1</sup>							
<u>Ft. Mott-Henlopen</u>							
Control	0	340 c <sup>†</sup>	382 e	140 c	151 d	11.5 d	14.2 d
CaSiO <sub>3</sub>	0.25	487 c	519 d	163 bc	174 cd	13.9 cd	16.2 cd
	0.5	710 b	659 c	170 bc	184 bc	17.9 bc	19.0 c
	1	845 b	871 b	208 b	207 b	19.3 b	23.5 b
	2	1380 a	1576 a	321 a	343 a	26.6 a	32.9 a
<u>Ingleside-Hammonton</u>							
Control	0	783 d	768 d	132 d	114 d	20.4 c	18.6 b
CaSiO <sub>3</sub>	0.25	962 c	881 d	166 cd	148 d	21.9 b	19.6 b
	0.5	1063 c	1113 c	187 c	178 c	22.9 b	22.8 b
	1	1319 b	1354 b	232 b	230 b	23.7 b	27.4 a
	2	1903 a	1829 a	343 a	330 a	30.0 a	30.9 a
<u>Mullica-Berryland</u>							
Control	0	652 d	633 e	111 e	115 c	6.46 d	6.42 c
CaSiO <sub>3</sub>	0.25	747 d	800 d	135 d	149 c	6.82 cd	6.11 c
	0.5	938 c	980 c	171 c	218 b	7.38 c	7.39 bc
	1	1185 b	1262 b	229 b	259 b	10.0 b	8.73 b
	2	1628 a	2031 a	327 a	449 a	12.2 a	13.3 a

<sup>†</sup>Values within each soil with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

Table 4.4: Effect of Si treatments with time on water extractable P (WEP) in three legacy P impacted agricultural soils sampled at multiple days after Si incorporation during one growing season of winter wheat.

Treatment	Total Si rate	4 d	40 d	80 d	98 d	129 d	161 d	189 d	209 d	
	Mg ha <sup>-1</sup>	mg kg <sup>-1</sup>								
<u>Ft. Mott-Henlopen</u>										
CaSiO <sub>3</sub>	0.41	7.90 a <sup>†</sup>	8.11 b	8.21 c	7.74 bc	6.59 b	5.76 b	5.67 c	5.28 c	
Silicic acid	0.41	7.00 ab	10.0 a	9.53 bc	8.29 bc	8.37 ab	6.17 b	6.56 abc	5.79 bc	
	0.82	7.57 a	10.2 a	10.3 ab	8.92 ab	8.12 ab	6.57 ab	6.86 ab	6.21 ab	
	2	8.28 a	11.0 a	11.0 a	10.2 a	9.02 a	7.59 a	7.42 a	6.96 a	
Silica gel	2	7.76 a	10.0 a	9.55bc	9.03 ab	7.94 ab	6.35 b	7.35 a	6.65 ab	
Control	0	6.07 b	7.55 b	8.48 c	7.20 c	6.68 b	5.83 b	5.85 bc	5.19 c	
<u>Ingleside-Hammonton</u>										
CaSiO <sub>3</sub>	0.41	13.2 a	12.0 ab	13.7 a	11.8 ab	9.13 b	8.71 a	8.72 b	8.27 c	
Silicic acid	0.41	11.1 b	11.7 ab	12.2 a	11.6 ab	10.7 ab	9.72 a	10.1 ab	9.51 bc	
	0.82	11.8 ab	11.9 ab	13.8 a	11.5 ab	11.5 ab	10.0 a	11.0 ab	9.76 b	
	2	13.4 a	13.5 a	13.7 a	14.2 a	15.3 a	17.3 a	10.6 ab	11.3 a	
Silica gel	2	12.8 ab	11.8 ab	13.3 a	13.0 ab	11.7 ab	11.3 a	9.90 ab	9.85 b	
Control	0	11.1 b	11.4 b	12.7 a	10.5 b	11.1 ab	10.2 a	12.8 a	8.91 bc	
<u>Mullica-Berryland</u>										
CaSiO <sub>3</sub>	0.68	15.7 a	16.0 a	17.4 a	15.1 ab	14.4 a	10.9 b	11.7 c	9.69 b	
Silicic acid	0.68	13.5 bc	14.9 ab	16.8 a	14.4 b	13.9 ab	11.2 b	12.3 bc	10.4 b	
	1.36	14.4 ab	15.6 a	18.1 a	14.8 b	14.7 a	11.7 b	12.8 abc	10.8 ab	
	2	14.1 b	16.0 a	17.4 a	17.1 a	15.4 a	13.6 a	13.5 a	11.7 a	
Silica gel	2	13.6 bc	14.7 ab	17.4 a	15.1 ab	14.9 a	11.7 b	12.9 ab	10.5 ab	
Control	0	12.2 c	13.1 b	14.1 b	13.6 b	12.3 b	10.5 b	11.9 bc	9.96 b	

† Values within each soil with different letters were statistically different using Tukey's honestly significant difference test at  $P < 0.05$ .

Table 4.5: Summary of pH, concentrations of Mehlich-3 extractable P (M3P), degree of P saturation (DPS<sub>M3</sub>), and the ratio of water extractable P (WEP) to Mehlich-3 extractable P (M3P) of soil samples collected on 40 and 209 d after Si incorporation from evaluated three legacy P impacted agricultural soils.

Treatment	Total Si rate Mg ha <sup>-1</sup>	pH		M3P		DPS <sub>M3</sub>		WEP/M3P		
		40 d	209 d	40 d	209 d	40 d	209 d	40 d	209 d	
				—mg kg <sup>-1</sup> —		%				
<u>Ft. Mott-Henlopen</u>										
CaSiO <sub>3</sub>	0.41	6.23 b <sup>†</sup>	7.17 a	220 a	194 ab	27.0 b	27.5 a	3.69 cd	2.72 cd	
Silicic acid	0.41	6.30 ab	7.00 a	207 a	186 ab	28.3 ab	27.9 a	4.85 ab	3.11 bcd	
	0.82	6.23 b	6.90 a	212 a	188 ab	28.5 ab	28.3 a	4.81 ab	3.31 bc	
	2	6.27 ab	6.90 a	194 a	170 b	28.1 ab	30.0 a	5.67 a	4.10 a	
Silica gel	2	6.30 ab	6.93 a	220 a	188 ab	29.1 a	30.4 a	4.52 bc	3.55 ab	
Control	0	6.37 a	6.50 b	209 a	203 a	27.3 b	27.9 a	3.63 d	2.57 d	
<u>Ingleside- Hammonton</u>										
CaSiO <sub>3</sub>	0.41	6.00 c	6.30 a	415 a	361 a	47.2 a	48.1 a	2.89 a	2.32 b	
Silicic acid	0.41	6.23 b	6.27 a	419 a	386 a	48.5 a	51.9 a	2.80 a	2.48 ab	
	0.82	6.33 ab	6.20 a	405 a	372 a	44.3 a	51.0 a	2.95 a	2.62 ab	
	2	6.33 ab	6.33 a	388 a	376 a	42.6 a	49.8 a	3.55 a	3.00 a	
Silica gel	2	6.33 ab	6.17 a	396 a	348 a	48.9 a	48.5 a	2.98 a	2.83 ab	
Control	0	6.47 a	6.37 a	352 a	397 a	42.2 a	48.9 a	3.24 a	2.26 b	
<u>Mullica-Berryland</u>										
CaSiO <sub>3</sub>	0.68	5.53 c	6.47 a	646 a	577 a	39.2 a	33.0 a	2.47 a	1.68 a	
Silicic acid	0.68	5.67 bc	6.40 a	632 a	573 a	40.1 a	35.1 a	2.36 ab	1.81 a	
	1.36	5.73 abc	6.27 abc	621 a	633 a	38.3 a	37.6 a	2.52 a	1.70 a	
	2	5.80 ab	6.13 bc	634 a	602 a	38.6 a	37.2 a	2.53 a	1.95 a	
Silica gel	2	5.87 ab	6.33 ab	639 a	588 a	39.3 a	38.0 a	2.30 ab	1.79 a	

Control	0	5.93 a	6.10 c	623 a	610 a	37.6 a	38.0 a	2.1 b	1.64 a
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†Values within each soil with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

Table 4.6: Effect of Si treatments on the maximum soil sorption capacity ( $S_{max}$ ) in three legacy P impacted agricultural soils after one winter wheat growing season as determined by Langmuir isotherms.

Treatment	Ft. Mott-Henlopen	Ingleside- Hammonton	Mullica-Berryland
	mg kg <sup>-1</sup>		
CaSiO <sub>3</sub>	84 ab <sup>†</sup>	43 b	272 a
Silicic acid at CaSiO <sub>3</sub> Si rate	87 a	31 b	290 a
Silicic acid at two times CaSiO <sub>3</sub> Si rate	63 cd	40 b	283 a
Silica gel at Si rate of 2 Mg ha <sup>-1</sup>	68 c	33 b	332 a
Silicic acid at Si rate of 2 Mg ha <sup>-1</sup>	51 d	61 ab	280 a
No Si control	72 bc	87 a	284 a

<sup>†</sup>Values within each soil with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

Table 4.7: Effect of Si treatments on the yield of winter wheat and P and Si concentration of straw and grain in three legacy P impacted agricultural soils after one winter wheat growing season.

Treatment	Total Si rate	Yield		P concentration		Si concentration		Total crop P removal
		Straw	Grain	Straw	Grain	Straw	Grain	
		Mg ha <sup>-1</sup>		g kg <sup>-1</sup>				kg ha <sup>-1</sup>
<u>Ft. Mott-Henlopen</u>								
CaSiO <sub>3</sub>	0.41	7.68 a <sup>†</sup>	3.78 a	0.66 b	2.21 a	8.38 b	0.10 a	13.4 a
Silicic acid	0.41	5.82 b	3.50 a	0.79 ab	2.27 a	8.34 b	0.07 ab	12.6 a
	0.82	6.83 ab	3.18 a	0.89 ab	2.40 a	11.2 b	0.04 ab	13.7 a
	2	6.93 ab	3.69 a	0.99 a	1.57 a	18.3 a	0.03 b	12.8 a
Silica gel	2	7.07 ab	3.53 a	0.85 ab	2.25 a	15.2 a	0.05 ab	13.9 a
Control	0	7.25 ab	4.32 a	0.68 ab	1.48 a	2.74 c	0.02 b	11.2 a
<u>Ingleside- Hammonton</u>								
CaSiO <sub>3</sub>	0.41	7.23 a	3.28 a	1.25 a	2.48 ab	7.14 cd	0.03 a	17.2 a
Silicic acid	0.41	6.71 a	3.28 a	1.37 a	2.74 a	6.50 cd	0.03 a	18.2 a
	0.82	7.70 a	4.21 a	1.21 a	2.29 b	9.56 bc	0.04 a	19.0 a
	2	8.05 a	3.84 a	1.62 a	2.52 ab	16.6 a	0.04 a	22.9 a
Silica gel	2	8.02 a	3.71 a	1.17 a	2.39 ab	15.4 ab	0.04 a	18.4 a
Control	0	6.67 a	3.60 a	1.19 a	2.47 ab	1.47 d	0.01 b	16.8 a
<u>Mullica-Berryland</u>								
CaSiO <sub>3</sub>	0.68	8.04 ab	3.99 a	1.05 a	3.24 a	11.0 a	0.05 a	21.7 a
Silicic acid	0.68	8.58 ab	4.43 a	1.01 a	2.65 a	5.89 bc	0.03 b	20.3 a
	1.36	7.80 ab	3.70 a	1.06 a	2.36 a	9.30 ab	0.03 ab	17.1 a
	2	8.82 ab	3.89 a	1.00 a	2.16 a	11.0 a	0.03 b	17.2 a
Silica gel	2	9.43 a	4.72 a	1.04 a	2.30 a	11.2 a	0.03 ab	20.4 a
Control	0	7.11 b	4.04 a	1.15 a	2.47 a	1.95 c	0.02 b	18.1 a

† Values within each soil with different letters were statistically different using Tukey's honestly significant difference test at  $P < 0.05$ .

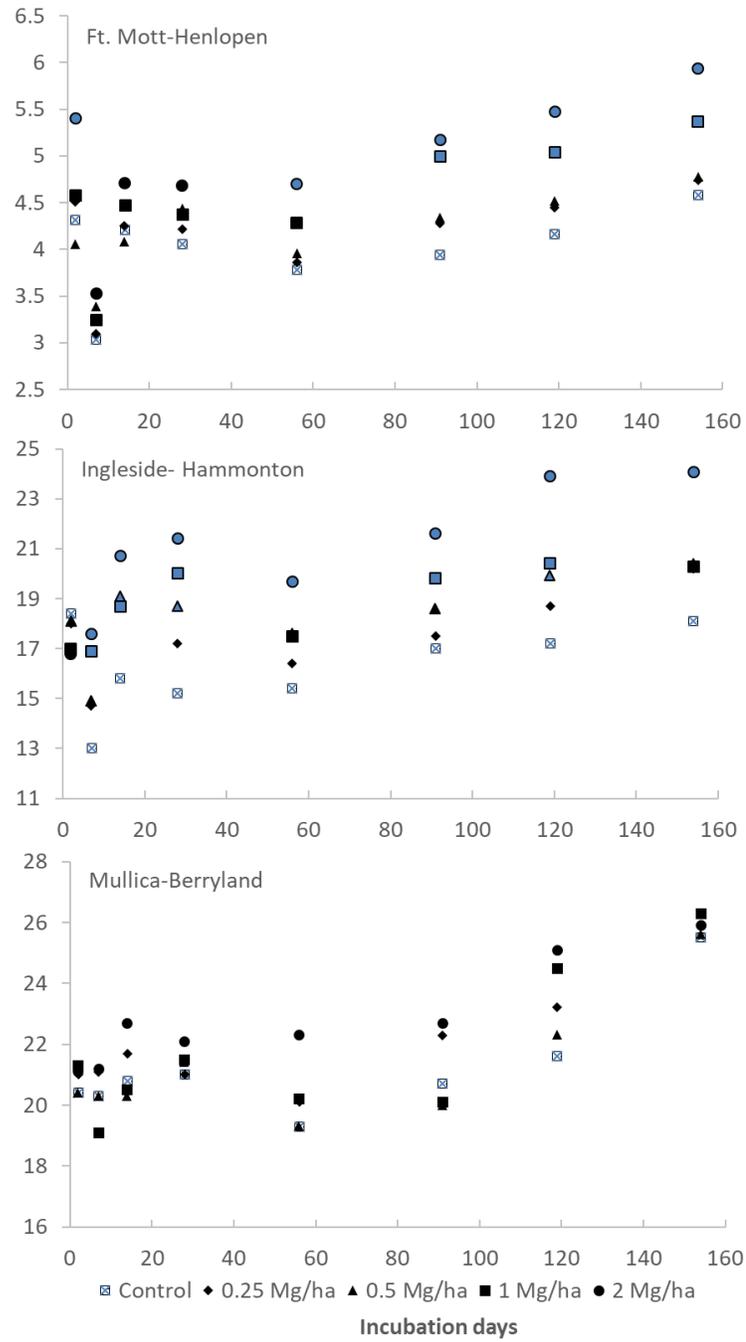


Figure 4.1: Effect of silicic acid application on soil water extractable P (WEP) during the soil only incubation study. Data points shown in blue were significantly different than the controls using Tukey's honestly significant difference test at  $P < 0.05$ .

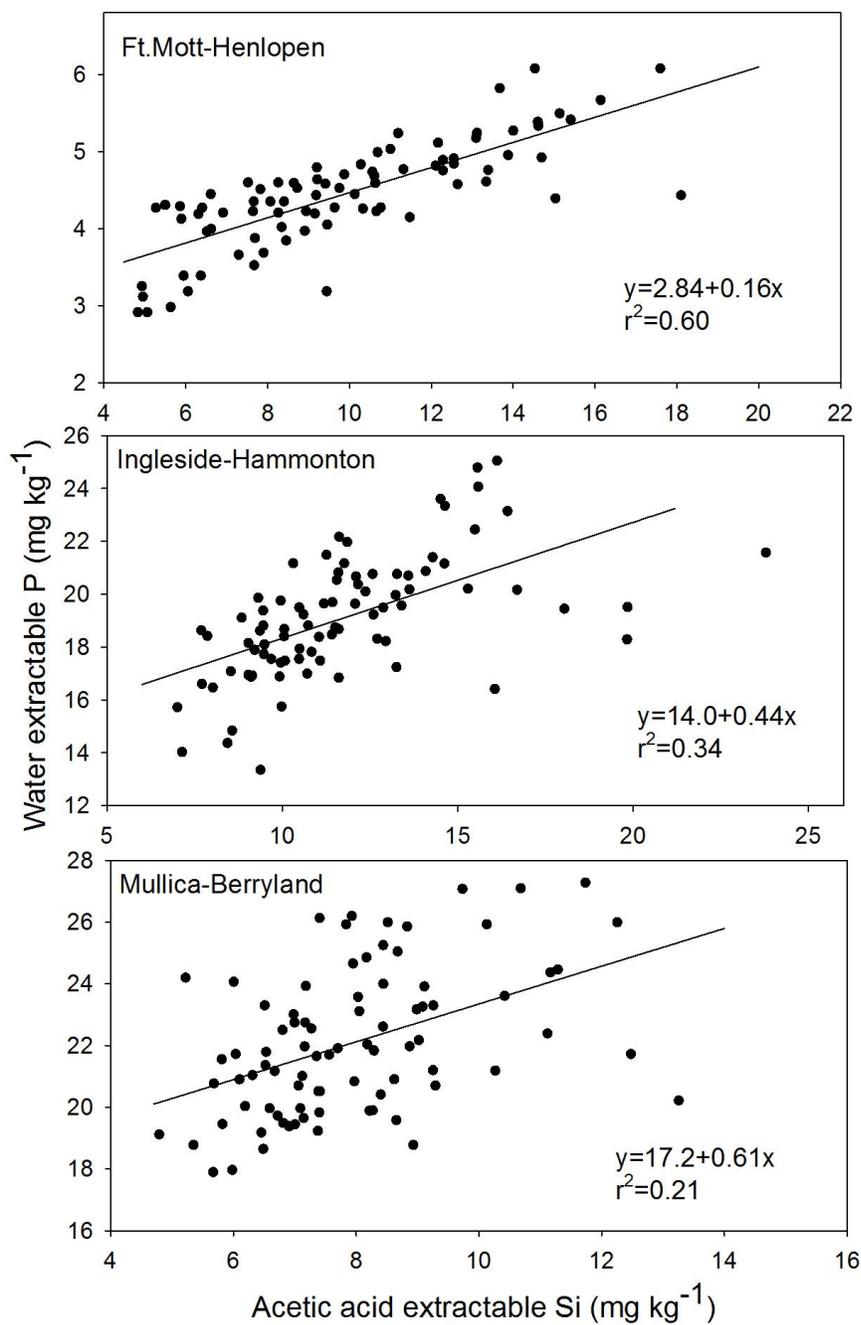


Figure 4.2: Relationship between acetic acid extractable Si and water extractable P when silicic acid was applied as the Si source to three legacy P impacted agricultural soils during the soil only incubation study. All relationships were significant at  $\alpha$  level of 0.001.

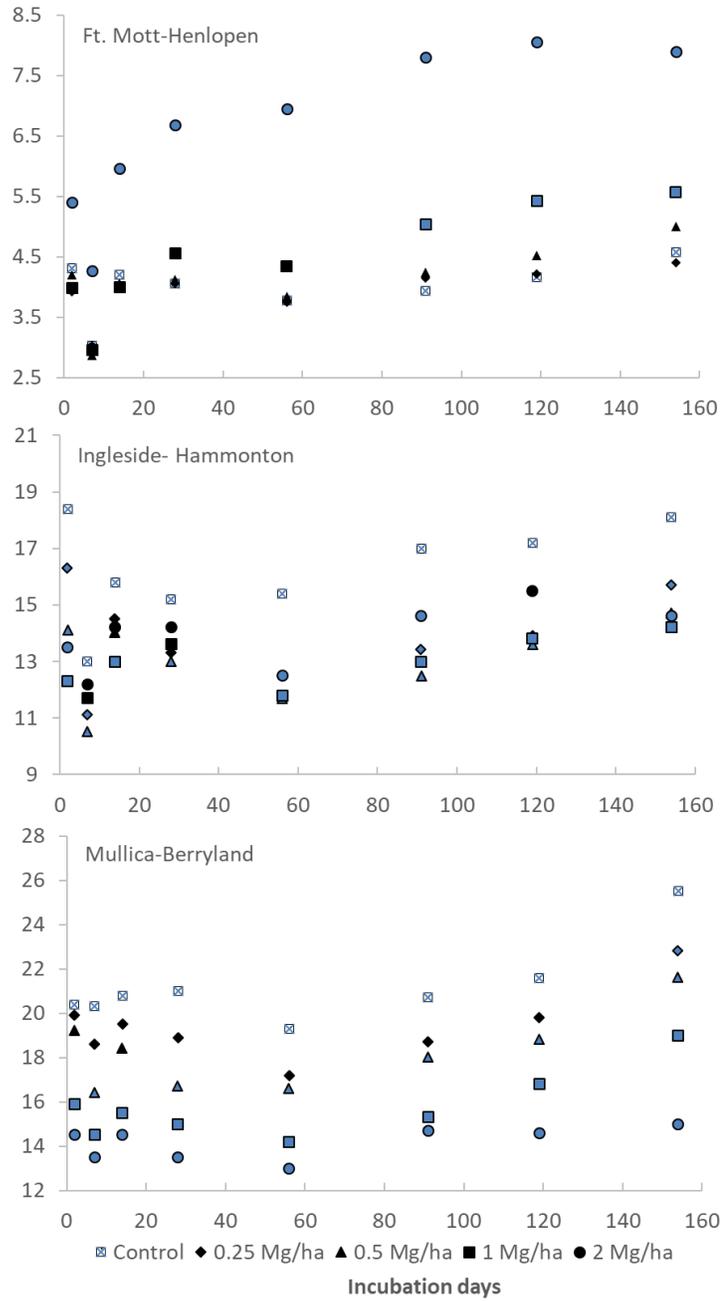


Figure 4.3: Effect of  $\text{CaSiO}_3$  application on soil water extractable P (WEP) during the soil only incubation study. Data points shown in blue were significantly different than the controls using Tukey's honestly significant difference test at  $P < 0.05$ .

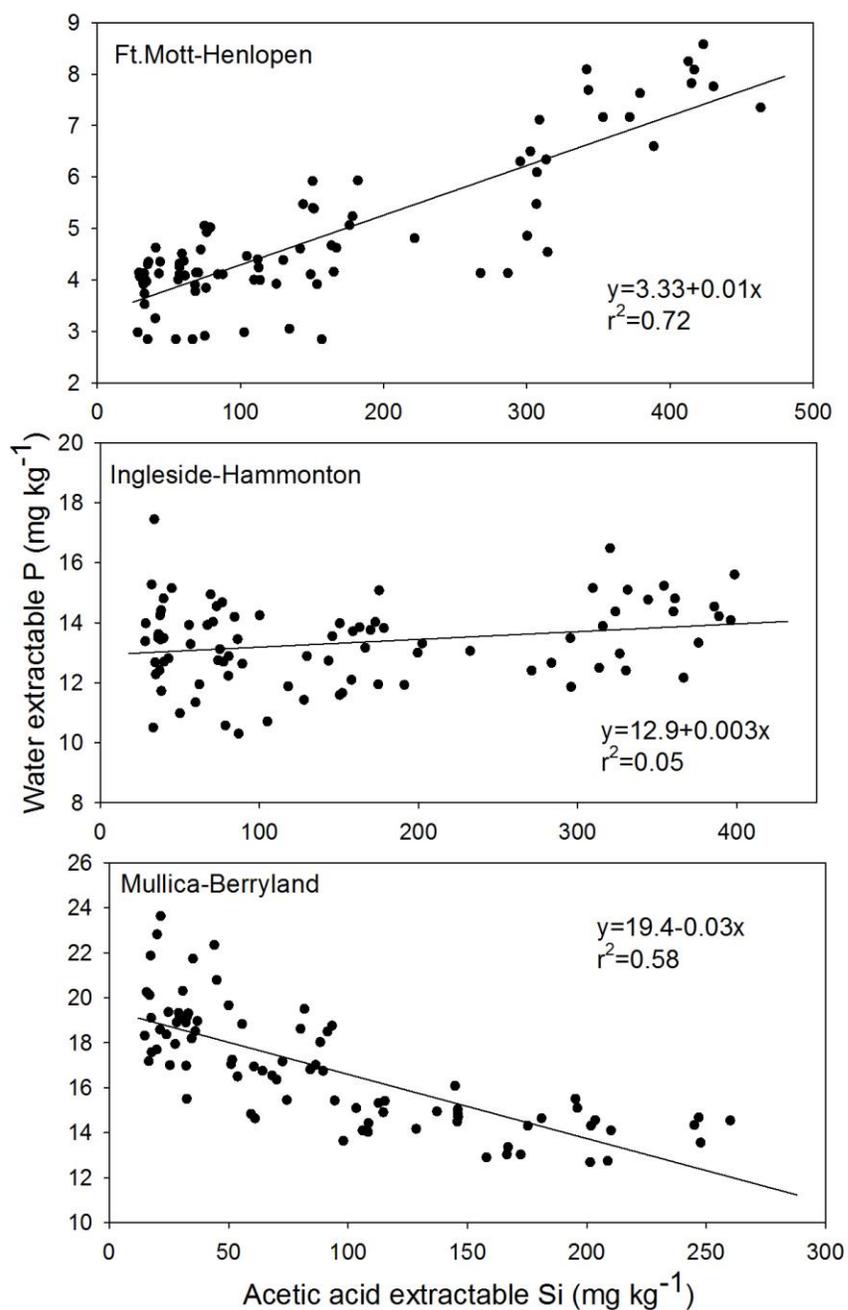


Figure 4.4: Relationship between acetic acid extractable Si and water extractable P when  $\text{CaSiO}_3$  was applied as the Si source to three legacy P impacted agricultural soils during the soil only incubation study. Relationship were significant at  $\alpha$  level of 0.001 for Ft. Mott-Henlopen and Mullica-Berryland soil series, and at  $\alpha$  level of 0.05 for Ingleside-Hammonton soil series.

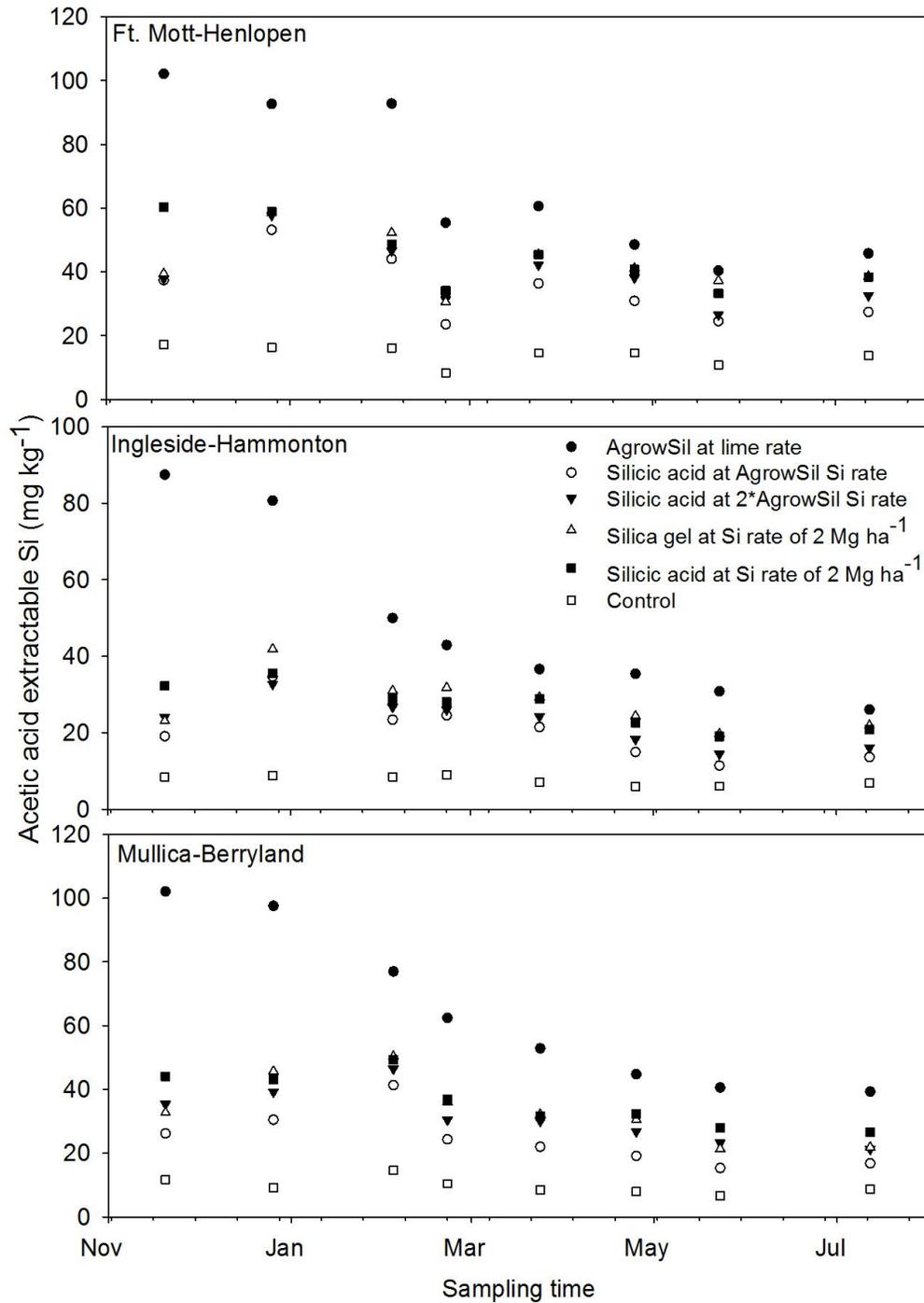


Figure 4.5: Temporal trends in acetic acid extractable Si concentrations in three legacy P impacted agricultural soils receiving Si fertilization during one winter wheat growing season.

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## Appendix A

### SILICON FERTILIZERS ENHANCE SOIL P AVAILABILITY AND UPTAKE FROM LEGACY P SOILS BY WINTER WHEAT

Table A.1: Effect of Si treatments over time on acetic acid extractable Si in three legacy P impacted agricultural soils during a 154-d incubation.

Source	Total Si rate Mg ha <sup>-1</sup>	Acetic acid extractable Si mg kg <sup>-1</sup>						
		7 d	14 d	28 d	56 d	91 d	119 d	154 d
<u>Ft. Mott-Henlopen</u>								
Control	0	4.35 c <sup>†</sup>	4.68 c	5.32 d	6.52 d	11.8 a	6.63 e	9.33 d
Switchgrass ash	0.25	5.33 bc	5.51 bc	6.87 cd	6.85 cd	12.3 a	7.39 de	10.6 cd
	0.5	5.64 bc	6.99 bc	6.85 cd	9.60 bcd	8.36 a	9.07 cd	11.3 cd
	1	6.73 bc	7.90 b	7.63 cd	11.2 abcd	11.2 a	9.78 bc	13.1 bcd
	2	9.89 a	11.8 a	13.5 a	16.9 a	15.7 a	14.6 a	19.0 a
Silicic acid	0.25	4.90 bc	5.63 bc	6.54 cd	7.98 bcd	8.88 a	9.03 cd	12.0 bcd
	0.5	5.32 bc	6.33 bc	7.36 cd	8.94 bcd	10.4 a	9.97 bc	11.9 bcd
	1	7.15 b	7.81 b	8.43 bc	13.3 ab	12.8 a	11.6 b	14.3 abc
	2	7.11 b	10.7 a	10.4 b	12.8 abc	14.4 a	14.1 a	16.1 ab
<u>Ingleside-Hammonton</u>								
Control	0	6.00 b	7.36 c	6.92 b	7.35 d	8.31 d	7.29 f	8.33 e
Switchgrass ash	0.25	7.51 ab	7.93 bc	7.90 b	8.25 cd	9.08 d	8.72 ef	9.76 de
	0.5	12.6 a	8.10 bc	8.59 b	9.82 bcd	10.0 cd	10.1 cde	10.6 cde
	1	9.43 ab	11.3 abc	9.80 b	12.4 abc	12.0 b	10.9 cde	12.8 bc

	2	12.6 a	15.5 ab	18.3 a	14.7 ab	15.5 a	13.8 ab	16.0 a
Silicic acid	0.25	7.53 ab	8.13 bc	9.77 b	12.0 bcd	9.90 cd	9.62 def	11.3 cd
	0.5	8.66 ab	9.26 abc	10.2 b	10.8 bcd	11.5 bc	12.7 abc	12.6 bc
	1	8.45 ab	14.7 abc	10.5 b	12.5 abc	12.3 b	11.7 bcd	14.9 ab
	2	9.24 ab	16.9 a	11.9 ab	17.2 a	14.6 a	14.9 a	16.0 a
<u>Mullica-Berryland</u>								
Control	0	4.77 c	6.79 a	7.05 a	8.13 a	5.90 b	5.49 e	7.69 c
Switchgrass ash	0.25	5.33 c	8.12 a	8.91 a	6.17 a	6.39 ab	5.72 de	7.19 c
	0.5	5.81 c	8.51 a	8.89 a	6.95 a	7.03 ab	6.37 de	8.49 bc
	1	6.27 bc	7.47 a	7.21 a	8.85 a	6.87 ab	7.10 cd	8.76 bc
	2	9.24 a	9.56 a	9.92 a	8.18 a	8.69 ab	8.96 b	10.0 ab
Silicic acid	0.25	5.80 c	6.94 a	6.68 a	6.90 a	6.46 ab	7.14 cd	7.92 bc
	0.5	5.41 c	6.66 a	7.65 a	7.43 a	9.49 ab	6.89 cde	8.67 bc
	1	6.17 bc	7.79 a	8.00 a	7.26 a	8.28 ab	8.19 bc	9.23 bc
	2	7.74 ab	9.00 a	8.10 a	10.2 a	10.2 ab	10.8 a	11.7 a

†Values within each soil with different letters were statistically different using Tukey's honestly significant difference test at  $P < 0.05$ .

Table A.2: X-ray fluorescence analysis of selected elemental composition on calcium silicate ( $\text{CaSiO}_3$ ) liming alternative.

Material	P	Fe	Al	Ca	Mg	Mn	Si
	$\text{g kg}^{-1}$						
$\text{CaSiO}_3$	2.34	32.3	69.4	267	97.5	9.16	121

Table A.3: Initial characterization of operationally-defined soil P pools on three legacy P impacted agricultural soils evaluated for the winter wheat pot experiment.

Soils	H <sub>2</sub> O- extractable P	NaHCO <sub>3</sub> - extractable P	NaOH- extractable P	HCl- extractable P
	mg kg <sup>-1</sup>			
Ft. Mott-Henlopen	21.0 c <sup>†</sup>	119 c	210 c	21.4 b
Ingleside-Hammonton	42.8 b	175 b	408 b	48.8 a
Mullica-Berryland	65.1 a	281 a	690 a	53.7 a

<sup>†</sup>Values within each extraction with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

Table A.4: Characterization of operationally-defined soil P pools on three legacy P impacted agricultural soils evaluated for the winter wheat pot experiment after receiving Si treatments for 40 d.

Treatment	H <sub>2</sub> O- extractable P	NaHCO <sub>3</sub> - extractable P	NaOH- extractable P	HCl- extractable P
	mg kg <sup>-1</sup>			
	<u>Ft. Mott-Henlopen</u>			
CaSiO <sub>3</sub>	25.1 b <sup>†</sup>	75.6 a	220 ab	23.8 a
Silicic acid at CaSiO <sub>3</sub> Si rate (0.41 Mg ha <sup>-1</sup> )	27.9 ab	68.4 ab	219 ab	28.3 a
Silicic acid at two times CaSiO <sub>3</sub> Si rate (0.82 Mg ha <sup>-1</sup> )	28.2 a	71.4 a	227 a	27.9 a
Silica gel at Si rate of 2 Mg ha <sup>-1</sup>	28.8 a	73.7 a	214 ab	30.1 a
Silicic acid at Si rate of 2 Mg ha <sup>-1</sup>	29.4 a	72.4 a	204 b	24.8 a
No Si control	26.5 ab	63.4 b	222 ab	30.0 a
	<u>Ingleside-Hammonton</u>			
CaSiO <sub>3</sub>	38.3 b	83.3 a	361 a	44.8 a
Silicic acid at CaSiO <sub>3</sub> Si rate (0.41 Mg ha <sup>-1</sup> )	43.8 a	88.4 a	364 a	60.3 a
Silicic acid at two times CaSiO <sub>3</sub> Si rate (0.82 Mg ha <sup>-1</sup> )	40.8 ab	87.2 a	335 a	51.4 a
Silica gel at Si rate of 2 Mg ha <sup>-1</sup>	42.6 ab	88.5 a	348 a	46.4 a
Silicic acid at Si rate of 2 Mg ha <sup>-1</sup>	45.6 a	89.4 a	334 a	52.1 a
No Si control	40.9 ab	89.1 a	364 a	49.3 a
	<u>Mullica-Berryland</u>			
CaSiO <sub>3</sub>	59.6 abc	191 a	615 a	61.9 b
Silicic acid at CaSiO <sub>3</sub> Si rate (0.68 Mg ha <sup>-1</sup> )	58.2 bc	179 a	619 a	62.5 b
Silicic acid at two times CaSiO <sub>3</sub> Si rate (1.36 Mg ha <sup>-1</sup> )	61.6 ab	186 a	653 a	60.5 b
Silica gel at Si rate of 2 Mg ha <sup>-1</sup>	59.7 abc	183 a	663 a	68.3 ab
Silicic acid at Si rate of 2 Mg ha <sup>-1</sup>	64.0 a	191 a	614 a	85.6 a
No Si control	55.1 c	182 a	627 a	65.3 b

<sup>†</sup>Values within each soil with different letters were statistically different using Tukey's honestly significant difference test at P<0.05.

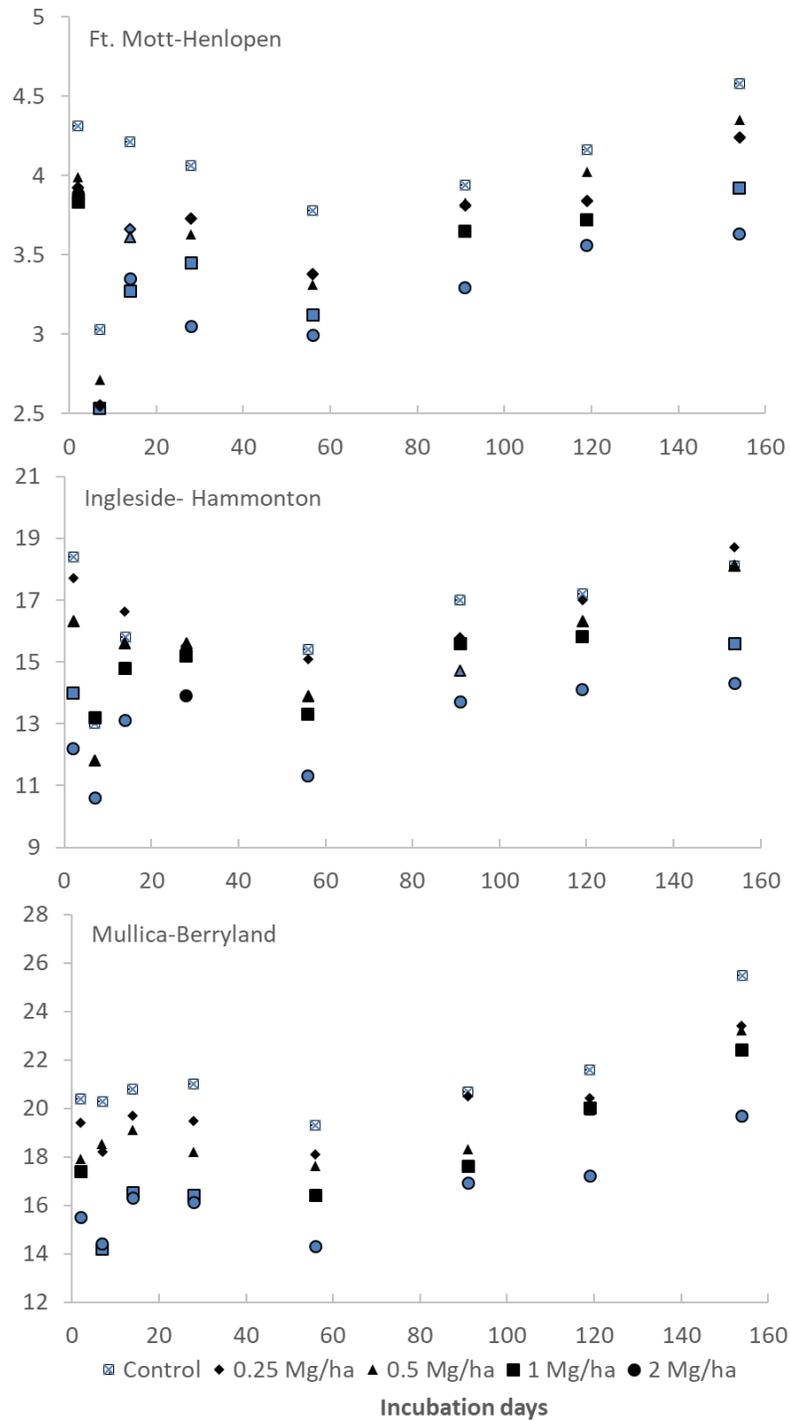


Figure A.1: Effect of switchgrass ash application on soil water extractable P (WEP) during the soil only incubation study. Data points shown in blue were significantly different than the controls using Tukey's honestly significant difference test at  $P < 0.05$ .