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MECHANISMS OF PHOSPHORUS REMOVAL BY PHOSPHORUS SORBING MATERIALS

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Abstract

Stormwater filtration units are a structural best management practice designed to reduce dissolved P losses from runoff. Various industrial by-products are suitable for use as P sorbing materials (PSMs) for treatment of drainage water; P sorption by PSMs varies with material physical and chemical properties. Previously, P removal by PSMs was estimated using chemical extractions. We determined speciation of P when reacted with various PSMs using X-ray absorption near edge structure (XANES) spectroscopy. Twelve PSMs were reacted with P solution in the laboratory under batch or flow-through conditions. In addition, three slag materials were collected from working stormwater filtration structures. Phosphorus K-edge XANES spectra were collected on each reacted PSM and compared with spectra of 22 known P standards using linear combination fitting (LCF) in Athena. We found evidence of formation of a variety of Ca-, Al-, and/or Fe-phosphate minerals and sorbed phases on the reacted PSMs, with exact speciation influenced by the chemical properties of the original unreacted PSM. We grouped PSMs into three general categories based on the dominant P removal mechanism: 1) Fe and Al mediated removal (i.e., adsorption of P to Fe/Al-(hydro-)oxide minerals and/or precipitation of Fe-/Al-phosphate minerals); 2) Ca mediated removal (i.e., precipitation of Ca-phosphate mineral); and 3) both mechanisms. We prefer the use of Fe/Al sorbing PSMs for use in stormwater filtration structures where stormwater retention time is limited because reaction of P with Fe or Al generally occurs more quickly than Ca-P precipitation.

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Supplemental Materials: Information on the methods used to prepare and synthesize reference standards is included in the Supplemental Materials. The Supplemental Materials section also includes a table showing the chemical analysis of reacted PSMs.

Introduction

Widespread implementation of best management practices (BMPs) has significantly reduced agricultural non-point P pollution over the past few decades (Mulla et al., 2008; Meals et al., 2010; Sharpley et al., 2011; McDowell and Nash, 2012). However, traditional BMPs, such as fertilizer management (Fiorellino et al., 2017) and conservation tillage (Sharpley and Smith, 1994; Sharpley et al., 2011; Jarvie et al., 2017) to reduce soil erosion, are not particularly effective at controlling dissolved P losses 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 pose a risk for dissolved P losses (Sharpley et al., 2011; Jarvie et al., 2017). Some entities recommend eliminating application of manures and commercial P fertilizers to agricultural soils with agronomically excessive concentrations of STP to allow draw-down of P through crop removal, even when risk assessment tools (i.e., P Index) do not indicate a significant risk of P loss (Maryland Department of Agriculture, 2016). However, widespread elimination of manure application in areas with intensive animal production, such as the Delmarva Peninsula, could result in serious waste disposal issues (Withers et al., 2015) and burden growers economically by requiring a shift to commercial fertilizers to supply N, K, and other essential plant nutrients. Elimination of manure application could also eliminate the soil health benefit gained by adding organic amendments to soils as part of the soil fertility program (Romano et al., 2017).

By-products generated from a variety of industries, such as steel manufacturing, electrical power production, drinking water treatment, and fertilizer production, can serve as low-cost PSMs that can be applied to soils to reduce P solubility (Leader et al., 2008), applied to streambeds to remove P from slow streamflow (McDowell et al., 2007), or used in filtration structures (as PSMs; Penn et al., 2007; Penn et al., 2016) or tile drainage system (as drainage medium; McDowell et al., 2008) to remove P from drainage water. These PSMs commonly contain significant concentrations of Al, Fe, Ca, or Mg that can react with and bind P (Stoner et al., 2012). Several researchers have described how PSMs can reduce soluble P concentrations in soils (Stout et al., 1998) and manures (Staats et al., 2004) or 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 (fluidized bed combustion fly-ash and flue gas desulfurization by-products) reduced soil Mehlich 3 P by 20–110 mg kg⁻¹ and water extractable P concentrations by 7–9 mg kg⁻¹ in seven soils representing a wide range of soil P concentrations, textures, and organic matter content collected from three locations in Pennsylvania, two locations in Delaware, and one location in Washington and Ohio. The reduction in soil STP and water extractable P following application of PSMs 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) showed that water treatment residuals significantly reduced total cumulative leachate P loads within four months of application to sandy Florida soils planted with Bahiagrass (*Paspalum notatum* Flueggé) when compared with leachate P loads from an unamended soil in a greenhouse column study.

Industrial PSMs also serve as effective media for use in storm water filtration structures. A stormwater filter is a structural BMP that removes soluble P from agricultural drainage water by forcing water through a sorbent material. Stormwater 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; Penn et al., 2014; Penn et al., 2017). However, the overall P sorption capacity of specific PSM-based filtration media varies based on the chemical and physical properties of the material. In addition, all PSM-based filter media will eventually become saturated with P, thereby reducing their ability to remove P from stormwater runoff. Several studies have indicated performance of several PSMs and provided estimates of P sorption capacity under flow-through conditions (Stoner et al., 2012; Penn et al., 2012; Penn et al., 2016; Penn et al., 2017). Yet, comprehensive information about the P speciation and removal mechanisms of PSMs is lacking. Synchrotron-based XANES is an effective, in-situ tool that can be used 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 technique can be used to evaluate P sorption by PSMs. This technique allows us to probe the molecular level P speciation information, which extends beyond the information provided by traditional bulk chemical analysis that only quantify operationally defined soil P pools (Prietzel et al., 2016). The objective of this research is to: 1) determine detailed P speciation and sorption mechanisms of 12 common PSMs used in stormwater P filtrations structures using XANES spectroscopy, and 2) compare the differences in P speciation when PSMs were reacted under different conditions (i.e., laboratory batch reaction, laboratory flow-through reaction, or field reaction).

MATERIALS AND METHODS

Preparation and Chemical Characterization of Phosphorus Sorbing Materials

A total of 12 PSMs, including three acid mine drainage residuals (AMDR), two drinking water treatment residuals (WTR), one Ca/Mg silicate soil amendment, two fly-ashes, and four electric arc furnace steel slags of various particle-size compositions were evaluated in this study. The elemental composition and chemical properties of these unreacted PSMs (with the exception of slag2) were previously reported in the literature (Stoner et al., 2012) and are summarized in Supplemental Information (Table S1). Specifically, AMDR1 and AMDR3 were naturally formed at mining sites in Pennsylvania when acid mine drainage water flowed from 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 goethite was the main crystalline minerals (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 calcite was the main crystalline minerals 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 AB-Jewell and

Mohawk drinking water treatment plants in Tulsa, OK, where Al-sulfate was used as the flocculating agent (Stoner et al., 2012); these neutral pH materials had the highest total digestible and oxalate Al concentrations (when compared to other PSMs), and quartz was the main crystalline minerals (Stoner et al., 2012). The Ca/Mg silicate soil amendment (Excell Minerals, Harsco Corp., Camp Hill, PA) is a material that is used to supply 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 particle size compositions 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 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 for the purpose of increasing the hydraulic conductivity; Al-sulfate treatment resulted in the precipitation of amorphous Al-hydroxide on the slag surface (Penn and McGrath, 2011). The Ca/Mg silicate soil amendment, fly-ash, and all un-coated slags were alkaline materials, while the coated slag was pH neutral. The Ca/Mg silicate soil amendment, fly ashes, slag materials, and AMDR4 had the highest total digestible Ca concentrations of any evaluated PSMs; the slags materials also contained relatively high concentrations of total digestible Fe (Stoner et al., 2012). Previously, Stoner et al. (2012) also detected some Fe-, Ca-, and/or Si-associated crystalline minerals in unreacted Ca/Mg silicate soil amendment, fly-ashes, and slags (Table S1).

Slag1 and slag2 were available as spent materials removed from filter structures that are currently deployed to remove P from stormwater runoff at field sites in Stillwater, OK (Penn et al., 2012). Coated slag was also available as spent field material that was removed from a pond-filter structure located on the turfgrass research farm at Oklahoma State University (Penn and McGrath, 2011). AMDR1 and Al-WTR2 were previously reacted with P solution (Stoner et al., 2012) in a flow-through cell, which was constructed as described in DeSutter et al. (2006) and Penn and McGrath (2011). Briefly, materials were reacted with 5 mg L^{-1} 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. The P sorption results from those flow-through experiments are presented in Stoner et al. (2012). Ten previously unreacted (fresh) PSMs were also treated with P in the laboratory under batch conditions. Unreacted samples of slag1 and slag2 were not available at the time of this study, and therefore, were not reacted in the laboratory under batch conditions. For batch reactions, fresh PSMs were ground into a fine powder and reacted with 5 mg L^{-1} P solution (as KH_2PO_4) 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 $0.45 \mu\text{m}$ filter. The residual PSMs were again reacted with a fresh 5 mg L^{-1} P solution. 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^{-1} . We did not react the fresh PSMs in a flow-through setting because the equipment used to react the samples under flow conditions was not available at the time of this work.

All lab and field reacted PSMs were air-dried at room temperature and stored until analysis. After laboratory reaction, all PSMs were analyzed by X-ray fluorescence (XRF; Supermini200, Rigaku Americas, Inc., The Woodlands, TX) to determine total elemental composition, and by X-ray diffraction (D8 XRD, Bruker AXS, Madison, WI) to identify crystalline mineral components.

Phosphorus K-edge X-ray Absorption Near Edge Structure Spectra Collection

Phosphorus K-edge XANES spectra were collected on all reacted PSMs and 22 reference standards. Details on the reference preparation and synthesis methods are outlined in the Supplemental Information. Spectra collection for 19 of the 22 reference standards was conducted at the bending magnet beamline 9-BM at Advanced Photon Source, 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 helium 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 P 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 reference standards in total electron yield (TEY) mode using an electron yield detector to minimize the effects of self-absorbance (i.e., 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. We recognize that comparing standard spectra collected in TEY mode with sample spectra collected in fluorescence mode can be problematic since the former method only probes the surface of the samples while the latter method evaluates the bulk samples (Toor et al., 2006). As a result, it is possible that the surface structure of the samples differs from the bulk structure of the material, thus yielding different spectral features. We were not able to collect quality spectra of our standards in fluorescence mode despite numerous attempts to dilute samples (e.g., using boron nitride, spreading thin on Kapton tape, etc.). As such, we opted to generate spectra for our sample library in TEY to preserve the integrity of the white line peak.

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 eV relative to the white line peak and a normalization range of 15–150 and 15–115 eV relative to the white line peak 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 K-edge XANES spectra of reacted PSM samples were compared with spectra of 22 P reference standards (Figure S1) using the LCF tool in Athena to identify the P forms and respective contributions of reference P species in each PSM; the P K-edge XANES spectra of Heterosite with Mn, Bobierite, and Newberyite (Figure S1) from the study of Ingall et al. (2011) were also used in the fitting analysis as potential Mn- or Mg-associated P species. The linear fitting range was -5 to 50 eV relative to the white line peak. 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). 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. The E_0 of reference standard spectra was allowed to shift up to ± 1 eV during the fitting. Residual factor (R-factor) and χ^2 values were generated by the LCF tool in Athena to evaluate the goodness of fit, with smaller values indicating a better fit. The fluorapatite standard was not used for LCF analysis because no fluorine was detected in any of our PSMs using XRF. We also eliminated the phytic acid from LCF analysis for the laboratory-reacted PSMs, since those materials were not likely to contain organic forms of P after reaction with inorganic P standard (as KH_2PO_4).

RESULTS AND DISCUSSIONS

Characterization of Elemental and Mineral Compositions of Reacted Phosphorus Sorbing Materials

The overall composition of Al, Fe, and Ca of the unreacted PSMs was evaluated in previous studies using chemical digestion (Table 1). We also found that most of the reacted PSMs contained relatively high Si concentrations (estimated concentration $>100 \text{ g kg}^{-1}$ as determined by XRF). Materials that were rich in Ca (Ca/Mg silicate soil amendment, fly-ashes, slags, and AMDR4) also contained relatively high concentrations of Mg (as determined by XRF; data not shown). We did not detect crystalline P species in any of the laboratory-reacted PSMs using XRD, which was likely due to the relatively low concentration of P in the evaluated materials (about 1 g kg^{-1}). As a result, any crystalline P mineral that may have 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, which was generally consistent with those detected in fresh PSMs evaluated in previous studies (Table 1). However, we did not detect gypsum, tricalcium magnesium orthosilicate, or portlandite in the laboratory-reacted coated slag, Ca/Mg silicate soil amendment, 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 may have resulted from their relatively high solubility in water (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, for the laboratory-reacted PSMs, we detected quartz in AMDR3, merwinite in Ca/Mg silicate soil amendment, and calcite and

periclase in the 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 (Ruiz-Agudo et al., 2013). However, it is not likely that other minerals were formed during the P reaction process since minerals, such as 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.

Characterization of Phosphorus Species on Phosphorus Sorbing Materials

Acid Mine Drainage Residuals and Drinking Water Treatment Residuals—Based on the LCF results 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, with formation of non-crystalline Fe-phosphates under batch conditions (Figure 1) and semi-crystalline Fe-phosphates under flow-through conditions (Table 2). Under both batch and flow-through conditions, a small amount (16–17%) of total P precipitated as strengite (a crystalline Fe-phosphate mineral) when P solution was reacted with AMDR1. Reaction of AMDR3 with P solution resulted in adsorption of phosphate to Al-hydroxides and ferrihydrite (to a lesser extent), as well as precipitation of semi-crystalline Fe-phosphates (Figure 1). Reaction of AMDR4 with P solution resulted mainly in precipitation of strengite, with a smaller fraction of total P precipitated as monetite or phosphate sorbed to ferrihydrite (Figure 1).

The LCF results for WTR materials (Al-WTR1 and Al-WTR2) revealed that reaction with P solution resulted in the formation of Al-phosphate species, namely wavellite and other Al-phosphates of varying crystallinity (Figure 1). Reaction of the Al-WTR1 with P solution also resulted in adsorption of phosphate to Al-hydroxide. Semi-crystalline Al-phosphates did not form when Al-WTR2 was reacted with P under flow conditions; a similar amount of strengite was formed instead (Table 2).

The formation of Fe- and/or Al- phosphates following reaction of AMDRs and WTRs with P solution was consistent with elevated total digestible and oxalate-extractable (amorphous) Al and/or Fe content of these materials (Table 1). Most of the AMDRs and WTRs materials (except AMDR4) also had a pH lower than 7.5, which favors the reaction of phosphate with Al- and/or Fe- oxides (Penn and Zhang, 2010; Penn et al., 2011). 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 Fe and Al mineral surfaces (Rhoton and Bighan, 2005). The dominant formation of surface-adsorbed P species for AMDR3, but not AMDR1, is expected due to the lower pH of AMDR1 (3.2) compared to AMDR3 (6.4). Formation of a small amount of Ca-associated phosphate (monetite) following reaction of AMDR4 with P solution was likely due to the higher total Ca concentration and pH compared with other AMDRs and WTRs (Table 1).

Ippolito et al. (2003) also confirmed the association of P with Al in a WTR that was reacted with P solution using electron microprobe-wavelength dispersive spectroscopy. The authors hypothesized that phosphate initially adsorbs to the Al minerals as outer-sphere complex and, as time passes, forms a stronger inner-sphere complex and eventually amorphous

variscite. In another study, Penn et al. (2011) found that ammonium fluoride (NH_4F)-extractable P (i.e., Al-associated P) accounted for 56 and 69% of the total P removed by an AMDR and WTR material, respectively. However, Penn et al. (2011) also noted that sulfuric acid (H_2SO_4)-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 association of P with the calcite coating that formed on the Fe and Al oxides/hydroxide minerals in the AMDR when lime was used to increase pH and precipitate Fe in the acid mine drainage treatment systems (Penn et al., 2011). Pierzynski et al. (1990a) also found that P-rich particles in over-fertilized soils were predominantly associated with Al irrespective of soil pH. Using scanning transmission electron microscopy with an energy dispersive X-ray analyzer, Pierzynski et al. (1990b) further concluded that those P-Al particles can be described as an amorphous mixed Al-Si-P substance.

Ca/Mg silicate soil amendment, Fly-ash, and Slags—The two fly-ash materials evaluated in this study had very similar elemental concentrations and material pH (Table 1). Consequently, reaction of both fly-ash materials with solution P resulted in the formation of Ca-phosphates (based on LCF results), either in the form of octacalcium phosphate or hydroxyapatite (Figure 2). Similar to fly-ash, the Ca-rich, alkaline Ca/Mg silicate soil amendment also formed Ca-phosphate minerals (i.e., hydroxyapatite and monetite) when reacted with P (Figure 2).

Reaction of all evaluated slag materials with P (either in the laboratory or in the field) resulted in the formation of hydroxyapatite (37–87% of total P; Figure 2 and Table 3). In addition, Fe- and/or Al- associated phosphates (non-crystalline and/or semi-crystalline) also formed when P came into contact with the slag materials (Figure 2 and Table 3), with the exception of field-reacted slag1 (Table 3). However, the batch-reacted coated slag only formed 15% Al-associated phosphate, which was lower than expected considering material surface was coated with Al-sulfate. We believe that the act of grinding the samples before reacting with P destroyed the Al coating and diluted the Al concentration in the ground samples. As a result, the ground coated slag material behaved like the uncoated Ca-rich slag materials when reacted with P during the laboratory batch reaction. Another possibility is that the majority of the detected Ca-phosphate minerals were already present in the slag, prior to reaction with P, as the unreacted slag samples used in this study contained considerable P concentrations (Yildirim and Prezzi, 2011; Penn, 2012 unpublished data)

The formation of Ca-phosphates during reaction of P with Ca-rich, alkaline PSM (i.e., Ca/Mg silicate soil amendment, fly-ashes, and uncoated slag materials) is consistent with the chemical composition of those materials, which had among the highest total and/or water-soluble Ca and relatively high pH (>9; Table 1). Others also reported that 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 of an argon oxygen decarburization slag following laboratory batch reaction with P solution using a combined Visual MINTEQ and XANES analysis. The authors reported the precipitation of Ca-phosphate minerals when the slag materials were reacted with P solution under highly alkaline (apatite) or neutral (brushite) solution conditions, respectively. Hussain et al. (2014) reported the formation of

Ca-phosphate dibasic dehydrate or sorption of P onto calcite using multiple spectroscopic tools when P-rich lake water was filtered through alkaline oxygen furnace slag. 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 resulted in the formation of crystalline Ca-phosphates (e.g., octacalcium phosphate, hydroxyapatite, and/or monetite; accounting for >30% of total P). Amorphous Ca-phosphate (14–63% of total P) also formed when Filtralite P, Filtra P, Polonite, or Absol were reacted with wastewater. In addition, reaction of Filtralite P and blast furnace slag with wastewater also resulted in the association of P with Fe and/or Al (e.g., hydrated Al-phosphate, phosphate adsorbed to Al-oxide or ferrihydrite; >35% of total P). Contrary to our findings, Penn et al. (2011) reported that the formation of Al-bound P (NH_4F -extractable P) dominated when P solution was reacted with a Pennsylvania 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 g kg^{-1}) and pH (8.2) than the untreated fly-ash materials evaluated in our study (and Table 1), which explains the variation in P speciation with our study.

Other researchers also reported the formation of amorphous Ca-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) when our evaluated PSMs were reacted under laboratory or field conditions. Drizo et al. (2002) 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 ($\text{pH} > 9.3$). Therefore, we suggest that amorphous Ca-phosphate could potentially 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). Additionally, the XRD analysis on the reacted coated slag indicated the presence of calcite (Table 1) and when combined with a pH close to 7, could result in the sorption of phosphate to calcite when reacted with P. Since we did not include non-crystalline Ca-phosphates or sorbed phases of Ca in our standards library, we are unable to eliminate the possibility that amorphous Ca-phosphate formed when slag and/or Ca-rich alkaline materials were reacted with P.

Phosphorus Removal Mechanisms of Phosphorus Sorbing Materials

Based on the XANES LCF characterization of P species associated with 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 Ca/Mg silicate soil amendment was mostly by Ca-phosphate precipitation. The P removal by AMDRs and WTRs was a result of adsorption 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 slag2) used in field scale filtration structures occurred through 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, 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 investigating the major P removal mechanism of PSMs, since they represent the most reactive forms of the sorbing elements (Stoner et al., 2012). However, the 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 (Table 2) formed more semi-crystalline and/or highly crystalline Fe- and/or Al-phosphate compared with those reacted under batch conditions (Figure 1). 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). It is also possible that the accumulation of reaction products under batch condition influenced the system chemistry, while this effect was largely prohibited under flow-through conditions; reaction products were removed quickly in the latter case. When PSMs were reacted in stormwater filtration structures at field site, its P removal efficiency may be affected by the presence of dissolved organic carbon in stormwater. Specifically, previous studies have shown that dissolved organic carbon can compete with P for adsorption sites in soils, clay, and synthetic minerals, leading to decreased P sorption (Nagarajah et al., 1970; Sibanda and Young, 1986; Hue, 1991). Overall, the PSMs that were 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 change 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 (Filtral 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 were gradually exhausted, the solution pH dropped, 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 both the Fe/Al and Ca based mechanisms in removal of stormwater dissolved P by field-reacted coated slag and slag2 materials as predicted by our XANES LCF analysis. It is also possible that Fe and/or Al played a more important role in removing dissolved P once the Ca in field-reacted coated slag and slag2 had fully reacted and the pH had decreased. However, we noticed that Fe- and/or Al-associated P did not form in field-reacted slag1 material, which might due to reaction environment variability (chemical and physical environment) when slag1 was reacted with P in the field compared with coated slag and slag2.

Moreover, even if PSMs exhibit the same dominant P removal mechanism, there can still be significant differences in the chemical species that accumulate (i.e., adsorbed phases vs. precipitates, non-crystalline species vs. crystalline species). For example, AMDR1 and

AMDR3 both removed P by Fe and/or Al sorption; but Fe-phosphate precipitates were the main P species formed when P was reacted with AMDR1. In contrast, P removed by AMDR3 was mainly adsorbed to Fe- and/or Al- (hydr-)oxides (Figure 1), because this material possessed a higher pH that is more accustomed to ligand exchange reactions. 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 Mn can also potentially play an important role in some of the evaluated PSMs. 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, formation of Mg-phosphate precipitate is mostly likely to occur in our slags and Ca-rich alkaline PSMs since those reacted PSMs also contained notable amounts of Mg (Table 1). Phosphate precipitation with Mn is another important mechanism that removes dissolved P in solution (Leader et al., 2008), which happens mostly between pH 6.5–9 (Heintze, 1968). Considering the material pH (Table S1) and the amount of Mn in the reacted PSMs (Table 1), it is mostly likely that Mn-phosphate precipitates formed when P was reacted with WTRs, AMDR4, and coated slag samples. However, our LCF fitting result did not support the presence of Mg or Mn phosphate species in any of those PSMs when comparing with Mg- and Mn-P species presented by Ingall et al. (2011) (Figure 1 and 2).

Phosphorus Sorbing Materials Selection in Use for Stormwater Filtration

The determination of P removal mechanism and P speciation can shed light on the selection of PSMs for use in stormwater filtration structures. From the perspective of effective P removal, PSMs that remove P via the Fe/Al mechanism are generally considered more efficient filtration media than PSMs that rely on Ca-based removal mechanisms (Dou et al., 2003; Penn et al., 2016). Removal of P via adsorption to the surface of Fe and/or Al minerals occurs more rapidly than P removal via Ca precipitation (Lyngsie et al., 2015). In addition, Fe-/Al- oxides also potentially bind P more strongly than Ca-based sorbents; the latter normally have higher likelihood of desorption (Lyngsie et al., 2015). As such, PSMs that remove P via the Fe/Al mechanism are preferred for use in stormwater filtration structures, with materials that mainly remove P through chemisorption on the surface of Fe- and/or Al- (hydr-) oxides (e.g., AMDR3) preferred for structures with relatively high flow rates as the chemisorption process is 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 reaction environment (e.g., solution pH, redox condition, etc.) are also important to consider when selecting appropriate materials for filtration structures (Richardson and Craft, 1993; Drizo et al., 1999; Lyngsie et al., 2014). For example, PSMs that remove P by the Fe/Al mechanism may have reduced sorbing capacity in alkaline reaction environments since these metal (hydr-)oxides can potentially release P when subjected to elevated solution pH (Hietjes and Lijklema, 1980). In contrast, PSMs that remove P by the Ca/Mg mechanism may have reduced efficacy under acidic conditions (Leader et al., 2008). Crystallinity of the Fe/Al minerals in the PSM will also affect the ability of PSMs remove dissolved P from stormwater. In general, sorption of P to Fe-/Al-rich materials is greater for non-crystalline or amorphous minerals, such as

ferrihydrite, when compared with PSMs that are dominated with crystalline minerals like goethite or gibbsite (Stoner et al., 2012).

Recycling Options for Spent Phosphorus Sorbing Materials

The determination of P removal mechanism and P speciation can provide valuable information for the recycling of spent (P-saturated) materials. Materials 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, AMDR and WTR materials 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 S1). Although the concentrations of most trace elements were generally low (estimated concentrations $<10 \text{ g kg}^{-1}$) 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. Moreover, the cost of land application needs to be considered to determine whether this recycling option is economically feasible.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations:

AMDR	acid mine drainage residuals
BMP	best management practice
LCF	linear combination fitting
PSM	P sorbing material

STP	soil test P
TEY	total electron yield
WTR	drinking water treatment residuals
XANES	X-ray absorption near-edge structure
XRF	X-ray fluorescence
XRD	X-ray diffraction

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Core ideas:

- P speciation of PSMs was determined using XANES for stormwater filtration media.
- PSMs remove P via Al/Fe sorption, Ca sorption, or both mechanisms.
- P speciation is valuable in guiding the selection of PSMs for stormwater filtration structures.

Figure 1.

Linear combination fitting (LCF) results for P K-edge X-ray absorption near-edge structure spectra of acid mine drainage residuals (AMDR) and drinking water treatment residuals (WTR) materials that were reacted with phosphate solution in the laboratory under batch conditions. The spectra of the reference standards represent the relative proportion of the total that each reference P species in the fitted spectra.

Figure 2.

Linear combination fitting (LCF) results of P K-edge X-ray absorption near-edge structure spectra of Ca/Mg silicate soil amendment, fly-ashes, and slag materials that were reacted with phosphate solution in the laboratory under batch conditions. The spectra of the reference standards represent the relative proportion of the total that each reference P species in the fitted spectra.

Table 1. Selected 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>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	— [§]	-	5.8	7.1	Calcite, Gypsum,	Penn and McGrath (2011)
Ca/Mg silicate soil amendment	Batch	268	20	71	2.3	19	0.2	10.9	Tri-calcium magnesium 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 [‡]		245	28	112	0.3	2.2	-	11.6	-	Penn (2017), unpublished data

[†] AMDR, acid mine drainage residuals; WTR, drinking water treatment residuals.

[‡] pH was determined using a 1:1 w/v ratio instead of 1:5 w/v; Total element concentrations were determined by EPA 3050 digestion instead of EPA3051 digestion.

[§] Data not available

Table 2.

X-ray absorption near-edge structure spectroscopy linear combination fitting results showing the relative proportion of phosphate (PO_4) standards giving the best fit (from -5 to 50 eV relative to the white line peak) to spectra from acid mine drainage residual (AMDR) and Al drinking water treatment residual (Al-WTR) reacted with P solution in the laboratory under flow-through conditions.

Material ID	Wavellite	FePO_4 (3d) [‡]	Strengite	R-factor	χ^2
% of total P					
AMDR1	— [‡]	82	17	0.0007	0.12
Al-WTR2	37	-	60	0.0084	1.02

[‡]Species not identified using linear combination fitting.

[‡]Semi-crystalline P species. The reaction days are specified in the parenthesis

Table 3.

X-ray absorption near-edge structure spectroscopy linear combination fitting results showing the relative proportion of phosphate (PO₄) standards giving the best fit (from -5 to 50 eV relative to the white line peak) to spectra collected on field reacted slag materials.

Material ID	PO ₄ sorbed to Al hydroxide	Amorphous Al-PO ₄	Al-PO ₄ (10d) [‡]	Al-PO ₄ (30d)	Amorphous Fe-PO ₄	Monetite	Hydroxy-apatite	R-factor	χ ²
-----% of total P-----									
Slag1	- [‡]	-	-	-	-	25	73	0.0407	3.42
Slag2	-	40	-	-	14	-	44	0.0048	0.54
Coated slag	21	-	13	27	-	-	37	0.0008	0.13

[‡] Species not identified using linear combination fitting.

[‡] Semi-crystalline P species. The reaction days are specified in the parenthesis.