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Iron Hydroxide from Coal Mine Drainage to Remove and Reuse Phosphorus from Greenhouse and Plant Nursery Runoff

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IRON HYDROXIDE FROM COAL MINE DRAINAGE TO REMOVE AND REUSE
PHOSPHORUS FROM GREENHOUSE AND
PLANT NURSERY RUNOFF

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Toxicology

by
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ABSTRACT

Irrigation runoff from agriculture and specialty crops production remains a source of excess phosphorus (P) loading into aquatic systems. Iron hydroxide from coal mine drainage (CMD) was investigated in this study as an adsorbent for low-cost P removal from greenhouse and plant nursery runoff. The overall objectives of this study were to quantify the P sorption capacity, desorbability of P, and plant availability of P adsorbed to Blue Valley iron hydroxide (BVIO), a granular adsorbent obtained from oxidation of CMD. Batch sorption experiments were conducted to measure the effect of mixing BVIO with silica sand (1:1; BVIO:Sand, by weight) on P sorption capacity. Two solutions, deionized (DI) water and pond water, were evaluated for their effect on P sorption. The sorption capacities of BVIO and BVIO-amended sand (17.76 ± 0.77 and 21.45 ± 0.75 mg P/g BVIO, respectively) were well above those previously reported for BVIO (8-11 mg P/g BVIO). Water source (DI or pond) did not influence substrate P sorption capacity. Desorption of P from BVIO-amended sand was measured using batch experiments and a series of extracting solutions. Phosphorus desorption was measured over 96 hours for pond water (adjusted to either pH 6 or pH 10) and a 0.01 M CaCl_2 solution. Exposure of P-saturated BVIO-amended sand to CaCl_2 aided more P desorption than either pond water solution. The potential for reuse of P-saturated BVIO-amended sand as a fertilizer amendment was investigated through extraction with Mehlich III, a solution developed to measure plant-available nutrients in soils. Phosphorus adsorbed to BVIO is not readily available as assessed via Mehlich III extraction; rather CaCl_2 -labile P may better represent the plant-available fraction of total P. Concentrations of P desorbed

after exposure to CaCl_2 solutions (0.1 - 0.12 mg/L) were within nutrient recommendations for most plants. Low amounts of P may become available over time, similar to a controlled-release fertilizer. Results from this study demonstrated that BVIO-amended sand is a viable, low-cost adsorbent with potential for use to both remove P and permit its reuse in the greenhouse and plant nursery industry.

DEDICATION

This thesis is dedicated to my parents, David and Karen DeLaBarre Chase, whose love and support facilitated my education and the completion of this research. I also dedicate this thesis to the protected lands, wetlands, and wild and scenic rivers that helped shaped me (the Shenandoah, the Chesapeake, and the Chattooga) and to those who aim to protect and restore them.

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CHAPTER 1

INTRODUCTION

Phosphorus (P) is often the most limiting nutrient in freshwater systems among nutrients required for plant growth (Hecky and Kilham, 1988). Eutrophication is a response to increased P availability and is a natural process that occurs on geologic time scales. Anthropogenic (accelerated) eutrophication occurs when excess P is available in surface waters, primary productivity exceeds a sustainable rate, and phytoplankton populations overwhelm surface communities, disturbing bacterial community diversity and composition (Newman, 2009; Berry et al., 2017). Increased bacterial processing of decaying organic matter can lead to greater biological oxygen demand and subsequent decreases in dissolved oxygen available for other organisms. The economic impacts of harmful cyanobacterial blooms include costs associated with illness from algal toxins, fish kills from depleted dissolved oxygen, damage to drinking water sources, declines in recreation and tourism, and the cost of monitoring and management (Lopez et al., 2008; CDC, 2017). As a result, more attention is being directed toward mitigating the risks associated with eutrophication. To limit excessive algal growth, EPA water quality criteria state that phosphate (PO_4^{3-}) should not exceed 0.05 mg/L in streams that discharge into lakes or reservoirs, 0.025 mg/L within a lake or reservoir, and 0.1 mg/L in streams that do not discharge into lakes or reservoir (USEPA, 1986).

Irrigation runoff from agriculture and specialty crops production remains a source of excess P loading into aquatic systems. As water quality monitoring and remediation

efforts increase to limit harmful algal and cyanobacterial blooms, greenhouse and plant nursery operators need to manage P export in their irrigation runoff. Strategies to reduce P export include vegetative buffers, constructed wetlands, and efficient fertilizer application. Success with P reduction in runoff varies, and concentrations often exceed 0.05 mg/L P (White, 2007). Sorption to substrate is an effective mechanism for P removal from municipal and agricultural wastewater (Penn et al., 2011), and P removal efficiencies have been characterized for a variety of sorbents (e.g., calcined clay, crushed brick, iron oxide-coated sand, blast furnace slag) (Arias et al., 2006; Hylander et al., 2006; Penn et al., 2011; White et al., 2011). Iron hydroxide residuals produced by neutralization of coal mine drainage (CMD) are a promising medium for P sorption and are a low-cost alternative to conventional methods of P removal (e.g., chemical precipitation) (Fish and Dietz, 2009; Penn et al., 2011; Sibrell et al., 2015).

Iron Hydroxides from Coal Mine Drainage

Alternative use of residuals from coal mine drainage was first investigated in western Pennsylvania by Robert Hedin, who began production of iron hydroxides for use in the pigment industry (Neely, 2010; Hedin, 2002). Hedin's innovation has developed into an area of ongoing research that includes applications in agricultural runoff, dairy wastewater, secondary wastewater effluent, and aquaculture effluent (Penn et al., 2007; Sibrell et al., 2013; Wang et al., 2013; Fish and Dietz, 2009; Sibrell and Kehler, 2016). Philip Sibrell, a researcher for the United States Geological Survey (USGS), was instrumental in developing filtration systems that incorporate CMD residuals for PO_4^{3-}

recovery. In a study conducted in 2003, Adler and Sibrell reported P sorption capacities of 10 – 20 g P/kg floc using CMD floc, demonstrating the use of residuals from neutralized CMD to sequester phosphorus. After a patent was granted in 2007 for the use of CMD sludges for the removal of P from solution in columns and filtration systems (US Patent No. 7,249,275, 2007), Sibrell et al. (2008) used column and field tests to confirm P removal success measured in laboratory sorption experiments. Iron hydroxides from abandoned mine drainage have also been used in hydrosol amendments within constructed wetlands and incorporated in drainage ditch filter boxes to remove P from agricultural runoff (Evenson and Nairn, 2000; Penn et al., 2007).

The rate and extent of phosphate adsorption to CMD residuals is strongly dependent on a variety of factors, including the age of the iron oxide (i.e., crystallinity), sludge composition (i.e., iron, calcium, and aluminum content) and other physical properties. Sibrell et al. (2009) reported that the P sorption capacities of six CMD Fe oxide sources ranged from 1,820 mg/kg to 23,900 mg/kg. Variability in sorption capacity was likely due to contamination with Ca oxides, silicate soil, and clay from settling basins. Sibrell et al. (2009) also observed a positive correlation between Al substitution in goethite and P sorption, indicating that CMD sludge sources with both high Fe and Al content adsorb more P. In a study conducted to remove P from municipal wastewater effluent, Fish and Dietz (2009) similarly reported variable sorption capacities among different sources of CMD Fe oxides due to differences in age and physical properties. The P sorption capacity of dried Fe oxides (7 mg P/g) was compared to the sorption capacity of amorphous Fe oxides that had never been dried (12 mg P/g). These values

are 13 to 23 times lower than the P sorption capacity of newly precipitated Fe oxides prepared from ferric chloride (160 mg P/g Fe oxide; Fish and Dietz, 2009). These findings demonstrate the importance of characterizing the source of iron oxides used for remediation.

Blue Valley Iron Oxide

Coal mine drainage (CMD) is formed by the oxidation of sulfur in minerals associated with coal deposits, forming sulfuric acid that solubilizes other metals present in the host rock (i.e., Fe, Al, Mn). Iron hydroxides investigated in this study were collected from the Blue Valley discharge, a deep coal mine portal in the Toby Creek watershed in western Pennsylvania. Before development of a treatment facility, the slightly acidic discharge (average pH 6.1) directly flowed into a creek (250 – 500 gpm) and contained 19 mg/L total dissolved iron (Keister et al., 2009). William Sabatose, of the Toby Creek Watershed Association, initiated a novel treatment plant, with funding from the PA Department of Environmental Protection, Commonwealth of PA, and the PA Fish and Boat Commission, to process water discharged from Blue Valley. In the treatment process, water is cleaned to satisfy drinking water standards and is directed to a recirculating fish culture facility. Water pumped into the plant undergoes mechanical aeration and oxidation with potassium permanganate (KMnO_4) (Keister et al., 2009). After oxidation, ferric hydroxide precipitates from solution and is collected in the clarifiers, while overlying water circulates through two large tanks with 3,000 rainbow trout and flows through a wetland prior to discharge back into the creek. Sludge

collected from clarifiers and settling ponds is cleaned, dewatered, and transported to a processing facility at Iron Oxide Recovery, Inc.

Phosphate Adsorption to Iron Oxide in Pond Water

To assess the suitability of Blue Valley iron oxide (BVIO) to remove P from irrigation runoff containment ponds, the P sorption capacity of BVIO was determined through batch sorption experiments. Most laboratory batch P sorption experiments use solutions of KH_2PO_4 and deionized water to measure sorption capacity. While this method reduces inherent variability and increases replicability, the applicability to more complex systems is limited. Phosphate adsorption to iron oxides can be influenced by the solution properties of the source water, such as the pH, ionic strength, presence of competing anions, sorbing substrates (e.g., organic matter), or organic acids (Mao and Yue, 2016). To anticipate the performance of a substrate for removal of P from pond water, it is essential to measure the sorption capacity in natural waters that contain a complex matrix of constituents. More specifically, this study characterized P sorption using the pond water source targeted for P treatment at a greenhouse and plant nursery operation. With the exception of one study conducted by Lalley et al. (2016), there is a lack of batch sorption studies which use pond or other natural waters as a sorption solution. The studies detailed in this thesis measured and compared the P sorption capacities of BVIO in pond water and deionized water to determine potential effects to P adsorption efficiency.

Rapid sand filtration is used by greenhouse and nursery operators to manage suspended solids loading from surface waters prior to the waters' use for irrigation. In a

novel approach to P sorption, this study began preliminary research with BVIO to investigate the effect of mixing CMD iron oxide with sand for use in a P filtration system. Results of this study can then be used to inform design parameters (e.g., sorption capacity, contact time, breakthrough) of a pilot-scale rapid sand filter.

Current removal strategies for P in wastewater focus on the capture and retention of dissolved and particulate-bound P through filtration systems, with little consideration of reuse of the P-saturated product. The adsorbent must be replaced when sorption capacity is achieved and spent substrates are typically disposed of at landfill sites (Hylander and Siman, 2001). Within the greenhouse and nursery industry, there is potential for incorporating P-saturated materials within potting substrates as a fertilizer amendment, provided the adsorbed-P is slowly available to plants. Certain extraction techniques can help to determine plant availability of P and other elements in soils (i.e., Mehlich III, Bray, Olsen, 0.01 M CaCl_2) (Wuenschel et al., 2015), though their applicability to iron oxide sorbents has not been characterized. This study investigated two extraction methods to determine plant availability of P after adsorption to BVIO sorbents.

The final component of this research was to gain understanding of P mobility as a function of pH in pond water. Irrigation containment ponds undergo diurnal fluctuations in water quality characteristics (e.g., pH, dissolved oxygen, temperature, and nutrient concentrations). Adsorption and desorption of P from adsorbents can be influenced by solution pH; therefore, it is essential to be able to anticipate P mobility during diurnal changes (Neely, 2010). We used batch desorption experiments to characterize the

reversibility of P adsorption to BVIO and the extent of P expected to desorb in certain conditions (Kose and Kivanc, 2011; Roy, 2017).

Numerous studies have investigated sorption of phosphorus to iron oxide, finding sorption capacities ranging from 1,000 to 160,000 mg/kg (Sibrell et al., 2009; Fish and Dietz, 2009). Most of these studies focused on the sorption properties of costly reagent-grade iron oxide in experiments using deionized water, which limits the applicability to field-scale operations (i.e., greenhouse and plant nursery operations). This research investigated the use of BVIO as a low-cost iron oxide product by anticipating its use by greenhouse and plant nursery operators. The use of BVIO to capture P from runoff and the reuse of the P-enriched product on site is a strategy that minimizes waste and closes the loop in remediation.

Goal and Objectives

The goal of this study was to characterize the suitability of BVIO for use in a P filtration system treating water from irrigation runoff containment ponds and to evaluate the potential to reuse BVIO as a fertilizer amendment. We accomplished this by focusing on the following three objectives:

1. To measure and quantify the P sorption capacity of BVIO, sand, and BVIO-amended sand from DI water and irrigation pond water at pH 7 (Chapter 2).
2. To measure and quantify the effect of pH on the desorbability of P adsorbed to BVIO-amended sand in pond water (Chapter 3).
3. To assess the plant availability of P adsorbed to BVIO-amended sand, BVIO,

and sand from pond water using a Mehlich III extraction solution and a 0.01M CaCl₂ solution (Chapter 3).

References

Arias, M., Da Silva-Carballal, J., Garcia-Rio, L., Mejuto, J., & Nunez, A. 2006. Retention of phosphorus by iron and aluminum-oxides-coated quartz particles. *Journal of colloid and interface science*, 295(1), 65-70.

Berry, M. A., Davis, T. W., Cory, R. M., Duhaime, M. B., Johengen, T. H., Kling, G. W., and Denef, V. J. 2017. Cyanobacterial harmful algal blooms are a biological disturbance to western Lake Erie bacterial communities. *Environmental microbiology*, 19 (3), 1149-1162.

Centers for Disease Control and Prevention (CDC). 2017. Harmful Algal Bloom (HAB)-Associated Illnesses. Fact Sheet.

Evenson, C. J., and R. W. Nairn. 2000. Enhancing phosphorus sorption capacity with treatment wetland iron oxyhydroxides. Conference Proceedings for the 17th National Meeting of the American Society for Surface Mining and Reclamation, Tampa, FL. June 5-11.

Fish, D. H., & Dietz, J. M. 2009. Use of iron oxides produced from the treatment of coal mine drainage as adsorbents to remove phosphorus from secondary wastewater effluent. Final Report for OSM PA (AMD-04) Grant. Submitted to the Pennsylvania Department of Environmental Protection, Harrisburg, PA. USA.

Hecky, R. E., and Kilham, P. 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: a review of recent evidence on the effects of enrichment. *Limnology and Oceanography*, 33 (4:2), 796-822.

Hylander, L. D., & Simán, G. 2001. Plant availability of phosphorus sorbed to potential wastewater treatment materials. *Biology and fertility of soils*, 34(1), 42-48.

Hylander, L. D., Kietlińska, A., Renman, G., & Simán, G. 2006. Phosphorus retention in filter materials for wastewater treatment and its subsequent suitability for plant production. *Bioresource technology*, 97(7), 914-921.

Keister, T., Sleigh, J., Sabatose, W.J. 2009. The Blue Valley Fish Culture Station: Treatment and Beneficial Use of Abandoned Mine Drainage. Pennsylvania Association of Environmental Professionals. 2009 Annual Conference. State College, PA.

Köse, T.E., Kivanc, B. 2011. Adsorption of phosphate from aqueous solutions using calcined waste eggshell. *Chem. Eng. J.* 178, 34–39.

Lalley, J. Changseok H., Xuan L., Dionysios D. Dionysiou, Mallikarjuna N. Nadagouda. 2016. Phosphate Adsorption Using Modified Iron Oxide-Based Sorbents in Lake Water: Kinetics, Equilibrium, and Column Tests. *Chemical Engineering Journal* 284:1386-96.

Lopez, C. B., Jewett, E. B., Dortch, Q. T. W. B., Walton, B. T., & Hudnell, H. K. 2008. Scientific assessment of freshwater harmful algal blooms. Washington DC: Interagency Working Group on Harmful Algal Blooms, Hypoxia, and Human Health of the Joint Subcommittee on Ocean Science and Technology. Washington DC; 2008.

Mao, Y., & Yue, Q. 2016. Kinetic Modeling of Phosphate Adsorption by Preformed and In situ formed Hydrrous Ferric Oxides at Circumneutral pH. *Scientific reports*, 6, 35292.

Neely, C.A. 2010. Characterization and possible sustainable sorbent use of iron oxides from abandoned mine drainage discharges. Doctoral dissertation, University of Oklahoma.

Newman, M. C. 2015. *Fundamentals of Ecotoxicology: The Science of Pollution*. Fourth edition. CRC Press.

Penn, C. J., Bryant, R. B., Callahan, M. P., & McGrath, J. M. 2011. Use of industrial by-products to sorb and retain phosphorus. *Communications in Soil Science and Plant Analysis*, 42(6), 633-644.

Penn, C.J., Bryant, R. B., and Kleinman, P.A. 2007. Sequestering dissolved phosphorus from ditch drainage water. *Journal of Soil Water Conservation*. 62:269-272.

Roy, E. D. 2017. Phosphorus recovery and recycling with ecological engineering: a review. *Ecological engineering*, 98, 213-227.

Sibrell, P.L., 2007. Method of Removing Phosphorus from Wastewater. U.S. Patent 7,294,275.

Sibrell, P. L., Penn, C. J., & Hedin, R. S. 2015. Reducing soluble phosphorus in dairy effluents through application of mine drainage residuals. *Communications in Soil Science and Plant Analysis*, 46(5), 545-563.

Sibrell, P. L., Tucker, T. W., Kehler, T., & Fletcher, J. W. 2008. Removal of phosphorus from wastewater using ferroxysorb sorption media produced from AMD sludge. In *Hydrometallurgy 2008: Proceedings of the Sixth International Symposium* (p. 86). SME.

Sibrell, P. L., and Tucker, T. W. 2012. Fixed bed sorption of phosphorus from wastewater using iron oxide-based media derived from acid mine drainage. *Water, Air, & Soil Pollution*, 223(8), 5105-5117.

Sibrell, P. L., & Kehler, T. 2016. Phosphorus removal from aquaculture effluents at the Northeast Fishery Center in Lamar, Pennsylvania using iron oxide sorption media. *Aquacultural Engineering*, 72, 45-52.

U.S. Environmental Protection Agency. 1986. Quality Criteria for Water. USEPA Rep. 440/5-86-001. USEPA Office of Water Regulations and Standards. U.S. Gov. Washington, DC.

Wang, Y. R., Tsang, D. C., Olds, W. E., & Weber, P. A. 2013. Utilizing acid mine drainage sludge and coal fly ash for phosphate removal from dairy wastewater. *Environmental technology*, 34(24), 3177-3182.

White, S. 2007. Constructed Wetlands for the Landscape Nursery Industry: Nutrient Assimilation and Removal. TigerPrints. *All Dissertations*. 162. https://tigerprints.clemson.edu/all_dissertations/162

White, S. A., Taylor, M. D., Albano, J. P., Whitwell, T., & Klaine, S. J. 2011. Phosphorus retention in lab and field-scale subsurface-flow wetlands treating plant nursery runoff. *Ecological Engineering*, 37(12), 1968-1976.

Wuenschel, R., Unterfrauner, H., Peticzka, R., & Zehetner, F. 2015. A comparison of 14 soil phosphorus extraction methods applied to 50 agricultural soils from Central Europe. *Plant Soil Environ*, 61(2), 86-96.

CHAPTER 2

IRON HYDROXIDE FROM COAL MINE DRAINAGE TO REMOVE PHOSPHORUS FROM GREENHOUSE AND PLANT NURSERY RUNOFF

Abstract

Iron hydroxide from coal mine drainage (CMD) was investigated as a low-cost adsorbent for phosphorus (P) removal from greenhouse and plant nursery runoff. Batch sorption experiments measured the sorption capacity of Blue Valley iron oxide (BVIO), a CMD residual. Rapid sand filtration is a technology already used by greenhouse and nursery operators; thus, we studied the effect of mixing BVIO with silica sand on the P sorption capacity of BVIO. Adsorption of P onto BVIO and BVIO-amended sand followed the Langmuir isotherm with sorption capacities of 17.8 ± 0.76 mg P/ g BVIO and 21.5 ± 0.75 mg P/g BVIO, respectively. We then rinsed BVIO and silica sand individually with deionized (DI) water to discern effects to adsorbent efficacy when fine particles (<150 μm) were removed. The sorption capacities for BVIO and BVIO-amended sand were 15.4 ± 0.76 mg P/g BVIO and 19.1 ± 0.87 mg P/g BVIO, respectively. In each experiment, substrates were saturated by P within 1-6 hours. Sorption capacities of substrates in DI water were compared to those in water collected from an irrigation runoff containment pond to determine solution effects to substrate performance in the field. No changes in sorption capacity were noted, regardless of water source, indicating that P removal efficacy will not be negatively affected in irrigation pond water. Sorption capacities of BVIO-amended sand and BVIO used in this study

were higher than those measured in other studies that have used BVIO for P removal, which confirms the use of BVIO as a promising adsorbent for P removal in the greenhouse and nursery industry.

Introduction

Runoff from greenhouse and plant nursery operations contributes excess phosphorus (P) loading into aquatic systems. Phosphorus remediation strategies are essential to mitigate risks associated with eutrophication, such as harmful algal blooms, release of algal toxins (e.g, microcystin), depletion of dissolved oxygen, and loss of ecosystem functions (Lopez et al., 2008; Newman, 2009; CDC, 2017). Best management practices such as vegetative buffers, slow sand filters, and constructed wetlands can be implemented within greenhouse and nursery operations to control nutrients, pathogens, and other constituents of concern. Within a constructed wetland, P can be taken up by vegetation and sorbed to suspended solids within the water column. Plant uptake has been shown to be a minor pathway in P removal, highlighting the importance of sorption processes (Taylor et al., 2006). Adsorption to a substrate (e.g., calcined clay, crushed brick, and blast furnace slag) is a well-established mechanism for P removal from municipal and agricultural wastewater (White et al., 2011; Cui et al., 2008; Penn et al., 2011). Residuals produced by neutralization of coal mine drainage (CMD) are a promising medium for P sorption, due to their high iron oxide content. A low-cost alternative to conventional methods of P removal (e.g., chemical precipitation), several studies have demonstrated the effectiveness of CMD iron oxides for P removal from

wastewater (Wei et al., 2008; Fish and Dietz, 2009; Sibrell et al., 2009; Penn et al., 2011; Sibrell et al., 2015). There are few options for use of CMD produced iron oxides in industrial applications, which presents an opportunity for use of these products within the greenhouse and plant nursery industry.

The affinity of phosphate (PO_4^{3-}) to iron oxide is well-characterized for a variety of iron oxide forms, from iron oxide tailings to iron oxide – coated sand and crushed brick (Zeng et al., 2004; Boujelben et al., 2008; Yaghi and Hartikainen, 2013; Wang et al., 2013). Edwards and Benjamin (1989) developed a method to coat filter sand with ferrihydrate in fixed-bed filtration of metals in wastewater. Ayoub et al. (2001) applied this technology to the removal of PO_4^{3-} from wastewater and reported that iron oxide-coated sand was successful in removing low levels of PO_4^{3-} (0.5 mg/L) to less than 0.1 mg/L. Building on these findings, Arias et al. (2006) precipitated iron oxides onto quartz particles and measured a sorption capacity of 4.4 mg P/g. This low sorption capacity could have been attributed to the low iron content after precipitation (4.5%). In a study that investigated the effectiveness of hydrous iron oxide – coated diatomite (HIOMD) on P removal, Wang et al. (2016) reported a sorption capacity of 35.71 mg P/g HIOMD; this was considerably more successful than previous efforts for P removal. Their study reported that coated iron oxide was unstable and easily shed by friction between sand particles. Coating of sand and diatomite with iron oxide produced sorbents with small particle sizes ($\leq 150\mu\text{m}$), large surface areas, low iron content ($< 5\%$) and variable P adsorption capacities. These studies hold promise for developing technologies to reduce and reuse P in wastewaters, though their applicability for field-scale filtration systems is

limited by costly chemical reagents.

The rate and extent of PO_4^{3-} adsorption to CMD residuals is strongly dependent on sludge composition (i.e., Fe, Ca, and Al content), crystallinity, and other physical properties. Sibrell et al. (2009) reported that the sorption capacities of six CMD Fe oxide sources ranged from 1,820 mg/kg to 23,900 mg/kg, demonstrating the importance of characterizing the source and consistency of iron oxides used for remediation. Investigated in our study, Blue Valley iron oxide (BVIO) is primarily composed of goethite ($\alpha\text{-FeOOH}$), the most frequently encountered oxy hydroxide in nature (Sibrell and Tucker, 2012) (Table 2.1). Goethite is a highly adsorptive medium for anions, due to its relatively high surface area (50 -300 m^2/g) and surficial hydroxide functional groups, making this mineral class a great candidate for PO_4^{3-} adsorption (Lalley et al., 2016).

Table 2.1 Physical properties of Blue Valley iron oxide.

Properties	
$\alpha\text{-FeOOH}$	95% (dry)
Si and Al minerals	5% (dry)
Surface area	150– 175 m^2/g
PZC (point of zero charge)	pH 8.5
Moisture	35%
Grain size	0.6 – 4 mm
Loss on Ignition	24.2%

Source: Sibrell and Tucker (2012)

The main adsorption mechanism occurs as an inner-sphere complex, where the phosphate ion reacts with two Fe-OH groups directly, forming a bidentate bridge ((Fe-O)₂ PO₂H) (Lalley et al., 2016), contributing to the stability of adsorbed PO_4^{3-} . The formation reaction for this complex can be written as: $2\equiv\text{FeOH}^{-0.5} + \text{PO}_4^{3-} + 2\text{H}^+ =$

($\equiv\text{FeO}$)₂ PO_4^{2-} + 2H₂O (Weng et al., 2012). Sludges produced by neutralization of coal mine drainage usually contain much lower levels of copper (Cu), lead (Pb), cadmium (Cd), and arsenic (As) than sludges produced from metal mine drainage and are therefore more suitable for use in water filtration studies (Sibrell et al., 2008). To assess the potential risk of metals leaching from this product, the metal content of BVIO was compared to the USEPA Eco-Soil Screening Level toxicity thresholds for plants and to the USEPA Part 503 trace metal ceiling concentrations for land application of sludges (Table 2.2; Hedin, personal communication). With the exception of arsenic (As) and Zinc (Zn), concentrations of metals fall below toxicity thresholds. Due to the high binding affinity of As for Fe hydroxides, leaching of As into overlying water does not present a profound risk.

Table 2.2 Metal content of Blue Valley iron oxide compared to toxicity thresholds

Metal (mg/kg dry weight)	Blue Valley	Eco-SSL^b	EPA^c
Arsenic	36.9 ^a	18	75
Cadmium	0.5	32	85
Cobalt	5.2	13	25 ^d
Chromium	<10	---	3,000
Copper	17	70	4,300
Lead	11	120	840
Mercury	0.018	---	57
Nickel	32	38	420
Selenium	1.7	---	75
Zinc	305 ^a	160	7,500

^aValues highlighted in blue are above the Eco-SSL toxicity threshold

^bEPA Eco-Soil Screening Level Toxicity Threshold for plants

^cEPA Part 503 trace metal ceiling concentrations for land application of sludges

^dEPA Risk Reduction Standards: Type I Soil Criteria; values that pose no significant risk in residential settings

Sources: Sibrell and Tucker (2012); Sibrell and Kehler (2016)

Phosphate adsorption to iron oxides can also be influenced by the presence of competing anions, sorbing substrates (e.g., organic matter), or organic acids (Mao and Yue, 2016). Adsorption of organic functional groups onto iron oxides can promote anion adsorption via cation bridges (Al^{3+} and Fe^{3+}), alter surface charges, or compete with PO_4^{3-} and other anions for adsorption sites (Hinsinger, 2001; Hinsinger et al., 2011; Borggaard et al., 2005; Guppy et al., 2005). Conversely, Weng et al. (2012) demonstrated that dissolved organic carbon had a negative impact on PO_4^{3-} adsorption to iron oxides. An increase in dissolved organic carbon from 0.5 to 50 mg/L decreased the amount of PO_4^{3-} adsorbed by over 50%. Citrate, an organic anion, is also reported to block goethite pores and prevent PO_4^{3-} adsorption (Mikutta et al., 2006). If adsorbed, organic anions can alter the surface charge of goethite and cause PO_4^{3-} to be electrostatically repelled (Antelo et al., 2007). These findings highlight the importance of measuring sorption capacity in natural waters that contain a complex matrix of constituents. With the exception of a study conducted by Lalley et al. (2016) using lake water and a study conducted by Wei et al. (2008) using river water, there is a lack of batch sorption studies which use natural surface waters as the sorption solution. Although use of natural waters introduces inherent variability, the variability can be minimized through experimental design, while simulating conditions that are more realistic than those of studies using deionized (DI) water spiked with a counter-ion.

Recovery of iron oxides from CMD represents the kind of innovation essential for addressing complex ecological issues in the future. Use of CMD-derived sorbents as a P management strategy has not been established in the greenhouse and nursery industry.

To date, one study has been published on the use of P-sorbing materials (calcium-based waste materials, basic oxygen furnace slag, and concrete waste) to remove PO_4^{3-} from greenhouse effluent (Dunets et al., 2015). Phosphorus in greenhouse runoff exists predominantly as orthophosphate-P ($\text{PO}_4\text{-P}$), but P can also be assimilated by bacteria or sorbed to organic matter and other suspended solids. Removal of these fractions can be achieved by incorporating a P sorbent within a sand filter, a technology already used by greenhouse and nursery operators. In a novel approach to P removal from greenhouse and nursery effluent, this study investigated the effect of mixing BVIO with silica sand and its potential for use in a P filtration system. To ensure adoption of BVIO for P removal in the greenhouse and nursery industry, the capacity of the BVIO was characterized in bench-scale batch experiments. Anticipating the use and realistic exposure of this material used in a filtration system, the effect of adding sand, rinsing the material, and use of pond water on the sorption capacity of BVIO were also investigated.

Goal and Objectives

The goal of this study was to quantify the capacity of BVIO-amended sand to sorb P. The specific objectives were (1) to measure and compare the P sorption capacities of BVIO-amended sand, BVIO, and sand, (2) to measure and compare sorption capacities of washed and unwashed substrate, (3) to measure and compare sorption capacities of each substrate in deionized water and pond water, and (4) to quantify the contact time required to reach sorption capacity.

Materials and Methods

Experimental Conditions

All experiments were performed in 50-mL centrifuge tubes. The P sorption capacities of three unwashed and washed substrates (BVIO, sand, and BVIO-amended sand) in DI water spiked with KH_2PO_4 (CAS # 7778-77-0; Fisher Chemical) were quantified and compared. BVIO-amended sand was prepared by adding 0.5 g of BVIO to 0.5 g of silica sand. In experiments using “washed” substrate, sand and BVIO were separately rinsed on a 100 mesh sieve (150 μm) using DI water, and air dried for 72 hours. All size fractions of silica sand and BVIO were used in the unwashed sorption capacity experiments to represent how greenhouse and plant nursery operators might realistically incorporate these materials within a P filtration system. A particle size analysis was performed on BVIO and is presented in Table 2.3.

Table 2.3 The particle size distribution of unwashed BVIO. All size fractions of BVIO were used in sorption capacity experiments*.

U.S. Standard Sieve Size	Size Fraction	Weight (g)	Percentage of Total
No. 10	>2 mm	61.4	30.25
No. 18	1 mm	77.2	38.03
No. 35	0.5 mm	50.0	24.63
No. 60	0.25 mm	11.4	5.62
No. 120	0.125 mm	1.3	0.64
No. 200	0.075 mm	1.1	0.54

BVIO: Blue Valley iron oxide

Total weight of BVIO analyzed: 203.00 g

* In experiments using “washed” substrate, the fine fraction (<150 μm ; <1% of total BVIO) was washed out.

Two solutions, DI water and pond water, were evaluated for their effect on the P sorption capacities of unwashed BVIO, sand, and BVIO-amended sand. Pond water was collected from an irrigation runoff containment pond at a plant nursery in South Carolina at approximately 10 AM on October 11, 2017, and the water quality of this pond is characterized in Table 2.4. The P sorption capacities of unwashed BVIO, sand, and BVIO-amended sand in DI water were compared to the sorption capacities of the same substrates in pond water.

Table 2.4 Physio-chemical parameters of the irrigation runoff containment pond.

Parameter	Value
pH (SU)	6.52 [*]
Dissolved oxygen (mg/L)	8.02 ^{**}
Specific Conductivity (μS/cm)	100 ^{**}
Alkalinity (mg/L as CaCO ₃)	26 [*]
P (mg/L)	0.01 – 0.06 ^{***}
K (mg/L)	1.97 – 2.35 ^{***}
Ca (mg/L)	3.61 – 4.95 ^{***}
Mg (mg/L)	0.84 – 1.28 ^{***}
Fe (mg/L)	0.06 – 0.20 ^{***}
S (mg/L)	0.88 – 1.20 ^{***}
Na (mg/L)	1.37 – 2.48 ^{***}

^{*}Measured in the laboratory after samples were collected at 10 AM on 10/11/17. In situ pH values in the pond, however, range from 6.2 – 8.8.

^{**} Measured in situ when samples were collected.

^{***}Measured using ICP-AES analysis; range represents values from individual 1L samples. All other standard elements were below detection limits.

Contact Time

The time required to reach sorption equilibrium (i.e., contact time) was determined by exposing 1g of unwashed BVIO and BVIO-amended sand to a solution of 6.0 mg/L P for one of ten contact times (0, 0.01, 0.05, 0.1, 0.5, 1, 6, 12, 24, and 48 hours). Unwashed silica sand (1g) was exposed to a solution of 0.5 mg/L P for each

contact time. Solutions of 0.5 mg/L P and 6.0 mg/L P were prepared by adding 5mL and 60 mL of a 100 mg/L P stock solution to 1L of DI water. The stock solution was prepared with DI water and 439.4 mg KH_2PO_4 . Solution pH was adjusted to 7.0 ± 0.1 in bulk solutions using 1M KOH. Forty-five mL of solution was poured over 1g of substrate in a 50mL tube. Three replicates of each treatment type ($n=90$) were prepared. Each tube was placed horizontally on a shaker table set at 150 rpm for its corresponding contact time. For the 0 h treatment, a contact time of under 10 seconds was considered sufficient. Ten mL of each sample was filtered through a $0.45\mu\text{m}$ filter into 15 mL centrifuge tubes; 3 drops of concentrated HNO_3 (trace metal grade) were then added to each sample. Samples were analyzed for total dissolved P using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (P detection limit = 0.0022 mg/L P). The instrument (Spectro Arcos ICP-OES; Spectro Analytical Instruments) was equipped with a UV-Plus Purifier gas cleaning system with argon gas flow and a Cetac autosampler and was calibrated using commercially available ICP standard solutions (Inorganic Ventures) each time the method was used. A check standard was analyzed along with samples, every 55 samples, to ensure calibration, and the instrument was maintained biannually by Ametek service technicians. In each experiment, samples were organized in the autosampler from lowest expected concentrations of P to highest to minimize carryover.

Sorption Capacity

To quantify sorption capacity, nine concentrations of P were evaluated. DI water and pond water were spiked with KH_2PO_4 to achieve a nominal concentration of 0.0, 0.5, 1.0, 10.0, 50.0, 100.0, 200.0, 500.0, or 1000.0 mg P/L as KH_2PO_4 . The pH of each

solution was adjusted to 7.0 ± 0.1 with 1M KOH to minimize variation from the consecutively greater amounts of KH_2PO_4 added to attain experimental P range.

After each tube was filled with 1g of substrate (unwashed or washed BVIO, sand, and BVIO-amended sand), 45 mL of the KH_2PO_4 -spiked solutions (DI water and pond water) was poured into each tube, and the initial overlying pH was recorded. Three replicates of each treatment type were prepared ($n=81$) and placed horizontally on a Thermo Scientific MaxQ Orbital shaker set at 150 rpm for 24 hours at 25°C . After 24 hours, 10mL of each sample was filtered through a $0.45\text{-}\mu\text{m}$ nylon filter (Thermo Scientific) into 15mL centrifuge tubes. Three drops of concentrated HNO_3 (trace metal grade, CAS# 7697-37-2; Fisher Chemical) were added to each sample, and 10 mL of filtrate from each sample was analyzed for total P, K, Ca, Mg, Zn, Cu, Mn, Fe, S, Na, B, and Al using ICP-OES (Spectro Arcos ICP-OES; Spectro Analytical Instruments).

Sorption capacities were determined by plotting the mass of P adsorbed per gram of substrate (C_s) from each replicate ($n=3$) against the concentration of P remaining in solution (C_w). Equation 1 was used to derive C_s values:

$$C_s = \frac{C_0 - C_w}{m_s} \quad \text{Equation 1}$$

where C_0 is the initial concentration of P introduced to each substrate and m_s is the mass of substrate (1g). All raw data from each treatment (i.e., unwashed and washed substrates in DI water and unwashed substrates in pond water) were plotted ($n=25$). Isotherm data were then fit to a non-linear Langmuir model using an Excel spreadsheet designed by Bolster (2010), and non-linear least squares regression used to predict the sorption capacity (C_{smax} ; mg P/g) and the equilibrium constant of the sorption reaction (K_L ; L/mg).

The accuracy of the spreadsheet was thoroughly tested by Bolster and Hornberger (2007) by comparing model fits and parameter estimates with the software package SAS 9.2.

To determine if the non-linear Langmuir model was an appropriate fit for the sorption data, C_s values from the raw datasets were plotted against the predicted model values for C_s for each treatment (Appendix A, Figure A1). The resulting regressions were found to have slopes near 1 and intercepts near 0, indicating the model provided a good fit of the data. Additionally, narrow 95% confidence intervals indicated good precision of the parameter estimates. The model was verified by plotting two data series in one figure; the first plotted raw data vs equilibrium concentration and the second plotted the predicted values from the model vs initial concentrations of P (i.e., 0.0, 0.5, 1.0, 10.0, 50.0, 100.0, 200.0, 500.0, or 1000.0 mg P/L) (Figures 2.1 and 2.2).

The parameters predicted using the non-linear Langmuir method were compared to those calculated using a linearization of the Langmuir isotherm (Bolster and Hornberger, 2007). For the purposes of this thesis, the linearization methods and comparisons are presented in Appendix B.

Unwashed vs washed substrate

In preliminary sorption tests, solutions appeared cloudy in 50-mL tubes that contained BVIO, indicating very fine iron oxide particles were suspended after mixing on the shaker table. The effect of washing substrates on P sorption capacity was investigated by comparing the P sorption capacity of unwashed sand, BVIO, and BVIO-amended sand in pond water to the P sorption capacity of sand, BVIO, and BVIO-amended sand that had been rinsed with DI and air-dried at 25°C for 72 hours.

Monitoring pH

To ensure consistency of pH throughout the treatments, the effect of BVIO-amended sand on the pH of a solution of KH_2PO_4 was tested. Forty-five mL of a 100 mg P/L stock solution was adjusted to pH 7. The solution was added to 1g of unwashed substrate in a 50mL centrifuge tube. The pH was recorded after 10 minutes and at the conclusion of the experiment (24 h). Initial and final (post 24 h) pH values were recorded for each unwashed treatment in sorption capacity experiments.

Statistical Analysis

Sorption isotherm data were fitted to a non-linear Langmuir model (Bolster, 2010) and statistical analyses were performed using the software package JMP Pro 13.2 (SAS Institute Inc., Cary, NC). Non-linear least squares regression of the sorption isotherm data was used to estimate the sorption capacity (C_{smax}) and the equilibrium constant of the sorption reaction (K_L). The parameters, C_{smax} and K_L , were predicted from the data set ($n=25$) of each treatment (unwashed substrates (BVIO, sand, and BVIO-amended sand) in DI water, washed substrates in DI water, and unwashed substrates in pond water). Treatments were considered statistically different from one other if the confidence intervals for the predicted parameters did not overlap (Ott and Longnecker, 2010). To compare C_{smax} and K_L values among substrates (BVIO, sand, and BVIO-amended sand), sorption isotherm data were normalized to the mass of BVIO added to each 50-mL centrifuge tube.

Results and Discussion

Phosphorus Sorption Capacity of Unwashed vs Washed substrate

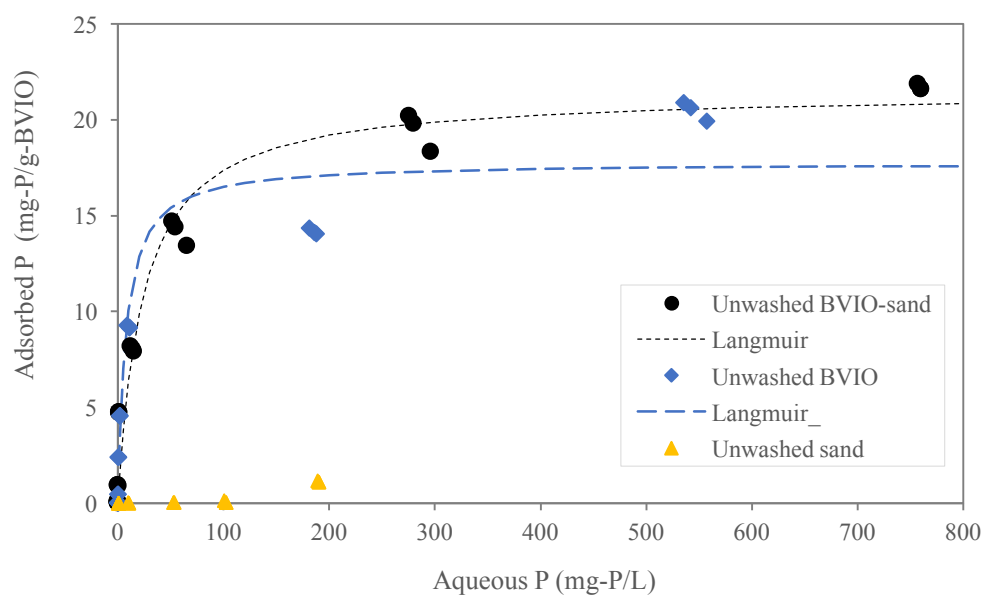
Fine particles (<0.25 mm) often have high sorption capacities for various sorbates, due to the high surface area to volume ratio. As BVIO-amended sand was investigated for use in a P filtration system, it was necessary to determine if sorption capacity would be affected when fine particles washed out of a filter. Results of sorption tests of washed and unwashed substrates are summarized in Table 2.5. Phosphorus sorption to unwashed BVIO and BVIO-amended sand in DI water saturated around 20 mg P/g BVIO and 21 mg P/g BVIO, respectively (Figure 2.1A). Phosphorus sorption to washed BVIO and BVIO-amended sand in DI water saturated around 15 and 20 mg P/g substrate, respectively (Figure 2.1 B).

Table 2.5. Langmuir parameters calculated using the non-linear Langmuir model for BVIO and BVIO-amended sand in deionized water

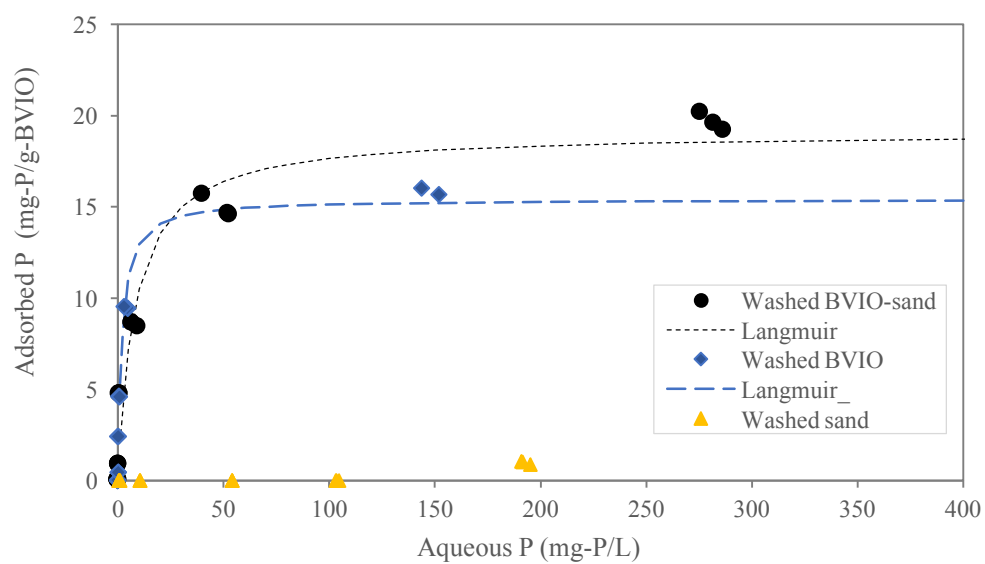
Treatment	Parameter	Estimate	Approximate Standard Error	Lower CL	Upper CL
Unwashed BVIO-sand in DI water	C _{smax}	21.450	0.747	19.867	23.122
	K _L	0.043	0.007	0.029	0.064
Washed BVIO-sand in DI water	C _{smax}	19.086	0.867	17.175	21.146
	K _L	0.122	0.027	0.072	0.2198
Unwashed BVIO in DI water	C _{smax}	17.762	0.775	16.113	19.454
	K _L	0.131	0.029	0.076	0.227
Washed BVIO in DI water	C _{smax}	15.409	0.763	13.723	17.142
	K _L	0.531	0.099	0.346	0.858

BVIO: Blue Valley iron oxide; C_{smax}: sorption capacity (mg P/g BVIO); K_L: Langmuir constant (L/mg)

A.



B.



C.

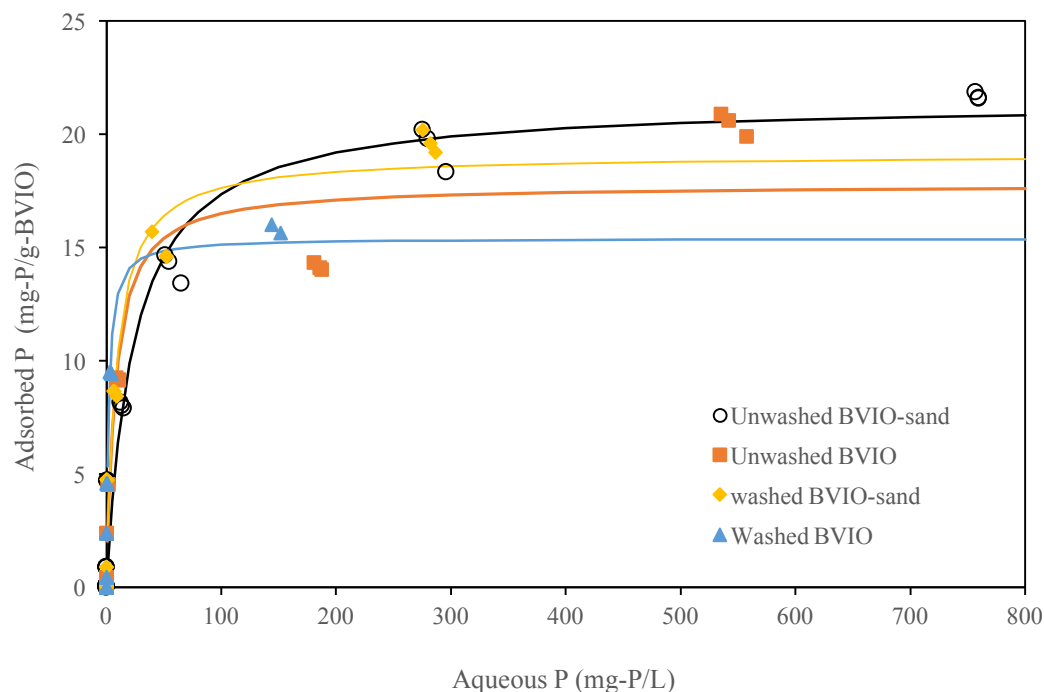


Figure 2.1. Phosphorus sorption isotherms of unwashed (A) and washed (B) Blue Valley iron oxide (BVIO) and BVIO-amended sand in DI water. Data from each of the three replicates are presented along with the fitted Langmuir models. Sorption isotherms of unwashed substrates are compared to those of washed substrates in Figure 2.2 C. The detection limit of P was 0.0022 mg/L.

Comparison of the confidence intervals for C_{smax} revealed that between the unwashed treatments in the DI sorption solutions, BVIO-amended sand had a higher sorption capacity than BVIO (Table 2.5). Mixing BVIO with sand enhanced P sorption. The potential to mix BVIO with sand and use that substrate in a rapid filter is intriguing, as a grower could use existing infrastructure to introduce a new treatment technology.

The sorption maximum for unwashed BVIO-amended sand was higher than that of washed BVIO-amended sand (Figure 2.1), but the relative P capacity of washed and

unwashed BVIO and BVIO-amended sand were similar (Figure 2.1). This finding has implications for substrate performance in a flow-through filter, potentially indicating that filter performance will not decline as water moves through the system and washes out fine particles (<0.15 mm).

Phosphorus sorption capacities of BVIO substrate in DI water vs pond water

The P sorption isotherms of BVIO and BVIO-amended sand in DI water were compared to those in pond water to determine if solution type impacted substrate performance in the field. Phosphorus sorption trends to BVIO and BVIO amended-sand in pond water were similar to those in DI water (Figure 2.2). Phosphorus sorption to unwashed BVIO and BVIO-amended sand in pond water saturated around 18 mg P/g substrate and 20 mg P/g substrate, respectively (Figure 2.2). The fitted Langmuir models slightly underestimated adsorbed P at higher aqueous concentrations, which could have been a function of model inadequacy or of the small sample sizes ($n=25$) used in the model estimations.

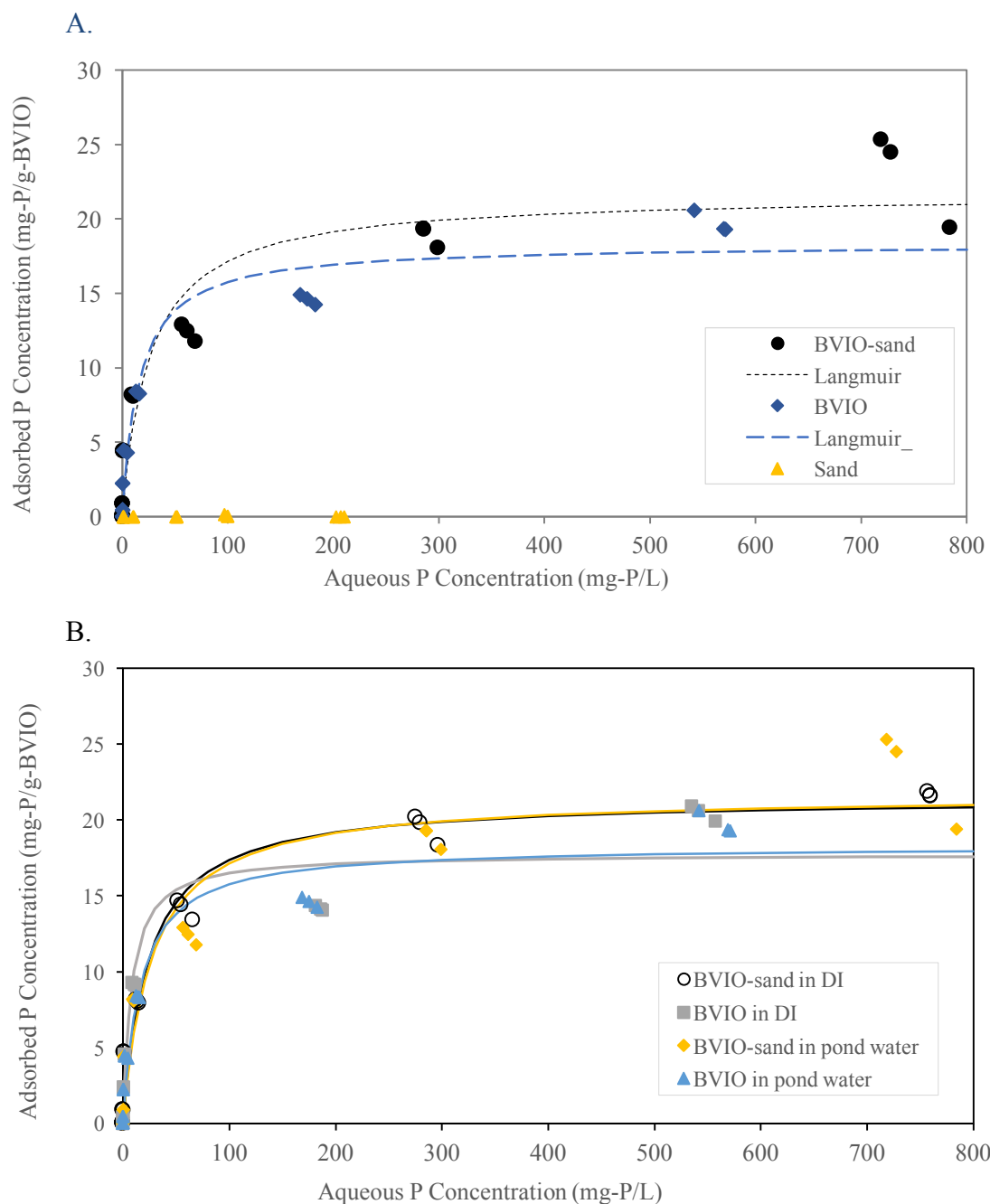


Figure 2.2 A -B. Phosphorus sorption isotherms of unwashed Blue Valley iron oxide (BVIO) and BVIO-amended sand in pond water. Sorption isotherms of substrates in pond water are compared to those in DI water in Figure 2.2 B. Data from each of the three replicates are presented along with the fitted Langmuir models. The detection limit of P was 0.0022 mg/L.

Table 2.6. Sorption parameters calculated using the non-linear Langmuir model for Blue Valley iron oxide (BVIO) and BVIO-amended sand in pond water and DI water

Treatment	Parameter	Estimate	Approximate Standard Error	Lower CL	Upper CL
Unwashed BVIO-sand in DI water	C_{smax}	21.450	0.747	19.867	23.122
	K_L	0.043	0.007	0.029	0.064
Unwashed BVIO-sand in pond water	C_{smax}	21.657	1.164	19.019	24.845
	K_L	0.038	0.010	0.018	0.085
Unwashed BVIO in DI water	C_{smax}	17.762	0.775	16.113	19.454
	K_L	0.131	0.029	0.076	0.227
Unwashed BVIO in pond water	C_{smax}	18.302	0.799	16.613	20.098
	K_L	0.062	0.013	0.037	0.105

BVIO: Blue Valley iron oxide; C_{smax} : sorption capacity (mg P/g BVIO); K_L : Langmuir constant (L/mg)

When working with non-ideal conditions and complex matrices, such as pond water, lower P sorption capacities are not unexpected. However, no changes in sorption capacity were detected in our experiments using pond water for either BVIO or BVIO-amended sand (Table 2.6). These results differ from those reported by Weng et al. (2012), who demonstrated lower PO_4^{3-} adsorption with increasing dissolved organic carbon (DOC), a constituent of natural waters, and other studies that argue for the influence of competitive anions, such as sulfate or nitrate, on PO_4^{3-} adsorption. Lalley et al. (2016) compared the effectiveness of modified iron oxide- based sorbents for PO_4^{3-} removal in lake water and similarly reported decreased PO_4^{3-} adsorption due to the presence of dissolved organic matter. While we did not observe changes in sorption capacity from the use of pond water, this could have been an artifact of low concentrations of DOC and other anions. To make proper comparisons between the results of our study to those from Lalley et al. (2016) and Weng et al. (2012), it would be necessary to measure DOC

concentrations and competitive anion concentrations in the sorption solutions prior to use in experiments.

Our findings support the consistency of P sorption to BVIO across treatments and suggest that sorption capacities of BVIO substrates will not be negatively affected in pond water collected from the irrigation runoff containment pond. Further testing is needed to confirm the consistency of this result among different samples collected from the same source over time and among different pond water sources. Sorption capacities of BVIO-amended sand and BVIO used in this study were higher than those measured in other studies that have used BVIO for P removal (Table 2.7). Results from this study suggest that mixing BVIO with inert substrates (e.g., sand) can enhance P sorption and filter substrate performance. These findings are in agreement with Menon et al. (1989), who reported a positive correlation of P extracted from soils with HCl and sand content, suggesting that a substantial amount of P had adsorbed to the sandy soil.

Table 2.7 Phosphorus sorption capacities calculated in this study compared to those reported in other studies that have used BVIO for phosphorus removal

Sorbent	Description	C_{smax} (mg P/g BVIO)	Source
BVIO	1g of BVIO-amended sand in pond water	21.7 ±1.16	Current study
BVIO	1g of BVIO in pond water	18.3 ±0.80	Current study
BVIO	Ground BVIO in filtered secondary effluent	8.20	Fish and Dietz (2009)
BVIO	0.1g of <0.15mm BVIO in KH ₂ PO ₄	8.70	Sibrell et al. (2008)
BVIO	0.1g of <0.15mm BVIO in KH ₂ PO ₄	11.0	Sibrell and Tucker (2012)

Contact Time

Phosphorus remaining in solution after each time interval (i.e., 0-48 hours) was used to calculate the mass of P that had adsorbed to the substrate, which was then plotted against contact time (Figure 2.3). The time required to reach sorption capacity (i.e., contact time) was estimated from the time correlating to the point where the asymptotic curve reached the sorption capacity value determined in the previous experiment. For each substrate, sorption capacity was reached within the first few hours.

BVIO-amended sand removed 99% of initial P (0.27 mg) within 1 hour (Figure 2.3A). BVIO removed 93.7% of initial P (i.e., 0.27 mg) within 1 hour of exposure, and 98.8% of initial P within 6 hours, indicating perhaps a slightly longer contact time (e.g., 2-3 hours) would be needed to achieve sorption capacity (Figure 2.3B). Pond water did not influence the BVIO P-sorption capacity of BVIO substrates; thus it is not expected to influence the contact time. However, this may be dependent on the amount of dissolved organic matter in the source water, as shown by Weng et al. (2012) and Lalley et al. (2016).

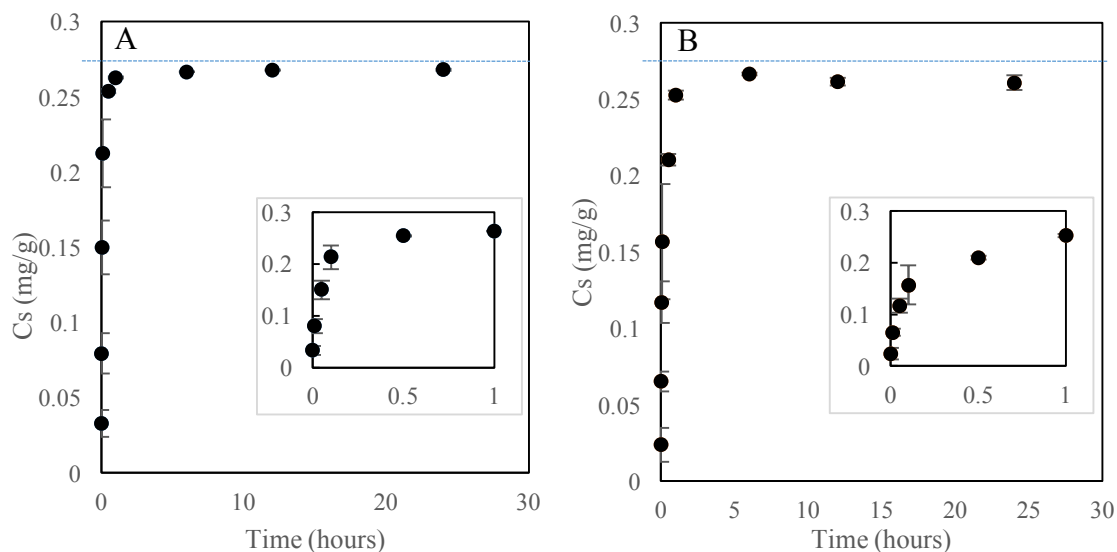


Figure 2.3 Phosphorus adsorbed to BVIO-amended sand (A) and BVIO (B) over time in solutions of KH_2PO_4 and DI. Each data point represents the average of three samples. The dashed line represents the initial concentration of $\text{P} = 6 \text{ mg/L} = 0.27 \text{ mg}$.

Monitoring pH

Exposure of unwashed substrate (i.e., BVIO, sand and BVIO-amended sand) to unbuffered solutions of DI and KH_2PO_4 water resulted in changes to overlying solution pH that were dependent on the substrate and initial concentration of P (Table 2.8). Exposure to sand resulted in a 0.76 to 0.79 decrease in pH in the 0.5 and 1.0 mg/L P solutions, respectively, while there was less of an effect at higher concentrations of P. Changes to solution pH followed similar trends for BVIO and BVIO-amended sand. Generally, pH increased with increasing initial exposure concentration. This experiment was conducted to ensure the consistency of pH throughout the sorption experiments. While the solution pH increased after 24 hours from exposure to BVIO, the pH never rose above 8.5, the reported point of zero charge (PZC) of this iron oxide, which signifies

that PO_4^{3-} will continue to be electrostatically attracted to the iron oxide surface, although less strongly as the pH increases (Table 2.1; Sibrell and Tucker, 2012).

Table 2.8. Changes in solution pH after sorption capacity experiments of 1g of unwashed Blue Valley iron oxide (BVIO), sand, and BVIO-amended sand.

Substrate	Initial P (mg/L)	Initial pH	Final pH after 24 h Mean \pm (Standard Error) ($n=3$)
Sand	0.5	7.00	6.24 (0.01)
Sand	1	7.10	6.31 (0.01)
Sand	10	7.09	7.00 (0.04)
Sand	50	7.08	6.99 (0.02)
Sand	100	7.01	6.99 (0.01)
Sand	200	7.02	7.04 (0.00)
BVIO-sand	0.5	7.00	7.96 (0.01)
BVIO-sand	1	7.10	7.88 (0.03)
BVIO-sand	10	7.09	7.94 (0.03)
BVIO-sand	50	7.08	8.07 (0.01)
BVIO-sand	100	7.01	8.35 (0.01)
BVIO-sand	200	7.02	8.40 (0.04)
BVIO	0.5	7.00	7.89 (0.03)
BVIO	1	7.10	8.02 (0.03)
BVIO	10	7.09	8.01 (0.01)
BVIO	50	7.08	8.17 (0.01)
BVIO	100	7.01	8.35 (0.01)
BVIO	200	7.02	8.70 (0.02)

Implications of mixing sand with BVIO

Compared to other studies using BVIO as a P sorbent, findings from this study suggest that mixing BVIO with inert sand can enhance P sorption through a number of possible mechanisms. In visual observations of sorption tests, the BVIO-amended sand substrate was evenly distributed after 24 hours of mixing on a shaker table. Mixing inert sand with BVIO might encourage particle movement by breaking up iron oxide clumps. The purpose of the sand could be two-fold: (1) to create more interconnected pore spaces, increasing the hydraulic conductivity and the surfaces exposed to aqueous P, and (2) to serve as a substrate to which dissolved Fe can bind to. In all samples analyzed, Fe concentrations were under the detection limit (0.01 mg/L) suggesting that any dissolved Fe may bind to sand once it goes into solution after shaking. Further investigation is needed to confirm this observation.

Filter clogging is a concern in many studies investigating the use of iron oxide sorbents for P removal. Dunets et al. (2015) reported clogging in columns filled with basic oxygen furnace slag when larger particles and aggregates collapsed into fines that blocked pore space. They suggested clogging could be minimized by using coarse particle size fractions or mixing a P-sorbing material with an inert material. Findings from our study could provide benefits to greenhouse and plant nursery operators using sand filters and researchers using column filtration that experience filter clogging when large particles collapse into fines that block pore space. Mixing BVIO with sand may reduce filter clogging as sand is likely less friable and may facilitate more interconnected pore space.

Conclusions

This study measured the efficacy of BVIO and BVIO-amended sand to adsorb P. The P sorption capacities of unwashed sand, BVIO, and BVIO-amended sand in solutions of KH_2PO_4 and DI water were 0 mg P/g sand, 17.76 ± 0.76 mg P/ g BVIO, and 21.45 ± 0.75 mg P/g BVIO, respectively. Whether washed or unwashed, the BVIO and BVIO-amended sand were similarly able to sorb P from solution, which has implications for substrate performance in a flow-through filter, and indicates filter performance will not decline as water moves through the system and carries fine particles with it. When BVIO was exposed to more environmentally realistic P exposure scenarios (pond water vs. DI water), no differences were observed in how P sorbed to BVIO. The sorption capacity of BVIO and BVIO-amended sand remained unaffected when pond water was used.

In a novel approach to P sorption, this study demonstrated that mixing iron hydroxides with inert sand can improve the P sorption capacity and decrease time required to bind P to substrates. As sand filters are used by many operations for control of suspended solids, there is potential that these filters may be adopted for P removal. Our findings support the consistency of BVIO across different treatments, which improves the applicability of this product for use by greenhouse and nursery operators in P filtration systems that can treat pond water.

References

- Adler, P. R., and P. L. Sibrell. 2003. Sequestration of Phosphorus by Acid Mine Drainage Floc. *J. Environ. Qual.* 32:1122-1129. doi:10.2134/jeq2003.1122
- Antelo, J., Arce, F., Avena, M., Fiol, S., López, R., & Macías, F. 2007. Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma*, 138(1-2), 12-19.
- Arias, M., Da Silva-Carballal, J., Garcia-Rio, L., Mejuto, J., & Nunez, A. 2006. Retention of phosphorus by iron and aluminum-oxides-coated quartz particles. *Journal of colloid and interface science*, 295(1), 65-70.
- ASTM D6913-04. 2009. Standard Test Methods for Particle-Size Distribution (Gradation) of Soils Using Sieve Analysis, ASTM International, West Conshohocken, PA, 2009, www.astm.org
- Ayoub, G. M., Koopman, B., & Pandya, N. 2001. Iron and aluminum hydroxy (oxide) coated filter media for low-concentration phosphorus removal. *Water Environment Research*, 73(4), 478-485.
- Bolster, C.H. 2007. A convenient spreadsheet method for fitting the nonlinear langmuir equation to sorption data. Internet Web Page.
- Bolster, C. H., & Hornberger, G. M. 2007. On the use of linearized Langmuir equations. *Soil Science Society of America Journal*, 71(6), 1796-1806.
- Borggaard, O.K., B. R.-L., A.L. Gimsing, B.W. Strobel. 2005. Influence of humic substances on phosphate adsorption by aluminium and iron oxides. *Geoderma*, 127(3-4), 270-279. doi: 10.1016/j.geoderma.2004.12.011
- Boujelben, N., Bouzid, J., Elouear, Z., Feki, M., Jamoussi, F., & Montiel, A. 2008. Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents. *Journal of Hazardous Materials*, 151(1), 103-110.
- Centers for Disease Control and Prevention (CDC). 2017. Harmful Algal Bloom (HAB)-Associated Illnesses. Fact Sheet.
- Cui, L., Zhu, X., Ma, M., Ouyang, Y., Dong, M., Zhu, W., & Luo, S. 2008. Phosphorus sorption capacities and physicochemical properties of nine substrate materials for constructed wetland. *Archives of environmental contamination and toxicology*, 55(2), 210-217.

Del Bubba, M., Arias, C. A., & Brix, H. 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Water Research*, 37(14), 3390-3400.

Dunets, C. S., Zheng, Y., & Dixon, M. 2015. Use of phosphorus-sorbing materials to remove phosphate from greenhouse wastewater. *Environmental technology*, 36(14), 1759-1770.

Edwards, M., & Benjamin, M. M. 1989. Adsorptive filtration using coated sand: a new approach for treatment of metal-bearing wastes. *Research Journal of the water pollution control federation*, 1523-1533.

Erickson, A. J., Gulliver, J. S., & Weiss, P. T. 2007. Enhanced sand filtration for storm water phosphorus removal. *Journal of Environmental Engineering*, 133(5), 485-497.

Evenson, C. J., and R. W. Nairn. 2000. Enhancing phosphorus sorption capacity with treatment wetland iron oxyhydroxides. *Conference Proceedings for the 17 Th National Meeting of the American Society for Surface Mining and Reclamation*, Tampa, FL. June 5-11.

Fish, D. H., & Dietz, J. M. 2009. Use of iron oxides produced from the treatment of coal mine drainage as adsorbents to remove phosphorus from secondary wastewater effluent. Final Report for OSM PA (AMD-04) Grant. Submitted to the Pennsylvania Department of Environmental Protection, Harrisburg, PA. USA.

Georgia Department of Natural Resources: Environmental Protection Division (GADNR). 2018. Risk Reduction Standards for Type 1 Soil Criteria: Appendix III (391-3-19). <http://rules.sos.state.ga.us/cgi-bin>.

Guppy, C. N., Menzies, N. W., Moody, P. W., & Blamey, F. P. C. 2005. Competitive sorption reactions between phosphorus and organic matter in soil: a review. *Soil Research*, 43(2), 189-202.

Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant and soil*, 237(2), pp.173-195.

Hinsinger, P., Brauman, A., Devau, N., Gérard, F., Jourdan, C., Laclau, J. P., ... & Plassard, C. (2011). Acquisition of phosphorus and other poorly mobile nutrients by roots. Where do plant nutrition models fail?. *Plant and Soil*, 348(1-2), 29.

Houba, V.J., E.J.M. Temminghoff, G.A. Gaikhorst & W. van Vark. 2000. Soil analysis procedures using 0.01 M calcium chloride as extraction reagent, *Communications in Soil Science and Plant Analysis*, 31:9-10, 1299-1396, DOI: 10.1080/00103620009370514

Hyde, J.E. and Morris, T.F., 2004. Phosphorus availability from phosphorus-amended water treatment residual. *Communications in soil science and plant analysis*, 35(7-8), pp.1033-1046.

Keister, T., Sleight, J., Sabatose, W.J. 2009. The Blue Valley Fish Culture Station: Treatment and Beneficial Use of Abandoned Mine Drainage. Pennsylvania Association of Environmental Professionals. 2009 Annual Conference. State College, PA.

Lalley, J. Changseok H., Xuan L., Dionysios D. Dionysiou, Mallikarjuna N. Nadagouda. 2016. Phosphate Adsorption Using Modified Iron Oxide-Based Sorbents in Lake Water: Kinetics, Equilibrium, and Column Tests. *Chemical Engineering Journal* 284:1386-96.

Lopez, C. B., Jewett, E. B., Dortch, Q. T. W. B., Walton, B. T., & Hudnell, H. K. 2008. Scientific assessment of freshwater harmful algal blooms. Washington DC: Interagency Working Group on Harmful Algal Blooms, Hypoxia, and Human Health of the Joint Subcommittee on Ocean Science and Technology. Washington, D.C.

Mao, Y., & Yue, Q. 2016. Kinetic Modeling of Phosphate Adsorption by Preformed and In situ formed Hydrous Ferric Oxides at Circumneutral pH. *Scientific reports*, 6, 35292.

Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* 15:1409-1416.

Menon, R. G., Chien, S. H., & Hammond, L. L. 1989. Comparison of Bray I and Pi tests for evaluating plant-available phosphorus from soils treated with different partially acidulated phosphate rocks. *Plant and soil*, 114(2), 211-216.

Mikutta, R., Kleber, M., Torn, M. S., & Jahn, R. 2006. Stabilization of soil organic matter: association with minerals or chemical recalcitrance? *Biogeochemistry*, 77(1), 25-56.

Neely, C. A. 2010. Characterization and possible sustainable sorbent use of iron oxides from abandoned mine drainage discharges. Doctoral dissertation, University of Oklahoma.

Newman, M. C. 2009. Fundamentals of ecotoxicology. CRC press.

Ott, R. L., & Longnecker, M. T. 2015. An introduction to statistical methods and data analysis. Nelson Education.

Penn, C., Bowen, J., McGrath, J., Nairn, R., Fox, G., Brown, G., and Gill, C. 2016. Evaluation of a universal flow-through model for predicting and designing phosphorus removal structures. *Chemosphere*, 151, 345-355.

- Penn, C.J., R.B. Bryant, and P.A. Kleinman. 2007. Sequestering dissolved phosphorus from ditch drainage water. *Journal of Soil Water Conservation*. 62:269-272.
- Penn, C. J., Bryant, R. B., Callahan, M. P., & McGrath, J. M. 2011. Use of industrial by-products to sorb and retain phosphorus. *Communications in Soil Science and Plant Analysis*, 42(6), 633-644.
- Sibrell, P. L., Montgomery, G. A., Ritenour, K. L., & Tucker, T. W. 2009. Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge. *Water research*, 43(8), 2240-2250.
- Sibrell, P. L., & Kehler, T. 2016. Phosphorus removal from aquaculture effluents at the Northeast Fishery Center in Lamar, Pennsylvania using iron oxide sorption media. *Aquacultural Engineering*, 72, 45-52.
- Sibrell, P. L., Tucker, T. W., Kehler, T., & Fletcher, J. W. 2008. Removal of phosphorus from wastewater using ferroxysorb sorption media produced from AMD sludge. In *Hydrometallurgy 2008: Proceedings of the Sixth International Symposium* (p. 86). SME.
- Sibrell, P. L., and Tucker, T. W. 2012. Fixed bed sorption of phosphorus from wastewater using iron oxide-based media derived from acid mine drainage. *Water, Air, & Soil Pollution*, 223(8), 5105-5117.
- Sibrell, P. L., Penn, C. J., & Hedin, R. S. 2015. Reducing soluble phosphorus in dairy effluents through application of mine drainage residuals. *Communications in Soil Science and Plant Analysis*, 46(5), 545-563.
- Taylor, M.D., White, S.A., Chandler, S.L., Klaine, S.J., Whitwell, T., 2006. Nutrient management of nursery runoff water using constructed wetland systems. *Hort-Technology* 16 (4), 610–614.
- U.S. EPA 1993. 40CFR Part 503 - Standards for use and disposal of sewage sludge: Final rules. *Federal Register* 58:9248-9415.
http://www.gadnr.org/epd/Files_PDF/techguide/wpb/smplasguidelinerev_June2006.pdf
- Wang, Y. R., Tsang, D. C., Olds, W. E., & Weber, P. A. 2013. Utilizing acid mine drainage sludge and coal fly ash for phosphate removal from dairy wastewater. *Environmental technology*, 34(24), 3177-3182.
- Wang, Z., Lin, Y., Wu, D. and Kong, H. 2016. Hydrous iron oxide modified diatomite as an active filtration medium for phosphate capture. *Chemosphere*, 144, pp.1290-1298.

Wei, X., Viadero, R.C., Bhojappa, S. 2008. Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants. *Water Res.* 42, 3275–3284.

Weng, L., Van Riemsdijk, W. H., & Hiemstra, T. 2012. Factors controlling phosphate interaction with iron oxides. *Journal of environmental quality*, 41(3), 628-635.

White, S. A., Taylor, M. D., Albano, J. P., Whitwell, T., & Klaine, S. J. 2011. Phosphorus retention in lab and field-scale subsurface-flow wetlands treating plant nursery runoff. *Ecological Engineering*, 37(12), 1968-1976.

Wuenschel, R., Unterfrauner, H., Peticzka, R., & Zehetner, F. 2015. A comparison of 14 soil phosphorus extraction methods applied to 50 agricultural soils from Central Europe. *Plant Soil Environ*, 61(2), 86-96.

Yaghi, N., and Hartikainen, H. 2013. Enhancement of phosphorus sorption onto light expanded clay aggregates by means of aluminum and iron oxide coatings. *Chemosphere*, 93(9), 1879-1886.

Zeng, L., Li, X. & Liu, J. 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Res.* 38, 1318–1326.

CHAPTER 3

DESORPTION AND PLANT AVAILABILITY OF PHOSPHORUS ADSORBED TO IRON HYDROXIDE FROM COAL MINE DRAINAGE

Abstract

Phosphorus (P) presence in irrigation runoff from greenhouse and nursery plant production operations contributes to eutrophication of surface water, if the runoff is not captured and treated. Blue Valley iron oxide (BVIO) is a waste product that can be used to sorb P from irrigation runoff. Greenhouse and nursery growers use rapid sand filtration to treat water, thus there is potential to mix sand and BVIO in a filter to remediate P, but what does one do with the saturated waste product? We quantified both the effect of mixing BVIO with silica sand on the desorbability of P and the mass of P desorbed from the mixed substrate. Bench-scale batch desorption experiments measured the extent of P desorbed from BVIO-amended sand (initial adsorbed P = 6 mg/L; 0.27 mg P/g substrate) using several extracting solutions. To measure the effect of pH on the desorbability of P from BVIO-amended sand, we compared 3 extracting solutions: (1) pond water adjusted to pH 6, (2) pond water adjusted to pH 10, and (3) a 0.01 M CaCl₂ solution. After an initial spike in P desorbed from the substrate in the pH 6 and 10 solutions (0.70 mg/L P and 0.87 mg/L P, respectively), concentrations decreased asymptotically over 96 hours. The CaCl₂ solution desorbed 0.10 - 0.12 mg/L P consistently over 96 hours. We then investigated the potential for reuse of P desorbed from P-saturated BVIO-amended sand. The reuse of P is contingent on the availability of P to plants. Mehlich III extractions indicate that P adsorbed to BVIO alone is not available to plants, but P desorbed from the BVIO-amended sand mixture was slightly

more available, with concentrations less than 0.5 % of adsorbed P. Concentrations of CaCl_2 -labile P (0.10 – 0.12 mg/L P; 2% of adsorbed P) may be more representative of the plant available fraction of total P and indicate that low concentrations of P may be slowly available over time, similar to a controlled-release fertilizer. In general, concentrations above 0.07 mg/L P are considered sufficient for commercially-grown ornamental plants. Concentrations of desorbed metals and minerals (K, Ca, Mg, Zn, Cu, Mn, Fe, S, Na, B, and Al) were also assessed and were below EPA toxicity thresholds and water quality criteria.

Introduction

Eutrophication resulting from excess phosphorus (P) loading into aquatic systems remains a potential risk from greenhouse and plant nursery irrigation runoff. Phosphorus is present in irrigation runoff in a number of different forms, including dissolved inorganic phosphate (PO_4^{3-}), P adsorbed onto soil particles, and as chemical precipitates (e.g., CaPO_4) (Haygarth and Jarvis, 2001). When P-bound particles are transported by surface runoff into water bodies, P can desorb and become available to support growth of undesirable algal communities (McGeechan, 2002). Filtration systems can reduce the risk of excess P in runoff containment ponds by targeting physical and chemical mechanisms for capturing P, such as sediment removal and adsorption by strong sorbents. Blue Valley Iron Oxide (BVIO), a residual of abandoned coal mine drainage (CMD), can effectively adsorb PO_4^{3-} from pond water (Table 2.7). Results from Chapter 2 established that P sorption capacity of BVIO increased when it was mixed with sand, creating a low-cost product that can be implemented within a filter.

The goal of this research was to inform the design of a P filtration system for irrigation runoff containment ponds and vegetative channels, which can have low alkalinity, high algal activity, and can experience diurnal fluctuations in water quality (e.g., pH, dissolved oxygen, temperature, dissolved organic carbon, and nutrient concentrations). Changes in pH are often intensified in eutrophic systems from the coupled respiration and photosynthesis of algal communities (Wetzel, 2001). During the day, pH can increase as algae reduce CO_2 to glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in photosynthesis. Influenced by the population density of the algal communities, pH can reach > 10 in poorly buffered systems. At night, respiration by algae releases CO_2 , and pH decreases from the formation, and subsequent dissociation, of carbonic acid (H_2CO_3) (Wetzel, 2001). Adsorption and desorption of P from adsorbents can be influenced by solution pH and the types of adsorption complexes formed on adsorbent surfaces (Neely, 2010; Mao et al., 2016). It is essential to be able to anticipate P mobility during diurnal fluctuations. Desorption experiments can characterize the reversibility of P adsorption and binding strength between P and the sorbent, and the extent of P expected to desorb in certain conditions can be measured through a series of extracting solutions (Kose and Kivanc, 2011; Roy, 2017). When an extracting solution is added to a P-saturated adsorbent, P can be removed from the solid phase through the dissolving action of acids, anion replacement, and complexation or hydrolysis of cations binding P (Elrashidi, 2010). Desorbability, defined as the ratio of P desorbed over the total P adsorbed by the adsorbent, can indicate the extent of desorption from different adsorbents (Lalley et al., 2016).

Current P reduction strategies from wastewater focus on the capture and retention of dissolved and particulate-bound P through filtration systems, with little consideration of reuse of the P-saturated product. The adsorbent must be replaced when P-binding sites are saturated. Spent substrates are typically disposed of at landfill sites (Hylander and Siman, 2001; Roy, 2017). Although considerable efforts have been made to develop P recovery and recycling systems that incorporate captured P, their applicability to low-cost remediation systems is limited (Roy, 2017). Within the greenhouse and nursery industry, there is potential for incorporation of P-saturated materials within potting mixes as a fertilizer amendment, provided the adsorbed-P is available to plants. Several studies have addressed plant availability of P sorbed to filter substrates. In a study measuring the biomass yield of barley, *Hordeum vulgare*, in response to incorporation of P-saturated materials into potting soil, Hylander and Simon (2001) found that application of P at 0.3 g P /pot with crystalline slag resulted in a higher yield than the application of fertilizer P. The rate of release of P from the slag likely corresponded to the P requirements of the Barley plants, compared to the more soluble fertilizer P that likely was released quickly and sorbed to soil particles (Hylander and Siman, 2001). Dobbie et al. (2005) similarly found that P-saturated iron hydroxide functioned as a slow-release fertilizer in pot and field experiments. For effective use of a P-saturated product, the growth requirements for plants in container production must be considered as well as the plant availability of the P that is bound to the adsorbent. These studies demonstrated that recalcitrant P desorbed at lower rates over time resulted in higher plant yield than easily-soluble fertilizer P, and that initially unavailable P was gradually converted into plant-available forms.

In acidic soils, inorganic PO_4^{3-} can form highly insoluble compounds with trivalent cations (e.g., Fe^{3+} , Al^{3+}) and is readily adsorbed by natural Fe-oxide sources. In alkaline soils, PO_4^{3-} complexes with divalent cations (e.g., Ca^{2+}) and can be adsorbed by calcium carbonate (CaCO_3) (Tan, 2010). As a result, P concentrations in soil solution are typically low (ppb), and very little P is available for biological uptake. As plants deplete P in soil solution, it is replenished by solubilization of P-containing particles, desorption of P from charged surfaces, and the hydrolysis of organic P compounds (Hocking et al., 2000). Organic acids, such as acetic, citric and malic acid, exuded from plant roots can alter the availability of P compounds directly through a few mechanisms: (1) lowering the pH of the soil solution to increase the dissolution of P compounds, (2) altering the surface charge of soil particles, (3) competing with PO_4^{3-} for adsorption sites and inducing ligand exchange, and (4) forming complexes with P-bound cations (Hocking et al., 2000; Pinton et al., 2007; Hinsinger, 2001). The first evidence of P solubilization by plant root exudates was reported by Gardner et al. (1982), where the roots of white lupin (*Lupinus albus*) exuded citric acid to form a ferric-hydroxy-phosphate polymer, showing that organic acids could form complexes with P-bound minerals (Hocking et al., 2000). Once these complexes are formed, they can diffuse back to the root where the complex is absorbed, or P is separated from the ligand after reduction and is then absorbed (Pinton et al., 2007). These complex interactions occurring at the soil-root interface are expected to influence availability of P-bound BVIO when mixed with potting soil as a fertilizer amendment.

Several extraction techniques have been developed to determine plant availability of P in soils (e.g., Mehlich-III, Bray, Olsen), though their applicability to iron oxide sorbents has not been characterized. The Mehlich-III extraction is a method commonly used by soil laboratories in fertilizer recommendations to determine the quantity of P immediately available to crops in mineral soils (Mehlich, 1984; McGechan 2002). The Mehlich-III extraction was selected for investigation in this study to determine plant availability of P for a number of reasons. The Mehlich-III extraction estimates nutrient availability to plants in neutral and acidic soils using a several compounds dissolved in a pH 2.5 solution (acetic acid, ammonium nitrate, ammonium fluoride, nitric acid, and EDTA); these compounds solubilize P using different mechanisms (Zhang et al., 2009). Nitric acid and acetic acid increase the solubility of Fe and Al-phosphates. Fluoride (F^-) ions promote P desorption by ligand exchange with PO_4^{3-} , and by complexing with aluminum cations that can bind with PO_4^{3-} . Acetic acid keeps the solution buffered below pH 2.9 to prevent CaF_2 precipitation. Ammonium nitrate serves to extract exchangeable cations (K, Ca, Mg), and EDTA acts as a chelating agent to bind metal ions (Fe, Mn, Zn, Cu).

Phosphorus removal from irrigation runoff can be achieved by incorporating a P sorbent within a sand filter, a technology already familiar to greenhouse and nursery operators. This study investigated mixing BVIO with sand for use in a P filtration system. Studies assessing the availability of soil P to crops have suggested that an increase in sand content is correlated with an increase in plant-available P. In a study that measured extractable P content of soils, Menon et al. (1989) reported a positive correlation of HCl-

extracted P and sand content. Similarly, Wuenscher et al. (2015) compared 50 agricultural soils and reported P extracted with Mehlich-III and CaCl_2 solutions was positively correlated with sand content. The implication of these findings is that mixing the sorbent with sand could increase the recoverability of P.

Research Goal and Objectives

The goal of this study was to characterize desorption dynamics of P adsorbed to BVIO-amended sand. The specific objectives of this study were to:

- (1) measure the effect of two pH conditions (pH 6 and 10) on the extent of phosphorus desorption over time from BVIO-amended sand in pond water,
- (2) assess the plant availability of P adsorbed to BVIO-amended sand, BVIO, and sand in pond water using standard extraction solutions,
- (3) measure the extent of desorption of metals and other elements (K, Ca, Mg, Zn, Cu, Mn, Fe, S, Na, B, and Al) over time from BVIO-amended sand in pond water.

Materials and Methods

Desorption

Desorption and extraction experiments were performed with unwashed BVIO-amended sand. To measure the effect of pH on the desorbability of P adsorbed from BVIO-amended sand, we prepared 3 extracting solutions: (1) pond water adjusted to pH 6 (1 M HNO_3), (2) pond water adjusted to pH 10 (1 M KOH), and (3) a 0.01 M CaCl_2 solution (pH 6), widely-used to extract soluble P, as a positive control (Appendix C,

Figure C1; Hyde and Morris, 2000; White et al., 2011). Desorption was also measured as a function of contact time (0, 24, 48, 72, and 96 hours). Three replicates were prepared per substrate per treatment type ($n=135$). All size fractions of silica sand and BVIO were used to represent realistic use of materials in P filtration systems by plant nursery operators, and a particle size distribution is presented in Table 2.3.

To prepare a P-equilibrated product, each substrate (1.000g per experimental unit of BVIO-amended sand, BVIO, and sand) was added to a 50mL centrifuge tube containing 45 mL of a 6 mg/L P solution (Appendix C; Figure 2). The 6 mg/L P bulk solution was prepared by adding KH_2PO_4 to pond water and was adjusted to 7.0 ± 0.1 with 1M KOH. After 24 hours of horizontal shaking on an orbital shaker table set at 150 rpm at 25°C , each tube was centrifuged at 5000 rpm for 15 min. The supernatant was poured through a vacuum filtration apparatus ($0.22 \mu\text{m}$) and P remaining in solution was measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (detection limit= 0.0022 mg/L). The instrument (Spectro Arcos ICP-OES; Spectro Analytical Instruments) was equipped with a UV-Plus Purifier gas cleaning system with argon gas flow and a Cetac autosampler and was calibrated using commercially available ICP standard solutions (Inorganic Ventures) every time the method was used. A check standard was analyzed along with samples, every 55 samples, to ensure calibration, and the instrument was maintained biannually by Ametek service technicians. Any fines remaining in solution were retained in the paper filter used during vacuum filtration, as the sorbing solution was poured off the vials.

The concentration of phosphorus remaining in solution was used to calculate the initial amount of adsorbed P (C_s ; Equation 1), and subsequently the amount of desorbed P:

$$C_s = \frac{C_0 - C_w}{m_s} \quad \text{Equation 1}$$

where C_s is the mass of P adsorbed per gram of substrate, C_0 is the initial concentration of phosphorus introduced to each substrate (i.e., 0 – 1000 mg/L), C_w is the concentration of P remaining in solution, and m_s is the mass of substrate (1.000g) minus the mass of fines retained on the filter paper during vacuum filtration. The remaining P-saturated substrate was left under a fume hood to dry for 24 hours at 25°C, 45mL of desorbing solution was poured over the dried substrate.

Desorbing solutions were prepared using pond water collected from an irrigation runoff containment pond at a plant nursery in South Carolina. The water quality parameters for this water source were measured before desorption experiments were initiated and included P content (mg/L) and concentrations of K, Ca, Mg, Cu, Fe, S, Na, Zn, Mn, B, and Al (Table 3.1).

Table 3.1. Analysis of pond water before desorption experiments*

Element	Average concentration ($n=4$) (mg/L)	S.E. ^z
P	0.054	0.007
K	2.298	0.015
Ca	3.611	0.031
Mg	0.867	0.006
Cu	0.09	0.007
Fe	0.041	0.001
S	1.008	0.007
Na	1.259	0.007

^z S.E. = standard error of the mean

*Concentrations of Zn, Mn, B, and Al were below detection limits

Three desorbing solutions (Pond 6.0, Pond 10.0, and CaCl_2 6.0) were evaluated for their ability to induce desorption of P from the substrate, and no buffering agent was added to the solutions, to better mimic water with the low alkalinity (~ 25 mg/L CaCO_3). Treatments were prepared in triplicate and placed horizontally on an orbital shaker table set at 150 rpm for either 24, 48, 72, or 96 hours. After contact time of under 10 seconds, which was considered sufficient for the 0-hour treatments, 10mL of overlying solution was filtered (0.45 μm), acidified with concentrated HNO_3 and measured for desorbed P via ICP-OES (detection limit = 0.0022 mg/L). Desorbed elements from BVIO-amended sand (K, Ca, Mg, Zn, Cu, Mn, Fe, S, Na, B, and Al) were measured in overlying solutions of all treatment replicates and were handled similarly to P samples. Corrections for P, K, Ca, Mg, Cu, Fe, S, and Na initially present in the pond water were made.

Plant Availability

A Mehlich-III extraction was performed on P-saturated substrate to estimate plant availability. The Mehlich-III extracting solution, a pH 2.5 solution of 0.05M acetic acid, 0.083 M ammonium nitrate, 0.038M ammonium fluoride, 0.013M nitric acid, and 0.001M EDTA, was prepared according to Zhang et al. (2009) and Hyde and Morris (2000). To saturate each substrate with P, 45 mL of 10 mg/L P pond water solution was poured over 2g of substrate (BVIO, sand, and BVIO-amended sand) in a 50 mL centrifuge tube (Appendix C; Figure C3). After 24 hours of contact time on an orbital shaker table set at 150 rpm, each tube was centrifuged at 5000 rpm for 15 min. The supernatant was poured through a vacuum filtration apparatus (0.22 μm), and the solution

was measured for P via ICP-OES. The remaining P-saturated substrate (~2g) was left under a fume hood to dry for 24 hours at 25°C. Twenty mL of Mehlich-III solution was poured over the air-dried substrate. Five replicates were prepared for each substrate and placed horizontally on an orbital shaker table for 5 minutes. Ten mL of overlying solution was filtered (0.45 µm), acidified with 1 M HNO₃, and measured for extracted P via ICP-OES. In BVIO treatments, concentrations of desorbed P were under the detection limit (0.015 mg/L P). When measured values were below the detection limit, the minimum detection limit was divided by two according to Hewett and Ganser (2007), who state that if the percent of non-detectable (D) values is <50% and the number of observations between 20 and 100, substitution of D/2 is an appropriate approximation for statistical analyses.

Statistical Analysis

Statistical analyses were conducted using the software package JMP Pro 13.2 (SAS Institute, 1990). Significance level for all evaluations $\alpha < 0.05$. Desorption data from all treatments were tested for distribution normality using the Shapiro-Wilk W test, and for homogeneity of variance using Levene's test. When appropriate, one-way analyses of variance were performed on pH 6, pH 10, and CaCl₂ –extractable P concentrations to discern differences among the means of desorption data from the three treatments (Ott and Longnecker, 2010). When appropriate, treatment means for pH 6, pH 10, and CaCl₂ –extractable P concentrations were separated by contact time (0, 24, 48, 72, and 96 hours) using Tukey's HSD. Treatment means of Mehlich III- extractable P

were separated by substrate (sand, BVIO-amended sand, and BVIO) using Tukey's HSD. Student's t-tests were used to discern differences between initially adsorbed P and Mehlich-III extractable P for the substrates. Treatments means of desorbed metals (K, Mg, Cu, Fe, Na) and S were separated by desorbing solution (pH 6, pH 10, and CaCl₂) using Tukey's HSD. Treatment means for desorbed constituents were then separated from the mean values of the background pond water concentrations using Student's t-tests.

Results and Discussion

The effect of pH on desorption of P from BVIO-amended sand

Concentrations of P desorbed from BVIO and BVIO-sand were assessed in solutions of pond water adjusted to pH 6 and 10 and DI water amended with 0.01M CaCl₂ (Figure 3.1). After an initial spike in P desorbed from the substrate, concentrations decreased with time in the pH 6 and 10 treatments. After a contact time of 10 seconds, 0.07 mg/L P was desorbed from BVIO-amended sand in the pH 6 solution, and less P was desorbed at 24, 48, 72, and 96 hours ($p=0.0025$, 0.0044 , 0.0044 , and 0.0060 , respectively). A similar trend was observed in the pH 10 solution; after 10 seconds, 0.09 mg/L P was desorbed from BVIO-sand, and less P was desorbed at 24, 48, and 72 hours ($p=0.034$, 0.0124 , and 0.0089 , respectively), but not at 96h ($p=0.168$). Phosphorus desorption from iron oxide by mild treatments, such as solutions of indifferent electrolytes (i.e., 0.01 M NaCl) or pond water, can be explained through considerations of chemical equilibrium (Madrid and Posner, 1979; Cabrera et al., 1981). The equilibrium

between PO_4^{3-} in solution and solid surfaces may be altered by changing the concentration of PO_4^{3-} ions in solution, the pH of the suspension, or ionic strength (Cabrera et al., 1981). The initial equilibrium of the substrate with solution was disrupted by initiating the desorption trial, which introduced physical shaking and pH changes.

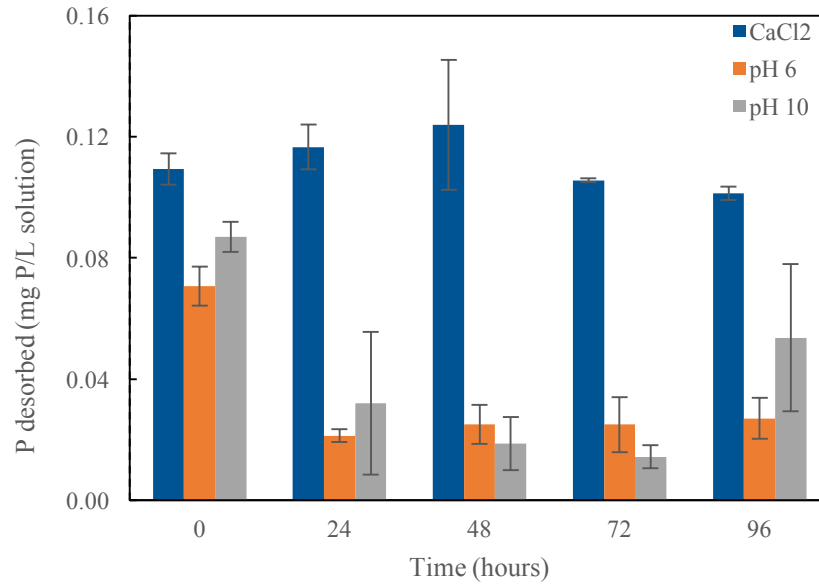


Figure 3.1. Phosphorus desorption from Blue Valley iron oxide (BVIO)-sand in 0.01 M CaCl_2 and in pond water adjusted to pH 6 and pH 10. Values represent the average of three samples and error bars represent standard error from the mean.

The initial spike in P concentration, followed by declining P concentrations indicates that after initial desorption, some P re-adsorbed to the iron oxide surface, potentially reaching equilibrium in the pH 6 solutions. The pH 10 solutions may have eventually been influenced by the increase in pH above the PZC of 8.5. Above the PZC, the Fe-hydroxide surface becomes more negatively charged and the sorption affinity for anions such as PO_4^{3-} declines (Neely, 2010). Results from the pH 6 and 10 desorbing solution could also be an artifact of physical shaking; as particles are broken up, new

sorption sites are created for PO_4^{3-} to quickly adsorb. These observations are supported by the findings of Madrid and Posner (1979), who reported some re-adsorption of P-bound goethite in P-free solutions of the same ionic strength, and Barrow and Shaw (1975), who measured re-adsorption of some P after desorption with 0.01 M CaCl_2 from P-saturated soil. Barrow and Shaw (1975) suggested that this was due to the breakdown of soil particles and exposure of new surfaces. An alternative explanation is that the PO_4^{3-} moves toward chemical equilibrium between the P-bound to the iron oxide surface and P in solution, and that this is influenced by the pH of the desorbing solution. Supporting this concept, Atkinson et al. (1972) and Neoh (1975) found that most PO_4^{3-} adsorbed on goethite was isotopically exchangeable, which means that it should be in equilibrium with the solution. Building on the findings of Barrow and Shaw (1975), Cabrera et al. (1981) reported slight re-adsorption of P after initially rapid desorption from goethite ($\sim 16 \mu\text{mol/g}$ at pH 3.3 in 0.1 M NaCl). They found that the amount of P remaining adsorbed to goethite after 240 hours was dependent on the initial pH of the desorbing solution and total P concentration. It is feasible that the adsorption/desorption dynamics observed in this study were influenced by chemical equilibrium as well as the physical shaking of the substrate on the shaker table.

The 0.01 M CaCl_2 solution facilitated desorption of more P than the pH 6 solution at 0h, 24h, 48h, 72h, and 96h ($p=0.0066, 0.0078, 0.0057, 0.0001, \text{ and } 0.0115$, respectively), and the pH 10 solution at 24h, 48h, and 72h ($p=0.0136, 0.0042, \text{ and } 0.0001$, respectively) (Figure 3.1). Despite these differences, CaCl_2 extracted only 2% of adsorbed P (0.267 mg/g) over 96 hours. The 0.01 M CaCl_2 solution was used a positive

control to compare against concentrations of P desorbed from changes in pH, and to serve as an indicator of desorbability when compared to other studies that have also used CaCl_2 . Also reported by some studies as the fraction of labile, plant-available P in soils, CaCl_2 extracts P through ion exchange and the dissolution of P compounds in the extraction solution (Wuenschel et al., 2015; Van Raij, 1998). Results of this study indicate that P desorption can be initiated by the presence of calcium, which could be useful to greenhouse and plant nursery operators who incorporate P-saturated sorbent within potting mixes. For example, the use of lime (CaCO_3) may cause P to slowly desorb and become available for plant uptake.

Low desorbability is expected for P that is adsorbed to a strong sorbent such as iron hydroxide. Zeng et al. (2004) reported that PO_4^{3-} had a desorbability of 13-14% (0.73 mg P/g - 0.99 mg P/g), noting the strong bonding between adsorbed PO_4^{3-} and iron oxide tailings (a waste byproduct from mineral processing facility composed mainly of magnetite (Fe_3O_4)). Hyde and Morris (2000) reported that concentrations of CaCl_2 -soluble P required for plant growth vary by plant and soil composition, but concentrations less than 0.07 mg/L are considered deficient for most plants (Kamprath and Watson, 1980; Hyde and Morris, 2000). Well above this threshold, concentrations of P desorbed from BVIO-amended sand ranged from 0.01 – 0.12 mg/L, indicating that this product may be suitable as a fertilizer amendment.

Plant Availability of P

Plant availability of P was assessed through extraction with Mehlich-III solution to determine if P-saturated BVIO-amended sand could act as a P source for fertilizer

Table 3.2. Mehlich-III-extractable P concentrations in sand, BVIO-amended sand, and BVIO. Values represent the mean ($n=5$) \pm standard error (S.E.) from the mean.

	Initial Adsorbed P (mg/g) (S.E.)	Desorbed P (mg/g) (S.E.)	% P Desorbed
Sand	0.012(0.008)	0.031 (0.004)	262 %
BVIO-sand	0.238* (0.001)	0.001 (0.001)	0.363%
BVIO	0.238* (0.000)	0.000 (0.000)	0.032%

^z BVIO = Blue Valley iron oxide; S.E. = standard error from the mean

*Samples from initial sorption tests were below detection limits for P (0.015 mg/L); these values were divided by two according to Hewett and Ganser (2007).

when mixed with potting soil. Less P was extracted from unwashed BVIO and BVIO-amended sand using Mehlich-III solution than from unwashed silica sand ($p<0.001$) (Figure 3.2 and Table 3.2). The addition of BVIO to sand reduced Mehlich-III P concentrations compared to the un-amended sand control ($p= <0.0001$) (Figure 3.2). Only 0.3% of initially adsorbed P was extracted from the BVIO-amended sand, and only 0.03% of initially adsorbed P was extracted from BVIO alone. By mixing sand with BVIO, the percent of plant-available P (i.e., from the total mass of P adsorbed) increased by an order of magnitude (from 0.03% to 0.36%).

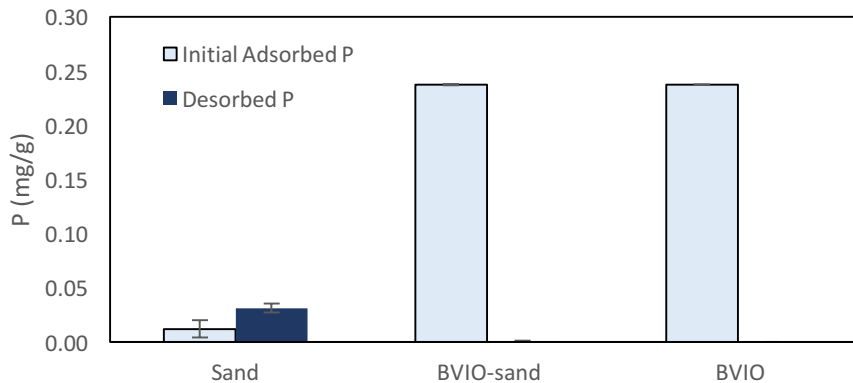


Figure 3.2. Initial adsorbed P compared to Mehlich-III extractable P concentrations in sand, Blue Valley iron oxide (BVIO)-amended sand, and BVIO. Values represent the average of 5 samples and error bars represent standard error of the mean.

Mehlich III solution extracted less than 1% of P adsorbed to BVIO and BVIO-amended sand. The amount of CaCl_2 -labile P was higher (0.005 mg P or 2.1 %), indicating that more P may be available than suggested by the Mehlich III method. The Mehlich-III method extracts P when acetic acid promotes the dissolution of Ca-phosphates, and ammonium fluoride releases P when F^- ions compete with PO_4^{3-} for Fe^{3+} as well as Al^{3+} . While these mechanisms may facilitate removal of some P from the BVIO surface, the ionic strengths of each of these constituents are relatively low when considering the P binding affinity of BVIO, and perhaps a stronger Mehlich-III solution could extract more P. The Mehlich III extraction is an agronomic method developed for a wide range of mineral soils to indicate the quantity of P immediately available to growing plants (McGeechan, 2002), and may not be the best extraction for measuring plant availability of P adsorbed to Fe-hydroxides. Iron hydroxides generally have a stronger binding affinity for P than other soil constituents at acidic to neutral pH values. It is also important to note that while the 1:10 solid to liquid ratio used in these experiments is standard for Mehlich-III extractions, the volume of extracting solution can have a substantial impact on desorption.

Results from this study highlight the strong binding affinity of P for iron-hydroxide surfaces and suggest that P adsorbed to BVIO and BVIO-amended sand is not immediately available to plants. This observation may not be the limiting factor in the reuse of this product; previous studies have demonstrated that unavailable P slowly desorbed over time resulted in higher plant yield than soluble P in commercial fertilizer (Hylander and Siman, 2001; Dobbie et al., 2005).

Desorption of other elements from BVIO-amended sand

To assess the suitability of P-saturated BVIO-amended sand for reuse as a fertilizer amendment, the degree of metals and other elements leaching from the sorbent must be negligible to minimize risk to container-grown plants. Aquatic organisms could also be exposed to leachate from the sorbent if runoff from container areas flowed into a containment pond, vegetative channel, or creek.

Concentrations of desorbed elements in 0.01 M CaCl_2 , pH 6 and pH 10 pond water were compared to concentrations measured in pond water before pH adjustments and P additions (Table 3.3). Background P and Fe concentrations measured in pond water were 0.005 mg/L and 0.041 mg/L, respectively. After exposure to 0.01 M CaCl_2 , S concentrations were higher (~6 mg/L) than background pond water concentrations ($p=0.0001$). Potassium, Cu, and Na concentrations measured in CaCl_2 solutions were lower than background pond water values ($p < 0.001$), indicating possible formation of surface complexes (Martin, 2005). Concentrations of Fe over time did not differ from the background Fe concentrations. Concentrations of Ca were not appropriate to report in Table 3.3 as concentrations attributed to desorption from BVIO were masked by CaCl_2 in the desorbing solution.

After exposure to pH 6 pond water, K and Na concentrations were higher than background pond water concentrations ($p < 0.0001$), and after 24 hours in pH 6 pond water, Ca and S were higher than background concentrations ($p < 0.0001$) (Table 3.3.), which suggests these elements desorbed from BVIO-amended sand. After 24 hours,

Table 3.3. Elements desorbed from BVIO-amended sand in 0.01 M CaCl₂, pH 6, and pH 10 desorbing solutions over time. Concentrations of desorbed minerals (mean (n=3) ± standard error from the mean) were compared to background concentrations of minerals analyzed in pond water before desorption experiments were initiated.

Solution	Background	K		Mg		Cu		Fe (mg/L)	S		Na		Ca	
		2.3 (0.02)		0.87 (0.01)		0.09 (0.01)			1.01 (0.01)		1.26 (0.01)		3.61 (0.03)	
0.01 M CaCl ₂	0 h	0.87 (0.09)	***	0	***	0.004	***	0.029 (0.037)	4.51 (0.182)	***	0.145 (0.028)	***	NA	
	24 h	1.45 (0.03)	***	0.73 (0.06)	***	0.004	***	<0.002 (0)	6.27 (0.18)	***	0.14 (0.01)	***	NA	
	48 h	1.46 (0.07)	***	0.86 (0.04)	***	0.004	***	0.03	6.43 (0.11)	***	0.23 (0.05)	***	NA	
	72 h	1.44 (0.07)	***	0.86 (0.04)	***	0.004	***	0.01 (0.01)	6.48 (0.07)	***	0.16 (0.01)	***	NA	
	96 h	1.22 (0.23)	***	0.94 (0.07)	***	0.005	***	0.01 (0.01)	6.48 (0.09)	***	0.18 (0.04)	***	NA	
pH 6	0 h	3.71 (0.06)	*** C	0.92 (0.03)	C	0.08	C	0.10 (0.09)	1.73 (0.06)	C	2.5 (0.07)	*** C	7.85 (0.39)	C
	24 h	3.67 (0.06)	*** C	0.47 (0.01)	*** C	0.007	*** C	0.02 (0.01)	4.49 (0.12)	*** C	2.35 (0.03)	*** C	22.9 (0.32)	*** C
	48 h	3.84 (0.04)	*** C	0.457 (0.02)	*** C	0.004	***	0.01 (0.00)	5.01 (0.11)	*** C	2.48 (0.03)	*** C	28.32 (0.49)	*** C
	72 h	3.93 (0.08)	*** C	0.45 (0.02)	*** C	0.004	***	0.002	5.19 (0.48)	*** B	2.52 (0.06)	*** C	29.6 (1.07)	*** C
	96 h	3.81 (0.06)	*** C	0.43 (0.03)	*** C	0.004	***	0.11 (0.18)	5.09 (0.22)	*** C	2.48 (0.04)	*** C	30.16 (0.69)	*** C
pH 10	0 h	11.80 (0.26)	*** C	0.75 (0.02)	** C	0.1	C	0.05 (0.01)	1.88 (0.1)	C	2.66 (0.18)	*** C	5.76 (0.17)	C
	24 h	12.23 (0.03)	*** C	0.35 (0.02)	*** C	0.01	***	0.21 (0.26)	5.72 (0.54)	***	2.66 (0.14)	*** C	19.81 (0.11)	*** C
	48 h	11.64 (0.04)	*** C	0.23 (0.02)	*** C	0.00 (0.00)	***	0.24 (0.34)	5.18 (0.26)	*** C	2.48 (0.04)	*** C	22.52 (1.04)	*** C
	72 h	11.36 (0.01)	*** C	0.22 (0.01)	*** C	0.00 (0.00)	***	0.01 (0.01)	5.35 (0.38)	*** B	2.54 (0.05)	*** C	23.17 (0.35)	*** C
	96 h	11.57 (0.21)	*** C	0.26 (0.04)	*** C	0.00 (0.00)	***	0.03 (0.03)	5.44 (0.24)	*** C	2.54 (0.10)	*** C	23.69 (0.32)	*** C

When compared with background pond water concentrations within a column, * $p = 0.05$, ** = 0.01 to 0.05, *** = <0.01

When mineral concentrations of pH 6 and pH 10 were compared with CaCl₂ by contact time, A $p = 0.05$, B = 0.01 to 0.05, and C = <0.01

NA= not appropriate to report; Ca concentrations attributed to BVIO desorption were masked by CaCl₂ in the desorbing solution

concentrations of Mg and Cu were lower in the pH 6 solution than background concentrations ($p= 0.0001$), indicating possible formation of surface complexes (Martin, 2005). Similar trends were observed for each element in pH 10 desorbing solutions (Table 3.3).

Elements not included in Table 3.3 were below detection limits (DL) and include Zn, Mn, B (DL = 0.01 mg/L) and Al (DL=0.033). Studies investigating metal desorption from CMD iron oxides have reported similar findings. In a study using a slurry of BVIO to reduce P in secondary wastewater effluent, Fish and Dietz (2009) found that As, Ca, Cd, Co, Cr, Fe, Ni, Pb, Se, and Zn did not desorb from BVIO after 12 hours of stirring. To assess the potential risks of desorbed metals, concentrations of metals and other elements in 0.01 M CaCl₂, pH 6 and pH 10 pond water were compared to EPA toxicity criteria for aquatic life (Table 3.4). Developed by the EPA's Office of Water, the criteria presented in Table 3.4 serve as conservative toxicity threshold values for the protection of aquatic life (USEPA, 1992). Organisms used for the development of these values include the Fathead minnow (*Pimephales promelas*), Cutthroat trout (*Oncorhynchus clarkia*), Chinook salmon (*Oncorhynchus tshawytscha*), *Ceriodaphnia dubia*, and *Daphnia magna*. While concentrations of Ca, K, Na, and S were above background levels in the pH 6 and 10 solutions after contact with P-saturated BVIO, the concentrations reported do not present considerable risk to plants or aquatic life (USEPA, 1998).

Table 3.4. EPA toxicity threshold values for the protection of aquatic life.

Metal	Freshwater CCC (Chronic) *	Freshwater CMC (Acute) *	Freshwater TRV
		µg/L	
Arsenic (III)	150	340	190 **
Cadmium	0.7 -2.0	1.8 - 8.6	0.7 **
Calcium			116000 ***
Chromium (III)	120-370	98-310	117 **
Copper	6.5-21	9.2-34	6.5 **
Iron	1000		1000 **
Lead	1.3-7.7	34-200	1.3 **
Magnesium			82000 ***
Mercury (III)		24	0.01 **
Nickel	88-280	790-2500	87.7 **
Potassium			53000 ***
Sodium			680000 ***
Sulfur			5000000 ****
Zinc	59-190	65-210	120 **

Sources: *USEPA, 1993; **USEPA, 1992; ***Suter and Tsao (1996), ****USEPA (1982)

CCC: Criterion continuous concentration; values reported to elicit toxicological effects organisms are exposed continuously over time

CMC: Criterion maximum concentration; values above this concentration are expected to elicit toxicological effects from a single exposure

* and ** Lowest acute and chronic values for: *Pimephales promelas*, *Oncorhynchus clarkia*, *Oncorhynchus tshawytscha*, *Ceriodaphnia dubia*, and *Daphnia magna*

***Lowest chronic value for *Daphnia magna*

****48-hour LC50 for *Daphnia magna*

Conclusions

The goal of this study was to characterize desorption dynamics of P adsorbed to BVIO-amended sand. Characterization of P mobility within a BVIO-sand filtration system and within a plant container is an essential component to that understanding. To limit excessive algal growth, EPA water quality criteria state that PO_4^{3-} should not exceed 0.05 mg/L in streams that discharge into lakes or reservoirs, 0.025 mg/L within a lake or reservoir, and 0.1 mg/L in streams that do not discharge into lakes or reservoir (USEPA, 1986). We found that P concentrations were mostly within this range after contact with pond water adjusted to pH 6 (0.021 – 0.071 mg/L P) and 10 (0.014 – 0.087 mg/L P) (Fig

3.1). Initial spikes in desorbed P followed by declining concentrations suggest that equilibrium between the P sorbed to iron hydroxide surfaces and P in solution was eventually reached. Considering the use of BVIO-amended sand in a filtration system, pH changes in pond water flowing through the filter might cause more P to desorb immediately. This effect could be mitigated by designing the filter to have certain retention times to achieve equilibrium before water is discharged. Other management decisions for effective P filtration may include choosing to program the filter to pump water during certain times of the day or adjusting the pH before pond water enters the filter.

Reuse of P-saturated BVIO-amended sand is contingent on the availability of P to plants. Results of this study indicate that P adsorbed to BVIO is not available when assessed through Mehlich III extraction. When mixed with sand, Mehlich III-extractable P increased by an order of magnitude, although concentrations were still less than 0.5 % of adsorbed P. The amount of CaCl_2 -labile P may be more representative of the plant available fraction of total P, which could be confirmed with a study of biomass yield from containers amended with P-saturated BVIO-amended sand. Previous studies have used CaCl_2 to estimate plant availability and suggested that low amounts of P may become available over time (Hyde and Morris, 2000; Koopmans et al., 2004; White et al., 2011), affirming this study's findings. In concept, this would be similar to a controlled-release fertilizer. Additionally, our findings suggest that external changes to soil solution pH and introduction of calcium-based materials (e.g., lime (CaCO_3)) could facilitate P desorption within the container. This process could benefit growers targeting P release

for higher plant yield. Overall, results of this study are promising for reuse of the spent substrate as a soil amendment.

Just as root exudates in soils cannot be simply explained by a single mechanism, but rather by a complex web of equilibria between constituents, P mobility in soils and solution is continuously governed by multidirectional fluxes. By considering the mechanisms and investigating the extents of P removal and desorption by BVIO-amended sand, we can inform the design of a P-filtration system for irrigation runoff. Extrapolation of results from batch-scale laboratory experiments to pilot-scale or field-scale, however, would be too great a leap for proper implementation of this substrate. Rather, a vertical column study that manipulates pressure, ratios of BVIO to sand, and flow rate would be a more appropriate scale to investigate at the next stage of this research.

References

- Atkinson, R. J., Posner, A. M. and Quirk, J. P. 1972. Kinetics of heterogeneous isotopic exchange reactions. Exchange of phosphate at the at-FeOOH-aqueous solution interface. *J. inorg. nucl. Chem.* 34, 2201-11.
- Barrow, N. J. and Shaw, T. C. 1975. The slow reactions between soils and anions: Effects of period of prior contact on the desorption of phosphate from soils. *Soil Sci.* 119:311-20.
- Cabrera, F., de Arambarri, P., Madrid, L. and Toca, C.G., 1981. Desorption of phosphate from iron oxides in relation to equilibrium pH and porosity. *Geoderma*, 26: 203-216.
- Dobbie, K. E., Heal, K. V., & Smith, K. A. 2005. Assessing the performance of phosphorus-saturated ochre as a fertilizer and its environmental acceptability. *Soil Use and Management*, 21(2), 231-239.
- Elrashidi, M.A., 2010. Selection of an appropriate phosphorus test for soils. USDA NRCS, Lincoln, NE.
- Fish, D. H., & Dietz, J. M. 2009. Use of iron oxides produced from the treatment of coal mine drainage as adsorbents to remove phosphorus from secondary wastewater effluent. Final Report for OSM PA (CMD-04) Grant. Submitted to the Pennsylvania Department of Environmental Protection, Harrisburg, PA. USA.
- Gardner, W.K., et al., The acquisition of phosphorus by *Lupinus albus* L. I. Some characteristics of the soil/root interface, *Plant Soil* 68:19-32.
- Haygarth, P., & Jarvis, S. 2001. *Agriculture, hydrology and water quality*. Wallingford: CABI.
- Hewett, P. and Ganser, G.H. 2007. A comparison of several methods for analyzing censored data. *Annals of Occupational Hygiene*, 51(7), pp.611-632.
- Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant and soil*, 237(2), pp.173-195.
- Hocking, P. J., Randall, P., Delhaize, E., & Keerthisinghe, G. 2000. The role of organic acids exuded from roots in phosphorus nutrition and aluminium tolerance in acidic soils. *Management and conservation of tropical acid soils for sustainable crop production*, 61-73.
- Houba, V. J. G., Temminghoff, E. J. M., Gaikhorst, G. A., & Van Vark, W. 2000. Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. *Communications in soil science and plant analysis*, 31(9-10), 1299-1396.

- Hyde, J. E., & Morris, T. F. 2000. Phosphorus availability in soils amended with dewatered water treatment residual and metal concentrations with time in residual. *Journal of environmental quality*, 29(6), 1896-1904.
- Hyde, J.E. and Morris, T.F., 2004. Phosphorus availability from phosphorus-amended water treatment residual. *Communications in soil science and plant analysis*, 35(7-8), pp.1033-1046.
- Hylander, L. D., & Simán, G. 2001. Plant availability of phosphorus sorbed to potential wastewater treatment materials. *Biology and fertility of soils*, 34(1), 42-48.
- Hylander, L. D., Kietlińska, A., Renman, G., & Simán, G. 2006. Phosphorus retention in filter materials for wastewater treatment and its subsequent suitability for plant production. *Bioresource technology*, 97(7), 914-921.
- Kamprath, E. J., & Watson, M. E. 1980. Conventional soil and tissue tests for assessing the phosphorus status of soils. *The role of phosphorus in agriculture*, 433-469.
- Kõiv, M., Ostonen, I., Vohla, C., Mõtsep, R., Liira, M., Lõhmus, K., Kirsimäe, K. & Mander, Ü. 2012, "Reuse potential of phosphorus-rich filter materials from subsurface flow wastewater treatment filters for forest soil amendment", *Hydrobiologia*, vol. 692, no. 1, pp. 145-156.
- Koopmans, G. F., Chardon, W. J., Ehlert, P. A. I., Dolfing, J., Suurs, R. A. A., Oenema, O., & Van Riemsdijk, W. H. 2004. Phosphorus availability for plant uptake in a phosphorus-enriched noncalcareous sandy soil. *Journal of environmental quality*, 33(3), 965-975.
- Köse, T.E., Kivanc, B. 2011. Adsorption of phosphate from aqueous solutions using calcined waste eggshell. *Chem. Eng. J.* 178, 34–39.
- Lalley, J. Changseok H., Xuan L., Dionysios D. Dionysiou, Mallikarjuna N. Nadagouda. 2016. Phosphate Adsorption Using Modified Iron Oxide-Based Sorbents in Lake Water: Kinetics, Equilibrium, and Column Tests. *Chemical Engineering Journal* 284:1386-96.
- Madrid, L., & Posner, A. M. 1979. Desorption of phosphate from goethite. *European Journal of Soil Science*, 30(4), 697-707.
- Mao, Y., & Yue, Q. 2016. Kinetic Modeling of Phosphate Adsorption by Preformed and In situ formed Hydrrous Ferric Oxides at Circumneutral pH. *Scientific reports*, 6, 35292.
- Martin, S. T. 2005. Precipitation and dissolution of iron and manganese oxides. *Environmental Catalysis*, 61-81.

- McGechan, M. B. 2002. SW—soil and water: sorption of phosphorus by soil, part 2: measurement methods, results and model parameter values. *Biosystems Engineering*, 82(2), 115-130.
- Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* 15:1409-1416.
- Menon, R. G., Chien, S. H., Hammond, L. L., & Henao, J. 1989. Modified techniques for preparing paper strips for the new P i soil test for phosphorus. *Fertilizer research*, 19(2), 85-91.
- Neely, C. A. 2010. Characterization and possible sustainable sorbent use of iron oxides from abandoned mine drainage discharges. Doctoral dissertation, University of Oklahoma.
- Neoh, L. S. 1975. Desorption of phosphate from goethite. Doctoral dissertation, Univ. Western Australia.
- Ott, R. L., & Longnecker, M. T. 2015. An introduction to statistical methods and data analysis. Nelson Education.
- Pinton, R., Varanini, Z., & Nannipieri, P. 2007. The rhizosphere: biochemistry and organic substances at the soil-plant interface. CRC press.
- Roy, E. D. 2017. Phosphorus recovery and recycling with ecological engineering: a review. *Ecological engineering*, 98, 213-227.
- Sibrell, P. L., and Tucker, T. W. 2012. Fixed bed sorption of phosphorus from wastewater using iron oxide-based media derived from acid mine drainage. *Water, Air, & Soil Pollution*, 223(8), 5105-5117.
- Sibrell, P. L., Tucker, T. W., Kehler, T., & Fletcher, J. W. 2008. Removal of phosphorus from wastewater using ferroxysorb sorption media produced from CMD sludge. In *Hydrometallurgy 2008: Proceedings of the Sixth International Symposium* (p. 86). SME.
- Suter, G.W. and C.L. Tsao. 1996. Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Aquatic Biota: 1996 Revision. ES/ER/RM-96/R2. Oak Ridge National Laboratory, Oak Ridge, TN.
- Tan, K.H., 2010. Principles of soil chemistry. CRC press.

U.S. Environmental Protection Agency. 1998. National Recommended Water Quality Criteria. FRL-OW-6186-6a. Federal Register, Vol. 63 (237). US EPA, Washington, D.C.

U.S. Environmental Protection Agency. December, 1982. Sulfur Pesticide Registration Standard, L. Rossi, et al. US EPA, Office of Pesticides and Toxic Substances, Washington, DC.

U.S. Environmental Protection Agency. 1986. Quality Criteria for Water. USEPA Rep. 440/5-86-001. US EPA, Office of Water Regulations and Standards. Washington, DC.

U.S. Environmental Protection Agency. 1998. National Recommended Water Quality Criteria. FRL-OW-6186-6a. Federal Register, Vol. 63 (237). US EPA, Office of Water Regulations and Standards. Washington, D.C.

U.S. Environmental Protection Agency. 1992. National Recommended Water Quality Criteria. Federal Register 57-60848. US EPA, Office of Water Regulations and Standards. Washington, D.C.

U.S. Environmental Protection Agency. 1993. 40CFR Part 503 - Standards for use and disposal of sewage sludge: Final rules. Federal Register 58:9248-9415. US EPA, Washington, D.C.

Van Raij, B. 1998. Bioavailable tests: alternatives to standard soil extractions. Communications in Soil Science and Plant Analysis, 29 (11-14), 1553-1570.

Wetzel, R. G. 2001. Limnology: lake and river ecosystems. gulf professional publishing.

White, S. A., Taylor, M. D., Albano, J. P., Whitwell, T., & Klaine, S. J. 2011. Phosphorus retention in lab and field-scale subsurface-flow wetlands treating plant nursery runoff. Ecological Engineering, 37(12), 1968-1976.

Wuenschel, R., Unterfrauner, H., Peticzka, R., & Zehetner, F. 2015. A comparison of 14 soil phosphorus extraction methods applied to 50 agricultural soils from Central Europe. Plant Soil Environ, 61(2), 86-96.

Zeng, Le & Li, Xiaomei & Liu, Jindun. 2004. Adsorptive Removal of Phosphate From Aqueous Solutions Using Iron-Oxide Tailings. Water research. 38. 1318-26. 10.1016/j.watres.2003.12.009.

Zhang, H., S. Kariuki, J. Schroder, M. Payton, and C. Focht. 2009. Inter-laboratory validation of the Mehlich 3 for extraction of plant-available phosphorus. J. AOAC International Vol. 92 (1): 91-102.

CHAPTER 4

SUMMARY AND CONCLUSIONS

Iron hydroxide from coal mine drainage (CMD) strongly sorbs phosphorus (P). Mixing Blue Valley iron oxide (BVIO) with silica sand enhanced the P sorption capacity of BVIO, possibly by breaking up particles and increasing surface area of sites for P adsorption. The P sorption capacity of BVIO-amended sand was similar to that of BVIO alone when normalized to BVIO content. One implication of this finding is that greenhouse and plant nursery operators could achieve comparable P removal efficiencies with less BVIO, though the substrate life-span may be reduced. For BVIO to be incorporated into P management strategies within the greenhouse and nursery industry, it must be an effective adsorbent for P removal and be low in cost. Iron oxides from CMD are available at about \$500 per ton (\$10 per cubic foot; Iron Oxide Recovery, Inc.); this cost is about 10% of the cost of commercially available iron oxide sorbents (Sibrell and Kehler, 2016). Mixing sand with BVIO could help to reduce the costs associated with the use of iron oxide while increasing P removal from irrigation runoff. That sand filters are already used by the industry is a huge step toward making adoption of BVIO-sand filters for P remediation and water filtration feasible. Additionally, it provides the added benefit to CMD managers and greenhouse and plant nursery operators by converting a waste product (BVIO) to a resource for contaminant removal.

Phosphorus sorption to BVIO-amended sand under realistic exposure conditions (water collected from a pond) was as consistent as in experiments conducted solely with deionized water. No differences in sorption capacity were noted between substrates

exposed to P in deionized water or in pond water. Rinsing BVIO-amended sand to remove fine particles did not reduce the capacity of the substrate to sorb P. Future research should address the influence of particle size on P sorption to confirm this observation.

The mobility of P sorbed to BVIO upon exposure to pond water was a function of chemical equilibrium. After initial desorption, some P re-adsorbed to BVIO-amended sand. The amount of P re-adsorbed depended on the PO_4^{3-} concentration, solution pH, and the ionic strength of the solution (Cabrera et al., 1981; Madrid and Posner, 1979). In looking at the potential to reuse P-saturated BVIO, external changes to soil solution pH (e.g., lime (CaCO_3) application) could affect P mobility within a potting substrate (P recycling). Additionally, the breakdown of BVIO particles by shaking could expose new surfaces to adsorption and affect the concentration of P remaining in solution (Barrow and Shaw, 1975).

Evaluation of the potential for reuse of P-saturated BVIO and BVIO-amended sand as a fertilizer amendment was assessed using the Mehlich-III extraction at the laboratory batch-scale. Phosphorus sorbed to BVIO was not readily available in solution after Mehlich III extraction. When BVIO was mixed with sand, Mehlich-III-extractable P increased by an order of magnitude, although concentrations were still less than 0.5 % of adsorbed P. Upon considering the limitations of the Mehlich-III extraction method and the physical properties of BVIO, we determined that CaCl_2 -labile P may be more representative of the plant available fraction of total P. More P desorption was facilitated using the 0.01 M CaCl_2 solutions than the pH 6 and pH 10 desorbing solutions at 0, 24,

48, and 72 hours, although only 2% of adsorbed P (0.267 mg/g) was extracted over 96 hours. This suggests that small amounts of P may be released over time, similar to a controlled-release fertilizer. Previous studies have demonstrated that unavailable P slowly desorbed over time resulted in higher plant yield than soluble P in commercial fertilizer, which supports the use of this P-saturated product. Current extraction methods to assess plant availability were developed for soils (e.g., Mehlich, Bray, Olsen) and may not accurately represent the fraction of plant available P in P sorbed to BVIO. Future research should include developing an extracting solution for plant availability that is suitable for sorbents with strong binding affinities, such as iron hydroxide. A long-term plant-growth study incorporating P-saturated BVIO-amended sand with potting substrates would give a more definitive answer to the question of plant availability.

Future research using BVIO-amended sand for P removal and recycling in greenhouse and plant nursery operations should consider questions of scalability. A flow-through column study would be an appropriate design to assess the capacity of this substrate to adsorb P in a filtration system. A column study would represent conditions that are more analogous to a P filtration system than batch studies in 50mL tubes on an orbital shaker table and would be more repeatable than a pilot-scale study. The effect of seasonal and diurnal water quality fluctuations on adsorbent performance (i.e., sorption capacity and contact time) should also be considered. As with pH, dissolved oxygen, temperature, and nutrient concentrations, dissolved organic carbon (DOC) is a water quality parameter that fluctuates diurnally (Weng et al., 2012). Typical DOC concentrations in irrigation runoff ponds range from 1-30 mg/L non-purgeable organic

carbon (unpublished data from a plant nursery study in Cairo, Georgia by Sarah White), and in a study measuring phosphate adsorption to iron oxides, Weng et al. (2012) demonstrated that an increase in DOC from 0.5 to 50 mg/L decreased the amount of PO_4^{3-} adsorbed by over 50%. While this study did not monitor DOC in sorption and desorption experiments, we found that the use of pond water did not decrease the P sorption capacity of BVIO or BVIO-amended sand. Future studies should monitor DOC concentrations to confirm the efficacy of BVIO sorbents for use in P filtration systems.

While there are many important parameters to consider when assessing the efficacy of a sorbent for P removal and recycling, it is imperative to remember the application of the technology and its realistic use. The use of recovered iron hydroxides from CMD treatment to remove P from greenhouse and plant nursery irrigation runoff represents the kind of remediation strategy that will be essential to addressing complex ecological issues in the future. This study demonstrated comparable P removal efficiencies using less adsorbent by mixing it with silica sand. This method reduced the cost of the adsorbent required for P removal and while making the media more adaptable for use in rapid sand filtration, a technology already familiar to greenhouse and plant nursery operators. Additionally, the reuse of the P-enriched product minimizes waste and closes the loop in P remediation.

Acknowledgements

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References

- Barrow, N. J. and Shaw, T. C. 1975. The slow reactions between soils and anions: Effects of period of prior contact on the desorption of phosphate from soils. *Soil Sci.* 119:311-20.
- Cabrera, F., de Arambarri, P., Madrid, L. and Toca, C.G., 1981. Desorption of phosphate from iron oxides in relation to equilibrium pH and porosity. *Geoderma*, 26: 203--216.
- Madrid, L., & Posner, A. M. 1979. Desorption of phosphate from goethite. *European Journal of Soil Science*, 30(4), 697-707.
- Sibrell, P. L., & Kehler, T. 2016. Phosphorus removal from aquaculture effluents at the Northeast Fishery Center in Lamar, Pennsylvania using iron oxide sorption media. *Aquacultural Engineering*, 72, 45-52.
- Weng, L., Van Riemsdijk, W. H., & Hiemstra, T. 2012. Factors controlling phosphate interaction with iron oxides. *Journal of environmental quality*, 41(3), 628-635.

APPENDICES

APPENDIX A

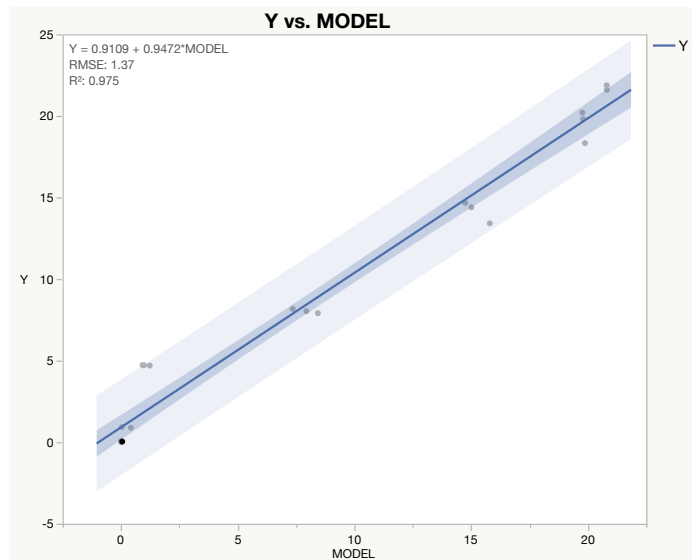
Verification of the non-linear Langmuir model as an appropriate fit for phosphorus sorption experiments

To determine if the non-linear Langmuir model was an appropriate fit for the sorption data, C_s values from the raw datasets were plotted against the predicted model values for C_s for each treatment. The resulting regressions were found to have slopes near 1 and intercepts near 0, indicating the model provided a good fit of the data.

Unwashed BVIO-sand:

$$Y = 0.9109 + 0.9472 \cdot \text{MODEL}$$

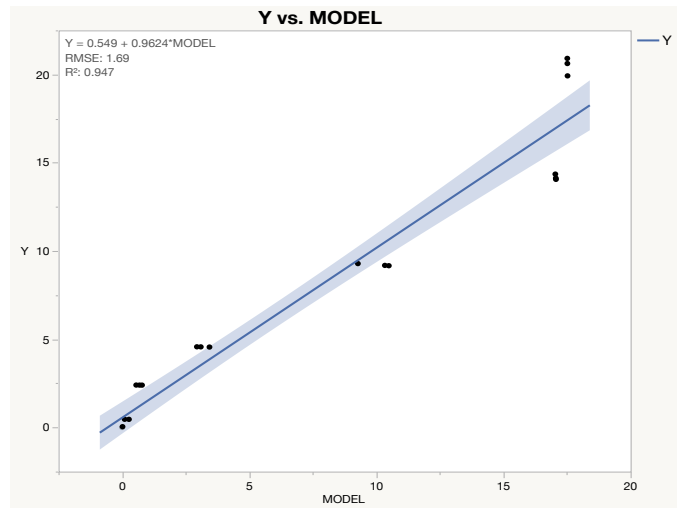
RMSE: 1.37
 $R^2 = 0.975$



Unwashed BVIO:

$$Y = 0.549 + 0.9624 * \text{MODEL}$$

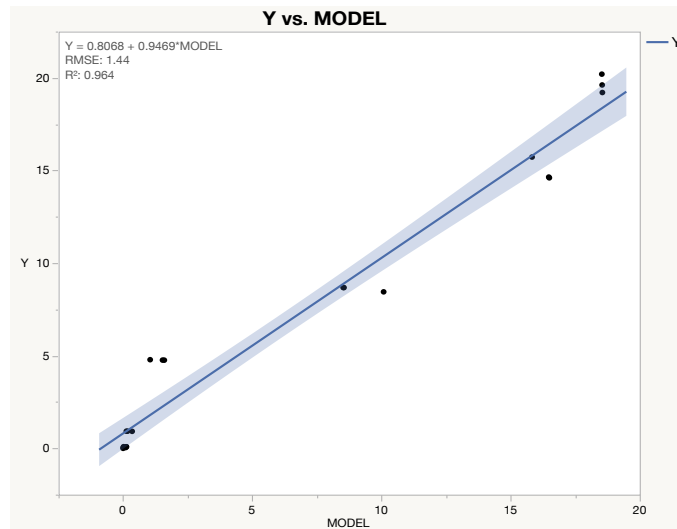
RMSE: 1.69
 $R^2 = 0.947$



Washed BVIO-sand:

$$Y = 0.8068 + 0.9469 * \text{MODEL}$$

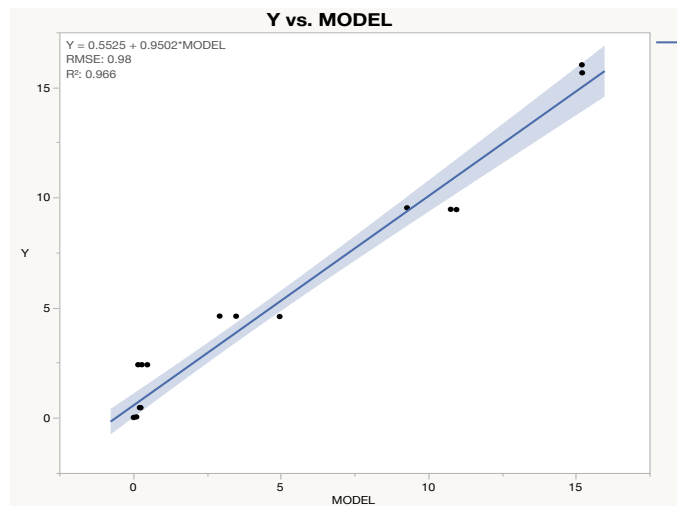
RMSE: 1.44
 $R^2 = 0.964$



Washed BVIO:

$$Y = 0.5525 + 0.9502 * \text{MODEL}$$

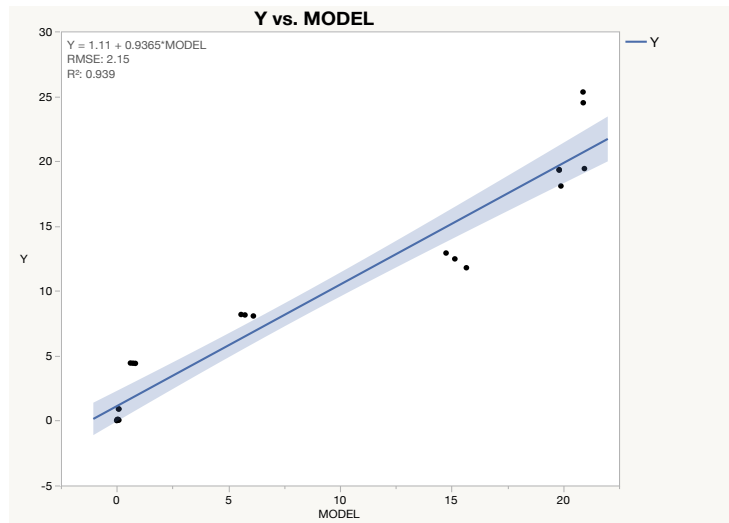
RMSE: 0.98
 $R^2 = 0.966$



Unwashed BVIO-sand in pond water

$$Y = 1.11 + 0.9365 * \text{MODEL}$$

RMSE: 2.15
 $R^2 = 0.939$



Unwashed BVIO in pond water

$$Y = 0.7817 + 0.9473 * \text{MODEL}$$

RMSE: 1.49
 $R^2 = 0.958$

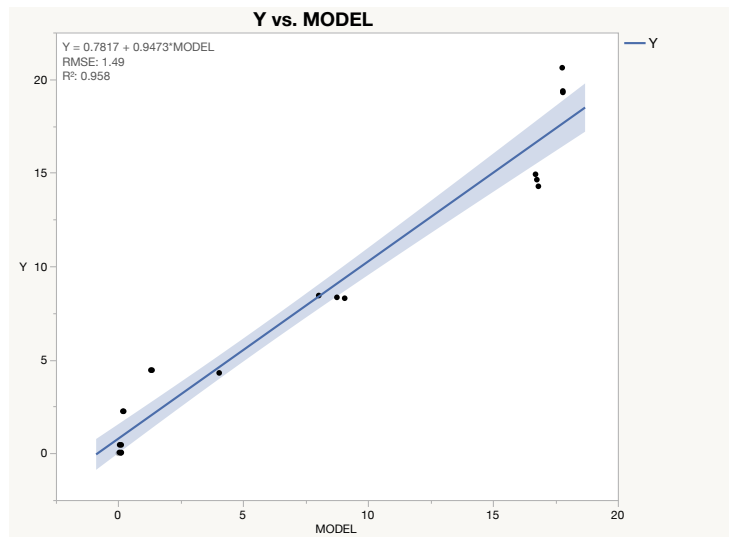


Figure A.1. Verification of the non-linear Langmuir model. C_s values from the raw datasets were plotted against the predicted model values for C_s for each treatment.

APPENDIX B

Parameters predicted using the non-linear Langmuir model compared to those calculated using the Hanes-Woolf linearization of the Langmuir isotherm

Throughout the sorption capacity experiments outlined in this thesis, several methods were investigated for analysis of sorption behavior, capacity, and equilibrium constants. The first method investigated was the Hanes-Woolf linearization of the Langmuir isotherm (Equation 1). Commonly used in P sorption studies, it provides data more similar to the nonlinear equation (Chapter 2) than other linearization methods (Bolster and Hornberger, 2007).

Methods

To calculate P sorption capacity, data were plotted (C_w/C_s vs. C_w) and linearized using the Hanes-Woolf form of the Langmuir isotherm (Equation 1; Bolster and Hornberger, 2007):

$$\frac{C_w}{C_s} = \frac{1}{C_{smax}} C_w + \frac{1}{K_L C_{smax}} \quad \text{Equation 1}$$

where C_w is the concentration of P remaining in solution, C_s is the mass of P adsorbed per gram of substrate, C_{smax} is the sorption capacity (mg/g), and K_L (L/mg) is defined as the equilibrium constant of the sorption reaction, which reflects the binding affinity of the sorbent for the sorbate. C_s was derived from:

$$C_s = \frac{C_0 - C_w}{m_s} \quad \text{Equation 2}$$

where C_0 is the initial concentration of phosphorus introduced to each substrate and m_s is the mass of substrate (1g).

Observed sorption data were fit to linearized Langmuir isotherm model (Equation 1) and statistical analyses were performed on the linearized data and fitted parameters using the software package JMP Pro 13.2 (SAS Institute Inc., Cary, NC). Sorption data from all treatments (i.e., unwashed and washed sand, deionized water and pond water) were tested for normal distribution (Shapiro-Wilk W Test) and for homogeneity of variance (Levene's test). The significance level for all analyses was set at $\alpha < 0.05$. The Generalized Linear Model procedure was used to test for differences among treatment means through Analysis of Variance (ANOVA).

Results

Phosphorus Sorption Capacity of Unwashed vs Washed substrate

Results of sorption tests of washed and unwashed substrates are summarized in Table B.1. Phosphorus sorption to unwashed BVIO and BVIO-amended sand in DI water saturated around 1 mg P/g substrate and 11 mg P/g substrate, respectively (Figure B.1A), slightly lower than the sorption capacities calculated in Table 2.5. Linearized data from unwashed BVIO, sand, and BVIO-amended sand in DI water were normally distributed ($p > 0.05$) and differences were detected among the treatment means ($p = 0.029$) (Figure B.1B). Unwashed BVIO and BVIO-amended sand sorbed more P than sand

($p=0.009$ and 0.01 , respectively), and BVIO removed more P than BVIO-amended sand ($p<0.05$).

Table B.1. Langmuir parameters calculated using the Hanes-Woolf linearization for BVIO and BVIO-amended sand in deionized water

Substrate	Regression Equation	Slope	C_{smax} (mg P /g substrate)	K_L	R^2
Unwashed BVIO	$y = 0.0497x + 0.618$	0.0497	20.1	0.080	0.981
Unwashed BVIO-sand	$y = 0.0915x + 1.37$	0.0915	10.9	0.067	0.997
Washed BVIO	$y = 0.0623x + 0.133$	0.0623	16.1	0.470	0.999
Washed BVIO-sand	$y = 0.0996x + 0.76$	0.0996	10.0	0.131	0.998

BVIO: Blue Vally iron oxide; C_{smax} : sorption capacity; K_L : Langmuir constant; R^2 : regression coefficient

Sorption data from washed substrates followed trends similar to unwashed substrates. Data from washed BVIO and BVIO-amended sand in DI water were normally distributed and differences were detected among the treatment means ($p=0.0001$). Linearized data from washed sand were not suitable for linear regression as the data were not normally distributed ($p=0.073$) (Figure B.1C). While statistical comparisons between BVIO substrates and sand could not be made, BVIO and BVIO-amended sand removed more P than washed sand (Figure B.1C). More notably, washed BVIO also removed more P than washed BVIO-amended sand ($p=0.0001$) (Figure B.1D). Phosphorus sorption to washed BVIO and BVIO-amended sand in DI water saturated around 15 and 11 mg P/g substrate, respectively (Figure B.1 C); the calculated sorption capacities were slightly lower than these values (Table B.1).

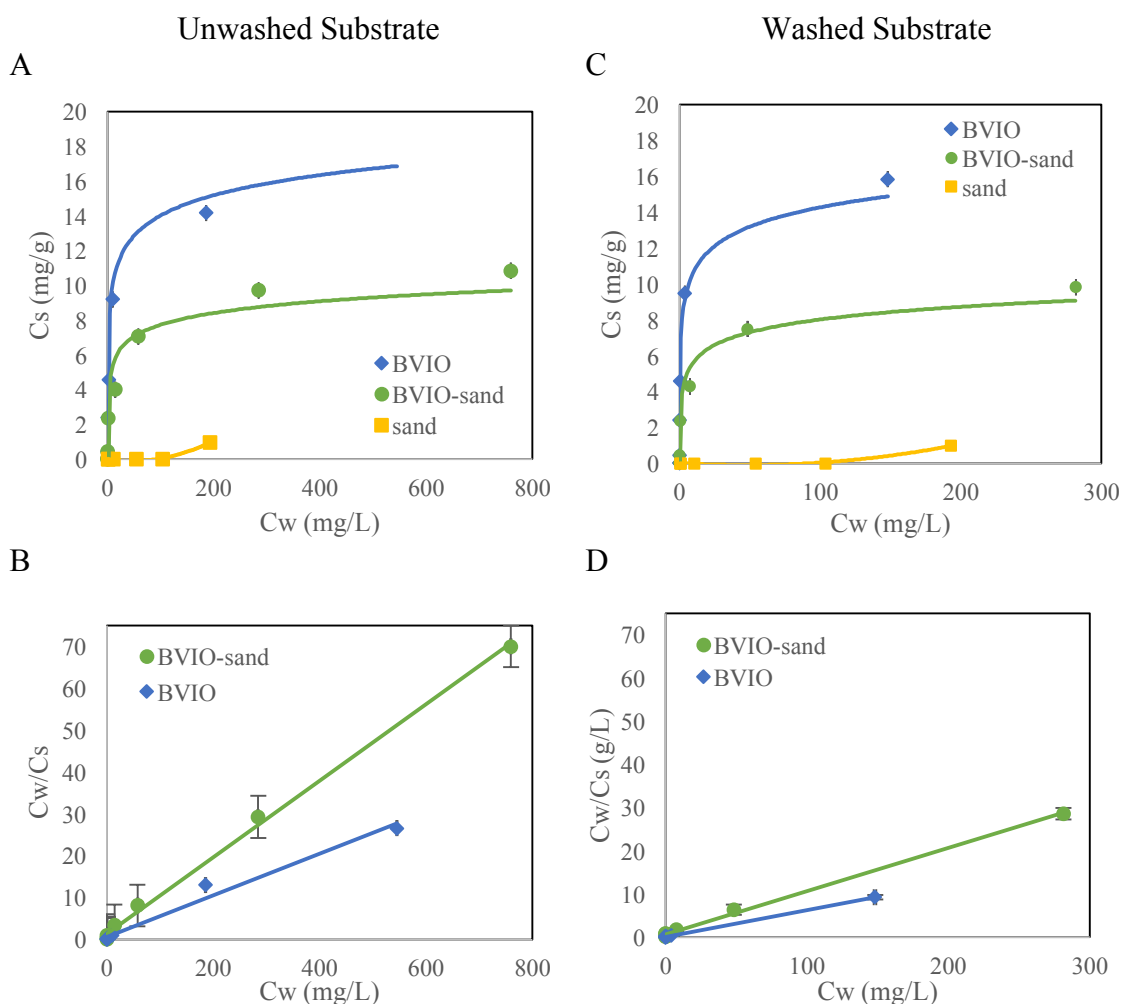


Figure B.1A-D. Phosphorus sorption capacity of unwashed (A and B) and washed (C and D) substrates in DI water. Raw data are presented in A and C. Langmuir-transformed data are presented in B and D. Each data point represents the average of three replicates and error bars represent standard error from the mean. The detection limit of P was 0.0022 mg/L.

Sorption data from unwashed and washed BVIO-amended sand were obtained using 0.5 g BVIO. When sorption data were normalized to the mass of BVIO (0.5 g), sorption capacities of unwashed BVIO-amended sand and washed BVIO-amended sand increased to 21.8 g P/g BVIO. Sorption data from unwashed and washed substrates were compared to discern effects of removal of fine particulates on P sorption capacity. Although the sorption capacity of BVIO decreased from 20.1 mg/g to 16.1 mg/g after the

substrate was rinsed with DI water (Table B.1), no differences between the slopes of the regressions from unwashed BVIO and washed BVIO ($p=0.687$) were noted, nor between the slopes from unwashed BVIO-amended sand and washed BVIO-amended sand ($p=0.56$).

Phosphorus sorption capacities of BVIO substrate in DI water vs pond water

Phosphorus sorption trends to BVIO and BVIO amended-sand in pond water were similar to those in DI water (Table B.2). Linearized data from BVIO and BVIO-amended sand in pond water were normally distributed, and BVIO removed more P than BVIO-amended sand ($p=0.001$). Linearized data from sand in pond water revealed that P did not sorb to sand in any solution of pond water after 24 hours, and the data were not suitable for linear regression (Figure B.1C). Phosphorus sorption to unwashed BVIO and BVIO-amended sand in pond water saturated around 18 mg P/g substrate and 10 mg P/g substrate, respectively; the calculated sorption capacities were slightly lower than these values (Table B.2). When normalized to the mass of BVIO (0.5 g), the sorption capacity of unwashed BVIO-amended sand in pond water increased from 11.5 to 23 mg P/g BVIO.

Table B.2. Langmuir parameters calculated using the Hanes-Woolf linearization for BVIO and BVIO-amended sand in pond water

Substrate	Regression Equation	Slope	C_{smax} (mg P/ g substrate)	K_L	R^2
BVIO	$y = 0.0498x + 1.1433$	0.0498	20.1	0.0435	0.987
BVIO-sand	$y = 0.0871x + 2.2885$	0.0871	11.5	0.038	0.992

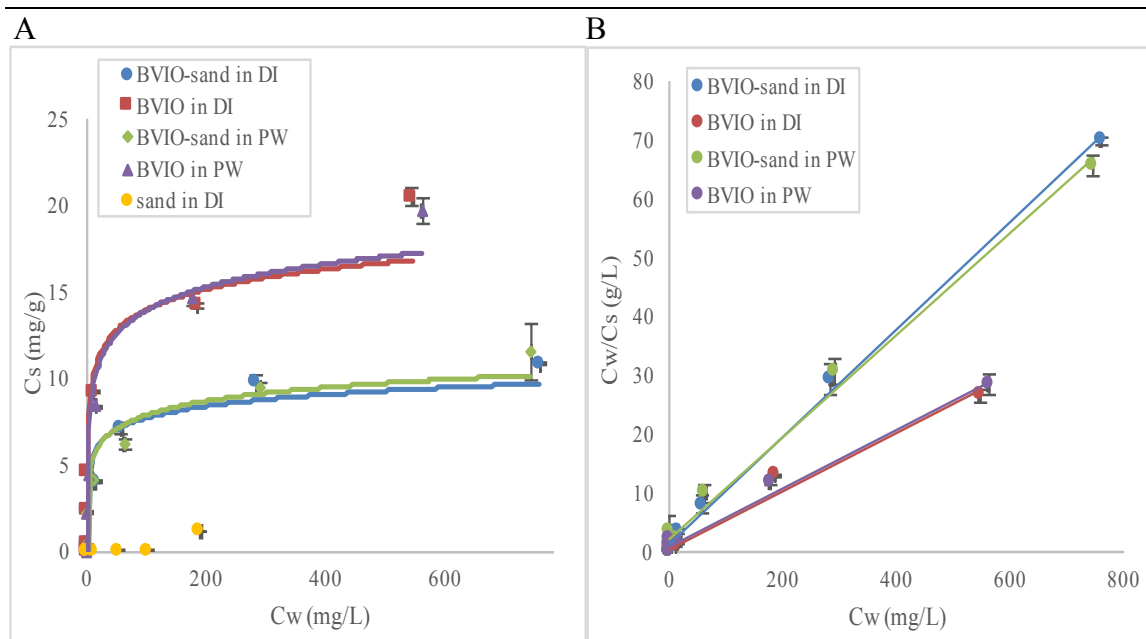


Figure B.2 A-B. Sorption capacities of unwashed substrate in pond water and deionized water. Raw sorption data are presented in A and Langmuir- transformed data are presented in B. Data were linearized using the Hanes-Woolf form of the Langmuir isotherm. Each data point represents the average of three replicates and error bars represent standard error from the mean.

Sorption data from unwashed BVIO and BVIO-amended sand in DI water were compared to unwashed BVIO and BVIO-amended sand in pond water, and no differences were found in the slopes of BVIO-amended sand ($p=0.617$); nor were there differences in the slopes of BVIO ($p=0.444$).

Discussion

Comparison of the Hanes-Woolf linearization to the nonlinear Langmuir model

Analyses of sorption data using the Hanes-Woolf linearization resulted in overestimation of the C_{smax} in each treatment. One limitation of this linearization is that it was fitted to sorption data using least squares regression, which assumes that the predictor

variable (i.e., equilibrium concentration) is error free, introducing the potential for bias. Bolster and Hornberger (2007) tested this linearization against the nonlinear Langmuir model and found they provided similar estimates of C_{smax} and K_L . The C_{smax} value calculated for each treatment in the sorption experiments using the Hanes Woolf linearization are compared to the nonlinear Langmuir estimates in Table B.3. The nonlinear Langmuir model was found to reduce the error in the predictor variable by modifying the Langmuir equation so that the true independent variable (i.e., the initial concentration of P) is used as the predictor variable (Bolster, 2016).

Table B.3. Parameter estimates from a nonlinear Langmuir model and a linearized model

Treatment	Parameter	Estimate	ApproxStd Err	Lower CL	Upper CL	Csmax (Hanes Woolf)
Unwashed BVIO-sand in DI water	C_{smax}	21.450	0.747	19.867	23.122	21.8
	K_L	0.043	0.007	0.029	0.064	
Unwashed BVIO in DI water	C_{smax}	17.762	0.775	16.113	19.454	20.1
	K_L	0.131	0.029	0.076	0.227	
Washed BVIO-sand in DI water	C_{smax}	19.086	0.867	17.175	21.146	20.1
	K_L	0.122	0.027	0.072	0.2198	
Washed BVIO in DI water	C_{smax}	15.409	0.763	13.723	17.142	16.1
	K_L	0.531	0.099	0.346	0.858	
Unwashed BVIO-sand in pond water	C_{smax}	21.657	1.164	19.019	24.845	23
	K_L	0.038	0.010	0.018	0.085	
Unwashed BVIO in pond water	C_{smax}	18.302	0.799	16.613	20.098	20.1
	K_L	0.062	0.013	0.037	0.105	

References

Bolster, C.H. 2007. A convenient spreadsheet method for fitting the nonlinear langmuir equation to sorption data. Internet Web Page.

Bolster, C.H. 2016. Microsoft Excel Spreadsheets for Fitting Sorption Data. USDA-ARS. Internet Web Page.

Bolster, C. H., & Hornberger, G. M. 2007. On the use of linearized Langmuir equations. *Soil Science Society of America Journal*, 71(6), 1796-1806.

APPENDIX C

Conceptual diagrams for methods in sorption and desorption experiments

Sorption Experiments: Chapter 2

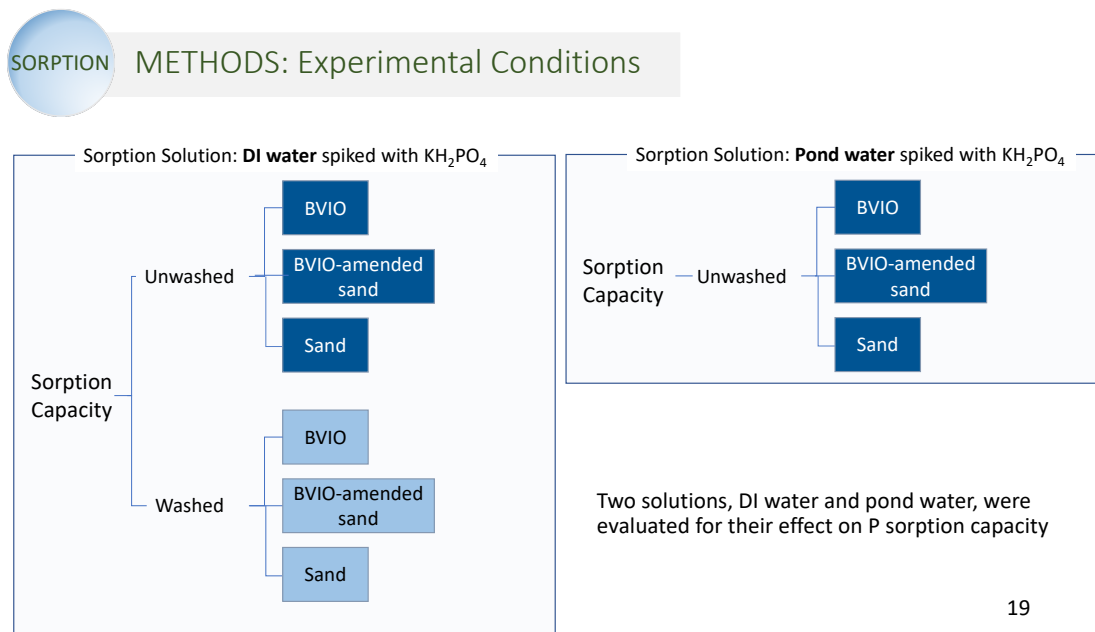


Figure C1. Conceptual diagram for comparison of treatments in sorption experiments

SORPTION METHODS: Sorption Capacity Experiments

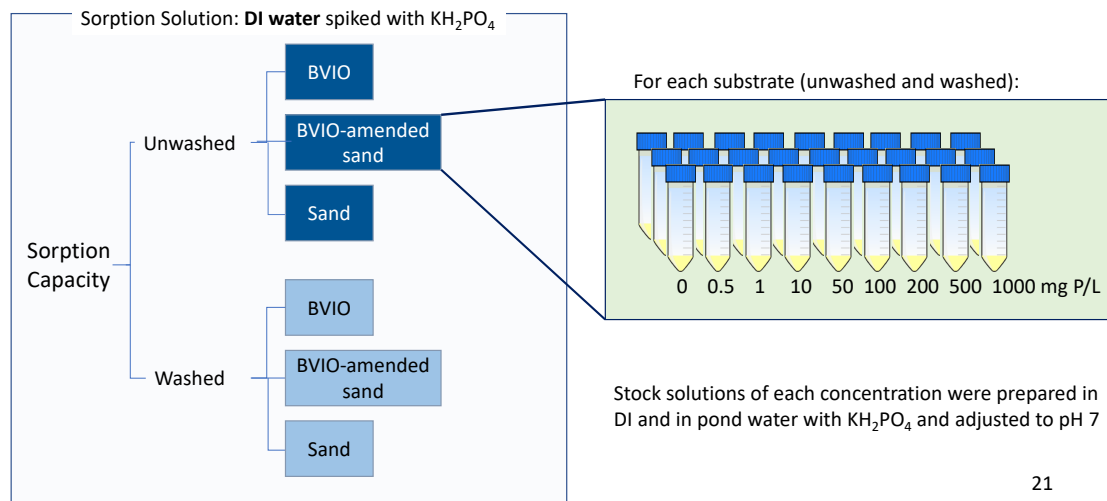


Figure C2. Conceptual diagram for exposure concentrations in sorption experiments

SORPTION METHODS: Contact Time

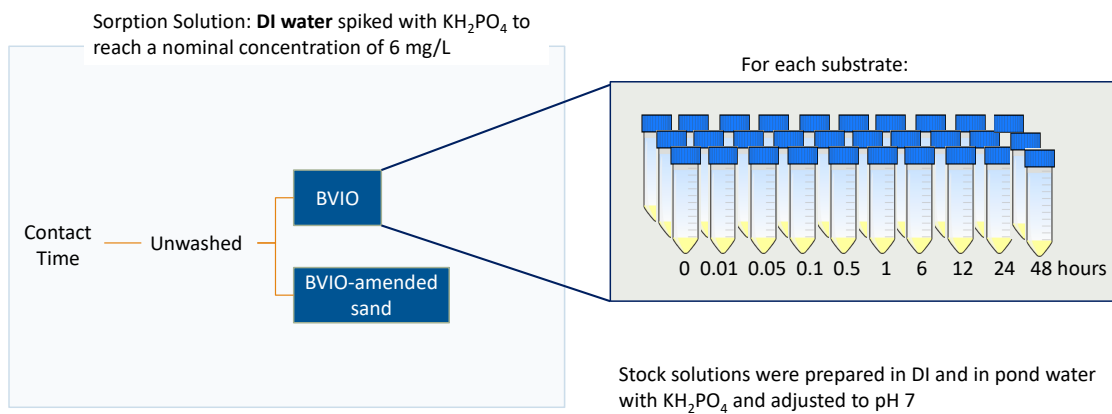


Figure C3. Conceptual diagram for contact times in sorption experiments

Desorption Experiments: Chapter 3

DESORPTION METHODS: Experimental Conditions

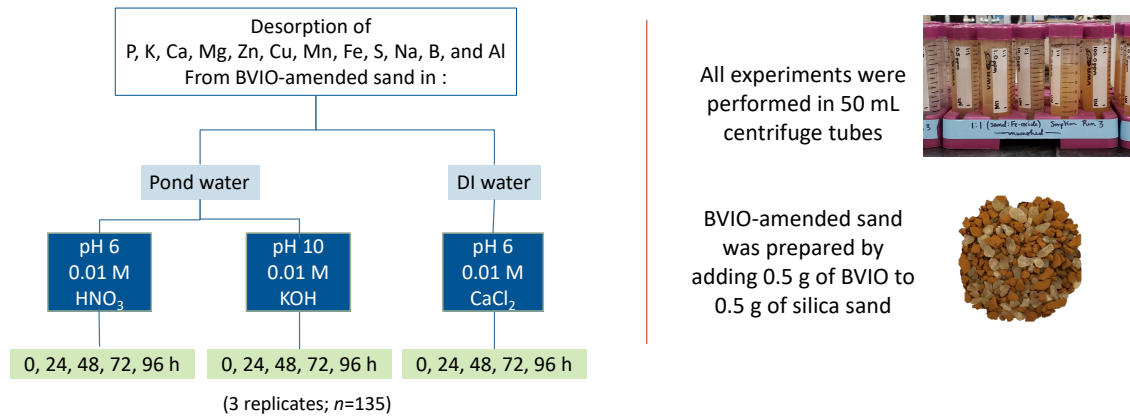


Figure C4. Conceptual diagram for comparison of treatments in desorption experiments

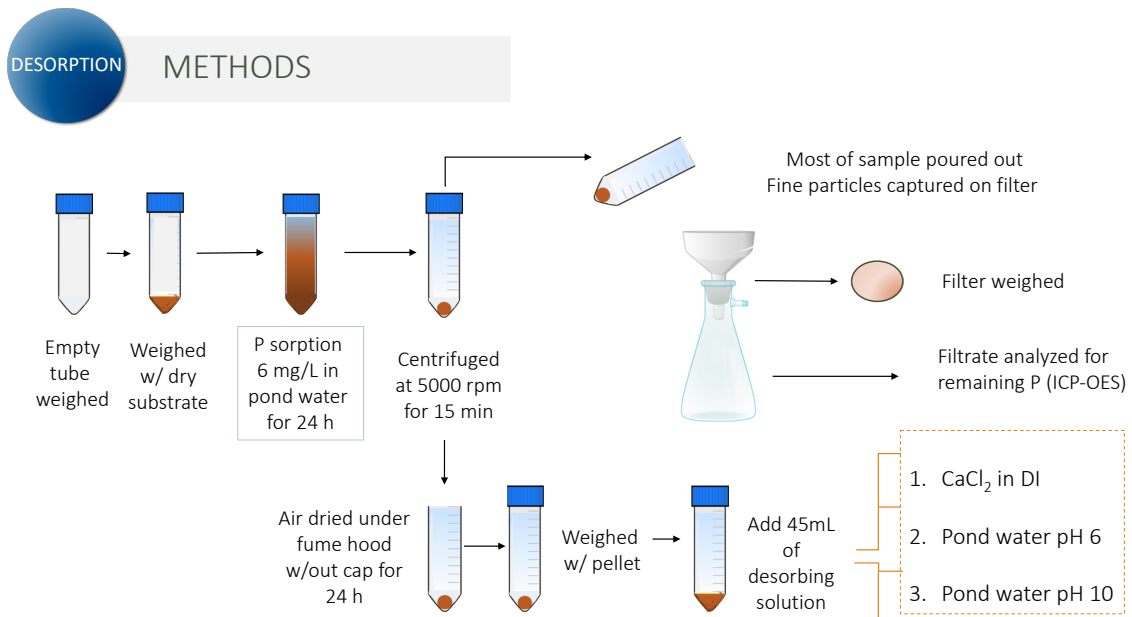
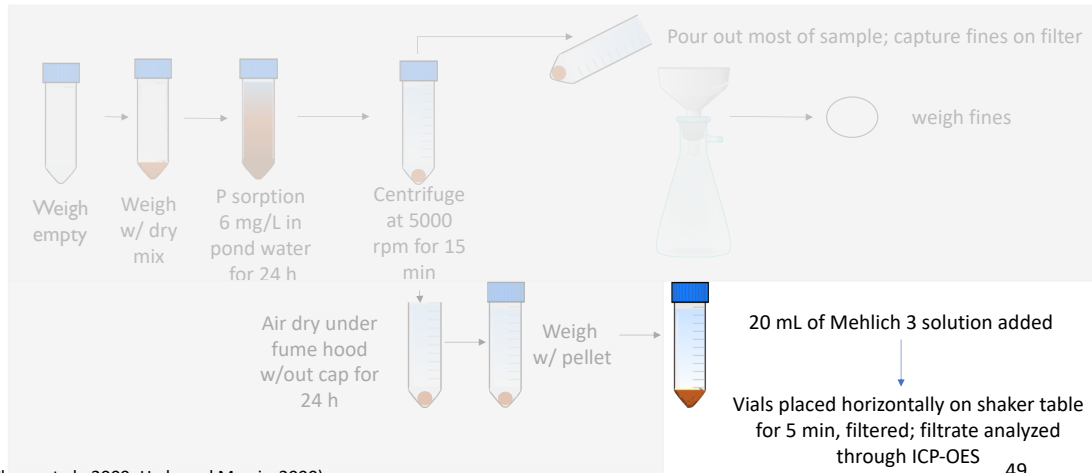


Figure C5. Conceptual diagram for methods in desorption experiments



METHODS: Plant Availability

Similar to Desorption experiment, except 2g of BVIO- amended sand used



(Zhang et al., 2009; Hyde and Morris, 2000)

Figure C6. Conceptual diagram for methods in plant availability experiments