Examining reduction of phosphorus and copper release from bioretention soil media components using phosphorus saturation ratio

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Abstract

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Bioretention is an effective means of treating urban runoff, however, organic soil components are known to export P and Cu. Drinking water treatment residuals (WTRs) are cost-effective P sorbents and may also be useful in Cu retention. To optimize bioretention soil mixtures (BSMs), predictive measures of P and Cu mobility are needed for application across a range of materials. A series of batch studies was conducted with WTRs and organics to determine the relationship between P and Cu export and soil physiochemical characteristics. Materials were incubated separately and in combination, and net release was calculated on a mass basis from the media. P release from combinations increased with increases in either phosphorus saturation index (PSI) or phosphorus saturation ratio (PSR), determined by oxalate or Mehlich 3 extraction, respectively. Variation in P release increased at higher PSI and PSR values, but decreased at low values (PSI <

0.5, PSR < 1). Keeping the PSI and PSR of BSMs low should help reduce or eliminate P release from bioretention systems and improve water quality. Other factors, including total C of media and specific surface area of WTRs, were also significant but contributed only moderately to an explanation of the variation seen. Total Cu was a predictive factor of Cu release from the combinations, however, variation in this response was high and the predictive strength of total Cu as an explanatory variable was low.

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Chapter 1. LITERATURE REVIEW

Stormwater management requires balancing multiple objectives. With aging built infrastructure further strained by continued urban growth and changing climate patterns (Archer, 2012; Trenberth, Dai, Rasmussen, & Parsons, 2003), additional capacity is greatly needed in cities like Seattle. As in many cities, Seattle's stormwater runoff into local receiving waters is regulated by the Clean Water Act through the National Pollutant Discharge Elimination System (NPDES), which requires certain actions be taken to protect receiving waters by controlling combined sewer overflow events (CSOs). Additionally, Seattle is currently under a consent decree with the United States Department of Justice, United States Environmental Protection Agency (EPA), and the Washington State Department of Ecology, which requires the reduction of CSOs in order to come into compliance with the NPDES permit and the Clean Water Act, and leverages penalties for non-compliance. While both the frequency and volume of combined sewer overflows (CSOs) have decreased over the past several years, in 2018 1,724 CSO events brought over 52,000,000 gallons of combined stormwater and sewage into local waterways (Seattle Public Utilities, 2019). This is an expensive problem with big implications for local wildlife, recreation, and human health. In areas with separated sewer systems, untreated stormwater also brings heavy metals, organic pollutants, and other harmful constituents to surface waters (Washington State Deptartment of Ecology Water Quality Program, 2012).

Bioretention, as a type of green stormwater infrastructure, represents a powerful tool for additional, cost-effective stormwater management, easily distributed throughout the urban landscape, while providing supplementary benefits from like neighborhood beautification and engagement from increased urban greenspace (Wang, Eckelman, & Zimmerman, 2013; Wendel, Downs, & Mihelcic, 2011). However, current soil specifications are not sufficient to keep bioretention systems from exporting phosphorus in effluent waters (Li & Davis, 2016), limiting their installation near sensitive receiving waters due to concerns about eutrophication (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017). This constrains the use of bioretention to its full extent across the urban landscape. By learning to control phosphorus export from bioretention soil, the use of bioretention can be expanded to help meet stormwater challenges.

1.1 STORMWATER

Rain falling on a landscape interacts with the surfaces it contacts as it makes its way to rejoin surface waters. In an undisturbed forest, most of the water that falls as rain is either intercepted by vegetation and re-released to the atmosphere through transpiration, or infiltrates into soil to recharge groundwater. The small proportion that remains flows over the surface of the ground as runoff. In an urban system, where impervious surfaces dominate, there is less vegetation, and access to soil and groundwater is largely impeded, surface runoff is greatly increased. As this runoff flows over roofs and asphalt roads, it picks up contaminants and carries them to local waterways. To reduce contamination of local rivers and lakes and prevent flooding during heavy storms, municipalities rely on a combination of techniques to manage stormwater. Traditional built infrastructure, referred to as “gray” systems, include storm drains, sewers, and treatment plants. Separated systems (called municipal separated sewer systems, or MS4) divert stormwater directly to local waterways, while combined sewer systems (CSS) treat stormwater and municipal wastewater together (Wang et al., 2013). To deal with the rising need for managing more water to increasingly stringent water quality standards, cities have been turning to “green” stormwater infrastructure (GSI), which uses an engineered approach to mimic natural water filtration mechanisms in order to minimize runoff, reduce peak flows, and improve water quality, and can bring additional benefits to the urban landscape (Wang et al., 2013). These systems work to allow rapid infiltration and contaminant removal in areas that look like natural soil and plant systems. However, the success of GSI depends on a complex balance of design features, which include infiltration rates, specialized soil, plants, and maintenance considerations, to get the job done.

In Western Washington state, the top stormwater pollutants of concern for are suspended solids; metals including copper, lead, and zinc; nutrients including nitrogen and phosphorus; certain bacteria and viruses; and organic contaminants like petroleum hydrocarbons and pesticides (Washington State Deptartment of Ecology Water Quality Program, 2012). In order to improve water quality, these are the stormwater constituents that bioretention systems need to address. Although bioretention has been shown to be an effective and important component of stormwater control in an urban landscape, field and lab studies of these systems have reported wide variation in several performance metrics. Total suspended solids (TSS) are generally considered to be well treated by bioretention systems of varying design, with retention rates frequently cited around 90% (Allen P. Davis, Hunt, Traver, & Clar, 2009; Hatt, Fletcher, & Deletic, 2009). Mean TSS removal across a range of field conditions was 94% (range of 89-99%) in one study, independent of storm size (Shrestha, Hurley, & Wemple, 2018), and >95% in another (Bratieres, Fletcher, Deletic, & Zinger, 2008). However, retention as low as 54 and 59% has also been reported (Allen P. Davis et al., 2009). Jay et al. (Jay, Brown, Tyler-Plog, Brown, & Grothkopp, 2018) found effluent from the first leachings of a new sand-only column to have higher turbidity, a proxy measurement for TSS, than influent stormwater, but turbidity had leveled off to the influent concentration by the 12th leaching. Columns in the same study amended with a range of organics and residual solids from drinking water treatment (water treatment residuals, or WTRs) leached effluent with a range of turbidity, mostly exhibiting retention while a few were statistically similar to influent. Brown et al. (S. Brown, Corfman, Mendrey, Kurtz, & Grothkopp, 2016) found that varying organic matter used in BSM columns did not impact turbidity, but that turbidity was lowest in columns that included WTRs, which makes sense due to their original purpose in removing particulates from drinking water, and that turbidity from all columns decreased over time. Different bioretention soil mixtures have also been shown to remove or reduce concentrations of most metals (Bratieres et al., 2008; Hatt et al., 2009; Jay et al., 2018), and polyaromatic hydrocarbons (PAHs) (Jay et al., 2018) from influent stormwater. Another study showed removal of E. coli and fecal coliform bacteria as well (Hunt, Smith, Jadlocki, Hathaway, & Eubanks, 2008).

Despite a mostly successful track record of bioretention performance, phosphorus (P) and copper (Cu) levels in bioretention effluent remain inconsistent. Nutrient concentrations in bioretention effluent are highly variable and dependent on system configuration, especially the bioretention soil mixture (BSM) (Li & Davis, 2016). Phosphorus retention has been reported as high as 65% to as low as -240% (240% of influent concentration exported to effluent) (Hunt, Jarrett, Smith, & Sharkey, 2006). Although bioretention systems of varying design specifications typically remove 90% of influent Cu regardless of configuration (Hatt et al., 2009), wide variation in performance has also been reported, and Cu leaching from compost in the BSM to effluent has also been seen (Chahal, Shi, & Flury, 2016; Mullane et al., 2015). A study examining varying compost feedstocks at equal quantities in BSM reported retention of total Cu ranging from 4.5 to 85%, and retention of dissolved Cu from 93% to -66% (export to effluent) (Jay et al., 2018). These two elements, and predictive measures for optimizing bioretention soil specifications, are the focus of the present study.

1.1.1 *Phosphorus in stormwater*

While phosphorus is a key component of productive soil, excess concentrations can cause problems, especially when it ends up in surface waters. It is essential for plant and animal growth, but a limiting nutrient in many natural environments, including most freshwater systems. The addition of P to freshwater systems can cause rapid changes in biological productivity (Sharpley et al., 2003). Increased organic enrichment and biological productivity of aquatic systems is known as eutrophication. Many organisms will take advantage of the additional nutritional resource, but most notable are algae and bacteria, which produce explosions of biomass. The subsequent decay of that biomass depletes oxygen in aquatic systems, stressing aquatic organisms, causing problems for fisheries, recreational and industrial use, and sometimes leading to toxic algal blooms and simplified trophic structure (Schoumans, 2009; Sharpley et al., 2003; Sindelar, Brown, & Boyer, 2015). The EPA considers eutrophication to be the leading cause of impaired surface water quality (U.S. Environmental Protection Agency (US EPA), 1996). Phosphorus concentrations in lake water above 0.02 mg L^{-1} can lead to eutrophication (Sharpley et al., 2003). Urban stormwater runoff is a major vector for excess nutrients like P entering local surface waters and causing eutrophication (O'Neill & Davis, 2012a).

Controlling phosphorus levels in stormwater reaching surface waters is therefore important for protecting water quality and minimizing the risk of eutrophication. EPA reports background reference concentrations of 10.0 µg L^{-1} total P in rivers and streams in Aggregate Ecoregion II (which includes western Washington state), based on 25th percentiles (US EPA, 1996). For Level II Ecoregion II (which includes the Puget Lowlands), background reference conditions are 19.5 µg L^{-1} total P. These values represent "conditions of surface waters that are minimally impacted by human activities and protective of aquatic life and recreational uses" (p. v) and are presented as recommended criteria for water quality to avoid nutrient over-enrichment from eutrophication (United States Environmental Protection Agency, 2000).

Total phosphorus (TP) in stormwater exists in dissolved forms and particulate forms (P associated with particulates) (Li and Davis 2016). Dissolved phosphorus (DP) includes both dissolved organic phosphorus (DOP), and inorganic ortho-phosphate, also called soluble reactive phosphorus (SRP) (Lefevre et al., 2015). Particulate P (PP) is generally thought to be the larger P fraction in stormwater, about 70-80% of TP, with 20-30% dissolved P (DP), about half of which is soluble reactive P (SRP) and half dissolved organic P (DOP) (Yan, James, & Davis, 2018). However, concentrations of all forms vary widely, affected by interactions between land use, precipitation patterns, and seasonality (Pitt, Maestre, & Clary, 2018), and the dissolved fraction of P in stormwater can be much higher; up to 90% in some cases (Lefevre et al., 2015; Shrestha et al., 2018). DOP may be more difficult to treat with bioretention and requires more research (Yan, James, & Davis, 2017). A range of P in stormwater is shown in Table 1.1.

Table 1.1. Common concentrations of phosphorus in stormwater (adapted from Shrestha et al. (2018) with additional data).

Watershed Land use	Reference	Region	Stormwater input concentrations (mg L^{-1})		
			Ortho-P	DP	TP
Roadway	Shrestha et al. (2018) (mean, median)	Vermont	0.139, 0.105		0.256, 0.214
Mixed land use	Pitt, Maestre, & Morquecho (2004) (median)	Nationwide		0.13	0.27
Municipal parking lot	Hunt et al. (2008)	North Carolina	nm*		0.19
Shopping center (G1 cell)	Hunt et al. (2008)	New York	0.05		0.11
Urban catchments with mixed land use	Ippolito (2015)	Boise, Idaho	nm*	0.19	nm*
Major urban highway	Jay et al. (2018)	Seattle, Washington	nm*	0.04	0.08

* constituent not measured

1.1.2 *Copper in stormwater*

Copper (Cu) is another essential nutrient which can cause environmental damage in excess quantities. It is a micronutrient needed for animal and plant growth, and is naturally present in all soil in the range of 5-50 mg Cu kg^{-1} as a result of weathering of primary and secondary minerals (Mengel, Kirkby, Kosegarten, & Appel, 2001). In agricultural soils in the US, the average soil Cu concentration is 18.5 mg Cu kg^{-1} (Holmgren, Meyer, Chaney, & Daniels, 1993). It is present in soil pore water in very low concentrations, usually in the range of (0.64 to 38 μg m^{-3}), depending on soil properties that control its mobility, including pH, organic material, and metal oxides (Mengel et al., 2001).

Copper is also a common constituents of urban stormwater runoff as a result of anthropogenic activities and have negative effects on aquatic ecosystems (Paus, Morgan, Gulliver, & Hozalski, 2014; United States Environmental Protection Agency, 2000). Copper in stormwater primarily come from motor vehicles, specifically wear on parts like brake pads and tires, as well as Cu-coated roofs and industrial and manufacturing sources (Lefevre et al., 2015). These elements can also be associated with soil particles.

Median concentrations of total Cu in stormwater nationally have been reported at 16 μg L^{-1}, with dissolved Cu concentrations at 8.0 μg L^{-1}. These values vary by land use, ranging from 12 to 22 μg L^{-1} median concentration of total copper from residential and industrial landcover, respectively, and from 5.5 to 10 μg L^{-1} median concentration of dissolved copper from mixed residential and mixed commercial (Pitt et al., 2004). “First flush” concentrations of metals in roof runoff (in this case the first rain after a week or more of dry weather) can range from 11 to 166 μg L^{-1} total copper and from 2 to 128 μg L^{-1} dissolved copper, depending on roofing material. The high end of that range was reported from tar-covered roofs (Good, 1993). In a survey of NPDES permit holders, 66% of stormwater monitoring samples exceeded the 4.7 μg L^{-1} limit set by the EPA as the acute ambient water quality criteria for aquatic life (Maestre and Pitt 2005, LeFevre 2015). Stormwater collected from a major urban highway in the Seattle area showed Cu concentrations higher than the reported national average: total Cu ranging from 18 to 77 μg L^{-1} with a mean of 39.8 ± 19.1 μg L^{-1}, and dissolved Cu ranging from 9.6 to 25 μg L^{-1} with a mean of 18.2 ± 7.2 μg L^{-1} (Jay et al., 2018).

Even very low concentrations of Cu can cause toxicity in aquatic systems. In plant tissues, >50 mg kg^{-1} can negatively impact many biochemical and physiological processes, reduce nitrogen metabolism, and reduce overall growth (Brady & Weil, 2008). In animals it is a neurotoxin, lethal to fish and other wildlife. Even concentrations as low as 5 μg L^{-1} in surrounding water causes loss of sensory function in salmon that can directly or indirectly lead to death (McIntyre, Baldwin, Meador, & Scholz, 2008). Copper speciation is an important factor in environmental toxicity, as free ionic Cu (Cu^{+2}) is the most toxic to fish even at very low concentrations, while Cu complexed with DOM has been shown to be much less harmful (McIntyre et al., 2008). Copper is of particular interest in the Puget Sound region because of its negative impact on salmon, even at sub-lethal concentrations, and the fact that conventional stormwater treatment may not be adequately addressing Cu (Hinman, 2009).

1.1.3 *Climate change exacerbates stormwater issues*

While population and human development impact the physical landscape of the region, changing global climate patterns are bringing more changes in precipitation that further intensify demands on our stormwater infrastructure. At the global level, total atmospheric moisture, a factor of temperature, has already been increasing since the 1970s (Trenberth et al., 2003). The distribution of that precipitation varies widely, however in general, areas of the globe that are currently relatively wet are expected to get even wetter, and areas that are currently dry are expected to get drier (Archer, 2012). A historically wet, coastal, mid-latitude location like Western Washington lines up multiple factors all predicting increased annual precipitation (Allen & Ingram, 2002; Archer, 2012), and climate change-induced shifts in midlatitude and North Pacific storm tracks are expected to bring more precipitation to the Pacific Northwest in particular (Salathe, 2006).

In addition to overall precipitation increases, the additional heat energy in atmospheric water vapor and higher sea-surface temperatures will drive more storms, meaning that individual precipitation events will also be more extreme than we have seen in the recent past, with fewer, but more intense events (Archer, 2012; Trenberth et al., 2003), and a corresponding decrease in summer rainfall, by as much as 14% to 40%, depending on models used (Mote & Salathe, 2010). Further exacerbating changing intensity, warming temperatures cause more precipitation that would previously have fallen in the Pacific Northwest as snow to turn to rain (Mote & Salathe, 2010; Salathe, 2006; Trenberth et al., 2003). Rather than snow building up over a season and replenishing rivers with melt in spring and early summer, groundwater and surface water recharge happen immediately with each rain event. Combined with greater intensity of precipitation events overall, hydrographs of rivers are subsequently "flashier:" having sharper oscillations between higher highs and lower lows (Trenberth et al., 2003). Changes in snowfall and snowpack are pronounced in the Pacific Northwest since the cold season coincides with most of the annual precipitation. These trends point to more water hitting our region in shorter periods of time over the next hundred years. Although the Pacific Northwest is famous for its rain, that rain has typically come in a slow, steady drizzle throughout the winter – or at least in the time since we've built most of our gray stormwater infrastructure.

Flood risk in the Pacific Northwest is expected to intensify as soon as 2040-2069 for two primary reasons: more extreme and earlier storms, and snow shifting to rain with increasing temperatures (Salathe et al., 2014). In urban areas, where a significant amount of paved ground surfaces funnel rainfall into storm drains and a smaller area of natural vegetation, changes in distribution and timing of precipitation are amplified. And in rapidly growing urban centers like Seattle, where paved surfaces and precipitation patterns change concurrently, impacts are more pronounced still. In some highly urban environments with a large percentage of paved surfaces, even small storms can produce floods (Hunt et al., 2008). Managing this increase in quantity of both stormwater and pollutants entering the system will require changes to our stormwater infrastructure.

1.2 BIORETENTION

1.2.1 *General features and function*

Low impact development, an approach to landscape development aimed at stormwater management, attempts to mimic pre-development hydrologic functions at the parcel and subdivision scale to protect streams, lakes, wetlands, and other aquatic systems from negative impacts of development (Hinman, 2005). Green Stormwater Infrastructure (GSI) comprises various methods of treating urban or suburban stormwater that also mimic certain landscape features or functions that occur in nature in order to minimize runoff quantity and peak flow, improve water quality, and contribute positively to the urban landscape. GSI is typically used in combination with gray infrastructure and can increase the total stormwater treatment capacity of a city or region (Wang et al., 2013). GSI such as bioretention, vegetated roofs and permeable pavement, are considered low impact development (LID) techniques, although LID also includes other actions such as site assessment and homeowner education (Hinman, 2005) that are not considered GSI.

A bioretention system is a shallow basin or box filled with an engineered soil mix (called a bioretention soil mixture, or BSM) and specially-selected plants. An individual bioretention basin or box is referred to as a cell (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017). Shapes and sizes of bioretention systems vary, but cells are typically 0.7-1 m in depth. In the City of Seattle, the bottom area of a single bioretention cell must be at least 4 square feet (0.37 m^2) and no more than 800 square feet (74.3 m^2) and can receive and process runoff from a maximum of 5,000 square feet (465 m^2) of impervious surface. These size requirements can be exceeded if a bioretention system includes a series of multiple, connected bioretention cells. (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017).

The overall design includes an inlet for runoff entering the system, outlet for treated water called effluent (either direct connection to groundwater or an underdrain pipe, or both), and some kind of overflow mechanism (Allen P. Davis et al., 2009). Direct infiltration to groundwater without an underdrain is possible where underlying soils are porous enough to meet the minimum subgrade infiltration rate (1.5 cm hr^{-1}), and where other site conditions like steep slopes or high groundwater are not limiting. (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017). The makeup of the soil media within the bioretention system varies widely, and there is no unified standard (Allen P. Davis et al., 2009).

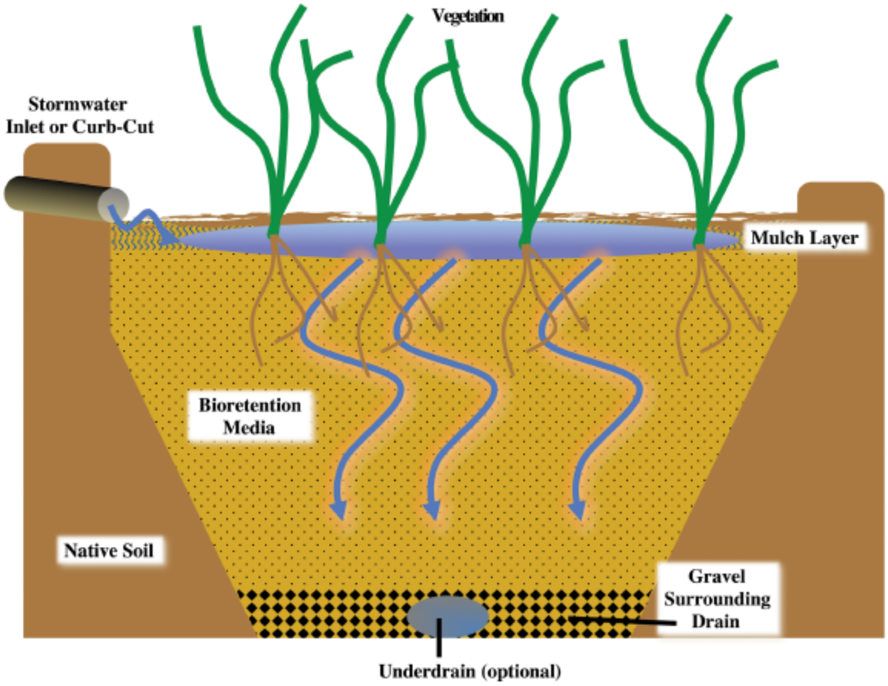


Figure 1.1. Cross section diagram of conventional bioretention cell (Lefevre et al., 2015).

Bioretention systems greatly reduce the cumulative volume of outflow by slowing influent water and allowing evaporation and evapotranspiration to occur, reducing total volume load on built infrastructure when underdrains connect to storm sewers. They also greatly reduce peak flows, important for preventing overflow events in combined sewer systems and helping to regulate the flashiness of flows to surface waters. In both Hunt et al. (2018) and Shrestha et al. (2018), outflow volume was a mean of 25% of inflow volume per storm event. This was especially pronounced in "small storms" (rainfall depth ≤1 inch, or 0.025 cm), which resulted in 100% volume retention (no effluent) within the bioretention system. Peak flow rate was reduced by a mean of 91% (86-96% range) across all storm types. Even without reduction in overall peak flow volume, delay of peak flow is also an important contribution of bioretention, as it gives built systems more time to process higher volumes of runoff. Bioretention can delay peak flows by a factor of 2 (A. P. Davis, 2008).

The lifespan of a bioretention basin depends on several variables. Retention of heavy metals from influent stormwater depends on soil specifications, especially the compost volume fraction of the BSM. Research suggests 4 years at minimum and possibly up to 19 years for retention of Cu, cadmium (Cd), and zinc (Zn) in a BSM containing at least 30% compost by volume (Paus et al., 2014). Because heavy metals are generally retained in the top few centimeters of soil, service lifetimes can be extended by removing or replacing that portion of the BSM (Feng, Hatt, McCarthy, Fletcher, & Deletic, 2012; Paus et al., 2014). Retention of P depends on release rates of organic components, retention rates of P-sorbing soil amendments, basin and catchment sizing, and influent P. Research on bioretention lifespan from a P standpoint suggests that under typical conditions, systems with correct soil specifications can easily manage both influent and internally-released P for 20 years or more (O'Neill & Davis, 2012b).

Like other GSI, bioretention systems provide interception of urban stormwater runoff, decreased pollutant discharge to local surface water and groundwater, and groundwater recharge (O'Neill & Davis, 2012a). A life cycle assessment of various GSI (bioretention, green roofs, and permeable pavement) and gray infrastructure (CSS or MS4) compared options by equivalent reductions in effluent P. The study found that bioretention basins offered phosphorus treatment equivalent to other stormwater control measures for the least dollar and carbon emission costs (see Figure 2). Bioretention basins were found to cost an estimated $98 per kg P reduction from treated stormwater, and result in emissions of 61 kg CO_2-equivalent; about 23% of the dollar cost of the same P reduction by a wastewater treatment plant (or less than 4% of the cost when capital expenses are included in the accounting) (Wang et al., 2013). This assessment assumes that bioretention systems will successfully retain P and not export it to effluent – a big assumption that is not assured by all systems with current soil specifications. In general, GSI of all kinds appear to be more robust and flexible than gray infrastructure to uncertainties and changes in future conditions, with less compromise on performance objectives regarding flooding, water quality, human health impacts, greenhouse gas emissions, and costs. A scenario combining all GSI options offered the same stormwater treatment with 75-95% lower greenhouse gas emissions than either gray infrastructure option (CSS or MS4) over the lifetime of the infrastructure, including materials, maintenance, and electricity use. GSI was also successful at reducing the incidence of combined sewer overflow (CSO) events, which occur when heavy storms cause combined sewer pipes carrying both stormwater and municipal wastewater to exceed their volume capacity and discharge excess water to nearby surface waters. However, the analysis suggested that the most realistic and robust strategy overall may be a combination of green and gray alternatives (Casal-Campos, Fu, Butler, & Moore, 2015).

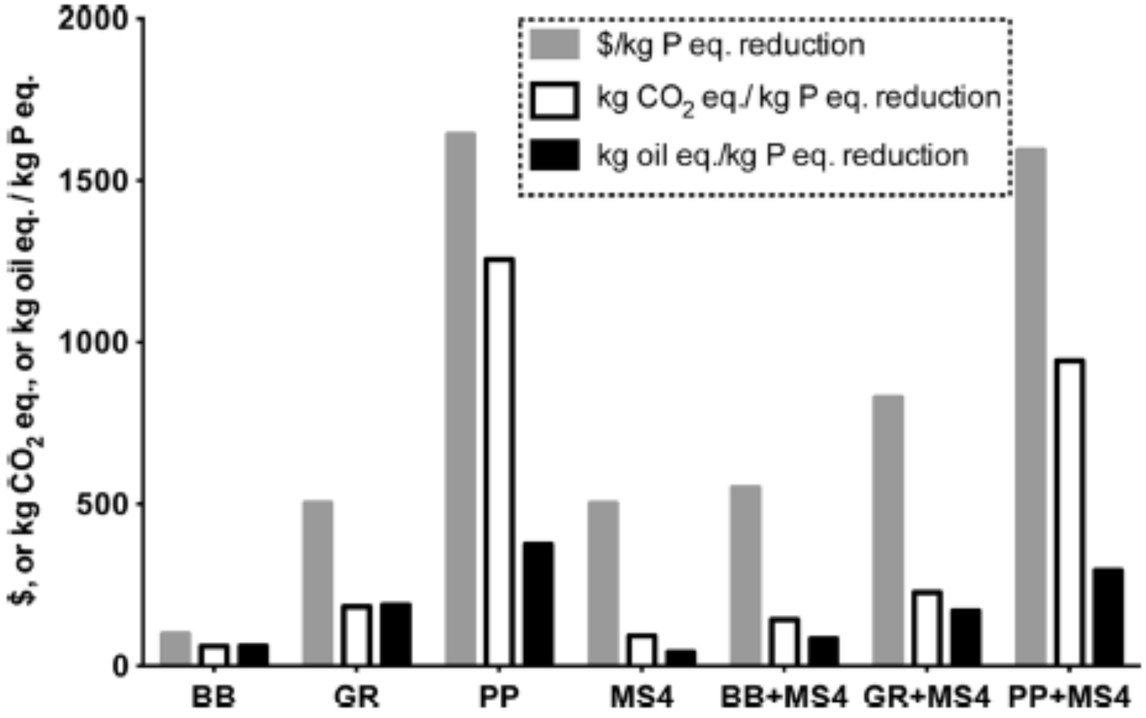


Figure 1.2. Cost-benefit ratios of water improvement: reduction of freshwater eutrophication impacts at the expense of economic costs ($/kg P eq), climate impacts (kg Co2 eq/kg P eq), and energy consumption (kg oil eq/kg P eq). From Wang et al. (2013).

Bioretention systems have become increasingly popular and are now one of the most widely-used stormwater control measures nationally and in many other countries as well. Green building design standards and the leadership in energy and environmental design (LEED) certification program consider bioretention a preferred site practice (Allen P. Davis et al., 2009).

1.2.2 *Bioretention soil mixture*

Bioretention media is generally a mixture of sand, topsoil and organic matter such as mulch, compost, or peat. Each component will have its own characteristics which it will contribute to the total BSM: infiltration, initial nutrient or contaminant content, and capacity for removal of various elements and compounds (Li & Davis, 2016). A BSM removes particulate pollutants from influent water by physical filtration and interception, and removes dissolved pollutants by biochemical and physiochemical processes. (Shrestha et al., 2018).

1.2.2.1 Mineral component

A mineral aggregate generally makes up the largest component of a BSM. Usually this is sand, although a sandy loam soil is frequently used either instead or in addition (Collins et al., 2010; A P Davis, Shokouhian, Sharma, Minani, & Winogradoff, 2003; Feng et al., 2012; Yan et al., 2017). Due to its large particle size and low specific surface area, sand does not hold water well and drains quickly (Brady & Weil, 2008). This is good for mitigating high peak flows, and generally for treating large volumes of water without requiring a large footprint (Yan et al., 2018).

However, sand particles have low surface area and low sorption capacity. Sand contains relatively few nutrients and is not very good at supporting the nutrient needs of plants (Brady & Weil, 2008). For many stormwater contaminants, including P, there is a tradeoff between removal efficiency and infiltration (Yan et al., 2018). Flow rate through the bioretention system needs to be fast enough to prevent overflow, but slow enough to allow sufficient contact time between runoff and soil particles, as the biochemical and physiochemical processes that remove dissolved pollutants are dependent on soil conditions and to some extent, retention time within soil media (Shrestha et al., 2018). However, overflow must be avoided as this leads to flooding, as well as the bypass of excess water from the treatment system. Bioretention in Seattle must have an infiltration rate sufficient to achieve a maximum surface pool drawdown time of 24 hr (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017).

The sandy loam, loamy sand, and loam soil textural classifications prevalent in early bioretention soil specifications (and still currently in use by many jurisdictions) include some clay content which influences bioretention system function (Allen P. Davis et al., 2009). Clay, due to its very small particle size (< 2 μm) and consequently high specific surface area, has a collectively large surface area available for many active processes including adsorption, catalysis, precipitation, microbial colonization, and other surface phenomena. Surface charges on clay particles consist of both permanent charges and pH-dependent charges. The negative permanent charges are the result of cation substitution in the clay mineral structure, allowing clays to readily attract cations (cation exchange capacity). Positive charges (anion exchange capacity) on clays are typically found on oxides and decrease with increasing soil pH. Highly acidic soils (especially below pH 4.4) and soils with high Fe and Al oxide content may have an overall positive charge (Brady & Weil, 2008). However, due to its high surface area, clay also has a high water holding capacity and drains slowly. Infiltration rates into clay are slow and high clay content in a BSM can cause drainage problems and possible system failure. As a result, best management practices have moved away from clay in favor of better-draining media components (Allen P. Davis et al., 2009).

1.2.2.2 Organic matter

1.2.2.2.1 Function within the BSM

Most BSMs also include some kind of organic matter, such as mulch, compost, or peat (Li & Davis, 2016). Organic matter (OM) impacts many of a soil's physical, chemical, and biological properties, and helps BSMs regulate moisture and support plant growth (Paus et al., 2014), The addition of OM from a range of organic waste sources (including food and yard waste compost, manure, and biosolids) increases soil organic carbon, nutrient content, and water holding capacity, and reduces bulk density (S. Brown & Cotton, 2010; Khaleel, Reddy, & Overcash, 1981). The impact of OM on reducing bulk density is especially pronounced in coarse-textured soil (Khaleel et al., 1981), such as the sand frequently used as the majority of a BSM.

Organic matter from a wide range of sources has also been shown to contribute to the pollutant removal capacity of the BSM (S. Brown et al., 2016; Paus et al., 2014). One study using a variety of composts from feedstocks including leaves, grass, and woody debris and excluding food waste and manure found that all composts tested exhibited over 90% retention of Cu, Cd, and Zn. Increasing the proportion of compost in a BSM otherwise composed of sand resulted in increased capacity for Cd and Zn and longer service lifetimes until a 10% breakthrough of either metal was observed, estimated at a minimum of 2 years with 10% CVF and increasing up to 41 years for Zn and 84 years for Cd with 50% CVF. A breakthrough for Cu was never observed over 1,000 pore volumes of synthetic stormwater containing 1.0 mg L^{-1} Cu, even in the treatment with the smallest compost fraction (10% by volume), however, increased compost fraction further decreased effluent Cu concentrations (Paus et al., 2014). Another study using BSMs with a variety of organics including biosolids with and without iron addition, and composts derived from food waste, yard waste, and biosolids, found that all treatments removed Cu and Zn, with varying efficiency. In the same study, BSMs containing food and yard waste compost also removed 61% or more of influent PAHs, and BSMs containing biosolids and yard waste compost achieved 99% removal of PAHs (Jay, Brown, Kurtz, & Grothkopp, 2017).

Compared to larger-sized media such as sand, the higher surface area of small organic particles offers the potential for better sorption of influent pollutants, as well as functional groups like carboxyls and phenolics that can form complexes with metal cations (Paus et al., 2014). These small particles, present in compost, should also increase physical filtration of particulate pollutants (Paus et al., 2014). However, particle loading from a larger number of small particles in the BSM poses two potential risks to overall bioretention function: clogging, and hydraulic failure. The optimum compost content in bioretention systems must balance infiltration rates and system bed lifetimes with particle capture and pollutant removal efficiency. There is some evidence that increasing the compost fraction of a BSM decreases hydraulic conductivity; however, even at 50% compost fraction (50% sand), infiltration was still 37 cm hr^{-1}, well above required rates (Paus et al., 2014). Other research is mixed on the effect of compost amendment on soil infiltration rates, showing decreased infiltration in some locations, and increases in others, possibly due to decreased bulk density of amended soil (S. Brown & Cotton, 2010). A review of organic waste addition and its impact on agricultural soil physical properties noted increased hydraulic conductivity resulting from increased porosity in soils with added OM, despite the increased water holding capacity. The magnitude of change was variable and depended on soil texture, but was always positive (Khaleel et al., 1981). The size of compost particles may impact infiltration, with very fine particles playing a role more similar to clay.

1.2.2.2.2 Design specifications

Like other aspects of the BSM, compost and other organic components vary widely, and specifications for sources and chemical composition are inconsistent and often not given at all (Hurley, Shrestha, & Cording, 2017). Frequently the organic component is compost, which can range from 10-50% of a BSM by volume, a huge variation which impacts system performance (Paus et al., 2014).

Currently, bioretention design standards vary widely in the amount of OM recommended or required and leave room for a large amount of variation in feedstocks. Seattle specifications require that at least 65% (by volume) of the compost component in a BSM must come from recycled plant waste, such as yard waste and crop residue. Post-consumer food waste can be up to 35% (by volume) of the recycled plant waste content but must be at least 10% of the total compost content. Compost from biosolids or manure feedstocks are not allowed (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017). This means that the post-consumer component of the total BSM can range from as little as 2.3% to as much as 14%, and yard waste and crop residue, which can vary greatly in nutrient content, can be used interchangeably.

Compost for bioretention can come from a wide variety of feedstocks, including grass, leaves, and woody debris (Paus et al., 2014), food waste (pre- and post-consumer), yard waste, livestock bedding, wood chips, and manure from various animals (Hurley et al., 2017). Some municipalities regulate feedstocks allowable for use in bioretention. Municipal biosolids are generally not permitted in bioretention soil although they have been studied as a bioretention soil amendment (S. Brown et al., 2016; Jay et al., 2017, 2018). Biosolids may or may not include additives, such as Fe, added during the wastewater treatment process to reduce P, which could also be beneficial in a BSM (Jay et al., 2017). Regardless of feedstock, compost can be the result of either thermophilic or vermicomposting processes, and of varying age, which may also affect their performance in a BSM (Paus et al., 2014).

City of Seattle Standard Specification for bioretention soil is a well-blended, homogenous mixture of 35-40% fine compost to 60-65% mineral aggregate, by volume. The compost must contain a minimum of 40% organic matter content by dry weight (according to loss-on-ignition) and meet certain requirements for maturity and stability. The C:N ratio of compost used must be less than 25:1, determined by total carbon and total Kjeldhal nitrogen. If all plants are native species, the C:N ratio of the compost can be up to 35:1, under the assumption that hardier native plants have lower fertilizer needs (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017).

1.2.2.2.3 Leaching of Phosphorus

Organic soil amendments also have the capacity to leach certain elements into water; nitrogen, phosphorus, and copper being a substantial concern (Mullane et al., 2015). Total nutrient and metal concentrations in composts are typically higher than in sand (Paus et al., 2014). For example, total P and N concentrations in composts are typically greater than 2,500 and 10,000 mg kg^{-1}, respectively (Basta et al., 2015; Mullane et al., 2015). Nutrient export from bioretention systems is widely recognized to be caused by initial levels of phosphorus in the BSM and its release during the breakdown of organic material such as compost and mulch (Bratieres et al., 2008; Hunt et al., 2006; Hurley et al., 2017; Li & Davis, 2016; Mcphillips, Goodale, & Walter, 2018; Paus et al., 2014; Shrestha et al., 2018). Stable nutrient pools in the organic matter are converted by microbial activity to more soluble forms which can be transported down through the soil profile in subsequent high flow storm events (Shrestha et al., 2018).

Effluent P concentrations from bioretention soil leaching can exceed influent concentrations by an order of magnitude or more (Chahal et al., 2016; Mcphillips et al., 2018; Paus et al., 2014). The general pattern seen is an initial spike in the first one or two storm events, followed by a steady but slow decline in each subsequent event (S. Brown et al., 2016; Chahal et al., 2016; Jay et al., 2017; Mullane et al., 2015). Effluent from one column study with a BSM typical of that used in the Pacific Northwest (60:40 mix of sand to compost by volume; the compost being about 80% yard waste feedstock and 20% food waste) contained total P in excess of 40 mg L^{-1} during the first simulated rainstorm with new compost. After 7 consecutive heavy storms, P leaching had significantly reduced, but never fell below 5-6 mg L^{-1} (Chahal et al., 2016). In another column study with a BSM also intended to match typical Seattle area specifications (60:40 sand to food and yard waste compost) and using similar rainfall intensity and assumptions for catchment area, effluent total P concentration was much lower, <6 mg L^{-1} initially, decreasing over 12 successive heavy storm events but never going below a minimum of 1.48 mg L^{-1} (Jay et al., 2018). In these column studies, dissolved P in the form of bioavailable ortho-phosphate made up the majority of total effluent P in compost leachate, 73-90% was measured by Chahal et al. (2016) and effluent from the corresponding Jay et al. (2017) treatment also fell within that range.

The mass of P leaching from compost from various leaf and wood chip feedstocks has been measured as high as 203 ± 24 mg P kg^{-1} compost (Paus et al., 2014). Food and yard waste compost in the Mullane et al. (2015) study leached an average of 7.73 – 8.87 % of its initial total P over the course of 18 heavy storms. A sandy loam column that had been performing at 83% PO_4^{3}- removal without the organic addition became a net P source to effluent following the addition of 10% compost and 10% wood mulch (Bratieres et al., 2008).

Because of the widespread problem of nutrient leaching, some jurisdictions have called for restrictions on organic material in bioretention systems, but there is no consensus on criteria. One soil specification requires that organic material make up only 3% of a total BSM (Allen P. Davis et al., 2009), while another recommends that total P content of bioretention soil be either 30 mg P kg^{-1} of BSM or less, contain less than 5% OM, or include P-sorbing amendments like Fe, in order to reduce P loads to receiving waters (Minnesota Pollution Control Agency, 2018). Some researchers even recommend a sandy loam BSM with no further added organic matter at all (Bratieres et al., 2008). However, design specifications are not necessarily based on science or tied to performance. Many jurisdictions borrow or adapt guidelines from other agencies without a good understanding of their limitations or modifications for local conditions, and out-of-date information is often used (Allen P. Davis et al., 2009). Although P leaching has been shown to be correlated with particular chemical content of soil components used (Hunt et al., 2006; Jay et al., 2017; Mcphillips et al., 2018), many bioretention specifications continue to call for minimum or maximum organic content by weight or volume, regardless of initial nutrient content.

Given the wide variation in sources and nutrient content, it makes sense that not all composts are equal when it comes to nutrient leaching. However, to date there are no clear means of predicting P leaching potential based on total P concentrations in composts and BSM and the total P concentrations of different organic materials varies widely (S. Brown et al., 2016; Hurley et al., 2017; Jay et al., 2017). Brown et al. (2016) found that, when controlling for total Al, Fe, and P in BSM from different feedstocks, feedstock was not a significant factor in P export. Testing BSM columns containing composts from different feedstocks in equal and varying amounts, Jay et al. (2018) found that P export was correlated with relative available fractions of Fe, Al and P rather than total P.

1.2.2.2.4 Leaching of Copper

Organic material may also leach metals, including copper. A batch study using compost from leaves, grass, and woody debris reported 0.10 mg Cu leached kg^{-1} compost (Paus et al., 2014). This amount accounted for less than 0.4% of the compost's total Cu content, indicating that the large majority of the Cu present was fixed in the compost, not bioavailable or likely to leach (Paus et al., 2014). The Mullane et al. (2015) study using compost feedstocks more typical of the Pacific Northwest (a mix of yard and food waste) reported leached Cu accounting for 1-3% of initial total copper content of the compost. These are relatively small amounts of the total copper content but can contribute to effluent Cu concentrations above acceptable levels for environmental health.

Another study testing different compost feedstocks and amounts found that all soil treatments tested were sinks for total Cu. However, 3 out of 14 treatments were a net source of dissolved Cu to effluent water, while the rest were sinks, and there was a wide range of total Cu content in composts themselves (from 11.6 – 180 mg kg^{-1}), suggesting that all compost is also not equal in terms of Cu performance (Jay et al., 2018).

Like P, Cu tends to be released from new compost in an initial spike followed by a gradual decline (Chahal et al., 2016; Mullane et al., 2015). Leaching from compost alone remained high for the first 5 or 6 storm events in one study, then dropped to a much lower level but that still remained significant even after 18 successive simulated storm events each equivalent to the heaviest 24-hour storm seen in a 6-month period in the Seattle-Tacoma region (Mullane et al., 2015). A compost-amended BSM leached Cu for the first 4-6 simulated storm events and became a sink for subsequent events, however effluent Cu concentrations remained above 20 μg L^{-1}, which is higher than the 14 μg L^{-1} benchmark in Washington State for stormwater discharge from industrial areas (Chahal et al., 2016). Most bioretention effluent Cu, whether leached from compost or remaining from influent content, is generally in a dissolved form (Chahal et al., 2016; Jay et al., 2018; Mullane et al., 2015).

Adding compost to soil can add a large and rapid flux of dissolved organic carbon (DOC) into pore water, which can affect other soil constituents, such as metals, that may be bound to organic matter (Beesley & Dickinson, 2010). Mullane et al. (2015) and Chahal et al. (2016) reported pulses of DOC from compost alone and compost-amended BSM with each of subsequent storm events, peaking in the first few and decreasing thereafter as seen with other leached constituents. Although both studies observed Cu export from fresh, mature compost, all or nearly all effluent Cu was complexed with dissolved organic matter (DOM) (Chahal et al., 2016), which is much less toxic to fish and other aquatic organisms than the free ionic form (Cu^{+2}) (McIntyre et al., 2008).

1.2.2.3 Nutrient-control amendments and water treatment residuals

As concerns about nutrient leaching from bioretention systems gain attention, other materials may be considered for inclusion in the BSM to aid in nutrient retention and sorption of other pollutants. Such materials, with high surface area for increased adsorption and/or high chemical affinity for P, include blast furnace vermiculite, perlite, slag, fly ash, iron-amended sand, alum and partially hydrolyzed aluminum, or residuals from drinking water treatment (Feng et al., 2012; Li, Liang, Li, Li, & Jiang, 2018; Paus et al., 2014; Yan et al., 2018). Of these, the last presents a low-cost opportunity to create a beneficial use for what is otherwise a waste product.

Al salts (alum, [$Al_2(SO_4)_3$ x $14H_20$]) and Fe salts (ferric chloride, $FeCl_3$, and ferric sulfate, $Fe_2(SO_4)_3$) are used in drinking water treatment as coagulants in the sedimentation-flocculation process, producing residual solids in large quantities (Elliott, O’Connor, Lu, & Brinton, 2002; Ippolito, 2015). These solids, known as drinking water treatment residuals, or WTRs, are composed of sediment from the initial drinking water source influent, and coagulant hydroxide precipitate. Depending on the primary coagulant used, the residual material is typically characterized as either Al-WTR or Fe-WTR. When lime is used in drinking water treatment for hardness removal, a third type, Ca-WTR is produced. It has potential for use in beneficial P retention, although it produces a soil suspension with higher pH than when Al or Fe-WTRs are used. As in calcareous soils, the primary P-removal mechanism of Ca from Ca-WTR is co-precipitation, not adsorption (Elliott, O'Connor, Lu, et al., 2002).

Despite being a waste product of drinking water treatment, this material retains a large capacity to adsorb phosphorus and many pollutants from water, and can be readily and cheaply obtained, avoiding landfill disposal (Agyin-Birikorang, O'Connor, Jacobs, Makris, & Brinton, 2007). As population growth and increased drinking water treatment standards result in an increase of coagulant use in drinking water treatment, WTRs will only become more readily available and the demand for beneficial use and landfill diversion higher (Ippolito, Barbarick, & Elliott, 2011). Because of the nature of WTR production, the quality of source water is an important concern. Before they are used in any land application, potential toxicity issues stemming from source water constituents need to be considered, as these can sometimes end up in WTRs (Ippolito et al., 2011). In regions fortunate enough to have high-quality source drinking water without persistent harmful contaminants, this should not be prohibitive to WTR use in bioretention.

Many studies have tested WTR sorption under a wide range of conditions, with a wide range of results, from 700 – 37,000 mg sorbed P kg^{-1} WTR (Elliott, O'Connor, Lu, et al., 2002; Ippolito et al., 2011). They are capable of strongly sorbing both inorganic soluble reactive phosphorus (SRP) and dissolved organic phosphorus (DOP) (Yan et al., 2017). Use of WTR as a soil amendment to reduce P leaching was first done in the agricultural sector (Agyin-Birikorang et al., 2007; Elliott, O'Connor, Lu, et al., 2002). The success of that work led to similar research focused specifically on stormwater control measures (Li & Davis, 2016; Lucas & Greenway, 2008; O'Neill & Davis, 2012b, 2012a).

1.2.2.4 Plants

Plants are an integral component of bioretention systems as they improve the appearance of these systems and also impact their function. Plants used in bioretention systems need to be adapted to local climatic conditions and the stress of alternating wet and dry periods (City of Seattle Department of Construction & Inspections & Seattle Public Utilities, 2017). Vegetation helps maintain hydraulic capacity of the bioretention system, and cycles of root growth and senescence can help prevent compaction and clogging of the BSM (Hatt et al., 2009). Greater root density is correlated with reduced peak flow rate, which may be due to roots slowing infiltration rates (Shrestha et al., 2018). However, other research shows increased infiltration rates from plant growth, due to roots and root channels creating flow paths within the BSM (Ippolito, 2015), and increasing treatment efficiency by maintaining soil porosity (Bratieres et al., 2008).

Plant growth and uptake of nutrients reduces nutrient concentrations in bioretention effluent (Shrestha et al., 2018), possibly by as much as 50% (Ippolito, 2015). While P uptake by bioretention plants represents a very small portion of overall potential removal, the presence of mature vegetation and a well-developed rhizosphere greatly enhances the BSM's capacity for sorption. In addition to what can be attributed directly to plant uptake, a well-developed rhizosphere may facilitate interactions between plants, fungi, microrganisms, and soil media that aid further P removal (Lucas & Greenway, 2008).

1.2.3 *Research on BSMs*

Research on BSM and soil components include lab studies at various scales, or field studies of full-scale bioretention systems, to test the movement of various constituents between influent, soil, and effluent water. Column and mesocosm studies construct soil profiles of varying specifications through which to run influent water: small-scale versions of field conditions. Batched assays test even smaller amounts of specific soil components in tubes, cups, or bottles, incubated with controlled solutions. In all cases, studies attempt to determine the potential for various components and design features to contribute to optimal bioretention performance, and to link performance to various measurable physical, chemical, and biological characteristics.

Many studies use synthetic solutions that recreate concentrations of contaminants similar to those seen in actual stormwater (Jay et al., 2017; O'Neill & Davis, 2012a, 2012b), or use stormwater collected from roads or other areas to more closely reflect real-world conditions (Chahal et al., 2016; Hatt et al., 2009; Jay et al., 2018). Others spike solutions with heightened levels of nutrients or pollutants to test extreme conditions, or to determine the upper limit of a soil or amendments' ability to remove contaminants from water over a longer timeline. Paus et al. (2014) used concentrations of Cd, Cu, and Zn at 1.0 mg L^{-1} of each metal to try to find breakthrough over the course of 1,000 pore volumes of solution. Batch studies creating sorption isotherms of media response over a range of conditions use higher concentrations, such as when testing WTR's P sorption capacity. Yan (Yan, Davis, F.ASCE, & James, 2016) and O'Neill and Davis (O'Neill & Davis, 2012a) used P solutions up to 2.0 and 9.0 mg L^{-1}, respectively, while Dayton and Basta (2005) used P solutions up to 3.5 g L^{-1}. Studies focusing on the export of nutrients or contaminants *from* the BSM *to* effluent may use influent or initial incubation water without anything added to it (Mullane et al., 2015; Paus et al., 2014). The use of deionized (DI) water, with an ionic strength lower than that of actual stormwater (as stormwater contains at least some dissolved ionic content), facilitates the release of chemical constituents from soil and therefore represents a "worst-case" leaching scenario (Mullane et al., 2015).

Although differences in particle size and surface area have been shown to impact soil function with respect to contaminant removal, including adsorption by WTRs (E. A. Dayton &

Basta, 2005; Makris, Harris, O’Connor, Obreza, & Elliott, 2005), many BSM studies use material sieved to <2 mm as a standard practice (Hurley et al., 2017; Mcphillips et al., 2018; O’Neill & Davis, 2012a, 2012b; Paus et al., 2014; Yan et al., 2016). This particle size is also frequently used for WTRs and soils tested for P leaching potential in agricultural sector research (Agyin-Birikorang et al., 2007; Elizabeth A. Dayton, Basta, Jakober, & Hattey, 2003; Maguire & Sims, 2002).

Batch studies generally include incubating samples for varying periods of time, often with mechanical shaking to increase contact between soil and liquid. Dayton and Basta (2005) found that WTRs continued to adsorb additional P from solution up to 6 days into incubation. However, because fast infiltrations rates are necessary in order to prevent flooding, and are required by BSM specifications (Seattle Public Utilities, 2014), a long contact time between stormwater and BSM may not be practical in real-world conditions. A 24-hour incubation study is common (O’Neill & Davis, 2012a; Yan et al., 2016) and mimics a longer rain event which might cause temporary ponding and potentially increased P release over a short rain event (Hurley et al., 2017), but still meets the maximum draw-down time required by the City of Seattle.

1.3 MANAGING PHOSPHORUS IN BIORETENTION SYSTEMS

1.3.1 *Particulate phosphorus*

Removal of P in particular is heavily dependent on physiochemical processes within soil (Shrestha et al., 2018). Particulate P is effectively managed by bioretention systems through sedimentation and filtration, and effluent levels are generally very low. This is because total suspended solids (TSS) are generally well removed by bioretention systems as they are currently commonly designed (Li & Davis, 2016), and the removal of particulates and particulate-bound pollutants is not significantly impacted by changes in BSM characteristics (Allen P. Davis et al., 2009). However, Brown et al. (2016) did find that the addition of 5-10% Fe-WTR by volume decreased turbidity by an order of magnitude or more, consistent with the intended role of WTRs as polishing material in drinking water treatment. Some amount of particulate P will also leach and become dissolved P at some point (Li and Davis 2016).

1.3.2 *Dissolved phosphorus*

The most important removal mechanism for DP from stormwater by bioretention systems is adsorption onto the BSM, although precipitation is also an important retention pathway (Li & Davis, 2016; Lucas & Greenway, 2008). A small amount of additional DP is removed via uptake by vegetation and immobilization by microbial activity (Lucas & Greenway, 2008). Adsorption of P is controlled by the combination of the adsorption capacity of the media and its previous exposure to the adsorbate (in this case, P). Dissolved P uptake can be highly pH-dependent, primarily as co-precipitation with Ca in calcareous soils, and as sorption to Al and Fe hydroxides and hydroxylated mineral surfaces in acidic soils (Li & Davis, 2016).

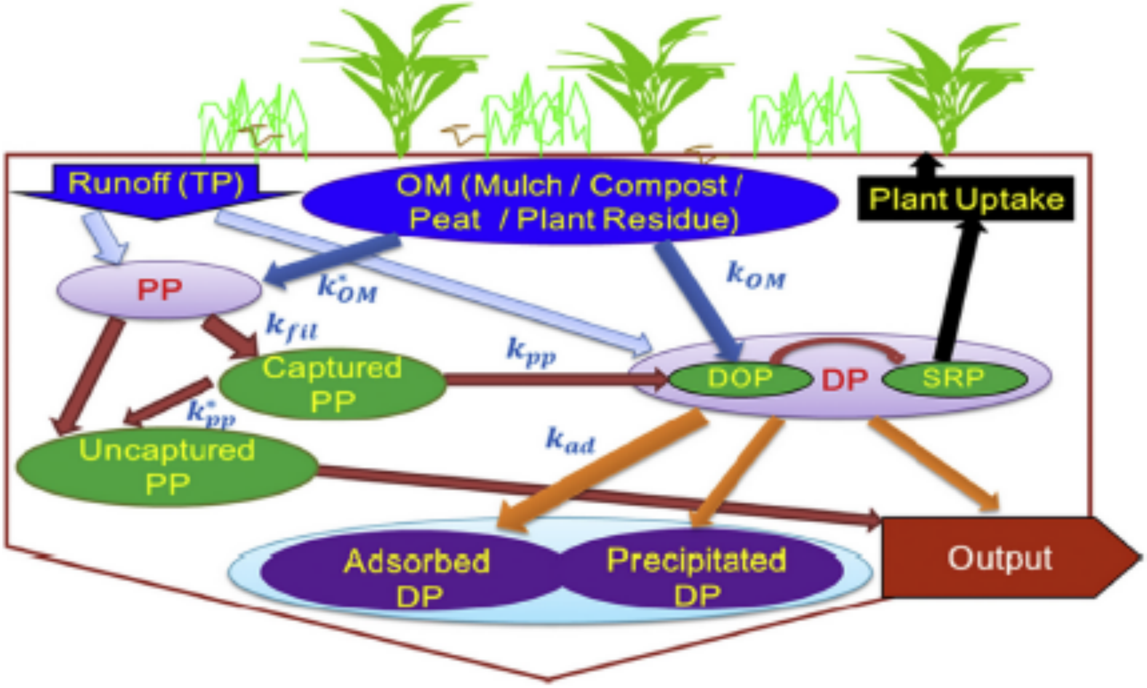


Figure 1.3. Fate of P in a bioretention system (Li & Davis, 2016).

1.3.2.1 Stages of sorption

The process of adsorption within a BSM happens in several stages as the adsorbed P transitions from weakly to very strongly bound to the soil. Generally, the process is broken up into two general phases: one that is fast, and relatively reversible, and a second that is slower, and creates a stronger, long-term bond. Within minutes of contact, as runoff flows through the bioretention media, a highly reversible electrostatic ion-exchange reaction happens in the outer sphere of Al and Fe oxide sorbents present (Li & Davis, 2016; Lucas & Greenway, 2008). This "fast" sorption process can take several minutes to several hours to fully proceed (Ippolito et al., 2011) Next, the sorbed P moves into relatively labile monodentate inner sphere specific surface complexes, and then more stable bidentate complexes (Li & Davis, 2016; Lucas & Greenway, 2008). These "slow" sorption processes take 24 hours to several days (Ippolito et al., 2011). Eventually, over the course of months, even slower reactions take place, moving P into even more stable bonds within the soil. Following these slowest processes, the result of intraparticle diffusion of P into soil micropores, P is essentially immobilized within the soil and does not desorb, even after years of weathering (Li & Davis, 2016; Makris, Harris, O'Connor, & Obreza, 2004). As P moves from the "rapid-reversible" to the "slow-irreversible" sites, rapid-reversible sites are emptied to become occupied by new P entering the bioretention system (Li & Davis, 2016; Lucas & Greenway, 2008).

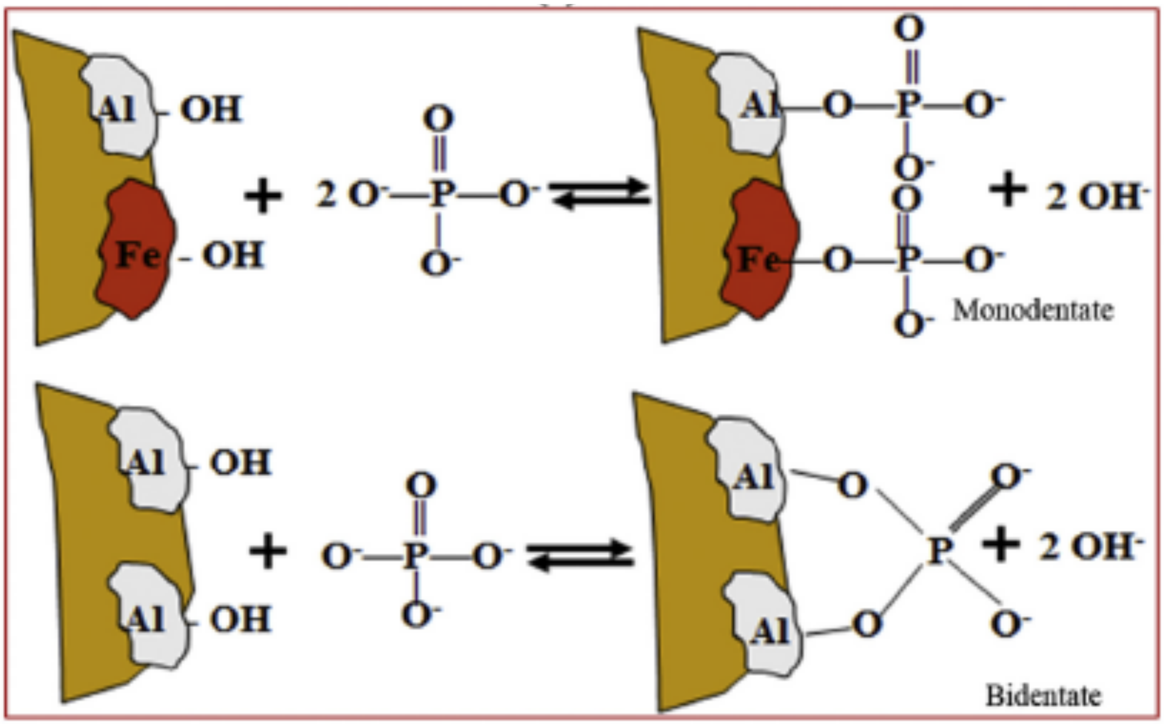


Figure 1.4. P adsorption onto Al and Fe oxides in soil (Li & Davis, 2016).

1.3.2.2 Precipitation with calcium

The co-precipitation of P with Ca is a natural mechanism of P removal in many natural systems, especially in alkaline environments. This reaction, which forms precipitates of calcium phosphate or calcium carbonate ($CaCO_3$) such as calcite with P adsorbed, is highly dependent on pH and Ca concentrations in the water, with more co-precipitation (higher DP remaining in solution) occurring with high pH and high Ca concentrations (Diaz, Reodyit, & Jr, 1994; Sindelar et al., 2015). At Ca concentrations < 50 mg L^{-1}, little to no co-precipitation occurs, even at a pH as high as 9. At Ca concentrations > 50 mg L^{-1}, co-precipitation increases with increased pH, starting around a pH of 8 and showing the most dramatic increase above pH of 8.5. In one study, at a pH of 9, more than 60% of all DP had co-precipitated with Ca, across a range of Ca concentrations, and by a pH of 11, very little P remained in solution (Diaz et al., 1994).

Phosphorus co-precipitated with Ca is much less stable than P sorbed onto amorphous Al and Fe hydroxides. A decrease in pH below 8 can cause rapid dissolution of previously co-precipitated P (beginning immediately and concluding by 24 hr after pH change); in one study, 70% to > 90% of the Ca phosphate came back into solution as pH decreased in two out of three water bodies, and 50% in a third water body that had conditions of supersaturated phosphate and high magnesium concentration which favor increased precipitation (Diaz et al., 1994). Another study showed that DOC inhibits the co-precipitation of P with Ca by competing for free calcium ions. At a pH of 8.5, the presence of DOC at a concentration of 0.5 mg C L^{-1} was enough to effectively cease all Ca precipitation, which stopped Ca-P co-precipitation. A higher pH of 9.5 allowed increased precipitation of Ca even in the presence of DOC, due to the supersaturation of calcite, however, precipitation rates decreased with increased DOC (Sindelar et al., 2015). Because of the circumneutral pH of stormwater (median 7.5 across landcover types, ranging in median by landcover type from 7.1 to 7.9), and the dissolved organic matter present in both stormwater influent (Pitt et al., 2004) and released by OM within many BSMs (Mullane et al., 2015), Ca-P co-precipitation should be a less effective mechanism of P removal than sorption by Al and Fe hydroxides in bioretention systems.

1.3.3 *Measurement and mechanisms to predict availability and movement*

A traditional tool for measuring sorption capacity of a soil is through batch equilibrium experiments, where a potential sorbent is exposed to known quantities of P. Sorption performance is measured using plotted isotherms relating initial vs. equilibrium P concentrations. Commonly-used isotherm equations include Langmuir, Freundlich, and Tempkin models. However, this procedure is time-consuming, complicated, and expensive to do across a range of soil types, so proxy measurements were determined using certain soil characteristics that can help estimate future sorption performance (Schoumans, 2009).

Because of the time-dependent nature of P sorption through the physical structure of soil, including some very long-term processes over the course of days to months, the concept of a finite P sorption capacity of a soil is not entirely accurate, and soils continue to sorb P as the slowest processes re-release reactive surfaces to additional influent. However, within a range of other factors, sorption capacity is useful to illustrate the reduced ability of a soil to adsorb additional P from solution as its exposure increases (P. J. A. Kleinman, 2017). This concept of sorption capacity should be especially useful on the timeframe of 24 hours or less, as slow sorption processes will not have taken place and fast sorption processes will be predominate (Ippolito et al., 2011). Over the course of months, as the slow processes move phosphorus into the inner structure of the particle, eventually even those sites should become full and reach an eventual saturation.

A simple and straightforward method for determining a high-P soil's capacity to release P into effluent or runoff is the determination of water-extractable P (WEP). Details of WEP protocol vary between studies, but Kleinman et al. (2007) recommend the following, which had the highest correlation with runoff P from packed soil boxes amended with biosolids and manure, following a study comparing variations in protocol: 100:1 ratio of water to soil solid, 1h of shaking, centrifuge for 10 min at 1500 x soil weight, filtration with Whatman #1 paper if necessary, and determination of P by inductively coupled plasma-atomic emission spectrometry or colorimetric methods. Soil solids are extracted “as-is” (not dried) but measured on a dry-weight equivalent basis. Although Whatman #1 paper is specified if filtration is necessary, the difference between WEP measurements using centrifuge only (no filtration), Whatman #1, Whatman #40, or 0.45-µg filters should not be significant (P. Kleinman et al., 2007).

While WEP is useful in determining the amount of P expected to be released by a soil under field conditions, a measure of the potential binding capacity of soil components is needed in order to manipulate soil amendments for desired sorption performance. The concept of soil phosphorus saturation is a measure of a soil’s current P content over its total capacity to bind P. A soil that is saturated is expected to release excess P to runoff, and a soil that is not saturated has the capacity to sorb additional P (P. J. A. Kleinman, 2017).

1.3.3.1 Amorphous aluminum and iron content

Aluminum and iron hydroxides are naturally present in soils as the result of both primary and secondary mineral weathering. They have large specific surface areas (SSAs), and play a major role in regulating fate and availability of macronutrients, including phosphorus (Makris, Harris, O’Connor, & El-Shall, 2005). Oxyanions like phosphate sorb to these hydroxides and become tightly bound (Agyin-Birikorang et al., 2007). In many soils, naturally-occurring levels of these Al- and Fe-hydroxides are sufficient to prevent eutrophication of nearby surface waters (Elliott, O’Connor, & Brinton, 2002).

1.3.3.1.1 Oxalate ratio, phosphorus saturation index, and phosphorus saturation ratio

By accounting for Al and Fe present in a soil in relation to its P content, the soil's potential to release P to the environment can be measured with greater accuracy, as soils with low sorption capacity can leach P even at low levels of soil test P (STP) (V.D. Nair & Harris, 2004). Total elemental content of Al and Fe in the soil is not a good predictor of P sorption capacity (Elliott, O'Connor, Lu, et al., 2002; Gallimore et al., 1999). Instead, it is specifically the amorphous (non-crystaline) iron oxide and aluminum oxide content that is related to a soil's capacity for P sorption (Gallimore et al., 1999; Li & Davis, 2016). Several soil tests measure the quantity of elemental content in a soil or soil amendment (such as WTR or organic material) specific to a certain goal or property (such as P sorption), by using a specified solution to extract the element in a way that is useful for determining certain soil behavior. Rather than determining the total content of a given element present in the soil, an extraction solubilizes only a certain fraction of the elemental content, intended as an indicator of various soil properties. A soil extraction using a solution of acid ammonium oxalate to measure the non-crystalline or amorphous Al and Fe present in a solid (Agyin-Birikorang et al., 2007; McKeague, Brydon, & Miles, 1971) is the most widely-used method of measuring P saturation (P. J. A. Kleinman, 2017). The Mehlich 3 method is another soil extraction which has been shown to extract similar amounts of Al, Fe, and P to the oxalate extraction (Maguire & Sims, 2002). Further complicating the study of Ca-P co-precipitation, Ca cannot be accurately measured by oxalate extractions, and methods to determine P sorption capacity of alkaline soils primarily rely on batch sorption studies (P. J. A. Kleinman, 2017).

Oxalate extraction methods originate with McKeague and Day (1966), using air-dried soil samples ground to 0.15mm and extracted with 200mM solution of acid ammonium oxalate at a 1:40 ratio of solid to solution, shaken in the dark, centrifuged, and analyzed colorimetrically. This method has been modified and varied. Many studies use dried media ground to < 2mm (Elizabeth A. Dayton et al., 2003; Jay et al., 2017; O'Neill & Davis, 2012a; Yan et al., 2016). Sparks indicated a 1:60 solid to solution ratio that has been repeated (Bai, Wang, He, & Pei, 2014; S. Brown et al., 2016; Oladeji, O'Connor, Sartain, & Nair, 2007) and specified 2 hours of shaking prior to analysis by ICP. Brown et al. (2016) and Jay et al. (2017) used a 4 hr shaking time followed by filtration with Whatman #40 paper prior to analysis by ICP.

The phosphorus saturation index (PSI) is the molar ratio of oxalate-extractable P (P_{ox}) to oxalate-extractable Al (Al_{ox}) and Fe (Fe_{ox}), and measures the degree to which readily-soluble P may be potentially bound to amorphous Al or Fe within a soil (Elliott, O'Connor, & Brinton, 2002). Agyin-Birikorang et al. (2007) showed an inverse relationship between the sum of Al_{ox} and Fe_{ox} in agricultural soil and bioavailable P. As such, PSI and its reciprocal, the oxalate ratio (OR), are frequently used in studies of the P adsorption/leaching potential of a soil in the agricultural sector (Elliott, O'Connor, & Brinton, 2002; Maguire & Sims, 2002; Oladeji et al., 2007), and has since been used in studies of BSM as well (S. Brown et al., 2016; O'Neill & Davis, 2012b).

$$PSI = P_{ox}/(Al_{ox} + Fe_{ox}) \tag{1.1}$$

$$OR = (Al_{ox} + Fe_{ox})/P_{ox} \tag{1.2}$$

The Mehlich 3 soil test is a multi-element extractant commonly used on a wide range of soils, including a wide range of pH (Schoumans, 2009). It is an adjustment to earlier Mehlich 1 and 2 methods, which enhances the extraction to allow for a wider range of soils (Mehlich, 1984). The Mehlich 3 method uses a different extracting solution from the oxalate method: one made from ammonium nitrate, ammonium fluoride, acetic acid, nitric acid, and ethylenediaminetetraacetic acid (EDTA), but the molar ratio of Mehlich 3-extractable P (P_{M3}) to Mehlich 3-extractable Al and Fe (Al_{M3} and Fe_{M3}), or phosphorus saturation ratio (PSR), has also been used as a predictor of P leaching potential in both agricultural and bioretention soil contexts (Jay et al., 2017; Maguire & Sims, 2002). The standard Mehlich 3 method uses a 1:10 ratio of solid to extracting solution; samples are shaken for 5 minutes, and then filtered through a medium-porosity filter paper (such as Whatman #2 or Whatman #40) before analysis of the supernatant (Jay et al., 2017; Maguire & Sims, 2002; Mehlich, 1984).

$$PSR = P_{M3}/(Al_{M3} + Fe_{M3}) \tag{1.3}$$

The PSI ratio of oxalate-extractable elements is sometimes alternatively referred to as the phosphorus saturation ratio (Oladeji et al., 2007), and the Mehlich 3 ratio is sometimes called PSI. For the purposes of this paper, to distinguish the two extraction methods, $P_{ox}/(Al_{ox} + Fe_{ox})$ will always be referred to as PSI, and $P_{M3}/(Al_{M3} + Fe_{M3})$ will be referred to as PSR, following Jay et al. (2017).

A column study on P movement across a range of BSM mixtures was conducted by Jay et al. (2017), and both PSR and PSI were compared in their ability to predict P movement. In this study, PSR was better correlated with effluent P concentrations than PSI. This could be because much of the initial P content of certain high P-sorbing soil amendments such as WTRs is thought to be tied up in Al-P and Fe-P solids. These Al-P and Fe-P compounds are amorphous, and thus susceptible to oxalate extraction, but have limited solubility, shown to result in much lower Mehlich 1-extractable than oxalate-extractable P (Elliott, O'Connor, Lu, et al., 2002). Maguire and

Sims (2002) found that P_{M3}, Al_{M3}, Fe_{M3} of an agricultural soil were closely related to its oxalate-extraction analogues (p ; r2 = 0.93, 0.87, 0.80, respectively), however, oxalate was able to extract greater amounts of all three elements, and the difference in Al and Fe was especially pronounced at higher soil concentrations (above approximately 1,000 mg P kg^{-1} by either extraction). Jay et al. (2017) also found higher Al_{ox}, Fe_{ox}, and P_{ox} than P_{M3}, Al_{M3}, Fe_{M3}, with the difference between the two extracts most pronounced in high-Fe biosolids. These differences could point to a fundamental limitation of the Mehlich 3 extraction, or could simply indicate a higher solution to solid ratio needed for Mehlich 3 extractions on media with high amorphous Al and Fe content, as suggested by Dayton and Basta (2005) for oxalate extractions on WTRs. As the Mehlich-3 soil test is more widely available in commercial labs than the oxalate extraction (P. J. A. Kleinman, 2017), PSR may also be a more practical and accessible metric to use, if they can successfully predict P movement.

Several studies propose a linear relationship between extractable Al, Fe, and P, and expected leaching or sorption behavior of soil. PSI has been shown to be correlated with P release in agricultural soil (Elliott, O'Connor, & Brinton, 2002; Oladeji et al., 2007). O'Neill and Davis (2012a) present the following equation to describe the relationship found between oxalate ratio (OR) and the total adsorption capacity of a given soil media, q. Using batch and minicolumn studies on a sandly loam BSM amended with Al-WTR, they found variation in sorption performance based on flow regime, media composition, and fine particle composition; however, these additional sources of variation were relatively small and the overall relationship with the oxalate ratio still held across all data:

$$q\ (\text{mg P kg}^{-1}\ \text{media}) = 1.363 * OR - 0.564 \quad (1.4)$$

Using an influent concentration of 120 μg P L^{-1} (average concentration of soluble P in stormwater), 120 cm average annual rainfall in the Washington Metropolitan Region, a desired bioretention system lifespan of 20 years and sized at 5% of completely impervious catchment area, O'Neill and Davis (2012a) set a benchmark desired adsorption at 34 mg P kg^{-1} media. To achieve that benchmark given their equation, an ideal OR is between 20 and 40.

Brown et al. (2016) also showed that a combined PSI of all BSM components was correlated with P concentration in BSM effluent, and that BSMs with a PSI of 0.5 or higher were net contributors of P to effluent, while a BSM with a PSI of 0.1 was not. In a column study using BSMs with varying sources of organic matter (food and yard waste compost, biosolids, and biosolids compost) and P sorbing components (Fe-WTR, oyster shells, soil, and sawdust), Jay et al. (2017) found a linear relationship between the PSR of a BSM and its expected P release, determined by the following relationship for a first leaching event with fresh media:

$$\text{Ln(effluent P (mg L}^{-1}\text{))} = 1.10 \text{ x } \ln(\text{PSR}) + 2.79 \tag{1.5}$$

The columns in this study were of equal volume (1365 cm^3) and received equal volumes (either 900 or 1600 mL) of either synthetic stormwater containing 15.6 ± 1 mg DP L^{-1}, or collected highway runoff containing 1.71 ± 0.30 mg DP L^{-1}. Leaching of P by BSM has been shown to peak with the addition of fresh organic matter and decrease over time (S. Brown et al., 2016; Chahal et al., 2016; Jay et al., 2017; Mullane et al., 2015). In the Jay et al. (2017) column study, differences between the 1st and 12th subsequent leaching events were large enough to producing a distinct predictive equation for expected P leaching for the 12th leaching event:

$$\mathrm{Ln}(\text{effluent P (mg L}^{-1})) = 0.97 \times \ln(\text{PSR}) + 1.61 \qquad (1.6)$$

Yan et al. (2018) found that the addition of 10% Al-WTR by mass to a high-flow media (56% very coarse sand, 26% coarse sand, 16% medium sand, 2% fine sand, mixed on a volume basis) increased the OR of the overall BSM from 5 to 59 and increased the quantity of P removed from 149 to 467 mg P kg^{-1}. Further media enhancement with partially-hydrolyzed aluminum increased the OR to 232 and the quantity of P removed to 1,399 mg P kg^{-1}.

Some research suggests a tipping point, or change point, above which P leaching can be expected from soil, and below which there may be potential for additional P loading or sorption. Elliott, O'Connor, and Brinton (2002) looked at agricultural soil amended with a biosolids or synthetic P source equivalent to 224 kg P ha^{-1} and 2.5% WTR, and found a change point at a combined PSI of 1.1, nearly equal amounts of P and (Al + Fe). The change point found by Maguire & Sims (2002), however, at a PSR of 0.23, indicates much more Al and Fe needed to prevent leaching from agricultural soil with existing P content ranging from 87 to 328 mg PM3 kg^{-1}. Some degree of difference is expected due to the different extractants used. Nair and Harris (2004) found a change point using a Mehlich 1-based PSR of 0.15 for minimally- to heavily P-loaded agricultural soil (up to 229 mg kg^{-1} of Mehlich 1-extractable P), and Nair (2014) reported the change point for the same soils at a PSI of 0.1. Maguire & Sims (2002), showed that that while both PSI and PSR were useful in identifying a change point, PSR was more useful in predicting P release.

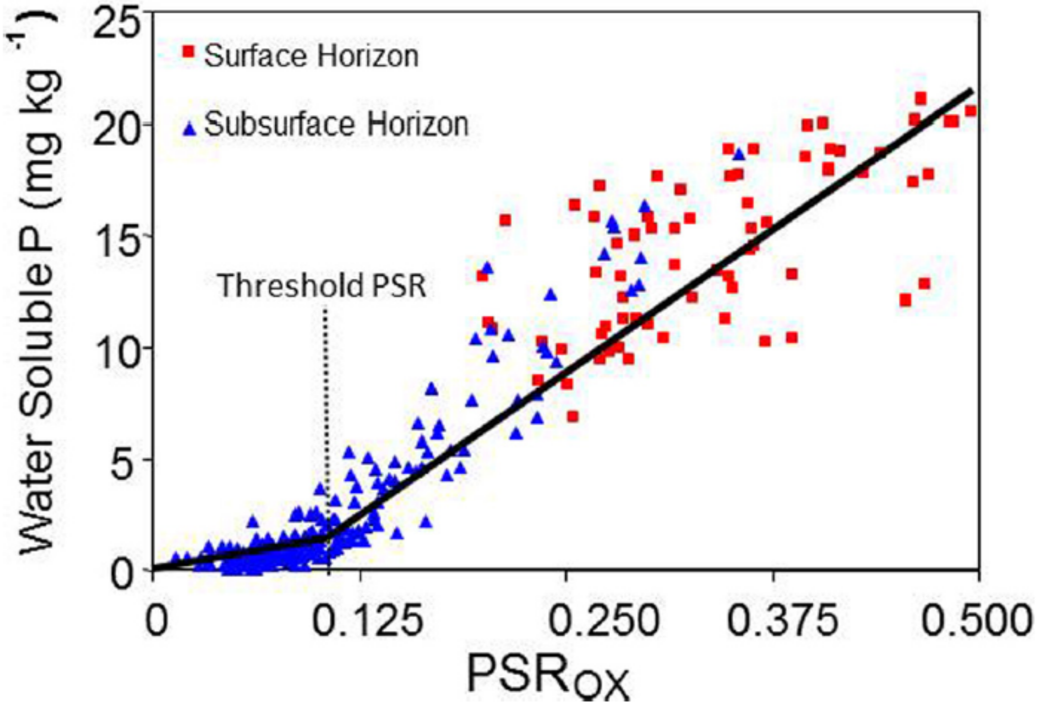


Figure 1.5. Relationship between the concentration of water soluble phosphorus (WSP) and the phosphorus saturation ratio (PSR) for manure-impacted surface and subsurface horizons. The threshold PSR = 0.1. From Nair .

1.3.3.1.2 Phosphorus saturation capacity

Combining the concept of a linear relationship between amorphous Al, Fe, and P, with a change point experienced between sorption and leaching, Nair and Harris (2004) proposed a calculation of the total capacity of soil to sorb or leach P, called soil P storage capacity (SPSC), working backwards from a change point set where no leaching occurs. A measure of a soil's degree of P saturation (DPS), introduced by van der Zee et al. (van der Zee, Fokkink, & van Riems-dijk, 1987) and Breeuwsma & Silva (1992), accounts for the extractable P, Fe, and Al in a soil to predict soil solution P concentration. Extractable elemental values used in DPS were originally oxalate-extractable values, but the calculation was later extended to be used with Mehlich 1 and Mehlich 3 extractions as well (V.D. Nair & Harris, 2004). The SPSC, initially based on Mehlich 1-

extractable P, Al, and Fe (P_{M1}, Al_{M1}, and Fe_{M1}), shows a soil's position in relation to a threshold value for P release, and estimates either the capacity to sorb additional P or the risks of further loading a soil with inherently low P sorption capacity.

$$SPSC = (0.15 - PSR_{M1})(Al_{M1} + Fe_{M1}) \times 31 \quad (1.7)$$

where all values are expressed in moles.

The PSC equation as stated above uses a 0.15 soil PSI threshold specified by Nair & Harris (2004) as the point at which no excess P remains to be released and pose environmental threats, but P pools needed to meet plant requirements are not impacted. Above this threshold value, P concentration in soil solution increases rapidly and leaching is likely. Thus, soils with PSC > 0 should act as sinks, and those with PSC < 0 should act as sources. This threshold value has been suggested with regards to agricultural soils in Florida (Oladeji et al., 2007).

Oladeji et al. (2007) extended to SPSC calculation to be used with oxalate-extractable P, Al, and Fe, as in the original DPS measurements of Breeuwsma & Silva (1992), and showed that the phosphorus storage capacity (PSC) calculation can be used for either soil (SPSC) or amendments such as WTRs (PSC of ammendments, or APSC), or a combination. The calculations are identical, with positive values for media that retains the capacity for sorbing additional P, and negative values for highly P-affected media (or very low-sorbing media) with the potential to leach. Data were combined from greenhouse experiments and field studies using high-P agricultural soil amended with Al-WTR. For the purposes of this paper, calculations for either media will be referred to simply as PSC.

$\text{PSC (mg P kg-1)} = (0.15 - \text{PSI})(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}) \text{ x } 31$ (1.8)

where all elements are expressed in moles, and the value of 31 in the equation represents the atomic mass of P expressed in g mol^{-1} (Oladeji et al., 2007).

The concept of threshold PSR and SPSC can also be used with wetland soils, including those with organic matter ranging from 0-95%, and the threshold PSR or PSI can be altered as appropriate to the system (Vimala D. Nair, 2014). A total PSC for a combined agricultural soil and WTR amendment was tested empirically and the tipping point for water-extractable P was confirmed at a PSC of 0. While expected (calculated from the equation above) and observed PSC values did not exactly match (reasons were not fully understood, but could have been due to insufficient media mixing), they were closely related ($r^2 = 0.8$; $p < 0.05$) (Oladeji et al., 2007). The idea is that P sources and sinks can be co-applied to a soil, as long as relative amounts of amorphous Al, Fe, and P are balanced so as to achieve a PSC of zero:

$\text{SPSC}_{\text{expected}} = (\text{SPSC}_{\text{soil}} \text{ x Weight}_{\text{soil}} + \text{APSC}_{\text{P-source}} \text{ x Weight}_{\text{P-source}} + \text{APSC}_{\text{WTR}} \text{ x Weight}_{\text{WTR}})\ /$
$(\text{Weight}_{\text{soil}} + \text{Weight}_{\text{P-source}} + \text{Weight}_{\text{WTR}})$ (1.9)
(Oladeji et al., 2007).

1.3.3.2 Other factors

Going beyond measures of amorphous Al, Fe, and P, and incorporating other media characteristics relative to P sorption, Li and Davis (2016) derived a theoretical equation based on a review of previous research to predict effluent P concentration from a bioretention system for a given rainfall event:

$$C_e = C_0 exp^{-ß2/Q} + (C^0_{eq} exp^{ß1\,BV})(1 - exp^{-ß2/Q}) \qquad (1.10)$$

Where effluent concentration (C_e) is a function of influent concentration (C_0), initial equilibrium concentration of DP or PP (C^0_{eq}), a coefficient of the rate at which C_{eq} approaches C_0 ($ß_1$), a coefficient of the phosphorus sorption rate constant ($ß_2$), and the cumulative run time of the event (BV), expressed as # of bed volumes. The equilibrium concentration, C_{eq}, occurs at the boundary layer at the surface of the adsorbent, and is a factor of the adsorption characteristics of the BSM. A gradient created between C_{eq} and the aqueous concentration of DP determines the rate of adsorption. If the C_{eq} of a given media is small enough, C_e becomes independent of C_0 , meaning that if the sorption power of the media is strong enough, effluent will be more or less the same (low) regardless of the influent concentration. Effective values of C_{eq} for a given media will change over time as the media is exposed to more P, toward an eventual saturation or "breakthrough" point. In the case of media that does not have any P-sorption capacity at all, but in fact leaches P, the equation still applies, but a high C_{eq} means that negative sorption (ie. leaching) causes $C_e > C_0$. C_{eq} will still approach C_0 over time, as the leaching capacity of the media is eventually exhausted (Li and Davis 2016).

The lower C_{eq} of low-P media (achieved by addition of Al and Fe) is less variable than that of high-P media, which means effluent P will also be less variable for low-P media. So the addition of highly P-sorbing amendments can reduce not only effluent P concentrations, but also variability and uncertainty in bioretention system performance (Li & Davis, 2016).

1.3.3.2.1 Time

In addition to media characteristics, time scale is stressed as an important factor in predicting effluent concentrations of P. Li and Davis (2016) define three timeframes relevant to P fate in a bioretention system. Very generally, "high P" media will leach P and effluent > influent; "low P" media will adsorb P and effluent < influent (Li and Davis 2016).

During the "event-term" (a single rainfall event), effluent P concentration in both P-sorbing and P-leaching media decreases from its starting point, meaning that P-sorbing media will sorb more as the event progresses, and P-leaching media will leach less. This was modeled by Li and Davis (2016) and also measured in column studies by Chahal et al. (2016), where leachate P concentration was highest at the start of an individual rain event, decreased throughout the event, and then peaked again at the start of the next rain event. Lower moisture content of the media at the beginning of an event leads to a relatively high C_{eq}, as soluble P leaches from the media due to crystallization of mineral compounds, breakdown of soil aggregates, and disruption of clay organic matter coatings (Li & Davis, 2016; O'Neill & Davis, 2012a). Media that is continuously saturated performs better from a P sorption standpoint than media exposed to periodic drying between events by avoiding this cycle (O'Neill & Davis, 2012a). This would impact the performance of bioretention systems in Seattle, especially in the early fall when they are likely to be dry. This could contribute additional phosphorus to "first flush" effluent from storm events after a period of dry weather.

The longer the dry period between events and the lower the sorption strength of the BSM, the more variation in effluent P. Consequently, the "fast" adsorption sites are overwhelmed and P is leached. As the media becomes saturated, "fast" adsorption sites come back into play and effluent concentrations decrease (Li & Davis, 2016; O'Neill & Davis, 2012a). This event-term increase and decrease of effluent concentrations occurs around a central mean specific to the given media.

“Short-term” is defined by Li and Davis (2016) as multiple event-terms before the exhaustion of the media’s ability to either sorb or leach additional P. According to Li and Davis (2016)’s model, effluent P concentrations do not change significantly during the short-term duration, but rather oscillate around a relatively steady point with peaks at the start of each individual event. The “long-term” encompasses the time it takes for a media’s capacity to sorb or leach to be exhausted, and effluent concentrations of either media type will approach influent concentrations by the end of the long-term timeframe (Li & Davis, 2016; O’Neill & Davis, 2012a, 2012b). This is dependent on both media characteristics and P loading. Chahal et al. (2016) did see a new peak in leached P at the start of each subsequent simulated storm event, but they, Brown et al. (2016), and Mullane et al. (2015) all saw decreased leachate concentrations over the course of successive storm events, using BSM columns amended with organic matter.

1.3.3.2.2 Media depth and volume

Highly-sorptive media will adsorb influent P in shallowest depths first, closest to the soil surface or inflow location. As that media becomes saturated and loses its sorption capacity, P flows further down and is adsorbed by media at greater depth. Similarly, a larger system of equal depth will provide greater volume of sorptive media for P uptake. Given media of the same initial P sorption capacity, and assuming the P source is influent water (not the BSM itself as would be the case with high-P media), a larger system will have greater sorption capacity and therefore a longer effective lifespan (O’Neill & Davis, 2012b). Li and Davis (2016) model an increase in P sorption with increased depth up to an optimum depth dependent on media type and influent concentration, with diminishing returns for additional depth beyond this point. More sorptive media requires less depth or volume for P removal. Bratieres et al. (2008) found that sandy loam columns receiving 0.35 mg L^{-1} TP influent (approximately 30% dissolved PO43-) achieved effective PP filtration and DP sorption (82% TP retention) in 300mm, with no additional benefit of increased depth. O'Neill and Davis (2012b) found that, after 20 years' worth of typical stormwater P influent (120 cm $year^{-1}$ at 120 µg L^{-1}, with the bioretention system sized at 5% of the completely impervious catchment area), a high-sorbing media containing 5% Al-WTR, 3% hardwood bark mulch, and 92% loamy sand had accumulated enough sorbed P in the top 2 cm to alter the oxalate ratio from 23.1 to 14.5 (5.52 mmol kg-^{1} more P_{ox} than unused soil). By contrast, soil from 11-22cm accumulated a very small amount of additional P (2.11 mmol kg-^{1} more P_{ox} than unused soil), and deeper soil below 43 mm retained its original sorption capacity and an OR of 22.8 (0.11 mmol kg-^{1} more P_{ox} than unused soil). Using an estimate of the P sorption mass capacity per mass of media, an ideal total volume of media can be calculated for a given expected P loading from influent stormwater and desired lifespan of the system (O'Neill & Davis, 2012a). Low- or non-sorbing media would not benefit from increased media depth, as P will not be retained anyway regardless of depth (O'Neill & Davis, 2012b). In the case of P-leaching media, increased depth within the same footprint would lead to increased effluent P, as the total volume of leachable soil would be greater (Li & Davis, 2016).

1.3.3.2.3 Other sources of variability

Other factors, such as flow rate, presence of fine particles in media, total C content, pH, and surface area can introduce variability into overall trends and relationship between sorption and amorphous Al, Fe, and P content measurement (Bai et al., 2014; Makris, Harris, O'Connor, Obreza, et al., 2005; O'Neill & Davis, 2012a). Makris et al. 2005 noted a negative correlation between total C content and P adsorption by WTRs, suggesting that organic C content prevents the diffusion of P into internal sites within WTR micropores.

1.3.3.3 Water treatment residuals as phosphorus sinks in bioretention systems

1.3.3.3.1 Measuring sorption capacity of WTRs

Water treatment residuals can have a range of chemical and physical characteristics depending on the treatment process used to create them, and the characteristics of the drinking water source. Average chemical characteristics of Al and Fe WTRs are presented in Table 2, however since the turbidity of the drinking water source determines the amount of coagulant needed in the drinking water treatment process, it also determines the amount of Al, Fe, and Ca present in the resulting WTR and is responsible for the wide range of values seen (Elliott, O'Connor, Lu, et al., 2002). Total Al in Al-WTR has been reported as low as 15 and as high as 177 g Al kg^{-1} (Agyin-Birikorang & O'Connor, 2007). Total Fe in Fe-WTR can be as high as 250 g Fe kg^{-1} WTR (Ippolito et al., 2011). While Al-WTR naturally contain much higher levels of Al, and Fe-WTR higher levels of Fe, both contain some amount of both constituents (Ippolito et al., 2011). Either type may also contain Ca, derived either from source water or Ca-based additives like $Ca(HCO_3)_2$ which can be used as softening agents in the treatment process (Bai et al., 2014).

Large amorphous Al and Fe content, along with high porosity and specific surface area (SSA), make WTRs ideal for adsorbing high amount of anions (Ippolito et al., 2011). Al and Fe present in WTRs are almost entirely amorphous in form, as evidenced by the high proportion of oxalate-extractable components reported; 80-98% of total Al in Al-WTR is in an oxalate-extractable form (Agyin-Birikorang & O'Connor, 2007; Makris, Harris, O'Connor, Obreza, et al., 2005). Similar high proportions of oxalate-extractable Fe exist in Fe-WTR (Ippolito et al., 2011). Variation in amorphous Al, Fe, and P will affect the sorption performance of WTRs, so these values should be used to determine quantities of amendment added to a BSM (O'Neill & Davis, 2012a). An important caveat is the case of Ca-WTRs, which, because of their different P-removal mechanism, do not have P-removal capacity tied to their amorphous Al and Fe content. The principle P removal pathway for Ca-WTRs is co-precipitation, not sorption (Elliott, O'Connor, Lu, et al., 2002).

Table 1.2. Chemical characteristics of aluminum- and iron-based water treatment residuals from published research, 2005-2008. Reported numbers are means ± SEM. Table adapted from Ippolito et al. (2011).

Parameter	Al-WTR*	Fe-WTR**
pH	6.5± 0.3	7.0 ± 1.3
	mg kg^{-1}	
Total N	4,065 ± 740	10,000
Total P	2,157 ± 361	710
Total Al	118,700 ± 24,260	61,390 ± 35,920
Total Fe	37,000 ± 19,740	220,900 ± 32,200
Total Ca	10,360 ± 4,299	Not determined
Total Cu	624 ± 581	46 ± 12
Oxalate-extractable Al	65,820 ± 9,030	927 ± 498
Oxalate-extractable Fe	13,930 ± 7,695	109,300 ± 29,780
Oxalate-extractable P	2,320 ± 451	610

* Mean and SEM values for Al-WTR calculated from Agyin-Birikorang et al. (2007, 2008), Babatunde et al. (2008), Bayley et al. (2008), Codling et al. (2007), Hseigh et al. (2005), Ippolito and Barbarick (2006), Madhy et al. (2007), Makris et al. (2006), Mortula et al. (2007), Novak et al. (2007), Oladeji et al. (2007, 2008), Ramirez Zamora et al. (2008), Razali et al. (2007), Sarkar et al. (2007a, b), Sotero-Santos et al. (2005), Wagner et al. (2008), Yang et al. (2006), and Zhao et al. (2007).

** Mean and SEM values for Fe-WTR calculated from Agyin-Birikorang and O'Connor (2007), Leder et al. (2008), Sarkar et al. (2007a, b), and Sotero-Santos et al. (2005).

Al-WTRs are generally circumneutral to slightly acidic (6.5 on average) (Ippolito et al., 2011), possibly due to alkaline materials such as calcium hydroxide used for pH adjustment in the drinking water treatment process (Agyin-Birikorang & O'Connor, 2007). Fe-WTRs are also generally circumneutral, although usually higher in pH than Al-WTRs. Fe-WTRs have an average pH of 7.0 (Ippolito et al., 2011), but have been reported as low as 4 and as high as 9.2 (Agyin-Birikorang & O'Connor, 2007).

WTR addition tends to buffer the pH of an overall BSM, and changes in pH may not make much of a difference in P sorption by WTR-amended BSM, regardless of variation in initial BSM components before amendment (O'Neill & Davis, 2012a). Within the circumneutral pH range that WTRs normally occur (pH 5-7), variation in pH does not seem to influence sorption by WTRs (Makris et al., 2004). For example, O'Neill and Davis (2012a) saw final pH values from 5.9 to 7.4 of WTRs after equilibration with added P, trending slightly higher with more WTR content. At very low pH (3 or lower), WTRs can be destabilized and release previously-sorbed P (Agyin-

Birikorang & O’Connor, 2007), however this low pH is very unlikely to occur in a bioretention system and would also not support plant growth and so would not be acceptable in a BSM.

Potential contaminants originating in source water influent or from other parts of the drinking water treatment process that can be passed on to or accumulate in WTRs should also be considered when WTRs are used as a soil amendment (Ippolito, 2015). Trace metal content in WTRs, a potential concern for land application, has gone down since an initial characterization done by the American Society of Civil Engineers in 1996, coinciding with the implementation of the United States National Pollutant Discharge Elimination System program (USNPDES) (American Society of Civil Engineers, American Water Works Association, & United States Environmental Protection Agency, 1996; Ippolito et al., 2011).

An acknowledgement of the differences between WTRs produced at different treatment facilities revealed a need for predictive qualities that could accommodate those differences. Because the amorphous fractions of Al and Fe are known to be excellent P sorbents, as with agricultural soil and BSM more generally, research on predictive measurements has generally focused on extractable concentrations of these elements. Dayton and Basta (2005) showed the relationship between Langmuir Q_{max} (maximum P adsorption capacity determined by equilibrium batch tests) and the oxalate-extractable Al (Al_{ox}) content of drinking water treatment residuals (WTR) used as a soil amendment in the following equation:

$$P_{max}\ (\mathrm{g\ kg^{-1}}) = 0.156 \times Al_{ox} + 11.3 \qquad (1.11)$$

In Dayton and Basta’s (2005) study, including oxalate-extractable levels of Fe (Fe_{ox}) along with Al_{ox} did not significantly improve the predictive equation (p=0.001). However, the Al-WTRs used in the study contained, on average, 10 times the amount of Al_{ox} as Fe_{ox} on a mass basis. Later studies showed that neglecting Fe content was insufficient to explain the P sorption capacity of WTRs with a higher Fe content (Bai et al., 2014; Jay et al., 2018). However, the WTRs used in that study were Al-based, and so naturally had very high levels of amorphous aluminum (mean of 54.5 g Al_{ox} kg^{-1} by 40:1 oxalate solution to solid ratio; mean of 73.1 g Al_{ox} kg^{-1} by 100:1 ratio). The WTRs in their study also had very low levels of iron and phosphorus (mean of 5.17 g total Fe kg^{-1} and 1.39 total P), probably negligible to the relationship with P_{max}. Other studies have shown that the oxalate-extractable Fe (Fe_{ox}) is important in P sorption by WTRs, particularly in WTRs with higher Fe content (Bai et al., 2014; O'Neill & Davis, 2012a). There may also be a range of initial P content in WTRs from different treatment plants, owing to the influent water source (Agyin-Birikorang & O'Connor, 2007; Makris, Harris, O'Connor, Obreza, et al., 2005), although this is generally relatively very low (Ippolito et al., 2011). Because the overall P reduction performance of Al and Fe can be inhibited by simultaneous mineralization of soluble P from organic matter (OM), which contributes P to the combined media (Li & Davis, 2016; Mcphillips et al., 2018), initial P content must also be accounted for. This is more consistent with the PSR and PSI calculations used for determining P sorption and release by soil.

Dayton and Basta (2005) tested several ratios of solid to oxalate extracting solution and found a 1:100 ratio (a 2.5-fold increase from the original) to be ideal for WTRs in particular, because their Al and Fe content is so much higher than for a typical soil. This practice has been referenced and repeated (O'Neill & Davis, 2012a; Yan et al., 2016, 2018). O'Neill and Davis used a 275mM solution for 2mm dried media, with McKeague and Day's 1:40 solid to solution ratio for soil and compost and Dayton and Basta's 1:100 ratio for WTRs.

While amorphous Al and Fe content in WTR has gotten a lot of attention, their P-sorption capacity may also depend on other factors. Oladeji et al. (2007) looked at agricultural soil amended with WTRs and found the PSC based on PSR for the soil as a whole (including amendments) to be a good predictor of P release. Brown et al. (2016), and O'Neill and Davis (O'Neill & Davis, 2012a, 2012b) also used WTRs to alter the PSI or PSR of the BSM they used and found P sorption or release to be correlated with changes in PSI or PSR. However, Jay et al. (2017) found that while a general trend correlated P release from BSM with PSR across all amendments used, BSM with WTR added released less P than paired treatments at the same PSR, suggesting that the WTRs used contributed more to P sorption within the BSM than their PSR alone would imply.

WTRs have very high SSA and porosity, although these characteristics will vary with each material (Makris et al., 2004; Makris, Harris, O'Connor, Obreza, et al., 2005) (see Table 3). More surface area means more reactive surfaces for amorphous Al and Fe to adsorb P, however, SSA alone is not shown to be well correlated with P sorption capacity of WTRs (Makris, Harris, O'Connor, Obreza, et al., 2005). Differences in microporosity seem to make big distinction in WTR performance, since research suggests most anion sorption by WTRs of either type occurs in micropores (<2 nm) (Ippolito et al., 2011; Makris, Harris, O'Connor, Obreza, et al., 2005). Micropores are critical to the slow sorption processes responsible for the long-term stability of sorbed P within WTRs. Total carbon is thought to increase WTR microporosity, but it can also reduce sorption per unit pore volume or surface area, so this measurement cannot be used alone to predict P movement. In one study, a combined effect of total C, N_2-based SSA, and CO_2-based SSA explained 82% of the variability in WTR's ability to sorb P, with increased total C being detrimental to P sorption (Makris et al., 2004). Total C in Al-WTRs has been reported in the range of 23-205 g C kg^{-1} WTR. High values of C content in WTRs could be due to additives used in the drinking water treatment process, including lime for pH adjustment and activated carbon for taste and odor (Agyin-Birikorang & O'Connor, 2007).

Table 1.3. Surface area and microporosity of WTRs from published studies.

WTR type	Reference	BET-N2 SSA (m^2 g^{-1})	Micropore area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	Total pore volume (cm^3 g^{-1})
Al	Makris et al. (2004)	36	104.9	0.042	
Al	Makris et al. (2005)	40-100		0.0105-0.08	0.092-0.12
Fe	Makris et al. (2004)	3.9	27.5	0.012	
Fe	Makris et al. (2005)	5-65		0.0012-0.00145	0.0043-0.012

A principal component analysis performed by Bai et al. (2014) attributed 36.5% of variation in P sorption by various WTRs to amorphous Al in the form of 200 mmol L-1 oxalate-extractable Al. An integrated factor of pH, total Fe, 200 mmol L-1 oxalate-extractable Fe, surface area, and organic matter content of the WTRs contributed another 28.5% of variation. Non-significant factors included Ca, P, and 5 mmol L-1 oxalate-extractable Fe and Al content. The WTRs used in this study contained Al and Fe in closer to equal quantities than is typically seen in the US. It is conceivable that, for example, in a Fe-WTR with vastly more Fe than Al, Fe content could be an even more significant factor in sorption.

1.3.3.3.2 Long-term adsorption

Desorption of previously-sorbed P from WTRs is not seen to be a problem, as P diffuses deep into the pore structure of the WTR during the "slow-irreversible" period of sorption (Makris et al., 2004). Agyin-Birikorang et al. (2007) found that even after 7.5 years of field use, WTRs did not desorb P into effluent. Various lab studies involving P-loading at high levels, exposure to KCl, simulated aging under high temperatures, low pH, two years of alternating wet and dry periods, and shaking for over 200 days, found WTR-bound P remained fixed and not readily released (Agyin-Birikorang & O'Connor, 2007; Ippolito et al., 2011). Cu sorbed to WTRs also seems to be tightly bound and not likely to desorb or be re-released into effluent (Castaldi, Silvetti, Garau, Demurtas, & Deiana, 2015).

1.3.3.3.3 Al- and Fe-based WTRs

There is some concern about using Fe-based WTRs because they can release previously sorbed P under reducing conditions if iron(III) minerals are dissolved (O'Neill & Davis, 2012a). Therefore, it is important to maintain oxygenated conditions in a BSM amended with Fe-based material (Lefevre et al., 2015). Al-based WTRs are considered a stronger sorbent of phosphorus than Fe-based WTRs according to some studies (Elliott, O'Connor, Lu, et al., 2002; Makris et al., 2004). In the Elliott et al. (2002) study, the Al-WTRs tested contained more amorphous Al than the amorphous Fe contained in the Fe-WTRs, and in the Makris et al. (2004) study, the Al-WTRs tested had larger surface area and more micropore volume, all of which is associated with sorption capacity. It is not clear whether those characteristics always differ between the WTR types.

There has also been some concern expressed about Al toxicity to plants and/or Al leaching. However, Al solubility and resulting plant toxicity is enhanced only at pH values less than 5, so this is not considered to be a problem under expected conditions (Ippolito, 2015), especially given the small fraction of a BSM potentially made up by WTRs. Average pH of Al-WTR is 6.7.

1.3.3.3.4 Effect on plant growth

Despite their ability to prevent P leaching out of the bioretention system, the effect of WTR on plant growth in a bioretention system is not entirely clear. Ippolito (2015) found that fescue growth, and P concentrations in fescue plants in a column study simulating an engineered wetland soil, all increased with Al-WTR application, possibly due to the WTR's sorption of P making P more plant-available. However, WTR application in many other cases has been shown to cause P deficiency in plants, especially in studies on agronomic crops (Ippolito et al., 2011), so the calculation of appropriate application rates remain important for considering bioretention plant needs, as well as in order to accurately estimate sorption needs.

1.4 MANAGING COPPER IN BIORETENTION SYSTEMS

Copper is another stormwater constituent whose fate within a bioretention system can vary widely, from excellent retention to net export. Copper in stormwater generally includes both dissolved and particulate forms, but may occur as 50% or more in a dissolved form (Paus et al., 2014), so while sedimentation and filtration of particulate Cu is important, removal of dissolved Cu is also essential for maintaining low effluent concentrations. Both dissolved and particulate forms of copper are generally removed from stormwater very efficiently by bioretention systems; removal rates regularly top 90% and total effluent concentrations are frequently in the parts per billion (ppb) (Allen P. Davis et al., 2009). Particulate copper is especially well-managed by filtration in even basic sand-only bioretention columns; removal of remaining dissolved copper occurs through both sorption and precipitation (Allen P. Davis et al., 2009; Paus et al., 2014). Shrestha et al. (2018) found good retention of particulate metals, including Cu (as well as Zn, Cr, Pb, and Co), within the bioretention systems tested, due to good retention of TSS. Unlike with the case of nutrients like P, metals like Cu are typically removed from soil through plant uptake only in very small amounts. Although plants do require Cu, this generally accounts for less than 7% of retention, so the primary Cu treatment is via the BSM (Paus et al., 2014).

1.4.1 *Copper mobility*

Precipitation within the BSM is an important pathway of dissolved copper removal, resulting in as much as 78% of influent copper precipitating as $Cu(OH)_s$. In a BSM with good particulates filtration, this copper precipitate is then retained (Paus et al., 2014).

Of all adsorbants with a strong affinity for Cu, Mn oxide is the strongest, followed by organic matter, Fe oxide, and clay minerals. Metal concentration, distribution within the soil, soil pH, and contact time between metals and soil all affect sorption. Soil texture also plays a big role in heavy metal sorption, with course-grained soils sorbing less, and fine-grained soil fractions sorbing more due to their larger surface areas and larger surface reactivities (Bradl, 2004).

Organic matter is a good sorbent of metals generally within soil, (Bradl, 2004), making OM an important component of many BSM. The addition of organic matter in the form of compost has been shown to significantly reduce ($p < 0.05$) metal availability in contaminated yard soil and mine tailings, with the combination of compost and Al-WTR having the greatest effect (57% removal) on reducing bioaccessible lead in the yard soils than any other treatment tested (S. L. Brown, Compton, & Basta, 2007). This is due to functional groups like carboxyl and phenolic groups in OM, which remove dissolved metals from influent water by forming complexes with metal cations (Paus et al., 2014). These OM functional groups are generally considered to be more chemically reactive with metals than are inorganic sorbents, and therefore more successful at treating metals in bioretention systems (Lefevre et al., 2015), making them important components of the BSM.

Copper has an even stronger affinity for sorbing to OM than other metals, and in solution complexes with soluble organic matter (Bradl, 2004). In bioretention soil receiving 0.5 mg L^{-1} influent Cu, even a 10% addition of compost from leaves, grass, and woody debris feedstock to a sand column resulted in a drop in total effluent Cu from 0.39 to 0.04 mg L^{-1}, and Cu removal continued to increase with increasing BSM compost fraction. When the BSM contained 50% compost (50% sand), total effluent Cu was reduced to 0.004 mg L^{-1} (Paus et al., 2014). A study using synthetic stormwater found that a BSM compost of 60% sand and 40% compost (by volume) of varying feedstocks removed >90% of the Cu (total and dissolved) from synthetic stormwater starting at 1 mg L^{-1} Cu influent concentration (S. Brown et al., 2016). Another study found 97-99% Cu removal from stormwater by a sandy loam BSM with a 2.5-cm mulch layer on top (A P Davis et al., 2003).

Because of the strong affinity of Cu for OM, in the presence of DOM, Cu ions will readily form Cu-DOM complexes, which has important implications for environmental availability of Cu in stormwater (Chahal et al., 2016). Copper in this organically complexed form is much less environmentally toxic than free ionic Cu, which has neurotoxic effects on fish. The protective effects of DOM against fish toxicity were much larger than that caused by either water hardness or alkalinity, both of which also reduced negative fish responses to Cu. Copper entering aquatic systems from vehicles, pesticides, boats, buildings, or other sources have been found to be in forms that harm Pacific salmon, especially when sources of Cu reach fresh water, which is typically much lower in naturally-occurring dissolved organic carbon (DOC). However, at DOC concentrations as low as 3.8 mg L-1, Cu-induced neurotoxicity in juvile coho salmon exposed to 20 μg L^{-1} for 30 minutes was reduced by 50%, and at 6 mg L^{-1}, it was reduced by 100%, as the Cu ions were sufficiently complexed with DOC (McIntyre et al., 2008). Bioretention effluent water has been found in some cases to contain high levels of dissolved Cu, sometimes higher than influent concentrations due to additional Cu exported from organic matter in the BSM. However, in a study of compost typical of that used in Pacific Northwest BSMs (80% yard waste and 20% food waste by volume), the export of dissolved Cu in leachate from compost-only columns coincided with DOC. Both Cu and DOC were exported in pulses with intermittent rain events, starting high and decreasing over time (Mullane et al., 2015). In another column study, using a standard BSM composed of 60% sand by volume and 40% food and yard waste compost previously mentioned, dissolved Cu export was measured as high as 100 μg L^{-1} for the first rain event, and both concentrations of total and dissolved Cu effluent exceeded influent concentrations for the first 4 to 5 rain events. By the 6th and 7th rain events, columns were retaining Cu and effluent concentrations were lower than influent, although concentrations never decreased below 20 μg L^{-1} over 7 rain events. However, this exported Cu seemed to be nearly completely if not completely complexed with DOC (Chahal et al., 2016).

Soil pH is also an extremely important factor controlling heavy metal movement between soil surfaces and solution. Sorption of heavy metals (including Cu) is maximized at a pH of about 6.5 (Brady & Weil, 2008), which is right within the usual range of urban stormwater pH from 6-8 (Yan et al., 2018), and precipitation of Cu oxide or hydroxide from solution also increases with solution pH (Castaldi et al., 2015). Less sorption and therefore higher solution concentration of Cu occurs as pH deceases (Bradl, 2004; Brady & Weil, 2008), as protons and metal ions at lower pH compete for sorption sites (Bradl, 2004).

At a pH of 4.5, Cu precipitation ceases. However, even at this pH, both Al and Fe-WTR were still able to pull Cu out of solution via sorption. The pH of soil and solution are also important factors because acidic conditions can also lead to the dissolution of Cu sorbents, including DOC, Al- and Fe-hydroxides. Release of DOC from Fe-WTR peaks at pH 5.5 and from Al-WTR at 4.5. Solubilization of the Al and Fe itself from the WTR can occur at very low pH; this has been observed at pH 3.5. This would cause re-mobilization of metals sorbed to these substances (Castaldi et al., 2015), but again this is not expected in the typical pH range of stormwater.

Chemical reactions involving other elements present in stormwater can complicate sorption of certain metals. Minervini (2013) critiqued a synthetic stormwater study by Wium-Anderson et al. (2012) by discussing potential confounding effects of other chemicals that might be found in real stormwater that could change how different chemicals of interest respond to various sorbents. Chloride is specifically mentioned as a potentially confounding ion in real stormwater. Pitcher, Slade, and Ward (2004) reported that sorption performance (onto natural zeolite mordenite) of Pb, Cu, Zn, and Cd was lower from real stormwater spiked with those metals than from a synthetic solution, suggesting that some dissolved contaminants in the real stormwater runoff could be interfering in the exchange of heavy metal ions. The difference could have been caused by metal speciation or cation competition. Minervini (2013) also speculates that the change in pH between the real and synthetic stormwater could affect changes in sorption.

Even with a synthetic stormwater solution, Cd, Cu, and Zn appeared to compete for sorption sites, evidenced by the stratification of metal accumulation in bioretention soil at varying distances from the inlet (Paus et al., 2014). Metals are generally retained within the top 50-100mm of a BSM and tend to accumulate there without movement over time (Feng et al., 2012). Due to its high affinity for organic matter, a BSM containing organic material should retain Cu more readily than other metals (Paus et al., 2014).

1.4.2 *Phases of copper sorption*

The general term of "sorption" of heavy metals refers to several processes. Sorption can be either non-specific cation exchange, producing a faster, but weaker covalent bond with the outer sphere of charged particles, or specific, inner-sphere complexation, a slower and less reversible process. Metals can also form precipitate as oxides, hydroxides, carbonates, sulfides, or phosphates on the surface of soil particles. The most stable sorption mechanism is absorption, also known as fixation, where metals that have been adsorbed onto the surfaces of clays or metal oxides then diffuse into pore spaces and become locked into the particle structure. Clays and metal oxides remove heavy metals from solution through cation exchange and specific adsorption. Organic matter uses cation exchange, surface complexation, and surface precipitation (Bradl, 2004).

As with P, adsorption of Cu is biphasic. The fast-sorption phase occurs in approximately the first hour, followed by slow sorption. In one study, about 60% of the total Cu sorbed by both Al and Fe-WTR over a 24 hr period was sorbed in the first hour. In the slow-sorption phase that follows, Cu moves into less accessible sites or possibly those with lower affinity for Cu (Castaldi et al., 2015). Brown et al. (2016) found that removal efficiency of BSM with compost from varying feedstocks increased over time through 12 subsequent leaching events.

1.4.3 *WTRs and copper removal*

The use of WTR in bioretention has so far been focused on reducing soluble P in effluent, however, there has been some research suggesting that they may also be used for removing other contaminants, especially anions (Ippolito et al., 2011). Adsorption and coprecipitation of Cu in runoff by hydrous oxides of Al and Fe has been researched following similar use in treating contaminated wastewater, and WTRs have been shown to be capable of removal of Cu by both mechanisms (Karthikeyan, Elliott, & Cannon, 1997). These reactions are highly pH-dependent and Al- and Fe-WTRs have different optimal pH windows. Fe-WTR may be a more powerful Cu sorbent, however other factors including SSA and organic content of WTR particles are also significant for both WTR types (Castaldi et al., 2015).

Fe-WTR may be a stronger sorbent of Cu than Al-WTR. In one study, Fe-WTR was able to sorb 63% more than Al-WTR, despite the lower molar quantity of total values of both metals (Al_T and Fe_T) in the Fe-WTR (0.0028 mol g^{-1} of $Al_T + Fe_T$, compared with 0.0035mol g^{-1} in the Al-WTR). This could have been due to greater surface area or CEC of the Fe-WTR. It could also have been affected by the low pH (4.5) in which this experiment occurred. The Fe-WTR used also had a higher total Mn content (11.21 mg g^{-1} in the Fe-WTR, compared with 2.33 mg g^{-1} in the Al-WTR) (Castaldi et al., 2015).

Cu sorption by Al and Fe-WTR increased with increasing time and solution concentration. The maximum amount of Cu sorbed by Fe-WTR at pH 4.5 in one study was 0.089 mmol Cu (II) g^{-1}, 63% more than sorbed by Al-WTR at the same pH. This maximum was reached at a solution concentration of 0.8 mM Cu, at which point sorption plateaued, suggesting that all sorption sites had been saturated. The organic content of Al and Fe-WTRs was responsible in one study for 8.5% and 26% of total Cu sorbed by the WTR, respectively. The authors speculated that the WTR's organic content contributed both additional Cu sorption sites and negative charge to the WTR surface from the presence of humic acids (Castaldi et al., 2015).

1.4.4 *Predicting copper movement*

Because organic matter is one of two main Cu sorbents in soil, increasing organic matter in a BSM should increase Cu sorption, however results are mixed. In one study, increased compost volume fraction (CVF) was associated with increased Cu removal from water in bioretention systems. Looking at varying CVFs, total Cu was effectively removed (down to a 0.04mg L^{-1} effluent, a 95.7% removal rate from influent concentrations) by a BSM with 10% compost and 90% sand, the lowest CVF tested. Effluent concentrations continued to decrease with increased CVF, to 0.004 mg L^{-1} for the BSM that was 50% compost and 50% sand (a 99.6% removal rate). By contrast, the control BSM consisting only of sand had an average effluent concentration of 0.39 mg L^{-1} Cu. The sand-only and 10% compost BSMs were still able to remove most particulate Cu through filtration; dissolved Cu made up 75-95% of total effluent Cu in those treatments. Another study showed that CVF did not significantly affect concentrations of either total or dissolved Cu in bioretention effluent, especially at very high CVFs (80% by volume) (Jay et al., 2018). Faster infiltration showed a slight but significant relationship (r^2=0.32) with reduced Cu removal efficiencies in a column study testing multiple types of BSM; however, all infiltration rates were very high across treatments (up to 0.35 cm s^{-1}) (Jay et al., 2018). It is possible that OM amendment could impact Cu retention by altering infiltration rates and stormwater-soil contact time.

Because Al and Fe oxides are involved in sorption of Cu as well as P, PSI may be indicative of BSM Cu sorption. Brown et al. (2016) found that, although all compost-amended BSMs of varying feedstock and PSI removed Cu from synthetic stormwater, feedstock and PSI were both significant factors of variation in degree of removal ($p < 0.0001$)., with the lowest PSI media retaining the most Cu regardless of feedstock. However, as WTR had been added to the low PSI BSM in order to bring down the PSI, the authors suggested that the Cu sorption may have been due to the presence of the WTR in the media, rather than specifically an effect of PSI. Jay et al. (2018) found that the addition of WTR or biosolids with high Fe content reduced dissolved Cu in the effluent from BSMs of varying components. Variation in the compost itself, including feedstocks, initial Cu content, PSI or PSR, or other factors, could play a role in its performance as an effective Cu sorbent. The LID Technical Guidance Manual for Puget Sound recommends initial Cu content in BSM or compost used in a bioretention system not exceed 750mg kg^{-1} (Hinman, 2012).

The lifespan of a bioretention system is generally thought to be very good from a Cu treatment perspective. Davis et al. (2003) calculated that, based on observed retention, their mulch-topped sandy loam boxes could be expected to adequately treat copper in stormwater influent for 77 years. Paus et al. (2014) found that all BSM treatments tested (sand-only and with varying additions of compost) continued to remove influent copper without breakthrough even after 1,000 pore volumes.

1.5 CONCLUSION

Bioretention offers an effective option for stormwater treatment that can augment a city's gray infrastructure and add capacity for reduction of runoff volume, delayed peak flows, and contaminant removal for increased water quality in local groundwater and surface waters. However, specifications for soil media and other components vary widely and may not be optimized to best suit desired performance. By properly selecting BSM components, P leaching from bioretention systems can be entirely eliminated (Li & Davis, 2016) and Cu can be completely retained (S. Brown et al., 2016; A P Davis et al., 2003; Paus et al., 2014). Due to their high amorphous Al and Fe content, their proven ability to adsorb large amounts of P, and suspected ability to remove additional stormwater constituents such as Cu, WTRs are a promising BSM amendment. However, as WTRs vary widely in their physical and chemical characteristics, the most useful guidelines for bioretention practitioners will need to take these differences into account in order to match sorption needs with sorbent capacity for pollutants of concern and selected BSM components. Previous research has already shown PSR and PSI to be correlated with P movement in agricultural soils and in BSMs, including WTR amendments in both. However, as yet no predictive measure of soil components based on chemical or physical characteristics has been shown to produce a BSM that can meet desired effluent standards, and more research is required to generate these measures. Such a tool would inform BSM installation regardless of media components under consideration, as long as component characteristics were measured.

Chapter 2. PREDICTING PHOSPHORUS AND COPPER RELEASE FROM BIORETENTION SOIL MEDIA COMPONENTS USING PHYSIOCHEMICAL CHARACTERISTICS

2.1 INTRODUCTION

Stormwater management is a growing need as cities expand their impervious surface cover, industry increases the contaminant load on the landscape, and water quality gets more attention as an environmental concern. Climate change is increasing the magnitude and decreasing the frequency of precipitation in many areas including the Pacific Northwest (Allen & Ingram, 2002; Archer, 2012; Salathe, 2006; Trenberth et al., 2003), causing further strain on aging built stormwater infrastructure. To augment existing built or "gray" infrastructure such as pipes and water treatment plants, "green infrastructure" such as bioretention mimics the natural ability of soil and plants to hold and filter water (Wang et al., 2013). Used in combination with gray systems, green stormwater infrastructure (GSI) can offer additional capacity to treat stormwater for flood prevention and water quality improvement that is both cost-effective and offers additional benefits to the urban landscape (Wang et al., 2013).

Bioretention systems are a type of GSI using a soil mixture generally comprised of sand and an organic material, and often with additional components, with specially-selected plants, installed in a shallow basin or box with an inflow, overflow mechanism, and either an underdrain or direct connection to infiltrating subsurface soil (Allen P. Davis et al., 2009). These systems can effectively reduce and delay peak flows, and treat a range of contaminants, from heavy metals to organic pollutants, and has become increasingly popular nationally and world-wide (A. P. Davis, 2008; Allen P. Davis et al., 2009; Hatt et al., 2009; Jay et al., 2018). However, bioretention specifications are not consistent from one jurisdiction to the next, and are often not based on the best available science, producing a range of performance (Allen P. Davis et al., 2009). Because bioretention effluent can be in contact with groundwater, or in many cases connected directly to freshwater systems via underdrain pipes, nutrient export can lead to eutrophication and decreased water quality (Schoumans, 2009; Sharpley et al., 2003; Sindelar et al., 2015). Nutrients such as phosphorus (P) and nitrogen (N) can be released from organic components of bioretention soil mixtures (BSMs) (Bratieres et al., 2008; Hunt et al., 2006; Hurley et al., 2017; Li & Davis, 2016; Mcphillips et al., 2018; Paus et al., 2014; Shrestha et al., 2018). Phosphorus is especially problematic because of the extremely varied performance seen across bioretention systems, from 65% removal of influent P concentrations to 240% P export to effluent, making the bioretention system frequently a P source to receiving waters, instead of a sink (Hunt et al., 2006; Li & Davis, 2016). While particulate stormwater constituents are generally well-managed by bioretention systems by sedimentation and filtration, dissolved constituents, which require sorption or precipitation for removal, and are often highly depended on soil physiochemical processes, can be more difficult (Allen P. Davis et al., 2009; Li & Davis, 2016; Shrestha et al., 2018).

Because aluminum (Al) and iron (Fe) regulate P in natural soils, they have gotten some attention as a possible key to solving the P release problem in bioretention (Li & Davis, 2016). Measures of amorphous Al and Fe have been shown to be predictive of P leaching and runoff from agricultural soils, and Al- and Fe-containing amendments have been successful in reducing releases of P (Agyin-Birikorang et al., 2007; Elliott, O'Connor, Lu, et al., 2002; Oladeji et al., 2007). While many such amendments have been studied, a promising option comes in the form of Al- and Fe-based residual solids from the drinking water treatment process. These water treatment residuals (WTRs), are locally readily available across the country, low-cost, and offer an opportunity to create a beneficial use for a waste product. Due to their high surface area and amorphous Al and Fe content, they have been shown as effective sorbents of anions such as phosphate (Agyin-Birikorang et al., 2007; S. Brown et al., 2016; Elliott, O'Connor, Lu, et al., 2002; Gallimore et al., 1999; Jay et al., 2017; O'Neill & Davis, 2012a, 2012b; Oladeji et al., 2007).

The relationship between amorphous Al and Fe in a soil or soil amendment and the existing P content has been expressed in a number of similar ratios that have been linked to P mobility. The phosphorus saturation ratio (PSR) uses measurements of the three elements as determined by Mehlich 3 soil extraction, and is expressed as [P/(Al+Fe)], where all units are in moles. The phosphorus saturation index (PSI) is the same molar ratio using elemental content determined by acid ammonium oxalate extraction, and the oxalate ratio (OR) is the inverse of PSI, [(Al+Fe)/P]. These ratios have been shown to be predictive of P sorption and release by soil mixtures, especially in an agricultural context, and WTRs have been used to manipulate the ratios in the direction of increased P sorption and decreased release (Elliott, O'Connor, Lu, et al., 2002; Maguire & Sims, 2002; Makris et al., 2004). These ratios and the use of WTRs has also been explored to some extent in the bioretention context (S. Brown et al., 2016; Jay et al., 2017; Yan et al., 2016). Physical characteristics of WTRs have also been shown to impact their capacity for P sorption (Makris et al., 2004; Makris, Harris, O'Connor, Obreza, et al., 2005). However, a predictive measure of either chemical or physical soil characteristics that has been tested across a wide range of WTRs and organic components has not yet been produced. Such a tool would enable the creation of optimized BSMs that could protect receiving waters against eutrophication without sacrificing bioretention system performance for other water quality and quantity control metrics.

Copper (Cu) is another stormwater constituent for which bioretention has shown inconsistent results. Some studies have shown retention of Cu as high as 97%, while others show release of Cu, especially from fresh organic components like compost (Chahal et al., 2016; A P Davis et al., 2003; Hatt et al., 2009; Jay et al., 2018; Mullane et al., 2015). Although Cu is also an essential nutrient for plant and animal life (Mengel et al., 2001), excess Cu in receiving waters can be toxic to wildlife (McIntyre et al., 2008). However, the Cu released from organic matter in soil has been shown to be complexed with dissolved organic carbon (DOC), a form that is much less toxic (Chahal et al., 2016; McIntyre et al., 2008; United States Environmental Protection Agency, 2000). Nevertheless, predictive measures of Cu mobility within BSMs would help to better manage this constituent.

To explore these topics, the following research questions were posed:

1) What is the relationship between PSR or PSI and P released from the organic components of BSMs, and can that relationship be manipulated with WTR amendments to reduce P release from the BSM as a whole?
2) Does this relationship hold across a range of organic materials and a range of WTRs?
3) What role to other media characteristics, such as surface area and porosity, play in P mobility within a BSM?
4) What are some predictive measures of Cu mobility within a BSM, and can WTR amendments also help reduce Cu release?

Sorption needs in bioretention systems can be calculated as a mass balance based on pollutant concentrations in influent stormwater, and catchment area and desired lifespan of the system (Ippolito, 2015). In theory, this could then be matched with the sorption capacity of soil components to create a BSM best suited to desired performance. However, predictive measures of sorption have not yet been validated across a range of materials. Additionally, the role of BSM components as sources of certain constituents also needs to be better understood. To explore the P and Cu sorption and release potential of two BSM components, organic materials as sources, and WTRs as sinks, were used in a series of batch studies.

Four WTRs, two Al-based, one Fe-based, and one Ca-based, were combined in pairs with eight organic materials, including composts of varying feedstock, biosolids, and a potting soil blend. One of the composts (ComFY), made from a food and yard waste feedstock, is commonly used in BSMs in the Seattle area. All media was characterized for a range of factors that could be related to P or Cu mobility, including total and extractable Al, Fe, P, Ca, and Cu, surface area, and porosity. The pairs were combined in a range of relative proportions of each component to create a spectrum of combined chemical content and therefore a range of combined PSR and PSI values, and incubated with dionized (DI) water. WTRs were also incubated with controlled synthetic solutions of P and Cu to test their sorption capacity alone, and organics were incubated alone with DI water to assess their release rates. Batches were incubated for 24 hours, shaken to facilitate chemical release and sorption, filtered to separate particulate and dissolved constituents. The supernatant was then tested for dissolved P and Cu, and these measurements were used to correlate chemical and physical characteristics of BSM components with performance. Using a sorptive amendment like WTRs to retain P released by organic components of the BSM would allow the continued use of organic components, which contribute to overall bioretention system function, without degrading surface water quality. This study was conducted to assess how physiochemical characteristics of BSM components can be predictive of performance with respect to P and Cu and used to create better functioning bioretention systems.

2.2 METHODS

2.2.1 *Preparation of media*

A total of 4 different WTRs and 8 different organic materials were used in this study (Table 2.1. Media used). Three drinking water treatment plants in the Pacific Northwest provided WTRs as screw-pressed wet material: one Fe-based from Seattle, Washington (Fe-WTR), one Al-based from Tacoma, Washington (Al-WTR1), and another Al-based from Vancouver, British Columbia (Al-WTR2). A fourth Ca-based WTR from Chicago was used in preliminary tests (Ca-WTR), but it was not included in most of the study due to poor P sorption. The organics used were a range of composts, biosolids, and other organic materials. The three composts are designed for home gardens and each is derived from different feedstocks: 75% sawdust and 25% Class B biosolids stabilized via anaerobic digestion (ComBS), food scraps and yard waste (ComFY), and yard waste alone (ComY). The four biosolids each came from a different wastewater treatment plant, the three King County plants (BioKC1, BioKC2, BioKC3), and a fourth from San Francisco (BioFe), which is known to include Fe addition as ferric chloride ($FeCl_3$) for struvite control during the wastewater treatment process. They were collected as biosolids cake- suitable for use on agronomic crops but not permitted for general use. A biosolids-based potting soil product, also designed for home gardens, was also used (BioPot). It is made from 20% Class A biosolids, 20% maple sawdust, and 60% aged bark, with a small amount of course bark and mineral component.

Table 2.1. Media used

Media name	Description
WTR	

Al-WTR1	Al-based WTR from Tacoma
Al-WTR2	Al-based WTR from Vancouver
Ca-WTR	Ca-based WTR from Chicago
Fe-WTR	Fe-based WTR from Seattle
Organics	
BioFe	Biosolids from San Francisco (Fe added)
BioPot	Sawdust/bark/biosolids potting soil (Tagro)
BioKC1	Biosolids from King County's South Plant
BioKC2	Biosolids from King County's Brightwater Plant
BioKC3	Biosolids from King County's West Point Plant
ComBS	Sawdust/biosolids compost (Groco)
ComFY	Food/yard waste compost (Cedar Grove)
ComY	Yard waste compost (LRI)

All WTRs and organics were stored wet at room temperature until they were dried and prepared for use. WTRs were kept in sealed buckets to minimize oxidation and organics were kept loosely covered to prevent anaerobic conditions from developing. Wet material of both media types was air-dried at room temperature for at least a week or dried in an oven at 40°C for 48 hours, then sieved to <2 mm before being used for either media characterization or batch incubation. Dried materials were lightly ground until particles and aggregates passed through the 2 mm sieve.

2.2.2 *Media characterization*

2.2.2.1 Chemical analysis

Samples of all media were prepared for total elemental analysis following EPA method 3050B (U.S. EPA, 1996) and the digestate was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (7900 octopole reaction system ICP-MS, Agilent, Santa Clara, California). One sample of each media was tested, and one method blank was used for every seven media samples. Total C and total N were determined by combustion using a CHNS/O analyzer (Series II Analyzer, Model 2400, PerkinElmer, Waltham, Massachusetts). A duplicate sample was added for every third media tested.

2.2.2.2 Surface area and porosity

Surface area and porosity of WTRs were calculated using N_2 adsorption and desorption isotherms, measured at 77°C on a TriStar II Plus analyzer (Micromeritics Instrument, Norcross, Georgia). Prior to data collection, the samples were outgassed at 100°C for 24 hours in a vacuum. The specific surface area (SSA) and pore size distributions of the WTRs were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Barrett, Joyner, & Halenda, 1951; Brunauer, Emmett, & Teller, 1938). Micropore area and volume were determined using the t-plot based on the N_2 sorption isotherms. Total pore volumes were determined from the nitrogen adsorbed at a relative pressure of 0.99.

Because the Fe-WTR and Al-WTR2 were so far below the recommended minimum SSA for high instrument accuracy (10 m^2 g^{-1}), they were re-tested using a larger sample and the results confirmed initial measurements. Duplicate samples of each WTR were tested and all samples showed highly repeatable results as duplicates were very similar. Means from duplicate samples are presented in the results.

Dayton and Basta (2005) suggested that performing oxalate extractions on WTR ground and sieved to <150 µm increases the accuracy of the measurement of amorphous oxides and their correlation with P adsorption, when compared to more commonly-performed extractions on material ground and sieved to <2 mm. This is thought to be due to the increased surface area available for reactions to occur and simulates the slaking action that happens naturally to the material over time in field conditions. Slaking during short-term batch studies could introduce a source of variability into the results. Additional samples of Fe-WTR were tested using material ground and sieved to <150 µm to test the relationship of particle size, surface area, and porosity.

2.2.2.3 pH measurements

A glass electrode probe and pH meter was used to determine the pH of all WTRs and organics, using a ratio of 1:2, 1:3, or 1:4 dry media to deionized water (v:v) as needed to produce sufficient fluid for the probe.

2.2.2.4 Phosphorus binding capacity

The potential P binding and release characteristics of the WTRs and organics were measured using three extraction methods. Chemical extractions using Mehlich 3 and ammonium oxalate solutions are soil tests designed to measure both the amorphous Al and Fe content important for binding P, as well as environmentally-relevant quantities of P in different media (P. J. A. Kleinman, 2017; Maguire & Sims, 2002; McKeague et al., 1971; Mehlich, 1984). They have been used with both agricultural as well as bioretention soils (Jay et al., 2017; Maguire & Sims, 2002). The phosphorus saturation ratio (PSR) and phosphorus saturation index (PSI) are molar ratios of extractable P to extractable Al and Fe, and have been shown to be related to leachable P from soils and soil mixtures (S. Brown et al., 2016; E. A. Dayton & Basta, 2005; Jay et al., 2017; Maguire & Sims, 2002; Oladeji et al., 2007). Water-extractable P was also measured to estimate environmentally-leachable P in runoff concentrations (P. Kleinman et al., 2007)

2.2.2.5 Chemical extractions of WTRs and organics

Mehlich 3-extractable Al, Fe, Ca, Cu, and P in all WTRs and organics was measured using a 10:1 solution to solid ratio with 2 g of dried and sieved media and 20mL Mehlich 3 extracting solution per sample (Mehlich, 1984). Samples were shaken for 5 minutes on a shaker table and filtered using 8-µm filter paper (Whatman #2 qualitative filter paper, GE Healthcare Life Sciences, United Kingdom). Filtered extracting solution was refrigerated until being analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (7300 DV ICP-AES, PerkinElmer, Waltham, Massachusetts). Three replicates were used for each material and two blanks, containing only extracting solution, were used for each extraction.

The Mehlich 3 extraction was done on four separate occasions. Samples were tested internally as well as sent to the Kansas State University soil testing laboratory (second extraction). Data from the third Mehlich 3 extraction are reported in the results of this study because samples of all media were analyzed, including three biosolids that were added late in the study. Means of replicate samples are reported in results. The fourth extraction was intended to confirm the results of the third extraction, but two of the WTRs (Fe-WTR and Al-WTR2) were below detectable limits for phosphorus (960 µg L^{-1} for Fe-WTR and 240 µg L^{-1}, due to different dilutions used, equivalent to 9.6 and 2.4 mg kg^{-1} WTR, respectively), so the results of that extraction were not used.

In the third Mehlich 3 extraction, additional samples were prepared for the WTRs using 25mL of extracting solution and 1g of dried and sieved WTR, a 2.5-fold increase in solution to solid ratio from the original Mehlich (1984) method, to see if extractable content would be higher. Dayton and Basta (2005) reported that a 2.5-fold increase in oxalate extracting solution, using 100:1 ratio of solution to solid instead of the original 40:1 ratio (McKeague & Day, 1966), produced more accurate results for WTRs due to their high Al and Fe content, and several subsequent studies have followed their suggestion (O'Neill & Davis, 2012a; Yan et al., 2016, 2018). To my knowledge this increased extracting solution ratio has not been done with the Mehlich 3 extraction.

The PSR of each material was calculated using its Mehlich 3-extractable P, Al, Fe content (Jay et al., 2017; Maguire & Sims, 2002).

$$PSR = (P_{M3})/(Al_{M3} + Fe_{M3}) \tag{2.1}$$

Early in the study, the contribution of Ca in the WTR to its ability to sorb P was explored, and Mehlich 3-extractable Ca was included in an alternative calculation of PSR.

$$PSR_2 = (P_{M3})/(Al_{M3} + Fe_{M3} + Ca_{M3}) \tag{2.2}$$

The sum of extractable Al and Fe in a media (the denominator of the PSR), is also used in certain analyses and is referred to as reactivity.

$$\text{Reactivity}_{M3} = \text{Al}_{M3} + \text{Fe}_{M3} \qquad (2.3)$$

Oxalate-extractable Al, Fe, P, and Cu, were determined following the method outlined in Jay et al. (2017), using a 60:1 solution to solid ratio modified from the original procedure of McKeague and Day (1966). Because the increased solution to solid ratio did not yield a significant change in Mehlich 3-extractable elemental content, an increased oxalate solution ratio was not used. Sieved media (0.5 mg) and 30mL of extracting solution were combined in each sample. Samples were immediately placed in the dark and shaken for 4 hours, then filtered using 8-µm ashless filter paper (Whatman #40 ashless quantitative filter paper, GE Healthcare Life Sciences, United Kingdom), diluted to a 1:4 ratio of filtrate to 0.01M HCl, and stored refrigerated in the dark until they were analyzed by ICP-AES. Three replicates were used for each material and two blanks, containing only extracting solution, were used for each extraction. Means of replicate samples are reported in results, with one exception. Two out of three replicates of Al-WTR2 were below detectable limits for P (96 µg L^{-1}, equivalent to 5.76 mg kg^{-1}); in the case of this media, the result from the third replicate, 97.2 µg L^{-1}, was used as the sole measurement.

The PSI of each material was calculated using its oxalate-extractable Al, Fe, and P (Elliott, O'Connor, & Brinton, 2002; Jay et al., 2017), and reactivity$_{ox}$ was calculated as the sum of oxalate-extractable Al and Fe.

$$\text{PSI} = (\text{P}_{OX})/(\text{Al}_{OX} + \text{Fe}_{OX}) \qquad (2.4)$$

$$\text{Reactivity}_{ox} = \text{Al}_{OX} + \text{Fe}_{OX} \qquad (2.5)$$

2.2.2.6 Water extraction of organics

Water-extractable phosphorus and copper were also measured for all organics to determine release rates expected to be comparable to runoff seen in field conditions (P. Kleinman et al., 2007). Dried and sieved aliquots of organic material were weighed into 120mL plastic specimen cups, to which DI water was added, in specified amounts of organic and water (Table 2.2. Water extractions performed on organic materials), beginning with one treatment water:solid ratio of 25:1 (O'Neill & Davis, 2012a), plus one more and one less concentrated treatment. Cups were then placed side by side on a shaker for 24 hours (± 2 h), and the supernatant was filtered through 0.45-µm membrane vacuum filters (Hurley et al., 2017; O'Neill & Davis, 2012a). Filtrate was analyzed for total dissolved P and Cu by ICP-MS. At least two lab blanks containing only DI water were used per extraction. Each sample was incubated in triplicate.

Shaking the samples increases contact between the solid and water in each sample. The use of DI water (instead of tap water or stormwater), due to its low ionic strength, also facilitates release of P from the organics, representing a "worst case scenario" that should be equal to if not greater than what would be expected in real bioretention systems (Mullane et al., 2015).

An initial water extraction was done using 1, 2, or 5g of dried and sieved organics per sample and 50mL DI water, for a total of three treatments for each organic (Table 2.2. Water extractions performed on organic materials). Results from this extraction showed that the organic material with the highest P release (ComBS) decreased P leaching per g as more organic was used in the sample, suggesting that the water was saturated and true P release rates were not reflected (assuming a much larger volume of water would be available in field conditions). A second water extraction was done using more diluted samples: either 0.5 or 1g of solid and 50 or 100mL DI water, for a total of four treatments for each organic. A third water extraction was done with the three King County biosolids alone (BioKC1, BioKC2, and BioKC3), because they were added to the study after the first two water extractions had already been done. These biosolids had higher amounts of P_{M3} and P_{ox} than the other organics, and higher PSRs, so to attempt to avoid the water saturation problem previously encountered, the last water extraction was even more dilute than the previous two. Samples of BioKC1, BioKC2, and BioKC3weighing 0.3, 0.5, or 1g of dried and sieved material were combined with 100mL DI water (three treatments per organic).

Table 2.2. Water extractions performed on organic materials

Water extraction number	DI water (mL)	Organic (g)	Water:solid ratio	Organics tested
1	50	1.0, 2.0, 5.0	50:1, 25:1, 10:1	ComFY, ComBS, ComY, BioPot, BioFe
2	50, 100	0.5, 1.0	200:1, 100:1, 50:1	BioFe, BioPot, ComBS, ComFY, ComY
3	100	0.3, 0.5, 1.0	300:1, 200:1, 100:1	BioKC1, BioKC2, BioKC3

2.2.3 *Batch sorption experiments*

Previous studies have used either the PSR or PSI (or its inverse, oxalate ratio) to predict P movement from BSM in both batch adsorption and column leaching studies (S. Brown et al., 2016; Jay et al., 2017; Yan et al., 2016). Although these prior studies have shown PSR and PSI to be related to P movement, no predictive equation has been able to produce BSMs from a range of WTR and organic components with sufficiently low P release to meet bioretention goals. An equation determined by Jay et al. (2.6), based on the PSR of a sample, suggests that this should be possible. In our research project, a series of batch studies, first using WTRs alone in synthetic solutions, and then different combinations of WTRs and organics together, was conducted to test the P release (organics) and P adsorption (WTR) of BSM components as well as the behavior of different blends. Different combinations of organics and WTRs were made to exhibit a wide range of PSR ratios. Effluent copper was measured in addition to P, to examine PSR as a possible predictor of Cu sorption as well.

$$\mathrm{Ln}(\text{effluent P (mg L}^{-1}\text{)}) = 1.10 * \ln(\mathrm{PSR}) + 2.79 \tag{2.6}$$

Air dried and sieved (< 2 mm) aliquots of WTRs and organics were weighed into 120mL plastic specimen cups. Solutions (assays 1-6) of DI water (assays 7-12) were added and samples were placed side by side on a shaker for 24 hours (± 2 h), then filtered through 0.45-µm membrane vacuum filters. In the case of assay 10, all samples were centrifuged and 1-µm filters were used due to excessive clogging of the 0.45-µm filters. The results from this assay were compared against assay 9 in a paired t-test. Filtrate from all assays was analyzed for total dissolved P and Cu by ICP-MS. Three replicate samples were done for each treatment, and blank samples were used routinely throughout as described below. In addition to lab blanks, which were prepared alongside treatments in the same specimen cups and received the same shaker time, one process blank was prepared per assay using only DI water poured through a clean filter and analyzed with the rest of the samples.

2.2.3.1 First incubations: testing WTR sorption with synthetic solutions of known concentration

An initial set of six assays was done with WTRs to test the potential for a previously-determined equation (2.6) to predict P adsorption based on the PSR of media used, and to examine the relationship between PSR and Cu removal. In each of the assays, the WTRs were incubated with synthetic solutions of varying amounts of P and Cu, and influent and effluent concentrations were compared to measure the response of the WTRs as sinks, or possibly sources, of either element.

As Ca was still being included in PSR equations at this stage in the study, equation (2.2) was adapted as equation (7) below, to calculate a combined PSR_2 for a sample containing both WTR and solution to use in equation (6). Since the solutions contained no additional Al, Fe, or Ca, the elemental contribution of the solution to the combined PSR was only relevant in the numerator. All WTR values are Mehlich 3-extractable molar quantities of each element, and all terms are expressed in mol sample^{-1}.

$$PSR_{2\text{-sample}} = (P_{WTR} + P_{solution})/(Al_{WTR} + Fe_{WTR} + Ca_{WTR}) \qquad (2.7)$$

Equation (7) was rearranged with the new target PSR_2 of 0.0422 as equation (8) to determine the mass of P, expressed in mol and converted to mol P kg^{-1} WTR, that a WTR could theoretically adsorb.

$$P_{solution} = 0.0422*(Al_{WTR} + Fe_{WTR} + Ca_{WTR}) - P_{WTR} \qquad (2.8)$$

The Mehlich 3 extractable concentrations of Fe, Al, Ca, and P for the four WTRs from the first Mehlich 3 extraction were used in equation (8) to calculate a unique $P_{solution}$ for each WTR on a mass basis. Accounting for 2 g of WTR and 50 mL solution in each sample, four $P_{solution}$ concentrations were calculated (Table 4), which were used in assay 1. These solution concentrations, as predicted by the $PSR_{2\text{-sample}}$, were each calculated to match one of the four WTRs so that the remaining solution after incubation would be below a set target value of 0.5 mg P L^{-1}.

As each WTR had a different initial PSR_2, the 4 solutions were expected to provide the $PSR_{2\text{-sample}}$ required for each WTR to achieve the target post-incubation concentration with its own solution, as well produce as a range of $PSR_{2\text{-samples}}$ and P sorption responses among the full set of WTRs and solutions.

Table 2.3. Concentrations of P calculated for synthetic solutions used in assay 1. The solutions were intended to deliver a mass of P that each of the four WTRs could adsorb in a single sample. P_{solution} concentrations, expressed in mol P kg^{-1} WTR, were calculated according to equation (1.8), using Mehlich 3-extractable content of the WTR. Psolution concentrations, expressed in mg P L^{-1}, are equivalent to the Psolution concentrations in mol P kg^{-1} WTR, assuming that each sample contains 2 g WTR and 50 mL of solution. The $PSR_{2\text{-sample}}$ of each sample (accounting for both WTR and solution) is 0.0422.

Matching WTR	**PSR_2 of WTR**	**P_{solution} concentration (mg L^{-1})**
Ca-WTR	0.00090	49.6
Fe-WTR	0.0014	24.8
Al-WTR1	0.0046	6.20
Al-WTR2	0.0062	3.10

KH_2PO_4 was measured into DI water to prepare four solutions at the P concentrations listed in Table 4 for assay 1, so that each of the original 4 WTRs had a matching solution intended to produce effluent concentrations at or below the 0.5 mg L^{-1} target. Each WTR was tested with its own solution, and with the other three solutions strengths, to get a range of response data.

Five more batched assays were then performed, for a total of six: using the 4 P solutions as initially calculated, using solutions containing 4 times the initial amount of P, and each with either 0, 1, or 100 µg L-1 Cu (Table 5), added as $Cu(NO_3)_2$. Within each assay, all 4 WTR were tested with their own solution and with the other three solutions to get a range of response data. Three replicates of each WTR were done with each of the treatment solutions. Two lab blanks were used for each of the four solutions used in each assay, containing only the treatment solution and no WTR.

The concentrations of P used in these solutions is much higher than the 0.13 mg L^{-1} national average for concentrations in runoff (Pitt et al., 2004). As the main source of P to bioretention effluent is organic matter in the BSM, not influent stormwater (McPhillips, etal. 2018; Paus et al. 2014; Chahal, Shi, and Flury 2016), we wanted to test the WTRs with higher P concentrations. Solution concentrations were designed to explore the capacity of the WTRs used in the study to adsorb P and to generate a range of response data. The range of concentration of Cu used in these solutions (0 – 100 µg L -1) spans a range wider than reported for dissolved Cu in stormwater runoff (5.5 – 25 µg L -1) (Jay et al., 2018; Pitt et al., 2004), also intended to generate a range of responses.

Table 2.4. Intended and measured concentrations of phosphorus and copper in the first set of assays (assays 1-6)

			Solution							
			1		2		3		4	
Assay	Treatment	Addition	Intended	Measured	Intended	Measured	Intended	Measured	Intended	Measured
1	Low P, no Cu	P (mg L $^{-1}$)	49.6	59.6	24.8	31.8	6.20	8.58	3.10	9.15
		Cu (µg L $^{-1}$)	0	*	0	*	0	*	0	*
2	Low P, low Cu	P (mg L $^{-1}$)	49.6	46.2	24.8	22.2	6.20	5.62	3.10	2.78

		Cu (μg L $^{-1}$)	1	1.04		0.70		0.80		0.80
3	High P, no Cu	P (mg L $^{-1}$)	198	168	99.2	81.9	24.8	19.4	12.4	10.2
		Cu (μg L $^{-1}$)	0	6.45	0	3.80	0	2.69	0	2.40
4	High P, low Cu	P (mg L $^{-1}$)	198	188	99.2	91.6	24.8	23.7	12.4	9.9
		Cu (μg L $^{-1}$)	1	8.03		6.48		2.28		1.55
5	Low P, high Cu	P (mg L $^{-1}$)	49.6	47.5	24.8	23.2	6.20	5.30	3.10	1.88
		Cu (μg L $^{-1}$)	100	88.9		74.5		68.2		30.2
6	High P, high Cu	P (mg L $^{-1}$)	198	194	99.2	92.5	24.8	24.0	12.4	6.16
		Cu (μg L $^{-1}$)	100	92.4		92.6		96.2		44.5

* Effluent Cu was not measured for assay 1.

Individual samples were prepared by adding 50mL of synthetic stormwater solution to 2g of WTR in 120mL plastic specimen cups. Samples were shaken for 24 hours (± 2 h), then filtered through 0.45-μm membrane vacuum filters. Filtrate was analyzed for total dissolved P and Cu by inductively coupled plasma mass spectrometry (ICP-MS) (7900 octopole reaction system ICP-MS, Agilent, Santa Clara, California).

In order to correct for discrepancies between intended and actual influent concentrations of P and Cu in these solutions, and also because the DI water was found to be a source of Cu, all influent concentrations were set according to measurements in blanks. Adsorbed or released P and Cu are calculated as the difference between measured effluent of a given sample and influent concentrations in blanks for the same treatment solution.

2.2.3.2 Final incubations: Leaching-sorption with WTR and organic combinations.

A final set of six batched assays was conducted using WTRs and organics in paired combinations, using a range of relative quantities of each to generate a range of PSR values. For the first assay of this set (assay 7), WTRs and organics were combined according to an estimated P adsorption or release based on the difference in P between their individual PSR_2 values from the first Mehlich 3 extraction, and the target PSR of 0.0422 from equation (2.6). Three organics, BioKC1, BioKC2, and BioKC3, were not included in this assay.

$$PSR_{2\text{-target}} = 0.0422 = (P_{WTR} + P_{adsorb})/(Al_{WTR} + Fe_{WTR} + Ca_{WTR}) \tag{2.9}$$

$$P_{adsorb} = [(Al_{WTR} + Fe_{WTR} + Ca_{WTR})*0.0422] - P_{WTR} \tag{2.10}$$

$$PSR_{2\text{-target}} = 0.0422 = (P_{organic} - P_{release})/(Al_{organic} + Fe_{organic} + Ca_{organic}) \tag{2.11}$$

$$P_{release} = P_{organic} - 0.0422*(Al_{organic} + Fe_{organic} + Ca_{organic}) \tag{2.12}$$

Pairs of WTR and organic were then combined in relative proportions so that the weighted average of each component would match P_{adsorb} for each WTR with $P_{release}$ for each organic (Table 2.5).

$$P_{release} * weight_{organic} = P_{adsorb} * weight_{WTR} \qquad (2.13)$$

Table 2.5. Relative amounts of WTR and organics used in assay 7.

Combination	WTR (g)	Organic (g)	$PSR_{2\text{-sample}}$
Al-WTR1/BioFe	0.17	1.83	1.19
Al-WTR1/BioPot	0.14	1.86	0.73
Al-WTR1/ComBS	0.28	1.72	1.98
Al-WTR1/ComFY	0.044	1.96	0.56
Al-WTR1/ComY	0.13	1.87	0.76
Al-WTR2/BioFe	0.24	1.76	1.14
Al-WTR2/BioPot	0.21	1.79	0.71
Al-WTR2/ComBS	0.40	1.60	1.88
Al-WTR2/ComFY	0.066	1.93	0.74
Al-WTR2/ComY	0.20	1.80	0.55
Ca-WTR/BioFe	0.018	1.98	1.45
Ca-WTR/BioPot	0.015	1.98	0.84
Ca-WTR/ComBS	0.033	1.97	2.55
Ca-WTR/ComFY	0.0045	2.00	0.59

Ca-WTR/ComY	0.014	1.99	0.89
Fe-WTR/BioFe	0.034	1.97	1.43
Fe-WTR/BioPot	0.030	1.97	0.83
Fe-WTR/ComBS	0.062	1.94	2.50
Fe-WTR/ComFY	0.0087	1.99	0.58
Fe-WTR/ComY	0.027	1.97	0.88

The subsequent five assays then combined WTRs and organics in set proportions on a dry weight basis (Table 2.6). Each sample contained between 2 and 5g of combined media, to which was added 50mL DI water. As in the water extractions of organics previously mentioned, the use of DI water is intended to provide maximum facilitation of P release from the organics in combination samples, as well as to isolate the samples from confounding effects of dissolved elements in tap water. This should provide a conservative baseline of high P release from the organics against which high sorption by the WTR will be necessary to achieve desired low effluent results. All samples within a given assay contained the same amount of total media. Once DI water was added, samples were set on a side to side shaker for 24 hours (± 2 h) and then filtered. Many samples, especially those containing biosolids that tended to clog the filters quickly, were centrifuged at 3500 rpm for 5 minutes prior to filtration. Two lab blanks containing only DI water were used per assay.

Table 2.6. Relative amounts of WTR and organic media used per sample in batch combination incubation assays**.**

Assay	WTR (g)	Organic (g)

7	Varied based on component pairs (see Table 2.5)	
8	1	2
9	0.5	2
10	1	4
11	1	1
12	2	1
	additional combinations with BioKC1 and each WTR (see Table 2.7)	

On the final assay (assay 12), additional samples were prepared with the highest-P-releasing organic (BioKC1) and each WTR in proportions expected to yield effluent P concentrations at or below the 0.5 mg L^{-1} target according to preliminary results from earlier assays, suggesting that a PSR of around 0.05 should produce effluent at or below the target. In the case of the Fe-WTR and Al-WTR2 combinations, media was mixed in larger quantities, and 2-g aliquots were taken for each sample. PSR for this final assay was calculated using the standard format, including only Mehlich 3-extractable P, Al, and Fe, as in equation (2.14), and a weighted average of each present in WTRs and organic. P, Al, and Fe terms are expressed in mol sample^{-1}.

$$PSR_{sample} = (P_{WTR} + P_{organic})/(Al_{WTR} + Fe_{WTR} + Al_{corganic} + Fe_{organic}) \qquad (2.14)$$

Table 2.7. Relative amounts of WTR and organics used per sample in assay 12.

Combination	WTR (g)	Organic (g)
Fe-WTR/BioKC1	1.9	0.1
Al-WTR1/BioKC1	4	0.5
Al-WTR2/BioKC1	1.8	0.2

The result of assays 7-12 was a range of PSR_{sample} values tested for each WTR and organic combination. PSR values in Figures 1 and 2 below, and those reported in the results section of this study use Mehlich 3-extractable content of media based on the third Mehlich 3 extraction, This PSR range, according to a weighted average of extractable Al, Fe, and P for each media (as in equation 14), is presented in Figure 1 for each organic. The minimum PSR_{sample} was 0.13 (a 2:1 combination of Al-WTR1 and ComFY). The maximum was 6.5 (a 1:4 combination of Fe-WTR and BioKC3).

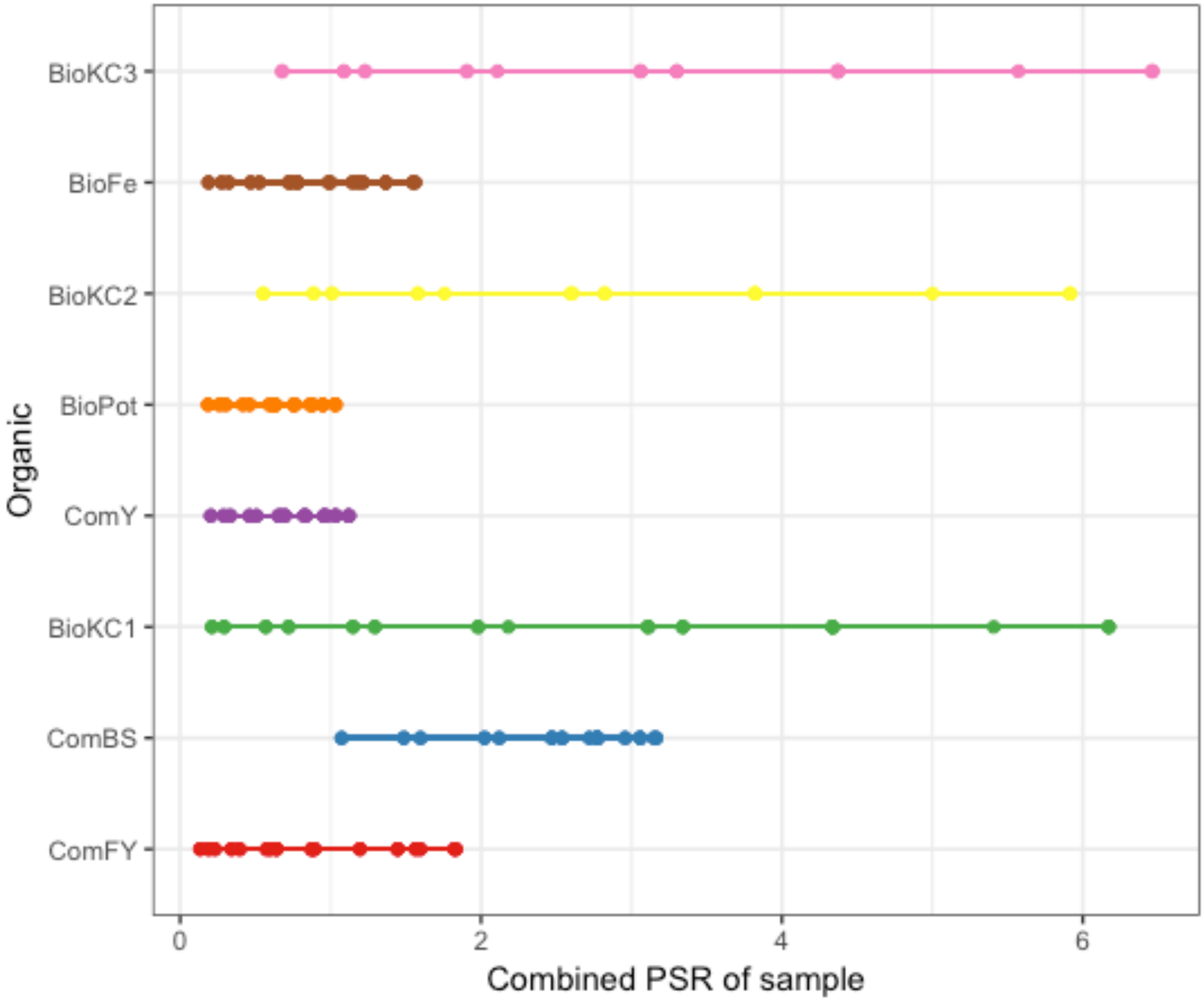


Figure 2.1. Range of PSR values tested across all combinations by organic (assays 7-12).

In addition to the PSR, we also calculated the PSI of materials. The PSI range of the combination samples, according to oxalate-extractable Al, Fe, and P for each media, is presented in Figure 2 for each organic. The minimum PSI_{sample} was 0.046 (a 19:1 combination of Fe-WTR and BioKC1). The maximum was 1.4 (a 1:4 combination including Al-WTR2 and BioKC1).

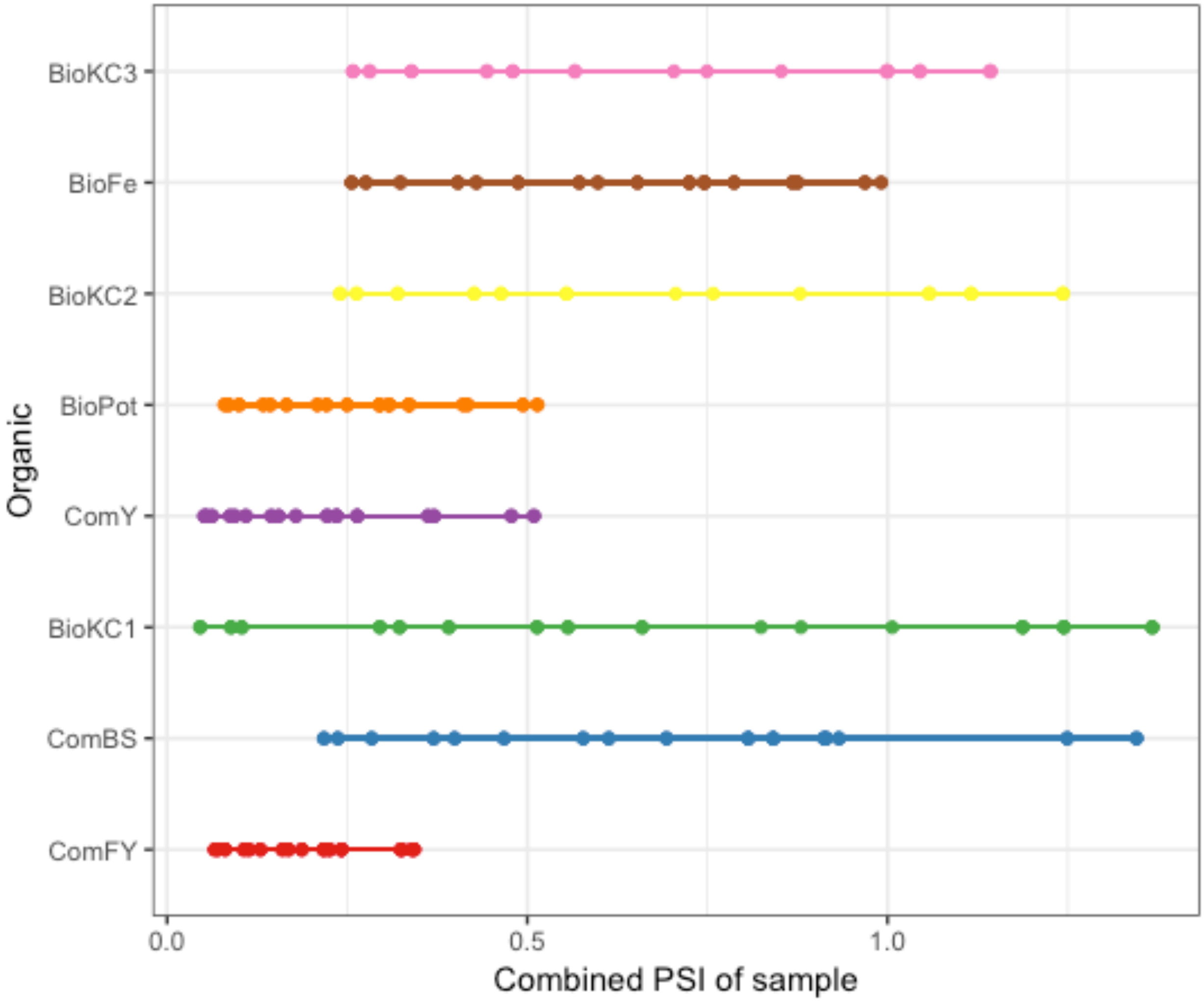


Figure 2.2. Range of PSI values tested across all combinations by organic (assays 7-12).

2.2.4 *Data analysis*

Data analysis was done in R (R Core Team, 2018) using an alpha of 0.05 for all significance tests. Significance of correlation coefficients was determined by one- and two-way ANOVA, and pairwise comparison of means was done with the Tukey HSD test. Individual linear regression models were assessed by their R^2 and by p-values of coefficients. Multiple candidate variables in nested sets were tested for inclusion in linear regression models using forward subset selection, and candidate models were compared by their R^2 and Akaike information criterion (AIC) values.

Two or more non-nested linear models were also compared by their R^2 and AIC values. The Akaike information criterion is a method of model comparison that takes into account both descriptive accuracy and parsimony of model parameters. Raw AIC values were also converted into Akaike weights as suggested by Wagenmakers and Farrell (2004) to ensure that models with the lowest raw AIC values were also those with the highest probability of approximating the data. Figures were made in base R or with the ggplot2 package (Wickham, 2016). Theme selection was aided by the ggthemes package (Arnold, 2019), and color selection was aided by the colorspace package (Ihaka, Murrell, Hornik, Fisher, & Zeileis, 2016) and viridis package (Garnier, 2018).

2.3 RESULTS AND DISCUSSION

2.3.1 *Phosphorus release and retention*

2.3.1.1 Phosphorus binding capacity

2.3.1.1.1 Extractable chemical components

All media were analyzed for total and extractable Al, Fe, and P (Table 2.8). Extractable content was determined by both Mehlich 3 and acid ammonium oxalate extractions. The Ca-WTR was not analyzed, because it performed poorly in the initial assays (low P sorption) and was removed from the study before most of the media characterization was completed.

Ammonium oxalate extracted higher quantities of elements tested (Al, Fe, P) from all media than Mehlich 3 in all but a few cases. Higher values for oxalate-extractable vs. Mehlich 3-extractable Al, Fe, and P have also been reported by other studies in both soils and bioretention mixes (Jay et al., 2017; Maguire & Sims, 2002). Since both oxalate and Mehlich 3 extractions are intended to measure the amorphous fractions of Al and Fe, this discrepancy suggests that either oxalate could be overestimating or Mehlich 3 could be underestimating these fractions. For this study, on the whole, results from the two extractions were fairly well-correlated, with p-values < 0.01 for linear regression for all mutually-tested elements (Figure 2.3), meaning that, while the elemental measurements are different in magnitude, they may be extracting similar proportions of elemental content from both low-content and high-content media, and may be useful for similar predictive calculations. The values from the two extractions were best correlated for P measurements, and least correlated for Fe (Al: $p \leq 0.006$, $R^2 = 0.54$; Fe: $p \leq 0.004$ and $R^2 = 0.20$, P: $p \leq 0.03$, $R^2 = 0.42$;). These R^2 values are lower than those reported by Maguire and Sims (2002). The low R^2 for Fe and P by the two extractions suggests that the two methods are not extracting similar proportions of these elements, and measurements may not predict similar P sorption and release behavior by the media. The fact that the correlation coefficients are different for the three elements (Figure 2.3) suggests that the two methods are not extracting the same proportions of each element relative to each other.

Table 2.8. Al, Fe, and P content of WTRs and organic as measured by Mehlich 3, oxalate, and total elemental extractions.

	Al_{M3}*	**Fe_{M3}***	**P_{M3}***	**Al_{ox}***	**Fe_{ox}***	**P_{ox}***	**Total Al**	**Total Fe**	**Total P**
WTR	**mg kg^{-1}**						**g kg^{-1}**		
Al-WTR1	743 ± 87.9	48.4 ± 3.61	20.6 ± 2.82	2092 ± 66.1	132 ± 4.01	22.8 ± 1.17	108	18.9	1.47
Al-WTR2	406 ± 12.2	60.1 ± 2.19	0.600 ± 0.265	1396 ± 187	233 ± 33.1	5.83‡	65.2	20.4	0.543
Fe-WTR	9.13 ± 1.48	208 ± 12.5	5.67 ± 0.176	258 ± 20.7	3460 ± 273	17.4 ± 1.22	10.2	72.9	0.846
Organics									
BioFe	52.9 ± 0.49	274 ± 25.1	333 ± 24.6	235 ± 40.5	2512 ± 426	1648 ± 263	9.04	52.7	26.5
BioKC1	41.6 ± 2.87	256 ± 38.2	1363 ± 257	183 ± 8.35	1010 ± 66.3	1644 ± 147	4.53	20.4	29.9
BioKC2	47.7 ± 3.05	152 ± 22.3	1008 ± 162	210 ± 22.1	658 ± 85.2	1290 ± 117	3.05	7.86	15.8
BioKC3	28.2 ± 6.77	238 ± 13.9	1263 ± 85.7	243 ± 13.0	1000 ± 53.3	1446 ± 88.8	6.27	17	23.7
BioPot	205 ± 24.7	183 ± 13.4	348 ± 39.5	399 ± 8.35	632 ± 7.21	415 ± 11.5	7.67	12.2	3.93
ComBS	629 ± 54.5	291 ± 48.9	2797 ± 150	431 ± 10.2	758 ± 10.6	1232 ± 30.3	4.63	7.59	8.1
ComFY	37.4 ± 3.96	128 ± 1.86	209 ± 3.21	447 ± 17.7	916 ± 31.7	351 ± 13.4	6.10	10.5	2.98
ComY	246 ± 59.9	115 ± 23.9	388 ± 120	240 ± 6.72	333 ± 5.11	234 ± 8.07	8.19	10.2	2.19

* Mean of three samples tested, ± standard error.

[1] Only one of three samples tested registered above detectable limits of 96 μg L^{-1}, equivalent to 5.76 mg kg^{-1} for these samples.

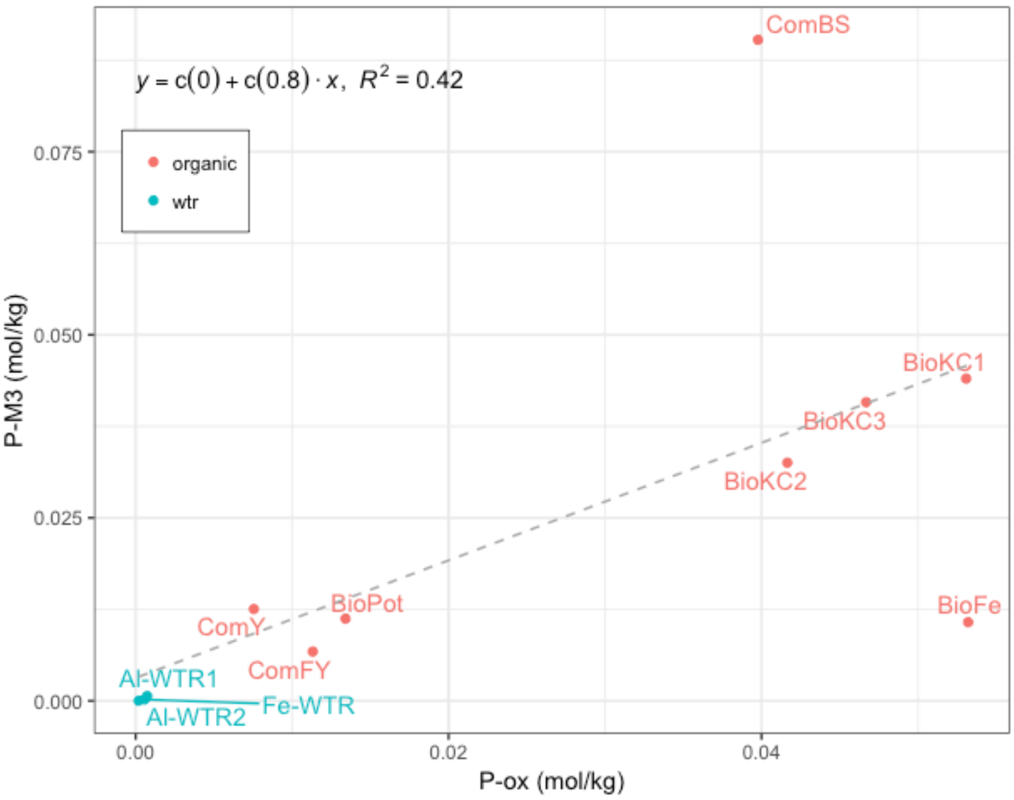
Extractable P from both methods was in general much higher for organics than for WTRs, as was total P. As expected, both the Mehlich 3 and oxalate extractable P for the WTRs tested was very low. It ranged from 0.600 to 20.6 mg P kg^{-1} for the Mehlich 3 and 5.83 to 22.8 mg P kg^{-1} for the oxalate extraction. Both extractions showed the least extractable P in Al-WTR2 and the most in Al-WTR1. In contrast, the extractable P for the organics was high. It ranged from 209 to 2797 mg P kg^{-1} for the Mehlich 3 and 234 to 1648 mg P kg^{-1} for the oxalate. The four biosolids and the biosolids/sawdust compost (ComBS) contained more total P and extractable P by either method than did the food and yard waste composts, ComFY and ComY, or the potting soil mix, BioPot (Figure 2.3a). While for most of the media, the two P extractions were very well correlated, two outliers were ComBS and BioFe. Figure 2.3 shows the correlation between extractable P, Al, and Fe by the two extraction methods.

Data points above the dotted correlation lines in Figure 2.3 (for example, ComBS in all three measurements) show media for which the Mehlich 3 extraction measured proportionally more of a given elemental content than did the oxalate extraction, when compared with the other media. While ComBS fell around the middle of the range of all media tested in terms of oxalate-extractable elemental content (Al, Fe, and P), it was among the highest of all media in Mehlich 3-extractable content, second only to Al-WTR in Mehlich 3-extractable Al. Conversely, BioFe falls well below the correlation line in extractable P; oxalate-extractable P was much higher for this media than was Mehlich 3-extractable P.

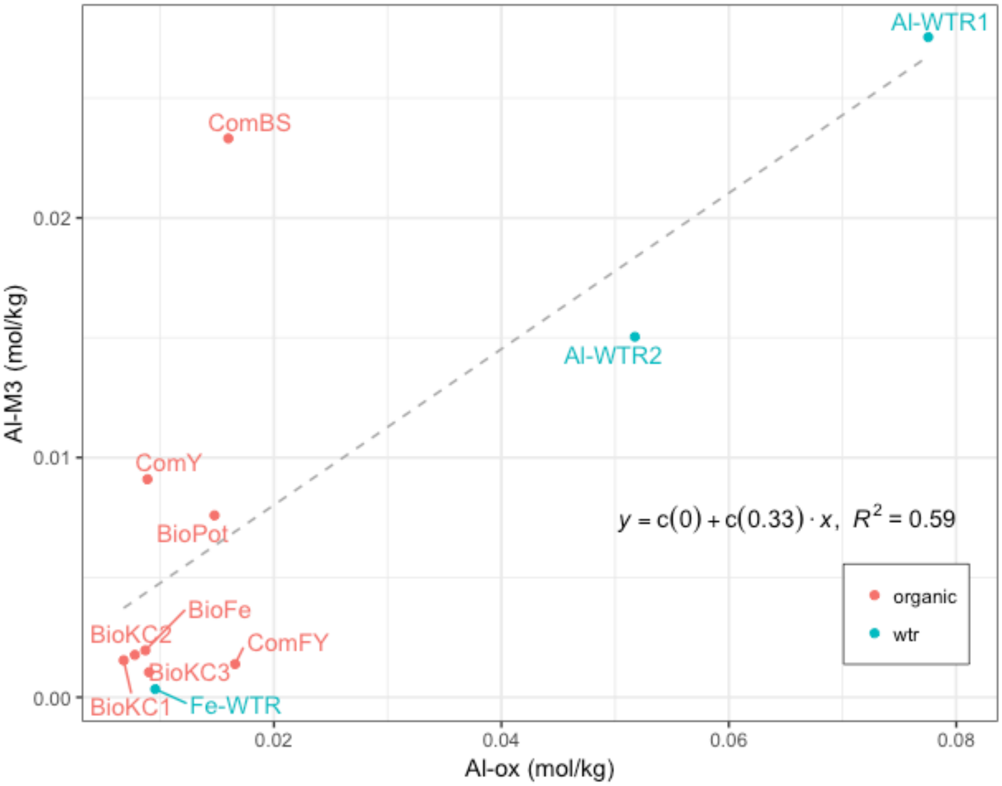
The discrepancy between the two extractions for Fe increased at higher concentrations of Fe in the media (Figure 2.3c). This trend was also observed by Maguire and Sims (2002), who found Mehlich 3 to be a poorer extractor of Fe than of Al, and suggested that Mehlich 3 may not be as good of a predictor of phosphorus saturation in soils with high pH or where Fe oxides are a bigger component than Al, both of which is the case with the Fe-WTR in this study. The two media known to have high Fe addition, BioFe and WTR-Fe, had higher oxalate-extractable Fe than the other media, but their Mehlich 3-extractable Fe was within the range of the other media.

As expected, the Fe-WTR had much higher total Fe than the other WTRs and all of the organics. BioFe is known to have Fe added as a flocculant in the wastewater treatment process and tested higher for total Fe than any of the other organics. Both Al-based WTRs had much higher total Al than did Fe-WTR or any of the organics. The WTRs had generally higher extractable Al or Fe (depending on the WTR type) than did the other media, however this was more pronounced in the oxalate-extractable numbers. Although the WTRs had total Al and Fe levels comparable to those reported by other studies, the oxalate- and Mehlich 3-extractable levels of these metals were much lower. Ippolito et al. (2011) reported a range of characteristics of WTRs from 21 studies using Al-based WTRs and 5 studies using Fe-based WTRs. The average oxalate-extractable Al in Al-based WTRs reported from those studies was over 30 times higher than in Al-WTR1 in the present study (even more when compared to Al-WTR2), and the average oxalate-extractable Fe in Fe-based WTRs reported was also over 30 times higher than in Fe-WTR in the present study. This means that the proportion of amorphous to total Al and Fe is also much lower than average. O'Neill and Davis (2012a) used Al-based WTR containing 91% of their total Al as oxalate-extractable Al; in the present study, total Al in Al-WTR1 is 1.8% oxalate-extractable, and in Al-WTR2 it is 2.1%. Total Fe in Fe-WTR is 4.7% oxalate-extractable. The percentage according to Mehlich 3 numbers is even lower. This could be due to various factors involved in the drinking water treatment process that creates the WTRs in this region, but regardless it should greatly reduce their effectiveness as P sorbents (Gallimore et al., 1999; Ippolito et al., 2011).

a)


$y = c(0) + c(0.8) \cdot x, \; R^2 = 0.42$
organic
wtr
ComBS
BioKC1
BioKC3
BioKC2
BioPot
BioFe
ComY
ComFY
Al-WTR1
Al-WTR2
Fe-WTR
P-M3 (mol/kg)
0.075
0.050
0.025
0.000
0.00
0.02
0.04
P-ox (mol/kg)

b)


Al-WTR1
ComBS
Al-WTR2
ComY
BioPot
$y = c(0) + c(0.33) \cdot x, \; R^2 = 0.59$
organic
wtr
BioFe
BioKC2
ComFY
BioKC3
BioKC1
Fe-WTR
Al-M3 (mol/kg)
0.02
0.01
0.00
0.02
0.04
0.06
0.08
Al-ox (mol/kg)

c)

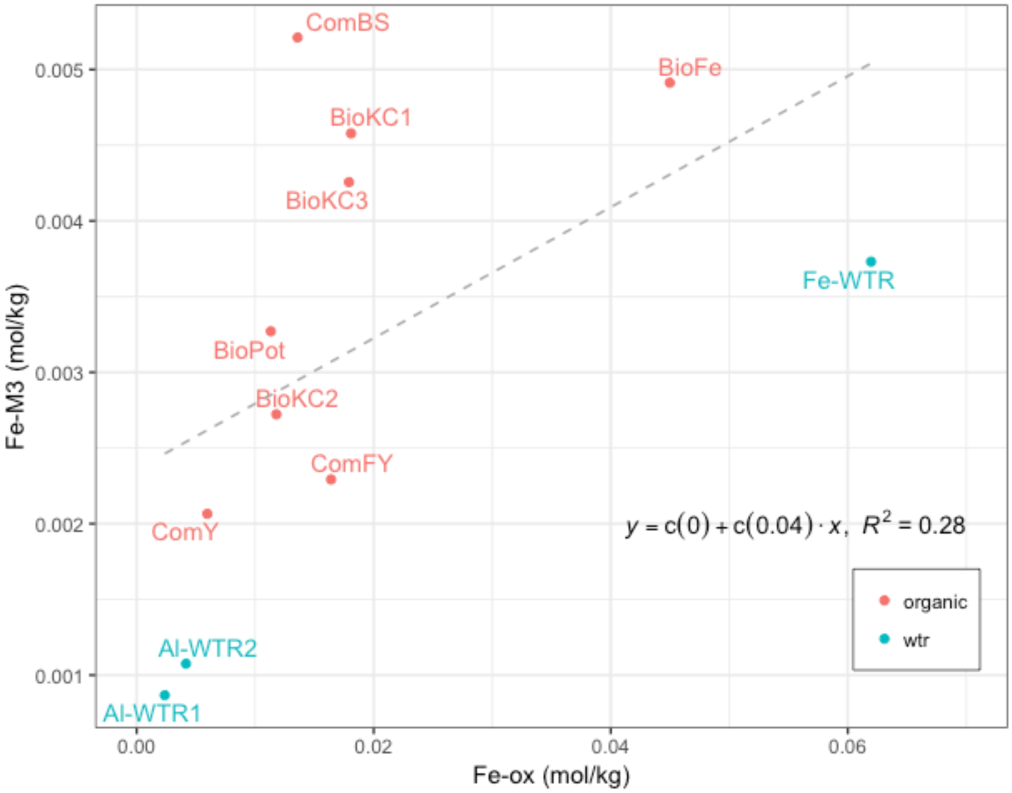


Figure 2.3. Comparison of Mehlich 3-extractable and oxalate-extractable elements in media. a) Phosphorus, b) Aluminum, and c) Iron.

The differences between the two extractions carries into measures of expected sorption between the three WTRs. The sum of oxalate-extractable Al and Fe, referred to as reactivity$_{ox}$, is the denominator of PSI and is a measure of the P binding capacity of a WTR. For the WTRs tested in this study, the reactivity$_{ox}$ of the Fe-WTR and Al-WTR1, (71.5 and 79.9 mmol kg$^{-1,}$ respectively), was similar. This suggests that their absorption capacity for P would also be similar. In contrast, the reactivity$_{ox}$ of the AlWTR2 was lower (55.9 mmol kg^{-1}), suggesting it would be less effective at absorbing P. However, reactivity$_{M3}$ (the same sum for Mehlich 3-extractable metals) for Fe-WTR, at 4.07 mmol kg^{-1}, was much lower than for either Al-WTR1 or Al-WTR2, (28.4 and 16.1 mmol kg^{-1}, respectively). This suggests that the Fe-WTR would be less effective than the Al based WTR at absorbing P. If, as previous literature suggests, this difference is due to an under-extraction of Fe by Mehlich 3, that would lead to an underestimation of P sorption by the Fe-WTR and the absorptive capacity of this material would likely be higher than predicted.

Many of the organics tested also had a high P adsorptive capacity (reactivity) as measured by both the M3 and oxalate extractions. Reactivity_{M3} in the organics ranged from 3.7 to 11 mmol kg^{-1} and reactivity_{ox} ranged from 15 to 54 mmol kg^{-1}. This suggests that the adsorptive capacity of extractable Al and Fe in the organics may play a part in predicting whether they will leach significant quantities of P in bioretention systems (Oladeji et al., 2007), in conjunction with their P content. In several cases (ComBS, BioKC1, BioFe, and BioKC3), Fe_{M3} of the organics exceeded Fe_{M3} of the Fe-WTR. Al_{M3} of one of the organics (ComBS) also exceeded Al_{M3} of Al-WTR2, although none of the organics exceeded Al-WTR1 in Al_{M3}. In oxalate-extractable Al and Fe, Al-WTR1 and Al-WTR2 exceeded all organics in Al_{ox}, and Fe-WTR exceeded all organics in Fe_{ox}. BioFe, the San Francisco biosolids with Fe added, had by far the highest reactivity_{ox} of all of the organics, but mid-level reactivity_{M3}.

The ratio of extractable P to the extractable Fe and Al gives the unitless ratios PSR and PSI. Despite differences in extractable amounts of individual elements the two ratios were well correlated, with a highly significant ($p < 0.0001$) correlation coefficient of 3.5 and an R^2 of 0.89. The mean PSR across all organics and WTRs was 2.80 ± 0.52, higher than the mean PSI of 0.88 ± 0.14. BioKC1, BioKC2, and BioKC3 had the highest PSR (7.1 ± 0.41, 7.2 ± 0.45, and 7.7 ± 0.50, respectively) and PSI (2.1 ± 0.71, 2.1 ± 0.80, and 1.7 ± 0.015, respectively) of all media. BioFe, the other Class B biosolid included in the study, had Fe added during wastewater treatment. The reduced PSR (1.6 ± 0.034) due to a relatively low P_{M3}, and reduced PSI (0.99 ± 0.011) due to a high reactivity$_{ox}$ set this material apart from the other biosolids in the study. The PSR of all organics ranged from 1.0 ± 0.027 (BioPot) to 7.7 ± 0.50 (BioKC3). The corresponding PSI range was 0.34 ± 0.0037 (ComFY) to 2.1 (± 0.071 for BioKC1 and ± 0.080 for BioKC2). High-PSR and PSI media are expected to release the most P (S. Brown et al., 2016; Jay et al., 2017; O'Neill & Davis, 2012a; Oladeji et al., 2007). In this case we would expect all three King County biosolids (BioKC1, BioKC2, and BioKC3) to release the most P. We would expect BioPot and ComY to release the least P according to PSR values, and ComFY to release the least P according to PSI values. All WTR had much lower PSR and PSI than all organics, as expected due to the high Al and Fe and low P content of the WTRs and the relatively high P content of organic matter. Al-WTR2 had the lowest PSR (0.0012 ± 0.00054) and PSI (0.0027) than the other two WTR (0.0450 ± 0.0023 and 0.0079 ± 0.00010, respectively, for Fe-WTR, and 0.023 ± 0.0012 and 0.0092 ± 0.00039, respectively, for Al-WTR1), making Al-WTR2 the expected best performer in terms of P adsorption.

Table 2.9. Reactivity$_{M3}$, reactivity$_{ox}$, PSR, and PSI of media used. Reactivity$_{M3}$ and PSR are calculated from Mehlich 3-extractable elemental content, and reactivity$_{ox}$ are calculated from oxalate-extractable elemental content (shown in Table 2.8). Reactivity$_{ox}$ and reactivity$_{M3}$ are the sum of extractable Fe and Al, expressed in mmol kg^{-1}, and represent the binding capacity of each material.

	Reactivity$_{M3}$*	**Reactivity$_{ox}$***	**PSR***	**PSI***
WTRs	**mmol kg^{-1}**			
Al-WTR1	28 ± 3.1	80 ± 2.5	0.023 ± 0.0012	0.0092 ± 0.00039
Al-WTR2	16 ± 0.49	56 ± 7.5	0.0012 ± 0.00054	0.0027[1]
Fe-WTR	4.1 ± 0.26	72 ± 5.6	0.045 ± 0.0023	0.0079 ± 0.00010
Organics				
BioFe	6.9 ± 0.46	54 ± 9.1	1.6 ± 0.034	0.99 ± 0.011
BioKC1	6.1 ± 0.78	25 ± 1.5	7.1 ± 0.41	2.1 ± 0.071
BioKC2	4.5 ± 0.49	20 ± 2.3	7.2 ± 0.45	2.1 ± 0.080
BioKC3	5.3 ± 0.52	27 ± 1.4	7.7 ± 0.50	1.7 ±0.015
BioPot	11 ± 1.1	26 ± 0.43	1.0 ± 0.027	0.51 ± 0.0086
ComBS	29 ± 2.9	30 ± 0.57	3.3 ± 0.45	1.3 ± 0.0073
ComFY	3.7 ± 0.12	33 ± 1.2	1.8 ± 0.071	0.34 ± 0.0037
ComY	11 ± 2.6	15 ± 0.34	1.1 ± 0.075	0.51 ± 0.0063

* Mean of three samples tested, ± standard error.

[1] Only one of the three Al-WTR2 samples tested registered above detectable limits for P$_{ox}$ (96 μg L^{-1}, equivalent to 5.76 mg kg^{-1} for these samples); this sample was used to calculate PSI.

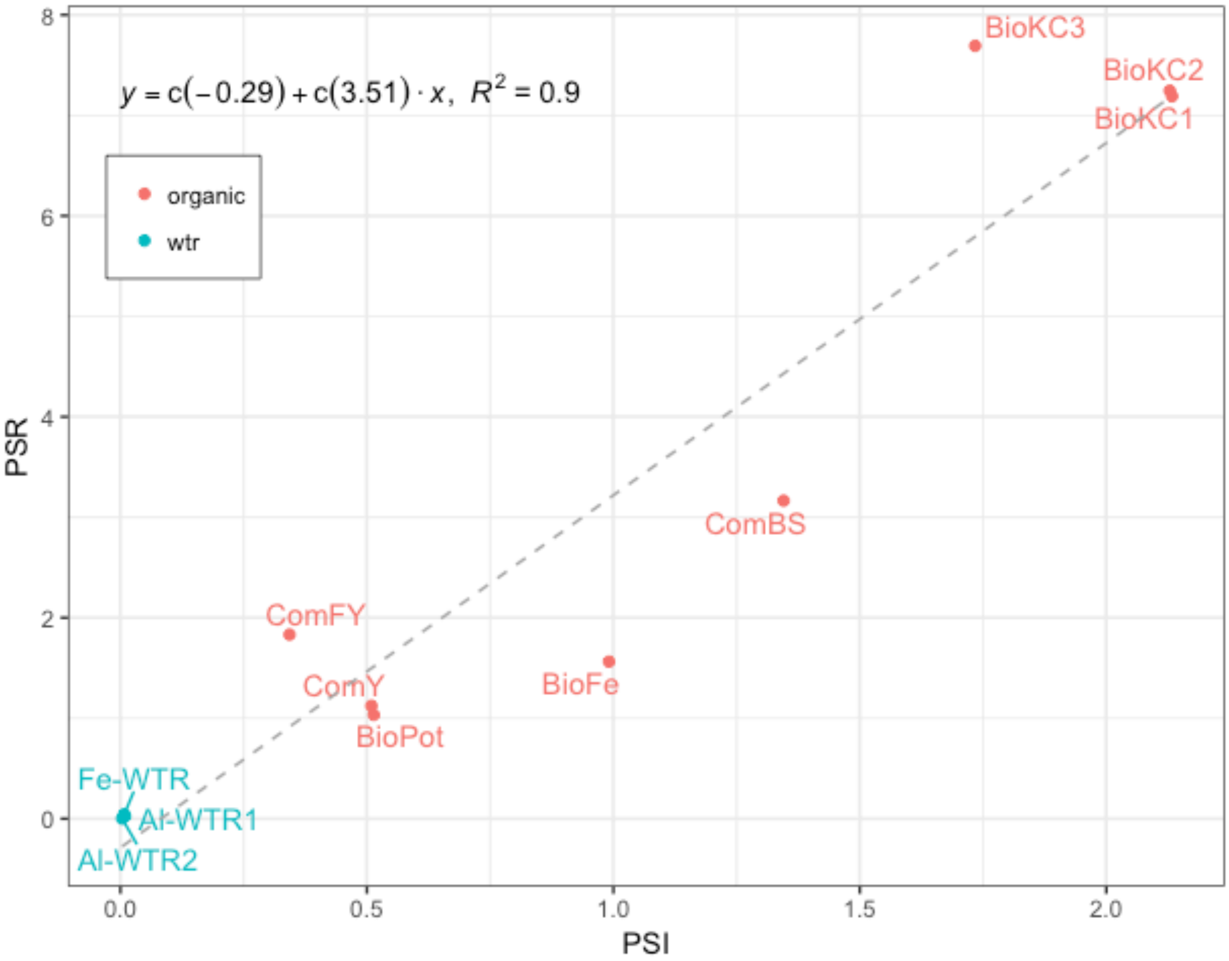


Figure 2.4. Comparison of PSI and PSR values for media.

All media were also analyzed for pH, total C, and total N. The Fe-WTR had the highest pH of all media in the study, still circumneutral with a pH of 7.22, whereas the two Al-WTRs were slightly acidic, with pHs of 5.89 and 5.35. A review suggested that Fe-WTR are usually slightly more alkaline than Al-WTR, the former averaging pH 7.0, and the later 6.5 of the materials sampled (Ippolito et al., 2011). The average pH of the two Al-WTR at 5.62 was very similar to that of the organics at 5.51. The total C in the WTRs ranged from 153 to 206 g kg^{-1} and total N ranged from 9.99 to 16.2 g kg^{-1}. In general, the organics had similar to higher total C than the WTRs (199 to 400 g kg^{-1}) and higher N (9.43 to 66.3 g kg^{-1}). Previous work has suggested that C in WTRs may inhibit P adsorption (Makris et al, 2005). The relatively high carbon content of the WTRs included in this study may impact their ability to absorb P.

Table 2.10. pH, total C, and total N of media used.

	pH	**Total C**	**Total N**
WTR		g kg^{-1}	
Fe-WTR	7.22	205.5	16.2
Al-WTR1	5.89	152.8	9.99
Al-WTR2	5.35	203 ± 7.96*	14.4 ± 0.005*
Organics		g kg-1	
BioFe	5.68	262	37.7
BioKC1	5.72	366 ± 1.56*	62.7 ± 0.22*
BioKC2	6.46	400	66.3
BioKC3	6.44	306	50.7
BioPot	4.42	199 ± 10.6*	9.43 ± 0.48*
ComBS	4.93	344	13.3
ComFY	5.49	274	21.1
ComY	6.05	253	19.04

* Mean of two samples tested ± standard error.

2.3.1.1.2 Surface area and porosity

Physical characterization was done for the WTRs (Table 2.11). Previous work has suggested that the physical characteristics of the material can impact their sorption performance (Makris et al., 2004; Makris, Harris, O'Connor, Obreza, et al., 2005). One of the Al-WTR (Al-WTR1) had a much higher specific surface area (SSA), micropore area, micropore volume, and total pore volume than the other two WTR, suggesting a higher sorption capacity. Although the Fe-WTR had the highest micropore area ratio and volume ratio, it had the lowest SSA and total pore volume, as well as the largest peak pore size, with the majority of pores in the mesopore (not micropore) range, suggesting it may not have a high adsorptive capacity.

Makris et al. (2004; Makris, Harris, O'Connor, Obreza, et al., 2005) reported higher SSA for Al-based WTRs than for Fe-based, as seen here. However, the difference in SSA between Al-WTR1 and the other two WTRs in the present study was much greater than the difference between Al-WTR2 and Fe-WTR, suggesting that the WTR type (Al or Fe) may not be the defining factor in SSA. In general, the WTRs measured by Makris et al. (2004; Makris, Harris, O'Connor, Obreza, et al., 2005) were much higher in SSA (4- 200x) than the materials measured here. Measured micropore area and micropore volume were also at least one order of magnitude lower for the WTRs measured here than reported by Makris et al. (2004; Makris, Harris, O'Connor, Obreza, et al., 2005). These characteristics are all associated with increased P sorption capacity (Makris et al., 2004; Makris, Harris, O'Connor, Obreza, et al., 2005). In addition to the lower amorphous Al and Fe measurements, this suggests that our WTRs may have a lower capacity for P sorption than what has been reported in other studies.

Table 2.11. Physical characterization of WTRs.

WTR	**Specific surface area**	**Micropore area**	**Micropore area ratio**	**Micropore volume**	**Total pore volume**	**Micropore volume ratio**	**Peak pore size**
	------- (m^2 g^{-1}) -------		**(micropore/ total surface area)**	**------- (cm^3 g^{-1}) -------**		**(micropore/ total pore volume)**	**(nm)**
Fe-WTR	0.304	0.377	1.24	0.000139	0.00157	0.089	50
Al-WTR1	9.44	1.81	0.192	0.000711	0.029694	0.024	4.5
Al-WTR2	1.66	0.30	0.179	0.000107	0.007714	0.0139	4

The results from the comparison of PSR and PSI of the media used suggest that Al-WTR2 is most likely to be the best sorbent of P, although Al-WTR1 had the highest measure of reactivity by either extraction, which may increase its total capacity for P sorption. On the high end of the ranges, the three King County biosolids, BioKC1, BioKC2, and BioKC3, had higher PSRs and PSIs than the other media, and are therefore most likely to leach the most significant quantities of P. BioKC3 had the highest PSR of all, while BioKC1 had the highest PSI.

2.3.1.2 Removal of phosphorus from synthetic solution

2.3.1.2.1 Effect of WTRs

All WTRs removed a significant amount of P from the synthetic solutions ($p < 0.0001$) (Figure 2.5). Phosphorus removed from influent solutions was calculated using a mass balance as follows:

P removed (mg P kg^{-1} WTR) = [Influent P (mg L^{-1}) – effluent P (mg L^{-1})]*solution volume (L)/WTR weight (kg) (2.15)

Removal varied by WTRs, with the Al-WTR1 and Fe-WTR showing the highest removal efficiency and the Ca-WTR showing the lowest removal efficiency.

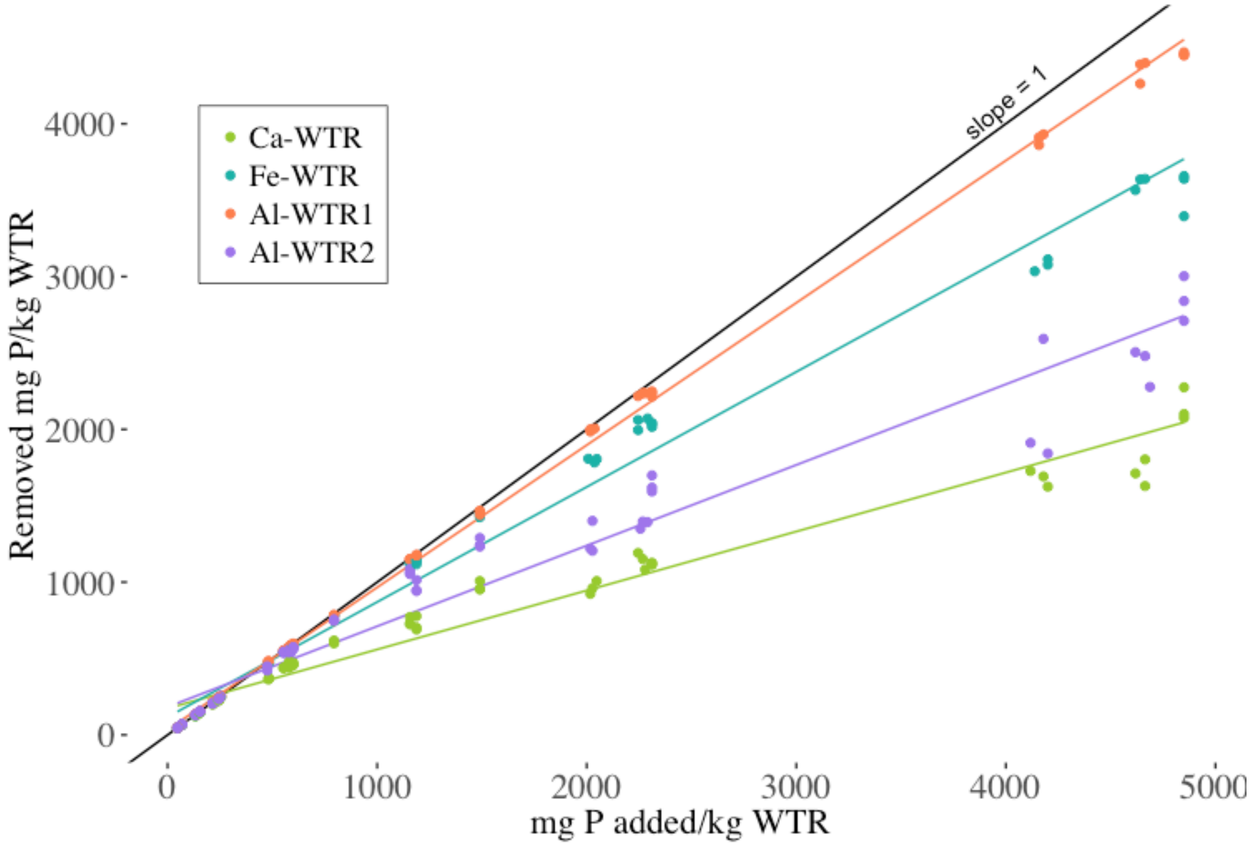


Figure 2.5. P added to synthetic solutions vs. removed by WTR. The line with a slope of 1 represents complete removal. Points below the line indicate that there was P remaining in solution.

All four WTRs removed all influent P from the solutions with the lowest concentrations of P. As influent P concentrations increased, removal efficiencies decreased and associated effluent P concentrations increased. All four WTRs removed more P but at incrementally smaller amounts at greater solution concentrations. Since we did not continue testing higher concentrations of P, we cannot say for sure if adsorption would have completely leveled off, as is seen with most sorbents as they become saturated (Hemond & Fechner, 2015). The (influent) solution with the highest concentration of P was 194 mg L^{-1}, which amounts to 4850 mg P added kg^{-1} WTR for the solution volume and WTR weights used per sample. The solution with the lowest concentration was 1.88 mg L^{-1}, amounting to 47 mg P added kg^{-1} WTR. Although degree of removal varied across that influent range as described, the average reduction of P concentration from the influent to the effluent was the highest by Al-WTR1, followed by Fe-WTR, Al-WTR2, and finally Ca-WTR (Table 2.12). The performance of the four WTRs in relation to each other was consistent across all assays and treatments. The % reduction by Al-WTR1 and Fe-WTR were statistically similar; % reduction by Al-WTR2 was significantly lower, and by Ca-WTR lower still. After these first six assays, the Ca-WTR was dropped from the remainder of the study due to its poor performance compared to the other WTRs.

Table 2.12. Mean reduction of influent to effluent P concentrations (mg L^{-1}) in synthetic solutions by the WTRs. Means followed by different letters are significantly different according to Tukey's honest significant difference (HSD).

WTR	**Mean reduction (%)**
Al-WTR1	98 ± 0.28 *a*
Fe-WTR	93 ± 0.90 *a*
Al-WTR2	86 ± 2.0 *b*
Ca-WTR	75 ± 2.4 *c*

2.3.1.2.2 PSI and PSR as predictive measures of phosphorus sorption

As expected, there was a relationship between the PSR of the WTR, and the amount of P adsorbed from solution. A combined PSR of the sample was calculated as the molar ratio of the sum of extractable P in the WTR and dissolved P in the influent, over the sum of extractable Al and Fe in the WTR, so that relative PSR of samples with each of the WTRs could be tracked as more P was added to the treatment solutions. These ratios did not include Ca content, as preliminary results and the poor performance of the Ca-WTR suggested that the inclusion of Ca did not yield a good correlation with P adsorption or release.

$$PSR_{sample} = (P_{WTR} + P_{solution})/(Al_{WTR} + Fe_{WTR}) \qquad (2.16)$$

In these calculations, P, Al, and Fe from the WTR and solution are expressed in moles sample^{-1}.

Since all WTR received all of the same treatment solutions, this comparison is appropriate. The relationship between combined PSR of the sample and P sorption by WTR held well within each WTR, but less so across WTR types (Figure 2.6). The relationship between combined PSI and P sorption was better than PSR across WTR types, but better still within each WTR (Figure 2.7).

Within each WTR, the combined PSR of the sample was a highly significant factor ($p < 0.0001$) for P adsorption on a mass basis, with $R^2 > 0.95$ for each of the three WTR. Across all WTR the combined PSR was still highly significant, ($p < 0.0001$), however the R^2 was 0.42, suggesting that much less variability was accounted for. The spread in adsorption by the WTRs can be seen in Figure 2.6, where each WTR shows a different slope of change in sorption over change in PSR.

The relationship between the combined PSI of the samples and P adsorption by the WTRs was very similar to the PSR response. Across all WTRs, the combined PSI was highly significant ($p < 0.0001$), with an R^2 of 0.8; PSI was a better fit than PSR. However, this response also varied by WTR, each of which shows its own slope in Figure 2.7. Within each WTR, the combined PSI was also highly significant ($p < 0.0001$) with an $R^2 > 95$ for each of the three WTR. These trends suggest that both PSI and PSR are impacting adsorption by all WTRs, but that other factors differentiating the WTRs from each other also influence their adsorption capacity.

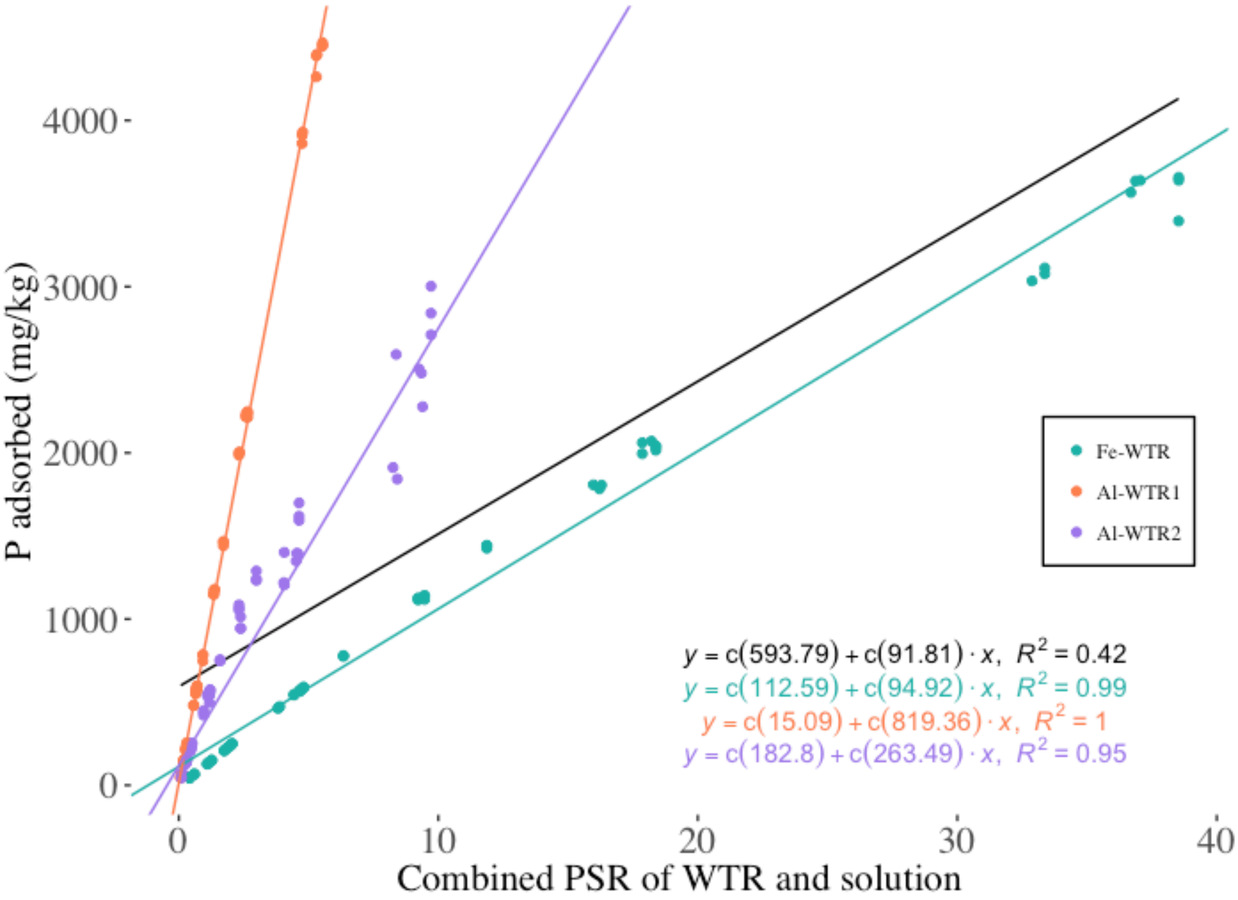


Figure 2.6. Combined PSR of sample (molar ratio of Mehlich 3-extractable P in WTR and solution over Mehlich 3-extractable Al and Fe) as a predictive measure of adsorbed P. Linear regression for all media is shown as a black line with confidence interval shown in gray; individual regression lines for each media are shown in color.

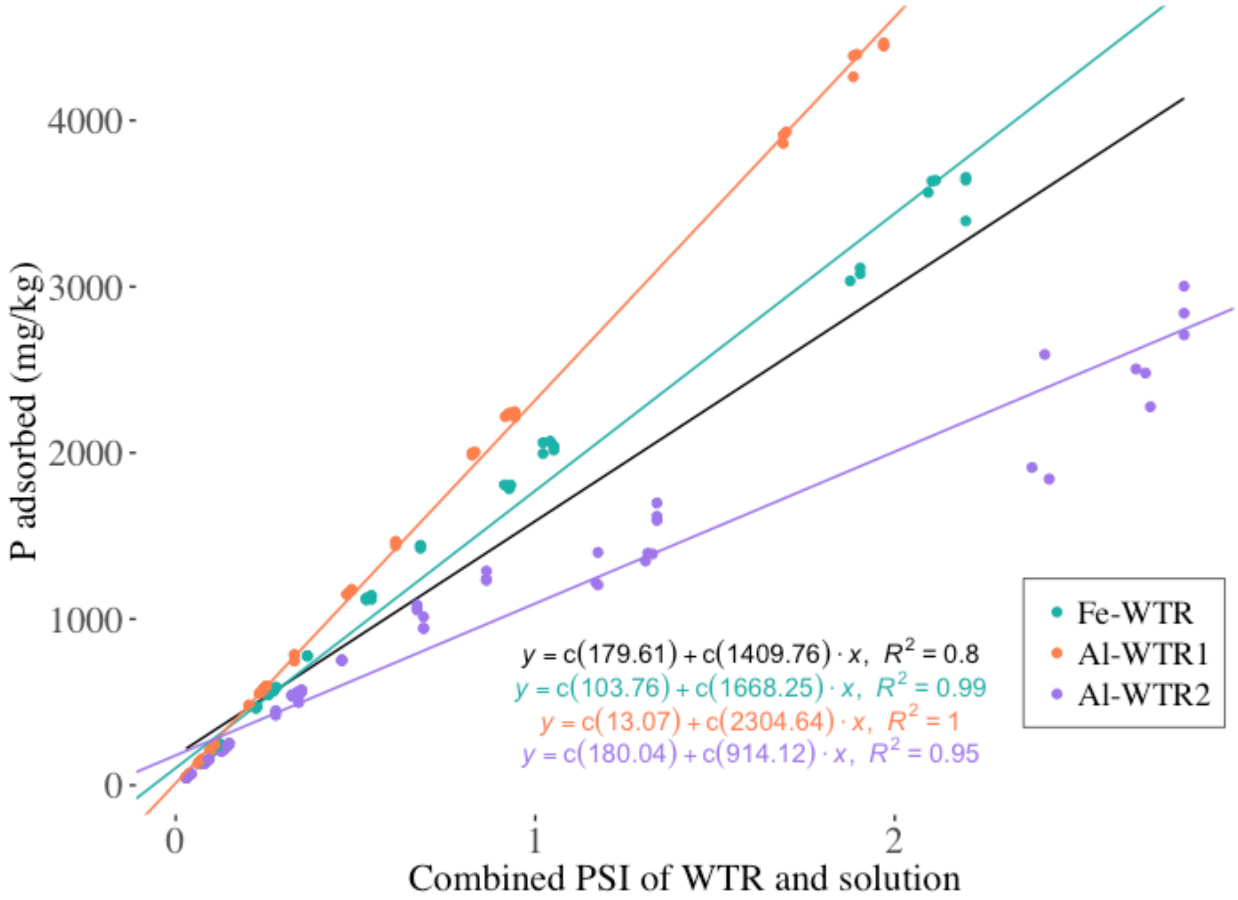


Figure 2.7. Combined PSI of sample (molar ratio of oxalate-extractable P in WTR and solution over oxalate-extractable Al and Fe) as a predictive measure of adsorbed P. Linear regression for all media is shown as a black dotted line with confidence interval shown in gray; individual regression lines for each media are shown in color.

2.3.1.2.3 Reactivity

Because PSR and PSI are unitless ratios, 1g and 2g of the same WTR will have the same ratio. Since P is adsorbed by WTR on a mass basis, 2g should adsorb more P than 1g. Reactivity$_{M3}$ of the WTR, or the sum of Mehlich 3-extractable Al and Fe, expressed as mol kg^{-1}, allows us to control for the amount of "sorbing power" (amorphous Al and Fe) per P added on a mass basis and to account for different reactivity between media with the same PSR or PSI. As Figure 2.8 illustrates, samples with the same initial PSR respond differently to added P. The WTR reactivity$_{M3}$, or the denominator of the PSR, appears to determine both the additional binding capacity and the associated change in the PSR as P was added to the solution. This is seen in the figures by the different slopes or reactivity for the different WTRs. Reactivity$_{M3}$ of the 3 WTR match the relative slopes of the lines in Figure 2.8: Fe-WTR being the lowest (4 mmol kg^{-1}), then Al-WTR2, then Al-WTR1 being the highest (28 mmol kg^{-1}). The same trend is seen in PSI, although in this case Al-WTR2 has the lowest reactivity$_{ox}$ and the least steep slope, Fe-WTR is in the middle, and Al-WTR1 has the highest reactivity$_{ox}$ and the steepest slope (Figure 2.9). Nair and Harris (2004) described this in terms of the soil phosphorus storage capacity. They developed an equation to illustrate that the rate of change in PSR vs. sorption (if sorption capacity is positive) or P release (if sorption capacity is negative) is determined by the reactivity$_{ox}$ of the media.

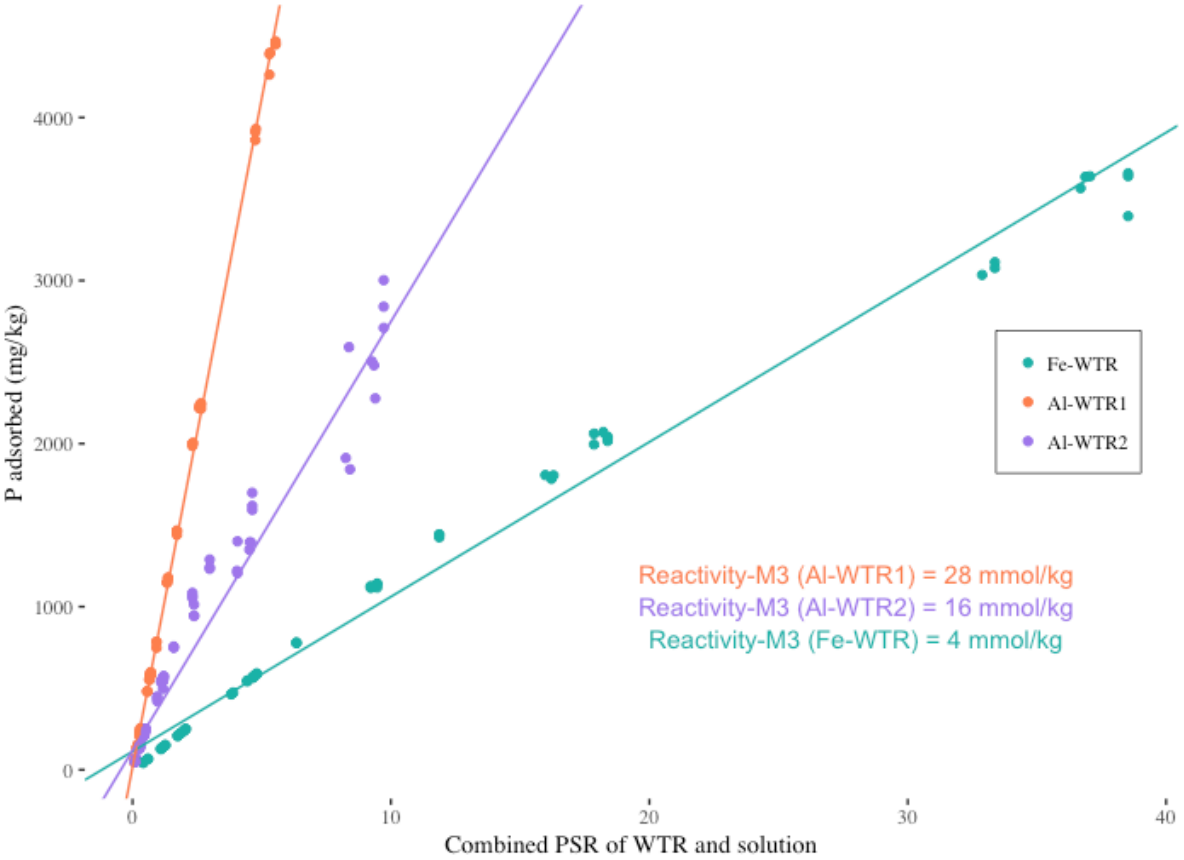


Figure 2.8. Combined PSR of sample (molar ratio of Mehlich 3-extractable P in WTR and solution over Mehlich 3-extractable Al and Fe) as a predictive measure of adsorbed P. Reactivity$_{M3}$ of each WTR is shown.

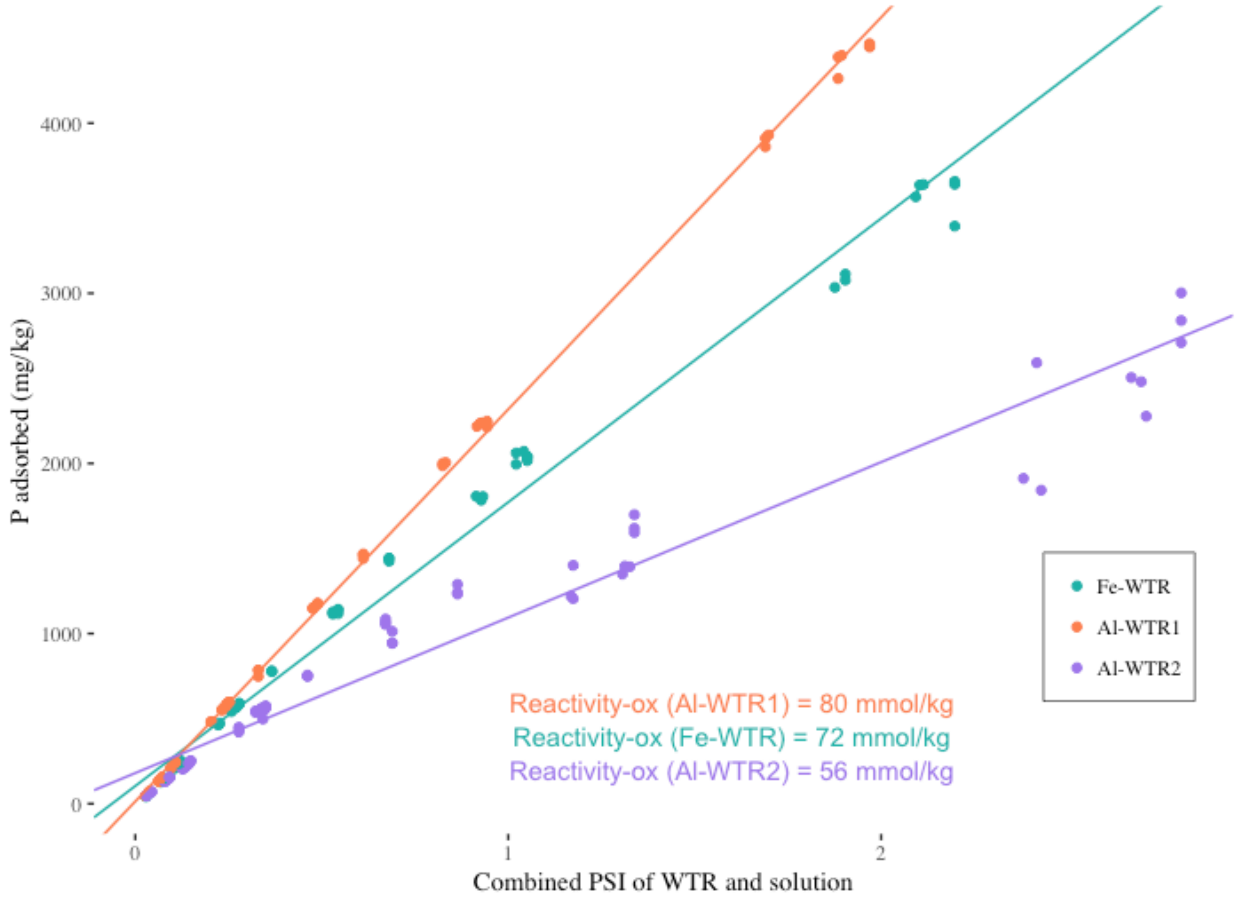


Figure 2.9. Combined PSI of sample (molar ratio of oxalate-extractable P in WTR and solution over oxalate-extractable Al and Fe) as a predictive measure of adsorbed P. Reactivity$_{ox}$ of each WTR is shown.

We tested this by developing a model using the combined PSR of the sample as a whole (combining the extractable P, Al, and Fe of the WTR with influent P). The model also included the reactivity$_{M3}$ of the WTR as a separate term and an interaction term between reactivity and the combined PSR. Both reactivity$_{M3}$ and an interaction term between reactivity$_{M3}$ and PSR were significant ($p \leq 0.004$); the R^2 of the model is 0.93, and the AIC is reduced to 3075, from 3524 without the reactivity term. Both Al-WTRs adsorbed slightly more P from solution than the model predicted, and Fe-WTR adsorbed slightly less than predicted (Figure 2.10).

$$\text{P sorption (mg kg}^{-1}\text{)} = 7296{*}\text{reactivity}_{\text{M3-WTR}} + 22121{*}\ \text{reactivity}_{\text{M3-WTR}}{*}\text{PSR}_{\text{sample}} \qquad (2.17)$$

We also tested this approach using the PSI (Figure 2.11). The model had an R^2 of 99, suggesting that it explained a greater amount of the variability than the associated model based on the PSR, and the Akaike information criterion (AIC) was reduced to 2727, from 3293 without the reactivity term. The model using oxalate-extractable variables includes PSI as a main effect (PSR as a main effect is absent in the Mehlich 3 model), and both PSI and $\text{reactivity}_{\text{ox-WTR}}$ terms have negative correlation coefficients, while the largest correlation coefficient in both models is for the interaction term.

$$\text{P sorption (mg kg}^{-1}\text{)} = -2198{*}\text{PSI}_{\text{sample}} - 6220{*}\text{reactivity}_{\text{ox-WTR}} + 55360{*}\ \text{reactivity}_{\text{ox-WTR}}{*}\text{PSI}_{\text{sample}} + 529 \qquad (2.18)$$

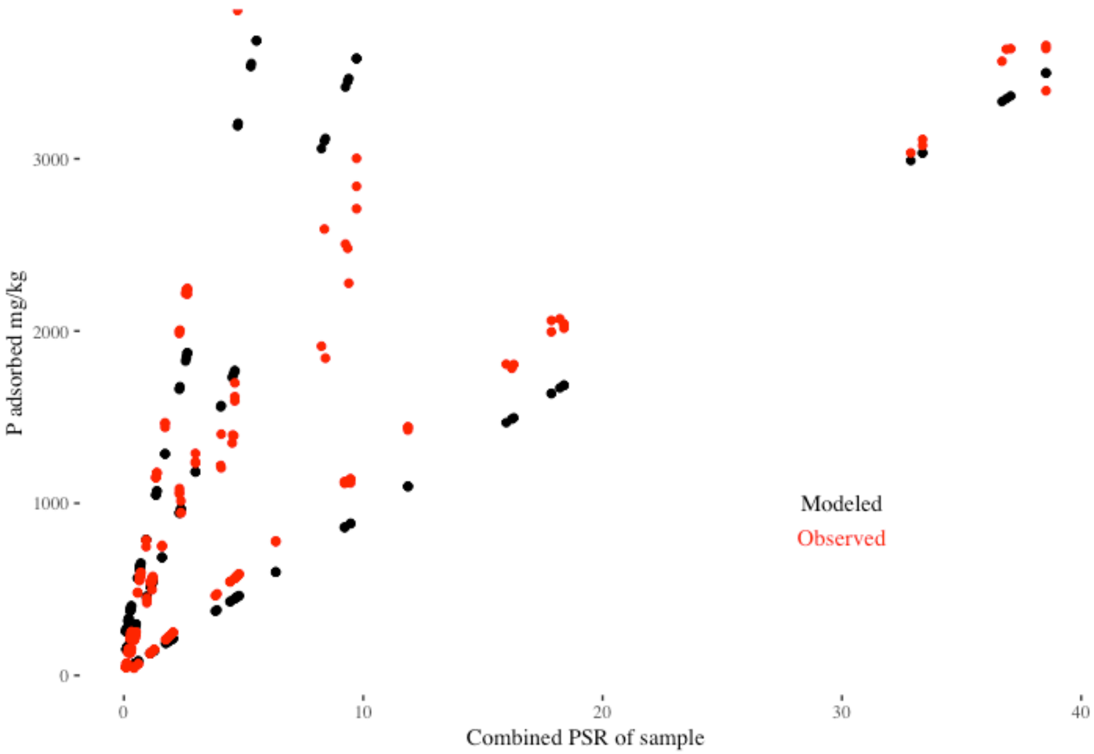


Figure 2.10. Modeled (using Mehlich 3-extractable values) and observed P sorption by the WTRs vs. PSR of the combined sample.

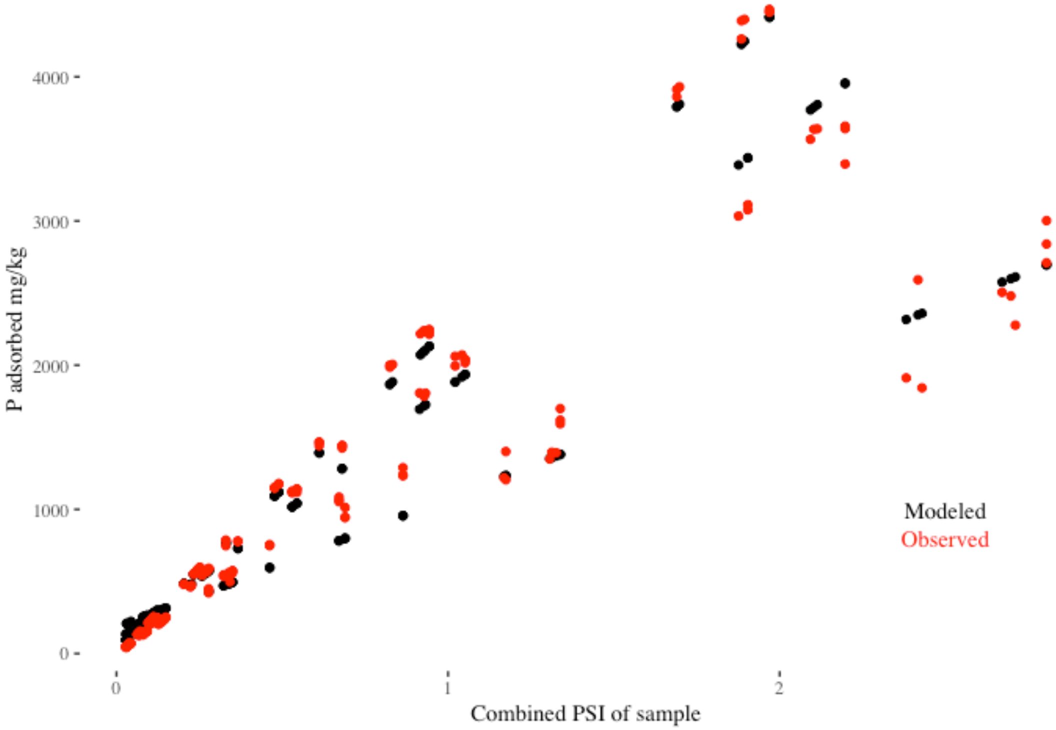


Figure 2.11. Modeled (using oxalate-extractable values) and observed P sorption by the WTRs vs. PSI of the combined sample.

2.3.1.2.4 Other variables

Other studies have suggested that other factors may impact the adsorption capacity of WTRs. These include specific surface area (SSA), micropore volume, total C, and pH of the WTRs (Bai et al., 2014; Makris et al., 2004; Makris, Harris, O'Connor, Obreza, et al., 2005). None of these were a significant factor of P sorption (in mg P kg^{-1}) in this study (p = 0.19, 0.12, 0.15, 0.46, respectively). Only when these variables were added to models which already included PSR and $reactivity_{M3}$, or PSI and $reactivity_{ox}$, did they improve the models' ability to explain variation in the results, and even then, the improvement was moderate.

We tested each additional variable along with PSR and $reactivity_{M3}$, and PSI and $reactivity_{ox}$, in two nested sets by forward selection, alternating the order of variables in the model (Table 2.13), and compared models by Akaike information criterion (AIC) and R^2. Each were significant and moderately improved the predictive ability of the PSR and $reactivity_{M3}$ model, when added as a third variable, increasing the R^2 from 0.93 to 0.99 and reducing the AIC from 3075 to 2697 in each case. Of the additional variables tested, only SSA and micropore volume improved the PSI and $reactivity_{ox}$ model when added as a third variable, in both cases also reducing the AIC to 2697; the R^2 remained at 0.99. In the case of both Mehlich 3 and oxalate model sets, none of the additional variables improved the models when added as a fourth variable, regardless of which variable was added. The equations for the models that offered improvement over models stated previously are shown below.

Table 2.13. Comparison of Mehlich 3 (a) and oxalate (b) nested sets of candidate models using PSR, reactivity, SSA, micropore volume, total C, and pH of the WTRs as predictors of P sorption.

a)

Model	R^2	**AIC**
P sorption ~ PSR	0.42	3525
P sorption ~ PSR * reactivity_{M3}	0.93	3075
P sorption ~ PSR * reactivity_{M3}* SSA	0.99	2697
P sorption ~ PSR * reactivity_{M3}* micropore volume	0.99	2697
P sorption ~ PSR * reactivity_{M3}* total C	0.99	2697
P sorption ~ PSR * reactivity_{M3}* pH	0.99	2697

b)

Model	R^2	**AIC**
P sorption ~ PSI	0.80	3293
P sorption ~ PSI * reactivity_{ox}	0.99	2727
P sorption ~ PSI * reactivity_{ox} * SSA	0.99	2697
P sorption ~ PSR * reactivity_{ox} * micropore volume	0.99	2697
P sorption ~ PSR * reactivity_{ox} * total C	0.99	2697
P sorption ~ PSR * reactivity_{ox} * pH	0.99	2697

P sorption ~ PSR * reactivity * SSA:

$$\text{P sorption (mg kg}^{-1}) = 47*\text{PSR}_{sample} + 10040*\text{reactivity}_{M3\text{-}WTR} - 37*\text{SSA (m}^2\text{ g}^{-1}) + 7244*\text{reactivity}_{M3\text{-}WTR}*\text{PSR}_{sample} + 60*\text{PSR}_{sample}*\text{SSA (m}^2\text{ g}^{-1}) + 83 \quad (2.19)$$

P sorption ~ PSR * reactivity * micropore volume:

$$\text{P sorption (mg kg}^{-1}) = -52*\text{PSR}_{sample} + 4830*\text{reactivity}_{M3\text{-}WTR} - 376300*\text{micropore volume (cm}^3\text{ g}^{-1}) + 15600*\text{reactivity}_{M3\text{-}WTR}*\text{PSR}_{sample} + 603300*\text{PSR}_{sample}*\text{micropore volume (cm}^3\text{ g}^{-1}) + 145 \quad (2.20)$$

P sorption ~ PSR * reactivity * total C:

$$\text{P sorption (mg kg}^{-1}) = 1705*\text{PSR}_{sample} + 6901*\text{reactivity}_{M3\text{-}WTR} + 5*\text{total C (g kg}^{-1}) + 12278*\text{reactivity}_{M3\text{-}WTR}*\text{PSR}_{sample} - 8*\text{PSR}_{sample}*\text{total C (g kg}^{-1}) - 951 \quad (2.21)$$

P sorption ~ PSR * reactivity * pH:

$$\text{P sorption (mg kg}^{-1}) = -1193 * PSR_{sample} - 9348 * reactivity_{M3\text{-}WTR} - 97 * pH + 38330 * reactivity_{M3\text{-}WTR} * PSR_{sample} + 156 * PSR_{sample} * pH + 856 \quad (2.22)$$

P sorption ~ PSI * reactivity * SSA:

$$\text{P sorption (mg kg}^{-1}) = -1938 * PSI_{sample} - 5321 * reactivity_{ox\text{-}WTR} + 50322 * reactivity_{ox\text{-}WTR} * PSI_{sample} + 23 * PSI_{sample} * SSA + 486 \quad (2.23)$$

P sorption ~ PSI * reactivity * micropore volume:

$$\text{P sorption (mg kg}^{-1}) = -1782 * PSI_{sample} - 4699 * reactivity_{ox\text{-}WTR} + 47428 * reactivity_{ox\text{-}WTR} * PSI_{sample} + 417908 * PSI_{sample} * \text{micropore volume} + 452 \quad (2.24)$$

In each case, correlation coefficients for the additional variable are very small in comparison to those for PSR and reactivity or PSI and reactivity. The exception to this is the large correlation coefficient for micropore volume in the PSR model, and for the interaction term between micropore volume and PSI in the PSI model. This suggests that, while SSA, total C, and pH may impact the P sorption of the WTRs, these variables played a much smaller role than PSR, PSI, and reactivity. Although the added variables were statistically significant, they did not explain a large amount of additional variation. Micropore volume may have played a larger role in sorption by the WTRs as it interacted with PSR and PSI. In all cases, the addition of a third variable, either micropore volume, SSA, total C, and pH of WTRs, to a model already including PSR and reactivity or PSI and reactivity, explained additional variation in the samples.

2.3.1.3 Phosphorus release by organics

2.3.1.3.1 Magnitude of phosphorus release

Three water extraction assays were done on the organics with differing solid to deionized water ratios. For all ratios across the three extractions, all 8 organics released P into solution and did so at different rates. Phosphorus released by the organics on a mass basis was used to compare results across the different water extractions, accounting for differences in sample weight and water per sample:

P release (mg kg^{-1} organic) = effluent P (mg L^{-1}) * volume of water used (L)/organic weight (kg)

(2.25)

In the first extraction, 1, 2, and 5 g of organic media was used per 50 mL of DI (1:50, 1:25, and 1:10 solid: water ratio), for a total of three treatments per organic. The quantity of P released by each material was inconsistent and varied based on the solid: solution ratio. If true release rates had been reflected by the data, we would expect to see a steady release of P expressed in mg P g^{-1} organic for each of the different organics, and the solid: water ratio of the sample should not be a significant factor in release. There are not enough degrees of freedom to do pairwise comparisons between treatments for the individual organics. However, on a mass basis, P release in mg P g^{-1} organic declined for all organics as the solid:water ratio of the sample increased (Table 2.14).

Table 2.14. Mean P release in mg P g^{-1} organic for the first water extraction by organic and treatment (solid:water ratio of samples).

Organic	**P release (mg P kg^{-1} organic) by solid:water ratio**		
	1:50	**1:25**	**1:10**
BioFe	392 ± 24	212 ± 2.7	111 ± 6
BioPot	360 ± 30	282 ± 11	176 ± 4
ComBS	2650 ± 80	2304 ± 35	2080 ± 49
ComFY	193 ± 6.2	105 ± 4.1	45 ± 0.3
ComY	378 ± 11.	289 ± 5.5	265 ± 11

A second water extraction was done with lower solid:water ratios (1:50, 1:100, 1:200). A third extraction was done with the three additional biosolids that were added later in the study (BioKC1, BioKC2, and BioKC3). The third extraction used lower solid: water ratios (1:100, 1:200, 1:300), because of the high P_{M3} and P_{ox} of these materials. In this third extraction, solid:water ratio was again a significant factor in P release on a mass basis for two of the three organics used, and samples with higher solid:water ratio released less P on a mass basis (expressed in mg P g^{-1} organic).

Table 2.15. Mean P release in mg P g^{-1} organic for the third water extraction by organic and treatment (solid:water ratio of samples).

Organic	**P release (mg P kg^{-1} organic) by solid:water ratio**		
	1:333	**1:200**	**1:100**
BioKC1	6100 ± 569	7227 ± 1277	6193 ± 396
BioKC2	3278 ± 61.2	3107 ± 85.1	2650 ± 32.1
BioKC3	6467 ± 430	5047 ± 539	4013 ± 201

Because the data from the first and third extractions suggested that P release rates were not accurately reflected across all treatments, mean P release from all assays was not used to compare organics; instead, only the 1:200 solid:water ratio treatment was used (Figure 2.12). This was the most dilute (lowest solid:water ratio) treatment that was performed on all organics, and therefore should avoid some of the inconsistencies of the less dilute treatments. During one of the assays, the lids of a few samples became loose while on the shaker box, and the contents were lost, including all replicates of BioPot at the 1:200 treatment, so there is no data for that organic. The three low-Fe Class B King County biosolids cakes released the most P, with BioKC1 releasing the most of all, followed by BioKC3, and BioKC2. ComFY, ComY, BioFe, and ComBS released the smallest amounts and their means were statistically similar to each other. Organic was determined by Anova to be a significant factor of P release, and pairwise means comparison was done with the Tukey honest significant difference (HSD) method.

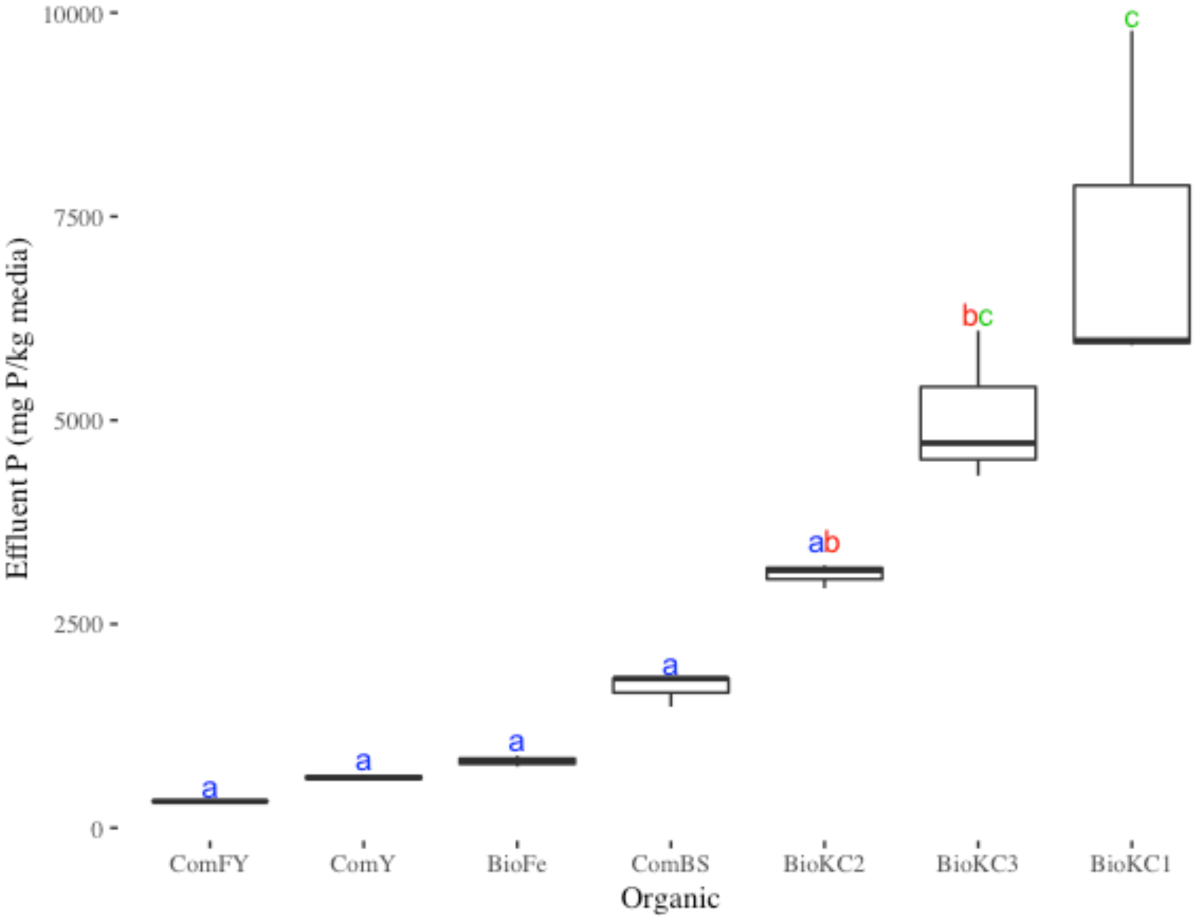


Figure 2.12. P release by organics in 1:200 solid:water ratio treatment water extractions. Lowercase letters indicate media with statistically similar means.

The lowest P release was from a food yard compost that is commonly used in bioretention soil mixtures in Western WA (ComFY). Previous column studies with this material have also shown it to release relatively low quantities of P (Jay et al., 2017). All of the other organics tested for this study released higher quantities of P than the food/yard compost. The range between the lowest-releasing organic (ComFY at 326 mg P kg^{-1}) and highest-releasing organic (BioKC1 at 9780 mg P kg^{-1}) was large, and release did not follow a pattern by type of organic, for example, the four biosolids released very different amounts of P. Paus (2014) reported a cumulative release of 203 ± 24 mg kg^{-1} from a compost made from leaves, grass, and woody debris during a batch incubation using an even lower solid:water ratio than used in this study (1:230 to 1:2300) and a longer shaking time (up to 96 hr). All organics in the present study released more P than the compost used by Paus (2014). The yard waste compost in the present study (the most similar in feedstock to the compost used by Paus (2014)) released three times the amount of P. Looking at biosolids used in agricultural application, Oladeji (2007) found 1.16 ± 0.16 to 5.52 ± 0.18 g kg^{-1} water-extractable P. In the present study, the biosolids-sawdust compost (ComBS) and two of the King County biosolids (BioKC2 and BioKC) fall in this range, while BioKC1 is considerably higher, and the biosolids with added Fe (BioFe) is lower.

Mullane et al. (2015) set up columns using the same food and yard waste compost used in the present study (ComFY), and subjected them to simulated rainstorms. These composts leached 8.87% ± 0.44%, or 7.73 ± 1.39% of initial total P content over the course of 9 storms (the difference depended on the age of the compost; 6-month aged compost leached more P than 12-month). In the present study, maximum P release by the organics in the water extraction represented a mean of 22 ± 4% of their initial total P. The maximum P release by ComFY alone was 11% of its initial total P, higher than reported by Mullane et al. (2015), but lower than the mean of all organics in this study.

2.3.1.3.2 Extractable P, PSI, and PSR

PSR and PSI were both significant factors for P release from the organics ($p < 0.001$, $R^2 = 0.65$ for PSR, 0.58 for PSI) (Figures 2.13, 2.14). In general, many of the highest-releasing organics (namely, the three Class B low-Fe biosolids) had the highest oxalate- and Mehlich 3-extractable P (P_{ox} and P_{M3}). Two of the lowest-releasing organics (yard waste and food/yard waste composts, ComY and ComFY) were also those with the least P_{ox} and P_{M3}. However, two of the organics tested, BioFe and ComBS, had high P_{ox} (1648 ± 263 and 1232 ± 30.3 mg kg^{-1}, respectively) but their release was limited by correspondingly high reactivity. BioFe had high amounts of Fe_{ox} (2512 ± 426 mg kg^{-1}), and ComBS had high amounts of Al_{ox} (431 ± 10.2 mg kg^{-1}). ComBS also had high P_{M3} accompanied by high reactivity$_{M3}$ due to high Al_{M3} (629 ± 54.5 mg kg^{-1}). As a result, both of these two organics had lower PSR and PSI than the low-Fe biosolids, and both released less P than their P-content alone would suggest. In fact, Melhich 3-extractable P content was not a significant of water-extractable P across the range of organics ($p = 0.49$). Oxalate-extractable P was a significant factor ($p = 0.01$), however with an R^2 of 0.29, it explains much less of the variability seen in the results than either PSR or PSI. Many bioretention soil specifications call for limited P content in organics, however, these data suggest that accounting for P binding capacity (reactivity) by using PSR or PSI would give a more accurate estimate of bioretention system performance.

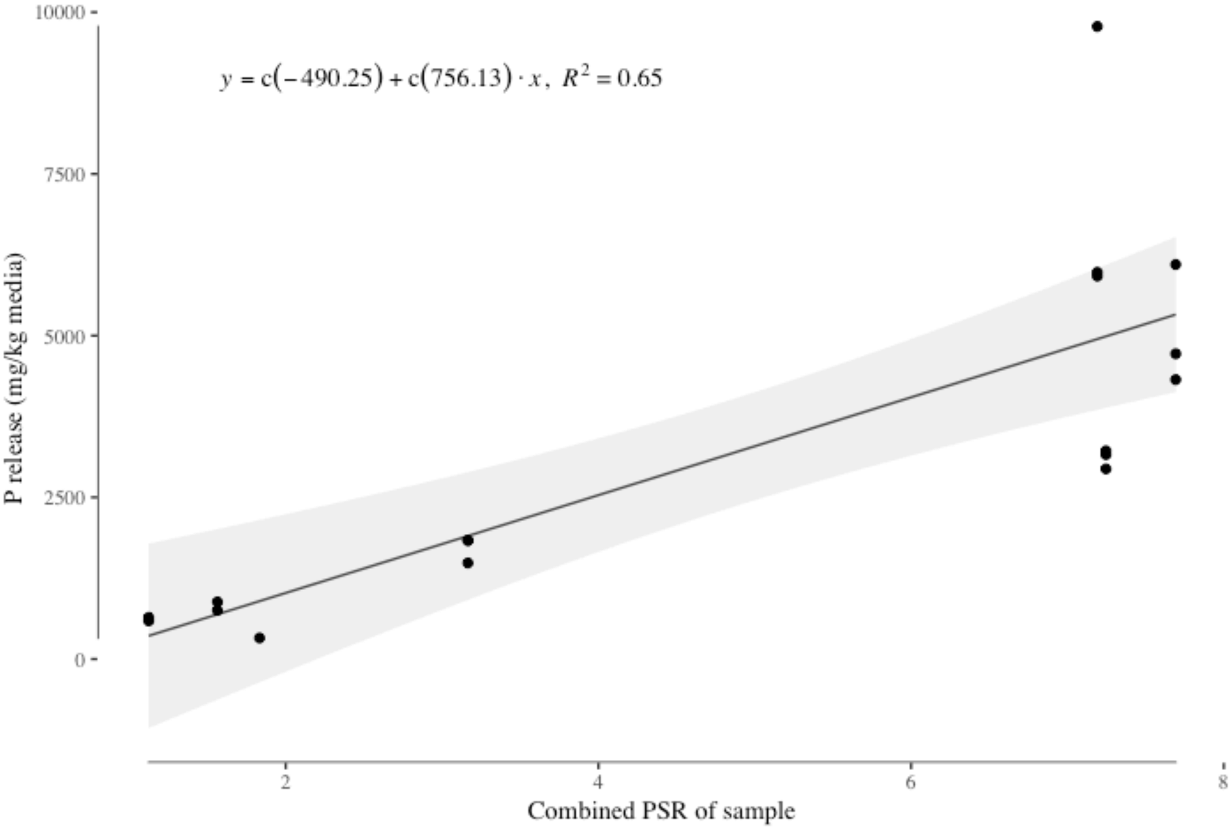


Figure 2.13. PSR of organics as a predictive measure of P release. Only the 1:200 solid:water treatment is used. The linear relationship between the two variables is shown as a solid black line, and confidence interval is shown in light gray.

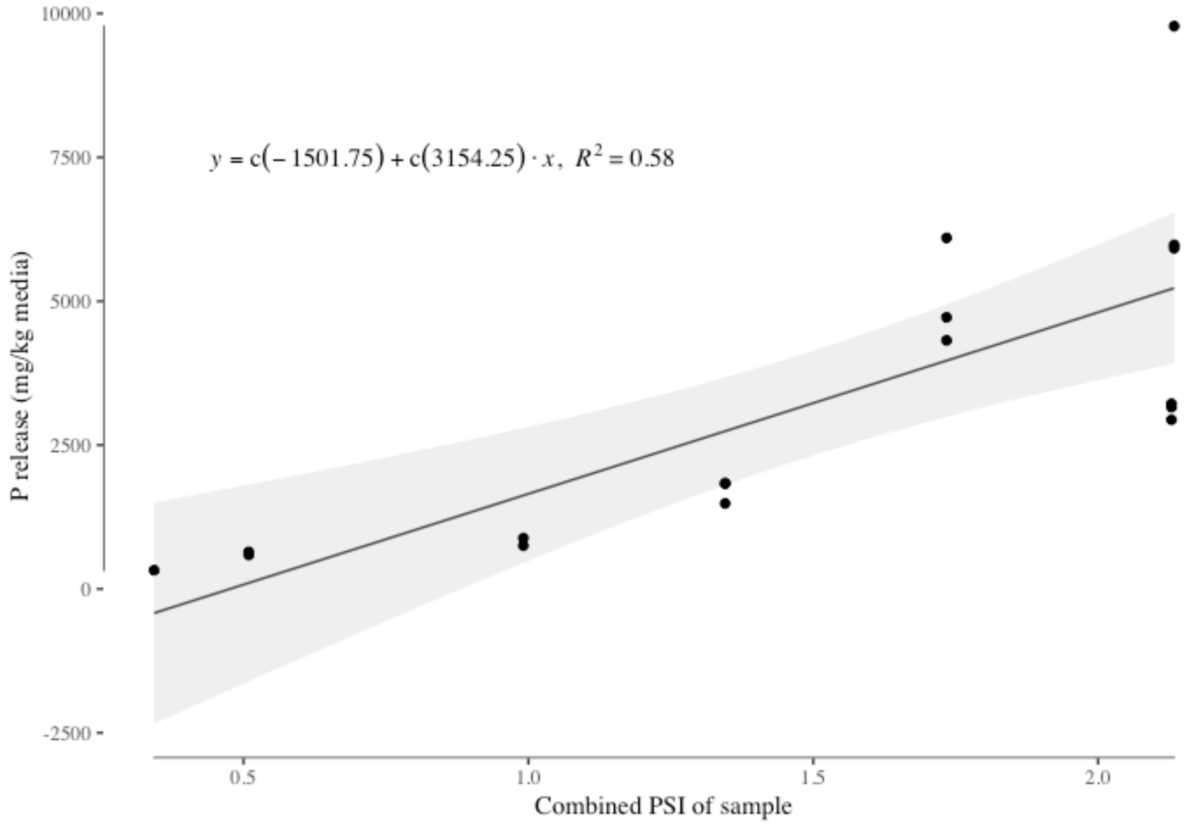


Figure 2.14. PSI of organics as a predictive measure of P release. Only the 1:200 solid:water treatment is used. The linear relationship between the two variables is shown as a dashed black line, and confidence interval is shown in light gray.

2.3.1.4 Phosphorus release by organic and WTR combinations

We tested a range of combinations of the different organics and WTRs to examine the predictive abilities of the PSI and PSR for determining P release. The results of assays 9 and 10, which used the same proportions of WTR to organic (0.5:2 in assay 9, and 1:4 in assay 10), were compared in a paired t-test to determine the effect of the 1-µm filters used in assay 10 due to problems with filter clogging. Phosphorus release by the two assays was not significantly different, and the results of assay 10 were included in the following analysis along with results from all other assays.

The PSR ratios tested ranged from 0.13 (a 2:1 combination of Al-WTR2 and ComFY) to 6.5 (a 1:4 combination of Fe-WTR and BioKC3). The PSI ratios tested varied from 0.046 (a 19:1

combination of Fe-WTR and BioKC1) to 1.4 (a 1:4 combination of Al-WTR2 and BioKC1). Because different assays used varying amounts of total media in each sample, results are compared on a mass basis as was done with the P release by organics alone. P released by the combination as a whole was calculated as follows:

P release (mg kg^{-1} media) = effluent P (mg L^{-1}) * volume of water used (L) / [WTR weight (kg) + organic weight (kg)] (2.26)

The maximum P release by any combination was 2500 mg kg^{-1} media, for a 1:4 combination (by mass) of Al-WTR2 and BioKC1. This combination had a PSI of 1.4 (the highest tested) and a PSR of 4.3. The minimum P release by any combination registered below detectable limits for effluent P concentration (0.1 mg L^{-1}, equivalent to 0.0017 mg kg^{-1} media), for a 1:2 combination by mass of Al-WTR1 and BioPot. The PSI for this combination was 0.08 and the PSR was 0.19.

2.3.1.4.1 PSI and PSR

The combined sample PSR or PSI ratio for the different combinations was calculated as a weighted average using the equations below. All values in the ratios were based on moles per mass of media.

$$\text{Combined sample PSR} = (P_{M3\text{-}WTR} + P_{M3\text{-}org})/(Al_{M3\text{-}WTR} + Al_{M3\text{-}org} + Fe_{M3\text{-}WTR} + Fe_{M3\text{-}org}) \quad (2.27)$$

$$\text{Combined sample PSI} = (P_{ox\text{-}WTR} + P_{ox\text{-}org})/(Al_{ox\text{-}WTR} + Al_{ox\text{-}org} + Fe_{ox\text{-}WTR} + Fe_{ox\text{-}org}) \quad (2.28)$$

The PSR and PSI of the different organic/ WTR mixtures was tested for its ability to predict P release. The interaction between PSR/PSI and the different organics and WTRs was also considered. PSR and PSI were both highly significant factors in P release from combined samples ($p < 0.0001$). A linear model using PSI as the predictive factor was marginally more effective (R^2= 0.54) than the equivalent model based on the PSR (R^2=0.49) for predicting P release across the range of combinations tested. A significant amount of the observed variability appeared as the PSR and PSI values increased with less variability observed at the lower range (Figures 2.15, 2.18).

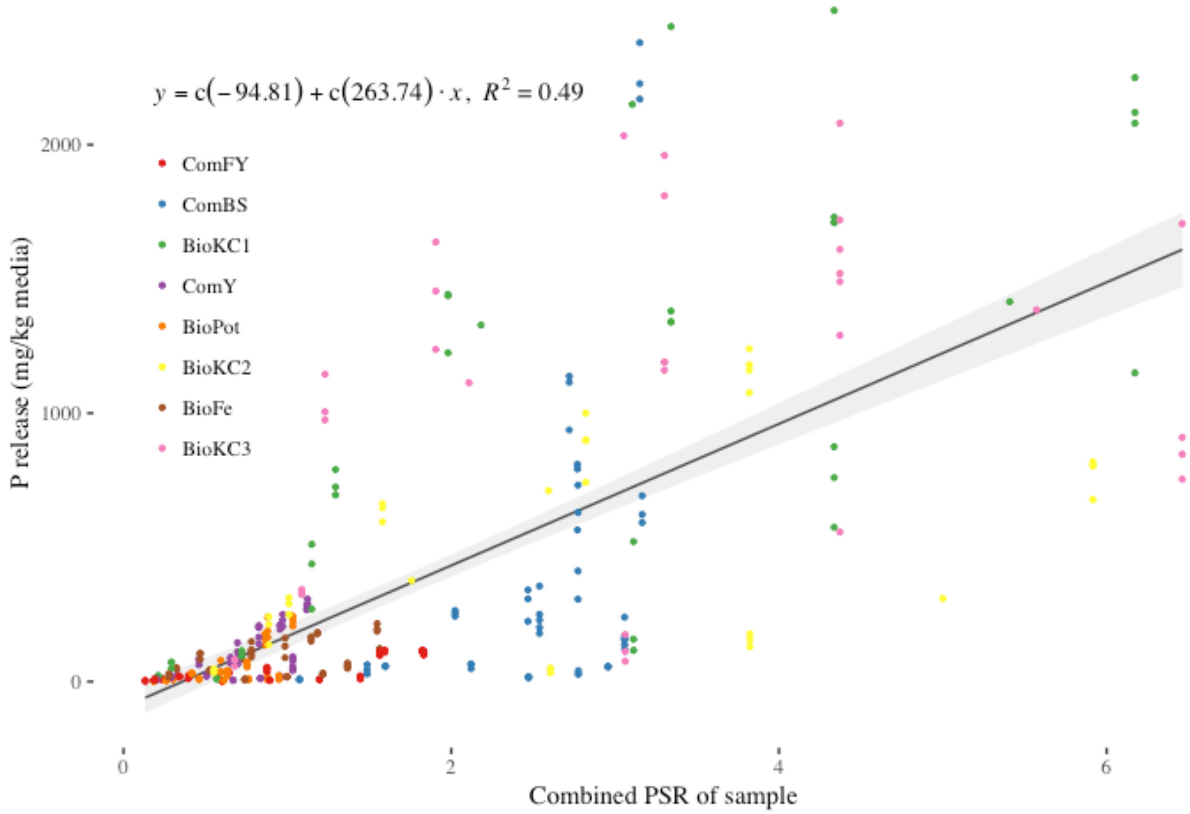


Figure 2.15. Combined of sample PSR as a predictive measure of P release by combinations.

Previous work found a more effective fit between PSR and P release when the results were described using natural ln-transformed data (Jay et al., 2017). This was also the case in the present study (Figure 2.16). The natural log transformation diminishes the spread of release response observed at the high end of the PSR range on a linear scale. The P release by the combinations presented a similar trend to that reported by Jay et al. (2017) (Figure 2.17). These studies used very different methods; the Jay et al. study was a column design, rather than a batch incubation as performed in the current study. The results cannot be compared exactly, however, a similar general trend was seen with a positive relationship between the two variables in both studies. The current study allowed for greater contact time between media and water, and overall release of P from samples was higher than reported by Jay et al. (2017). For comparison, total mass of dissolved P reported in the Jay et al. (2017) study was used, summed across all 12 subsequent leaching events. Because a mass of 5.3 mg dissolved P was included in the influent water, this amount was subtracted from the mass exported by the columns. A mass for the media in the columns was calculated as 3.89 kg from the column volume of 3241 cm^3 and an estimated bulk density of 1.2 g cm^3.

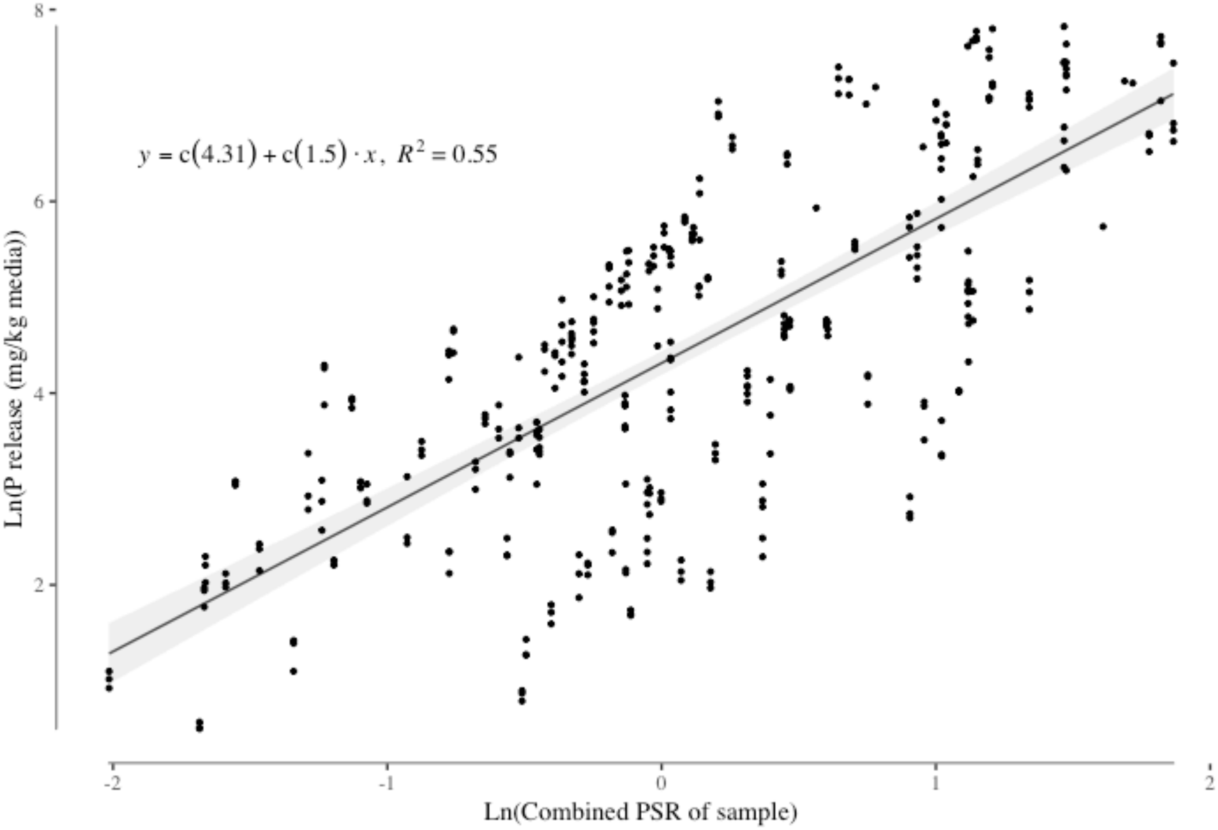


Figure 2.16. Combined sample PSR as a predictive measure of P release by combination on a natural log-natural log scale.

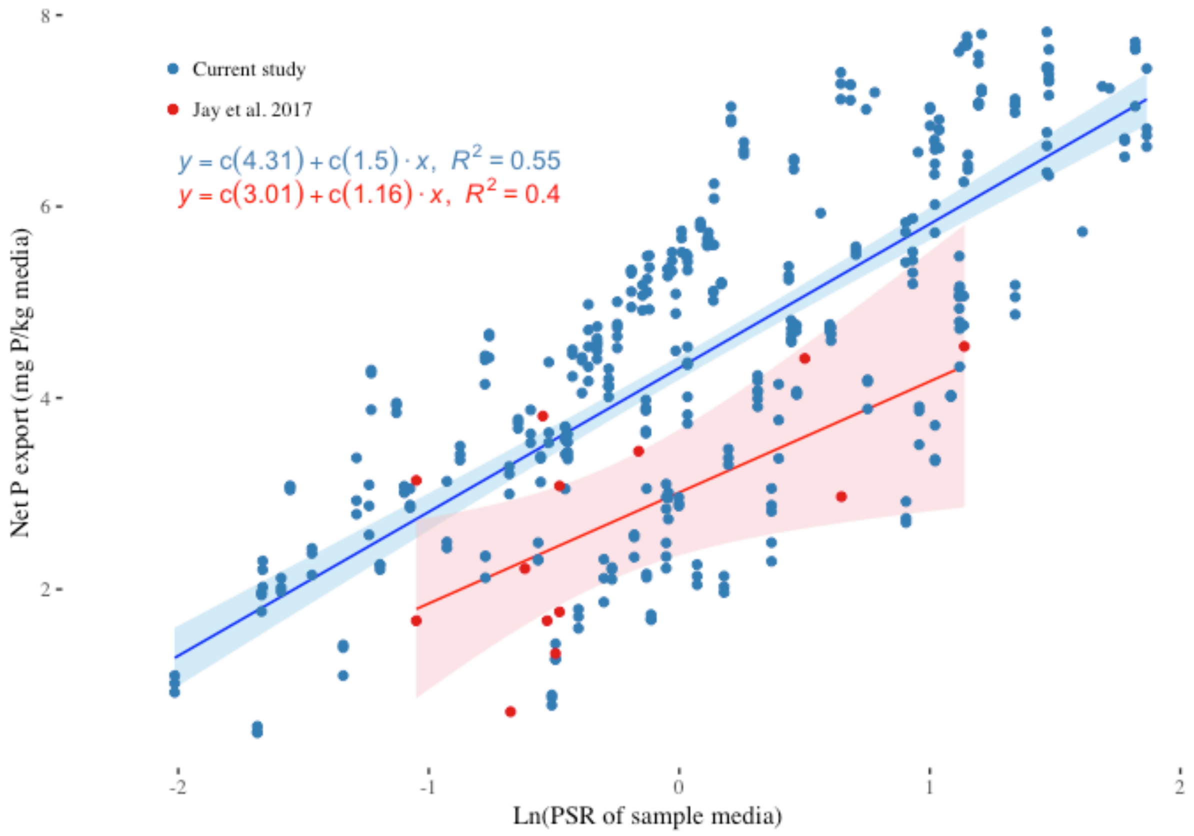


Figure 2.17. Combined sample PSR as a predictive measure of mass of P release in sample effluent on a natural log-natural log scale, shown in blue, and comparison with the results of a previous study by Jay et al. (2017), shown in red.

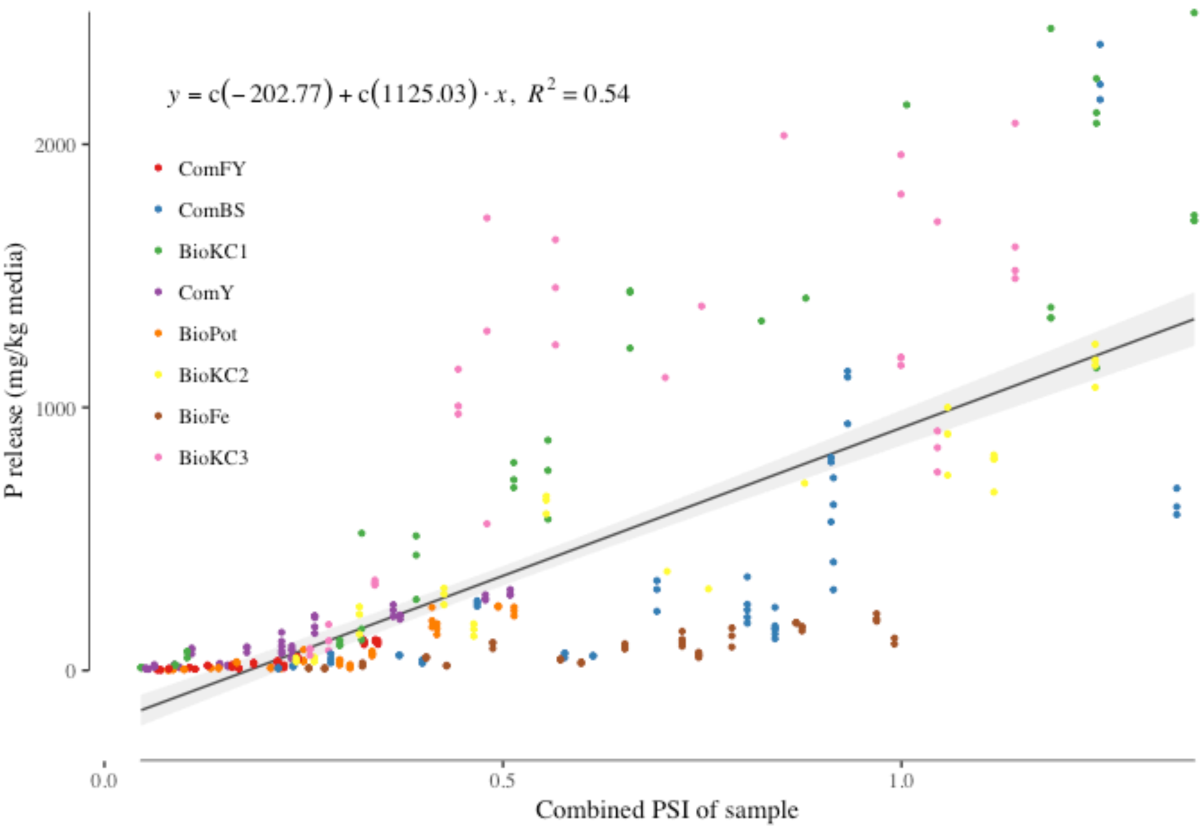


Figure 2.18. Combined sample PSI as a predictive measure of P release by combination.

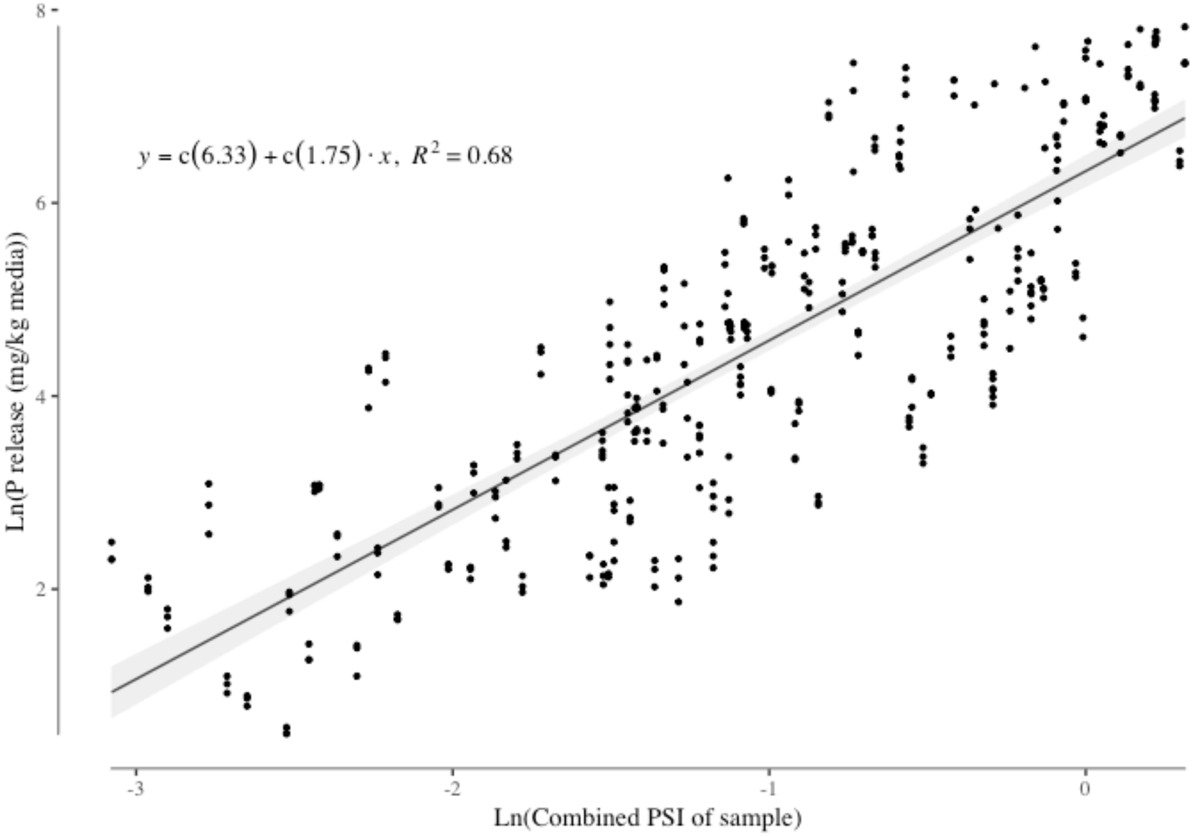


Figure 2.19. Combined sample PSI as a predictive measure of P release by combination on a natural log-natural log scale.

At the low end of the PSR and PSI range, P release by combinations of all media decreased substantially, especially at PSR < 1 and PSI < 0.5 (Figures 2.20, 2.21). This is where future research should be targeted to better understand the relationship between the variables with P release reduced below levels which are acceptable for water quality. However, across these ranges, the strength of the predictive linear relationship between P release and either PSR or PSI decreased, with R^2 of 0.28 and 0.26, respectively.

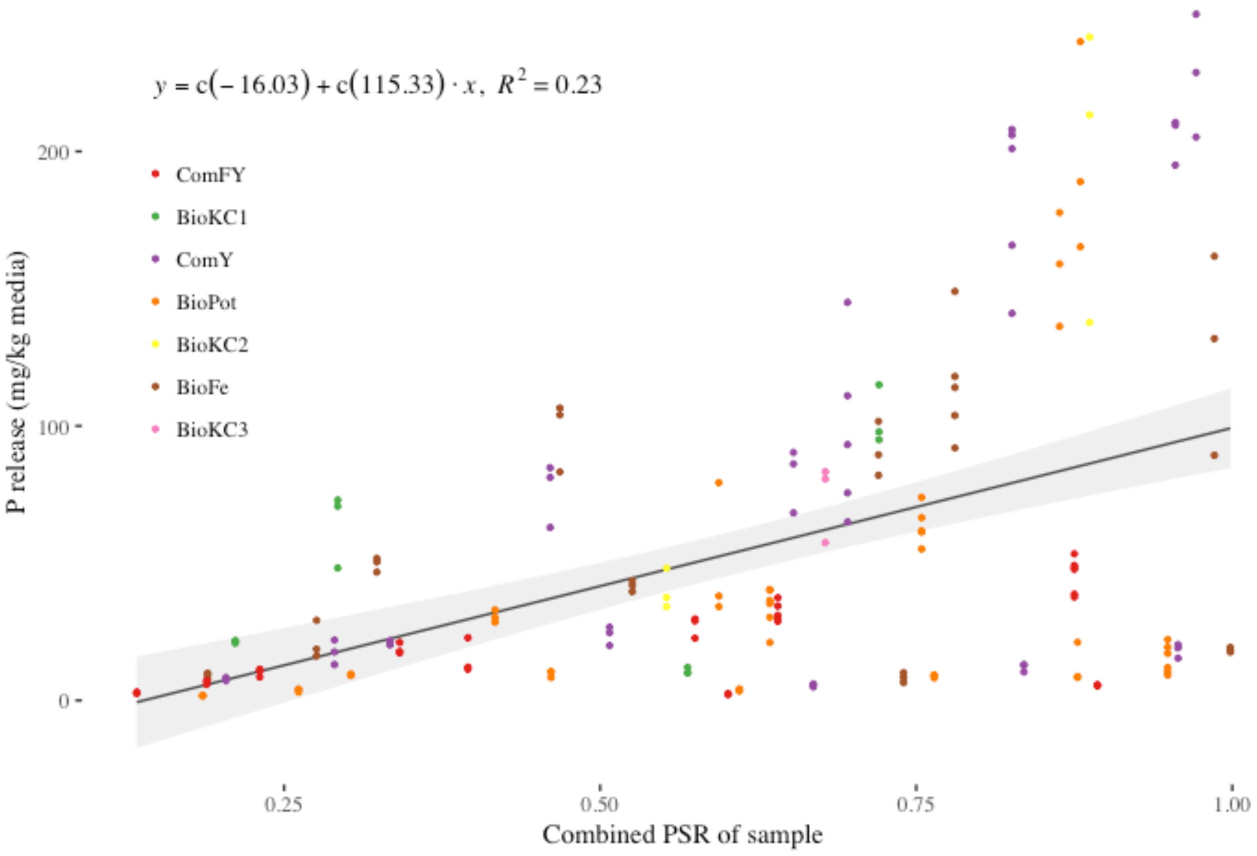


Figure 2.20. Combined sample PSR as a predictive measure of P release by combinations with a PSR ≤ 1.

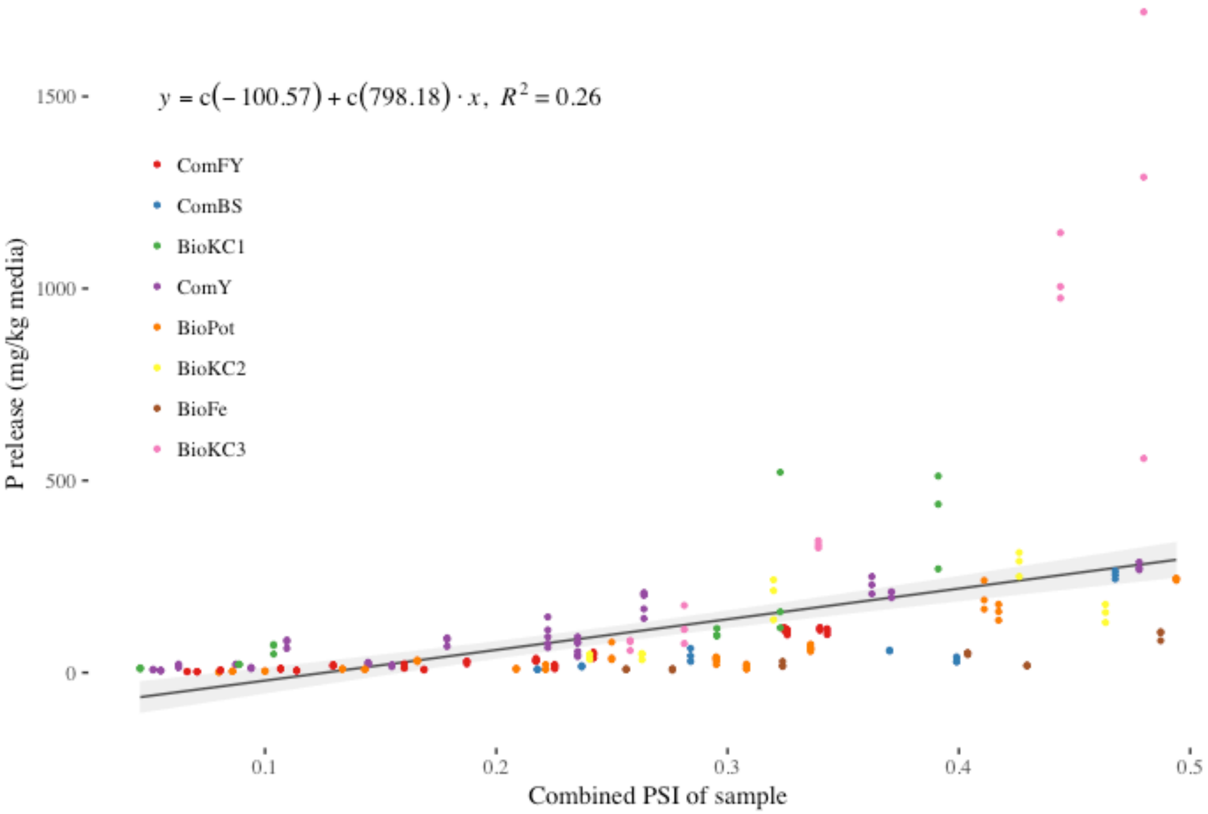


Figure 2.21. Combined sample PSI as a predictive measure of P release by combinations with a PSI ≤ 0.5.

P released by combinations of WTRs and organics was substantially higher than that of earlier samples consisting of WTRs and synthetic P solution at the same PSR or PSI values, although both data sets exhibited a similar overall positive trend between P release and PSR or PSI (Figures 2.22, 2.23). In the case of the WTRs in synthetic solution, P release shown represents the effluent P remaining in solution after incubation with the WTRs. Despite the highly significant ($p < 0.0001$) positive relationship between effluent P and the PSR of these samples, the R^2 suggests that only a portion of the observed variability was explained using this measure alone.

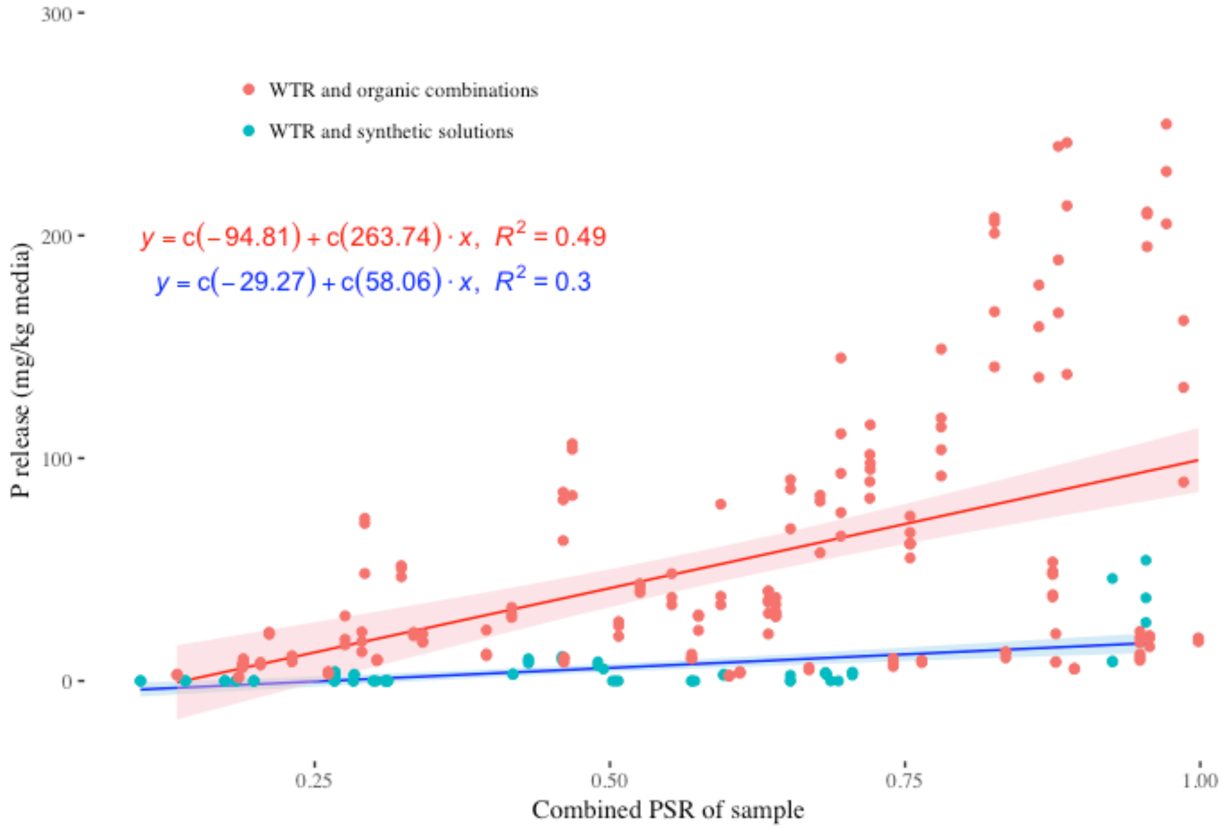


Figure 2.22. Combined sample PSR as a predictive measure of P release for WTRs and organic combinations, and for WTRs in synthetic solution, at combined PSR values ≤ 1. WTRs and organic combinations are shown in red, and WTRs and synthetic solution are shown in blue.

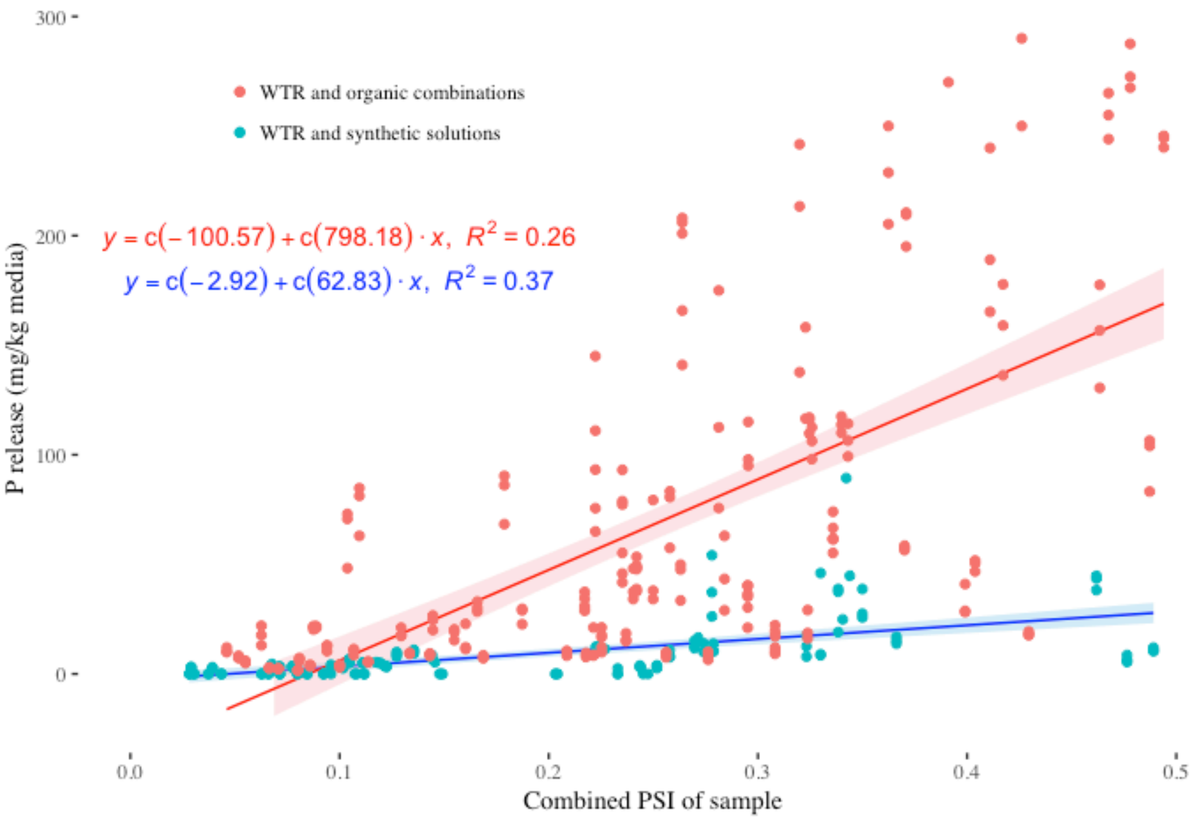


Figure 2.23. Combined sample PSI as a predictive measure of P release for WTRs and organic combinations, and for WTRs in synthetic solution, at combined PSI values ≤ 0.5. WTRs and organic combinations are shown in red, and WTRs and synthetic solution are shown in blue.

2.3.1.4.2 Effect of organic and WTR

PSR and PSI values for combinations were rounded to the nearest 0.1 to allow for comparisons among organics at equivalent PSR and PSI. This also enabled an examination of interaction effects between PSI or PSR and WTR or organic. Both PSR and organic were significant factors of P release by the combinations when tested together, and an interaction term was also significant ($p < 0.0001$ for all effects and interactions). The same was true for PSI and organic. This suggests that, in addition to the effect of PSR and PSI across all samples, all organics did not behave the same way. Combinations with some organics released more P, and some released less, even at the same PSR or PSI. However, the presence of the interactions suggests that this behavior was not consistent across the PSR and PSI ranges; some organics released more than others and some PSR or PSI values, and less at other values. Phosphorus release from combinations by organic is shown in Table 2.16 and Figure 2.24 for select PSR values at the low end of the range, which is pertinent for bioretention systems, and in Table 2.17 and Figure 2.25 for all rounded PSI values ≤ 0.5.

Table 2.16. P released from combinations of organic and WTR at selected PSR values, by organic used. Combined PSR values for samples are rounded to the nearest 0.1. PSR values at the low end of the range that represented the most organics were selected for inclusion in this table.

	PSR value					
	0.1	0.2	0.3	0.7	1	1.1
Organic	Mean P release (mg P kg^{-1} media)					
BioFe		8.86 ± 0.691	35.5 ± 6.61	49.7 ± 18.7	73 ± 26.2	161 ± 5.03
BioKC1		21.4 ± 0.267	64 ± 7.9	103 ± 6.25		407 ± 71.5
BioKC2					284 ± 18.3	
BioKC3				73.8 ± 8.2		334 ± 5.3
BioPot		1.14 ± 0.573	6.55 ± 1.28		234 ± 6.05	
ComBS						8.6 ± 0.528
ComFY	2.76 ± 0.14	8.44 ± 0.896	18.8 ± 1.2			
ComY		7.69 ± 0.327	19.4 ± 1.42	68.3 ± 13.8	116 ± 22.8	285 ± 5.74

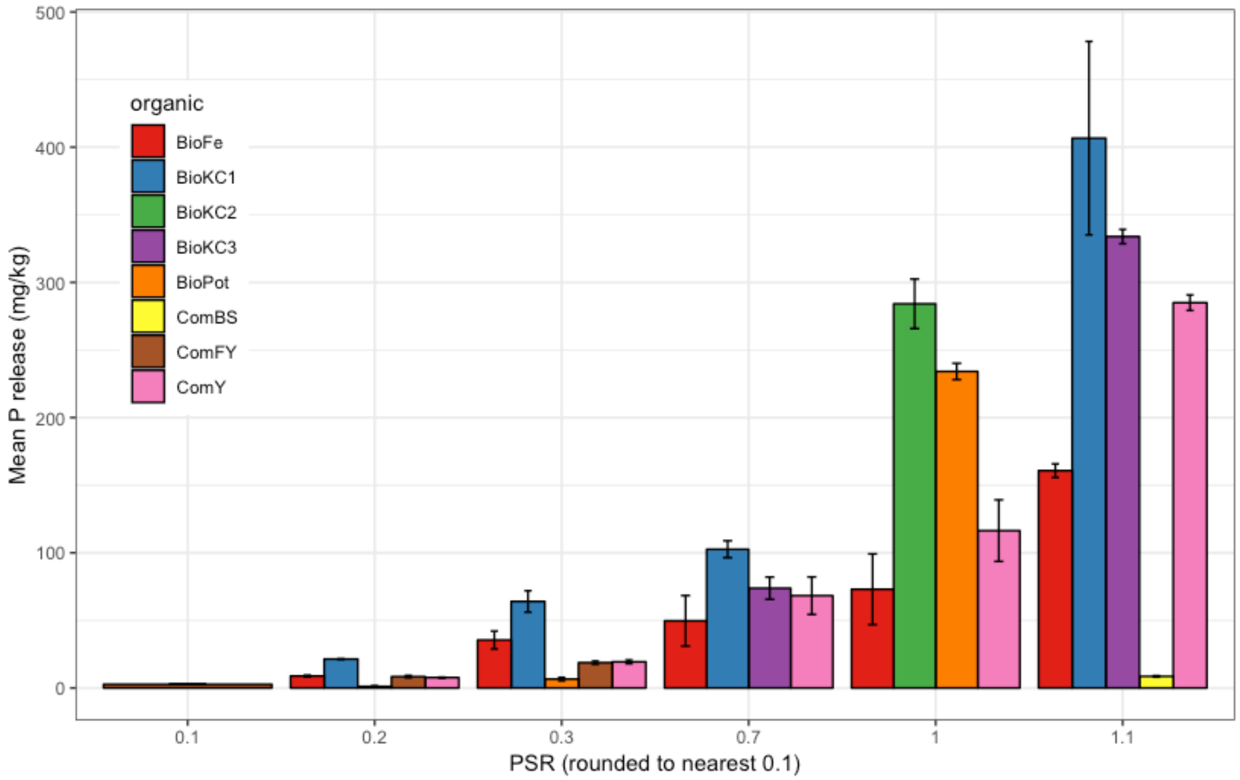


Figure 2.24. P released from combinations of organic and WTR at selected PSR values, by organic used. Combined PSR values for samples are rounded to the nearest 0.1. PSR values at the low end of the range that represented the most organics were selected for inclusion in this table.

Table 2.17. P released from combinations of organic and WTR at selected PSI values, by organic used. Combined PSI values for samples are rounded to the nearest 0.1. PSI values at the low end of the range were selected for inclusion in this table.

	PSI value					
	0	0.1	0.2	0.3	0.4	0.5
Organic	Mean P release (mg P kg^{-1} media)					
BioFe				12.8 ± 2.45	34 ± 7.03	97.9 ± 7.37
BioKC1	10.7 ± 0.658	42.7 ± 10.2		184 ± 68.2	407 ± 71.5	737 ± 28
BioKC2			39.9 ± 4.22	121 ± 37.2	284 ± 18.3	155 ± 13.6
BioKC3				176 ± 41	1040 ± 52.4	1190 ± 339
BioPot		5.37 ± 0.867	25.9 ± 5.88	37.5 ± 5.03	178 ± 14.4	234 ± 6.05
ComBS			12.4 ± 1.81	36 ± 18.1	45.1 ± 5.86	255 ± 6.06
ComFY		7.71 ± 1.37	26.6 ± 2.85	110 ± 1.88		
ComY		23.4 ± 5.11	69.5 ± 8.33	184 ± 13.3	216 ± 8.05	285 ± 5.74

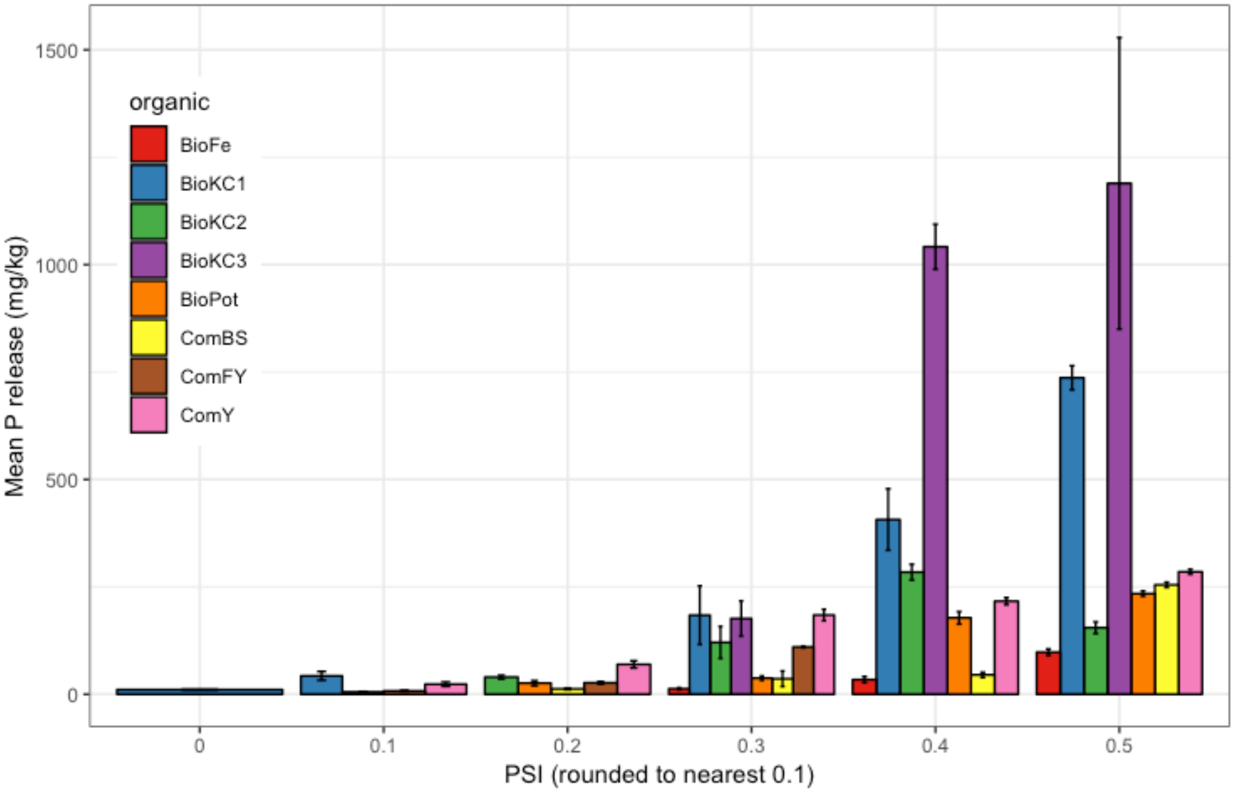


Figure 2.25. P released from combinations of organic and WTR at selected PSI values, by organic used. Combined PSI values for samples are rounded to the nearest 0.1. PSI values at the low end of the range were selected for inclusion in this figure.

P release increases as PSR or PSI increases for all individual organics. P release decreases as PSR or PSI decrease, and variation between organics also decreases. Additionally, despite variability seen from one organic to the other, some organics do stand out. BioKC1, BioKC2, and BioKC3, the Class B biosolids, often released a higher amount of P than the other organics at the same PSR or PSI values. BioFe, BioPot, and ComBS often released a smaller amount of P.

Rounded PSR and PSI values were also used to compare WTRs at equivalent PSR and PSI. Both PSR and WTR were significant factors of P release by the combinations when tested together, and an interaction term was also significant ($p < 0.0001$ for all effects). Both PSI and WTR were also significant when tested together ($p < 0.0001$, and $p = 0.0008$, respectively), as was their interaction ($p = 0.01$). This suggests that all WTRs did not behave the same way at equivalent PSI/PSR values. Combinations with some WTRs released more P, and some released less than others at the same PSR or PSI. However, again the presence of the interactions suggests that differences were not consistent across the PSR and PSI ranges, with some WTRs releasing more than others at some PSR or PSI values, and less at other values. Phosphorus release from combinations by WTR is shown in Table 2.18 and Figure 2.26 for select PSR values at the low end of the range where data points exist for the most WTRs to allow for comparison, and in Table 2.19 and Figure 2.27 for all rounded PSI values ≤ 0.5.

Overall, P release increases as PSR or PSI increases for all individual WTRs as was seen with the organics. P release decreases as PSR or PSI decrease, and variation between WTRs also decreases. Although individual WTRs did not stand out quite as much as some of the organics, combinations including Fe-WTR released less P than those with other WTRs at the same PSR value.

Table 2.18. P released from combinations of organic and WTR at selected PSR values, by WTR used. Combined PSR values for samples are rounded to the nearest 0.1. PSR values at the low end of the range that represented the most WTRs were selected for inclusion in this table.

	PSR value				
	0.1	0.2	0.3	0.7	1
WTR	Mean P release (mg P kg^{-1} media)				
FeWTR				6.89 ± 0.797	82.2 ± 22.5
AlWTR1	2.76 ± 0.14	9.86 ± 1.77	26.7 ± 6	92.6 ± 7.47	245 ± 19.6
AlWTR2		6.67 ± 0.404	25.1 ± 5.68	86.3 ± 4.49	178 ± 25

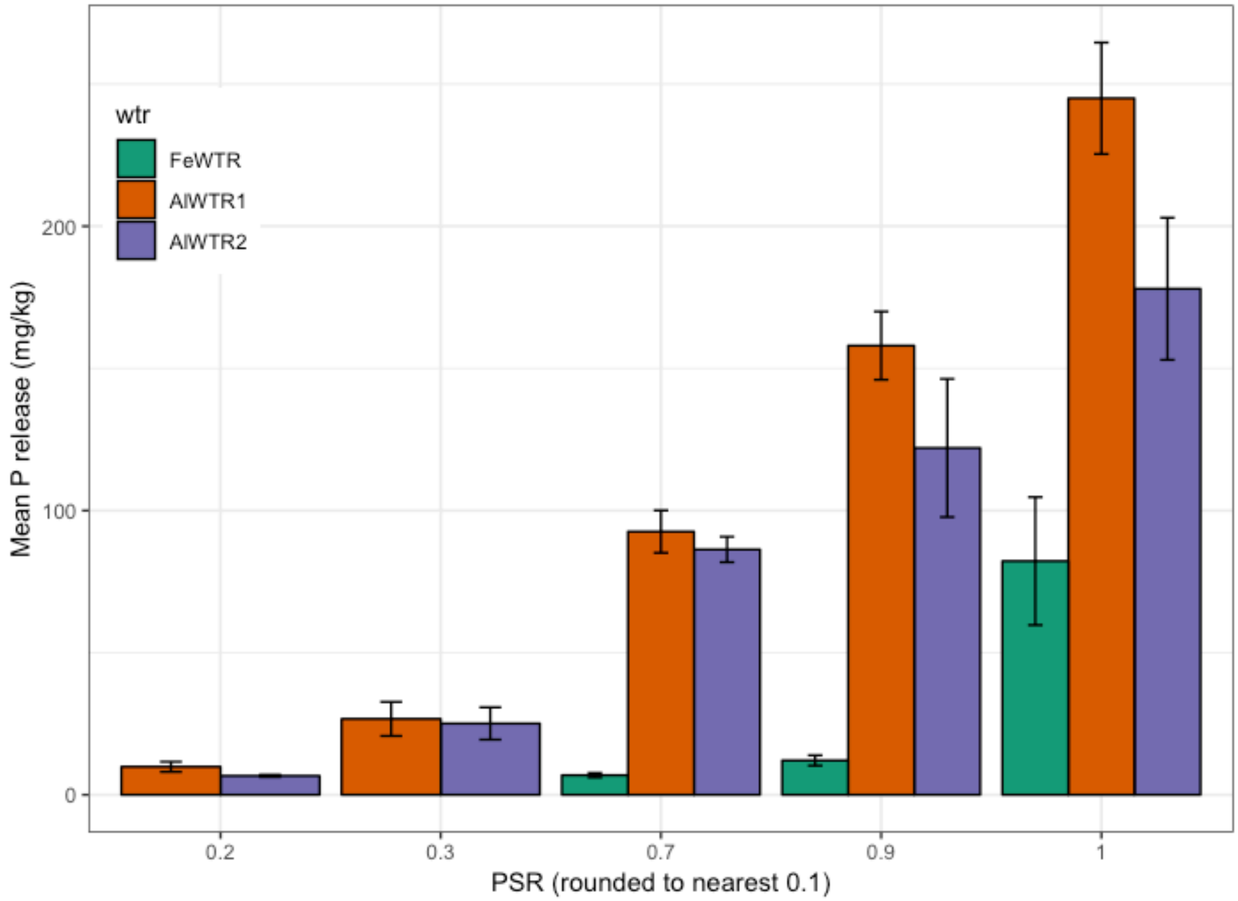


Figure 2.26. P released from combinations of organic and WTR at selected PSR values, by WTR used. Combined PSR values for samples are rounded to the nearest 0.1. PSR values at the low end of the range that represented the most different WTRs were selected for inclusion in this figure.

Table 2.19. P released from combinations of organic and WTR at selected PSI values, by WTR used. Combined PSI values for samples are rounded to the nearest 0.1. PSI values at the low end of the range were selected for inclusion in this table.

	PSI value					
	0	0.1	0.2	0.3	0.4	0.5
WTR	Mean P release (mg P kg^{-1} media)					
FeWTR	10.7 ± 0.658	6.33 ± 0.799	27.6 ± 5.28	83.2 ± 24.9	25.5 ± 3.71	466 ± 146
AlWTR1		12.2 ± 146	39.7 ± 7.9	59.8 ± 9.07	299 ± 83.3	737 ± 28
AlWTR2		31.2 ± 7.03	46.9 ± 4.92	131 ± 19.8	278 ± 39.3	176 ± 35.3

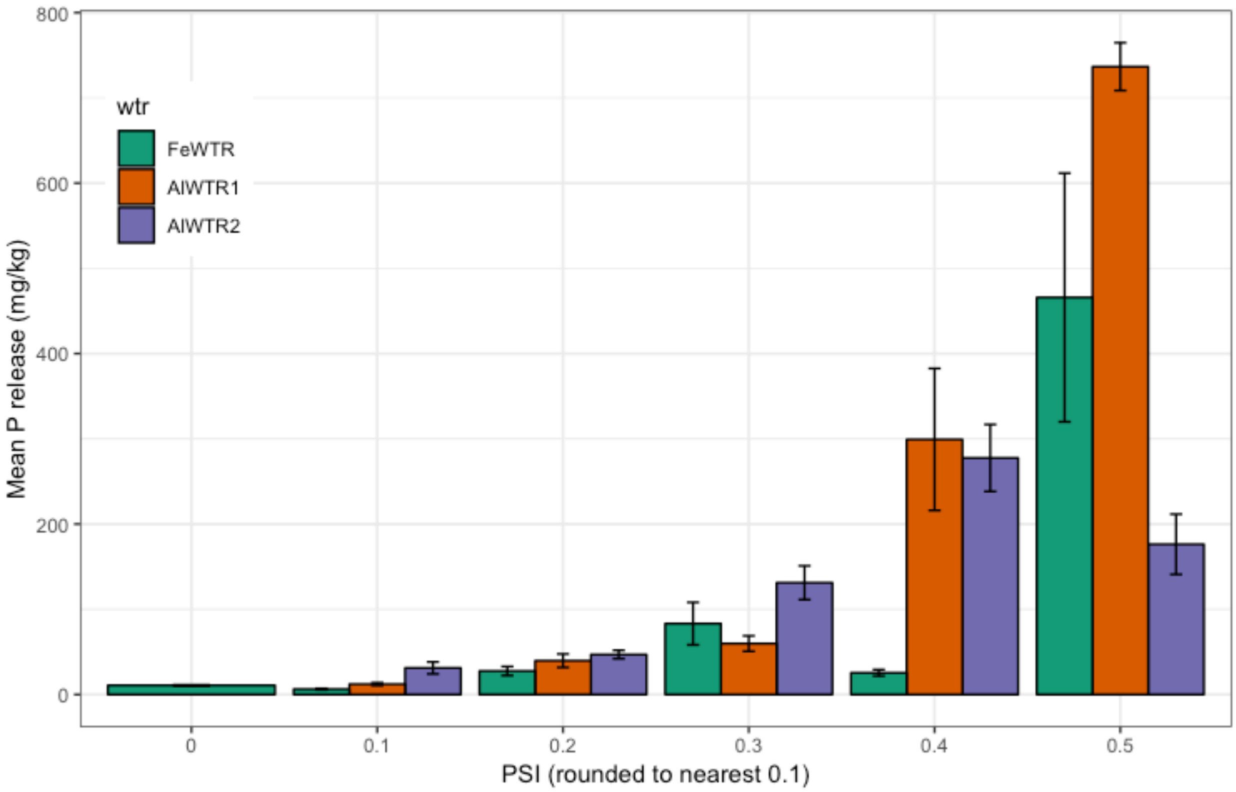


Figure 2.27. P released from combinations of organic and WTR at selected PSI values, by WTR used. Combined PSI values for samples are rounded to the nearest 0.1. PSI values at the low end of the range were selected for inclusion in this figure.

Although both PSR and PSI were excellent predictors of P release, P release at corresponding values was very different; generally much lower at the same number PSR compared with PSI. The two measurements are not equivalent and cannot be used interchangeably to make statements about soil performance at the same value. As the study was not a complete factorial design, we do not have data to compare for all media at all PSR and PSI values. Additionally, this batch incubation design is not necessarily indicative of how soil mixtures would perform in a bioretention system in an individual rain event.

2.3.1.4.3 Reactivity and other variables

The addition of the reactivity term greatly improved the predictive model for P sorption by WTRs in synthetic solution. To see if including reactivity would also improve the predictive capacity for mixtures, the interaction between extractable P, Al, and Fe within the mixture was explored. We separated these terms using a linear model that considered the combined amount of each element in the sample, expressed in moles. Extractable elemental values were calculated using a weighted average for the sample, accounting for relative amounts of WTR and organic. Candidate models compared three different ways of using P, Al, and Fe content of the sample as predictors of P release: one model used the PSR or PSI as a set ratio, one used extractable P and reactivity as two separate terms, and one used extractable P, Al, and Fe as three separate terms. Oxalate- and Mehlich 3-extractable variables were compared separately as nested sets, and models were compared by R^2 and AIC values. In the case of both oxalate and Mehlich 3 sets, the model containing all three variables separately (model 3) was the most predictive (Table 2.20). This suggests that the relationship between P, Al, and Fe may be more complex than the ratio used for both the PSI or PSR. The separation of these variables may also account for the additional P sorption capacity of a high-reactivity media having the same PSI or PSR as a low-reactivity media. Our results suggest that the oxalate-extractable variables may explain slightly more of the variation seen, but that the two extraction methods were similar for this purpose.

Table 2.20. Comparison of Mehlich 3 (a) and oxalate (b) nested sets of candidate models using extractable P, Al, and Fe as predictors of P release by combinations of WTRs and organics. In models 2 and 3, each variable included in the model is expressed in moles kg^{-1}.

a)

#	**Model**	**R^2**	**AIC**
1	P release ~ PSR	0.49	5627
2	P release ~ P_{M3} * $reactivity_{M3}$	0.57	5570
3	P release ~ P_{M3} * Al_{M3}* Fe_{M3}	0.63	5517

b)

#	**Model**	**R^2**	**AIC**

1	P release ~ PSI	0.54	5589
2	P release ~ P_{ox} * reactivity_{ox}	0.64	5495
3	P release ~ P_{ox} * Al_{ox}* Fe_{ox}	0.65	5491

Full oxalate model:

$$\text{P release (mg kg}^{-1}\text{ media)} = -508 + 80491 * P_{ox} + 9626 * Al_{ox} + 15396 * Fe_{ox} - 1055729 * P_{ox} * Al_{ox} - 1513932 * P_{ox} * Fe_{ox} \quad (2.29)$$

The variation in P release was partly, but not fully, explained by the independent relationships between extractable P, Al, and Fe. Additional variation suggests the effect of another factor, or factors. Additional candidate factors were considered across the full range of organics and WTRs used. Mehlich 3- and oxalate-extractable measures for P, Al, and Fe were kept together, and specific surface area (SSA), micropore volume, and total C were tested with each set, creating a series of nested sets of variables for comparison (Table 2.20). Candidate variables within each nested set were tested and compared using the R^2 and AIC of the resulting model, and the best models from each set was also compared against each other.

Table 2.21. Candidate variables tested in nested sets.

Nested set	**Restricted model**	**Additional variables tested**	**R2**	**AIC**
Oxalate	P_{ox} * Al_{ox} * Fe_{ox}	SSA * micropore volume * total C	0.83	5262
Mehlich 3	P_{M3} * Al_{M3} * Fe_{M3}	SSA * micropore volume * total C	0.9	5081

The best model from all of the nested sets (the model with the highest R^2 and lowest AIC) was the full model from the Mehlich 3 set using all 6 variables in Table 2.21.

Mehlich 3 model:

$$\text{P release (mg kg}^{-1}\text{ media)} = 1.444e{+}06 - 5.602e{+}08 * Al_{M3} * Fe_{M3} - 2.072e{+}08 * Fe_{M3} * P_{M3} - 7.724e{+}03 * Al_{M3} * \text{total C} + 1.645e{+}09 * Al_{M3} * P_{M3} * \text{micropore volume} + 7.920e{+}02\ Al_{M3} * SSA * \text{micropore volume} + 2.553e{+}04 * Fe_{M3} * SSA * \text{micropore volume} + 2.705e{+}06 * Al_{M3} * Fe_{M3} * \text{total C} + -9.120e{+}01 * Fe_{M3} * SSA * \text{micropore volume} * \text{total C} \quad (2.30)$$

Including extractable P, Al, Fe, reactivity, SSA, micropore volume, and total C, an estimate of P release by the BSM could be made. An optimal BSM would minimize P loss into bioretention effluent, and retain enough sorption capacity to treat P concentrations in influent stormwater. We can use our predictive model to see if new BSM under consideration is expected to release P, and to calculate necessary amounts of amendments to counter the expected release.

2.3.1.4.4 Threshold PSI and PSR

A threshold PSI or PSR would describe the relative maximum amount of extractable P that can be bound by the reactivity$_{M3}$ of the media. A "change point" like this has been observed by other studies such as Elliott, O'Connor, and Brinton (2002), Maguire and Sims (2002), Oladeji et al. (2007), and Nair and Harris (2004), using agricultural soil. After the threshold is exceeded, P release is expected to increase relative to the combined PSR for the media, with a rate of change determined by the reactivity of the media. The threshold would suggest that, while PSR or PSI alone may not be an accurate predictor of P release across a wide PSR range, it could be a good predictor of the *presence or absence* of P release, as long as the PSR or PSI of the combination was *below* the threshold. The 0.15 threshold proposed by Nair and Harris (2004) and others is a good starting place. The mean P release for samples in our study with a PSR < 0.15, 2.76 ± 0.14 mg P kg^{-1}, is very low, however there were only three samples in this range. The mean P release for samples with a PSI < 0.15, 63 samples in total, was 15.87 ± 2.44 mg P kg^{-1}. This is low compared to P release at higher PSI values but may not be sufficient for very strict bioretention specifications.

Figures 2.28 and 2.29 show the probability density distribution of combination samples that exceeded a 0.5 mg P L^{-1} effluent target at PSR and PSI values across the range tested. PSI and PSR were both significant factors of the probability of exceeding the effluent target. At a PSI of 0.11, there was a 50% probability of meeting the target (above that PSI, there was a > 50% chance of exceeding the target). Of all of the samples tested, 48 had a PSI ≤ 0.11; effluent P concentrations were below 0.5 mg P L^{-1} for 31 of them. Similarly, at a PSR of 0.22 there is a 50% probability of meeting the release target. Only 18 samples had a PSR of ≤ 0.22; effluent P concentrations were below 0.5 mg P L^{-1} for 13 of them. For a stronger analysis, more data points are needed at the low end of both ranges, especially in the case of the PSR range. For comparison with previous studies, however, Jay et al. (2017) found effluent P concentrations from an all-sand column with a PSR of 0.05 to be lower than influent concentration in 8 out of 12 leaching events (in the 3 leaching events where the sand column was a net source of P to effluent, influent P concentrations were close to detection levels). Other columns with PSRs ranging from 0.35 to 3.12 were a source of total and dissolved P to effluent in all events and all treatments. Brown et al. (2016) found columns with a PSI of 0.1 removed P from influent concentrations in all but one treatment, while columns with PSIs of 0.5 and 1.0 exported P to effluent. These ratios are similar to those seen in the present study. O'Neill and Davis (O'Neill & Davis, 2012a) suggested an oxalate ratio (OR; the inverse of PSI) between 20 and 40 to not only prevent P release, but to be able to retain additional P equivalent to 20 years of treatment of average influent stormwater P concentrations for the Washington, D.C., Metropolitan area (120 μg L^{-1}), equivalent to 34 mg kg^{-1} media (calculated for the BSM as a whole). An OR between 20 and 40 is equivalent to a PSI between 0.025 and 0.05.

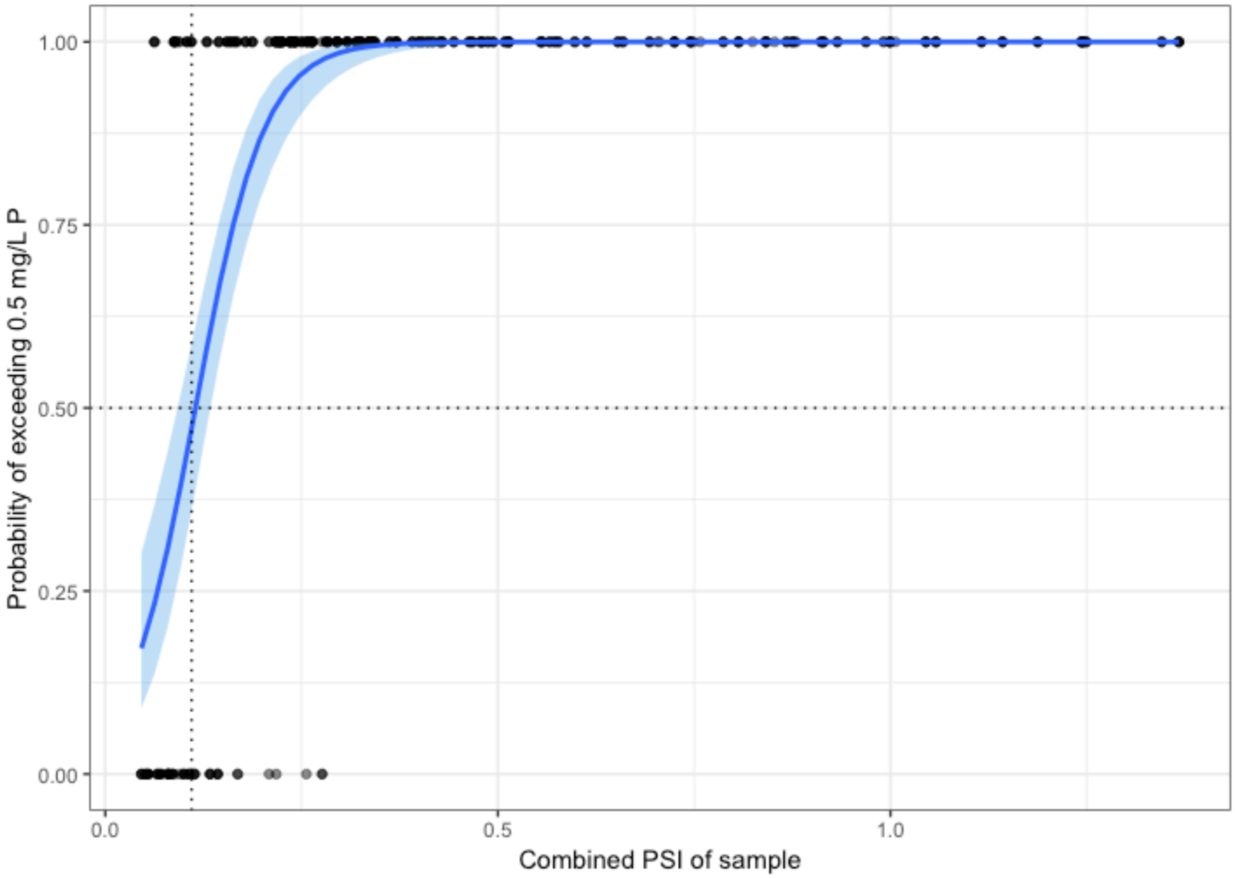


Figure 2.28. Probability of exceeding a target effluent P concentration of 0.5 mg L^{-1} across the range of PSI values seen in combination samples, shown by the blue line. A confidence interval is shown in light blue shading. The PSI values of samples which either met or exceeded the target are shown as black dots. A 50% probability of meeting the release target is seen at a PSI of 0.11 and indicated by the dotted lines.

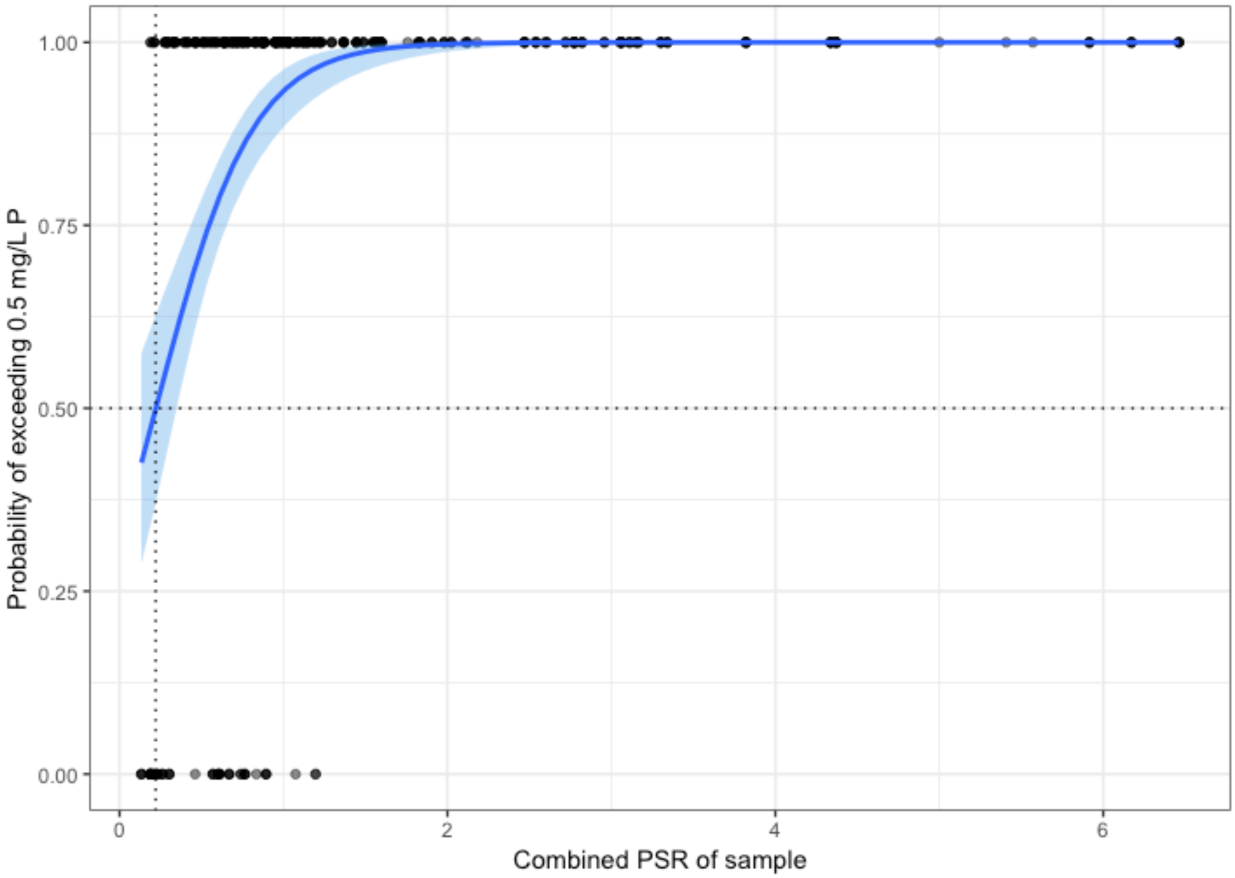


Figure 2.29. Probability of exceeding a target effluent P concentration of 0.5 mg L^{-1} across the range of PSR values seen in combination samples, shown by the blue line. A confidence interval is shown in light blue shading. The PSR values of samples which either met or exceeded the target are shown as black dots. A 50% probability of meeting the release target is seen at a PSR of 0.22 and indicated by the dotted lines.

The methods used in a batch incubation study like this are very different from a column study or real bioretention conditions in the field. The 24-hour incubation is longer than rainwater is generally retained in a bioretention system (except for a case of clogging or backup which results in system failure) and shaking the samples further increased contact between liquid and solid media, both of which should accelerate P release from the organics and adsorption by the WTRs. In addition, effluent concentrations are in part dependent on the volume of liquid and mass of media used in each sample cup, which can produce numbers that are very different from the results of rainwater flowing through a bioretention soil in vertical profile. If a desired performance standard for a bioretention system is based on effluent concentrations, as is often the case, these will need to be determined by column and field studies.

2.3.1.4.5 Recommendations for bioretention installations

These data indicate that PSR or PSI may be a useful predictor of a BSM's potential to release excess P into effluent, and that WTRs can be used to manipulate the PSR or PSI of the BSM components. Addition of amorphous Al and Fe from WTR amendment in a BSM serves to bind available P in the soil media and reduce P release. The PSI of the food and yard waste compost, ComFY, was 0.34, and its PSR was 1.8. Since this organic is currently commonly-used in bioretention systems and known to produce large pulses of P in effluent water (Chahal et al., 2016; Mullane et al., 2015), it is advised that PSI or PSR measurements of organic-WTR combinations for bioretention are at least lower than this starting point to improve on existing conditions.

In the results of this study, large increase in P release occurred when the PSI of samples exceeded 0.2, or when the PSR exceeded 0.25 (Fig. 2.20, 2.21). To further reduce effluent P concentrations in P-limited systems, it is advised to keep organic-WTR combinations below these ratios, as shown in Figure 2.30, or with a similar process using PSR. In order to achieve these PSI and PSR values, not all media is equally advisable for use in a BSM. The highest PSI/PSR organics, BioKC1, BioKC2, and BioKC3, also the highest P-releasing, would require a lot of WTR to perform at standards required for P-limited receiving waters. With enough WTR addition it could be done, however, an organic that requires more than 1 part WTR to 1 part organic (on a mass basis) to achieve optimal PSI or PSR values may not be practical, as the reduction in organic fraction of the overall BSM to make room for the WTR will start to impede on other functionality, such as metal retention (Paus et al., 2014). It is also important to note that, due to the much higher bulk density of WTRs than organics, a 1:1 ratio of media by mass will still result in a much larger volume fraction of organic (Jay et al., 2017).

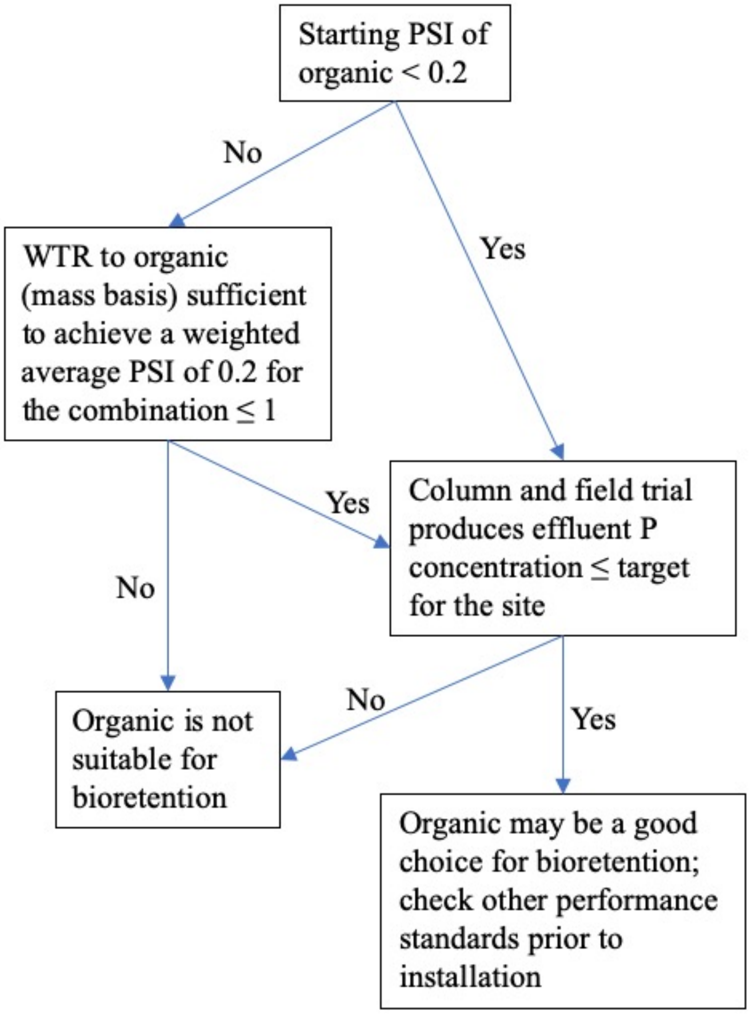


Figure 2.30. Decision tree for use of hypothetical organic and WTR in bioretention installation.

On the other end of the BSM combination, Al-WTR2 was the lowest P-sorbing WTR of the three used throughout the study (not including Ca-WTR). While it had very low starting PSI and PSR values, its low reactivity gave it less sorption capacity in combination with organics. It would take more of this media to amend the organic components for optimal P performance. Al-

WTR1 and Fe-WTR may be better choices, however, WTRs from other sources with even higher reactivity could be even more desirable.

Additional variables including surface area, micropore volume, total C, and pH may play a role in P release, although they provided only minor contributions to an explanation of variability in the results of this study. Another aspect of P mobility is that P sorption is in part dependent on the concentration gradient between P in solution and P in the sorbent (Hemond & Fechner, 2015; Li & Davis, 2016). The results from the synthetic solutions emphasize this point, as more P was adsorbed by the WTRs from solutions with high P concentrations, even when not all P in the solution was adsorbed. Combination samples with very low WTR:organic ratios also show that adding a small amount of WTR to an organic changed the P released by the combination by a lot, while smaller returns were seen with more WTR addition. Removing low concentrations of P from solution may be the most difficult. To address these issues, more testing is needed. Column and field studies will also be critical for understanding how P release examined in this study translate to effluent P concentrations in individual rain events, and to account for additional factors such as influent P concentration and volume, and P uptake by plants.

While PSI or PSR may be used to estimate the effluent P for a bioretention media, the desired PSI or PSR, and the amount of WTR amendment required to achieve the desired ratio, ultimately depends on the acceptable concentration of effluent P for a given scenario. If influent P is to be managed as well, influent concentrations, bioretention basin sizing, and desired effective lifespan all need to be considered (O'Neill & Davis, 2012a).

2.3.2 *Copper release and retention*

2.3.2.1 Copper and Phosphorus

Comparing the effluent P in assays with differing amounts of Cu, and the effluent Cu in assays with differing amounts of P allows us to look for evidence of competitive sorption or other interactions. Effluent P from the two assays with no added Cu was not significantly different from that of the two assays with the most added Cu (one low-P and one high-P assay in each pair) ($p=0.20$). Effluent Cu from the two assays with low P was not significantly different from that of the two assays with high P (one low-Cu and one high-Cu assay in each pair) ($p = 0.25$). These data suggest that P and Cu did not impact each other, positively or negatively, in sorption or release by WTRs.

2.3.2.2 Copper content of media

All media were analyzed for Mehlich 3-extractable and total Cu (Table 2.22). All four biosolids contained higher amounts of total Cu than the other media. Al-WTR1 and ComY had the least Cu content overall by all measurements.

Table 2.22. Copper content of media as measured by Mehlich 3 and total elemental analysis.

	Cu_{M3}*	Total Cu
	mg kg^{-1}	
WTR		
Fe-WTR	4.03 ± 0.186	119
Al-WTR1	0.933 ± 0.088	30.7
Al-WTR2	0.700 ± 0.058	69.5
Organics		
BioFe	7.40 ± 0.757	485
BioKC1	0.867 ± 0.120	318
BioKC2	0.567 ± 0.088	233
BioKC3	0.800 ± 0.058	349
BioPot	3.53 ± 0.561	60.3
ComBS	16.4 ± 0.982	161
ComFY	2.53 ± 0.203	57.2
ComY	1.17 ± 0.371	32.2

**Mean and standard error of three replicate samples tested.*

2.3.2.3 WTRs in Cu solution

The first six assays had synthetic Cu concentrations ranging from 0 to 96 μg L^{-1}. Effluent Cu did not change significantly across the range of influent Cu concentrations (Figure 2.31). Influent Cu concentration was a significant factor of effluent concentration, across all WTRs and for each WTR individually, but coefficients were < 1 in all cases (0.26 for Fe-WTR, 0.08 for Al-WTR1, 0.11 for Al-WTR2). Even as influent concentration increased, effluent concentration increased at a slower rate.

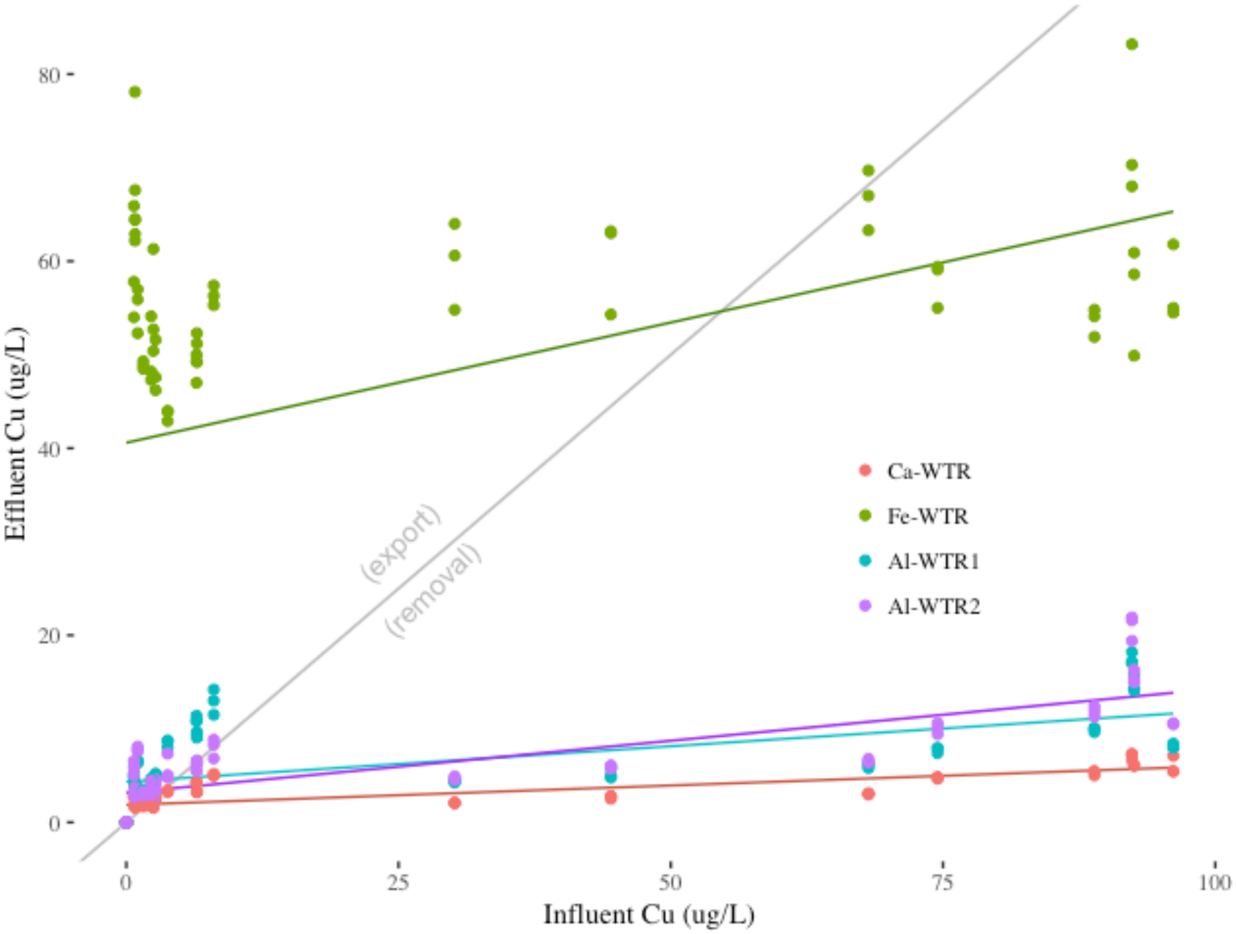


Figure 2.31. Concentrations of Cu before (influent) and after (effluent) incubation with WTR. Colored dashed lines indicated lines of best fit for each WTR. Gray dashed line represents line of best fit across all WTRs. Solid gray line has a slope of 1 and indicates the boundary between removal of Cu from influent and export of Cu to effluent.

WTR was a significant factor of both effluent Cu and Cu removal by WTRs. Effluent Cu concentrations in samples incubated with Fe-WTR were consistently and significantly higher than with any of the other WTR across all treatments in all five assays (Figure 2.30). Effluent Cu from the other three WTRs was statistically similar. While Fe-WTR did remove Cu from the solutions with the highest influent concentrations (> 70 μg L^{-1}), it exported Cu to all solutions with influent < 60 μg L^{-1}. All three of the other WTR consistently had effluent Cu concentrations below 22 μg

L^{-1}, regardless of influent concentrations, while Cu concentrations in the Fe-WTR effluent ranged between 42 and 84 μg L^{-1}.

At the lowest influent concentrations, effluent Cu for all three of the other WTRs also exceeded influent concentrations, suggesting that these WTRs may also have exported a small amount of Cu into the solutions. However, blank samples from assays in which no Cu was intentionally added all contained small concentrations of Cu, ranging from 0.60 to 6.78 μg L^{-1}, with a mean of 2.56 μg L^{-1}. The last four combination assays used Milli-Q water from a different tap, and only one of the 7 blanks in those assays contained detectable concentrations of Cu (the one outlier measured 0.22 μg L^{-1}). It was determined that the lab DI tap water was the source of additional Cu in the earlier assays. As Cu pipes leach the most when the faucet is first turned on, and the order in which samples were filled was not recorded, it is impossible to know if blank samples are representative of the additional Cu from tap water added to other samples. However, the additional Cu from the tap water is assumed to be small, most likely less than 10 μg L^{-1}. As influent concentrations were set according to blanks, the true effects of treatments should be close to those measured, although they may not be exact. No blanks were found to contain P unless it was intentionally added via synthetic solution or organic media.

Since effluent was only measured at higher concentrations than influent for Al-WTR1, Al-WTR2, and Ca-WTR when influent concentrations were < 10 μg L^{-1}, it is hard to say confidently whether the WTR were actually exporting Cu in these cases, or whether the measurement was due to an error in the study. At higher influent Cu concentrations, all WTRs removed more Cu. During the final two assays of the set (containing the highest influent Cu concentrations), even Fe-WTR removed Cu from solution.

Table 2.23. Percent removal of Cu from solutions by WTRs**.**

	% removal from selection solutions	
WTR	**All solutions**	**High Cu solutions only**
Ca-WTR	8.6 ± 14	94 ± 0.19
Al-WTR1	-95 ± 28	88 ± 0.72
Al-WTR2	-77 ± 31	86 ± 0.80
Fe-WTR	-2100 ± 380	3.8 ± 9.6

2.3.2.4 WTRs in Cu solution

Effluent Cu concentrations were also measured following the water extraction of the organics, and Cu release was calculated on a mass basis.

Cu release (mg kg^{-1} organic) = effluent Cu (mg L^{-1}) * volume of water used (L)/organic weight (kg) (2.31)

As in the case of P, the solid:water ratio used in the extractions was a highly significant ($p < 0.0001$) factor of Cu release by the organics on a mass basis. Cu release increased as the solid:water ratio decreased, suggesting that release may have been limited in the treatments using lower solid:water ratios. To compare organics, only the 1:200 solid:water treatment was used, as this was the most dilute extraction performed on all organics, and should therefore provide conditions for greater Cu release. However, no data is available for the BioPot organic at this treatment, due to those samples being destroyed during the 24 hr shaking period.

Table 2.24. Cu released by organics in 1:200 solid:water treatment of water extractions. Means and standard error shown for mass of Cu released per mass of organic, and for effluent Cu concentration.

Organic	**Cu released (mg kg^{-1})**	**Effluent concentration (mg L^{-1})**
BioKC1	12.1 ± 0.183 *a*	60.73 ± 0.913 *a*
BioFe	7.60 ± 0.040 *b*	38.0 ± 0.200 *b*
BioKC3	4.73 ± 0.401 *c*	23.6 ± 2.00 *c*
BioKC2	3.80 ± 0.321 *c*	19.0 ± 1.61 *c*
ComBS	2.04 ± 0.138 *d*	10.21 ± 0.692 *d*
ComFY	1.88* *d*	9.39* *d*
ComY	0.937 ± 0.009 *d*	4.69 ± 0.0450 *d*

*Two of three replicates leaked during shaking; only one replicate used in analysis.

Type of organic was highly significant ($p < 0.0001$) in Cu release in the water extraction. All four biosolids cakes, including the high-Fe biosolids (BioFe), released significantly more Cu than the composts. Of the biosolids, BioKC1 released the most Cu, followed by BioFe, and then BioKC3 and BioKC2 which were statistically similar. Total Cu and Mehlich 3-extractable Cu (Cu_{M3}) of the organics were tested as factors of Cu release, and total Cu was found to be highly significant ($p = 0.003$) with an R^2 of 0.45, while CuM3 was not significant ($p = 0.23$).

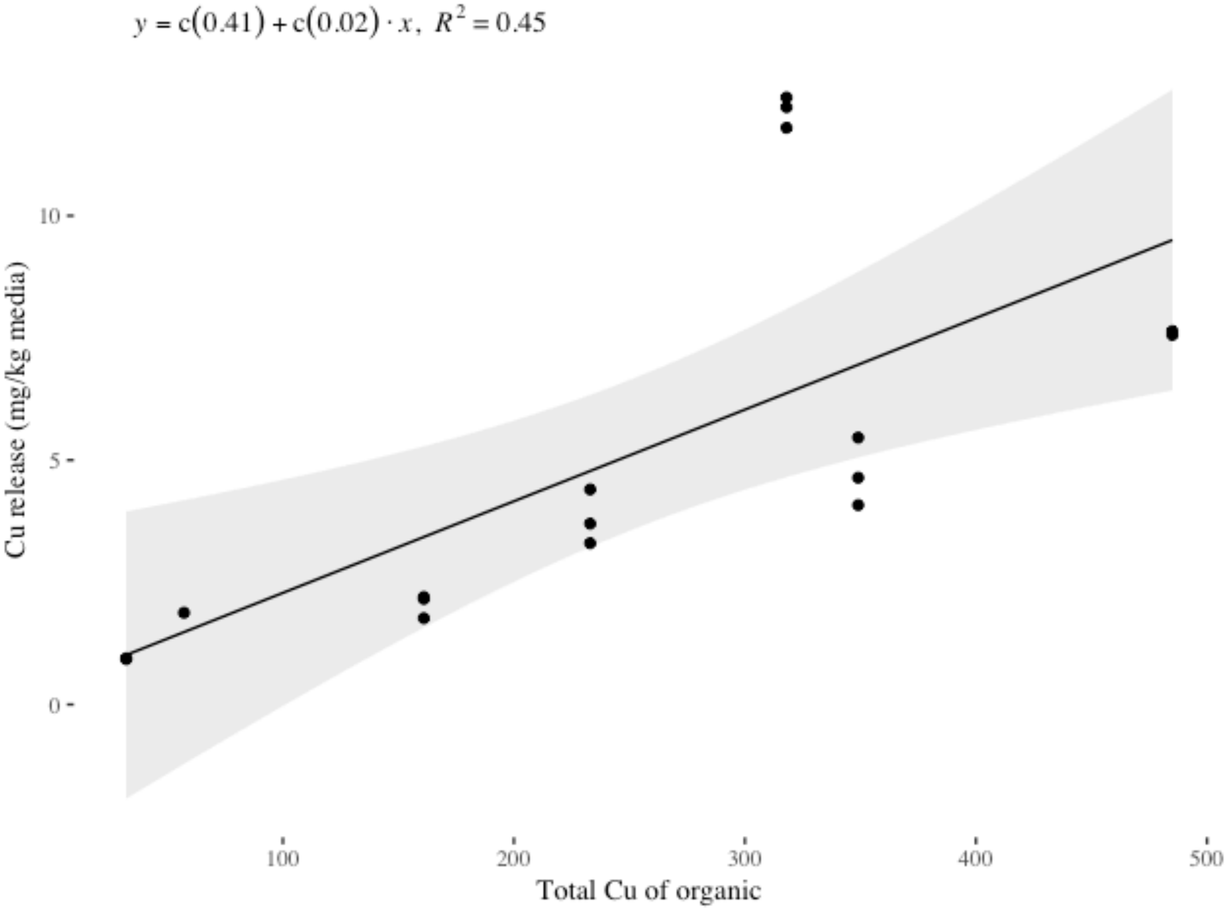


Figure 2.32. Total Cu in organics as a predictive measure of Cu release from 1:200 solid:water treatment of water extraction.

Total Fe and Fe_{M3} were also tested as factors of Cu release, as Fe plays a role in limiting Cu mobility in soil (Bradl, 2004). Total Fe was significant (p = 0.04), although the correlation coefficient (0.00014) was positive, indicating that higher total Fe was associated with more Cu release. However, the low R^2 of this relationship (0.26) and the very small magnitude of the correlation coefficient suggests that total Fe explained only a minor amount of variability seen in these data. Fe_{M3} was not a significant factor of Cu release by the organics. PSR and PSI were also tested as factors; PSR was not significant (p = 0.08), while PSI was significant (p = 0.02) but had a low R^2 (0.3), suggesting that it is a poor fit for the data as a predictor of Cu release.

2.3.2.5 Cu release from organic and WTR combinations

In combinations, WTR and organic were both significant factors for Cu concentration in effluent. Combinations containing Fe-WTR released more Cu than those containing Al-WTR1 or Al-WTR2 (Table 2.25, Figure 2.32). Fe-WTR contained more total Cu, and Cu_{M3} than either of the Al-based WTRs. However, observed Cu release was not proportional to the differences in total or extractable Cu across the combinations.

Table 2.25. Mean and SE of Cu released by combination samples containing the three WTRs**.**

WTR	**Mean (mg Cu kg^{-1} media)**
Fe-WTR	2.2 ± 0.26 *a*
Al-WTR2	1.2 ± 0.12 *b*
Al-WTR1	1.1 ± 0.11 *b*

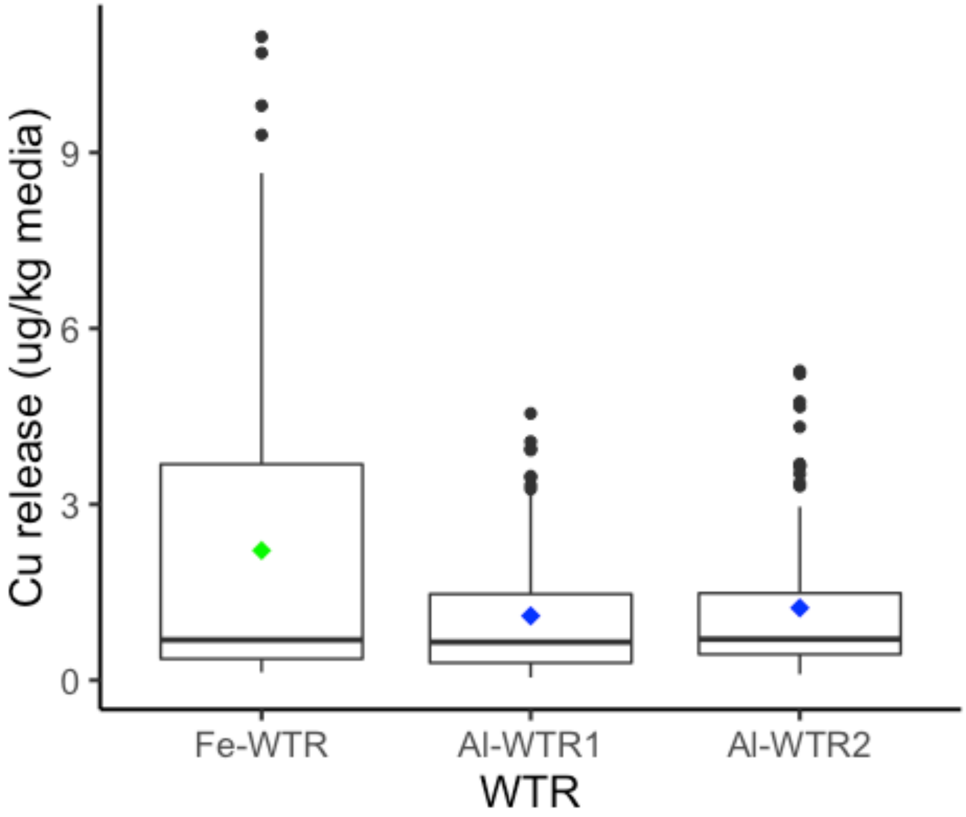


Figure 2.33. Cu released by combination samples as affected by WTRs. Means are shown in color; significantly different means are shown in different colors.

Cu release by the combinations followed a similar pattern by organic as Cu release by organics alone in the water extraction. Of the organics, combinations of WTRs and one of the Class B biosolids materials (BioKC1) had the highest overall Cu release. Copper release from combinations with two other biosolids (BioKC3, and BioFe) were lower than those with BioKC1 but elevated above the other media (Table 2.26, Figure 2.33).

Table 2.26. Mean and SE of Cu released by combination samples containing the different organics**.**

Organic	**Mean (mg Cu kg^{-1} media)**
BioKC1	4.35 ± 0.52 *a*
BioFe	3.30 ± 0.30 *b*
BioKC3	2.22 ± 0.29 *b*
BioKC2	1.17 ± 0.16 *c*
ComFY	0.62 ± 0.035 *c*
ComBS	0.59 ± 0.031 *c*
ComY	0.42 ± 0.46 *c*
BioPot	0.35 ± 0.031 *c*

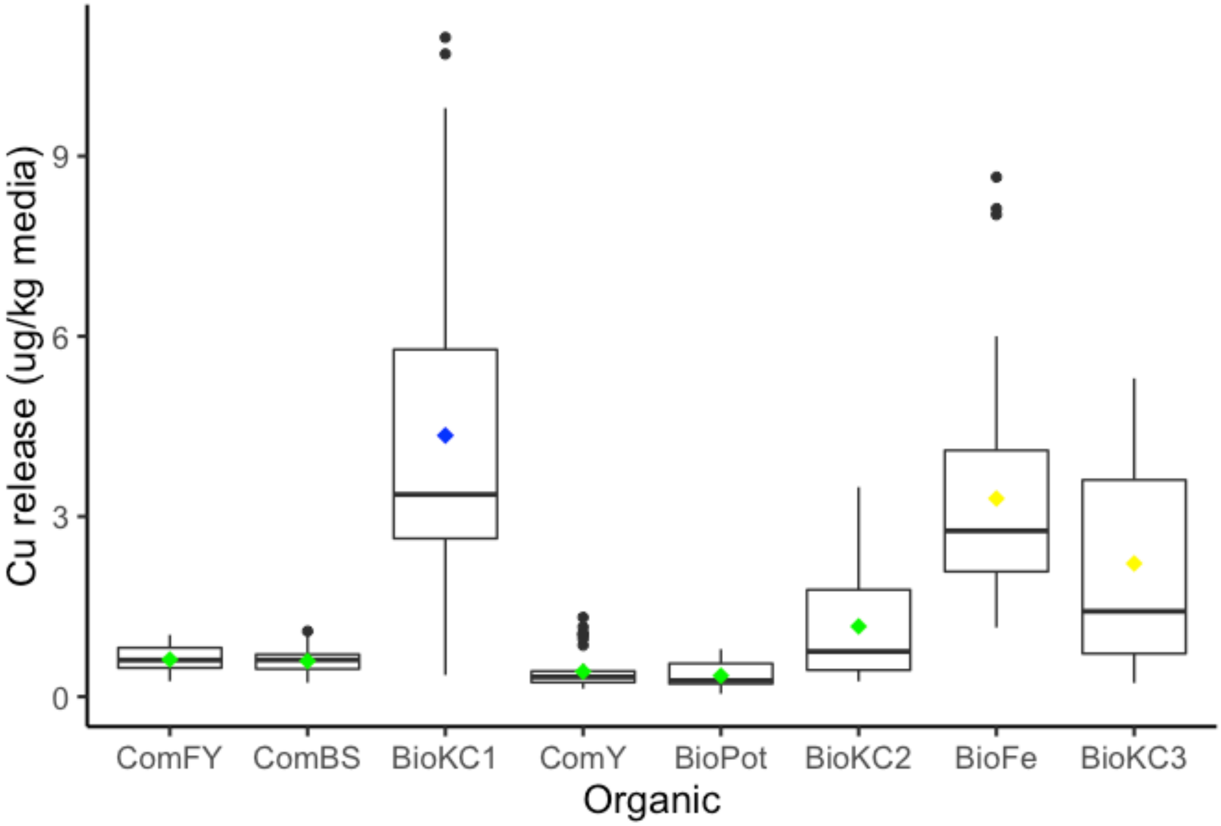


Figure 2.34. Cu released by combination samples containing the different organics. Means are shown in color; significantly different means are shown in different colors.

2.3.2.6 Predictors of Cu sorption and release

Copper release from combinations of organic and WTR ranged from 0.048 – 11 mg Cu kg^{-1} media. This produced effluent concentrations ranging from 2.9 – 630 ug L^{-1}, although, as with the P data, the unequal solid:water ratio across the samples makes comparison of raw effluent numbers somewhat difficult. Only three samples produced effluent concentrations ≥ 5 ppb; these were the three replicates of a 1:2 (by weight) combination of BioPot and Al-WTR1. Mean effluent concentration of these samples was 3.31 ± 0.22 μg L^{-1}.

It is unclear what factors are driving the differences in Cu release between all of the samples. Total Cu, calculated as a weighted average of component media (total Cu from both organic and WTR in mg Cu kg^{-1} media), was a significant factor in Cu release (also expressed as mg Cu kg^{-1} media), although the R^2 was only 0.24. Fe-WTR contained the most total Cu of all WTRs, and was associated with samples with more Cu release. BioFe, BioKC1, and BioKC3, the organics associated with samples with more Cu release, all had higher total Cu than the other organics. Combinations with the lowest overall total Cu released the least Cu into solution, however, there was a high degree of variability in the response across the range of total Cu of all combinations, especially with some very high levels of Cu release in the middle of the range of total Cu values (Figure 2.34).

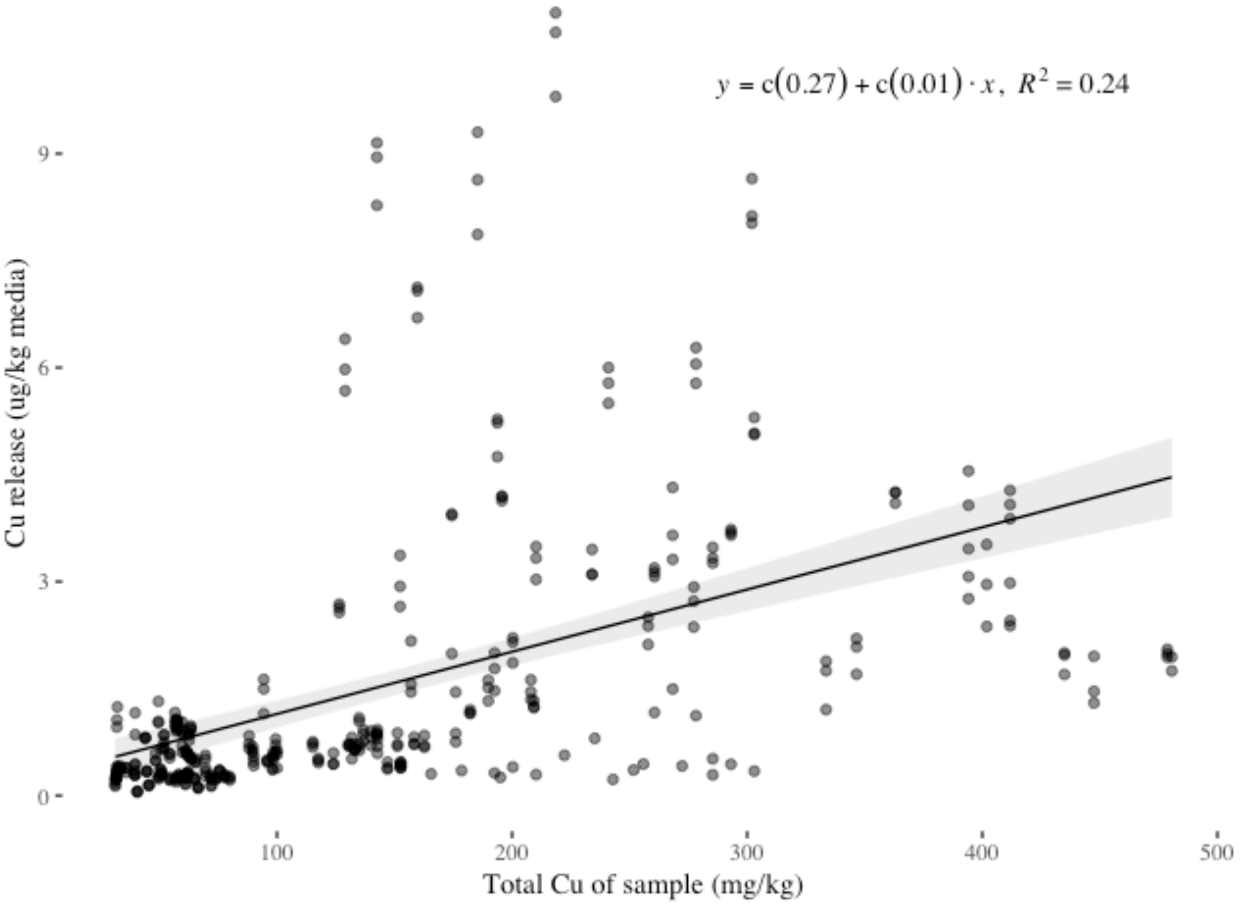


Figure 2.35. Total Cu of combination samples (calculated as a weighted average of component media) as a predictive measure of Cu release.

PSI and PSR were both significant factors of Cu release with R^2s of 0.12 and 0.14, respectively. This suggests that these ratios explain only a small portion of the observed variability seen in the data and were not strong predictors of Cu release. The following additional candidate factors of Cu release from combined samples were examined: reactivity_{M3}, reactivity_{ox}, Total C, Total Cu, Cu_{M3}, Total Fe, Fe_{M3}, Fe_{ox}, all as weighted averages of contributions of both WTR and organics in the combination. Reactivity was expressed as mol kg^{-1} media, and the other variables were expressed as mg kg^{-1} media. pH of both WTR and organic were also tested, as were physical characteristics of the WTRs, micropore volume (cm^3 g^{-1}), micropore area (m^2 g^{-1}), and specific surface area (m^2 g^{-1}). All variables tested were significant, but R^2 values were low, ranging from 0.009 (micropore volume of WTRs) to 0.22 (Fe_{M3}). It is strange that total Fe, Fe_{M3} and Fe_{ox} were all positively correlated with increase Cu release, since Fe plays a role in binding Cu within soil (Bradl, 2004).

It is clear that not all WTRs and organics behave in the same way with regards to Cu removal from or export into solution. However, from the above analysis, it is unclear what causes the media to perform in the way we observed, or how Cu release could be predicted without incubation assays. The analysis suggests that it is a complex combination of media characteristics that determines Cu release. Many organics exported very little Cu, however a few exported significantly more. The highest Cu export in this study was by some of the biosolids tested, although not all of the biosolids tested exported such high amounts. Previous work has also shown no relationship between total Cu in the BSM and Cu in effluent. It is also important to consider that not all Cu in effluent may be bioavailable to aquatic organisms. Copper released from organics is likely complexed with dissolved organic carbon (DOC) (Chahal et al., 2016; McIntyre et al., 2008). This is a form that is much less toxic to wildlife than ionic Cu in stormwater runoff. We do not know the status of Fe exported from WTR such as Fe-WTR, but since the combinations contain such a high amount of organic matter, Cu released by WTRs within the combination is still likely to become complexed with DOC before leaving the BSM, as has been seen with influent Cu (Chahal et al., 2016).

2.4 CONCLUSIONS

Soil physiochemical characteristics are correlated with the performance of a BSM as either a source or sink of P to effluent, and eventually to receiving waters. The ratio of available P to the amorphous Al and Fe content of the soil, measured using either oxalate or Mehlich 3 extractions and expressed as either PSR or PSI, is a factor of the net P released by a soil mixture and can be used to estimate and correct for that release. All organic materials included in this study, compost of various feedstocks, biosolids, and potting soil blends, were sources of P to water in the batched incubations performed, and all WTRs were P sinks. Because of their high amorphous Al and Fe content, WTRs may be used as an effective amendment to offset the high amount of available P in organic materials, and PSR or PSI of the mixture can be used to calculate the relative proportions of each component for decreased P release to effluent. However, to better understand how this relationship can inform bioretention soil installations in a field setting, more study is needed. Other variables, such as total C and porosity, may also play a role in P release from soil and soil amendments, although this study found the effects of those variables to be smaller than that of PSR or PSI.

Factors of Cu release from organic materials and soil mixtures are less clear. Total Cu was a significant factor of Cu release, although this does not represent the total picture of Cu mobility as there was still a large amount of variability in the relationship between the two variables. In the case of both P and Cu, field-scale studies will need to be conducted to better understand these materials and how optimal BSMs can be created to maximize stormwater treatment benefits of bioretention systems and improve receiving water quality.

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