Bioretention Soil Media:

Understanding the effects of compost and finding predictors for phosphorus leaching

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A thesis

submitted in partial fulfillment of the

requirements for the degree of

Master of Science

University of Washington

2016

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Program Authorized to Offer Degree:

School of Environmental and Forest Sciences

University of Washington

Abstract

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Chair of the Supervisory Committee:

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This study is intended to 1) investigate the effect of compost rate and compost type on bioretention soil media (BSM) performance, and 2) explore possible predictors of phosphorus leaching from bioretention systems. Columns with 14 different bioretention soil media (BSMs) were analyzed in a greenhouse over the course of 60 weeks, during which 14 storm events were staged. Removal rates of metals (Cu, Pb, and Zn) and nutrients (N and P) were analyzed, as well as infiltration rate, plant yield, and chemical soil properties. All BSMs acted as sinks for copper and zinc when real stormwater was used as influent, with BSMs containing pure biosolids showing most effective removal. BSMs with 80% compost by volume were less effective than 40% or 20% compost mixtures at metals removal when varying influent levels

were used. Nitrogen leaching results were counter to expectations - it is posited that hydraulic features of the BSMs may have played a larger role than BSM ingredients in determining nitrogen leaching. Mehlich-III phosphorus saturation ratio (PSR) was found to be an adequate predictor of phosphorus leaching from all BSMs, while the ammonium oxalate phosphorus saturation index (PSI) was a poor predictor, possibly due to the wide variety of BSMs in this study.

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Acknowledgements

First and foremost I have to thank my advisor, Sally Brown, for the enormous role she has played in the creation of this thesis. Without her committed guidance and invaluable knowledge of the field, this thesis project would not have succeeded. Not only that, but the course of my education would have gone in an entirely different direction. Not everyone would be willing to take on the task of molding someone with a liberal arts background into a scientist in two years, so I am sincerely grateful for Sally's openness and commitment to helping me along that path!

Further recognition must go to my thesis committee members, Kate Kurtz and Susan Bolton, for helping me refine the topic and present it at its best. I am grateful for your guidance, interest, and time. I am also very grateful to Northwest Biosolids and DC Water, both of which helped fund this project and helped direct it by acting as real-world reference points.

This project required a lot of work in the greenhouse over a long period time, and for their help with that I must thank Amber Corfman, Megan Plog, and Ashley Blazina. Amber Corfman especially deserves thanks as she was responsible for the set up and maintenance of the greenhouse columns before I arrived on the scene. All three contributed long hours and a fair amount of sweat to the success of this project. I also owe gratitude to Dongsen Xue, who helped run hundreds of samples and patiently taught me how to prepare them for different tests.

Finally, I want to thank my partner Harris Schwartzreich, who was supportive of my choice to move all the way across the country to pursue this degree, and who has made grad school life a great adventure.

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Figure 4.3. Effluent concentration of total Cu from all reps of C40-FY, C20-W, Sand, and DCB8-LCS, for events 9-12. Average influent concentration of Cu for these events was 39.76 µg/L. DCB8-LCS was consistently below the detection limit of 4 µg/L.

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Introduction

Bioretention systems offer a green alternative to conventional stormwater management by allowing stormwater to infiltrate into groundwater and removing contaminants along the way. Though many factors contribute to the effectiveness of bioretention systems, the make-up of the bioretention soil media (BSM) is crucial to contaminant removal as well as plant growth.

Many bioretention guidelines across the country suggest including compost in BSMs, but the recommended rate varies widely (SWMMWW 2014; Carpenter et al 2010). Furthermore, although "compost" is an umbrella term that can describe soils with very different properties, the term is not always accompanied by appropriate specification (Philadelphia 2015; Georgia 2001). This may be due in part to the paucity of scientific research into the effect of compost on BSM performance. Though many batch and column studies have included one or two BSMs containing compost and compared them to non-compost BSMs, few have compared the performance of BSMs with different rates of compost, and even fewer have looked at the effect of composts with different feedstocks, C/N ratios, or other properties (Brown et al. 2016; Charlesworth et al. 2013; Hatt et al. 2008; Bratieres et al. 2008). This study is intended to address that knowledge gap by analyzing the effect of compost rate and compost type (i.e., compost feedstock) on characteristics of effluent by comparing the performance of BSMs with 20%, 40%, and 80% compost as well as BSMs with food/yard and biosolids/yard compost.

One common issue with BSMs is phosphorus (P) removal. BSMs must contain a certain level of P in order to support robust plant growth, and that P can also wash out with stormwater. In fact, many BSMs act as sources of P in stormwater rather than sinks.

Researchers have identified additives that can reduce P mobility – water treatments residuals (WTRs) are an especially effective example (Brown et al. 2016, Lucas and Greenway 2011, O'Neill and Davis 2011). However, limited research has been put into finding ways to predict P leaching based on chemical or physical properties of BSMs. Methods that have been developed to predict P leaching from agricultural soils offer a good first step for bioretention research. This study will investigate whether two tools developed in agricultural settings – the phosphorus saturation index (PSI) and the phosphorus saturation ratio (PSR) – are predictive of P leaching from bioretention soils.

Literature Review

Stormwater runoff in urban areas poses several environmental problems, including increased flooding, potential lack of groundwater recharge, and surface water contamination. With the proliferation of impervious surfaces in urban environments, rain is largely unable to infiltrate soils and instead runs over the surface as stormwater directly into water bodies, or to combined sewer pipes that transport the stormwater to wastewater treatment plants. This leads to flashy hydrology (Figure 1.1) in which floods are more intense and frequent, and base flow of rivers in between storm events is lower (Ward and Trimble 2004). Post-development hydrology is referred to as "flashy' because runoff volumes reach their peak more quickly and the peak volume is much higher than it would be under pre-development conditions. Post-development peak flow is brief, and runoff volumes quickly return to their baseflow, which is lower than it would be pre-development. In addition to direct runoff, sewer pipes and wastewater treatment plants in regions with combined sewers can become overwhelmed during intense storms, resulting in combined sewer overflows (CSOs); this is where raw or partially treated sewage and stormwater are released to surface water bodies to prevent sewage backup.

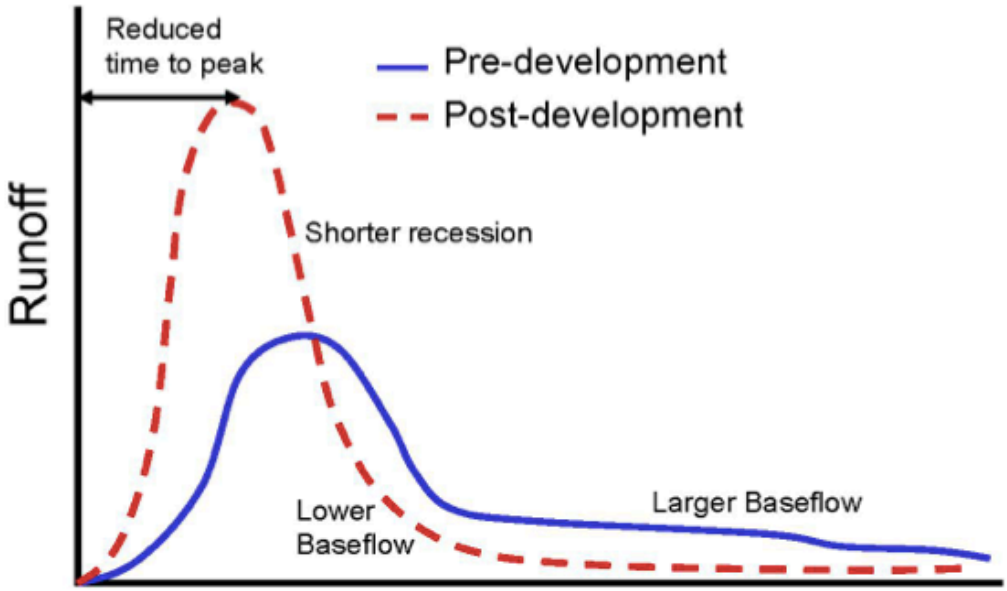

Figure 1.1. This simplified chart depicts the conceptual difference between pre-development and post-development in the relationship between runoff volume (y-axis) and time (x-axis). Taken from Liu et al (2014).

As stormwater runs over streets, buildings, lawns, and other impervious surfaces, it picks up contaminants and delivers them into nearby surface water bodies where they can negatively affect aquatic life and threaten public health. Stormwater contamination and volume varies with land use and climate; stormwater in heavy industrial areas typically has higher levels of contamination than in residential or undeveloped areas. It has been shown that 1 acre of paved parking lot generates 16 times more runoff than a meadow of the same size (Schueler 1995). Common contaminants of concern include sediment, heavy metals such as copper (Cu), zinc (Zn), lead (Pb), arsenic (As), and cadmium (Cd), nutrients including nitrogen (N) and phosphorus (P), and organic compounds such as bisphenols, polycyclic aromatic hydrocarbons (PAHs), and pesticides. Table 1.1 below shows median values for a variety of contaminants in

stormwater from areas with different land use patterns (Pitt et al. 2005). These data are from the National Stormwater Quality Database, which aggregated data from more than 200 communities throughout the United States over a 10-year period.

Table 1.1. Median values for common stormwater contaminants according to land use, as reported in the National Stormwater Quality Database report (Maestre and Pitt 2005).

Parameter	Overall	Residential	Commercial	Industrial	Freeways	Open Space
Area (acres)	56	57.3	38.8	39	1.6	73.5
% Imperv.	54.3	37	83	75	80	2
Precip. Depth (in)	0.47	0.46	0.39	0.49	0.54	0.48
TSS (mg/L)	58	48	43	77	99	51
BOD5 (mg/L)	8.6	9	11.9	9	8	4.2
COD (mg/L)	53	55	63	60	100	21
Fecal Coliform (mpn/100 mL)	5081	7750	4500	2500	1700	3100
NH3 (mg/L)	0.44	0.31	0.5	0.5	1.07	0.3
N02+NO3 (mg/L)	0.6	0.6	0.6	0.7	0.3	0.6
Nitrogen, Total Kjeldahl (mg/L)	1.4	1.4	1.6	1.4	2	0.6
Phos., filtered (mg/L)	0.12	0.17	0.11	0.11	0.2	0.08
Phos., total (mg/L)	0.27	0.3	0.22	0.26	0.25	0.25
Cd, total (ug/L)	1	0.5	0.9	2	1	0.5
Cd, filtered (ug/L)	0.5	ND	0.3	0.6	0.68	ND
Cu, total (ug/L)	16	12	17	22	35	5.3
Cu, filtered (ug/L)	8	7	7.6	8	10.9	ND
Pb, total (ug/L)	16	12	18	25	25	5
Pb, filtered (ug/L)	3	3	5	5	1.8	ND
Ni, total (ug/l)	8	5.4	7	16	9	ND
Ni, filtered (ug/L)	4	2	3	5	4	ND
Zn, total (ug/L)	116	73	150	210	200	39
Zn, filtered (ug/L)	52	33	59	112	51	ND
ND = not detected, or insufficient data to present as a median value.						

In order to protect the health of aquatic life, maintain water quality, and prevent flooding and drought, environmental managers have turned to low-impact development (LID) to manage stormwater in a way that aims to mimic pre-development hydrology. LID best management practices (BMPs) include a variety of options including bioretention systems, which will be the focus of this paper.

Bioretention systems are shallow depressions backfilled with engineered soil media and planted with water-tolerant species (Figure 1.2). Instead of flowing into drains and sewers, stormwater from an impervious area is directed into a bioretention cell. Many bioretention cells allow water to infiltrate directly into the groundwater (Figure 1.2). However, if the soil in a

given area is clay-heavy or has a very low hydraulic conductivity, the bioretention cell may be fitted with an underdrain to prevent saturation of the cell (Figure 1.3). Underdrains can lead to pipes that go to wastewater treatment plants or directly to surface water bodies. Bioretention systems are physically depressed to allow water to pool over the bioretention soil media, and a weir or other mechanism is sometimes built to prevent overflow. The purposes of bioretention systems are primarily to 1) control stormwater flows by allowing water to infiltrate and be retained temporarily by the cell, and 2) to remove pollutants from the stormwater as it infiltrates. (Liu et al. 2014; SWMMWW 2014; Palmer et al. 2013)

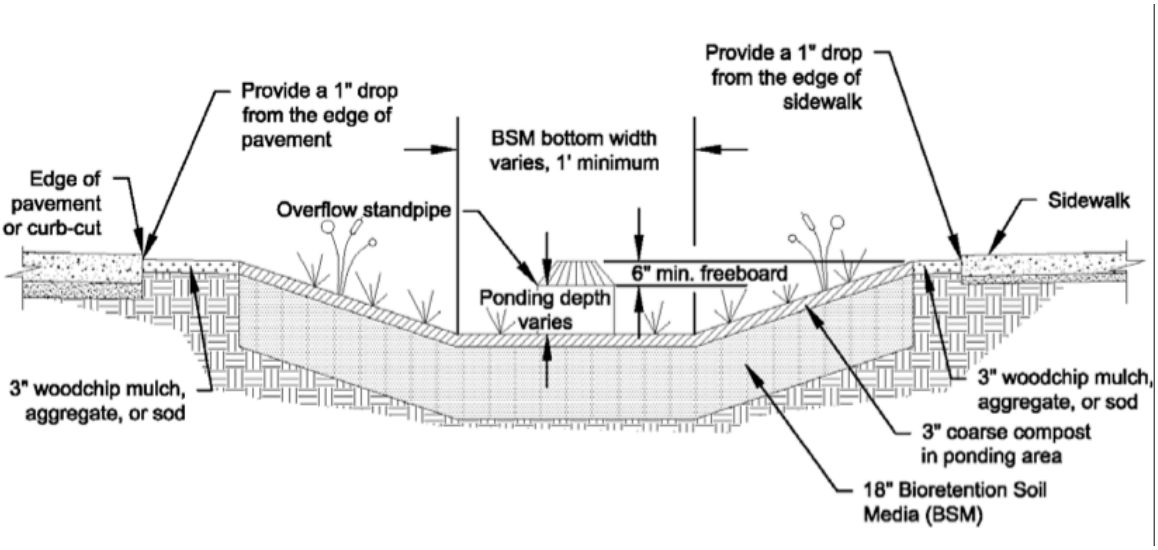

Figure 1.2. A typical bioretention system that drains into the underlying soil. Illustration taken from Washington Department of Ecology's Stormwater Management Manual for Western Washington (2014).

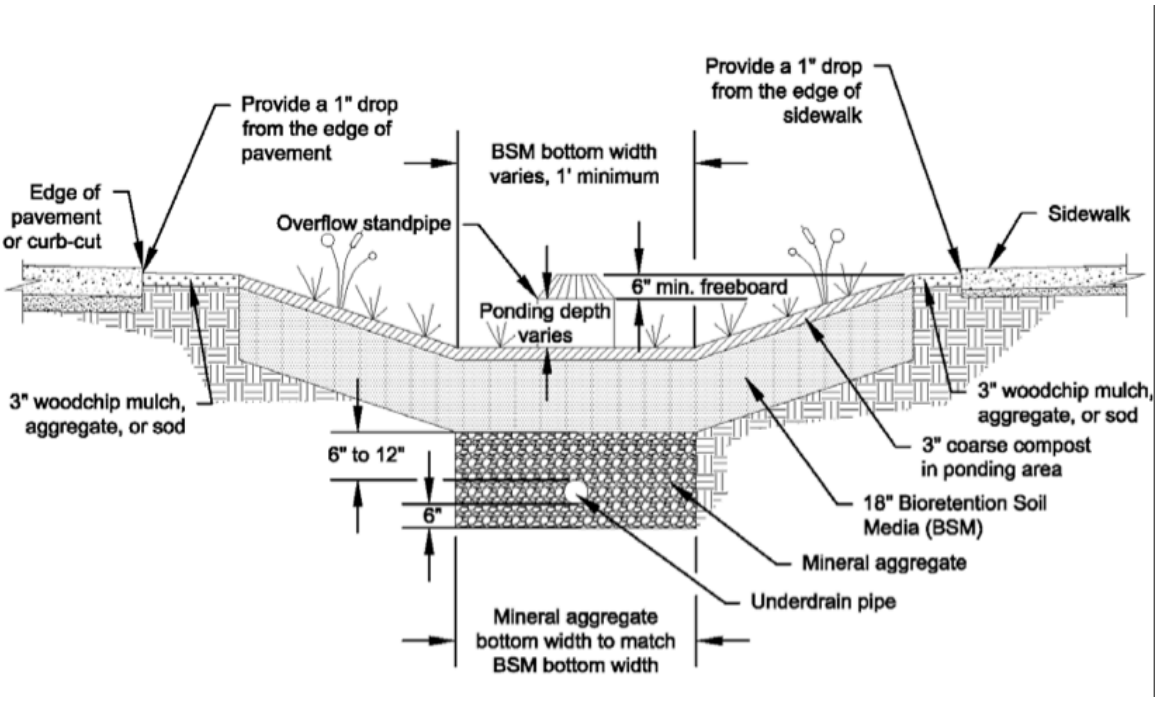

Figure 1.3. A typical bioretention system with an underdrain. Illustration taken from Washington Department of Ecology's Stormwater Management Manual for Western Washington (2014)

It has been shown that bioretention systems are able to effectively control runoff by reducing peak flows in streams and rivers, enhancing base flows, and increasing lag time (the time between a storm event and peak flow), thereby mimicking pre-development hydrology in post-development areas (Liu et al. 2014; Li et al. 2009; Davis 2008; Hunt et al. 2008). A recent study of water quality of effluent from these systems demonstrates the capability of bioretention treatment to protect aquatic organisms through contaminant removal. McIntyre et al. (2015) tested the response of juvenile coho salmon, mayfly nymphs, and cladocerans to untreated stormwater and to stormwater that had been treated by columns set up to mimic bioretention systems, and found sharply different responses. While the juvenile salmon in untreated stormwater had a 100% mortality rate, all of those exposed to stormwater treated by

bioretention soil survived. Cladocerans and mayfly nymphs followed a similar pattern, as can be seen in Figure 1.4. In that study, the bioretention soil media (BSM) was made up of 60% sand, 15% compost, 10% Water Treatment Residuals (WTR) and 15% shredded bark, by volume. It was further found that concentrations of metals in the fish that were exposed to water treated by bioretention soil were not significantly higher than levels in the control fish, which were exposed to DI water.

Similar studies directly linking bioretention to survival of biota are lacking, however, many studies have examined the ability of bioretention systems to reduce concentrations of particular contaminants of concern in stormwater. Research into bioretention systems is active, in particular work to optimize the performance of bioretention soil media (BSM).

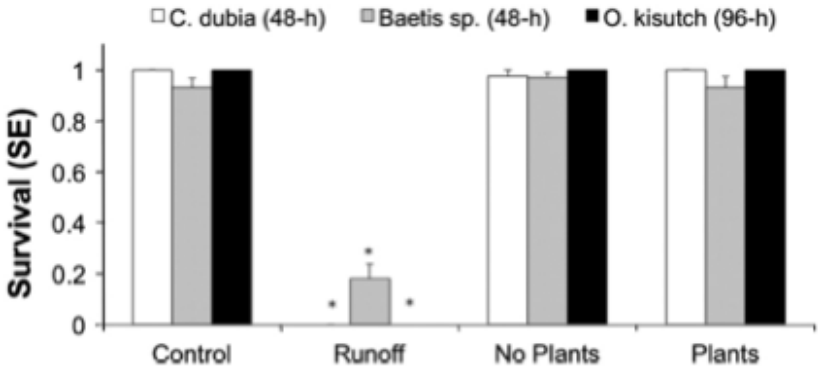

Figure 1.4. The survival of three aquatic species – mayfly nymphs (Baetis sp.), cladocerans (C. dubia) and juvenile salmon (O. kisutch) – exposed to different water types. In order from left to right, these water types are DI water (control), untreated stormwater runoff from a Seattle, WA, U.S.A. highway bridge (runoff), runoff treated by bioretention systems with no plants (no plants), and runoff treated by bioretention systems with plants (plants). Stars indicate survival significantly lower than the control. Taken from McIntyre et al. (2015).

Stormwater contaminants

The sources and threats of nutrient and metal contaminants will be discussed below, as well as their chemical behavior in soils.

Phosphorus

Phosphorus (P) is a contaminant of particular concern in stormwater, as it often is the limiting nutrient for eutrophication in freshwater bodies. Excess P in runoff causes algal blooms that can lead to fish kills, reduced usability for recreation and industry, and in some cases toxicity, which threatens public health (Kotak et al. 1993; Sharpley et al. 1994; Sharpley 2000). It has been estimated that problems associated with freshwater eutrophication have an economic cost exceeding $2.2 billion a year in the United States (Dodds et al. 2009). In urban and suburban areas, P in stormwater runoff comes from fertilizers used on lawns or other green spaces, as well as atmospheric deposition, soil erosion, and animal waste (US EPA 2009).

The soil processes involved in the sorption and desorption of P are complex. These processes can be divided into the "fast" sorption process, which is a reversible sorption of P onto the surface of soil particles or colloids, and the "slow" sorption processes. The "slow" processes involve deposition of inorganic P onto amorphous oxides of calcium (Ca), iron (Fe) and aluminum (Al) (Kovar and Pierzinski 2009). Fe and Al hydroxides have especially high charges and large surface areas when compared to other oxides, making them ideal bonding sites for inorganic P (Lucas and Greenway 2011). The deposition process is pH dependent, with Ca becoming a more prevalent deposition site above a pH of 5.8 (McDowell et al. 2001). The deposition process is described as "slow" because with time, P is incorporated into the interior of the oxide particle, and once this has occurred P is unlikely to desorb. P is also known to sorb

to organic matter, but the mechanism behind this is unclear and changes with pH (McGechan and Lewis 2002). Under reducing conditions, P can be released as Fe and other oxides are transformed. P in runoff is typically either dissolved in the form of PO_4^{3-} or sorbed to particles suspended in the water.

Nitrogen

Nitrogen (N) in stormwater has similar sources to P – stormwater picks up N from fertilizers, animal waste, and atmospheric deposition. In urban areas an important N source is fixation of N from the atmosphere in internal combustion engines in cars (Elliott et al. 2007; Baker et al. 2001). While elevated N in drinking water has been associated with a range of health impacts, the primary concerns with elevated N in stormwater are related to the potential for eutrophication (Ward et al 2005; Weyer et al. 2001; Carpenter et al. 1998; Howarth et al. 1996).

N takes multiple forms in soil and goes through various transformative processes depending on conditions. Fertilizers contain N predominantly in the form of ammonium (NH_4^+) and nitrate (NO_3^-), both of which are water-soluble and plant available. Although both ions are soluble, ammonium (which is positively charged) easily sorbs to negatively charged colloids in the soil, while negatively charged nitrate moves freely in soil water. Nitrate is therefore the most mobile form of N and the main species of concern for stormwater issues. Ammonium and nitrate can both be immobilized by microorganisms, which convert them to organic forms of N – ammonium is preferred in this process due to the highly reduced state of NH_4^+-N (Dell and Rice 2005; Melzer and Exler 1982). The opposite of this process is mineralization, in which

organic forms of N decompose to inorganic N in the form of ammonium or nitrate. Organic N is largely in particulate form, but a small percentage is dissolved organic N, which can be taken up by plants and contribute to N leaching, especially during the first rain after a dry season (Mullane et al. 2015; Brady and Weil 2010; Flint and Davis 2007).

Even if the soil lacks nitrates initially, it may still leach nitrates as other forms of soil N are transformed. Mineralization is the major process that can increase inorganic N in soils, but inorganic species can change from one to another as well. Microbes in aerobic soil conditions oxidize ammonium to nitrite (NO_2^-) and then to nitrate in a process called nitrification. The opposite of this process is dissimilatory nitrate reduction to ammonium (DNRA), which reduces nitrate to nitrite and then to ammonium, but it is much less common than nitrification. Ammonium can be removed from the soil through volatilization, in which ammonium in the soil volatilizes to ammonia gas – this process is more prevalent in soils with high pH. Nitrate can also leave the soil through the denitrification process, where it is converted to nitrogen gas (N_2) or nitrous oxide (N_2O), typically under anaerobic conditions. Nitrates are reduced in the denitrification process, so a source of electrons is also necessary in this process and is usually found in soil carbon. (Collins et al. 2010; Brady and Weil 2010)

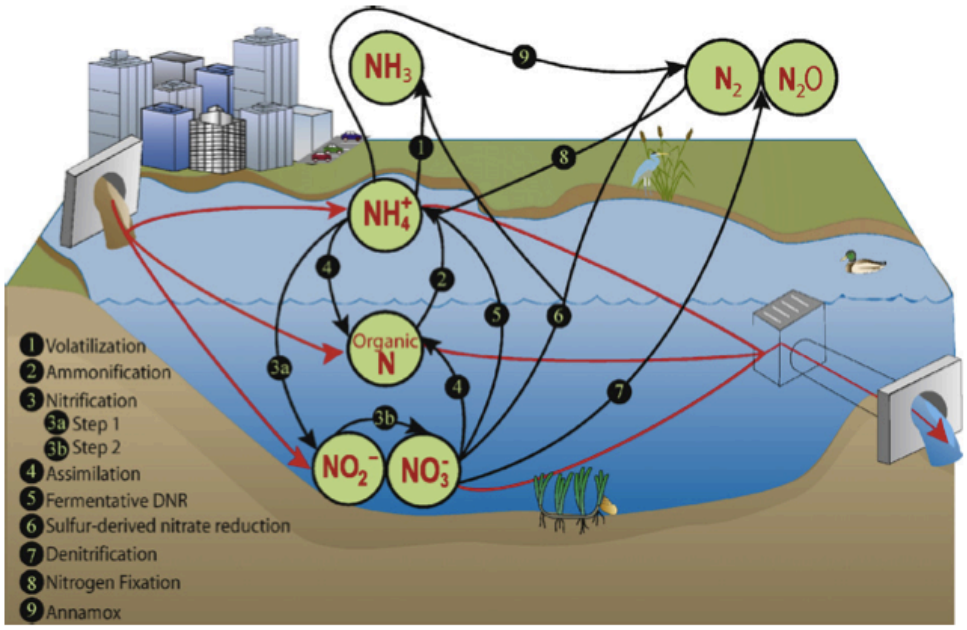

Figure 1.5: A simplified depiction of the N cycle, illustrating nitrification, denitrification, immobilization (called assimilation in the figure), mineralization (called ammonification), volatilization, and DNRA. Taken from Collins et al. (2010).

Metals

Heavy metals including copper (Cu), chromium (Cr), zinc (Zn), manganese (Mn), lead (Pb), iron (Fe), and arsenic (As) are a long-term concern as they do not degrade over time. Metals in stormwater mainly come from traffic-related sources, soil particles, and litter – common sources of different metals in stormwater can be seen in Figure 1.6 (Sansalone and Buchberger, 1997). High metal concentrations in drinking water can have grave human health effects (one of the most notorious being lead poisoning). Aquatic life is also extremely sensitive to high concentrations of some metals, especially Cu. For instance, juvenile coho salmon have reduced alarm response when exposed to waters containing Cu in concentrations as low as 5 µg/L, making them more susceptible to predation (McIntyre 2012).

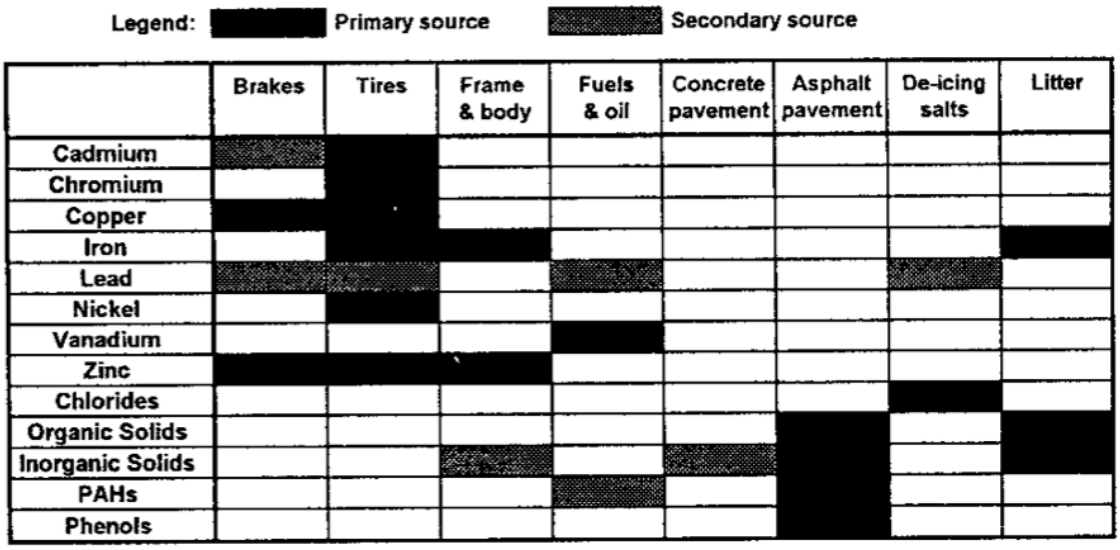

Figure 1.6. Primary and secondary sources of metal and organic contaminants in urban stormwater. Taken from Sansalone and Buchberger (1997)

Metals are generally partitioned between dissolved and particulate forms. Fewer soil processes affect heavy metals than N and P – primarily metal cations sorb to negatively charged soil particles through ion exchange. Therefore, cation exchange capacity (CEC) is usually negatively correlated with metals mobility in soils (Sun and Davis 2007). Pb, Cu, and Ni can also form covalent bonds with Fe, Al, or Mg oxides, which exist naturally in the soil (Wenjun et al. 2012). Metal sorption is directly related to pH – lower pH can cause metals to desorb from soil particles. Sorption is also affected by oxygen levels - under reducing conditions, Fe, Mn, and Cu are more soluble and likely to desorb, and oxides can be reduced and release sorbed metals in the process. (Brady and Weil 2010)

Cu, Zn, Mn, Ni, and Cl though considered toxic at high concentrations, are all micronutrients which are essential to plant growth and health. Therefore these metals are taken up by plants in their dissolved forms, albeit at much slower rates than macronutrients such as N and P. Organic matter is known to complex with certain metal cations (Cu, Zn, Mn,

and Fe) to form organic chelates, some of which are immobile, and most of which are nontoxic to aquatic biota (McIntyre 2015). However, degradation of organic matter can release organic acids and lower soil pH, which may cause metals to desorb from soil particles. Despite this complexity, organic matter content is usually negatively correlated with metals mobility in soils. (Brady and Weil 2010; Sun and Davis 2007)

Phosphorus in Soil

Since phosphorus (P) is an essential plant nutrient and one of the main components of commercial fertilizers, agricultural fields have long been a source of excess P. In fact, farms are a major non-point source of P pollution, and thus play a large contributing role in the eutrophication problems in many water bodies. To help farmers determine the ideal amount of P to apply to their fields in order to support robust crops without over-applying and releasing excess P to the environment, soil scientists have developed many mechanisms for measuring soil P and predicting the rate at which it will be taken up by plants and/or mobilized into runoff. With bioretention systems facing similar concerns, it makes sense to investigate these mechanisms for possible applications in this field.

Multiple soil extractions have been proposed to measure soil P in agronomic settings. Some are designed to measure plant available P (Olsen, Bray, Mehlich-I and -III), while others measure environmentally active P (water soluble P, $CaCl_2$, KCl, ammonium oxalate, and Mehlich-I and -III) (Sharpley et al. 2002; McDowell et al. 2001). When soil test P is related to P leaching, researchers often find a "change point" – a certain level of soil P past which P leaching

increases quickly with increased soil P concentration, but before which P leaches at very low levels and does not change with soil P concentration.

The standard agronomic extraction in the southern U.S. is the Mehlich-III extraction (Mehlich 1984; Tucker 1992). Various ranges for Mehlich-III-P have been proposed to support crop growth but minimize environmental risk: Maguire and Sims (2001) claim 50-100 mg/kg Mehlich-III-P is ideal, while Kovar and Pierzinski (2009) give a range of 45-50 mg P/kg. The Virginia Department of Conservation and Recreation recommends that soil Mehlich-III-P levels be between 18-40 mg/kg (Virginia 2005). In fact, the relationship between Mehlich-III-P levels and P leaching appears to change depending on the soil type, pH, and other factors. One variable of note is that the Mehlich-III extraction solution is highly acidic and it is thus a less accurate measure of labile P in calcareous soils, as it gives falsely elevated P levels by dissolving Ca oxides, which would not release P to runoff in field conditions (Sharpley and Smith 1994). A field study looked at Olsen and Mehlich P in 8 different soils, and found widely varying change points for each one (McDowell et al. 2001). One field study of two bioretention sites did find that P leaching was greater where soil Mehlich-P levels were higher, but this relationship was not investigated further (Hunt et al. 2006). Kleinman et al. (2001) found that the relationship between soil Mehlich-III-P and dissolved P in runoff for three different soils (Berks, Lewbeach, and Honeoye) was distinct for each soil. One soil showed a clear positive correlation (i.e. P in runoff increased as soil Mehlich-III-P increased, which would be expected), but the others had no significant relationship, indicating that soil-specific management may be necessary. Similarly, Elliott et al. (2002) found that Mehlich-I P (which is functionally similar to Mehlich-III P) was poorly correlated with P leaching in biosolids-amended soils. Due to this complexity, a

national study performed by the USDA, U.S. EPA and multiple universities concluded that a specific threshold of soil P to prevent P leaching is unrealistic, stating that P behavior is too variable with soil type, topography and management (Sharpley et al. 2002). When considering these results in the context of bioretention systems, it is important to note that studies done on agricultural fields are usually analyzing runoff water rather than leachate that has passed through a greater depth of soil, and also that very small concentrations of P are a concern for some bioretention systems that may not be for agricultural runoff.

To better predict runoff P, some soil scientists combine soil P with other soil or environmental factors to describe the P "saturation" of a soil. The P Saturation Index (PSI) is one such combination. It takes into account the importance of Fe and Al oxides as sorbents of P, representing the P saturation of a soil with the molar ratio P/(Al+Fe), where P, Fe, and Al are the ammonium oxalate-extractable molar concentration of each element in the soil. Soils with PSI< 1 would be expected to leach less P, while soils with PSI>1 would be expected to leach P increasingly as the PSI increases (Breeuwsma and Schoumans 1987; Breeuwsma et al. 1995). The same molar ratio, P/(Al+Fe), has also been proposed using P, Al and Fe extracted using the Mehlich-III reagent; this is called the P saturation ratio (PSR) (Maguire et al. 2001). Schoumans and Groenendijk (2000) amended this ratio to include a saturation index α as follows: P/(α{Fe+Al}), where α=0.3-0.5. This revised ratio is called the dissolved P saturation (DPS) index, and was developed to better fit experimental data.

In a lab study of 6 biosolids-amended agricultural soils, the only soil with PSI above 1.1 was the only soil that leached significant amounts of P, despite variation in Mehlich-P and oxalate-P. The authors conclude by recommending PSI to predict P leaching (Elliot et al. 2002).

O'Neill and Davis (2011) also recommend PSI for this purpose, as they found a linear relationship between P leaching and PSI with an R^2 of 0.725 from their batch study of water treatment residuals (WTR)-amended soils. They recommend that bioretention soils intended to efficiently remove P should have a PSI below 0.05. Maguire and Sims (2002) demonstrated in batch tests that P leaching began to increase quickly when PSR exceeded 0.2.

Lu and O'Connor (2001) studied the effect of three different land-applied biosolids on two sandy soils in Florida – they hypothesized that the high Al and Fe content of the biosolids would increase the P retention. Although PSI was not specified, the ratio of P/(Al+Fe) was at the center of the study. They found that P sorption increased with oxalate extractable Al and Fe content of the soil, with an R^2 value of 0.7 (see Figure 1.7). Biosolids failed to impact the P retention in soils which already had high Al and Fe content, but significantly increased P retention where soil Fe and Al content was low. They caution, however, that this effect faded after four years and show that Fe and Al disappear from the soil A horizon during this time period, possibly due to organic acid produced as biosolids degraded.

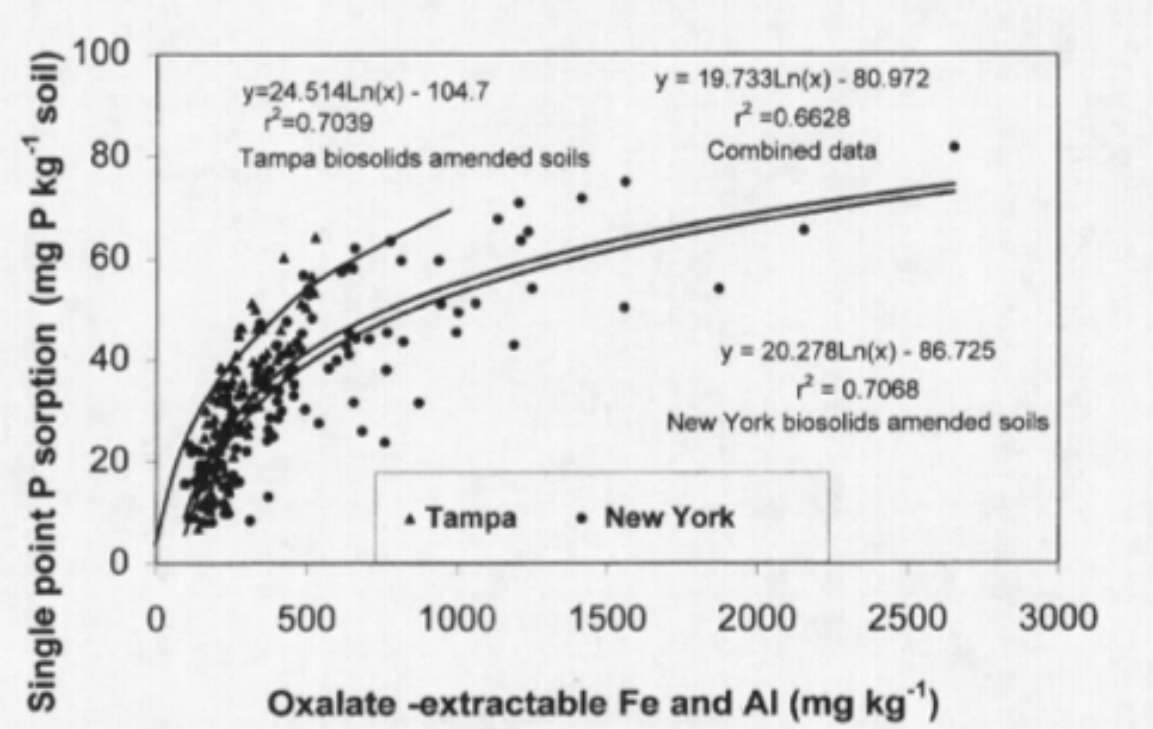

Figure 1.7. The relationship between P sorption capacity and oxalate-extractable Al and Fe in two different sandy soils, with biosolids from Tampa and New York applied. Taken from Lu and O'Connor (2001).

In Brown et al. 2016, PSI was investigated by creating soil columns with the same soil components and bringing them to PSIs of 0.1, 0.5, and 1.0 by adding either Fe-based WTRs to reduce the PSI or ammonium phosphate to increase the PSI. Clear differences in P leaching were seen between all three PSI levels (see Figure 1.8), with the soil with the highest PSI leaching the most P and the soil with the lowest PSI leaching the least P. It was also noted in this study that P leaching from all PSI levels decreased over time (Brown et al. 2016).

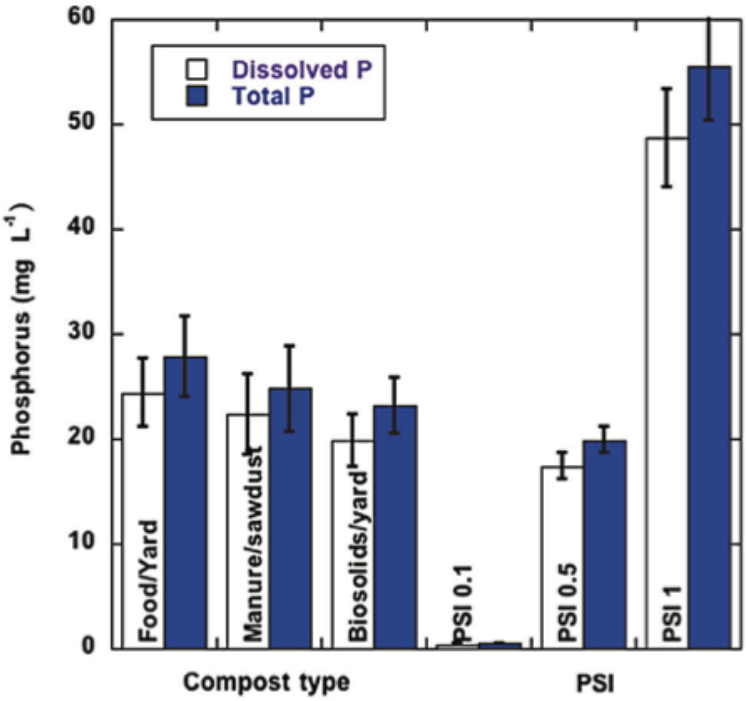

Figure 1.8. Dissolved and total P in effluent from bioretention columns contain three different composts, and columns containing those composts which have been chemically brought to PSI levels of 0.1, 0.5, and 1.0 with the addition of WTR or ammonium phosphate. Taken from Brown et al. (2016).

Bioretention Soil Media: Contaminant Removal

Many of the studies discussed below are monitoring studies performed on existing bioretention systems in the field to determine actual nutrient, metals, and water retention capacity. Others have been performed in labs or greenhouses on mesocosms or soil columns created to simulate the functioning of real bioretention systems. Mesocosm and column studies are idealized and do not fully represent bioretention in the field, as they do not account for things like changing seasons, irregular precipitation, freezing and thawing, clogging, compaction, and other unexpected influences (Liu et al. 2014; Carpenter et al. 2010).

Potential differences between greenhouse columns studies and real-world bioretention systems are exemplified by the differences between contaminant removal efficiency during dry-wet cycles (which reflects real-world precipitation patterns) versus during continuous flow or constantly moist conditions, which are found in most greenhouse studies. Research into the effects of dry-wet cycles on N removal indicates that dry periods in between precipitation events allow nitrate to build up as nitrification proceeds in the aerobic soil, resulting in a flush of nitrates in the first wetting after a dry period (Li and Davis 2014; Hsieh et al. 2007). It has also been suggested that dry-wet cycles negatively affect P sorption, possibly by encouraging the crystallization of metal oxides and subsequent desorption of P (O'Neill and Davis 2011; Baldwin and Mitchell 2007). However, Hsieh and Davis (2007) found that a soil that had sorbed high quantities of P and had started showing decreased P removal rates regained the capacity to sorb P after drying for 14 days and subsequent re-wetting. They posit that the dry period allows the slow sorption of P to proceed such that P sorbed to the exterior of oxides can be brought into the interior of their structure, thereby freeing surface sorption sites for stormwater P. It may be true that dry-wet cycles could be prevented in the field with application of mulch to aid in moisture retention, but this has not been thoroughly explored in the literature (O'Neill and Davis 2011). Due to the potential variation between greenhouse and field data, the type of each study discussed below will be noted.

A further source of confusion when comparing bioretention studies arises when looking at contaminant removal rates. Many studies present removal rates in terms of concentration by comparing the concentration of a contaminant in effluent leachate to the concentration in influent stormwater. This is useful but does not always tell the whole story, because

bioretention systems retain water as well as contaminants. Thus, for instance, if 1 mg/L nitrate is in influent stormwater, and the bioretention system retains 90% of water and 90% of nitrate by mass, the effluent concentration of nitrate will still be 1 mg/L and removal rate will be 0 when comparing concentrations, even though 90% of the nitrate by mass has been retained. For this reason, some studies present removal rates in terms of mass balance, comparing the total mass of a contaminant that exits a system to the total mass of the contaminant in the influent. Removal rates by mass are generally much higher than removal rates by concentration, and thus should not be compared directly. This is illustrated by a field study in Virginia conducted by Debuske and Wynn (2011), where 99% removal of N and P are reported by mass. That same study reports 99% retention of water from precipitation events, and does not include concentration levels in effluent, so it is impossible to determine whether N and P removal was due to treatment by the BSM or simply due to water retention. In discussion of bioretention studies below, removal rates will describe concentrations unless otherwise noted.

Metals

Bioretention tests have reliably removed metals at high rates, despite widely varying designs. Davis et al. (2001) did a column study followed by a field test of two bioretention sites to examine removal rates of Cu, Zn, and Pb, and found that removal rates of all of these metals were close to 100% in the columns (which were filled with sandy loam soil). Effluent Cu and Pb concentrations were under 5 µg/L, and effluent Zn concentrations were under 25 µg/L. One of the field sites removed all metals at a rate at or above 95%, but the other had much poorer removal ranging from 43-70%. The cause of this difference in the field is only guessed at in this

study, but shows that not all bioretention systems are equal when it comes to metals removal. Unusually high influent concentrations of the contaminants were used in this study for both the column and field tests, but their results are mirrored in many other studies showing high metal removal (Wenjun et al. 2012; Blecken et al. 2009; Faucette et al. 2009; Hatt et al. 2008; Sun and Davis 2007).

Sun and Davis (2007) looked at Cu, Zn, Pb, and Cd removal in bioretention "pots" (only 31 cm in height) with BSM consisting of 50% sand, 30% planting soil, and 20% leaf compost. They grew three different types of grass in these pots, with the expectation that they would bioaccumulate some of the metals. They found 88.4-98% removal for all metals, and further determined that 88–97% was captured in soil media while only 0.5–3.3% were accumulated in plants. They attribute this low plant uptake to the low biomass of grass in the study, and suggest that different plants that have more biomass may have more of an impact on metals removal.

A larger scale greenhouse experiment involving 120 columns looked at the effect of vegetation and different BSM components on removal of Fe, Cu, Cr, Zn, Pb, and Al (Wenjun et al. 2012). BSMs consisting of sandy loam, sandy loam with vermiculite and perlite (which were added to increase CEC), and sandy loam with leaf compost were compared. Once again, high removal rates were found for all columns, with 80-99% removal of Cu, Zn, Pb, Fe, and 70-99% removal of Cr and Al. Like the study above, no significant influences of vegetation were found, with the exception of one species, *C. appressa*, which appeared to remove a significant amount of Fe. Though there were small statistical differences, BSMs with compost performed similarly to sandy loam BSMs in removing all metals, but the authors note that variance in metals

removal was smaller for the compost BSM, implying that compost may be the more reliable treatment.

By investigating the mechanism of metals removal in bioretention systems, Li and Davis (2008) showed that most metals are removed from stormwater in the thin top layer of bioretention media by a combination of physical filtration and sorption. Jones and Davis (2013) confirmed this by sampling the top soil layer of a 4-year old bioretention system, where they observed the majority of metal accumulation in the top 3-12 cm of the BSM. Since metals do not degrade over time, Davis et al. (2003) had projected that BSMs may need to be changed out every 15 years to avoid accumulation of metals at toxic levels in the soil. Jones and Davis (2013) did find that Cu, Zn, and Pb concentration in the 4-year old BSM had increased significantly in the top layer, but they were well below regulatory limits, and it was estimated that BSM replacement would not be necessary as long as the bioretention system was routinely maintained.

Phosphorus

Nutrient removal in bioretention systems has been less reliable than metals removal – many BSM mixtures struggle with removing N and P, especially in their dissolved forms. Time is an important factor for both P and N leaching. Concentrations of both of these nutrients in effluent have been shown to decrease over time (Brown et al. 2016; Hatt et al. 2008; Dietz and Clausen 2006; Hsieh and Davis 2003). Other studies have shown P concentrations increase over time (Yang et al. 2010; Lu and O'Connor 2001).

Since P leaching can be particularly harmful to freshwater systems, many BSM components specifically chosen to increase P retention have been suggested. Erickson et al. (2007) did batch tests on calcareous sand, limestone, three blast oxygen furnace byproducts, aluminum oxide, and chopped granular steel wool to determine effectiveness at P sorption, and from that information picked calcareous sand, steel wool, and limestone to investigate further as amendments in bioretention columns of sand. The addition of steel wool to sand columns increased P sorption from 2% to 34-81% of influent mass. However, removal decreased over time and was very low (though still positive) by the end of the trial. Zhang et al. (2007) did a similar study of sand columns amended with fly ash, expanded shale, limestone, and peat moss, and found that both fly ash and one type of expanded shale would effectively reduce P concentration in effluent to below 0.37 mg/L for a projected lifetime of 12 years. These are promising numbers, but the 12-year lifetime was determined using an accelerated loading procedure that may not accurately reflect the behavior of a bioretention system over time in the field. Many similar studies of "enhanced" sand and other industrial media have been done: granulated activated carbon, granulated ferric hydroxide, bauxsol-coated sand, aluminum oxide-coated sand, iron oxide-coated sand, spinel, tire crumb and red mud have all been suggested (O'Reilly et al. 2012; Wium-Andersen 2012; Lucas and Greenway 2011; Liu et al. 2005). Some of these (Al-coated sand, for instance) are too expensive to be a realistic component of most bioretention systems. Still, many of these enhancements are low in cost and have been shown to increase P retention, but the columns they were tested in did not contain compost or soil that would support plant growth, so their behavior in a functioning bioretention system can only be deduced.

Many studies have shown that P leaching in agricultural soils can be controlled by the addition of water treatment residuals (WTRs) (Agyin-Birikorang et al. 2007; Dayton and Basta, 2005a; Elliott et al., 2005; Novak and Watts, 2004), and that P sorbed to WTRs does not desorb over time (Agyin-Birikorang et al. 2007; Agyin-Birikorang and O'Connor 2007; Makris et al. 2004; Ippolito et al. 2003). WTRs are Al- or Fe-based byproducts of the drinking water treatment process: Al and Fe salts are added to water as flocculants to create clearer water, and WTR are the Al and Fe hydroxides that result. WTR are generally disposed of in landfills, and thus can be obtained for free or low-cost (Agyin-Birikorang et al. 2007; Makris et al. 2005).

WTRs have been tested in bioretention systems for the same purpose. Lucas and Greenway (2011) tested P removal in bioretention mesocosms with Al-WTRs, red mud, and clay by loading the systems with effluent over 80 weeks that they claim is equivalent to 40 years' worth of P loading in the field. The mesocosms with WTR removed P most efficiently, with 90% removal throughout the course of the trial. O'Neill and Davis (2011) did a batch and minicolumn study of sandy loam soil with varying amounts of Al-WTR added, and found that increased WTR content resulted in increased P sorption capacity. They noted further variables influencing P sorption: decreasing fines content increased P sorption, and intermittent flow (i.e. drying and wetting of the soil versus continual moisture) reduced P sorption. A column study based on their findings was performed, and it was found that loamy sand columns with 5% Al-WTR and 3% bark mulch removed 88.5% of P by mass, compared to similar columns without WTR which actually added 71.2% the mass of influent P (O'Neill and Davis 2012). Komlos et al. (2013) did batch sorption tests on Al-WTRs that had been baked, dried, or unchanged from their original

form, and found that drying did not affect the P sorption capacity of the WTRs, and that drying and baking both increased the WTRs' hydraulic conductivity by two orders of magnitude.

Finally, Palmer et al. (2013) did a greenhouse study of columns with BSM composed of sand, food/yard waste compost, shredded bark, and Al-WTRs, and found that inorganic phosphate was removed from all columns at rates between 58 and 81%. They compared columns with and without a saturated zone, and found that those with the saturated zones removed significantly less inorganic P than those without. To explain this, they suggest that P was prone to desorb from the WTRs in the anoxic environment created by the saturated zone. This is supported by Baldwin and Mitchell (2007), who describe a tendency for P to desorb under reducing conditions in riverine soils. This study shows only a snapshot, as it was conducted over a period of one month and thus ignored any possible changes over time. Despite these limitations, Palmer et al. conclude that Al-WTRs are an effective P removal component.

Nitrogen

Like phosphorus, nitrogen export is also a common problem with BSMs, especially export of nitrate and nitrite. A summary of N removal rates found in studies of conventional bioretention studies can be seen in Table 1.3, taken from Collins et al. (2010). While the majority of systems tested remove total N, the highest removal rate is only 58%. Furthermore, when looking at nitrate/nitrite, the most mobile form of N, almost half of systems tested actually add nitrate/nitrite to stormwater, rather than remove it.

Table 1.3. N removal rates based on concentration in studies of conventional bioretention systems. Taken from Collins et al. (2010).

Study	NH_3–N	$NO_{3,2}$–N	TKN	TN	Study location
Blecken et al. (2007)	58.3	−650	–	−72.7	Laboratory
Bratieres et al. (2008)	–	−562	–	−202	Greenhouse
Bratieres et al. (2008)	–	74.1	–	58.4	Greenhouse
Bratieres et al. (2008)	–	−520	–	−182	Greenhouse
Cho et al. (2009)	92.6	−144	–	–	Laboratory
Davis et al. (2001)	25.8	–	66	–	Laboratory
Davis et al. (2001)	73.3	−89.2	55.9	–	Laboratory
Davis et al. (2006)	–	−54.	60.9	42.9	Laboratory
Davis et al. (2006)	–	−12.8	55.4	47.2	Laboratory
Davis et al. (2006)	–	18.0	55.0	51.9	Field, Maryland, USA
Davis (2007)	–	84.6	–	–	Field, Maryland, USA
Dietz and Clausen (2005)	75.0	30.0	28.6	25.0	Field, Connecticut, USA
Dietz and Clausen (2006)	–	66.7	33.3	50.0	Field, Connecticut, USA
Hatt et al. (2009)	53.9	−10.8	–	0.1	Field, eastern Australia
Hsieh and Davis (2005)[a]	13	11	–	–	Laboratory
Hsieh and Davis (2005)	21.2	41.0	–	–	Field, Maryland, USA
Hsieh and Davis (2005)[a]	5	15	–	–	Field, Maryland, USA
Hsieh et al. (2007)[a]	14.7	−15.8	–	–	Laboratory
Hunt et al. (2006)	−600	40	−545	−312	Field, North Carolina, USA
Hunt et al. (2008)	70.6	−4.9	44.4	32.1	Field, North Carolina, USA
Kim et al. (2003)	–	8	−25	–	Laboratory
Line and Hunt (2009)	−3	28	−257	42	Field, North Carolina, USA
Lucas and Greenway (2008)	–	−13.3	–	23.0	Field mesocosms, Queensland, Australia
Lucas and Greenway (2008)	–	45.3	–	54.5	Field mesocosms, Queensland, Australia
Read et al. (2008)	−327	5.1	–	−114	Greenhouse
Read et al. (2008)	−318	79.5	–	−65.7	Greenhouse
Median	21.2	8.0	44.4	25.0	
Mean	−49.6	−61.2	−38.9	−30.7	
Maximum	92.6	84.6	66.0	58.4	
Minimum	−600	−650	−545	−312	

[a] Equation used for calculating percent removal not reported.

To address this problem, Kim et al. (2003) proposed the engineering bioretention systems to include a saturated zone, where the media would remain anoxic in order encourage denitrification (illustrated in Figure 1.9). Since denitrification is a reduction reaction, for the reaction to occur there must be a source of electrons. In this initial paper, Kim et al. demonstrated this by mixing a variety of possible electron donors into sand columns with saturated zones. All columns with electron sources performed better than the control column of pure sand at nitrate removal, with the best performing ingredient being shredded newspapers, which achieved 100%, nitrate removal compared to 10% from the control. Using this information a pilot-scale bioretention system using sand and shredded newspaper was built with a saturated zone, and was found to have 70-80% mass removal efficiency of nitrate/nitrite.

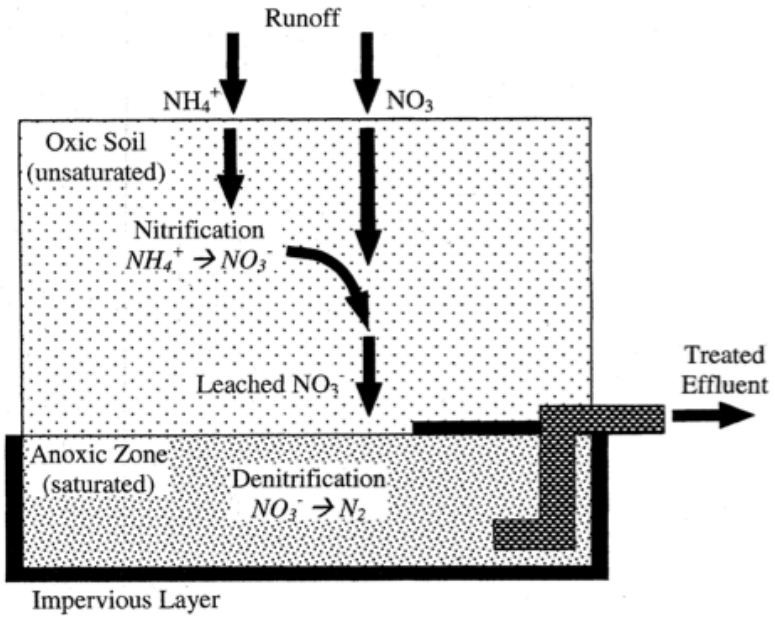

Figure 1.9. Illustration of the N processes that occur in a bioretention cell modified to include a saturated zone. Taken from Kim et al. (2003).

Since this paper, many studies have tested saturated zones in bioretention systems and found them effective at nitrate/nitrite removal - a summary of studies on bioretention systems with saturated zones before 2010 can be found in Table 1.4 below. By comparing removal rates in conventional bioretention systems (table 1.3) with removal rates in systems containing saturated zones (table 1.4), it is clear that saturation improves nitrate/nitrite removal. The median removal rate without saturation is 8.0%, compared to the median with saturation at 43.2%. For instance, Lucas and Greenway (2011) compared bioretention columns with and without saturated zones created by regulated outlets, and found that nitrate removal increased 2.7 times and total N removal increased 2.2 times with the creation of saturated zones.

Still, saturated zones may not be the whole solution – several studies included in table 1.4 still exported nitrate/nitrite even with saturated zones. Li and Davis (2014) found that saturated zones improved total N and nitrate/nitrite concentrations in effluent from their

column study, but they still saw export of nitrate/nitrite with saturated zones, so recommend that saturated zones be used in conjunction with other controls on N leaching for maximum effectiveness.

Table 1.4. N removal rates based on concentration in studies of bioretention systems modified to improve N removal. Taken from Collins et al. (2010).

Study	NH_3–N	$NO_{3,2}$–N	TKN	TN	Study location
Alcala et al. (2009)	–	84.5	–	–	Laboratory
Bratieres et al. (2008)	−158	−101	–	–	Greenhouse
Cho et al. (2009)	41.5	−40.8	–	–	Laboratory
Davis (2007)	79.2	–	–	–	Field, Maryland, USA
Dietz and Clausen (2006)	–	77.8	33.3	62.5	Field, Connecticut, USA
Hatt et al. (2009)	25.0	65.0	–	−18.2	Field, Victoria, Australia
Hsieh et al. (2007)[a]	68.3	−46.3	–	–	Laboratory
Hunt et al. (2006)	−1080	17.6	60.0	−224	Field, North Carolina, USA
Kim et al. (2003)[a]	–	78.7	−725	–	Laboratory
Kim et al. (2003)	–	91.0	–	–	Laboratory
Passeport et al. (2009)	77.9	21.4	54.1	54.2	Field, North Carolina, USA
Smith and Hunt (2006)	79.1	43.2	65.3	60.9	Field, North Carolina, USA
Smith (2008)	–	–	98.1	–	Laboratory
Smith (2008)	–	–	29.5	–	Laboratory
Median	54.9	43.2	46.7	54.2	
Mean	−108.4	26.5	−73.1	−12.9	
Maximum	79.2	91.0	98.1	62.5	
Minimum	−1080	−101	−725	−224	

[a] Equation used for calculating percent removal not reported.

A field test of two bioretention sites in Connecticut was performed by Dietz and Clausen (2006) to compare the performance of the systems before and after retrofitting for a saturated zone. Nitrate levels in effluent were very low before the creation of saturated zones and remained similarly low after the fact; total N concentrations, however, decreased by 18% in effluent with the installation of saturated zones. Another field monitoring test in North Carolina found less evidence for the effectiveness of saturated zones. Hunt et al. (2006) looked at three bioretention systems with sandy BSM, two of which were in the same parking lot. One of those had an engineered saturated zone of 1.5-2 feet. They found no significant difference in nitrate removal when comparing the saturated system to the non-saturated system nearby. Both, however, removed nitrate at a high rate (75% by mass, with removal by concentration as well but no specified number). It is possible that the system without an engineered saturated zone

actually had natural anaerobic zones within due to the high organic matter content. This theory is supported by the third system, which had lower organic matter content and no saturated zone, and removed only 13% of nitrate by mass. Other research confirms that denitrification can occur in small anaerobic pockets within soil micropores, especially where there is high organic matter (Kremen et al. 2005; Gold et al. 1998).

Denitrification without an engineered saturated zone was also witnessed by Hsieh et al. (2007) in a greenhouse column experiment. The experiment was set up to compare the hydraulic and pollutant removal effectiveness of bioretention systems with a low conductivity layer of sandy loam soil over a high conductivity layer of sand, and vice versa. These configurations removed 12% and 68% of ammonium, respectively, but exported nitrate at 109% and 154% (with large variation) respectively. It is hypothesized that these differences in N removal may be due to the hydraulic relationship between low and high permeability media creating an anoxic zone in the low permeability media when it is at the bottom, and thus allowing nitrification to occur in the aerobic top layer and then denitrification to occur in the anaerobic bottom. This implies that it may be possible to tweak the BSM itself to create saturated zones without changing the structure of the system.

Yang et al. (2010) attempted to create this coupled nitrification and denitrification with a further engineered “biphasic” system, which consisted of a saturated sand column emptying into an aerobic sand column before draining. All columns had BSM consisting of 60% sand, 20% topsoil, and 20% compost. When comparing this biphasic design to conventional bioretention columns with no saturated zone, a significant difference in nitrate removal was found. With influent nitrate at 5 mg/L, biphasic systems removed 60% of nitrate, compared to 37% removal

in the conventional systems. When influent N was 50 mg/L, removal rates were reduced nearly by half, but the same difference between the two systems was evident. This experiment also explored the importance of carbon as an electron donor for denitrification by adjusting the C/N ratio of soils in the biphasic systems with glucose. The result was a clear positive relationship between soil C/N ratio and nitrate removal efficiency (see Figure 1.10), which would be expected considering the mechanism of denitrification.

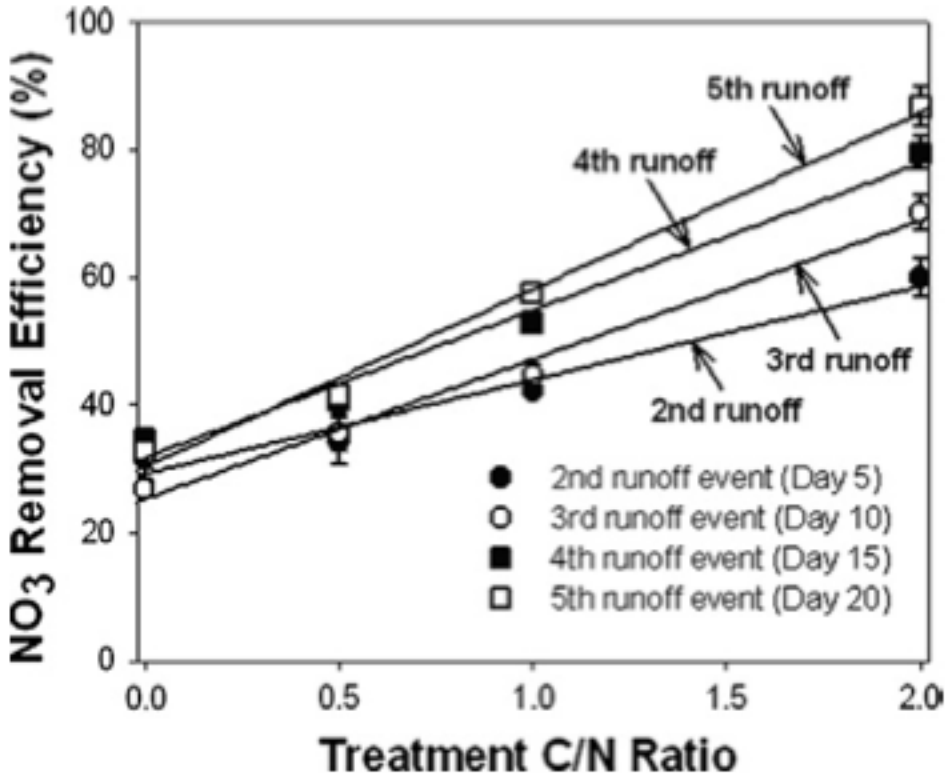

Figure 1.10. Relationship between soil C/N ratio and nitrate removal efficiency in "biphasic" bioretention systems with a saturated zone, as found in Yang et al. (2010).

Interestingly, several recent studies have considered the importance of denitrification in saturated zones alongside N uptake by plants. Zinger et al. (2013) set up a column study to investigate whether systems could be effectively retrofit with saturated zones after functioning

without them. They planted sandy loam columns with three different plant species, analyzed their effectiveness at removing nutrients from stormwater, and then created saturated zones in the same columns and compared performance. The creation of saturated zones was found to increase nitrate/nitrite removal rates for columns planted with two of the species by 370% and 180% respectively; however, columns planted with *C. appressa* saw no improvement with saturated zones because they were already removing nitrate at high rates. These results are echoed by a larger study performed by Payne et al. (2014) comparing columns planted with 20 different plant species as well as columns with and without saturated zones. This study similarly found that although saturated zones did improve total N and nitrate removal in some columns, the improvement in N removal due to different plant species was more important than the improvement due to saturated zones. These studies make it clear that plants are a crucial factor for pollutant removal in bioretention systems.

Plant uptake

Despite their importance, many bioretention experiments performed in the lab neglect to incorporate plants into the systems being studied. Plants take up nitrate, ammonium, phosphate, and other pollutants such as Cu and Zn in trace amounts. Plants also take up water, reducing effluent volume and associated contaminants. Plant uptake of N varies with plant species and climate, as well as with season (Greenway and Lucas 2010; Read et al. 2008). Most N is taken up by plants in spring and summer, peaking in late summer and stopping in autumn. Plants actually return N to the soil in autumn and winter as they senesce (Kadlec and Wallace, 2009). Because of this cycle, N taken up by plants is not considered to be removed from the system, unless the plants are harvested. When plants are harvested annually, this has the

added benefit of increasing their N uptake (Tuncsiper et al., 2006). Furthermore, plants preferentially take up nitrate and nitrite, the main N species of concern, due to microbial competition for ammonium (Lucas and Greenway 2011c; Dell and Rice 2005; Recous et al. 1992). Plants also encourage robust microbial populations in soils, which in turn can speed up the microbial processes like denitrification that help remove contaminants (Muerdter et al. 2015; Brady and Weil 2010). Lucas and Greenway (2011c) demonstrated the importance of plant uptake to N removal in their study of vegetated bioretention mesocosms: They demonstrated 10-30% improvement in N retention during summer versus winter, and the pattern of retention over time matched their projections for plant uptake over time, indicating that plants were the main sink of N in their systems.

In a greenhouse study of compost/sand BSMs with and without vegetation, Palmer et al. (2013) found a mixed influence of vegetation: the columns with vegetation had nitrate removal up to 19% better than barren columns on some collection dates, but were not significantly different on others. They attribute this to the fact that their plants were newly established (7 weeks old) and thus plant uptake was too slow of a process to have a significant impact on nitrate uptake; they project that vegetation with a more established rhizosphere would have a greater effect.

Bratieres et al. (2008) also found that vegetation had a mixed influence on nutrient leaching. In their large-scale greenhouse study involving 125 columns, they compared columns planted with five different species, as well as non-vegetated columns, for contaminant removal. They allowed vegetation to establish for seven months in their bioretention columns before

sampling effluent. Even with established plants, all but two of the planted treatments exported total N and nitrate. Columns planted with *Carex appressa* or *Melaleuca ericifolia*, however, removed total N at respective rates of 71 and 46%, and removed nitrate at respective rates of 96 and 52%. Removal rates in columns with these plants also significantly improved over time. All of the other plant columns exported N along with the non-vegetated column, and showed increasing export over time. While all columns removed total P at rates above 76%, columns planted with *C. appressa* had significantly higher total P removal than the other treatments. This plant likely performed best due to its particularly dense root structure with high numbers of microscopic root hairs, increasing the surface area able to take up nutrients. This indicates that not only length of establishment, but also species of plant is important to adequate nutrient retention. A comparison of 20 different plant species for their removal of nutrients and heavy metals in bioretention columns was done by Read et al. (2009), and *C. appressa* was found to be one of the most effective here as well.

Compost

Although compost is included in many recommended mixtures for BSMs, the amount of research done on the performance of compost in bioretention systems is limited. Several studies have shown that compost is effective at removing metals, but exports nutrients to varying degrees (Palmer et al. 2013; Bratieres et al. 2008; Hatt et al. 2008; Hatt et al. 2007; Seelsaen et al. 2007). Two of the studies discussed above in the section on metals demonstrated BSMs with compost removing metals at rates above 80% (Wenjun et al. 2013; Sun and Davis 2007). Further evidence of metals removal is in McIntyre et al. (2015), the study of juvenile salmon viability in bioretention- treated stormwater. This study showed no elevated

levels of metals and 100% survival in fish exposed to stormwater treated by bioretention systems that contained 15% compost.

These results are reflected in Hatt et al. (2008), which compared six different BSM treatments which included sandy loam mixed with 10% compost and 10% mulch, sandy loam with 20% compost and 20% mulch, unamended sandy loam, and unamended sand. Before leaching, columns were flushed with 15 months' worth of stormwater over 17 weeks in an effort to stabilize the BSMs. Nevertheless, the compost treatments exported nutrients in large quantities, adding 400+% total P, 100+% total N, and 100+% manganese (Mn) to effluent (calculated in terms of mass loading). The compost treatments performed well, however, in removing metals with 93, 97, 96, and 92% removal of Cu, Pb, Zn, and TSS respectively. This study also considered the hydraulics of their columns, and noted that the compost treatments clogged at the surface, with 64-68% reduction in hydraulic conductivity from pre-trial to post-. They see this as an advantage of compost and other fine-grained media, however, since a clog at the surface is easy to scrape off and replace. Coarse-grained media such as sand has the tendency to clog at the base of the system as fines accumulate at the bottom, and this type of clog is more difficult to rectify (Siriwardene et al. 2007). The authors recommend that in bioretention systems containing compost, the top few inches should be removed and replaced every 2 years to maintain hydraulic conductivity. They also suggest that the presence of vegetation would likely prevent the surface clogging problem altogether.

Not all studies agree that BSMs containing compost export nutrients. Yang et al. (2010) investigated an alternative "biphasic" bioretention design that involved one saturated column flowing into one unsaturated column. This study was discussed above in the context of

saturated zones for nitrate removal, but is relevant here as the BSM in all columns contained 20% compost by volume. Even with this proportion of compost, all columns achieved 89-100% removal of total P, and 37-60% removal of nitrate. This contrasts with other trials, which have shown that BSMs containing compost export nutrients. Hsieh and Davis (2005) also show BSMs containing compost which remove total P and nitrate: one of their treatment which was 11% compost by weight removed 54% of total P, and 27% of nitrate.

Many column studies are done with barren soil, and it is assumed that vegetation of any sort will decrease nutrient export. This did not prove true in a large-scale greenhouse experiment involving 125 bioretention columns by Bratieres et al. (2008). Among other things, three BSMs were compared: sandy loam, sandy loam with 10% compost and 10% mulch, and sandy loam with 10% vermiculite and 10% perlite, all with vegetation that had been allowed to establish for 7 months. The compost BSM was the only one of the three that exported total N (only 1% higher than influent concentration), nitrate (58% higher than influent concentration), and dissolved P (78% higher than influent, but with a standard deviation greater than 100). All three BSMs removed total P, but compost had the lowest removal rate at 38% compared to 91 and 95% removal in the other two.

Another vegetated study done by Palmer et al. (2013) analyzed pollutant removal by BSMs which closely reflect the City of Seattle guidelines: 15% food/yard waste compost, 10% water treatment residuals, and 15% shredded bark by volume. This study found nitrate removal of 33-71% depending on column design, and phosphate removal of 67-80%. Despite removal of the dissolved forms of N and P, the columns exported total N. This study also saw mixed effects of vegetation, as discussed above.

The above studies compare BSMs with compost to those without, but even fewer studies have attempted to make comparisons between different composts, despite the fact that composts can vary widely in composition. Charlesworth et al. (2013) set up 2-liter bottles as bioretention columns to compare the oil/grease and metals (Cd, Zn, Pb, Cu and Ni) removal of yard waste compost, food/yard waste compost, and topsoil (texture not specified). The results of this study showed effluent from all treatments had concentrations of Cr, Zn, Ni and Cd at below detection limits; both composts performed better than the topsoil at removing oil and grease, but the food/yard waste compost performed worse than the other two with respect to Cu and Pb. Influent levels of metals were below detection, however, and remained low even in food/yard waste column effluent – Cu peaked at 0.1 mg/L, and Pb at 0.05 mg/L. Charlesworth et al. also assessed the media for oil degrading bacteria and fungi, and found that food/yard waste compost had the most in total, followed by yard compost and then topsoil.

Three food/yard composts were compared in Paus et al. (2014). Columns containing 10%, 30%, or 50% food/yard waste compost by volume, layered with sand, were analyzed for Cu, Zn, and Cd, and P release. They found that the higher the compost volume fraction for all three compost types, the more efficient the Cd and Zn removal. Cu was filtered out to below detection levels by all mixtures, but more P was exported as the compost volume fraction increased. However, mixtures with only 10% compost exported the same amount of P as pure sand did. Hydraulic conductivity also decreased with greater compost proportion, which would be expected as compost is a finer media than sand. Three different food/yard waste composts were tested here, and it was found in separate batch sorption tests that sorption varied between the three. Two of the composts tested had similar or higher metal sorption capacities

than activated bauxsol-coated sand, fly ash, GAC, iron oxide-coated sand, zeolites, spinel, olivine I, limestone, and shell sand. Returning to the column tests, it was found that the 50% compost mixture had a predicted lifetime of 41-84 years, compared to 1-3 years for pure sand. "Lifetime" here indicates the time before 10% breakthrough of Zn or Cd. This study indicates that compost can be a great advantage for long-term metals removal, and also that different composts vary in their sorption capacities. The authors conclude by recommending a two-layer bioretention system, with a top layer of compost to remove metals and a bottom layer of oxide-coated sand to remove P.

Brown et al. (2016), in Phase I of this study, analyzed columns containing food/yard waste compost, manure/sawdust compost, and biosolids/yard waste compost with varying amounts of Al-WTRs added. With no WTR added, it was found that the three compost types exported similar levels of dissolved and total P (23-25 mg/L), with the exception of food/yard waste compost, which exported significantly more total P (28 mg/L). The three composts also performed similarly with regards to nitrate and ammonium leaching, with average effluent concentrations of 6.3-10.9 mg/L and 0.9-3.0 mg/L for nitrate and ammonium, respectively. The three compost types removed copper and zinc at different rates (biosolids compost removed less Cu than the other two), but all were efficient with removal of dissolved Cu and dissolved Zn above 90% for all treatments. Columns containing all three composts were brought to PSI of 0.1 by added Al-WTRs, and these columns had average effluent P concentrations below 1 mg/L. Concentrations of effluent P decreased over time, with reductions in of 35% by event 4 and 80% by event 9 seen in 0.1 PSI columns. These results agree with Palmers et al. (2013) that a proper combination of compost and Al-WTR in BSMs can lead to substantial P removal. Though

N leaching concentrations in this experiment are high, this may be due in part to the fact that NH_4HPO_3 salts were added to some columns to elevated their PSI.

Conclusion

With their aesthetic qualities and the impressive contaminant removal capabilities shown in many of the studies mentioned in this review, it is no wonder that bioretention systems are an increasingly important best management practice. Much information can be extrapolated from the bioretention articles reviewed here, but there are noticeable gaps. Most articles compare selected BSMs but fail to develop relationships or tools that can predict efficacy in BSMs that were not directly studied. Focus has been placed on the performance of general BSM components (compost, WTR, sand, topsoil), but there can be wide variation within these categories in terms of particle size, OM content, and nutrient and metals concentrations, and thus the predictive capacity of this general parameter is limited. For bioretention systems to reliably succeed in a wide variety of circumstances, more research is needed to develop models for predicting performance.

Understanding the Effect of Compost Rates and Types in Bioretention Soil Media

Introduction

Compost is included in most recommended mixtures for bioretention soil media (BSMs), however the amount of research done on the performance of compost in bioretention systems is limited (SWMMWW 2014; Carpenter 2010). Several studies have shown that compost is effective at removing metals, but exports nutrients to varying degrees (Palmer et al. 2013; Bratieres et al. 2008; Hatt et al. 2008; Hatt et al. 2007; Seelsaen et al. 2007). Two recent studies demonstrated BSMs with compost removing metals at rates above 80% (Wenjun et al. 2013; Sun and Davis 2007). Further evidence of metals removal is in McIntyre et al. (2015), the study of juvenile salmon viability in bioretention- treated stormwater. This study showed no elevated levels of metals and 100% survival in fish exposed to stormwater treated by bioretention systems that contained 15% compost by volume.

The results of the above salmon study are reflected in Hatt et al. (2008), which compared six different non-vegetated BSM treatments that included sandy loam mixed with (by volume) 10% compost (feedstock not specified) and 10% mulch, sandy loam with 20% compost and 20% mulch, unamended sandy loam, and unamended sand. Before leaching, columns were flushed with 15 months' worth of stormwater over 17 weeks in an effort to stabilize the BSMs. Nevertheless, the compost treatments exported nutrients in large quantities, adding 400+% total P, 100+% total N, and 100+% manganese (Mn) to effluent (calculated in terms of mass loading). The compost treatments performed well, however, in removing metals with 93, 97, 96, and 92% removal of Cu, Pb, Zn, and TSS respectively.

Not all studies have found that BSMs containing compost export nutrients. Yang et al. (2010) investigated an alternative "biphasic" bioretention design that involved one saturated column flowing into one unsaturated column. The BSM in all columns in this study contained 20% compost by volume. All columns achieved 89-100% removal of total P, and 37-60% removal of nitrate. This contrasts with other trials, both in the field and in lab environments, which have shown that BSMs containing compost export nutrients. Hsieh and Davis (2005) also show BSMs containing compost which remove total P and nitrate: one of their treatments, which was 11% compost by weight, removed 54% of total P, and 27% of nitrate.

Compost types

The above studies compare BSMs with compost to those without, but even fewer studies have attempted to make comparisons between different composts, despite the fact that composts can vary widely in composition. Charlesworth et al. (2013) set up 2-liter bottles as bioretention columns to compare the oil/grease and metals (Cd, Zn, Pb, Cu and Ni) removal of yard waste compost, food/yard waste compost, and topsoil (texture not specified). The results of this study showed effluent from all treatments had concentrations of Cr, Zn, Ni and Cd at below detection limits. Both composts performed better than the topsoil at removing oil and grease. However, the food/yard waste compost performed worse than the other two with respect to Cu and Pb. Influent levels of metals were below detection, but in food/yard waste column effluent, Cu peaked at 0.1 mg/L, and Pb at 0.05 mg/L. Charlesworth et al. also assessed the media for oil degrading bacteria and fungi, and found that food/yard waste compost had the most in total, followed by yard compost and then topsoil.

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Brown et al. (2016) analyzed columns containing food/yard waste compost, manure/sawdust compost, and biosolids/yard waste compost with varying amounts of Fe-WTRs added. With no WTR added, it was found that the three compost types exported similar levels of dissolved and total P (23-25 mg/L), with the exception of food/yard waste compost, which exported significantly more total P (28 mg/L). The three composts also performed similarly with

regards to nitrate and ammonium leaching, with average effluent concentrations of 6.3-10.9 mg/L and 0.9-3.0 mg/L for nitrate and ammonium, respectively. The three compost types removed copper and zinc at different rates (the biosolids/yard waste compost removed less Cu than the other two), but all were efficient with removal of dissolved Cu and dissolved Zn above 90% for all treatments. Columns containing all three composts were brought to PSI of 0.1 by added Fe-WTRs, and these columns had average effluent P concentrations below 1 mg/L. Concentrations of effluent P decreased over time, with reductions of 35% by event 4 and 80% by event 9 for all composts in the 0.1 PSI columns. These results confirm the findings of Palmer et al. (2013) by showing that a proper combination of compost and Al-WTR in BSMs can lead to substantial P removal. Though N leaching concentrations in Brown et al. (2016) were high, this may be due in part to the fact that NH_4HPO_3 salts were added to some columns to elevated their PSI.

Vegetation

Once installed, all bioretention systems include actively growing plants. Plants enhance the appearance of these systems and can also affect their efficacy. Plants take up nitrate, ammonium, phosphate, and other pollutants such as Cu and Zn in trace amounts. Plants also take up water, reducing effluent volume and associated contaminants. Plant uptake of N varies with plant species and climate, as well as with season (Greenway and Lucas, 2010; Read et al. 2008). Most N is taken up by plants in spring and summer, peaking in late summer and stopping in autumn. Plants actually return N to the soil in autumn and winter as they senesce (Kadlec and Wallace, 2009). Because of this cycle, N taken up by plants is not considered to be removed

from the system, unless the plants are harvested. When plants are harvested annually, this has the added benefit of increasing their N uptake (Tunçsiper et al., 2006). Furthermore, plants preferentially take up nitrate and nitrite, the main N species of concern, due to microbial competition for ammonium (Lucas and Greenway 2011c; Dell and Rice 2005; Recous et al. 1992). Plants, along with soil organic matter, also encourage robust microbial populations in soils, which in turn can speed up the microbial processes like denitrification that help remove contaminants (Muerdter et al. 2015; Brady and Weil 2010). Lucas and Greenway (2011c) demonstrated the importance of plant uptake to N removal in their study of vegetated bioretention mesocosms: They demonstrated 10-30% improvement in N retention during summer versus winter, and the pattern of retention over time matched their projections for plant uptake over time, indicating that plants were the main sink of N in their systems.

Despite their importance, many bioretention experiments performed in the lab do not incorporate plants into the systems being studied. In a greenhouse study of compost/sand BSMs with and without vegetation, Palmer et al. (2013) found a mixed influence of vegetation: the columns with vegetation had nitrate removal up to 19% higher than barren columns on some collection dates, but were not significantly different on others. They attributed this to the fact that their plants were newly established (7 weeks old) and thus plant uptake was too slow of a process to have a significant impact on nitrate uptake; they projected that vegetation with a more established rhizosphere would have had a greater effect.

Bratieres et al. (2008) also found that vegetation had a mixed influence on nutrient leaching. In their large-scale greenhouse study involving 125 columns, they compared columns

planted with five different species, as well as non-vegetated columns, for contaminant removal. They allowed vegetation to establish for seven months in their bioretention columns before sampling effluent. Even with established plants, all but two of the planted treatments exported total N and nitrate. Columns planted with *Carex appressa* or *Melaleuca ericifolia*, however, removed total N at respective rates of 71 and 46%, and removed nitrate at respective rates of 96 and 52%. Removal rates in columns with these plants also significantly improved over time. N was exported from all other vegetated columns, although at lower rates than N export from the non-vegetated column – the exception being the column planted with *Leucophyta brownii*, which exported more N than the non-vegetated column. While all columns removed total P at rates above 76%, columns planted with *C. appressa* had significantly higher total P removal than the other treatments. This plant likely performed best due to its particularly dense root structure with high numbers of microscopic root hairs, increasing the surface area able to take up nutrients. This indicates that not only length of establishment, but also species of plant is important to nutrient retention. A comparison of 20 different plant species for their removal of nutrients and heavy metals in bioretention columns was done by Read et al. (2009), and *C. appressa* was found to be one of the most effective here as well.

This study was conducted to examine the impact of bioretention soil compost content on characteristics of effluent. The impact of compost feedstock, compost proportion, and active plant growth were evaluated. The study looked at heavy metals (Cu, Zn, and Pb), nutrients (N and P), and total suspended solids in effluent to determine BSM efficacy.

Methods

BSM preparation

Columns measuring 9.5 cm in diameter and 45.75 cm in height were set up in a randomized complete block design with four replicates of each treatment. This study focused on four BSM treatments, which are described below in Table 2.1. The columns had 2 cm holes in the center of the base for leachate collection, which were covered with mesh to prevent loss of soil media and fitted with plastic tubes to direct flow into collection buckets. The insides of the columns were sanded with coarse sandpaper to prevent preferential flow of water along the sides. To ensure even packing of BSM, each column was filled to the top then dropped three times from 5 cm above the work surface. Columns were then refilled to the top and tamped down with a 1kg weight dropped from 5cm above the column three times. Columns were kept in a controlled environment greenhouse at the University of Washington.

The four treatments are have the following components: 20% biosolids/yard compost/80% sand (C20), 40% food/yard waste compost/60% sand (C40-FY), 40% biosolids/yard compost/60% sand (C40-B), and 80% biosolids/yard compost/20% sand (C80). These percentages represent volume proportions, but since both volume and mass proportions are used in bioretention depending on region and convention, both measures are shown in Table 2.1 below. It should be noted that volume and dry weight proportions can be very different and do not necessarily change at the same rate – for instance, doubling the volume proportion of compost from 40 to 80% corresponds to more than quadrupling the dry weight proportion of compost from 9 to 38%. Treatment C40-FY is the standard BSM used in King County, WA region and was used as a control (City of Seattle 2011).

Table 2.1. Description of experimental column media.

	Components	Volume (%)	Dry Weight (%)
C40-FY	Food/Yard Waste Compost	40	9
	Sand	60	91
C40-B	Biosolids/Yard Compost	40	9
	Sand	60	91
C80	Biosolids/Yard Compost	80	38
	Sand	20	62
C20	Biosolids/Yard Compost	20	4
	Sand	80	96

Sand for the study was a silica sand with d_{60} of 0.4 mm, and was obtained from a commercial landscape materials supplier where it had been stored outdoors (Sawdust Supply 2016). The yard/food compost used in C40-FY was produced from yard waste and food scraps by a Seattle area composter and is the compost that is most commonly used in bioretention system treatments in the Seattle area. The biosolids/yard compost was provided by Sawdust Supply, Inc.; it was produced from King County biosolids and yard waste.

Prior to column packing, aliquots of each BSM were taken for preliminary soil analysis. Samples were dried at room temperature. Soil pH was measured at a 2:1 volume ratio of DI water to dry soil. Total C and N were analyzed by combustion using a Perkin Elmer CHN analyzer model 2400. Phosphorous Saturation Index (PSI) of each BSM was determined by analyzing for P, Fe and Al using a 6:1 ratio of 0.2 M acid oxalate solution to soil, followed by agitation for four hours, filtration using #40 Whatman paper, 1:4 dilution with 0.01 M HCl, and analysis using a Thermo Scientific Co. inductively coupled plasma mass spectrometer (ICP-MS) Model 6300 (modified from McKeague and Day 1966 as described in Sparks 1996). BSMs were also analyzed for total Cd, Cr, Cu, Pb, P and Zn using the aqua regia extraction method and the ICP-MS

(McGrath and Cunliffe, 1982). BSMs were also assessed for Mehlich-III extractable Al, Ca, Cd, Cr, Cu, Fe, Mg, P, Pb, and Zn using 2 g soil: 20 mL Mehlich-III solution, followed by agitation for 5 minutes, filtration using #40 Whatman paper and analysis using the ICP-MS (Mehlich 1984). Duplicate, blanks and known standards were routinely used in all analyses.

Leaching events

Storm events were simulated by pouring stormwater into columns at predetermined volumes. Water was allowed to pool at the top of the columns to simulate bioretention conditions in the field. Storm events represented 24 hour storms in Seattle, WA with return frequencies of either 0.2 years for a rainfall depth of 0.9 inches (900 mL per column) or one year for a rainfall depth of 1.8 inches (1600 mL per column) (City of Seattle 2016). Water volumes were calculated to reflect a bioretention system that was designed to collect 90% of the runoff from an impervious catchment of which the bioretention surface represents 6.5% of the area. Leachate was collected through the tubes at the bottoms of the columns during each event and for four hours after.

The first 4 leaching events were done with synthetic stormwater spiked with high concentrations of metals and typical concentrations of nutrients. The synthetic stormwater (high metal) was made by diluting concentrated solutions of $CuSO_4$, $(CH_3CO_2)_2Zn{\bullet}2H_2O$, $NH_4H_2PO_4$, $CdCl_2$, $CrCl_3{\bullet}6H_2O$, and $(CH_3COO)_2Pb{\bullet}3H_2O$ into tap water at predetermined quantities. The subsequent or 5^{th} leaching was done with tap water to assure that there was no carry over of metals. The 6^{th} -8^{th} leaching's were carried out with a synthetic stormwater that had lower concentrations of metal contaminants more typical of real-world stormwater, made

with the same chemicals described above (Maestre and Pitt 2005). The remaining leachings (9-12) were carried out using actual stormwater collected as runoff from a major Seattle highway bridge and stored in plastic carboys at 3°C for no longer than seven days. Rye grass was planted in the columns after leaching event 12 and allowed to mature, after which the final two leachings, 13a and 13b, were conducted on select treatments. Leaching 13a was performed on all four treatments presented here and was done with synthetic stormwater that was spiked only with $NH_4H_2PO_4$, as the main interest of this event was in the effect of plant growth on nutrient leaching. Of the four treatments of interest in this chapter, only C40-FY was included in event 13b, as a point of comparison for other treatments that will be discussed in later chapters. A schedule of the leachings is shown below (Table 2.2), followed by a description of the metals and nutrient concentrations in each type of stormwater (Table 2.3). Columns were kept moist with tap water until the first leaching and were also kept moist in between leaching events to avoid the complicating effects of drying and wetting seen in previous studies (Mullane et al. 2015; Li and Davis 2014; Hsieh et al. 2007).

Table 2.2. Schedule of water type and volume used for each leaching.

Event	Date	WA Return Interval	Stormwater Type
		yrs	
1	5/12/14	0.2	High metal synthetic
2	5/27/14	1	High metal synthetic
3	6/9/14	0.2	High metal synthetic
4	7/7/14	1	High metal synthetic
5	7/21/14	0.2	Tap
6	8/4/14	1	Low metal synthetic
7	8/18/14	0.2	Low metal synthetic
8	9/22/14	1	Low metal synthetic

9	11/4/14	0.2	Actual
10	12/2/14	0.2	Actual
11	1/20/15	1	Actual
12	1/27/15	1	Actual
		Grass planted	
13a	6/8/15	0.2	Synthetic (nutrients only)
13b	7/3/15	0.2	Tap

Table 2.3. Concentration of metal and nutrient contaminants in all water types.

			Tap water	High metal synthetic	Low metal synthetic	Actual stormwater*
P	Dissolved	mg/L	<MDL	0.52 ± 0.28	0.60 ± 0.84	0.04 ± 0.01
	Total		0.04 ± 0.02	1.49 ± 0.22	2.01 ± 0.08	0.08 ± 0.03
NO_3^-	Dissolved		0.04 ± 0.02	0.07 ± 0.01	0.05 ± 0.01	0.40 ± 0.32
NH_4^+	Dissolved		0.007 ± 0.001	0.79 ± 0.09	1.13 ± 0.10	0.57 ± 0.40
TN	Total		0.12 ± 0.01	0.95 ± 0.10	1.08 ± 0.04	1.79 ± 0.97
Cd	Dissolved	µg/L	13.2 ± 12.6	3792 ± 1283	124 ± 187	4.08 ± 2.67
	Total		13.5 ± 12.9	3864 ± 1317	436 ± 16	5.97 ± 4.37
Cr	Dissolved		0.31 ± 0.04	27.0 ± 40.1	0.53 ± 0.24	3.12 ± 1.30
	Total		0.32 ± 0.05	1267 ± 193	400 ± 111	6.90 ± 3.07
Cu	Dissolved		21.7 ± 2.4	211 ± 173	5.78 ± 7.49	18.25 ± 5.76
	Total		25.4 ± 3.0	2882 ± 1243	525 ± 132	39.8 ± 19.1
Pb	Dissolved		10.4 ± 4.9	93.8 ± 48.1	4.39 ± 6.29	1.91 ± 1.64
	Total		12.4 ± 5.4	7827 ± 1698	781 ± 197	20.83 ± 2.89
Zn	Dissolved		116 ± 5.5	2772 ± 482	40.1 ± 58.7	113 ± 90.8
	Total		113 ± 4.2	3503 ± 498	950 ± 178	172 ± 87
Turbidity		BTU	0.41 ± 0.06	18.5 ± 8.4	2.67 ± 1.63	28.4 ± 11.3

*Actual stormwater has a high standard deviation for all values due to variations between stormwater collected on different days. **Event 13a had metal concentrations matching those presented for tap water. Nutrient concentrations for this event were (in mg/L) TN: 3.81 ± 0.02, NO_3^-: <MDL, NH_4^+: 36 ± 0.06, TP: 9.04 ± 0.14.

Leachate volume was recorded and then the leachate was divided into aliquots for different analyses and delivered to the King County Environmental Lab for analysis of total and dissolved Cd, Cr, Cu, Pb, Zn, P and N. Leachate samples for determination of dissolved metals and P were prepared using EPA Method 200.8, while total metals and P were analyzed using

EPA Method 200.7, and all were run with a Thermo X-series II ICPMS with Collision Cell Technology (Brockhoff et al., 1994). Samples were analyzed for total N (TN), NO_3-N, and NH_4-N using SM4500-NO3F NO3, SM4500-N-C, and the procedure described in Keruoel and Aminot (1997), respectively. Finally, one aliquot per column was measured on-site for turbidity using a Hatch 2100b turbidity meter.

Infiltration Rate and Vegetation

The infiltration rate of each column was measured three times using the single-ring falling head procedure: at the beginning of the trial before any leachings occurred, after the 12^{th} leaching before grass was planted, and after all leachings were completed. Each column was wetted with 500 mL of tap water and allowed to drain. An additional 500 mL was then added, and the time required to infiltrate the soil was measured.

After the 12^{th} leaching event, 0.8 grams of rye grass seed was planted in each column based on a seeding rate of 420 kg ha-1 (Oregon Ryegrass Commission 2013). Grass was allowed to grow for 4 weeks, at which point the grass was harvested to 2 cm above the soil. Biomass was rinsed and dried in a drying oven at 105°C, weighed to determine dry yield, and then ground into a fine powder using a mortar and pestle. This powder was analyzed for total C and N content by combustion using a Perkin Elmer CHN analyzer model 2400.

The grass was allowed to regrow for two months after this harvest, at which time the 13^{th} leaching was performed. The leachate from events 13a and 13b was analyzed only for total N, P, and NO_3^-, to gain an understanding of the impact of growing grass on the mobility of these

nutrients. Grass was harvested a second time following these leachings and measured for yield as described above.

Final soil analysis

The soil media were extracted from their columns. Grass roots were separated out by hand and the BSM from each column was homogenized, after which an aliquot was separated from each column and allowed to dry at room temperature for 5 days. The air-dried soil was sieved to 2 mm. Soil pH was measured at a 2:1 volume ratio of DI water to dry soil. PSI, total C and N, and Mehlich-III extractable Al, Ca, Cd, Cr, Cu, Fe, Mg, P, Pb, and Zn were analyzed as described above. Duplicate, blanks and known standards were routinely used in all analyses.

Data analysis

Results were normalized by either log transformation or 1/sqrt(x) transformations to minimize skewness and kurtosis. Data were then analyzed in R using one- and two-way ANOVAs and the Tukey HSD post-hoc test for multiple means comparison, using an alpha of 0.05. Linear and logarithmic regression models were run and analyzed for R^2, p-value and mean squared error.

Results and Discussion

Phosphorus Saturation Index (PSI)

The ammonium oxalate extractable P in the different mixtures increased as the portion of compost in the mixtures increased. The increases followed the change in compost content on

a dry weight basis. This was expected since sand has negligible P. The differences in extractable P also help to emphasize the differences in mix characteristics when dry weight rather than volume is used. For example, C80 has twice the volume portion of compost as C40, but it has slightly over 4 times the weight portion of compost (Table 2.1). This is due to the high bulk density of sand – when the volume portion of compost is increased, the volume portion of sand decreases and thus the overall dry weight of the soil mixture decreases. The decreased overall dry weight combined with the higher volume proportion of compost result in the greater increase in compost dry weight proportion. Thus the ammonium oxalate extraction data in Table 2.4 confirm expectations, as C80 P concentration is close to 4 times higher than C40-B P, which is twice C20 P. Though C40-FY and C40-B have the same proportion of compost, the compost type is different, so C40-FY's lower PSI value in Table 2.4 is also in line with expectations.

The phosphorus saturation index (PSI), which is the molar ratio of P/(Fe+Al), should not vary greatly between BSMs with different proportions of the same type of compost, since it is a ratio of elements mainly found in compost. However, the table below shows P content increasing with compost portion as described above, but Al and Fe content do not increase proportionally to the compost increase and thus PSI is higher for BSMs with higher proportions of compost (i.e., higher P content). This pattern indicates that the sand component of the BSM contained enough Al and Fe to lower the PSI when compost proportion (and thus P content) was low.

Table 2.4. Pre-trial Ammonium Oxalate-extracted P, Al, Fe, and PSI (P/(Fe+Al).

P	Al	Fe	PSI

		mmol/kg		
C20	6.8 ± 0.4	5.0 ± 0.1	11.0 ± 0.3	0.43 ± 0.02
C40-FY	10.0 ± 0.3	12.6 ± 0.5	21.0 ± 1.4	0.30 ± 0.03
C40-B	15.4 ± 0.9	7.8 ± 0.1	15.0 ± 0.1	0.68 ± 0.03
C80	89.1 ± 1.1	23.0 ± 0.3	47.7 ± 0.3	1.26 ± 0.02

The PSI was also measured on BSM mixtures at the end of the study (Table 2.5). There were notable changes in soil PSI between the beginning and end of the trial, although no change had been expected. The PSI of C20, C40-FY, C40-B, and C80 decreased significantly by the end of the trial. A similar decrease in PSI was seen in Brown et al., 2016, but the mechanism is not clear.

The observed changes in the PSI can be seen in Figure 2.1 and understood in terms of the individual components of the ratio. For both the C20 and C40-B treatments, extractable P decreased and Al and Fe showed slight increases between the initial measure and the completion of the trial. Phosphorus in the high compost treatment (C80) decreased, as did Al and Fe. However, loss of P was more pronounced than the decrease in Al and Fe. Finally C40-FY lost soil P but saw little change in Al or Fe. The loss of soil P corresponds with the finding that these four treatments were all sources of P for the majority of the experiment – this will be discussed in a later section. The slight gain in Al and Fe seen in C20 and C40-B may be explained by changes in speciation making soil Al and Fe more available to extraction.

Table 2.5. Post-trial Ammonium Oxalate-extracted P, Al, Fe, and PSI (P/(Fe+Al).

	P	**Al**	**Fe**	**PSI**
		mmol/kg		
C20	4.8 ± 0.3	9.3 ± 0.6	21.0 ± 3.9	0.16 ± 0.02
C40-FY	4.4 ± 0.3	11.8 ± 0.4	23.8 ± 2.2	0.13 ± 0.01

C40-B	8.0 ± 0.8	10.9 ± 0.8	23.2 ± 2.7	0.23 ± 0.01
C80	29.5 ± 2.1	17.3 ± 1.4	32.0 ± 1.8	0.60 ± 0.03

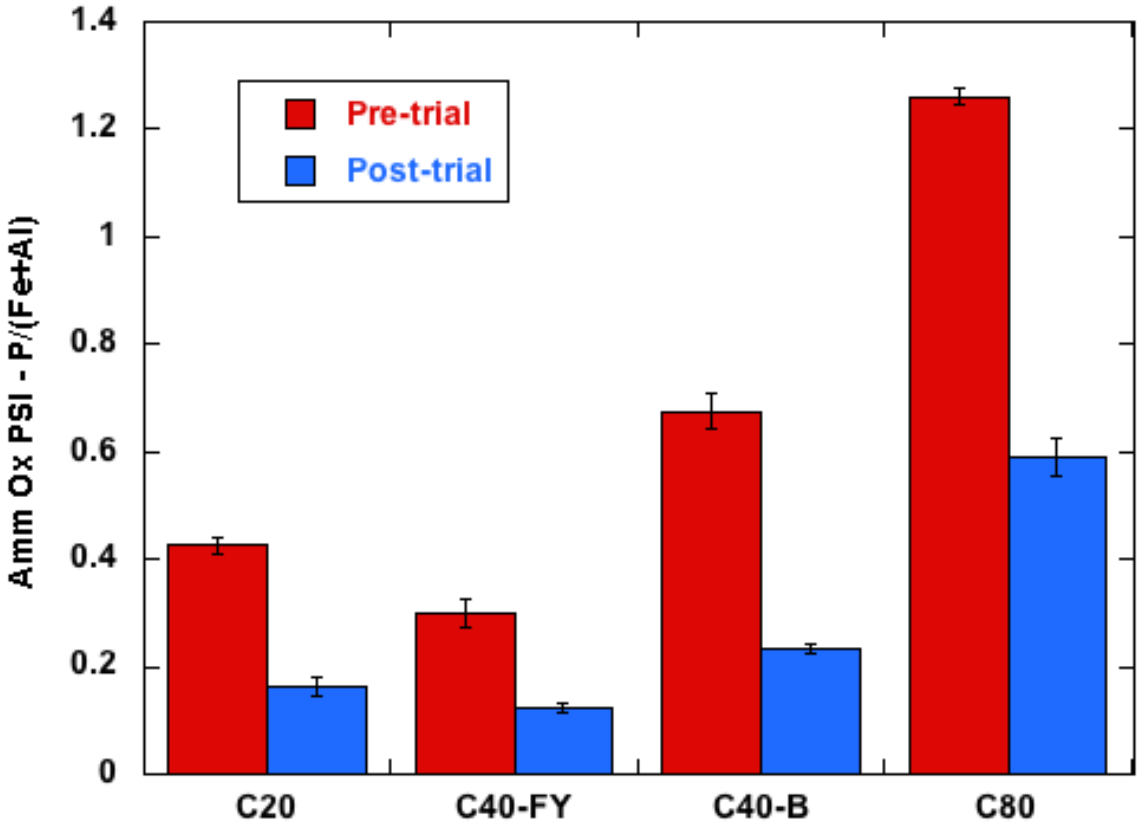


Figure 2.1. Pre- and post-trial ammonium oxalate PSI for C20, C40-FY, C40-B, and C80. Error bars represent +/- one standard deviation.

Total Metals

The total Cu, Pb, Zn, and P content of pre-trial treatments C20, C40-FY, C40-B, C80, and sand are shown below in Table 2.6. As with P above, the Cu, Pb and Zn content increase with compost proportion. Values for sand are included to indicate which portion of total metals in each mixture is due to compost. Although the values for C80 appear unexpectedly high, this is due to the large difference in compost weight proportion that goes along with doubling the compost volume proportion. Keeping weight proportions in mind, the C20, C40, and C80 values are as expected.

Table 2.6. Total Cu, Pb, Zn, and P content of treatments, from aqua regia extraction.

	Total Solids	Cu	Pb	Zn	P
	%	mg/kg			
C20	99.9	14.4	2.1	33.5	576
C40-FY	99.6	14.1	6.3	39.1	706
C40-B	99.7	17.1	3.0	40.6	766
C80	99.3	56.7	12.5	134	3250
Sand	99.9	10.6	1.4	25.6	330

Carbon to Nitrogen Ratio

As with P content, C and N would also be expected to increase with the weight proportion of compost. The C/N ratios of the BSMs in this experiment were all below the maximum for C/N ratio of compost in the western Washington BSM regulations (SWMMWW 2014). Since sand does not have a significant amount of C or N, it was expected that the C/N ratio would be consistent for BSMs containing different proportions of the same compost. Indeed, C20, C40-B, and C80, which all contained biosolids compost, had pre-trial C/N ratios close to 20, while C40-FY with food/yard waste compost had a lower ratio of 15 (Table 2.7). However, the pre-trial C and N content (which were expected to increase with weight portion of compost) is much higher than expected in C80. Since its C/N ratio is similar to C40-B and C20, and since its P content and metals content met expectations (metals are discussed below), it may be that these heightened levels of C and N are due to variations within the compost, or measurement error.

C/N ratios of C20, C40-B, and C40-FY fell over the course of the experiment, while that of C80 stayed constant. These differences in C/N ratio are due to very small changes to C and N

content, which cannot be distinguished from measurement errors and differences between replicates.

Table 2.7. C, N, and C/N ratio of BSMs before and after trial.

	Pre-trial			Post-trial		
	%C	%N	C/N	%C	%N	C/N
C20	0.57 ± 0.03	0.03 ± 0.00	21.85 ± 2.62	0.80 ± 0.21	0.07 ± 0.01	11.02 ± 1.68
C40-FY	3.02 ± 0.24	0.20 ± 0.02	15.16 ± 0.39	2.33 ± 0.40	0.20 ± 0.03	11.84 ± 0.36
C40-B	1.24 ± 0.04	0.07 ± 0.01	17.78 ± 0.97	1.28 ± 0.58	0.11 ± 0.04	11.76 ± 1.27
C80	13.04 ± 2.74	0.67 ± 0.11	19.26 ± 0.76	7.29 ± 0.74	0.39 ± 0.06	18.80 ± 0.80

pH

The pre- and post-trial pH for all of the treatments is shown in Table 2.8. All pre-trial pH values were within western Washington BSM guidelines (which require a pH between 5.5 and 7.0) with the exception of C80, which was too acidic. The C40-FY was more basic than the treatments that contained biosolids compost. The pH of the mixtures remained consistent through the study period for the C20 and C40-FY mixes. The C40-B and C80-B mixtures became less acidic during the trial with each showing an increase of approximately 0.5 in pH value.

Table 2.8. Value of pH of BSMs before and after trial.

Treatments	pH pre-trial	pH post-trial
C20	6.02	6.15
C40-FY	6.68	6.46
C40-B	5.83	6.34
C80	5.17	5.71

BSM performance: Infiltration rate

All treatments had infiltration rates well above the minimum of 1 in./hr in the western Washington guidelines (Figure 2.2). Measured rates were variable across replicates. The Infiltration rate increased from C20 to C40-B, and increased even more greatly from C40-B to C80. These results contrast with the findings of Paus et al. (2014) and Hsieh and Davis (2005), which show that increasing compost proportion caused a decrease in infiltration rate. These authors explained slower infiltrations rates with higher quantities of compost by suggesting that a finer media such as compost would slow infiltration.

One possible explanation for this divergence could be that infiltration rate was measured near the end of the trial (after event 12, before grass was planted) rather than the beginning. Anecdotally, it was observed that infiltration rates increased over the course of the trial, and it is possible that preferential flow paths formed. This would reflect a study by Carpenter et al. (2010), in which preferential flow paths were found to be the cause of high infiltration rates in a functioning bioretention cell with BSM containing 80% compost. Preferential flow was also posited by Hsieh and Davis (2005) in a column study.

An alternative explanation may be simply that the biosolids compost used in this trial had a larger average particle size than the composts used in the trials mentioned above, and thus larger pores which would allow for faster infiltration. The particle size distribution of the compost in this study was not measured.

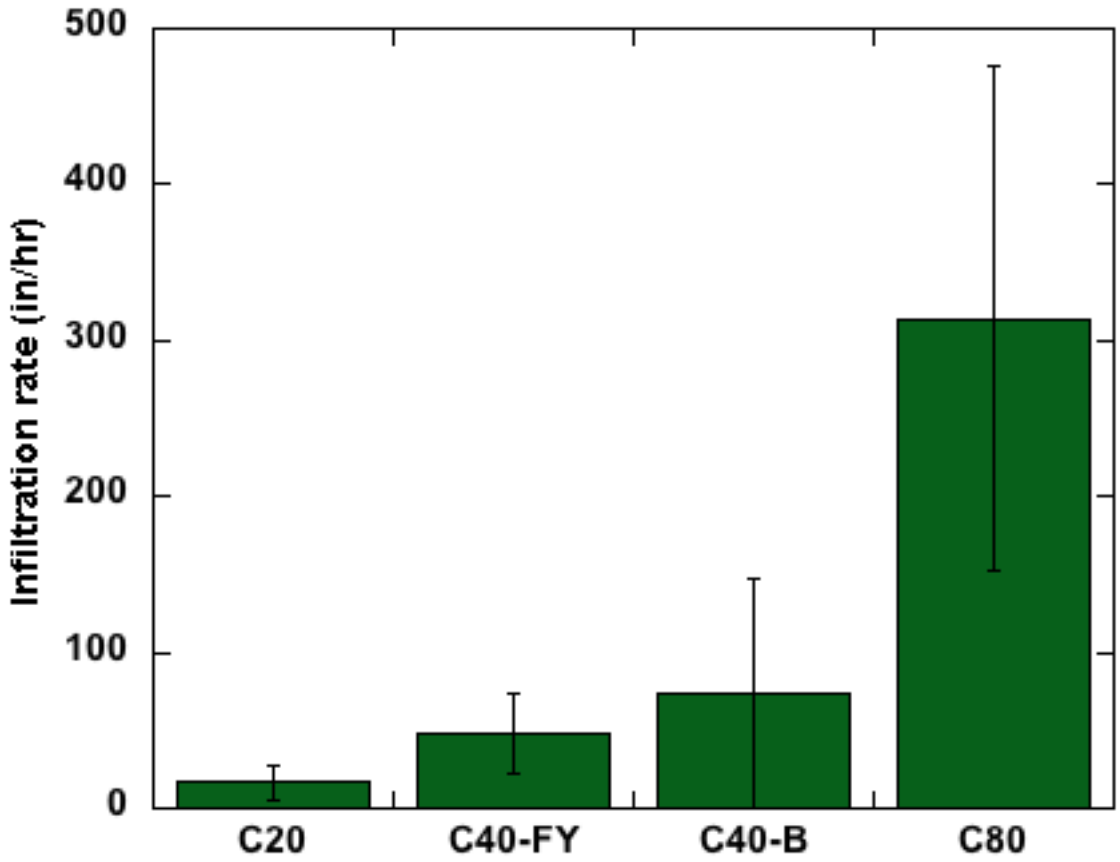


Figure 2.2. Average infiltration rate of columns, measured with the single-ring falling head procedure after event 12 (before grass was planted).

BSM Performance: Metals and TSS removal

The effect of increasing compost portion and the effect of different compost types on metals removal will be discussed below. Results for Cu, Pb, and Zn removal will be shown first, followed by a brief discussion.

Copper

Four types of influent stormwater were used throughout this experiment, each with a different concentration of metals. High metal synthetic stormwater was used for events 1-4, tap water was used in event 5, low metals synthetic stormwater was used for events 6-8, and

actual stormwater collected from a highway bridge was used for events 9-12 (see schedule of influent waters in Table 2.3 above). Total Cu concentrations in these influent types were as follows: 2882 ± 1243 µg/L in high metal synthetic, 525 ± 132 µg/L in low metal synthetic, 40 ± 19 µg/L in actual stormwater, and 25 ± 3 µg/L in tap. Dissolved concentrations were an order of magnitude lower in the synthetic influent waters, and about half the total concentration in actual stormwater - see Table 2.9 below for dissolved concentrations.

Table 2.9. Effluent concentration in µg/L from C20, C40-FY, C40-B, and C80, averaged over events with the same stormwater type. Influent concentrations are missing for event 1, so are not included in the average for high metal synthetic influent.

	High metal synthetic water		Low metal synthetic water		Actual stormwater	
	Cu dissolved	**Cu total**	**Cu dissolved**	**Cu total**	**Cu dissolved**	**Cu total**
	µg/L		µg/L		µg/L	
Influent	*211.4 ± 173.4*	*2882 ± 1243*	*5.8 ± 7.5*	*525.1 ± 131.7*	*18.3 ± 5.8*	*39.8 ± 19.1*
C20	29.7 ± 7.5	55.7 ± 13.6	17.3 ± 3.5	22.6 ± 3.5	17.6 ± 8.4	21.2 ± 8.8
C40-FY	29.1 ± 2.5	128.5 ± 35.7	17.8 ± 2.9	36.0 ± 9.1	9.8 ± 1.3	12.9 ± 2.2
C40-B	33.0 ± 6.7	44.5 ± 8.4	27.3 ± 6.4	30.0 ± 7.1	28.9 ± 8.3	31.9 ± 9.7
C80	316.6 ± 117.2	517.1 ± 145.8	117.6 ± 23.9	140.7 ± 20.0	30.3 ± 6.4	37.7 ± 8.0

The variables of water type and time covary, so it is difficult to separate their effects. A two-way ANOVA with water type and treatment as the independent variables and total Cu concentration (transformed for normality) as the dependent show that treatment, water type, and the water type/treatment interaction are significant with $p<0.000$. The basis for this interaction is visible in Figures 2.3 and 2.4. These figures show effluent Cu concentration from C80 (Figure 2.3) and C40-FY (Figure 2.4) changing noticeably with each shift in water type, while effluent Cu from C20 and C40-B remains relatively constant throughout. Due to the significance of the interaction, patterns and relationships with respect to effluent Cu

concentrations will be discussed separately for events with different influent water types. Tap water will not be included since it was used only in event 5 to flush out any excess metals that had built up from the high influent concentrations of the first four events.

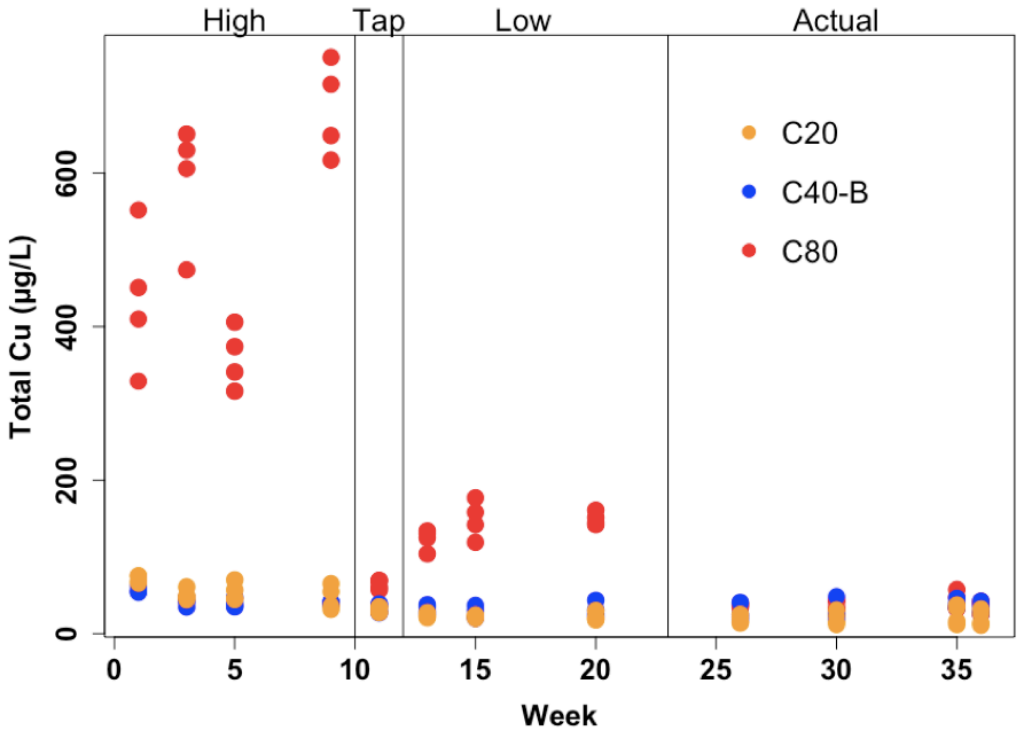


Figure 2.3. Effluent concentrations of total Cu from C20, C40-B, and C80 from each of the first 12 storm events. Vertical lines indicate divisions between water types.

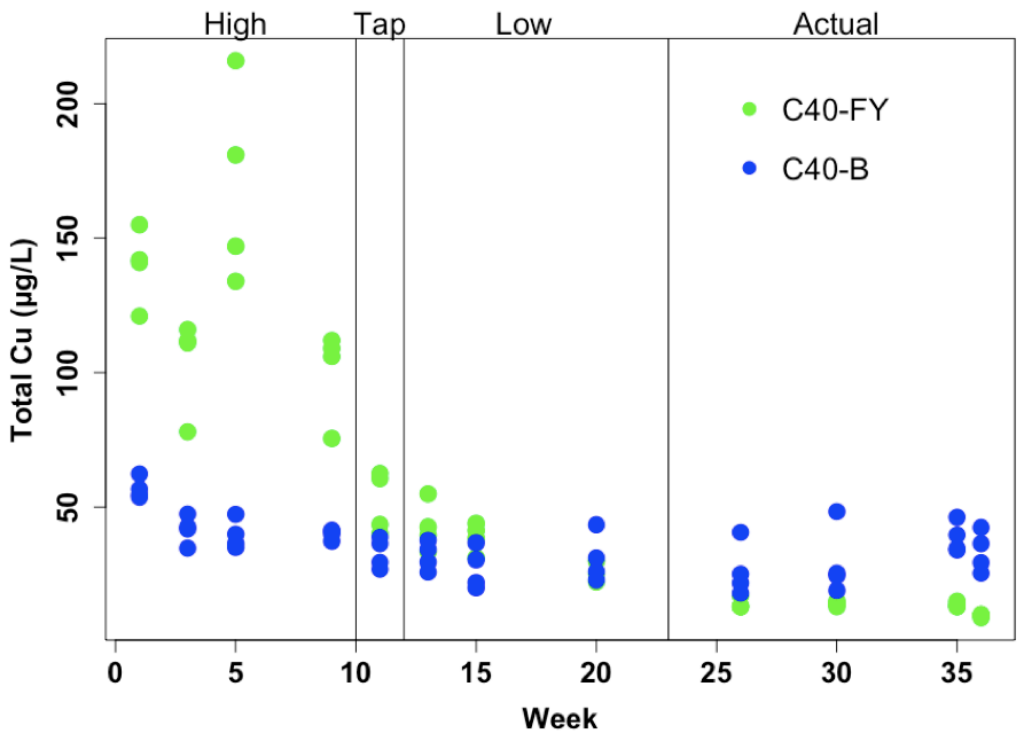


Figure 2.4. Effluent concentrations of total Cu from C40-FY and C40-B from each of the first 12 storm events. Vertical lines indicate divisions between water types.

For events 1-4, which used high metal synthetic stormwater, an ANOVA with time and treatment as independent variables shows that time, treatment, and time/treatment interaction are significant with $p<0.000$, $p<0.004$, and $p<0.007$ respectively. The effect of increasing compost portions is visualized in the high metal stormwater portion of Figure 2.3 - C80 has high effluent Cu compared to C20 and C40-B. C20 and C40-B have low effluent Cu during these events, comparable to their concentrations from the other water types (see Table 2.9). The effect of compost type is visualized in Figure 2.4, which shows C40-FY releasing more Cu than C40-B for these high metal events and showing more variability between events. Even with these high influent Cu concentrations, all four treatments act as a sink for Cu.

For events 6-8, which used low metal synthetic stormwater, an ANOVA with time and treatment as independent variables shows that only treatment and time/treatment interaction

are significant, with $p<0.000$ and $p<0.021$ respectively. Once again, the significance of the interaction appears to come from C80, which increases slightly over the three events while C20, C40-FY and C40-B all remain relatively constant with C40-FY decreasing slightly. Here, the effect of compost type appears negligible, with C40-FY and C40-B largely overlapping (see Table 2.9 for average values). Increasing compost portions from 20% to 40% also has negligible effects, but the increase from 40% to 80% more than triples the average Cu effluent concentration.

For events 9-12, which used actual stormwater, an ANOVA with time and treatment as independent variables shows that only BSM treatment is significant, with $p<0.000$. A Tukey HSD post-hoc test indicates that average effluent concentrations of total Cu from C80 was similar to C40-B, but both were statistically higher than that from C20. The differences here are small – doubling the compost volume from 20% to 40% resulted in an average increase of only 11 µg/L of Cu in effluent per event. Finally, Cu effluent concentration from C40-FY is statistically lower than all of the biosolids compost treatments regardless of portion, but again the difference is minimal. Looking at the performance of the three biosolids compost treatments overall, it can be extrapolated that a higher proportion of compost in a BSM makes it less robust to high influent concentrations of Cu, but has a minimal effect on Cu removal under normal circumstances. When considering the effect of compost type, food/yard waste compost removed Cu more effectively from actual stormwater than biosolids compost, but was less robust than the same proportion of biosolids compost to higher influent Cu concentrations.

Despite the variability of C80 and lower removal efficiency for the higher metal waters, all four treatments currently being discussed were sinks for Cu from all influent water types. However, change in concentration from influent to effluent does not take into account one of

the most important functions of a BSM – water volume reduction. Some portion of influent water is retained in BSMs, resulting in a lower volume of effluent than influent. Therefore, if contaminant mass were neither removed nor added by a BSM, there would still be an increase in the contaminant's concentration in effluent water, since the volume of effluent water would be lower than the volume of influent water. Most regulations for contaminant levels in water are concentration-based, but reduction of total mass of a contaminant is still useful to consider.

An overall picture can be seen in Table 2.10 and Figure 2.5, which show influent and effluent mass numbers for the entire trial. These mass numbers are calculated for each replicate by multiplying the effluent concentration of the contaminant by the volume of effluent for each event, and then summing these values over all 14 events, as follows: *total mass = Σ(event n concentration)*(event n volume).* The final values are averages and standard deviations of these mass numbers for all four replicates in a treatment. The same equation is used for influent mass numbers, but using influent concentration and volume and averaging the totals from each of 3 samples taken from influent water per event. These numbers show a mass removal rate of total Cu of over 97%, 95%, 97%, and 81% for C20, C40-FY, C40-B and C80 respectively. A Tukey HSD post hoc test shows that C20 and C40-B had similar mass removal effects, C40-FY was less effective, and C80 was the least effective overall. This is a simple way to compare the overall effect of the different BSMs, but it should be understood in the context of the interactions with time and water type described above.

Table 2.10. Total mass of Cu, Pb, and Zn in effluent through all leaching events(µg). Values are averages and standard deviations of mass numbers for all four replicates in a treatment. Shared letters indicate statistically similar means.

	Cu	**Pb**	**Zn**

		Mg					
Influent			*16727 ± 828*		*41498 ± 2742*		*22282 ± 1335*
C20		a	427 ± 41	a	3317 ± 250	a	441 ± 48
C40-FY	Total	b	762 ± 75	a	4790 ± 531	a	629 ± 87
C40-B		a	481 ± 50	a	4394 ± 456	a	505 ± 91
C80		c	3084 ± 224	b	13549 ± 1732	b	2454 ± 259
Influent			*998 ± 180*		*448 ± 79*		*12263 ± 1155*
C20		a	278 ± 44	a	391 ± 53	a	163 ± 26
C40-FY	Dissolved	a	257 ± 9	b	885 ± 148	a	241 ± 60
C40-B		b	408 ± 44	b	1148 ± 198	b	313 ± 64
C80		c	2050 ± 369	c	3267 ± 1086	c	1497 ± 125

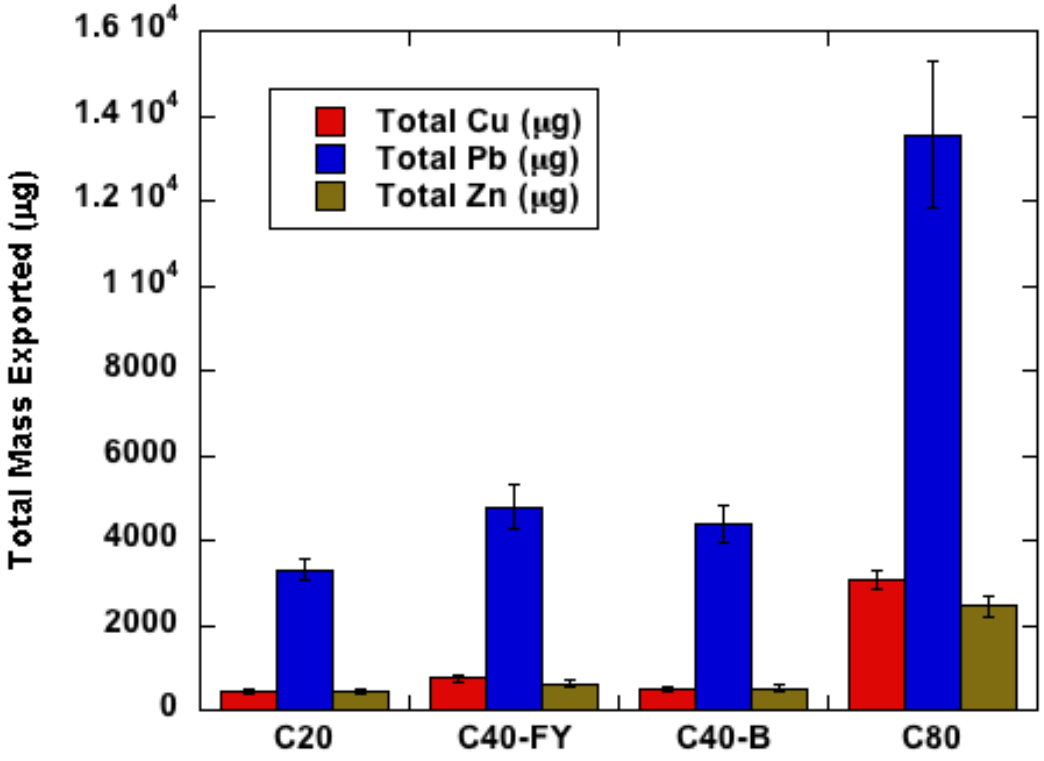


Figure 2.5. Mass export of total Cu, Pb, and Zn over entire trial expressed in µg. For reference, total mass of Cu, Zn, and Pb in influent water was 16727, 22282, and 41498 µg.

So far only total Cu has been discussed, but dissolved Cu was also measured and is shown in Tables 2.9 and 2.10 alongside total figures. A review of the mass dissolved Cu in effluent as well as the effluent concentrations of dissolved Cu over time shows that it followed

the same patterns over time and upheld similar relationships described for total Cu for treatments with increasing compost portions. This is underlined by Figure 2.6, which shows total and dissolved Cu concentrations in effluent over time from the four treatments under focus. The relationship between the compost types is flipped for dissolved Cu – C40-FY releases around half as much dissolved Cu as C40-B by mass, and in fact is statistically similar to C20. Food/yard waste compost released more total Cu than biosolids compost in the same portions, so release of total suspended solids may play a role in this difference and will be explored in a later section.

It is important to note that although similar patterns are followed, the removal rate of dissolved Cu is much lower than it is for total Cu, and in fact C80 acts as a net source of dissolved Cu despite removing 81% of total Cu. Since similar performance is seen with Pb and Zn as well, possible reasons for this will be discussed at the end of the metals section.

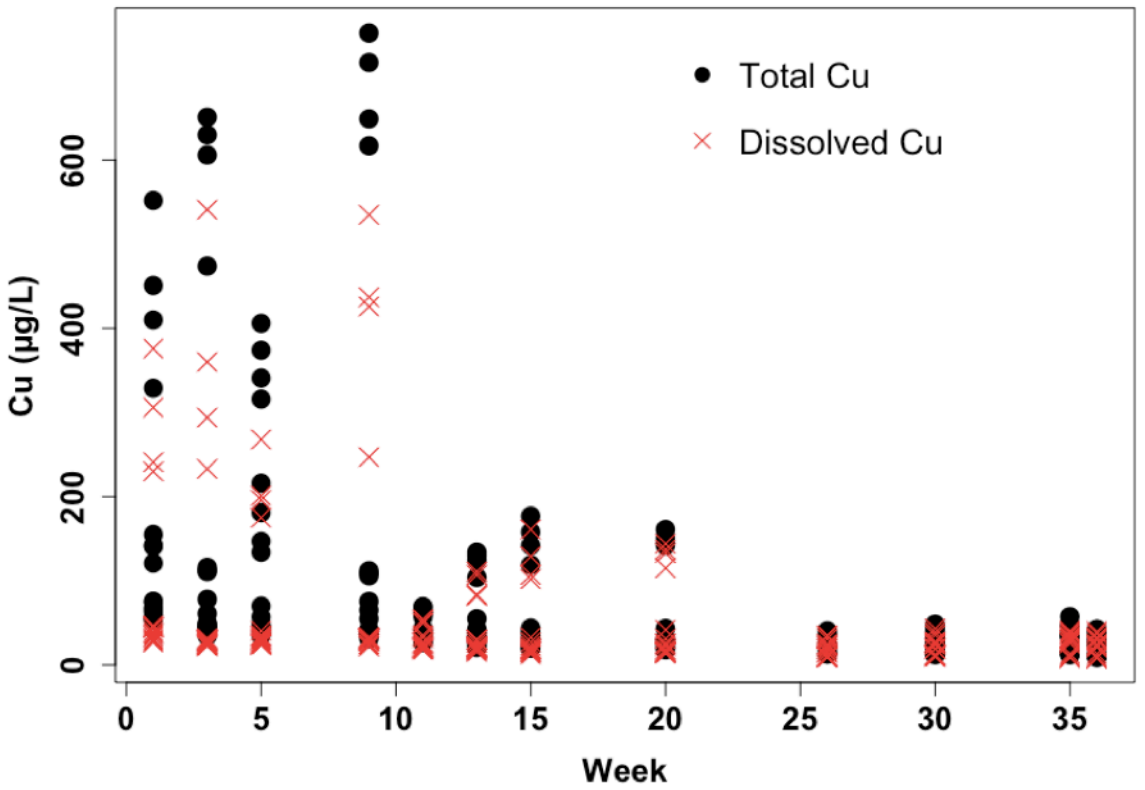


Figure 2.6. Effluent concentrations of total and dissolved Cu from C20, C40-FY, C40-B, and C80 from each of the first 12 storm events.

Lead

As above, influent water type is a significant factor for Pb removal. Pb concentrations in influent were as follows: 7827 ± 1699 µg/L in high metal synthetic water, 781 ± 197 µg/L in low metal synthetic water, and 21 ± 3 µg/L in actual stormwater. Dissolved concentrations were 1-2 orders of magnitude lower than total concentrations, and can be seen in Table 2.11 below. A two-way ANOVA with water type and treatment as the independent variables and total Pb concentration as the dependent show that treatment, water type, and the water type/treatment interaction are significant with $p<0.000$. This interaction is visible in Figures 2.7 and 2.8. In these figures, effluent Pb concentration from C20, C40-FY, C40-B, and C80 all are

high and with high variability during the initial 4 events with the high metal synthetic influent, but quickly lower to a stable and low concentration for the remainder of the water types. As with Cu above, Pb concentrations will be discussed separately for events with different influent water types.

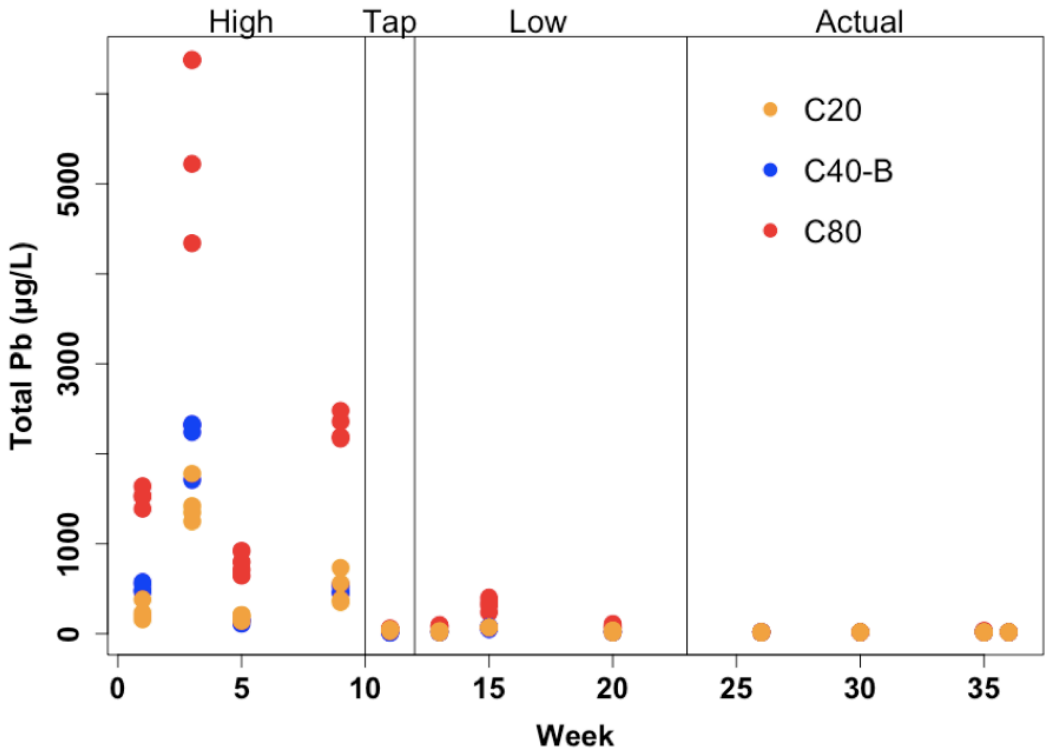


Figure 2.7. Effluent concentrations of total Pb from C20, C40-B, and C80 from each of the first 12 storm events. Vertical lines indicate divisions between water types.

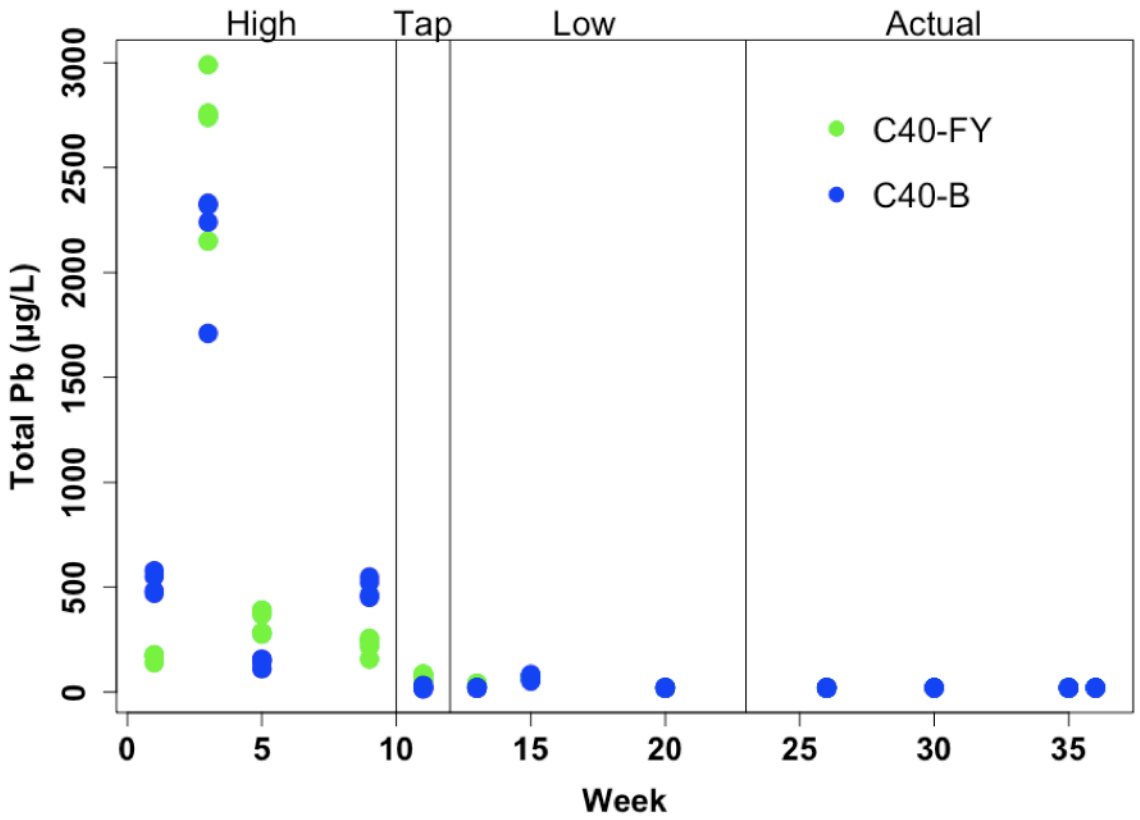


Figure 2.8. Effluent concentrations of total Pb from C40-FY and C40-B from each of the first 12 storm events. Vertical lines indicate divisions between water types.

For events 1-4, which used high metal synthetic stormwater, an ANOVA with time and treatment as independent variables shows that only treatment is significant, with $p<0.000$. The effect of increasing compost portions is visualized in the high metal stormwater portion of Figure 2.7 - C80 has high effluent Pb compared to C20 and C40-B for all events. All three appear to spike in events 2 and 4, but time was not a significant factor perhaps due to the high variability between replicates. The effect of compost type is shown in Figure 2.8, which shows C40-FY and C40-B with similar values. A Tukey HSD post-hoc test shows that all of these treatments have statistically similar values with the exception of C80, which has higher effluent Pb concentrations than the rest. Nevertheless, all treatments are a sink for total Pb (see Table 2.11).

Table 2.11. Effluent concentration of Pb in µg/L from C20, C40-FY, C40-B, and C80, averaged over events with the same stormwater type. Influent concentrations are missing for event 1, so are not included in the average for high metal synthetic influent.

	High metal stormwater		Low metal synthetic water		Actual stormwater	
	Pb dissolved	**Pb total**	**Pb dissolved**	**Pb total**	**Pb dissolved**	**Pb total**
	µg/L		µg/L		µg/L	
Influent	*93.8 ± 48.2*	*7827 ± 1699*	*4.4 ± 6.3*	*780.8 ± 197.2*	*1.9 ± 1.6*	*20.8 ± 2.9*
C20	66.7 ± 53.7	597.1 ± 541.5	13.2 ± 13.6	41.4 ± 23.9	1.7 ± 0.5	<MDL
C40-FY	153.8 ± 198.7	843.8 ± 1097.0	12.2 ± 7.7	40.8 ± 22.9	2.5 ± 0.9	<MDL
C40-B	209.9 ± 201.8	826.9 ± 815.5	13.5 ± 16.8	36.2 ± 25.3	0.9 ± 0.3	<MDL
C80	585.4 ± 504.3	2543 ± 1947	70.8 ± 68.6	164.0 ± 125.8	1.6 ± 0.4	21.1 ± 4.3

For events that used low metal synthetic influent, both treatment and time are significant factors, with $p<0.000$ and $p<0.044$. The significance of time likely results from the bump in Pb from C80 in week 15 in Figure 2.7. A post-hoc Tukey HSD test gives similar results– all treatments are similar with the exception of C80, which is higher. Interestingly, for events using actual stormwater, none of the factors were significant. In fact, effluent concentrations of Pb were below detection limit for all treatments but C80. Influent concentrations for this water type were so low that C80 was a source of Pb in these events, but was still statistically similar to the other treatments, which were below the detection limit.

Pb follows the same pattern as Cu – C80 was less robust to high influent concentrations of Pb, but performed similarly to C20 and C40-B when actual stormwater was used as the influent. These differences are shown in the mass data in Table 2.10 and Figure 2.5 above, where C80 is again the only statistically distinct treatment of the four. C20, C40-FY, C40-B, and C80 had Pb mass removal rates of over 92%, 88%, 89%, and 67% respectively.

Finally, dissolved Pb followed similar patterns over time as total Pb, as shown in Figure 2.9 below. Like with Cu, removal rates were much lower for dissolved Pb than for total, and in fact all treatments except C20 were overall sources of dissolved Pb. However, since influent concentrations of dissolved Pb were so low, the majority of Pb movement is associated with particulates. This is expected, as Pb is highly insoluble in soils.

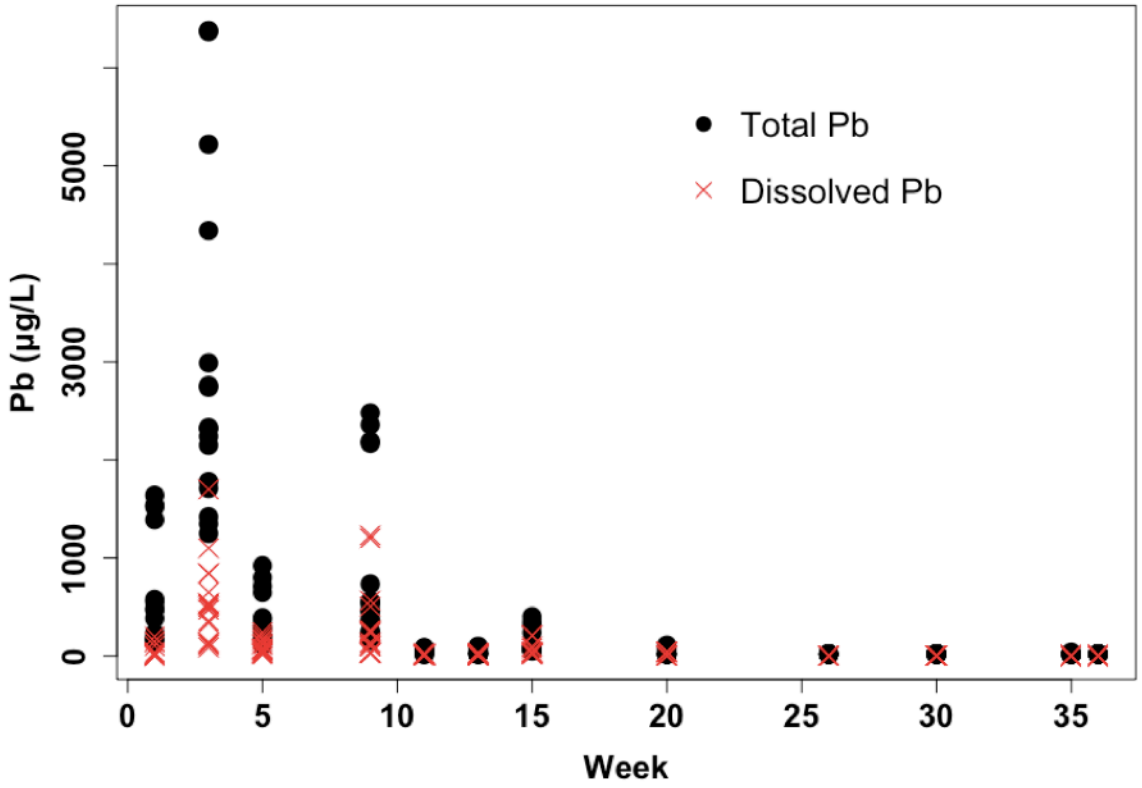


Figure 2.9. Effluent concentrations of total and dissolved Cu from C20, C40-FY, C40-B, and C80 from each of the first 12 storm events.

Zinc

Zn concentrations in influent were as follows: 3503 ± 498 µg/L in high metal synthetic water, 950 ± 178 µg/L in low metal synthetic water, and 172 ± 87 µg/L in actual stormwater. Dissolved concentrations in influent were 2772 ± 482, 40 ± 59, and 113 ± 91 µg/L respectively. A two-way ANOVA with water type and treatment as the independent variables and total Zn

concentration as the dependent show that treatment, water type, and the water type/treatment interaction are significant with $p<0.000$. This interaction is shown in Figures 2.10 and 2.11. Effluent Zn follows a similar pattern to effluent Cu in that there are visible "steps" between water types for C80 – higher effluent concentrations in the high metal influent events, lower concentrations from the low metal influent events, and the lowest from the actual stormwater influent events. C20, C40-FY and C40-B are much less variable, with a slight downward trend that is more pronounced during the high metal events. Zn concentrations will be discussed separately for events with different influent water types.

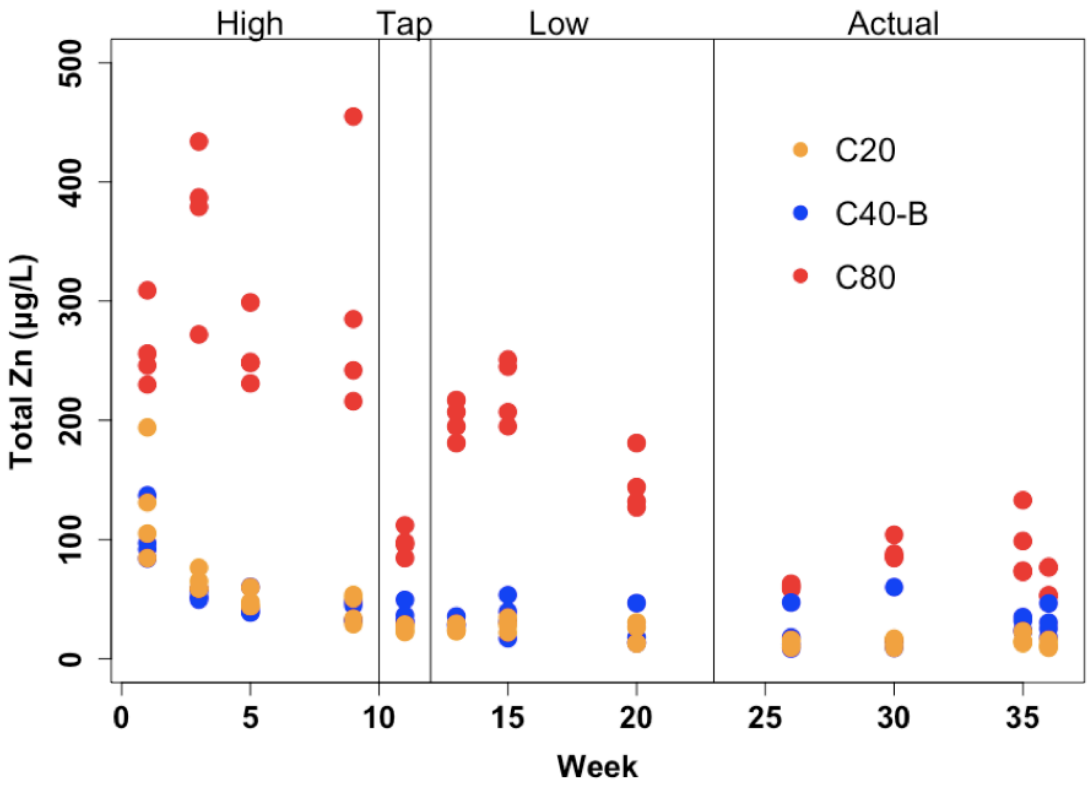


Figure 2.10. Effluent concentrations of total Zn from C20, C40-B, and C80 from each of the first 12 storm events. Vertical lines indicate divisions between water types.

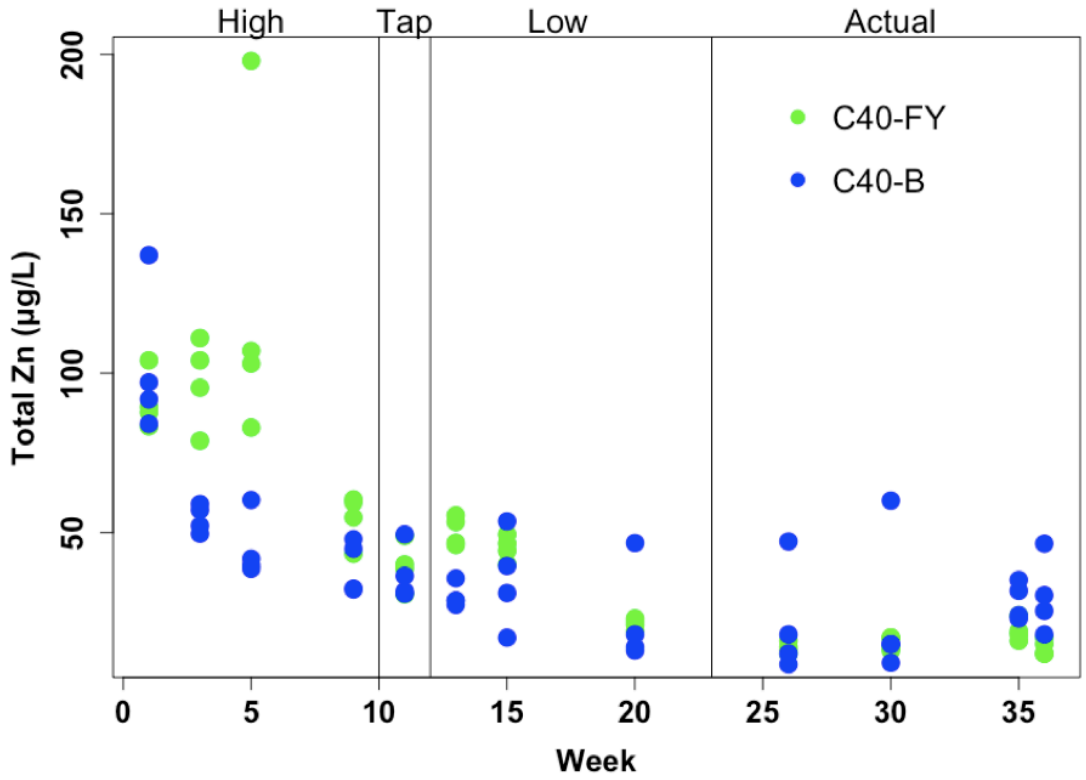


Figure 2.11. Effluent concentrations of total Zn from C40-FY and C40-B from each of the first 12 storm events. Vertical lines indicate divisions between water types.

For high metal synthetic stormwater events, an ANOVA with time and treatment as independent variables shows that time and treatment are both significant with $p<0.000$ and no significant interaction. Effluent Zn from all four treatments decreases over the course of the high metal events. A Tukey HSD post-hoc test shows again that the effect of increasing compost portion is not linear: C20 and C40-B performed similarly, while C80 was statistically higher. The effect of compost type for these events is statistically significant, with C40-FY absorbing less total Zn than C40-B. As with Cu and Pb above, these four treatments are all sinks for Zn.

Treatment and time are significant with $p<0.000$ for low metal synthetic events as well. Total Zn in effluent continues to decrease from all four treatments during these events. Fewer differences are found between treatments here – all are similar except for C80, which is higher

than the rest. The significance of time decreases for actual stormwater events to $p<0.032$, but treatment remains significant with $p<0.000$. For these events, C40-FY and C20 perform similar and release the lowest concentrations of Zn, followed by C40-B and then C80. Effluent concentrations of Zn can be seen in Table 2.12.

Table 2.12. Effluent concentration of Zn in µg/L from C20, C40-FY, C40-B, and C80, averaged over events with the same stormwater type. Influent concentrations are missing for event 1, so are not included in the average for high metal synthetic influent.

	High metal stormwater		Low metal synthetic water		Actual stormwater	
	Zn dissolved	**Zn total**	**Zn dissolved**	**Zn total**	**Zn dissolved**	**Zn total**
	µg/L		µg/L		µg/L	
Influent	*2772 ± 481.9*	*3503 ± 498.3*	*40.1 ± 58.7*	*950.3 ± 178.4*	*112.6 ± 90.8*	*172.0 ± 86.8*
C20	23.4 ± 19.0	71.0 ± 42.0	10.1 ± 3.8	24.9 ± 6.6	7.9 ± 3.2	13.6 ± 3.6
C40-FY	27.5 ± 12.2	91.4 ± 35.0	13.3 ± 2.1	38.9 ± 13.6	10.0 ± 2.7	15.6 ± 3.2
C40-B	30.5 ± 14.6	60.3 ± 28.5	18.7 ± 9.3	29.4 ± 12.9	20.2 ± 12.0	26.2 ± 14.9
C80	166.4 ± 47.5	296.1 ± 76.1	113.3 ± 17.4	190.2 ± 40.1	57.6 ± 17.5	77.7 ± 21.3

Zn, Pb, and Cu thus all follow similar patterns with respect to influent concentrations, with C80 and to a lesser extent C40-FY being less robust to high influent metals concentrations. All four treatments were sinks for total metals, both with respect to concentration and total mass, regardless of influent concentration. For total Zn, C20, C40-FY, C40-B, and C80 had mass removal rates of over 98%, 97%, 97% and 89% respectively (see Table 2.10 and Figure 2.5).

The pattern of dissolved Zn over time is compared to that of total Zn in Figure 2.12 below. As with Cu and Pb, removal of dissolved Zn was much lower than total removal throughout. C80 was a source of dissolved Zn concentration during the low metal stormwater events, but dissolved Zn was still removed by all other treatments and all other water types.

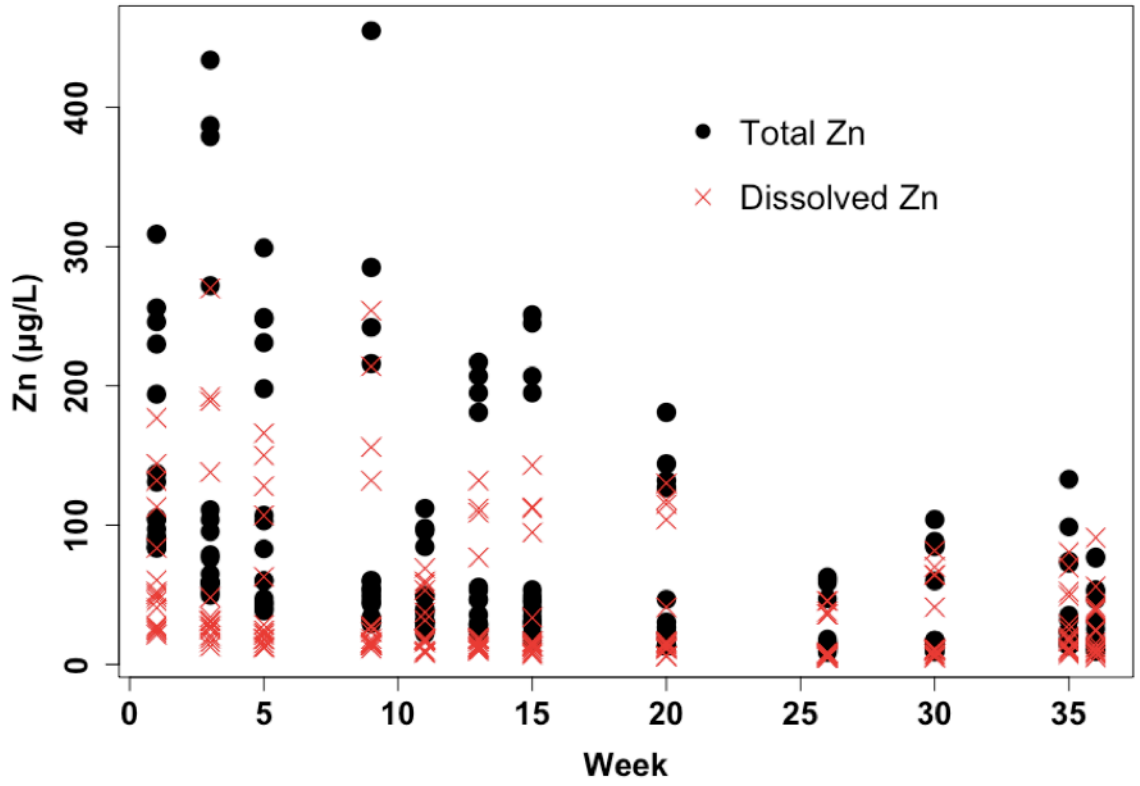


Figure 2.12. Effluent concentrations of total and dissolved Cu from C20, C40-FY, C40-B, and C80 from each of the first 12 storm events.

Total Suspended Solids

Turbidity was used in this experiment as an approximate measure of total suspended solids (TSS), as the two are directly related (Clark and Siu 2008). Turbidity changed between water types as follows: 18 ± 8 BTU in high metal synthetic stormwater, 3 ± 2 BTU in low metal synthetic stormwater, and 28 ± 11 BTU in actual stormwater. Note that, unlike with metals, actual stormwater had higher levels of TSS than either of the synthetic waters. A two-way ANOVA with water type and treatment as the independent variables and turbidity as the dependent show that treatment, water type, and the water type/treatment interaction are significant with $p<0.000$. Looking at Figures 2.13 and 2.14, it appears that the significance of water type may be due to its covariance with time, since the turbidity of effluent appears to

decrease smoothly with time even though the final four events have actual stormwater as influent, which has the highest turbidity of the water types. In fact, all treatments acted as a sink for TSS when actual stormwater was used as the influent, but acted as a source when synthetic influents were used.

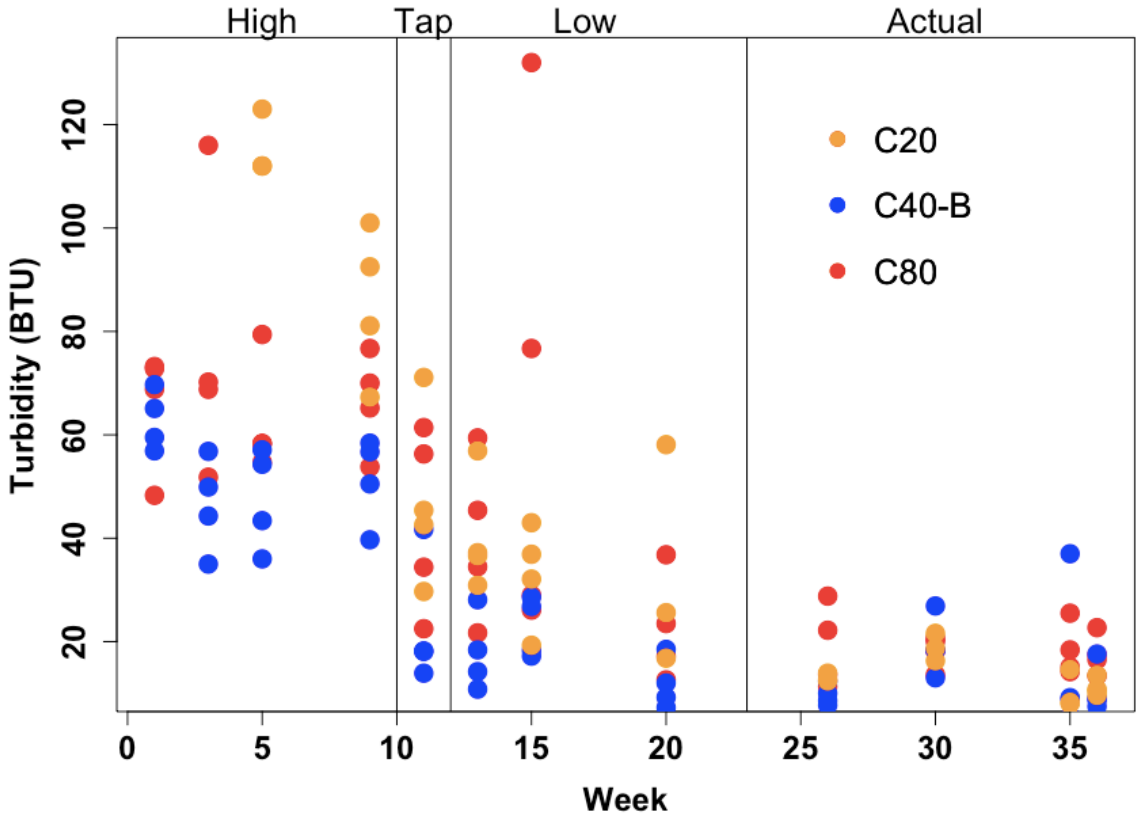


Figure 2.13. Turbidity of effluent from C20, C40-B, and C80 from each of the first 12 storm events. Vertical lines indicate divisions between water types.

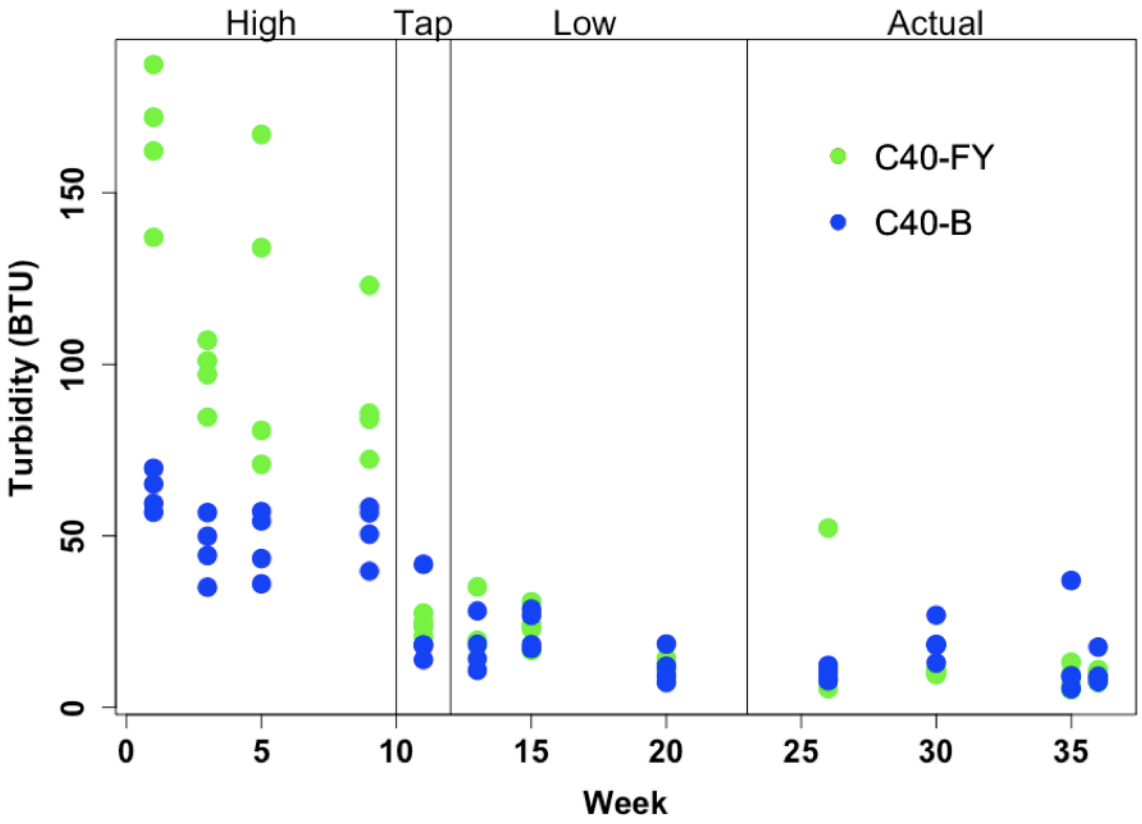


Figure 2.14. Turbidity of effluent from C40-FY and C40-B from each of the first 12 storm events. Vertical lines indicate divisions between water types.

For the first four events, with influent water of 18 BTU, all treatments were a source of turbidity. An ANOVA with time and treatment as independent variables shows that time, treatment, and time/treatment interaction are all significant with $p<0.000$, $p<0.000$, and $p<0.001$ respectively. Variability is high during these first four events and it is therefore difficult to find patterns, but the averaged values indicate that TSS in effluent during these events was lower as the compost portion of the mixtures increased (see Table 2.13 for averaged values). C40-FY also had higher effluent turbidity than C40-B throughout these events, but decreased more steeply than C40-B, so the difference is less pronounced by event 4.

Table 2.13. Average turbidity in effluent from C20, C40-FY, C40-B, and C80, separated by water type. Influent data are missing for event 1 so it is not included in the average.

	High metal synthetic	Low metal synthetic	Actual
	BTU	BTU	BTU
Influent	*18.5 ± 8.4*	*2.7 ± 1.6*	*28.4 ± 11.3*
C20	159.2 ± 89.0	35.8 ± 13.3	12.6 ± 4.4
C40-FY	100.6 ± 28.5	19.6 ± 7.6	12.7 ± 11.0
C40-B	48.5 ± 8.6	17.4 ± 7.3	13.7 ± 8.4
C80	68.6 ± 17.5	42.9 ± 33.5	18.2 ± 4.9

For events 6-8, with influent turbidity of 3 BTU, only time and treatment are significant with $p<0.000$, and no significant interaction. Here two replicates of C40-B have a spike in effluent turbidity during week 15, but this is likely an outlier as the other replicates do not spike nor do the other treatments. A Tukey HSD post-hoc test shows that for these events, C20 and C80 were similar and lower than both C40-B and C40-FY, which were also statistically similar. Only treatment was significant ($p<0.004$) for the final events, which had influent turbidity of 28 BTU. For these events, C20, C40-FY, and C40-B were statistically similar, with C80 releasing statistically lower turbidity than all except C20. These final events had actual stormwater as the influent, and thus realistic turbidity levels, so it is important to note that all treatments reduced turbidity during these events.

These results indicate that increasing compost portion in BSM decreases TSS in effluent for the first four events. However, the differences between C20, C40, and C80 after the first four events were essentially insignificant, so this relationship may only be relevant directly after installation. Similarly, compost type appears to have minimal effect with the exception of an initial flush of TSS from C40-FY that is not seen from C40-B. All treatments started out as sources of TSS, but acted as sinks during the final four events when actual stormwater was used. Since all treatments had decreasing TSS throughout and were a sink for TSS in the final

events, it is possible that high levels of removal could be reached were the experiment continued. This would reflect results from other studies, which found high TSS removal rates after initial flushing (Hatt et al. 2008, Hsieh and Davis 2005). It is also worth noting that the measure used in this study to indicate total suspended solids – turbidity – is not perfect. Dissolved organic carbon, which commonly leaches from nutrient rich media like compost, can color water without contributing greatly to the suspended solids load. Without further tests it is difficult to say how much of the effluent turbidity seen in the initial events was due to dissolved organic carbon rather than suspended solids.

Metals and TSS Discussion

The literature has shown high metals removal by a variety of BSMs (Brown et al. 2016; Paus et al. 2014; Hatt et al. 2008; Sun and Davis 2007; Hsieh and Davis 2005; Davis et al. 2001). With total mass removal of over 80% for all treatments for Cu, Pb, and Zn, results from this experiment support that assertion with regard to metals. However, some studies have shown that higher proportions of compost in BSM result in higher metals removal, or that OM content is positively correlated with higher metals removal (Paus et al 2014). These results show a different pattern – mass removal by C80 was consistently lower than C20 or C40. The variability of the influent water type played a role in this difference, but even from events with actual stormwater as influent, C80 had higher Zn and Cu effluent concentrations, although Pb was similar. Other studies saw little difference between metals removal in BSMs with differing levels of compost (Wenjun et al. 2013; Hatt et al. 2008). However, these studies did not include BSMs with more than 50% compost by volume, while this study included a mixture with 80%

compost. Since this study found that 20% and 40% compost portions performed similarly, it is possible that there is somewhere a "breaking point" between 40 and 80% compost volume, past which metals removal begins to fall.

The reason for the difference in C80's performance may be understood from the difference between removal of total and dissolved metals. Removal of dissolved metals was lower for all treatments than total metals removal, and C80 was in fact a net source of dissolved Cu, Pb, and Zn despite total metal removal rates above 80%. While particulate metals are captured by filtration, dissolved metals are captured by sorption to OM particles, and these sorption processes are directly affected by pH (Brady and Weil 2010; Li and Davis 2008). Although C80 likely had high OM content due to its high compost portion, it also had the lowest pH of all four treatments. It is possible that this acidity encouraged metals present in the BSM to desorb and wash out as dissolved metals, thus acting as a net source for dissolved metals while still acting as a sink for total metals by filtering out the particulate metals. There is also the possibility that higher OM content resulted in more soluble metal-OM complexes. Studies have found that the majority of captured metals are caught in the top layer of a BSM, so if this hypothesis were true, the top layer of the BSM would be expected to increase in metals content over the course of the experiment, while the remainder would slightly decrease (Dietz and Clausen 2006, Sun and Davis 2007). Unfortunately, this study did not sample different layers of the BSMs but instead homogenized the mixtures prior to analysis, leaving the precise mechanisms ambiguous. Furthermore, the effect of C80's low pH may have been exacerbated by C80's unexpectedly high infiltration rate: reduced contact time in C80 would limit sorption of dissolved metals from stormwater.

The effect of compost type on metals removal was minimal. Brown et al. (2016) found that BSMs containing biosolids compost removed Cu and Zn less effectively than BSMs containing food/yard waste compost, but both had removal rates above 90%. This study confirms those results: C40-FY and C40-B both removed Cu and Zn with mass removal rates above 95%, and Pb with rates above 85% over the entire experiment – see Table 2.10. When actual stormwater was the influent, C40-B had statistically higher Cu and Zn concentrations in effluent than did C40-FY, with statistically similar for Pb concentrations. C40-FY, however, was less robust than C40-B at higher influent concentrations of Cu and was less effective at removing suspended solids. Paus et al. (2014) found that different food/yard waste composts had varying sorption capacities, so taking into account that there is variation within compost types, the performance of C40-B and C40-FY is similar enough to imply that compost feedstock does not affect metals removal in BSMs.

Nitrogen

Unlike metals and turbidity, nitrogen concentrations in the influent water remained relatively consistent across the study. Total N values were as follows: 0.95 ± 0.10 mg/L for high metal synthetic stormwater, 1.08 ± 0.04 mg/L for low metal synthetic stormwater, and 1.79 ± 0.97 mg/L in actual stormwater. Therefore, influent water type will be disregarded during the analysis of N leaching.

Mass numbers for N can be seen in Table 2.14 and Figure 2.15. These mass numbers were calculated in the same way as mass numbers for metals as described above, and represent the total mass of N in effluent summed over the entire experiment. An initial

evaluation shows that all treatments were overall sources of total N and NO_3-N, but sinks for NH_4-N. It was expected that increased volume of compost would result in increased N movement through the columns, since compost contains high levels of N compared to sand. However, compost volumes did not follow a linear pattern for N movement according to the mass numbers. C40-B exported about twice as much total N and NO_3-N as C20, as expected. However, C80 fell in between the two, exporting less N and NO_3-N than C40-B but more than C20. It was expected that C80 would export around four times as much as C40-B, due to the relative weights of compost and the N content of the mixture.

Table 2.14. Total mass of NO_3-N, NH_4-N, and total N in effluent. Values are averages and standard deviations of mass numbers for all four replicates in each treatment. Shared letters indicate statistically similar means.

	TN		**NO_3-N**		**NH_4-N**
		Mg			
Influent		*22.1 ± 0.5*	*3.0 ± 0.0*		*14.4 ± 0.8*
C20	a	143.4 ± 5.3	a 64.1 ± 10.7	b	7.6 ± 2.3
C40-FY	ab	157.9 ± 9.5	a 83.2 ± 6.3	a	2.7 ± 0.4
C40-B	c	271.3 ± 34.1	b 165.1 ± 30.4	ab	5.0 ± 1.0
C80	bc	205.2 ± 26.7	a 96.9 ± 25.7	ab	3.6 ± 0.5

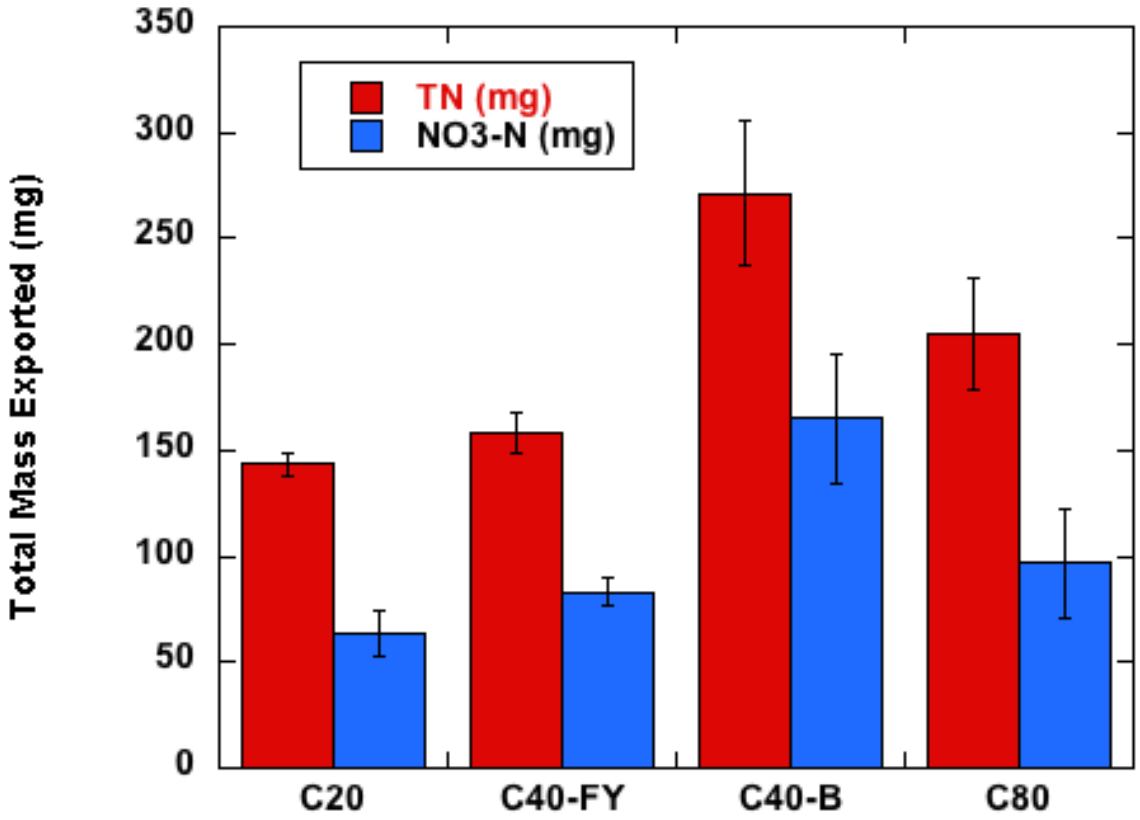


Figure 2.15. Mass export of total N and NO_3-N over entire trial in mg. For reference, total mass of N and NO_3-N in influent water was 22.0 and 2.9 mg, respectively.

A two-way ANOVA with time and treatment as independent variables and total N as the dependent variable shows that time, treatment, and time/treatment interaction are all significant with $p<0.000$, $p<0.000$, and $p<0.005$ respectively. Therefore, it is important to look at effluent concentrations from each event as well as overall mass data. Effluent data are in Table 2.15 below, and demonstrates that all treatments are indeed sources of total N and NO_3-N throughout the experiment. Other studies have found a wide variety of BSMs to be sources of N (Hatt et al. 2008, Hsieh and Davis 2005).

Looking at the patterns of export over time in figure 2.16 and 2.17, we see similar patterns in total N and NO_3-N: After an initial flush in event 1, effluent levels of both remain low for a few events, begin to increase steadily, and then decrease to their lowest levels in event 13, which takes place after grass is established. This pattern describes leaching from C40-B and C80; C20 leaching follows a different pattern. Total N from C20 is relatively constant throughout until a noticeable decrease in export during the final vegetated event, and NO_3-N increases slightly between events 4 and 6 but then also falls at the final vegetated event. Since they increase at the same rate, it appears that the increase of total N is due to the increase in NO_3-N. The fact that the increase in effluent NO_3-N is delayed a few weeks from the initial event indicates that it is a result of mineralization (and thus mobilization) of organic N from the BSMs during the first three events. This is supported by the findings in Li and Davis (2014), which similarly suggested that the conversion of captured N to more mobile forms was the main cause of N leaching from BSMs.

Table 2.15. Average influent and effluent concentrations of NO_3-N and total N from select events, for C20, C40-FY, C40-B, and C80. Influent data are missing for event 1.

Treatment	Event	NO_3-N (mg/L)	Total N (mg/L)
Influent	1	-	-
	3	0.08 ± 0.00	0.94 ± 0.04
	6	0.05 ± 0.00	1.09 ± 0.04
	9	0.09 ± 0.00	1.04 ± 0.08
	12	0.32 ± 0.00	1.47 ± 0.05
	13	0.03 ± 0.00	3.81 ± 0.02
C20 Effluent	1	0.12 ± 0.08	13.68 ± 2.04
	3	0.13 ± 0.05	9.11 ± 1.02
	6	7.16 ± 2.35	11.48 ± 0.87
	9	6.07 ± 3.02	10.32 ± 3.20
	12	5.14 ± 1.65	7.93 ± 2.24
	13	0.03 ± 0.02	4.78 ± 0.72

C40-FY Effluent	1	1.13 ± 0.72	15.40 ± 1.59
	3	1.46 ± 0.58	12.10 ± 1.56
	6	9.33 ± 2.76	12.10 ± 1.24
	9	6.56 ± 0.88	11.18 ± 1.83
	12	5.10 ± 0.72	7.41 ± 0.67
	13	0.34 ± 0.14	3.48 ± 0.39
C40-B Effluent	1	2.79 ± 1.79	21.58 ± 4.33
	3	0.11 ± 0.04	11.43 ± 0.40
	6	12.89 ± 4.72	17.75 ± 4.73
	9	23.48 ± 11.17	29.25 ± 13.19
	12	10.79 ± 1.12	15.48 ± 0.95
	13	0.05 ± 0.00	5.08 ± 1.18
C80 Effluent	1	0.64 ± 0.14	20.95 ± 1.41
	3	0.27 ± 0.10	12.73 ± 0.87
	6	1.12 ± 0.84	9.88 ± 2.32
	9	13.19 ± 7.92	16.81 ± 8.19
	12	13.23 ± 3.40	17.25 ± 4.47
	13	0.05 ± 0.01	4.22 ± 0.66

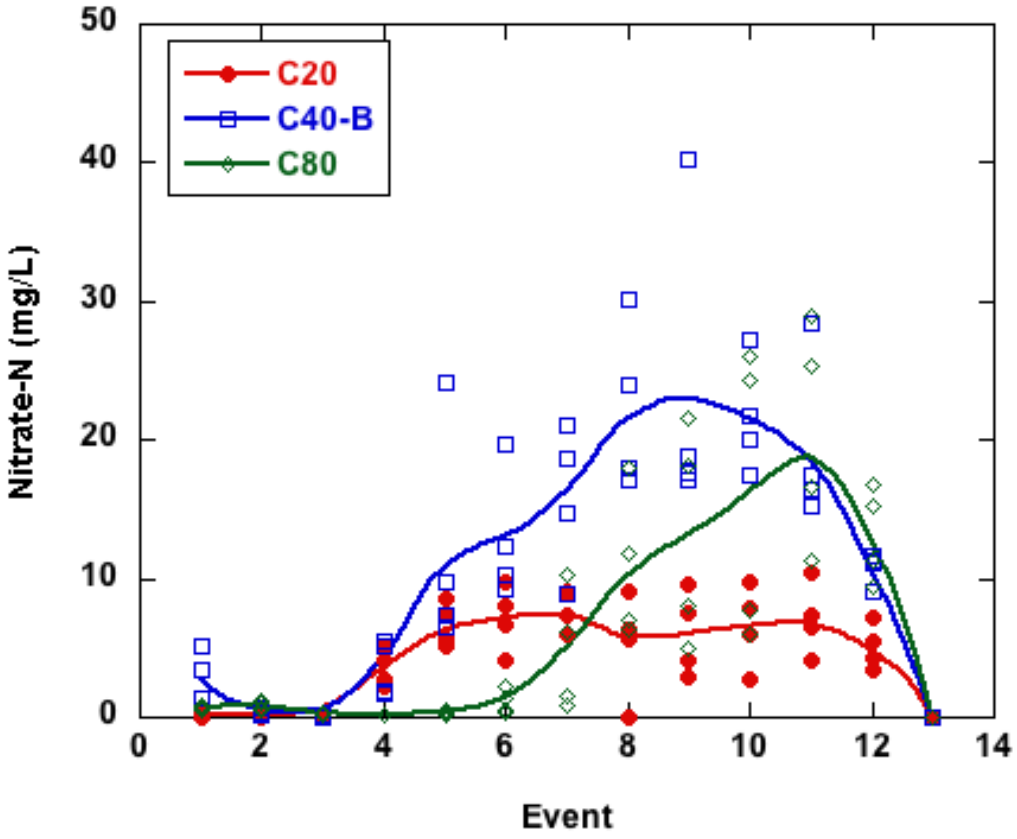


Figure 2.16. Concentration of NO_3-N in effluent (mg/L) from C20, C40-B, and C80 columns shown by event. Grass was planted and allowed to establish between events 12 and 13. Lines are Loess curve fits.

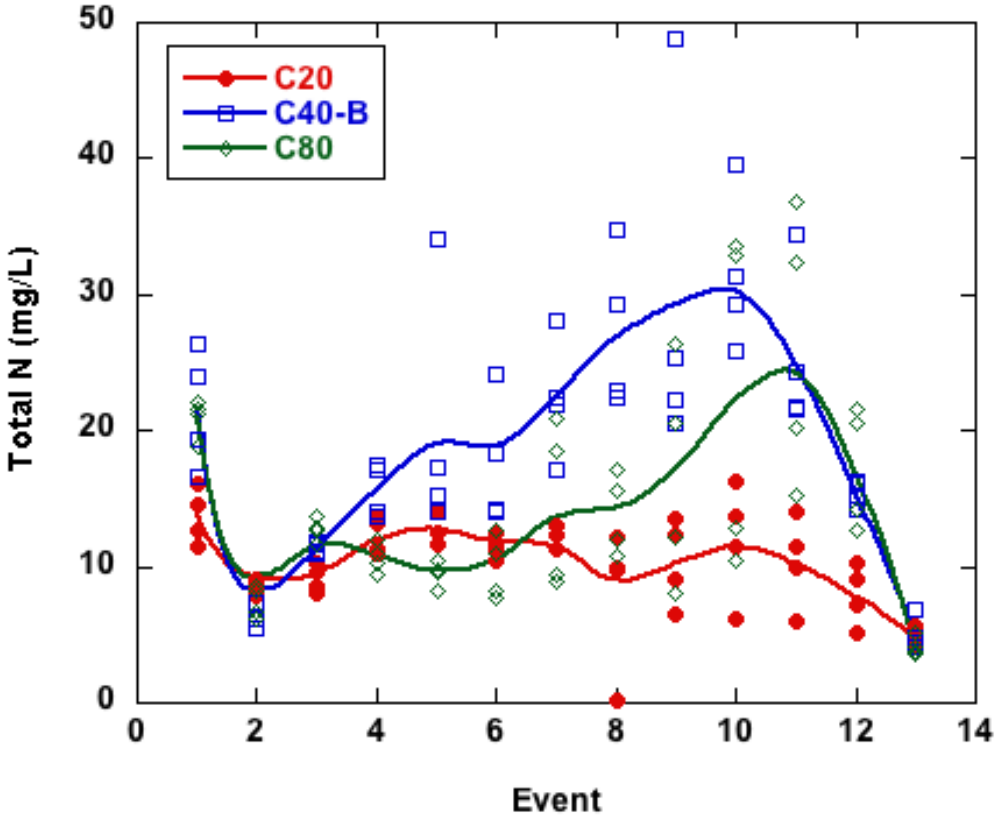


Figure 2.17. Concentration of total N in effluent (mg/L) from C20, C40-B, and C80 columns shown by event. Grass was planted and allowed to establish between events 12 and 13. Lines are Loess curve fits.

From Figure 2.18 below, we can begin to posit an explanation for the low mass export from treatment C80. It appears that effluent N concentrations from C80 do not begin to increase until event 6, while C40-B begins to increase much earlier at event 3. They increase at a similar rate, and thus it is possible that C80 would have continued increasing over time and eventually surpassed C40 were it not cut off by the grass planted before event 13. C80 did show some decrease in effluent N concentration between events 11 and 12, however, so it is difficult to predict what the next event would have looked like had grass not been planted.

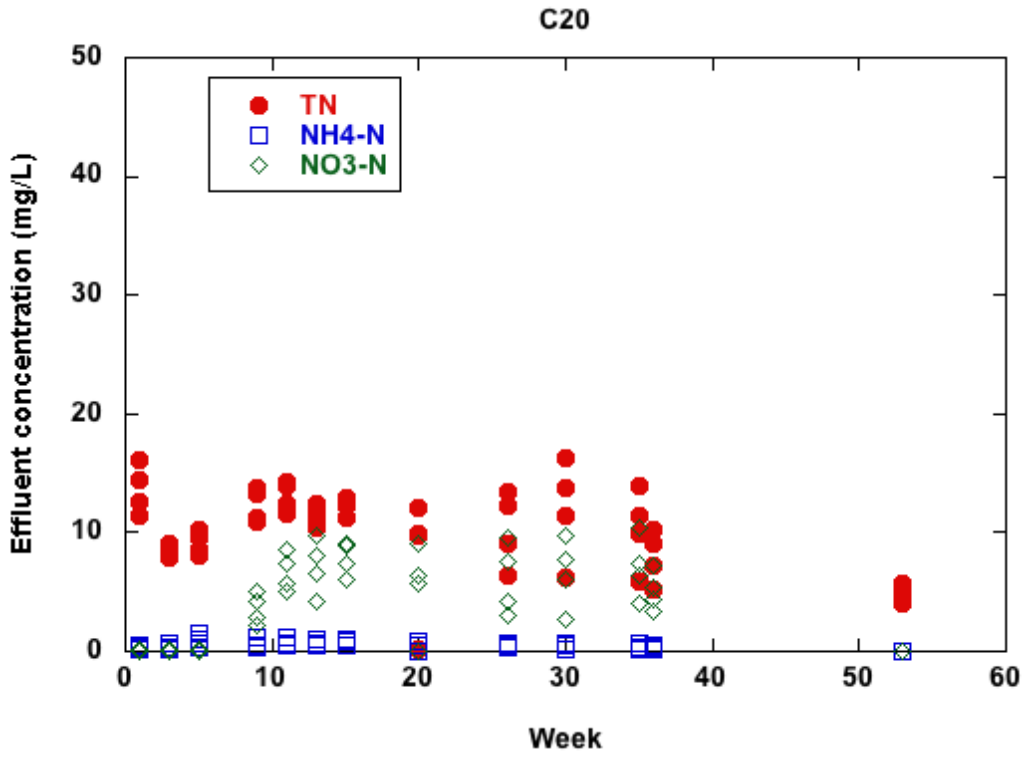
For both events, it is clear that the increase in total N is due to the release of NO_3-N, and it is likely that this NO_3-N increase is due to mineralization of N, likely from the BSM mixtures. Several studies have suggested that mineralization occurs preferentially in the aerobic environment that forms in BSMs when they dry in between leaching events (Mullane et al. 2015; Li and Davis 2014; Hsieh et al. 2007). Although it was intended that the BSMs be kept moist in between storm events in order to avoid this complication, the amount and frequency of watering for this purpose was loosely estimated and may have been too little to prevent drying and thus mineralization from taking place in the majority of treatments. This seems likely, since mineralization appears to be the main cause of N leaching. If this were the case, it would explain why less mineralization occurred in C80 – with such a high proportion of compost, C80 would be expected to have a very high water retention capacity, which may have prevented it from fully drying in between storm events. Other treatments with lower compost portions and thus lower water retention capacity would dry more quickly. If C80 did not dry out between events, NO_3-N would not have built up due to mineralization, which would explain why NO_3-N concentrations in effluent from C80 were lower than those in effluent from C40-B.

This idea is supported by the fact that time in between events was longer beginning with event 8, which is also the point at which NO_3-N concentrations from C80 begin to climb. The longer time in between events would make it more likely for C80 to fully dry out and for mineralization to occur.

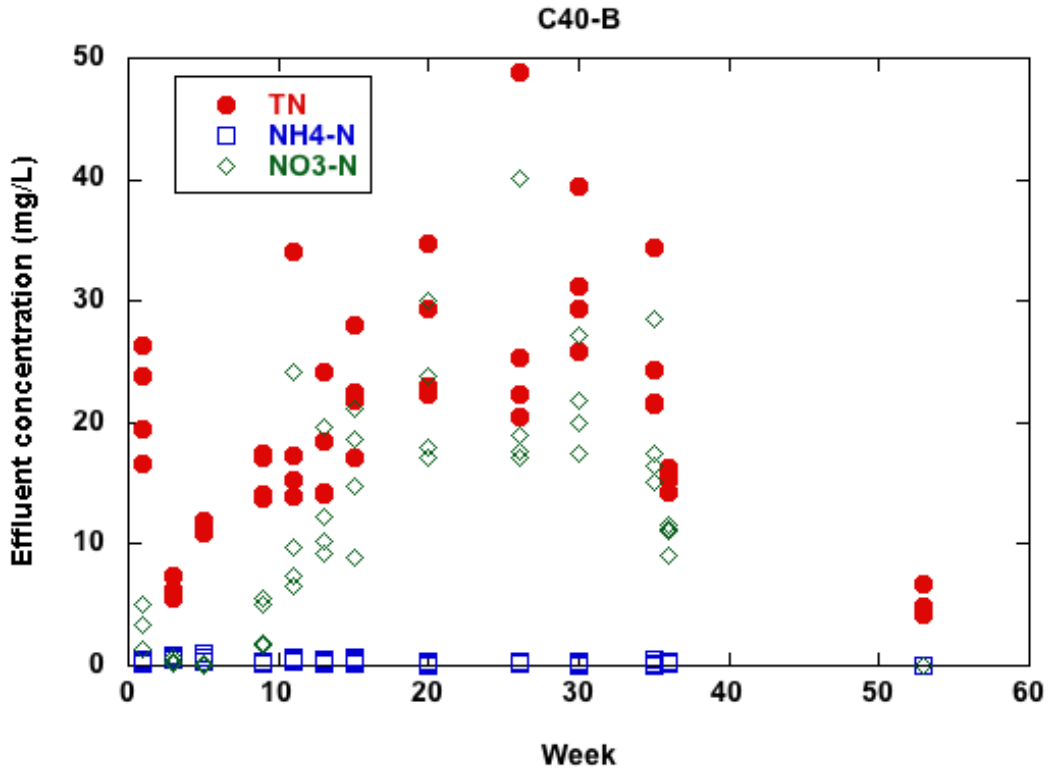
More research is necessary to confirm this theory, but it could have important implications for bioretention systems. C80 has twice the volume of compost as C40-B, but it appears that the lack of a wetting/drying cycle caused C80 to export less total N than C40-B.

This could mean that effective management of a bioretention system may be even more important than the mix components of the BSM. An alternative explanation for this difference could lie in the differing infiltration rates – C80 had a much higher infiltration rate than C40-B or C20 (Figure 2.2) and it is possible that the lower contact time in C80 was responsible for its reduced N leaching, or at least compounded the differences in the wet/dry cycle.

a)



b)



c)

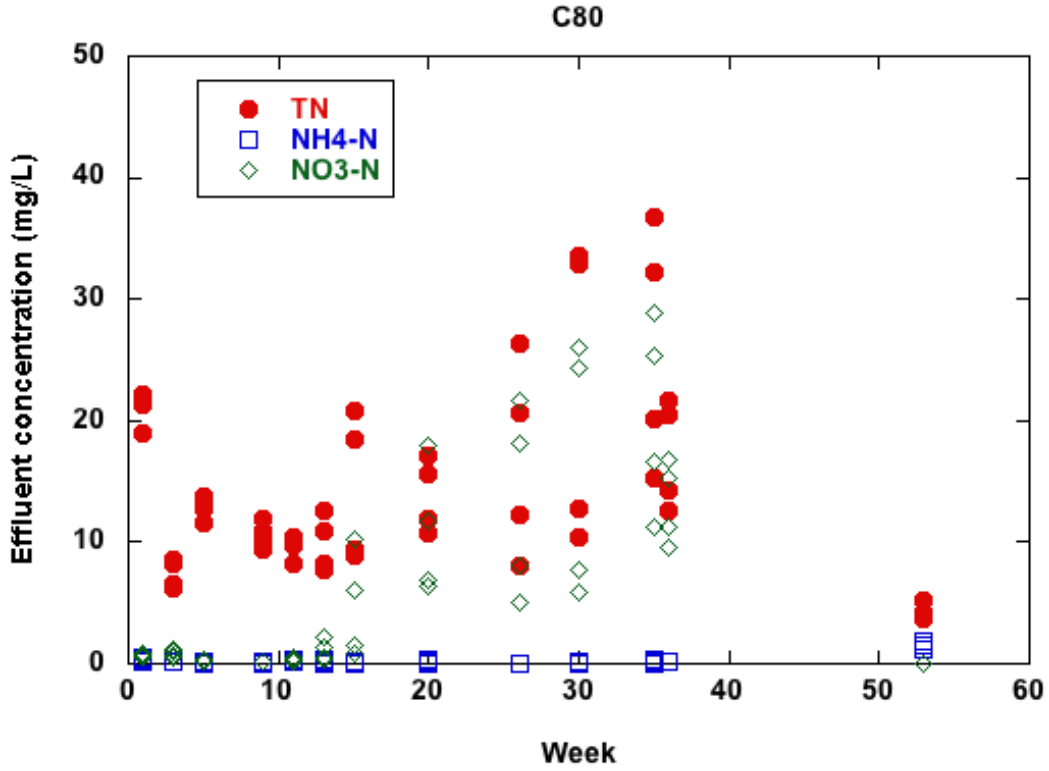
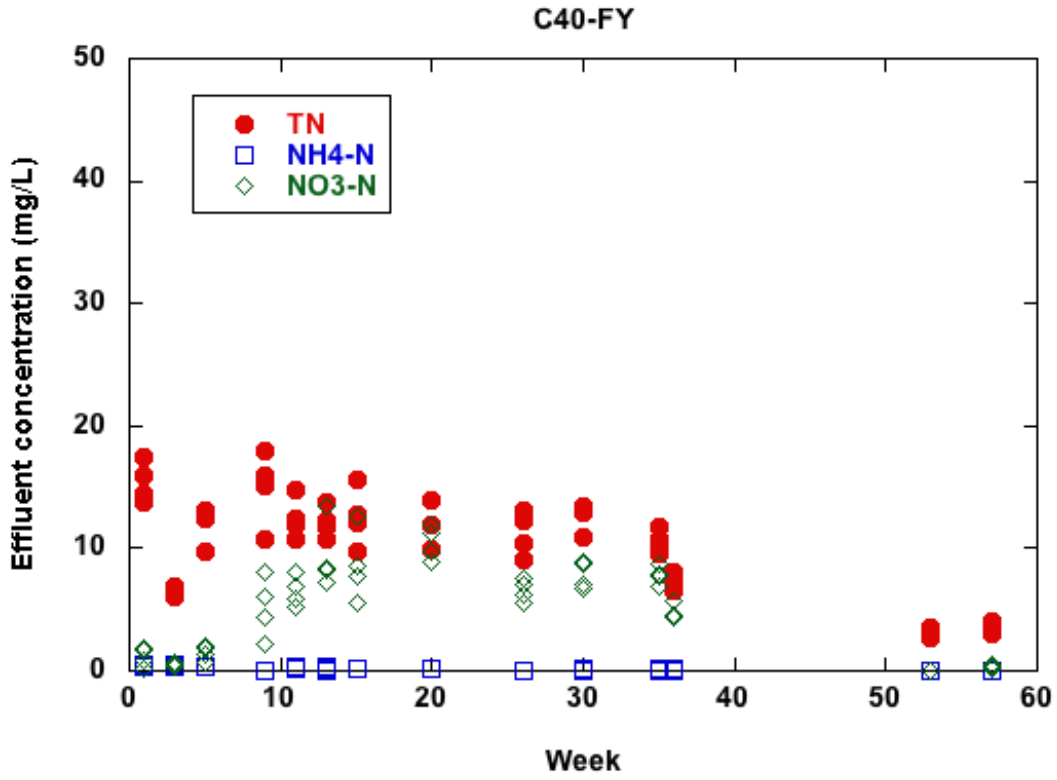


Figure 2.18. Concentration of total N, NO_3-N, and NH_4-N (mg/L) in effluent from BSMs with increasing proportions of biosolids compost. In order: C20 (a), C40-B (b), and C80 (c).

Finally, it is interesting to compare the different compost types used in this experiment. C40-FY and C40-B behaved very differently, which underlines the claim that "compost" as a term can encompass soils with widely varying properties. Though both had the same proportions of compost and sand, C40-FY exported significantly less total N and NO_3-N than C40-B did. In fact, C40-FY's mass N export was statistically similar to C20, indicating that the biosolids/yard waste compost had a higher N leaching potential than the food/yard waste compost in this experiment, but this difference was eliminated by simply adjusting proportions. Perhaps more interestingly, Figure 2.19 shows that total N leaching from C40-FY decreased steadily over time before falling when vegetation was established, which directly contrasts with C40-B where total N leaching increased over time before vegetation. Nitrate -N and NH_4-N leaching in C40-FY and C40-B followed similar patterns, both increasing over time before vegetation. Since the total N leached at the beginning by the food/yard waste compost was high but the NO_3-N concentration at the beginning was low, it is likely that the food/yard waste compost was releasing organic N during the first few events. Organic N is usually in particulate form, and thus for this to be true it would be expected that C40-FY leached higher levels of TSS than C40-B during the first few events, which was shown to be true in the suspended solids section above (see Figure 2.14).

a)


C40-FY
TN
NH4-N
NO3-N
Effluent concentration (mg/L)
Week
0
10
20
30
40
50
60

b)

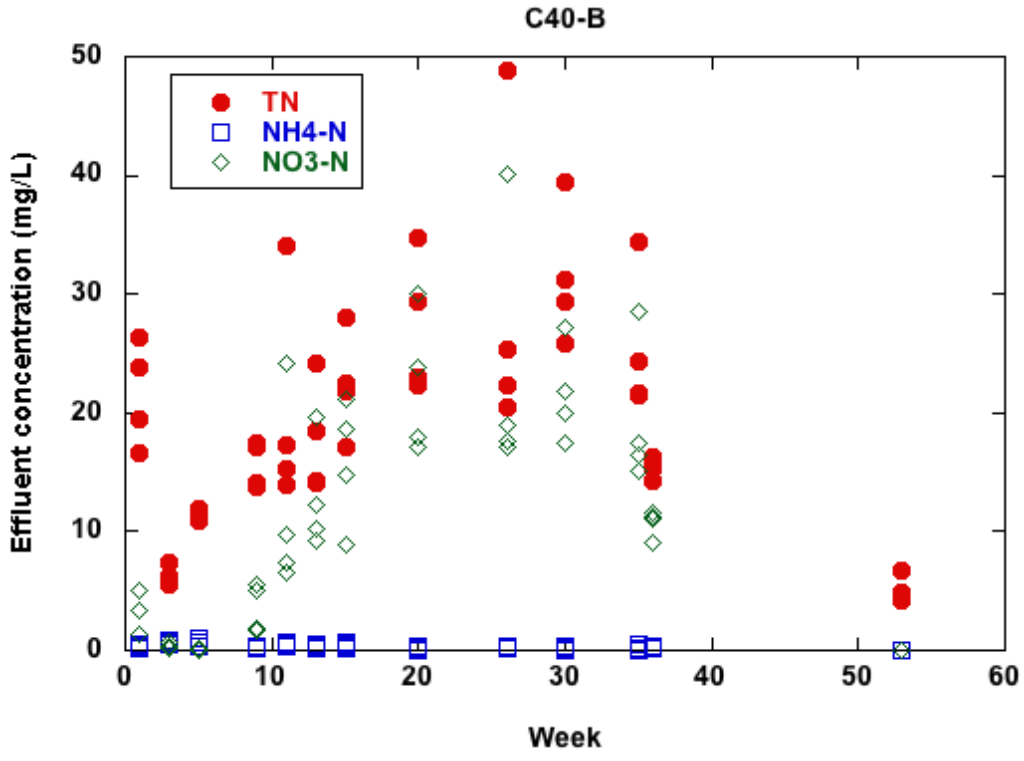

C40-B
TN
NH4-N
NO3-N
Effluent concentration (mg/L)
Week
0
10
20
30
40
50
60

Figure 2.19. Concentration of total N, NO_3-N, and NH_4-N (mg/L) in effluent from BSMs with different compost type but same compost proportion, shown by event. In order: C40-FY (a), C40-B (b).

Phosphorus

As with N, influent concentrations of P were relatively constant throughout the experiment, so water type will be disregarded when analyzing P export. Concentrations of P in influent stormwater were: 1.49 ± 0.22 mg/L in high metal stormwater, 2.01 ± 0.08 mg/L in low metal synthetic stormwater, and 0.08 ± 0.03 mg/L in actual stormwater. Although the concentration in actual stormwater appears much lower, the difference is minimal when compared to effluent concentrations.

Unlike what was observed with N, both total and dissolved P in leachate increased as the volume fraction of compost in the BSM increased. As with metals and N, mass export data for P was calculated for each replicate by multiplying the effluent concentration of the contaminant by the volume of effluent for each event, and then summing these values over all 14 events, as follows: *total mass = Σ(event n concentration)*(event n volume).* This data is shown in Table 2.16, and it is clear that all treatments were overall sources of P. Overall mass export data in Figure 2.20 show that C20, C40-B, and C80 behaved mostly as expected, i.e. P export increased with compost portion. This relationship was not linear, however – C80, which contained 4 times by volume the compost of C20, leached less than twice as much P overall. The smaller difference between C40-B and C80 may be due to the higher infiltration rate in C80 columns, and the possibility of preferential flow. Reduced contact time in C80 would likely decrease soil P mobilization. Compost type also played a large role in P leaching, with C40-FY

leaching much less P than C40-B. In fact, C40-FY leached less than 25% the mass of P that C20 did (see Table 2.17).

In both agriculture and bioretention studies, it has been suggested that the PSI of a soil is a good predictor of its capacity to leach P (Brown et al. 2016; Elliott et al. 2002; Lu and O'Connor 2001). The results of this trial support those findings. PSI increased with compost fraction: C20 had a PSI of 0.43 ± 0.02, C40-B had a PSI of 0.68 ± 0.03, and C80 had a PSI of 1.26 ± 0.02. A higher PSI indicates a higher portion of P to Al and Fe in the soil, meaning less Al and Fe oxides are available in the soil to sorb P. Therefore it would be expected that P export would increase with increases in the PSI. The significance of PSI as a possible predictor of P leaching is further supported by the fact that C40-FY had a PSI of 0.30 ± 0.03, much lower than any of the biosolids treatments. Despite having a higher portion of compost than C20, the increased availability of Fe and Al sorption sites in the soil resulted in lower levels of P leached overall. It is also interesting to note the C40-FY had higher initial levels of extractable P than C20, but a lower PSI and lower overall P leaching. This indicates that soil P alone should not be considered a good predictor of BSM performance.

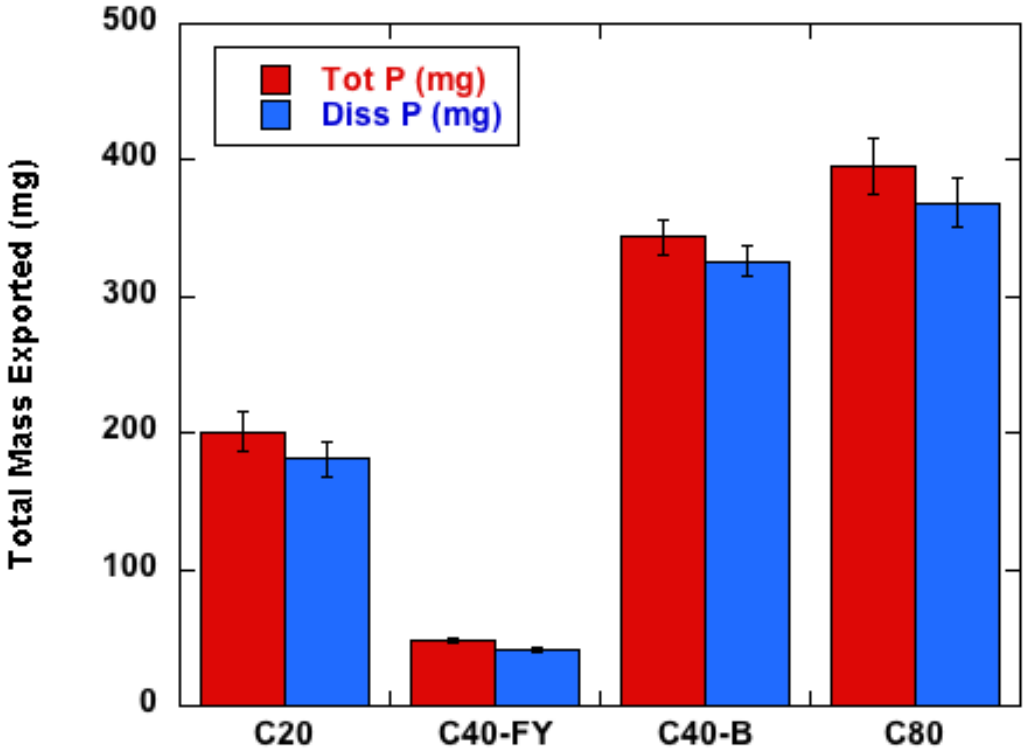


Figure 2.20. Mass export of total and dissolved P over entire trial, in mg. For reference, mass of total and dissolved P in influent water was 24.2 and 5.3 mg, respectively.

Table 2.16. Total mass of dissolved and total P in effluent. Values are averages and standard deviations of mass numbers for the four replicates in each treatment. Shared letters indicate statistically similar means.

	Dissolved P		**Total P**	
		Mg		
Influent		*5.3 ± 0.4*		*24.2 ± 0.4*
C20	b	181.3 ± 12.6	c	201.1 ± 14.7
C40-FY	a	40.8 ± 2.1	a	48.3 ± 2.1
C40-B	c	326.2 ± 11.2	b	343.6 ± 12.5
C80	c	368.6 ± 18.3	b	395.1 ± 20.8

A two-way ANOVA with time and treatment as the independent variables and total P as the dependent variable shows that time, treatment, and time*treatment interaction are all significant with $p<0.000$. Therefore, it is important to look at effluent concentrations over time,

which are presented below in Table 2.17. All treatments are sources of P throughout the experiment, with the exception of C40-FY in the final event. However, influent concentrations in that event were unexpectedly high, and the concentration in that event was actually higher than in the previous event when C40-FY was still a source of P.

Figure 2.21 shows that effluent concentrations of P from C20, C40-B, and C80 are initially high and decrease logarithmically over the course of the experiment, reaching 1/6 their original concentration by the final event. This is in keeping with previous studies, which have shown initial flushing of P from BSMs containing compost (Brown et al. 2016; Hatt et al. 2008; Dietz and Clausen 2006; Hsieh and Davis 2003). Figure 2.22 shows that most P in effluent was in dissolved form.

Table 2.17. Average influent and effluent concentrations of dissolved and total P from select events, for C20, C40-FY, C40-B, and C80. Influent data are missing for event 1. Dissolved P was not measured for event 13.

Treatment	Event	Dissolved P (mg/L)	Total P (mg/L)
Influent	1	-	-
	3	0.94 ± 0.04	0.75 ± 0.01
	6	1.09 ± 0.04	1.16 ± 0.12
	9	1.04 ± 0.08	0.17 ± 0.00
	12	1.47 ± 0.05	0.46 ± 0.02
	13	-	3.60 ± 0.06
C20 Effluent	1	30.13 ± 2.29	35.65 ± 3.60
	3	24.70 ± 3.99	20.45 ± 3.69
	6	15.63 ± 1.08	16.40 ± 1.22
	9	7.34 ± 3.12	8.63 ± 3.36
	12	4.81 ± 0.68	5.49 ± 0.80
	13	-	3.70 ± 0.98
C40-FY Effluent	1	3.76 ± 0.31	5.24 ± 0.20
	3	4.29 ± 0.10	4.98 ± 0.16
	6	3.26 ± 0.53	3.76 ± 0.50
	9	2.29 ± 0.11	2.70 ± 0.07
	12	1.68 ± 0.23	1.88 ± 0.21

	13	-	2.95 ± 0.29
C40-B Effluent	1	55.03 ± 2.54	60.90 ± 3.53
	3	42.48 ± 1.80	39.18 ± 2.02
	6	18.63 ± 2.13	23.90 ± 2.98
	9	14.50 ± 1.27	16.38 ± 1.74
	12	11.23 ± 0.85	12.48 ± 0.80
	13	-	8.73 ± 1.05
C80 Effluent	1	69.23 ± 6.51	75.55 ± 7.35
	3	48.40 ± 3.59	45.90 ± 3.94
	6	23.30 ± 2.00	29.18 ± 3.79
	9	13.45 ± 2.15	14.98 ± 2.70
	12	9.53 ± 1.90	10.73 ± 2.12
	13	-	11.53 ± 0.31

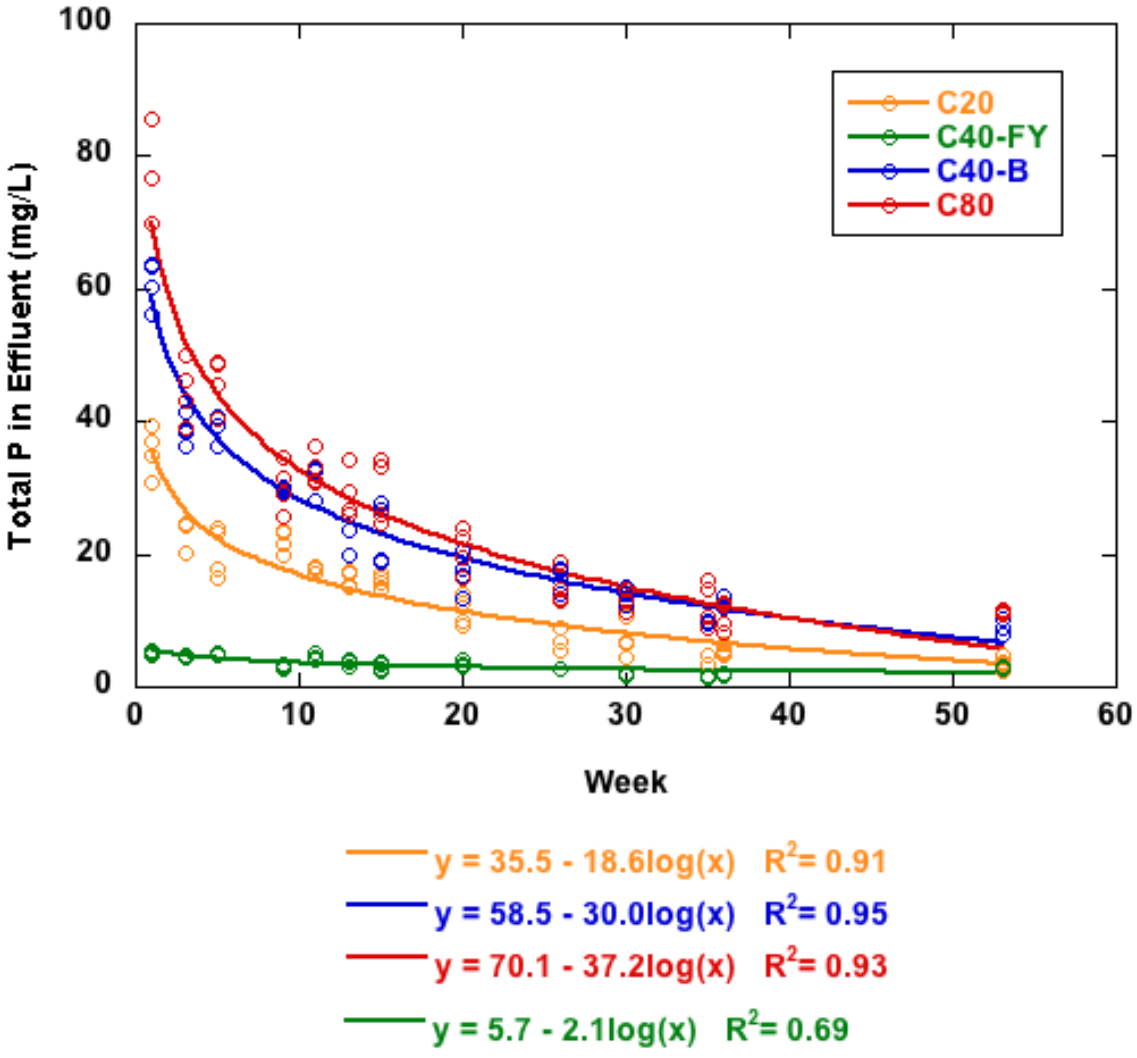


Figure 2.21. Concentration of dissolved P in effluent (mg/L) from C20, C40-B, and C80, Sand columns shown by event. Lines are logarithmic fits, equations and R^2 presented below the graph.

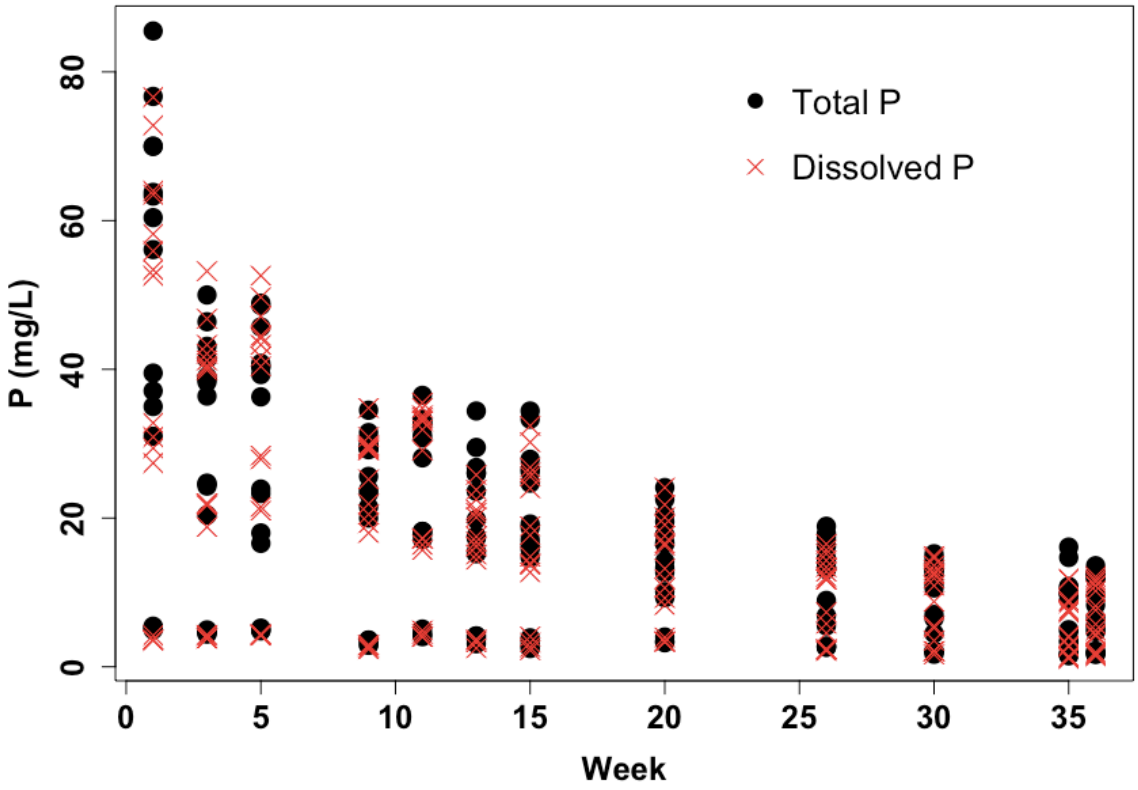


Figure 2.22. Total and Dissolved P in effluent (mg/L) from all four treatments, by week.

Grass

As expected, grass yield increased with increasing levels of compost, as can be seen in Figures 2.23 and 2.24. C40-FY had lower yield than C40-B, which is consistent with the lower N and P leaching that was seen for C40-FY: lower growth would result from lower N and P availability.

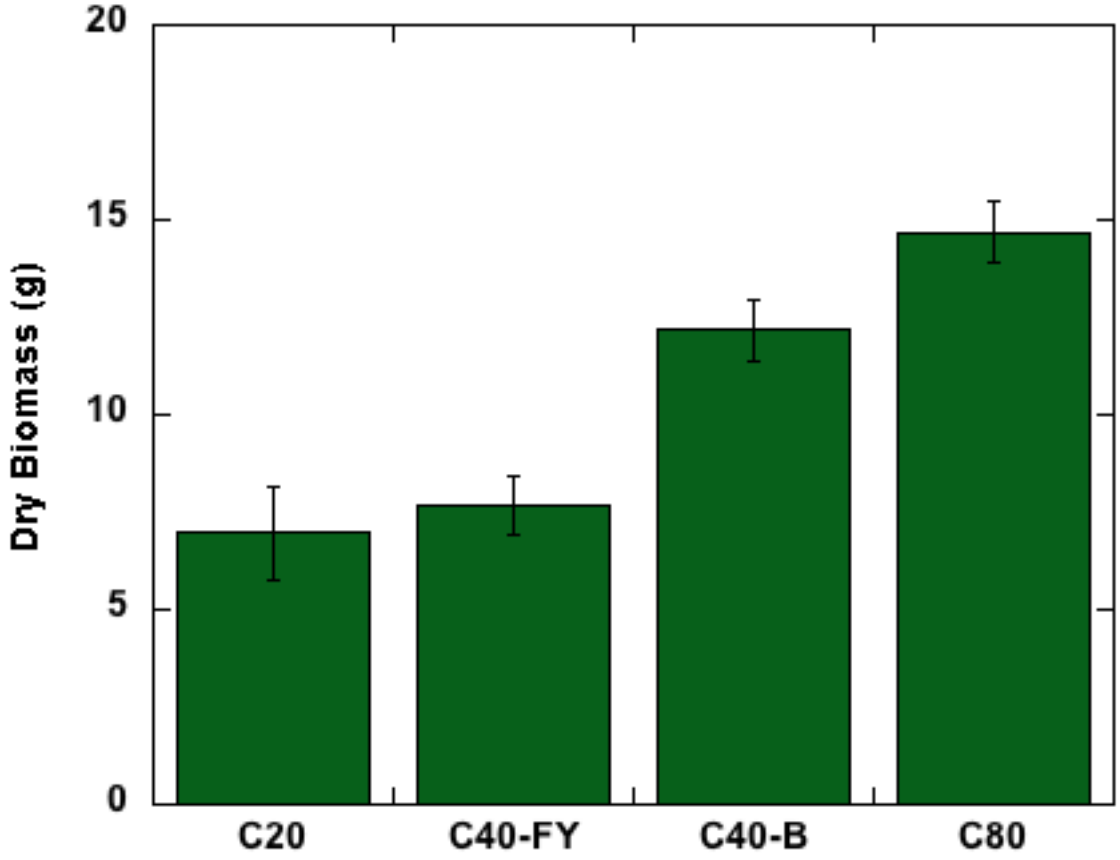


Figure 2.23. Average biomass (g) of grass harvested from columns after one month of growth and dried in a drying oven at 105°C.

Figure 2.24. Grass 5 months after first harvest. Top row from left to right: C20, C40-FY. Bottom row: C40-B, C80.

Studies have shown that plants can reduce nutrient leaching and minimize differences between effluent concentrations from barren BSMs (Brown et al., 2016; Payne et al 2014; Zinger et al. 2013). In this experiment, grass was planted and allowed to establish before leaching event 13, and effluent N from C20, C40-B and C80 was at its lowest in this event. In fact, before event 13, effluent concentrations from each treatment followed a somewhat linear pattern, which is noticeably broken by the low concentration of N in effluent after grass was

established (see Figure 2.18 above). Furthermore, differences in N leaching between the treatments were minimal in event 13 - average effluent concentrations of total N in this event differed by less than 2 mg (see Table 2.15 above).

No effect from vegetation was seen with P leaching – C80 and C40-FY actually leached higher concentrations of total P after grass was established, but this may have been due to the unexpectedly high concentration of P in the influent for this event. Unfortunately time constraints of the experiment did not allow for further events, so it is not known whether P removal would have been affected over time, or whether the effluent N concentrations would have rebounded or remained at low levels as the grass grew.

Conclusion

Increasing proportions of compost in BSMs had mixed effects on BSM efficacy. All treatments were found to be sinks for total Cu, Pb, and Zn, with overall mass removal rates of above 80%. Little effective difference was found between 20% and 40% compost BSMs, but 80% compost BSMs removed metals less effectively. We posited that this difference may be due to a combination of low pH and high infiltration rate in C80 – other studies have found that increasing compost portions either increase or have no effect on metals removal rates in BSMs (Paus et al. 2014; Wenjun et al. 2013; Hatt et al. 2008).

N leaching did not meet expectations – although all BSMs were sources of N, it was expected that compost portion and N leaching would be positively correlated. Instead, the 80% compost BSM leached less N than the 40% compost BSM. A possible explanation for this is that C80 did not experience wet/dry cycles as the other treatments did, and thus did not undergo as

much mineralization and washing out of NO_3-N. If this is true, it emphasizes the significant influence that wet/dry cycles have on BSM performance. C80 also had a much higher infiltration rate than C20 and C40-B, which likely contributed to its reduced N leaching. These findings imply that proper management of a BSM may be even more important than the contents of the BSM itself, as here a higher infiltration rate and the absence of wet/dry cycles more than compensated for doubling the volume portion of compost in terms of N leaching.

The type of compost in the BSM had minimal effects on metal removal - when actual stormwater was used as influent, the biosolids compost was slightly less effective at removing Cu and Zn than the food/yard waste compost used in this experiment when they were in the same proportions (i.e., C40-B and C40-FY). Larger differences were seen between compost types with respect to N and P. The food/yard waste compost leached less N than the biosolids compost in the same portion, but similar results were attained by simply halving the portion of biosolids compost in the BSM. The food/yard waste compost also leached less P than the biosolids compost in similar proportions.

Finally, the results of this study indicate that plant growth is not only crucial to a BSM for aesthetic reasons, but also for its contribution to N removal. Differences between BSMs with respected to N were minimized when grass was established, suggesting that future column studies should include plant growth throughout in order to more accurately reflect the functioning of a BSM in the field. This is supported in some of the literature (Brown et al., 2016; Payne et al 2014; Zinger et al. 2013), but other studies have found that plants have a mixed effect on N leaching (Palmer et al. 2013; Bratieres et al 2008). More research is needed to understand the immediate and long-term effects of vegetation on nutrient leaching from BSMs.

Predictors of Phosphorus Leaching from Bioretention Soil Media

Introduction

Phosphorus (P) is a contaminant of particular concern in stormwater, as it is most commonly the limiting nutrient for eutrophication in freshwater bodies (Ward and Trimble 2004). Total P concentrations in stormwater are usually between 0.2 and 0.3 mg/L, depending on land use (Maestre and Pitt 2005). Excess P in runoff causes algal blooms that can lead to fish kills, reduced usability for recreation and industry, and in some cases toxicity that threatens public health (Kotak et al. 1993; Sharpley et al 1994; Sharpley 2000). It has been estimated that problems associated with freshwater eutrophication have an economic cost exceeding $2.2 billion a year in the United States (Dodds et al., 2009). In urban and suburban areas, P in stormwater runoff comes from fertilizers used on lawns or other green spaces, as well as atmospheric deposition, soil erosion, and animal waste (US EPA 1998).

Research on excess P in soils has focused on soil mechanisms to absorb P as well as predictive tests to estimate the potential for P movement through soils. Both of these have been developed in soil science and agronomy, but have potential applications to bioretention systems.

Phosphorus in Soil

Phosphorus is an essential plant nutrient and is often bound in soils. To help farmers determine the ideal amount of P to apply to their fields in order to support robust crops without over-applying and releasing excess P to the environment, soil scientists have developed

many mechanisms for measuring environmentally relevant P and predicting the rate at which it will be taken up by plants, mobilized into runoff, and/or leached through the soil profile. With bioretention systems facing similar concerns, it makes sense to investigate these mechanisms for possible applications in this developing field.

Multiple soil extractions have been proposed to measure soil P in agronomic settings to predict P leaching. The standard in the southern U.S. is the Mehlich-III extraction (Mehlich 1984; Tucker 1992). Various ranges for Mehlich-III-P have been identified to support crop growth and minimize environmental risk, but in fact the relationship between Mehlich-III-P levels and P leaching appears to change depending on the soil type, pH, and other factors (Maguire and Sims 2001, Kovar and Pierzinski 2009, Virginia 2005). One field study of two bioretention sites found that P leaching was greater where soil Mehlich-III-P levels were higher, but this relationship was not investigated further (Hunt et al. 2006). Kleinman et al. (2001) found that the relationship between soil Mehlich-III-P and dissolved P in runoff for three different soils (Berks, Lewbeach, and Honeoye) was distinct for each soil. One soil showed a clear positive correlation, but the others had no significant relationship, indicating that soil-specific management may be necessary. Similarly, Elliott et al. (2002) found that Mehlich-I P (which is functionally similar to Mehlich-III P) was poorly correlated with P leaching in biosolids-amended soils.

To better predict runoff P, some soil scientists combine soil P with other soil or environmental factors to describe the P “saturation” of a soil. The P Saturation Index (PSI) is one such combination. It takes into account the importance of Fe and Al oxides as sorbents of P, representing the P saturation of a soil with the molar ratio P/(Al+Fe), where P, Fe, and Al are

the ammonium oxalate-extractable molar concentration of each element in the soil (Breeuwsma and Schoumans 1987; Breeuwsma et al. 1995). The same molar ratio, P/(Al+Fe), has also been proposed using Mehlich-III-extractable P, Al and Fe and called the P saturation ratio (PSR) (Maguire et al. 2001).

Many agricultural studies have tested the effectiveness of these ratios. In a lab study of six biosolids-amended agricultural soils with varying concentrations of Mehlich-III- and oxalate-extracted P, the authors conclude by recommending PSI to predict P leaching (Elliot et al. 2002). Maguire and Sims (2002) demonstrated in batch tests that P leaching began to increase quickly when PSR exceeded 0.2. Lu and O'Connor (2001) studied the effect of three different land-applied biosolids on two sandy soils in Florida – they hypothesized that the high Al and Fe content of the biosolids would increase the P retention. Although PSI was not specified, the ratio of P/(Al+Fe) was at the center of the study. They found that P sorption increased with oxalate extractable Al and Fe content of the soil, with an R^2 value of 0.7 (see Figure 3.1).

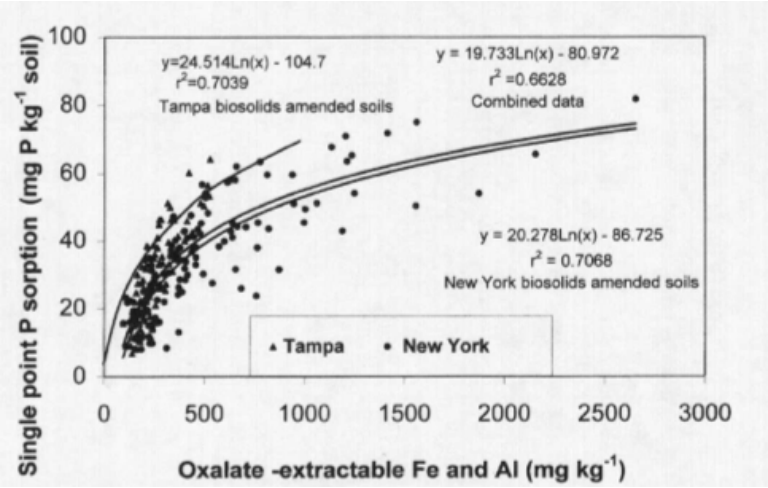


Figure 3.1. The relationship between P sorption capacity and oxalate-extractable Al and Fe in two different sandy soils, with biosolids from Tampa and New York applied. Taken from Lu and O'Connor (2001).

These ratios have also been applied to bioretention soils. O'Neill and Davis (2011) recommend PSI for predicting P leaching from BSMs, as they found a linear relationship between P leaching and PSI with an R^2 of 0.725 from a batch study of water treatment residuals (WTR)-amended soils. They recommend that bioretention soils intended to efficiently remove P should have a PSI below 0.05.

In Brown et al. (2016), PSI was investigated by creating soil columns with the same soil components and bringing them to PSIs of 0.1, 0.5, and 1.0 by adding either Fe-based WTRs to reduce the PSI or ammonium phosphate to increase the PSI. Clear differences in P leaching were seen between all three PSI levels (see Figure 3.2), with the soil with the highest PSI leaching the most P and the soil with the lowest PSI leaching the least P. It was also noted in this study that P leaching from all PSI levels decreased over time.

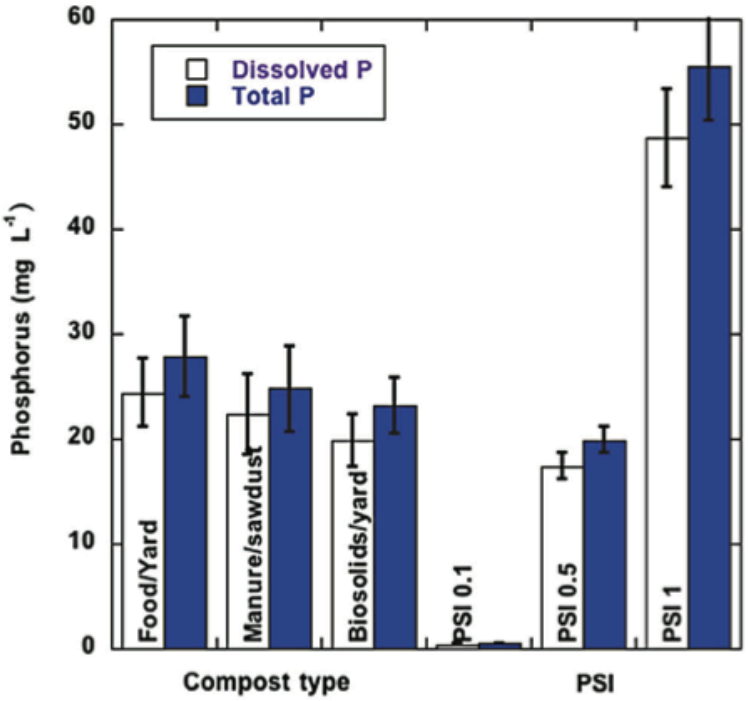


Figure 3.2. Dissolved and total P in effluent from bioretention columns contain three different composts, and columns containing those composts which have been artificially brought to PSI levels of 0.1, 0.5, and 1.0. Taken from Brown et al. (2016).

Phosphorus in Bioretention

Many bioretention soil media (BSMs) have been found to act as source of P rather than a sink. There have been conflicting results with how performance of these mixtures changes with time, with some studies showing that concentrations of P in effluent water from BSMs decrease over time (Brown et al. 2016; Hatt et al. 2008; Dietz and Clausen 2006; Hsieh and Davis 2003) and other studies have shown P concentrations in effluent increase over time (Yang et al. 2010; Lu and O'Connor 2001).

With the exception of those studies mentioned above which look at PSI or PSR as predictors, most bioretention studies that have looked at P leaching have taken the approach of adding and testing specific components to BSMs that are expected to bind P. Water treatment

residuals (WTRs) are one such component. Many studies have shown that the addition of WTRs controls P leaching in agricultural soils (Novak and Watts, 2004; Dayton and Basta, 2005a; Elliott et al., 2005; Agyin-Birikorang et al. 2007). Furthermore, it has been shown that P sorbed to WTRs does not desorb over time (Agyin-Birikorang et al. 2007; Agyin-Birikorang and O'Connor 2007; Ippolito et al., 2003; Makris et al., 2004). WTRs are Al- or Fe-based byproducts of the drinking water treatment process. Al and Fe salts are added to water as flocculants to create clearer water and to remove contaminants, and WTR are the Al and Fe hydroxides that result. WTRs are generally disposed of in landfills, and thus can be obtained for free or at low cost (Agyin-Birikorang et al. 2007; Makris et al. 2005).

WTRs have been tested for their effectiveness at controlling P leaching in bioretention systems. Lucas and Greenway (2011) tested P removal in bioretention mesocosms with Al-WTRs, red mud (a by product of aluminum processing), and clay mixed with sand. The mesocosms were dosed with synthetic stormwater for over 80 weeks to achieve the equivalent to 40 years' worth of P loading in the field. The mesocosms with WTR removed P most efficiently, with 90% removal throughout the course of the trial. O'Neill and Davis (2011) did a batch and mini-column study of sandy loam soil with varying amounts of Al-WTR added, and found that increased WTR content resulted in increased P sorption capacity. They noted further variables influencing P sorption – decreasing fines content increased P sorption, and intermittent flow (i.e. drying and wetting of the soil versus continual moisture) reduced P sorption. A column study based on their findings was performed, and it was found that loamy sand columns with 5% Al-WTR and 3% bark mulch removed 88.5% of P by mass. This was

compared to similar columns without WTR that actually added 71.2% to the mass of influent P (O'Neill and Davis 2012).

Finally, Palmer et al. (2013) did a greenhouse study of columns with BSM composed of sand, food/yard waste compost, shredded bark, and Al-WTRs, and found that inorganic phosphate was removed from all columns at rates between 58 and 81%. This study shows only a snapshot, as it was conducted over a period of one month and thus ignored any possible changes over time. Despite these limitations, Palmer et al. conclude that Al-WTRs are an effective P removal component.

Although much research has been done to compare the effectiveness of BSMs at removing P from stormwater, little has been done to find predictive measures for P leaching in bioretention. Measures such as the ammonium oxalate PSI and the Mehlich-III PSR have been used in agriculture to predict P leaching, but it has not been thoroughly demonstrated that these tools translate to bioretention systems. This study was conducted to evaluate the PSI and Mehlich-III extractions for their predictive ability across a wide range of BSM mixtures. In addition, the importance of WTR in bioretention mixtures was examined by establishing paired treatments at similar PSI both with and without WTRs.

Methods

BSM preparation

Columns measuring 9.5 cm in diameter and 45.75 cm in height were set up in a randomized complete block design with 4 replicates of each treatment. A range of different BSMs was included in the design. These are described below in Table 3.1. The columns had 2 cm holes in

the center of the base for leachate collection, which were covered in mesh to prevent loss of soil media and fitted with plastic tubes to direct flow into collection buckets. The insides of the columns were sanded with coarse sandpaper to prevent preferential flow of water along the sides. To ensure even packing of BSM, each column was filled to the top then dropped three times from 5 cm above the work surface. Columns were then refilled to the top and tamped down with a 1kg weight dropped from 5cm above the column three times. Columns were kept in a controlled environment greenhouse at the University of Washington.

Table 3.1. Description of 14 BSMs

Label	Treatment	Volume (%)	Dry Weight (%)
C40-FY	Food/Yard Compost	40	9
	Sand	60	91
C40-B	Biosolids/Yard Compost	40	9
	Sand	60	91
C40-W*	Biosolids/Yard Compost	35	8
	Sand	60	90
	Water Treatment Residuals	5	2
C80	Biosolids/Yard Compost	80	38
	Sand	20	62
C20	Biosolids/Yard Compost	20	4
	Sand	80	96
C20-W **	Biosolids/Yard Compost	17.5	3
	Sand	80	96
	Water Treatment Residuals	2.5	1
Sand	Sand	100	100
C15-SS	Biosolids/Yard Compost	15	3
	Sand	80	97
	Sawdust	5	0
C15-OS	Biosolids/Yard Compost	15	3
	Sand	80	92
	Oyster Shells	5	6
DCB8-LCS	Sand	49	80
	Loamy Clay	30	12
	High Fe Biosolids	20	8
DCB20	Sand	49	80
	High Fe Biosolids	51	20
DCC20	Sand	49	80
	High Fe Biosolids Compost	51	12
DCB40-FSS	Sand	1.2	15
	Sawdust	85.5	40
	High Fe Biosolids	12.9	40
	Mineral Fines	0.4	5
DCB50-SS	Sand	3	25
	Sawdust	75	25
	High Fe Biosolids	23	50

* Brought to same PSI as C40-B with addition of P salts, ** Brought to same PSI as C20 with addition of P salts

Mix proportions are presented in Table 3.1 above by volume and by dry weight. Both methods are used independently in different stormwater guidelines depending on region and convention. It should be noted that volume and dry weight proportions can be very different and do not necessarily grow at the same rate – for instance, doubling the volume proportion of compost from 40 to 80% corresponds to more than quadrupling the dry weight proportion of compost from 9 to 38%. This is due to the greater bulk density of sand – when compost volume increases, sand volume must decrease, and thus the overall weight is lowered.

This chapter will begin by focusing on the four "paired" treatments: C40-B/C40-W and C20/C20-W. The "-W" treatments have 5% and 2.5% less compost (respectively) than their pairs but the same proportion of sand; the difference is made up by the addition of WTRs. Calcium phosphate was added to C20-W and C40-W during mixing in order to bring the PSI to equal that of their paired treatments. This was done so that the effects of WTR on contaminant removal could be seen independent of its effect on PSI. Salts were dissolved in 500ml water and poured onto the soil mixture by alternating aliquots of soil and salt solution and thoroughly mixing between additions. Treatment C40-FY is the standard BSM used in the Seattle, WA metropolitan area and was included for the purposes of comparison (City of Seattle 2011).

Sand for the study was a silica sand with d_{60} of 0.4 mm, and was obtained from a commercial compost and soil supplier where it had been stored outdoors (Sawdust Supply 2016). Loamy clay soil for the study was a commercial topsoil, and sawdust was a fine alder sawdust, both obtained from the same supplier described above. The high Fe biosolids and high Fe biosolids compost were provided by District of Columbia Water. This compost was made from biosolids and wood chips in equal portion by wet weight. These biosolids and the

compost made from these biosolids are high in Fe because Fe is added during DC Water's wastewater treatment process to precipitate P from the effluent. The yard/food compost used in C40-FY was produced from yard waste and food scraps by a Seattle, WA area composter and is the compost that is most commonly used in bioretention system treatments in the Seattle area. The biosolids/yard compost was provided by Sawdust Supply and produced from anaerobically digested biosolids and yard waste. WTRs were acquired from Seattle Public Utilities, where they were used for drinking water treatment. Oyster shells were acquired from a Seattle, WA area restaurant and shattered with a hammer into small shards.

Prior to column packing, aliquots of each BSM were taken for preliminary soil analysis. Samples were dried at room temperature. Total C and N were analyzed by combustion using a Perkin Elmer CHN analyzer model 2400. Phosphorous Saturation Index (PSI) of each BSM was determined by analyzing for P, Fe and Al using a 6:1 ratio of 0.2 M acid oxalate solution to soil, followed by agitation for four hours, filtration using #40 Whatman paper, 1:4 dilution with 0.01 M HCl, and analysis using a Thermo Scientific Co. inductively coupled plasma mass spectrometer (ICP-MS) Model 6300 (modified from McKeague and Day 1966 as described in Sparks 1996). BSMs were also assessed for Mehlich-III extractable P, Al, and Fe using 2 g soil: 20 mL Mehlich-III solution, followed by agitation for 5 minutes, filtration using #40 Whatman paper and analysis using the ICP-MS described above (Mehlich 1984). Blanks and duplicates were routinely used in analysis.

Leaching events

Storm events were simulated by pouring stormwater into the columns at predetermined volumes. Water was allowed to pool at the top of the columns to simulate bioretention conditions in the field. Storm events represented 24 hour storms in Seattle, WA with return frequencies of either 0.2 years for a rainfall depth of 0.9 inches (900 mL per column) or one year for a rainfall depth of 1.8 inches (1600 mL per column) (City of Seattle 2016). Water volumes were calculated to reflect a bioretention system that was designed to collect 90% of the runoff from an impervious catchment of which the bioretention surface represents 6.5% of the area. Leachate was collected through the tubes at the bottoms of the columns during each event and for four hours after.

The first 4 leaching events were done with synthetic stormwater spiked with high concentrations of metals and typical concentrations of nutrients. The synthetic stormwater (High metal) was made by diluting concentrated solutions of $CuSO_4$, $(CH_3CO_2)_2Zn\ 2H_2O$, $NH_4H_2PO_4$, $CdCl_2$, $CrCl_3\ 6H_2O$, and $(CH_3COO)_2Pb\ 3H_2O$ into tap water at predetermined quantities. The subsequent or 5^{th} leaching was done with tap water to assure that there was no carry over of metals. The 6^{th} -8^{th} leachings were carried out with a synthetic stormwater that had lower concentrations of metal contaminants, made with the same chemicals described above (Brown et al. 2016; Maestre and Pitt 2005). The remaining leachings (9-12) were carried out using actual stormwater collected as runoff from a major Seattle highway bridge and stored in plastic carboys at 3°C for no longer than seven days. Rye grass was planted in the columns after leaching event 12 and allowed to mature, after which the final two leachings, 13a and 13b, were conducted as follows: leaching 13a was performed only on the first 10 treatments (those without high Fe biosolids) and was done with synthetic stormwater that was spiked only

with $NH_4H_2PO_4$, while leaching 13b was performed on the last 5 treatments (those containing high Fe biosolids) as well as the sand and C40-FY treatments and was done with tap water. A schedule of the leachings is shown below (Table 3.2), followed by a description of the metals and nutrient concentrations in each type of stormwater (Table 3.3). Columns were kept moist with tap water until the first leaching and were also kept moist in between leaching events to avoid the complicating effects of drying and wetting seen in previous studies (Mullane et al. 2015; Li and Davis 2014; Hsieh et al. 2007).

Table 3.2. Schedule of water type and volume used for each leaching.

Event	Date	WA Return Interval	Stormwater Type
		yrs	
1	5/12/14	0.2	High metal synthetic
2	5/27/14	1	High metal synthetic
3	6/9/14	0.2	High metal synthetic
4	7/7/14	1	High metal synthetic
5	7/21/14	0.2	Tap
6	8/4/14	1	Low metal synthetic
7	8/18/14	0.2	Low metal synthetic
8	9/22/14	1	Low metal synthetic
9	11/4/14	0.2	Actual
10	12/2/14	0.2	Actual
11	1/20/15	1	Actual
12	1/27/15	1	Actual
Grass planted			
13a	6/8/15	0.2	Synthetic (nutrients only)
13b	7/3/15	0.2	Tap

Table 3.3. Concentration of metal and nutrient contaminants in all water types. Numbers represent means ± one standard deviation for all events of the same water type.

Contaminant	Tap water	High metal	Low metal	Actual

				synthetic	synthetic	stormwater*
P	Dissolved	mg/L	<MDL	0.52 ± 0.28	0.60 ± 0.84	0.04 ± 0.01
	Total		0.04 ± 0.02	1.49 ± 0.22	2.01 ± 0.08	0.08 ± 0.03
NO_3-N	Dissolved		0.04 ± 0.02	0.07 ± 0.01	0.05 ± 0.01	0.40 ± 0.32
NH_4-N	Dissolved		0.007 ± 0.001	0.79 ± 0.09	1.13 ± 0.10	0.57 ± 0.40
Total N	Total		0.12 ± 0.01	0.95 ± 0.10	1.08 ± 0.04	1.79 ± 0.97
Cd	Dissolved	µg/L	13.2 ± 12.6	3792 ± 1283	124 ± 187	4.08 ± 2.67
	Total		13.5 ± 12.9	3864 ± 1317	436 ± 16	5.97 ± 4.37
Cr	Dissolved		0.31 ± 0.04	27.0 ± 40.1	0.53 ± 0.24	3.12 ± 1.30
	Total		0.32 ± 0.05	1267 ± 193	400 ± 111	6.90 ± 3.07
Cu	Dissolved		21.7 ± 2.4	211 ± 173	5.78 ± 7.49	18.25 ± 5.76
	Total		25.4 ± 3.0	2882 ± 1243	525 ± 132	39.8 ± 19.1
Pb	Dissolved		10.4 ± 4.9	93.8 ± 48.1	4.39 ± 6.29	1.91 ± 1.64
	Total		12.4 ± 5.4	7827 ± 1698	781 ± 197	20.83 ± 2.89
Zn	Dissolved		116 ± 5.5	2772 ± 482	40.1 ± 58.7	113 ± 90.8
	Total		113 ± 4.2	3503 ± 498	950 ± 178	172 ± 87
Turbidity		BTU	0.41 ± 0.06	18.5 ± 8.4	2.67 ± 1.63	28.4 ± 11.3

*Actual stormwater has a high standard deviation for all values due to variations between stormwater collected on different days. **Event 13a had metal concentrations matching those presented for tap water. Nutrient concentrations for this event were (in mg/L) Total N: 3.81 ± 0.02, NO_3-N: <MDL, NH_4-N: 36 ± 0.06, Total P: 9.04 ± 0.14.

Leachate volume was recorded and then the leachate was divided into aliquots for different analyses and delivered to King County Environmental Lab for analysis of total and dissolved Cd, Cr, Cu, Pb, Zn, P and N. Leachate samples for determination of dissolved metals and P were prepared using EPA Method 200.8, while total metals and P were analyzed using EPA Method 200.7, and all were run with a Thermo X-series II ICPMS with Collision Cell Technology (Brockhoff et al., 1994). Samples were analyzed for total N (TN), NO_3-N, and NH_4-N using SM4500-NO3F NO3, SM4500-N-C, and the procedure described in Keruoel and Aminot

(1997), respectively. Finally, one aliquot per column was measured on-site for turbidity using a Hatch 2100b turbidimeter.

Infiltration Rate and Vegetation

The infiltration rate of each column was measured using the single-ring falling head procedure after the 12th leaching before grass was planted. Each column was wetted with 500 mL of tap water and allowed to drain. An additional 500 mL was then added, and the time required to infiltrate the soil was measured.

After the 12th leaching event, 0.8 grams of rye grass seed was planted in each column based on a seeding rate of 420 kg ha-1 (Oregon Ryegrass Commission 2013). Grass was allowed to grow for 4 weeks, at which point the grass was harvested to 2 cm above the soil. Biomass was rinsed and dried in a drying oven at 105°C, and weighed to determine dry yield. The grass was allowed to regrow for two months after this harvest, at which time the 13th storm event was simulated. The leachate from events 13a and 13b was analyzed only for total N, P, and NO_3^- N, to gain an understanding of the impact of growing grass on the mobility of these nutrients.

Final Soil Analysis

Once all leachings were complete, the soil media were extracted from their columns. Grass roots were separated out by hand and the BSM from each column was homogenized, after which an aliquot was separated from each column and allowed to dry at room temperature for 5 days. The air-dried soil was sieved to 2 mm. Soil pH was measured at a 2:1 volume ratio of DI water to dry soil. Ammonium oxalate-extractable P, Al, and Fe, as well as

total C and N were analyzed as described above. BSMs were also assessed for Mehlich-III extractable P, Al, and Fe as described above. Duplicates, blanks and known standards were routinely used in all analyses.

Data Analysis

Results were normalized by either natural log transformation, 1/sqrt(x), or $\ln(x)^2$ transformations to minimize skewness and kurtosis. Data were then analyzed in R using one- and two-way ANOVAs and the Tukey HSD post-hoc test for multiple means comparison. Linear and logarithmic regression models were made to investigate different predictors of performance, and were analyzed for R^2 and p-value. Outliers were identified using standard residuals and removed from ANOVAs and regression models. A stepwise regression was also performed in R to narrow down predictors for a multiple regression.

Results and Discussion

Soil Analysis of BSMs: Ammonium Oxalate Extraction

The results of ammonium oxalate extractions of P, Fe, and Al from the pre- and post-treatment BSMs are shown below in Table 3.4. The pre-trial results confirm the BSMs were mixed successfully – extractable P increases with compost portion (by weight) as expected, and the paired WTR/non-WTR treatments are shown to have similar PSI. Treatments C20 and C20-W have PSIs of approximately 0.4 and C40-B and C40-W have PSIs of approximately 0.7. The treatments containing WTRs would be expected to have higher Fe content than their paired treatments, which was also observed. They would also be expected to have higher P content

than their paired treatments due to the addition of P salts to raise PSI, and this was observed as well.

Ammonium oxalate extractions were also performed on BSM mixtures at the end of the trial. There was a notable decrease in soil PSI in all treatments between the beginning and end of the trial, although no change had been expected. The change is shown below in Figure 3.3. The treatments containing high Fe biosolids saw a smaller reduction in PSI than the other 9 treatments. Those without high Fe biosolids had their PSI reduced by over half. The change in PSI can partially be attributed to a universal loss of extractable P over the course of the trial, which may be explained by the finding that these treatments were all sources of P for the majority of the experiment – this will be discussed for select treatments below. Treatments with the largest decrease in PSI also had increased levels of extractable Al and Fe by the end of the trial as well as decreased extractable P – this is true of C20, C40-B, C15-OS, C15-SS, and sand. C20-W, C40-FY, DCB8-LCS, and DCB40-FS all saw no significant change in extractable Al and Fe over the course of the trial. Finally, C40-W, C80, DCB20, DCC20, and DCB50 all saw decreases in extractable Al and Fe over time.

Table 3.4. Pre- and post-trial ammonium oxalate-extractable P, Fe and Al as well as the Phosphorus Saturation Index (PSI), which is the molar ratio of ammonium oxalate P/(Fe + Al).

	Pre-trial			
	P	**Al**	**Fe**	**P/(Fe+Al)**
	mmol kg^{-1}			
C20	6.8 ± 0.4	5.0 ± 0.1	11.0 ± 0.3	0.43 ± 0.02
C20-W	14.7 ± 0.2	8.1 ± 0.5	24.9 ± 1.3	0.45 ± 0.02
C40-FY	10.0 ± 0.3	12.6 ± 0.5	21.0 ± 1.4	0.30 ± 0.03
C40-B	15.4 ± 0.9	7.8 ± 0.1	15.0 ± 0.1	0.67 ± 0.03
C40-W	62.5 ± 5.3	16.3 ± 0.4	72.5 ± 2.4	0.70 ± 0.04
C80	89.1 ± 1.1	23.0 ± 0.3	47.7 ± 0.3	1.26 ± 0.02

SAND	3.6 ± 2.3	4.9 ± 1.0	9.9 ± 0.8	0.26 ± 0.18
C15-SS	12.9 ± 1.6	6.9 ± 0.9	15.3 ± 1.1	0.58 ± 0.02
C15-OS	3.9 ± 0.6	5.9 ± 0.2	11.2 ± 0.5	0.23 ± 0.03
DCB8-LCS	53.6 ± 10.2	33.1 ± 5.5	67.8 ± 9.2	0.53 ± 0.02
DCB20	240.7 ± 57.9	116.3 ± 26.8	226.4 ± 49.1	0.70 ± 0.01
DCC20	121.5 ± 41.4	55.8 ± 17.6	119.5 ± 33.8	0.69 ± 0.03
DCB40-FS	46.0 ± 6.4	26.3 ± 2.6	45.0 ± 4.2	0.64 ± 0.03
DCB50-SS	492.8 ± 21.6	186.9 ± 8.4	362.2 ± 15.0	0.90 ± 0.00

	Post-trial			
	P	**Al**	**Fe**	**P/(Fe+Al)**
	mmol kg^{-1}			
C20	4.8 ± 0.3	9.3 ± 0.6	21.0 ± 3.9	0.16 ± 0.02
C20-W	5.9 ± 0.5	11.9 ± 3.3	31.5 ± 8.0	0.14 ± 0.03
C40-FY	4.4 ± 0.3	11.8 ± 0.4	23.8 ± 2.2	0.12 ± 0.01
C40-B	8.0 ± 0.8	10.9 ± 0.8	23.2 ± 2.7	0.23 ± 0.00
C40-W	28.2 ± 1.9	14.0 ± 1.1	49.3 ± 2.5	0.45 ± 0.01
C80	29.5 ± 2.1	17.3 ± 1.4	32.0 ± 1.8	0.60 ± 0.03
SAND	1.6 ± 0.3	13.4 ± 1.0	32.2 ± 4.9	0.04 ± 0.00
C15-SS	2.6 ± 0.3	13.3 ± 2.2	33.3 ± 4.4	0.06 ± 0.01
C15-OS	2.4 ± 0.4	10.3 ± 0.2	29.1 ± 1.9	0.06 ± 0.01
DCB8-LCS	34.4 ± 7.1	29.1 ± 3.6	57.2 ± 5.6	0.39 ± 0.04
DCB20	49.1 ± 9.1	30.5 ± 3.1	70.0 ± 8.1	0.48 ± 0.04
DCC20	36.8 ± 3.1	26.6 ± 1.1	60.8 ± 4.9	0.42 ± 0.02
DCB40-FS	31.5 ± 4.5	26.3 ± 5.1	43.3 ± 4.5	0.46 ± 0.06
DCB50-SS	319.2 ± 38.3	145.4 ± 17.7	283.8 ± 31.8	0.74 ± 0.00

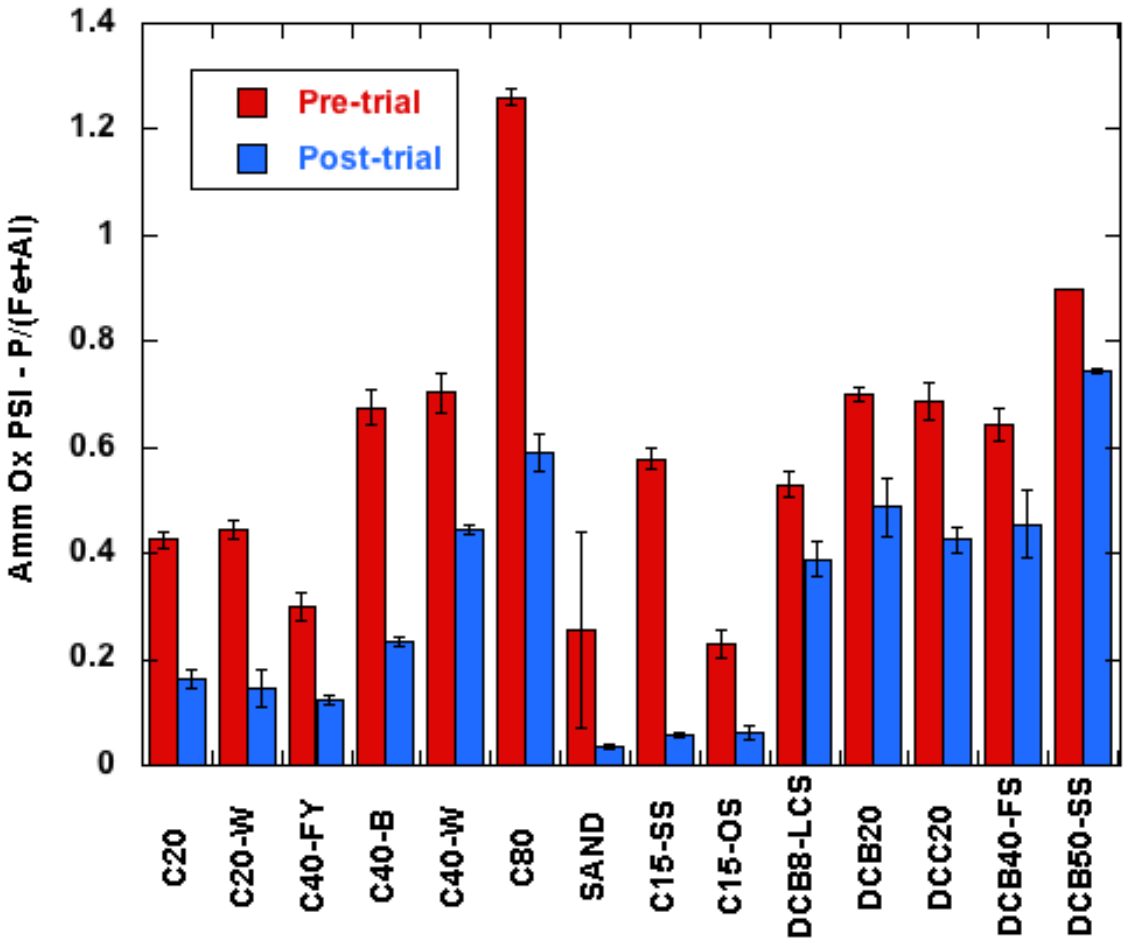


Figure 3.3. Pre- and post-trial Phosphorus Saturation Index (PSI), which is the molar ratio of ammonium oxalate P/(Fe + Al). Error bars represent +/- one standard deviation.

Soil Analysis of BSMs: Mehlich-III Extraction

The results of Mehlich-III extractions of P, Fe, and Al from the pre- and post-trial BSMs are shown in Table 3.5. The pre-trial Mehlich-III extraction data follow similar patterns to the ammonium oxalate extraction data above. For instance, the paired WTR/non-WTR treatments were chemically brought to the same oxalate PSI, and since the Mehlich-III PSR describes the same ratio with the only change being the extraction reagent, the PSR of the paired treatments were expected to be similar. They were not necessarily expected to be identical, however, since different reagents potentially target different fractions of total Al, Fe and P. This was achieved,

with C20/C20-W at PSRs of ~0.6 and C40-B/C40-W at PSRs of 1.6 and 1.9, respectively. The treatments containing WTRs were shown to have higher P and Fe content than their paired treatments, as shown above.

Similar to oxalate PSI, the Mehlich-III PSR decreased for all treatments from pre- to post-trial extractions (Table 3.5). This change is shown below in Figure 3.4. Here the decrease in PSI is due to a universal increase in extractable Al and Fe over the course of the trial – the only exception is treatment C40-W, which saw a decrease in Al. Treatments behaved differently with respect to extractable P over the course of the trial – C20, DCB8-LCS, DCB20, and DCB40 saw an increase in extractable P; C40-FY, C80, and C15-SS saw a decrease; and C20-W, C40-B, C40-W, sand, C15-OS, and DCB50 all saw no significant change in extractable P.

The discrepancy between the changes shown by the oxalate extraction and the Mehlich-III extraction suggests that the fraction of total P solubilized by the two extractions is not identical. The differences between the two extractions will be explored in more depth later in this chapter.

Table 3.5. Pre- and post-trial Mehlich-III-extractable P, Fe and Al as well as the Phosphorus Saturation Ratio (PSR), which is the molar ratio of Mehlich-III extractable P/(Fe + Al).

	Pre-trial			
	P	**Al**	**Fe**	**P/(Fe+Al)**
		mmol kg^{-1}		
C20	3.8 ± 0.0	4.2 ± 0.0	2.4 ± 0.0	0.58 ± 0.01
C20-W	6.1 ± 0.6	4.3 ± 0.2	5.6 ± 0.1	0.62 ± 0.04
C40-FY	5.6 ± 0.6	7.2 ± 0.4	3.1 ± 0.2	0.54 ± 0.03
C40-B	9.1 ± 0.2	3.2 ± 0.2	2.3 ± 0.1	1.65 ± 0.15
C40-W	26.4 ± 0.6	8.5 ± 0.1	5.3 ± 0.1	1.91 ± 0.02
C80	46.9 ± 1.5	10.4 ± 0.0	4.6 ± 0.0	3.12 ± 0.12
SAND	0.3 ± 0.0	3.4 ± 0.1	1.6 ± 0.1	0.05 ± 0.00
C15-SS	5.9 ± 0.6	4.4 ± 0.1	2.6 ± 0.0	0.85 ± 0.10

C15-OS	1.8 ± 0.2	3.3 ± 0.2	1.8 ± 0.0	0.35 ± 0.06
DCB8-LCS	9.2 ± 0.5	13.6 ± 1.3	4.5 ± 0.1	0.51 ± 0.01
DCB20	11.1 ± 1.1	13.3 ± 1.3	4.7 ± 0.1	0.62 ± 0.01
DCC20	11.6 ± 0.1	14.0 ± 0.1	5.0 ± 0.2	0.61 ± 0.01
DCB40-FS	4.6 ± 0.0	9.3 ± 0.0	3.6 ± 0.1	0.35 ± 0.00
DCB50-SS	17.2 ± 0.3	21.7 ± 0.1	7.6 ± 0.1	0.59 ± 0.01

	Post-trial			
	P	**Al**	**Fe**	**P/(Fe+Al)**
		mmol kg^{-1}		
C20	5.2 ± 1.4	9.6 ± 2.2	5.7 ± 1.4	0.34 ± 0.03
C20-W	6.4 ± 0.9	8.7 ± 0.4	7.7 ± 0.7	0.39 ± 0.03
C40-FY	3.9 ± 0.7	9.6 ± 1.0	4.6 ± 0.6	0.28 ± 0.02
C40-B	10.8 ± 3.7	10.0 ± 3.0	6.6 ± 1.6	0.64 ± 0.07
C40-W	24.3 ± 4.4	5.0 ± 1.3	10.7 ± 0.4	1.58 ± 0.40
C80	26.3 ± 2.0	15.6 ± 1.1	9.1 ± 0.5	1.06 ± 0.02
SAND	0.4 ± 0.0	7.5 ± 0.5	3.0 ± 0.2	0.04 ± 0.01
C15-SS	1.8 ± 0.4	7.8 ± 0.5	4.5 ± 0.8	0.15 ± 0.02
C15-OS	1.9 ± 0.4	7.9 ± 0.4	3.6 ± 0.2	0.16 ± 0.03
DCB8-LCS	16.6 ± 1.2	24.6 ± 2.9	12.7 ± 0.3	0.45 ± 0.01
DCB20	16.1 ± 0.9	20.6 ± 0.9	12.5 ± 0.5	0.49 ± 0.01
DCC20	17.6 ± 1.8	21.9 ± 2.9	12.8 ± 0.7	0.51 ± 0.01
DCB40-FS	11.2 ± 3.8	22.7 ± 6.3	11.6 ± 1.5	0.32 ± 0.03
DCB50-SS	18.8 ± 1.7	40.7 ± 1.8	12.2 ± 0.2	0.35 ± 0.02

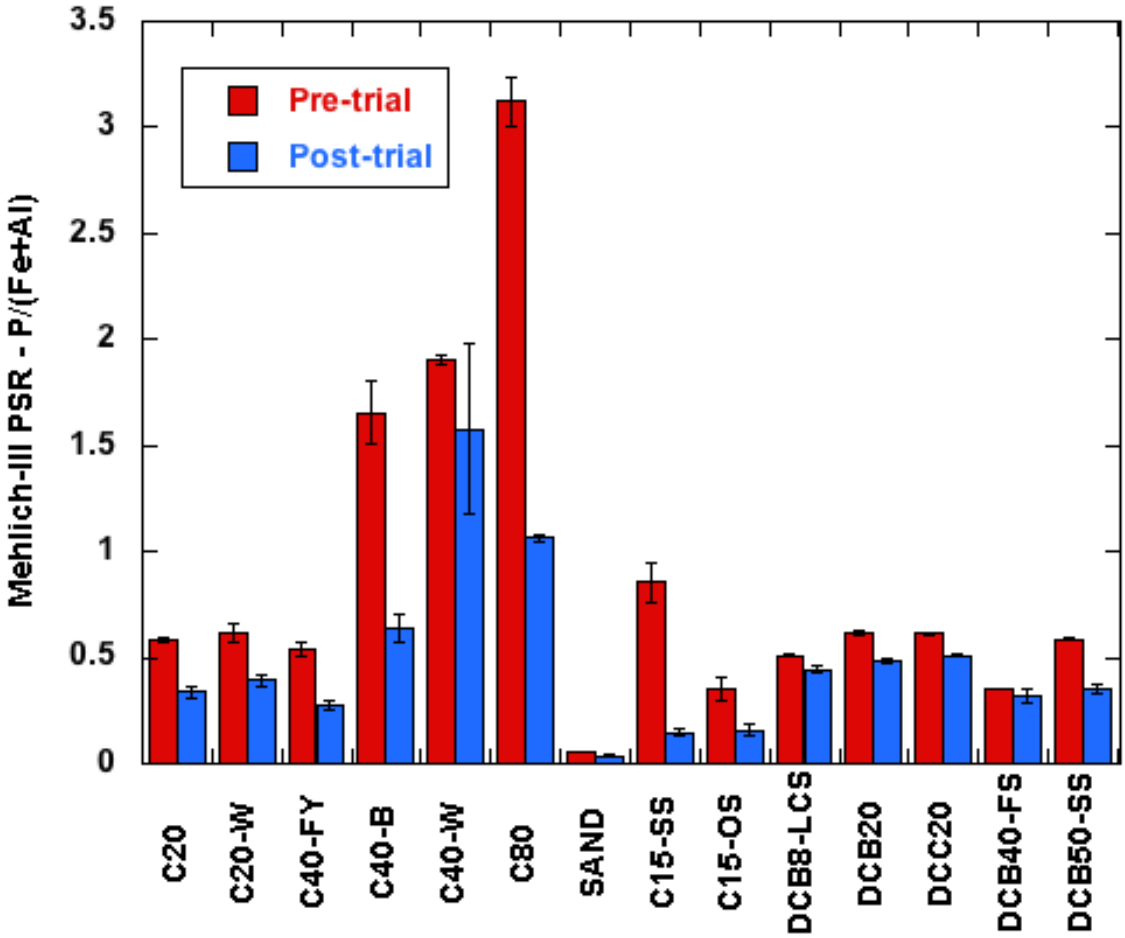


Figure 3.4. Pre- and post-trial Phosphorus Saturation Ratio (PSR), the molar ratio of Mehlich-III extractable P/(Fe + Al). Error bars represent +/- one standard deviation.

Phosphorus Leaching in Paired Treatments

Four treatments (C20/C20-W and C40-B/C40-W) were specifically paired to have the same PSI with and without WTRs. The performance of these treatments will provide some insight into the impact of WTRs on BSM performance and the effectiveness of PSI as a predictor of P leaching.

The influent concentrations of P were relatively consistent across influent water types (see Table 3.3 above), so water type will be ignored as a variable. A two-way ANOVA for effluent P concentrations with time and BSM treatment as independent variables shows that

both independent variables and their interaction are significant with $p<0.000$. Dissolved and total P concentrations in leachate from each treatment were similar throughout the trial (see Table 3.6), so only total P will be discussed here in detail.

Table 3.6. Effluent concentrations of dissolved and total P from selected events. Data from every third event are included in order to show the pattern over time. Influent data are missing for event 1. Groups are the result of a post hoc Tukey HSD test on all 14 treatments for each event. Shared letters indicate statistically similar means.

Event	Treatment	Dissolved P (mg/L)		Total P (mg/L)	
1	Influent		-		-
	C20	d	30.13 ± 2.29	c	35.65 ± 3.60
	C20-W	c	10.61 ± 1.83	b	12.30 ± 2.17
	C40-FY	a	3.76 ± 0.31	a	5.24 ± 0.20
	C40-B	e	55.03 ± 2.54	d	60.90 ± 3.53
	C40-W	b	6.91 ± 0.70	b	8.99 ± 0.61
3	Influent		0.94 ± 0.04		0.75 ± 0.01
	C20	c	24.70 ± 3.99	c	20.45 ± 3.69
	C20-W	b	11.62 ± 1.30	b	10.57 ± 1.03
	C40-FY	a	4.29 ± 0.10	a	4.98 ± 0.16
	C40-B	d	42.48 ± 1.80	d	39.18 ± 2.02
	C40-W	b	8.40 ± 0.41	b	8.44 ± 0.39
6	Influent		1.09 ± 0.04		1.16 ± 0.12
	C20	c	15.63 ± 1.08	c	16.40 ± 1.22
	C20-W	b	7.89 ± 1.31	b	8.12 ± 1.50
	C40-FY	a	3.26 ± 0.53	a	3.76 ± 0.50
	C40-B	c	18.63 ± 2.13	d	23.90 ± 2.98
	C40-W	b	6.37 ± 0.34	b	7.58 ± 0.60
9	Influent		1.04 ± 0.08		0.17 ± 0.00
	C20	b	7.34 ± 3.12	b	8.63 ± 3.36
	C20-W	b	4.50 ± 0.96	b	5.24 ± 1.06
	C40-FY	a	2.29 ± 0.11	a	2.70 ± 0.07
	C40-B	c	14.50 ± 1.27	c	16.38 ± 1.74
	C40-W	b	4.52 ± 0.49	b	5.44 ± 0.33
12	Influent		1.47 ± 0.05		0.46 ± 0.02
	C20	c	4.81 ± 0.68	c	5.49 ± 0.80
	C20-W	b	3.21 ± 0.58	b	3.67 ± 0.65

	C40-FY	a	1.68 ± 0.23	a	1.88 ± 0.21
	C40-B	d	11.23 ± 0.85	d	12.48 ± 0.80
	C40-W	bc	3.70 ± 0.65	bc	4.24 ± 0.81

The patterns over time of P leached from the paired treatments are seen in Figures 3.5 and 3.6. P concentrations in leachate from the WTR treatments stay consistently low throughout the experiment, while the treatments without WTR start out with high effluent P and decrease over time. The difference in behavior over time is evident in the curve fits presented in Figures 3.5 and 3.6. The best fit for both non-WTR treatments was logarithmic due to the high initial concentrations of P in effluent, while the best fit for both WTR treatments was simply linear. For both paired treatments, the effluent concentrations of P from the WTR and non-WTR treatment are similar for the final three events. All four paired treatments were sources of P throughout the experiment.

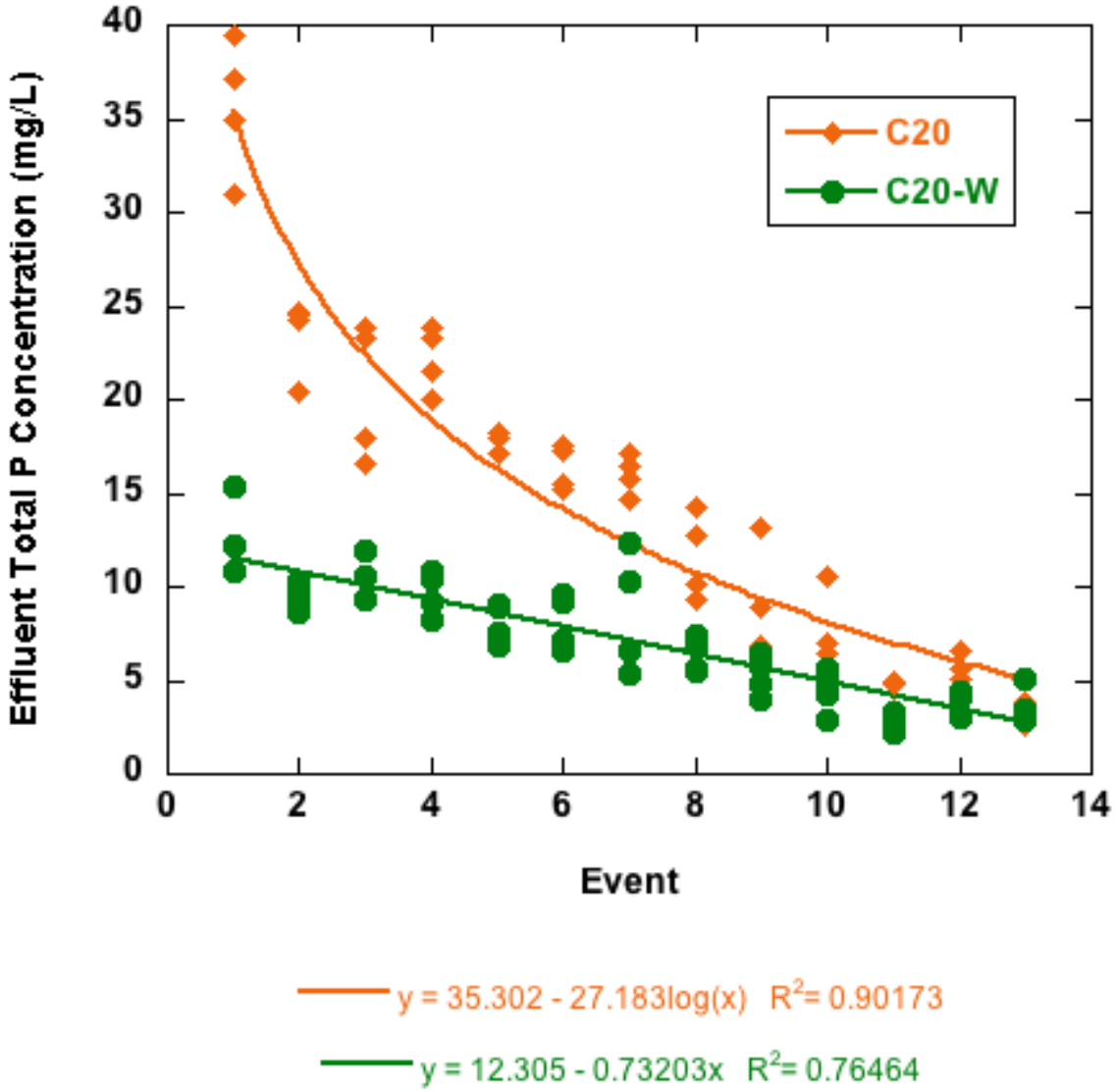


Figure 3.5. Concentration of total P in effluent (mg/L) from C20 and C20-W, both of which had a PSI of approximately 0.4. Curve fit equations and R^2 values are included below the graph.

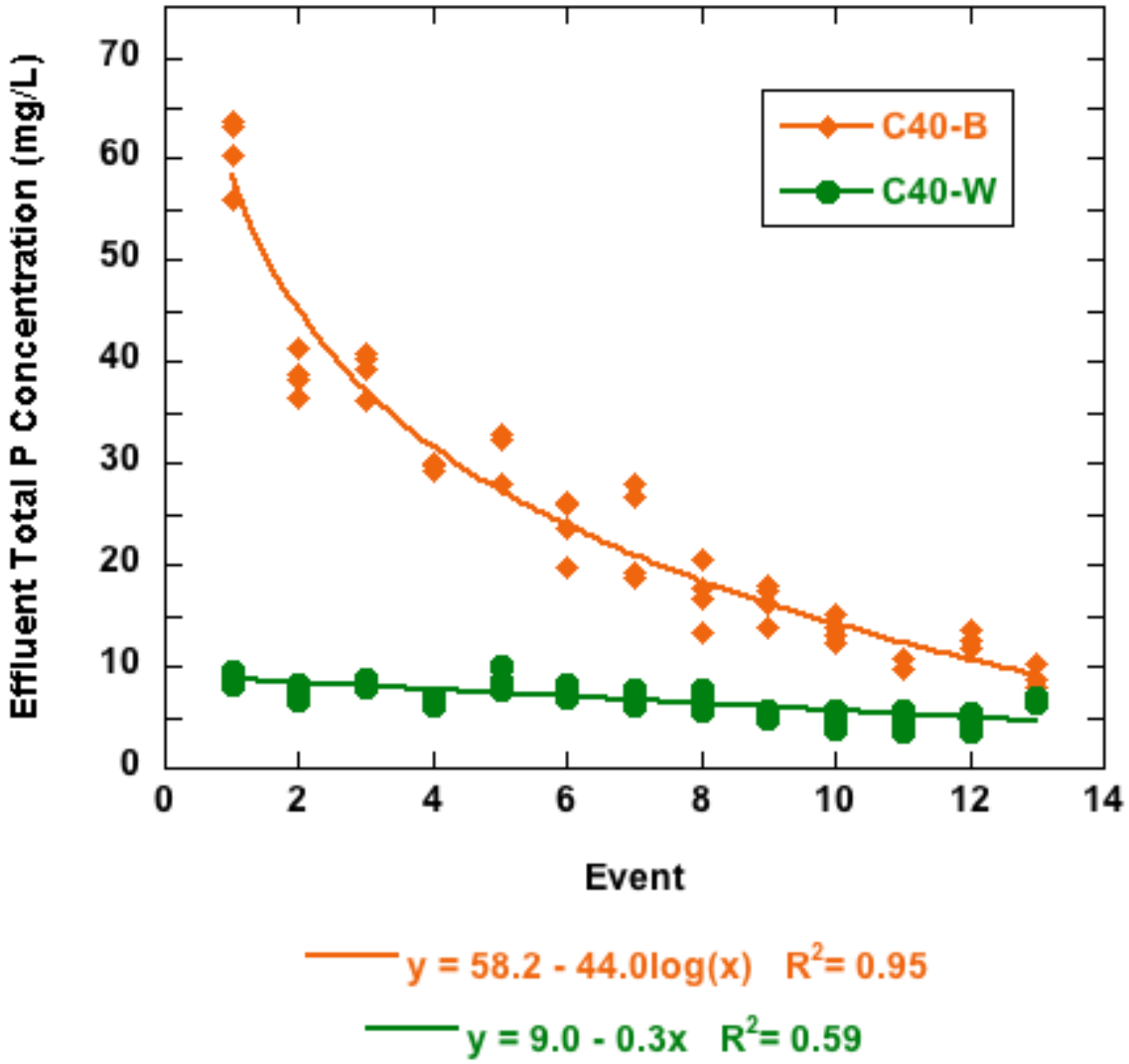


Figure 3.6. Concentration of total P in effluent (mg/L) from C40-B and C40-W, both of which had a PSI of approximately 0.7. Curve fit equations and R^2 values are included below the graph.

The overall effect of WTRs can be understood by comparing the total mass export of P from the paired treatments. These mass numbers are calculated for each replicate by multiplying the effluent concentration of the contaminant by the volume of effluent for each event, and then summing these values over all 14 events, as follows: *total mass = Σ(event n concentration)*(event n volume).* The final values are averages and standard deviations of these mass numbers for all four replicates per treatment. The same equation is used for influent mass

numbers, but using influent concentration and volume and averaging the totals from each of 3 samples taken from influent water per event. The mass export numbers in Table 3.7 and Figure 3.7 show that WTRs significantly decreased the export of both total and dissolved P in the paired treatments. All treatments were an overall source of total and dissolved P.

Table 3.7. Total mass of dissolved and total P in effluent. These mass numbers are calculated for each replicate as follows: *total mass = Σ(event n concentration)*(event n volume).* The final values are averages and standard deviations of these mass numbers for the four replicates in each treatment. Groups are the result of a post hoc Tukey HSD test on all 14 treatments tested; shared letters indicate statistically similar means.

	Dissolved P	**Total P**
	mg	
Influent	5.3 ± 0.4	24.2 ± 0.4
C20	c 181 ± 12.6	c 201.1 ± 14.7
C20-W	b 90 ± 6.6	b 100.5 ± 7.5
C40-FY	a 41 ± 2.1	a 48.3 ± 2.1
C40-B	d 326 ± 11.2	d 343.6 ± 12.5
C40-W	b 81 ± 6.0	b 94.5 ± 6.0
C80	d 369 ± 18.3	d 395.1 ± 20.8

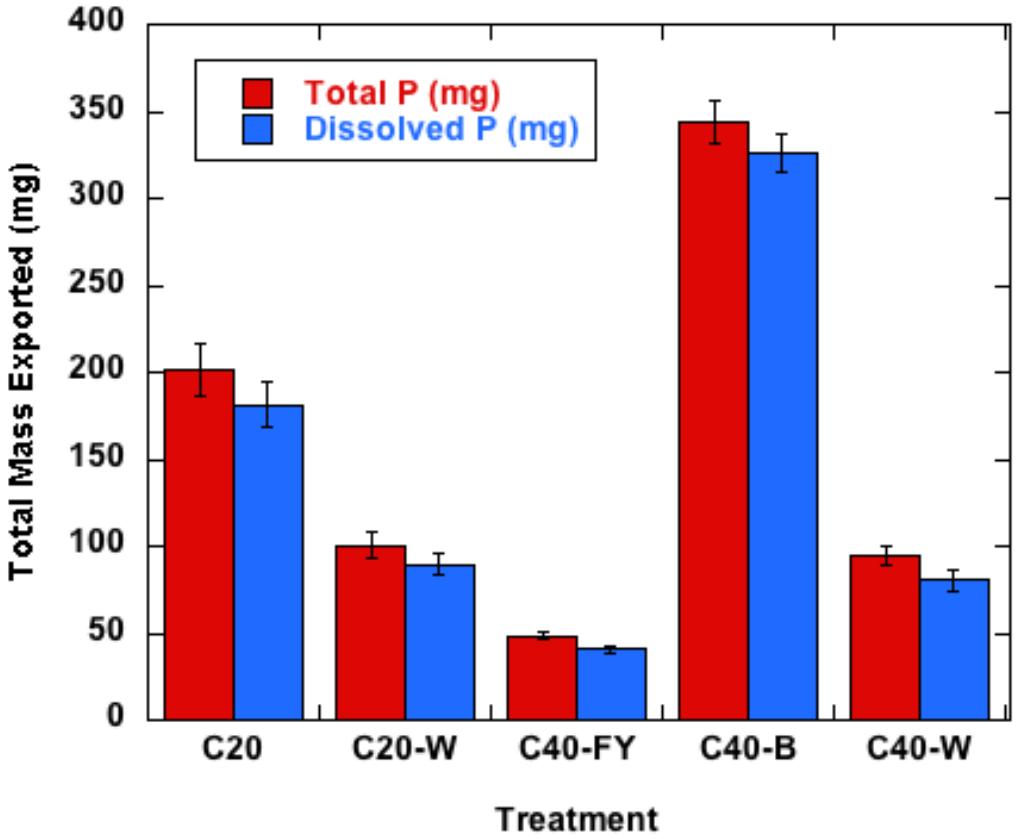


Figure 3.7. Mass export of total and dissolved P from C20, C20-W, C40-FY, C40-B, and C40-W. Total mass of P and dissolved P in influent were 24.2 and 5.3 mg respectively.

The differences in P leaching from the paired treatments were unexpected. Since paired treatments were chemically brought to the same PSI, it was expected that they would perform similarly with respect to P leaching, as previous studies have shown that PSI is a good predictor of soil P loss (Brown et al. 2016; O'Neill and Davis 2011; Lu and O'Connor 2001). Instead, it was found that even with the same PSI as the treatments that did not contain WTR, treatments with WTR exported less P. Furthermore, the two WTR treatments leached statistically similar amounts of P, even though C40-W began at a higher PSI than C20-W. The non-WTR treatments,

C40-B and C20, did behave as expected, with the higher PSI treatment (C40-B) leaching more P than the lower PSI treatment (C20).

These unexpected results may be due to the effect that WTRs had on infiltration rate. Figure 3.8 shows that C40-W and C20-W both had higher infiltration rates than their non-WTR pairs. This would have reduced contact time in the WTR treatments and may thereby have limited P mobilization. This would also explain why C40-W and C20-W leached similar levels of P: although C40-W had a higher PSI than C20-W, it also had nearly quadruple the infiltration rate, and thus P in C40-W may not have been as thoroughly mobilized as that in C20-W due to reduced contact time. Differences in pH were also considered as a possible explanation, but the WTR/non-WTR pairs had similar pre-trial pH values and thus pH was likely not a factor here. C20, C20-W, C40-B, and C40-W had pre-trial pH values of 6.02, 6.48, 5.83, and 6.01 respectively.

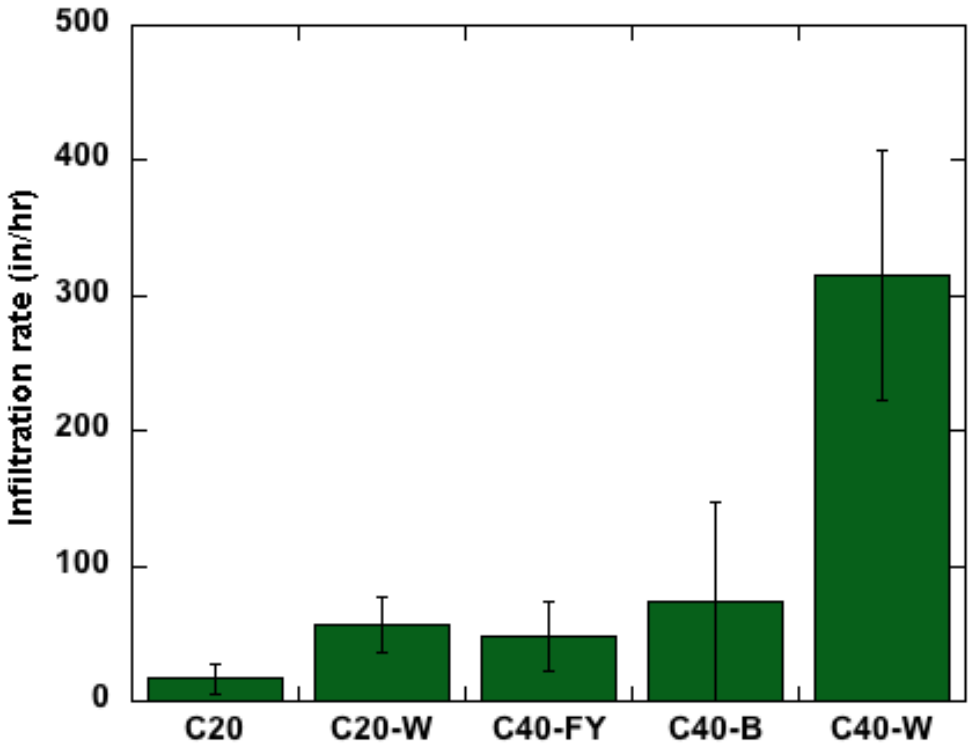


Figure 3.8. Infiltration rates of C20, C20-W, C40-FY, C40-B, and C40-W measured after event 12, before grass was planted. Error bars represent +/- one standard deviation.

Predicting P leaching

To better understand P leaching and how it can be predicted, we will now expand the discussion to include all 14 treatments that were tested in this experiment. The treatments have diverse ingredients and proportions (see Table 3.1 in methods), but all were sampled before and after the trial and subjected to ammonium oxalate and Mehlich-III extractions.

P leaching in this section is quantified as the sum total mass of P exported by each replicate over the course of the entire experiment, as described above. Thus, graphs below will show four data points per treatment, one for each replicate. The intricacies of changing effluent concentration with time are not described by these numbers, but they are useful in that they allow for valid comparisons of overall BSM performance.

Molar ratio as predictor

As stated above, previous studies have suggested that the molar ratio of ammonium oxalate-extracted P/(Fe+Al), i.e. the phosphorus saturation index (PSI), be used to predict P leaching in both agricultural soils and bioretention media (Brown et al. 2016; O'Neill and Davis 2011; Lu and O'Connor 2001; Breeuwsma and Schoumans 1987). Others have suggested using Mehlich-III-extracted elements for the identical ratio of P/(Fe+Al), and calling it the phosphorus saturation ratio (PSR) (Hsieh et al. 2007; Maguire and Sims 2002). Both will be investigated here, and henceforth referred to as the oxalate PSI and the Mehlich-III PSR, for the sake of clarity.

A graph of pre-trial Mehlich-III PSR vs. total P mass export (transformed with $\ln(x)^2$ for normality) was plotted, and from its appearance as well as from line fits in the literature, it was inferred that the best curve fit would be logarithmic (Lu and O'Connor 2001). This was the case: a logarithmic regression showed that Mehlich-III PSR was a good predictor, with $p<0.000$ and an R^2 of 0.67. The curve is plotted below in Figure 3.9; its equation is $y=20.2\log(x)+25.7$. The relationship between post-trial Mehlich-III PSR vs. total P mass export is not as clear (Figure 3.10), with an R^2 of only 0.34.

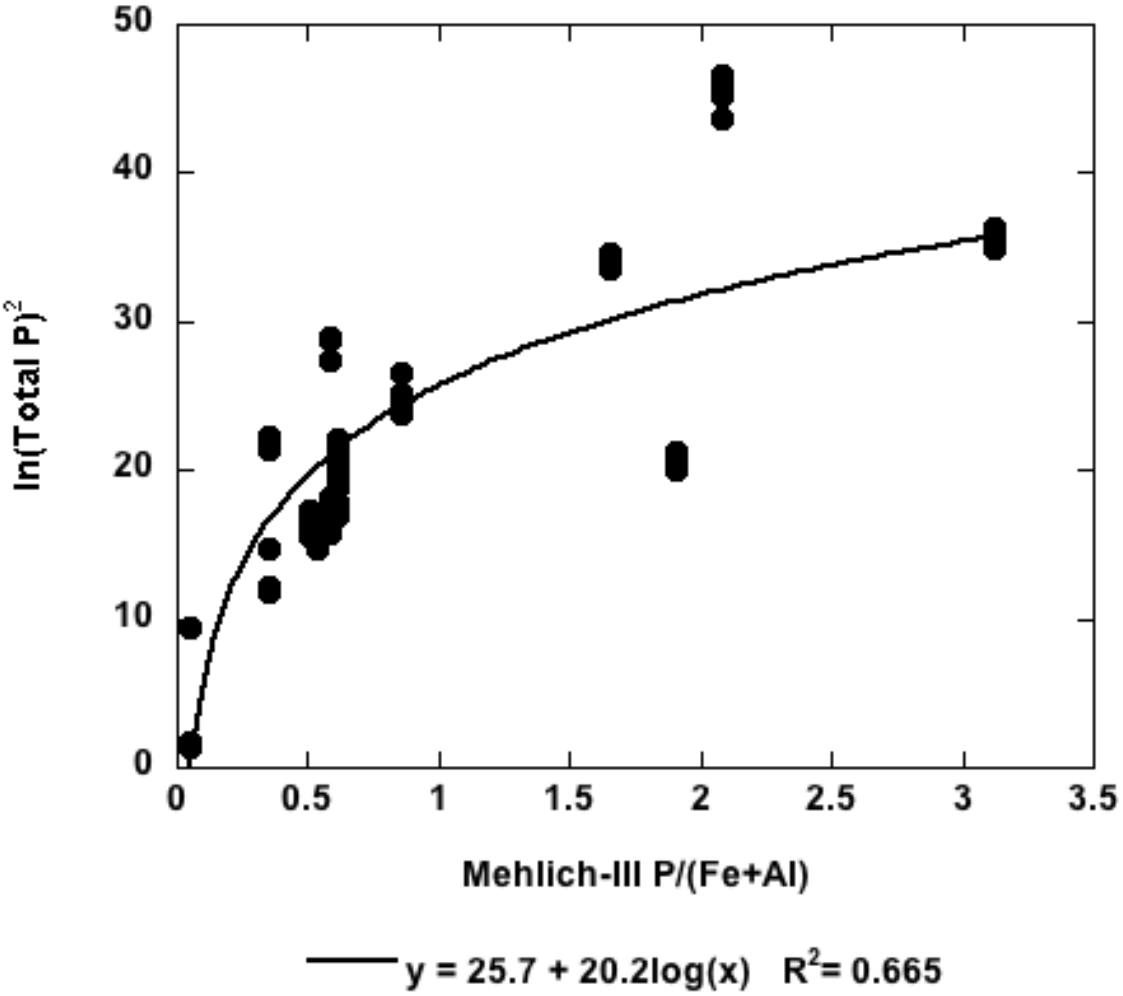


Figure 3.9. Pre-trial Mehlich-III molar ratio of P/(Fe+Al) as a predictor of P leaching.

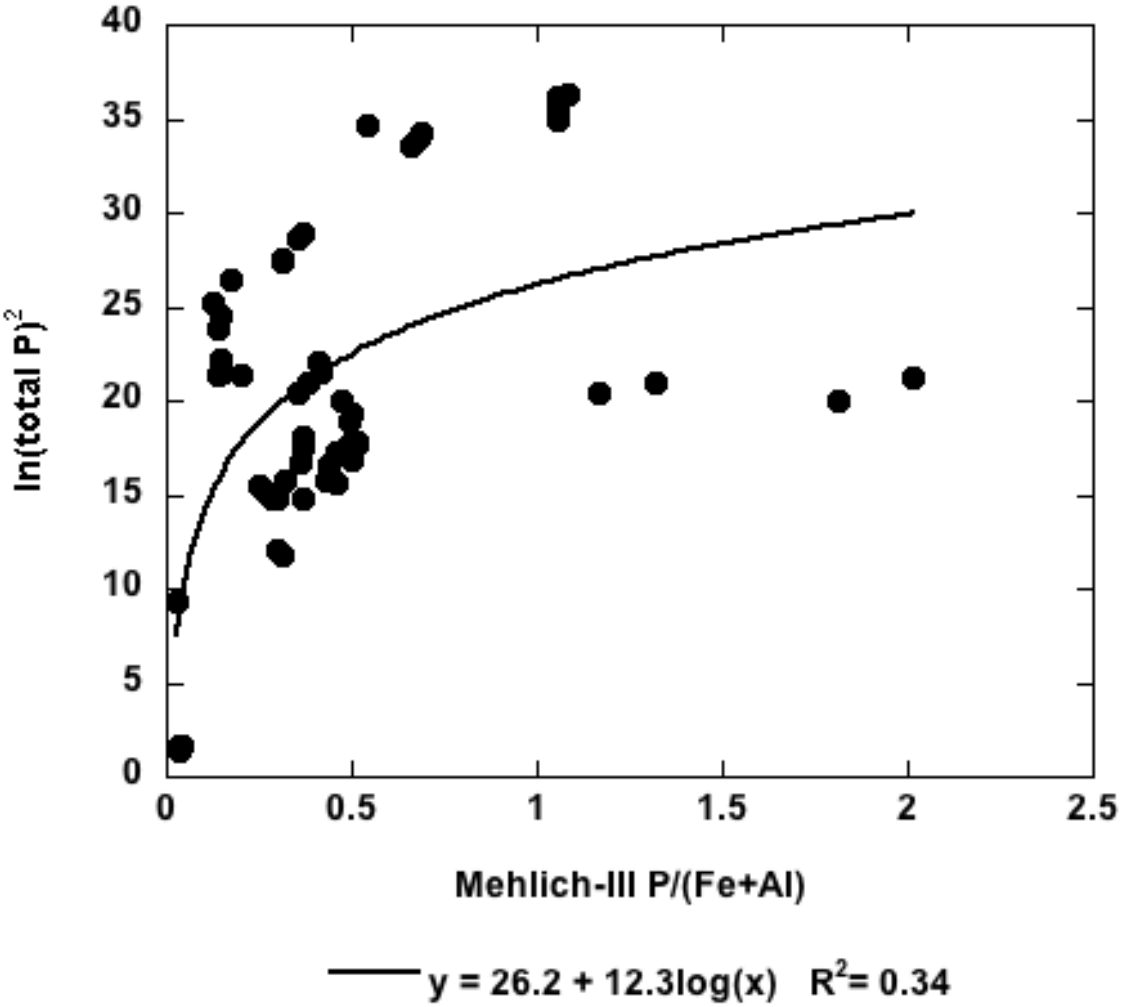


Figure 3.10. Post-trial Mehlich-III molar ratio of P/(Fe+Al) as a predictor of P leaching.

The same process was followed for oxalate PSI, with both a linear and a logarithmic regression. Although oxalate PSI was a significant factor in both cases ($p<0.000$), neither a linear nor a logarithmic regression created a successful curve fit, with R^2 values of 0.203 and 0.207 respectively. These fits are plotted below in Figure 3.11 along with their equations. The post-trial ammonium oxalate ratio had a similarly poor fit (Figure 3.12). An explanation for the difference in predictive capacity between ammonium oxalate and Mehlich-III molar ratios will be attempted in the next section.

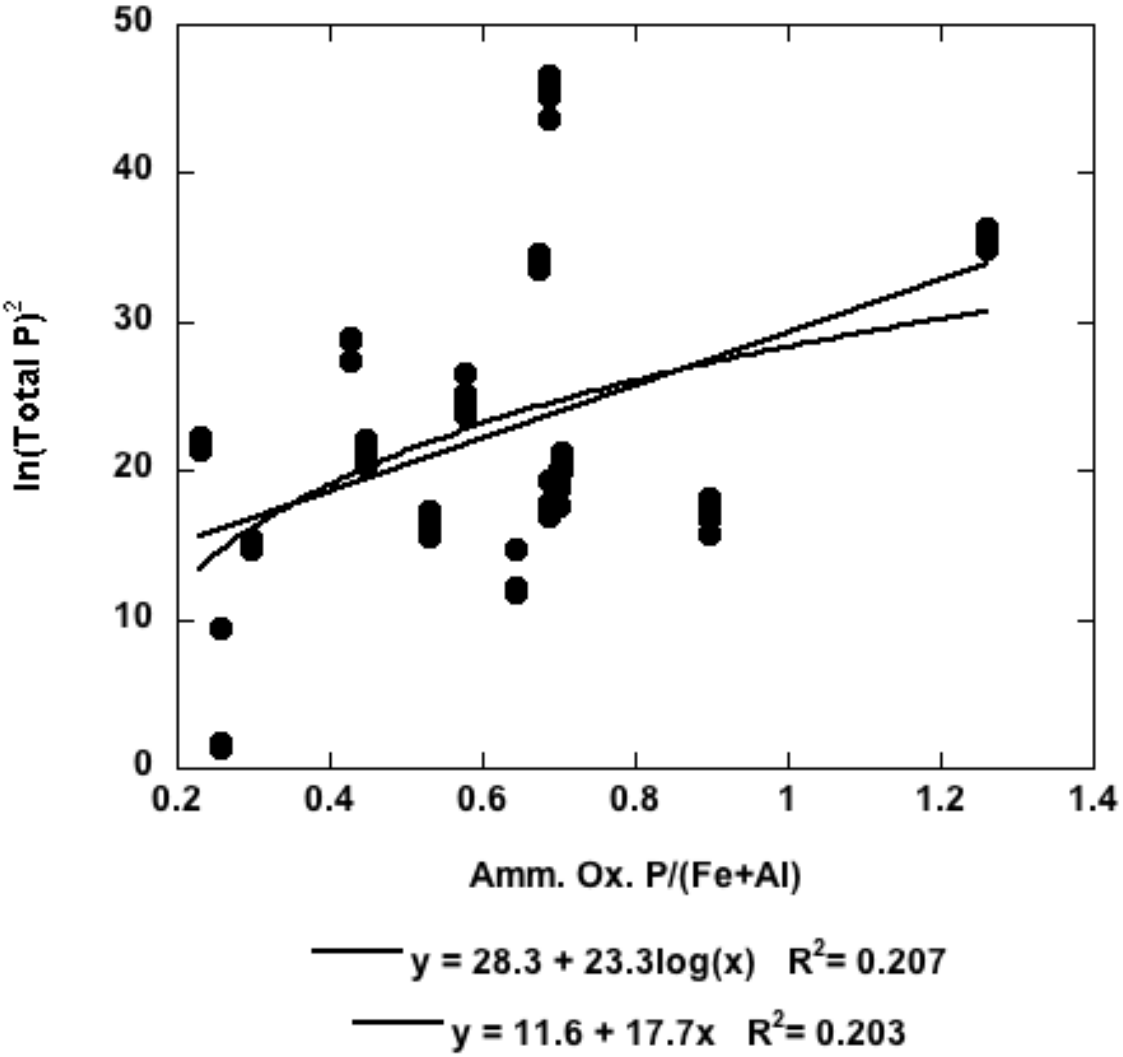


Figure 3.11. Pre-trial Ammonium Oxalate molar ratio P/(Fe+Al) as a predictor of P leaching.

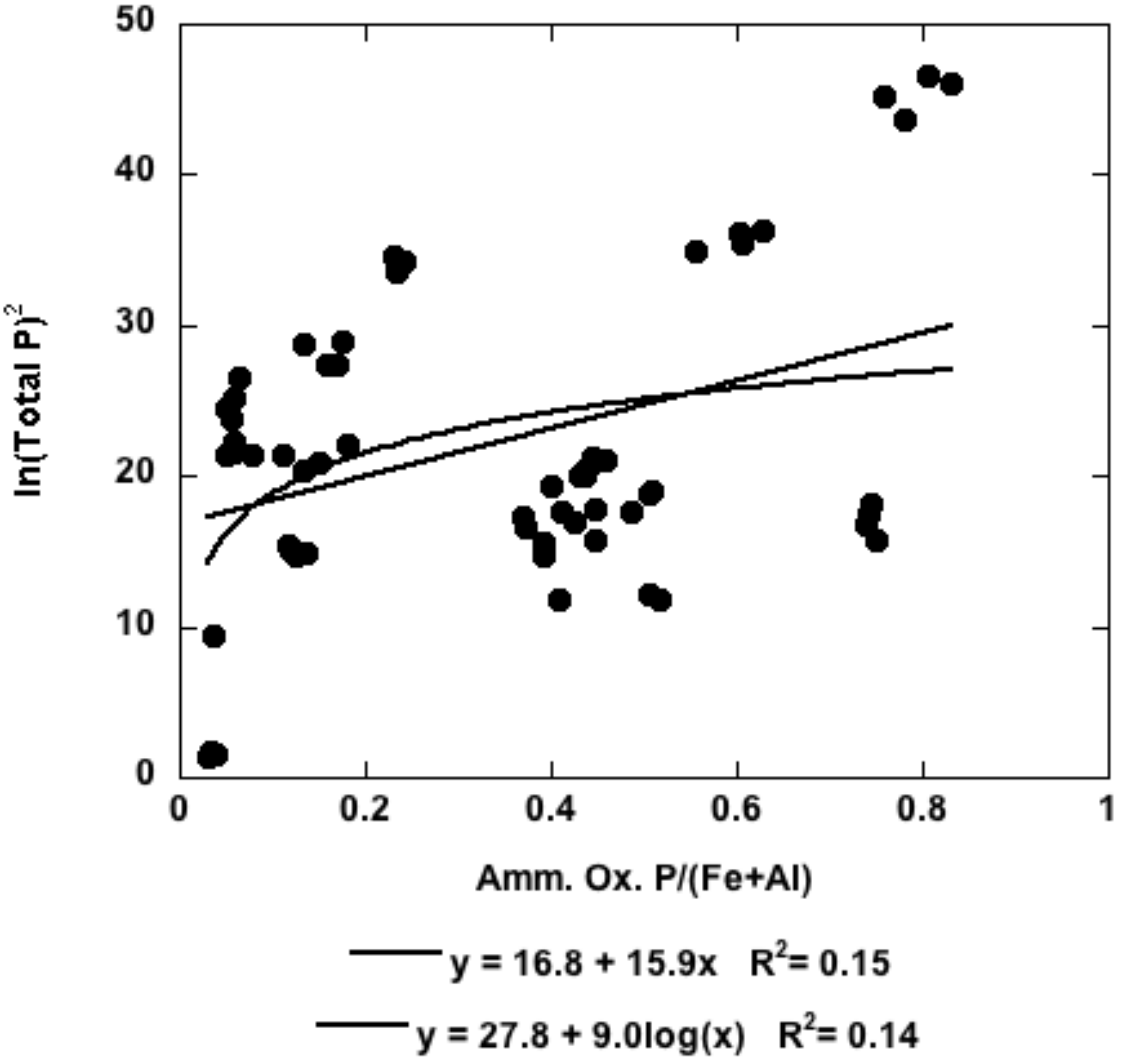


Figure 3.12. Pre-trial Ammonium Oxalate molar ratio P/(Fe+Al) as a predictor of P leaching.

The fit found for the pre-trial Mehlich-III PSR (R^2=0.67) is similar to fits found in the literature. Lu and O'Connor (2001) found an R^2 of 0.7 using oxalate PSI as a predictor of P leaching in sandy agricultural soils; O'Neill and Davis also found a linear fit of 0.7 with the same variables applied to bioretention soils. Mallarino et al. (2006) found correlations of 0.52, 0.73 and 0.69 between Mehlich-III PSR and P leaching for three different agricultural soil types, although even higher correlations were found in that study with Mehlich-III P alone.

Many studies have noted a change point in Mehlich-III and oxalate molar ratios, below which minimal P is leached and above which P leaches with increasing amounts as the molar ratio increases (McDowell et al. 2001, USDA 2002, Maguire and Sims 2002). Change points vary widely depending on the study and the soil types. Change points were not seen in this study, but this may be because P saturation was relatively high in most treatments. It is possible that there were not enough treatments with low molar ratios to distinguish a change point. However, it should be noted that change points are not always found – for instance, McDowell et al. (2001) found change points for fewer than half of the soils when using Mehlich-III and oxalate extractions.

Agricultural studies have shown that the relationship between soil P, molar ratios, and P leaching is different for every soil type (USDA 2002, McDowell et al. 2001). The USDA recommended that no universal limit be adopted for soil P since there was such variation across different soil types in how P leaching could be predicted. Here, soil parameters were compared with P leaching for a varied group of BSMs, and it was found that the Mehlich-III molar ratio was a reasonably good predictor of total P leaching despite differences in BSM components.

Other factors

In an effort to explore the full range of factors that influenced P leaching, a stepwise regression was done using R, starting with the following independent factors which were deemed to be potentially important: Mehlich-extractable P, Al, Fe, Ca, and Mg; infiltration rate and pH. All of these, with the exception of infiltration rate, were pre-trial measures of the

BSMs. The interactions between each factor and Mehlich-III extractable P were also included, with the dependent factor being the mass total of leached P, transformed for normality.

The stepwise regression eliminated all individual factors except for Mg, but kept each of the interactions between extractable P and the other variables. A linear model with only the interactions and Mg has an R^2 of 0.54 – the results of an ANOVA of this model can be seen below in Table 3.8. If the individual factors are included in the model, the R^2 rises to 0.97 – the results of an ANOVA for that model are in Table 3.9.

Ca and Mg have not yet been discussed, but it is clear from this regression analysis that they must be considered as important factors. P has been shown to bond with both Ca and Mg in soils, but these elements are not included in established predictive ratios like oxalate PSI or Mehlich-III PSR (Brady and Weil 2010). In fact, Lindsay (1979) indicated that P solubility in soil is controlled by Al and Fe only below a pH of 5.8, with control shifting to Ca above this pH. With the pH of all BSMs in this experiment all above 5.8, and with the p-values associated with Ca and Mg in the ANOVAs in Tables 3.8 and 3.9, Ca and Mg appear to have been important factors for limiting P leaching.

Table 3.8. P-values from ANOVA of linear model resulting from stepwise regression. P, Al, Fe, Mg, and Ca are Mehlich-III extracted from pre-trial BSMs. Italicized p-values are significant with an α of 0.05.

Factor	**p-value<**
Mg	*0.000*
P*pH	*0.011*
P*Al	*0.000*
P*Fe	*0.002*
P*Inf. Rate	0.522
P*Ca	0.095
P*Mg	*0.000*

Table 3.9. Resulting p-values from ANOVA of linear model including interactions and independent variables. P, Al, Fe, Mg, and Ca are Mehlich-III extracted from pre-trial BSMs. Italicized p-values are significant with an α of 0.05.

Factor	p-value <
P	*0.000*
pH	*0.000*
Al	*0.000*
Fe	0.061
Inf. Rate	*0.000*
Ca	0.426
Mg	*0.000*
P*pH	*0.000*
P*Al	*0.000*
P*Fe	*0.000*
P*Inf. Rate	*0.000*
P*Ca	*0.000*
P*Mg	0.292

The relationship between extractable P, Al, Fe, Ca, and Mg does not appear to be simple or straightforward. To investigate the impact of Ca and Mg, several possible variations of the Mehlich-III PSR including Ca and/or Mg as well as Al and/or Fe were tested for predictiveness of P leaching. The ratio P/Fe was also tried, since Fe has been shown to sorb P more efficiently than Al (Brady and Weil 2010). The same procedure shown above for testing the predictiveness of Mehlich-III PSR was followed, and the alternative ratios with the best curve fits were as follows when plotted against total mass of leached P: P/(Fe+Ca+Al) with R^2 of 0.60, P/Fe with R^2 of 0.57, and P/(Fe+Al+Ca+Mg) with R^2 of 0.50. The most predictive alternative ratio, P/(Fe+Ca+Al), is shown below in Figure 3.13. None of the alternative ratios exceed the established PSR in predictive ability, despite the significance of Mg and Ca to predicting P leaching. More research is needed to determine the precise relationships between Ca, Mg, Al, and Fe as sorbents of P.

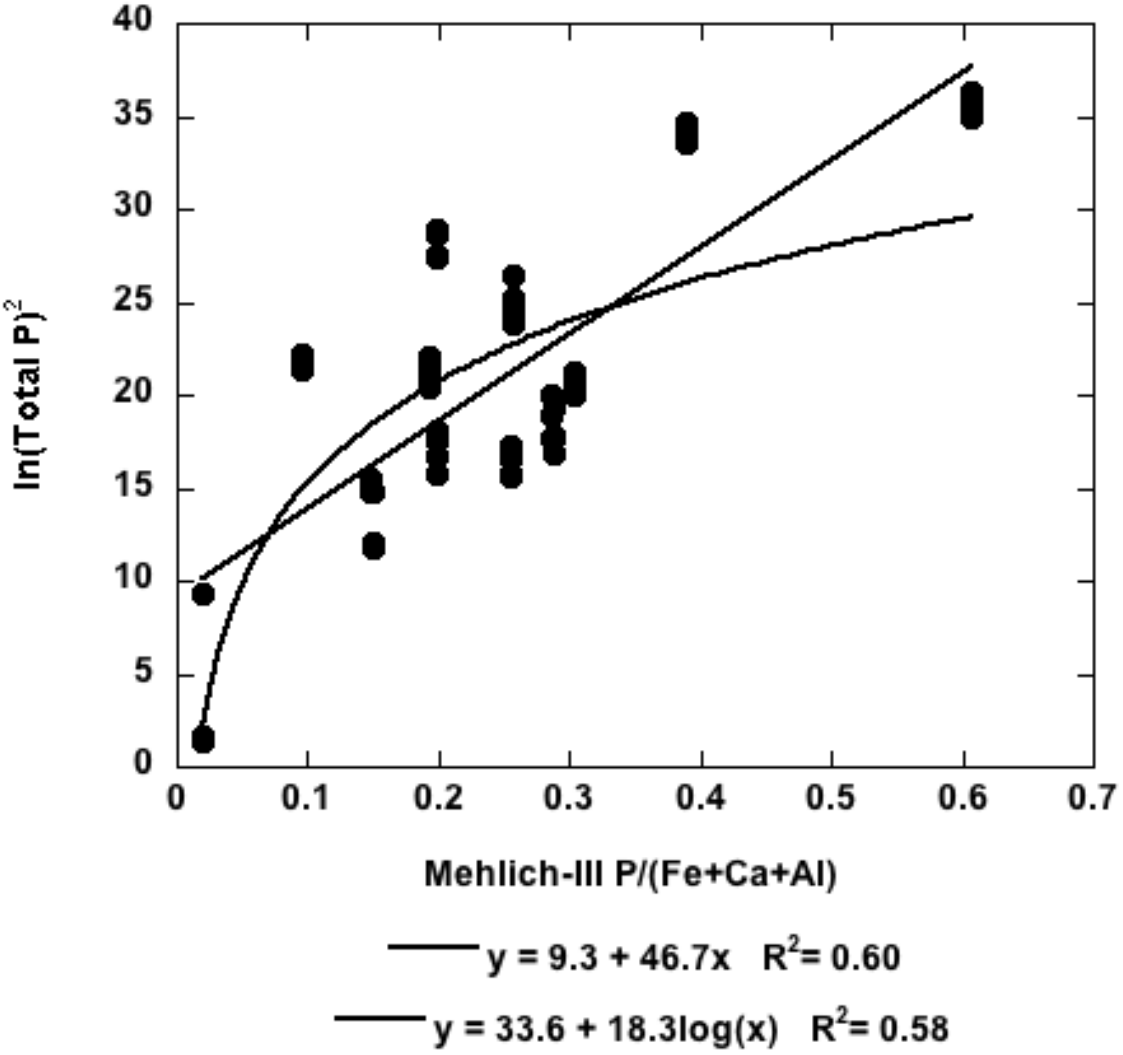


Figure 3.13. Pre-trial Mehlich-III molar ratio of P/(Fe+Al+Ca) as a predictor of total P leaching. Total P is in mg.

Combining this information with the results of the stepwise regression, it appears that P leaching is determined by a complex interaction among many soil factors. This finding helps explain why the PSI and PSR are most effective at predicting P leaching within rather than between soil types, since things like pH and infiltration rate are relatively constant within soil types.

Comparing Extraction Methods

Investigating the relationship between ammonium oxalate extractions and Mehlich-III extractions may explain why they were not equally predictive of P leaching in this experiment. For them to be equally predictive, they would need to rise together, i.e. the Mehlich-III ratio would have to be consistently lower than the oxalate ratio, or vice versa, throughout. The bar graph below in Figure 3.14 demonstrates that this is not the case – the oxalate ratio is lower than the Mehlich-III ratio for several of the treatments, but higher for others.

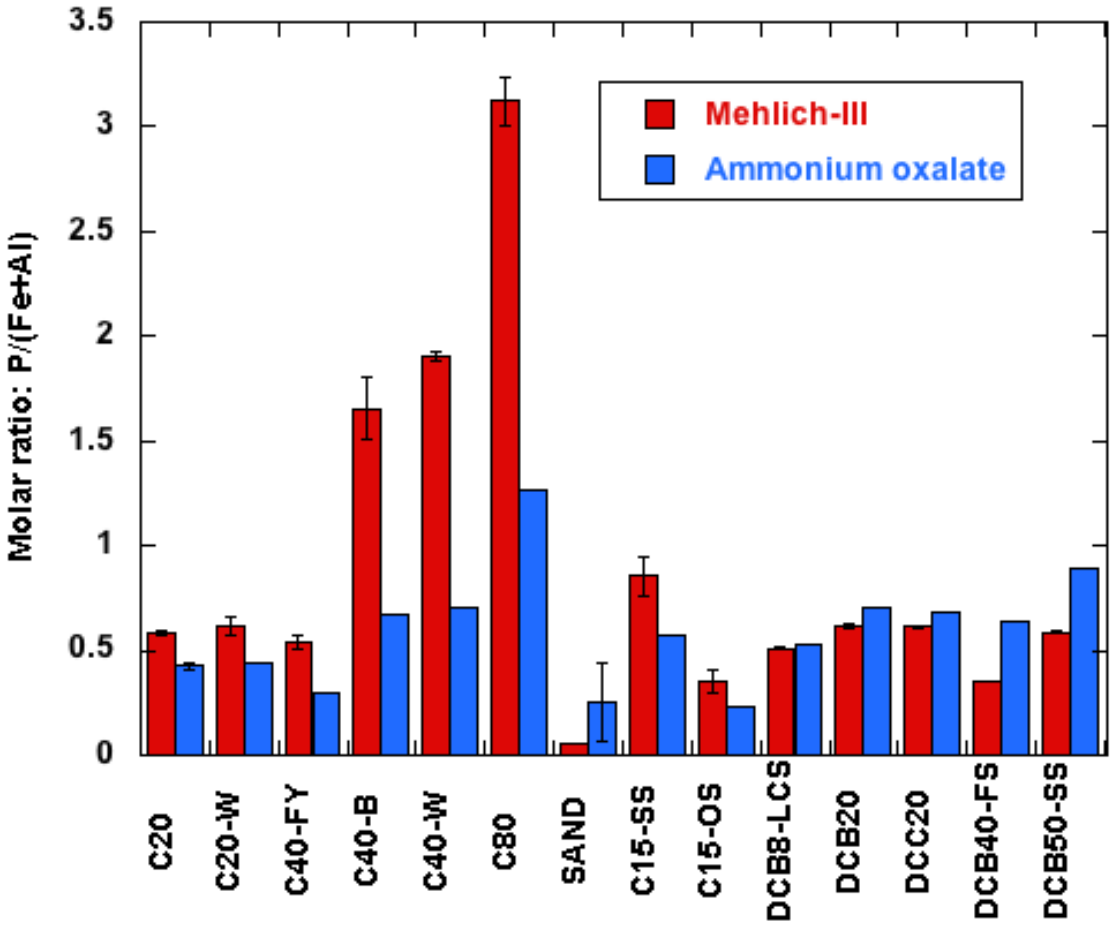


Figure 3.14. Ammonium oxalate and Mehlich-III molar ratios of P/(Fe+Al) for each treatment, measured before the trial. Error bars represent +/- one standard deviation.

To understand why the two ratios are not following the same pattern, it is necessary to compare the individual elements in the ratio: P, Fe, and Al. In Figure 3.15 below, the pre-trial results from the two extraction methods are plotted against each other for P, Al, and Fe and fitted with linear regressions. If the two extractions are equally precise, then there would be expected to be a linear relationship between their values for each element. Also, if Mehlich-III and ammonium oxalate ratios followed similar patterns, the fit lines of P, Al, and Fe in this graph would be expected to be parallel. This would indicate that oxalate-extractable P increases with Mehlich-III-extractable P at the same rate that oxalate-extractable Al increases with Mehlich-III Al, and the same for Fe.

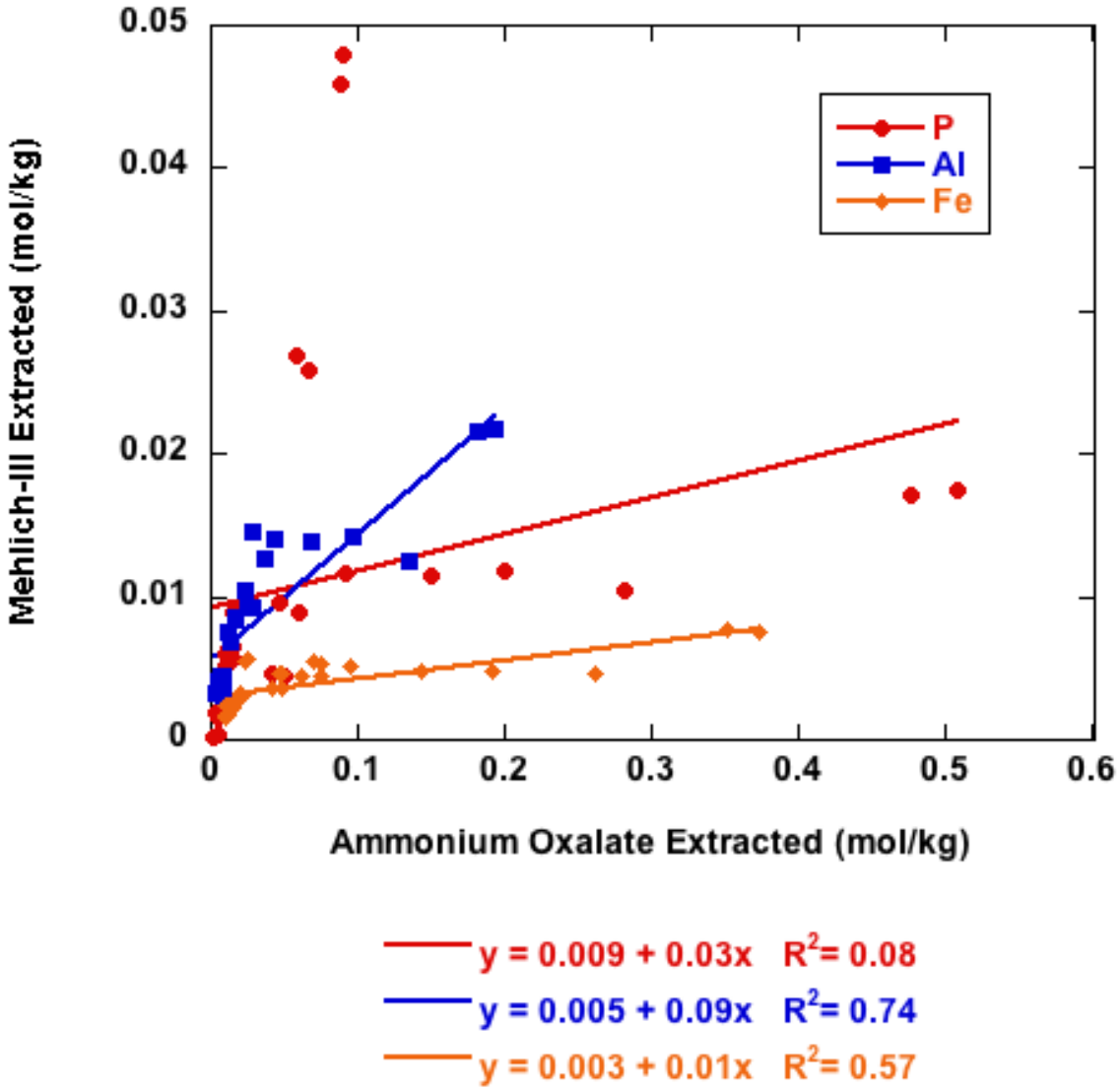


Figure 3.15. Pre-trial comparison of Ammonium Oxalate and Mehlich-III extractions of P, Al, and Fe from the 14 BSMs used in this experiment. Aliquots of each BSM were taken after mixing but before being packed into columns, and two different samples were taken from each aliquot and tested. Line fit equations and R^2 values are included below the graph.

It is obvious from Figure 3.15 that this is not the case. In fact, although Al and Fe have curve fits of 0.74 and 0.57 respectively, P is very scattered with an R^2 of only 0.08. This variability in P indicates either that different soil properties influence the effectiveness of the extraction processes, or that there was some systematic error in measurement. Looking at the bar chart in Figure 3.14 above, the treatments where oxalate PSI exceeds Mehlich-III PSR were

those that contain high Fe biosolids. Indeed, when those high Fe biosolids treatments are removed from the extractions comparison, the variability in P diminishes and the line fits for P, Al, and Fe improve to 0.98, 0.93 and 0.61 respectively (see Figure 3.16 below). This indicates that both extractions were similarly precise for all treatments whose major components were sand and food/yard or biosolids/yard compost, but that one extraction did not yield reliable results from the treatments containing high Fe biosolids or high Fe biosolids compost.

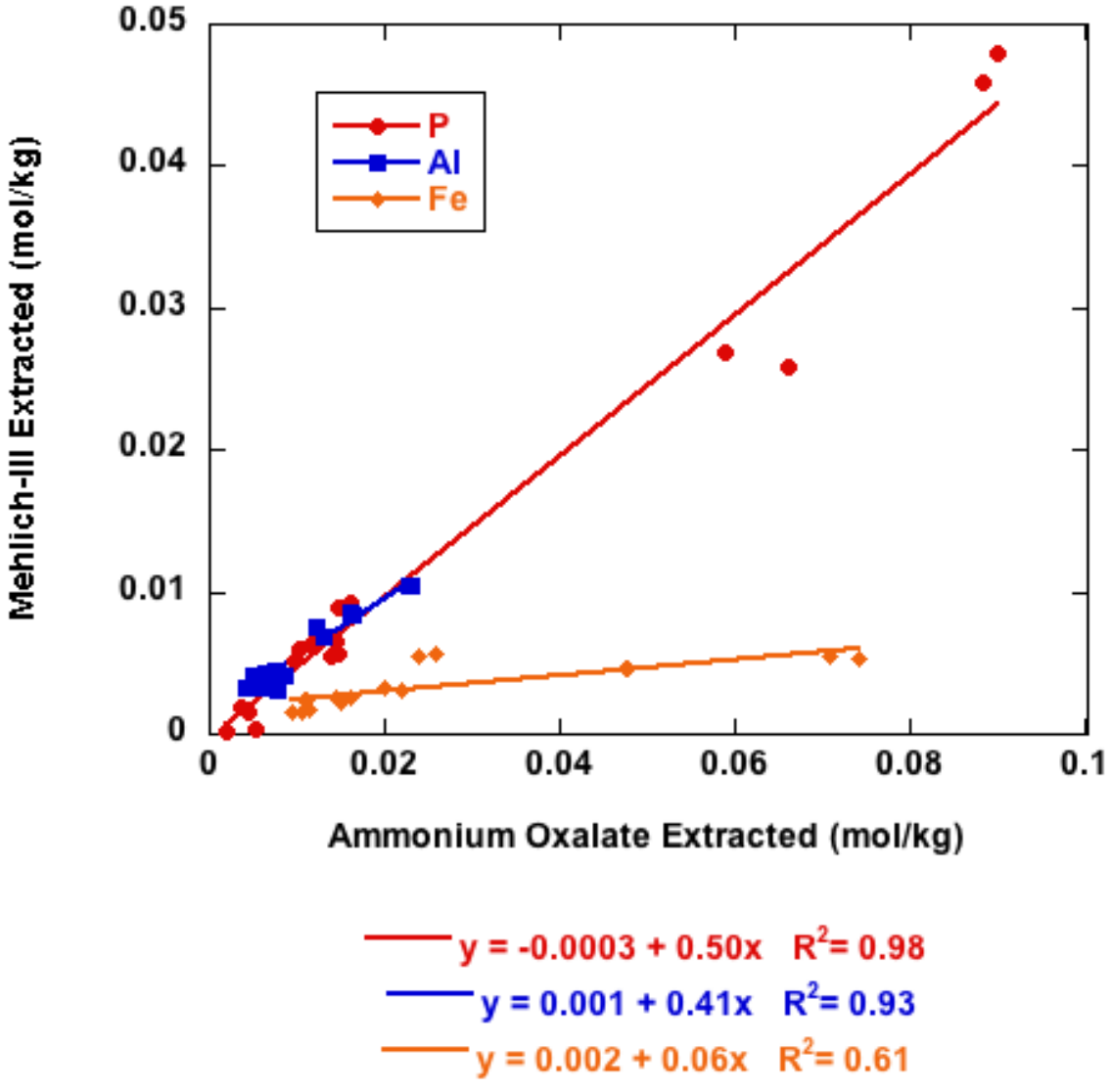


Figure 3.16. Pre-trial comparison of Ammonium Oxalate and Mehlich-III extractions of P, Al, and Fe only from the 9 BSMs not containing high Fe biosolids. Line fit equations and R^2 values are included below the graph.

This variability in soil P extraction for the high Fe biosolids treatments likely explains the observed difference in predictive capacity between the ammonium oxalate and Mehlich-III molar ratios. Since Mehlich-III was found to be predictive of P leaching as expected, it is likely the oxalate extraction that lost reliability in certain treatments. The reason for this difference is not known at this time, but the finding indicates that Mehlich-III is more robust to changing soil components.

One further point of note from Figure 3.16 is the difference in slope of the fit lines for P, Fe, and Al. The line fits are high in this graph, indicating that both extractions performed reliably for the nine treatments included. However, P and Al have relatively parallel line fits with respective slopes of 0.50 and 0.41, while Fe has a line fit with a much lower slope of 0.06. This indicates that a soil with high Fe content would have a much lower ammonium oxalate ratio than Mehlich-III ratio, as the ratio is inversely related to Fe.

Since the assignment of the reagents to axes was arbitrary, the graph can be interpreted one of two ways. Either the Mehlich-III reagent extracts Fe with decreasing efficiency as soil Fe content increases, or the ammonium oxalate reagent extracts P and Al with decreasing efficiency as soil P and Al content increase. Decreasing effectiveness here means decreasing more quickly (or increasing more slowly) than extraction of the other elements by the same reagent.

The post-trial extractions have a similar, though not identical, relationship. As above, for post-trial soils the two extraction methods are plotted against each other for P, Al, and Fe and

fitted with linear regressions in Figure 3.17. Post-trial extractions were done on soil from each rep of each treatment, so there are two times more data points in this comparison graph than there were in the above. Although the R^2 value here for P is much higher than in the pre-trial extraction containing all treatments, there is a visible divergence in pattern, with some points following a steep slope while others flatten out. As we saw above, this divergence disappears when the points representing the treatments containing high Fe biosolids are taken out (Figure 3.18). Without these treatments, the R^2 value of the line fit for P increases to 0.94. The slope of the Fe line fit is also lower than the slopes of the Al and P line fits as seen above, although it is worth noting that the fit of Al is poor, with an R^2 of only 0.086, when the high Fe biosolids treatments are removed from the graph (Figure 3.18). This may be due to the fact that the post-trial extractable Al content of the remaining nine treatments were similar and thus there was not enough spread to show a pattern. It is worth noting that P concentrations in effluent from all treatments were also more similar near the end of the trial than at the beginning (Figure 3.19), although there were still statistical differences. Since both pre- and post-trial extraction comparisons show similar but not identical patterns, more research is warranted here to better understand the relationship between these two extractions.

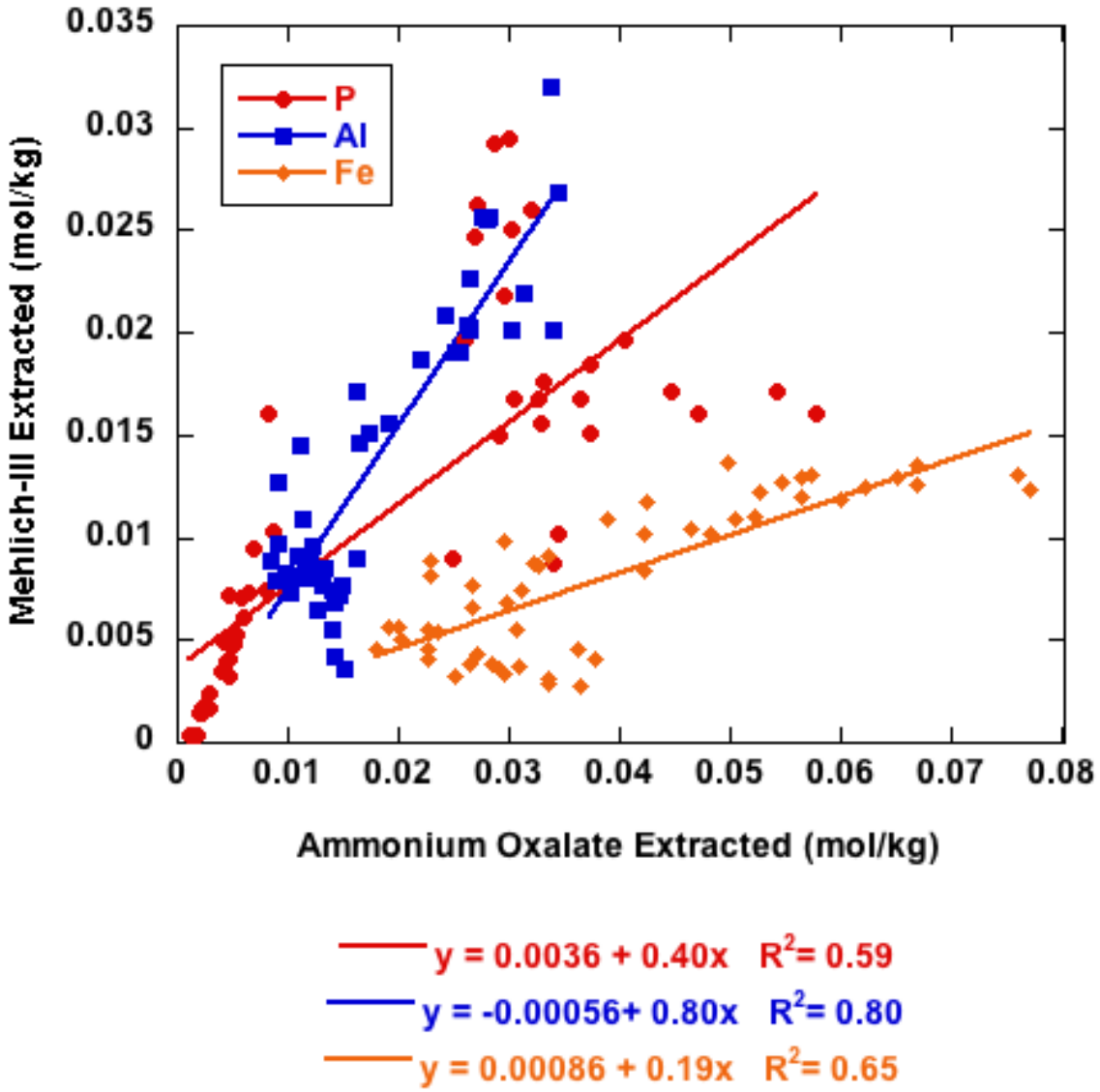


Figure 3.17. Post-trial comparison of Ammonium Oxalate and Mehlich-III extractions of P, Al, and Fe from the 14 BSMs used in this experiment. Treatment 15 was determined to be an outlier and thus is not included here. Line fit equations and R^2 values are included below the graph.

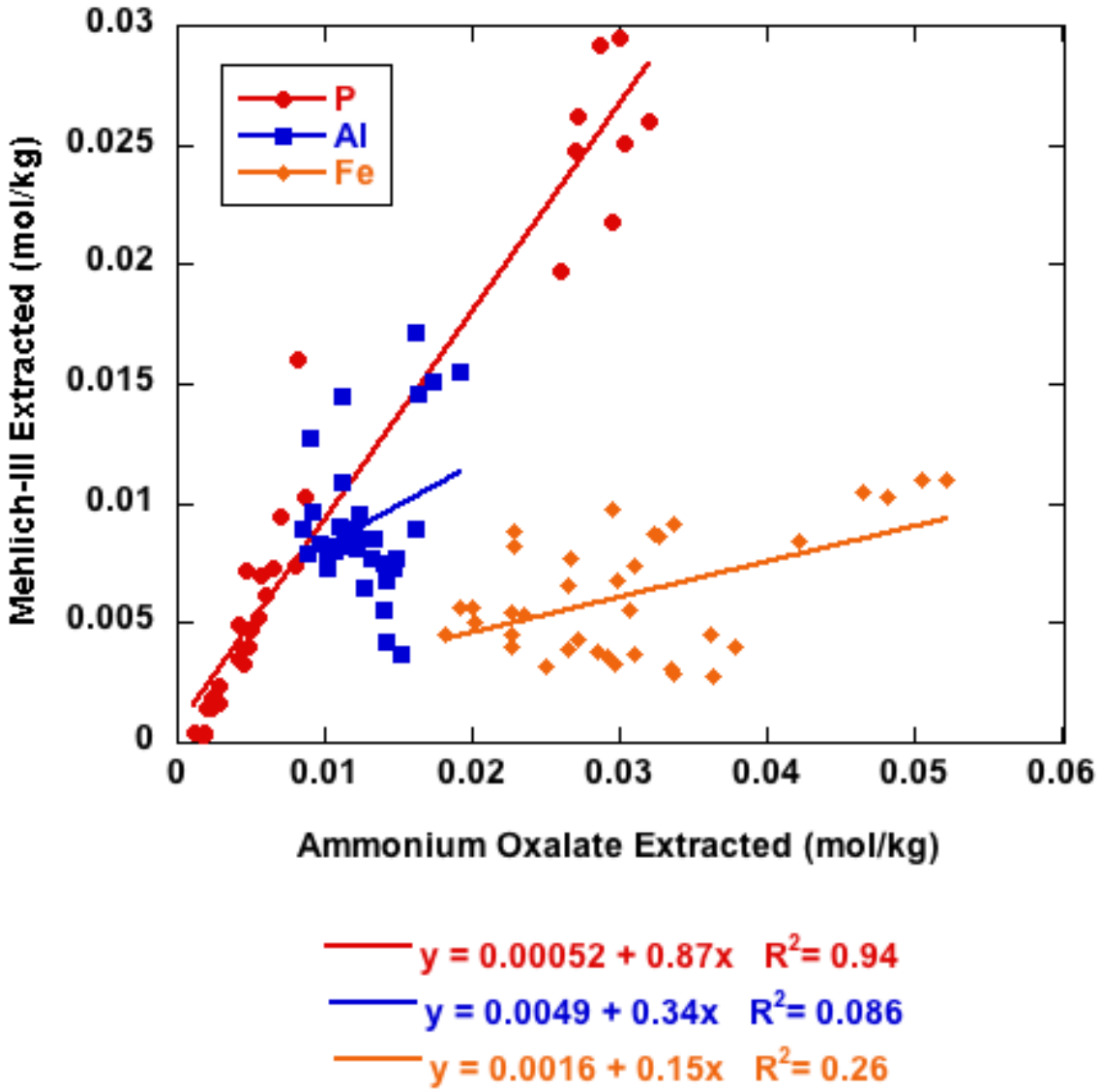


Figure 3.18. Post-trial comparison of Ammonium Oxalate and Mehlich-III extractions of P, Al, and Fe only from the 9 BSMs not containing high Fe biosolids. Line fit equations and R^2 values are included below the graph.

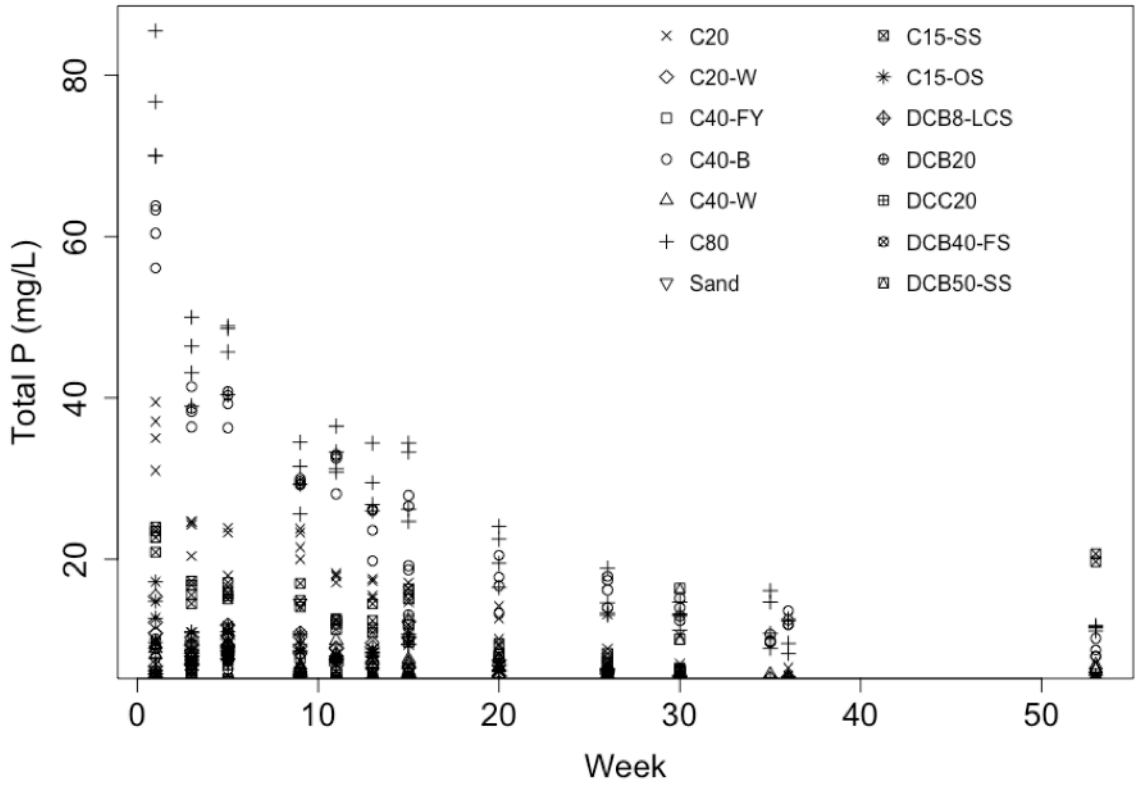


Figure 3.19. Concentration of total P in effluent from all treatments over time.

Conclusion

Finding a way to predict P leaching from BSMs will be crucial to optimizing bioretention design to protect water bodies. Steps toward this goal can be taken by looking to parameters developed by agriculture and soil science.

The Mehlich-III PSR was the best predictor of P leaching in this study, with an R^2 of 0.67. Oxalate PSI and alternative Mehlich-III ratios containing Mg and/or Ca were all found to be poor predictors of P leaching. More research is needed to analyze the relationship between Mehlich-III and ammonium oxalate extractions, but the results of this experiment indicate that the Mehlich-III extraction may be more robust to changing BSM components.

In addition, this study found that the addition of WTRs to a BSM lowers its rate of soil P leaching by reducing the initial flush of P. This was true even when the PSI of the WTR treatment was equal to the PSI of the non-WTR treatment. A stepwise regression analysis suggested that many soil factors beyond extractable P, Fe and Al may be important to predicting P leaching, including pH, extractable Ca, and extractable Mg.

Appendix: Copper and Zinc Removal

Introduction

Heavy metal contaminants in stormwater, such as Copper (Cu) and Zinc (Zn), commonly come from traffic-related sources, soil particles, and litter (Sansalone and Buchberger, 1997). It is important that Cu and Zn levels in surface water be controlled, as aquatic life has been shown to be extremely sensitive to such metals. For instance, juvenile coho salmon have reduced alarm response when exposed to waters containing Cu in concentrations as low as 5 µg/L, making them more susceptible to predation (McIntyre 2012).

A recent study of water quality of effluent from bioretention systems demonstrates the capability of bioretention treatment to protect aquatic organisms through contaminant removal. McIntyre et al. (2015) tested the response of juvenile coho salmon, mayfly nymphs, and cladocerans to untreated stormwater and to stormwater that had been treated by columns set up to mimic bioretention systems, and found sharply different responses. While the juvenile salmon in untreated stormwater had a 100% mortality rate, all of those exposed to stormwater treated by bioretention soil survived. Cladocerans and mayfly responded similarly. In that study, the bioretention soil media (BSM) was made up of 60% sand, 15% compost, 10% Water Treatment Residuals (WTR) and 15% shredded bark, by volume. It was further found that concentrations of metals in the fish that were exposed to water treated by bioretention soil were not significantly higher than levels in the control fish, which were exposed to DI water.

Though considered toxic at high concentrations in soils, Cu and Zn are both micronutrients which are essential to plant growth and health. Therefore these metals are taken up by plants in their dissolved forms, albeit at much slower rates than macronutrients

such as N and P. Organic matter is known to complex with Cu and Zn cations to form organic chelates, some of which are immobile, and most of which are nontoxic to aquatic biota (McIntyre 2015). However, degradation of organic matter can release organic acids and lower soil pH, which may cause metals to desorb from soil particles. Despite this complexity, organic matter content is usually negatively correlated with metals mobility in soils. (Brady and Weil 2010; Sun and Davis 2007)

As Cu and Zn are a concern even at low concentrations, this appendix will compare effluent Cu and Zn concentrations from 14 different BSMs. The focus will be on storm events that were simulated using actual stormwater as the influent, in an effort to model real-world conditions.

Methods

BSM Preparation

Columns measuring 9.5 cm in diameter and 45.75 cm in height were set up in a randomized complete block design with 4 replicates of each treatment. A range of different BSMs was included in the design. These are described below in Table 4.1. The columns had 2 cm holes in the center of the base for leachate collection, which were covered in mesh to prevent loss of soil media and fitted with plastic tubes to direct flow into collection buckets. The insides of the columns were sanded with coarse sandpaper to prevent preferential flow of water along the sides. To ensure even packing of BSM, each column was filled to the top then dropped three times from 5 cm above the work surface. Columns were then refilled to the top and tamped

down with a 1kg weight dropped from 5cm above the column three times. Columns were kept in a controlled environment greenhouse at the University of Washington.

Table 4.1. Description of 14 BSMs

Label	Treatment	Volume (%)	Dry Weight (%)
C40-FY	Food/Yard Compost	40	9
	Sand	60	91
C40-B	Biosolids/Yard Compost	40	9
	Sand	60	91
C40-W*	Biosolids/Yard Compost	35	8
	Sand	60	90
	Water Treatment Residuals	5	2
C80	Biosolids/Yard Compost	80	38
	Sand	20	62
C20	Biosolids/Yard Compost	20	4
	Sand	80	96
C20-W **	Biosolids/Yard Compost	17.5	3
	Sand	80	96
	Water Treatment Residuals	2.5	1
Sand	Sand	100	100
C15-SS	Biosolids/Yard Compost	15	3
	Sand	80	97
	Sawdust	5	0
C15-OS	Biosolids/Yard Compost	15	3
	Sand	80	92
	Oyster Shells	5	6
DCB8-LCS	Sand	49	80
	Loamy Clay	30	12
	High Fe Biosolids	20	8
DCB20	Sand	49	80
	High Fe Biosolids	51	20
DCC20	Sand	49	80
	High Fe Biosolids Compost	51	12
DCB40-FSS	Sand	1.2	15
	Sawdust	85.5	40
	High Fe Biosolids	12.9	40
	Mineral Fines	0.4	5
DCB50-SS	Sand	3	25
	Sawdust	75	25
	High Fe Biosolids	23	50

* Brought to same PSI as C40-B with addition of P salts, ** Brought to same PSI as C20 with addition of P salts

Mix proportions are presented in Table 4.1 above by volume and by dry weight. Both methods are used independently in different stormwater guidelines depending on region and convention. It should be noted that volume and dry weight proportions can be very different and do not necessarily grow at the same rate – for instance, doubling the volume proportion of compost from 40 to 80% corresponds to more than quadrupling the dry weight proportion of compost from 9 to 38%. This is due to the higher bulk density of sand – since the volume of

sand is reduced when the volume of compost is increased, the overall weight of the BSM is reduced.

There are four "paired" treatments in the chart above: C40-B/C40-W and C20/C20-W. The "-W" treatments have 5% and 2.5% less compost (respectively) than their pairs but the same proportion of sand; the difference is made up by the addition of Fe-based water treatment residuals (WTRs). Calcium phosphate was added to C20-W and C40-W during mixing in order to bring the PSI to equal that of their paired treatments. This was done so that the effects of WTR on contaminant removal could be seen independent of its effect on PSI. Salts were dissolved in 500ml water and poured onto the soil mixture by alternating aliquots of soil and salt solution and thoroughly mixing between additions. Treatment C40-FY is the standard BSM that has been used in the Seattle, WA metropolitan area and was included for the purposes of comparison (City of Seattle 2011).

Sand for the study was a silica sand with d_{60} of 0.4 mm, and was obtained from a commercial compost and soil supplier where it had been stored outdoors (Sawdust Supply 2016). Loamy clay soil for the study was a commercial topsoil, and sawdust was a fine alder sawdust, both obtained from the same supplier described above. The high Fe biosolids and high Fe biosolids compost were provided by District of Columbia Water. This compost was made from biosolids and wood chips in equal portion by wet weight. These biosolids and the compost made from these biosolids are high in Fe because Fe is added during DC Water's wastewater treatment process to precipitate P from the effluent. The yard/food compost used in the control treatment (treatment 1) was produced from yard waste and food scraps by a Seattle, WA area composter and is the compost that is most commonly used in bioretention system

treatments in the Seattle area. The biosolids/yard compost was provided by Sawdust Supply and produced from anaerobically digested biosolids and yard waste. WTRs were acquired from Seattle Public Utilities, where they were used for drinking water treatment. Oyster shells were acquired from a Seattle, WA area restaurant and shattered with a hammer into small shards.

Leaching Events

Storm events were simulated by pouring stormwater into the columns at predetermined volumes. Water was allowed to pool at the top of the columns to simulate bioretention conditions in the field. Storm events represented 24 hour storms in Seattle, WA with return frequencies of either 0.2 years for a rainfall depth of 0.9 inches (900 mL per column) or one year for a rainfall depth of 1.8 inches (1600 mL per column) (City of Seattle 2016). Water volumes were calculated to reflect a bioretention system that was designed to collect 90% of the runoff from an impervious catchment of which the bioretention surface represents 6.5% of the area. Leachate was collected through the tubes at the bottoms of the columns during each event and for four hours after.

Four leaching events were carried out using actual stormwater collected as runoff from a major Seattle highway bridge and stored in plastic carboys at 3°C for no longer than seven days. Prior to these events, the bioretention columns had been maintained and watered for 23 weeks and subjected to 8 leaching events using synthetic stormwater with high metal concentrations as influent. A schedule of the leaching events is shown below (Table 4.2), followed by a description of the metals and nutrient concentrations in the stormwater used for this study (Table 4.3). Columns were kept moist with tap water in between leaching events to

avoid the complicating effects of drying and wetting seen in previous studies (Mullane et al. 2015; Li and Davis 2014; Hsieh et al. 2007).

Table 4.2. Schedule of leaching events with volume of actual stormwater used as influent.

Event	Date	WA Return Interval
		yrs
9	11/4/14	0.2
10	12/2/14	0.2
11	1/20/15	1
12	1/27/15	1

Table 4.3. Concentration of metal and nutrient contaminants in influent stormwater. Numbers represent means ± one standard deviation for all events of the same water type.

Contaminant			Actual stormwater*
Cu	Dissolved	µg/L	18.25 ± 5.76
	Total		39.76 ± 19.13
Zn	Dissolved		113 ± 90.8
	Total		172 ± 87
Turbidity		BTU	28.4 ± 11.3

*High standard deviation for all values are due to natural variations between stormwater collected on different days.

Leachate volume was recorded and then the leachate was divided into aliquots for different analyses. Total and dissolved Cu and Zn were analyzed at the King County Environmental Lab. Leachate samples for determination of dissolved metals were prepared using EPA Method 200.8, while total metals were analyzed using EPA Method 200.7. All were analyzed using a Thermo X-series II ICPMS with Collision Cell Technology (Brockhoff et al., 1994). Finally, one aliquot per column was measured on-site for turbidity using a Hatch 2100b turbidimeter.

The infiltration rate of each column was measured using the single-ring falling head procedure after the 12th leaching before grass was planted. Each column was wetted with 500 mL of tap water and allowed to drain. An additional 500 mL was then added, and the time required to infiltrate the soil was measured.

Data analysis

As needed, results were normalized by either natural log transformation, 1/sqrt(x), or $\ln(x)^2$ transformations to minimize skewness and kurtosis. Data were then analyzed in R using one- and two-way ANOVAs and the Tukey HSD post-hoc test for multiple means comparison. Outliers were identified using standard residuals and removed from ANOVAs and regression models.

Results and Discussion

Copper

Average concentrations of total and dissolved Cu in effluent water from all four storm events can be seen in Table 4.4. Numbers in these tables show the mean and standard deviation of effluent concentrations from all reps of each treatment in all four leaching events with collected stormwater as the influent. Treatments with the same letter have statistically similar concentrations in effluent. These means are also shown in Figure 4.1.

All treatments acted as a sink for total Cu with varying degrees of removal. C40-B, C80, and DCB40-FSS all acted as sources of dissolved Cu, with the remainder of the treatments again acting as sinks. The most effective treatment at removing both dissolved and total Cu was

DCB8-LCS, whose effluent had an average dissolved Cu concentration of 1.08 µg/L and a total Cu concentration that was consistently below the detection limit of 4 µg/L.

Table 4.4. Mean concentration of dissolved and total Cu in effluent water from each treatment. Treatments with the same letter have statistically similar concentrations in effluent.

	Cu dissolved (µg/L)		**Cu total (µg/L)**	
Influent	*18.25 ± 5.76*		*39.76 ± 19.13*	
C20	17.64 ± 8.43	abc	21.15 ± 8.77	bc
C20-W	5.10 ± 1.61	ef	7.77 ± 2.19	f
C40-FY	9.75 ± 1.26	cd	12.85 ± 2.20	de
C40-B	28.87 ± 8.27	a	31.91 ± 9.68	ab
C40-W	12.79 ± 1.80	bc	19.33 ± 3.21	bc
C80	30.27 ± 6.36	a	37.73 ± 7.95	a
SAND	4.02 ± 1.26	fg	17.90 ± 4.24	cd
C15-SS	11.03 ± 1.87	c	17.02 ± 3.91	cd
C15-OS	6.31 ± 0.86	de	10.89 ± 1.85	e
DCB8-LCS	1.08 ± 0.31	h	<MDL	h
DCB20	3.35 ± 1.09	g	5.98 ± 1.94	g
DCC20	3.18 ± 1.16	g	6.94 ± 6.01	g
DCB40-FSS	21.26 ± 4.18	ab	25.77 ± 5.40	abc
DCB50-SS	16.09 ± 7.47	abc	32.31 ± 41.15	abc

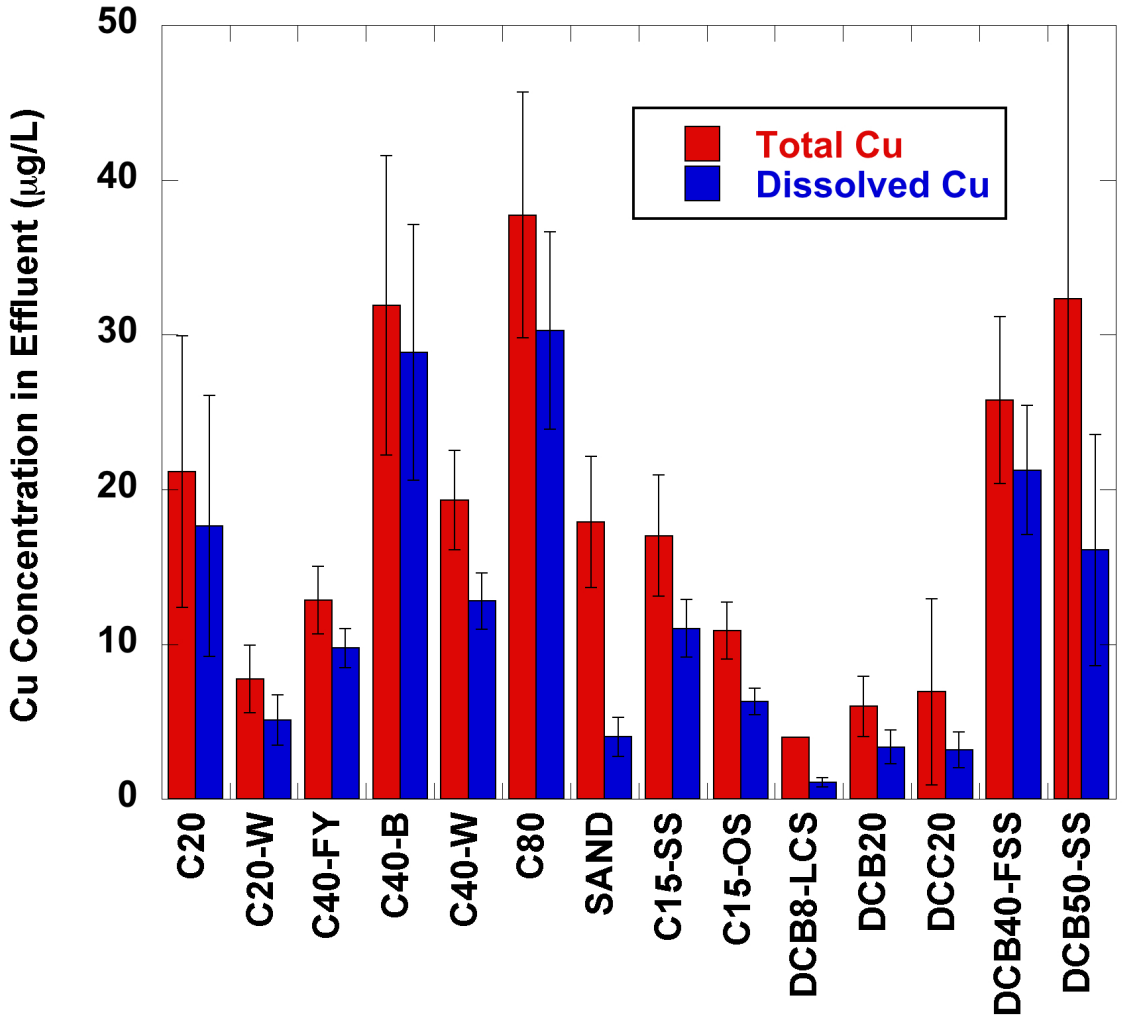


Figure 4.1. Mean concentration of dissolved and total Cu in effluent water from each treatment. Error bars represent plus or minus one standard deviation.

Certain patterns are evident in Figure 4.1. When comparing the treatments that contain only biosolids/yard compost and sand (C20, C40-B, and C80), it appears that total effluent Cu concentrations increase as the biosolids/yard compost fraction increases. However, statistically it can only be said that total Cu from C80 was higher than total Cu from C20, while C20 and C40-B were similar and C40-B and C80 were also similar. This indicates that doubling the compost volume proportion in a BSM does not significantly effect the dissolved or total Cu concentration in effluent.

Furthermore, when comparing paired treatments that have similar proportions of compost with and without WTRs added, it appears that the treatments with WTRs are more effective at removing Cu. Both dissolved and total Cu from C20-W is statistically lower than that from C20, while dissolved Cu from C40-W is statistically lower than that from C40-B (total Cu is similar). Other additives were less effective – C15-SS and C20 performed similarly, indicating that sawdust had negligible effect on Cu removal. The inclusion of oyster shells in C15-OS does appear to have affected performance, with C15-OS removing more copper than C20, but less than C20-W which contained WTR.

Finally, it is interesting to compare the three treatments with similar proportions of compost – C40-FY, C40-B, and C40-W. C40-FY, which contains 40% food/yard waste compost, had effluent concentrations of total and dissolved Cu that were statistically similar to C40-W, which had 35% biosolids/yard waste and 5% WTR. Cu concentrations from both treatments were statistically lower than those from C40-B. Figure 4.2 shows the same data as Figure 4.1 for total Cu effluent concentration, but uses a box plot to show the medians and quartiles.

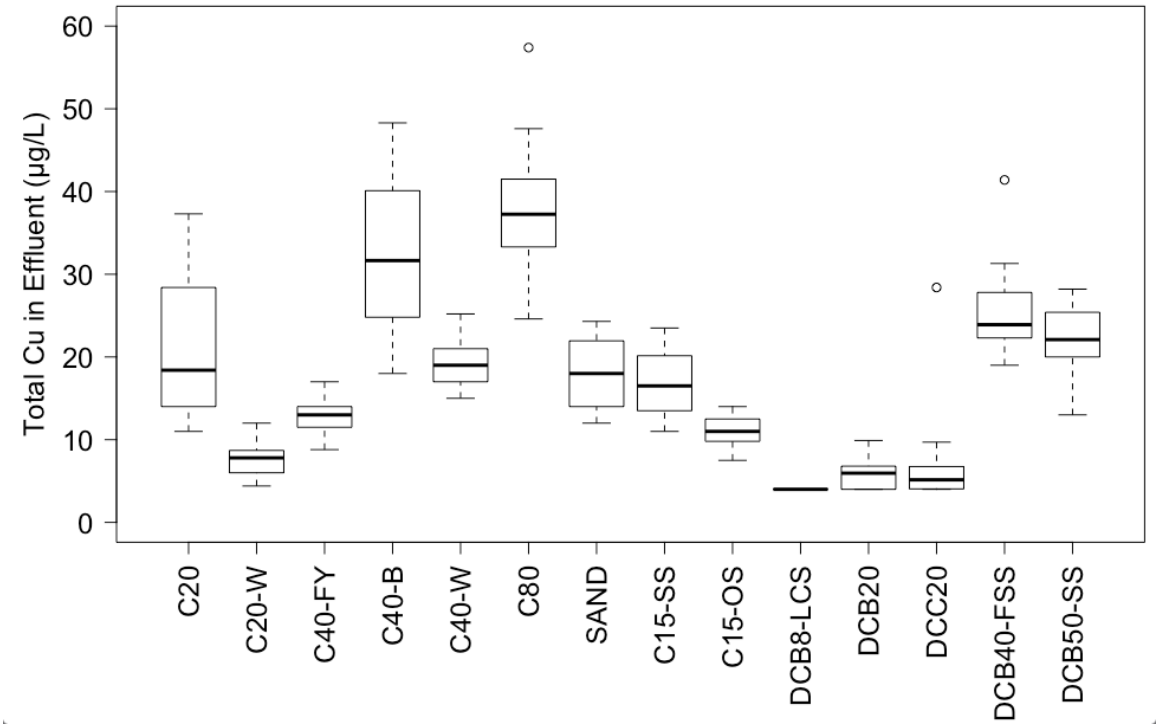


Figure 4.2. Total Cu concentration in effluent from all 14 treatments. Boxes show medians and upper and lower quartiles, whiskers show the minimum and maximum values. Points denote values outside the range of 1.5*IQR+Q3. One outlier for DCB50-SS is beyond the upper range of this plot but is nevertheless included in the calculation of the median and quartiles.

The data above synthesize the performance of 14 treatments over 4 separate storm events. In order to look more closely at each storm event, four treatments were chosen for comparison – C40-FY, the only treatment containing food/yard waste compost; Sand; C20-W, the best performing treatment containing biosolids/yard waste compost; and DCB8-LCS, the best performing treatment containing high Fe biosolids. Effluent concentrations of total and dissolved Cu for these treatments for all four events are shown in Figures 4.3 and 4.4.

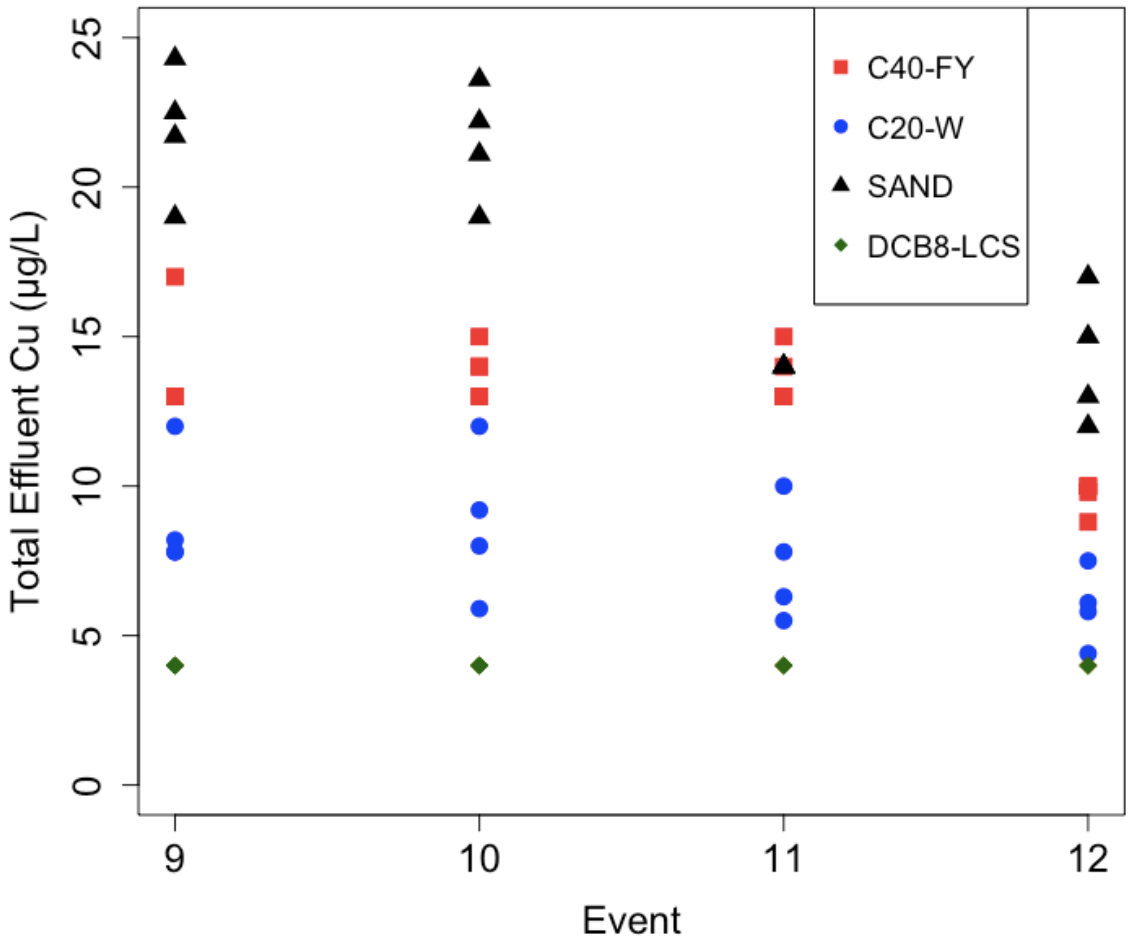


Figure 4.3. Effluent concentration of total Cu from all reps of C40-FY, C20-W, Sand, and DCB8-LCS, for events 9-12. Average influent concentration of Cu for these events was 39.76 µg/L. DCB8-LCS was consistently below the detection limit of 4 µg/L.

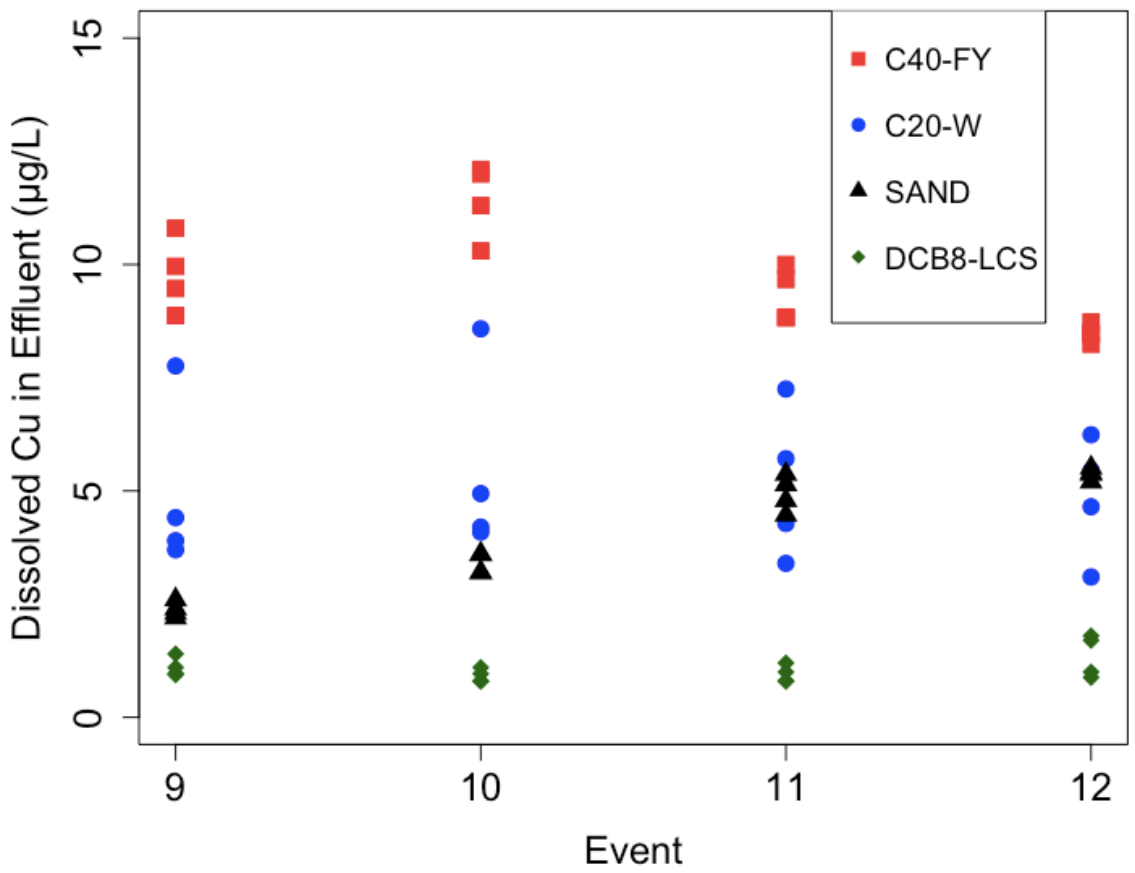


Figure 4.4. Effluent concentration of dissolved Cu from all reps of C40-FY, C20-W, Sand, and DCB8-LCS, for events 9-12. Average influent concentration of dissolved Cu for these events was 18.25 µg/L.

These graphs show that sand alone was less effective at removing total Cu than the other three treatments that contained organic matter. This was expected, since the presence of organic matter in soil tends to reduce metals mobility (Brady and Weil 2010; Sun and Davis 2007). For dissolved Cu, only DCB8-LCS was more effective than sand.

Zinc

Average concentrations of total and dissolved Zn in effluent water from all four storm events can be seen in Table 4.5. Numbers in this table show the mean and standard deviation of all reps of each treatment in all four leaching events that used actual stormwater as the

influent. Treatments with the same letter have statistically similar concentrations in effluent. These means are also shown in Figure 4.5.

All treatments acted as a sink for total and dissolved Zn, with varying degrees of removal. DCB8-LCS, DCB20, and DCC20 performed statistically similarly to each other and were the most effective at removing dissolved Zn, with average dissolved Zn below 3.15 µg/L. For total Zn, these three treatments along with C20-W were the most effective at removal, with average total Zn below 14.94 µg/L.

Table 4.5. Concentration of dissolved and total Zn in effluent water from each treatment. Treatments with the same letter have statistically similar concentrations in effluent.

	Zn dissolved (µg/L)		**Zn total (µg/L)**	
Influent	*112.56 ± 90.82*		*172.04 ± 86.77*	
C20	7.92 ± 3.22	bcd	13.61 ± 3.65	def
C20-W	4.30 ± 1.37	de	9.16 ± 2.60	fg
C40-FY	10.04 ± 2.70	bc	15.56 ± 3.18	cde
C40-B	20.18 ± 12.00	ab	26.18 ± 14.89	cd
C40-W	10.82 ± 2.44	bc	26.28 ± 7.31	bc
C80	57.56 ± 17.47	a	77.70 ± 21.34	a
SAND	3.90 ± 1.57	e	17.63 ± 3.18	cde
C15-SS	7.15 ± 1.54	bcd	15.88 ± 2.78	cde
C15-OS	5.97 ± 1.70	cde	11.17 ± 1.56	ef
DCB8-LCS	1.86 ± 0.89	f	14.94 ± 23.44	g
DCB20	2.50 ± 1.52	f	9.73 ± 4.61	fg
DCC20	3.15 ± 2.42	f	14.03 ± 14.40	fg
DCB40-FSS	37.28 ± 13.57	a	48.74 ± 18.38	ab
DCB50-SS	48.91 ± 24.83	a	89.88 ± 33.92	a

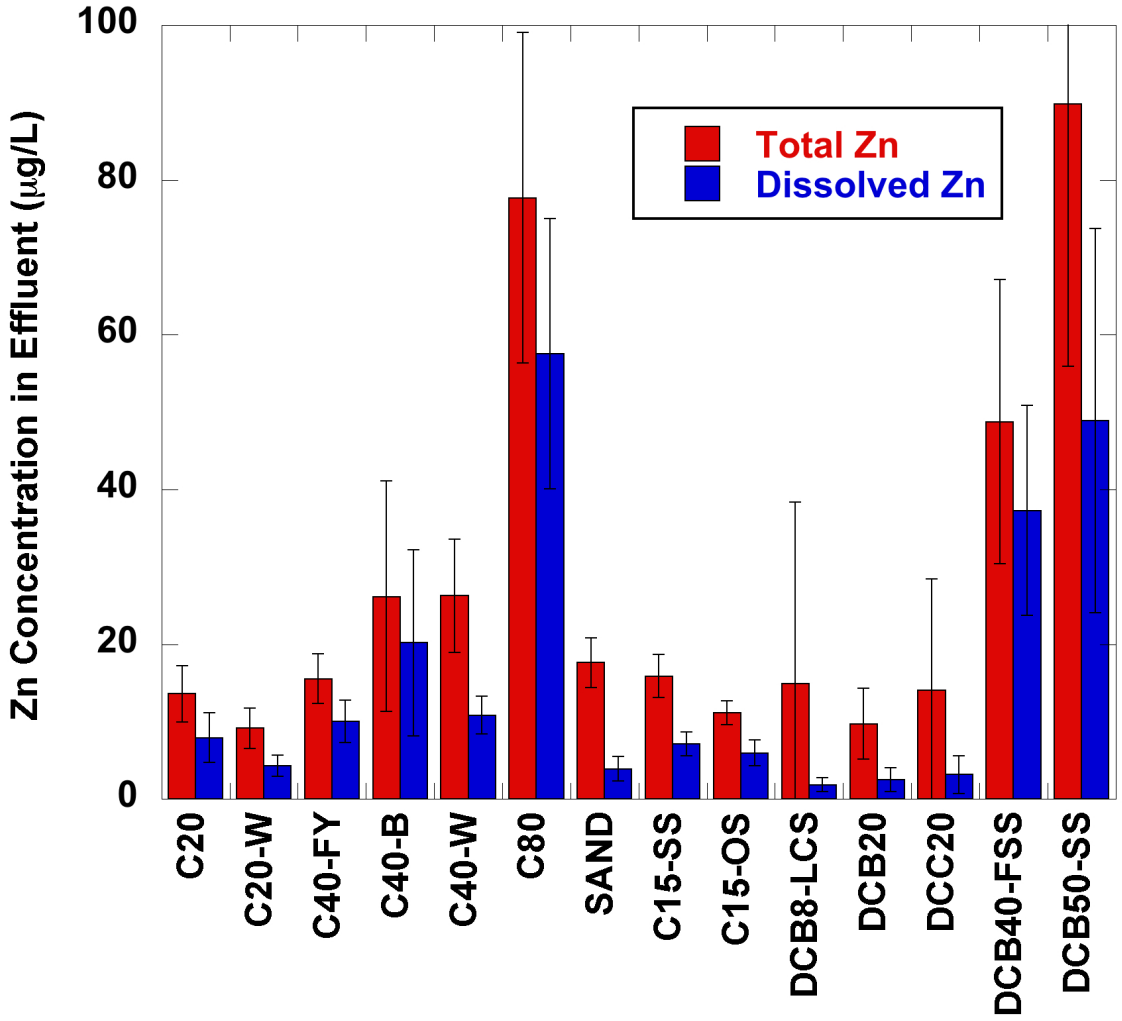


Figure 4.5. Mean concentration of dissolved and total Zn in effluent water from each treatment. Error bars represent plus or minus one standard deviation.

Results for effluent Zn resemble those for effluent Cu but are not identical. When considering the three treatments with increasing proportions of biosolids/yard compost (C20, C40-B, and C80), the means comparison shows that C40-B and C20 perform similarly for both total and dissolved Zn, but C20 and C80 are distinct with C80 performing less effectively. However, unlike with Cu, the paired WTR/non-WTR treatments did not perform significantly differently with respect to Zn. The other additives – sawdust and oyster shells – did not have a significant effect either. C40-FY also performed similarly to C40-B and C40-W, the other two

treatments containing similar proportions of compost. Figure 4.6 shows the same data as Figure 4.5 for total Zn effluent concentration, but uses a box plot to show the medians and quartiles.

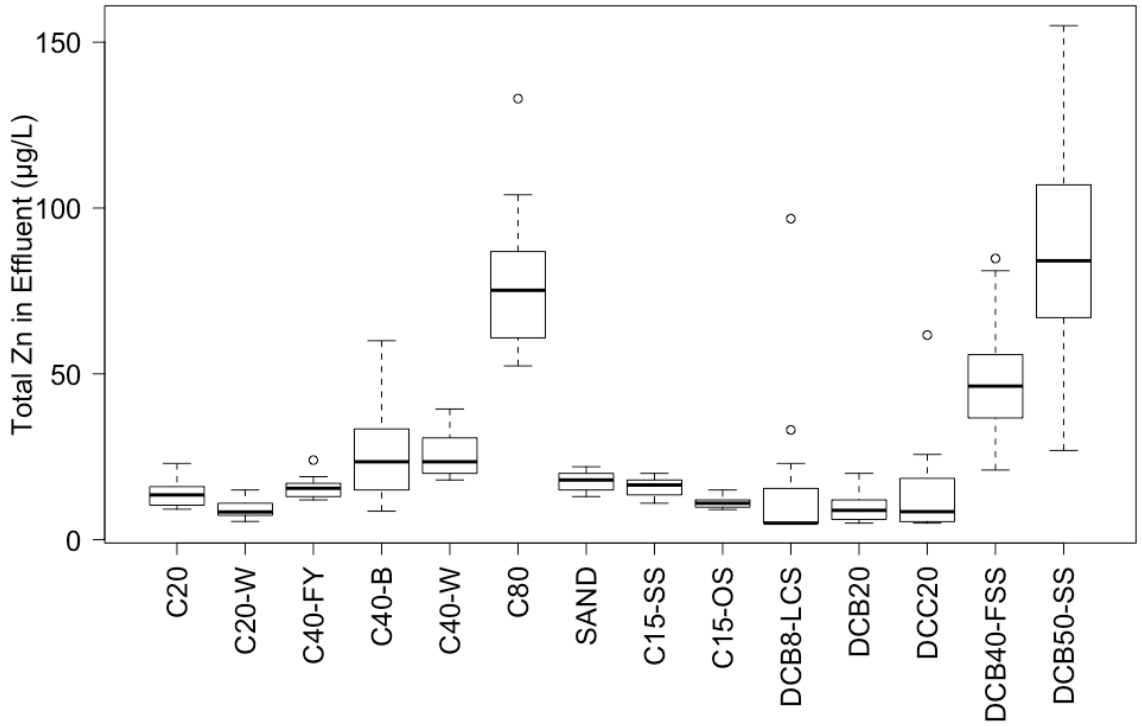


Figure 4.6. Total Zn concentration in effluent from all 14 treatments. Boxes show medians and upper and lower quartiles, whiskers show the minimum and maximum values. Points denote values outside the range of 1.5*IQR+Q3.

As above, four treatments were chosen for comparison in individual events – C40-FY, the only treatment containing food/yard waste compost; Sand; C20-W, the best performing treatment containing biosolids/yard waste compost; and DCB20, the best performing treatment containing high Fe biosolids (chosen arbitrarily from the three best performing treatments in this category which were statistically similar). Effluent concentrations of total and dissolved Zn for these treatments for all four events are shown in Figures 4.7 and 4.8.

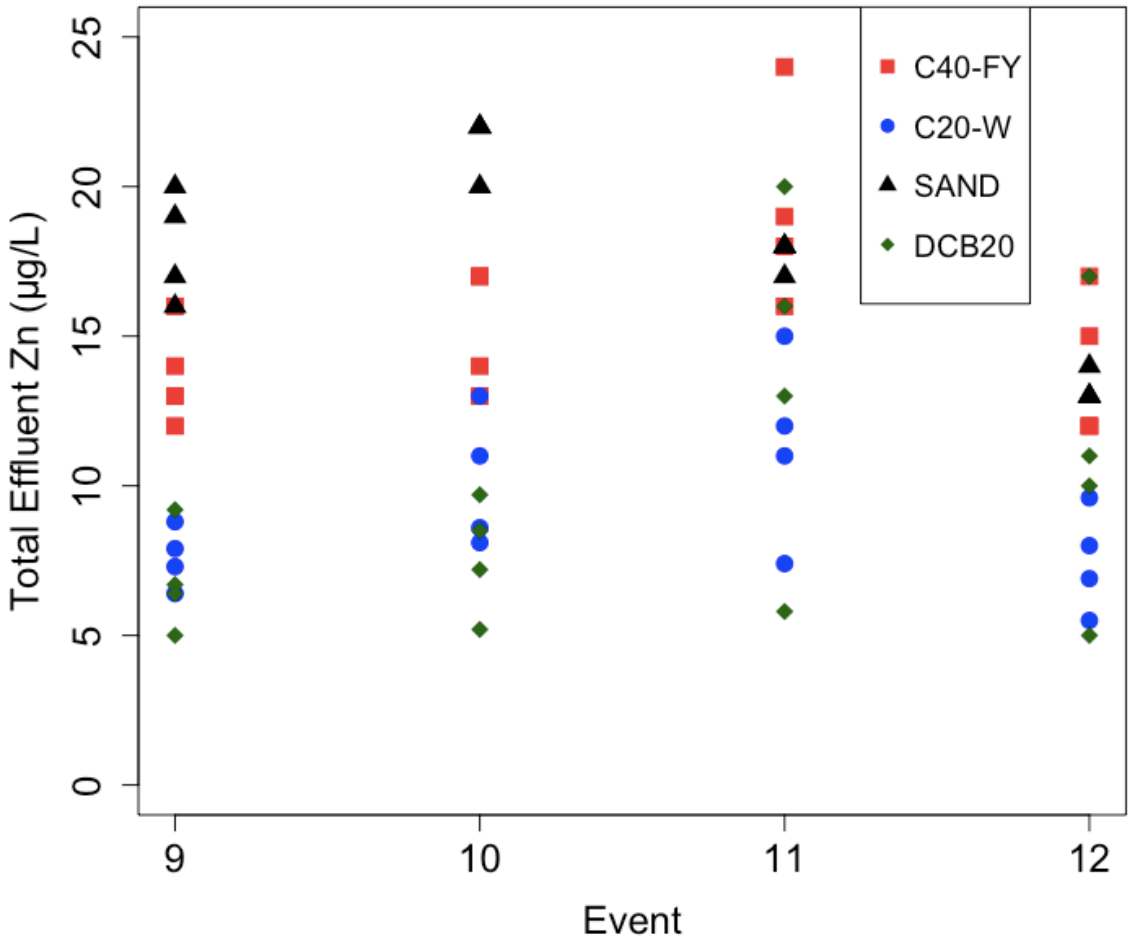


Figure 4.7. Effluent concentration of total Zn from all reps of C40-FY, C20-W, Sand, and DCB20, for events 9-12. Average influent concentration of total Zn for these events was 172 µg/L.

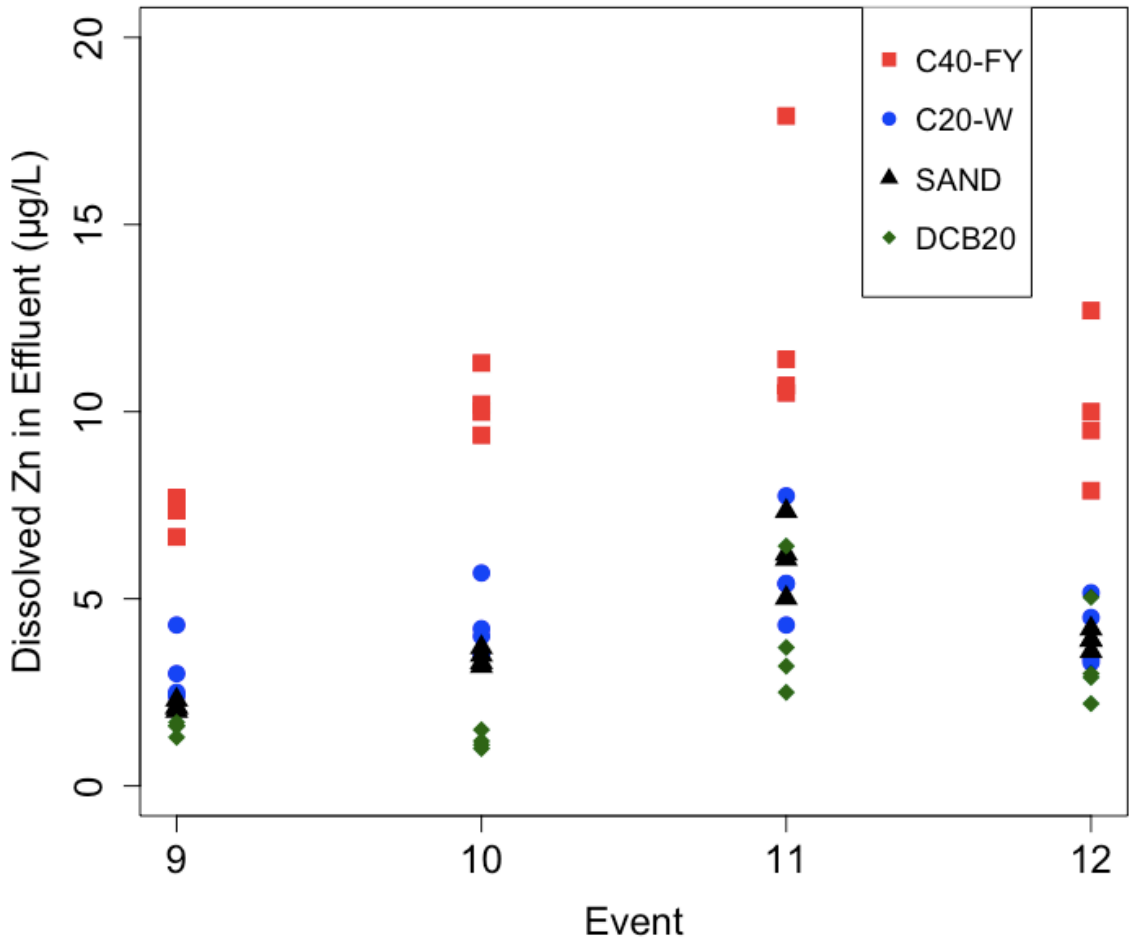


Figure 4.8. Effluent concentration of dissolved Zn from all reps of C40-FY, C20-W, Sand, and DCB20, for events 9-12. Average influent concentration of dissolved Zn for these events was 113 µg/L.

Once again, sand removes total Zn less effectively than the other three treatments, which contain organic matter. Sand is relatively more effective at removing dissolved Zn, where it is outperformed by only DCB20.

Discussion and Conclusion

It is worth noting that for both Zn and Cu, treatments containing high Fe biosolids – that is, pure biosolids – were most effective at removal. Comparing DCB20, which contains 20% high Fe biosolids cake by volume, to C20-W, which contained 17.5% biosolids/yard compost and 2.5% WTR by volume, we see that DCB20 was statistically more effective at removing total and dissolved Cu and dissolved Zn, and the two performed similarly with respect to total Zn. Although there is not a similarly one-to-one comparison available with a treatment containing food/yard compost (which was only included in C40-FY), it was established that the performance of treatments containing biosolids/yard compost did not significantly change when the compost portion was doubled – i.e., C20 and C40-B removed Zn and Cu equally effectively. If the same is true for food/yard waste compost, then a comparison between C40-FY and DCB20 may be useful. Looking at the mean separations, we see that DCB20 was statistically more efficient at removing total and dissolved Cu and Zn than C40-FY.

Despite these differences, all treatments acted as a sink for total Cu and Zn. Results in this study indicate how the different BSMs may perform in real-world bioretention systems with respect to Cu and Zn removal. When considering real-world applications, metals removal should be considered in the context of other crucial aspects of bioretention soils such as infiltration rate, plant growth, and removal of nonmetal contaminants.

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