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# Water Quality Performance And Greenhouse Gas Flux Dynamics From Compost-Amended Bioretention Systems & Potential Trade-Offs Between Phytoremediation And Water Quality Stemming From Compost Amendments

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# WATER QUALITY PERFORMANCE AND GREENHOUSE GAS FLUX DYNAMICS FROM COMPOST-AMENDED BIORETENTION SYSTEMS & POTENTIAL TRADE-OFFS BETWEEN PHYTOREMEDIATION AND WATER QUALITY STEMMING FROM COMPOST AMENDMENTS

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## ABSTRACT

Stormwater runoff from existing impervious surfaces needs to be managed to protect downstream waterbodies from hydrologic and water quality impacts associated with development. As urban expansion continues, increasing impervious cover, and climate change yields more frequent extreme precipitation events, this increases the need for improved stormwater management. Although green infrastructure such as bioretention has been implemented in urban areas for stormwater quantity and quality improvements, these systems are seldom monitored to validate their performance. Herein, we evaluate flow attenuation, stormwater quality performance, and nutrient cycling from eight roadside bioretention cells. Bioretention cells received varying treatments: (1) vegetation with high (7 species) and low-diversity (2 species) plant mixes; (2) proprietary SorbtiveMedia$^{TM}$ (SM) containing iron and aluminum oxide granules to enhance phosphorus sorption; and (3) enhanced rainfall and runoff (RR) to certain cells, mimicking anticipated precipitation increases from climate change. Bioretention water quality parameters monitored include total suspended solids (TSS), and dissolved and total nitrogen (N) and phosphorus (P) in the cells' inflows and outflows across 121 storms. Simultaneous measurements of flow rates and volumes allowed for evaluation of the cells' hydraulic performances and estimation of pollutant load and event mean concentration (EMC) removal. We also monitored soil $CO_2$ and $N_2O$ fluxes and determined C and N stocks in the soil media, microbial and vegetation biomass to determine the overall C and N balances in these systems.

Significant average reductions in effluent stormwater volumes and peak flows were reported, with 31% of the storms events completely captured. Influent TSS loads and EMCs were well retained by all cells irrespective of treatments, storm characteristics, or seasonality. Nutrient removal was treatment-dependent, where the SM treatments consistently removed P loads and EMCs, and sometimes N as well. The vegetation and RR treatments mostly exported nutrients to the effluent. We attribute observed nutrient exports to the presence of excess compost in the soil filter media. Rainfall depth and peak inflow rate undermined bioretention performance, likely by increasing pollutant mobilization through the filter media. While the bioretention cells were a source of $CO_2$, they varied between being a sink and source of $N_2O$. However, soil C and N, and plant C and N in biomass was seen to largely offset respiratory $CO_2$-C and biochemical $N_2O$-N losses from bioretention soil. The use of compost in bioretention soil media should be reduced or eliminated. If necessary, compost with low P content and high C: N ratio should be considered to minimize nutrients losses via leaching or gas fluxes.

To understand trade-offs stemming from compost amendments, we conducted a laboratory pot study utilizing switchgrass and various organic soil amendments (e.g., different compost types and coir fiber) to heavy metal contaminated soils and studied potential nutrient leaching and pollutant uptake. Addition of organic amendments significantly reduced metal bioavailability, and improved switchgrass growth and metal uptake potential. While no differences in soil or plant metal uptake were observed among the amendments, significant differences in nutrient leaching were observed.

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## DISSERTATION OVERVIEW

Stormwater is one of the pressing water quality challenges of today, and is responsible for impairing surface water bodies throughout the United States. Urban stormwater, which is runoff generated from developed lands, is major contributor to non-point source (NPS) pollution (NRC, 2008; Hsieh and Davis, 2005; Wang et al., 2000). Pollution from urban storm runoff is responsible for 15% percent of all impaired rivers (38,114 miles), 18% of all impaired lakes (1482 square miles) and 32% of all impaired estuaries (2742 square miles) in the United States (NRC, 2008). Pollutants commonly detected in urban storm runoff include nutrients such as phosphorus (P) and nitrogen (N), sediments, pathogens, and toxic substances such as heavy metals, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and pesticides (Davis et al., 2003a; Gilbreath and McKee, 2015; Klein, 1979; Walsh et al., 2005).

The Clean Water Act of 1972 spurred the development and widespread adoption of various stormwater best management practices (BMPs) to manage the quantity and quality of urban storm flows (Roy-Poirier et al., 2010). The low impact development (LID) approach was introduced in the 1990s in Prince George's County, Maryland as an alternative to conventional stormwater management approaches (LID Center, 2007). LID, also called Green Stormwater Infrastructure (GSI), comprises of a set of site design strategies which aims to mimic the hydrologic regime of predeveloped conditions by promoting infiltration, evapotranspiration, filtration, increasing concentration time for runoff, soil storage, groundwater recharge, and re-use of stormwater, while concurrently minimizing impervious cover and runoff (PGC, 1999; Davis, 2007; Hinman, 2005; Roy et al., 2008). LID or GSI employs wide array of small-scale technologies ranging from

bioretention, green roofs, pervious pavements, swales, planter boxes, infiltration trenches, rain barrels or cisterns, and constructed wetlands that treat water at the site level (PGC, 1999; LID Center, 2007; VT DEC[1]). However, the LID approach has historically focused on storm volume and peak flow reduction for flood control rather than targeting the treatment of specific contaminants in the stormwater (Roseen et al., 2006; Roy et al., 2008). More research is needed on the design choices that effectively target removal of specific pollutants through use of appropriate soil amendments, soil composition and plant selection. Improved understanding of subsurface flow, retention time needed for chemical sorption reactions and microbial transformations under various soil types, and the interplay between these factors can help enhance design features of GSI systems.

Bioretention, a prominent GSI option, is increasingly and commonly being implemented as a stormwater control measure in urbanized watersheds in the U.S. and abroad in the last decade (Davis et al., 2009a; Roy-Poirier et al., 2010). However, there has been very little monitoring to validate bioretention performance. Much of the research evaluating bioretention performances are from laboratory based column studies, and field performance data is lacking. Field confirmation of laboratory results is becoming more important because of the complexity associated with field installations, and the variability in the inputs of storm volumes and pollutant levels and plant survival (Davis, 2007). A limited number of field monitoring studies exist, which have showed that their performances are variable and the removal efficiencies are dependent on the pollutant type and the soil media composition itself. An increasing number of monitoring studies have in fact showed substantial leaching of phosphorus from compost-amended

[1] http://www.watershedmanagement.vt.gov/stormwater/htm/sw_gi_gsi.htm

bioretention systems (Dietz and Clausen, 2005, 2006a; Hatt et al., 2009; Hunt et al., 2006; McPhillips Lauren et al., 2018). In the light of this, it is becoming far more important to study and test the role of different soil amendments to enhance field performances of bioretention media.

Bioretention can increase urban landscape resiliency as an adaptation to mitigating climate change, but climate change could also affect bioretention functioning. Virtually no field installations have addressed the potential effects of climate change (i.e., altered precipitation regimes) on bioretention performances. With the projected increases in precipitation and extreme events for the northeastern U.S. including Vermont (Frumhoff et al., 2006; Hayhoe et al., 2007; Guilbert et al., 2014), it becomes important to understand the role of bioretention in not only mitigating water quality, but also in influencing urban landscape biogeochemical processes (Pataki et al., 2011) such as greenhouse gas (GHG) fluxes in meeting environmental goals.

Eight bioretention cells were constructed adjacent to paved roads at the University of Vermont (UVM) Bioretention Laboratory for improving storm runoff quality. The study included different treatments associated with bioretention soil, vegetation diversity and hydrology (e.g. drainage area and precipitation) that were informed particularly by pollution concerns in Lake Champlain (Guercio, 2010) and climate change predictions for Vermont (Guilbert et al., 2014). A fine-scale time resolution monitoring scheme was employed to sample influent and effluent water for comparing traditional water quality parameters. Gas fluxes from the soil were measured, and soil and vegetation nutrient content were quantified to study nutrient cycling dynamics from the cells. The results

from this study can inform stormwater design and management community about which attributes of bioretention design features are effective and resilient.

Chapter 1 is a comprehensive literature describing the impacts of urbanization and climate change on urban hydrology and watershed processes, the importance of bioretention as storm control measure, bioretention design features, major stormwater pollutants, precedent studies on bioretention performances, and biogeochemistry controlling nutrient fate in bioretention.

Chapter 2 is a field study investigating the water quality performance of eight roadside bioretention systems receiving different soil media, vegetation, and hydrologic treatments. The study evaluates (a) the composition of N and P species in bioretention inflows and outflows, (b) hydraulic performances, and pollutant (nutrients, sediments, metals) mass removal efficiencies (MRE), and event mean concentrations (EMCs) removal efficiencies from bioretention, (c) influence of environmental factors (precipitation depth, antecedent dry period (ADP), seasonality), hydrological factors (inflow volumes, inflow mass, peak flow, hydraulic loading ratio), and treatments (vegetation, soil media, hydrologic) on bioretention performance.

Chapter 3 investigates soil media $CO_2$ and $N_2O$ fluxes from the bioretention cells. Gas fluxes represent a potential nutrient loss pathway from bioretention, and must be evaluated. Most bioretention research focuses on water quality functions, but little is known about the potential for this practice to mitigate climate change. This chapter evaluates (a) soil media $CO_2$ and $N_2O$ fluxes (b) treatment, soil temperature and moisture effects on gas fluxes, (c) total amounts of C and N stored in the bioretention soil, microbes and aboveground plant biomass stocks to estimate overall C and N balance.

Lastly, the study compares fluxes to those from other bioretention studies, stormwater treatment systems, and land use types.

Chapter 4 is a laboratory pot study to explore water quality tradeoffs of using organic matter such as compost for phytoremediation. The study investigates the capacity for switchgrass, in combination with various organic amendments (e.g., different compost types and coconut coir fiber), to remediate soils contaminated by heavy metals. The study investigates the effects of the different organic amendments on pollutant uptake, plant growth, metal bioaccumulation, and nutrient leaching.

# CHAPTER 1: COMPREHENSIVE LITERATURE REVIEW

## 1.1 Urbanization impact on watershed processes

Urbanization is increasing rapidly around the world, and this trend is expected to continue with human populations expanding in future decades (United Nations World Urbanization Prospects 2008 Revision). More than 75% of the U.S. population lives in urban areas, and it is anticipated that over 60% of the world's population will live in urban areas by the year 2030, with the majority of growth occurring in the developing nations (Paul and Meyer, 2001). Urbanization brings about physical, chemical, and biological changes in watersheds by increasing areas that are largely impervious (e.g., roadways, sidewalks, parking lots, roofs) and inhibit natural infiltration of rainfall (Klein, 1979; Walsh et al., 2005, 2012). While in many natural ecosystems, more than 90% of water drains from uplands to streams by subsurface flow (Kaye et al., 2006). In contrast such hydrological flow paths are bypassed to produce moresurface runoff in urban areas. The reduction in infiltration and groundwater recharge seen in watersheds with greater impervious area, also reduces the influence of soil and plant on water chemistry and evapotranspiration (Gold et al., 2001; Walsh et al., 2012). In humid cities like Baltimore, a 10-20% in impervious surface area doubled the volume of surface runoff, reduced lag times between the onset of storms and peak discharge, and increased overall discharges during storms (Paul and Meyer, 2001). Higher peak discharges and runoff volumes increases the severity of flooding. Large runoff volumes and high intensity rains transport pollutants in the "first flush" of runoff and increase peak pollutant loading during storms (Aryal et al., 2010; Klein, 1979; Walsh et al., 2005). Physical effects from altering catchment hydrology with impervious surfaces can cause downstream channel erosion

and widening streams (Hollis, 1975; Klein, 1979; Ragan et al., 1977). In addition stream temperatures can increase (Galli, 1990), and water tables in riparian areas (known to be hotspots for nitrogen removal) might be lowered (Groffman et al., 2002), inhibiting denitrification functions. Meanwhile chemical changes can occur via elevated inputs of pollutants such as organics, nutrients (N and P), suspended solids, and heavy metals (Porcella and Sorensen, 1980) to public waters. Stream biology is also altered and compromised as a stream catchment is urbanized, with multiple studies having documented decreased fish, invertebrate and insect diversity with urbanization (Jones and Clark, 1987; Klein, 1979; Pratt et al., 1981; Shaver et al., 1995). Klein (1979) found that, across twenty-seven watersheds, and found that the stream quality was severely degraded in watersheds with greater than 30% imperviousness. Simulations predicted that water quality in small sub-watersheds (5 to 50 $km^2$ in area) declined when imperviousness exceeded 10% (Schueler. et al., 2009). Furthermore, rapid urban development (without retrofitting existing storm infrastructures) puts pressure on existing storm infrastructures, causing untreated sewage discharges to surface waters from combined sewer overflow, adversely affecting water quality and threatening aquatic health.

### 1.2 Climate change impacts on urban hydrology

Climate imposes uncertainties on urban runoff stressors; for example, increasing precipitation generates greater runoff volumes and subsequent wash-off of pollutants. When storms occur with greater intensity and duration, it is likely that the turbulence generated by the runoff will exceed critical shear stress and thus loosen and detach surface pollutants, availing them to transport (Vaze and Chiew, 2002). Climate change is

projected to bring more extreme rain events to certain regions, increasing the magnitude and frequency of floods (Frumhoff et al., 2006). As a result, the delivery rate of pollutant concentrations and loads to storm drains and surface waters may increase with the accentuated rainfall-runoff events. In other areas, climate change can result in less rainfall and increased risk of seasonal droughts (NRDC[2]). In cities, lack of infiltration and groundwater recharge due to impervious surfaces creates challenges in meeting public demands for water supply. Thus, there is urgent need for climate change adaptation strategies in stormwater management.

### 1.3 Importance of green stormwater management

Traditionally, urban storm runoff is collected and routed in closed engineered systems (i.e., storm pipes) to surface waters rapidly without treatment (PGC, 1999; Kaye et al., 2006). The conventional approach to dealing with storm runoff in urban areas is to take it off site as efficiently as possible via delivery conduits like catch basins to minimize local flooding and quickly convey runoff to receiving waters (such as streams and lakes and bays), or to a centrally located management system (i.e., wastewater facility in case of combined sewer system) (PGC, 1999; Walsh et al., 2012). There is little or no treatment of stormwater volume or quality, as a result of bypassing processes like natural filtering, or recharge to groundwater (Cook, 2007). Where the municipal sewer system is combined, the infrastructure is prone to failures during large storm events when its hydraulic treatment capacity is exceeded due to large runoff volumes. This results in combined sewer overflows, which directly releases untreated sewage and

[2] http://www.nrdc.org/health/climate/drought.asp

runoff, and associated nutrients and pathogens, into receiving waters (Roy et al., 2008). Such 'gray infrastructures' (i.e., catch basins, storm sewer) do not provide volume control and as a result, chances of flooding and streambank erosion are greater downstream of the built environment. In some cases, municipal water discharge can lead to riparian drying due to reduced groundwater recharge (Kaye et al., 2006). By contrast, GSI is a promising alternative for managing stormwater in urbanized areas and meeting Clean Water Act water quality goals (US EPA 2014).

GSI strategies involve the reduction or transformation of paved surfaces through the integration of plants, soils, and microbes in combination with hydrology and engineering design elements for stormwater management (Cook, 2007). GSI utilizes natural processes in order to modify post-development hydrology to closely mimic predevelopment conditions; GSI aims to achieve water quality goals by disconnecting impervious areas and hydrologic flow paths, retaining runoff volume, reducing peak discharge, and treating stormwater on-site (Davis et al., 2009a; Sansalone et al., 2013). Although GSI is primarily implemented as promising alternatives to the conventional "gray" stormwater management approach, their benefits can extend well beyond stormwater control. GSI may also provide a variety of ancillary benefits to urban environments ranging from regulation of the water cycle (Pataki et al., 2011), groundwater recharge (Davis et al., 2009a), countering the urban heat island effect (Brown et al., 2012), improved air quality (Grantz et al., 2003), aesthetics (Hurley and Forman, 2011), wildlife habitat and refugia (Liu et al., 2014), in addition to phytoremediation (Read et al., 2009) and carbon sequestration (Pataki et al., 2011). Therefore, GSI has the potential to effectively address different environmental issues

simultaneously. Integrating resilient and cost-effective GSI strategies in the way we manage urban stormwater can increase the capacity and longevity of storm sewer systems (Roy-Poirier et al., 2010), reduce pollutant loads to waterways, and foster environmental stewardship.

### 1.4 Bioretention for urban stormwater management

Bioretention systems (also commonly referred to as raingardens, bioswales or biofilters) are a type of GSI; bioretention cells are typically implemented on roadsides and within parking lots. Bioretention uses a combination of porous soils and vegetation media (Figure 1) to detain and infiltrate pollutant-laden runoff conveyed as sheetflow or via curb cuts of pipes from the impervious surfaces to the treatment unit (Cook, 2007). As the runoff percolates to ultimately restore groundwater and baseflow in streams, plant uptake and evapotranspiration of the water occurs, which substantially reduces stormwater volume and peak discharge (Davis et al., 2009a; Flynn and Traver, 2013). Within the bioretention media, as the runoff velocity is reduced, sediments and pollutants have longer periods of contact with the soil media and undergo physical (e.g. filtration), biochemical (e.g. denitrification) and physico-chemical reactions (e.g. removal of dissolved phosphorus and heavy metal through sorption) (Feng et al., 2012; Liu et al., 2014; Lucas and Greenway, 2007b), which overall reduces pollutant load in the effluent.

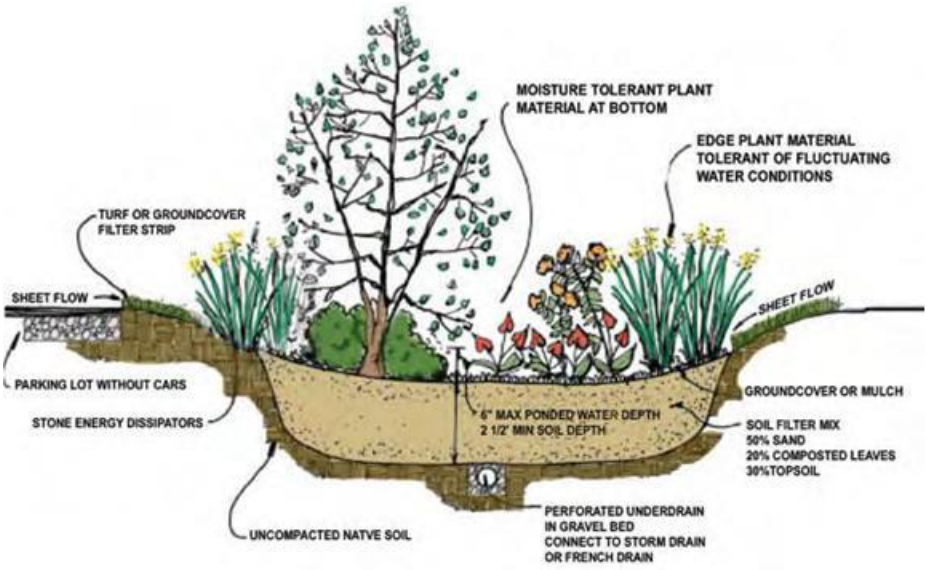


**Fig. 1.** Typical layout of a bioretention basin (Source: Low Impact Development Manual for Michigan)

Phytoremediation can contribute to uptake of pollutants like nutrients and heavy metals (Davis et al., 2003a). Runoff is also stored temporarily within soils and aboveground, in the ponding zone planted with vegetation, to be released slowly downstream. In intense storm events, this can alleviate pressure on existing storm infrastructure, and reduce peak discharge and downstream flooding. Additional benefits include shade, wind-breaks, noise absorption, wildlife habitat, aesthetic value (Cook, 2007) along with carbon sequestration through photosynthesis.

### 1.5 Bioretention features

Bioretention design must employ range of features that are targeted to perform specific functions to meet the water quality goals in the area. Design features vary in surface area, ponding depth, soil/filter media depth and composition, plant palette, time of concentration, and presence or absence of pre-treatment facility and drainage

configurations like perforated underdrain pipe and overflow design (Davis et al., 2009a). The filter media depth is typically 0.6 m up to 1.3 m deep to allow adequate time for filtration and pollutant removal. Bioretention is designed to maximize infiltration. The size of conducting pores affects the hydraulic conductivity of the media, and since larger pores conduct water more rapidly, sandy media is traditionally favored (Hsieh and Davis, 2005). Native soil with high permeability is also used, particularly when the soil is predominantly sand or belongs to the hydrologic soils group "A" classification such as sandy loam, loamy sand (UNHSC Report 2012). Clays tend to swell after absorbing water and shrink upon drying (Weil et al., 2016), which can impede infiltration rates. If the underlying native soil is clay and poorly drained, a perforated underdrain structure is installed at the bottom of the bioretention cell to prevent water from standing in the unit for prolonged periods (Roy-Poirier et al., 2010). The underdrain helps convey the water to a storm drainage network.

Vegetation and microorganisms in the bioretention unit are considered important in controlling the fate of nutrients (Davis et al., 2006), and provide ecological treatment of stormwater. Vegetation also plays an integral role in their functioning and longevity. In fact, the effluent quality from vegetated bioretention filters has been shown to be significantly better relative to effluent from unvegetated bioretention systems, in both laboratory (Bratieres et al., 2008; Denman et al., 2006; Henderson et al., 2007; Lucas and Greenway, 2007b) and field-based studies (Breen, 1990; Rogers et al., 1991; Song et al., 2001). Plants with shallow root systems provide less effective treatment relative to deep-rooted plants (Lintern et al., 2011; Read et al., 2008). Bioretention plants represent a small carbon sink, while contributing directly to pollution remediation via

phytoremediation processes. Plant root growth and senescence counters compaction and clogging of the pore spaces in the media through creation of soil macropores (Hatt et al., 2009; Read et al., 2009). The presence of macropores allows water to move to deeper soil layers, and overtime maintains the hydraulic conductivity and media filtering capacity (Quinton and Hess, 2002). Plants intercept precipitation and conduct evapotranspiration. Through root exudates and photosynthetic inputs to soil, plants continue to enhance soil physiochemical properties in order to sustain microbial populations (Read et al., 2009), which in turn facilitate nutrient transformations and subsequent removal from stormwater under ideal conditions (e.g. denitrification, which is pertinent for nitrate removal). Further, the aesthetic nature of plants has the potential to influence public acceptance of bioretention systems.

### 1.6 Lake Champlain Research Context

Lake Champlain is a freshwater lake located mainly within the borders of Vermont and New York, and partially located across the Canada-United States border. The Lake Champlain Basin (LCB) is a 21,326 $km^2$ watershed with 56% of it falling in Vermont, 37% in New York, and 7% in Canada. Over 90% of the water that flows to the lake drains from the surrounding watersheds (LCBP 2016[3] ). Historically, many of the water quality concerns surrounding Lake Champlain have been related to high levels of P, causing summer and fall algal blooms since the 1970s. In a 2015 Lake Champlain Basin Program (LCBP) study, 41% of the nonpoint source load for P was estimated to originate from agricultural lands, 18% from urban or developed lands, 16% from

[3] http://www.lcbp.org/about-the-basin/facts/

forestlands, 20% from streambank erosion, 4% from WWTFs, and 1% from wetlands[4]. Due to high levels of P concentrations in many lake segments, Vermont established the first total maximum daily loads (TMDL) in 2002 (Guercio, 2010). TMDL calculates the maximum amount of a given pollutant that is legally allowed to enter a waterbody from all the point and non-point sources daily and still meet the required water quality standards for that pollutant. To meet the state's TMDL standards, management strategies are being developed to clean up Lake Champlain by providing incentives to develop new and innovative stormwater BMPs to specifically reduce pollutant loads from urban landscapes. The lake serves as the primary source of drinking water for 35% of the basin's population, and is important for economic activities such as agriculture, recreation and tourism, which can be affected by climate change that Vermont is experiencing (Pealer, 2012).

Climate data from the past 40-year record (1963 to 2003) shows that precipitation in LCB has increased by 8% and 38% at low and high elevations, respectively (Beckage et al., 2008). Vermont is experiencing more extreme rain events, and that trend is anticipated to continue (Pealer, 2012). The region was impacted by extreme weather events including significant flooding in 2011 from heavy spring rainfall and Tropical Storm Irene that followed the very summer. These extreme storm events caused extensive damage to public infrastructure (i.e., wells submerged by floodwaters possibly exposing them to harmful chemicals or pathogens, release of 10 million gallons of untreated sewage from wastewater treatment facilities (WWTFs) and private property, and thus demands attention to the potential impacts of climate change (Pealer, 2012).

[4] http://sol.lcbp.org/Phosphorus_where-does-p-come-from.html

### 1.6.1 *Climate change prediction for Northeast U.S.*

From 1970 to 2011, every state in the U.S. experienced warming trends. Over this period, three of the ten fastest warming states were in the Northeast (Maine, Massachusetts, and Vermont; Climate Central 2012). Temperatures across the Northeastern U.S. are expected to rise further by 2.5 to 4°F in winter and 1 to 3°F in summer over the next few decades (Frumhoff et al., 2006). The warming has been correlated with observable hydrological changes such as increase in heavy rainfall events, earlier spring snowmelts resulting in earlier, higher spring river flows, and less precipitation falling as snow and more as rain (Frumhoff et al., 2006). For the contiguous United States, over the last several decades, there has been an increase in the occurrence of annual number of wet days (e.g., 5-10 days $yr^{-1}$ in the eastern U.S., and 10-15 days $yr^{-1}$ in the west) and heavy precipitation days and in the mean daily and annual total precipitation, despite regional variability (Higgins et al., 2007; Karl and Knight, 1998). In the upcoming several decades, Vermont and other Northeastern states are projected to experience more frequent and intense rainfall events (Frumhoff et al., 2006; Pealer, 2012). Average daily precipitation is projected to increase between 5 and 10% (10% being an increase of 4 inches $yr^{-1}$) by midcentury, and between 7 and 14% by late century (Guilbert et al., 2014; Hayhoe et al., 2007). Extreme precipitation events (amount of precipitation that falls over five consecutive days) will also progressively increase over the century, i.e., 8% by mid-century, and 12-13% by late century (Frumhoff et al., 2006).

## 1.7 Stormwater pollutants in urbanized watersheds and their impacts

Major pollutants in storm runoff include total suspended solids (TSS), nutrients such as P and N, heavy metals, pathogens, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and pesticides (Davis et al., 2003a; Gilbreath and McKee, 2015; Klein, 1979; Walsh et al., 2005). These pollutants can alter the turbidity, temperature, pH, and salinity of surface waters (Corcoran et al., 2010) and decrease water quality for aquatic biota (Pratt et al., 1981). TSS, N, P, and heavy metal pollutants will be discussed in the subsequent sections.

### 1.7.1 *Total suspended solids*

Total suspended solids (TSS) are any solid organic or inorganic materials that are suspended in the water[5] and will not pass through a 2-micron filter (NEMA 2014). While point source for TSS in urban areas can include WWTFs, nonpoint sources include erosion from bare lands and construction sites. Urban runoff is also a source/carrier of TSS, as heavy rainfall washes soil particles and debris from streets, commercial, and residential areas directly into streams, or storm drains that discharge directly to streams. Since infiltration is decreased due to large amount of imperviousness, and there are less natural areas for settling, runoff velocity is increased, which can increase the delivery of silt and clay particles, as well as larger sand-sized sediments and contribute to greater TSS amounts from land into surface waters. High water volumes and velocities resulting from urbanization can increase the speed of the water current downstream, resulting in streambank erosion and re-suspension of particulate matter from bottom sediments[6].

[5] https://www.ndhealth.gov/WQ/SW/Z6_WQ_Standards/WQ_TSS.htm

TSS impairs surface waters by increasing turbidity, which reduces sunlight penetration and subsequently slow down photosynthesis of benthic vegetation[6]. DO levels are decreased due to lower photosynthesis. Suspended solid particles can absorb heat from sunlight, which increases water temperature, which also affects DO levels, as warmer waters cannot hold as much oxygen as colder water. Further, suspended solids can clog fish gills, and their settling from the water column can smother eggs and larvae, and occupy void spaces between rocks. Prior to sedimentation, these microhabitats are used by various aquatic insects. Sedimentation limits the ability of the water to support a diverse aquatic life. Besides these direct effects, the sorption of dissolved substances (especially phosphate) and toxic heavy metals to TSS (Carritt and Goodgal, 1954) can lead to unintended consequences when, under turbulent flow caused by large storms contaminated sediments are resuspended to the water column and made bioavailable.

Measures to curb TSS from urban watersheds should focus on reducing loading suspended solids to storm drains, streams, and rivers. Apart from regular street-sweeping, proper GSI incorporation in urban areas can go a long way in effectively reducing TSS concentrations in urban runoff.

### 1.7.2 *P sources, sinks, and cycling in urbanized watersheds*

#### 1.7.2.1 *Land*

Sources of P in urban catchments include wastewater and fertilizers (La Valle, 1975). Lawns and streets were the primary source of P to urban streams in Madison, Wisconsin due to fertilizer application (Waschbusch et al., 1993). Soils under septic field

[6] https://www.ndhealth.gov/WQ/SW/Z6_WQ_Standards/WQ_TSS.htm

systems, while retaining some P, can also leach variable amounts of P to groundwater, which can affect stream P concentrations (Gerritse et al., 1995; Hoare, 1984). Construction activities including clearing of previously agricultural land for development can expose soils, and under heavy rain events, deliver P-laden sediment to waters (Paul and Meyer, 2001). In northern temperate climates, most of the P loading occurs in winter–spring from a combination of snowmelt and spring runoff, which is driven by weather conditions. Total dissolved inorganic phosphorus (DIP) concentrations of river water can increase by double up to four-fold during and following increases in river discharge from heavy rainfall events or in the early stages of snowmelt (Wetzel, 2001). Streambank erosion of land adjacent to urban, suburban or agricultural areas, from intense rainfall-runoff events, is another big source of P loading to streams (DeWolfe et al., 2004),which can impact downstream lakes that receive input from such waters.

P accumulates on land due to decadal application of fertilizer and manure excessive to crop requirements (Carpenter et al. 1998), which has been described as "legacy P" (Kleinman et al., 2011). Soils are typically considered a sink for P through chemical immobilization or sorption of orthophosphate (orthoP or phosphate) onto the finer clay and silt particles, and to iron (Fe) and aluminum (Al) hydroxides, and calcium carbonate ($CaCO_3$) compounds (Richardson 1985) present in the soil. In acid soils, P precipitates with Fe and Al hydroxides, whereas in alkaline soils, P precipitates with Ca minerals. Additionally, higher metal content (Fe, Al, and Ca), and electrical conductivity (indicator of total soluble metal ion content of substrate) has also shown to increase P sorption (Roy, 2016; Wang et al., 2013). Sorption is the removal of a compound from

solution by concentrating it in (absorption) or on (adsorption) a solid phase such as soil particles or organic matter (Figure 2), through one of two processes:

(i) Ligand exchange – an anion (i.e., orthoP) replaces a surface hydroxyl ion that is bonded with a metal cation in a solid phase (part of the clay layer). In acidic waters this occurs with Fe, Al, Mn, and in basic waters with Ca, Mg.

(ii) Ion exchange – ions are attracted to and loosely bound by negative and/or positively charged sites on permanent and variable charge soil surfaces (Rhue and Harris, 1999).

Phosphate sorption is influenced by pH, ionic strength, type of P compound, and other ion species competing with phosphate for adsorption (Hansen et al., 1999). Desorption reactions can also occur on clays, Al and Fe oxides to re-release orthophosphate ions from soil surfaces back in solution (Figure 2). Phosphorus can be removed from soil by plant uptake.

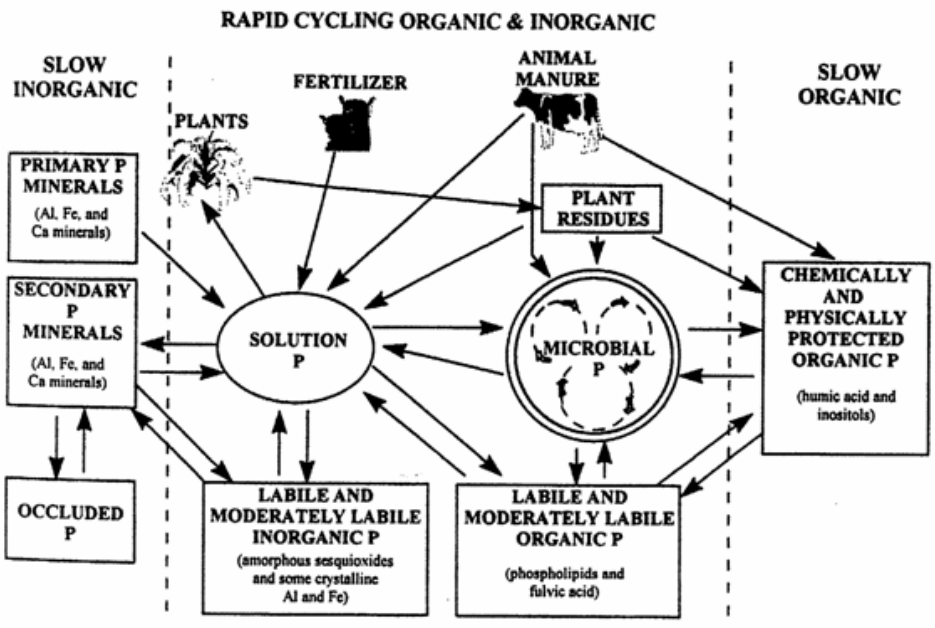


**Fig. 2.** Phosphorus cycle in the soil (Source: www.spectrumanalytic.com)

In soils prone to runoff during intense storms P can be transported to aquatic ecosystems as both dissolved and particulate (sediment-bound) P forms (Correll, 1998) through erosion and runoff, where it accumulates in sediments. Erosion moves particularly finer soil particles that are P-enriched (Kleinman et al., 2011). "Legacy P" is a problem in various lakes in the U.S. including Lake Champlain, Great Lakes, Lake Mendota, and Lake Erie, Lake Washington, Tabor Lake, among others. It is expected that even long after external P inputs to the lakes from urban, forest and agriculture runoff are ceased, the de-sorption and internal cycling of "legacy P" from mineral sediments in lake bottoms, can increase bioavailable or algal-available P, and delay the response of watersheds to land management efforts in mitigating eutrophication (Kleinman et al., 2011; Larsen et al., 1979; Scheffer et al., 1993). As lakes are enriched, P accumulates in the sediments, and the rates of recycling from sediments to the overlying water ("internal loading") increase. Whole-lake experiments show that cycling rates can build to significant levels in a matter of years (Schindler et al., 1971). On an annual basis, recycling from sediments to water of eutrophic lakes commonly exceeds external inputs of P (Nürnberg, 1984; Soranno et al., 1997).

**1.7.2.2** *Internal cycling of P in waters and sediments*

Inorganic orthophosphate (orthoP; $PO_4^{3-}$ either as $H_3PO_4$, pH<2.16; $H_2PO_4^-$; pH<7.2, or $HPO_4^{2-}$, pH<12.5, Stumm and Morgan, 1970), sometimes called soluble reactive phosphorus (SRP), ortho-P or dissolved inorganic P (Li and Brett, 2013), is considered the most mobile and bioavailable or algal-available form of P within sediments and the water column (Giles et al., 2015), though organisms may also utilize

dissolved organic P (DOP), when supply of ortho-P is limited for biomass growth (Lin et al., 2016). Eutrophication can accelerate desorption of e ortho-P from sediments to the overlying bulk water primarily by depleting dissolved oxygen (DO) (Correll, 1998; Giles et al., 2015). Oxygen is not able to diffuse into the water column as rapidly as the microbial consumption of oxygen, leading to anaerobic condition. This condition is more common in summers due to higher temperatures increasing microbial activity. Anoxic conditions in eutrophic waters (lakes and estuaries) leads to the reduction and dissolution of mineral-phosphate complexes (Giles et al., 2015; Lake et al., 2007; Norton et al., 2008) that otherwise remove P from the solution/bioavailable phase to solid/particulate phase, and act as P sinks. For example, iron hydroxide ($Fe(OH)_{3(solid)}$) has a strong binding capacity for inorganic phosphate in the water column and oxic sediments. Under anoxia and when certain pH conditions are met however, $Fe(OH)_3$ dissolves and releases adsorbed $PO_4$ (i.e., $Fe^{3+}$ is reduced to $Fe^{2+}$, a more soluble form of iron, and both $Fe^{2+}$ and the adsorbed P are released into the solution) thereby rendering the P bioavailable, where it can also diffuse more freely (Correll, 1998; Lake et al., 2007). Also under anoxic conditions, lower concentrations of oxidized Fe minerals are present that can adsorb P. Though the affinity of P is much stronger for Fe oxides, it is also known to bind with Al oxides and almost irreversibly so that even under reducing conditions, P is much less likely to desorb from Al hydroxides (Lake et al., 2007). Besides oxygen levels and pH controlling P cycling mechanisms, photo-redox reactions due to sunlight in shallow lakes can also degrade mineral-organic complexes, producing free radicals that are highly reactive and which decompose organic matter, releasing organically bound P in the process (Essington, 2015). In addition, if conditions in the bay allow for aerobic activity

in the sediment-water interface, P will also be made bioavailable by microbial mineralization or (aerobic) decomposition of organic matter (Andersen and Jensen, 1992).

Beside chemical adsorption of P by Fe and Al hydroxides in minerals soils and sediments in conjunction with aerobic conditions, phosphate ions also adsorb onto $CaCO_3$ (i.e., by replacing the carbonate, leading to formation of calcium phosphate minerals called apatite (Kitano et al., 1978; Schlesinger, 2005). However, $CaCO_3$ sorption is considered less important than iron-phosphate complexes in controlling the concentrations of phosphorus in sediments (Wetzel, 2001). P can be mobilized from its solid or "sorbed" phase in sediments (and soils) into the solution phase depending on certain pH changes in the environment. For example, when pH is lower or greater than 6.5, Al or Fe-phosphate complexes become soluble, and have decreased P sorption capacity, while calcium phosphates become soluble at lower pH (Wetzel, 2001).

Biological sinks of P include uptake by microorganisms, plants, algae and cyanobacteria (Wetzel, 2001), while their death releases P during decay. No significant gaseous component of P exists, and the atmospheric transport of P in soil dust is relatively small compared to other transfers (Schlesinger, 2005) such as erosion, river discharge, internal cycling in sediments and soils discussed above.

Algal blooms in Lake Champlain, first documented in the 1970s, are associated with increasing P concentrations in the lake, and intensify during summer months when increasing temperatures increase algae productivity. The detrimental effects of eutrophication have stimulated efforts to control P input to lakes.

### 1.7.3 *N sources and sinks in urbanized watersheds*

The various sources of N in urban systems include effluents from WWTFs, fertilizers applied to gardens, lawns and golf courses, human and pet wastes, landfill leachates, industrial processes, and atmospheric (wet and dry) transport and deposition of various N-containing compounds such as $NO_x$ (i.e., NO, $NO_2$) in the automobile exhausts and other fossil fuel combustion sources (Bouwman et al., 1997; Carpenter et al., 1998). Due to the short residence time of $NO_x$ in the atmosphere, most of it falls over land by precipitation, where it enters biogeochemical cycles (Schlesinger, 2005). Natural sources like biological N fixation (conversion of $N_2$ to $NH_4$) in the root nodules of leguminous plants, and lightning, though minor compared to anthropogenic sources, also makes oxidized nitrogen ($NO_x$) available (Schlesinger, 2005). Various other gaseous N oxides, although not generated directly from urban activities, come from natural soils, agriculture and forestry operations such as biomass burning, deforestation, cattle farming, manure application to soils (Bouwman et al., 2002), and forest fires (causing volatilization of $NH_3$, $NO_x$, and $N_2$; Schlesinger, 2005). Land use changes through urbanization can alter biogeochemical cycles of N, transforming the ecosystem from being a sink to source or vice versa of pollutant. For example, altering catchment hydrology in humid urban areas such as Baltimore negatively impacted the ability of urban riparian zones to intercept and subsequently remove upland-derived $NO_3^-$ via denitrification process, owing to water table lowering (Groffman et al., 2002; Kaye et al., 2006). Simultaneously, where riparian areas have been eliminated, human activities are also creating alternative hotspots for denitrification or $NO_3^-$ sink such as in stormwater detention basins, roadside ditches, and drainage swales (Groffman and Crawford, 2003a; Zhu et al., 2004), and in lawns and

other places where there is adequate water, nitrate and soil organic matter conducive for the reaction to occur (Kaye et al., 2006). Urban landscaping through vegetation planting also represents a small nutrient sink as plants accumulate nutrients in biomass and soil organic matter.

#### **1.7.3.1** *Atmospheric N forms*

N in precipitation is present as ammonium ($NH_4^+$), nitrate ($NO_3^-$), and dissolved organic N, and they all play major a role in the nutrient cycling of surface waters (Russell et al., 1998). $NH_4^+$ exists in precipitation due to dissolution of atmospheric $NH_3$ gas, whose major sources are from biomass burning, animal excreta, and synthetic fertilizer applications to soils (Bouwman et al., 1997; Prospero et al., 1996). Major N oxides from atmospheric transport and deposition standpoint include NO, $NO_2$ (collectively referred to as $NO_x$), and $NO_3^-$ (in the form of $NO_3^-$ aerosols and as gas phase $HNO_3$) (Bauer et al., 2007; Prospero et al., 1996). $NO_3^-$ mainly exists in rainwater because of dissolution of $HNO_{3\,(g)}$, which is primarily derived from $NO_x$. Major natural sources of $NO_x$ to the atmosphere include lightning and biological fixation, and major anthropogenic sources include fossil-fuel combustion by power plants and automobiles and biomass burning (Russell et al., 1998).

The sources of dissolved organic nitrogen (DON) are less well known, but they are present in precipitation, though they are poorly characterized (Jickells et al., 1990; Knap et al., 1986; Rendell et al., 1993). Studies have shown that phytoplankton are capable of using DON as a nutrient source (Antia et al., 1991; Timperley et al., 1985),

highlighting the importance of quantifying both inorganic and organic forms of nitrogen when studying eutrophication (Russell et al., 1998).

#### **1.7.3.2** *Terrestrial forms*

Soil organic matter, plants, and soil microbes in the upland ecosystems act as both sources and sinks of N, and the cycling of N between these entities can regulate N supply in the solution that is available for leaching into surface or ground waters. The main processes through which N is transformed and cycled between these entities are plant uptake during growth, N mineralization through decay, immobilization, nitrification and denitrification (Figure 3). Most of these processes are mediated by microorganisms. N mineralization is the conversion of organic N (i.e., N bound in dead plant biomass) to $NH_4^+$ by bacteria and fungi during decomposition. Volatilization may be responsible for the loss of $NH_3$ in soil-water systems. Volatilization in flooded soils occurs at pH above 7.5 or 8. However, since the pH of stormwater is unlikely to be higher than 8 (Hatt et al., 2004), volatilization is not expected to be a common nutrient removal processes in bioretention systems. Some of the $NH_4^+$ can be removed by sorption processes (Phillips, 2002), or taken up by plants for growth, while some is used by bacteria for growth or their own metabolism in the nitrification process, by converting $NH_4^+$ to $NO_3^-$, a highly mobile nutrient in the soil solution. Unlike $NH_4^+$ ions, which are positively charged, $NO_3^-$ ions are negatively charged and highly prone to leaching by rainfall. While the positive charge of $NH_4$ allows it to chemically sorb onto the negatively charged clay particles and soil organic matter and get held within the soil, $NO_3^-$ does not participate in sorption reactions significantly (Harrison, 2003). Unless $NO_3^-$intercepts plant roots and gets taken

up, or further gets transformed through the denitrification process, it leaches into groundwater and downstream surface waters, causing nutrient enrichment.

Nitrification, carried out by nitrifying bacteria, requires the presence of oxygen ($O_2$), and thus occurs in aerobic soils, flowing water, and surface layers of sediments (Harrison, 2003) at a redox potential above 350 mV (Patrick and Jugsujinda, 1992). $N_2O$ and NO, which are potent greenhouse gases, are released as by-products during nitrification (Wrage et al., 2004) when $O_2$ supplies are marginal (Weil et al., 2016). Nitrification is also likely to occur in waterlogged soils in the thin aerobic zone created around plant roots (Reddy et al., 1984). Nitrification appears to be a dominant process in many bioretention systems (Table 2). The presence of labile organic C can limit nitrification when the heterotrophic microbes consuming organic C can out-compete nitrifying organisms by immobilizing $NH_4$ (Butturini et al., 2000; Zhang et al., 1995). Aerobic heterotrophs also consume $O_2$ in the process of respiration, limiting its supply to the nitrifying organisms (Butturini et al., 2000).

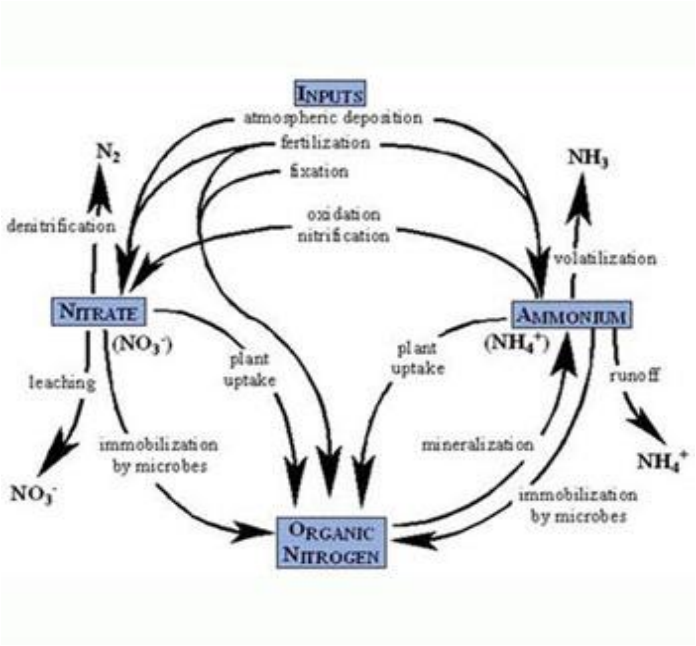


**Fig. 3.** Nitrogen cycle in soils (Source: U.S. Department of the Interior, National Park Service)

The N transformation that serves an important water quality benefit carried out by riparian ecosystems (Groffman and Crawford, 2003b) is denitrification, which is the anaerobic microbial conversion of $NO_3^-$ to N gases ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$). A soil is considered aerobic if it has a reduction-oxidation (redox) potential above 350 mV, and in such environment $O_2$ is used as the terminal electron acceptor. At redox potentials less than 350 mV, $O_2$ supply is depleted, and the denitrifying bacteria begin to use alternate electron acceptors such as $NO_3^-$ (below 350 mV), manganese – $Mn^{4+}$ (below 300 mV) and iron – $Fe^{3+}$ (below 150 mV) respectively (Patrick and Jugsujinda, 1992). The denitrifying bacteria, which are facultative anaerobes, using $NO_3^-$ or $NO_2$ as an alternative electron acceptor and ultimately reducing it to inert $N_2$ gas, if the reaction occurs all the way through (Bollmann and Conrad, 1998), removing N permanently from the system. If the end-product is not $N_2$ gas, NO or $N_2O$ gases are produced, which are

reactive and detrimental to the atmosphere. In the absence of denitrification, most N would occur in the form of $NO_3^-$ in seawater, raising the acidity of oceans as a result (Schlesinger, 2005). Denitrification requires ample availability of organic matter (labile C) supply to provide energy source for bacteria, so denitrification rates can slow down if C supplies are limited. Kim et al., (2003) designed bioretention systems using newspaper as an artificial C source to promote denitrification and measured significant $NO_3^-$ removal (up to 99 %), while observed little removal (up to 10%) in the non-amended bioretention system.

Denitrification is the only process that irreversibly removes N from ecosystems (Harrison, 2003), which can be replicated in stormwater ponds and detention basins to reverse nutrient enrichment in waters. Although most of the loss occurs as $N_2$, the small fraction that is lost to the atmosphere as $N_2O$ during denitrification (Schlesinger, 2005; Wrage et al., 2004) may have important implications for potential greenhouse warming and ozone destruction in the stratosphere (Bollmann and Conrad, 1998).

### 1.7.4 *Eutrophication from nutrients*

N and P (mostly in the form of $NO_3^-$ and $PO_4$) are the major limiting macronutrients in aquatic environments controlling photosynthesis (Galloway et al., 1996; Howarth, 1998; Nixon et al., 1996). While P is the key element limiting algae growth in fresh waters, particularly for many lakes including Lake Champlain, N is limiting in marine systems (Carpenter et al., 1998; Correll, 1998; Schindler, 1977). At excess concentrations, these nutrients lead to increased growth of algae and plants, which starts the process of eutrophication. The decaying algae and plant matter contribute to

high levels of organic matter, and the subsequent decomposition by microbes depletes DO levels in the process creating hypoxia or anoxia, leading to fish kills (Russell et al., 1998; Smith et al., 1998). Eutrophication can be accompanied by proliferation of toxic cyanobacterial blooms, also called blue-green algae, which causes poisoning and poses health risks to humans and animals alike. Myriad of other adverse effects include problems with odor, taste, and increased cost of water treatment, murky water column, and compromised aesthetics, altogether restricting the use for fisheries, recreational activities, industry and drinking water (Carpenter et al., 1998). In streams, excessive nutrient inputs can also stimulate the growth of undesirable rooted aquatic plants. According to US EPA, approximately 11% of the nation's assessed stream miles are threatened or impaired due to excess nutrients (Erickson et al., 2013).

### 1.7.5 *Heavy Metals*

Heavy metals (Copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), aluminum (Al)) enter water bodies via storm runoff, wastewater discharge where metal concentrations can be higher near sewage treatment plant outfalls (Lacey et al., 2001), runoff from industrial sites with longstanding history of contamination, and atmospheric deposition (LCBP 2011). Heavy metals constituents are typically dynamically partitioned into dissolved fraction or particulate fraction. Particulate-bound heavy metals are bound to road dust, particulate organic matter, and the suspended sediment component of the runoff (Brown and Peake, 2006), and get mobilized to water bodies where they accumulate in the sediments. Changes in redox features in the environment can desorb sediment-bound heavy metals into the water column (Pekey et al., 2004). Finer grain

sizes such as the negatively charged clays (< 2 micron) in soil and dust elements have higher metal adsorption capacity, due to their higher specific surface area to volume ration than coarser fractions (Brown and Peake, 2006; Mecray et al., 2001). Metals can also latch on to organic compounds (humic substances, low molecular weight organic ligands) bearing negative charges, and can subsequently get carried in the runoff as metal-organic complexes (Essington, 2015). Particulate metals are generally associated with the non-filterable fraction of stormwater where flow rates can affect mobilization rates from the road surface and drainage system. Metal removal efficiency in bioretention systems could thus be correlated to the efficiency of removal of clay and silt fractions of the sediment and particulate organic carbon (Maniquiz-Redillas and Kim, 2014).

Urbanized cities have higher concentrations of metals than rural areas (Kaye et al., 2006). Sources of heavy metals include vehicles (tire wear, brake pads, motor oil and gasoline, leakage of oil and lubricants), asphalt road, batteries, metal plating, roadway maintenance operations, corrosion of galvanized materials (i.e., building roofs, pipes), (Brown and Peake, 2006; Maniquiz-Redillas and Kim, 2014). Heavy metals persistent in the environment, and their potential to bioaccumulate can render them toxic to organisms (Pekey et al., 2004). Metals tend to build up within the water treatment facilities as well (Davis et al., 2003a). While some of the trace metals (Pb, Cd, As) are toxic to organisms at low concentrations, others (Cu, Zn) are biologically essential micronutrients and become toxic only at higher concentrations (Amundsen et al., 1997; Pekey et al., 2004).

### 1.8 Soil microbial biomass (SMB) and nutrient transformations

Green infrastructures including but not limited to bioretention systems are designed to amplify soil biological activity as they receive nutrient enriched influent waters. Soil microbial communities exert major influence on nutrient cycling (Bailey et al., 2002) such as decomposition and mineralization, immobilization, nitrification, and denitrification . As such they regulate the retention/release of nutrients from the bioretention filter media. Soils have large pool of soil microbial biomass (SMB) which is involved in extensive nutrient storage and transformation of C and nutrients (Weil et al., 2016).

Plants, essential parts of bioretention systems promote microbial growth through root exudates that contain C and nutrient. As a result, SMB density is two orders of magnitude higher in the rhizosphere relative to bulk soils (Atlas and Bartha 1998). Microbes immobilize nutrients  N from the soil solution for their own metabolism and growth (Schlesinger, 2005), and like plants, drive up nutrient sequestration which in turn reduces the  nutrients availabe  to leach below to groundwater.. Conversely, the ammonification potentials of soil and the decay of plant litter, which spur nutrient flush, are  closely associated with SMB (Wardle, 1992).

The balance between microbial immobilization, mineralization, and transformation determines the nutrient fate in the soil. During decomposition of organic material, the respiration of soil microbes converts organic C to $CO_2$, while some of the N and P contents are assimilated within microbial cells. Ruess and Seagle, (1994) found a direct correlation between SMB carbon and soil $CO_2$ efflux in African grassland, most likely because of decomposition by microbes driving subsequent release of $CO_2$. Another

study by Brookes et al., (1985) showed soil microbial biomass P was linearly related to soil microbial biomass C in 15 different soils (8 grassland, 6 arable, 1 deciduous woodland), likely due to microbial immobilization of P. Perhaps water quality benefit could arise from increasing SMB, but only if immobilization of influent stormwater N and P can exceed nutrient release from decomposition.

SMB, which is an index of microbial activity (Schlesinger, 2005), influence the extent to which the above biochemical processes are carried out in a system. SMB varies seasonally as its activity is affected by varying soil temperatures coupled with soil moisture conditions. Other factors that influence SMB are the amount of organic matter and specifically the labile C and N pool, inputs from root exudation and sloughing, plant production (Ruess and Seagle, 1994; Van Veen et al., 1989), plant species, functional groups and diversity (Bardgett and Shine, 1999; Lange et al., 2015; Wardle, 1992; Zak et al., 2003).

### 1.9 Bioretention performance: Precedent studies

Among the number of ecological technologies, best management practices, and land use and conservation measures that have the potential of decreasing the flow of nonpoint pollution into surface waters, bioretention is one of them, if designed properly. Bioretention focuses on implementing specific physicochemical and biological processes that naturally occur in the environment as a mechanism to remove pollutants (Davis et al., 2009b; Lucas and Greenway, 2007b). A growing body of literature over the past decade has shown that bioretention systems are effective water quality treatment devices with good load removal capacities for total suspended solids, heavy metals, organics, oil and

grease, and bacteria in the effluent (Table 1). On the other hand, nutrient (particularly dissolved ones not readily treated through filtration or sorption) retention and detention is not a focus in bioretention design as much as hydrological volumes and TSS. While total phosphorus (TP) and total nitrogen (TN) removal is decent compared to other stormwater treatment practices, removal of dissolved nutrients (organic N, $NO_3^-$ or $PO_4^{3-}$/SRP) are highly variable and sometimes poor (Davis et al., 2001, 2006; Dietz and Clausen, 2006a; Hatt et al., 2007; Hsieh and Davis, 2005; Hunt et al., 2006), unless specific design features are incorporated. These specific features could be increased fill media depth and composition or raised under-drain to prolong anaerobic conditions for denitrification (Davis et al., 2001, 2009b; Hong et al., 2006; Kim et al., 2003), and underlying less impervious media layer over a more pervious one (Cho et al., 2009; Hsieh et al., 2007). Nevertheless, the fact that bioretention design features and monitoring regimes also vary greatly among studies, could influence the variability in the resulting treatment efficiencies.

Leaching of N from bioretention has been attributed to mineralization of soil organic matter (Dietz and Clausen, 2006a) or the mulch used in the filter media (i.e. produced from leaves and grass clippings used by Hsieh and Davis 2005), nitrification of captured N between storm events and its subsequent wash-off (Davis et al., 2006; Hatt et al., 2007; Hsieh et al., 2007), or the mineralization of organic N as it gets mobilized through the soil profile (Duncan, 1999). Additional research is needed on the role of plants and soil additives that may better manage nitrate and phosphate while maintain (or even improve) soil structure and infiltration rates over time.

**Table 1.** Load based (with the exception for fecal coliform) pollutant removal efficiencies (%) by *in situ* bioretention systems.

| Pollutant | % Load Removal | Removal Phenomenon | Field Studies | Design recommendations to enhance removal |
|---|---|---|---|---|
| Fecal coliform | *69 to 95 | Filtration, decay/die-off | Passeport et al., 2009; Hunt et al., 2008 | Mature and dense vegetation |
| Total suspended solids (TSS) | 60 to 97 | Sedimentation, Filtration/ infiltration | Hatt et al., 2009; Hunt et al., 2008; Roseen et al., 2006 | Deep and extensive rooted plants<br>Soil depth > 300 mm |
| NUTRIENTS | | | | |
| Nitrate+Nitrite ($NO_{2,3}$-N) | -44 to 67 | Microbial mediated biotransformation (nitrification, denitrification)<br>Adsorption onto negatively charged soil particles<br>Plant uptake | Kim et al., 2003; Dietz and Clausen 2006; Davis et al., 2006; Dietz and Clausen, 2005; Hatt et al., 2009; Hunt et al., 2006; Li and Davis, 2014; Roseen et al., 2006 | Amending media with C source (pea straw, woodchips) to promote denitrification<br>Low N content in the organic material<br>Plants with higher N uptake capacity, extensive root systems, greater maturity and density<br>Plant harvest from time to time and before senescence |
| Ammonia ($NH_3$-N) | 64 to 96 | | | |
| Total nitrogen (TN) | -7 to 80 | | | |
| Orthophosphate ($PO_4$-P) | 52 to 77 | Adsorption onto silt, clay minerals, Ca and to hydrous oxides of Fe and Al<br>Plant uptake | Passport et al., 2009; Davis et al., 2006; Dietz and Clausen 2005; Hunt et al., 2006; Hatt et al., 2009 | Low P-index soil<br>Low organic matter content in filter media<br>Low P content in the organic matter<br>Incorporate silt & clay in soil media |
| Total phosphorus (TP) | -398 to 85 | | | |
| HEAVY METALS | | | | |
| Pb | 31 to 95 | Adsorption to mulch, organic matter layer | Davis et al., 2003; Hunt et al., 2006; Roseen et al., 2006; Hunt et al., 2008 | Filter media depth > 300 mm |
| Cu | 43 to 98 | | | |
| Zn | 64 to 95 | | | |
| Cd | 91 | | | |
| Fe | -13000 | | | |

*Concentration (mg $L^{-1}$) instead of load

**Table 2.** Summary of soil media and associated pollutant removal mechanisms by bioretention systems in selected studies.

| Study | Bioretention Soil Media Composition | Pollutant removal pathways described |
|---|---|---|
| Dietz and Clausen, 2006 | Shredded hardwood bark mulch, native soil, woody shrubs | $NH_4^+$ adsorption, $NO_3^-$ denitrification, N and P released by decomposition of soil flora and fauna, mulch retained N & P, plant uptake of P < 3 %. |
| Davis et al., 2003 | Box: Sandy loam soil, creeping juniper<br>Field: 50% sand, 20-30% leaf mulch, 20-30% topsoil, grasses, bushes, small trees | Metal removal by sorption to mulch layer and influenced by flowrate and storm duration. Metal uptake by roots. Higher metal attenuation attributed to sites with finer media and mature plant growth in addition to mulch. |
| Davis et al., 2006 | Box: Mulch layer, sandy loam (76% sand), creeping juniper<br>Field: Mulch, sandy loam top soil, grasses, shrubs, small trees | Limited adsorption or physiochemical reaction with $NO_3^-$ expected, organic N sorption to mulch, limited denitrification responsible for N losses, plant uptake could remove 90 % of captured N. |
| Davis et al., 2001 | Shredded hardwood bark mulch, agriculture top soil (sandy loam) used for vegetable production, creeping juniper | Metal sorption to mulch layer greater than sorption to soil, P sorption or precipitation with Ca, Fe, Al, $NH_4^+$ sorption via ion exchange and electrostatic interaction, effluent $NO_3^-$ higher resulting from nitrification between dosing events. |
| Hsieh and Davis, 2005a | Mulch, local soil, sand | Mulch layer filtered most of TSS and reduced media clogging. TP and Pb removed by sorption to OM or precipitation. $NO_3^-$ denitrification. |
| Hsieh and Davis, 2005b | Mulch from leaves and grass clippings, porous soil, sand, | TP removal via physical filtration, sorption or precipitation, loss of N by denitrification, Pb removal through filtration of TSS as 56% of influent Pb was sorbed to TSS. |
| Lucas and Greenway, 2007 | Pea gravel, sand, loamy sand, gravel mulch; Swamp Foxtail Grass, Flax Lily, Banksia, Bottlebrush | P Sorption, $NO_3^-$ denitrification, plant and microbial uptake. |
| Bratieres et al., 2008 | 3 media types: sandy loam, sandy loam with 10% vermiculite and 10% perlite, 10% leaf-compost and 10% mulch, 5 types of grasses | TSS removal through soil-based filtering Columns with Carex and Melaleuca showed $NO_3^-$ and TN removal due to dense root architecture and arbuscular mycorrhizal fungi respectively. $NO_3^-$ export and poor TN removal from other plant columns attributed to poor root density and OM mineralization rate > plant and microbial uptake, biological transformation of captured $NH_3$ and organic N to $NO_x$ between runoff event, inadequate denitrification to complete the N removal process. |
| Zinger et al., 2007 | Sandy loam, fine sand mixed with shredded woodchips from pea straw and red-gum, river sand, tall sedge, SZ | $NO_3^-$ denitrification. Addition of organic C as an electron donor in the anaerobic zone was concluded beneficial to the rate of denitrification. |
| Blecken et al., 2009 | Sandy loam, fine sand, coarse sand, cellulose-based C source consisting of 1/3 pea straw and 2/3 Red River Gum wood chips, Tall sedge; SZ | Addition of SZ and C decreased DO and redox potential. Formation of dissolved Cu-organic matter complexes, but also sorption of Cu by solid OM particulate added by woodchips. SZ enhanced metal sorption by diminishing oxidizing conditions. $NO_3^-$ denitrification. SZ increased pH, which increases metal retention. |

SZ: Submerged zone

### 1.10 Soil $CO_2$ fluxes

Although $CO_2$ is only one aspect of the C cycling of terrestrial systems, it is essential to quantify as it is the most important GHG being produced in largest quantities. The residence time of $CO_2$ is 3 to 4 years in the atmosphere[7]. Soil $CO_2$ flux includes $CO_2$ released from soils due to respiration of soil heterotrophs (e.g., microbes and soil fauna which decompose organic substrates) and live roots and root-associated mycorrhizal fungi (Bond-Lamberty et al., 2011; Boone et al., 1998; Raich and Schlesinger, 1992). In fact, current estimates indicate that $CO_2$ emissions from soils by microbial respiration (60 Pg C $yr^{-1}$) are more than 10 times greater than from fossil fuels sources of combustion (5.5 Pg C $yr^{-1}$; Essington, 2015). Increased soil C sequestration could help offset the effects of anthropogenic emission of $CO_2$, and improve soil physical and chemical properties by maintaining nutrient cycling processes and soil biological activity (Rustad et al., 2000), processes closely related to soil sustainability. Biotical and abiotic factors that influence soil $CO_2$ fluxes are vegetation quantity and type, roots, microbial biomass, temperature, soil moisture and management activities. Soil saturation, a critical design consideration of GSIs, can impede diffusion of oxygen, which slows down the activity of microbes involved in decomposition and $CO_2$ production, but increases the production of more potent but trace biogenic GHGs, namely $N_2O$ and $CH_4$.

Lastly, soil $CO_2$ flux estimates can be used to fill gaps in the complete study of carbon cycling and budget of bioretention systems, in which other parameters required

[7] https://web.viu.ca/krogh/chem302/residence%20time%20of%20atmos%20gases%20Table%202.1%20Hobbs.pdf

are carbon stocks in soil and plants, as well as dissolved organic carbon in the soil solution (and inflows and outflows) some of which are beyond the scope of this study.

### 1.11 Trace soil $N_2O$ and $CH_4$ exchange

$CH_4$ and $N_2O$ are emitted in smaller quantities, but substantially contribute to global warming (Smith et al., 2003). Both $CH_4$ and $N_2O$ are radiatively active and potent greenhouse gases having greater warming potential than $CO_2$ in the atmosphere. The warming potential of 1 kg of $CH_4$ is 25 times greater than that of $CO_2$, while that of $N_2O$ is 300 times greater in a 100-year life span (Christiansen et al., 2012; Smith et al., 2003). The atmospheric residence times of $N_2O$ and $CH_4$ are 150 and 9 years respectively. Production of either gas is limited by oxygen and available C substrates (Christiansen et al., 2012), the latter of which can be provided by the soil media or by particulate organic matter (OM) or degradation products of hydrocarbons in the influent (McPhillips and Walter, 2015).

#### 1.11.1 *Soil $N_2O$ exchange*

$N_2O$, which is the third most important contributor to current radiative forcing, has increased by about 16% from its pre-industrial level of 270 ppb to 319 ppb in 2005 (Denman et al., 2006). There is growing concern about the flux of $N_2O$ as its concentrations in the atmosphere are increasing almost linearly at an annual rate of 0.26% for the last several decades (Denman et al., 2006). Such small atmospheric increases can have long lasting effects as $N_2O$ has an atmospheric residence time of 100-175 years.

Soils are an important source of $N_2O$ which is formed due to two microbial processes: nitrification, the aerobic conversion of $NH_4^+$ to $NO_2$ and then to $NO_3^-$, and denitrification, which involves reduction of $NO_3$, to atmospheric $N_2$ releasing $N_2O$ (Figure 1) as an intermediate product (Basiliko et al., 2009; Bollmann and Conrad, 1998). While denitrification produces $N_2O$ under anaerobic-saturated zone conditions, the intermediate wet, or saturated conditions within an unsaturated zone in which microsites vary between aerobic and anaerobic conditions, can promote cycling between nitrification and denitrification and subsequent $N_2O$ production (Burgin and Groffman, 2012; Christiansen et al., 2012; Firestone and Davidson, 1989). The complex interactions between production and consumption make field level $N_2O$ measurements extremely variable and difficult to interpret (Burgin and Groffman, 2012). Nitrification rates are controlled by $O_2$ and $NH_4^+$ availability, and the primary controls of denitrification rates are $O_2$, $NO_3^-$, and organic C availability. Any factor that slows the overall rate of denitrification can cause $N_2O$ to accumulate as a major end-product (Firestone and Davidson, 1989). From water quality standpoint, removal of $NO_3^-$ from stormwater is a desired ecosystem service, and thus an ideal GSI design would maximize the water quality service of denitrification while minimizing production of $CH_4$ and $N_2O$.

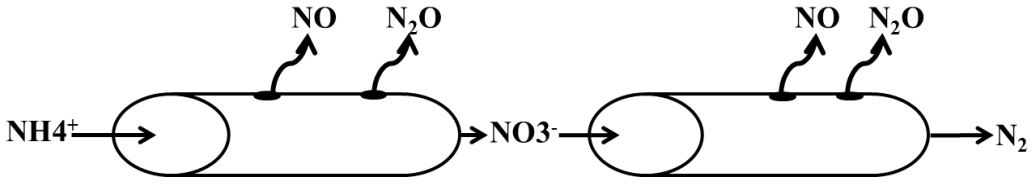


**Fig. 4.** A conceptual model of N gas production via nitrification and denitrification: (a) flux of N through process "pipes" and (b) holes in the pipes through which N-gases "leak" (Adapted from (Firestone and Davidson, 1989).

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# CHAPTER 2: EFFECTS OF DIFFERENT SOIL MEDIA, VEGETATION, AND HYDROLOGIC TREATMENTS ON NUTRIENT AND SEDIMENT REMOVAL IN ROADSIDE BIORETENTION SYSTEMS

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*Keywords: Bioretention, urban road runoff, sediment, nitrogen, phosphorus, stormwater management*

Abstract

Water quality performance of eight roadside bioretention cells in their third and fourth years of implementation were evaluated in Burlington, Vermont. Bioretention cells received varying treatments: (1) vegetation with high-diversity (7 species) and low-diversity plant mix (2 species); (2) proprietary SorbtiveMedia$^{TM}$ (SM) containing iron and aluminum oxide granules to enhance sorption capacity for phosphorus; and (3) enhanced rainfall and runoff (RR) to certain cells (including one with SM treatment) at three levels (15%, 20%, 60% more than their control counterparts), mimicking anticipated precipitation increases associated with climate change. A total of 121 storms across all cells were evaluated in 2015 and 2016 for total suspended solids (TSS), nitrate/nitrite-nitrogen ($NO_x$), ortho-phosphorus (Ortho-P), total nitrogen (TN) and total phosphorus (TP). Heavy metals were also measured for a few storms, but in 2014 and 2015 only. Simultaneous measurements of flow rates and volumes allowed for evaluation of the cells' hydraulic performances and estimation of pollutant load removal efficiencies and EMC reductions. Significant average reductions in effluent stormwater volumes (75%; range: 48-96%) and peak flows (91%; range: 86-96%) was reported, with 31% of the storms events (all less than 25.4 mm (1 in.), and one 39.4 mm (1.55 in.) depth completely captured by bioretention cells. Influent TSS concentrations and EMCs was mostly significantly reduced, and TSS loads were well retained by all bioretention cells (94%; range: 89-99%) irrespective of treatments, storm characteristics or seasonality. In contrast, nutrient removal was treatment-dependent, where the SM treatments consistently removed P concentrations, loads and EMCs, and sometimes N as well. The vegetation and RR treatments mostly exported nutrients to the effluent for those three metrics with varying significance. We attribute observed nutrient exports to the presence of excess compost in the soil media. Rainfall depth and peak inflow rate had consistently negative effects on all nutrient removal efficiencies from the bioretention cells likely by increasing pollutant mobilization. Seasonality followed by soil media presence, and antecedent dry period were other predictors significantly influencing removal efficiencies for some nutrient types. Results from the analysis will be useful to make bioretention designers aware of the hydrologic and other design factors that will be the most critical to

the performance of the bioretention systems in response to interactive effects of climate change.

## 2.1 Introduction

Urban waters are widely impaired by excess nutrients and sediments in the input stormwater, despite substantial efforts spent in stormwater management and control in the surrounding watersheds (Hobbie et al., 2017). Urban stormwater is a major contributor to nonpoint source pollution in surface waters nationwide. As nonpoint source pollution is much more difficult to regulate than point source pollution, stormwater is considered one of the most pressing water quality challenges of today (Wang et al., 2000; Hsieh and Davis, 2005; NRC 2008). Among many pollutants of concern, those commonly detected in urban storm runoff are nutrients (nitrogen; N and phosphorus; P), which are major culprits of eutrophication nationwide (Erickson et al., 2013), suspended solids, heavy metals, and organics (Porcella and Sorensen, 1980).

As cities are expanding rapidly, the impervious footprint increases, and natural hydrological flow paths that would have absorbed, filtered and treated stormwater through soils are bypassed (Cook, 2007). During high flow events, urban storm infrastructures may fail, leading to harmful combined sewer-storm-water overflows that contaminate surface waters with nutrients and pathogens (Kaye et al., 2006) intended to be kept out of those very waters. Thus, newer strategies to address urban stormwater management are needed to protect water quality. The low impact development (LID) approach was therefore introduced in the 1990s in Prince George's County, Maryland as an alternative to conventional stormwater management approach (LID Center 2007). LID, more broadly termed Green Stormwater Infrastructure (GSI), comprises landscape

design strategies that promote infiltration, filtration, soil storage, evapotranspiration, groundwater recharge and/or re-use of stormwater, while minimizing impervious cover and runoff (Davis, 2007; Roy et al., 2008) (PGC 1999, Hinman 2012).

Bioretention, a prominent type of green infrastructure, is increasingly being used as a sustainable stormwater control measure in urbanized watersheds within the U.S. and abroad (Davis et al., 2009; Roy-Poirier et al., 2010; Liao et al., 2017). The technology is an aesthetically pleasing, sunken (approx. <1.3m deep) planted basin filled with porous media that intercepts, filters, stores, and treats pollutant-laden runoff conveyed as sheet flow from impervious surfaces (Cook, 2007). Bioretention design allows for stormwater runoff to be treated for water quality on-site, close to the source of origination (Hurley and Forman, 2011), via different physical (filtration, evaporation), chemical (sorption, ion exchange, precipitation), and biological (phytoremediation, microbial-mediated transformation, transpiration) mechanisms, facilitated by the filter media (Davis, 2007; Feng et al., 2012; Liu et al., 2014; Lucas and Greenway, 2007). Runoff is detained and stored temporarily in the bioretention media and aboveground in the ponding zone, and is released slowly to the surrounding soil via infiltration or to an existing storm sewer system. Integrating bioretention systems throughout urban spaces (most commonly in roadsides, parking lots, and streets) offer more opportunities to restore natural hydrologic functions. Bioretention's storage of stormwater in the landscape can alleviate pressure on existing storm infrastructure by decreasing storm flow velocities and reducing peak discharge and downstream erosion and flooding. Furthermore, ancillary benefits from bioretention include wildlife and pollinator habitat, and enhanced urban biodiversity, and aesthetics (County, 1999).

A growing body of literature has shown that bioretention systems are effective water quality treatment devices with good removal capacities for total suspended solids (Hsieh and Davis, 2005; Bratieres et al., 2008; Hatt et al., 2009a), heavy metals (Davis et al., 2001, 2003; Hunt et al., 2006), fecal coliform (Hunt et al., 2008; Passeport et al., 2009), hydrocarbons and oil and grease (Hong et al., 2006). However, nutrient removal performance (specifically for N and P) is more variable (Davis, 2007). Field studies have shown successful removal of ammonium ($NH_4^+$) and Total Kjeldahl Nitrogen (TKN) from runoff (Davis et al., 2003; Birch et al., 2006; Dietz and Clausen, 2006; Hunt et al., 2006; Hatt et al., 2009b; Passeport et al., 2009), but removal of nitrate+nitrite ($NO_x$), total nitrogen (TN), total phosphorus (TP), and ortho-P have been shown in both lab and field studies to be highly variable and sometimes negative removals (or exports) have been reported (Davis et al., 2001; Hsieh and Davis, 2005; Birch et al., 2006; Davis et al., 2006; Dietz and Clausen, 2006; Hunt et al., 2006; Van Seters et al., 2006; Bratieres et al., 2008; Hatt et al., 2009b; Passeport et al., 2009).

This research evaluates water quality performances of seven roadside bioretention cells receiving different vegetation, soil media, and hydrologic (enhanced rainfall + runoff (RR)) treatments in Burlington, Vermont in the northeastern USA. The experimental design and its treatment variables were motivated particularly by concerns regarding elevated levels of P in the Lake Champlain Basin attributed to watershed inputs and internal cycling of phosphorus (P) from lake sediment bottoms, which causes algal and toxic cyanobacterial blooms in the summer. The hydrologic treatment is informed by climate change projections associated with frequent and intense rainfall events for Vermont and other Northeastern states (Frumhoff et al., 2006; Pealer, 2012). Average

daily precipitation is projected to increase between 5 and 10% (10% being an increase of 4 inches $yr^{-1}$) by midcentury, (Hayhoe et al., 2007; Guilbert et al., 2014), and extreme precipitation events (amount of precipitation that falls over five consecutive days) are also likely to progressively increase over the century, i.e., 8% by mid-century, and 12-13% by late century (Frumhoff et al., 2006).

Bioretention performance needs to be robust and responsive to various physical site conditions/constraints, variability in storm sizes, volumes and pollutant levels, plant survival, and non-steady environmental conditions. Thus, field studies such as the following are valuable in that they are exposed to natural variations not easily replicated in the lab. Bioretention monitoring results are critical to understand how small-scale bioretention retrofits implemented under constrained field conditions can provide stormwater controls and how their performance may vary based on different design attributes, hydrologic conditions, and other environmental factors.

The specific objectives of the study were:

1) to characterize the composition of N and P species in bioretention inflows and outflows in a roadside field study;
2) to characterize (A) stormwater volume and (B) pollutant retention capacities of bioretention cells across various storm sizes;
3) to evaluate and compare bioretention cells' (A) hydraulic performances, (B) pollutant mass removal efficiencies (MRE), and (B) event mean concentrations (EMCs) among vegetation, soil media, and hydrologic treatments; and
4) to investigate whether environmental factors (precipitation depth, antecedent dry period (ADP), seasonality), hydrological factors (inflow volumes, inflow mass,

peak flow, hydraulic loading ratio), and treatments (vegetation, soil media, hydrologic), are significant predictors of pollutant mass removal efficiencies.

## 2.2 Methods

### 2.2.1 *Study site description*

The study site consists of eight bioretention cells (Fig.1) located on both sides of a medium-traffic campus roadway at University of Vermont (Burlington, USA). Monitoring of the bioretention cells was carried out from May to November in the years 2015 and 2016. The cells were constructed in November 2012 (Cording et al., 2017). Vegetation was planted in May 2013 and was well established by the time this study commenced in Spring 2015. Table 1 describes the design parameters of the bioretention cells. Each cell collects stormwater runoff from road watersheds of varying sizes (30 to 120 $m^2$). Curb cuts along the road route the runoff to a shallow rock-lined swale, which then directs it to each bioretention cell's "inflow" where water samples are collected. The cells are rectangular with identical size (1.22m wide by 3.05m long by 0.9m deep) and drainage configurations. From top to bottom, the bioretention soil media is layered with two layers each 30.5 cm deep: the upper layer is a 60:40 sand compost mix (compost derived from cow manure, food scraps, and wood shavings); below is a pure sand layer (Fig. 2a). Below the sand media is a 7.6 cm-layer of pea stone, and the bottom 23 cm of the cell is occupied by 5-cm diameter stones or gravel. Two of the cells contain a soil additive treatment, where the bottom 7.6 cm of the pure sand layer is replaced by SortiveMedia$^{TM}$ (SM; Fig. 2b), described later in detail. The entire cell (sides and bottom) is lined using an impermeable ethylene propylene diene monomer (EPDM) liner to

isolate the cell and prevent water exchange with the underlying native soil and cross contamination of the water quality. The liner also accounts for all the water volume and pollutant loads for mass balance calculations. The bioretention cells are drained using an underdrain pipe at one end of the cell, a 26-cm long, 15.24 cm-diameter perforated PVC pipe that is placed 2.5 cm from the bottom of the cell within the gravel layer. The underdrain is connected to a solid PVC pipe outside the soil media where the effluent is sampled for water quality analysis. The pipes are connected to the existing storm sewer system. Additional details about construction of the bioretention cells and details regarding the monitoring infrastructure can be found in Cording et al., (2017).

Burlington (44°28′33″N 073°12′43″W) has a humid continental climate, with warm, humid summers and cold winters. The annual mean temperature is 7.7$^{o}$C (45.9$^{o}$F) and the average annual rainfall is 934 mm (US Climate Data 2017). The historical averages here are from year 1981-2010 and given by Burlington International Airport in South Burlington, administrated by the National Weather Service.

### 2.2.2 *Experimental design*

Our study examines a combination of vegetation, soil media, and hydrologic treatments assigned among eight bioretention cells. Unlike the latter two, the vegetation treatment does not have a true experimental control and comparisons are made between two pairs of cells, each containing a different plant palette. The vegetation treatment has two replicates per treatment: the low-diversity treatment (VL) contains 2 species, and the high-diversity treatment (VH) contains 7 species (Table 1). All plants are native perennials and selected for several reasons such as their tolerance of roadside conditions,

road salts, desiccation and inundation. Plantings in the high-diversity treatment include native species with varying root depths, and varying phenology so that flowering occurs throughout growing season. In both types of cells, the plants senesce in mid-October to mid-November, and begin to re-establish in early May.

The second treatment variable is soil media: two of the cells (cell 3 and 4) contain an engineered, P-sorbing amendment called SorbtiveMedia™ (Contech Engineered Solutions LLC, North Carolina). This product was donated by its developer to this research trial, and was not purchased with research funds, nor has the developer previously reviewed the results; there is no intention herein to advertise or promote its use. The material consists of fine granules of Fe and Al oxide, and is shown to have enhanced capacity for adsorption of dissolved P from influent water (Balch et al., 2013). In the two other cells (cell 3 and 4), the bottom 7.6 cm of the sand layer is replaced by the SorbtiveMedia™ (Fig. 2b), termed SM from here on.

The third treatment is an enhanced runoff plus rainfall (RR) treatment to increase precipitation and runoff input to three bioretention cells by 15%, 20%, and 60% (cell 1, 5 and 3 respectively). The additional runoff and rainfall treatment the cells are receiving is proportional to the paired cell's watershed size differences (Table 2). All hydrologic treatments are assigned to cells with the high-diversity plant mix (VH). Three cells have larger road watershed areas than their ambient counterparts: cell 1's road watershed is 15% larger than that of cell 2 (paired control), and cell 5's road watershed is 20% larger than that of cell 6 (paired control) (Table 2). The control, in this case, is high diversity plot with no addition of a rainpan or SM. Additionally, cell 3's road watershed is 60% larger than that of cell 4 (control), both of which have the SM treatment. Additional

rainfall is delivered via a corrugated, plastic "rainpan" (Appendix A) whose surface area is designed to be 15%, 20% or 60% of the cell's surface area of 3.72 $m^2$, thereby extending the cell's drainage area, and consequently the rainfall input by that much more. It is important to note that the construction and placement of the cells were constrained by site conditions including underground utilities and a variety of fill soils. Thus, the cells are designed to drain varying watershed sizes although the cell dimensions and surface areas are identical.

### 2.2.3 *Bioretention maintenance*

Vegetation maintenance occurred periodically throughout the growing season. Maintenance included removal of weeds every two to three weeks and clipping of all the aboveground stems to within a few inches of the soil line in early November before plant senescence, to reduce re-release of nutrients into the bioretention cell. Other maintenance activities included clearing sediment, garbage, and other coarse materials from the perforated gutters, curb cuts, and maintaining rainpan infrastructure to allow water movement into the bioretention soil surface, and setting up stakes and ropes outside the bioretention cells to reduce foot traffic passing through the research plots.

### 2.2.4 *Stormwater sampling*

Stormwater quality was monitored for 50 distinct storms (but total of 121 storms among all cells) in 2015 and 2016. Some water quality and soil analysis was also carried out in 2014. With eight autosamplers (Teledyne ISCO 6712/7400, Lincoln, NE), we could simultaneously monitor the inflow and outflow of four bioretention cells. Accordingly, we monitored in two phases, with each phase containing two statistically

paired cells (Table 2). However, equipment difficulties resulted in the VH vegetation pair, Cells 1 and 2, not being monitored simultaneously. Rainfall data from Burlington International Airport, 4 km away from the site, was used for collection of rainfall data.

**2.2.4.1** *Influent and effluent sampling design*

A 90$^{o}$ v-notch weir, set in a cedar box, is installed in the inflow of each bioretention cell. The weir box at the inflow can contain up to 5.5 L, before overflowing into the bioretention cell at the invert elevation of the v-notch. Notably, runoff from the road watersheds is first channeled into a high-density polyethylene (HDPE) plastic and rock-lined swale before entering the inflow weir (Appendix B); the swale serves as a conveyance, but potentially functions as a "pre-treatment," as sedimentation of large particles may occur there.

The underdrain pipe in each cell outflow is outfitted with a Thel-Mar plug-in weir (Thel-Mar, LLC, Brevard, NC). While the Thel-Mar plug-in weir came pre-calibrated, the inflow weir was constructed and calibrated in the lab experimentally (Cording et al., 2017). The area where the water pooled behind the weirs was cleaned with hose water before every storm to establish comparable starting conditions, and to clean the weirs of any previous storm residues. Water was filled up to the v-notch, and the stage or "level" was referenced to be zero. Stage values for both inflow weir boxes and ouflow Thel-Mar weirs were related to flow rates using weir-specific rating curve equations (Appendix C).

**2.2.4.2** *Water sample collection*

Flow measurements were taken using calibrated V-notch weirs on a 1-minute interval using a submerged probe flow module (Teledyne ISCO 720 module, Lincoln, NE), also known as pressure transducer. The pressure transducer is sensitive to direct sunlight and temperatures outside of 0o to 71oC, prohibiting winter sampling. Flow rates exceeding 0.94 to 1.17 L min-1 in the inflow (depending on the cell's weir dimension) and 0.046 L min-1 in the outflow triggered sample events.

A mix of discrete and composite time-based sampling approach was used to collect water samples every 4 and 2 minutes at the inflow and outflow, respectively. Twenty-four 1-litre polypropylene bottles were installed in the samplers to collect composites of 3 samples per bottle, switching bottles every 12 minutes in the inflow and 6 minutes in the outflow. Composite was done to lengthen the sampling duration, in effort to capture an entire storm event. Time-based samples are considered very accurate at small time intervals (Harmel et al., 2003). A fine time resolution monitoring was deemed the best to capture, with greater frequency, the temporal variabilities related with flow rate and pollutant concentration change to best represent true loads over the course of a storm hydrograph. Multiple sampling intervals were tested before determining these intervals, e.g., 15- minute intervals with 2 samples per bottle, and discrete samples at 30-minute increments. Short time intervals were chosen because the cells drain small watershed areas, and we wanted to capture the initial time of concentrations (approx. 5 to 9 minutes from smallest to largest watersheds (Cording et al., 2017). For each bottle, 1-cm diameter suction tubing was used to draw 900-ml sample, in 300-ml increments, from the influent, and 450-ml sample, in 150-ml increments, from the effluent. All samples (up

to 24 bottles per inflow or outflow with 3 sampling intervals per bottle; Appendix B) were analyzed separately to obtain a complete pollutograph.

#### **2.2.4.3** *Water quality analysis*

Water samples were transported to the Agriculture and Environmental Testing Laboratory within 24 hours after the precipitation event. Samples were analyzed for total suspended solids (TSS), nitrate/nitrite ($NO_x$), orthophosphate (ortho-P), total nitrogen (TN), and total phosphorus (TP). Dissolved heavy metals (Copper (Cu), Zinc (Zn), Lead (Pb), Cadmium (Cd), Chromium (Cr), Nickel (Ni)) concentrations were also analyzed, some of which are not reported due to large number of concentrations below the detection limit, which has occurred in other studies (Dietz and Clausen, 2006; Hatt et al., 2009b).

Samples were analyzed per the test methods specified in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). TSS measurements included shaking the bottle and vacuum-filtering an aliquot of the original samples through pre-rinsed and dried glass fiber filters. The filters retaining residue samples were oven dried and dry weights taken. TSS mass was the difference between final and initial dry weights. Results were expressed in concentration by dividing the mass by the volume of aliquot drained. Dissolved nutrient concentrations were analyzed after filtration through a 0.45 μm pore size nylon mesh filter by flow injection analysis on an automated colorimeter (Lachat Instruments QuickChem8000 AE, Hach Inc., Loveland, CO) using the Cd-reduction method for $NO_x$, and ammonium molybdate colorimetric method for ortho-P. TN and TP were analyzed by standard persulfate digest on unfiltered water samples. A value of one-half of the detection limit was used for any analyte below the detection limit

(Dietz and Clausen, 2006; Li and Davis, 2014). Heavy metal concentrations were determined using the inductively coupled plasma optimal emission spectrometry (ICP-OES, Optima 3000DV, Perkin Elmer Corp, Norwalk, CT, USA) after filtration through a 0.45 μm filter and acidification with concentrated hydrochloric (HCl) acid. For particulate metals in the runoff (measured in 2014), approximately 1000 ml of sample was filtered through Whatman 47-mm standard glass fiber filters to collect suspended sediments. Nitric acid digestion procedure was carried out on the residue filters, and filtrate was analyzed for heavy metals.

**2.2.4.4** *Pollutant loads and mass removal efficiency*

Pollutant cumulative mass at the inflow and outflow was calculated for each rainfall event by taking the integral of the product of concentrations and flow rates over the total time of the flow during an event (Davis et al., 2006).

$$\text{Total Pollutant Mass} = \int_0^{t_r} C(t)Q(t)dt$$

(Equation 1)

where:

C(t) = concentration

Q(t) = runoff flow rate

Limits of integration refer to time 0 (runoff initiation) and time $t_r$ (time at which runoff ceases).

Pollutant mass removal efficiency (RE) was calculated based on the following formula: RE (%) = (mass in - mass out) × 100/mass in (Dietz and Clausen, 2006). If the value is positive, the system retains pollutant mass; if the value is negative, the system exports/leaches pollutant mass.

Event mean concentration (EMCs) was also calculated for individual storms by dividing total pollutant load washed off during storm event by the total runoff volume over that duration (Lee and Bang 2000).

$$\text{EMC} = \frac{\text{Total Pollutant Mass}}{\text{Total Runoff Volume}} = \frac{\int_0^{t_r} C(t)Q(t)dt}{\int_0^{t_r} Q(t)dt}$$

(Equation 2)

### 2.2.5 *Soil CN content, plant tissue nutrient content, and root biomass*

Soil C: N ratio was measured from all cells by grinding oven-dried soils at 60$^{o}$C into a fine powder and combusting in the CN analyzer. Plant tissue samples were taken in July and August in 2015 and 2016 respectively to determine tissue nutrient content of total C, N and P. Plant tissues (only leaves in 2015, and all above-ground plant parts which included stems, leaves, pods, flowers in 2016) were collected from at least two different individuals of all species from VH and VL treatments only. Samples were composited and dried in 60$^{o}$C oven for 3 days. Samples were ground into fine powder, and analyzed in triplicates for total C and N by a combustion method in a CN elemental analyzer (Flash EA-1112, CE Elantech, Lakewood, NJ). Total P was determined on ICP-OES following a nitric acid- microwave digestion. Additionally, plant health and survival/absence and percent cover in each cell was also recorded intermittently throughout the monitoring period. Root biomass was measured in November 2014 from fresh soil cores taken from up to 45 cm depth from three equally divided transects from the cells' (VH and VL treatments only) center. Final root biomass was expressed per volume basis (i.e., root biomass density in mg cm$^{-3}$ soil).

### 2.2.6 *Statistical analysis*

No significant differences for water quality and soil parameters were found between the VH replicates, nor between the RR15 and RR20 bioretention cells. Therefore, data were averaged for the VH replicate cells, and for the VH RR15 and RR20 cells. Each sampling event was considered a replicate for statistical purposes (Winston et al., 2013). Influent and effluent concentration and loads differences within each cell were statistically compared. The difference between paired "in" and "out" data from each event was tested for normality using the Shapiro-Wilk goodness-of-fit test. A Wilcoxon Signed Rank test for matched pairs, a non-parametric analogue to the paired t-test (Zar 1999), was used, due to a non-normal distribution of the differences (Davis, 2007; Winston et al., 2013). Whenever the paired sample t-test is applicable, the Wilcoxon Signed Rank test for matched pairs is also applicable (Zar 1999). There were difficulties transforming the negative differences to fit a normal distribution, and Wilcoxon test is appropriate because it does not require the data to fit a certain distribution. Statistical analyses were performed using JMP Pro 12.0.0 (SAS Institute Inc., Cary, NC, 2015). All results are reported as mean with standard deviation or standard error. A criterion of 95% confidence ($\alpha$=0.05) was used.

An attempt was made to relate effluent peak flow rates and volumes to five predictor variables such as storm size, inflow peak flow rate, inflow volume, antecedent dry weather period (ADP), and month of the year using multiple linear regression analysis in R software version 3.1.1 (www.r-project.org).

A multiple linear regression model (Hatt et al., 2009b) was used in R software version 3.1.1 (www.r-project.org) to evaluate the correlation of nine to ten predictor

variables with effluent peak flow rates and volumes, and percent volume and pollutant mass RE across the entire monitoring duration. The nine predictors included: environmental parameters such as precipitation depth, antecedent dry weather period (ADP), seasonality, hydrological factors such as inflow volumes, peak flows (which could affect pollutant mobilization rates), hydraulic loading ratio, and the different treatment variables (soil, vegetation, and RR). The tenth predictor, which was the pollutant loads infiltrating into the cell, was included in the model to predict pollutant load RE. All the above predictor variables were included in the regression model as independent or explanatory variables at the start, while effluent peak flow and volume, and percent volume and mass RE was input as a dependent variable. Seasons were divided into spring (May and June), summer (July and August) and fall (September to November) and input as categorical. The soil, vegetation, and RR treatments were input as binary categorical, while the rest of the variables were input as continuous. The variables that were found to be the least significant were eliminated from the model, and the model was re-run. Parameter estimates of the final chosen model are presented containing slope estimates, p values, and model $R^2$. For regression models, $\alpha$=0.1 was considered as marginally significant.

## 2.3 Results

### 2.3.1 *Storms sizes and pollutant loadings*

Fifty individual storms were sampled from May to November in the years 2015 and 2016 (23 and 27 storms respectively) that produced both inflow and outflow samples. Storm sizes in 2015 ranged from 0.3 mm to 85 mm (0.01 to 3.3 in.), with a median at

15.2 mm (0.6 in.) precipitation depth (Fig. 3). Storm sizes in 2016 ranged from 1.27 mm to 39 mm (0.05 to 1.5 in.), with 50% of the storms below 10 mm (0.4 in) (Fig 3). 2016 was a dry year relative to 2015, characterized by storm events of lower magnitude along with longer antecedent dry periods between consecutive storm events. Overall, antecedent dry periods for the storms sampled ranged from minimum 0 to maximum of 13 days.

Runoff resulting from 90$^{th}$ percentile rainfall is equivalent to the first inch (25.4 mm) of rainfall in a 24-hour storm event (VSMM 2016). One inch is the water quality design storm criteria in Vermont for stormwater best management practices (VSMM 2016). Thus, storms above and below 25.4 mm (1 in.) were characterized as large and small storms respectively.

Across all road watersheds and their respective bioretention cells, 96 out of 121 storms (79%) that were monitored across all cells were small storms, and 25 storms (21%) were large storms. The largest 21% of the storm events (ranked by precipitation depth) accounted for 68% of the total TSS loadings, 45% TN, 37% $NO_x$-N, 50% TP, and 39% of $PO_4$ loadings (Table 3), indicating that several of the pollutants, especially TSS and TP, were transported in just a fewer larger events.

### 2.3.2 *Nitrogen and phosphorus species composition in storm runoff and bioretention effluent*

Among over 800 samples collected at the bioretention research site, TN in storm runoff was largely composed of TKN (Organic N+$NH_3$-N or TN−$NO_x$-N, 63%), while $NO_x$ only comprised 37% of the TN. When looking at P species, 48% of the TP was

ortho-P, while the remaining 52% was particulate-P (part-P; TP−ortho-P). While there were no dramatic changes in the composition of N species in the effluent relative to the influent, P species composition changed dramatically from influent to effluent (Fig. 3). A much greater portion of the effluent total P was ortho-P relative to part-P (69% vs. 31% respectively).

### 2.3.3 *Volume and pollutant retention capacity of bioretention in various storm sizes*

Storm sizes resulting in 100% volume retention ranged from 1.3 mm (0.05 in.) up to 39.4 mm (1.55 in.). Among these storms, 37 events, out of 121 monitored, among all bioretention cells resulted in no outflows (100% volume and pollutant retention in this case), and all but an individual 39.4 mm (1.55-in.) storm were small storms.

For all pollutants, mean percent retention (for all cells combined) was always higher for small storms relative to large storms, but storm size did not make a difference for percent TSS retention (Table 4). Mean TSS removal was always over 90%. When comparing median to mean values, the median retentions were always greater for all parameters (Table 4). Over 60% of dissolved and total nitrogen species were retained by bioretention cells in small storms, whereas large storms always showed negative removal for all nutrient species, especially with mean removal of dissolved P being greatly negative. When examining the medians, only the dissolved N and P were exported in large storms, while removal was observed for everything else (Table 4).

### 2.3.4 *Hydraulic performance (peak flow and volume) of bioretention cells*

During 2015 and 2016, flow rates and runoff volumes were measured from each of the seven bioretention cells. On average, all cells reduced both peak flows and cumulative volumes, and no surface overflow was observed. The average peak flow rate reduction was 91% across all cells (range: 86-96%; See Appendix E for detailed averages). Of the nine predictor variables, peak outflow rates were most strongly correlated to peak inflow rates, explaining most of the explained variation alone ($p<0.0001$, $R^2=0.47$, Fig. 5, compared to $R^2=0.56$ for the whole model). Additionally, precipitation depth, ADP, and VH treatment also significantly and positively correlated with peak outflow rates ($p<0.0001$, $p=0.012$, $p=0.024$ respectively) out of the nine variables in the model.

On average, 75% of the inflow volume was retained (range: 48-86%; Table 5) by the bioretention cells. Outflow volumes were strongly proportional with inflow volumes ($R^2=46\%$, $p<0.0001$, Fig. 6), peak inflow rates ($R^2=47\%$, $p<0.0001$), and precipitation depth ($R^2=20\%$, $p<0.0001$). The three predictor variables together explained 60% of the variation in the outflow volumes, and were positively significant. Similar to results indicated by Hatt et al., 2009b, our results suggest that outflow volumes expected from bioretention cells could be modelled using inflow volumes as one of the strongest predictor variables (Hatt et al., 2009b). Caution should be taken however to avoid extrapolating results to larger storms that may be over 4 inches, which were not observed in the study, as the linear relationship may not hold true for these storms.

Volume retention was mostly positive, except for a few rare occasions. Four storms (two in June; VH and VH SM cells, and one in July and October each; VHRR and

VH cells) had greater outflow volumes relative to inflow volumes. The June and July storms had a total 3-day antecedent period rain of 2.76, 1.68, and 1.04 inches respectively, suggesting that media may have been somewhat saturated prior to storms, and flushing of retained water from previous storm may occur along with "new" water (Subramaniam et al., 2015) in which outflow exceeded inflow. Passeport et al. (2009) also measured greater outflows than inflows on certain occasions. For the October 29 storm, small volumes of inflow and outflow were observed (only 2.63 vs. 3.1 L respectively) with a 3-day antecedent rainfall of 0.62 inches. Season (excluding winter) did not have any significant effects on outflow volume or percent volume retention. Thus, the effects of hydrological factors on the outflow generated from these bioretention cells are more important than seasonality.

Conversely, percent volume retention did not show any strong pattern with inflow volumes (Fig. 6). Precipitation was the only variable out of the nine predictors that showed significant and negative correlation with volume retention ($p=0.041$, $R^2=3.4\%$, compared to $R^2=11\%$ for the full model).

### 2.3.5 *Influent and effluent pollutant concentrations*

The change in pollutant concentrations from influent to effluent from bioretention cells were highly variable and treatment dependent. Across all cells, mean influent concentrations for TSS, $NO_x$, TN, ortho-P, and TP were in the following order: 28, 0.661, 1.32, 0.139, and 0.256 mg $L^{-1}$. Mean effluent concentrations for the five pollutants were 8.9, 1.3, 2.7, 1.3, 1.4 mg $L^{-1}$ respectively. TSS was the most effectively retained pollutant by all bioretention cells across all storms. All treatments lowered influent TSS

concentrations, but the reduction was only significant for VL, VH and VH RR treatments (Fig. 7).

Different media configuration resulted in varying P removals. The two cells amended with the SM additive reduced ortho-P concentrations in the effluent (significant for VH SM cell only), in contrast to all other cells that did not receive the additive (Fig. 7). While the SM cell also significantly reduced influent TP concentrations, lower (but not statistically significant) effluent TP concentrations were measured in the SM+RR60 cell relative to influent. SM cell was the only cell that resulted in lower effluent $NO_x$ concentrations. Export of TN concentrations in the effluent was observed for all other cells (Fig. 7).

Overall, the dissolved metal concentrations for Cu, Zn, Cr, Pb, and Co were low, and non-detectable at times, with influent mean values, pooled across all cells, of 13.7, 148, 11.1, 9.1, and 16.5 μg $L^{-1}$ respectively. For those same elements, effluent concentrations were 21.2, 144, 10.7, 8.9, and 17.8 μg $L^{-1}$, respectively, showing no notable change in concentration within bioretention cells, except for a small export of Copper. Particulate metal concentrations for the above elements were much lower than their dissolved constituents: below 19 μg $L^{-1}$ for influent, and below 3 μg $L^{-1}$for effluent concentrations, indicating positive retention within the bioretention cells.

### 2.3.6 *Cumulative pollutant mass and EMC removal efficiency by treatment*

Cumulative (over the study duration) pollutant load retention from the bioretention cells varied with pollutant types and treatments (Table 5). Mass removal efficiencies were calculated on the cumulative loads (Table 5). Overall, TSS loads were

well retained across all cells (range: 89-99%). Interestingly, the two SM cells retained all four nutrient pollutants based on loads for $NO_x$, TN, ortho-P and TP (over 20% removal for N species, and over 80% for P species; Table 5). All other cells showed negative removals for P species, while N species retention varied depending on the treatment (Table 5). Positive retention of TN was also observed from VL and VH cells. VL showed positive retention for $NO_x$ as well (Table 5).

We examined the EMC data to determine statistical differences between the influent and effluent for the different treatments, by considering each sampling event across the whole monitoring duration as a replicate. Significant reduction in TSS EMCs was observed for all cells (Fig. 8). Ortho-P and TP EMCs were found to be significantly lowered by the two SM cells only, irrespective of the RR treatments. More ortho-P and TP were present in the outflow than the inflow for the non-SM cells (mean negative cumulative mass retention: -427%, -163%, respectively; Table 5), with varying significances for those cells (Fig. 8). The SM treatment also lowered $NO_x$ (significantly) and TN EMCs (Fig. 8). The non-SM cells show mixed results with respect to nitrogen (Fig. 8).

### 2.3.7 *Factors affecting mass removal efficiencies of the different pollutants*

Ten variables were input into a multiple linear regression model to better assess the various factors influencing pollutant removal by bioretention cells. For $NO_x$ and TN, the observed variation in load reduction was a function of the variation in precipitation depth ($p<0.0003$), inflow volume ($p=0.002$ and 0.01 respectively), peak inflow discharge ($p<0.003$), and seasonality ($p=0.1$ and 0.04 respectively), with a model $R^2$ of 28% for

NOx and 24% for TN (Table 6). Out of the ten variables that were selected to explain the total variation in ortho-P removal, precipitation depth, seasonality and peak inflow discharge were highly significant (p=0.002, 0.007 and 0.02 respectively). Inflow volume (p=0.06) and soil media treatment were marginally significant (p=0.08). Together these variables explained 20% of the total variation. For TP, multiple predictor variables were highly or marginally significant, including precipitation depth (p=0.0006), seasonality (p<0.0001), peak inflow discharge (p=0.0004), ADP (p=0.004), inflow TP mass (p=0.001), and soil treatment (p=0.06), explaining 40% of the total variation (Table 6). None of the variables were influential predictors of TSS removal efficiency, except for soil media (p=0.01) and hydraulic ratio (p=0.05), but these predictors only explained as little as 7% of the variation in TSS removal, arguably making them poor model predictors.

### 2.3.8 *Soil and plant nutrient concentration, root biomass density*

Soil C and N content consistently decreased in all cells from year 2014 to 2016 (Table 7). An increase in the CN ratio was observed in 2016 as N decreased more than C content. Plant tissue N concentrations were approximately 6-7 times higher than P concentrations (Fig. 9), which is typical (Tanner and Headley, 2011). Leaf N concentrations were greater than "all plant parts" N concentrations for all species, while for P, this varied with species. *Hemerocallis* and *Symphyotrichum* had the highest tissue N concentrations. *Symphyotrichum* also had the slightly highest P concentrations (Fig. 9). Root biomass density between VH and VL treatments were not significantly different,

but slightly greater density was measured in the VL treatment (0.664 vs. 0.556 mg $cm^{-3}$ soil).

## 2.4 Discussion

### 2.4.1 *Stormwater N and P composition*

The overall composition of N and P species and their concentrations in influent stormwater measured at our bioretention site in Burlington, Vermont over 50 storm events were in the mid-range for $NO_x$ and TN, and high range for ortho-P and TP compared with other urban stormwater findings in the literature (Table 8). Overall, measured P concentrations were much lower (approx. five times) than N concentrations, which is typically the case in urban stormwater (Pitt et al., 2003; Dietz and Clausen, 2006; Winston et al., 2013). TSS was comparatively lower in this research (Table 8).

Median stormwater N and P composition (i.e. proportion of different "species" of each nutrient) in our work align with a few other studies. For example, Taylor et al. (2005) found very similar median numbers in Melbourne, Australia where 30% of the TN (1.8 mg $L^{-1}$) in the storm runoff was $NO_x$ (0.54 mg $L^{-1}$), compared to the reported 40% in our study (TN and $NO_x$: 0.933 and 0.372 mg $L^{-1}$ respectively) (Table 8). Taylor et al. (2006) reviewed the international stormflows from residential, commercial, industrial, parkland landscapes in various cities with separate stormwater systems (Duncan, 1999) and reported that only 24% of TN was attributed to $NO_x$ (this is based on means).

To put our study into a more local context, our N and P species median data were compared to a study conducted by Pitt et al. (2003) which examined stormwater outfall samples from over 200 municipalities nationwide in the U.S. covering mixed land uses (residential, mixed residential, commercial, industrial, institutional, freeway) and

comparable results were found. 25% of TN (2.36 mg $L^{-1}$) was composed of $NO_x$ (0.6 mg $L^{-1}$; Table 8). $NH_4^+$ proportion was smaller, at 19% (0.44 mg $L^{-1}$) and 9% (0.17 mg $L^{-1}$), while greater than 40% of TN was made up of dissolved and particulate organic N in the in the Pitt et al. (2003) and Taylor et al. (2006) studies respectively. From the evidence in the international literature for urban stormwater (Duncan, 1999), we can assume that ammonia may only constitute a small proportion of TN in our data, but we cannot separately quantify the proportions of organic N that are in dissolved (DON) or particulate (PON) forms, apart from concluding that they together may make up majority of the TN. $PO_4$ made up 49% of TP compared to 44% in the Pitt et al. (2003) study, with little variation in the concentration values (Table 8). In fact, a number of studies have measured a greater proportion of soluble ortho-P making up TP in influent stormwater (range: 44-71%, Table 8).

### 2.4.2 *Importance of hydrology on volume and pollution retention capacity of bioretention cells*

Our data shows that bioretention systems exhibit a relatively higher treatment capacity for small storm events because of increased volume retention and subsequently reduced outflow volumes (Table 4). Complete capture of small storms was observed in the study, e.g., 31% over 121 storms monitored. (Davis, 2008) reported complete capture of 18% of 49 storms, all from smaller storm events, and overall delayed times to effluent peak flows. In this study, bioretention was also functional at retaining portion of large storm runoff volumes (70% mean volume retention; Table 4) from the roads. This shows that bioretention has the capacity to maintain predevelopment hydrologic regimes in

urban areas, and by keeping pollutant-laden runoff from entering the sewer, alleviate pressures on existing storm infrastructure. It is also likely that the existence of the shallow swale which resulted in initial abstraction of storm runoff and entrapment of pollutants, a portion of storm volume and pollutants do not make it to the cells' inflows in small storms, if at all, until a bigger big storm flushes them through the cells. Treatment capacity for nutrients, especially dissolved ones, is challenged under changing hydrologic conditions, e.g., for storm sizes greater than 25 mm (1 in.) (Table 4). The challenges of dealing with dissolved nutrients under larger storm events (either longer duration or greater intensity) is that water and nutrients can bypass sorption capacity of the subsoil layers and their susceptibility of leaching from the soil media can greatly increase, particularly when the media is predominantly sand (Djodjic et al., 2004) mixed with compost like here. While particulate pollutants are primarily removed by physical filtration, dissolved pollutants are removed by biochemical (denitrification) or physiochemical (sorption) processes, which require certain soil conditions and retention times in the media.

### 2.4.3 *Cumulative Loads and EMC-based treatment effectiveness*

This study selected experimental treatments to evaluate certain design parameters: vegetation, media additives, and hydrologic regime. All treatment cells performed consistently well for TSS with an average (±SD) MRE of 94±5% (Table 5), and significant effluent EMC reduction (Fig. 8). TSS load removal reported in other field bioretention studies range from 60 to 97% (Roseen et al., 2006; Hunt et al., 2008; Hatt et al., 2009b). TSS is removed via physical filtration of the particulates and colloids during

percolation through the soil profile. The bioretention cells were consistently effective in removing TSS irrespective of the storm sizes, ADP, peak influent discharges, runoff volumes and influent loads amounts, and treatments. Though the cells are functioning well for TSS at present, monitoring long-term removal efficiency is critical, as soil matrix characteristics are may change with time due to influx of sediments, and influence of vegetation, stormwater input, soil moisture changes, and climate.

The soil media additive treatment was the most effective at improving effluent water quality regarding nutrients. P removal efficiencies were highly dependent on the soil treatment. Only the SM treatments, irrespective of whether there was added rainfall and runoff, removed ortho-P, TP cumulative loads (94%, 90%) and EMCs from the influent (Table 5 & Fig. 8 respectively), despite the relatively low P road runoff input to the cells (Fig. 7 & 8). The SM additive cells interestingly also removed both $NO_x$ and TN loads (39% and 48% respectively) and EMCs except for the slight export of average $NO_x$ and TN EMC observed from the SM+RR60 cells (Table 5 & Fig. 8). This cell with the slight export also received approximately 3 times more influent runoff (Table 5) and average (±SD) peak discharge (47±52 vs. 14±27 L/min) than its control SM cell, which most likely contributed to increased N leaching from the bioretention media. Although removal efficiencies for N by the SM treatment were lower relative to P, the added N removal benefit provided by the additive is promising, and not something that was anticipated. Adsorption of $NH_4^+$ ions to iron and aluminum oxide and hydroxide ions (Westerhoff and James, 2003; Belchinskaya et al., 2013) in the additive layer could have reduced $NO_x$ formation via nitrification. It is also possible that concurrent nitrification/denitrification within the soil microsites (Parkin, 1987; Robertson and

Tiedje, 1987) and within same soil aggregates (Stevens et al., 1997) removed portion of the $NO_x$. It is critical to continue testing the long-term field performance of the additive to understand what service lifetime it carries before reaching P saturation potential.

The net retention of nutrients achieved by the bioretention systems was mostly through reduction in runoff volumes, rather than reduction in the actual concentrations of the input runoff, except for the SM treatments, which removed concentrations of either N or P, or both (Fig. 7). While we observed that the SM treatments consistently had positive effects on P removal based on all the metrics examined (loads, EMCs, and actual concentrations), the removal results for N species were inconsistent across the metrics, particularly for cells that did not receive the SorbtiveMedia™. Multiple linear regression results also support this conclusion, as design treatment was not a significant predictor of N load removal, while the SM treatment was a marginally significantly positive function of P load removal (Table 6). Although the SM treatment was not a significant predictor for N removal, the fact that it generally had a consistently positive effect on N removal across all metrics may indicate that it is somewhat promising for N, as it is greatly promising for P. It can be concluded that neither the vegetation nor RR treatments on EMC-based N removal were significantly different, with the exception that VL significantly exported TN EMCs to the effluent (Fig. 8). However, examining the EMCs (Fig. 8) and loads (Fig. 7) data in combination, the effects of vegetation and RR treatments seem to be irrelevant or inconsequential compared to the soil media effects, which appears to be largely governing the nutrient balance from the cells. The VH and RR treatments were overlaid on a soil composition and configuration that was identical among cells. The large amounts of composts that the media contained could have

dampened the possible vegetation and RR effects. Additionally, for bioretention of the depth and configuration utilized in the study, it can be concluded that a 15% to 20% change in hydrologic regime may alter loading patterns (Table 5) and increase variability in the effluent (Fig. 8), albeit not significantly.

We have now attributed nutrient export from the cells to the presence of excess compost in the soil media profile, which has also been known to occur in laboratory studies (Mullane et al., 2015; Hurley et al., 2017). Compost is a rich organic matter nutrient source, and its input to soil enhances C, N, and P mineralization (Tabatabai and Dick, 1979; Busby et al., 2007) due to the presence of active microbial biomass (Li et al., 2004; Goberna et al., 2006), converting more stable pools of organic N and P to soluble inorganic forms (Vitousek and Matson, 1988; Escudero et al., 2012) that are easily transportable. Nutrient transformations from mineralization continues to occur between storm events in the soils layers, and the soluble nutrients that are generated as a result are mobilized downwards by the next high flow event. This is particularly true when the initial nutrient content of the media is high (Hunt et al., 2006; Clark and Pitt, 2009). In our study, net N mineralization rates (±SE) estimated from the upper soil layers averaged 190±14 mg kg dry soil$^{-1}$ per year$^{-1}$, while net N nitrifications rates averaged 134±16 mg kg dry soil$^{-1}$ per year$^{-1}$ from the ambient cells (See Appendix F for detailed methods). Although the total soil N content has decreased over the years (Table 7), due to the "slow nutrient release" nature of composts, it is possible that nutrient mineralization by microbes (Connell et al., 1995) and leaching effects of $NO_x$ (and dissolved organic N) and ortho-P could be observed for at least another few years in the study, if not longer, highlighting the importance of long-term monitoring of bioretention soil media

performance. Typically soil microbes mineralize 1-3% of the N pool back in the soil each year (Connell et al., 1995). Although microbes also remove a portion of the N and P pool via microbial immobilization, assimilated nutrients are re-mineralized back to soil overtime via microbial decomposition of roots and organic matter, and microbial death and lysis (Ladd et al., 1981; Turner and Haygarth, 2001). Nitrate leaching has in fact been observed in several laboratory (Davis et al., 2001, 2006; Hatt et al., 2007; Blecken et al., 2010) and field studies (Hunt et al., 2006; Hatt et al., 2009b; Brown et al., 2013) of bioretention systems, highlighting challenges in dealing with a nutrient that is in a dynamic state of flux. Similarly, P export has also been observed in field studies either due to the disturbance of the soils at the initial phase of the study (Dietz and Clausen, 2005), use of high P-index media (Hunt et al., 2006), or leaching of the mulch and organic soil in the media (Toronto and Region Conservation 2006).

### 2.4.4 *Removal efficiency predictors and implications for bioretention design*

Precipitation depths, inflow volumes, and peak inflow rates had significant negative impact on N and P retention by the cells, suggesting that increases to storm volumes and intensities associated with climate change could undermine bioretention functioning. This could be exacerbated by the phenomenon observed in this research that it was a few larger storm events, as opposed to those less than 1 inch, that tended to mobilize the most TSS and TP from the roadway and into the stormwater treatment system. In a study by Davis et al. (2006), where a series of tests were performed with different runoff inflow characteristics, a reduction in treatment efficiency of nutrients was observed when both the rainfall duration or the flow rate through the bioretention soil

was doubled. Lower rainfall depth and duration also favored effluent peak flow and volume reduction by bioretention in other studies (Li et al., 2009; Mangangka, 2013). In fact, Vermont and other Northeastern states are projected to experience more frequent and intense rainfall events in the future (Frumhoff et al., 2006; Pealer, 2012). Bioretention design factors should be ameliorated to accommodate for the increased water quality volumes anticipated due to climate change. Further, increased rainfall intensities can increase pollutant mobilization and delivery rates, and decrease pollutant retention times provided by a system, as result of increased peak flow rates (Fig. 5). Peak flow rates were significantly positively correlated to increased peak flow rates, precipitation depth, ADP, and surprisingly the VH treatment in the study. This can be explained by the fact that greater diversity may not matter as much as plant selection and their respective functional traits. For example, *Panicum* is known to have deep extensive root systems (McLaughlin et al., 1999). Plants used in the VH treatment have not been a subject of research, but a one-time measurement of root biomass in the VH versus VL plots showed greater root density from the VL plots containing the *Panicum*. Greater proliferation of root density may have subdued the peak flow rates in LD plots by slowing infiltration. This suggests that plant diversity may not matter as much as individual plant functional traits. Designs features should therefore address the interaction of climate effects on hydraulic, hydrology and biogeochemical parameters within bioretention systems.

ADP was not a good predictor for removal efficiencies of most pollutants, only appearing significantly negative for TP (Table 6). This could be because the effect of ADP on pollutant build up on the road surfaces at this site is confounded due to campus

management activities requiring occasional street-sweeping, removing some fraction of dust and particulates that would otherwise be captured in the influent during rain events, or that the maximum ADP observed over the course of this research was only 13 days. Several other studies have showed little or no correlation of removal efficiency with ADP (max of 15 days) (Lewis et al., 2008; Winston et al., 2010), or mixed correlation depending on the pollutant type (Mangangka et al., 2015). Greater atmospheric buildup and deposition of certain pollutants may occur when ADP is longer (Kayhanian et al., 2003), but that would also lead to decreased soil moisture and thus increased soil storage capacity of runoff, improving pollutant retention (Mangangka et al., 2015) under certain storm sizes, but treatment may decrease for larger storms once media reaches saturation. The negative correlation between ADP and TP removal efficiency observed in our study is opposite to the trend reported by Mangangka et al. (2015). This reduction could be attributed to P being primarily present in particulate form (Miguntanna et al., 2013), and higher particulate loads associated with pollutant build-up on the surface (Vaze and Chiew, 2002). Though to support their observation, Mangangka et al. (2015) argue that with longer ADP the average particulate size is expected to increase, and they become more easily removable by bioretention system, this was not supported by our study. On the other hand, the role of soil media control on P removal is particularly an important one to consider owing to the effectiveness shown by this study as well (Table 5 and 6, Fig. 8). Seasonality was a significantly predictor in the model for all N and P removal efficiency, where a significant reduction in spring season (May-June) were observed relative to fall (September-early November) for bioretention performance of those nutrients, despite the largest storm depth of 85.09 mm occurring in September. The

results can be attributed to differences in plant growth that is closely tied to seasonality. Percent cover estimates from Spring to Fall roughly increased from average of 76% to 91% across the cells. Because plants are cut back to only a few inches off the ground in November, the plants are shorter in spring and get increasingly taller as the season progresses. Almost all the plants except the *Anemone* and *Baptisia*, reach full maturity only around July.

### 2.4.5 *Plant assimilation of nutrients*

Across all the herbaceous plant species, nutrient composition patterns were similar where N concentrations were much greater in magnitude than P concentrations in both leaves and "all plant parts" examined, agreeing with other research in the past (Han et al., 2005; Tanner and Headley, 2011; Winston et al., 2013). Tissue nutrient concentration ranged from 1.14 to 2.91% dry weight for N, and from 0.22 to 0.39% for P (McJannet et al., 1995) among the species used in the study, indicating that a percent of pollutant removal mechanism can be contribution from plant uptake of nutrients of dissolved N ($NH^{+}_{4}$, $NO^{-}_{3}$) and P pool, which is variable by species (Fig. 9). However, for accurately estimating the total nutrient amounts removed by species, bioretention plant nutrient concentration acquisition capacity should be paired with aboveground and/or belowground plant biomass data for the species. Examining concentrations and biomass together will allow for the estimation of areal uptake of species, which is a more complete metric of nutrient removal than tissue nutrient concentrations alone.

We also recorded plant growth, survival and composition changes within the cells over time in 2015 and 2016. Our observations will be useful for informing designers

about bioretention plant selection in a cold climate region. Disappearance of several species was observed over time despite plant maintenance through weed removal and careful attention towards mulching the stocks of the cold sensitive plants (e.g., *Lobelia and Aquilegia*) with thick layer of straw for protection. By 2016, *cardinalis* had disappeared from four out of five VH bioretention cells (and all cells by 2017). *Aquilegia* and *Asclepias* were outcompeted in three of the cells by 2016. It is possible that the aggressive growth of *Anemone* in spring (late May to early June), occupying from 20 to 60% of the coverage among the cells, could have drowned out the later emerging species like *Lobelia* and *Aquilegia*. 2016 was also a remarkably dry year compared to 2015, so it provided us with the opportunity to observe and record plant health and survival against the natural mini-droughts conditions occurring that year. All plants but the *Hemerocallis* and *Baptisia*, appeared to have been affected by the drought. *Panicum* height was stunted compared to the year before, while *Helenium* and *Symphyotrichum* contained many dead leaves, but continued growing new ones following wet conditions, while *Aquilegia* and *Asclepias* were mostly wilted and dead by late August. Overall, *Helenium*, *Symphyotrichum* and *Panicum* appeared the most robust against the drought. *Cardinalis*, *Asclepias* and *Aquilegia* appeared to be the least robust species in general; however, they may be able to survive competition and prolong if spacing between plants are wide enough.

### 2.4.6 *Informing design through research results*

By understanding N and P composition in storm runoff, designers can optimize critical bioretention design elements required to effectively target the removal of major

pollutant constituents, and subsequently minimize their transport to water bodies downstream.

#### **2.4.6.1** *Nitrogen*

Given the relatively high organic N proportion of TN (Fig. 3), promotion of aerobic conditions is primarily required in the soil media to drive mineralization in a two-step process: ammonification, the conversion of organic N to $NH^{+}_{4}$ (ammonium) ion (Wood, 1988; Gumbricht, 1993), and nitrification, where $NH^{+}_{4}$ is oxidized, forming first nitrites ($NO_2$), which are highly reactive and gets oxidized to $NO^{-}_{3}$ immediately (Okano et al., 2004). $NO^{-}_{3}$, a highly mobile anion, is ultimately removed via anaerobic denitrification process to achieve complete N removal from the system (Knowles, 1982; Firestone and Davidson, 1989; Bollmann and Conrad, 1998). These processes are microbial-mediated. For N, effective treatment systems must therefore first rely on physical process of aerobic filtering (Taylor et al., 2005; Passeport et al., 2009), followed by a continuously saturated anaerobic zone, with a reliable carbon source as electron donating energy substrates for microbes (Kim et al., 2003). Systems that rely solely on physical filtration with short detention/retention times may not perform adequately for N.

Both lab and field studies have also showed successful N removal in other cases, by incorporating internal saturated zones (ISZ) in the design to promote denitrification, which is the major pathway of N removal. Studies involving N have utilized various carbon substrates ranging from newspaper (Volokita et al., 1996), wheat straw (Soares and Abeliovich, 1998), sawdust (Robertson and Cherry, 1995), woodchips and leaf mulch compost (Blowes et al., 1994) for denitrification potential. Kim et al. (2003) did a column

study utilizing all five organic substrates in sand and observed 100% removal from newspaper columns, 60% from leaf mulch, and greater than 95% removal from sawdust, wheat straw and woodchips columns. In another study, Dietz and Clausen (2006) found that the presence of an ISZ reduced TN concentrations significantly, but did not affect $NO_x$ concentrations, and significantly exported TP loads. Passeport et al. (2009) found ISZs did not lower $NO_x$ concentrations, but lowered various other N species (TN, TKN, $NH_3$), and surprisingly TP and ortho-P EMCs and loads as well.

Apart from hydrologic and soil modification to the treatment system, a pre-treatment could greatly enhance performance. Observationally, the shallow rock-lined inflow swale in our system appeared to slow runoff flow, and to settle and entrap a portion of coarse sediments and particulates, offering promise of a pre-treatment that can increase cell longevity.

#### **2.4.6.2** *Phosphorus*

In contrast to N removal from a system, saturation might have unwanted effects on P solubility, as P becomes increasingly soluble due to desorption under extended saturation (Ann et al., 1999; Hurley et al., 2017; Lintern et al., 2011). This is important to consider in ecosystems challenged predominantly by P pollution, or both P and N pollution. Whereas N removal is closely linked to microbial processes, both short and long-term P removal is heavily relied on soil chemical parameters. Unlike $NO_x$, phosphates are removed from soil solution through sorption reactions with metal cations (mainly Al, Fe, Ca) and chemical precipitation in soils. Thus, design features targeting P retention should try to optimize those physiochemical soil properties that have the largest

role in P removal (Babatunde et al., 2010). This research evaluated the use of SorbtiveMedia™, which contains Fe and Al, and found promising results (Table 5, Fig. 7&8). The SorbtiveMedia™ is a fine reactive media, with a projected service life of 10-30 years when used as a soil and sand amendment, depending on the site loading characteristics and amount utilized[8]. High Fe and Al content are characteristic of an effective filter substrate for P removal (Roy, 2016; Wang et al., 2013). Phosphates bind to organic matter or soil substrates surfaces containing Fe and Al oxides (present in high amounts in clays and silt) through ligand exchange reactions, and are taken out of the dissolved phase (the most bioavailable and transportable) into solid phase (insoluble compounds). Phosphates can also form precipitate with dissolved metal ions and get filtered out during percolation (Roy, 2016). However, Fe treatment for P should be considered carefully because of its sensitivity to redox potential as Fe solubilizes and desorbs P under reduced conditions. Al treatment may be recommended for immobilizing P under wet conditions as it is not affected by redox potential changes. Lime materials ($CaCO_3$, $Ca(OH)_2$), may be better than Al and Fe due to their effectiveness in immobilizing P under heavily reduced conditions (Ann et al., 1999), although they will release P under low pH and in acid soils in the presence of carbonates (Martens and Harriss, 1970; Stumm and Leckie, 1970), high Mg concentration (Martens and Harriss, 1970), and organic acids (Inskeep and Silvertooth, 1988).

As this study indicates that SorbtiveMedia™ as a bioretention soil amendment is promising, other naturally available sequestering materials (adsorbents), which accelerate sorption exchange reactions, as alternatives can also be examined, e.g., red mud,

[8] http://www.imbriumsystems.com/stormwater-treatment-solutions/sorbtive-media

dolomite, limestone, zeolite, bauxite, calcined waste eggshells, and oyster shells (Drizo et al., 1999; Köse and Kıvanç, 2011; Vohla et al., 2011; Wang et al., 2013). Locally produced industrial by-products such as gypsum and drinking water treatment residuals are also other alternatives (Leader et al., 2008).

## 2.5 Conclusion

Bioretention cells at this site were largely successful at mitigating volume and peak flow retention, and reducing TSS concentrations, loads and EMCs. Nutrient loads reduction, however, was more a function of runoff capture and storage, rather than of actual water quality improvements, except for the additive treatment cells, which reduced $NO_x$, TN, ortho-P and TP concentrations, loads and EMCs with variable significance. Our results indicate that P removal can be greatly enhanced by soil media additives (e.g., substrates having higher Fe and Al metal content). The additive layer of SM applied to two of the eight bioretention cells studied successfully negated the inputs of N and P generated by both compost leaching and storm runoff. In non-additive cells, the transformations of input nutrients, and mineralization of compost P forms to ortho-P and compost N forms to ammonium/nitrate and DON could be the major reason for highly variable and poor removal efficiency of the cells. N (and P) removal could be enhanced in future designs by reducing nutrient content of compost (if it must be used), or using little to no compost in the soil media, and/or through deliberate engineering designs to promote microsite conditions of saturation within the soil layers to achieve N transformations via denitrification.

Our multiple linear regression results indicated increased storm sizes and peak flow rates to be the top significant hydrologic predictors of negative nutrient removal

efficiencies (pollutant export) from the cells. Local climate predictions for New England include increased rainfall volumes and intensities in the long-term, suggesting that, for bioretention performances to improve, design initiatives should be driven by the different local climate challenges including extreme precipitation events and flood risks, as well as addition to water quality treatment. Selection of water quality volumes (such as the "WQ volume" calculation used by the State of Vermont, Connecticut and Maryland in stormwater permitting**)** should also be carefully considered. Both N and P in bioretention systems are dynamic and exhibit variation in forms over the course of individual storm events, after and between inter events. Therefore, considering their dynamic speciation, transport, and fate, bioretention design that relies solely on volume reduction is not enough to achieve nutrient removal successes. Promising alternative materials and hydrologic design variables that enhance N and P capture mechanisms should continue to be explored and researched. Appropriate plant species, for example ones that reach maturity faster alongside occupying greater soil coverage and accumulating larger aboveground and belowground biomass, while tolerate changing environmental conditions should be considered for bioretention in cold climate regions.

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**Table 1.** Bioretention watershed and cell characteristics.

| Characteristics | Description |
|---|---|
| Watershed description | Low to medium traffic paved asphalt road |
| Watershed area | 30 – 120 $m^2$ |
| Bioretention cell area | 3.72 $m^2$ (40 $ft^2$) |
| Bioretention maximum ponding depth | 15.2 cm (6 in.) |
| Soil media depth | 61 cm (2 ft) |
| Soil media characteristics | 60:40 sand: compost (upper 30.5cm; 1ft), pure sand (lower 30.5cm; 1ft) |
| Pea stone depth | 7.6 cm (3 in.) |
| Gravel media depth | 22.9 cm (9 in.) |
| Underdrain system | 15.2 cm (6 in.) diameter perforated PVC pipe |
| *Soil media available-P | 27.08 ppm |
| Soil media CEC (top layer) | 6.7 meq/100 g soil |
| Soil media OM (top layer) | 1.99 % |
| Soil pH | 6.27-7.36 |
| Soil media total C and N | 1.6% C, 0.099% N (CN ratio of 15.7) |
| Vegetation types | Low diversity palette: Daylilies 'Stella d'Oro' (*Hemerocallis spp.*) and Switchgrass 'Shenandoah' (*Panicum virgatum*)<br><br>High Diversity palette: Butterfly Milkweed 'Tuberosa' (*Asclepias tuberosa*), Windflower (*Anemone canadensis*), Columbine (*Aquilegia canadensis*), New England Aster 'Purple Dome' (*Symphyotrichum novae-angliae*), Blue False Indigo 'Capsian' and 'Midnight Prairiebliss' (*Baptisia australis*), Sneezeweed 'Red+Gold' (*Helenium autumnale*), and Cardinal Flower (*Lobelia cardinalis*) |

*Note: See Appendix D for detailed soil chemical parameters.

**Table 2.** Treatments in the experimental design for each of the eight bioretention cells.

| Cell | Soil | Vegetation | Vegetation treatment watershed area difference (%) | Rainfall | Runoff treatment watershed area difference (%) | Drainage Area, ($m^2$) |
|---|---|---|---|---|---|---|
| 7 | | VL | 11 | Ambient | | 30 |
| 2 | | VH | | Ambient | 20 | 33 |
| 1 | | VH | | Ambient+RR20 | | 40 |
| 8 | | VL | 13 | Ambient | | 61 |
| 6 | | VH | | Ambient | 15 | 54 |
| 5 | | VH | | Ambient+RR15 | | 63 |
| 4 | SM | VH | | Ambient | 60 | 64 |
| 3 | SM | VH | | Ambient+RR60 | | 120 |

*Cells inside the rectangular are paired cells, for example cell 2 is paired with cell 7 for the purpose of comparing vegetation diversity and with cell 1 for the purpose of comparing rainfall rates.
*Cells highlighted in gray were monitored simultaneously in 2015 (May 10 - July 1) and 2016 (July 15 - November 4). Remaining cells were monitored simultaneously, but in reverse order in 2015 (July 15-October 31) and 2016 (May 15 – July 10) to cover all seasons. VL= low diversity plant mix, VH= high diversity plant mix, RR= enhanced rainfall + runoff, SM= SorbtiveMedia™.

**Table 3.** Cumulative volume and pollutant influent loadings, and percentage of total loadings accounted by small (≤ 1 in. depth; n= 96) and large storms (>1 in. depth; n=25) for the storm events sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont.

| | Cumulative volume and load | | | | | |
|---|---|---|---|---|---|---|
| | Volume | $NO_x$ | TN | Ortho-P | TP | TSS |
| | (L) | ----------(mg)---------- | | | | (g) |
| Small (79%) | 35389 | 11593 | 27348 | 2715 | 5130 | 475 |
| Large (21%) | 27454 | 6665 | 22521 | 1733 | 5198 | 997 |
| | Volume and load contribution (%) | | | | | |
| Small | 44 | 63 | 55 | 61 | 50 | 32 |
| Large | 56 | 37 | 45 | 39 | 50 | 68 |

**Table 4.** Mean (SE, in parenthesis) and median (IQ, in paranthesis) percent loads reduction for all cells combined for small (≤1 in. depth; n= 96) and large (>1 in. depth; n=25) storms for the different water quality parameters across all cells that was sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont.

| Parameter | Storm Size | Mean (SE) | Median (IQ) |
|---|---|---|---|
| Volume | Small | 83 (3) | 98 (21) |
| | Large | 70 (5) | 77 (34) |
| $NO_x$ | Small | 77 (6) | 100 (10) |
| | Large | -272 (127) | -58 (440) |
| TN | Small | 67 (11) | 99 (18) |
| | Large | -24 (34) | 40 (152) |
| Ortho-P | Small | -34 (40) | 99 (26) |
| | Large | -1199 (635) | -84 (719) |
| TP | Small | -35 (19) | 99 (22) |
| | Large | -285 (133) | 5 (365) |
| TSS | Small | 93 (2.9) | 100 (2) |
| | Large | 93 (2.7) | 97 (7) |

**Table 5.** Reduction of overall cumulative volume and pollutants from inflow to outflow from the different bioretention cells, and calculated percentage volume and mass removal efficiency (% RE) for the storm events sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont.

| *Cell | | n | In | Out | % RE |
|---|---|---|---|---|---|
| VL | **Volume (L)** | 17 | 7955 | 1580 | 80 |
| VH | | 37 | 26613 | 4693 | 82 |
| VH RR | | 35 | 11668 | 2678 | 77 |
| VH SM | | 16 | 4295 | 2217 | 48 |
| VH SM RR60 | | 16 | 12423 | 1791 | 86 |
| VL | **$NO_x$ (mg)** | 14 | 1440 | 1414 | 2 |
| VH | | 31 | 4810 | 6213 | -29 |
| VH RR | | 29 | 3338 | 3416 | -46 |
| VH SM | | 12 | 4033 | 1802 | 55 |
| VH SM RR60 | | 13 | 4677 | 3614 | 23 |
| VL | **Ortho-P (mg)** | 14 | 628 | 3578 | -470 |
| VH | | 31 | 784 | 5365 | -584 |
| VH RR | | 29 | 1451 | 4736 | -226 |
| VH SM | | 12 | 643 | 37 | 94 |
| VH SM RR60 | | 13 | 1303 | 79 | 94 |
| VL | **TSS (g)** | 13 | 164 | 14 | 92 |
| VH | | 31 | 266 | 3 | 99 |
| VH RR | | 28 | 358 | 38 | 89 |
| VH SM | | 12 | 65 | 6 | 91 |
| VH SM RR60 | | 13 | 620 | 20 | 97 |
| VL | **TN (mg)** | 12 | 5955 | 3256 | 45 |
| VH | | 28 | 15936 | 8823 | 45 |
| VH RR | | 25 | 7198 | 6159 | -14 |
| VH SM | | 11 | 5910 | 3689 | 38 |
| VH SM RR60 | | 13 | 14649 | 6305 | 57 |
| VL | **TP (mg)** | 14 | 1141 | 4430 | -288 |
| VH | | 30 | 3050 | 5106 | -67 |
| VH RR | | 26 | 1902 | 4449 | -134 |
| VH SM | | 12 | 1067 | 154 | 86 |
| VH SM RR60 | | 13 | 3163 | 190 | 94 |

*VL= vegetation low diversity, VH= vegetation high diversity, RR= enhanced rainfall+runoff, SM= SorbtiveMedia; n= number of storm events

**Table 6.** Significant predictors of regression models for pollutant mass removal efficiencies where (+) and (-) signs indicate the direction of the intercepts and slope estimates.

| | Equation | N | Model p-value | Model $R^2$ |
|---|---|---|---|---|
| **$NO_x$** | y = 203 − 11.7 × precipitation depth (mm) + 0.197 × inflow volume (L) − 2.48 × peak inflow rate (L $min^{-1}$) − 91.3 × season (Spring versus Fall) | 97 | <0.0001 | 28% |
| **TN** | y = 116 − 3.3 × precipitation depth (mm) + 0.07 × inflow volume (L) – 1.15 × peak inflow rate (L $min^{-1}$) − 44 × season (Spring versus Fall) | 87 | 0.0003 | 24% |
| **$PO_4$** | y = 604 − 34.6 × precipitation depth (mm) + 0.596 × inflow volume (L) – 9.95 × peak inflow rate (L $min^{-1}$) + 297 × soil media present − 709 × season (Spring versus Fall) | 98 | 0.0017 | 20% |
| **TP** | y = 233 – 7.27 × precipitation depth (mm) – 2.6 × peak inflow rate (L $min^{-1}$) + 0.824 × inflow TP mass (mg) + 70 × soil media present – 42 × ADP (days) − 202 × season (Spring versus Fall) | 93 | <0.0001 | 40% |

**Table 7.** Soil total C and N content (g kg $soil^{-1}$), and C/N ratios measured once per year in 2014 and 2016 from the bioretention soil media in Burlington, Vermont.

| | 2014 | | | 2016 | | |
|---|---|---|---|---|---|---|
| *Cell | Total C | Total N | C/N ratio | Total C | Total N | C/N ratio |
| | (g kg $soil^{-1}$) | | | (g kg $soil^{-1}$) | | |
| VL | 18.36 | 1.69 | 10.9 | 14.17 | 0.9 | 15.7 |
| VH | 17.78 | 1.63 | 10.9 | 16.66 | 1.06 | 15.8 |
| VH RR | 18.90 | 1.66 | 11.4 | 17.355 | 1.15 | 15.1 |
| VH SM | 15.57 | 1.49 | 10.4 | 14.65 | 0.94 | 15.6 |
| VH SMRR60 | 17.34 | 1.64 | 10.6 | 13.76 | 0.82 | 16.8 |

*VL= vegetation low diversity, VH= vegetation high diversity, RR= enhanced rainfall+runoff, SM= SorbtiveMedia

**Table 8.** Summary statistics (mean, median) of storm runoff concentrations for Burlington data (125 storm events) compared with other studies within the US and Australia. Concentrations reported are mean unless stated otherwise.

| | | | Stormwater input concentrations (mg $L^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|
| Watershed Land use | Reference | Region | $NO_x$ | TN | Ortho-P | TP | TSS |
| Roadway | This research (mean, median) | Burlington | 0.661, 0.372 | 1.32, 0.933 | 0.139, 0.105 | 0.256, 0.214 | 28, 18 |
| Mixed land use | Pitt et al. 2003 (median) | Nationwide | 0.6 | 2.36 | 0.12 | 0.27 | 63 |
| Interstate highway (pre-retrofit) | Winston et al. 2013 | North Carolina | 0.2 | 1.05 | 0.12 | 0.17 | 30 |
| Parking lot, maintenance building, picnic area (pre-retrofit) | Winston et al. 2013 | North Carolina | 0.12 | 1.01 | 0.13 | 0.26 | 216 |
| Municipal parking lot | Hunt et al. 2008 | North Carolina | 0.41 | 1.68 | na | 0.19 | 49.5 |
| Urban catchments with mixed land use | Taylor et al. 2006 (mean, median) | Melbourne, Australia | 0.74, 0.54 | 2.13, 1.8 | na | na | na |
| Roof | Dietz and Clausen 2006 | Connecticut | 0.9 | 1.6 | na | 0.009 | na |
| Shopping center (G1 cell) | Hunt et al. 2006 | North Carolina | 0.34 | 1.35 | 0.05 | 0.11 | na |


**Fig. 1.** Bioretention cell at the University of Vermont, Burlington, USA. The cell receives road runoff via curb cuts along the road. (A) Shallow rock-line inflow swale, underlain by high-density polyethylene (HPDE) plastic, conveys runoff into the cell's weir. (B) Rainpan and attached PVC precipitation-distribution pipes. The rainpan is installed outside of the cell. Rainwater from the corrugated pan drains into gutters, vertical downspouts, and to pipes that run horizontally along the length of the cell and contains perforations at the bottom to deliver water evenly across the cell. Photo credit: Lindsay Cotnoir.

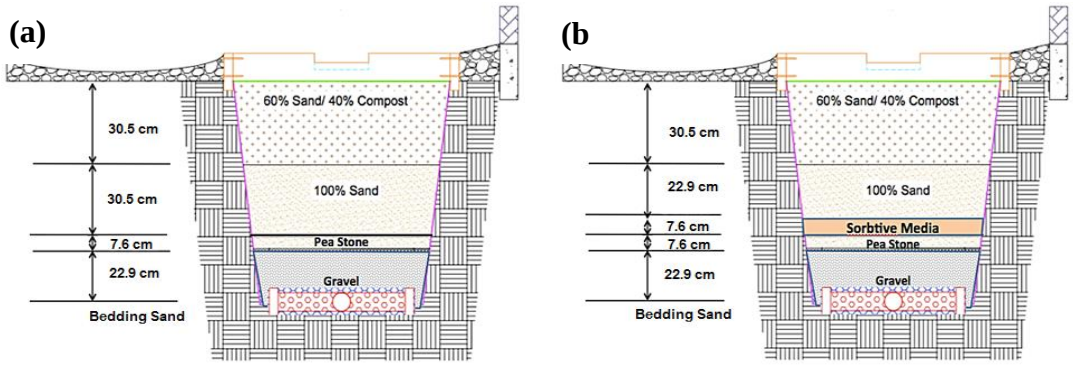


**Fig. 2.** (a) A typical cross section of bioretention soil media in UVM Bioretention Lab, (b) Cross section of bioretention soil amended with SorbtiveMedia$^{TM}$.

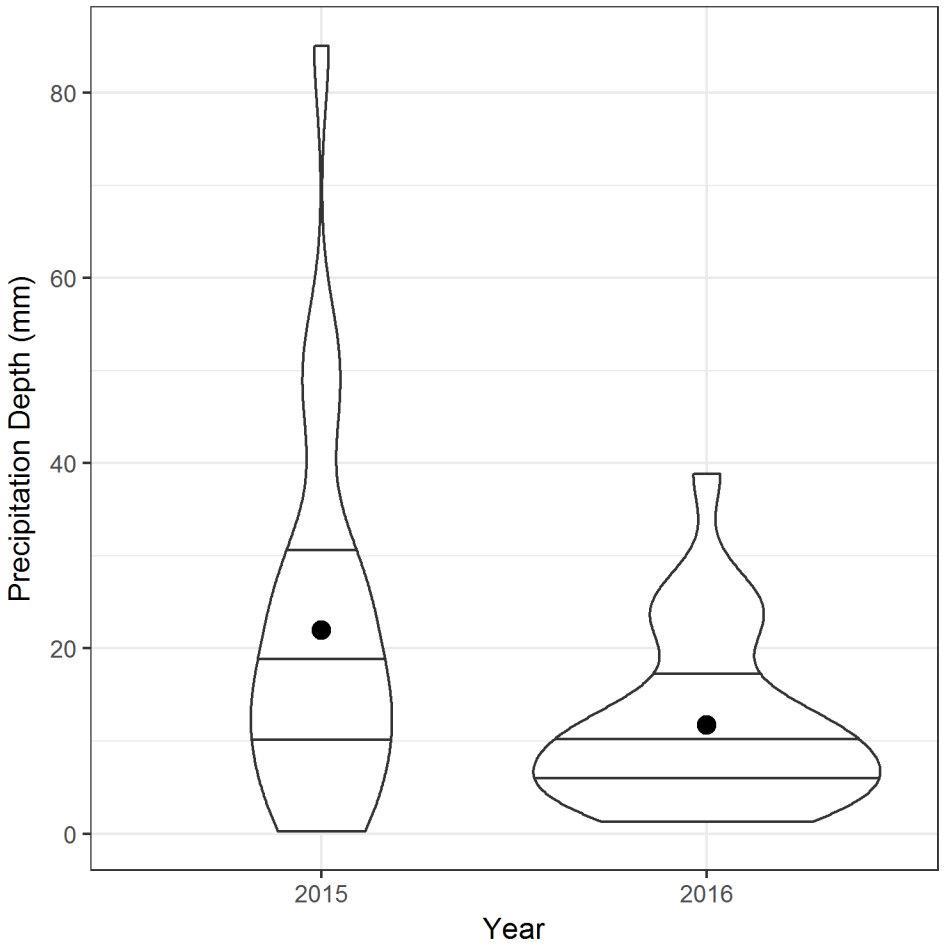


**Fig. 3.** Distribution of precipitation depth (mm) values in year 2015 (N= 23 storms) and 2016 (N= 27 storms) for the storm events sampled from May to October/November in Burlington, Vermont. Straight lines indicate median and interquartile range, dot indicates mean. Area of the violin plot is proportional to count (number of storms).

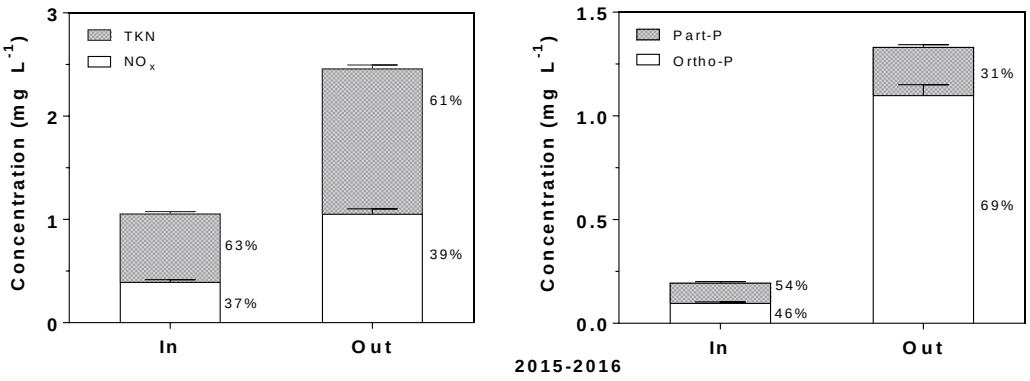


**Fig. 4.** Nitrogen and phosphorus composition for storm inflows and outflows (for matched samples only) monitored across all storm events from May to October/November 2015 and 2016 ($802 \leq n \leq 843$). Numbers beside each box show the percent mean, and error bars are ± 1 SE. The total bars represent total nitrogen (TKN + $NO_x$) and total phosphorus (Part-P + Ortho-P).

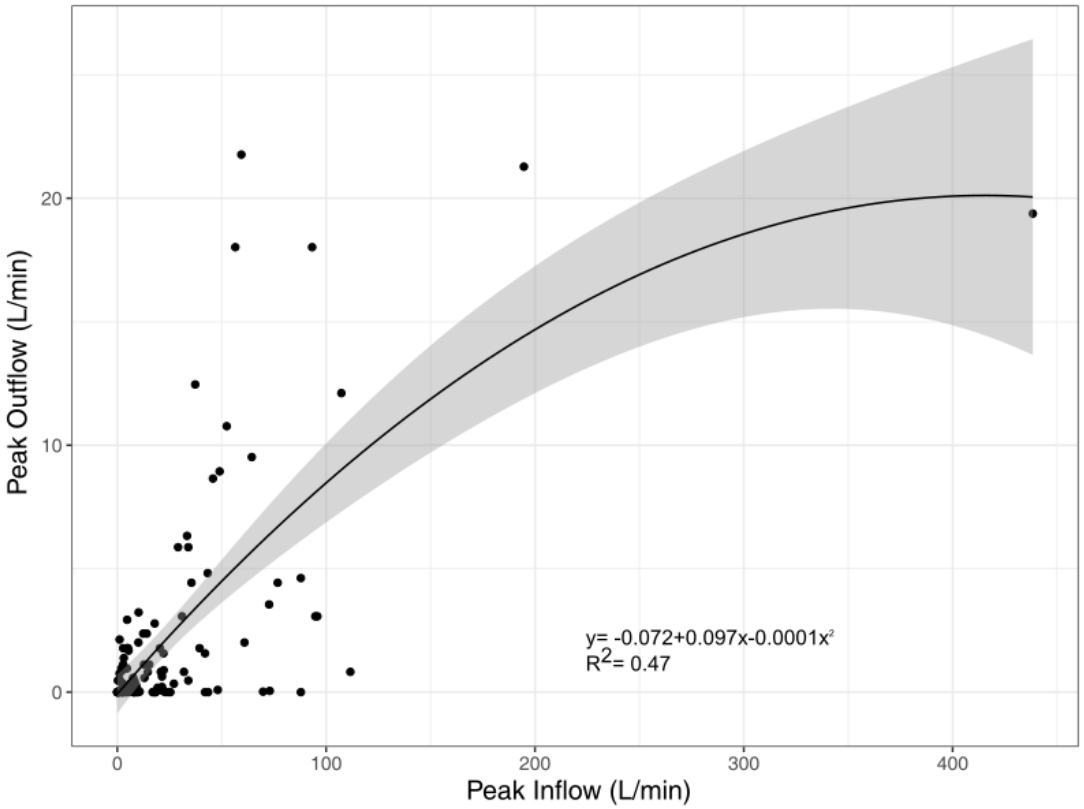


**Fig. 5. R**elationship between peak inflow and peak outflow rate (L $min^{-1}$) for the storm events sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont.

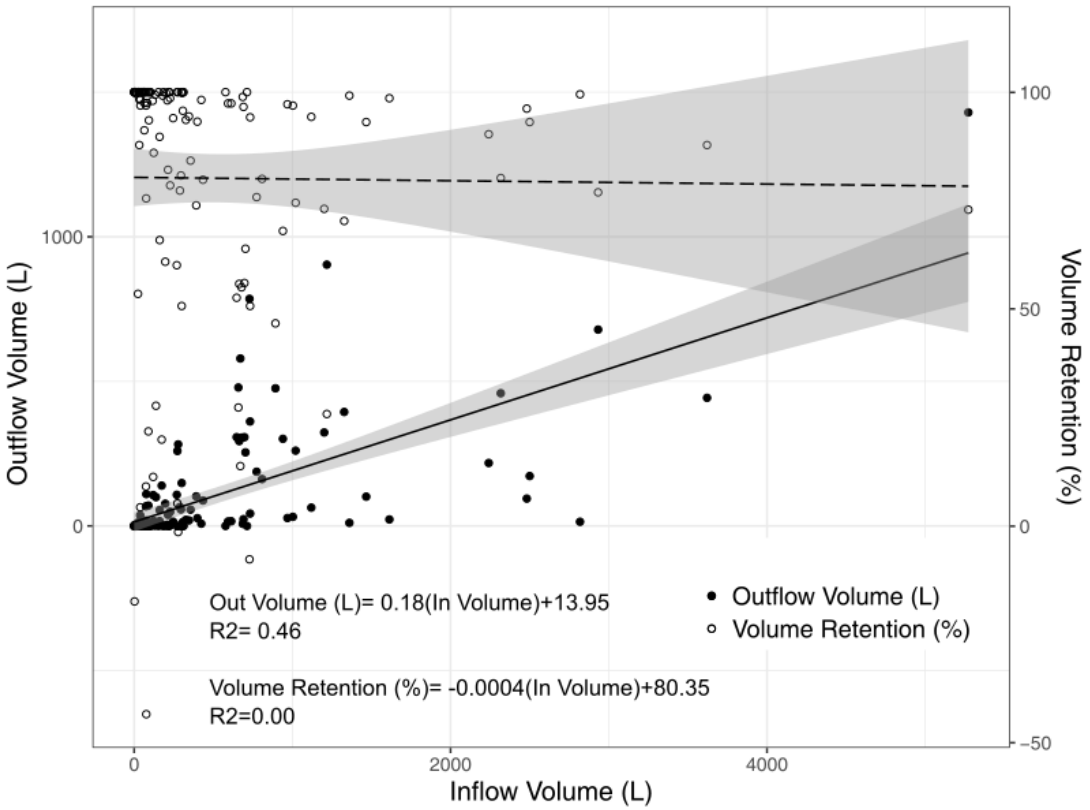


**Fig. 6.** Relationship between outflow volume (black circles) and volume reduction (gray circles) with inflow volumes for the storm events sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont. Solid line represents linear regression line between outflow volume and inflow volume. Dotted line represents linear regression line between volume retention and inflow volume.

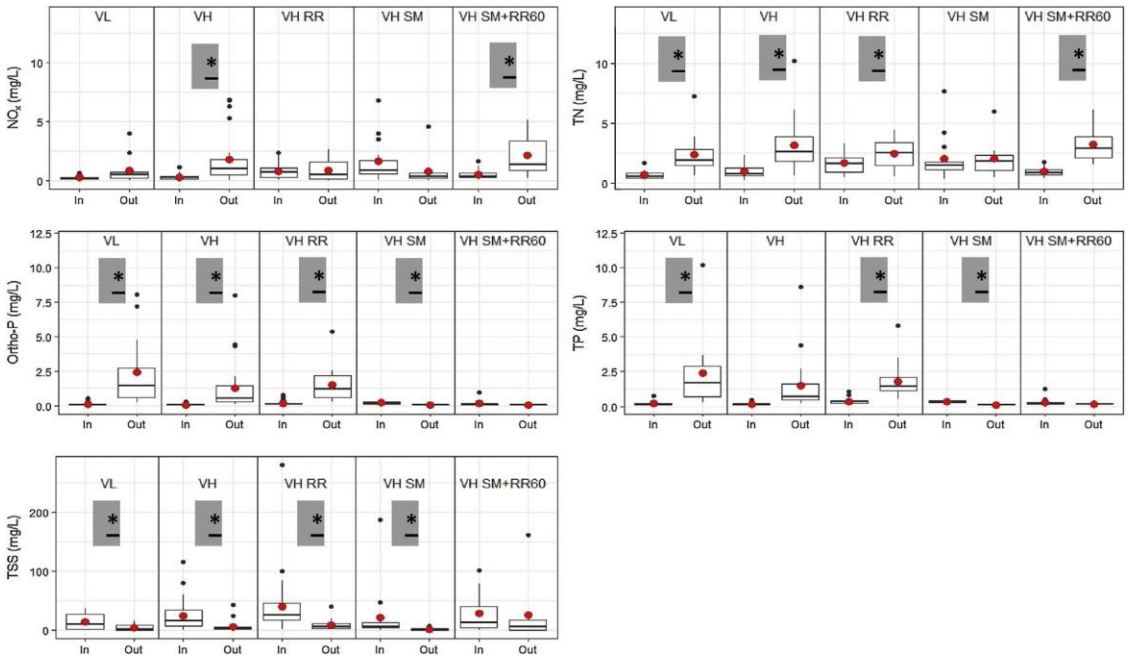


**Fig. 7.** Influent and effluent pollutant concentration (mg $L^{-1}$) during storm events sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont. Significance on the difference between influent and effluent EMC concentrations ere determined by Wilcoxon Signed Rank matched pairs test for non-normal data. Underlined asterisk on the shaded gray bars indicate significance at $p<0.05$. Black dots indicate outliers and red dots indicate mean.

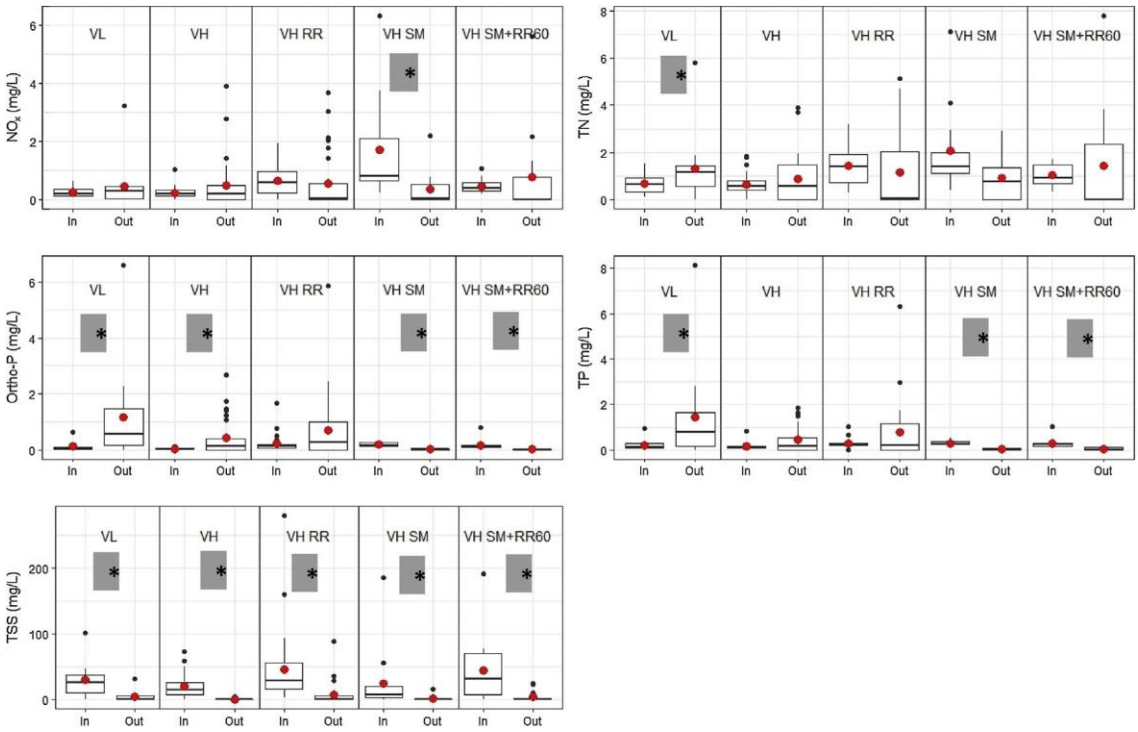


**Fig. 8.** Influent and effluent pollutant event mean concentrations (EMC; mg $L^{-1}$) during storm events sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont. Significance on the difference between influent and effluent EMC concentrations were determined by Wilcoxon Signed Rank matched pairs test for non-normal data. Underlined asterisk on the shaded gray bars indicate significance at $p<0.05$. Black dots indicate outliers and red dots indicate mean.

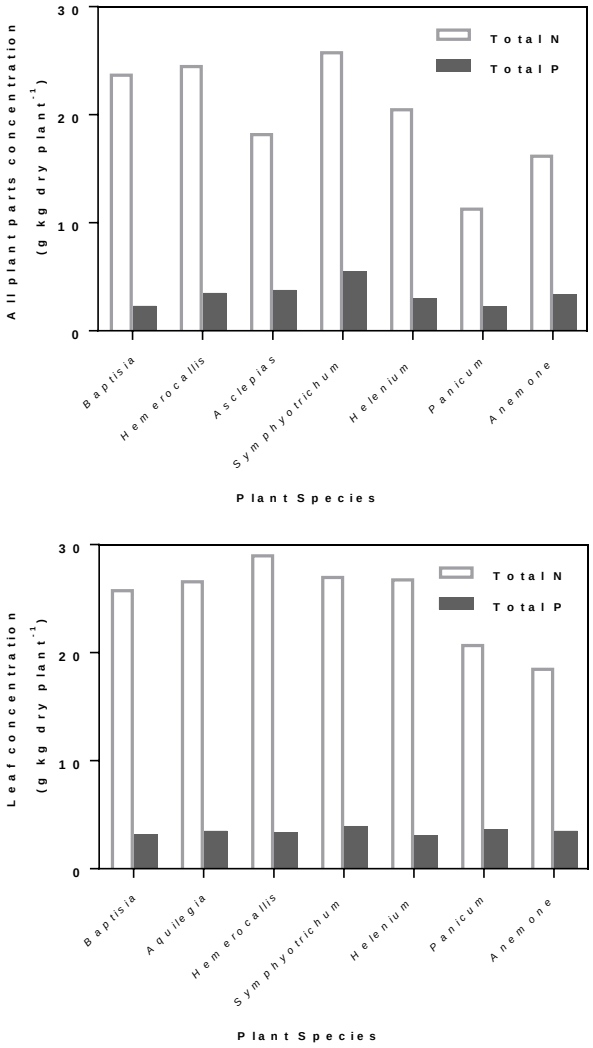


**Fig. 9.** Plant tissue total nitrogen (N) and total phosphorus (P) concentrations in samples pooled from all aboveground plant tissues such as leaves, stems, flowers and pods (left), and only leaves (right) of the different bioretention plant species in Burlington, Vermont.

# CHAPTER 3: SOIL MEDIA $CO_2$ AND $N_2O$ FLUXES DYNAMICS FROM SAND-BASED ROADSIDE BIORETENTION SYSTEMS

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*Keywords: Green stormwater infrastructure, Bioretention, Soil $CO_2$ fluxes, Soil $N_2O$ fluxes, Soil microbial biomass, Plant nutrient sequestration.*

## Abstract

The need for stormwater management is increasing as urban expansion continues at a rapid pace and climate change yields more frequent extreme precipitation events. Although green infrastructure such as bioretention is commonly implemented in urban areas for stormwater quality improvements, various ecosystem co-benefits, including ground water recharge, landscape beautification, and carbon (C) and nutrient sequestration must be evaluated to fully understand the impact of bioretention at the ecosystem scale. Most bioretention research focuses on water quality functions, but little is known about the potential for this practice to mitigate climate change. While bioretention infrastructure may increase C storage, it is also important to understand whether there is an impact of bioretention on greenhouse gas emissions, which could occur as a result of natural biogeochemical processes in the filter media. Gas fluxes are a pathway by which C and nitrogen (N) in the soil and vegetation systems may be lost to the atmosphere. We monitored eight roadside bioretention cells for $CO_2$-C and $N_2O$-N fluxes during the growing seasons over two years in Vermont, USA. Additionally, C and N stocks in the soil media layers and aboveground vegetation biomass were quantified to determine the overall C and N balance. Our bioretention cells contained three different treatments: plant species mix (high diversity versus low diversity), soil media (presence or absence of P-sorbent filter layer), and hydrologic (enhanced rainfall and runoff in some cells). $CO_2$-C fluxes from all cells averaged 194 mg $m^{-2}$ $hr^{-1}$. Average $N_2O$-N fluxes were 0.01 mg $m^{-2}$ $hr^{-1}$, varying between being a sink and source. There were no treatment-induced changes on gas fluxes, but instead $CO_2$-C fluxes were highly significantly correlated with soil temperature ($R^2$= 0.68, $p$ <0.0001), while $N_2O$-N fluxes were weakly correlated ($R^2$= 0.017, $p$ =0.04). This is one of three studies evaluating gas fluxes from bioretention. Compared with the existing two studies on bioretention (Grover et al., 2013 & McPhillips et al., 2018), average $CO_2$-C fluxes fell in the mid-range, while average $N_2O$-N fluxes were lower in this study. In a spectrum of least (urban/rural forest, native grassland) to highly intensively managed systems (landscaped sites, fertilized lawns/turf, mulch beds, constructed wetlands), average bioretention C and N fluxes from this study was at the lower end of the management spectrum mostly likely due to organic matter influence on decomposition processes.

## 3.1 Introduction

Globally, many cities are concerned about coping with the deleterious effects of climate change, such as increasing frequency of extreme events (e.g., heavy rainfall and droughts) and associated threats from flooding, scarcity of water, and extreme heat events ( IPCC, 2007; Zahran et al., 2008; VCA Full Report 2014). Along with increased consideration of climate change adaptation strategies, mitigation of greenhouse gases (GHGs), to slow the progress of climate change, is also critical. GHGs absorb long wave radiation emitted from the earth's surface thereby contributing to warming. Cities are important contributors to GHG emissions, typically from energy production and transportation systems (i.e. fossil fuel combustion; Grimm et al., 2008) combined with relatively low potential for carbon (C) sequestration due to absence of plants and soils (Brown et al., 2012). However, many cities have increasingly been taking measures to reduce their emissions (Kaye et al., 2006; Kennedy et al., 2009) for both economic and environmental reasons (Pataki et al., 2011). The role of cities in altering biogeochemical cycling has received increased attention as well (Pataki et al., 2011). More people currently live in urban areas than in rural areas (UN 2010), and as urban expansion continues, if appropriate counter measures are not taken, the rate of biogeochemical alteration may continue to increase, possibly worsening some climate effects. Additionally, climate change, which is predicted to increase precipitation volumes and intensities, e.g., the Northeastern United States (IPCC, 2007; NECIA 2006) will challenge cities to effectively manage stormwater runoff without negatively impacting water bodies or greenhouse gas emissions.

One of the ways cities are increasingly making efforts to improve their stormwater management capacities is through the integration of innovative green strategies in urban landscapes, broadly defined as green stormwater infrastructure (GSI), including but not limited to bioretention. Bioretention (also known in the literature as "biofilters" and "raingardens") is a porous vegetated media filter, which reduces impervious cover and consequently mitigate the hydrologic "flashiness" of urban runoff and its associated pollution (Nocco et al., 2016; United States Environmental Protection Agency 2012). It is a form of GSI that relies upon soil media and vegetation to slow, retain, and filter stormwater runoff to mitigate hydrological and water quality effects of urbanization. Although bioretention is primarily implemented for ecological treatment of urban stormwater, their benefits can extend well beyond stormwater control. Bioretention can lead to C and nitrogen (N) sequestration in the soils and plants that make up the filter. However, this presumed positive effect may be unique to an installation type and must be empirically documented.

Bioretention cells foster biogeochemical cycling processes, particularly C and N cycling, as they support active soil microbial communities (Liu et al., 2014) and may receive influxes of nutrient-enriched water (Bratieres et al., 2008; Hatt et al., 2009; Grover et al., 2013). The combination of nutrient influxes and variable soil moisture patterns can thus make bioretention systems hotspots for C and N transformation via biological processes such as root respiration and organic matter decomposition releasing $CO_2$ (Ewel et al., 1987; Lytle and Cronan, 1998), and microbial-mediated nitrification and denitrification releasing $N_2O$ (Verstraete and Focht, 1977). While carbon dioxide ($CO_2$) is the most important greenhouse gas, being produced in largest quantities, nitrous

oxide ($N_2O$) is emitted in smaller quantities but has 300 times the global warming potential of $CO_2$ (Smith et al., 2003), and plays an important role in the depletion of the stratospheric ozone layer (Johnston, 1971). As bioretention designs can greatly influence the extent of such biological processes, this has design implications and one must consider environmental tradeoffs accordingly. For example, from a water quality standpoint, removal of stormwater nitrate ($NO_3^-$) is a design goal, particularly in watersheds draining to N-sensitive water bodies (e.g., Chesapeake Bay; Groffman et al., 2002). Thus, an ideal GSI design would maximize the water quality service of denitrification while minimizing production of nitrous oxide ($N_2O$).

Thus far, only two studies exist that have examined GHG fluxes from bioretention in Melbourne, Australia (Grover et al., 2013), and New York, United States (McPhillips et al., 2018). However, no study exists to our knowledge that has quantified overall nutrient storage/stocks from a bioretention cell. As urban expansion continues, implementation of stormwater control structures such as bioretention will likely increase. It therefore becomes important to understand whether and how bioretention might contribute to urban climate change mitigation efforts, including C and N storage and GHG fluxes, to evaluate their benefits or trade-offs in meeting environmental goals. Additionally, a better evaluation and understanding of nutrient dynamics from bioretention cells will inform us on how to improve their design attributes to minimize detrimental and maximize beneficial functions.

In this paper, we examine soil fluxes of $CO_2$-C and $N_2O$-N from eight sand-based bioretention systems that had been previously maintained for 2.5 years, and receive different vegetation, soil media, and hydrologic treatments. We evaluate whether gas

fluxes vary significantly among cells receiving the different treatments. Since gas fluxes are tightly coupled with soil temperature (Pang et al., 2013) and moisture (Maier and Kress, 2000), which vary seasonally, we explore relationships between the observed gas fluxes and those environmental parameters derived from the bioretention soil media across all treatments. We quantify the total amounts of C and N stored in bioretention cell. For this, we chose one of the eight cells to determine soil, microbial, and plant sequestration of nutrients (C and/or N) to fill gaps in our understanding of nutrient stocks/accumulation and partitioning of the stocks among soil and plant biomass components in a bioretention system. Lastly, we compare fluxes from this bioretention study to other stormwater treatment systems, and some of the least and highly intensively managed land use types to contextualize our findings in a broader scale.

## 3.2 Methods

### 3.2.1 *Study site description and experimental design*

The study examines eight bioretention cells in an outdoor research laboratory situated adjacent to a medium-traffic road in the University of Vermont campus in Burlington, Vermont, USA (Shrestha et al. (in press)). Burlington is the largest and most populous city in Vermont (US Census Bureau, 2013), and has a humid continental climate, with mean summer and winter temperatures of and 20$^{o}$C and -6$^{o}$C, respectively, and a mean annual precipitation of 94 cm (National Climatic Data Center 2017). The bioretention cells were constructed in November 2012 and have identical sizes (1.22m wide, 3.05m long, 0.9m deep) and drainage configurations, but drain road watersheds of varying sizes, ranging from 30 to 120 $m^2$ (See Shrestha et al. (in press) for experimental

design details). The bioretention soil media consists of two layers, each approximately 30 cm deep: the upper layer is a 60:40 sand-compost mix, the lower layer is pure sand. A 7.6 cm-layer of pea stone was placed below the sand layer and the bottom 23 cm of each cell is occupied by 5-cm diameter stones. The cells are drained using a 26-cm long perforated PVC underdrain pipe that is placed 2.5 cm from the bottom of the cell within the stone layer, and which conveys effluent to the campus storm sewer system. For the purposes of water quality monitoring, the entire cell (sides and bottoms) is lined using an impermeable rubber liner.

The eight bioretention cells received combinations of three treatments, previously described in Shrestha et al. (in press): (1) vegetation with low-diversity (VL; 2 species) or high-diversity (VH; 7 species) plant mixes (See Appendix G for a detailed planting list); (2) presence or absence of a proprietary SorbtiveMedia$^{TM}$ (SM) layer containing iron and aluminum oxide granules to enhance sorption capacity for phosphorus; and (3) "ambient" or "enhanced rainfall and runoff" (RR) at three levels (15%, RR15; 20%, RR20; and 60%, RR60) mimicking a range of anticipated precipitation increases associated with climate change. The additional rainfall and runoff that each of the three RR cells receives is proportional to the paired cell's watershed size differences, such that each "enhanced" RR cell receives either 15%, 20%, or 60% more runoff and rainfall (via attached rain pan- see Shrestha et al. (in press) than its paired "ambient" cell (Table 1).

### 3.2.2 *Gas flux measurements*

In 2013, two PVC collars (18 cm height with 25 cm inner diameter) were installed permanently in each bioretention cell a soil depth of 5-10 cm (Hutchinson and Livingston, 2001). The collars were kept free of aboveground vegetation by clipping to

the soil surface to prevent aboveground plant respiration and photosynthesis (Tufekcioglu et al., 1998) and a bare soil surface was maintained by removing trash or leaf litter. $CO_2$-C and $N_2O$-N fluxes were measured at roughly 2 to 3-week intervals from May to October 2015 and 2016. Two subsample locations were sampled repeatedly from each of eight cells in 2015, while one location per cell was sampled in 2016. At each sampling date, flux measurements on the eight cells occurred within 45 minutes to 4.5 hours in 2015, and within 2 to 2.5 hours in 2016. All measurements were conducted in daylight between 9:30 am and 2:30 pm. In the wetter year 2015, only drier days were chosen for gas sampling due to logistical reasons and no post-storm sampling was conducted. In 2016, however, efforts were made to sample immediately after storm events. However, this was a drier year and only 6 storms (ranging from 0.762 mm (0.03 in) to 42.41 mm (1.67 in) was sampled for fluxes on the day of or the next day following storms.

Gases were analyzed using two different protocols during this study. From May 15 to June 26, 2015 sampling, a vented static chamber method was used for gas exchange measurements (n= 32) between the soil surface and atmosphere (Hutchinson and Livingston, 2001). At the time of sampling, a PVC lid containing a gas sampling port equipped with a butyl rubber septum and a vent tube to allow equilibration of internal and external atmospheric pressures was used to enclose the chamber. An instantaneous measurement was taken immediately upon sealing of the chamber head (time-zero concentration) with a 20-ml polypropylene syringe fitted with one-way stop-cock valve. Headspace gas samples were withdrawn from the chamber at regular intervals over a period of 45 minutes (i.e., 0, 15, 30, 45 min), which allowed the sampling of all cells to occur within an hour. Air samples were immediately transferred to a pre-evacuated 10-ml

glass vial sealed with butyl rubber septum. Vials were over-pressurized by injecting 15 ml of gas samples , which is considered to maintain the integrity of samples until analysis (McPhillips and Walter, 2015). Glass vials were transported to the laboratory and analyzed for $CO_2$-C and $N_2O$-N concentrations on a Shimadzu AOC-5000 gas chromatograph (GC) equipped with an electron capture detector (ECD) and flame ionization detector (FID). All samples were analyzed on the GC within 1 to 3 days.

From July 2015, due to mechanical malfunction with the GC, all the subsequent gas exchange measurements (n=144) were conducted using 1412 Photoacoustic multi-gas monitor (PAS; INNOVA Air Tech Instruments, Denmark; calibrated by California Analytical Instruments, as in Iqbal et al., 2013). The same PVC lids were modified to be compatible with the PAS analyzer. When the PAS was in use, sampling intervals were shortened such that headspace gas samples were withdrawn every 2 minutes over a period of 12 minutes (i.e., 2, 4, 6, 8, 10, 12 min; Iqbal et al., 2012) in 2015, and at every one minute up to 10 minutes in 2016, and concentrations detected *insitu* by the PAS analyzer. No observable differences in fluxes (e.g., <0.04% difference) were noted between the 12 vs. 10-minute duration. Atmospheric air samples were pulled as a "blank" before starting the actual sampling to check if concentrations were far from the typically expected 400 to 430 ppm range.

Soil surface gas fluxes were determined by calculating the linear regression slope of the gas concentrations over time after chamber closure (Hutchinson and Mosier, 1981; Rochette and Bertrand, 2008). Regression slopes with *p* values lower than 0.05 were assigned flux values of zero (assuming no measurable increase or decrease in concentrations; proc lm in R; R reference). All measured concentrations, originally in

ppm, were converted to mass units and corrected for 20$^{o}$C and 1 atm (because PAS instrument calculates the concentration of each gas at 20$^{o}$C) and field chamber volume and surface area, based on which final flux values were calculated (See Appendix H for additional detail on flux calculation).

Iqbal et al., 2013 found PAS readings to be comparable to GC readings when calibrated properly. In this study, overall, 22% and 78% of samples were analyzed on GC and PAS respectively. Soil temperature and volumetric moisture content at a depth of 10 cm was taken concurrently, once every sampling occasion in each of the sample locations in the chamber using a digital thermometer and a time-domain reflectometry moisture probe (FieldScout TDR300, Spectrum Technologies, Inc.).

### 3.2.3 *Soil and plant measurements*

Following GHG sampling, three random subsamples of the top 10 cm of soil outside of the chamber was collected from the ambient high and low diversity (VH and VL) plots for soil microbial biomass (SMB) C determination monthly from May to September 2014 and 2015. SMB measurements in 2015 coincided with the gas flux measurements. The chloroform fumigation-incubation extraction method (Jenkinson and Powlson, 1976; Vance et al., 1987) was used to determine SMB, following the extraction of soil samples with 0.5 M $K_2SO_4$ (Brookes et al., 1985). Analysis was done on field-moist soil within several hours from collection. The filtrate from the extraction procedure was analyzed for total organic carbon (TOC) on a TOC analyzer (TOC-L Shimadzu TOC Analyzer, Shimadzu Corporation). The difference in TOC between the chloroform-fumigated and non-fumigated soils divided by the kEC constant estimated as 0.45 is the

chloroform-labile C pool (EC), and is proportional to microbial biomass C (Vance et al., 1987; Beck et al., 1997). Moisture-correction was done for each sample to correct for differences in soil water content and results are expressed in dry weight equivalents (See Appendix I for detailed methods). Microbial biomass C concentration was measured from the top 10 cm soil media, but given the upper 30 cm soil media profile had the same soil media composition, we assumed this concentration to stay constant over the top 30 cm.

Total C and N content from the top 10 cm of the bioretention soil from all eight cells were measured in May 2014 and 2016. Three 0-10 cm soil cores, taken near the influent, center, and effluent locations, were composited for each cell. Soil bulk density was measured twice, and soil organic matter (OM) and pH were also measured six times from all cells during the sampling duration. Additionally, we wanted to estimate the total amount of standing C and N in bioretention soil media and plants from one of the chosen VL treatment at plot level. For this, soil C and N content was measured from one of the VL cells (cell 7) in November 2016 at depth increments of 0-30 cm and 30-40 cm. Soils were oven dried at 60$^{o}$C for 2 days, sieved through a 2-mm screen, homogenized, and ground into fine powder (<0.5 mm). Samples were analyzed in triplicate for C and N content by combustion method in a CN elemental analyzer (Flash EA-1112, CE Elantech, Lakewood, NJ). The mass of total soil C and N in the upper and lower 30- cm soil media layers were determined by multiplying the concentrations of soil total C and N by the total soil mass in their respective layers, estimated using soil bulk density measurements (1.19 and 1.59 g cm$^{-3}$ in upper and lower 30 cm layer respectively; See Appendix K for additional details). Mass of carbon derived from microbial contribution was also

determined by multiplying microbial biomass C concentration with the total soil mass in the upper 30 cm layer.

Aboveground plant tissues from the same VL cell were analyzed for C and N content in August and November 2016, where plant tissue samples were composited from three different individuals and analyzed in triplicate by combustion method. Since tissue C and N concentrations differed in summer versus fall, their average was used in the final calculations. Estimates for the aboveground plant biomass from the literature were used as proxy. *Panicum* biomass of 10 kg $m^{-2}$ (or 10 Mg $ha^{-1}$) estimated by Heaton et al. (2004), which examined 77 different observations from various peer reviewed literature in North America and Europe, was used to extrapolate carbon and nutrient capture at the bioretention plot level. Due to lack of biomass data for *Hemerocallis*, half of *Panicum* biomass (e.g., 5 kg $m^{-2}$) was assumed, given that their height in the plots were approximately half of *Panicum*, and their spread over a given area was relatively equal., 55% of the plot area (3.72 $m^2$) was covered by *Panicum*, and 45% by *Hemerocallis* (2.046 vs. 1.674 $m^2$ respectively). *Panicum* and *Hemerocallis* coverage, in a 3.72 $m^2$ cell, was determined through visual estimates. Tissue concentrations were multiplied by the total aboveground plant biomass and scaled to plot coverage level. In general, percent coverage of bioretention plants in all cells was also determined using visual estimates every 3 to 4 weeks in 2015 and 2016.

Additionally, dissolved organic C in the effluent water exiting from few of the cells (VH; cell 2, SM; cell 4, and VL; cell 7 treatments) was also measured in three different storm events on September 23, October 28, and November 3, 2016. Effluent samples were collected real-time over the course of the storms using autosamplers

(Teledyne ISCO 6712/7400, Lincoln, NE) in up to 24 bottles. If all 24 bottles were filled, every three consecutive bottles were composited into one sample, otherwise samples were analyzed discretely for dissolved organic C concentrations on a TOC analyzer (TOC-L Shimadzu TOC Analyzer, Shimadzu Corporation).

### 3.2.4 *Statistical analyses*

Gas fluxes from the VHRR15 and VHRR20 treatments were averaged, as no differences were observed between the two treatments, and will hereafter be called VHRR. The two treatments also had very similar plant cover throughout the monitoring period. Treatment effects on soil $CO_2$-C and $N_2O$-N flux, temperature, moisture and SMB carbon were examined using repeated measures (Proc mixed model) analysis in SAS 9.4 software (SAS Institute Inc., Cary, NC, USA) using the cell as a random effect, and treatment and day as fixed effects. The relationships between gas fluxes and environmental variables of soil temperature and soil moisture were examined using linear regression analysis in JMP Pro 12 (SAS Institute Inc., Cary, NC, USA). When necessary, soil $CO_2$-C efflux, temperature, moisture, and microbial C biomass data were log transformed to meet normality assumptions. Means are followed by standard errors where indicated.

## 3.3 Results

### 3.3.1 *Gas flux analysis*

No significant treatment effects on either of the gas fluxes, soil temperature, or soil moisture were observed. During the sampling period, the mean growing season soil

$CO_2$–C flux across all eight bioretention cells was 194±7 mg $m^{-2}$ $hr^{-1}$ (May-October), with a range 37 (May 9, 2016) to 374 mg $m^2$ $hr^{-1}$ (September 7, 2015). Mean growing season soil $N_2O$-N fluxes were thousands of orders of magnitude smaller than $CO_2$-C fluxes with a mean of 10±20 µg $m^{-2}$ $hr^{-1}$, and ranged from -1100 (September 18, 2016) to 330 µg $m^2$ $hr^{-1}$ (August 10, 2015). $N_2O$-N fluxes were below zero for many sampling events in all cells, indicating $N_2O$ uptake (Fig. 1). Overall, the soil $CO_2$-C fluxes paralleled soil temperature changes with strong seasonal patterns, increasing in summer and decreasing in spring and fall (Fig. 1). Soil $CO_2$-C fluxes appeared to be strongly driven by soil temperatures in a linear fashion ($R^2$= 0.68, $p$ <0.0001; Fig. 2). $N_2O$-N fluxes also slightly positively correlated with soil temperature ($R^2$= 0.017, $p$ =0.04; Fig. 2), but the resulting linear correlation was poor (Fig. 2). Soil moisture did not significantly affect $CO_2$-C or $N_2O$-N fluxes. Both soil temperature ($R^2$= 0.81, $p$<0.0001) and moisture ($R^2$= 0.49, $p$<0.0001) showed significant temporal variability (Fig. 1).

### 3.3.2 *Bioretention C and N pools*

The low diversity (VL) cell that was chosen for a more in-depth analysis of belowground C and N storage showed a dramatic decrease in both total soil C and N content with depth (Table 2). The top 30 cm of soil profile stored approximately five times the C and N stored in the lower 30-40 cm soil profile (C:10.27 vs. 1.82 g $kg^{-1}$ dry soil; N: 0.73 vs. 0.14 g $kg^{-1}$ dry soil respectively; Table 2). The SMB concentration in the VL cell made up approximately 9% of the average total soil concentration measured (Table 2). Average SMB carbon concentration measured the same in both the VL and VH treatments: 1.436 ± 0.15 versus 1.436 ± 0.14 g C $kg^{-1}$ dry soil respectively. Repeated

measures analysis showed no significant differences in SMB carbon between the high and low diversity treatments, but significant temporal variation in SMB carbon were observed for each of the two years (Fig. 3).

Plant concentration of C and N by far exceeded soil storage concentration in the VL cell per unit dry weight. Plant C and N concentrations were 28 and 5 times greater that than of the bioretention soil in the top 10 cm (Table 2 and 3). Between *Hemerocallis* and *Panicum*, *Panicum* appeared to have higher tissue C concentrations, while *Hemerocallis* had higher tissue N concentrations (Table 3). Tissue N concentrations were considerably higher in summer than fall for *Panicum* and *Hemerocallis*, while C concentrations seemed to have increased a little in the fall compared to summer (Table 3).

When extrapolating soil nutrient sequestration to the entire cell's soil media volume (calculations detailed in Appendix K), C sequestered in the top 30 cm vs. the lower 30 cm soil media was estimated to be 13844 g and 3278 g respectively (Fig. 4). A portion of the soil C is sequestered in the microbial biomass fraction. Estimated C stored in the microbial biomass portion amounted to 1936 g, which was 14% of the total soil C in the upper 30-cm layer.

Plants are larger reservoirs of C and N per unit dry mass relative to soil (Table 2 and 3). The amount of C sequestered by *Panicum* and *Hemerocallis* were 9279 and 3741 g C $yr^{-1}$ respectively (Fig. 4). The total amount of N sequestered by the two species was 176 and 144 g N $yr^{-1}$ respectively (Fig. 4). Excluding the winter months (November to April where no gas flux measurements were taken), gas fluxes represents 0.13% (17g C

$day^{-1}$) of total soil C, and $9\times10^{-5}$ % (0.9mg N $day^{-1}$) of total soil N lost from the top 30-cm of the bioretention soil media to the atmosphere per day (Fig. 4).

### 3.4 Discussion

Our objective was to provide baseline estimates of soil $CO_2$-C and $N_2O$-N fluxes from the bioretention soils, as the fluxes represent a potential nutrient loss pathway from the system. We examined whether these fluxes significantly varied with the different treatments associated with vegetation diversity, soil, and hydrologic (increased rainfall and runoff; RR) conditions, along with soil temperature and moisture. Estimating GHG fluxes is important for assessing potential environmental trade-offs associated with the water quality service provided by bioretention systems, as well as to better understand the mechanisms driving bioretention's role in biogeochemical cycling within the greater urban context. We also provide estimates of C and N in the soil media layers and plants, which are the different design elements critical to any bioretention, to quantify the overall C and N balance of the system. We compare fluxes to a variety of land-use types that will indicate relative C and N footprint of bioretention based on gas flux metrics.

#### 3.4.1 *Treatment effects on gas fluxes*

Gas fluxes of $CO_2$-C and $N_2O$-N did not vary significantly with the different vegetation, soil, and hydrologic treatments. Gas fluxes increased significantly with temperature but not soil moisture. Average $CO_2$ fluxes were slightly higher in the treatments receiving the enhanced rainfall and runoff (RR and SMRR60 treatments), but results were not significant. From the percent cover measurements, all RR treatment cells

had the maximum amount of plant coverage throughout the monitoring period in both years (up to 100% coverage in RRSM60, and up to 98% coverage in RR15 and RR20 cells from June through August). The higher percent vegetation cover could be associated with greater root proliferation. Belowground C allocation (e.g, roots, root exudates) could therefore influence root respiration (Hoegberg et al., 2001), and increase microbial respiration (Paul 2014), both of which contribute to the soil $CO_2$-C efflux. For $N_2O$-N fluxes, the highest average flux observation was made in the VL treatment, and lowest (and negative) was in the SM treatment. Interestingly, VL had the highest soil $NH_4^+$ concentrations, while SM had the lowest $NH_4^+$ concentrations (0.575 ± 0.08 ppm vs. 0.0137 ± 0.4 ppm respectively) among the five treatments (Detail averages shown in Appendix J), though the difference was not significant due to large variability in the data. Nevertheless, higher $NH_4^+$ concentrations can lead to increase nitrification potential, and as more $NH_4^+$ is available to undergo nitrification, this can increase nitrification contribution to $N_2O$ (Avrahami et al., 2002), which could corroborate the trend observed here.

### 3.4.2 *$CO_2$ fluxes*

As expected for any soils containing organic matter, the bioretention soils here were always source (or efflux) of $CO_2$ (Fig. 1). Soil $CO_2$ efflux is the pathway by which stored soil C is returned to the atmosphere via autotrophic root respiration and heterotrophic microbial respiration. Besides this study, there are only two published studies examining $CO_2$ fluxes from bioretention filters by Grover et al. (2013) and McPhillips et al. (2017). Grover et al. (2013) measured mean $CO_2$-C fluxes of 102.2 mg

$m^{-2}$ $hr^{-1}$ from a sandy loam bioretention, and 98.3 mg $m^{-2}$ $hr^{-1}$ from another sandy loam (80%) bioretention amended with compost (10%) and hardwood mulch (10%) with an internal saturated zone (ISZ). McPhillips et al. (2017) measured higher fluxes of 367.9 mg $m^{-2}$ $hr^{-1}$ from a bioretention amended with 40% compost (15 cm of compost mixed to an approximately 38 cm soil depth). Compared to Grover et al., this study observed much higher $CO_2$-C fluxes with a mean of 194±7 mg $m^2$ $hr^{-1}$, which may be attributed to the high amounts of compost (40%) present in the top 30 cm of the soil media. Composts adds C, N and P, stimulating microbial biomass and activity (Tabatabai and Dick, 1979; Goberna et al., 2006), which likely increases the microbial contribution to soil $CO_2$-C evolution. McPhillips et al., observed almost twice the amount of $CO_2$-C fluxes than this study, which could have also resulted from compost amendments, as well as initial soil disturbances from tillage (Calderón et al., 2001), given that they conducted gas measurements approximately one month following cell establishment during which period the soil was tilled to 38 cm depth.

The positive fluxes of $CO_2$-C from bioretention soils to the atmosphere, however, can likely be offset by photosynthetic uptake and sequestration of C by biomass (Dietz and Clausen, 2006; Lucas and Greenway, 2007; Pataki et al., 2011) and soil (Schlesinger and Lichter, 2001). This is also highlighted later by our study (see 'Carbon and nitrogen partitioned stocks in soils, microbial biomass, and plants' below).

### 3.4.3 *$N_2O$ fluxes*

Bioretention was not a significant source of $N_2O$. $N_2O$-N fluxes varied between uptake and emission, like in a study by McPhillips and Walter (2015), which examined

$N_2O$-N fluxes in dry and wet grassed detention basins. Across the wet and dry basins, their $N_2O$-N fluxes ranged from -2.4 to 26.9 µg $m^{-2}$ $h^{-1}$. Their maximum peak of 26.9 µg $m^{-2}$ $h^{-1}$ is orders of magnitude lower than the peak observed in this study of 330 µg $m^{-2}$ $h^{-1}$ (Fig. 1). Surprisingly, although they observed greater $N_2O$-N fluxes from dry detention basins relative to wet basins, due to wetter conditions promoting denitrification fully to $N_2$, the fluxes were not significantly different between the two basins. This suggests $N_2O$ production associated with nitrification rather than denitrification in these stormwater basins. The same author measured average $N_2O$-N fluxes of 367.9 µg $m^{-2}$ $h^{-1}$ from a bioretention (McPhillips et al., 2017), which was derived by modifying an existing grassed detention basin mentioned above. Meanwhile, Grover et al. (2013) observed mean $N_2O$-N fluxes of 13.8 and 65.6 µg $m^{-2}$ $h^{-1}$ from two bioretention cells each. Our mean fluxes of $N_2O$-N (10 µg $m^{-2}$ $h^{-1}$) are lower than mean fluxes of McPhillips et al. (2017) and Grover et al. (2013) study, despite having a greater proportion of compost in the soil than the Grover study. High fluxes from McPhillips et al. (2017) could result from tillage increasing microbial activity and therefore mineralization of compost N. Compost application increases microbial biomass and functional diversity (Nair and Ngouajio, 2012), and C and N nutrients are plentiful in the compost for the various microbes to mediate nitrification and denitrification reactions when conditions are ideal.

Soil $NO_3^-$ concentrations in the bioretention units were much higher (13 times) than soil $NH_4^+$ concentrations (Table 1; Also see Appendix J for full data) suggesting a strong possible occurrence of nitrification (Malhi and McGill 1982), forming $NO_3^-$ in the soil, which subsequently is also the substrate for denitrification. $N_2O$ efflux from the soil can be due to nitrification and denitrification (Stevens et al., 1997). These reactions can

occur simultaneously as aerobic and anaerobic microsites can develop within the same soil aggregate (Stevens et al., 1997), and their relative contribution to $N_2O$ efflux must be studied either isotopically through $^{15}N$-labelled compounds (Yoshinari et al., 1977), or in the laboratory using acetylene inhibition techniques (Sørensen, 1978). The case for nitrification induced $N_2O$-N is stronger relative to denitrification in our study since the soil moisture during the sampling period was relatively low at an average of 6% (maximum of only 16%; Fig. 1), and it is likely that nitrification rates exceeded denitrification rates at the relatively low soil moisture range observed here. Denitrification requires waterlogged conditions, which were not observed during the sampling period, but periodic $N_2O$ flux stemming from denitrification likely occurred from saturated microsites within the soil media layers. In addition, occasional $N_2O$ production could be a result of incomplete denitrification due to the low soil moisture levels observed in the bioretention cells, where the $N_2O$ produced as an intermediate in the denitrification reaction could not be further reduced to inert $N_2$ gas.

### 3.4.4 *Environmental effects on fluxes*

Fluxes of $CO_2$-C were very predictable throughout the season, significantly increasing with warmer temperatures and decreasing with cooler temperatures (Fig. 1 and 2), while $N_2O$-N showed no seasonal pattern (Fig. 1). Temperatures are likely tied to corresponding plant and microbial activity, which strongly drive soil $CO_2$ efflux rates (Raich and Schlesinger, 1992; Raich and Tufekciogul, 2000; Schlesinger and Andrews, 2000). Strong relationships between soil $CO_2$-C efflux and soil temperature are well documented in the literature (Liikanen et al., 2006). Soil temperature was weakly

correlated with soil $N_2O$ fluxes ($p=0.04$, $R^2=0.017$; Fig. 2), due to large variability in fluxes at relatively higher temperatures, and near zero fluxes evident throughout the season (Fig. 2). Neither $CO_2$-C or $N_2O$-N was significantly influenced by soil moisture, as it may be that respiration was never water limited in the study as the range of values was limited (i.e., not very large). Soil moisture impacts on gas fluxes may only be important in extreme conditions or times, i.e., very dry (desert, drought) or wet (waterlogged soils, wetlands and bogs). (Søvik et al., 2006) measured $CO_2$ efflux, with summer and winter averages of 187.5 and 50 mg $m^{-2}$ $h^{-1}$ respectively. Summer and winter $N_2O$ efflux averaged 3790 and 192 µg $m^{-2}$ $h^{-1}$ respectively in the same study. For both gases, temperature was positively correlated with gas fluxes. Various other environmental factors besides soil temperature and water content, and $NH_4^+$ and $NO_3^-$ concentrations regulate gas fluxes such as the amount of organic matter, mineralizable carbon, microbial biomass (Bettez and Groffman, 2012; Decina et al., 2016; Smith et al., 1998), which are relevant to various stormwater control structures. Decina et al., (2016) observed significant and positive correlation of soil $CO_2$ efflux with soil organic matter concentration, soil C: N ratio and the depth of the leaf litter layer. Bettez and Groffman (2012), who measured denitrification rates (1.2 mg N $kg^{-1}$ $hr^{-1}$) from stormwater control measures (wet ponds, dry detention ponds, dry extended detention, infiltration basin, filtering practices), observed that the rates strongly correlated with soil moisture, organic matter, microbial biomass, and soil $CO_2$ efflux across sites.

### 3.4.5 *Carbon and nitrogen partitioned stocks in soils, microbial biomass, and plants*

Rapidly growing urbanization characterized by expansion of impervious cover results in loss of soil C. Since urban development occurs at the expense of agricultural and forest lands, it is therefore necessary to consider the potential of developed lands to sequester C (Brown et al., 2012). Green spaces like bioretention, by replacing impervious surfaces with porous soils and vegetation, offer opportunities to increase C (and N) sequestration in urban landscapes (Brown et al., 2012), while simultaneously mitigating stormwater problems (e.g., stormwater infiltration, peak flow attenuation, groundwater recharge) and restoring ecosystem functions within built environments (e.g., wildlife refuge, cooling of air, beautification of landscapes, benefits to human health; Tzoulas et al., 2007; Pataki et al., 2011; Brown et al., 2012).

The VL treatment cell was chosen to study C and N partitioning in the different soil, microbial biomass, and plant stock components within a bioretention cell. No previous study of which we are aware has calculated C and N partitioning among the soil, microbes and plant stocks within a single bioretention cell. The two depth increments (0-30 cm vs. 30-40 cm) that were analyzed to assess nutrient storage in the entire soil media profile showed much higher total C and N concentrations (10.27 and 0.73 g $kg^{-1}$ dry soil respectively) in the surface soils than in the lower depths (1.82 and 0.14 g $kg^{-1}$ dry soil respectively; Table 2). Thus, the total C and N stored in the upper soil media layer was approximately four times greater than the layer below (C: 13844 vs. 3278 g, N: 984 vs. 252 g). This is not surprising given that 40% of the upper soil media consists of compost, with the remaining 60% being sand. Though the lower media (below 30 cm depth) consists entirely of sand, migration of nutrients and organic particulates from the upper

layers over time as well as belowground inputs from plants (roots) may have contributed to C and N observed there. In fact, the bottom profile may have greater ability to capture and sequester C and N throughout the lifetime of the cell, although a portion of those may be taken up by microbes and plants, be recycled back to the atmosphere in gaseous losses, or leached out in bioretention effluent as dissolved organic carbon. In fact, average dissolved organic carbon leaching of 6.1±1.6 mg $L^{-1}$ was measured in the effluent from few of the cells (VL, VH and SM treatments) across three rain events.

The total soil C held in the bioretention unit, including in plant biomass, was 17222 g, while the annual loss (excluding winter months) of C to the atmosphere from soil respiration was approximately 17.32 g, which represented very small portion (0.13%) of the total soil C pool (Fig. 4). The total standing C in bioretention vegetation was 13020 g, representing the second largest C pool in the unit. Generally, approximately 40% of a plant's dry mass consists of C fixed by photosynthesis (Lambers et al., 1998). Some portion of the assimilated C in vegetation is lost to atmosphere in plant respiration, which is a component of the ecosystem C balance (Ryan 1991). The net ecosystem C flux will change as the balance between photosynthesis and respiration changes (Ryan 1991). These would need to be quantified to accurately determine ecosystem level C-sequestration, which this study did not measure. Nevertheless, plants are net C sink, where photosynthetic uptake of atmospheric C greatly exceeds respiratory losses of C.

As previously described, one of the two VL bioretention cell plant species is *Panicum*. Beyond bioretention this species has been well-studied due to its restoration, agricultural, and biomass applications. Sanderson et al., (1996) measured leaf photosynthesis and respiration rates of various *Panicum* cultivars in three different

regions in the Southeastern US. Average *Panicum* photosynthesis rates were fourteen times higher than respiration rates: 31 vs. 2.18 g C $day^{-1}$ (Fig. 4). Therefore, the net C sequestration potential of bioretention systems renders promising due to the ability of soils and plants to act as great C sinks. However, it is important to consider the various factors influencing the C balance, as fluxes (both respiratory and/or photosynthetic) can vary with soil media composition, addition of compost/fertilizer, plant species, plant size and age, seasonality, soil temperature, and soil moisture (precipitation and evaporation balance) (Raich and Tufekciogul, 2000; Brown et al., 2012; Raich and Schlesinger, 1992; Davidson et al., 2002).

Not only is the size of N pool in bioretention soils and plants smaller relative to the size of C pool, the magnitude of soil N fluxes is also much smaller compared to C fluxes (0.89 mg $day^{-1}$ vs. 17 g $day^{-1}$ (this excludes winter months from November to April); Fig. 4). This is a favorable outcome considering that $N_2O$ is a potent gas, with 300 times greater global warming potential relative to $CO_2$-C. N fluxes may seem negligent at the site scale in relation to C fluxes, but large-scale implementation of bioretention and other green infrastructure may bring about indirect changes in the urban landscapes which could potentially influence N fluxes and cycling at an ecosystem scale, and in areas downstream. On the other hand, where cities have expanded in their impervious surfaces instead, catchment hydrology has been altered due to routing stormwater into closed engineered pipes and sewers resulting in lowering of the water table and riparian drying (Groffman et al., 2002). There, this has negatively impacted the ability of urban riparian zones to intercept stormwater and function as sinks for upland-derived $NO_3^-$ via

denitrification process (Kaye et al., 2006). This can cause shift in N forms, fluxes, and balance.

### 3.4.6 *Comparison of bioretention fluxes to other stormwater systems*

In some of the other managed stormwater structures such as constructed wetlands which are constantly waterlogged, the emissions of $CO_2$ and $N_2O$ are likely to be high (Søvik et al., 2006). Søvik et al. (2006) observed $CO_2$-C fluxes in the range of -35 to 3875 mg $m^{-2}$ $h^{-1}$ in constructed wetlands from several northern European countries, where even though the fluxes varied between sink and source, the maximum flux was orders of magnitude higher than found in our study (Fig. 5). High fluxes in the constructed wetlands could be attributed to intermittent loading (Jia et al., 2011) and fluctuating water levels bringing intermittent oxygen into the system, increasing $CO_2$ efflux via decomposition, and affecting both nitrification (increasing the rates) and denitrification (interrupting the last biochemical step conversion to $N_2$) in a way that contributes to more $N_2O$ release (Dotro et al., 2011; Mander et al., 2014). Søvik et al., (2006) measured $N_2O$-N fluxes of up to 41600 µg $m^{-2}$ $h^{-1}$ from the same constructed wetlands. The average fluxes of $CO_2$-C and $N_2O$-N in this study are lower than average fluxes measured from fertilized urban lawns and turfs and mulched garden beds (Livesley et al., 2010; Townsend-Small and Czimczik, 2010), but greater than in native grasslands and wheat ecosystems (Kaye et al., 2004; Fig. 5). Average $CO_2$-C fluxes observed in this study are lower than fluxes reported by Decina et al., (2012) from urban lawn and landscaped sites, but greater than average fluxes from urban (Decina et al., 2012) and rural forest (Giasson et al., 2013; Fig. 5). Our findings indicate the fact that bioretention C and N fluxes

generally fall between the least (urban/rural forest, native grassland) and highly intensively managed systems (landscaped sites, fertilized lawns, constructed wetlands). Among bioretention, fluxes may vary due to differences in design configuration, soil media composition, and spatial and temporal factors. These results underscore the need for more research that should focus on maximizing the nutrient capturing efficiencies of these systems.

### 3.5 Conclusion

This study assessed $CO_2$-C and $N_2O$-N fluxes from eight roadside bioretention cells in their third and fourth year of implementation in Vermont, USA. The cells received different vegetation, soil, and enhanced rainfall and runoff treatment designs. Results indicate no significant effects of the design variables on either type of GHG flux. Like all soils, the bioretention soil media was a source for $CO_2$ fluxes, increasing in warmer months and decreasing in colder months. Soil C, and plant C in biomass is seen to largely offset respiratory $CO_2$-C loss from bioretention soil, therefore suggesting that the bioretention is an overall net C sink, which may contribute to climate change mitigation. Bioretention was not a significant source of $N_2O$ fluxes, which altered between uptake and emission. This is a favorable outcome given the high global warming potential of the gas. Both C and N gas (and peak) fluxes can be arguably decreased by eliminating or reducing the amount of organic matter such as compost in filter media. If necessary, compost with a greater C: N ratio (>20; McPhillips et al. 2017) to promote N immobilization should be considered, the adoption of which may also benefit water quality where nutrients are concerned.

Plant tissue analysis suggests that the C and nutrient sequestration potential of bioretention can be further promoted by selecting plants that not only incorporate greater concentrations of nutrients, but also gain greater aboveground and belowground biomass over the growing season. Plants which shed less, producing lower levels of litter, may be preferred to minimize nutrient re-release (in gaseous or soluble form) via microbial decomposition, meanwhile suggesting possibilities for reducing the need for vegetation maintenance by landscapers. Future work should measure the magnitude of the gas fluxes in correlation to dramatic changes in wide range of biogeochemical parameters ranging from soil moisture (resulting from small to large storm events), soil organic carbon, soil microbial biomass, and soil nitrogen and parallel the understanding of the trade-offs that may exist between gas fluxes and water quality function of a bioretention.

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**Table 1.** Soil properties from the top 10 cm of soil media in the bioretention cell averaged among the eight cells. Standard errors of the mean (n= number of sampling times) in parenthesis.

| **Soil OM (%)** | **Soil CN** | **Soil pH** | **Soil EC ($\mu S\ cm^{-1}$)** | **Soil media bulk density ($g\ cm^{-3}$ dry soil)** | **Soil $NH_4$-N concentration (ppm)** | **Soil $NO_3$-N concentration (ppm)** |
|---|---|---|---|---|---|---|
| 1.95 (0.09) | 13.39 (0.65) | 7.04 (0.02) | 30.18 (0.23) | 1.19 (0.03) | 0.311 (0.10) | 3.932 (0.69) |
| n=7 | n =2 | n =7 | n =7 | n =2 | n =3 | n =3 |

**Table 2.** Soil total carbon (C) and nitrogen (N) concentration ($mg\ kg^{-1}$) from top 10 cm of soil media in May 2016, and two depth increments (0-30 cm and 30-40 cm) in November from low diversity (VL) bioretention cell in 2016.

| Sampled year | Soil depth | Total C | Total N | C/N |
|---|---|---|---|---|
| | | ---- $g\ kg^{-1}$ dry soil ---- | | |
| May 2014 | 0-10 cm | 18.36 | 1.69 | 10.9 |
| May 2016 | 0-10 cm | 14.17 | 0.9 | 15.7 |
| November 2016 | 0-30 cm | 10.27 | 0.73 | 14.1 |
| November 2016 | 30-40 cm | 1.82 | 0.14 | 13.5 |

**Table 3.** Plant tissue carbon (C), nitrogen (N), and phosphorus (P) concentrations ($g\ kg^{-1}$) from low diversity (VL) bioretention cell in August (peak growing season) and November (after plant senescence) in 2016.

| Season | Plant species | C | N | CN |
|---|---|---|---|---|
| | | ---- $g\ kg^{-1}$ dry plant---- | | |
| Summer (August) | *Panicum* | 446 | 11.4 | 39 |
| | *Hemerocallis* | 445 | 24.6 | 18 |
| Fall (November) | *Panicum* | 461 | 5.85 | 79 |
| | *Hemerocallis* | 449 | 9.76 | 46 |

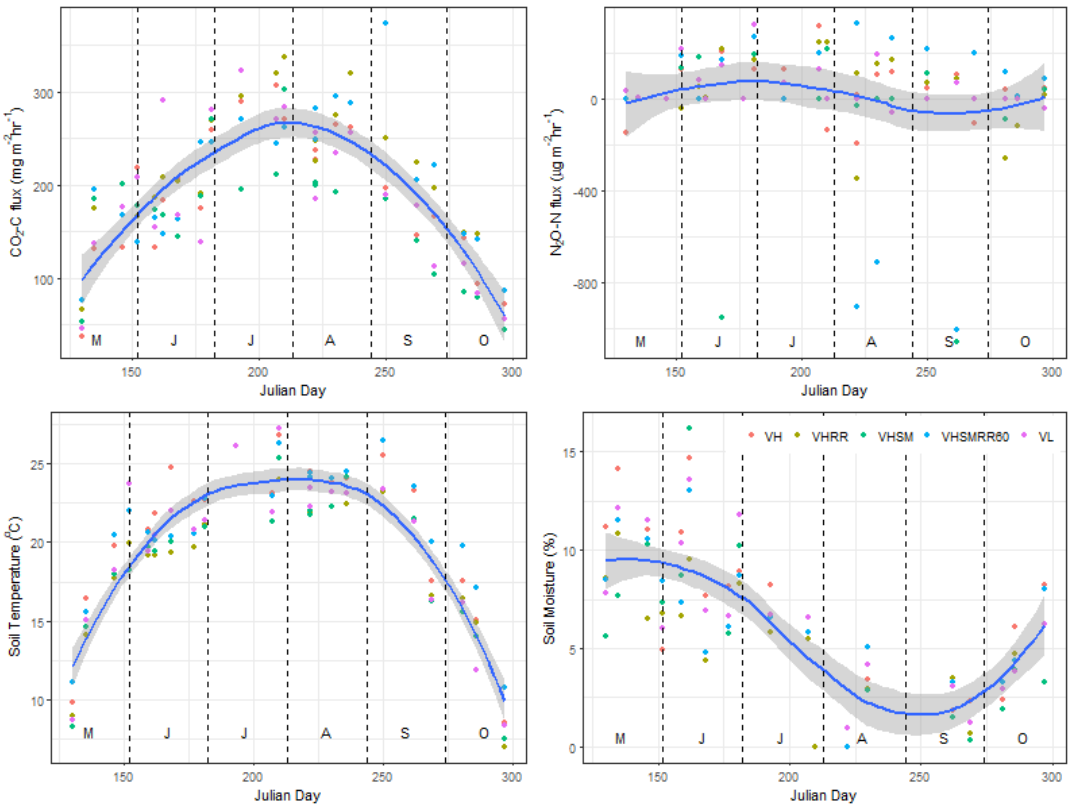



**Fig. 1.** Approximately biweekly measurements of $CO_2$-C flux (mg $m^{-2}$ $hr^{-1}$), $N_2O$-N flux (µg $m^{-2}$ $hr^{-1}$), soil temperature ($^oC$), and soil volumetric moisture content (%) from May to October 2015 and 2016 from all the cells receiving the five treatments, where VL= vegetation low diversity, VH= vegetation high diversity, RR= enhanced rainfall and runoff, SM= SorbtiveMedia™. Blue lines are smoothed conditional means using LOESS (locally weighted scatterplot smoothing) method. Gray shadings are 95% confidence intervals.

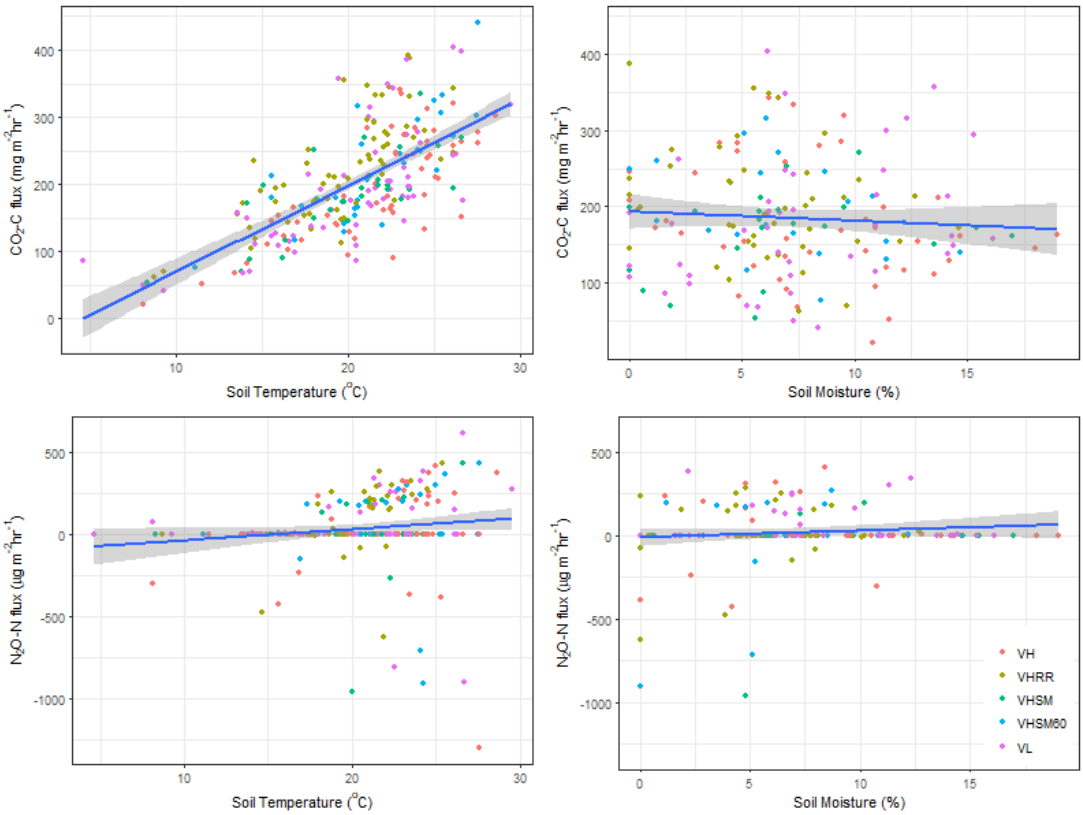



**Fig. 2.** Relationships between $CO_2$-C flux (mg $m^{-2}$ $hr^{-1}$) and $N_2O$-N flux (µg $m^{-2}$ $hr^{-1}$) with soil temperature (ºC) and soil volumetric moisture content (%) from May to October 2015 and 2016 from all the cells receiving the five treatments, where VL= vegetation low diversity, VH= vegetation high diversity, RR= enhanced rainfall and runoff, SM= SorbtiveMedia™. Blue lines represent the best fit line using linear regression. Gray shadings are 95% confidence intervals.

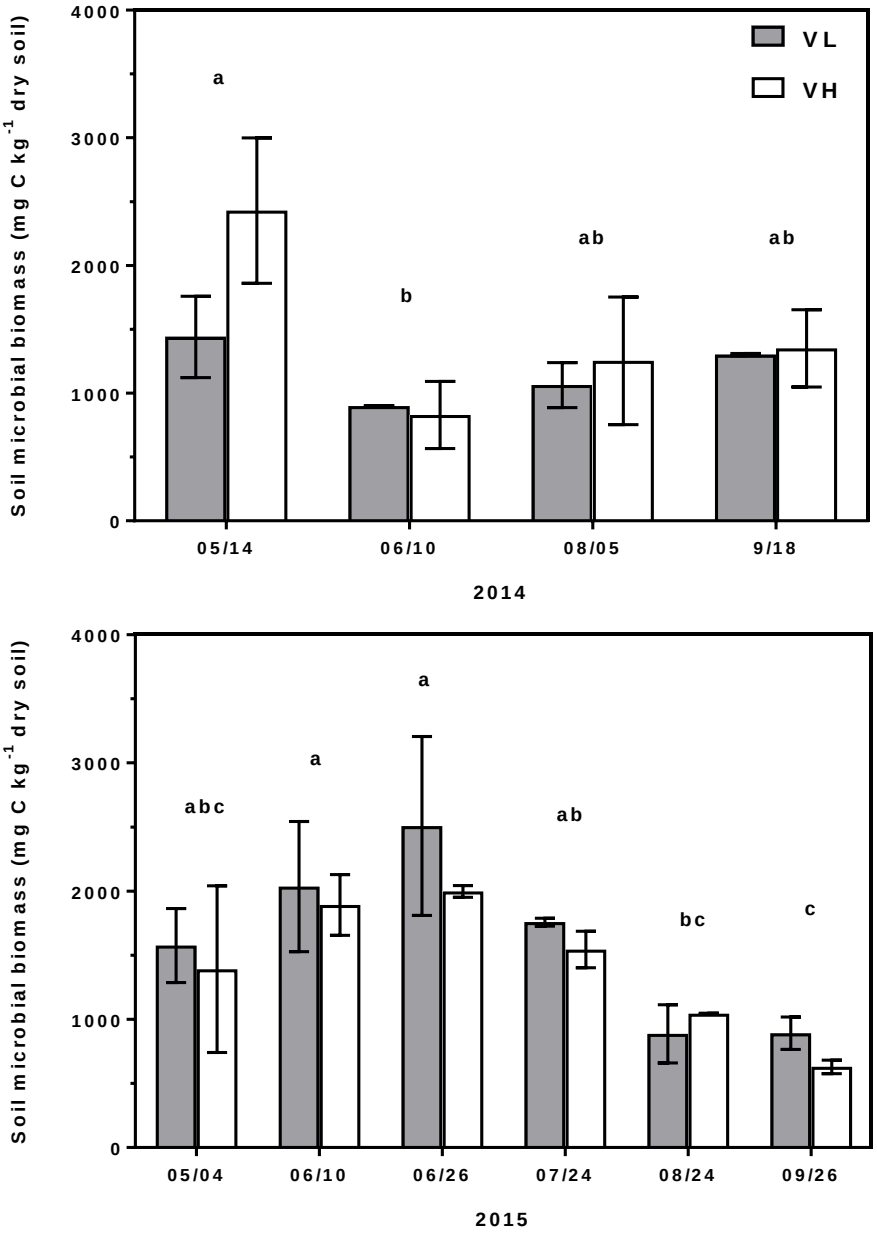



**Fig. 3.** Monthly mean (± 1 S.E.) measurements of soil microbial biomass carbon from May to September 2014 (top) and 2015 (bottom) from cells receiving the ambient vegetation low (VL) and high diversity (VH) treatments. No significant differences were observed between the two treatments. Different letters indicate significant differences between months as determined using Tukey-Kramer HSD at $p<.05$.

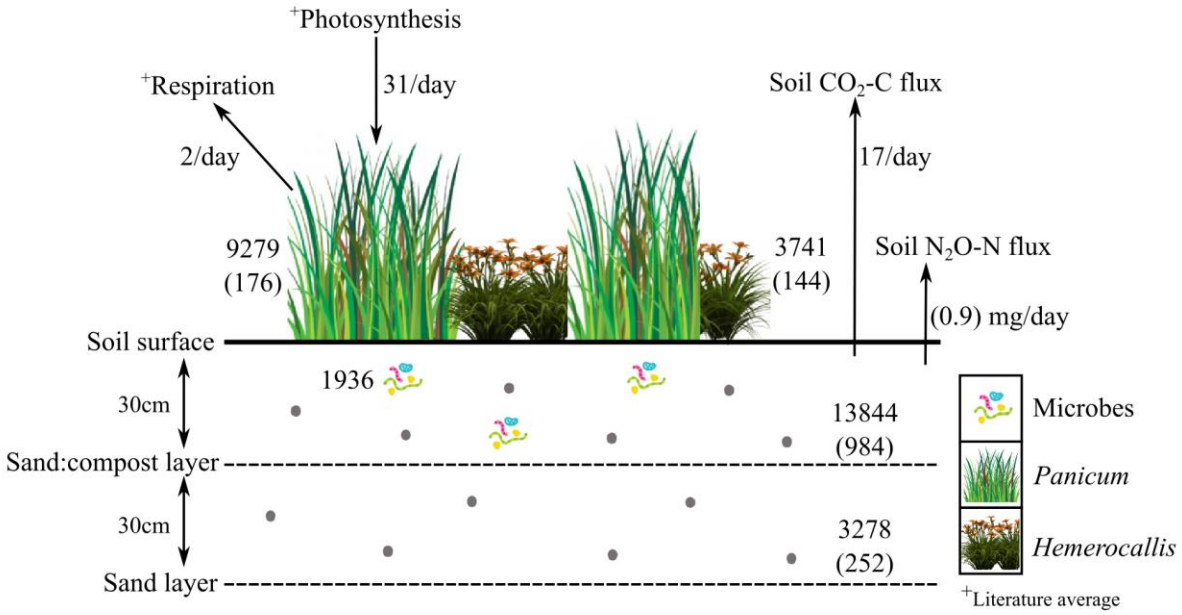
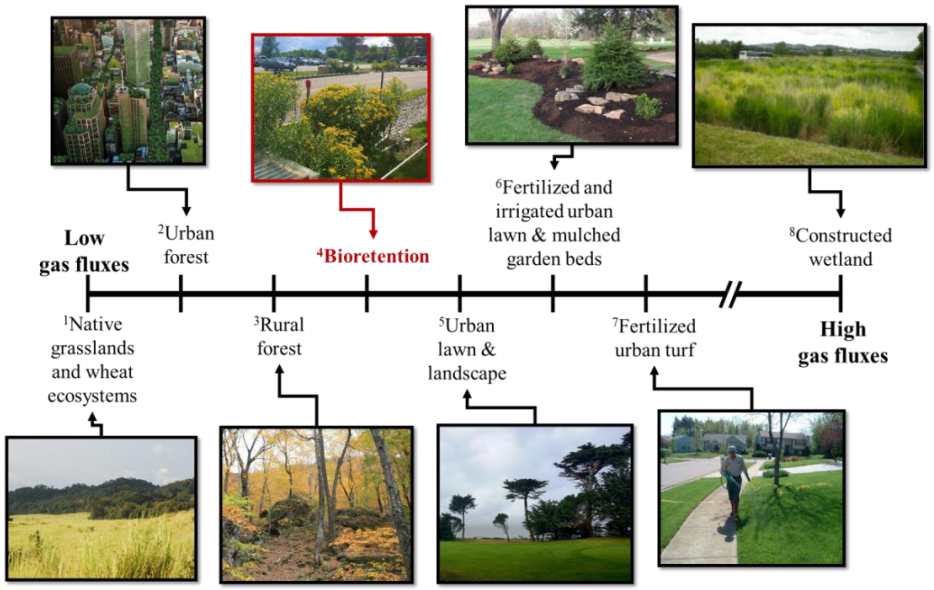



**Fig. 4.** Carbon (C) and/or nitrogen (N) fluxes and stocks (g, unless stated otherwise) in soil media layers, microbial biomass, and bioretention plants (*Panicum* and *Hemerocallis*) from a low vegetation diversity (VL) treatment cell. Numbers outside parenthesis are for C, and those inside parenthesis are for N.




| System | Reference | Study location | $CO_2$-C flux (mg C $m^{-2}$ $h^{-1}$) | $N_2O$-N flux (µg N $m^{-2}$ $h^{-1}$) | Image Reference |
|---|---|---|---|---|---|
| [1]Native grasslands and wheat ecosystems | Kaye et al. (2004) | Colorado, USA | na | <4 | www.worldwildlife.org |
| [2]Urban Forest | Decina et al. (2016) | Massachusetts, USA | 113 | na | dirt.asla.org |
| [3]Rural forest | Giasson et al. (2013) | Massachusetts, USA | 133 | na | Original |
| **[4]Bioretention** | **This Study** | **Vermont, USA** | **194** | **10** | Original |
| [5]Urban lawn & landscaped | Decina et al. (2016) | Massachusetts, USA | 194 & 291 | na | Original |
| [6]Fertilized and irrigated urban lawn & mulched garden beds | Livesley et al. (2010) | Melbourne, Australia | ~450 | 17 to 28 & 14 | www.medium.com |
| [7]Fertilized urban turf | Townsend-Small and Czimczik (2010) | Southern California, USA | na | 93 | mda.maryland.gov |
| [8]Constructed Wetland | Sovik et al. (2006) | Northern Europe (Estonia, Finland, Norway, Poland) | -35 to 3875 | -88 to 41600 | Vyzamal (2010) |

**Fig. 5.** This study's bioretention gas fluxes in relation to fluxes from other natural and artificial systems.

# CHAPTER 4: PHYTOREMEDIATION OF HEAVY METAL CONTAMINATED SOIL BY SWITCHGRASS: A COMPARATIVE STUDY UTILIZING DIFFERENT COMPOSTS AND COIR FIBER ON POLLUTION REMEDIATION, PLANT SURVIVAL, AND NUTRIENT LEACHING

Paliza Shrestha, Korkmaz Bellitürk, Josef Görres, Stephanie E. Hurley

**Keywords:** *Phytoremediation, heavy metals, bioremediation, Switchgrass, thermophilic compost, vermicompost, coco coir*

## Abstract

We investigated the effects of organic amendments (thermophilic compost, vermicompost, and coconut coir) on the bioavailability of trace heavy metals of Zn, Cd, Pb, Co, and Ni from metal-spiked soils under laboratory conditions. To test Switchgrass (*Panicum virgatum*) as a potential crop for phytoremediation to remove metal from soil, we investigated whether the addition of organic amendments promoted Switchgrass growth, and consequently, uptake of metals. Compost is a valuable soil amendment that makes nutrients available for plant establishment and growth, which is beneficial for phytoremediation. However, excess application of compost can result in nutrient leaching, which has adverse effects on water quality. We tested the nutrient leaching potential of the different organic amendments to identify trade-offs between phytoremediation and water quality. Results showed that the amendments decreased the amount of bioavailable metals in the soils. Organic amendments increased soil pH, electrical conductivity (EC), and soil nutrient status. Switchgrass shoot and root biomass was significantly greater in the amended soils compared to the non-amended control. Amended treatments showed detectable levels of metal uptake in Switchgrass shoots, while the control treatment did not produce enough Switchgrass biomass to uptake metals. Switchgrass uptake of certain metals and leachate concentrations of some nutrients significantly differed between the amended treatments. Overall, by improving soil properties, reducing metal solubility, and attenuating bioavailable metals that can otherwise hamper plant survival, organic amendments can greatly enhance phytoremediation in metal-contaminated soils.

## 4.1 Introduction

Phytoremediation is a set of ecological strategies that utilizes plants, *in situ*, to promote the breakdown, immobilization and removal of pollutants from the environment (Murphy and Coats, 2011; Peer et al., 2005; Salt et al., 1998). Plants have a more direct effect on contaminant levels via phytoextraction, which concentrates contaminants (e.g., heavy metals) from the environment into plant tissues. Phytoremediation is a cost-effective remediation solution for removing pollutants (mainly heavy metals and organics) from contaminated soils and waters at site level with little disturbance to the landscape (Itanna and Coulman, 2003; Salt et al., 1998). It also reduces the cost of alternatively disposing hazardous wastes to a landfill or a storage facility located off-site (Salt et al., 1998).

Efficient plants for phytoremediation are highly productive, good bioaccumulators, and tolerant to high levels of pollution. Switchgrass (*Panicum virgatum*) is known for its high biomass production (McLaughlin et al., 1999; Chen et al., 2012) that allows it to remove excess nutrients from sites amended with dairy manure (Sanderson et al., 2001). In the presence of Switchgrass, the degradation of herbicide such as atrazine may be accelerated (Murphy and Coats, 2011). Other researchers have proposed that Switchgrass might extract heavy metals from contaminated soils (Balsamo et al., 2015; Chen et al., 2012). Switchgrass has also been used in bioretention systems for urban storm runoff treatment (Shrestha et al., in press). In this paper, we focus on the ability of Switchgrass to extract toxic trace metals with and without yield-enhancing organic amendments. Since it is expensive to treat large amounts of metal polluted soils

with the conventional techniques of mechanical removal (Khan et al., 2000) or chemical immobilization (Basta and McGowen, 2004), the combined *in situ* approach of using recycled organic waste (compost) and plants is less expensive (or more affordable) (Salt et al., 1995) and may be a promising phytoremediation strategy.

The efficiency of phytoremediation using Switchgrass or other plants on contaminated soil can be enhanced through additions of composts and other organic matter sources (e.g., coir) that are locally and cheaply available. The proposed mechanism is that metal uptake and assimilation increases with biomass. Composts differ both in the feedstock materials and the processes used to create them. There are two common, aerobic processes to produce composts. Thermophilic composts encourage thermophilic microorganisms to decompose organic wastes (temperatures reaching 45 to 70$^{o}$C) followed by a mesophilic maturation process (Fornes et al., 2012) where organic matter becomes more stable and may resist further decomposition. Vermicomposting relies on earthworms and their gut flora to decompose the organic wastes but is frequently preceded by a thermophilic stage (temperatures between 25 to 40$^{o}$C; Fornes et al., 2012; Hashemimajd et al., 2004) when organic certification is required. This process occurs at mesophilic temperatures and fosters a very different microbial community (Neher et al., 2015). In broad strokes, thermophilic composts are mature at C:N ratios between 15-20:1 (Tognetti et al., 2005), and have low available nitrogen content. In contrast, vermicompost is mature at CN ratios of 10-15:1 (Austin, 2015) and has high available nutrient contents. However, these benchmarks may differ depending on the feedstocks.

This paper reports on a lab study that explores the efficacy of Switchgrass at removing metals from soils amended with composts and coir fiber. Composts contribute to soil quality by improving aeration, moisture holding capacity, carbon supply, microbial activity, cation exchange capacity, and controlled release of macro and micronutrients (Ansari, 2008; Mudhoo et al., 2012; Pereira and Arruda, 2003a; Sarkar et al., 2005; Weil et al., 2016) in the soil. However, stimulation of plant growth on contaminated soils depends on the quality and type of compost. Thus, compost may increase plant contaminant uptake by stimulating plant productivity, while compost itself can also directly influence bioremediation (Chen et al., 2015; Clemente et al., 2006; Farrell and Jones, 2010a; Sarkar et al., 2005). The humic substances in compost remove dissolved metals from the soil solution (Mora et al., 2005; van Herwijnen et al., 2007; Shuman, 1999) through complexation, sorption, and precipitation (Castaldi et al., 2005; Chen et al., 2015; Farrell and Jones, 2010a). The resulting solid complexes are less mobile and consequently pose less threat to the environment (Ogundiran and Osibanjo, 2009; Clemente et al., 2006; McGrath and Cegarra, 1992; Narwal and Singh, 1998; Ross, 1994; Shuman, 1999). However, this may also counteract the ability of a phytoextracting plant to remove the metals.

Coconut coir fiber (or coir) has also been shown to be a promising bio-adsorbent for remediation of heavy metals. Coir is the fiber that is derived from the inner shell of the coconut, which may be added as a substrate to compost soils to enhance its performance. Previously considered a waste product and as a result dumped or incinerated, new uses are being developed over the last decade, including using the coir

as a soil amendment for degraded soils (Abad et al. 2002). Most results are however inferred from laboratory batch sorption experiments using aqueous solutions containing heavy metals (Abdulrasaq and Basiru, 2010; Chaudhuri et al., 2010) with concentrations similar to those of wastewaters (Baes et al., 1996). Coir is an organic waste product that may be added as a substrate to compost soils to enhance soil and plant performance. Coir is a source of organic matter, and though it contains few nutrients itself, it has high nutrient retention capacity (Somasiri and Vidhanaarachchi, 1997; Abad et al., 2002), and improves the overall quality of the soil, although it alone cannot be a sufficient growing media (Hernández-Apaolaza et al., 2005). Coir is resistant to environmental biodegradation (Somasiri and Vidhanaarachchi, 1997); as a result, the slow breakdown of coir can release a steady supply of carbon. The proposed mechanism in the case of this research is that coir has a high C:N ratio substrate (ratio of 75 to 186: Abad et al., 2002; Noguera et al., 2000), and therefore rendering greater microbial immobilization of metals and nutrients from the soil to enhance phytoremediation benefits.

The main objective of our experiment was to investigate whether promoting growth of plants by organic matter additions increases the uptake of metals. Organic additions included thermophilic compost (hereby called compost), vermicompost, and coir in various combinations. We specifically studied the effects of heavy metals on Switchgrass (*Panicum virgatum*) productivity, and metal uptake potential of Switchgrass in pots with and without soil amendments. Switchgrass was chosen because of its high biomass production capacity, and versatility. To our knowledge, no pot study has been conducted that studied phytoremediation of heavy metals by Switchgrass in the presence

of different organic soil amendments. In addition, we also examined soil without plants to assess the effect of organic amendments on metal mobility in the absence of vegetation, and evaluated nutrient leaching to examine possible trade-offs between phytoremediation and water quality.

## 4.2 Methods

### 4.2.1 *Experimental design*

The following laboratory experiment is a complete block design with ten treatments replicated four times (Table 1; Fig. 1) resulting in 40 pot-scale, experimental units. The experiment explores blends of thermophilic compost (T), vermicompost (V), and coconut coir (C) mixed in different combinations (substrate chemical properties outlined in Table 2) with and without Switchgrass. The resulting treatments are soil (S), soil + thermophilic compost (ST), soil + thermophilic compost + coir (STC), soil + vermicompost (SV), and soil + vermicompost + coir (SVC) (Table 1). Thermophilic compost was collected from Green Mountain Compost Facility located in Williston, Vermont. Vermicompost was obtained from Worm Power, an organic composting facility located in Avon, New York. Coconut coir, here on called coir, was purchased from Gardeners Supply Company located in Burlington, Vermont.

### 4.2.2 *Soil collection and pot culture preparation*

Native soil was collected from a mixed hardwood forest located adjacent to University of Vermont Horticulture Research Center, Burlington, USA. The soil is a very well drained Windsor (mixed, mesic Typic Udipsamments) series (NRCS Web Soil

Survey). The fine earth fraction of the soils was obtained using a 2-mm stainless steel sieve. Any roots and stones in the pass fraction were further removed by hand. Sifted soils were left to air dry for over a week. The compost samples were also left to air dry in lab conditions for two weeks. The coir, which was purchased as a brick of dried coconut husk fiber, was soaked in de-ionized water to pull the fibers apart, and then left to air dry for over a month. Soil or amended soil was added to pots lined with coffee filters (Mellita brown coffee filters). Amended soil was created by mixing 1.5 kg dry soil with either 0.12 kg of air-dried compost or vermicompost, and 0.06 kg of air-dried coir (8% and 4% of dry soil weight respectively) to make up the recipes in Table 1. In non-amended soil control pots, the soil equivalent of these weights was added so that the resulting weight in all pots was 1.68 kg. To each substrate type, Switchgrass plants were either added or were not added (Table 1). Each plant by substrate combination had 4 replicates for a total of 20 pots.

### 4.2.3 *Switchgrass seed preparation*

Switchgrass seeds were grown in small plugs that were pre-filled with the experimental soil obtained from the Horticulture Research Center. 15 Switchgrass seeds were sowed into each plug. 4 ml of solution NPK fertilizer (100, 80, 100 ppm respectively) was added to the soil at the start. $NO_3^-$-N was made from 1000 mg/L pure $NO_3^-$ stock solution. P and K were made from $KH_2PO_4$ powder by mixing 0.349 grams of the compound into 1 L de-ionized water. The plugs were transported to the UVM Campus Greenhouse. They were irrigated every day, kept in 12-hour day/night cycle, and

temperature was maintained at 21$^{o}$C. In the greenhouse, plants were not further fertilized until they germinated. Once germinated, plants were fertilized six times, every Monday and Friday for three weeks, using the facility's standard NPK fertilizer at 17-4-17 at 150 ppm nitrogen.

### 4.2.4 *Phytoremediation experiment*

The different soil mixes in the 40 pots were spiked with 32 mg of each of five heavy metals: Zinc (Zn), Cadmium (Cd), Lead (Pb), Cobalt (Co), and Nickel (Ni) based on soil dry weight. Zn, Cd, Pb, Co, and Ni solution was prepared in five separate solutions using de-ionized water and their respective metal salt compounds: Zinc Chloride ($ZnCl_2$), Cadmium Chloride ($CdCl_2$), Lead Chloride ($PbCl_2$), Cobalt Chloride ($CoCl_2.6H_2O$), and Nickel Chloride ($NiCl_2.6H_2O$). The total mass of the metals in soil for each treatment after contamination is given in Table 3 (See Appendix L for data on the metal mass of the original substrates before and after combining them to make the recipes in Table 1).

Four days after heavy metal application to the soil mixes, the plugs containing the largest Switchgrass seedlings (8 to 10 cm) were transplanted. Each pot received two plugs. The pots were brought to equal soil moisture content once before planting of the Switchgrass to account for the loss of moisture through evaporation. Each plug contained one or two Switchgrass plants at the time of transplanting (only a few seeds had germinated in that time out of the 15 seeds that were originally sowed). All pots, regardless of whether Switchgrass was present, were irrigated with 50 ml de-ionized

water twice a week for the first two weeks, and then every other day as the Switchgrass plants grew taller. Any leachate collected in the plastic container beneath the pots was poured back into their respective pots. The pots containing Switchgrass were kept under 24-hr light in the laboratory with the help of growth lights for approximately 7 weeks, and at temperatures around 25$^{o}$C (Fig. 1).

### 4.2.5 *Plant-available or bioavailable heavy metals*

At the end of the 54-day incubation period, soils from the 'no plant' pots were analyzed for metal bioavailability (i.e., plant available metals) using a nonaggressive extractant method. 10 g subsample of air-dried soils from the 'no plant' pots were taken, combined with 25 ml of 0.01 M $CaCl_2$ solution, and the suspension was shaken for 24 hours on a mechanical shaker at room temperature (McBride et al., 2009). Solution was filtered through Ahlstrom filter paper 642 (particle retention of 2 µm), and filtrate was analyzed in triplicates using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES/AES, Optima 3000DV, Perkin Elmer Corp, Norwalk, CT, USA).

### 4.2.6 *Plant analysis (tissue metal concentrations and loads)*

From the planted pots, Switchgrass plants were harvested, and separated into roots and shoots at the end of the 54-day lab incubation period. The plant samples were washed with de-ionized water, oven dried at 70$^{o}$C for at least 5 days and weighed for dry biomass. The dried plant samples were stored in brown paper bags until further analysis. Plant samples were ground and digested (approximately 0.5 g) with 10 ml of 16N

concentrated nitric acid diluted to 50 ml with deionized water, and the extract was used to determine heavy metal concentrations. Total mass of metal uptake in each of the pots was estimated as the product of tissue metal concentrations and Switchgrass biomass.

### 4.2.7 *Soil analysis*

The entire soil content from all pots, including those planted to harvest, were transferred into large plastic containers and mixed thoroughly. Water content was determined gravimetrically for each experimental unit as the difference between fresh and oven-dry mass (about 10 g were dried for 48 hours at 105$^{o}$C). pH and EC were also determined using 10 g of fresh soil mixed in 20 ml distilled water using Fisher Scientific Accumet Portable APILO (pH/ORP meter) and Thermo Scientific Orion Star A222 Conductivity meter respectively. The remaining soils in the plastic container were left to air dry for one week before being analyzed for total metals. Soils were ground using mortar and pestle. The ground soil was screened through 0.5 mm sieve, and dried at 60$^{o}$C for several hours. Total heavy metal concentrations were analyzed using the ICP after following a microwave-assisted digestion of approximately 0.5 g soil in 16N concentrated nitric acid diluted to 50 ml with deionized water (USEPA 2007).

### 4.2.8 *Leachate nutrient analysis ($NH_4^+$-N, $NO_3^-$-N, $PO_4^{3-}$-P)*

A short experiment to investigate the nutrient losses through leaching was carried out for the treatments without plants soon after the pots were established at the start of the incubation experiment. 700 ml of de-ionized water was slowly applied to the ‘no plant’

pots containing the different soil mixes (Table 1). Water was applied evenly to cover the entire soil surface. The water addition (700 ml) produced enough leachate to allow nutrient analysis. Clear plastic containers were placed under each pot to collect the leachate water (Fig. 1). The leachate samples were filtered using a 0.45-µm nylon mesh filter (Fisher Scientific) and analyzed for available dissolved nutrients ($NH_4^+$-N, $NO_3^-$-N, $PO_4^{3-}$-P) by flow injection analysis on an automated colorimeter (Lachat Instruments QuickChem8000 AE, Hach Inc., Loveland, CO) using the Cd-reduction method for $NO_3^-$, the salicylate-nitroprusside method for $NH_4^+$, and the ammonium molybdate colorimetric method for $PO_4^{3-}$ (APHA 1998).

#### 4.2.9 *Statistical analysis*

The effects of soil organic amendments on heavy metal bioavailability, soil properties, Switchgrass biomass, and metal uptake were analyzed using the analysis of variance (ANOVA) in JMP Pro 13 (SAS Institute Inc., Cary, NC, USA). Tukey's Honestly Significant Difference (HSD, $\alpha = 0.05$) post hoc test was used to test for significant differences in the treatment means. When necessary, log transformations on the data were carried out to satisfy the assumption of normality and equal variance required by ANOVA.

### 4.3 Results

#### 4.3.1 *Bioavailable metals*

The fraction of bioavailable metal mass for all metal species (Zn, Cd, Pb, Co, and Ni) was significantly highest from the control soil treatment, compared to all the

organically amended treatments (Table 4). No significant differences were found in the leaching of bioavailable mass of metals among the amended soil treatments. In the control soil, the percentage of total metal mass that was bioavailable was in the range of 0.33% up to 70%, while only 0.04% to 1.02% of total metals mass were bioavailable in the compost-amended soils (Table 3 and 4).

### 4.3.2 *Soil pH and EC*

All organic amendments significantly increased soil pH (from slightly acidic at 4.65 in the control to more neutral at 6.43) and EC ($\mu S\ cm^{-1}$; from approx. 80 in control to upwards of 290 to 900) in both plant and no-plant treatments (Table 5). In the no-plant treatments, no significant difference in pH was observed among the organic treatments, while in the plant treatments, greater pH was observed in the compost treatments relative to the vermicompost treatments. EC was three times higher in vermicompost treatments compared to compost treatments, but this increase was only significant in plant treatments (Table 5).

### 4.3.3 *Switchgrass biomass*

All organic amendments improved Switchgrass productivity, both aboveground and belowground, over the study duration (Fig. 2). Switchgrass shoot and root biomass was significantly greater because of the organic amendments, while the type of organic amendments did not have significant effects on either root or shoot biomass. No

harvestable/quantifiable Switchgrass roots were present in the planted control treatment. Overall, the shoot biomass exceeded root biomass in all the planted treatments (Fig. 2).

### 4.3.4 *Total metal mass in Switchgrass and soils*

The mass of Switchgrass samples in the control (non-amended) soil treatment was too small to conduct tissue metal analysis for either shoots or roots. Thus, shoot metal masses were only determined in the four organic treatments. SV treatments had the greatest shoot metal mass for all metal species, significantly differing from ST for Cd and Co (Fig. 3). No significant differences in mass uptake were observed among the remaining treatments. Relative to the other trace metals (Cd, Pd, Co, and Ni), Zn uptake by Switchgrass was the highest (two to thirteen times higher in mass) in each of the treatments (Fig. 3). In all treatments, total soil metal mass at the end of the experiment was lower for all metals (Table 6) relative to their initial conditions (Table 3), except for Cd in the planted control treatment, which increased slightly. On average, mass of Zn, Cd, and Pb was lower in soils with Switchgrass than without, while the reverse was observed for Co and Ni.

### 4.3.5 *Nutrient ($PO_4^{3-}$-P, $NO_3^-$-N, and $NH_4^+$-N) leachate concentrations*

Soils receiving the organic matter amendments leached significantly higher nutrients than the control soil with no amendments (Fig. 4). Between the two compost types with or without coir, nutrient leachate was the highest from soils amended with vermicompost (SV and SVC). While there were no significant differences among the

compost types for leaching of $PO_4^{3-}$-P, $NO_3^-$-N leachate concentrations were significantly higher from vermicompost-amended soil without coir (SV only), and $NH_4^+$-N concentrations in the leachate was significantly higher from vermicompost-amended soils with and without coir (SVC and SV respectively; Fig. 4). $NO_3^-$-N in S, ST, STC, SV and SVC treatments were approximately 5, 122, 77, 38, and 21 times greater than $NH_4^+$-N leachate concentrations in the respective treatments. Relative to $NH_4^+$-N and $NO_3^-$-N on average, $PO_4$-P concentrations were orders of magnitude lower (15 and 550 times lower respectively).

## 4.4 Discussion

### 4.4.1 *Effect of amendments without plants*

Composts addition to heavy metal contaminated soil significantly reduced the bioavailable fraction of all metal constituents (Table 4). Soils naturally reduce solubility and mobility of heavy metals through sorption, precipitation and complexation reactions (Farrell and Jones, 2010; Kiikkilä et al., 2001). Organic amendments to soils can accelerate this natural attenuation process (Bolan and Duraisamy, 2003) due to high cation exchange capacity (Pereira and Arruda, 2003) through formation of stable complexes of metals with humic acids through chemical adsorption (Castaldi et al., 2005; Clemente et al., 2006; Kashem and Singh, 2001), and microbial immobilization (Haldar and Mandal, 1979). A study by O'Dell et al. (2007) showed that addition of yard waste-derived compost rich in humic and fulvic acid favored the fixation of heavy metals in an acidic Cu-Zn minespoil, and reduced bioavailable concentrations of Cu and Zn.

Complexes of some metals like Pb are found to be more stable (i.e., less bioavailable) than other metal complexes such as Cd (Table 4; Tack et al., 1996), which was observed in the current study (Table 4). Soil pH also affects metal solubility. The control soil was more acidic with pH of 4.63 contrary to amended soils with pH of 6.42 to 6.79 (Table 5). Reduced pH can result in much higher metal solubility (Kashem and Singh, 2001), which could explain why metal bioavailability was significantly higher in control soils. Chuan et al., (1996) observed higher metal solubilities of Zn, Cd, and Pb under slightly acidic conditions (pH=5). In contrast, increased pH due to composts can induce gradual alkalinisation of the soil, favoring the formation of metal hydroxides and carbonate complexes (Chlopecka and Adriano, 1996; Farrell and Jones, 2010; Mench et al., 1994), which can decrease metal bioavailability.

### 4.4.2 *Effects of amendments with plants*

Composts also improve soil properties. All the organic amendments containing compost alone, and compost plus coir lowered soil acidity by increasing soil pH and EC (Table 5), as in other studies (Hernández-Apaolaza et al., 2005; Mora et al., 2005). The pH observed in the amended treatments with plants ranged from 6.08 to 6.40 (Table 5), which is in the optimal range for Switchgrass (USDA 2009). In contrast, soil pH in the control was outside the range considered suitable for Switchgrass, which may have negatively affected plant growth (Table 5, Fig. 2). Negligible shoots and no roots were harvested from the control treatment. On the other hand, significantly greater shoot biomass (11 times) was measured on average from the amended treatments relative to the

control treatment (0.661 ± 0.29 g versus 0.058 respectively; Fig. 2) indicating that organic amendments enhanced plant productivity.

Through enhancing plant productivity on metal contaminated soil (Fig. 2), the ability of plants to absorb ('phytoextraction' or plant assisted uptake) and bioaccumulate pollutants from the soil (Gaur and Adholeya, 2004) can be made possible as a long-term phytoremediation strategy. While the attenuation of metal contaminants reduces metal solubility due to higher pH (Chlopecka and Adriano, 1996; Farrell and Jones, 2010b), providing direct remediation benefits, the improved survival and productivity of plants (Fig. 2), due to compost acting as slow-release fertilizers (Gutser et al., 2005), will increase the success of the phytoremediation strategy.

Switchgrass present in the organically amended soils had measurable levels of heavy metals in their shoots (Fig. 3). Shoot concentrations of metals varied, but were present in the order Zn> Cd> Co> Ni> Pb. Zn is a micronutrient essential for plant growth, so it is not surprising that they were present in the shoots in much higher concentrations compared to other metals. Other less essential metals for plant growth which can also be removed from soils via phytoextraction are Co, Ni, Fe, Mn, Cu, and Mo (Tangahu et al., 2011). Plants are also successful in absorbing metals that lack a known biological function, such as Cd, Pb, and Cr (Balsamo et al., 2015; Gaur and Adholeya, 2004; Shahandeh and Hossner, 2000). Plant roots release organic compounds (e.g., chelators) which, along with plant-induced pH changes, enhance the solubility of adsorbed metals in the soil, and in turn, facilitate their uptake by plants even at low concentrations and from nearly insoluble precipitates (Tangahu et al., 2011). If the

growth had continued longer than the duration of our experiment, additional growth may have extracted metals from a greater soil volume through a more extensive root systems (McLaughlin et al., 1999). In contrast to the amended soils, the control soil did not produce sufficient amounts of Switchgrass shoots or roots for analysis during the study period (Fig. 2). This likely means that metal uptake is negligible when compost was absent. Additionally, in the planted control treatments, the metal toxicity may have occurred because composts were not available to attenuate bioavailability of metals that can harm roots (Chatterjee et al., 2013; Kiikkilä et al., 2001).

The study shows that organic amendments boost plant survival and improve nutrient availability (Fig. 2 and 5) and soil properties (Table 5) on contaminated soils, while reducing metal bioavailability. In this experiment, plants assisted with pollutant uptake, but over the time period we examined, it was not a major effect. In this study, there were no significant differences in plant production among the organic amendments (Fig. 2), despite large variations in inorganic N in soil and leachate. There were large differences in N between the two compost types (Table 2, Fig 4). The lack of difference in plant biomass between the two compost treatments could be attributed to plants being very young over the study duration and –due to initial fertilizer applications in the pots— N may not have been limiting. If the study duration had been extended, differences in plant biomass may have developed between the two compost treatments, due to large differences between their nutrient supplies (Table 2). Coir did not have significant effects on plant biomass as it contains few nutrients itself (Somasiri and Vidhanaarachchi, 1997; Abad et al., 2002), but coir can improve soil performance overtime by increasing nutrient

retention capacity (Somasiri and Vidhanaarachchi, 1997). It could be that the applied amount of coir was limited and therefore its effects were not statistically apparent. Increasing the amount of coir in the mix may result in detectable results, but this needs to be investigated.

### 4.4.3 *Total metal mass in plant and no-plant pots*

The decrease in the total metal mass from the pots at the end of the experiment (Table 6) can be attributed to uptake of metals by Switchgrass. In pots without Swithchgrass, metals may have leached out from the soil during the watering process carried out for the nutrient leachate experiment. Some portion of metals may also have leached out of the soils during the weekly watering process in all the pots. Though we tried to pour the leachate back into the pots, it may be possible that we were unable to re-capture all the metals in time, due to possible adsorption of metals to the plastic container (Ashton et al., 2010; Holmes et al., 2012). Cd was the only metal found in slightly higher mass at the end of the study in two of the pots (Table 6). The discrepancy was small, and could result from detection limit of the instrument, as Cd was present in very low concentrations in all the initial substrates (Table 2). As expected, total metal mass was generally lower, but not always in planted treatments. Lack of noticeable differences may be due to small amounts of metal uptake by Switchgrass overall (Fig. 3) compared to the large amount of metal that was added (Table 3). The watering process for leachate nutrient analysis was also only subjected to the no-plant pots, thus loss of metals during this process could have resulted in smaller between treatment differences than expected.

### 4.4.4 *Phytoremediation trade-offs with water quality*

Use of compost for phytoremediation of post-industrial sites (contaminated with heavy metals) or in green stormwater infrastructure sites (e.g., bioretention) for stormwater treatment, may not always affect water quality positively. This is because nutrients can be leached from compost during and following wet events (e.g., rainfall, irrigation), which can pollute surface or groundwater. The resulting leachate nutrient concentrations from compost-amended soils were significantly greater than the control soil, even when compost made up as little as 8% of the total soil mix (Fig 5). The type of compost also controls the concentrations released in the leachate. We observed significantly higher $NO_3^-$-N concentrations from SV treatments relative to SVC, ST, and STC treatments. This is most likely due to lower CN ratio (Table 2), and higher extractable $NO_3^-$-N concentrations of vermicompost compared to compost (2230 vs. 505 mg $L^{-1}$ respectively; Table 2). Hurley et al. (2017) also observed significantly higher $NO_3^-$-N concentrations in the leachate originating from vermicompost compared to leachate from four different composts samples. Frederickson et al. (2007) observed similar trend of significantly higher extractable $NO_3^-$N concentrations (2660 mg $kg^{-1}$) from vermicompost relative to compost (1531 mg $kg^{-1}$). The addition of coir to the compost-amended soils did not significantly influence nutrient release in the leachate, except for $NO_3^-$-N which was significantly reduced in the SVC relative to SV (Fig 5). Coir, which provides an additional carbon source (Hernández-Apaolaza et al., 2005) in the SVC treatment, may have stimulated microbial biomass and activity leading to increased immobilization of $NO_3^-$ (Blumenthal et al., 2003).

While there were no differences in leachate $PO_4^{3-}$-P concentrations between the two compost types, $NH_4^+$-N leachate concentrations were significantly greater from both the vermicompost treatments (Fig. 5). Extractable $NH_4^+$-N concentrations measured were 34 times greater in the original vermicompost sample relative to the compost (Table 2). Higher $NH_4^+$-N concentrations also suggest the potential for high nitrification rates, which were indicative of the vermicompost treatments. Nitrates, the end products of nitrification reactions, are extremely mobile anions (Knowles, 1982), and hence leach out easily from the soil. This means, that depending on the compost type, an optimum proportion of compost and soil mix must be determined to ensure success for phytoremediation, while minimizing nutrient leaching potential. If compost with higher nutrient leaching potential is being applied to soils, appropriate best management practices should be implemented to minimize nutrient mobilization into sensitive water bodies.

**4.5 Conclusion**

Overall, the results of this work indicate that the effectiveness of phytoremediation can be increased by amending organic composts and vermicompost into heavy metal contaminated soil. Addition of organic amendments reduced metal solubility, and increased soil pH and EC, and soil nutrient status. Organic amendments significantly improved Switchgrass growth compared to the non-amended control. Amended treatments showed detectable levels of metal uptake in Switchgrass shoots, but extremely low growth in the non-amended planted controls suggests negligible metal

uptake (i.e., there was not enough biomass for analysis). If the study duration is extended, and Switchgrass continues to accumulate more biomass, this will likely increase the total metal uptake of Switchgrass shoots from the pots containing soil with organic amendments. As the roots exploit more soil volume and increase plant uptake, this could further prevent losses of bioavailable heavy metals, mineralized N (e.g. particularly $NO_3^-$ which is mobile), and P to the leachate. On the other hand, metal contaminated soils deprived of organic matter can increase metal bioavailability (Table 3 and 4), subsequently increasing toxicity to plants (Chatterjee et al., 2013; Kiikkilä et al., 2001). This hampers plant survival and performance (plants ability to uptake and sequester metals), thereby undermining phytoremediation as a strategy.

Some confounding factors in the study that were not controlled for are the maturity/age and feedstocks used to create the two composts; however, this should not have interfered with the results observed. We believe that by having an additional treatment of soil and coir alone, it would be possible to detect the effects of coir. The effects of coir in this study were not statistically apparent in any of the treatments for any of the parameters (except for leachate $NO_3^-$ concentrations). Increasing the proportion of coir in the mix could also result in detectable effects, but this needs to be studied.

Due to water quality implications of compost, the amount of compost deemed necessary for soil amendments to increase specific crop yield in phytoremediation should vary depending on the compost type. For example, based on this study, thermophilic compost may be substituted by smaller amounts of vermicompost based on their release

of inorganic N concentrations from a plant establishment perspective; however, what that will do in terms of impacting metal immobilization needs to be studied.

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**Table 1.** Experimental treatments.

| Substrate type | Composition | Plant | No Plant |
|---|---|---|---|
| Soil | Soil | S | S |
| Soil + Thermophilic Compost | 92% Soil + 8% compost | ST | ST |
| Soil + Thermophilic Compost+ Coir | 88% Soil + 8% compost + 4% coir | STC | STC |
| Soil + Vermicompost | 92% Soil + 8% compost | SV | SV |
| Soil + Vermicompost + Coir | 88% Soil + 8% compost + 4% coir | SVC | SVC |

S: Soil, P: Plant, T: Thermophilic Compost, V: Vermicompost, C: Coir

**Table 2.** Chemical properties of the experimental soil, composts (thermophilic and vermicompost) and coir.

| | Total Zn | Total Cd | Total Pb | Total Co | Total Ni | SOM | CN ratio | Total N | $NH_4^+$-N | $NO_3^-$-N |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm (mg $kg^{-1}$ dry soil) | | | | | (%) | | (%) | ppm | ppm |
| Soil | 68.1 | <0.2 | 16.9 | 9.2 | 27 | 0.7 | - | | | |
| Therm. Compost | 147 | <0.2 | 32 | 4.8 | 13.8 | 37.5 | 13.61 | 1.54 | 1.78 | 505 |
| Verm. Compost | 660 | <0.2 | 9.2 | 1.2 | 7.8 | 33.1 | 10.3 | 1.8 | 60.3 | 2230 |
| Coir | 12.7 | <0.2 | 1.2 | 0.2 | 2.6 | - | *75-186 | | | |

***** Values from Abad et al., 2002 and Noguera et al., 2000

**Table 3.** Total mass (mg) of metals in soil per pot in each treatment after contamination of the soil.

| | Total Zn | Total Cd | Total Pb | Total Ni | Total Co |
|---|---|---|---|---|---|
| | ---------- mg/pot ---------- | | | | |
| S | 148.01 | 33.94 | 61.99 | 78.96 | 49.06 |
| ST | 140.27 | 33.91 | 60.03 | 75.46 | 47.87 |
| STC | 135.72 | 33.90 | 58.90 | 73.66 | 47.25 |
| SV | 145.19 | 33.91 | 59.81 | 75.41 | 47.83 |
| SVC | 140.65 | 33.90 | 58.68 | 73.60 | 47.21 |

S: Soil, ST: Soil+compost, STC: Soil+compost+coir, SV: Soil+vermicompost, SVC: Soil+vermicompost+coir

**Table 4.** Bioavailable metal mass (mg) in soil per pot from control soil (S) and soils amended with thermophilic (T) and vermicompost (V) with and without coir (C) from the pots containing no Switchgrass plants. Numbers inside parenthesis indicate ± 1 S.E. Varying letters in each column indicate significant differences among the soil with and without the different organic amendments for each metal species at $p < 0.05$.

| [1]Treatment | n | Zn | Cd | Pb | Co | Ni |
|---|---|---|---|---|---|---|
| | | ---------- mg/pot ---------- | | | | |
| S | 3 | 20.104[a] (0.837) | 23.611[a] (0.875) | 0.204[a] (0.010) | 23.178[a] (0.909) | 25.225[a] (0.632) |
| ST | 4 | 0.342[b] (0.058) | 0.282[b] (0.067) | 0.027[b] (0.016) | 0.304[b] (0.089) | 0.388[b] (0.089) |
| STC | 4 | 0.231[b] (0.089) | 0.345[b] (0.021) | 0.030[b] (0.021) | 0.450[b] (0.063) | 0.456[b] (0.030) |
| SV | 4 | 0.442[b] (0.115) | 0.294[b] (0.024) | 0.042[b] (0.022) | 0.355[b] (0.023) | 0.529[b] (0.046) |
| SVC | 4 | 0.704[b] (0.077) | 0.309[b] (0.048) | 0.028[b] (0.014) | 0.449[b] (0.073) | 0.568[b] (0.075) |

[1]S: Soil, ST: Soil+compost, STC: Soil+compost+coir, SV: Soil+vermicompost, SVC: Soil+vermicompost+coir

**Table 5.** Soil pH and EC (μS $cm^{-1}$) from control soil (S), and control soil amended with thermophilic (T) and vermicompost (V) with and without cocopeat (C) from pots without (-) and with (+) plants. Numbers inside parenthesis indicate ± 1 S.E. Varying letters in each column indicate significate differences between treatments.

| Plants | [1]Treatment | n | pH | EC (μS $cm^{-1}$) |
|---|---|---|---|---|
| (-) | S | 3 | 4.63[b] (0.12) | 84[b] (15) |
| | ST | 4 | 6.79[a] (0.06) | 364[a] (49) |
| | STC | 4 | 6.53[a] (0.15) | 324[a] (26) |
| | SV | 4 | 6.44[a] (0.14) | 917[a] (51) |
| | SVC | 4 | 6.59[a] (0.04) | 1219[a] (104) |
| (+) | S | 3 | 4.67[c] (0.14) | 81[c] (0.99) |
| | ST | 4 | 6.40[a] (0.04) | 255[b] (27) |
| | STC | 4 | 6.34[a] (0.06) | 234[b] (8.3) |
| | SV | 4 | 6.08[b] (0.10) | 812[a] (99) |
| | SVC | 4 | 6.29[b] (0.03) | 776[a] (71) |

[1]S: Soil, ST: Soil+compost, STC: Soil+compost+coir, SV: Soil+vermicompost, SVC: Soil+vermicompost+coir.

**Table 6.** Total heavy metal mass in control soil (S), and control soil amended with thermophilic (T) and vermicompost (V) with and without coir (C) from pots without (-) and with (+) plants at the end of the 54-day incubation period. Numbers inside parenthesis indicate ± 1 S.E. Varying letters in each column indicate significate differences between treatments.

| Plants | [1]Treatment | n | Zn | Cd | Pb | Co | Ni |
|---|---|---|---|---|---|---|---|
| | | | | | mg | | |
| (-) | S | 3 | 105.38$^{b}$ (9.65) | 33.09$^{a}$ (0.60) | 47.52$^{a}$ (3.63) | 38.54$^{a}$ (2.55) | 57.54$^{a}$ (3.53) |
| | ST | 4 | 119.24$^{ab}$ (3.63) | 35.03$^{ab}$ (0.97) | 55.49$^{a}$ (1.52) | 33.67$^{ab}$ (0.79) | 46.51$^{b}$ (0.24) |
| | STC | 4 | 110.63$^{b}$ (6.72) | 29.87$^{b}$ (1.26) | 48.32$^{a}$ (3.16) | 29.36$^{b}$ (1.16) | 42.77$^{b}$ (1.65) |
| | SV | 3 | 143.44$^{a}$ (4.89) | 32.81$^{ab}$ (2.01) | 50.56$^{a}$ (4.24) | 32.13$^{b}$ (0.89) | 42.96$^{b}$ (1.90) |
| | SVC | 4 | 136.88$^{a}$ (4.70) | 30.93$^{b}$ (2.45) | 46.63$^{a}$ (3.77) | 30.53$^{b}$ (0.98) | 43.10$^{b}$ (1.26) |
| (+) | S | 3 | 102.69$^{a}$ (3.02) | 34.68$^{a}$ (1.28) | 50.60$^{a}$ (1.85) | 40.12$^{a}$ (1.22) | 55.52$^{ab}$ (1.43) |
| | ST | 4 | 110.45$^{a}$ (4.11) | 31.25$^{ab}$ (1.73) | 51.76$^{a}$ (1.89) | 33.55 (1.02) | 58.80$^{a}$ (8.42) |
| | STC | 4 | 109.91$^{a}$ (5.00) | 29.32$^{b}$ (3.71) | 48.86$^{a}$ (4.43) | 40.75$^{a}$ (8.26) | 47.57$^{ab}$ (2.72) |
| | SV | 4 | 120.28$^{a}$ (2.72) | 25.42$^{b}$ (0.29) | 44.57$^{a}$ (1.58) | 28.93$^{a}$ (0.84) | 42.29$^{ab}$ (0.76) |
| | SVC | 4 | 117.31$^{a}$ (4.45) | 24.18$^{b}$ (1.14) | 43.19$^{a}$ (0.86) | 26.09$^{a}$ (0.57) | 39.71$^{b}$ (1.35) |

[1]S: Soil, ST: Soil+compost, STC: Soil+compost+coir, SV: Soil+vermicompost, SVC: Soil+vermicompost+coir.

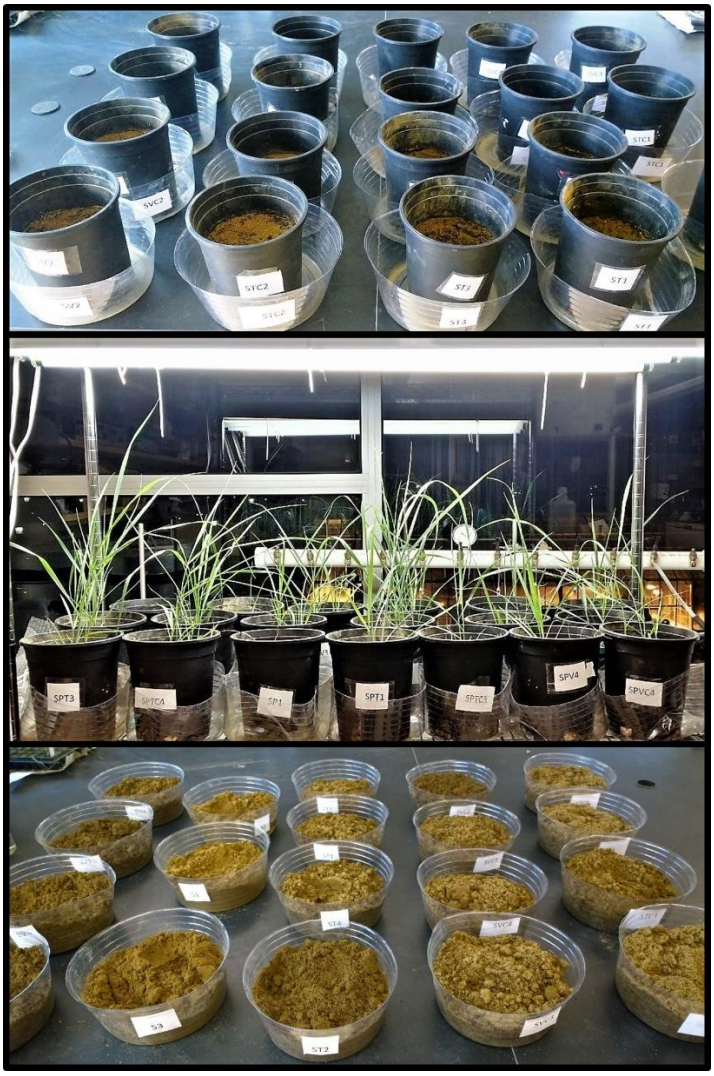


**Fig. 1.** (Top): Pots containing contaminated soils amended with the different organic treatments without Switchgrass placed over plastic containers used for leachate collection, (Middle): Planted pots containing Switchgrass growing in laboratory under 24-hour light conditions, (Bottom): Plastic containers holding soil that was removed from the pots at the end of the experimental phase for analysis.

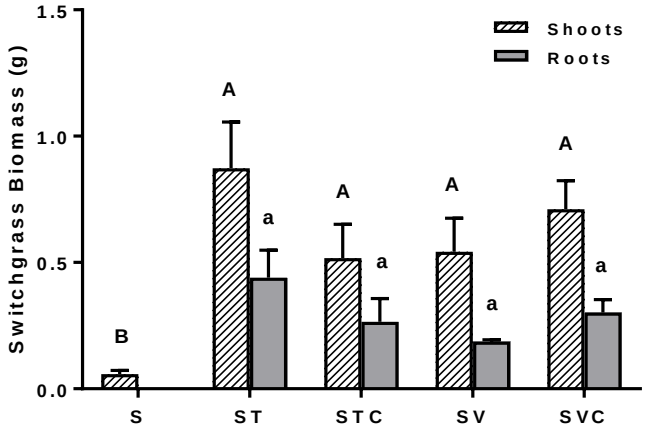


**Fig. 2.** Mean ± 1 S.E. Switchgrass shoot and root biomass (g) from control soil (S), and soil amended with thermophilic (T) and vermicompost (V) with and without cocopeat (C) from pots containing plants. Varying uppercase and lowercase letters indicate significant differences in shoot and root biomass respectively between the organically amended soils. S: Soil, ST: Soil+compost, STC: Soil+compost+coir, SV: Soil+vermicompost, SVC: Soil+vermicompost+coir.

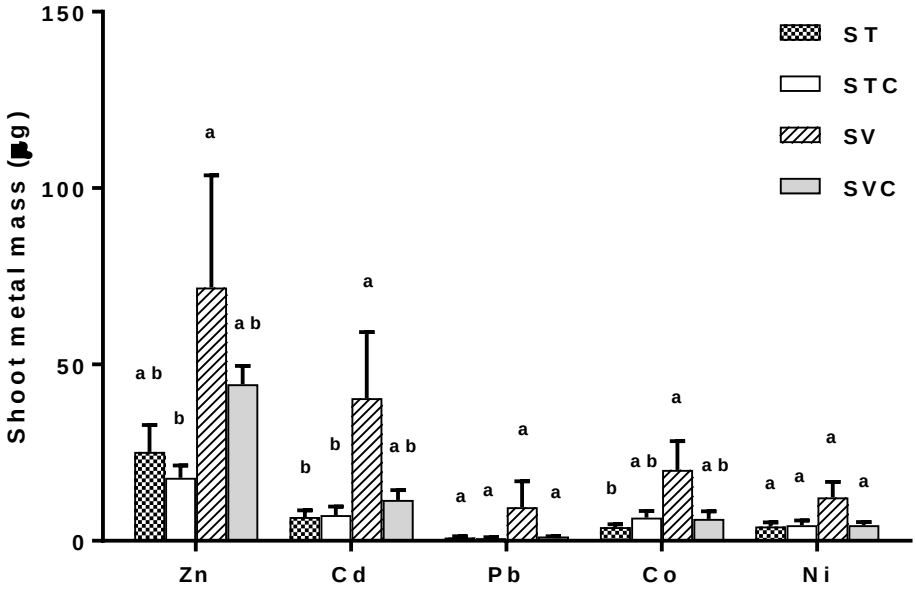


**Fig. 3.** Mean ± 1 S.E. Switchgrass shoot metal mass (µg) in Switchgrass shoots from soil (S) amended with thermophilic (T) and vermicompost (V) with and without coir (C) from pots containing plants. Varying letters indicate significant differences in shoot metal mass of Switchgrass between the organically amended soils. ST: Soil+compost, STC: Soil+compost+coir, SV: Soil+vermicompost, SVC: Soil+vermicompost+coir.

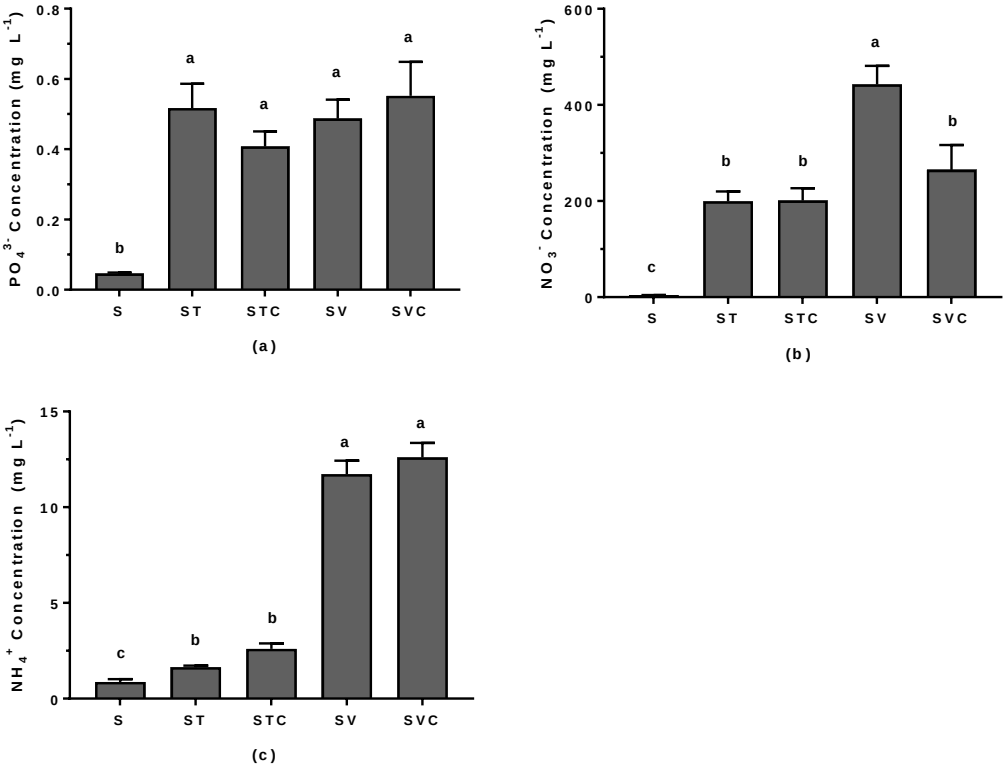


**Fig. 4.** (a-c) Mean ± 1 S.E. $PO_4^{3-}$, $NO_3^-$, and $NH_4^+$ concentrations analyzed in the leachate from control soil (S), and control soil amended with thermophilic (T) and vermicompost (V) with and without coir (C) from pots containing no plants. Different lowercase letters indicate significant differences in nutrient leachate concentrations among the soil and organically amended soil treatments. S: Soil, ST: Soil+compost, STC: Soil+compost+coir, SV: Soil+vermicompost, SVC: Soil+vermicompost+coir.

## DISSERTATION CONCLUSION

Green infrastructure such as bioretention can be implemented in urban areas for stormwater quality improvements and volume reductions. Bioretention reduces the impact of built environments on downstream waterbodies by retaining, filtering, and treating stormwater onsite. The ability of bioretention to reduce stormwater pollutants in the effluent depends on the various design elements which must be evaluated carefully. The soil filter media composition is especially critical to bioretention performance. Bioretention filter media is typically amended with compost for plant establishment and growth, as in this study. Compost contains nutrients in far greater quantities than typical urban storm runoff. Nutrient export observed in the study's bioretention cells (those without the SorbtiveMedia$^{TM}$ amendments) was due to the excess compost in the filter media. Despite beneficial qualities of compost, from improving soil biological properties to heavy metal retention, it should be used judiciously in N and P-impaired watersheds. Moreover, not all composts are created equal, and if necessary, compost with a greater C: N ratio to promote N immobilization, and lower P content should be considered, the adoption of which may also benefit water quality where nutrients are concerned, while simultaneously reduce greenhouse gas fluxes of $CO_2$-C and $N_2O$-N.

Bioretention plants have multitude of co-benefits including rainfall interception, erosion control, evapotranspiration, fostering microbial communities, and improving soil aeration and porosity in the filter media, all of which increase bioretention longevity. However, plants only take up a small portion of dissolved N and P contrary to the amount of nutrients that can be stored, retained or removed by the soil. Short and long-term ortho-

P removal must rely on soil chemical parameters in the filter media. Phosphates are removed from soil solution through sorption reactions with metal cations (mainly Al, Fe, and Ca) in soils. This research evaluated the use of SorbtiveMedia$^{TM}$ containing Fe and Al, and showed promising results for dissolved and total P removal. Alternatively, proprietary media such as the SorbtiveMedia$^{TM}$ can be replaced by locally and cheaply available native soil blends that are high in these cations. Additionally, Al-based drinking water treatment residuals, which are waste materials that are typically disposed to landfills, have potential use as bioretention soil amendments for P removal, but this needs to be studied. For dissolved N, effective treatment systems must rely on physical process of aerobic filtering in upper layers first, followed by a continuously saturated anaerobic zone with a reliable carbon source to promote microbial denitrification. Additional research should focus on increasing denitrification efficiency without releasing $N_2O$-N gas- a by-product of denitrification- to the atmosphere in order to achieve overall environmental benefits.

Currently, landscape architects and engineers are at the forefront of bioretention design implementation and at recognizing the "ecosystem services" provided by bioretention. Although engineering design and sizing of bioretention is critical for installation, collaboration across multiple disciplines to integrate complementary design ideas from soil science, hydrology, and horticulture is required. Bioretention is a complex treatment system which relies heavily on soil and water chemistry processes and plant-soil interaction for pollutant transformation and removal. Going forward, transdisciplinary research collaboration can help maximize bioretention design functions and should be the norm.

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# APPENDICES

## Appendix A

**Fig. 1.** Bioretention cell with rainpan and PVC precipitation-distribution pipes. The rainpan is installed outside of the cell. Rainwater from the corrugated pan drains into gutters, vertical downspouts, and to pipes that run horizontally along the length of the cell and contains perforations at the bottom to deliver water evenly across the cell.

**Appendix B**

**Fig. 2.** (Top left, Top Right, Bottom): Road runoff being conveyed via curb cut and rock-line swale into the v-notch weir where influent water is sampled, effluent water sampling location from an underdrain pipe 4ft deep belowground, stormwater samples collected in up to 24 bottles in the autosampler.

## Appendix C

**Table 1.** Weir equations for each cell's inflow and outflow.

| | Cell | Treatment | Weir equation |
|---|---|---|---|
| Inflow weir | 1 | VH RR20 | Q = 7.3858 * H^2.7088 |
| | 2 | VH | Q = 3.5975 * H^2.4424 |
| | 3 | VH SMRR60 | Q = 4.3192 * H^2.5137 |
| | 4 | VH SM | Q = 4.8798 * H^2.5761 |
| | 5 | VH RR15 | Q = 3.8256 * H^2.4750 |
| | 6 | VH | Q = 4.8967 * H^2.5735 |
| | 7 | VL | Q = 4.1210 * H^2.4923 |
| | 8 | VL | Q = 5.3260 * H^2.6022 |
| Outflow weir | 1-8 | | Q = 3.4166 * H^2.5515 |

Q: Flow rate (cfs) H: head (ft) above the 90° v-notch

*VL= vegetation low diversity, VH= vegetation high diversity, RR= enhanced rainfall+runoff, SM= SorbtiveMedia™

## Appendix D

**Table 2.** Mean soil chemical parameters including pH, organic matter percentage (OM %) using the loss-on-ignition method, available P (mg kg soil$^{-1}$), and exchangeable cation exchange capacity (ECEC; meg/100 g soil) averaged across all eight bioretention cells in Burlington, Vermont. Means are followed by ± 1 S.E.

| Date | pH | OM (% LOI) | Available P (mg kg soil$^{-1}$) | ECEC (meg/100 g soil) |
|---|---|---|---|---|
| 6/8/2015 | 6.92 ± 0.25 | 1.80 ± 0.56 | 12.24 ± 5.79 | 4.47 ± 1.04 |
| 8/24/2015 | 6.99 ± 0.13 | 2.25 ± 1.04 | 26.50 ± 4.03 | 7.25 ± 1.71 |
| 10/28/2015 | 7.14 ± 0.06 | 2.20 ± 0.49 | 23.12 ± 2.78 | 7.23 ± 0.92 |
| 5/17/2016 | 6.97 ± 0.24 | 1.45 ± 0.38 | 27.03 ± 6.30 | 5.51 ± 0.78 |
| 7/28/2016 | 7.09 ± 0.11 | 1.80 ± 0.30 | 32.83 ± 10.65 | 6.88 ± 1.13 |
| 9/8/2016 | 7.04 ± 0.12 | 1.97 ± 0.65 | 33.35 ± 6.59 | 7.14 ± 1.62 |
| 11/8/2016 | 7.20 ± 0.12 | 2.18 ± 0.55 | 39.94 ± 9.85 | 8.25 ± 1.28 |

## Appendix E

**Table 3.** Mean influent and effluent peak flowrates (L $min^{-1}$), and peak attenuation (%) in the bioretention cells treated with different soil, vegetation, and RR treatments from storm events sampled spanning May to October/November 2015 and 2016 in Burlington, Vermont. Significance determined by matched pair t-test on log-transformed data. P<0.001**, P< 0.05*.

| Cell | N | Peak Q In ± SD | Peak Q Out ± SD | Sig. diff. | % Peak Reduction | Average % Reduction ± SD | % Reduction Min-Max |
|---|---|---|---|---|---|---|---|
| VH | 37 | 30 ± 70 | 1.9 ± 3.9 | ** | 94 | 88 ± 28 | -63 -100 |
| VH RR | 35 | 21 ± 23 | 2.7 ± 5.5 | ** | 87 | 85 ± 33 | -92 -100 |
| VH SM | 16 | 14 ± 27 | 1.9 ± 3.7 | * | 86 | 83 ± 23 | 37-100 |
| VH SMRR60 | 16 | 47 ± 52 | 3.4 ± 5.4 | ** | 93 | 93 ± 9 | 68-100 |
| VL | 17 | 24 ± 35 | 1.0 ± 1.0 | ** | 96 | 88 ± 19 | 33-100 |

*VL= vegetation low diversity, VH= vegetation high diversity, RR= enhanced rainfall+runoff, SM= SorbtiveMedia™

## Appendix F

Nitrogen mineralization rates methods:

N mineralization and nitrification rates were measured two to three times a year from 2014 to 2016 (total of 8 sampling dates spanning spring, summer and fall) as an indicator of soil media microbial activity from ambient vegetation cells. KCl extraction was carried out on fresh soils for ammonium ($NH_4^+$) and nitrate ($NO_3^-$). At the time of soil collection, in-field incubation was carried out, where three 100-g subsamples of fresh soil were put into polyethylene bags and installed in three separate locations in each cell at 7 cm depth for 21 days, after which the soil was sampled for final $NH_4^+$ and $NO_3^-$ using a flow injection autoanalyzer. Net N mineralization (potential organic N transformation rates) rates were calculated by subtracting initial field $NH_4^+$ and $NO_3^-$ concentrations from final $NH_4^+$ and $NO_3^-$ concentrations. Net nitrification rate was calculated by final $NO_3^-$ concentrations minus initial field $NO_3^-$ concentrations (Ross et al., 2009). Moisture-correction was done for each sample to correct for differences in soil water content and express results in dry weight equivalents. N mineralization/nitrification rate were expressed in mg N per kg dry soil.

## Appendix G

**Table 4.** List of bioretention plant species.

| | Latin Name | Common Name |
|---|---|---|
| Low diversity (VL) cell | *Hemerocallis spp.* | Daylilies 'Stella d'Oro' (4*) |
| | *Panicum virgatum* | Switchgrass 'Shenandoah' (5) |
| High diversity (VH) cell | *Aesclepius incarnata* | Butterfly, Milkweed 'Tuberosa' (1*) |
| | *Anemone canadensis* | Windflower (2) |
| | *Aquilegia canadensis* | Columbine (2) |
| | *Symphyotrichum novae-angliae* | New England Aster 'Purple Dome' (2) |
| | *Baptisia australis* | Blue False Indigo 'Capsian' and 'Midnight Prairiebliss' (3) |
| | *Helenium autumnale* | Sneezeweed 'Red+Gold' (4) |
| | *Lobeliea cardinalis* | Cardinal Flower (1) |

*Numbers inside parenthesis indicate number of individuals planted per cell.

**Appendix H**

PAS gas flux calculation equation (used by Kaye, McCulley, Castellano, Adviento-Borbe Labs).

The method uses numbers (density, temperature, air pressure) based on 20°C and 1 atm and not the actual air temperature and pressure because the PAS instrument calculates the concentration of each gas at 20°C. Fluxes of $CO_2$ and $N_2O$ are computed by fitting a linear regression of gas concentration against time after chamber closure.

According to the PAS manual (14.11.2) to convert ppm (volume) to mg/m$^3$:

$$Concentration\ \left(\frac{mg}{m^3}\right) = ppm * molecular\ wt\ (\frac{g}{mol}) * \frac{1\ mol}{24.04\ m^3}$$

where 1 mol per 24.04 m$^3$ is the density of gas at 20°C and 0.101 MPa (ρ). Convert ppm to mg/m$^3$ using the above equation, then calculate the flux as below to get $CO_2$-C or $N_2O$-N in mg/(m$^2$*sec):

$$F = \frac{\Delta C}{\Delta t} * \frac{V}{A} * \alpha$$

$$F = \frac{mg}{m^3 sec} * \frac{m^3}{m^2} * \alpha$$

where $F$ is the gas production rate (mg m$^{-2}$ sec$^{-1}$), $\Delta C/\Delta t$ denotes the increase/decrease of gas concentration in the chamber (mg m$^{-3}$ sec$^{-1}$), $V$ is the chamber volume (in m$^3$), $A$ is the chamber soil surface area (in m$^2$), and α is a conversion coefficient (28/44 for $N_2O$-N; 12/44 for $CO_2$-C).

Example calculation: slope*44*(1/24.04) *0.17779*(12/44) *60*60

molecular weight of gas = 44 (CO2 or N2O)
1/24.04 = PAS conversion (see above)
chamber m3/m2 = 0.17779
12/44 = conversion to $CO_2$-C
*60*60 converts from seconds to hour

## Appendix I

Chloroform-fumigation extraction method:

Following GHG sampling, three random subsamples of soil was collected from the ambient high and low diversity vegetation plots (V1 and V2) for soil microbial biomass (SMB) carbon (C) determination monthly from May to November in 2015. Monthly SMB was also measured in year 2014. Chloroform fumigation-incubation method (Vance et al. 1987, Jenkinson and Powlson 1976) was used to determine SMB. Analysis was done on field-moist soil within several hours from collection. Chloroform fumigation is done to kill and lyse microbial cell membranes in the soil sample. Soils (11-12 grams) for fumigation were placed into 50 ml beakers and put in a vacuum desiccator. 20 ml of chloroform and some boiling chips were added to a beaker and placed in the center of the desiccator. The dessicator was sealed and evacuated using a vacuum pump for 2-3 minutes causing the chloroform to boil, exposing the samples to chloroform vapor (Alessi et al. 2011). This was followed by release of the vacuum to vent the desiccator. This step was repeated five times, not venting the last time. The desiccator was left under vacuum and stored in a dark box for 5 days before the vacuum was released again. Non-fumigated samples (10-11 grams) were weighted into 50 ml beakers but not fumigated. Chloroform fumigated and non-fumigated (control) soils were extracted with 50 ml of 0.5 M K2SO4. After shaking using a mechanical shaker and settling, the samples were passed through a pre-wetted (with 0.5 M K2SO4) Whatman 1 filter paper. The filtrate was frozen until ready to be determined for total organic carbon (TOC) on the TOC analyzer (TOC-L Shimadzu TOC Analyzer, Shimadzu Corporation). Control blanks containing only 0.5 M K2SO4 were included with every batch of samples. Blanks were subtracted from the data to correct for any background C present in the reagent. The difference in TOC between the chloroform-fumigated and non-fumigated soils is the chloroform-labile C pool (EC), and is proportional to microbial biomass C (Vance et al. 1987, Allison 2008). Moisture-correction was done for each sample to correct for differences in soil water content and to express final results in dry weight equivalents.

**Appendix J**

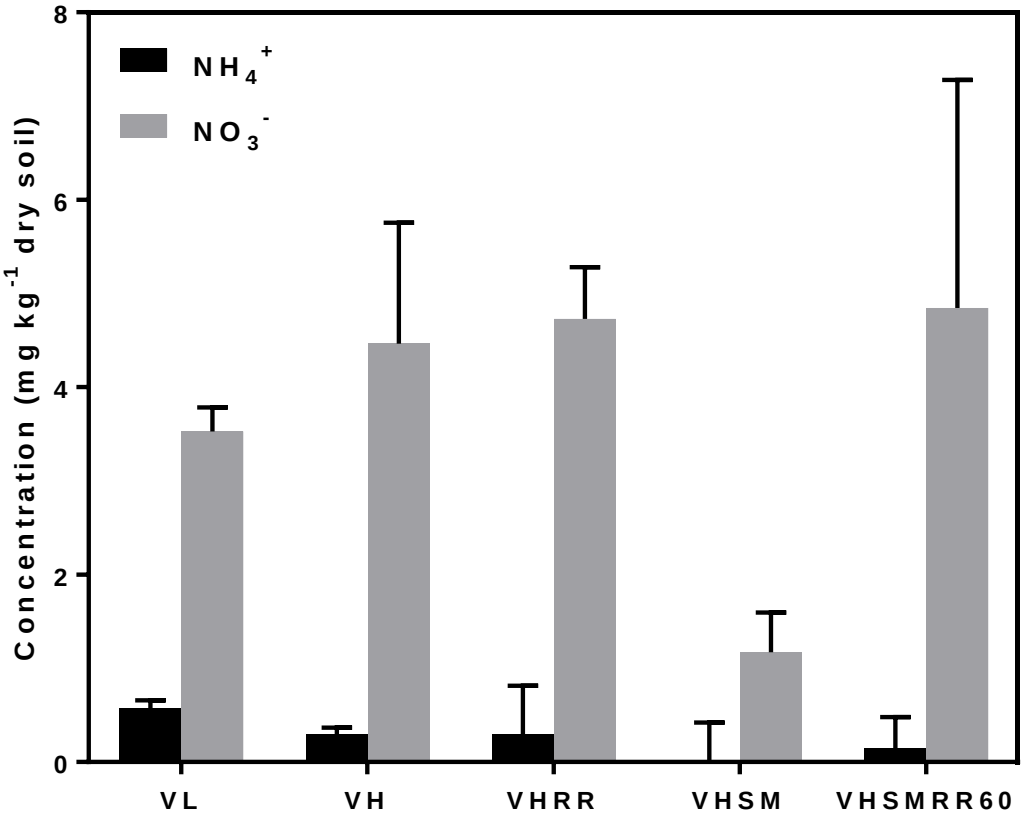


**Fig. 3.** Soil $NH_4^+$ and $NO_3^-$ concentrations averaged across three sampling dates (June 9, July 28, and November 2, 2016). VL= vegetation low diversity, VH= vegetation high diversity, RR= enhanced rainfall+runoff, SM= SorbtiveMedia$^{TM}$.

**Appendix K**

Estimation of carbon and nitrogen stocks in soil media layers, microbial biomass and plants.

Soil

Total volume of upper 30 cm soil media and lower 30 cm soil media = 1132674 $cm^3$
Total weight of upper 30 cm soil media = 1347.882 kg, given the bulk density 1.19 g $cm^{-3}$ (bulk density here is average bulk density and empirically derived from soil measurements taken on two separate occasions)
Total weight of lower 30 cm soil media = 1800.951 kg, given the bulk density 1.59 g $cm^{-3}$ (bulk density here is taken from USDA NRCS laboratory data[9])

Plants

Total cell area = 3.72 $m^2$
*Panicum* (switchgrass) coverage of cell area: 55% of 3.72 = 2.046 $m^2$
*Hemerocallis* (daylily) coverage of cell area: 45% of 3.72 = 1.674 $m^2$
Total biomass of *Panicum* per year = 10 kg $m^{-2}$ (extrapolated from Heaton et al., 2004)
Total biomass of *Hemerocallis* per year = 5 kg $m^{-2}$ (assumed to be half of *Panicum* as their height is measured to be half as well)
Total biomass of *Panicum* at plot coverage level = 20.46 kg (2.046 $m^{-2}$ x 10 kg $m^{-2}$)
Total biomass of *Hemerocallis* at plot coverage level = 8.37 kg (1.674 $m^{-2}$ x 5 kg $m^{-2}$)
Average *Panicum* C & N concentration: 453.5 and 8.625 g $kg^{-1}$ dry plant
Average *Hemerocallis* C & N concentration: 447 and 17.18 g $kg^{-1}$ dry plant

Loss from gas fluxes

$CO_2$ flux:

Average flux is 194±7 mg $m^2$ $hr^{-1}$
Average loss of C from $CO_2$ flux at plot level of 3.72 $m^2$ per day = 17.32 g

$N_2O$ flux:

Average flux is 0.01±0.02 mg $m^2$ $hr^{-1}$
Average loss of N from $N_2O$ flux at plot level per day = 0.893 mg

[9] https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/office/ssr10/tr/?cid=nrcs144p2_074844

**Appendix L**

**Table 5.** Total mass of metal in each substrate used in the experiment and calculated total mass of metals in the different treatments before contamination.

| | | Total mass (mg) of metal in each experimental substrate | | | | |
|---|---|---|---|---|---|---|
| Substrate | Weight (kg) | Zn | Cd | Pb | Ni | Co |
| Soil | 1.6 | 114.408 | 0.336 | 28.392 | 45.36 | 15.456 |
| Therm. Compost | 0.12 | 17.64 | 0.024 | 3.84 | 1.656 | 0.576 |
| Verm. Compost | 0.12 | 79.2 | 0.024 | 1.104 | 0.936 | 0.144 |
| Coir | 0.06 | 0.762 | 0.012 | 0.072 | 0.156 | 0.012 |

| | Total mass (mg) of metal per treatment pot before contamination | | | | |
|---|---|---|---|---|---|
| Treatment | Zn | Cd | Pb | Ni | Co |
| S | 114.41 | 0.34 | 28.39 | 45.36 | 15.46 |
| ST | 106.67 | 0.31 | 26.43 | 41.86 | 14.27 |
| STC | 102.12 | 0.30 | 25.30 | 40.06 | 13.65 |
| SV | 111.59 | 0.31 | 26.21 | 41.81 | 14.23 |
| SVC | 107.05 | 0.30 | 25.08 | 40.00 | 13.61 |