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Effects of different soil media, vegetation, and hydrologic treatments on nutrient and sediment removal in roadside bioretention systems



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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 highdiversity (7 species) and low-diversity plant mix (2 species); (2) proprietary SorbtiveMedia[™] (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/nitritenitrogen (NOx), 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 event mean concentrations (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.

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 diffused 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, proliferating the impervious footprint, natural hydrological flow paths resulting in absorption, filtering and treatment of stormwater through soils is bypassed (Cook, 2007). During high flow events, urban storm infrastructures can show failure, leading to harmful combined sewer-storm-water overflows, contaminating surface waters by nutrients and pathogens (Kaye et al., 2006) intended to be kept out of those very waters. Thus, newer

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strategies to address urban stormwater management are becoming increasingly necessary to improve surface water quality. 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; County, 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; Rov-Poirier et al., 2010; Liao et al., 2017). The technology is an aesthetically pleasing, sunken (approx. < 1.3 m 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 also 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 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., 2003, 2001; 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 (NH4⁺) 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) of these nutrient forms 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 informed particularly by concerns regarding the 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).

Field studies such as the following are valuable as there is insufficient number of field-performance data in the bioretention literature. 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. Monitoring results from our study will be important 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;
- 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. Methods

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 (30–120 m²). 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 (1.22 m wide by 3.05 m long by 0.91 m 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[™] (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 cmdiameter 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



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 highdensity 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.

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 °C (45.9°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. 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 to fill the bioretention

Table 1

Bioretention watershed and cell characteristics.

bed, and varying phenology so that, across the seven species, flowers bloom throughout the growing season. In both cells, the plants senesce in mid-October to mid-November, and begin to re-establish in early May.

The second treatment is a soil media treatment: two of the cells (cell 3 and 4) contain an engineered, P-sorbing amendment called SorbtiveMediaTM (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 cells (cell 3 and 4) with this treatment, the bottom 7.6 cm of the sand layer is replaced by the SorbtiveMediaTM (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

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 30.5 cm; 1 ft), pure sand (lower 30.5 cm; 1 ft)
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
^a 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)
	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)

^a Note: See Supplementary Materials section for detailed soil chemical parameters.



Fig. 2. (a) A typical cross section of bioretention soil media in UVM Bioretention Lab, (b) Cross section of bioretention soil amended with SorbtiveMedia[™].

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" (See Supplementary Materials) 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.

2.3. 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 likelihood of 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.

Table 2

Cell	Soil	Vegetation	Vegetation treatment watershed area difference (%)	Rainfall	Runoff treatment watershed area difference (%)	Drainage Area, (m²)
7		VL	11	Ambient		30
2		VH	11	Ambient	20	33
1		VH		Ambient+RR20	20	40
8		VL	13	Ambient		61
6		VH	15	Ambient	15	54
5		VH		Ambient+RR15	15	63
4	SM	VH		Ambient	60	64
3	SM	VH		Ambient+RR60	00	120

Treatments in the experimental design for each of the eight bioretention cells

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.

2.4.1. Influent and effluent sampling design

A 90° 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; 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

*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 = SorbtiveMediaTM.

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 (Supplemental Table 1).

2.4.2. Water sample collection

Flow measurements were taken using calibrated v-notch weirs on a 1-min 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 0°–71 °C, prohibiting winter sampling. Flow rates exceeding 0.94–1.17 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 min at the inflow and outflow, respectively. Twenty-four 1-l polypropylene bottles were installed in the samplers to collect composites of 3 samples per bottle, switching bottles every 12 min in the inflow and 6 min 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-min increments. Short time intervals were chosen because the cells drain small watershed areas, and we wanted to capture the initial time of concentrations (approx. 5–9 min) 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) were analyzed separately to obtain a complete pollutograph.

2.5. Water quality analysis

Water samples were transported to the Agriculture and Environmental Testing Laboratory within 24 h 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 $0.45 \,\mu m$ 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.

2.6. 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).

Total Pollutant Mass =
$$\int_{0}^{t_{r}} C(t)Q(t)dt$$
 (1)

where:

C(t) = concentration

Q(t) = runoff flow rate

Limits of integration refer to time 0 (runoff initiation) and time $t_{\rm r}$ (time at which runoff ceases).

Pollutant mass removal efficiency (RE) was calculated based on the following formula: RE (%) = (mass in – mass out) \times 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).

$$EMC = \frac{\text{Total Pollutant Mass}}{\text{Total Runoff Volume}} = \frac{\int_{0}^{t_{\text{r}}} C(t)Q(t)dt}{\int_{0}^{t_{\text{r}}} Q(t)dt}$$
(2)

2.7. 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 °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 °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).

2.8. 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 this test is appropriate because it does not require the data to fit a certain distribution. Results from Wilcoxon matched pair test were nevertheless compared against the paired *t*-test, and both tests were found to be comparable with each other in significant trends. Results presented are from the Wilcoxon test. 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 non-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.

3. Results

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 (0.01–3.3 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 (0.05–1.5 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 90th percentile rainfall is equivalent to the first inch (25.4 mm) of rainfall in a 24-h 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,



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).

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 PO₄ loadings (Table 3), indicating that several of the pollutants, especially TSS and TP, were transported in just a fewer larger events.

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 + NH₃-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. 4). A much greater portion of the effluent total P was ortho-P relative to part-P (69% vs. 31% respectively).

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

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.

Volume	NO _x TN Orth		Ortho-P	TP	TSS			
(L)	(mg)				(g)			
Cumulative volume and load								
35389	11593	27348	2715	5130	475			
27454	6665	22521	1733	5198	997			
Volume and load contribution (%)								
44	63	55	61	50	32			
56	37	45	39	50	68			
	Volume (L) Cumulative 35389 27454 Volume and 44 56	VolumeNOx(L)(mg)CumulativeJume and 35389274546665Volume and 4463 5637	Volume NOx TN (L) (mg)	Volume NO _x TN Ortho-P (L) (mg) <	Volume NO _x TN Ortho-P TP (L) (mg) -			



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 ($802 \le n \le 843$). 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).

(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 (Fig. 3).

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 dissolved P being greatly negative. When examining the medians, only the dissolved N and P were exported in large storms, while positive removal was observed for everything else (Table 4).

3.4. Hydraulic performance (peak flow and volume) of bioretention cells

During 2015 and 2016, flow rates and runoff volumes were collected 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%). Of the nine predictor variables, peak outflow rates were most strongly correlated to peak inflow rates, explaining most of the variation alone (p < 0.0001, $R^2 = 0.47$, Fig. 5, compared to $R^2 = 0.56$ for the whole model). Additionally,

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)

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 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).

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



Fig. 5. Relationship 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.

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 μ g L⁻¹ respectively. For those same elements, effluent concentrations were 21.2, 144, 10.7, 8.9, and 17.8 μ g L⁻¹ respectively showing no notable change in concentration within bioretention cells, except for a small export of Cu. Particulate metal concentrations for the above elements were much lower than their dissolved constituents: below 19 μ g L⁻¹ for influent, and below 3 μ g L⁻¹ for effluent concentrations, indicating positive

retention within the bioretention cells.

3.6. Cumulative pollutant mass and EMC removal efficiency from bioretention cells 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

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.

^a Cell		n	In	Out	% RE		n	In	Out	% RE
VL	Volume (L)	17	7955	1580	80	TSS (g)	13	164	14	92
VH		37	26613	4693	82		31	266	3	99
VH RR		35	11668	2678	77		28	358	38	89
VH SM		16	4295	2217	48		12	65	6	91
VH SM RR60		16	12423	1791	86		13	620	20	97
VL	NO _x (mg)	14	1440	1414	2	TN (mg)	12	5955	3256	45
VH		31	4810	6213	-29		28	15936	8823	45
VH RR		29	3338	3416	-46		25	7198	6159	-14
VH SM		12	4033	1802	55		11	5910	3689	38
VH SM RR60		13	4677	3614	23		13	14649	6305	57
VL	Ortho-P (mg)	14	628	3578	-470	TP (mg)	14	1141	4430	-288
VH		31	784	5365	- 584		30	3050	5106	-67
VH RR		29	1451	4736	-226		26	1902	4449	-134
VH SM		12	643	37	94		12	1067	154	86
VH SM RR60		13	1303	79	94		13	3163	190	94

^aVH = vegetation high diversity, RR = enhanced rainfall + runoff, SM = SorbtiveMedia, VL = vegetation low diversity, n = number of storm events.

Outflow Volume (L)



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 were determined by Wilcoxon Signed Rank matched pairs test for non-normal data. Underlined asterisk on the shaded gray bars indicate significance at p < .05. Smaller black dots indicate outliers and red dots indicate mean. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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).

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 R² 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

VH SM+RR60

VH SM+RR60



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 < .05. Smaller black dots indicate outliers and red dots indicate mean. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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	Ν	Model p-value	Model \mathbb{R}^2
NO _x	y = $203 - 11.7 \times \text{precipitation depth (mm)} + 0.197 \times \text{inflow volume (L)} - 2.48 \times \text{peak inflow rate (L min^{-1})} - 91.3 \times \text{season}$ (Spring versus Fall)	97	< .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	.0003	24%
PO ₄₃ .	$y = 604 - 34.6 \times \text{precipitation depth (mm)} + 0.596 \times \text{inflow volume (L)} - 9.95 \times \text{peak inflow rate (L min-1)} + 297 \times \text{soil media}$ present - 709 × season (Spring versus Fall)	98	.0017	20%
TP	y = 233 - 7.27 × precipitation depth (mm) - 2.6 × peak inflow rate ($Lmin^{-1}$) + 0.824 × inflow TP mass (mg) + 70 × soil media present - 42 × ADP (days) - 202 × season (Spring versus Fall)	93	< .0001	40%

(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.

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).

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		
^a Cell	Total C Total N (g kg soil ⁻¹)		C/N ratio	Total C Total N (g kg soil ⁻¹)		C/N ratio
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

 $^{a}VH =$ vegetation high diversity, RR = enhanced rainfall + runoff, SM = SorbtiveMedia, VL = vegetation low diversity.

4. Discussion

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,



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.

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	ТР	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

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, P concentrations measured 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. (2005) 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 also 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). NH₄⁺ 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_{4³} 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, number of studies have measured a greater proportion of soluble ortho-P making up TP in influent stormwater (range: 44–71%, Table 8).

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.

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 (\pm SD) MRE of 94 \pm 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 (Figs. 7 & 8). The SM additive cells interestingly also removed both NOx and TN loads (39% and 48% respectively) and EMCs except for the slight export of average NOx 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 (\pm SD) peak discharge (47 \pm 52 vs. $14 \pm 27 \, \text{Lmin}^{-1}$; Appendix B) 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 NH4⁺ 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_v 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 that removed concentrations of either N or P, or both (Fig. 7). While it is 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%-20% changes 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 lavers, 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 (\pm SE) estimated from the upper soil layers averaged 190 \pm 14 mg kg dry soil⁻¹ per year⁻¹, while net N ni-trifications rates averaged 134 \pm 16 mg kg dry soil⁻¹ per year⁻¹ from the ambient cells (See Supplementary Materials). 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 laboratories (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).

4.4. Removal efficiency predictors and implications for bioretention design

Precipitation depths and peak inflow rates had significant negative impact on N and P retention by the cells, suggesting that increasing storm sizes 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 utilized 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 VL 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 (Tables 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.

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 utilized 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 overtime 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 overtime 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 minidroughts 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.

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 waterbodies downstream.

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 (NO₂), 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, NH₃), 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 is also 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.

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; Lintern et al., 2011; Hurley et al., 2017). 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, Figs. 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.¹ 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 (CaCO₃, 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, 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).

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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¹ http://www.imbriumsystems.com/stormwater-treatment-solutions/sorbtive-media.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ecoleng.2017.12.004.

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