EVALUATING THE ROLE OF RAIN GARDEN SOILS IN NUTRIENT PROCESSING OF STORMWATER RUNOFF IN CHARLOTTE, NC

by

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ABSTRACT

CODY LEE STARNES. Evaluating the Role of Rain Garden Soils in Nutrient Processing of Stormwater Runoff in Charlotte, NC. (Under the direction of DR. SANDRA M. CLINTON)

As urbanization increases, Best Management Practices (BMPs) are used to reduce pollutants otherwise released to streams. Rain gardens are a type of BMPs that are vegetated depressions with highly permeable soil to treat urban runoff. These structures are traditionally assessed using inflow-outflow studies with an emphasis on quantifying removal efficiency. This approach neglects controls on nutrient processing within the rain garden and their role as potential hotspots in urban systems. To bridge this gap, three rain gardens in Charlotte, NC were quantified for soil water nutrient concentrations (ammonium, nitrate, phosphate, DOC) during storms and seasonal potential denitrification rates. The rain gardens were located at Myers Park High School (MP), Park Road Park (PR), and Bruns Academy Elementary School (BR) and vary with vegetation, size, treatment area, and age (4,7, and 15 respectively). The results identified no significant difference in the runoff between site or season which indicated differences within soil water concentrations were caused by structural variances of the rain gardens. Results identified soil water ammonium concentrations were significantly different between sites (p=0.0201). Soil water ammonium concentrations were also found to be significantly lower in the summer compared to the winter when all sites were aggregated together (p=0.0201). Nitrate concentrations were significantly higher (p<0.0001) in soil water across sites, and significantly lower (p<0.0001) in winter soil water compared to summer. These trends were caused by the presence of an underdrain and high infiltration rates that limited favorable denitrification conditions from existing. The potential denitrification rates were 0.39, 0.12, and 0.65 µg/gDM/hr at MP, PR, and BR respectively. Overall, the nitrification process attributed to the decrease in soil water ammonium and the accumulation of soil water nitrate. Without prolonged anoxic conditions present in the rain garden nitrate was stored until subsequent storms exported nitrate to the receiving stream. The sites with the highest soil moisture percent after the storm also had higher denitrification rates. Bruns Academy had very high soil nitrate (2.75 mg/L) compared to the other sites (0.42 and 0.28 mg/L at MP and BR respectively) which may have been caused by a pollutant exposure prior to this study. Phosphate was variable between sites and was likely due to the difference in phosphorus in the original soil media. Between similarly constructed MP and PR, soil water phosphate was higher at MP (0.032 mg/L) than PR (0.007 mg/L). This suggests more adsorption occurred due to an increased ratio of the rain garden area to the treatment area as well as plant assimilation. DOC was different among sites and had an inverse relationship with potential denitrification rates. PR had the lowest denitrification rate and presented the largest soil water DOC concentrations with an average concentration of 14 mg/L. The age gradient of the rain gardens in this study proved rain gardens still have the ability to remove pollutants as the structures age (with the exception of nitrate). The addition of soil water concentrations and potential denitrification rates in this study showed internal processes of rain gardens should be explored further to understand the longevity of these structures, as well as nutrient export as aging occurs.

DEDICATION

This work is dedicated to those nearest me who have provided the support needed to achieve my academic goals. To my wife and family, thank you for your endless encouragement and willingness to help in any way possible. To my professors at Wingate University, thank you for your guidance and the qualities you instilled to be successful in graduate school.

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Introduction

The ever-increasing volumes of stormwater runoff in urban communities constantly prompt the exploration and evaluation of new mitigation techniques. Urbanization causes the alteration of landscape structure and function in multiple ways including an increase in impervious cover (Leopold, 1968). Increased development disconnects the landscape from its natural hydrological cycle by decreasing infiltration and evapotranspiration while increasing surface runoff. This causes increased streamflow during storms and decreased flow in intermittent periods between storms (Leopold, 1968). Paved surfaces such as buildings, roads, and parking lots are a few of the driving forces that produce this disconnect. Increased surface runoff is problematic as it increases runoff volume, sediment, and contaminants transported to urban streams (Walsh et al., 2005). Furthermore, increased stream runoff causes direct physical changes to streams such as increased bank erosion, increased flashiness, and decreased richness in stream flora and fauna. These predictable changes have been summarized as the "urban stream syndrome" (Walsh et al., 2005).

Initially, the standard techniques used to mitigate increased stormwater included installing structures such as wet and dry ponds which have been studied extensively by researchers. Some structures such as wet ponds can require larger treatment areas, become a source of thermal pollution, and are not recommended for use in permeable soils (Charlotte-Mecklenburg Storm Water Services, 2014). Also, a wet pond's primary treatment mechanism is settling which stores the pollutant rather than removing it, which can lead to expensive dredging rehabilitation efforts (Marsalek et al., 2002). While traditional stormwater structures yield high potential denitrification rates, reducing the effects of the urban stream syndrome has shifted the focus of land planners (Bettez et al., 2012). More recently, construction has been completed with designs that attempt to minimize environmental impacts. Thus, alternative structures coined low impact development (LID), have been widely implemented because they harbor added ecosystem services that could make them favorable designs opposed to traditional stormwater structures (Davis et al., 2009). LIDs are also constructed to mitigate stormwater runoff and restore the hydrology of the treated area to pre-disturbed conditions or to mimic a lower percent impervious cover in the watershed (Davis, 2005). However, compared to some traditional stormwater treatment designs, LID projects mitigate more water quality problems associated with increased runoff without storage being the primary removal mechanism. In urban environments, LIDs excel in mitigating stormwater by balancing the needs of humans and nature, rather than dismissing the two as separate systems (Church, 2015).

Rain gardens are an example of how Charlotte, NC utilizes LIDs to improve the health of urban receiving waters. The primary goals of rain gardens and other LIDs are to reduce the runoff volume and pollutant/nutrient concentrations through processes such as adsorption, filtration, and biological uptake (Davis et al., 2009). Constructed rain gardens, also referred to as bioretention cells, appear as vegetated depressions in the landscape and vary in size, shape, vegetation as well as construction methods depending on regional preferences. Regardless of these differences rain gardens treat stormwater primarily through filtration. The runoff is captured in the rain garden and the highly permeable engineered soils allow for settling, filtration, and flow attenuation to abate the known effects of stormwater runoff (Hatt et al., 2009). The common rain garden design used in Charlotte, NC, can be seen in Figure 1. The versatility and prospect of using rain gardens for stormwater mitigation has caused research to shift towards analyzing their functions (Davis et al., 2009; Elliott et al., 2011; Hawrot et al., 2017; Hunt et al., 2008; Read et al., 2008).

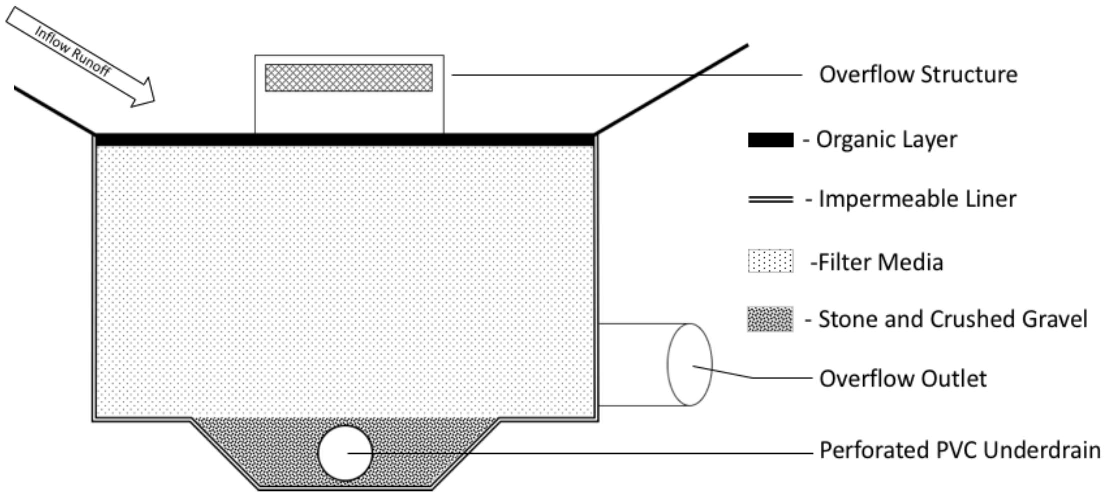


Figure 1: Charlotte, NC rain garden design adapted from the Charlotte Mecklenburg BMP design manual. Note Bruns Academy's overflow structure is an overflow spillway (Charlotte-Mecklenburg Storm Water Services, 2014).

Previous works suggest rain gardens are successful at reducing total suspended solids (TSS) and attenuating flow (Davis et al., 2009; Hunt et al., 2008; Li et al., 2009; Wossink et al., 2003). These findings are reported using percent reduction values comparing the outflow concentration of the observed pollutant to the initial amount entering the rain garden as runoff. Additional studies have assessed rain garden treatment abilities of pollutants associated with runoff (ammonium, nitrate, and phosphate), and much of these data are from the eastern United States (Bratieres et al., 2008; Hatt et al., 2009). Trends emerged in past research with an example being ammonium where concentrations were often significantly reduced, as much as 73% and 92% (Hunt et al., 2008; Jadlocki et al., 2015). Reported nitrate values have been highly variable with some rain gardens reducing nitrate as much as 75%, while other examples provided evidence of the nitrate export (-254%) from the structure (Hunt et al., 2006; Line et al., 2009). The differences in nitrate reduction have been attributed to the absence of anoxic zones in conventional rain gardens (Hunt et al., 2006). Orthophosphate has been understudied compared to the aforementioned nutrients and found by Hunt et al. (2006) to release an average of 9.3% larger outflow concentrations than runoff. Previous research has helped shape the understanding of rain garden performance by identifying efficiencies and design flaws. These traditional techniques of studying concentration reduction ignore the interaction of runoff with the structure of the rain garden. As a result, there has been a need to quantify stormwater attributes as runoff is treated through the rain garden itself. Few studies have begun to explore this relationship, however, only in specific ways that investigate a single factor.

The use of lysimeters to test soil water in the rain gardens has been underutilized in studying rain garden nutrient processing. A six-year study of runoff treatment in a rain garden that was connected to the native soil found a significant reduction of ammonium from runoff to soil water (Elliott et al., 2011). Nitrate produced more variable data with a 5% reduction at one site, and a 93% increase in soil water at the other (Elliott et al., 2011). In an additional study using lysimeters in rain gardens, Komlos et al. (2012) analyzed rain gardens' ability to treat orthophosphate in the runoff. This nine-year experiment found phosphate treatment had not declined throughout the length of the study. Additionally, due to the phosphorus gradient in their soil profile, they were able to predict that rain garden soils would not be saturated with phosphorus for an additional 20 years. Aside from the use of lysimeters to analyze internal processes of the rain garden, direct measurement of soil properties can also foster insight. Soil samples were used in a study to assess the potential denitrification capabilities of various SCMs (wet ponds, dry ponds, infiltration basins, and filtration systems) compared to natural riparian systems (Bettez et al., 2012). The average denitrification potential of five SCM soils had higher potential denitrification rates of 1.2 mg N/KgDM/hr, compared to riparian areas with 0.4 mg N/KgDM/hr (Bettez et al., 2012). The authors also identified that bioretention cells had been unobserved in this study due to a lack of access.

The overall objectives of this study were to 1) assess overall and seasonal water nutrient retention capabilities in regards to ammonium, nitrate, orthophosphate, and dissolved organic carbon (DOC), 2) explore hydrological and structural variables with water quality, and 3) obtain seasonal potential denitrification rates in rain garden soils. To assess these objectives I studied surface runoff and soil water for summer and winter storms across 3 rain gardens in Charlotte, NC. The rain gardens have similar design features and are spread across an age gradient (4, 7, 15 years old). These data will add to the overall knowledge of how urban rain gardens function and are a tool to help identify the long-term impacts of rain garden implementation.

Methods

2.1 Site Descriptions

To analyze how rain garden function varies in urban landscapes, three rain gardens were studied in Charlotte, NC. Field data collection occurred from July 2017 to February 2018, while December 1, 2017, marked the transition from the summer to winter sampling period. Two of the bioretention cells were located in southwest Charlotte, and one was located in northwest Charlotte (Figures 2-5, Table 1).

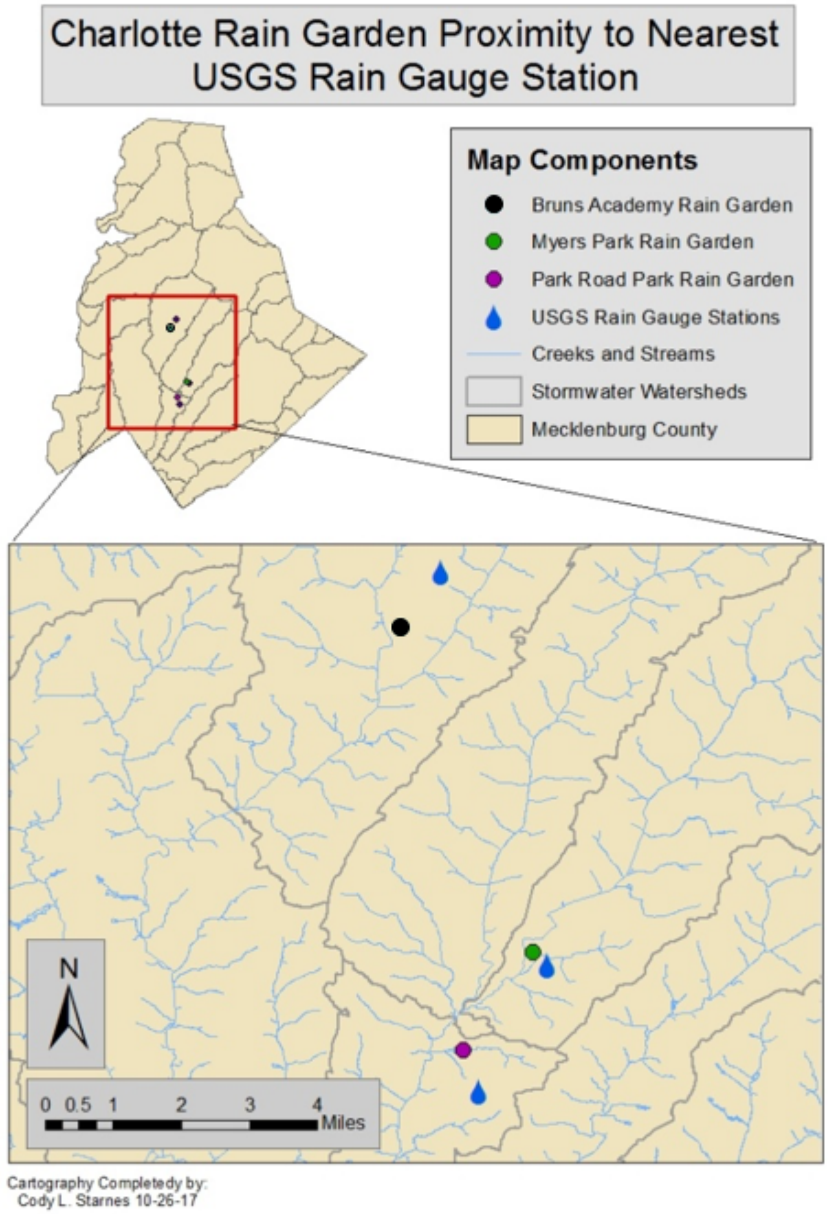


Figure 2: The locations of Rain Gardens and the corresponding USGS rain gauge locations.

Table 1: Site characteristics.

Site Name	Year Constructed	Age	Area (m^2)	Treatment Area (m^2)	Watershed	USGS Rain Gauge ID
Myers Park (MP)	2013	4	150	4000	Briar	351001080495845
Park Road (PR)	2010	7	350	4850	Lower Little Sugar	350823080505345
Bruns Academy (BR)	2002	15	250	4000	Irwin	351502080512045

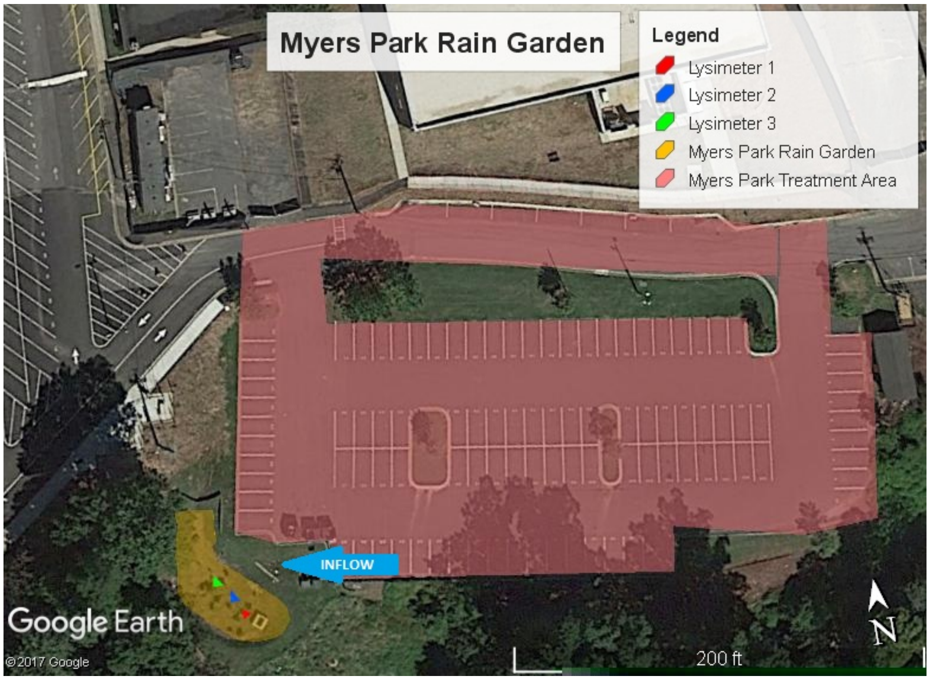


Figure 3: Rain Garden at Myers Park

Figure 4: Rain garden at Park Road Park

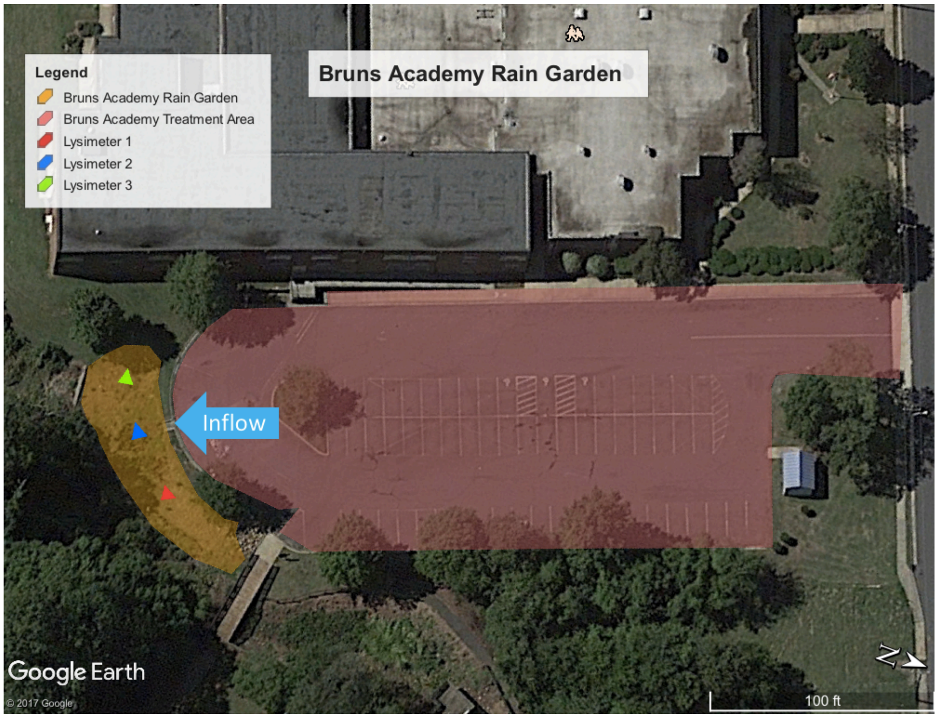


Figure 5: Rain garden at Bruns Academy

Each rain garden was constructed to the guidelines of the NCDEQ (2018) and Charlotte-Mecklenburg Storm Water Services (2014) design manuals and were designed to treat stormwater generated from an impervious parking lot adjacent an urban stream (Figure 6). The specific stormwater control measure design allows maximum runoff filtration, minimal erosion, and greater ecological availability in an urban environment. Furthermore, the City of Charlotte has collected composite inflow and outflow samples at each site for reporting purposes. The Myers Park site is the only site that is currently still being monitored by the City of Charlotte.

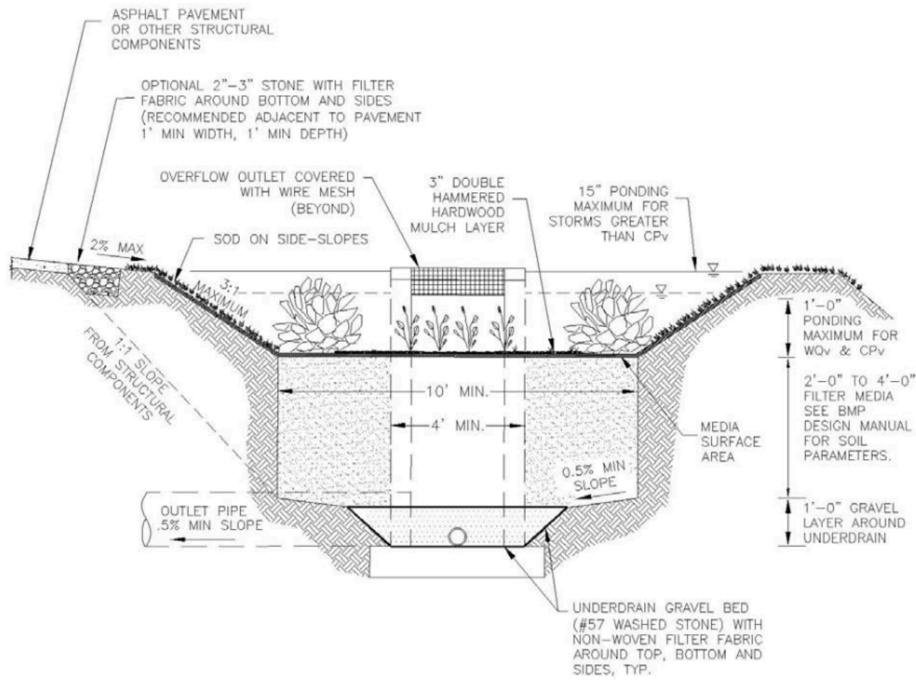


Figure 6: A cross section of a typical rain garden as diagramed in the Charlotte stormwater best management practices manual (Charlotte-Mecklenburg Storm Water Services 2014).

The study sites were constructed with long-term inflow monitoring structures installed to quantify runoff entering the rain garden across sites. Specifically, inflow and outflow 90-degree v-notch weirs were present. Bruns Academy did not have a weir due to vandalism; however, an inflow structure was present which funneled runoff to a specific entrance to the rain garden for sample collection.

Each study site was outfitted with three 24” 1900L Near Surface Samplers referred to as lysimeters (Appendix Figure 1). The lysimeters consist of a PVC body with a porous cup attached to its distal end. A rubber stopper attached to the exposed end at the surface sealed the lysimeter. A hand pump was used to create negative pressure (18mm/Hg) within the lysimeter which would draw water through the porous cup and was retained within the lysimeter. The soil water samplers were distributed evenly in the rain gardens to produce a total of three field replicates. Each site had lysimeters to the left of, centered within, and to the right of the bioretention cell inflow structure (Figures 3-5).

Throughout the sites, the lysimeters also served as reference points where additional data were collected. Soil moisture, denitrification, p-sorption, and infiltration rates were obtained within one meter of each lysimeter in every rain garden. Soil moisture was recorded at each site for one storm using a Hydrosense^{TM} soil moisture probe with a 20 cm probe rod. Readings were recorded prior to, and two times (within 24 and 48 hours) after the storm event. A total of four soil moisture readings were recorded at each lysimeter location to serve as sample replicates. These data were averaged and used to identify the variation of drainage responses at each site through the progression of the storm.

2.2 Sample Collection

A total of nine events were sampled during the summer, however, only the last three summer storm events were sampled at the Bruns Academy rain garden. Three storms were collected at each site from December 2017 to February 2018 to represent winter storm samples. Hydrological attributes of each storm event, such as quantity and duration of rainfall, were recorded at the nearest USGS rain gauge stations in 5-minute intervals (Table 2). Antecedent precipitation (AP_x) was calculated by adding the total precipitation in centimeters for *x* amount of days prior to the storm (Ali et al., 2010).

Multiple methods were used to collect the runoff samples including using Teledyne ISCO 6712 equipment, Nalgene Storm Water Samplers, and from hand collected samples of the first flush. Runoff samples were collected from Myers Park and Park Road park using a Teledyne ISCO 6712. A bubbler module was equipped and sample collection was triggered at a flow greater than 0.1 cubic foot per second. Once runoff was detected, three sequential first flush samples were acquired, followed by composite sampling designed to profile the rest of the storm's runoff. The composite sampling distributed six samples per bottle across a 10-minute interval. This sampling technique allowed the runoff to be assessed according to each hour of the storm's progression. Due to the absence of a weir at Bruns Academy, composite sampling was excluded and two Nalgene Storm Water Sampler bottles were used to collect the first flush at the site. Additionally, a hand grab sample of the rain garden underdrain outflow was collected if storm conditions were sufficient to sample.

Soil water was collected from the lysimeters using a kit consisting of a polyethylene tube, an Erlenmeyer flask, and a hand pump. The assembled collection kit was used to extract the volume of water collected in the porous cup of the lysimeter and the sample was transferred to a Nalgene bottle for short-term storage. All runoff samples were collected and filtered within 24 hours of the storm's end. Lysimeter sampling was completed within 24 and 48 hours of the storms, yielding two lysimeter samples per storm event at each lysimeter. Samples were then filtered through Whatman (GF/F; 0.7μm) glass microfiber filters. Once filtered, ammonium, nitrate, and phosphate samples were poured into a 50 mL centrifuge tube and frozen. DOC samples were poured into a 20 mL glass vial with no headspace and refrigerated.

Soil samples were collected at all three lysimeter locations within each rain garden for denitrification. Two samples at each lysimeter location were collected and composited into one sample approximately quarterly at 0-5 cm, and 5-10 cm depths. Soils were composited to increase the representativeness of overall soils adjacent to the lysimeters. Soil samples were refrigerated via dry ice and overnighted to Dr. Sara McMillan's laboratory at Purdue University. Once received, the samples were analyzed, which occurred within 48 hours of the initial collection.

2.3 Field and Laboratory Analysis

2.3.1 Sample Analysis

To complete the analysis for ammonia, the QuikChem® Method 10-107-06-1-C was implemented and has a detection limit of 4.0 µg/N. Nitrate/Nitrite concentrations were analyzed using the QuikChem® Method 10-107-04-1-A, which has a detection limit of 10.0 µg N/L. Orthophosphate was assessed using the QuikChem® Method 10-115-01-1-A method and has a detection limit of 10.0 µg P/L. DOC Samples were processed using the Shimadzu TOC-TN Analyzer Operational Procedure 2015 with a detection limit of 0.5 µg/L. Each site had three soil water samplers which served as three replicates for analysis. Additional sample replication was used to validate the results by rerunning five samples at the end of the sample query to confirm the instrument's output did not drift during the sample run. If sample analysis resulted in a negative value, the concentration was set to a value of 0. For this study, the values that fell between 0 and the analytical detection limit were left as reported by the initial analysis. Appendix Table 1 provides additional data with regards to the number of samples below the detection limit for each analysis.

2.3.2 Denitrification

Potential denitrification rates were measured using denitrification enzyme activity (DEA) assay for two depths (0-5, 5-10cm) at each lysimeter location. The DEA assay produced the potential denitrification rates by removing the limiting factors of denitrification (Smith et al., 1979). Denitrification was inhibited by acetylene (C_2H_2) and the production of nitrous oxide (N_2O) was measured as it is the end product with dinitrogen formation being blocked (Groffman et al., 2006). The production of N_2O was then measured as a peak area and converted to potential denitrification rates. The measurement conversions from N_2O area to potential denitrification rates were ascertained by adhering to methodology and considerations provided from previous authors (Groffman et al., 2006; Groffman et al., 1999; Smith, 1976).

Recorded N_2O peak areas were converted to volumetric concentrations of N_2O (µL/L) using an equation derived from a linear trendline of N_2O standards. The ideal gas law and Bunsen's coefficient (Equation 1) were used to convert the volumetric concentration of N_2O in the bottle to a mass of nitrogen (µg). The Bunsen coefficient accounts for the amount of dissolved N_2O in solution as well as N_2O in the headspace of the bottle. An additional linear line of fit was used to identify the slope of the relationship between the mass of nitrogen versus time (hr) at each site. This slope (µg/hr) was divided by the sample dry mass (µg) to produce the final potential denitrification value as µg/gDM/hr (Groffman et al., 2006; Groffman et al., 1999; Smith, 1976).

Equation 1. $$M = C_g \times (V_g + V_l \times \beta)$$

M= Total amount of N_2O in the water plus gas phase
C_g= Concentration of N_2O in the gas phase
V_g= Volume of the gas phase
V_l= Volume of the liquid phase
β=Bunsen coefficient (1.06 at 05°C; 0.882 at 10°C; 0.743 at 15°C; 0.632 at 20°C; 0.544 at 25°C; 0.472 at 30°C)

2.3.3 Phosphorus Sorption

Phosphorus sorption batch experiments were completed at each rain garden by compositing soil samples from each lysimeter location into two samples according to depth (0-5 and 5-10 cm). The two targeted values from this experiment were the equilibrium phosphorus concentration (E.P.C.), and the phosphorus adsorption index (P.A.I.). The procedure for the phosphorus batch experiments was adapted from Taylor et al. (1971). Soil samples were air dried and stored at 25°C. Three grams of soil was equilibrated for one hour in 25 mL of various concentrations (0, 10, 20, 50, 100, 200, 500, and 2000 μg P/L) of an anhydrous potassium phosphate monobasic (KH_2PO_4) solution. During the hour of equilibration, the samples were disturbed using a shaker table for 30 seconds every 10 minutes. Once complete, the samples were filtered with a GF/F filter and analyzed for orthophosphate (mg/L) using the Lachat.

To find the E.P.C. the final concentration of phosphorus in solution was plotted against the amount of phosphorus sorbed to the soil (Equation 2) which created an isotherm. The isotherm was then fitted by a linear trendline which was then solved to identify the specific concentration at which phosphorus was in equilibrium (Bache et al., 1971; Beckett et al., 1964; Meyer, 1979; Taylor et al., 1971). The P.A.I. was calculated (Equation 3) and provided a perspective of how much phosphorus the soil was capable of sorbing (Bache et al., 1971).

Equation 2. $$X_s = (s - c) \times F$$

X_s= Sorbed P at working solution concentrations (μg P/g soil)
s= μg P/mL of original working solution
c= μg P/mL in equilibrium solution
F= mL working solution/ g dry soil.

Equation 3. $$P.A.I. = \frac{X}{\log{(c)}}$$

X= Phosphorus adsorbed from initial concentration of 2000 μg P/L solution
c= Final concentration of phosphorus μg P/L after equilibration

2.3.4 Hydraulic Conductivity and Infiltration Rates

To quantify infiltration rates and conductivity of rain garden soils, a double ring infiltrometer, and a Guelph permeameter were used. Infiltration is the term used to identify water penetrating the surface of the ground (Soilmoisture Equipment Corp, 2009). The double ring infiltrometer simulates the infiltration rates in localized areas as if storm conditions were present. The Guelph permeameter was used to identify the field saturated hydraulic conductivity of the rain garden soils at various depths.

The double ring infiltrometer was installed by driving the rings 5 cm into the substrate. A ruler was fixed to the inner wall of the smallest ring to record the infiltration rate (length/time). The outer ring was filled to a depth of 10 cm, followed by the inner ring. The double ring technique ensures the downward movement of water into the soil while minimizing lateral spreading. Measurements were taken every 1 cm decrease in the water level of the inner ring. The rings were not allowed to go dry during the testing period and were gently filled back to the 10 cm mark once the inner ring dropped below 3 cm. The water level was kept at the same height in both of the rings to ensure water from one ring does not laterally move from the outer ring inward, or from the inner ring outward. Testing occurred until a steady state of flow was reached, or until water availability constrained the length of testing. Upon conclusion of testing, the infiltration rate was determined by the constant time interval between identical decreases in unit (cm) head (Soilmoisture Equipment Corp, 2009).

A Guelph permeameter was used to measure the field saturated conductivity (K_{sat}) value at various depths (10, 20, 30, and 50 cm) in the rain garden. The K_{sat} measurements were completed in areas of the rain garden that were visually identified during storms as having ponding and no ponding. Myers Park high school was the only rain garden that ponds across the entire area during a storm event. The K_{sat} experiment for the non-ponded sample was completed in the area that was the last to pond during the storm. The assembly and procedure were completed according to the operating instructions listed in the permeameter manual (Soilmoisture Equipment Corp, 2012). As boreholes were augured to create wells, a well prep brush was inserted and removed to minimize the smearing effect of the auger and return the soils to a natural state. Once assembled the permeameter was lowered to into the well and the reservoirs were filled leaving no void space. Due to the increased conductivity of the sites, both reservoirs were used in the experiment to prolong data collection and increase accuracy. The test was initiated by raising the air tube to a pre-determined well height (5cm and 10cm). The permeameter operates according to the Marriotte's Principle allowing a constant head to be created in the well (Soilmoisture Equipment Corp, 2012). As water in the well drops below the height of the well tube, air is released into the reservoir and the vacuum is temporarily relieved causing the well to stay at a constant height. Consequently, the water in the soil creates a bulb that allows the flow of water from the well to reach a steady state. To observe this, the decrease in height of the water column was documented in cm throughout the application.

At each depth, the steady state of water flowing from the permeameter was completed using two well head heights. These values were then used in Equation 4 or Equation 5 to obtain a final K_{sat} value. Equation 4 provided a K_{sat} value for the one head combined reservoir method and Equation 5 was the method used for the two head combined reservoir method (Soilmoisture Equipment Corp, 2012; Zhang et al., 1998). Few sites produced a negative K_{sat}, in which case a single head method was calculated to obtain the K_{sat} value (Reynolds, 2007; Reynolds et al., 1986; Soilmoisture Equipment Corp, 2012; Zhang et al., 1998).

Equation 4. $$K_{sat}=\frac{C_1\times Q_1}{2\pi H_1^2+\pi\alpha^2 C_1+2\pi(\frac{H_1}{\alpha^*})}$$

C_1= Shape factor (Equation 4b)
Q_1= Steady-state of flow (cm/sec)
α = Borehole radius (cm)
α^*= Microscopic capillary length factor due to soil texture (0.36)
H_1= Height of the water in the well

Where: $$C_1 = \left(\frac{H_1/\alpha}{2.074+0.093\left(H_1/\alpha\right)}\right)^{0.754}$$

C_1= The shape factor used in equation 4
H_1= Height of water within the well and
α= Borehole radius (cm)

Equation 5. $$K_{sat} = G_2Q_2 - G_1Q_1$$

Where: $$G_1 = \frac{H_2C_1}{\pi(2H_1H_2(H_2-H_1)+\alpha^2\,(H_1C_2-H_2C_1)}$$

And: $$G_2 = \frac{H_1C_2}{\pi(2H_1H_2(H_2-H_1)+\alpha^2\,(H_1C_2-H_2C_1)}$$

C = Shape factor for borehole heights 1 and 2 (see below)
Q= Steady-state of flow (cm/sec) for the borehole heights 1 and 2
H= Height of water in the borehole for runs 1 and 2 (cm)
α = Borehole radius (cm)

Where: $$C_1 = \left(\frac{H_1/\alpha}{2.074+0.093\left(H_1/\alpha\right)}\right)^{0.754}$$

And: $$C_2 = \left(\frac{H_2/\alpha}{2.074+0.093\left(H_2/\alpha\right)}\right)^{0.754}$$

C= Shape factors.
H= Heights of the water within wells 1 and 2
α= represents the borehole radius (cm)

2.3.5 Vegetation identification

Vegetation was surveyed once on July 13th, 2018 to identify typical vegetation found in the bioretention cells. To complete this survey, the Charlotte BMP manual planting list was referenced to identify vegetation. Vegetation identifications were noted to species if possible, if a species was unable to be identified it was generalized into the categories of grasses, shrubs, trees and other. A ¼ m^2 quadrat was randomly placed near each lysimeter throughout the rain garden to obtain a sample of the vegetation present (Hawrot et al., 2017). The identification and qualitative assessment using Shannon's diversity index (Shannon et al., 1949) of the vegetation in the rain gardens served as a preliminary inquiry into the vegetation present and could be expanded upon in future research.

2.4 Data Analysis

Differences in the overall concentrations of each constituent with respect to the runoff and soil water relationship were analyzed using a t-test. Specifically, this gathered the overall average values runoff and soil water values of each constituent at each site and identified if the values were significant. *P*-values below 0.05 were identified as significant. To identify the differences in concentrations for each constituent across the various seasons, the samples were divided into summer and winter storms and the t-tests were used for both. Two-way ANOVA was used to identify the effects of site, season, and the cross between the two on each constituent for runoff, soil water, and percent retention. Once significant values were identified, a Post hoc Tukey was used to identify which significant relationships were present.

In addition, multivariate and correlation analysis were also completed with multiple variables to identify how hydrological variables impacted percent retention. Additional bivariate analysis was used to obtain a *p*-value from two continuous variables that were plotted together. For data analysis involving potential denitrification rates, t-tests were used for testing the significance of potential denitrification rates at different depths, as well as different depths within each site specifically.

Lastly, the potential limitations of this research include the nutrient retention analysis assuming the soil water concentrations would be reflective of what would likely leave the rain garden system as well. The nutrient retention in this study is completed with the ratio of the soil water concentrations opposed to the traditional calculation of outflow concentrations. Also, the infiltration and hydraulic conductivity rates could be an overestimate of the actual infiltration and conductivity rates. Lastly, the sorption batch experiments used concentrations of solution that may have been too low and increased concentrations would help increase the confidence in the equilibria obtained.

Results

Through both seasons, hydrological variables pertaining to rainfall mirrored each other from site to site (Table 2). Each site experienced similar seasonal rainfall due to the proximity of the rain gardens. The average precipitation for all sites combined was lower for summer storms (2.03 cm/day) than winter storms (3.10 cm/day). The average duration of summer storms was approximately 2 to 4 hours less than the winter storms for each site. Additionally, antecedent precipitation was lower in the winter months suggesting longer periods between rain storms than summer storms. The only category that differentiated significantly between sites for the same season was maximum intensity (in/hr) during summer storms. A table of hydrological variables by individual storm events can be found in Appendix Table 2.

Table 2: Summary of the hydrological variables for the study. AP_x represents the antecedent precipitation value where x = number of days.

Hydrological Variables	MP Summer	MP Winter	PR Summer	PR Winter	BR Summer	BR Winter
Storms per season	8	3	8	3	3	3
Number of Runoff Samples	37	24	37	24	6	14
Number of Soil Water Samples	40	16	36	14	8	11
Average Precipitation (cm/day)	1.77	3.26	2.13	3.20	2.16	2.85
Average Duration (hr/day)	2.37	6.91	2.54	6.89	4.41	6.36
Average Max intensity (cm/hr)	0.99	0.84	1.24	0.74	0.46	0.74
Average AP_2 (cm)	0.58	0.10	0.71	0.10	0.51	0.08
Average AP_7 (cm)	2.16	2.08	2.08	2.11	1.45	1.73
Average AP_{14} (cm)	4.14	2.84	4.42	2.87	3.35	2.26

Soil moisture measurements were observed for one storm in February 2018. The average soil moisture percentages were recorded within 24, and 48 hours of the storm event. The average difference between one and two days post-storm was 1.28% drier for the latter collection. Between sites, Myers Park had an average of 2.13%, Park Road had an average of 0.53%, and Bruns Academy had an average of 1.2 % difference from 24 to 48 hours after the storm (Table 3). Since there were greater differences in percent soil moisture across sites and not between sample dates, both sample dates were averaged to identify site soil moisture for the storm event. Overall mean percent soil moisture was 37.3% at MP, 30.6% at PR, and 41.7% at BR for averaged 24 and 48 hour soil moisture measurements.

Table 3: Percent soil moisture data associated with the 2/4/18 storm. The "R" cells correspond to samples that were measured as the 48 hr post-storm.

Location	Storm date	Measured date	Average Soil Moisture (%)
MP 1	2/4/18	2/5/18	30.6
MP 1 R	2/4/18	2/6/18	31.0
MP 2	2/4/18	2/5/18	30.4
MP 2 R	2/4/18	2/6/18	29.8
MP 3	2/4/18	2/5/18	36.6
MP 3 R	2/4/18	2/6/18	38.6
PR 1	2/4/18	2/5/18	31.2
PR 1 R	2/4/18	2/6/18	30.4
PR 2	2/4/18	2/5/18	31.8
PR 2 R	2/4/18	2/6/18	30.0
PR 3	2/4/18	2/5/18	29.6
PR 3 R	2/4/18	2/6/18	30.6
BR 1	2/4/18	2/5/18	40.6
BR 1 R	2/4/18	2/6/18	38.0
BR 2	2/4/18	2/5/18	50.8
BR 2 R	2/4/18	2/6/18	51.8
BR 3	2/4/18	2/5/18	35.6
BR 3 R	2/4/18	2/6/18	33.6

3.1 Nutrient Retention

Nutrient concentrations for runoff and soil water were averaged across all storms and the overall mean concentrations (Table 4) and seasonal concentrations (Table 5) are summarized. Additionally, runoff values in Table 4 and Table 5 were averaged from first flush and composite runoff concentrations using data from every storm (except for Bruns Academy which was only First Flush). The one-way ANOVAs used to complete each of these analysis used every collected value for each storm to calculate the overall mean concentrations. Ammonium runoff concentration values ranged from 0.062- 0.122 mg N/L, while soil water values ranged from 0.012-0.027 mg N/L. Myers Park was the only site that did not have a statistically significant difference between runoff and soil water concentrations ($p = 0.058$). Even with a non-significant p-value between Myers Park runoff and soil water, the runoff concentration was almost twice the concentration of the soil water. Nitrate values for runoff were consistent with values ranging from 0.170-0.207 mg N/L. While these values were similar, the soil water concentrations varied with average values of 0.279, 0.424, and 2.748 mg N/L at Myers Park, Park Road, and Bruns Academy. When comparing these values Park Road was the only site that did not provide a statistical difference between the runoff and soil water concentrations. The relationship between nitrate and ammonium presented opposing trends as ammonium decreased from runoff to soil water at every site, while nitrate concentrations in the soil water increased. Phosphate at each site varied in comparison of runoff to soil water phosphorus between sites and yielded no consistent trends or differences among concentrations. DOC was significantly higher in soil water than parking lot runoff at Myers Park and Park Road having overall concentrations ranging from 5.59- 9.33 and 7.73-14.02 mg/L for runoff and soil water. Bruns Academy had a slight decrease in DOC concentration (8.78 mg/L to 7.73 mg/L) from average runoff to soil water concentrations.

Table 4: Overall average concentrations (mg/L) for surface runoff and soil water across all storms at each site. Significance was determined using a one-way ANOVA. Significant values identified with gray shading and bold text are $p<0.05$.

Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)
Myers Park:					
NH_4^+	Runoff	61	0.064	0.078	0.058
	Soil water	53	0.037	0.069	
NO_3^{2-}	Runoff	61	0.207	0.044	**0.002**
	Soil water	41	0.424	0.053	
PO_4^{3-}	Runoff	61	0.030	0.034	0.714
	Soil water	42	0.032	0.027	
DOC	Runoff	61	5.59	3.95	**0.001**
	Soil water	36	9.09	4.33	
Park Road:					
Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)
NH_4^+	Runoff	58	0.062	0.094	**0.004**
	Soil water	47	0.021	0.025	
NO_3^{2-}	Runoff	58	0.170	0.155	0.110
	Soil water	45	0.279	0.485	
PO_4^{3-}	Runoff	58	0.018	0.025	**0.003**
	Soil water	45	0.007	0.005	
DOC	Runoff	58	9.33	8.16	**0.003**
	Soil water	44	14.0	7.32	
Bruns Academy:					
Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)
NH_4^+	Runoff	14	0.122	0.095	**0.001**
	Soil water	25	0.012	0.015	
NO_3^{2-}	Runoff	14	0.179	0.149	**0.001**
	Soil water	21	2.75	2.41	
PO_4^{3-}	Runoff	14	0.035	0.034	**0.041**
	Soil water	21	0.082	0.078	
DOC	Runoff	14	8.78	6.78	0.615
	Soil water	14	7.73	3.71	

Table 5: Overall seasonal average concentrations (mg/L) for surface runoff and soil water across all storms at each site. Significance was determined using a one-way ANOVA. Significant values identified with gray shading and bold text are $p<0.05$.

Summer Samples						**Winter Samples**					
Myers Park:						Myers Park:					
Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)	Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)
NH_4^+	Runoff	37	0.041	0.039	0.088	NH_4^+	Runoff	24	0.099	0.107	0.322
	Soil water	37	0.025	0.038			Soil water	16	0.064	0.109	
NO_3^{2-}	Runoff	37	0.214	0.179	**0.001**	NO_3^{2-}	Runoff	24	0.195	0.123	0.990
	Soil water	34	0.478	0.546			Soil water	8	0.196	0.143	
PO_4^{3-}	Runoff	37	0.027	0.038	0.262	PO_4^{3-}	Runoff	24	0.033	0.005	0.071
	Soil water	34	0.036	0.026			Soil water	8	0.014	0.009	
DOC	Runoff	37	4.88	2.54	**0.001**	DOC	Runoff	24	6.68	1.03	0.476
	Soil water	32	9.63	4.28			Soil water	4	4.71	2.52	
Park Road:						Park Road:					
Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)	Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)
NH_4^+	Runoff	37	0.057	0.101	**0.024**	NH_4^+	Runoff	21	0.072	0.082	0.112
	Soil water	34	0.016	0.014			Soil water	13	0.032	0.039	
NO_3^{2-}	Runoff	37	0.136	0.121	0.098	NO_3^{2-}	Runoff	21	0.230	0.191	0.887
	Soil water	33	0.293	0.558			Soil water	12	0.239	0.184	
PO_4^{3-}	Runoff	37	0.019	0.028	**0.025**	PO_4^{3-}	Runoff	21	0.017	0.017	**0.018**
	Soil water	33	0.008	0.005			Soil water	12	0.004	0.002	
DOC	Runoff	37	7.72	4.58	**0.001**	DOC	Runoff	21	12.2	11.77	0.631
	Soil water	32	14.0	6.29			Soil water	12	14.1	9.88	
Bruns Academy:						Bruns Academy:					
Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)	Nutrient	Runoff / Soil water	Number of samples	Mean (mg/L)	Standard deviation (mg/L)	Significance (*p*-value)
NH_4^+	Runoff	6	0.066	0.064	**0.002**	NH_4^+	Runoff	8	0.163	0.096	**0.001**
	Soil water	14	0.007	0.008			Soil water	11	0.019	0.020	
NO_3^{2-}	Runoff	6	0.205	0.164	**0.001**	NO_3^{2-}	Runoff	8	0.159	0.144	**0.022**
	Soil water	13	3.91	2.35			Soil water	8	0.864	0.761	
PO_4^{3-}	Runoff	6	0.028	0.021	0.082	PO_4^{3-}	Runoff	8	0.040	0.042	0.506
	Soil water	13	0.101	0.094			Soil water	8	0.051	0.022	
DOC	Runoff	6	9.58	5.29	0.709	DOC	Runoff	8	8.18	8.02	0.503
	Soil water	10	8.70	3.94			Soil water	4	5.31	1.40	

The seasonal differences in rain garden nutrient processing presented multiple trends. Primarily, the ammonium present in runoff and soil water concentrations was higher during winter storms at every site compared to summer storms. Specifically, there was a significant increase at Myers Park and Bruns Academy for runoff across seasons (*p*= 0.0175, 0.0428 for MP and BR). While there were higher soil water concentrations in the winter, there was no significant increase across sites for seasonal soil water differences. Inversely, nitrate was lower in winter storms for all types of samples at each site with the exception of Park Road runoff and soil water. The summer values for nitrate runoff were approximately half of the soil water values except of Bruns Academy which had much larger soil water concentrations (Myers Park runoff = 0.214 mg/L, soil water = 0.478 mg/L, Park Road runoff = 0.136 mg/L, soil water 0.293 mg/L, and Bruns Academy runoff = 0.205 mg/L, soil water = 3.91 mg/L as seen in Table 5). The runoff to soil water concentrations were almost identical in the winter storms at Myers Park and Park Road Park (MP runoff = 0.195 mg/L, soil water = 0.196 mg/L, PR runoff = 0.230 mg/L, soil water =0.239 mg/L, and BR runoff = 0.159 mg/L, soil water = 0.864 mg/L as seen in Table 5). The number of significantly different results also differed from summer to winter. Summer storms presented a total of seven significant differences from runoff to soil water between sites, while winter storms had three significant differences. Most of the significant differences occurred at the Myers Park and Park Road sites. Specifically, there were five significantly different storms during the summer between the two sites and only one during the winter storms.

While the findings presented represent the overall means for each constituent and site, a two-way ANOVA was completed for each constituent to understand its response to site, season, and the interaction between the site and season (Table 6). To further explore runoff concentrations, the average runoff of each individual storm was used, rather than every sample individually. Using storm means in this scenario allowed the variance to be less affected by the unequal number of samples for the runoff. Due to a more equal number of samples for soil water collection at each site, each individual soil water sample was used when comparing the soil water samples in the two-way ANOVA. In addition, there was no significant difference between the soil water values from one day to two days post-storm event for each nutrient. With this lack of significance, the soil water values collected on both days were used as replicates in the soil water section of the two-way analysis. The mean runoff and mean soil water concentrations from each storm were used to obtain a percent retention of each individual storm (equation 6). This retention value identified the percent of soil water that was retained from the initial inflow concentration for each storm. A positive percent retention value signified an uptake of the nutrient in the rain garden, while a negative value indicated the release of the nutrients from the structures. Mean runoff values for each storm were not significantly different between site, season, or a cross between the two for any of the nutrients that were analyzed (Table 6). Therefore, the results presented hereafter analyze the soil water and percent retention findings that were statistically significant. The understanding of these significant relationships was furthered by the completion of a pairwise comparison of least squares using the Tukey-Kramer Honestly Significant Difference test (referred to as Tukey HSD).

Equation 6. $$\left(\frac{Runoff - Soil\ Water}{Runoff}\right) \times 100$$

Table 6: Summary of the two-way ANOVA results for each constituent. Significant values ($p < 0.05$) are highlighted in gray shading and bold text.

Constituent	Focus	Site	Season	Cross
Ammonium	Runoff	0.7561	0.4161	0.4767
	Soil Water	**0.0201**	**0.0201**	0.4277
	Retention	0.4065	0.4322	0.3145
Nitrate	Runoff	0.9930	0.8510	0.8211
	Soil Water	**<0.0001**	**<0.0001**	**<0.0001**
	Retention	**0.0004**	**0.0013**	**0.0107**
Phosphate	Runoff	0.8287	0.8729	0.6100
	Soil Water	**<0.0001**	**0.0035**	0.0829
	Retention	**0.0134**	0.0579	0.3096
DOC	Runoff	0.1224	0.4433	0.8318
	Soil Water	**<0.0001**	0.1096	0.3399
	Retention	0.1827	**0.0213**	0.1062

Soil water ammonium concentrations were significant for both site and season ($p<0.05$). The average soil water was significantly different between Myers Park (0.04 mg/L) and Bruns Academy (0.01 mg/L). Park Road was the location that did not significantly differ from either site with a mean value of (0.02 mg/L) (Figure 7A). In addition to site significance, seasonality yielded a lower amount of ammonium in the summer storms compared to the winter storms (Figure 7B). The average summer soil water with regards to ammonium was 0.02 mg/L, while the average winter concentration was 0.04 mg/L.

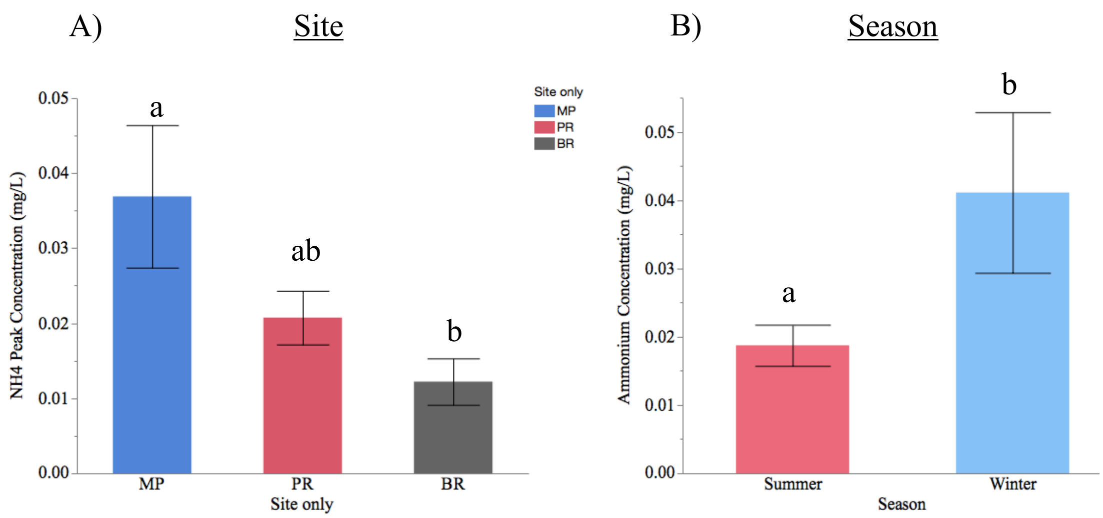


Figure 7: A) The results of the two-way ANOVA Tukey HSD test for site. Site had n value of 53,47, and 25 for MP, PR, and BR. B) The results of the two-way ANOVA Tukey HSD test for season. Seasonal n values were 85 for summer and 40 for winter. Significance level for both analysis was set at $p<0.05$.

Soil water nitrate values were identified as significant for the difference between all of the explanatory variables. The Bruns Academy site had a significantly higher concentration of 2.75 mg/L than the 0.40 mg/L at Myers Park and the 0.28 mg/L at Park Road Park ($p<0.05$). The summer mean soil water nitrate value of 0.96 mg/L (n=80 samples) was significantly higher compared to the mean winter soil water nitrate value of 0.41 mg/L (n=28 samples). The cross between the site and season found that the Bruns Academy site during the summer had a significantly different amount of soil water nitrate compared to all other sites and seasons (p-value <0.05) and is displayed in Figure 8 (as well as Appendix Figure 2 which displays an LS Means plot). The cross confirms that most of the significance between the previously discussed soil nitrate for site and season individually was due to the summer sample at Bruns Academy being so large at 3.91 mg/L for 14 samples.

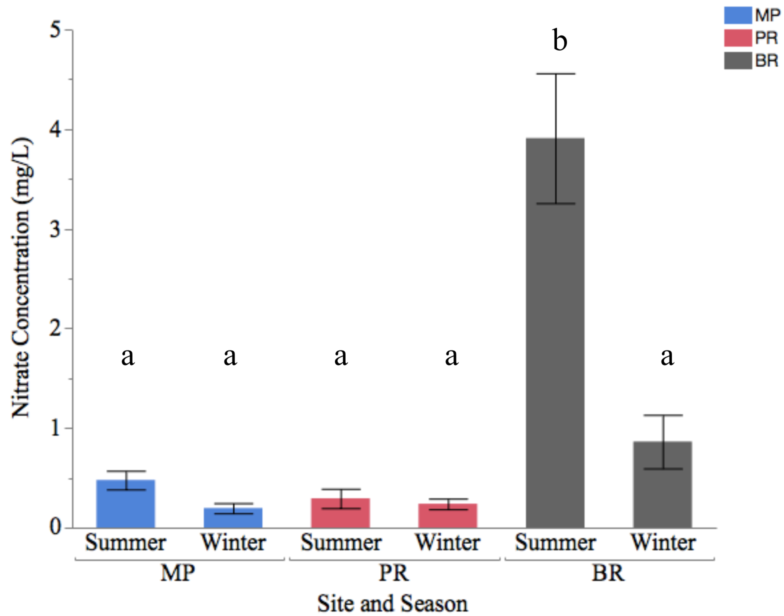


Figure 8: The Tukey HSD test result of the cross between site and season's effect on nitrate concentrations (mg/L). *p*-value <0.0001. Average mean values of 0.48 for MP Summer (n=34), 0.20 for MP Winter(n=8), 0.29 for PR Summer (n=33), 0.24 for PR Winter (n=12), 3.91 for BR Summer (n=13), 0.86 for BR Winter (n=8).

The soil water nitrate values of retention closely mimic the values of the significance for the soil water nitrate previously discussed. Because soil water concentration was used to calculate the overall percent retention of nitrate, the soil water effect on nitrate was also observed in retention. This specifically resulted in Bruns Academy having a highly negative mean retention value of -674% (Figure 9). Like soil water, Bruns Academy summer percent retention likely caused the site, and season to also be significant within the two-way ANOVA. Additionally, Appendix Figure 2 includes the LS-means plot for the Tukey HSD test.

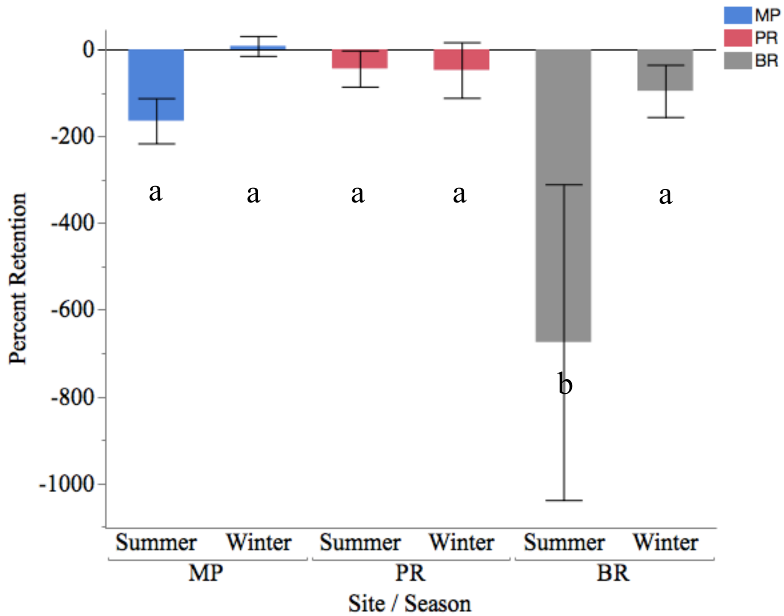


Figure 9: The results of the Tukey HSD test cross of site and season on percent retention. (p-value <0.05). Mean values are -164% for MP Summer (n=8), 8% for MP Winter (n=3), -44% for PR Summer (n=8), -47% for PR Winter (n=3), -674% for BR Summer (n=3), -96% for BR Winter (n=3).

The phosphate in soil water between sites was significantly different ($p<0.05$) from site to site (Figure 10A). The Bruns Academy site had the highest soil phosphate concentrations with a mean value of 0.082 mg/L (n=21). This concentration was followed by Myers Park having a mean concentration of 0.032 mg/L (n=42), and Park Road with 0.007 mg/L (n=45). The seasonal comparison yielded summer phosphate in soil water was significantly higher than winter phosphate in soil water (Figure 10B). Average summer samples measured 0.04 mg/L (n=80), while winter samples measured 0.02 mg/L (n=28).

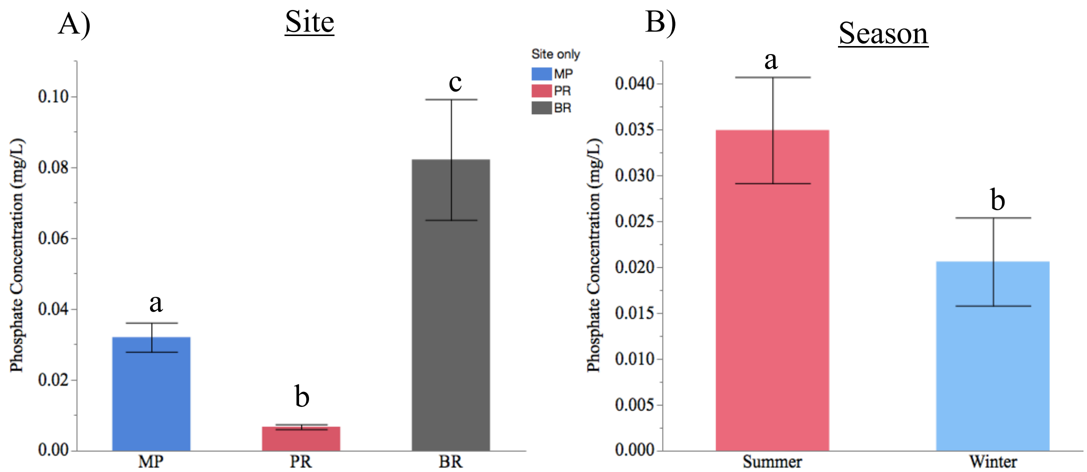


Figure 10: Represents the Tukey HSD test that was completed after the two-way ANOVA identified site (A) and season (B) were significantly different from in soil water phosphate concentrations.

Phosphate retention was only significant in the two-way ANOVA between sites (Figure 11). Park Road and Bruns Academy were identified as being significantly different from each other. Park Road was the only site to have a positive percent retention for phosphate with a value of 50.6%, signifying phosphate was taken up by the rain garden. The Myers Park was not statistically different from either site with a mean percent retention of -92.5%, while BR had an average retention value of -208.2%.

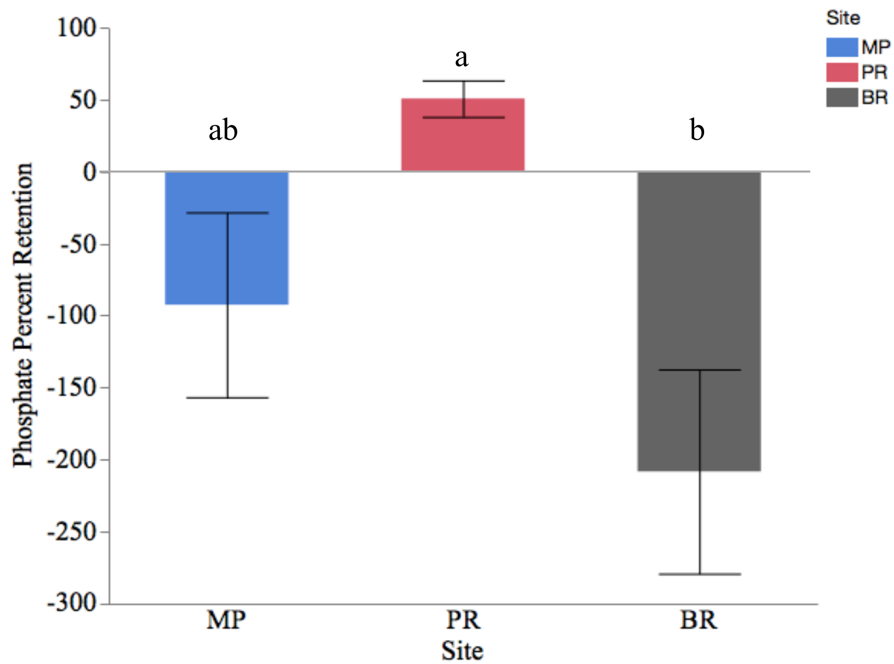


Figure 11: Identification of how sites differ with respect to phosphate retention. Significance was determined by a *p*-value <0.05, n=11,11, 6 for MP, PR, and BR.

The initial two-way ANOVA showed differing values for DOC soil water by site, as well as DOC percent retention across seasons. The results showed the DOC was significantly higher at Park Road compared to the other two sites (Figure 12A). Mean Park Road soil water DOC was 14.0 mg/L (n=44), while MP and BR were 9.1 mg/L (n=36), and 7.7 mg/L (n=14) respectively. Additionally, with regards to DOC retention, seasonal differences were also identified (Figure 12B). The summer DOC (-85.7%, n=19), retention was significantly more negative than for winter storms (-2.8%, n=9). DOC accumulated in the soil during the summer, while runoff and soil water were almost identical during the winter.

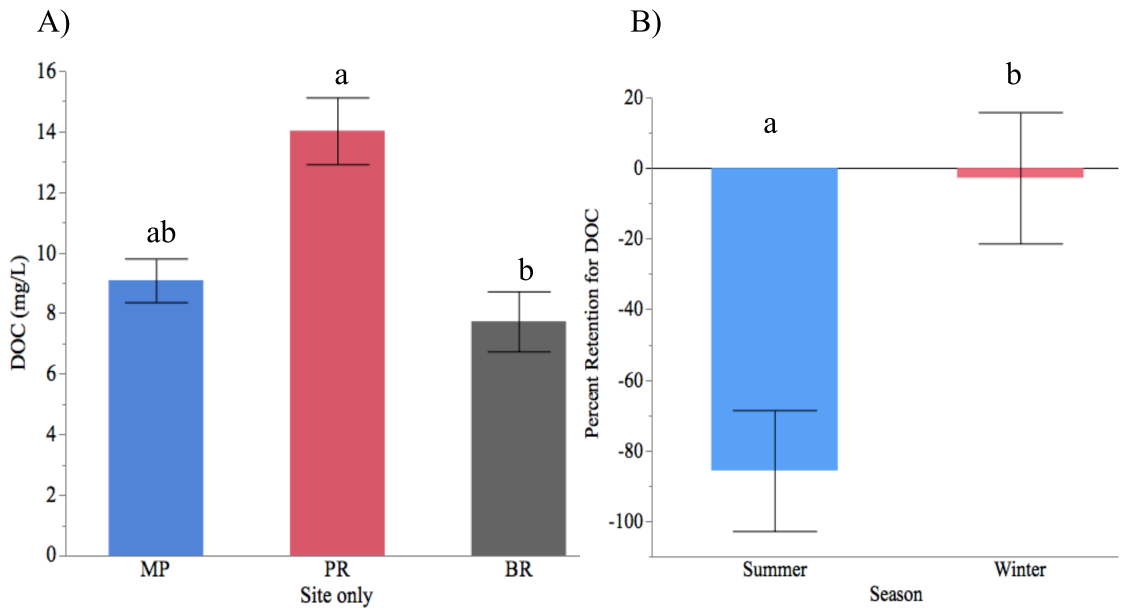


Figure 12: A) Site differences for soil water DOC. MP=8.46 mg/L, PR= 14.1 mg/L, BR= 6.88 mg/L with n= 11, 11, and 6 for MP, PR and BR Respectively. B) Seasonal differences of percent reduction for DOC. Summer retention = -85.7% while winter retention = -2.76%, n=19 and 9 for summer and winter.

3.2 Denitrification

When assessing denitrification with both depths aggregated together, there was a significant difference between the sites, but not between seasons or the interaction between the two (Table 7). Bruns Academy had the highest denitrification rates 0.65 µg/g DM/hr followed by Myers Park 0.40 µg/g DM/hr and Park Road 0.12 µg/g DM/hr (Figure 13).

Table 7: Two-way ANOVA testing for the effect of site, season, and the cross between the two on potential denitrification rates.

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Site	2	2	2.5006657	16.8744	<0.0001
Season	2	2	0.4322789	2.9170	0.0644
Site*Season	4	4	0.2176037	0.7342	0.5735

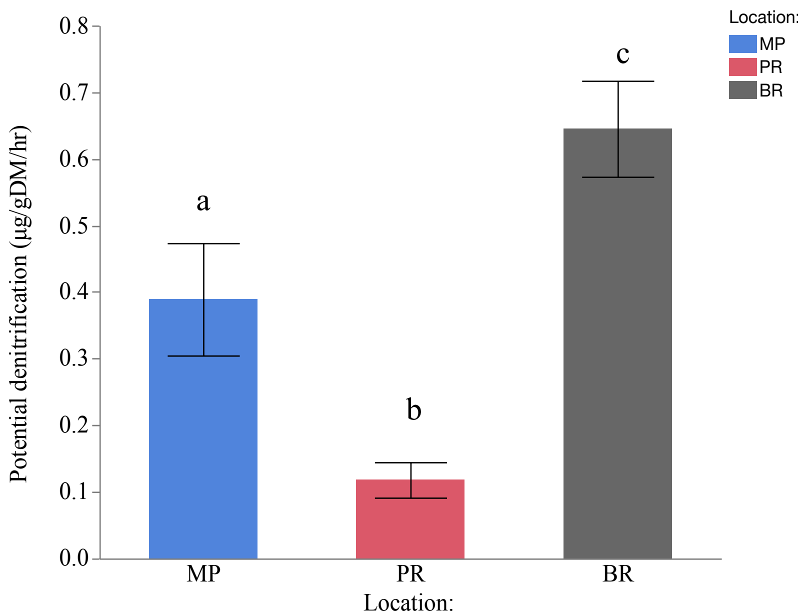


Figure 13: One-way ANOVA of potential denitrification values at each site. Significance identified by *p*-values <0.05. Means were 0.40, 0.12, and 0.65 for MP, PR, and BR respectively. n= 18 for each site. Specific *p*-values were <0.0001 for BR & PR relationship, 0.0145 for MP & PR, and 0.0222 for BR & MP.

An additional two-way ANOVA was used to explore the relationship between potential denitrification rates with the explanatory variables of depth and location. The results from the tests conclude that the 0-5 and 5-10cm depths, locations, and the interaction between the depths and locations were all significant ($p<0.05$) (Table 8).

Table 8: Two-way ANOVA results for depth, location, and the cross between them for denitrification values.

Source	**Nparm**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
Depth: (cm)	1	1	1.49	41.4533	<0.0001
Location:	2	2	2.50	34.8704	<0.0001
Location:*Depth: (cm)	2	2	0.78	10.8311	0.0001

Upon exploration of the first significant difference between depths, denitrification rates were significantly higher (p=0.0003) in the 0-5 cm depth of the rain gardens (Figure 14). The 0-5 cm depth had mean value of 0.55 µg/gDM/hr while the 5-10cm depth had a value of 0.22 µg/gDM/hr for the 5-10 cm depth. When the different depths were compared at each individual site, Myers Park and Bruns Academy had significantly higher rates at the 0-5 cm depth (p<0.0001 at Myers Park, p=0.0014 at Bruns Academy) compared to the 5-10 cm depth. The values reported from Park Road were similar with a 0-5 cm average value of 0.12 µg/gDM/hr, and a 5-10 cm average of 0.11 µg/gDM/hr. Figure 15 reports the values for overall site potential denitrification.

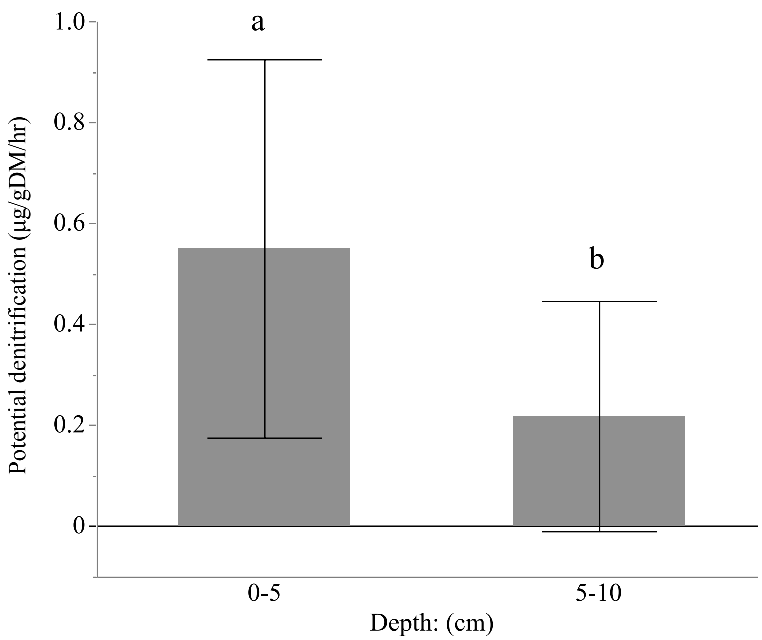


Figure 14: The average denitrification rate (µg/g DM/hr) at depths 0-5cm and 5-10cm. p<0.001 n=27 for each depth

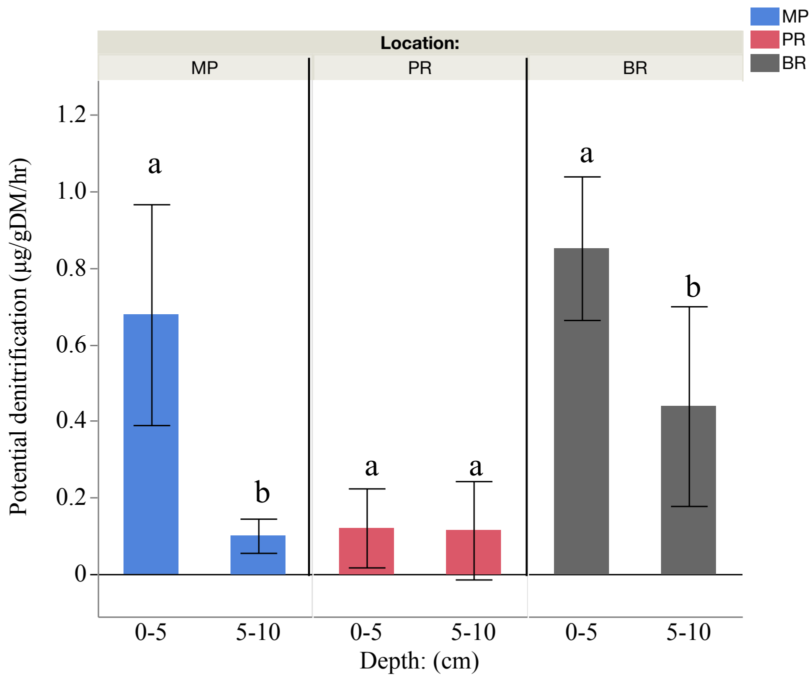


Figure 15: Potential denitrification differences between depths at each site. Pictured in order form left to right is Myers Park, Park Road Park, and Bruns Academy.

To finalize the understanding of the two-way ANOVA in Figure 15, a Tukey HSD analysis was completed (Figure 16) to understand the effect of the cross between site and depth on potential denitrification rates ($p<0.0001$). The findings showed a significant difference between depths at Myers Park and Bruns Academy, as well as an overall significant difference between Bruns Academy and Park Road Park.

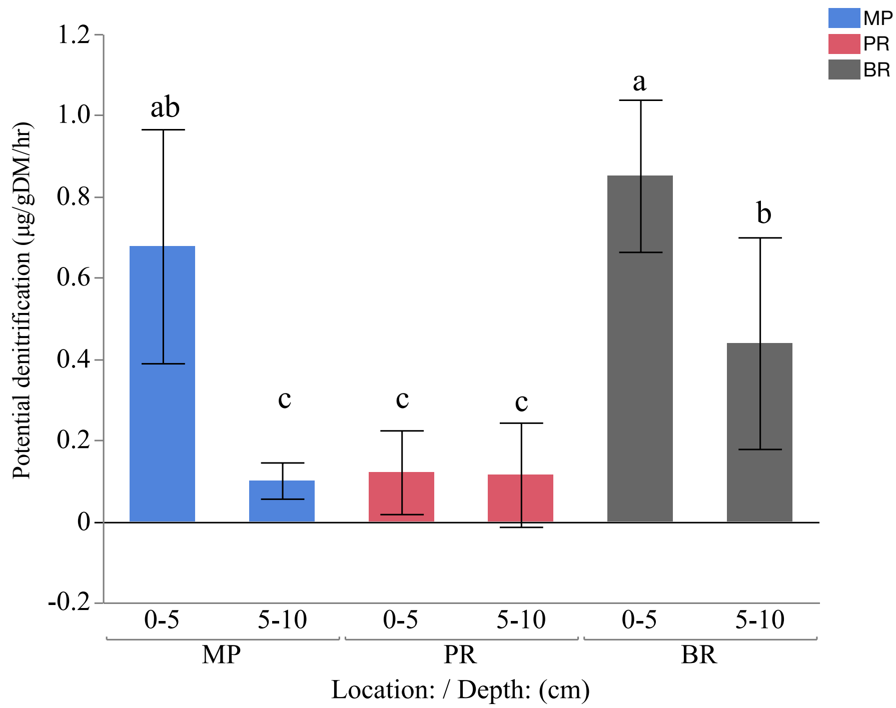


Figure 16: ANOVA exploring the cross between site and depth for denitrification. The resulting means were: MP 0-5cm= 0.68, MP 5-10 cm= 0.10, PR 0-5 cm= 0.12, PR 5-10 cm= 0.1, and BR 0-5 cm= 0.85, BR 5-10 cm= 0.44.

The DEA assay was completed at both depths for each lysimeter location in the rain garden. Figure 17 used the lysimeter location averages to display the differences between depths and seasons at each site. This figure reiterates the previous findings that Myers Park and Bruns Academy have large differences between depths, while the Park Road site has similar potential denitrification rates at both depths. However, this figure also expands upon the fact that the previously discussed trend is similar across summer, fall, and spring sampling.

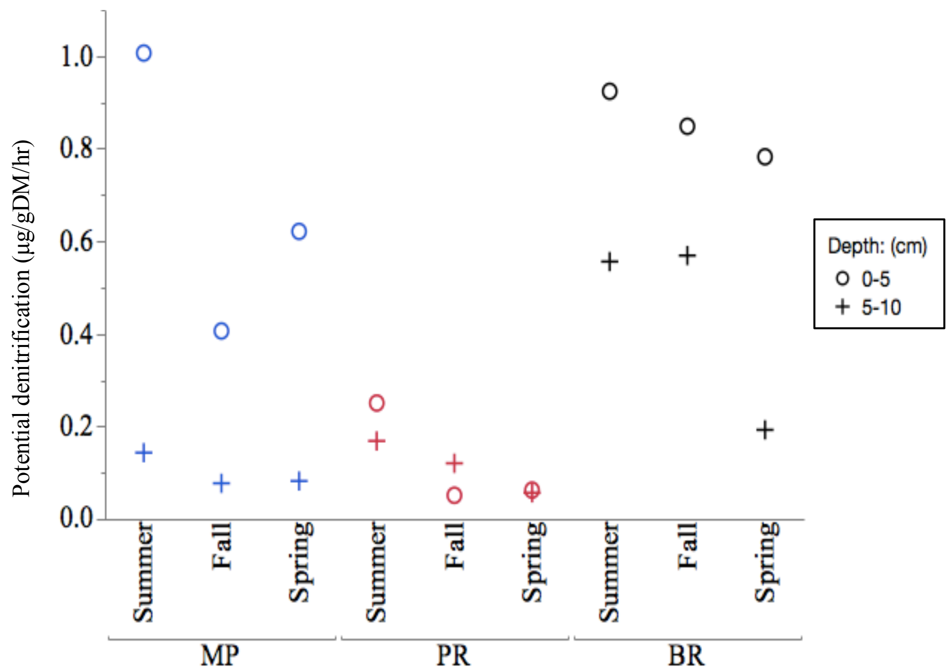


Figure 17: Potential denitrification differences between seasons, sites, and depths. Each point represents an average of the three lysimeter locations at each site where the samples were obtained.

3.3 Organic Matter

Percent organic matter was also calculated from the values obtained from the denitrification enzyme activity assay and analyzed. The 0-5 cm depth average percent organic matter was similar across all sites with means of 19.7%, 17.8%, and 13.8% at Myers Park, Park Road, and Bruns Academy. The 5-10 cm depth had one significant difference between sites which was between Myers Park and Bruns Academy (p=0.0428). The averages of the 5-10 cm depth organic matter percentages were 3.3%, 7.1%, and 7.7% at Myers Park, Park Road, and Bruns Academy respectively (Table 9).

Table 9: Average percent organic matter at 0-5 and 5-10 cm depths. See Appendix Figure 3 for an visual representation of the data.

		0-5cm			5-10cm		
Level	Number	Mean	Std Error	connecting letters	Mean	Std Error	connecting letters
MP	9	19.69	2.66	a	3.26	1.23	a
PR	9	17.79	2.66	a	7.10	1.23	ab
BR	9	13.80	2.66	a	7.74	1.23	b

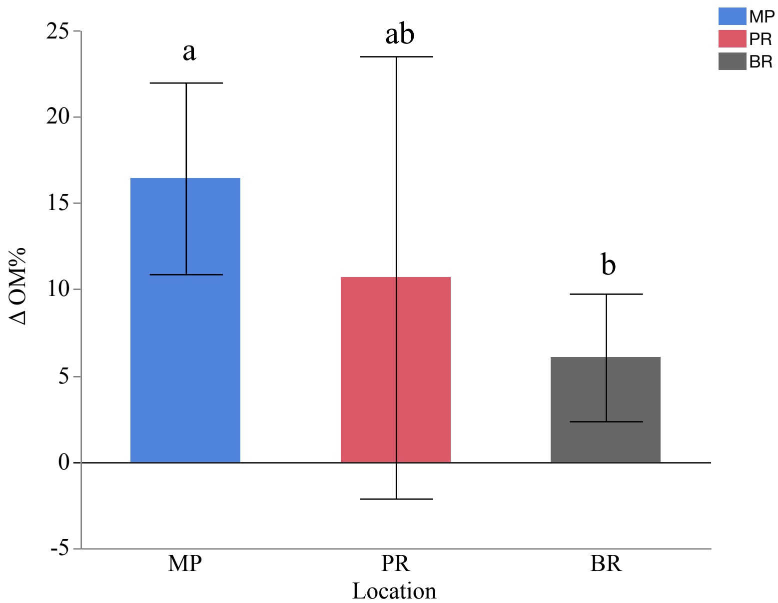


Figure 18: ANOVA results of the difference in percent organic matter across sites. ANOVA p-value= 0.0465, and a p-value of 0.0369 between MP and BR after a post hoc Tukey test was implemented. n= 9 for each site. Error bars represent one standard deviation from the mean.

In addition to these organic matter values, the difference between 0-5 cm and 5-10 cm percent organic matter was calculated and represented as "ΔOM%". This difference was analyzed across sites to assess the difference between organic matter at different depths. The results (Figure 18) showed there was a significant difference (p<0.05) between Myers Park and Bruns Academy. Specifically, there was a p-value of 0.0369 between the two sites which signified there was significantly less of a change in percent organic matter from 0-5cm to 5-10cm from Myers Park to Bruns Academy. Park Road

Park was in between these two values making the mean difference between the two depths 16.4, 10.7, and 6.1 at MP, PR, and BR.

A two-way ANOVA exploring the organic matter results identified depth and the interaction of age and depth to have significant effects on percent organic matter. As seen in Table 10, age does not have a significant impact on organic matter, however, when age and depth were observed, there was a significant difference. In addition, the percent organic matter values were also compared to potential denitrification rates (Figure 19).

Table 10: A two-way ANOVA between depth and age and the impact on percent organic matter.

Source	LogWorth		PValue
Depth: (cm)	7.607		0.00000
Age*Depth: (cm)	1.703		0.01981
Age	0.219		0.60329

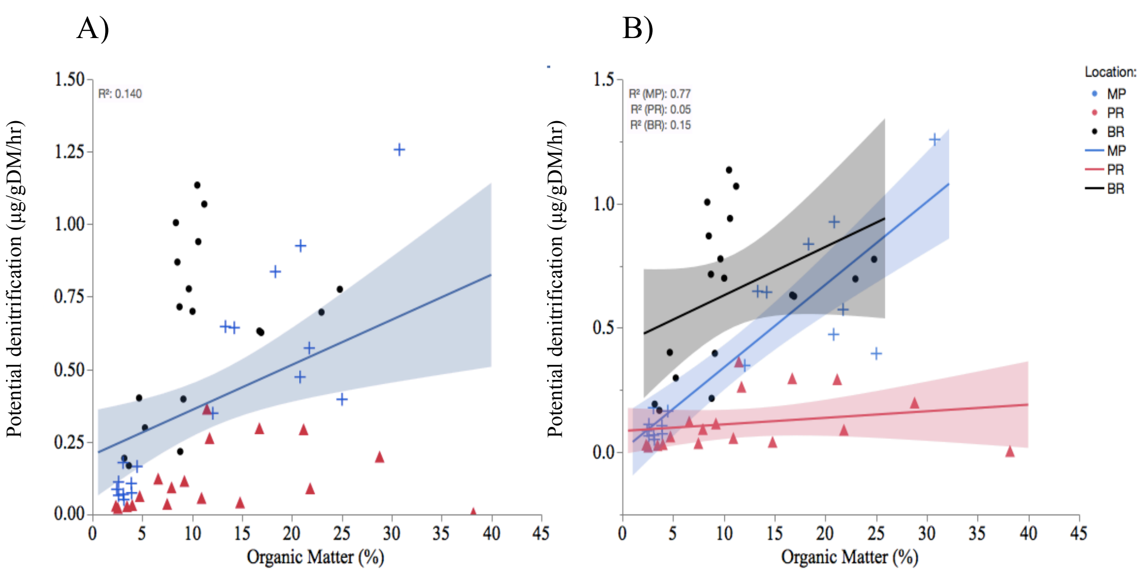


Figure 19: The relationship between potential denitrification rates and percent organic matter. A) The linear relationship with respect to all of the sites (r^2= 0.140). B) The linear relationships at each site which are color coordinated with blue, red, and black representing MP, PR, and BR. Myers Park r^2=0.77, Park Road Park r^2=0.05, and Bruns Academy r^2=0.15.

Figure 20 displays additional linear relationships between organic matter and potential denitrification rates. With all of the potential denitrification values aggregated into two separate depths (Figure 20A and Figure 20B), the linear relationship between 0-5cm depth potential denitrification rate and percent organic matter yielded an r^2 of 0.005, and the 5-10cm depth had an $r^2 = 0.371$. While the 5-10cm depth has an overall lower amount of potential denitrification, it has a stronger positive relationship with percent organic matter than the 0-5 cm depth. While the r^2 is not high, it is larger in the 5-10cm depth than the 0.005 at the shallow depth.

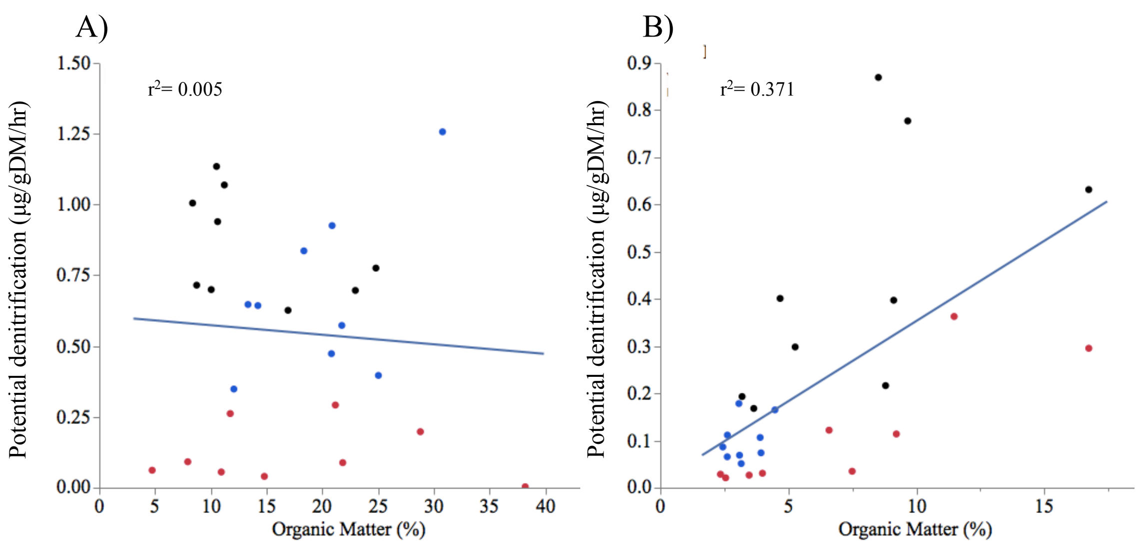


Figure 20: A) 0-5 cm. B) 5-10 cm. The graphs represent the relationships between % organic matter and potential denitrification rates.

3.4 Phosphorus Sorption

The p-sorption experiments were completed at each site for soil depths of 0-5 cm and 5-10 cm. The results were used to create a linear isotherm (Appendix Figure 4) which was then used to identify the equilibrium phosphorus concentration (EPC)(Table 11). Depth was not significantly different, but EPC was lower at each site for the deeper soil media tested. While the sample size was limited, the EPC nearly had a significant relationship with age (p-value = 0.0589) as the highest EPC in the youngest rain garden and lowest in the oldest was observed. More replicates are needed to address this relationship.

Table 11: The equilibrium phosphorus concentration (EPC) and p-sorption capacity at each site and depth.

Location	Depth	Age	P Sorption Capacity X/log10C	EPC
MP	0-5	4	-0.50	2930
MP	5-10	4	0.10	1620
PR	0-5	7	0.51	1370
PR	5-10	7	0.48	945
BR	0-5	15	2.30	649
BR	5-10	15	2.67	333

3.5 Hydraulic Conductivity and Infiltration Rates

All tests for the field saturated hydraulic conductivity (K_{sat}) using the Guelph permeameter were completed on the same date during dry conditions. The shallowest depth for each ponded and non-ponded location in the rain garden proved to have the highest K_{sat} (Table 12). In addition, there was no statistical difference between ponded and non-ponded sites when all of the sites were averaged together. However, when all of the depths were averaged together, the K_{sat} for the 10 cm depth was significantly higher (p=0.0011) than the other depths (Figure 21). The Charlotte BMP design manual lists rain garden soil hydraulic conductivity to range from 0.39-10.16 cm/hr (1-4 in/hr) (Charlotte-Mecklenburg Storm Water Services, 2014). The majority of values presented in Table 7 are much higher than the range given by Charlotte.

Table 12: Field saturated hydraulic conductivity values as a rate of cm/hr. The shaded values represent hydraulic conductivity rates that were calculated using the single head method and the unshaded values were completed using the double head calculation method. Values are in cm/hr.

Depth (cm)	MP Ponded	MP Not Ponded	PR Ponded	PR Not Ponded	BR Ponded	BR Not Ponded
10	29	110	62	50	120	78
20	8.0	4.0	26	32	55	56
30	16	25	36	14	39	44
50	13	25	19	2.0	26	18

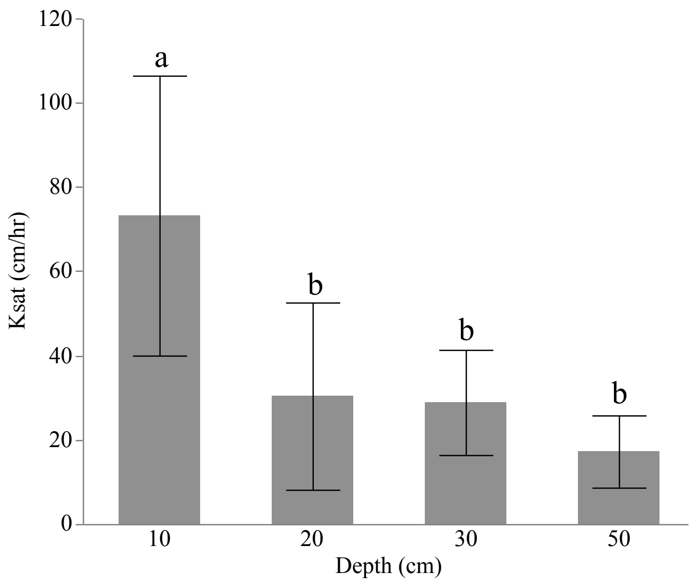


Figure 21: The K_{sat} values at each depth the procedure occurred. Error represents one standard deviation away from the mean.

Additionally, hydraulic conductivity showed a significant ($p = 0.0014$) trend regarding the depths the measurements were obtained (Figure 22). The field saturated hydraulic conductivity decreased with the depth of the rain garden.

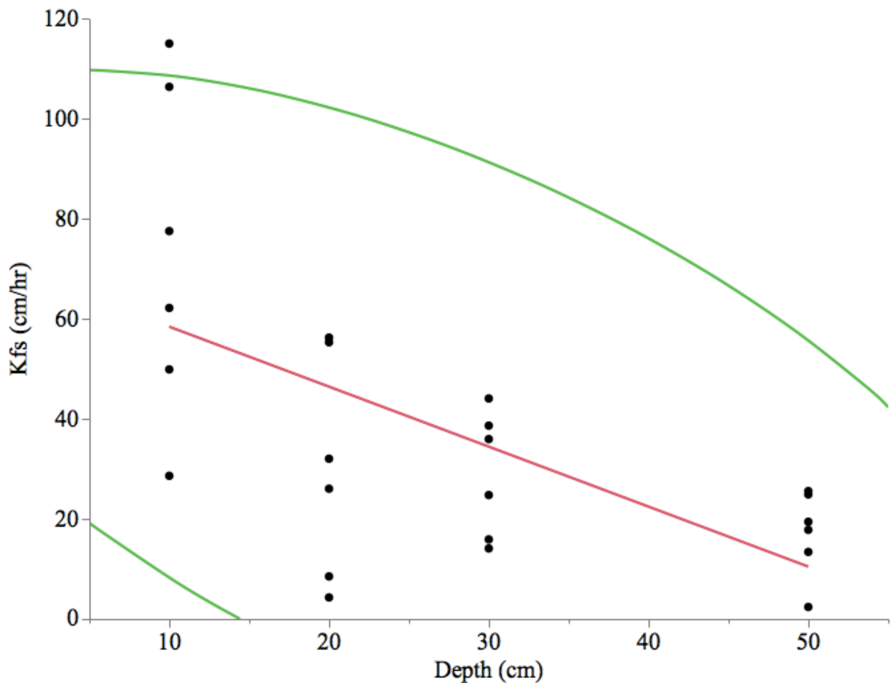


Figure 22: The relationship between field saturated hydraulic conductivity (cm/hr) through a profile of the rain garden (cm). r^2=0.377 with a density ellipse of 0.95. All sites are represented in the figure.

The infiltration rates from the study also yielded high values (Table 13). Overall, the average infiltration rate of 130 cm/hr was almost twice as fast at Bruns Academy compared to the other sites. In addition, the lowest values at each site are associated with areas that were the first to pond during storm events which were visually confirmed.

Table 13: Infiltration rates (cm/hr) at each site and lysimeter location.

Lysimeter Location	Infiltration Rate (cm/hr)		
	Myers Park	Park Road	Bruns Academy
1	71	65	147
2	62	77	9
3	82	74	235
Average	71	72	130

3.6 Vegetation Analysis

The results of the vegetation survey that took place on July 13, 2018 can be seen in Table 14 and Table 15. Appendix B has pictures of the unknown species 1 and 5 from the survey.

Table 14: The vegetation analysis completed 7-13-18. The unidentified plants were assigned a number to keep them separated during the analysis.

Location	Scientific name	Common Name	Count
MP	Ampelopsis brevipedunculata	Porcelain-berry	4
	Lythrum salicaria	Purple loosestrife	12
	Unknown 1	-	2
	Kummerowia striata	Japanese Clover	4
	Mollugo verticillata	Green Carpetweed	2
	Digitaria	Crabgrass	1
	Unknown 2	Moss	1
	Cephalanthus occidentalis	Buttonbush	1
	Eupatorium capillifolium	Dogfennel	1
PR	Sericea lespedeza	Sericea	2
	Persicaria perfoliata	Mile-a-minute	1
	Unknown 3	Tall Grass	28
	Mimosa pudica	Shameplant	4
	Lonicera japonica	Japandese Honeysuckle	8
	Unknown 4	Small Grass	1
	Parthenocissus quinquefolia	Virginia Creeper	16
BR	Digitaria	Crabgrass	8
	Cyperus	Nutsedge	14
	Unknown 5	-	18
	Dioscoreaceae	Wild Yam	9
	Cynoglossum virginianum	Wild Comfrey	9

Table 15: Additional analysis regarding the vegetation survey on 7-13-18.

Location	Shannon Index (H)
MP	1.77
PR	1.41
BR	1.55

Discussion

4.1 Sample collection differences among sites

Sample collection differences potentially impacted averaged nutrient concentrations. As stated previously, Bruns Academy lacked a weir which prevented composite sampling of all storms. Therefore, since no composite samples were collected at Bruns Academy, it was necessary to explore the differences between first flush and composite samples at the other sites (Figure 23). Myers Park had lower concentrations of ammonium, nitrate, and DOC in composite samples compared to the first flush. The volume of the first flush and composite samples were both 750mL. DOC was the only constituent at Myers Park with a significantly lower concentration in composite samples than the first flush. Park Road composite samples had significantly lower concentrations of ammonium, nitrate, and DOC than the first flush. Because both sites did not show significantly lower ammonium and nitrate it is not definite to assume Bruns Academy would likely have significantly lower composite concentrations. However, it is more likely to have significantly lower DOC composite concentrations than runoff concentrations at Bruns Academy based on the significant relationships at Myers Park and Park Road. These findings were further explained as Figure 24 identified a decreasing trend in concentrations from the first flush to composite samples. Therefore, when comparing Bruns Academy runoff concentrations to Myers Park and Park Road (if sampling techniques were similar throughout), Bruns Academy runoff would be slightly lower for ammonium, nitrate, and DOC. This could also potentially impact expected percent retention values at Bruns Academy to potentially be more negative (excluding phosphate). Phosphate does not show significance or trends regarding runoff concentrations between the two sites. Therefore Bruns Academy phosphate results were likely unaffected by the absence of composite sampling.

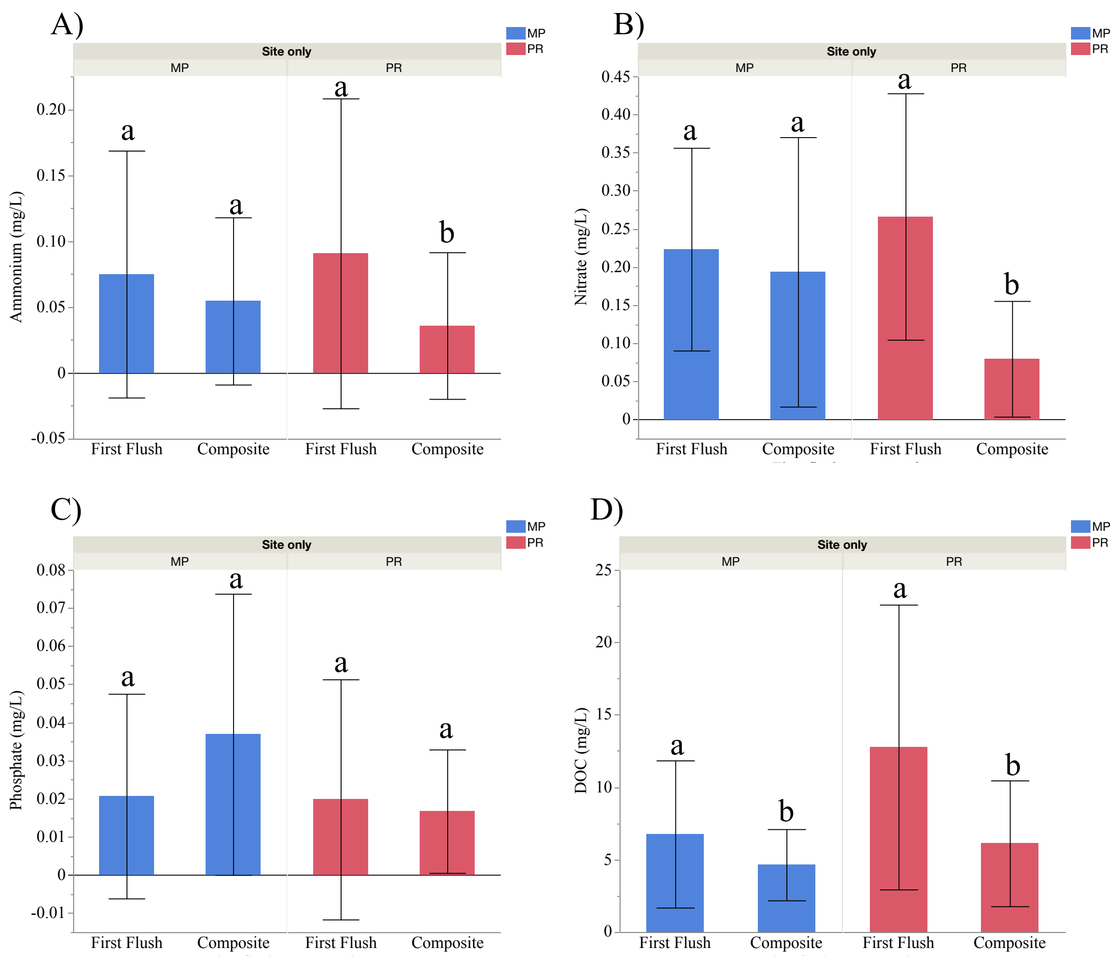


Figure 23: Blue represents Myers Park and the red represents Park Road. A-D are constituents ammonium, nitrate, phosphate and DOC respectively. Error bars represent standard deviation.

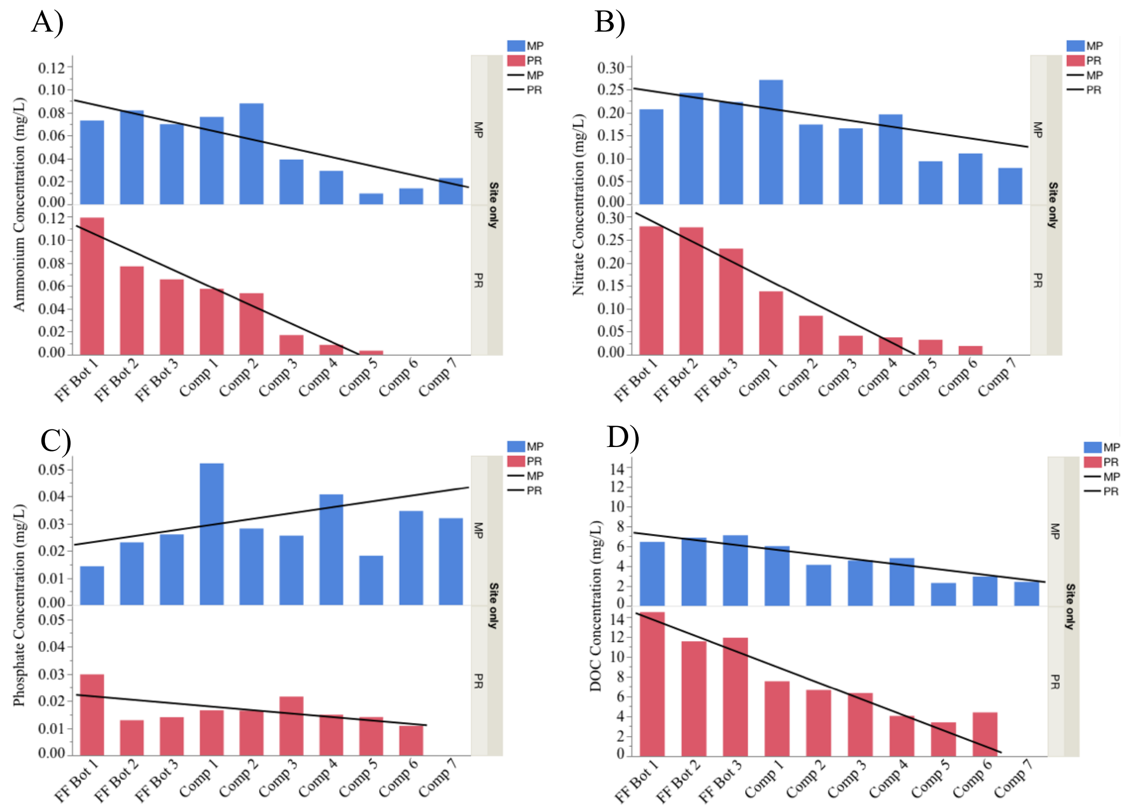


Figure 24: Chronological profile of runoff sampling per storm at Myers Park and Park Road Park. The black lines represent the line of fit to identify overall trends. A-D are constituents ammonium, nitrate, phosphate and DOC respectively.

4.2 Nutrient Retention

4.2.1 Ammonium

Throughout this study, ammonium decreased from average runoff concentrations to average soil water concentrations at every site as well as every season. The reduction of runoff ammonium in rain gardens has also been documented in previous studies (Davis et al., 2003; Dietz et al., 2005; Hsieh et al., 2007; Hunt et al., 2006; Strong, 2015). The decrease of runoff concentrations to soil water concentrations was potentially caused by plant and microbial assimilation and nitrifying bacteria. Ammonium is used by vegetation to create essential organic nitrogen molecules, and in the process reduce soil water ammonium. However, this ammonium represents uptake and not removal in the bioretention cell and is likely to become redeposited as plants die and decompose during the dormant season (Davis et al., 2006; Li et al., 2014). Also, nitrifying bacteria in the soil, such as *Nitrosomonas* and *Nitrobacter*, convert ammonium ions to nitrate (Hsieh et al., 2007). This occurs during aerobic conditions and is another explanation for the decreased ratio of runoff to soil water ammonium concentrations.

Temperature variance is likely an additional explanation for an increase in soil water ammonium from summer to winter. Optimal temperatures for the nitrification process have been identified as between 20 and 35°C (Barnard et al., 2005). Therefore, as the transition between summer and winter storms occurs, the temperature drops below optimal for nitrification and the conversion of ammonium to nitrate slows (Brown et al., 2013).

Bruns Academy likely had the lowest concentrations of ammonium in the soil water due to a larger presence of vegetation. Unsaturated rain gardens have been found to vary in nitrogen storage capabilities associated with differing antecedent soil moisture conditions among different vegetation (Nocco et al., 2016). Because Bruns Academy was covered with grass and the other two sites had dispersed shrubs with bare ground covered by mulch, these differences could potentially influence antecedent soil moisture. Nocco et al. (2016) explained vegetation differences cause rain gardens to dry at different rates due to evapotranspiration differences, and identified higher antecedent soil moistures with greater potential nutrient retention capabilities. This relationship could be present but was unlikely when the post-storm soil moisture percentages were observed. Bruns Academy had the highest soil moisture percentages which were contradictory of Nocco et al. (2016) and the aerobic conditions needed for nitrification. Additionally, while antecedent soil moisture was not observed, the antecedent precipitation was observed and did not have any correlation on nutrient retention. It could be assumed increased precipitation 2,7, and 14 days prior to the storm event would yield similar results as noted from antecedent soil moisture. However, with only one storm sampled, this relationship was assumed and is likely that this relationship may not be similar for every storm. Additional storm replicates would increase accuracy and better shape the understanding of soil moisture percentages after storms.

A site-specific difference at Bruns Academy involved the removal of vegetation, and repaving of the treatment area. While the repaved treatment area did not appear to have any impact on the concentrations of the water entering the rain garden, vegetation removal likely impacted soil water concentrations. The vegetation of the Bruns Academy rain garden was all clear cut and the vegetation was removed during the transition from summer to winter sampling. During the dormant season, plant growth is slowed and dead vegetation can release nutrients back into the rain garden (Davis et al., 2006; Li et al., 2014). This documented maintenance of Bruns Academy could potentially affect the results of the two-way ANOVA completed on ammonium for the site but not for the seasonal effects (Figure 25A&B). If the vegetation was not removed, it would have likely increased the winter soil water ammonium. This would not have changed the significance of the seasonal test but would have increased the average Bruns Academy site soil ammonium concentration and possibly altered the differences observed among sites.

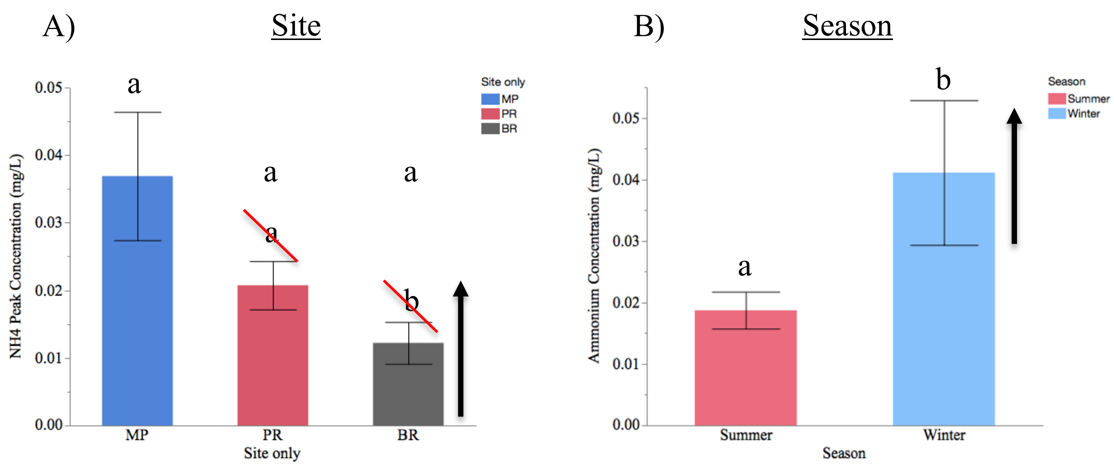


Figure 25: An edit of Figure 7 to identify potential differences in significance due to vegetation removal at the (A) site and (B) Season level. The red lines are over the initial values of Figure 7 to denote what changes could potentially occur. The black arrows identify the means that could potentially change if the vegetation was not removed at Bruns Academy between summer and winter storms. Additionally, theoretical connecting letters were added if any change could have occurred due to the change.

4.2.2 Nitrate

There were high levels of average soil water nitrate compared to average runoff concentrations which may be related to controls on nitrification rates discussed earlier. Prior studies have also identified the aerobic conditions of conventional rain gardens between storms as having fewer opportunities for denitrification to remove nitrate (Davis et al., 2001, 2006; Hatt et al., 2009). The lack of anoxic conditions was potentially the primary reason for the accumulation of soil water nitrate. Nitrate would be accumulating because there would be no additional flow through the rain garden or mechanism for the converted nitrate to leave the system in between storms. Layered rain garden materials in mesocosm and field scale rain garden studies have documented that accumulated nitrate then “washes out” during subsequent storms (Hsieh et al., 2007; Li et al., 2014; Lucas et al., 2008). Li et al. (2014) also identified nitrate as an anion which has a like charge with soil material and is therefore rather mobile in these systems. Exploratory outflow samples were taken during rain events by obtaining a hand grab sample at Myers Park and Park Road when conditions were suitable. Exploratory outflow samples varied in comparison to soil water concentrations but were usually higher than runoff concentrations (Figure 26). Thus, each location had storms that could have been representative of the "washout" effect often making rain gardens nitrate exporters. This is problematic as nitrogen exports can potentially lead to harmful algal blooms for the ecosystem as well as personal health risks in drinking water (Bernhardt et al., 2008). As the year progressed and temperatures grew cooler the average nitrate values of soil water decreased. This decrease was likely due to the aforementioned effect of cooler temperatures slowing nitrification rates.

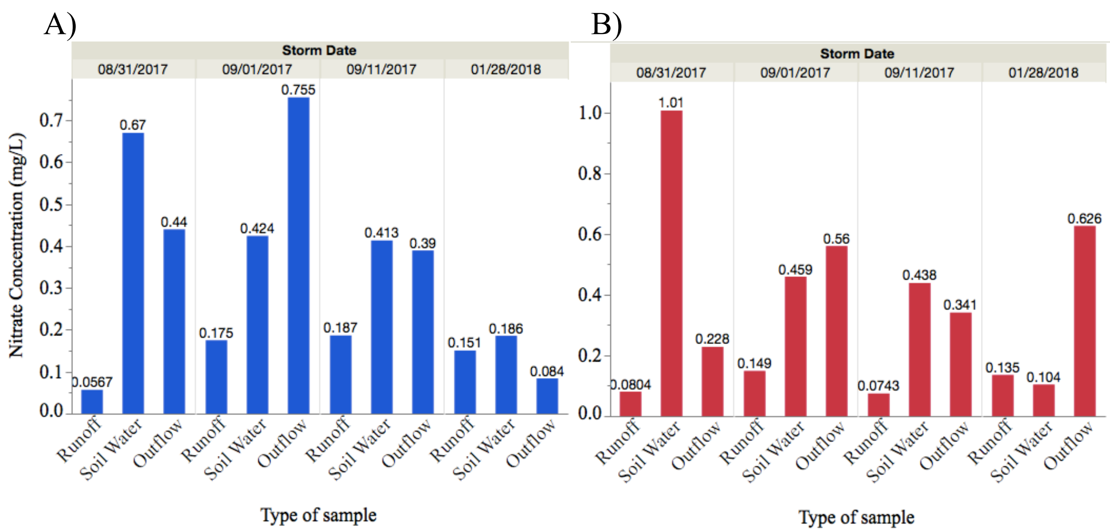


Figure 26: Mean nitrate concentrations by storm at Myers Park (A) and Park Road (B) in mg/L

A unique find of this research identified Bruns Academy having extremely negative nitrate retention with a value of -1420%. This is noteworthy because prior to this study, Strong (2015) studied a rain garden that had been exposed to a sewage spill and identified an average export for eight rain garden flooding events to have an average of

-785.35% retention of nitrate. Therefore, the negative retention average at Bruns Academy is not unique compared to previous research and potentially suggests this site was exposed to a pollutant source prior to this study. A wastewater performance report from July 1, 2016 through June 30, 2017 did not note any sewage spills near the Bruns Academy site (Charlotte Water, 2017). If a pollutant was introduced prior to this study, it could have originated from a wastewater leak. Additional knowledge of sewage lines in the site vicinity would be helpful to address this concern. Bruns Academy could have potentially been exposed to excess fertilizer at some point prior to the study, however, the treatment area is not well connected with the runoff that would be accumulating from neighboring lawns.

Further research should be conducted to identify the presence of mulch at Myers Park and Park Road as potential sources of nitrate. Hsieh et al. (2007) identified mulch to be a potential source of nitrate in rain garden effluent and mulch could potentially be a similar nitrate source for this study. Additionally, the time since the mulch was applied should also be addressed. If mulch was a significant source of nitrate into these systems, and mulch was only applied at the conclusion of rain garden construction, it could potentially explain soil water nitrate differences between similarly constructed rain gardens. Myers Park with mulch most recently applied (personal observation) had a soil water nitrate average of 0.42 mg/L while Park Road had an average of 0.28 mg/L.

4.2.3 Phosphate

Runoff concentrations for phosphate reported in this study were lower than runoff associated with commercial, freeway, industrial, open space, and residential stormwater (Bernhardt et al., 2008; Roy-Poirier et al., 2010). Phosphate removal results in rain gardens have been highly variable across studies and have been attributed to the various forms of soil media used in the bioretention cells during construction (LeFevre et al., 2014). The soil water values of phosphate for this study were in the range of effluent concentrations from other sites. Bioretention cells with a high p-index value have been shown to desorb phosphorus, leading to increased concentrations in outflow (Davis et al., 2006; Hunt et al., 2006; LeFevre et al., 2014; Roy-Poirier et al., 2010). Bruns Academy was documented in a published pilot study as having an extremely high p-index of 158 while the design limit is 30 (Charlotte-Mecklenburg Storm Water Services, 2014). This high index likely explains the high phosphate soil water concentrations at Bruns Academy compared to the other two sites. Myers Park and Park Road were proximal in distance and experienced almost identical hydrological storm variables. Therefore, the increased phosphate retention of Park Road is likely due to a structural variable opposed to hydrological differences. The differences between these rain gardens are the size, treatment area, vegetation present, and age. The overall rain garden size at Myers Park is roughly 3.8% of the treatment area, while the Park Road Park bioretention cell is about 7.2% of the size of the treatment area. This difference in size, as well as the fact that Park Road has a larger coverage of vegetation, could account for the significant difference between the two sites. The larger size of the Park Road site could result in a larger number of binding sites for phosphate to bind to in the rain garden soils. Vegetation has been shown to influence phosphorus concentrations as plants assimilate phosphorus for bioproduction (Brown et al., 2013; Lucas et al., 2008). While vegetation may also be influence the Park Road rain garden's ability to reduce phosphorus, additional research suggests only a small portion of phosphate runoff treatment (3-20%) is due to assimilation by plants (Dietz et al., 2005, 2006; Komlos et al., 2012; Lucas et al., 2008). Therefore, additional research needs to be completed prior to identifying vegetation as a main cause of phosphate reduction.

When exploring the seasonal differences for rain garden phosphate concentrations, the soil water phosphate concentration seasonal difference of 0.04 mg/L in the summer to 0.02 mg/L in the winter may have been attributed to the differences in storm duration and precipitation. The impact of winter storms being longer with more precipitation could potentially dilute the phosphate concentration of the rain gardens as water continually percolates through the rain garden.

4.2.4 DOC

DOC in urban runoff has been shown to be more hydrophobic and have lower molecular weights than runoff originating from other land uses (McElmurry et al., 2014). McElmurry et al. (2014) reasoned this was because of the lack of vegetation adding natural organic compounds to the impervious landscape, as well as the addition of petroleum hydrocarbons from transportation. Hydrophobic DOC in runoff is primarily retained by adsorption to the soil media in rain gardens and used as an energy source to reduce nitrate during the denitrification process (Davis et al., 2010). In this study, Park Road Park had the highest soil water DOC concentrations compared to the other two sites. The lower amount of soil moisture post-storm coupled with the lower nitrate concentrations potentially provides the explanation. The lower soil moisture and nitrate concentration likely indicate the lack of conditions needed for denitrification. It is possible that DOC concentrations were highest at Park Road because the organic matter was not being used as readily in the denitrification process and was therefore accumulated.

Seasonal percent retention was also identified as being significantly more negative in winter storms (Figure 27). It is possible the DOC is increased during the summer due to the presence of vegetation during the growing season. This vegetation would be labile and available for soil microbes. However, during the dormant season, the DOC in the rain garden would primary be derived from mulch and would be more refractory. These differences could potentially cause DOC concentrations to vary in soil water across seasons. The vegetation removal at Bruns Academy could have affected the winter percent retention values because soil water at this site would have been expected to be slightly increased due to decomposition of organic matter.

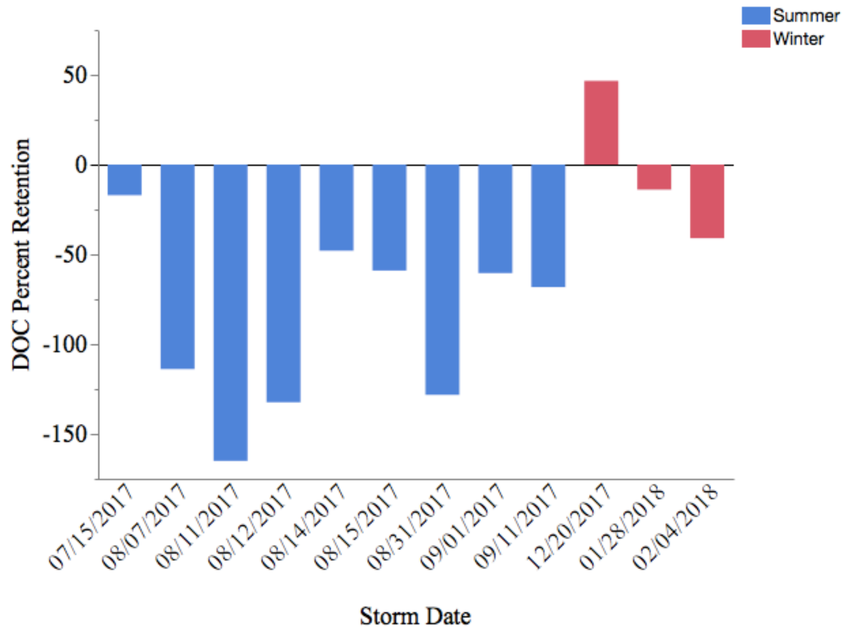


Figure 27: The figure represents percent retention for all sites for each sampling date. 8-31-17 and after represents storms with all three sites. Prior storms consist of Myers Park and Park Road only. 8-11-17 consists of only Myers Park data, and 8-14-17 consists of only Park Road data due to sampling errors.

4.3 Denitrification

While limited research has been completed to quantify denitrification rates in bioretention cells, Bettez et al. (2012) quantified varying types of constructed SCM denitrification rates with respect to riparian zones. The results of this study helped identify potential denitrification rates for the bioretention cells. The average potential denitrification rates of 0.39 at Myers Park, 0.12 at Park Road, and 0.65 µg/gDM/hr at Bruns Academy were more similar to riparian zone denitrification rates of 0.4 µg/gDM/hr than the similarly constructed infiltration SCMs with an average of 0.018 µg/gDM/hr (Bettez et al., 2012).

Seasonal potential denitrification rate differences were not significantly different; however, rates were lower in the fall and early spring compared to the summer. Similar to nitrification, this is likely due to decreasing temperatures slowing denitrification (Barnard et al., 2005). All sites were significantly different from each other in order of Bruns Academy, Myers Park, and Park Road having the largest to smallest potential denitrification rates. The soil moisture data corresponded to the denitrification as Bruns retained the most soil moisture (41%) followed by Myers Park (37%) and Park Road (30%). Additionally, the availability of nitrate in the soil water is likely linked to the denitrification rates, which followed the same trend as above (Barnard et al., 2005; Tuttle et al., 2014). When the denitrification potential was assessed by depth, the 0-5 cm layer was also representative of the previous conclusion. The 5-10 cm depth showed Bruns Academy had significantly higher rates (0.85 μg/gDM/hr) than Myers Park and Park Road which were similar (0.10 and 0.12 μg/gDM/hr). These values could be similar due to related construction techniques or the presence of microbial hotspots in the soil matrix at the site sampling locations (Reisinger et al., 2016).

4.4 Organic matter

The organic matter percent was largest in the younger rain gardens for the 0-5cm depth but was the lowest in the 5-10cm depths (Figure 28). This suggests that as rain gardens age, the percent organic matter leaches to lower layers. Specifically, as rain gardens have more growing and dormant seasons as they age, accumulated organic material is transported deeper into the rain garden soils during rain events.

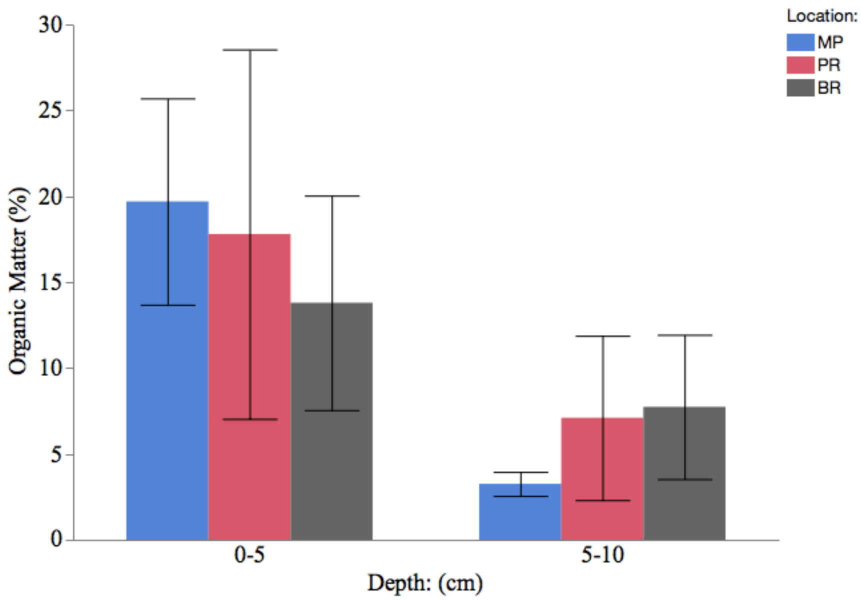


Figure 28: The difference in organic matter and depth. Standard deviation is represented on the figure for each site.

4.5 Phosphorus Sorption

The assessment of phosphate across an age gradient of rain gardens has been understudied. The age of a bioretention cell was not shown to influence phosphate retention rates in a nine-year study (Komlos et al., 2012). Komlos et al. (2012) found as the rain garden aged, the rain garden soil became saturated with phosphorus at the top, with the highest sorption availability at increased depths. This trend was not similar in this study and my data suggested the equilibrium concentration was lower at the deeper depths for each site. This implies that the uppermost layer of rain gardens have the highest potential for phosphorus sorption. Specifically, the upper most layer at each site had a higher potential to sorb phosphate as identified by the equilibrium concentrations from the sorption batch experiment. While there is the difference between depth, an age gradient persisted for the EPC concentrations which identified the oldest rain gardens reach equilibrium quickest and are closest to becoming saturated with phosphate. For this study, phosphorus sorption was only tested once during for each site. Additional soil sample collections and sorption batch experiments should be completed to increase accuracy of the assumptions in this research. Also, because phosphate is such a sticky nutrient, there is potential for error in the EPC analysis. Variations in the EPC methods have increased the equilibrating time to ensure the equilibrium can be reached and times possibly need to be increased moving forward.

4.6 Hydraulic Conductivity and Infiltration Rates

The infiltration rates at Myers Park and Park Road were almost identical which was likely due to the similarity in construction techniques. With the two values being so similar, the results suggest that clogging from fine particulate filtration would not affect infiltration with respect to age between the two sites. However, Bruns Academy had an overall higher infiltration rate but also had more heterogeneity within the site. The area that was in the middle of the rain garden and received most of the runoff after pretreatment was the location that had the lowest infiltration rate of 9 cm/hr (3.5in/hr). Even though this was the lowest infiltrating area of the rain garden it was still above the minimum requirement of 2.54 cm/hr (1 in/hr) by the state. This may suggest grassy rain gardens are more affected by clogging than the other sites. However, after 15, 7, and 4 years post installation the bioretention cells as a whole had infiltration rates that were exceptionally high. These high values were potentially due to the methodology used in this study. A falling head test was used for infiltration where a constant head method is used more often. The limited access to the necessary volume of water was an additional restriction for testing permeable soils.

Field saturated hydraulic conductivity exceeded the 2.54 to 10.16 cm/hr (1 to 4 in/hr) outlined in the Charlotte BMP design manual. As rain gardens age, compaction can potentially lower decrease rain garden permeability (Carpenter et al., 2009). As mentioned by Carpenter et al. (2009) increased field saturated permeability may have been higher than actual conductivity due to the disturbance of the soil during testing.

Conclusion

These findings provided insight into the internal processes of rain gardens that have been understudied in previous research. It is also necessary to understand the nutrient retention aspect of this research has been completed with the assumption the soil water is largely reflective of what would be in the outflow of the rain gardens during storms. Seasonal runoff was not significantly different across any nutrients studied, therefore differences in nutrient concentrations in rain gardens were driven by processes within the structure. Processes controlling the nitrogen cycle were interconnected and explained the overall trends of ammonium and nitrate concentrations. The aerobic condition of the soils promoted nitrification and removed ammonium from runoff and soil water. Consequently, this also increased soil water nitrate concentrations. Without sufficient saturated zones or hot spots of denitrification, nitrate accumulated via nitrification in rain garden soils until subsequent rain washed out much of the stored nitrate. However, seasonal changes caused the microbial processes to slow during the winter, which resulted in slight increases in soil water ammonium and decreases in nitrate compositions compared to the summer. No hydrological variables of the storm event had a significant effect on the retention of ammonium and nitrate. This further exemplified retention differences were due to processes within the rain garden. Potential denitrification rates appeared to be linked to the available nitrate concentrations in soil water since all sites had high infiltration rates and field saturated conductivities. The structural design proved to be the driving factor of the difficulty in standardizing potential denitrification rates in rain gardens. Mesocosm experiments showed denitrification of rain gardens soils (like the Charlotte sites) to have lower potential denitrification rates than identified in this study (Bettez et al., 2012). However, a similarly conducted study completed in Indiana concluded higher rates of potential denitrification in unlined rain gardens (Hawrot et al., 2017). This field scale research suggests higher potential denitrification was occurring than previously identified.

The variability of phosphate in the rain gardens was due to the fill media differences, the size of the rain gardens, as well as the vegetation present. Between similarly constructed Park Road and Myers Park, the site with the larger rain garden to treatment area ratio exemplified the increased area also increased opportunities for phosphate to bond to soil particles. The EPC in rain gardens appeared to decrease with age as well as depth. These tests should be repeated to identify the long-term removal performance before the structure is saturated with phosphorus.

DOC in the rain garden soils was different across sites may be driven by the denitrification process. Sites with the lowest nitrate concentrations and subsequent soil moisture had more DOC in the soil. Thus with low rates of denitrification occurring, DOC increases as it is not being used for energy.

While the aging Bruns Academy could not be compared directly to the pilot study report, varying infiltration rates suggest fine particulate clogging may be occurring. Overall, site compaction may cause decreased permeability at lower depths of the rain garden. The results of this study suggest the soil water at Bruns Academy had similar retention values compared to the pilot study retention with respect to inflow and outflow. The pilot study retention of ammonium was 92% and the soil water retention of ammonium was 87%. Results were also similar between nitrate in the regard that nitrate was exported from the system to the receiving stream. Nitrate had a runoff and outflow retention of -464% while the soil water retention was -1420%.

Various construction techniques should be explored moving forward in regard to Charlotte rain gardens. Charlotte rain gardens should remove the process of having one inflow location that channels sheet flow into the rain garden for sampling. Even with a level spreader or forebay present, portions of each rain garden were not in contact with stormwater throughout the storm. Allowing sheet flow into the rain garden would increase the surface area of the rain garden soils in contact with the runoff. This change could increase the microbial activity as well as disperse the fine particulate matter to slow clogging.

Further research needs to be completed to identify the specific relationship between the storage volume of the rain gardens with the runoff volume of each storm. Rain garden storage was loosely identified in this study by calculating the rain garden volume by incorporating the recommended optimal depth of 4 feet for rain gardens to treat for pollutants in the BMP manual by Charlotte-Mecklenburg Storm Water Services (2014). The rain garden storage volume was calculated by multiplying the overall rain garden volume by the percent porosity to identify the volume of void space that could be occupied by stormwater during events (rain garden storage). A porosity value of 40% was used in these calculations as it characterizes the average porosity of coarse sand which was the dominating soil type for these systems (Manger, 1963). The primary limitation to the site storage calculations is that they likely overestimate the site's storage. The storage was calculated as if the boundaries of the rain gardens immediately drop 1.2 meters when in reality the base of the rain gardens are likely to be more of a bowl shape with the deepest part in the center of the rain garden. As seen in Table 16 the overall storage of the rain gardens varied with the lowest runoff to storage volume ratio being 0.32, while the highest was 2.35. The runoff to storage ratio was an average of 1.2 at Myers Park, 0.70 at Park Road, and 0.82 at Bruns Academy. These runoff to storage ratios indicate that throughout this study, the rain garden was storing most or all of the runoff volume. This is relative to this study because, with moderate runoff to storage volume ratio values, it validates that the high concentrations of soil water nitrate are likely also exported.

Table 16: The exploratory storage calculations for each storm in relation to the overall storage of the rain garden. Values in bold text and shaded gray represent storms that had a higher runoff volume than rain garden storage.

Location	Storage volume with porosity at 40% (m^3)	Total runoff volume entering RG (m^3)	Ratio of runoff volume to storage volume	Event date	Total precipitation (m/day)
MP	73.2	47	0.64	7/15/17	0.012
		84	**1.15**	8/7/17	0.021
		23	0.32	8/11/17	0.006
		23	0.32	8/12/17	0.006
		85	**1.17**	8/15/17	0.021
		56	0.76	8/31/17	0.014
		77	**1.05**	9/1/17	0.019
		172	**2.35**	9/11/17	0.043
		103	**1.40**	12/20/17	0.026
		153	**2.10**	1/28/17	0.038
		135	**1.85**	2/4/17	0.034
PR	170.8	79	0.46	7/15/17	0.016
		94	0.55	8/7/17	0.019
		51	0.30	8/12/17	0.010
		113	0.66	8/14/17	0.023
		119	0.70	8/15/17	0.025
		63	0.37	8/31/17	0.013
		94	0.55	9/1/17	0.019
		214	**1.25**	9/11/17	0.044
		117	0.69	12/20/17	0.024
		191	**1.12**	1/28/17	0.039
		158	0.92	2/4/17	0.033
BR	122	56	0.46	8/31/17	0.014
		41	0.33	9/1/17	0.010
		163	**1.33**	9/11/17	0.041
		87	0.72	12/20/17	0.022
		135	**1.11**	1/28/17	0.034
		120	0.98	2/4/17	0.030

The implantation of internal water storage zones and the addition of organic matter such as newspaper to the soil matrix was shown to increase nitrate removal up to 80% in rain gardens (Kim et al., 2003). However, upon the perpetually improving nature of stormwater treatment, an additional adjustment of the rain garden structure could further the success of nitrogen removal. Bettez et al. (2012) identified stormwater control measures that alternate between wet and dry conditions are likely to have a higher denitrification potential. Bettez et al. (2012) also identified structures that permanently store water, such as wet ponds, had lower potential denitrification rates than expected due to permanent anoxic conditions and low nitrification. This relationship should be explored in rain gardens with raised and upturned underdrains that store water for long periods of time. A stacked underdrain system could potentially improve the balance of the nitrogen cycle by allowing the bottom underdrain with low permeability slowly release water from a temporary water storage zone. A second overlying underdrain would continue to function under current standards to transport most of the rain garden treated outflow to the stream. This stacked underdrain concept could potentially increase denitrification potentials without having effects of continual anoxic conditions.

Overall, the study of soil water concentrations in rain gardens has provided preliminary concentrations of soil water nutrients. As rain gardens have been proven to reduce peak flow and total suspended solids during rain events, future research will involve understanding the internal processes that can be compared to these findings.

References

Ali, G. A., & Roy, A. G. (2010). A case study on the use of appropriate surrogates for antecedent moisture conditions (AMCs). *Hydrology and Earth System Sciences, 14*(10), 1843.

Bache, B. W., & Williams, E. G. (1971). A phosphate sorption index for soils. *Journal of Soil Science, 22*(3), 289-301. doi:doi:10.1111/j.1365-2389.1971.tb01617.x

Barnard, R., Leadley, P. W., & Hungate, B. A. (2005). Global change, nitrification, and denitrification: a review. *Global biogeochemical cycles, 19*(1).

Beckett, P., & White, R. (1964). Studies on the phosphate potentials of soils. *Plant and soil, 21*(3), 253-282.

Bernhardt, E. S., Band, L. E., Walsh, C. J., & Berke, P. E. (2008). Understanding, managing, and minimizing urban impacts on surface water nitrogen loading. *Annals of the New York Academy of Sciences, 1134*(1), 61-96.

Bettez, N. D., & Groffman, P. M. (2012). Denitrification Potential in Stormwater Control Structures and Natural Riparian Zones in an Urban Landscape. *Environmental Science & Technology, 46*(20), 10909-10917. doi:10.1021/es301409z

Bratieres, K., Fletcher, T. D., Deletic, A., & Zinger, Y. (2008). Nutrient and sediment removal by stormwater biofilters: A large-scale design optimisation study. *Water research, 42*(14), 3930-3940. doi:https://doi.org/10.1016/j.watres.2008.06.009

Brown, R. A., Birgand, F., & Hunt, W. F. (2013). Analysis of consecutive events for nutrient and sediment treatment in field-monitored bioretention cells. *Water, Air, & Soil Pollution, 224*(6), 1581.

Carpenter, D. D., & Hallam, L. (2009). Influence of planting soil mix characteristics on bioretention cell design and performance. *Journal of Hydrologic Engineering, 15*(6), 404-416.

Charlotte Water. (2017). *Wastewater Performance Report July 1, 2016- June 30, 2017*. Retrieved from http://charlottenc.gov/Water/Documents/Wastewater%20Report.pdf

Charlotte-Mecklenburg Storm Water Services. (2014, January 1, 2014). BMP Design Standards Manual. Retrieved from http://charlottenc.gov/StormWater/Regulations/Pages/StormWaterDesignManual.aspx

Church, S. P. (2015). Exploring Green Streets and rain gardens as instances of small scale nature and environmental learning tools. *Landscape and Urban Planning, 134*, 229-240.

Davis, A. P. (2005). Green Engineering Principles Promote Low-impact Development. *Environmental Science & Technology, 39*(16), 338A-344A. doi:10.1021/es053327e

Davis, A. P., Hunt, W. F., Traver, R. G., & Clar, M. (2009). Bioretention technology: Overview of current practice and future needs. *Journal of Environmental Engineering, 135*(3), 109-117.

Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2001). Laboratory study of biological retention for urban stormwater management. *Water Environment Research, 73*(1), 5-14.

Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2006). Water Quality Improvement through Bioretention Media: Nitrogen and Phosphorus Removal. *Water Environment Research, 78*(3), 284-293. doi:10.2175/106143005X94376

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., & Winogradoff, D. (2003). Water quality improvement through bioretention: Lead, copper, and zinc removal. *Water Environment Research, 75*(1), 73-82.

Davis, A. P., Traver, R. G., & Hunt, W. F. (2010). Improving urban stormwater quality: Applying fundamental principles. *Journal of Contemporary Water Research & Education, 146*(1), 3-10.

Dietz, M. E., & Clausen, J. C. (2005). A field evaluation of rain garden flow and pollutant treatment. *Water, Air, and Soil Pollution, 167*(1-4), 123-138.

Dietz, M. E., & Clausen, J. C. (2006). Saturation to improve pollutant retention in a rain garden. *Environmental Science & Technology, 40*(4), 1335-1340.

Elliott, S., Meyer, M. H., Sands, G. R., & Horgan, B. (2011). Water quality characteristics of three rain gardens located within the twin cities metropolitan area, Minnesota. *Cities and the Environment (CATE), 4*(1), 4.

Groffman, P. M., Altabet, M. A., Böhlke, J., Butterbach-Bahl, K., David, M. B., Firestone, M. K., . . . Voytek, M. A. (2006). Methods for measuring denitrification: diverse approaches to a difficult problem. *Ecological Applications, 16*(6), 2091-2122.

Groffman, P. M., Holland, E. A., Myrold, D. D., Robertson, G. P., & Zou, X. (1999). Denitrification. In G. P. Robertson, D. C. Coleman, P. Sollins, & C. S. Bledsoe

(Eds.), *Standard Soil Methods for Long-term Ecological Research* (pp. 272-288): Oxford University Press.

Hatt, B. E., Fletcher, T. D., & Deletic, A. (2009). Hydrologic and pollutant removal performance of stormwater biofiltration systems at the field scale. *Journal of Hydrology, 365*(3), 310-321. doi:https://doi.org/10.1016/j.jhydrol.2008.12.001

Hawrot, H., McMillan, S., & Scarlett, R. (2017). *The assessment of the quality of ecosystem services provided by rain gardens.* Purdue University

Hsieh, C., Davis, A. P., & Needelman, B. A. (2007). Nitrogen Removal from Urban Stormwater Runoff Through Layered Bioretention Columns. *Water Environment Research, 79*(12), 2404-2411. doi:10.2175/106143007X183844

Hunt, W., Jarrett, A., Smith, J., & Sharkey, L. (2006). Evaluating Bioretention Hydrology and Nutrient Removal at Three Field Sites in North Carolina. *Journal of Irrigation and Drainage Engineering, 132*(6), 600-608. doi:doi:10.1061/(ASCE)0733-9437(2006)132:6(600)

Hunt, W., Smith, J., Jadlocki, S., Hathaway, J., & Eubanks, P. (2008). Pollutant removal and peak flow mitigation by a bioretention cell in urban Charlotte, NC. *Journal of Environmental Engineering, 134*(5), 403-408.

Jadlocki, S., & Hall, K. (2015). *Bruns Avenue School Bioretention Project- Final Monitoring Report*. Retrieved from http://charlottenc.gov/StormWater/SurfaceWaterQuality/Documents/BrunsAveSchoolBioretentionFinalReport.pdf

Kim, H., Seagren, E. A., & Davis, A. P. (2003). Engineered bioretention for removal of nitrate from stormwater runoff. *Water Environment Research, 75*(4), 355-367.

Komlos, J., & Traver, R. G. (2012). Long-Term Orthophosphate Removal in a Field-Scale Storm-Water Bioinfiltration Rain Garden. *Journal of Environmental Engineering, 138*(10), 991-998. doi:doi:10.1061/(ASCE)EE.1943-7870.0000566

LeFevre, G. H., Paus, K. H., Natarajan, P., Gulliver, J. S., Novak, P. J., & Hozalski, R. M. (2014). Review of dissolved pollutants in urban storm water and their removal and fate in bioretention cells. *Journal of Environmental Engineering, 141*(1), 04014050.

Leopold, L. B. (1968). Hydrology for urban land planning: A guidebook on the hydrologic effects of urban land use.

Li, H., & Davis, A. P. (2009). Water Quality Improvement through Reductions of Pollutant Loads Using Bioretention. *Journal of Environmental Engineering, 135*(8), 567-576. doi:doi:10.1061/(ASCE)EE.1943-7870.0000026

Li, L., & Davis, A. P. (2014). Urban Stormwater Runoff Nitrogen Composition and Fate in Bioretention Systems. *Environmental Science & Technology, 48*(6), 3403-3410. doi:10.1021/es4055302

Line, D. E., & Hunt, W. F. (2009). Performance of a Bioretention Area and a Level Spreader-Grass Filter Strip at Two Highway Sites in North Carolina. *Journal of Irrigation and Drainage Engineering, 135*(2), 217-224. doi:doi:10.1061/(ASCE)0733-9437(2009)135:2(217)

Lucas, W. C., & Greenway, M. (2008). Nutrient retention in vegetated and nonvegetated bioretention mesocosms. *Journal of Irrigation and Drainage Engineering, 134*(5), 613-623.

Manger, G. E. (1963). *Porosity and bulk density of sedimentary rocks* (1144E). Retrieved from http://pubs.er.usgs.gov/publication/b1144E

Marsalek, J., & Chocat, B. (2002). International Report: Stormwater management. *Water Science and Technology, 46*(6-7), 1-17.

McElmurry, S. P., Long, D. T., & Voice, T. C. (2014). Stormwater Dissolved Organic Matter: Influence of Land Cover and Environmental Factors. *Environmental Science & Technology, 48*(1), 45-53. doi:10.1021/es402664t

Meyer, J. L. (1979). The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. *Limnology and Oceanography, 24*(2), 365-375. doi:10.4319/lo.1979.24.2.0365

NCDEQ. (2018, 01/19/2018). Stormwater Design Manual Part C: Minimum Design Criteria and Recommendations for Stormwater Control Measures- Bioretention Cell. Retrieved from https://files.nc.gov/ncdeq/Energy%20Mineral%20and%20Land%20Resources/Stormwater/BMP%20Manual/C-2%20%20Bioretention%201-19-2018%20FINAL.pdf

Nocco, M. A., Rouse, S. E., & Balster, N. J. (2016). Vegetation type alters water and nitrogen budgets in a controlled, replicated experiment on residential-sized rain gardens planted with prairie, shrub, and turfgrass. *Urban Ecosystems, 19*(4), 1665-1691. doi:10.1007/s11252-016-0568-7

Read, J., Wevill, T., Fletcher, T., & Deletic, A. (2008). Variation among plant species in pollutant removal from stormwater in biofiltration systems. *Water research, 42*(4), 893-902.

Reisinger, A. J., Groffman, P. M., & Rosi-Marshall, E. J. (2016). Nitrogen-cycling process rates across urban ecosystems. *FEMS Microbiology Ecology, 92*(12), fiw198-fiw198. doi:10.1093/femsec/fiw198

Reynolds, W. D. (2007). Saturated Hydraulic Properties: Well Permeameter. In E. G. Gregorich & M. R. Carter (Eds.), *Soil sampling and methods of analysis* (2 ed., pp. 1025-1042). Boca Raton, FL: CRC Press.

Reynolds, W. D., & Elrick, D. E. (1986). A Method for Simultaneous In Situ Measurement in the Vadose Zone of Field-Saturated Hydraulic Conductivity, Sorptivity and the Conductivity-Pressure Head Relationship. *Groundwater Monitoring & Remediation, 6*(1), 84-95. doi:doi:10.1111/j.1745-6592.1986.tb01229.x

Roy-Poirier, A., Champagne, P., & Filion, Y. (2010). Bioretention processes for phosphorus pollution control. *Environmental Reviews, 18*, 159-173. doi:10.1139/A10-006

Shannon, C. E., & Weaver, W. (1949). The mathematical theory of communication. *Urbana, IL: University of Illinois Press*.

Smith, M., & Tiedje, J. (1979). Phases of denitrification following oxygen depletion in soil. *Soil Biology and Biochemistry, 11*(3), 261-267. doi:https://doi.org/10.1016/0038-0717(79)90071-3

Smith, R. E. (1976). Approximations for vertical infiltration. *Trans. American Soc. Agric. Engrs., 19*, 505.

Soilmoisture Equipment Corp. (2009). 2830K1 Double Ring Infiltrometer Kit Operating Instructions (pp. 1-12). P.O. Box 30025, Santa Barbara, CA 93105 U.S.A. : SoilMoisture Equipment Corp. .

Soilmoisture Equipment Corp. (2012). *2800 Guelph Permeameter Operating Instructions*. P.O. Box 30025, Santa Barbara, CA. 93130 U.S.A. .

Strong, P. (2015). *Efficiency of nitrate and phosphorus removal in a working rain garden.* (10034751 M.S.), University of North Texas, Ann Arbor. ProQuest Dissertations & Theses Global database.

Taylor, A. W., & Kunishi, H. M. (1971). Phosphate Equilibria on Stream Sediment and Soil in a Watershed Draining an Agricultural Region. *Journal of Agricultural and Food Chemistry, 19*(5), 827-831. doi:10.1021/jf60177a061

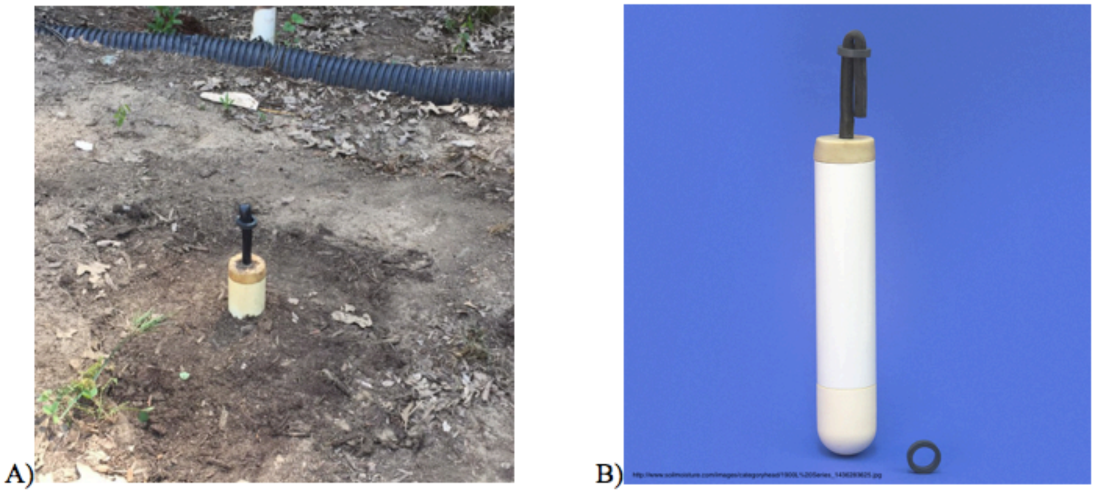
Tuttle, A. K., McMillan, S. K., Gardner, A., & Jennings, G. D. (2014). Channel complexity and nitrate concentrations drive denitrification rates in urban restored and unrestored streams. *Ecological Engineering, 73*, 770-777. doi:https://doi.org/10.1016/j.ecoleng.2014.09.066

Walsh, C. J., Roy, A. H., Feminella, J. W., Cottingham, P. D., Groffman, P. M., & Morgan, R. P. (2005). The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society, 24*(3), 706-723. doi:10.1899/04-028.1

Wossink, G., & Hunt, W. (2003). Cost effectiveness analysis of structural stormwater best management practices in North Carolina. *Rep, 344*.

Zhang, Z. F., Groenevelt, P. H., & Parkin, G. W. (1998). The well-shape factor for the measurement of soil hydraulic properties using the Guelph Permeameter. *Soil and Tillage Research, 49*(3), 219-221.

Appendix A Additional figures and tables



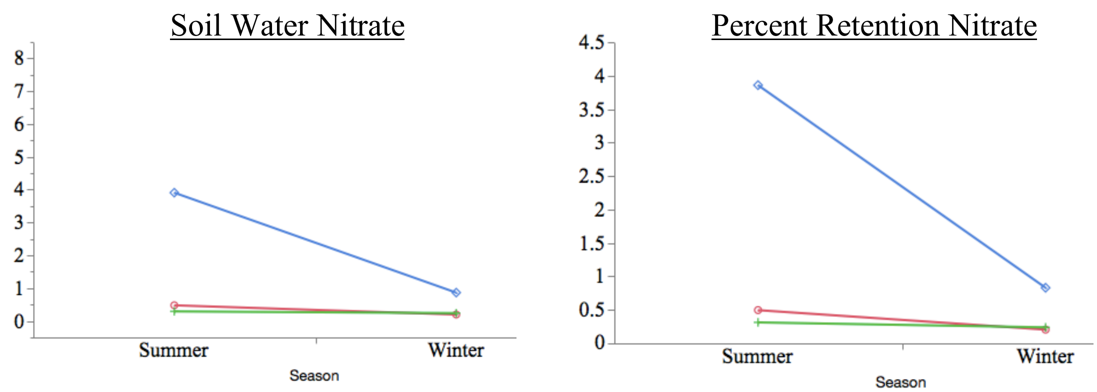
Appendix Figure 1: A) An installed lysimeter in a rain garden. B) A profile view of the 1900L Near Surface Samplers installed at each rain garden.

Appendix Table 1: Attribute information regarding sample analysis below detection limit.

	NH_4^+	NO_3^-	PO_4^{2-}	DOC
Number of samples	291	271	271	238
Number of samples below 0	40	0	14	0
Number of samples between 0 and detection limit	29	6	109	0
Detection limit	4.0 µg/L	10.0 µg/L	10.0 µg/L	0.5 µg/L

Appendix Table 2: Hydrological data for each individual storm. The red shades represent the summer storms, while the blue shades represent winter storms.

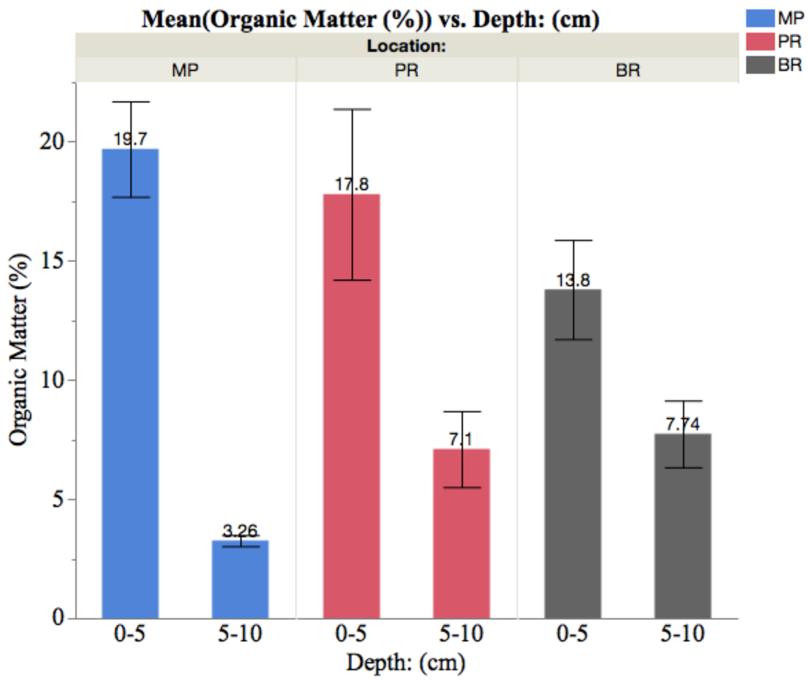
Location	Event Date	Total Precip (in/day)	Duration (hr/day)	Max Intensity (in/hr)	Max Intensity (in/day)	API 2(in)	API 7 (in)	API 14 (in)	Season
MP	7/15/17	0.46	0.75	0.45	0.45	0.03	0.32	1.59	Summer
PR	7/15/17	0.64	1	0.62	0.62	0	0.28	2.18	Summer
MP	8/7/17	0.83	2.41	0.26	0.3	0.08	0.79	1.14	Summer
PR	8/7/17	0.76	2.25	0.24	0.29	0.12	0.87	1.37	Summer
MP	8/11/17	0.23	0.91	0.08	0.17	0	1.8	2.15	Summer
MP	8/12/17	0.23	0.58	0.2	0.2	0.23	1.32	2.03	Summer
PR	8/12/17	0.41	0.91	0.34	0.34	0.24	1.28	2.03	Summer
PR	8/14/17	0.92	1.75	0.72	0.72	0.42	1.58	2.45	Summer
MP	8/15/17	0.84	0.83	0.83	0.83	0.96	1.6	3.22	Summer
PR	8/15/17	0.97	0.83	0.95	0.95	0.92	1.74	3.37	Summer
BR	8/31/17	0.55	2.83	0.26	0.26	0.04	0.04	0.67	Summer
MP	8/31/17	0.55	3.5	0.18	0.18	0.01	0.01	0.28	Summer
PR	8/31/17	0.51	3.33	0.17	0.17	0.01	0.02	0.16	Summer
BR	9/1/17	0.4	1.16	0.08	0.2	0.55	0.59	1.22	Summer
MP	9/1/17	0.76	0.66	0.72	0.72	0.55	0.56	0.83	Summer
PR	9/1/17	0.76	0.66	0.74	0.74	0.51	0.52	0.67	Summer
BR	9/11/17	1.6	9.25	0.21	0.21	0	1.07	2.06	Summer
MP	9/11/17	1.69	9.33	0.27	0.27	0	0.46	1.78	Summer
PR	9/11/17	1.74	9.58	0.24	0.24	0	0.43	1.71	Summer
BR	12/20/17	0.86	5.66	0.24	0.24	0	0	0.05 *	Winter
MP	12/20/17	1.01	6	0.23	0.23	0	0	0.08 *	Winter
PR	12/20/17	0.95	5.83	0.26	0.26	0	0	0.09	Winter
BR	1/28/17	1.33	9.5	0.19	0.19	0	0.59	0.59 *	Winter
MP	1/28/17	1.51	10.41	0.26	0.26	0.01	0.82	0.82 *	Winter
PR	1/28/17	1.55	10.58	0.15	0.25	0	0.8	0.80 *	Winter
BR	2/4/17	1.18	3.91	0.45	0.45	0.08	1.45	2.04	Winter
MP	2/4/17	1.33	4.33	0.49	0.49	0.11	1.64	2.46	Winter
PR	2/4/17	1.28	4.25	0.45	0.45	0.11	1.69	2.49	Winter
	* = Missing part of gauge data								



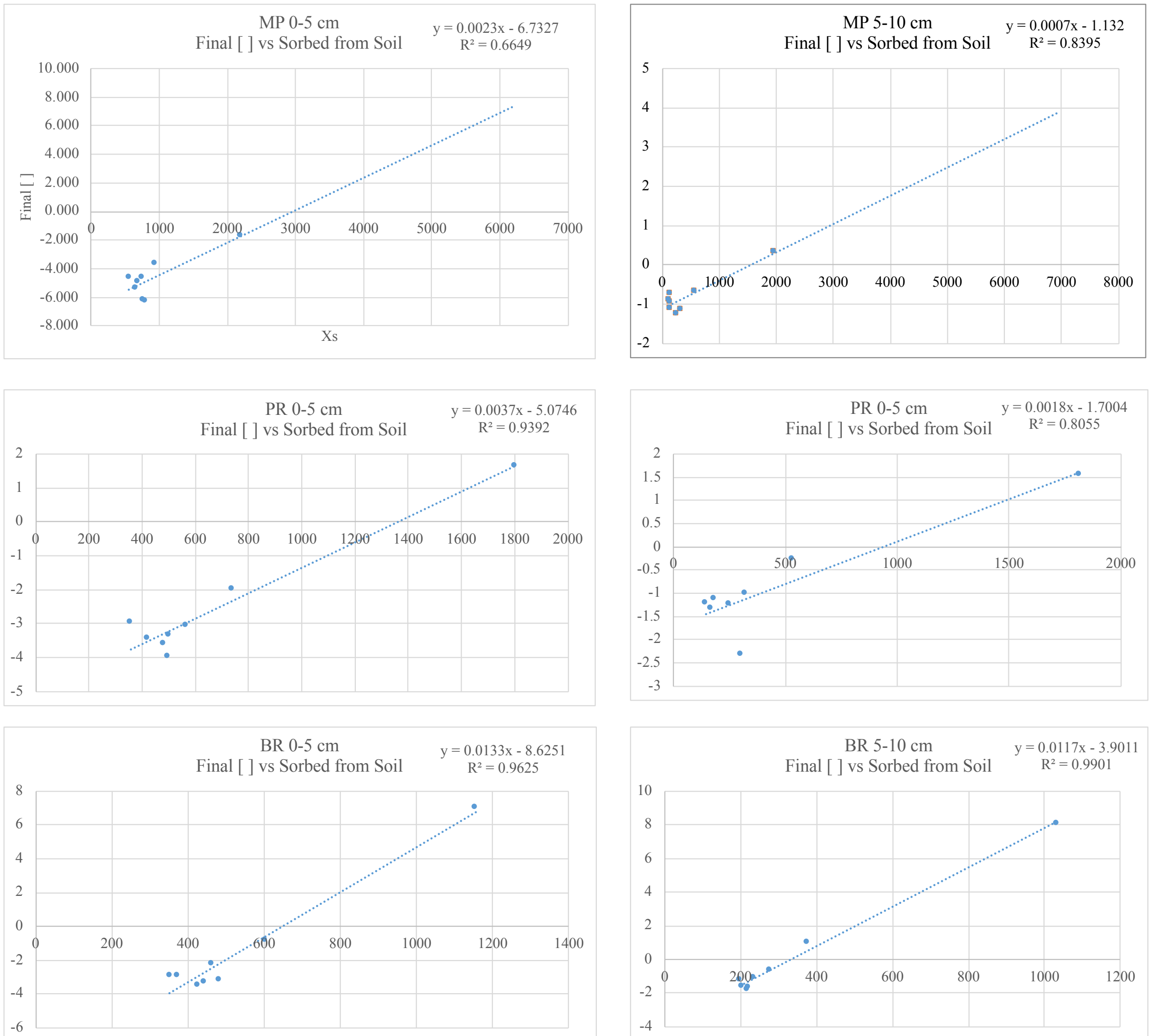
Appendix Figure 2: LS Means Differences Tukey HSD plot for site and season cross of the two-way ANOVA for soil water nitrate and retention.

Appendix Table 3: Values associated with Figure 17.

Site	Season	Depth	Denitrification µg/g DM/hr	DNF difference between 0-5 and 5-10 µg/g DM/hr
MP	Summer	0-5	1.01	0.86
		5-10	0.14	
MP	Fall	0-5	0.41	0.33
		5-10	0.08	
MP	Spring	0-5	0.62	0.54
		5-10	0.08	
PR	Summer	0-5	0.25	0.08
		5-10	0.17	
PR	Fall	0-5	0.05	-0.07
		5-10	0.12	
PR	Spring	0-5	0.06	0.01
		5-10	0.06	
BR	Summer	0-5	0.92	0.37
		5-10	0.56	
BR	Fall	0-5	0.85	0.28
		5-10	0.57	
BR	Spring	0-5	0.78	0.59
		5-10	0.19	



Appendix Figure 3: Figure to accompany
to show different mean organic matter percent across each site.

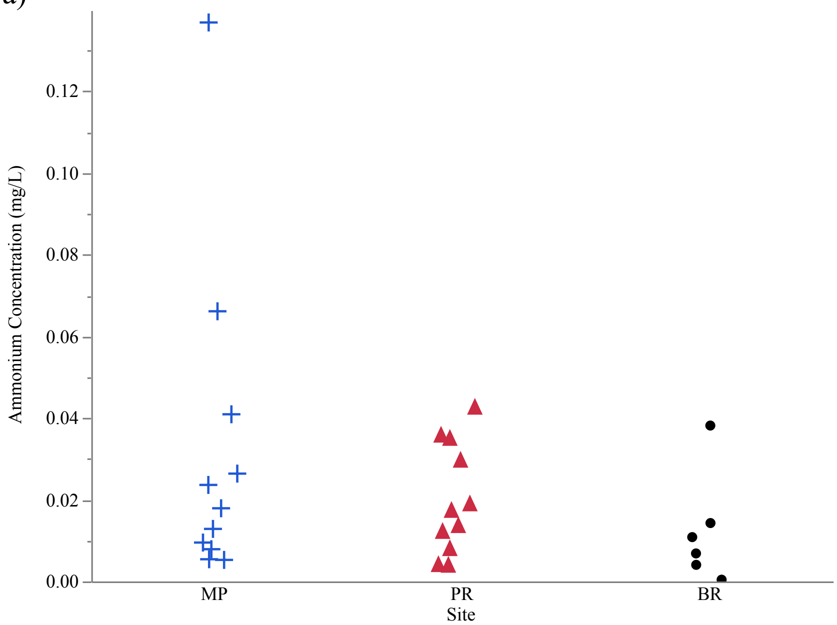


Appendix Figure 4: Isotherms used to identify the EPC.

Alternate figures of the bar graphs to display data points that were used to create the bar graphs. Note the figure number corresponds to the figure number in the text and figures that are not present below were not bar graphs in the original text.

Figure 7:

a)



b)

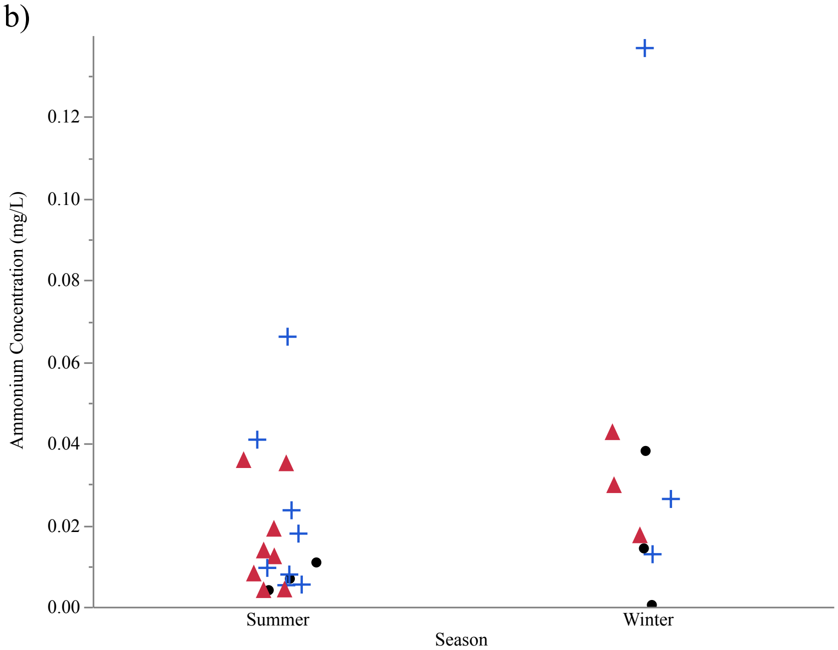


Figure 8:

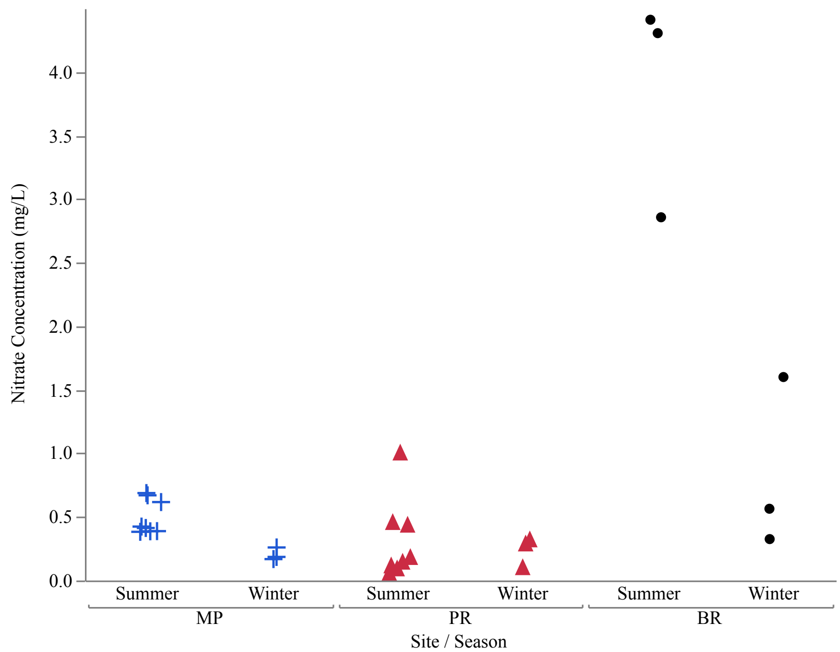


Figure 9:

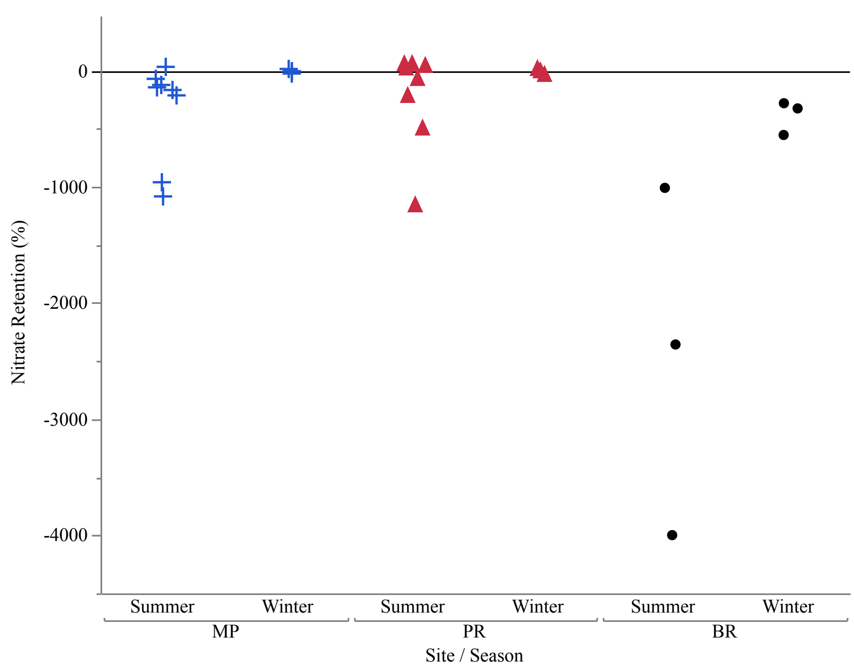
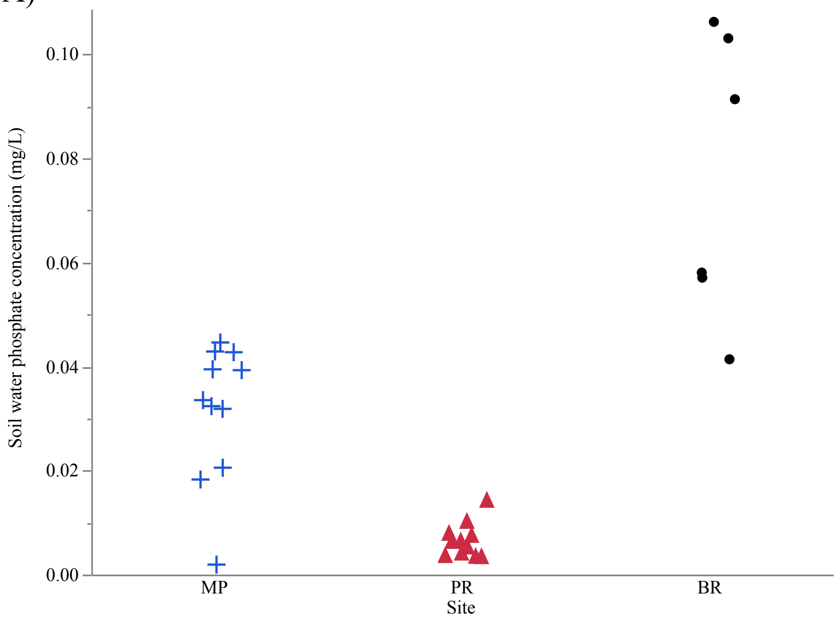


Figure 10:

A)


Soil water phosphate concentration (mg/L)
0.10
0.08
0.06
0.04
0.02
0.00
MP
PR
BR
Site

B)

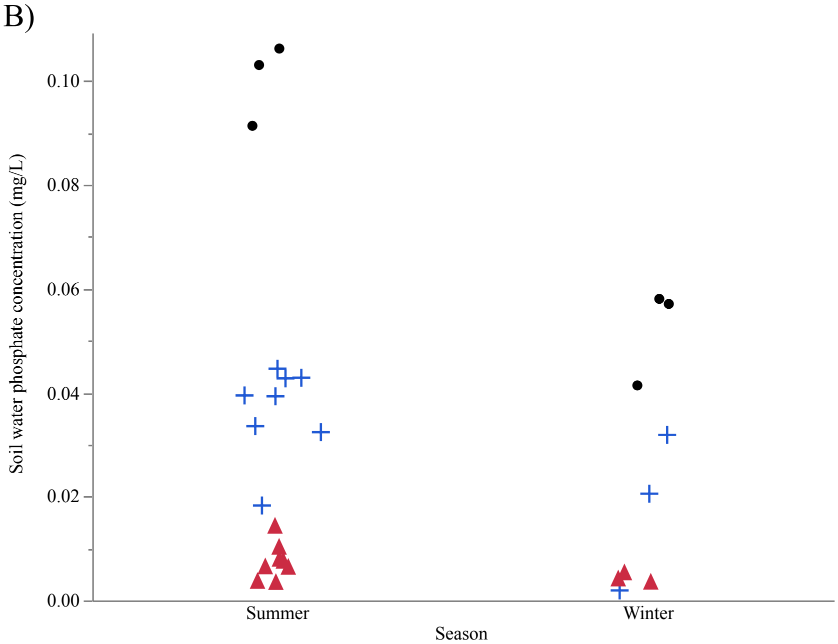

Soil water phosphate concentration (mg/L)
0.10
0.08
0.06
0.04
0.02
0.00
Summer
Winter
Season

Figure 11:

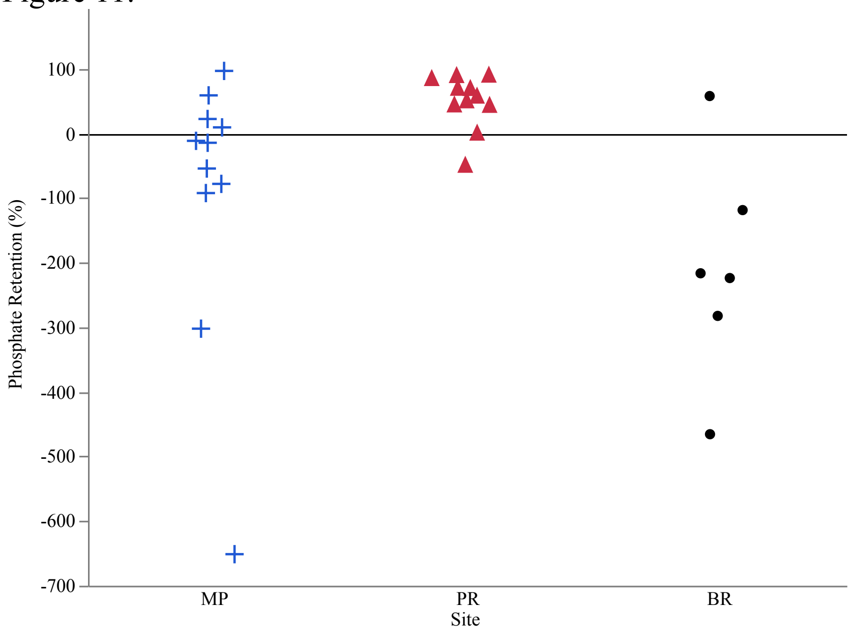
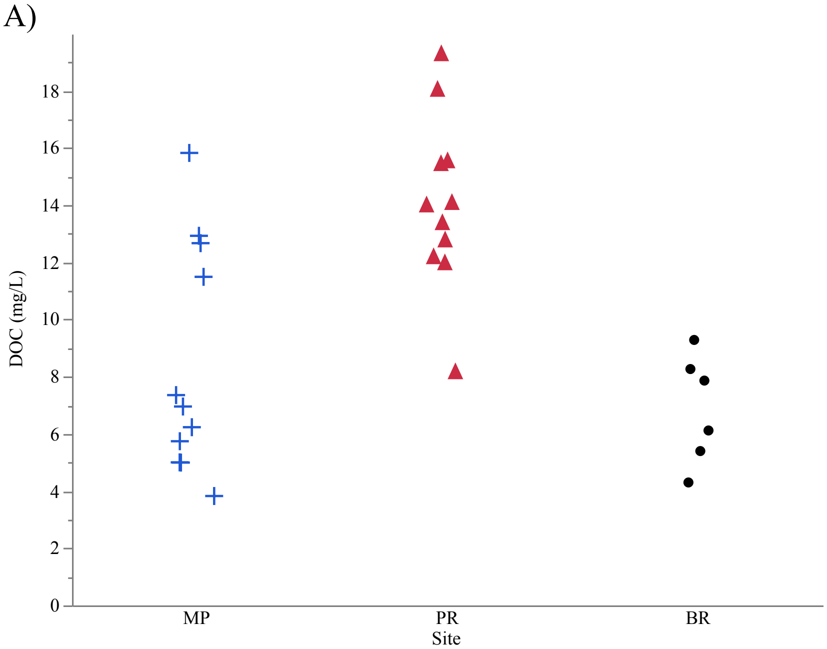
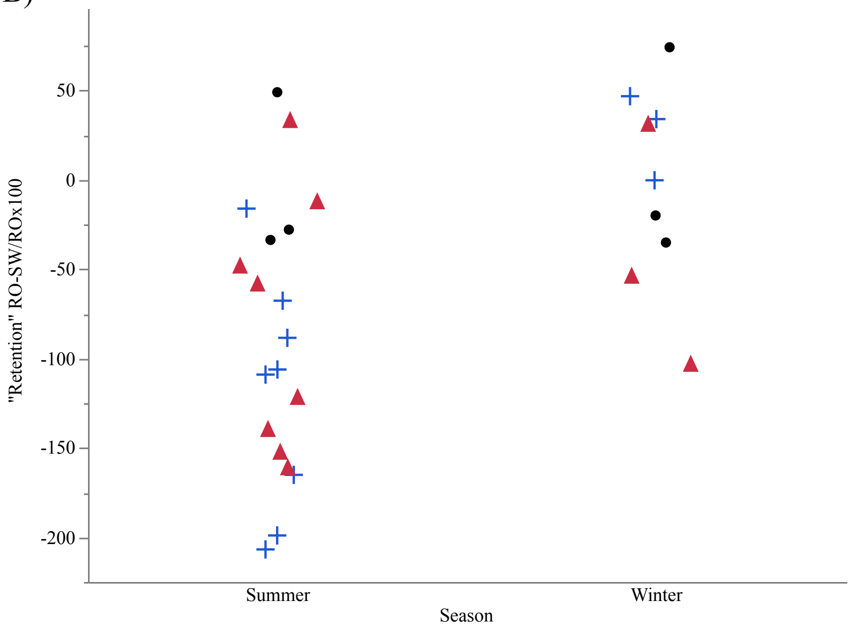


Figure 12:

A)

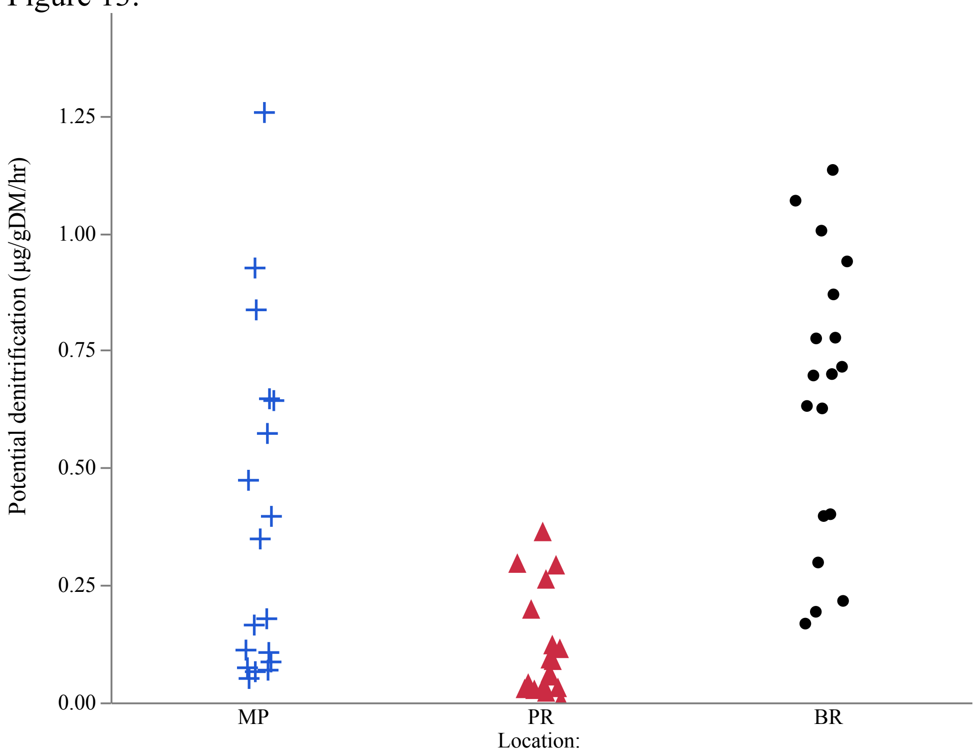


B)



"Retention" RO-SW/ROx100
50
0
-50
-100
-150
-200
Summer
Winter
Season

Figure 13:



Potential denitrification (μg/gDM/hr)
1.25
1.00
0.75
0.50
0.25
0.00
MP
PR
BR
Location:

Figure 14:

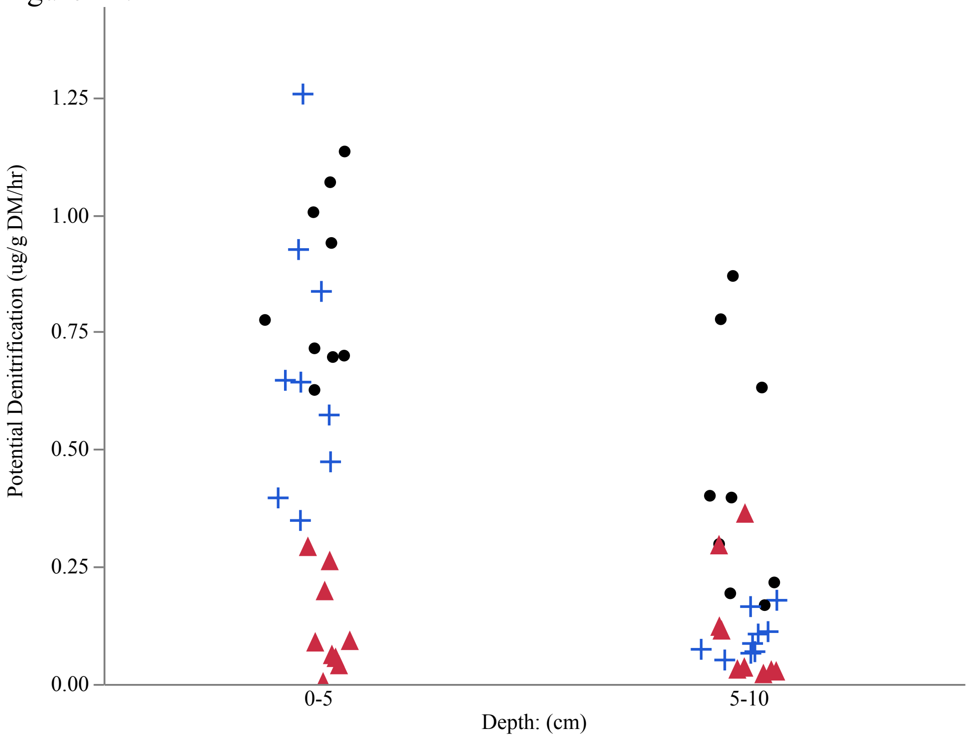


Figure 15 & 16:

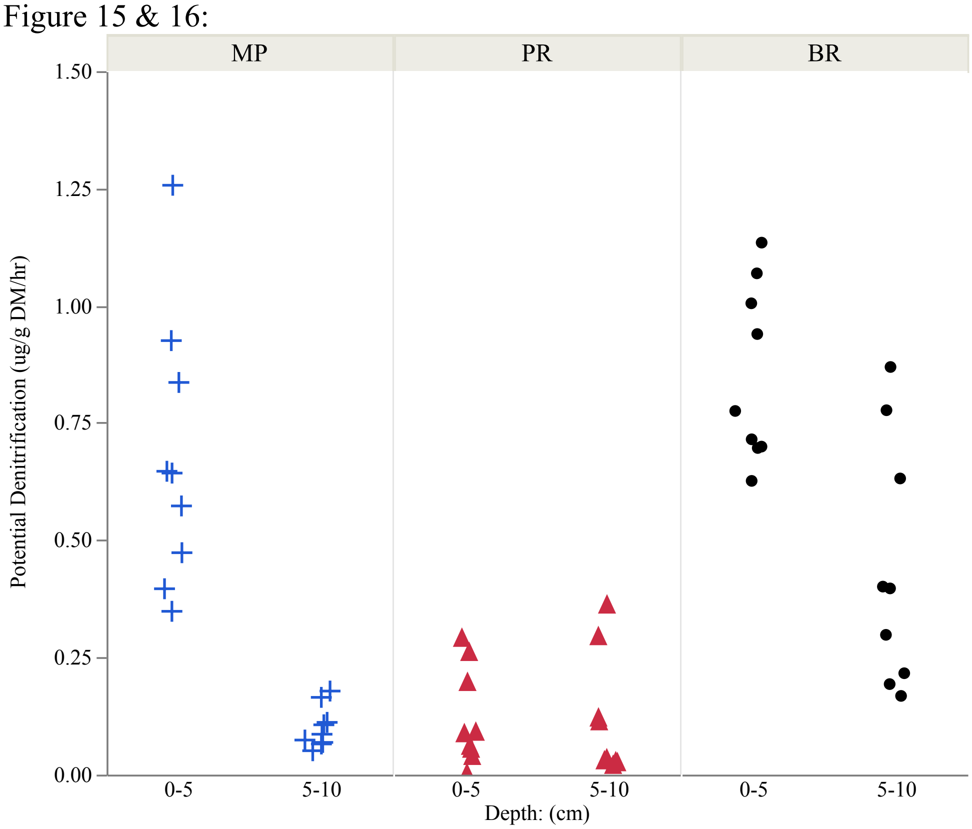


Figure 18:

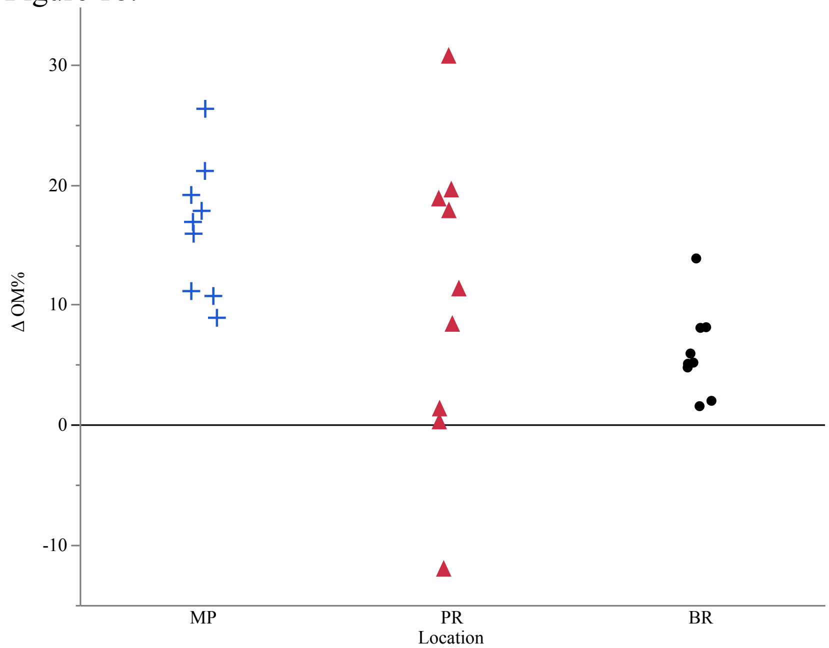


Figure 21:

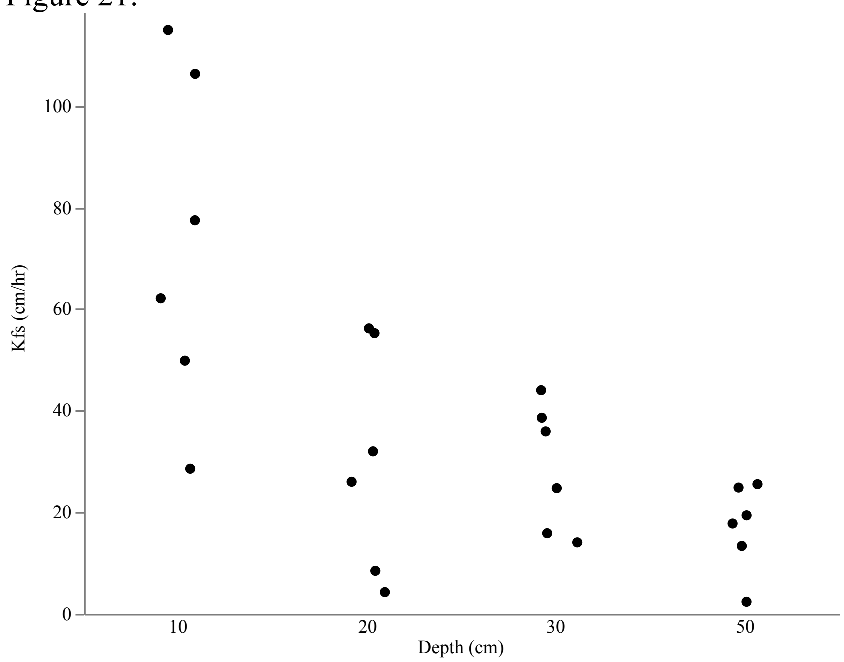
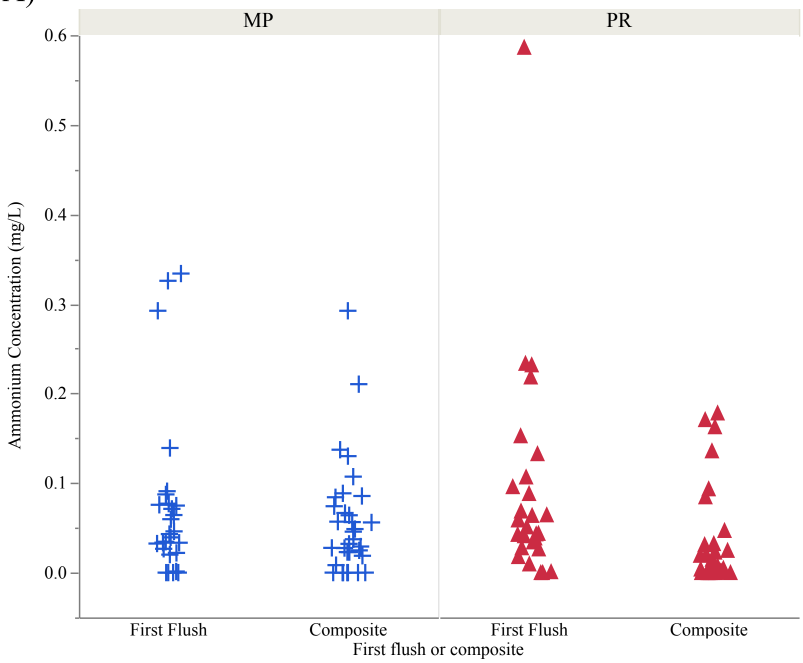


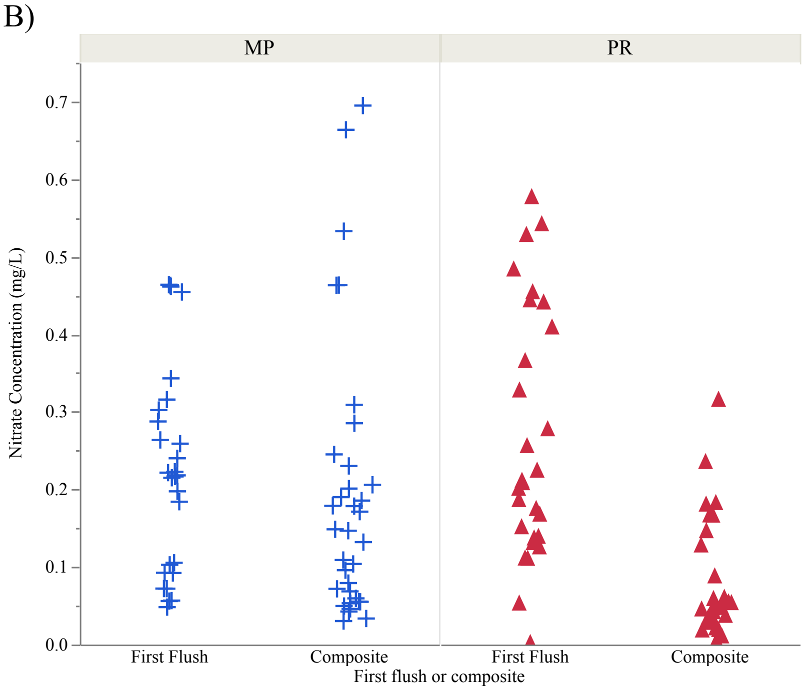
Figure 23:

A)



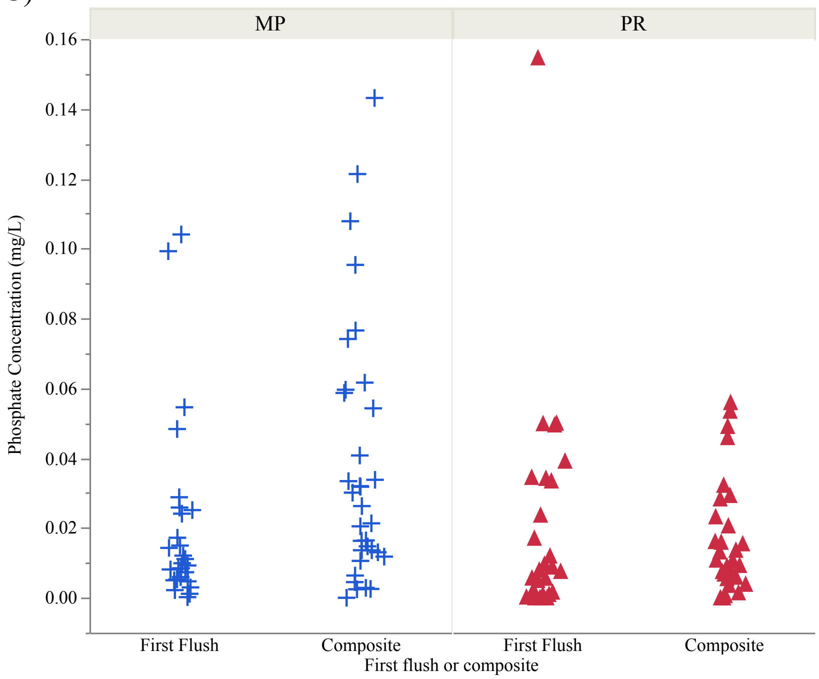
MP
PR
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Ammonium Concentration (mg/L)
First Flush
Composite
First Flush
Composite
First flush or composite

B)



MP
PR
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Nitrate Concentration (mg/L)
First Flush
Composite
First Flush
Composite
First flush or composite

C)


MP
PR
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Phosphate Concentration (mg/L)
First Flush
Composite
First Flush
Composite
First flush or composite

D)

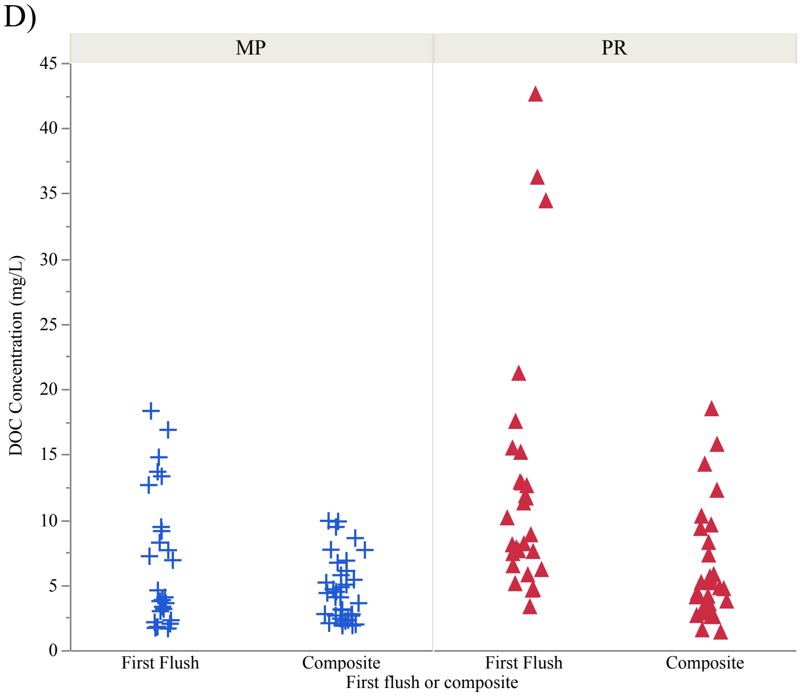
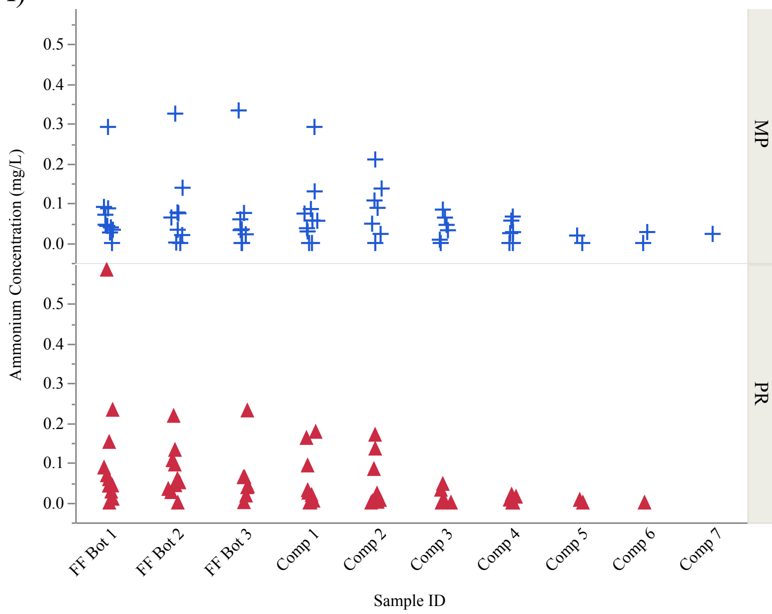
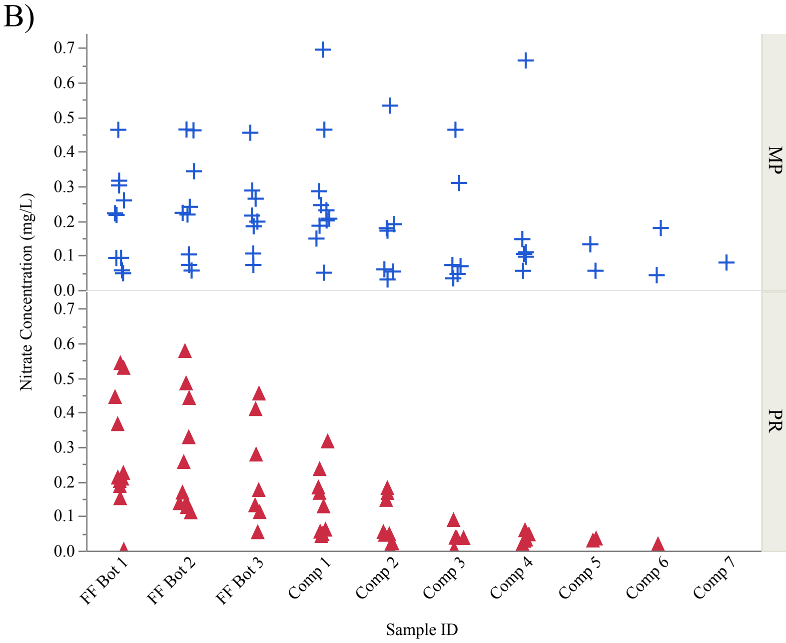

MP
PR
45
40
35
30
25
20
15
10
5
0
DOC Concentration (mg/L)
First Flush
Composite
First Flush
Composite
First flush or composite

Figure 24:

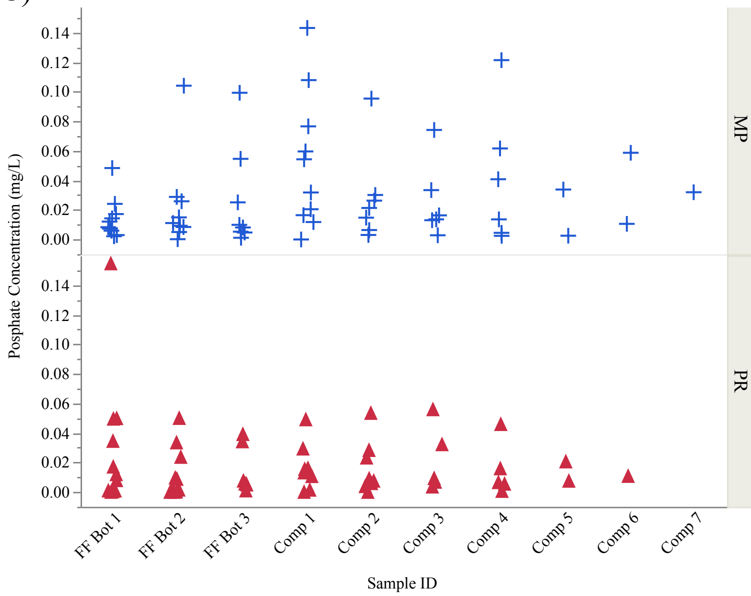
A)


Ammonium Concentration (mg/L)
0.5
0.4
0.3
0.2
0.1
0.0
MP
PR
FF Bot 1
FF Bot 2
FF Bot 3
Comp 1
Comp 2
Comp 3
Comp 4
Comp 5
Comp 6
Comp 7
Sample ID

B)

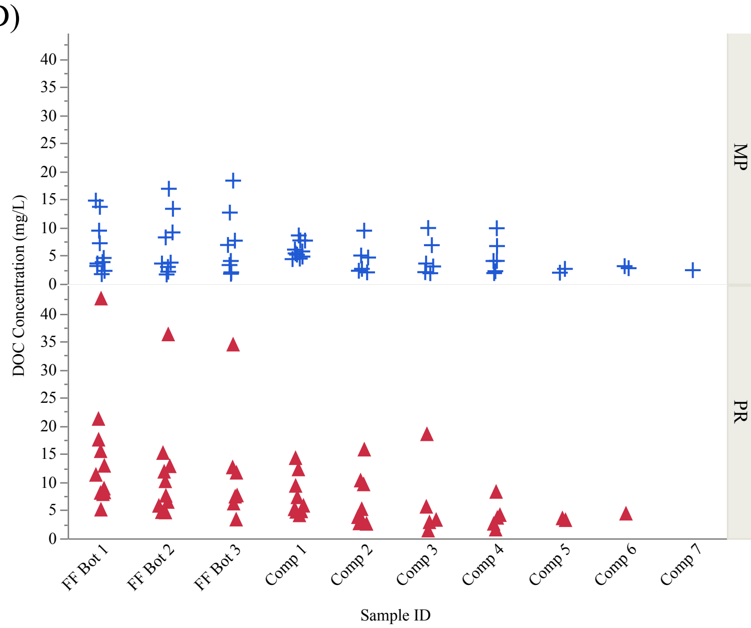

Nitrate Concentration (mg/L)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
MP
PR
FF Bot 1
FF Bot 2
FF Bot 3
Comp 1
Comp 2
Comp 3
Comp 4
Comp 5
Comp 6
Comp 7
Sample ID

C)



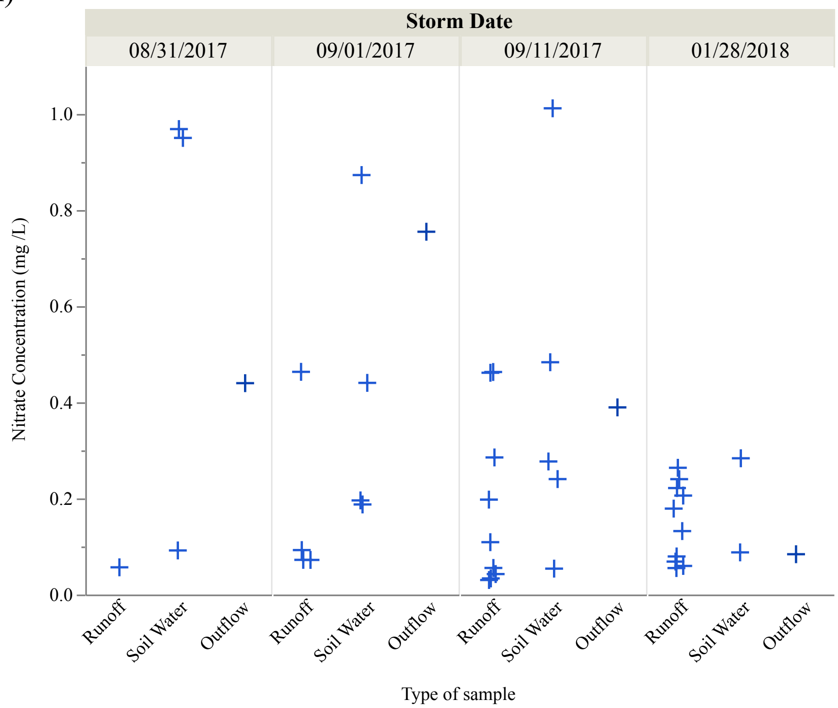
Posphate Concentration (mg/L)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
MP
PR
FF Bot 1
FF Bot 2
FF Bot 3
Comp 1
Comp 2
Comp 3
Comp 4
Comp 5
Comp 6
Comp 7
Sample ID

D)



DOC Concentration (mg/L)
40
35
30
25
20
15
10
5
0
MP
PR
FF Bot 1
FF Bot 2
FF Bot 3
Comp 1
Comp 2
Comp 3
Comp 4
Comp 5
Comp 6
Comp 7
Sample ID

Figure 26:
A)


Storm Date
08/31/2017
09/01/2017
09/11/2017
01/28/2018
Nitrate Concentration (mg /L)
1.0
0.8
0.6
0.4
0.2
0.0
Runoff
Soil Water
Outflow
Type of sample

B)

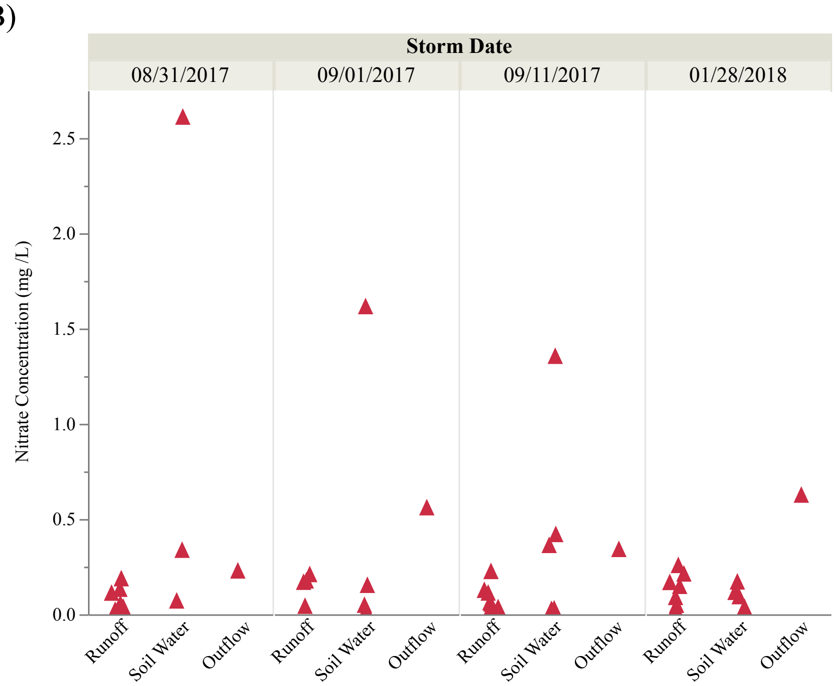

Storm Date
08/31/2017
09/01/2017
09/11/2017
01/28/2018
Nitrate Concentration (mg /L)
2.5
2.0
1.5
1.0
0.5
0.0
Runoff
Soil Water
Outflow

Figure 27:

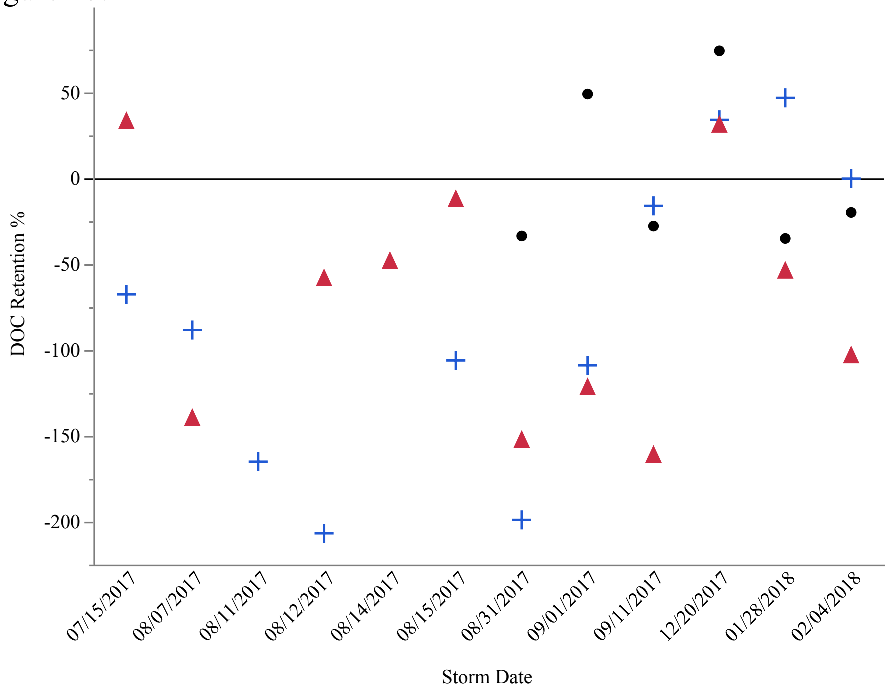
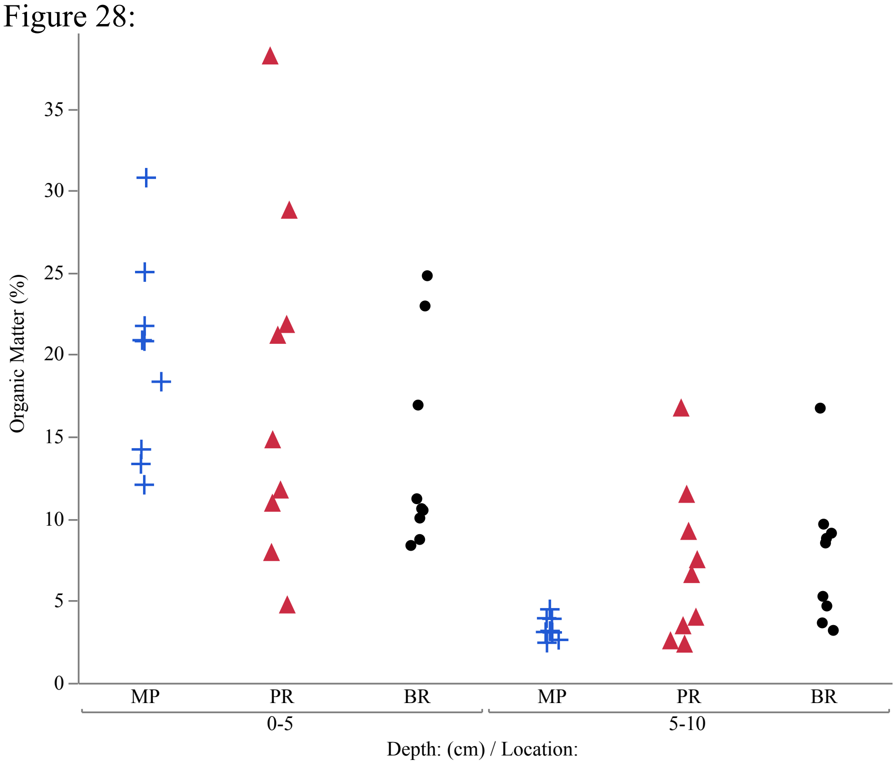


Figure 28:



Appendix B Raw Data

The raw data used to in this study with the negative values placed to zero. Each constituent had a measured concentration in mg/L. Blank spaces indicate no sample was obtained due water volume collected.

Original Sample ID	Season	Storm Date	Collection Date	NH_4^+	NO_3^{2-}	PO_4^{2-}	DOC	TN
MP Composite 1	Summer	07/15/2017	07/15/2017	0.086	0.695	0.143	8.587	1.043
MP Composite 2	Summer	07/15/2017	07/15/2017	0.089	0.533	0.095	9.439	1.116
MP Composite 3	Summer	07/15/2017	07/15/2017	0.084	0.463	0.074	9.908	1.122
MP Composite 4	Summer	07/15/2017	07/15/2017	0.067	0.664	0.121	9.863	1.116
MP Lys 1	Summer	07/15/2017	07/16/2017	0.030	0.039	0.022	18.970	0.590
MP Lys 1	Summer	07/15/2017	07/17/2017	0.043	0.032	0.019	15.460	0.513
MP Lys 2	Summer	07/15/2017	07/16/2017	0.045	0.571	0.054	13.560	1.112
MP Lys 2	Summer	07/15/2017	07/17/2017	0.041	1.417	0.052	15.340	1.841
MP Lys 3	Summer	07/15/2017	07/16/2017	0.045	0.146	0.062		
MP Lys 3	Summer	07/15/2017	07/17/2017	0.043	0.118	0.059		
PR FF Hand Grab	Summer	07/15/2017	07/15/2017	0.586	0.366	0.155	21.220	2.963
PR Lys 1	Summer	07/15/2017	07/17/2017	0.034	0.814	0.010	17.040	1.274
PR Lys 2	Summer	07/15/2017	07/16/2017	0.031	0.035	0.009	19.740	0.876
PR Lys 2	Summer	07/15/2017	07/17/2017	0.044	0.037	0.010	19.520	0.758
PR Lys 3	Summer	07/15/2017	07/16/2017	0.033	0.017	0.025		
PR Lys 3	Summer	07/15/2017	07/17/2017	0.038	0.016	0.018	0.137	0.000
MP FF Bot 1	Summer	08/07/2017	08/07/2017	0.071	0.092	0.012	3.155	0.235
MP FF Bot 2	Summer	08/07/2017	08/07/2017	0.077	0.103	0.015	2.984	0.243
MP Comp 1 Bot 4	Summer	08/07/2017	08/07/2017	0.130	0.201	0.032	4.829	0.473
MP Comp 2 Bot 5	Summer	08/07/2017	08/07/2017	0.137	0.190	0.030	4.662	0.453
MP Lys 1	Summer	08/07/2017	08/07/2017	0.014	0.063	0.009	12.090	0.458
MP Lys 1	Summer	08/07/2017	08/08/2017	0.010	0.021	0.010	7.546	0.261
MP Lys 2	Summer	08/07/2017	08/07/2017	0.000	1.127	0.071	10.130	1.233
MP Lys 2	Summer	08/07/2017	08/08/2017	0.008	0.343	0.081	6.495	0.491
MP Lys 3	Summer	08/07/2017	08/07/2017				0.042	0.000
MP Lys 3 Resample	Summer	08/07/2017	08/08/2017				7.852	0.405
PR FF Bot 1	Summer	08/07/2017	08/07/2017	0.153	0.152	0.017	5.097	0.416
PR FF Bot 2	Summer	08/07/2017	08/07/2017	0.133	0.140	0.033	4.601	0.387
PR Comp 1 Bot 4	Summer	08/07/2017	08/07/2017	0.163	0.183	0.029	5.168	0.459
PR Comp 2 Bot 5	Summer	08/07/2017	08/07/2017	0.171	0.181	0.028	5.184	0.472
PR Lys 1	Summer	08/07/2017	08/07/2017	0.008	0.259	0.006	11.070	0.633
PR Lys 1	Summer	08/07/2017	08/08/2017	0.033	0.098	0.006	8.481	0.337

PR Lys 2	Summer	08/07/2017	08/07/2017	0.002	0.109	0.012	14.860	0.553
PR Lys 3	Summer	08/07/2017	08/07/2017	0.023	0.005	0.009		
PR Lys 3	Summer	08/07/2017	08/08/2017	0.029			13.590	0.376
MP FF Bot 1	Summer	08/11/2017	08/11/2017	0.046	0.217	0.007	3.602	0.307
MP FF Bot 2	Summer	08/11/2017	08/11/2017	0.064	0.223	0.011	3.595	0.359
MP FF Bot 3	Summer	08/11/2017	08/11/2017	0.060	0.215	0.010	3.325	0.359
MP Comp 1 Bot 4	Summer	08/11/2017	08/11/2017	0.074	0.149	0.000	4.380	0.789
MP Comp 2 Bot 5	Summer	08/11/2017	08/11/2017	0.107	0.179	0.003	5.018	0.938
MP Comp 3 Bot 6	Summer	08/11/2017	08/11/2017	0.046	0.309	0.003	6.858	0.553
MP Comp 4 Bot 13	Summer	08/11/2017	08/11/2017	0.027	0.096	0.002	6.700	0.456
MP Lys 1	Summer	08/11/2017	08/12/2017	0.003	0.041	0.009	13.910	0.437
MP Lys 2	Summer	08/11/2017	08/12/2017	0.007	1.193	0.070	11.440	1.753
PR Rain	Summer	08/12/2017	08/12/2017	0.201	0.172	0.013	5.649	0.478
PR FF Bot 1	Summer	08/12/2017	08/12/2017	0.043	0.201	0.000	8.073	0.383
PR FF Bot 2	Summer	08/12/2017	08/12/2017	0.034	0.137	0.000	5.774	0.341
PR FF Bot 3	Summer	08/12/2017	08/12/2017	0.018	0.054	0.006	7.401	0.376
PR Comp 1 Bot 4	Summer	08/12/2017	08/12/2017	0.000	0.048	0.014	12.250	0.643
PR Comp 2 Bot 8	Summer	08/12/2017	08/12/2017	0.002	0.011	0.006	15.770	0.722
PR Lys 1	Summer	08/12/2017	08/13/2017	0.019	0.453	0.005	10.240	0.913
PR Lys 1	Summer	08/12/2017	08/14/2017	0.010	0.215	0.005	11.570	0.741
PR Lys 2	Summer	08/12/2017	08/13/2017	0.006	0.046	0.008	18.920	0.716
PR Lys 2 Resample	Summer	08/12/2017	08/14/2017				21.490	0.745
PR Lys 3	Summer	08/12/2017	08/13/2017	0.016	0.003	0.010	14.060	0.373
PR Lys 3	Summer	08/12/2017	08/14/2017	0.017	0.017	0.010	17.130	0.422
MP FF Bot 1	Summer	08/12/2017	08/12/2017	0.000	0.048	0.017	4.584	0.245
MP FF Bot 2	Summer	08/12/2017	08/12/2017	0.000	0.056	0.026	3.757	0.188
MP FF Bot 3	Summer	08/12/2017	08/12/2017	0.000	0.105	0.055	4.051	0.206
MP Comp 1 Bot 4	Summer	08/12/2017	08/12/2017	0.000	0.050	0.077	4.472	0.187
MP Lys 1	Summer	08/12/2017	08/13/2017	0.001	0.098	0.009	11.780	0.454
MP Lys 1	Summer	08/12/2017	08/14/2017	0.013	0.102	0.009		
MP Lys 2	Summer	08/12/2017	08/13/2017	0.009	0.937	0.067	11.650	1.515
MP Lys 2	Summer	08/12/2017	08/14/2017	0.004	2.253	0.078	16.000	2.046
MP Lys 3	Summer	08/12/2017	08/13/2017	0.021	0.049	0.035	9.972	0.371
MP Lys 3 Resample	Summer	08/12/2017	08/14/2017				15.260	0.804
PR Rainfall	Summer	08/14/2017	08/15/2017	0.312	0.257	0.010	5.898	0.775
PR FF Bot 1	Summer	08/14/2017	08/15/2017	0.088	0.444	0.001	11.280	0.892
PR FF Bot 2	Summer	08/14/2017	08/15/2017	0.096	0.484	0.000	10.140	0.881
PR FF Bot 3	Summer	08/14/2017	08/15/2017	0.064	0.278	0.008	6.178	0.464
PR Comp 1 Bot 4	Summer	08/14/2017	08/15/2017	0.019	0.128	0.016	4.088	0.269

PR Comp 2 Bot 5	Summer	08/14/2017	08/15/2017	0.023	0.048	0.053	9.590	0.520
PR Lys 1	Summer	08/14/2017	08/15/2017	0.024	0.248	0.005	8.587	0.646
PR Lys 2	Summer	08/14/2017	08/15/2017	0.055	0.029	0.005	14.690	0.638
PR Lys 3	Summer	08/14/2017	08/15/2017	0.026	0.006	0.009	13.360	0.484
PR Rainfall	Summer	08/15/2017	08/16/2017	0.089	0.119	0.000	2.274	0.357
PR FF 1	Summer	08/15/2017	08/16/2017	0.010	0.003	0.050	8.158	0.405
PR FF2	Summer	08/15/2017	08/16/2017	0.059	0.328	0.002	6.469	0.613
PR Lys 1	Summer	08/15/2017	08/16/2017	0.007	0.155	0.004	7.658	0.468
PR Lys 1	Summer	08/15/2017	08/17/2017	0.008				
PR Lys 2	Summer	08/15/2017	08/16/2017	0.002	0.069	0.007	5.659	0.578
PR Lys 3	Summer	08/15/2017	08/16/2017		0.010	0.002	9.725	0.315
PR Lys 3	Summer	08/15/2017	08/17/2017	0.000	0.001	0.002	9.709	0.230
MP Rainfall	Summer	08/15/2017	08/16/2017	2.141	0.250	1.305	14.190	11.35 0
MP FF Bot 1	Summer	08/15/2017	08/16/2017	0.033	0.259	0.003	2.294	0.344
MP FF Bot 2	Summer	08/15/2017	08/16/2017	0.001	0.218	0.000	1.654	0.243
MP FF Bot 3	Summer	08/15/2017	08/16/2017	0.000	0.184	0.001	2.024	0.219
MP Comp1 Bot 4	Summer	08/15/2017	08/16/2017	0.000	0.245	0.060	5.180	0.507
MP Lys 1	Summer	08/15/2017	08/16/2017	0.037	0.045	0.014	4.549	0.300
MP Lys 1	Summer	08/15/2017	08/17/2017	0.088	0.116	0.000		
MP Lys 2	Summer	08/15/2017	08/16/2017	0.022	0.262	0.058	7.518	1.730
MP Lys 2	Summer	08/15/2017	08/17/2017	0.001	1.439	0.006		
MP Lys 3	Summer	08/15/2017	08/16/2017	0.036	0.053	0.013	5.167	0.359
MP Lys 3	Summer	08/15/2017	08/17/2017	0.213				
PR Rainfall	Summer	08/31/2017	09/01/2017	0.211	0.098	0.000		
PR FF Bot 1	Summer	08/31/2017	09/01/2017	0.059	0.187	0.034	15.490	0.727
PR FF Bot 2	Summer	08/31/2017	09/01/2017	0.051	0.111	0.024	12.810	0.620
PR FF Bot 3	Summer	08/31/2017	09/01/2017	0.064	0.131	0.034	12.600	0.621
PR Comp 1 Bot 4+5	Summer	08/31/2017	09/01/2017	0.025	0.055	0.015	4.712	0.216
PR Comp 2 Bot 6+7	Summer	08/31/2017	09/01/2017	0.007	0.022	0.008	2.575	0.165
PR Comp 3 Bot 8+9	Summer	08/31/2017	09/01/2017	0.006	0.037	0.007	2.853	0.133
PR Comp 4 Bot 10 +11	Summer	08/31/2017	09/01/2017	0.007	0.019	0.007	2.581	0.118
PR Hand Grab Outflow	Summer	08/31/2017	09/01/2017	0.003	0.228	0.005	4.727	0.391
PR Hand Grab Outflow	Summer	08/31/2017	09/01/2017	0.001				
PR Lys 1	Summer	08/31/2017	09/01/2017	0.000	2.610	0.003		
PR Lys 2	Summer	08/31/2017	09/01/2017	0.007	0.336	0.013	20.290	1.056
PR Lys 3	Summer	08/31/2017	09/01/2017	0.017	0.070	0.015	18.340	0.584
MP Rain	Summer	08/31/2017	09/01/2017	0.438	0.150	0.799		

MP Hand Grab Inflow	Summer	08/31/2017	08/31/2017	0.039	0.057	0.024	3.846	0.239
MP Hand Grab Outflow	Summer	08/31/2017	08/31/2017	0.002	0.440	0.030	8.461	0.809
MP Lys 1	Summer	08/31/2017	09/01/2017	0.024	0.950	0.052	12.790	1.673
MP Lys 2	Summer	08/31/2017	09/01/2017	0.022	0.969	0.057	12.810	1.627
MP Lys 3	Summer	08/31/2017	09/01/2017	0.025	0.092	0.019	8.891	0.488
BR Rainfall	Summer	08/31/2017	09/01/2017	0.180	0.377	0.026		
Bruns FF True FF Sampler	Summer	08/31/2017	09/01/2017	0.083	0.198	0.068	7.267	0.592
Bruns Runoff Hand Grab	Summer	08/31/2017	09/01/2017	0.000	0.048	0.009	4.650	0.385
BR Forebay Sample	Summer	08/31/2017	09/01/2017	0.000	0.069	0.021	5.755	0.225
BR Lys 1	Summer	08/31/2017	09/01/2017	0.012	3.498	0.270		
BR Lys 2	Summer	08/31/2017	09/01/2017	0.000	2.485	0.019	10.770	6.809
BR Lys 3	Summer	08/31/2017	09/01/2017	0.021	6.933	0.020	4.963	16.070
PR Rainfall	Summer	09/01/2017	09/02/2017	0.115	0.153	0.026		
PR FF Bot 1	Summer	09/01/2017	09/02/2017	0.028	0.209	0.001	7.843	0.536
PR FF Bot 2	Summer	09/01/2017	09/02/2017	0.026	0.168	0.002	4.650	0.387
PR FF Bot 3	Summer	09/01/2017	09/02/2017	0.039	0.175	0.001	3.332	0.304
PR Comp 1 Bot 4	Summer	09/01/2017	09/02/2017	0.000	0.042	0.049	7.293	0.312
PR Outflow	Summer	09/01/2017	09/01/2017	0.001	0.560	0.001	15.190	1.111
PR Lys 1	Summer	09/01/2017	09/02/2017	0.001	1.615	0.004	11.720	2.813
PR Lys 2	Summer	09/01/2017	09/02/2017	0.014	0.048	0.008	14.020	0.451
PR Lys 3	Summer	09/01/2017	09/02/2017	0.024	0.152	0.006	13.490	0.657
PR Lys 3	Summer	09/01/2017	09/03/2017	0.009	0.020	0.007	11.970	0.406
MP Rainfall	Summer	09/01/2017	09/02/2017	0.390	0.238	0.155		
MP FF Bot 1	Summer	09/01/2017	09/02/2017	0.027	0.093	0.002	1.709	0.152
MP FF Bot 2	Summer	09/01/2017	09/02/2017	0.033	0.072	0.005	2.139	0.163
MP FF Bot 3	Summer	09/01/2017	09/02/2017	0.034	0.072	0.005	1.782	0.196
MP Comp 1 Bot 4	Summer	09/01/2017	09/02/2017	0.057	0.463	0.108	7.696	0.998
MP Outflow	Summer	09/01/2017	09/01/2017	0.001	0.755	0.030	12.540	0.798
MP Lys 1	Summer	09/01/2017	09/02/2017	0.001	0.196	0.012	6.488	0.478
MP Lys 1	Summer	09/01/2017	09/03/2017	0.004	0.188	0.007	7.935	0.703
MP Lys 2	Summer	09/01/2017	09/02/2017	0.000	0.441	0.071	7.105	0.743
MP Lys 2	Summer	09/01/2017	09/03/2017	0.007	0.873	0.044	6.310	1.602
MP Lys 3	Summer	09/01/2017	09/03/2017	0.015				
BR Rainfall	Summer	09/01/2017	09/02/2017	0.485				
BR FF Hand Grab 1	Summer	09/01/2017	09/01/2017	0.105	0.333	0.021	16.880	1.186
BR FF Hand Grab 2	Summer	09/01/2017	09/01/2017	0.163	0.463	0.034	15.640	1.148
BR Lys 1	Summer	09/01/2017	09/02/2017	0.013	2.519	0.205		

BR Lys 1	Summer	09/01/2017	09/03/2017	0.003	3.089	0.246		
BR Lys 2	Summer	09/01/2017	09/02/2017	0.000	5.261	0.052	9.280	6.187
BR Lys 2	Summer	09/01/2017	09/03/2017	0.000	2.757	0.069	10.160	3.877
BR Lys 3	Summer	09/01/2017	09/02/2017	0.012	8.201	0.036		
BR Lys 3	Summer	09/01/2017	09/03/2017	0.014	4.637	0.030	5.372	6.632
MP Rainfall	Summer	09/11/2017	09/12/2017	0.095	0.086	0.001	1.316	0.208
MP FF 1	Summer	09/11/2017	09/12/2017	0.043	0.463	0.006	9.439	0.809
MP FF 2	Summer	09/11/2017	09/12/2017	0.020	0.462	0.008	9.123	0.876
MP FF 3	Summer	09/11/2017	09/12/2017	0.022	0.198	0.005	7.662	0.751
MP Comp 1 Bot 4	Summer	09/11/2017	09/12/2017	0.037	0.285	0.016	6.073	0.583
MP Comp 2 Bot 6	Summer	09/11/2017	09/12/2017	0.000	0.030	0.006	2.652	0.211
MP Comp 3 Bot 8	Summer	09/11/2017	09/12/2017	0.000	0.034	0.013	3.598	0.201
MP Comp 4 Bot 10	Summer	09/11/2017	09/12/2017	0.000	0.109	0.004	4.060	0.333
MP Comp 5 Bot 12	Summer	09/11/2017	09/12/2017	0.000	0.055	0.003	2.644	0.174
MP Comp 6 Bot 14	Summer	09/11/2017	09/12/2017	0.000	0.043	0.011	3.125	0.210
MP Outflow	Summer	09/11/2017	09/12/2017	0.002	0.390	0.046	8.108	0.600
MP Lys 1	Summer	09/11/2017	09/12/2017	0.010	0.240	0.011	8.013	0.496
MP Lys 1	Summer	09/11/2017	09/13/2017	0.002	0.277	0.005	5.507	0.414
MP Lys 2	Summer	09/11/2017	09/12/2017	0.000	1.012	0.066	9.296	1.162
MP Lys 2	Summer	09/11/2017	09/13/2017	0.000	0.483	0.051	4.760	0.561
MP Lys 3	Summer	09/11/2017	09/12/2017	0.011	0.054	0.029	3.602	0.207
MP Lys 3	Summer	09/11/2017	09/13/2017	0.085				
PR Rainfall	Summer	09/11/2017	09/12/2017	0.089	0.084	0.009		
PR FF 1	Summer	09/11/2017	09/12/2017	0.043	0.225	0.012	8.841	0.962
PR FF 2	Summer	09/11/2017	09/12/2017	0.044	0.126	0.009	7.561	0.564
PR FF 3	Summer	09/11/2017	09/12/2017	0.041	0.112	0.005	7.622	0.566
PR Comp 1 Bot 4	Summer	09/11/2017	09/12/2017	0.005	0.061	0.001	4.790	0.343
PR Comp 2 Bot 6	Summer	09/11/2017	09/12/2017	0.000	0.054	0.004	3.764	0.204
PR Comp 3 Bot 8	Summer	09/11/2017	09/12/2017	0.000	0.005	0.056	18.500	0.216
PR Comp 4 Bot 10	Summer	09/11/2017	09/12/2017	0.000	0.032	0.001	3.647	0.189
PR Compt 5 Bot 12	Summer	09/11/2017	09/12/2017	0.000	0.035	0.008	3.233	0.232
PR Comp 6 Bot 14	Summer	09/11/2017	09/12/2017	0.000	0.019	0.011	4.385	0.209
PR Outflow	Summer	09/11/2017	09/12/2017	0.001	0.341	0.006		
PR Lys 1	Summer	09/11/2017	09/12/2017	0.000	1.354	0.003	9.877	2.210
PR Lys 1	Summer	09/11/2017	09/13/2017	0.002	0.419	0.000	15.060	0.734
PR Lys 2	Summer	09/11/2017	09/12/2017	0.011	0.362	0.002	14.340	1.001
PR Lys 3	Summer	09/11/2017	09/12/2017	0.007	0.029	0.007	37.450	0.402
PR Lys 3	Summer	09/11/2017	09/13/2017	0.000	0.026	0.006	13.620	0.319
BR Rain	Summer	09/11/2017	09/12/2017	0.175	0.069	0.036		

BR Inflow	Summer	09/11/2017	09/12/2017	0.045	0.116	0.016	7.269	0.620
BR Outflow	Summer	09/11/2017	09/12/2017	0.014	0.140	0.039	4.501	0.397
BR Lys 1	Summer	09/11/2017	09/13/2017	0.000	0.327	0.209	18.430	1.604
BR Lys 2	Summer	09/11/2017	09/12/2017	0.000	0.568	0.069	7.221	1.513
BR Lys 2	Summer	09/11/2017	09/13/2017	0.000			8.004	1.219
BR Lys 3	Summer	09/11/2017	09/12/2017	0.000	6.398	0.033	6.199	6.751
BR Lys 3	Summer	09/11/2017	09/13/2017	0.020	4.136	0.054	6.591	4.073
BR Rain	Winter	12/20/2017	12/21/2017	0.087	0.117	0.009		
BR FF Bottle 1	Winter	12/20/2017	12/21/2017	0.319	0.452	0.137	19.930	1.060
BR FF Bottle 2 Unanchored	Winter	12/20/2017	12/21/2017	0.272	0.304	0.059	22.100	0.840
BR Lys 2	Winter	12/20/2017	12/21/2017	0.011	0.783	0.003	3.953	0.992
BR Lys 2	Winter	12/20/2017	12/22/2017	0.048				
BR Lys 3	Winter	12/20/2017	12/21/2017	0.051	2.427	0.048	6.849	2.916
BR Lys 3	Winter	12/20/2017	12/22/2017	0.042	1.592	0.074		
PR Rainfall	Winter	12/20/2017	12/21/2017	0.220				
PR FF 1	Winter	12/20/2017	12/21/2017	0.000	0.542	0.050	42.610	1.170
PR FF 2	Winter	12/20/2017	12/21/2017	0.000	0.442	0.050	36.240	1.114
PR FF 3	Winter	12/20/2017	12/21/2017	0.001	0.409	0.039	34.430	1.158
PR Comp 1 Bot 4+5	Winter	12/20/2017	12/21/2017	0.031	0.236	0.013	9.325	0.623
PR Comp 2 Bot 6+7	Winter	12/20/2017	12/21/2017	0.004	0.046	0.023	2.656	0.131
PR Comp 3 Bot 8+9	Winter	12/20/2017	12/21/2017	0.000	0.037	0.032	3.274	0.167
PR Comp 4 Bot 10+11	Winter	12/20/2017	12/21/2017	0.000	0.059	0.046	8.253	0.401
PR Lys 1	Winter	12/20/2017	12/21/2017	0.029	0.446	0.000	3.631	0.806
PR Lys 1	Winter	12/20/2017	12/22/2017	0.015	0.129	0.002	7.338	0.456
PR Lys 2	Winter	12/20/2017	12/21/2017	0.152	0.576	0.008	3.690	0.220
PR Lys 2	Winter	12/20/2017	12/22/2017	0.004	0.140	0.004	31.970	1.286
PR Lys 3	Winter	12/20/2017	12/22/2017	0.014			20.390	0.569
MP Rainfall	Winter	12/20/2017	12/21/2017	0.117	0.089	0.010		
MP FF 1	Winter	12/20/2017	12/21/2017	0.087	0.316	0.048	13.670	1.318
MP FF 2	Winter	12/20/2017	12/21/2017	0.139	0.343	0.104	13.320	1.770
MP FF 3	Winter	12/20/2017	12/21/2017	0.032	0.288	0.099	12.650	1.622
MP Comp 1 Bot 4+5	Winter	12/20/2017	12/21/2017	0.029	0.186	0.054	5.391	0.377
MP Comp 2 Bot 6+7	Winter	12/20/2017	12/21/2017	0.023	0.053	0.026	2.024	0.142
MP Comp 3 Bot 8+9	Winter	12/20/2017	12/21/2017	0.008	0.072	0.033	2.065	0.186
MP Comp 4 Bot 10+11	Winter	12/20/2017	12/21/2017	0.000	0.147	0.041	4.048	0.242
MP Lys 1	Winter	12/20/2017	12/21/2017	0.443				
MP Lys 1	Winter	12/20/2017	12/22/2017	0.092	0.085	0.000		
MP Lys 2	Winter	12/20/2017	12/21/2017	0.049	0.455	0.000	5.006	0.651

MP Lys 2	Winter	12/20/2017	12/22/2017	0.013	0.057	0.002		
MP Lys 3	Winter	12/20/2017	12/21/2017	0.160				
MP Lys 3	Winter	12/20/2017	12/22/2017	0.064	0.077	0.006		
BR Rainfall	Winter	01/28/2018	01/29/2018	0.073	0.060	0.000		
BR FF Bottle 1	Winter	01/28/2018	01/29/2018	0.082	0.093	0.017	3.856	0.257
BR FF Bottle 2	Winter	01/28/2018	01/29/2018	0.168	0.080	0.036	5.212	0.596
BR Lys 2	Winter	01/28/2018	01/29/2018	0.000	0.469	0.057		
BR Lys 2	Winter	01/28/2018	01/30/2018	0.001				
BR Lys 3	Winter	01/28/2018	01/29/2018	0.000	0.660	0.059	6.121	1.118
BR Outflow	Winter	01/28/2018	01/29/2018	0.058	0.327	0.029		
PR Rainfall	Winter	01/28/2018	01/29/2018	0.019	0.064	0.000		
PR FF 1 Bottle 11	Winter	01/28/2018	01/29/2018	0.069	0.212	0.000	17.530	1.209
PR FF 2 Bottle 12	Winter	01/28/2018	01/29/2018	0.107	0.256	0.000	15.160	0.997
PR Comp 1 Bot 13	Winter	01/28/2018	01/29/2018	0.094	0.167	0.000	14.250	0.917
PR Comp 2 Bot 14+15	Winter	01/28/2018	01/29/2018	0.085	0.147	0.000	10.270	0.657
PR Comp 3 Bot 19+20	Winter	01/28/2018	01/29/2018	0.032	0.089	0.004	5.608	0.274
PR Comp 4 Bot 21+22	Winter	01/28/2018	01/29/2018	0.015	0.047	0.006	4.131	0.213
PR Comp 5 Bot 23+24	Winter	01/28/2018	01/29/2018	0.007	0.029	0.021	3.548	0.250
PR Lys 1	Winter	01/28/2018	01/29/2018		0.170	0.003		
PR Lys 2	Winter	01/28/2018	01/29/2018	0.022	0.037	0.005	11.000	0.412
PR Lys 3	Winter	01/28/2018	01/29/2018	0.011	0.115	0.005	16.550	0.629
PR Lys 3	Winter	01/28/2018	01/30/2018	0.020	0.093	0.004	18.860	0.968
PR Outflow	Winter	01/28/2018	01/29/2018	0.039	0.626	0.004		
MP Rainfall	Winter	01/28/2018	01/29/2018	0.054	0.052	0.002		
MP FF 1	Winter	01/28/2018	01/29/2018	0.091	0.222	0.008	14.780	0.701
MP FF 2	Winter	01/28/2018	01/29/2018	0.075	0.240	0.009	16.880	0.840
MP FF 3	Winter	01/28/2018	01/29/2018	0.076	0.264	0.008	18.330	0.922
MP Comp 1 Bot 4	Winter	01/28/2018	01/29/2018	0.056	0.206	0.012	7.674	0.458
MP Comp 2 Bot 5	Winter	01/28/2018	01/29/2018	0.049	0.060	0.015	2.311	0.163
MP Comp 3 Bot 6+7	Winter	01/28/2018	01/29/2018	0.032	0.069	0.016	3.075	0.191
MP Comp 4 Bot 8+9	Winter	01/28/2018	01/29/2018	0.025	0.055	0.014	1.890	0.137
MP Comp 5 Bot 10+11	Winter	01/28/2018	01/29/2018	0.019	0.132	0.034	1.970	0.251
MP Comp 6 Bot 12+13	Winter	01/28/2018	01/29/2018	0.028	0.179	0.059	2.768	0.338
MP Comp 7 Bot 14	Winter	01/28/2018	01/29/2018	0.023	0.079	0.032	2.415	0.350
MP Lys 1	Winter	01/28/2018	01/29/2018	0.003	0.088	0.009		
MP Lys 1	Winter	01/28/2018	01/30/2018	0.003			3.828	0.232
MP Lys 2	Winter	01/28/2018	01/29/2018	0.021	0.284	0.055		

MP Lys 2	Winter	01/28/2018	01/30/2018	0.007				
MP Lys 3	Winter	01/28/2018	01/29/2018	0.030				
MP Outflow	Winter	01/28/2018	01/29/2018	0.001	0.084	0.048		
BR Rainfall	Winter	02/04/2018	02/05/2018	0.075	0.045	0.001		
BR Hand Grab 1	Winter	02/04/2018	02/04/2018	0.167	0.112	0.019	4.281	0.345
BR Hand Grab 2	Winter	02/04/2018	02/04/2018	0.178	0.141	0.014	5.379	0.420
BR FF Bottle Anchored	Winter	02/04/2018	02/05/2018	0.051	0.040	0.020	2.310	0.192
BR FF Bottle Not Anchored	Winter	02/04/2018	02/05/2018	0.068	0.051	0.018	2.388	0.182
BR Lys 1	Winter	02/04/2018	02/05/2018	0.025				
BR Lys 2	Winter	02/04/2018	02/05/2018	0.001	0.296	0.049		
BR Lys 2	Winter	02/04/2018	02/06/2018	0.012	0.376	0.048		
BR Lys 3	Winter	02/04/2018	02/05/2018	0.019	0.306	0.073	4.302	0.706
PR Rainfall	Winter	02/04/2018	02/05/2018	0.061	0.053	0.001		
PR FF 1	Winter	02/04/2018	02/05/2018	0.234	0.529	0.008	12.890	1.360
PR FF 2	Winter	02/04/2018	02/05/2018	0.218	0.577	0.010	11.830	1.359
PR FF 3	Winter	02/04/2018	02/05/2018	0.232	0.455	0.006	11.660	1.355
PR Comp 1 Bot 4	Winter	02/04/2018	02/05/2018	0.178	0.316	0.011	5.789	0.734
PR Comp 2 Bot 5	Winter	02/04/2018	02/05/2018	0.136	0.167	0.009	3.264	0.466
PR Comp 3 Bot 6+7	Winter	02/04/2018	02/05/2018	0.047	0.038	0.009	1.388	0.145
PR Comp 4 Bot 8+9	Winter	02/04/2018	02/05/2018	0.020	0.029	0.016	1.559	0.151
PR Lys 1	Winter	02/04/2018	02/05/2018	0.016	0.536	0.004	4.188	0.669
PR Lys 2	Winter	02/04/2018	02/05/2018	0.005	0.092	0.005	5.160	0.288
PR Lys 2	Winter	02/04/2018	02/06/2018	0.038				
PR Lys 3	Winter	02/04/2018	02/05/2018	0.027	0.255	0.007	17.780	0.789
PR Lys 3	Winter	02/04/2018	02/06/2018	0.063	0.279	0.005	28.970	1.546
MP Rainfall	Winter	02/04/2018	02/05/2018	1.077	0.048	0.880		
MP FF 1	Winter	02/04/2018	02/05/2018	0.292	0.302	0.014	7.198	1.046
MP FF 2	Winter	02/04/2018	02/05/2018	0.326	0.464	0.029	8.238	1.060
MP FF 3	Winter	02/04/2018	02/05/2018	0.334	0.455	0.025	6.892	1.052
MP Comp 1 Bot 4	Winter	02/04/2018	02/05/2018	0.292	0.230	0.020	5.744	0.785
MP Comp 2 Bot 5	Winter	02/04/2018	02/05/2018	0.210	0.171	0.021	2.755	0.442
MP Comp 3 Bot 6+7	Winter	02/04/2018	02/05/2018	0.064	0.046	0.014	1.875	0.181
MP Comp 4 Bot 8+9	Winter	02/04/2018	02/05/2018	0.056	0.104	0.062	2.231	0.300
MP Lys 1	Winter	02/04/2018	02/05/2018	0.008	0.218	0.007	5.001	0.369
MP Lys 1	Winter	02/04/2018	02/06/2018	0.053				
MP Lys 2	Winter	02/04/2018	02/05/2018	0.007				
MP Lys 2	Winter	02/04/2018	02/06/2018	0.021	0.302	0.034	4.995	0.417
MP Lys 3	Winter	02/04/2018	02/05/2018	0.044				

Denitrification and organic matter % raw data:

Location:	Lysimeter Location	Depth: (cm)	Season	DNF (µg/g DM/hr)	Organic Matter (%)
MP	1	0-5	Summer	0.926	20.878
MP	1	5-10	Summer	0.178	3.071
MP	2	0-5	Summer	0.836	18.348
MP	2	5-10	Summer	0.086	2.443
MP	3	0-5	Summer	1.257	30.780
MP	3	5-10	Summer	0.165	4.479
MP	1	0-5	Fall	0.396	25.029
MP	1	5-10	Fall	0.106	3.901
MP	2	0-5	Fall	0.348	12.068
MP	2	5-10	Fall	0.051	3.161
MP	3	0-5	Fall	0.473	20.819
MP	3	5-10	Fall	0.074	3.934
MP	1	0-5	Spring	0.573	21.748
MP	1	5-10	Spring	0.111	2.621
MP	2	0-5	Spring	0.647	13.336
MP	2	5-10	Spring	0.065	2.616
MP	3	0-5	Spring	0.643	14.223
MP	3	5-10	Spring	0.069	3.095
PR	1	0-5	Summer	0.292	21.172
PR	1	5-10	Summer	0.028	2.351
PR	2	0-5	Summer	0.198	28.794
PR	2	5-10	Summer	0.114	9.221
PR	3	0-5	Summer	0.262	11.743
PR	3	5-10	Summer	0.363	11.479
PR	1	0-5	Fall	0.088	21.831
PR	1	5-10	Fall	0.031	3.991
PR	2	0-5	Fall	0.062	4.740
PR	2	5-10	Fall	0.295	16.739
PR	3	0-5	Fall	0.003	38.195
PR	3	5-10	Fall	0.035	7.495
PR	1	0-5	Spring	0.055	10.938
PR	1	5-10	Spring	0.021	2.553
PR	2	0-5	Spring	0.092	7.935
PR	2	5-10	Spring	0.122	6.593
PR	3	0-5	Spring	0.040	14.803
PR	3	5-10	Spring	0.027	3.470
BR	1	0-5	Summer	0.697	22.963
BR	1	5-10	Summer	0.397	9.118
BR	2	0-5	Summer	1.134	10.515
BR	2	5-10	Summer	0.869	8.520

BR	3	0-5	Summer	0.940	10.613
BR	3	5-10	Summer	0.401	4.681
BR	1	0-5	Fall	0.776	24.806
BR	1	5-10	Fall	0.632	16.738
BR	2	0-5	Fall	1.069	11.216
BR	2	5-10	Fall	0.777	9.667
BR	3	0-5	Fall	0.700	10.039
BR	3	5-10	Fall	0.298	5.269
BR	1	0-5	Spring	0.626	16.924
BR	1	5-10	Spring	0.216	8.801
BR	2	0-5	Spring	1.005	8.369
BR	2	5-10	Spring	0.193	3.195
BR	3	0-5	Spring	0.715	8.733
BR	3	5-10	Spring	0.168	3.652

Unknown plant species 1

Unknown plant species 5