Abstract

Title of Thesis: Advanced Denitrification in Bioretention Systems Using Woodchips as an Organic Carbon Source

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Bioretention systems still lack the ability to effectively mitigate nitrogen concentrations from urban stormwater. Column tests were conducted to evaluate the effect of nitrate concentration, stormwater retention time, limestone addition, and woodchip species, size, and mass percentage on the bioretention denitrification process. Denitrification of artificial stormwater appeared to follow pseudo-first-order kinetics. A 0.8 day average retention time showed the highest nitrate removal percentage of 82.4 $\pm$ 0.4%. Longer retention times correspond to greater removal efficiency. Willow Oak and Red Maple woodchips resulted in the highest total nitrogen removal efficiencies at 61.9 $\pm$ 0.8% and 61.8%, respectively. Smaller woodchips and higher woodchip mass percentage corresponded to greater nitrate removal efficiencies, but also higher organic nitrogen leaching. Media containing 4.5% 5 mm Willow Oak woodchips by mass represented optimum conditions with a pseudo-first-order denitrification rate of 4.1 $\pm$ 4.6 day^{-1} with nitrate concentrations of 1.5 to 4.5 mg/L N.

ADVANCED DENITRIFICATION IN BIORETENTION SYSTEMS USING
WOODCHIPS AS AN ORGANIC CARBON SOURCE

by

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1. Introduction

1.1. Background

Increases in pollutant and stormwater loads from urban areas have caused a push for mitigation. As urban areas develop, natural ecosystems, previously conducive to infiltration of stormwater, have become impervious (Davis et al. 2012, Morgan et al. 2013, Son et al. 2013). Roads, parking lots and buildings act as non-point sources of pollution (Davis et al. 2012, Morgan et al. 2013). As impervious surface area increases, runoff volumes become larger, which cause stream bank erosion and habitat loss (Davis et al. 2012). Increases in mobilized pollutants cause eutrophication of surface water bodies and other water quality concerns (Ergas et al. 2010, Morgan et al. 2013, Son et al. 2013). These adverse effects amount to losses in waterfront property, recreational areas, drinking water supply, and wildlife habitat (Ergas et al. 2010, Davis et al. 2012). As a way of mitigating the impact of urban development, stormwater control measures (SCM) are employed to increase water quality and decrease the amount of runoff discharged to water bodies (Brown and Hunt 2011, Davis et al. 2012, Hunt et al. 2012). Runoff from impervious surfaces is collected and managed in SCMs such as bioretention cells, rain gardens and vegetated swales (Brown and Hunt 2011, Davis et al. 2012, Hunt et al. 2012). Here water is allowed to infiltrate into the ground, naturally filtering out pollutants and returning urban areas closer to pre-development hydrologic conditions (Brown and Hunt 2011, Davis et al. 2012, Hunt et al. 2012). Although effective, these technologies are still somewhat immature and more research is needed to optimize their efforts.

Treatment for nitrogen using SCM's is one area that needs improvement. Nitrogen is one of the limiting nutrients associated with the eutrophication of lakes and rivers

(Ergas et al. 2010). Eutrophication is the change in the volume and diversity of biomass in an aquatic ecosystem (Ergas et al. 2010). Increases in nutrients that are usually scarce cause rapid growth of some species, resulting in the death of others (Ergas et al. 2010). Therefore, a spike in nitrogen can rapidly accelerate eutrophication when left unchecked. Bioretention is a very effective means of mitigating the effects of urban development and has shown some promise in the area of nitrogen treatment (Kim et al. 2003, Brown and Hunt 2011, Davis et al. 2012, Hunt et al. 2012). The goal of this research is to design a layered bioretention system that optimizes the efficiency of nitrogen removal from stormwater runoff. This will be achieved by determining the optimum conditions for denitrification.

1.1.1. Bioretention Systems

Bioretention cells are typically shallow (2-4 ft deep) areas of very porous media (Li and Davis 2009). The media is usually topped by a mulch layer to retain moisture and prevent unwanted vegetated species (Li and Davis 2009, Davis et al. 2012, Hunt et al. 2012). Selected vegetation is planted in the bioretention cell to promote evapotranspiration and uptake of pollutants (Li and Davis 2009, Davis et al. 2012, Hunt et al. 2012). Stormwater from the target watershed is directed into the bioretention cell where it quickly infiltrates. Pollutants are removed from the water as it passes through the media by means of filtration, adsorption, biological processes, and/or plant uptake (Li and Davis 2009, Davis et al. 2012, Hunt et al. 2012). Clean water can then recharge groundwater by infiltrating further or be taken up by plants (Li and Davis 2009, Davis et al. 2012, Hunt et al. 2012). What remains is usually collected by an underdrain that discharges into surface waters (Li and Davis 2009, Davis et al. 2012, Hunt et al. 2012). In

effect, this technology greatly reduces hydraulic and pollutant loads from urban stormwater.

Treatment of nitrogen using bioretention has been studied in a few different research endeavors (Kim et al. 2003; Hsieh et al. 2007; Ergas et al. 2010). Different designs have been able to remove anywhere from 70 to 90 percent of the total nitrogen in runoff when in highly controlled laboratory settings (Kim et al. 2003; Hsieh et al. 2007; Ergas et al. 2010).

1.1.2. Nitrogen in Stormwater

Typical urban stormwater event mean concentrations are approximately 1 to 3 mg/L total nitrogen depending on the land use (Collins et al. 2010). Typically one third of the total nitrogen will be in the form of organic nitrogen, one third will be ammonium, and one third will be oxidized nitrogen (Collins et al. 2010). The data collected by Collins et al. (2010) show that storms vary greatly in intensity and stormwater runoff also varies in nitrogen concentration. First flush is considered the first portion of a given storm (usually 1.3 to 1.9 mm of rainfall) on a watershed (Flint and Davis 2007). It is widely accepted that the runoff from the first flush contains the highest contaminant concentrations and could be as high as 90% of the total contaminant mass (Bach et al. 2010). Flint and Davis (2007) found that 85% of the total nitrogen mass is carried by the first 1.3 mm of runoff in storms that exceed 1.3 mm of rainfall.

A bioretention facility designed to incorporate nitrogen into its treatment processes must do so by following the nitrogen cycle (Ergas et al. 2010). Figure 1 shows a simplified version of how the nitrogen cycle occurs naturally and the corresponding valance states of each form of nitrogen. The goal in nitrogen treatment is to ultimately
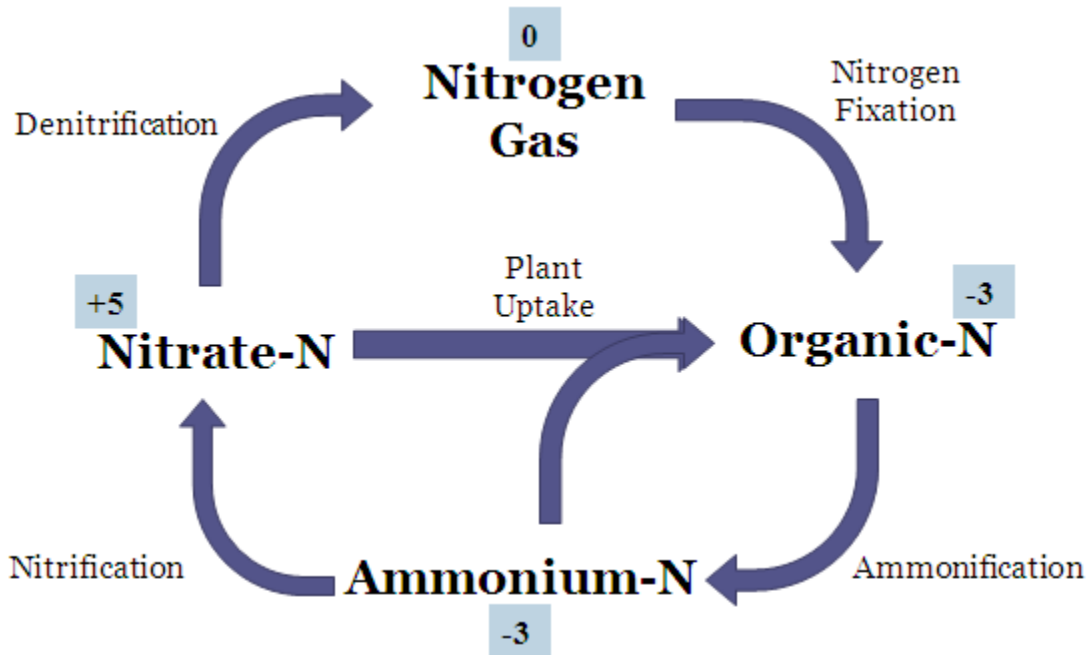
Figure 1: Simplified version of the nitrogen cycle. The highlighted numbers indicate the oxidation state of each form of nitrogen.

convert all forms to nitrogen gas which is released into the atmosphere. Organic nitrogen, from decaying organic matter, is converted to ammonium (ammonification). Ammonium is then oxidized to nitrite and then further oxidized to nitrate (nitrification). Nitrate can be returned to organic material because it is readily plant available (plant uptake). Uptake by plants is a significant pathway for nitrate loss (Bratieres et al. 2008). Nitrate can also be reduced by bacteria to nitrogen gas which is released into the atmosphere (denitrification).

These steps naturally occur very slowly if at all but are made more rapid by bacterial processes (Collins et al. 2010). Organic nitrogen is broken down over time and ammonium can then undergo nitrification. Nitrification requires the availability of oxygen. Typically, oxygen in air is used by bacteria to oxidize the ammonium. According to Hsieh et al. (2007), during storm events organic and ammonium nitrogen are the

adsorbed to media in a bioretention system and the nitrification process occurs in the time between storm events. In Maryland, on average there are six days between storm events (Hsieh et al. 2007).

Biologically, nitrate reduction can follow assimilatory or dissimilatory pathways (Blowes et al. 1994). Nitrate can be reduced to ammonia and assimilated by the bacterial cell or used as a terminal electron acceptor in respiration (Blowes at al. 1994). In stormwater treatment both processes take place to effectively remove nitrogen from aquatic/terrestrial systems. Denitrification reduces the valance state of nitrogen from +5 to 0 (Stumm and Morgan 1996). There are four steps in the denitrification pathway (Lee et al. 2000). Each step is carried out by a different enzyme produced by denitrifying microbes (Lee et al. 2000). The different steps are listed in equation 1.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad\qquad (1)$$
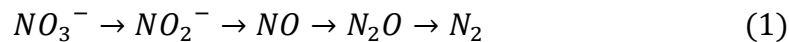
Denitrifying bacteria have their highest rate of nitrate reduction near pH 8 (Glass and Silverstein 1998). Ultimately, respiration will convert nitrate into nitrogen gas which is released into the atmosphere.

1.1.3. Denitrification

Denitrifying bacteria require anoxic conditions (the absence of molecular oxygen in the presence of nitrate) in order to reduce nitrate (Kim et al. 2003). This is because most denitrifying bacteria are facultative and will use oxygen as a terminal electron acceptor because it is more efficient (Blowes et al. 1994). After oxygen is depleted the bacteria will then begin to convert nitrate into nitrogen gas while using the attached oxygen as a terminal electron acceptor (Blowes et al. 1994).

Proper conditions for denitrification can be achieved by saturating the media in the lower layer of a bioretention cell (Kim et al. 2003, Ergas et al. 2010). This makes oxygen from the atmosphere inaccessible (Kim et al. 2003, Ergas et al. 2010). Therefore, the amount of time that stormwater runoff is retained in the bioretention system greatly effects the microbial processes that reduce nitrates to nitrogen gas (Leverenz et al. 2010; Robertson 2010). Several methods are used to saturate this layer. Some of these methods are using a media with low porosity (Hsieh et al. 2007; Ergas et al. 2010), using an upturned underdrain (Hunt et al. 2006, Chen et al. 2013, Zinger et al. 2013), or by controlling outflow (Lucas and Greenway 2011a). By slowing down flow through the system by using low porosity media or controlled outflow, the media becomes saturated. An upturned underdrain is implemented by placing the outlet of the underdrain higher than the collection piping. The upturned underdrain causes saturation by requiring hydraulic head in order to cause outflow.

Denitrifying bacteria also require a source of organic carbon (Kim et al. 2003). Several studies have been conducted to determine the best carbon source for denitrification in bioretention. Sawdust, woodchips, alfalfa, and newspaper are some of the sources studied (Kim et al. 2003; Leverenz et al. 2010; Robertson 2010). Woodchips appear to provide consistent, reliable and lasting results (Robertson 2010). Kim et al. 2003 determined that it was possible to achieve a steady state nitrate removal percentage with woodchips, alfalfa and newspaper near 100%. Sawdust was a bit lower but still showed above 90% removal in a steady state simulation (Kim et al. 2003). Kim et al. 2003 determined that, while woodchips provide adequate and high removal percentages,

newspaper provided the most consistent removal results based on fluctuations in hydraulics and nitrate concentrations.

Denitrification typically has a zero-order reaction rate in most SCMs (Leverenz et al. 2010). However, a first-order reaction rate can be used to model denitrification at low temperatures with low nitrate concentrations (Leverenz et al. 2010, Robertson 2010). Low concentrations were defined as concentrations less than 10 mg/L of nitrate as N (Leverenz et al. 2010).

Leverenz et al. (2010) determined that an anoxic environment of woodchips should exhibit a first-order denitrification rate constant between 1.41 and 1.30 days^{-1}. However, Robertson (2010) found that zero-order kinetics represented a better fit to collected data. In that study a zero order denitrification rate was observed at 15.4 to 23.0 mg N L^{-1} day^{-1} (Robertson 2010). After aging woodchips for 7 years the rate was found to be about half of the initial rate (Robertson 2010). Because nitrogen levels in stormwater are typically below the 10 mg/L level identified by Leverenz et al. (2010), first-order kinetics may be used. Following a first-order model for denitrification, it is estimated that concentrations of nitrate will be below 0.2 mg/L N if water is retained for more than 1 to 1.5 days. This calculation uses the rate constants reported by Leverenz et al. (2010) and assumes that stormwater contains initial nitrate concentrations of 1 to 3 mg/L N and nitrate is the limiting nutrient.

1.1.4. Woodchips

Robertson (2010) determined that woodchips had very good longevity for denitrification in agricultural runoff, approaching 10 years as an effective carbon source. One drawback of using woodchips is they initially cause a spike in organic carbon

effluent concentrations which diminishes over time (Robertson 2010). Typically, a system that induces denitrification uses a homogeneous media. For example, Robertson (2010) used a media consisting of only woodchips. While this has proven effective in a steady state system, the effluent concentrations of organic carbon are much higher than is necessary to sustain the microbial population (Leverenz et al. 2010, Roberson 2010). Therefore, media should be redesigned to limit the release of organic material in a system that operates more closely to field situations.

No available literature has defined the effect of woodchip size on the denitrification process. The size of the woodchips inversely relates to the total woodchip surface area which could contribute to
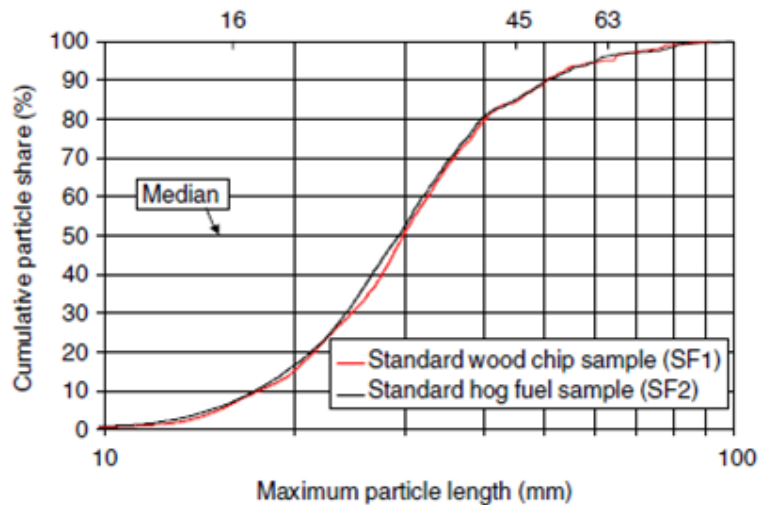
Figure 2: Standard woodchip particle size distribution from a disc chipper (Hartmann et al. 2006)

the availability of carbon. Larger woodchips have less surface area from which to leach organic carbon. Therefore, larger woodchips leach less organic carbon than smaller woodchips of the same mass. A standard woodchip size distribution from a disc chipper, developed by Hartmann et al. (2006), is presented in Figure 2. Different distributions of woodchip sizes would affect the woodchips surface area and adjust the availability of organic carbon.

Literature has yet to define the effect of woodchip species on the denitrification

process. Different types of wood have different carbon contents and vary in hardness. The carbon content of hardwoods ranges from 46.27 to 49.97 percent (Lamlom and Savidge 2003). Softwoods have slightly higher carbon contents ranging from 48.55 to 55.16 percent (Lamlom and Savidge 2003). These woods are not always easily attainable. Some of the most commonly harvested woods in Maryland are cherry, oak and maple for hardwoods and pine for softwoods (MCAE 2004; USFWS 2001).

1.2. Research Objectives

The goal of this research is to optimize the denitrification efficiency in a modified bioretention system design. In order to evaluate and optimize this design several objectives have been identified.

1. Develop a laboratory scale version of a denitrification layer, and provide media that create the conditions necessary for the growth and development of denitrifying bacteria.

In order to address this objective, columns are designed to provide conditions similar to those in the denitrification section of a bioretention system. The denitrification process is evaluated in column tests with media containing woodchips. These tests are compared to column tests where denitrification is inhibited. The contrast between these column tests provides evidence of the presence or absence of denitrifying microorganisms.

2. Model the denitrification process in the system using zero or first-order kinetics in order to determine which better describes the data. Use this model to determine how long stormwater should be retained in the media.

Zero and first-order models are developed using the column and assumptions… and applied to the denitrification data. These models are compared for goodness of fit and then used to evaluate the factors affecting the denitrification process in the system.

The amount of time that stormwater runoff is retained in the bioretention system greatly effects the microbial processes that reduce nitrates to nitrogen gas (Leverenz et al. 2010; Robertson 2010). The amount of time stormwater runoff is retained in the denitrification media is varied in a series of column tests. These provide insight into the effect of retention time on the efficiency of bioretention systems.

3. Evaluate different media compositions and their effect on microbial denitrification.

Adjusting the media composition of the denitrification layer in a series of column tests provides insight into how different media affects the denitrification process. The woodchip species, woodchip mass percentage, woodchip size, and limestone content in the media are varied in these column tests. The resulting data are compared to evaluate the effect of different media characteristics on the denitrification process

4. Provide design recommendations for a full scale bioretention system using the information gathered.

All of the factors evaluated with respect to denitrification in a bioretention system, when quantified, are optimized in order to further improve nitrogen removal using a variety of SCMs. Using the results of the column studies, optimum design conditions are used to form practical recommendations for nitrogen treatment bioretention systems.

2. Methodology

2.1.   Laboratory Design

In order to simulate a field situation in a newly designed bioretention layer, synthetic stormwater is passed through a column similar to the one depicted in Figure 3. The column will be used to address the goals identified previously for denitrification of first flush runoff using bioretention systems. The column was designed around typical bioretention parameters. Because excavation below 120 cm (4 feet) usually requires some kind of stabilization, bioretention cells are kept shallower than the 120 cm depth (Brown and Hunt 2011). The column constructed is 80 cm (~2.6 feet) high with media to the height of 70 cm (2.3 feet). This will provide enough height for a denitrification layer. The column is wrapped in foil, as shown in Figure 4, in order to prevent

Figure 3: Model bioretention system column design for testing the effect of identified factors affecting the denitrification process.

light from entering the media. In a field situation light will not penetrate the surface, so it is necessary to mimic that environment.

The column design includes three sampling ports. The bottom port is a valve that is adjusted to the appropriate effluent rate for each experiment. Before the test begins the effluent rate is set. This is done by filling an empty column to the point where media would be fully saturated and setting the flow rate to previously determined rates. An Orion redox/ORP electrode is placed in the middle sampling port in order to monitor the oxidation/reduction potential in the solution during the test (Figure 4).

Synthetic stormwater is used to represent typical first flush runoff pollutant concentrations of nitrate. Assuming that all the nitrogen carried by the stormwater is converted to nitrate before entering the denitrification layer, nitrate is the only source of nitrogen added to the synthetic stormwater in varying concentrations. The nitrate is added in the form of $NaNO_3$.

Phosphate, as $NaPO_4$, is added at urban

Figure 4: Constructed model bioretention system columns wrapped in aluminum foil to prevent light from entering.

runoff levels (0.1 mg/L) to encourage bacterial growth. Sodium chloride (NaCl) is added at 0.01 M in order to fix the ionic strength.

Synthetic stormwater is pumped into the top of the column using a peristaltic pump at 22.2 mL/min and an approach velocity of 0.32 m/min until the media is completely saturated. Pumping stops when the system is completely saturated because in a field setting, at saturation, it is expected that any excess water would overflow or bypass the denitrification layer.

Each test is conducted three times with 7 days in between loading events. This is done to mimic field conditions (Hsieh et al. 2007). The three replicates are conducted on the same media in succession. All three tests are conducted in the same manner according to the constraints identified herein.

All of the effluent is collected in order to conduct a water balance and determine the change in water quality parameters. Samples were collected in different time increments during the expected drainage period. Sample volumes are based on the volume needed to conduct different analytical methods. For each sample the pH, concentrations of nitrate, nitrite, Total Kjeldahl Nitrogen, phosphorus, and total organic carbon were determined. Sample temperature was also monitored using a mercury thermometer to ensure that the experiment remained at room temperature. The oxidation/reduction potential was monitored inside the column throughout the sampling event.

2.2. Experimental Sets

The media used in the columns consist of a mixture of woodchips and pea gravel. Pea gravel is used in order to optimize the structural capacity of the media as well as provide large porosity and thus large storage capacity. Each test will have different

variations of this media mixture.

Wood samples were collected from recently cut trees on University of Maryland
campus grounds. Bark from the samples was removed using a hammer and chisel.
Samples were then chipped by a Vermeer BC1000 XL 20" drum chipper. In order to
reduce the likelihood of contamination, the chipper was allowed to run for 5 minutes in
between each species that was chipped. Chips samples were thoroughly rinsed with tap
water and air dried for approximately two days. When dry, the samples were sieved
through 25.5 mm, 19 mm, 13 mm, 9.5 mm, and No. 4 (5 mm) sieves. This was done on
an automatic shaker for 15 minutes. The sorted chips were collected and sealed for
storage in large waterproof non-transparent plastic bags.

**Table 1: The factors investigated in the column studies are described. The
collected data will be used to provide design recommendations for the
optimization of nitrate removal in bioretention systems.**

Factor	Description
Inhibition	Adding Sodium Azide to the stormwater to inhibit microbial denitrification
Nitrogen Concentration	Adjusting the concentration of nitrate that enters the system
Retention Time	Varying the amount of time stormwater runoff is retained in bioretention
Woodchips Species	Different wood species used as a carbon source for denitrifying bacteria
Woodchip Size	Availability of carbon variation through differing chip sizes
Woodchip Mass	Varied carbon availability through woodchip content in bioretention media
pH	Media amended with limestone to raise the pH

In order to determine the most effective media for the nitrate treatment process,
tests were conducted with variations in the media. The different variations are referred to
in Table 1. For regional considerations the most available woods in Maryland were

evaluated for their effects on the denitrification process. Four different hard woods and one soft wood were chosen for their availability in the region. These woods can be found in Table 2 with their Latin names and corresponding carbon contents.

The amount of woodchips in the media was varied at 1%, 2.5%, and 4.5% by mass. The remaining media was pea gravel. The size of the woodchips was also evaluated for its effect on the denitrification process. Three different size distribution tests were conducted. The size rages were No. 4 (5 mm) to 9.5 mm, 9.5 mm to 13 mm, and 13 mm to 19 mm.

Table 2: Five wood species, available regionally, that were used to determine the effect of varying woodchip species on the denitrification process in a bioretention cell. Carbon contents for each wood species are identified as it may affect the culturability of denitrifying bacteria (USFWS 2001; Lamlom and Savidge 2003; MCAE 2004).

Wood Type	Species (Scientific Name)	Carbon Content (%)
Wild Cherry	Prunus serotina	49.53 ± 0.18
Willow Oak	Quercus phellos	49.57 ± 0.22
Red Maple	Acer negundo	49.34 ± 0.53
Virginia Pine	Pinus strobus	49.74 ± 0.16
American Beech	Fagus grandifolia	46.60 ± 0.39

The samples were soaked for a period of two days prior to being packed in the columns. Chips were completely submerged in the same solution as was used for artificial stormwater, which was described previously. This soaking has several purposes. Because it will take time to build a bacteria colony in the column it is advantageous to start growth prior to running the column. Soaking the woodchips will also allow the chips to become fully saturated; dry chips will absorb water. In order to conduct an accurate

water balance it is necessary to have as little influent water absorbed as possible.

Immediately after the soaking period the artificial stormwater was drained and the chips were mixed with washed pea gravel. Pea gravel was purchased in 50 lb bags from The Home Depot. The bags contained ASTM #8 pea gravel (0.3 mm to 9.5 mm). Peas gravel was thoroughly rinsed with tap water and then heated in the furnace for 4 hours at 600 °C. The mixed media was then packed into the column. The media was compacted using a compaction rod at six inch increments. Each layer received 20 blows from the compaction rod. Media was packed in layers until it reached a height of 70 cm. This provided a freeboard of 10 cm in the column.

In each set of experiments the outlet size is adjusted to drain stormwater at different rates. The effluent rate varies over time with the height of the water in the column. These varying flow rates are identified by the centroid retention time (CRT) for the runoff in the column. Centroids were calculated using a volume weighted average. The summation of the collected volumes multiplied by the respective times they were collected was divided by the total volume collected. Each set of experiments were averaged together to obtain the centroid.

$$CRT = \frac{\sum V_i * t_i}{V_{Total}} \tag{2}$$

Equation 1 shows the general form of the equation used to calculate the centroids; where V indicates volume, i indicates the sample number, and t indicates time. Table 3 provides the centroid times, initial flow rates, and sample collection times for the different tests.

Table 3: End times (min) at which samples were collected for the different centroid retention times. Samples were collected continuously (example: sample 1 for the 0.4 day centroid was collected from 0 to 150 min at which time sample 2 began to be collected). The initial effluent rate set before the test for each centroid is also shown.

Centroid	0.4 Days	0.6 Days	0.8 Days	1.0 Days	1.3 Days
Effluent Rate	2.1 (mL/min)	1.7 (mL/min)	1.4 (mL/min)	1.2 (mL/min)	1.0 (mL/min)
Sample #					
1	150 min.	180 min.	225 min.	270 min.	300 min.
2	195 min.	420 min.	1200 min.	1200 min.	1710 min.
3	660 min.	1200 min.	1860 min.	1860 min.	2640 min.
4	1050 min.	1680 min.	2640 min.	2700 min.	4080 min.
5	1110 min.	2730 min.	3450 min.	4080 min.	4620 min.
6	2100 min.				

A series of tests were conducted at the 0.8-day centroid in order to assess the ability

of the design to promote denitrification. First, a column was packed with media

containing 4.5% Willow Oak woodchips and 95.5% pea gravel by mass. The woodchips

used were those passing the 9.5 mm sieve and retained on the No. 4 (5 mm) sieve. The

concentration of nitrate in the artificial stormwater was 3 mg/L N in addition to the

phosphate and sodium chloride. Nitrate reduction was monitored in the effluent to show

that denitrification was taking place. These experimental conditions were used as a

standard for comparison with all the tests conducted. Unless otherwise noted, the

identified constraints were used in all of the tests discussed hereafter.

In order to prove that denitrification was the means by which nitrate concentrations

were being reduced, a set of tests were run that inhibited microbial denitrification.

Bremmer and Yeomans (1986) showed that denitrification in soil inoculated with

denitrifying bacteria was most retarded when using potassium azide as an inhibitor.

Azide is toxic and inhibits denitrification by killing the microorganisms that carry out

that process (Fiuza et al. 2002). Therefore, in the inhibited experiments of this research,

woodchips were soaked for 48 hours in artificial stormwater that also containing 1000

mg/L sodium azide (NaN$_3$) (Hong et al. 2006). In addition, artificial stormwater run through the system also contained 50 mg/L NaN$_3$ (Hong et al. 2006). The effects of the inhibited experiments were used for comparison with non-inhibited experiments. For comparison, a test was also run on media consisting solely of pea gravel.

To evaluate effects of N concentrations, different concentrations of nitrate in the artificial stormwater were evaluated to include 1.5 and 4.5 mg/L N. Five different centroids were used to determine the effect of time on the denitrification process. The initial flow rate for the 0.4, 0.6, 0.8, 1.0, and 1.3 day centroid times are 2.1, 1.7, 1.4, 1.2 and 1.0 mL/min respectively (Table 2).

Lastly the media was amended with limestone in order to raise the pH of the system. Media was amended with 5% and 10% limestone by volume. The size of the limestone used was passing the 13 mm sieve and retained on the 6.5 mm sieve.

2.3.   Analysis

All collected samples were tested for nitrate using Standard Method 4110-NO$_3^-$ Ion Chromatographic method (APHA, 1992). Nitrite was tested using Standard Method 4500-NO$_2^-$ C - Ion Chromatographic method (APHA, 1992). A Dionex ICS-1100 Ion Chromatography instrument was used for these measurements with an IonPac AS22 column. Eluent contained 4.5mM Na$_2$CO$_3$ and 1.5 mM NaHCO$_3$. Nitrite measurements were checked using Standard Method 4500-NO$_2^-$ B - Colorimetric method (APHA, 1992). TKN was measured using Standard Method 4500-N$_{org}$ B Macro-Kjeldahl method (APHA, 1992). The addition of nitrate, nitrite, and TKN resulted in the total nitrogen concentration. Total organic carbon was measured using Standard Method 505 Organic Carbon (Total) (APHA, 1992). Total phosphorus was measured using Standard Method

4500-P phosphorus (APHA, 1992). All chemicals and manufacturers are listed in Table 4.

Table 4: List of chemicals used in analytical methods with manufacturer and location of production.

Chemical Name	Formula	Manufacturer	Location of Production
Ammonium Molybdate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Fisher Scientific	Fair Lawn, NJ 07410
Ascorbic Acid	$C_6H_8O_6$	J.T. Baker	Phillipsburg, NJ 08865
Boric Acid	H_3BO_3	Fisher Scientific	Fair Lawn, NJ 07410
Cupric Sulfate	$CuSO_4$	Fisher Scientific	Fair Lawn, NJ 07410
Ethyl Alcohol	C_2H_6O	Pharco Products Inc.	Brookfield, CT 06804
Hydrochloric Acid	HCl	Fisher Scientific	Fair Lawn, NJ 07410
Methylene Blue	$C_{16}H_{18}N_3SCl$	Acros Organics	Geel, Belgium
Methyl Red	$C_{15}H_{15}N_3O_2$	Acros Organics	Geel, Belgium
N-(1-Naphthyl)-Ethylene-Diamine Dihydrochloride	$C_{12}H_{16}Cl_2N_2$	Acros Organics	Geel, Belgium
Nitric Acid	HNO_3	Fisher Scientific	Fair Lawn, NJ 07410
Phenolphthalein	$C_{20}H_{14}O_4$	Fisher Scientific	Fair Lawn, NJ 07410
Phosphate Standard	$NaPO_4$	Ricca Chemical	Arlington, TX 76012
Potassium Antimonyl Tartrate	$K(SbO)C_4H_4O_6 \cdot 0.5H_2O$	Fisher Scientific	Fair Lawn, NJ 07410
Potassium Persulfate	$K_2S_2O_8$	Fisher Scientific	Fair Lawn, NJ 07410
Potassium Sulfate	K_2SO_4	Acros Organics	Geel, Belgium
Sodium Azide	NaN_3	Fisher Scientific	Fair Lawn, NJ 07410
Sodium Bicarbonate	$NaHCO_3$	Fisher Scientific	Fair Lawn, NJ 07410
Sodium Carbonate	Na_2CO_3	Fisher Scientific	Fair Lawn, NJ 07410
Sodium Hydroxide	$NaOH$	Fisher Scientific	Fair Lawn, NJ 07410
Sodium Hydroxide-Thiosulfate	$NaOH \cdot Na_2S_2O_3$	Ricca Chemical	Arlington, TX 76012
Sodium Nitrate	$NaNO_3$	J.T. Baker	Phillipsburg, NJ 08865
Sodium Nitrite	$NaNO_2$	EM Science	Gibbstown, NJ 08027
Sulfuric Acid	H_2SO_4	Fisher Scientific	Fair Lawn, NJ 07410
Sulfuric Acid (Titrant)	H_2SO_4	HACH Company	Loveland, CO 80539

Using the data collected from these tests, combined with measurements of pH and oxidation reduction potential, a mass balance was constructed to show the inflow and outflow characteristics. Concentrations measured below the lowest standard are reported as half of the lowest standard (Table 5). Best practices were followed in regards to quality assurance and quality control. Regular standard checks were conducted every 10 samples. If the standard check was not within 10% of the expected value the system was recalibrated. All instruments are listed in Table 5 and undergo regular and continued maintenance according to instrument operation manuals. All glass and plastic-ware was hand washed and soaked in 0.5 N acids (HCl or HNO_3).

Table 5: List of analytical methods from Standard Methods and the corresponding instruments and detection limits.

Method	Instrument	Measured	Detection Limit (mg/L)
4110-NO_3^- Ion Chromatographic	Dionex ICS-1100	NO_3^- N	0.2
4500-NO_2^- C - Ion Chromatographic	Dionex ICS-1100	NO_2^- N	0.2
4500-NO_2^- B - Colorimetric	Shimadzu UV160U	NO_2^- N	0.02
4500-N_{org} B Macro-Kjeldahl	NA	TKN	0.2
505 Organic Carbon (Total)	Shimadzu TOC-5000	Total Organic Carbon	0.5
4500-P phosphorus	Shimadzu UV160U	Total P	0.01

3. Results and Discussion

3.1. Establishing Denitrification

The design of the column was able to provide the conditions required to induce the denitrification process. Synthetic runoff showed a decrease in the concentration of nitrate over time when passed through media containing woodchips. Figure 5 shows the nitrate-N concentrations in the effluent of a column packed with only pea gravel in comparison with the three runs for a column with 4.5% WO woodchips by mass. While the nitrate concentrations in the column with WO woodchips decreases from 3 mg/L-N until it reaches and remains below the detection limit of 0.2 mg/L-N, the concentration of nitrate in the pea gravel column remain near 3 ($\pm$ 0.11) mg/L-N. The pea gravel column provided little to no nitrate removal. This is in agreement with the fact that denitrifying
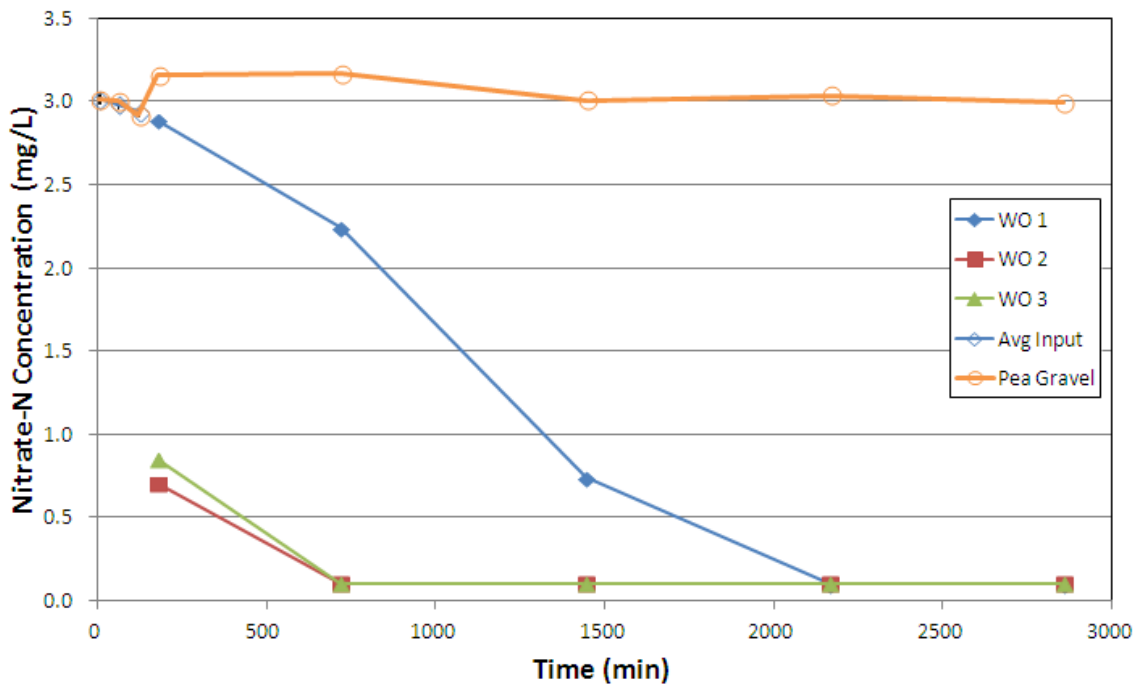
Figure 5: Nitrate-N concentrations of collected samples from a column packed with Willow Oak woodchips and samples collected from a column containing only pea gravel. These tests were conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column and one event for the pea gravel column. All columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

bacteria require anaerobic conditions and the presence of organic carbon (Blowes et al. 1994; Kim et al. 2003). With no organic carbon, denitrifying bacteria lack the ability to function and reproduce (Blowes et al. 1994; Kim et al. 2003).

Run 1 appears to have a delay in the nitrate reduction. This shoulder indicates that microbial populations have not been fully established nor produced the enzymes necessary to carry out denitrification. Runs 2 and 3, however, do not have a shoulder, indicating that microbial populations have been established. Runs 2 and 3 are also very similar which suggests that further tests would have similar results.

For all three runs the pH of WO column samples ranged from 5.90 to 6.72 with an average of 6.29. The values of pH from the blank column were slightly higher, between 6.60 and 7.07 with an average of 6.85. This suggests that the presence of organic material
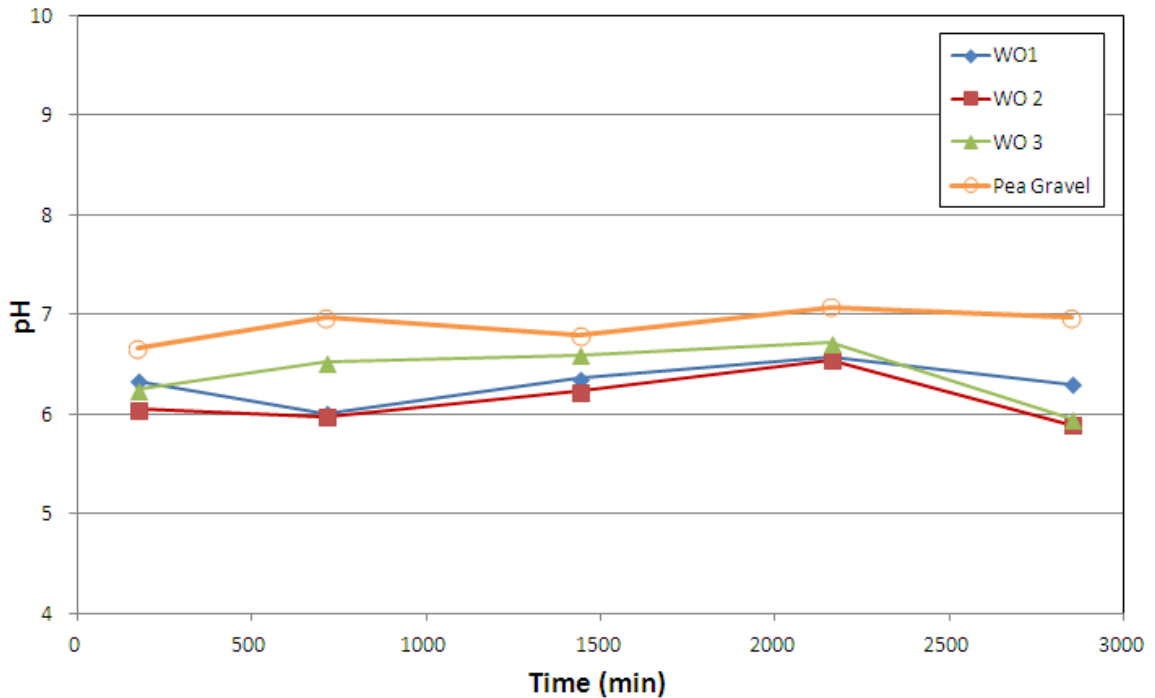
Figure 6: The pH of collected samples from a column packed with Willow Oak woodchips and a pea gravel column. This test was conducted with a centroid retention time of 0.8 days (1150 minutes). Three different events are displayed for the WO column and one event for the pea gravel column. All columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

slightly decreases the pH of the column. Figure 6 shows a comparison between the pH of the pea gravel column and the three WO column runs over time.
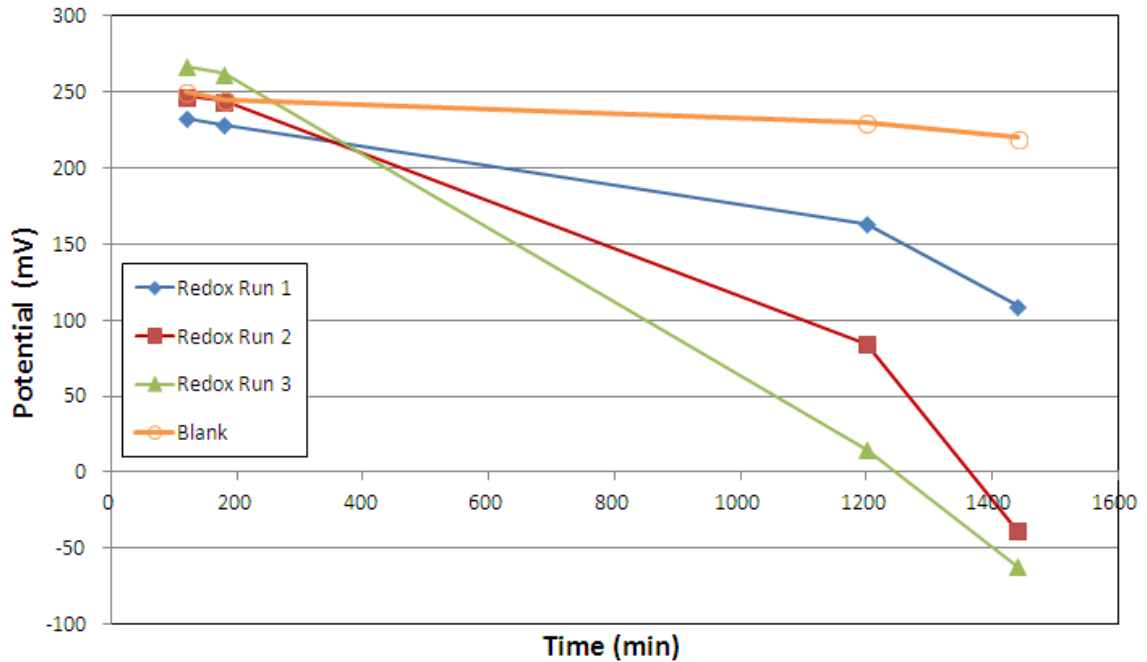
Figure 7: Oxidation Reduction Potential of collected samples from a column packed with Willow Oak woodchips and a pea gravel column. This test was conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column and one for the pea gravel column. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

The location of the oxidation/reduction probe allowed for readings for the first half of each test. The first run for a column containing woodchips shows an initially oxidizing environment with a potential near 250 mV (Figure 7). The potential slowly deceases over time suggesting that the environment is becoming more and more reducing (Figure 7). The reducing environment is conducive to denitrification (Blowes et al. 1994). Similar results are seen in the following runs, also shown in Figure 7. Again the potential starts near 250 mV and decreases over time, and, in these second two runs, reach below zero indicating a fully reducing environment. Denitrification takes place when the potential of an aquatic environment is between 200 and -200 mV (Stumm and Morgan 1996). The

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trend in the oxidation/reduction potential of column suggests that the media provides a good environment for denitrification. The potential in the column decreases below 200 mV, where denitrification is expected to be favorable, at around 400 minutes. The slope in the data indicates that oxygen is becoming much less available over time. In contrast, the oxidation reduction potential of the pea gravel column again starts near 250 mV but never reached below 200 mV (Figure 7). This suggests that the environment never becomes anaerobic when no organic carbon is present, and is not conductive to denitrification.

For comparison with the measured values, the equilibrium oxidation/reduction potential for the reduction of nitrate to nitrite was predicted using the Nernst equation (Eq. 3). The chemical formula for the half reaction of nitrate reduction to nitrite is shown in Equation 4.

$$E = E^0 - \frac{RT}{nF}\ln(Q) \tag{3}$$

$$NO_3{}^{-1} + 2H^+ + 2e^- = NO_2{}^{-1} + H_2O \tag{4}$$
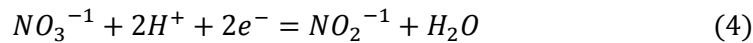
$$Q = \frac{[NO_2{}^-]}{[NO_3{}^-][H^+]^2} \tag{5}$$

E is the potential of the system, E^0 is the standard half reaction potential (+420 V for the reduction of nitrate to nitrite) (Stumm and Morgan 1996), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (298 K at room temperature), n is the number of electrons transferred (2 for the reduction of nitrate to nitrite), F is the Faraday constant (9.649 * 10^4 C mol^{-1}, and Q is the reaction quotient (Eq. 5). Table 6 shows the predicted potential in the column and the difference between those predicted values and the measured values.

Table 6: Predicted oxidation/reduction potential and corresponding measured potential for a column packed with Willow Oak woodchips. These tests were conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column. All columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

	Time(min)	pH	NO_2^- (mg/L)	NO_3^- (mg/L)	Oxidation Reduction Potential (mV) Measured	Predicted
Run 1	712.5	6.01	0.24	2.25	228.6	113.9
	1440	6.36	0.92	0.74	163.0	89.2
	2160	6.58	0.18	0.10	109.4	37.1
Run 2	712.5	5.98	0.01	0.10	244.1	112.8
	1440	6.23	0.01	0.10	84.6	92.0
	2160	6.55	0.01	0.10	-38.4	77.2
Run 3	712.5	6.53	0.01	0.82	261.9	103.4
	1440	6.60	0.01	0.31	15.3	59.4
	2160	6.72	0.01	0.10	-62.0	55.3

One reason that these predictions vary from the measured values is that the system is dynamic. This means that the nitrogen species are constantly changing and the potential changes accordingly. All of the species of nitrogen cannot be measured so some reactions are unaccounted for in the calculation of the potential. The electrode used to measure the potential in the column represents the environment as a whole. Nitrate reduction to nitrite is not the only process taking place that affects the system potential. However, those are the only measured concentrations that can be applied to the Nernst equation.

Early calculated values tend to underpredict the potential while later values tend to overpredict. This may be representative of a dynamic system. As nitrate is reduced to nitrite the concentration of nitrate decreases while nitrite increases. This would result in a decreasing potential, which is evident in both the measured and calculated values. When nitrite begins to be reduced to nitric oxide the concentration of nitrite also begins to

decrease. As a result, the potential of the system decreases much more quickly than the calculated values indicate. Therefore calculated values overpredict the potential.

The media containing woodchips resulted in leaching of phosphorus and organic carbon. Figure 8 shows the inflow and outflow concentrations of phosphorus over time for all three runs. Figure 8 is an example of effluent total phosphorus concentrations which closely reflects the total phosphorus concentration in all the experiments conducted. The empty markers show the inflow concentrations of 0.1 mg/L phosphorus and the solid markers show collected sample concentrations. The first sample of the first run showed a spike in phosphorus concentration. After the first sample the effluent had only slightly increased concentrations of phosphorus, near or below 0.15 mg/L phosphorus. This is consistent with all of the experiments being discussed unless otherwise mentioned.

Figure 9 shows the inflow and outflow concentrations of organic carbon over time for all three runs. Total organic carbon concentrations for WO 1 were at or near 50 mg/L
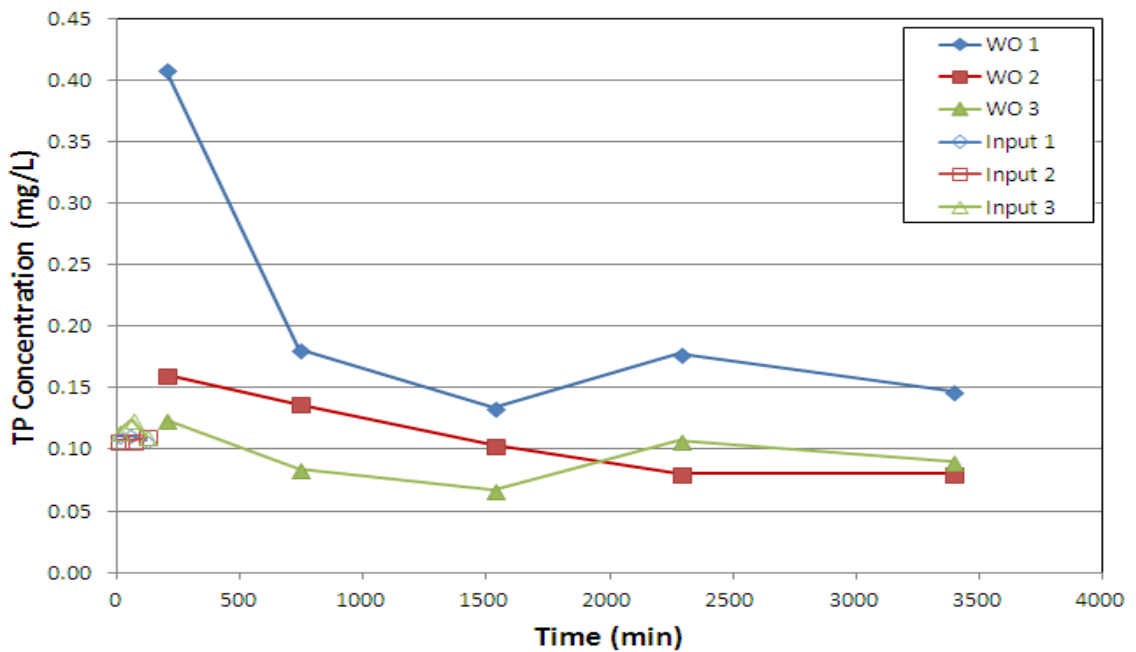
Figure 8: The concentration of total phosphorus in collected samples from a column packed with Willow Oak woodchips. This test was conducted with a centroid retention time of 1.0 days. Three different events are displayed. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

throughout the collection period. The subsequent runs showed lower concentrations with the exception of the first sample of WO 2 (Figure 9). In a study using woodchips as an organic carbon source for denitrification in septic systems, Robertson (2010) also found an initial spike in organic carbon concentrations in the effluent. In a steady state continuous flow system the organic carbon concentration decreased and began to stabilize over time (Robertson 2010). The consistency of the second two runs of this study suggests that steady state is reached after the first run is completed. The trend also suggests that, had testing continued, subsequent runs would have similar results. These observations are in close agreement with Robertson (2010). Robertson (2010) also attributed these concentrations of leached nutrients to the organic material in the media.

Nitrogen was also leached from the media, and measured as TKN. The TKN for WO 1 remained above 1 mg/L for all of the samples tested. The subsequent runs showed much lower concentrations near 0.5 mg/L. The TKN trend is similar to that of the total

Figure 9: Total organic carbon concentrations of collected samples from a column packed with Willow Oak woodchips. This test was conducted with a centroid retention time of 0.8 days. Three different loading events are displayed. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

organic carbon, suggesting that the two concentrations are linked or respond similarly to the changing environment. The pea gravel test was in agreement with these observations where no nitrogen, phosphorus, or organic carbon was leached. The source of those nutrients is therefore assumed to be the wood chips. Most of the research done on nitrate removal efficiency in bioretention systems does not account for other forms of nitrogen and therefore there are no specific examples to compare these data to. However, Robertson (2010) makes note of the link between organic material and leached nutrients, specifically organic carbon. That research suggests that adjustments in the amount of organic material would have significant effects on the leaching of these nutrients (Robertson 2010). Concentrations of each nitrogen species and the total nitrogen concentrations over time for run 3 of the WO column can be seen in Figure 10. The total nitrogen was calculated by adding the concentrations of TKN, nitrate, and nitrite.

The first run of the 0.8-day centroid retention time shows a nitrite concentration that starts below the detection limit (0.01 mg/ L-N) and increases over time until it peaks around 1.0 mg/L-N (Figure 10). This concentration is reached around halfway through the experimental duration, about 1500 minutes. Afterward the concentration decreased until it was below the detection limit (0.01 mg/L-N) in the final sample. This reflects, very clearly, the sequential microbial processes that reduce nitrate to nitrite and then to other forms of nitrogen and ultimately to nitrogen gas. As nitrate is converted to nitrate, nitrate concentrations decrease while nitrite concentrations increase (Blowes et al. 1994). As nitrite concentrations build, microbes begin to produce enzymes to convert that nitrite to nitric oxide, which is also depicted in Figure 10 by the decrease in nitrite concentrations after 1500 minutes (Blowes et al. 1994).
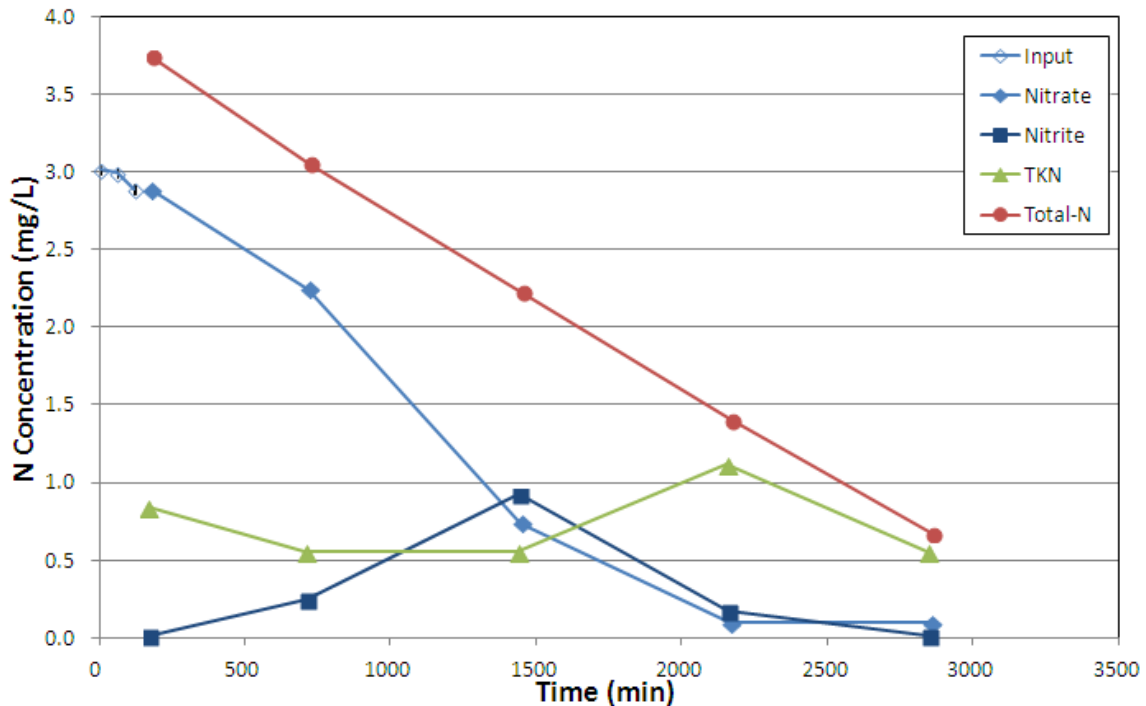
Figure 10: Nitrogen concentrations of collected samples from a column packed with Willow Oak woodchips. This test was conducted with a centroid retention time of 0.8 days. Run 3 of the different events are displayed. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

Data for the column with media containing WO woodchips was reproduced in a separate set of three runs. The average total nitrogen removal efficiencies for the two sets were 60.3% and 62.4%, which is the average difference between the total nitrogen mass in the influent and the effluent for the three runs. The average nitrate removal efficiencies for the two sets of data were 81.6% and 82.7%, which is similarly the average of the three runs' difference between the total nitrate-N mass in the influent and the total nitrate-N mass in the effluent. Figure 11 shows the second set of data. The similarity between these data and those presented in Figure 5 is clear. While run 1 of each set has a much slower reduction in the concentration of nitrate, runs 2 and 3 of each set have decreased to near 0.5 mg/L N by the first collected sample. Nitrate concentrations remain near or below the

detection limit for the remaining samples collected. This suggests that the data

presented herein are reliable and reproducible.
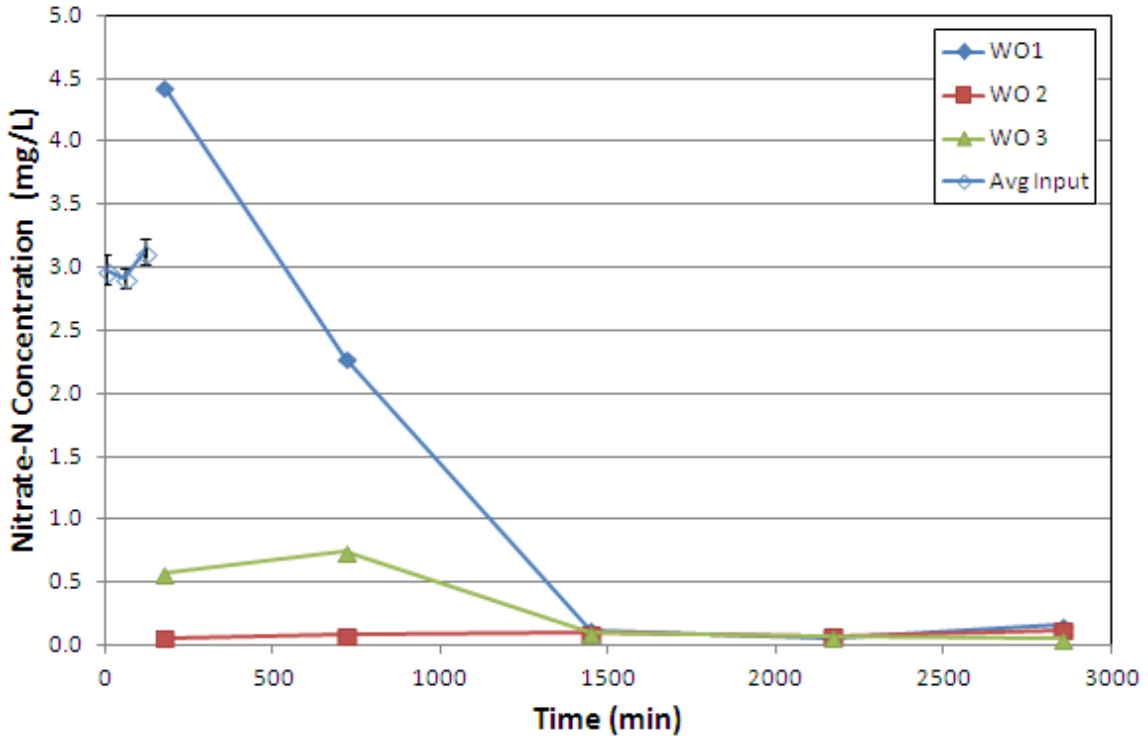
Figure 11: Nitrate-N concentrations of collected samples from a column packed with Willow Oak woodchips. These tests were conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

Similar to the pea gravel test, the tests inhibited with azide showed effluent

concentrations of nitrate at or near the inflow concentration of 3 mg/L-N (Figure 12).

Bremmer and Yeomans (1986) showed that azide has the greatest ability to retard

microbial denitrification. These data are in agreement and show that higher

concentrations of azide can fully inhibit denitrification. The pH of the inhibited samples

ranged from 5.86 to 6.56 with an average of 6.27. The oxidation/reduction potential in the

column showed a consistent oxidizing environment. Similar to the pea gravel column, the

potential in the inhibited column never reached below 200 mV. However, the inhibited

column leached much higher concentrations of phosphorus, organic carbon and TKN. These concentrations varied between runs and samples. The average concentrations of total phosphorus, total organic carbon, and TKN were 0.51, 106, and 2.50 mg/L, respectively.
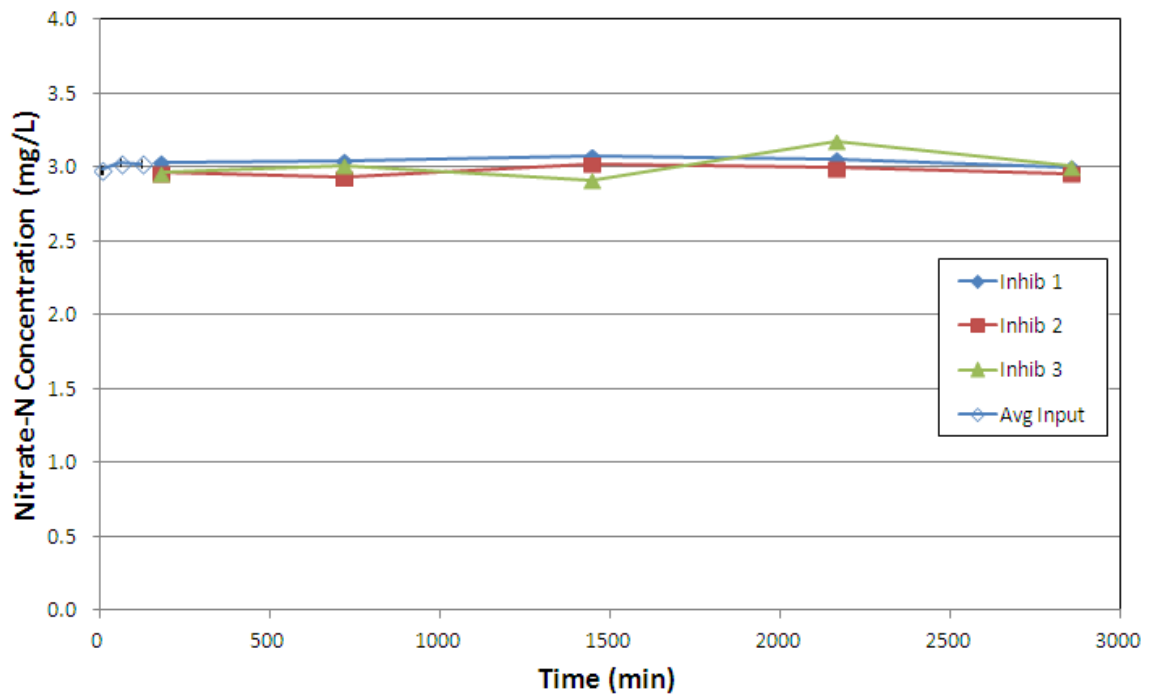
Figure 12: Nitrate-N concentrations of collected samples from a column packed with Willow Oak woodchips. These tests were conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column. Column was loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater containing 50 mg/L Sodium Azide for inhibition of microbial denitrification.

Because no reduction of nitrate is found when microbial denitrification is inhibited, these data suggest that the reduction of nitrate in the WO column was due to populations of denitrifying microbes. No other research has been identified that uses a similar method for identifying the effect of denitrifying microbes in a bioretention system. However, Chen et al. (2013) conducted quantitative PCR on media similarly designed for denitrification in bioretention systems. In the analysis, Chen et al. (2013) identified strains of denitrifying bacteria. While Chen et al. (2013) did not use woodchips as the sole source of organic carbon, the columns in that study created conditions similar to

those used in this study. That study had a saturated zone containing organic material that became anaerobic due to saturation (Chen et al. 2013). The similarities in environmental conditions and the contrasting nitrate concentrations from inhibitory and non-inhibitory columns strongly agree with the evidence presented in Chen et al. (2013).

The lack of nitrate reduction in the inhibited column also suggests that the scaled bioretention design provides the conditions necessary for improved nitrate removal from stormwater runoff. Kim et al. (2003), Hsieh et al. (2007), Bratieres et al. (2008), Ergas et al. (2010), Leverenz et al. (2010), Robertson (2010), Zinger et al. (2013), and Chen et al. (2013) all identify that the conditions needed for denitrification to take place in a stormwater management application are an anaerobic media, typically created by being fully saturated, containing a source of organic carbon. This research also found those conditions to be necessary and conducive to the growth of denitrifying microbes.

3.2. Effect of Nitrate Concentration

Varying the inflow concentrations of nitrate from 1.5 to 4.5 mg/L-N did not have an effect on the pH of the samples collected. The average pH for the 1.5, 3.0, and 4.5 mg/L N inflow columns were 6.30, 6.29, and 6.42, respectively. Collectively the samples ranged in pH from 5.75 to 7.32. The oxidation/reduction potential of the columns, however, varied greatly. While the potential in the 3.0 mg/L inflow column behaved as expected and decreased over time, the other two columns were less predictable. The 1.5 mg/L column started with a potential near 200 mV in all three runs but did not show any discernible trend thereafter (Figure 13). The 4.5 mg/L inflow column showed a decrease in potential over time in run 1 but increases in potential in runs 2 and 3 (Figure 14). This suggests that, for an unknown reason, the columns did not consistently create conditions

conducive to denitrification when varying the concentration of nitrate in the artificial stormwater.

While there were slight variations between the three different column studies, consistent nutrient concentrations were leached. Average concentrations of total phosphorus from the 1.5, 3.0, and 4.5 mg/L inflow columns were 0.11, 0.37, and 0.16 mg/L P, respectively. Average concentrations of total organic carbon were 28, 41, and 22 mg/L C, respectively, and TKN were 1.10, 0.78, and 0.90 mg/L N, respectively.
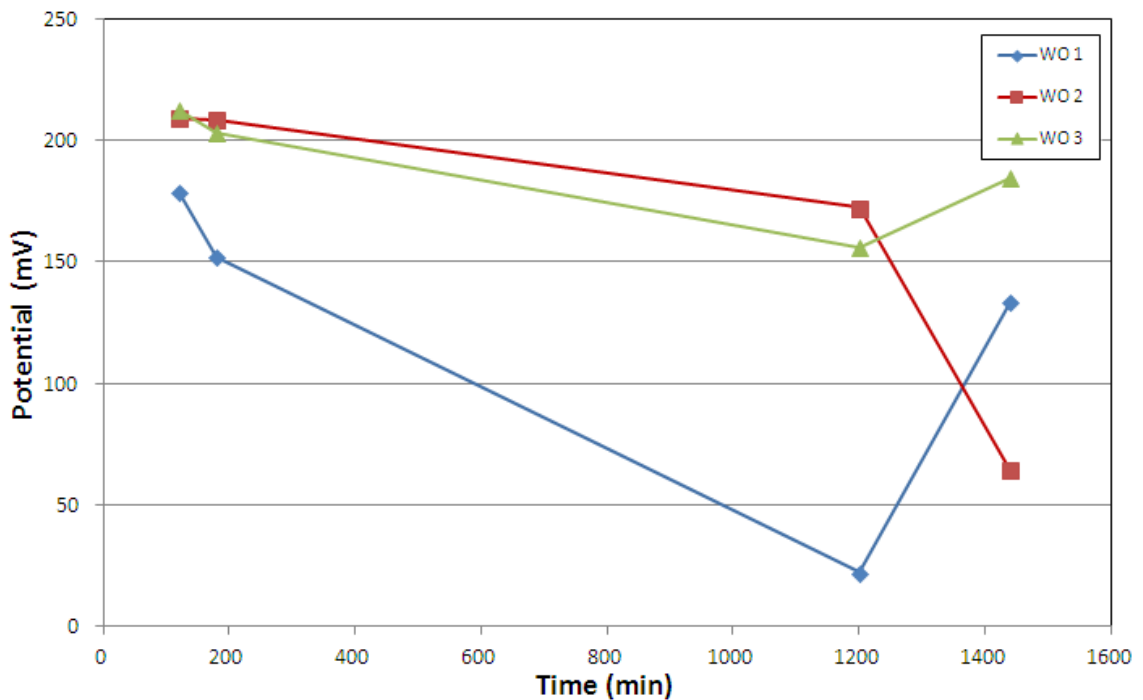
Figure 13: Oxidation Reduction Potential of collected samples from a column packed with Willow Oak woodchips. This test was conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater containing 1.5 mg/L N.

The removal of nitrogen by the column had no discernible pattern. Total nitrogen mass removal efficiencies for the 1.5, 3.0, and 4.5 mg/L N inflow columns were 13.7%,

60.3%, and 24.4%, respectively. Nitrate mass removal efficiencies for the 1.5, 3.0, and

4.5 mg/L N inflow columns were 67.9%, 81.6%, and 42.8%, respectively.
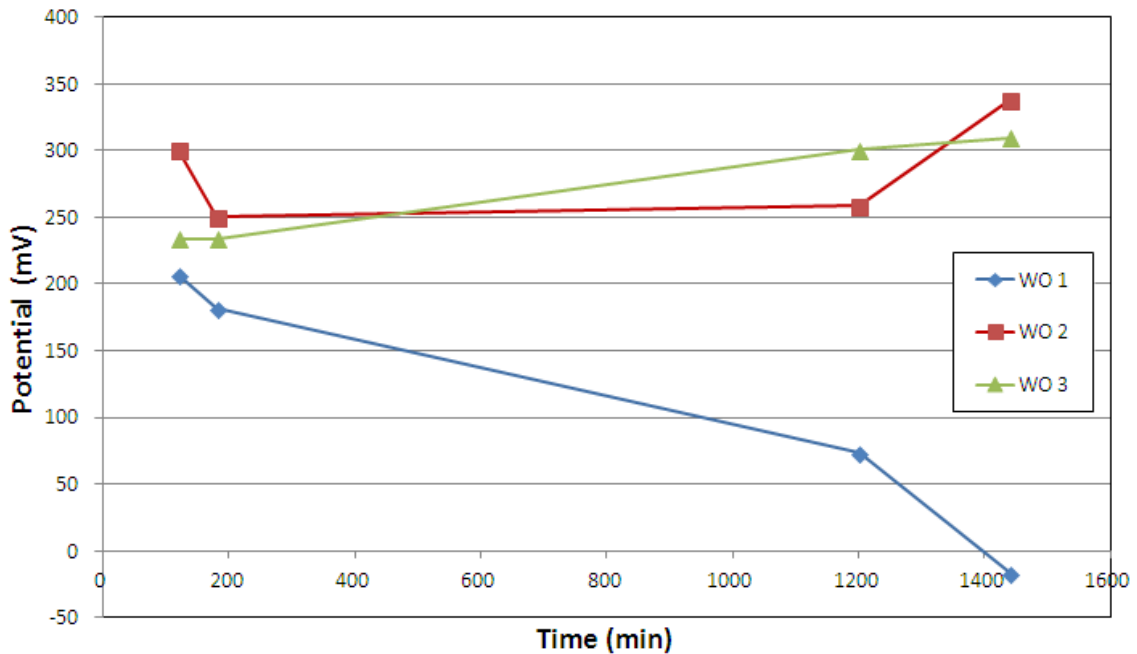
Figure 14: Oxidation Reduction Potential of collected samples from a column packed with Willow Oak woodchips. This test was conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater containing 4.5 mg/L N.

In order to better quantify and characterize the effect of varying inflow

concentrations of nitrate on the denitrification process, two models were developed.

Robertson (2010) and Leverenz et al. (2010) both evaluated modeling denitrification

using either zero or first order models. Robertson (2010) used a septic system design with

woodchips as an organic carbon source to accommodate treatment of agricultural runoff

and found that a zero-order model most accurately depicted the data. Leverenz et al.

(2010) conducted a lab scale evaluation of wetland treatment with woodchips as a carbon

source and found that first-order kinetics most accurately modeled denitrification. While

there are similarities, neither of these experiments accurately reflects the conditions in a bioretention system. Robertson (2010) is more closely related but has a more controlled environment than in a bioretention system and received stream runoff that contained much higher concentrations of nitrate (3.1 to 48.8 mg/L-N) than are typically seen in urban settings. Leverenz et al. (2010) had a horizontal continuous flow system modeled to represent a wetland and not a bioretention system. Both Robertson (2010) and Leverenz et al. (2010) have an abundance of organic material ensuring that carbon is not limiting.

Taking previous evaluations into consideration, pseudo-zero and first-order models were developed to represent the denitrification process in the present bioretention column. The rate constant for these models is a function of woodchip species, woodchip size, woodchip availability, pH, and temperature. The pseudo-zero and first-order model equations are shown in Eq. 7 and Eq. 8, respectively. These equations are derived from Eq. 6, which is a simple nitrate-N mass balance for the column. The full derivation of these models can be found in the appendix. Both models assume a completely mixed system because as water passes through the media it is mixed. There is no direct pathway through the column and the media is homogeneous. Therefore, it can be assumed that all stormwater retained in the column is in the same environment and undergoing the same processes. Outflow from the system is assumed to begin when the column is completely full. Therefore, inflow is not represented in Eq. 6. Very little effluent drains from the column during the filling period which is only a fraction of the total drainage time and the elimination of inflow from the equation greatly simplifies the derivation.

$$\frac{dM}{dt} = -Q * C - r * V \qquad (6)$$

$$C = C_0 + k_0 * t \qquad (7)$$

$$C = C_0 * e^{k_1 * t} \qquad (8)$$

For the pseudo-zero-order model rate, r, is equal to k_0, and for the pseudo-first-order model r is equal to k_1 times C. Q is the effluent rate, C is the concentration of nitrate-N of the sample at time t, and C_0 is the inflow concentration of nitrate-N. k_0 and k_1 are the rate constants for the psedo-zero and first-order models, respectively. These models were fitted to the collected data using least squares with a fixed intercept at the inflow concentration. Rate constants were used as fitting parameters. The pseudo-zero-order
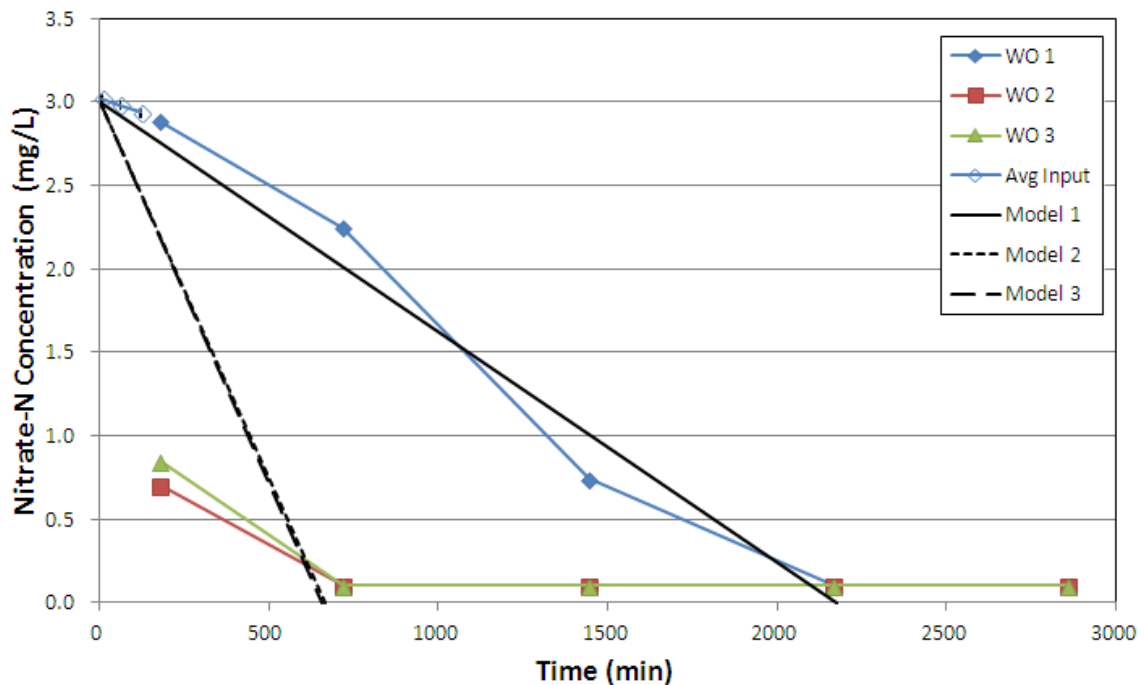
Figure 15: Fit of a pseudo-zero-order model to the Nitrate-N concentrations of collected samples from a column packed with Willow Oak woodchips. These tests were conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column.

model was fitted only to the points in the experimental phase where nitrate concentrations were decreasing. After the concentration of nitrate fell below the detection limit no more points were used (Figure 15). In Figure 15, model 1 and 2 overlap. All of the effluent data collected were used in fitting pseudo-first-order models to the data (Figure 16). The resulting rate constants were compiled in order to better compare each of the factors being discussed. pseudo-zero and first-order rate constants can be found in Table 7 for the average of all three runs, the average of runs 2 and 3, and run 3 alone for each set of data collected. Table 7 also shows the average total nitrogen and nitrate removal efficiencies for all of the factors being evaluated.

For the majority of the testing conducted the nitrate removal curve for Run 1 was very different from the subsequent two runs. The difference between run 1 and the

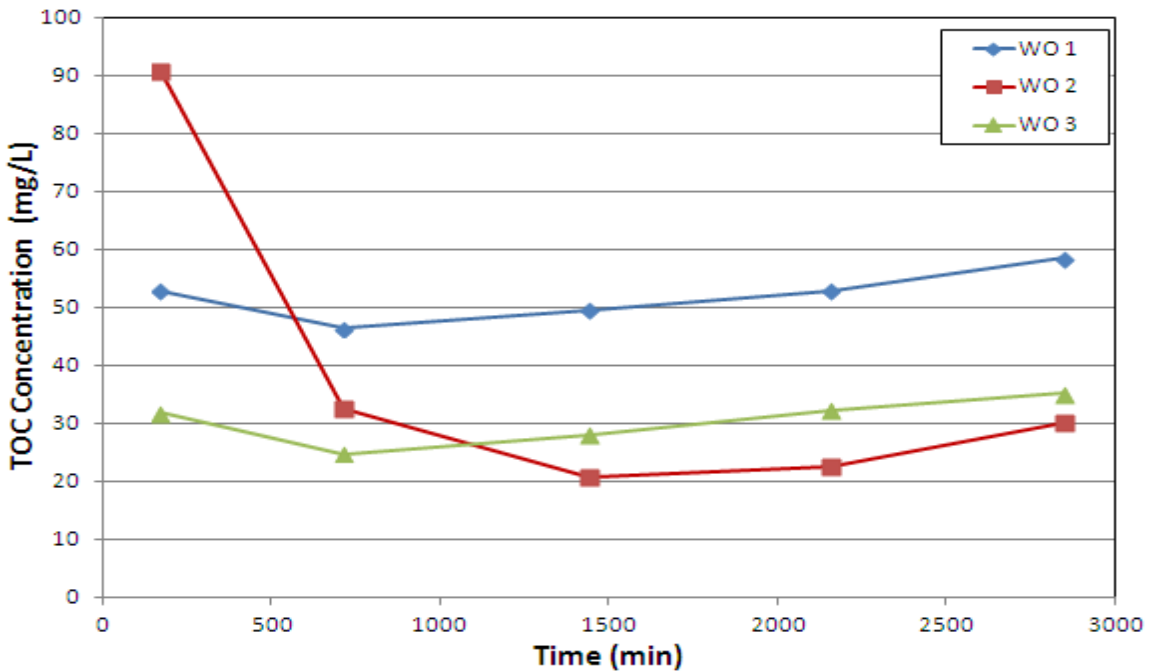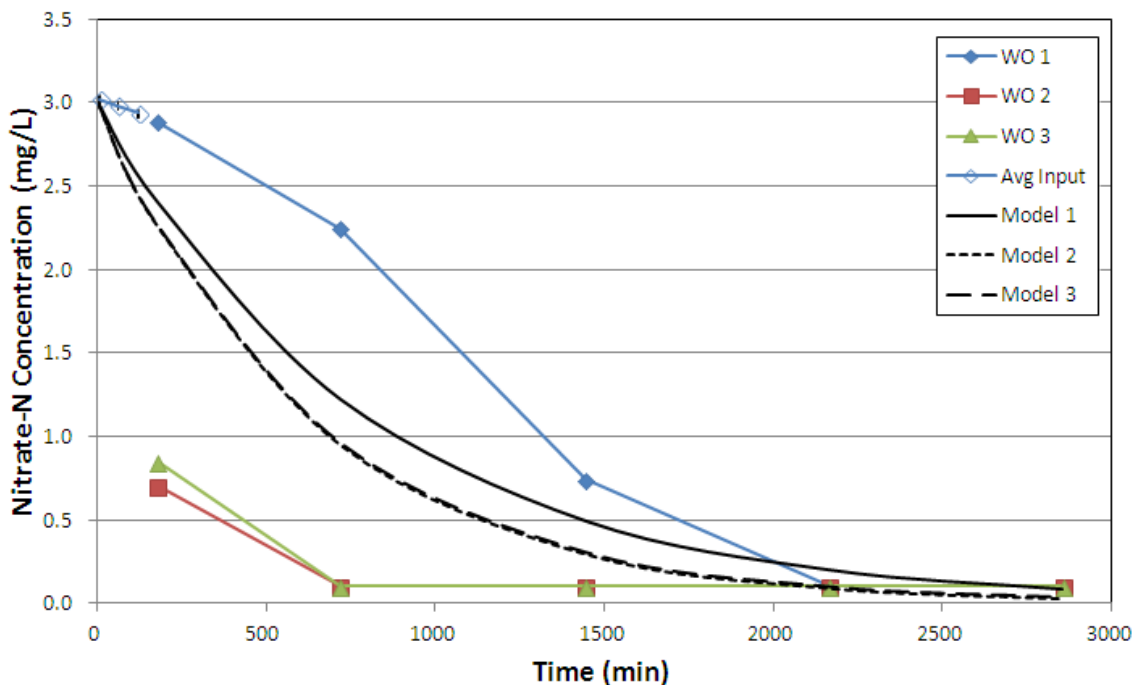**Figure 16: Fit of a pseudo-first-order model to the Nitrate-N concentrations of collected samples from a column packed with Willow Oak woodchips. These tests were conducted with a centroid retention time of 0.8 days. Three different events are displayed for the WO column.**

subsequent runs suggests that an average of the rate constants for all three runs does not accurately represent an established system. The average of the last two runs was more appropriate for most sets of data. The similarity of the last two runs suggests that subsequent runs would behave similarly. The second two runs did not have a shoulder, which was evident in run 1 (Figure 16). Therefore, it is expected that subsequent runs would not have a shoulder and an acclimation model would not accurately represent an established system. Some of the data sets continued to change from run 2 to run 3 suggesting that in some cases more than one run was necessary for the system to reach a steady state. Because run 3 represents the most established media, the discussion of rate constants will be based on the third run for each set of data. All of these data can be found in Table 7.

Altering the concentration of nitrate in the inflow did not have the expected effect. According to the models, the rate constants should not be affected by a change in the initial concentration of nitrate. However, 1.5, 3.0, and 4.5 mg/L N inflow columns had pseudo-zero-order rate constants of 1.30, 6.57, and 3.11 mg/L/day respectively for run 3. The pseudo-zero-order rate constants were not constant as the models predicted and neither was there a discernible trend in the change of the rate constants. The pseudo-first-order rate constants had less variability with inflow concentration of nitrate. The 1.5, 3.0, and 4.5 mg/L N inflow columns had pseudo-first-order rate constants of 1.39, 11.41, and 1.53 day^{-1} respectively for run 3.

One explanation of the non-conformity of the rate constants with the model predictions is different models may more accurately predict the data at different influent

Table 7:Rate constants and removal efficiencies for bioretention column denitrification. The three-run average, run 2 and 3 average, and run 3 pseudo-zero and first-order rate constants are listed for each column test. The corresponding combined three run total nitrogen and nitrate removal percentage is also shown for each column test.

Category		Pseudo-Rate Constants								Removal Efficiency	
		Zero Order				First Order				Total Nitrogen (%)	Nitrate (%)
		Total Avg (mg/L·day)	Run 2&3 Avg	Run 3 (mg/L·day)	Average R²	Total Avg (day⁻¹)	Run 2&3 Avg (day⁻¹)	Run 3 (day⁻¹)	Average R²		
Nitrate-N	Blank	ND	ND	0.01	0.00	ND	ND	0.00	0.00	-1.01	-1.01
	Inhibited	0.01	0.01	0.03	0.00	0.01	0.01	0.01	0.00	-80.58	0.37
	1.5 mg/L	1.85	1.40	1.30	0.91	2.20	1.76	1.39	0.93	13.7	67.9
	3.0 mg/L	5.02	6.53	6.57	0.64	10.39	14.98	11.41	0.92	61.9	82.4
	4.5 mg/L	3.12	2.16	3.11	0.62	1.87	0.91	1.53	0.74	24.4	42.8
Retention time	0.4 Days	4.51	4.13	4.20	0.87	3.07	2.89	3.04	0.93	6.5	51.0
	0.6 Days	2.99	2.07	1.94	0.61	1.94	1.70	1.46	0.74	30.1	49.5
	0.8 Days	5.02	6.53	6.57	0.64	10.39	14.98	11.41	0.92	61.9	82.4
	1.0 Days	2.34	2.28	1.86	0.64	1.52	1.63	1.45	0.78	41.8	59.6
	1.3 Days	1.58	1.30	1.34	0.89	1.21	0.85	0.94	0.95	50.1	65.9
Woodchip Species	Wild Cherry	2.83	3.23	3.24	0.83	2.34	2.92	3.02	0.93	37.5	71.4
	Willow Oak	9.94	13.68	3.46	0.60	13.15	19.13	12.73	0.88	61.3	82.1
	WO Repeat	5.02	6.53	6.57	0.69	7.62	10.83	10.09	0.97	62.4	82.7
	Red Maple	2.83	3.10	3.17	0.80	2.17	2.67	3.31	0.91	61.8	73.6
	Virginia Pine	2.78	3.39	3.20	0.60	9.77	14.20	4.21	0.90	47.4	78.4
	American Beech	4.22	3.31	3.31	0.75	4.18	4.08	4.00	0.96	34.4	87.2
Chip Size	5 mm	5.02	6.53	6.57	0.64	10.39	14.98	11.41	0.92	61.9	82.4
	9 mm	2.41	2.47	2.09	0.87	1.65	1.52	1.43	0.92	51.4	60.9
	13 mm	2.55	2.56	2.09	0.90	1.67	1.81	1.40	0.93	46.2	63.2
Chip Mass	1.0%	1.43	1.66	1.71	0.42	1.10	1.47	1.56	0.58	42.2	48.9
	2.5%	3.74	4.61	5.98	0.69	4.00	5.41	7.22	0.93	57.8	68.7
	4.5%	5.02	6.53	6.57	0.64	10.39	14.98	11.41	0.92	61.9	82.4
Limestone	0.0%	5.02	6.53	6.57	0.64	10.39	14.98	11.41	0.92	61.9	82.4
	5.0%	2.83	3.25	3.37	0.73	2.99	3.95	5.94	0.89	61.0	66.1
	10.0%	2.90	3.13	3.44	0.70	3.85	5.18	8.86	0.92	61.9	68.2

concentrations of nitrate. Robertson (2010) found that a zero-order model better fit the data. In that study influent nitrate concentrations were as high as 48.8 mg/L N (Robertson et al. 2010). Leverenz et al. (2010) suggested that denitrification may follow first order kinetics when the influent nitrate concentrations are low (less than 10 mg/L-N). The bioretention experiments fall below that suggested threshold, which suggests that first-order kinetics may be a better model. However, the average pseudo-zero-order model R^2 values for the 1.5, 3.0, and 4.5 mg/L N inflow columns were only 0.91, 0.64, and 0.62, respectively. The average pseudo-first-order model R^2 values for the 1.5, 3.0, and 4.5 mg/L N inflow columns were 0.93, 0.92, and 0.74, respectively. These goodness-of-fit statistics give a clear indication that the pseudo-first-order model better describes the data. The pseudo-zero-order model is fitted to fewer points. All of the points are used when fitting the pseudo-first-order model to the data. Even with fewer points fitted to the pseudo-zero-order model, the R^2 values pseudo-first-order kinetics better model the data.

Leverenz et al. (2010) found that after two years the first-order denitrification rate constant in a woodchip media was between 1.30 and 1.41 days^{-1}. Robertson (2010) reported first-order rate constants for fresh pine and fresh hardwood woodchip media to start at 2.3 day^{-1} and 2.4 day^{-1}, respectively. Further testing showed decreasing rate constants over time (Robertson 2010). The 3.0 mg/L N column had a pseudo-first-order rate constant of 11.4 ± 1.9 day^{-1}, for run 3. The rate constant for this column is higher than those reported in literature. However, this value has reproducibility and is, therefore, used in comparison with all of the tests conducted.

3.3. Effect of Retention Time

When varying the retention time of the columns, the pH of the samples remained relatively consistent and ranged from 5.90 to 7.50. The average pH of the 0.4 (575), 0.6 (860), 0.8 (1150), 1.0 (1450), and 1.3 days (1875 minutes) centroid retention time columns was 6.67, 6.47, 6.29, 6.53, and 6.69, respectively. The oxidation/reduction potential in the columns all started between 200 and 350 mV. However, the potential in shorter retention time columns did not reach the low levels that longer retention time columns did. The lowest potential measured for the 0.4 day centroid retention time column was 70.8 mV at 255 minutes while the lowest potential measured for the 1.3 day centroid retention time column was -454.5 mV at 2640 minutes. It is evident from these data that the longer the water is retained in the media the more reducing the environment becomes.
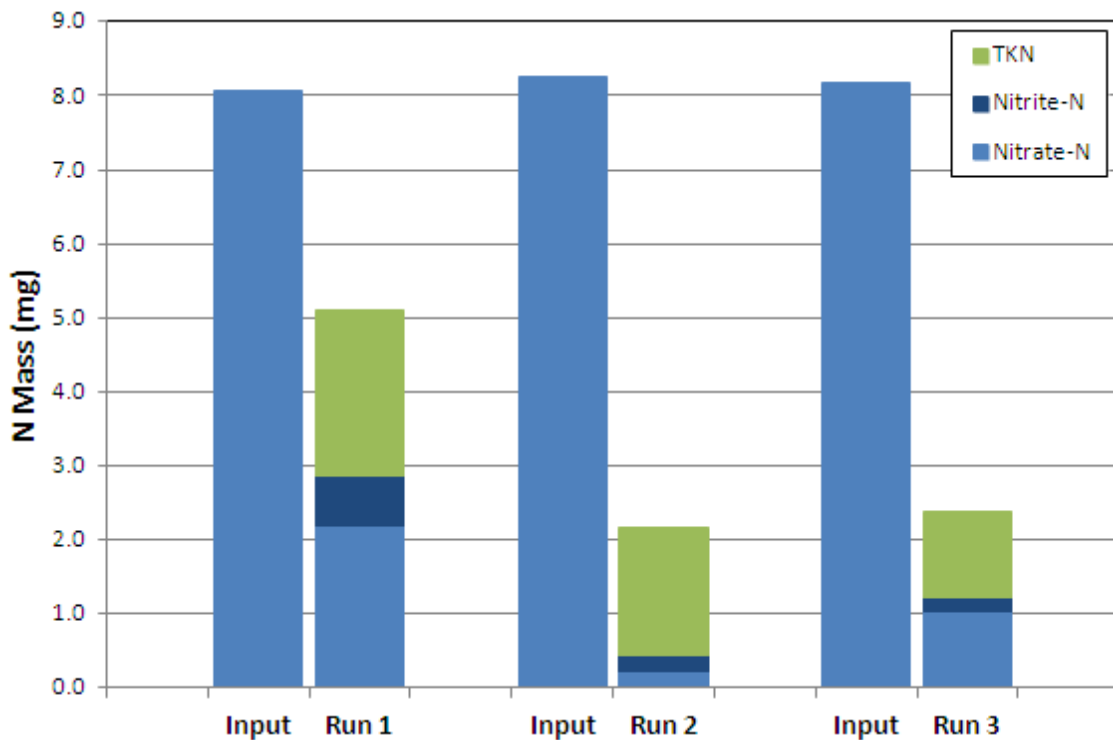
Figure 17: Total nitrogen mass in the effluent (Run #) is compared to its respective input mass from the artificial stormwater for a column packed with Willow Oak woodchips. This test was conducted with a centroid retention time of 0.8 days. Three different events are displayed. Columns were loaded at 1.2 L/hr for 2.25 hrs with artificial stormwater.

Nutrient concentrations were relatively unaffected by changing retention times as well. The average total phosphorus concentrations in samples from the 0.4, 0.6, 0.8, 1.0, and 1.3 days centroid retention time columns were 0.20, 0.14, 0.22, 0.14, and 0.13 mg/L P, respectively. The 0.4, 0.6, 0.8, 1.0, and 1.3 days centroid retention time columns produced average TKN concentrations of 1.16, 0.69, 0.78, 0.65, and 0.73 mg/L N, respectively, and average total organic carbon concentrations of 50.8, 28.7, 40.5, 29.6, and 21.8 mg/L C, respectively.

The total nitrogen mass in and out of the columns for the 0.8-day centroid retention time is presented in Figure 17. Each of the three successive runs is shown. It is evident that the TKN mass varies only slightly between runs. However, nitrate mass in the second and third runs are less than the first run suggesting that after the first run the microbial communities are established and can effectively reduce the nitrate concentrations.

In Figure 18 the amount of nitrogen mass in the effluent of the different centroid retention times are compared to the influent nitrogen mass. The three different runs for each retention time are combined in their respective columns. The far left column is the average total input nitrogen mass for the different centroid retention times. Research suggests that microbial denitrification requires time on the order of days to effectively reduce nitrate concentrations (Leverenz et al. 2010; Robertson 2010; Chen et al. 2013). Chen et al. (2013) suggests that prolonged periods of saturation are necessary to create anoxic environments that promote microbial denitrification. The use of a permanently saturated zone by means of an upturned underdrain is used in that lab scale study (Chen et al. 2013). The general trend in these data confirms that longer retention times have the effect of greater removal of total nitrogen mass and nitrate mass (Figure 18). The more
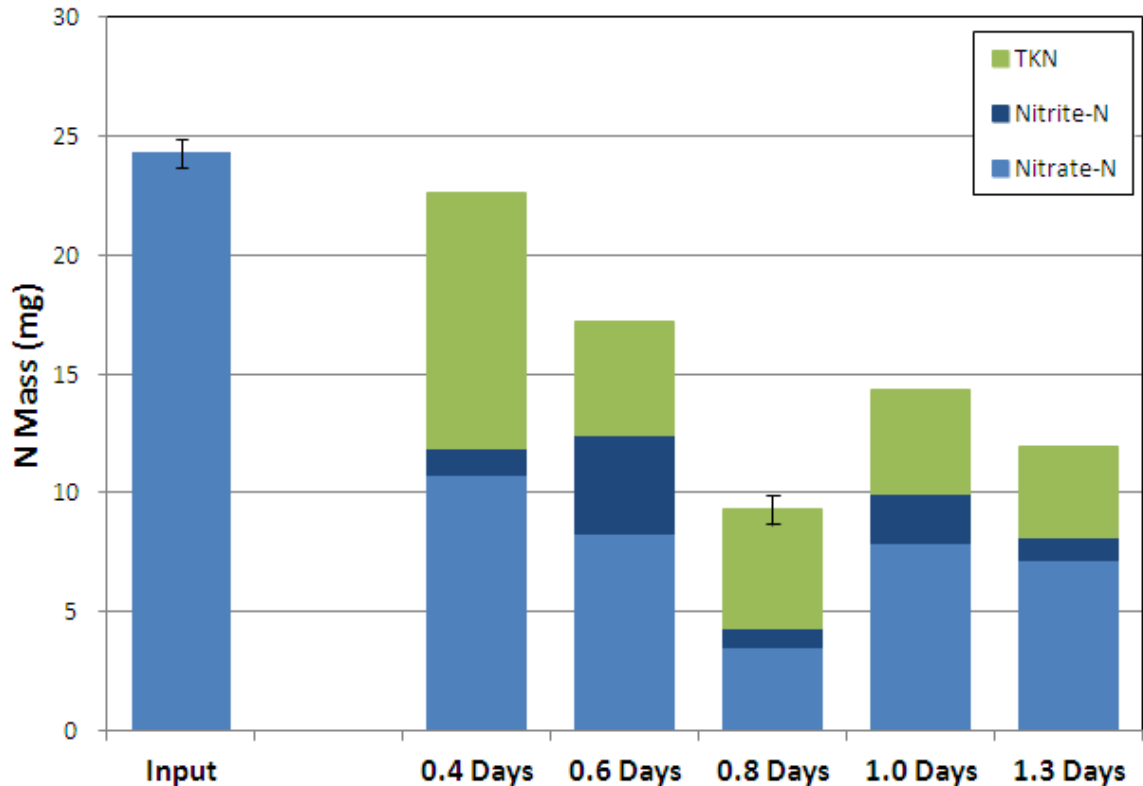
Figure 18: Nitrogen mass compared for different stormwater centroid retention times using Willow Oak woodchips. The columns are labeled by the centroid retention times used and are compared to the average input nitrogen mass. Each column represents the combined mass of the three successive runs conducted for each centroid retention time. The input mass is the average of the five combined masses.

time the stormwater remains in the saturated media, the greater amount of nitrogen removal is expected.

The pseudo-first-order model predicts that nitrate concentration decreases with time, but that time should not vary the rate constant. Therefore, it is expected that these rate constants are independent of the amount of time the water is in the column. The rate constants for the 0.4, 0.6, 0.8, 1.0, and 1.3 day centroid columns are 3.0, 1.4, 11.4, 1.4, and 0.9 day^{-1}, respectively for run 3 (Table 7). The trend in these numbers suggests that denitrification occurs more quickly with shorter retention times. This disagrees with the

mass analysis, the model, and other research (Robertson 2010, Leverenz et al. 2010, Chen et al. 2013).
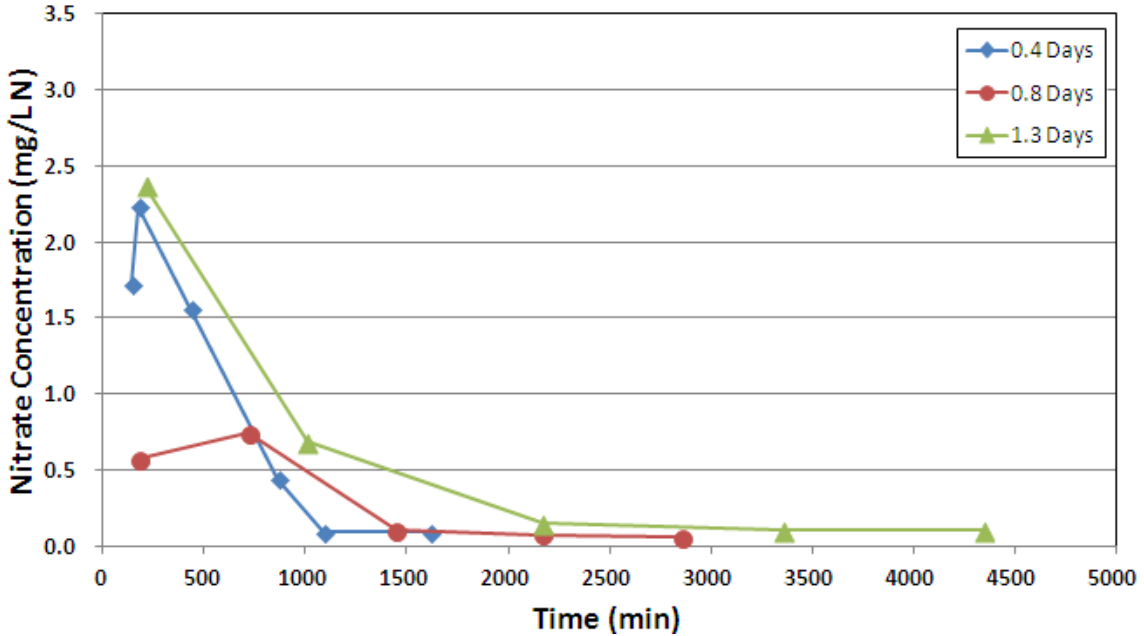
Figure 19: Nitrate-N concentrations of collected samples from run 3 for columns packed with Willow Oak woodchips. The tests were conducted with centroid retention times of 0.4, 0.8, and 1.3 days. The comparison among the three denitrification curves shows that the point at which the concentration reaches below the detection limit is stretched by greater amounts of time between samples.

One explanation of the trend in the data is that the time of sample collection skews the data. With shorter retention times, the points are grouped more closely together providing for a better fit to the data. With the longer retention times, the points are spaced farther apart. Later samples begin to fall below the detection limit and remain constant thus stretching the pseudo-first-order model to those later points that do not map the decreasing nitrate concentrations. Figure 19 compares the run 3 nitrate concentrations for the 0.4, 0.8, and 1.3 day centroid retention time. Notice that while the rate constant for the 0.4 day centroid is greater than all the other centroids, the trend in the curve of each data set is similar. The greater amount of time between detections for the longer retention times makes it more difficult to determine the precise time when nitrate concentrations

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reach the detection limit. This effectively stretches the denitrification process and results in decreased rate constants. Therefore, it is difficult to make an accurate comparison of the effect of retention time based on these rate constants.

3.4. Effect of Varying Media

3.4.1. Woodchip Species

When varying the woodchip species in the media, the pH of the samples again remained relatively consistent and ranged from 5.38 to 7.55. The oxidation/reduction potential in the columns all started between 200 and 400 mV. After 1200 min the potential decreased to between -100 and 200 mV for all columns. Nutrient concentrations varied slightly with changing chip type. The Wild Cherry (WC), Willow Oak (WO), Red Maple (RM), Virginia Pine (VP), and American Beech (AB) columns produced average TKN concentrations of 1.55, 0.78, 0.54, 0.99, and 2.14 mg/L N, respectively, and average total organic carbon concentrations of 152.9, 40.5, 42.4, 99.7, and 44.5 mg/L C, respectively. It appears that WC and VP leached greater amounts of TKN and organic carbon, suggesting that they degrade more quickly than the others woodchip species. The first run of AB leached a large amount of TKN which brought its average concentration up. While the second two runs did not leach as much TKN, significant amounts were still leached, averaging 1.40 mg/L N in the second two runs. The high amounts of TKN in the AB samples suggest that the carbon to nitrogen ratio is lower than the other woodchip species. According to Lamlom and Savidge (2003) AB has the lowest carbon content of the woodchip species being tested (Table 2). This agrees with the results of this study and the amount of TKN leached from the AB column
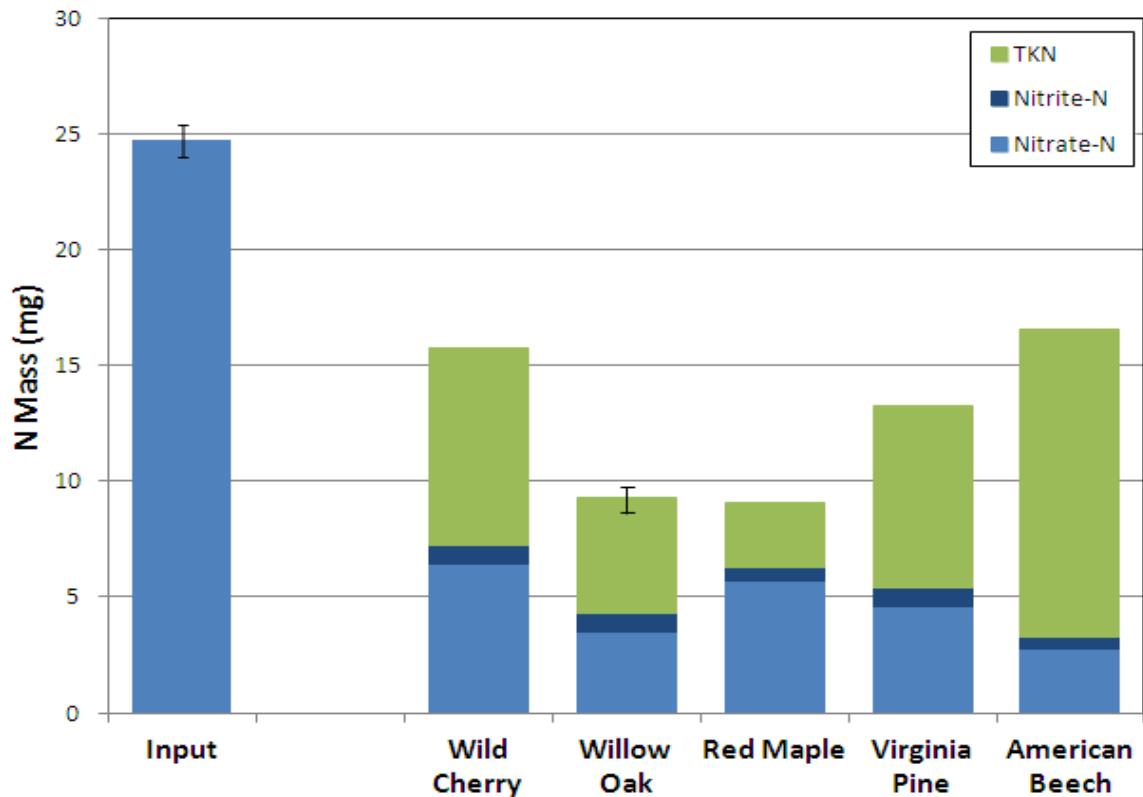
Figure 20: Total nitrogen mass compared for different woodchip species used in the media. The columns are labeled by the wood species used and are compared to the average input nitrogen mass. Each column represents the combined mass of the three successive runs conducted for each species. The input mass is the average of the five combined masses.

suggests that AB also degrades more quickly than the remaining two chip types, WO and RM.

Figure 20 shows the amount of nitrogen mass in the effluent of the columns with different woodchip species compared to the influent nitrogen mass. While AB is the most effective at nitrate removal, it leaches the largest amount of TKN, and it has the highest combined total nitrogen mass in its effluent. Willow Oak is the most effective at reducing the total nitrogen concentration in the effluent by not only substantially reducing nitrate concentrations but also leaching less TKN than the other wood types. RM shows the greatest overall reduction in nitrogen mass because very little TKN leached out of the

system. No significant variation can be seen between the effluent nitrite mass for each of the wood species.

The pseudo-first-order rate constants for the WC, WO, RM, VP, and AB columns were 3.0, 11.4, 3.3, 4.2, and 4.0 day^{-1}, respectively, for run 3 (Table 7). The similarity in rate constants suggests that the denitrification process is unaffected by woodchip species with the exception of WO which had a much higher rate constant than the other woodchip species. However, the nutrient data reveal that different woodchips leach varying amounts of organic carbon and TKN. WO and RM provide the necessary environment for microbial denitrification while leaching the least organic carbon and TKN. Therefore, of the five woodchips species tested, WO and RM woodchips provide the optimum treatment media for bioretention denitrification.

3.4.2. Woodchip Size

The pH of the collected samples was unaffected by differing woodchip sizes in the media. In each case the pH of the samples collected remained relatively consistent, between 5.55 and 6.97 throughout the tests. The oxidation/reduction potential in the columns all started between 200 and 300 mV, and followed the same trend as was indicated previously, decreasing over time making the environment more reducing. Slight decreases of nutrient levels were noted in the effluent with increasing size of the woodchips in the media. The 5 mm (No. 4 to 9.5 mm), 9.5 mm (9.5 mm to 13 mm), and 13 mm (13 mm to 19 mm) woodchip columns produced average total phosphorus concentrations of 0.22, 0.10, and 0.12 mg/L P, respectively, average TKN concentrations of 0.79, 0.35, and 0.54 mg/L N, respectively, and average total organic carbon concentrations of 40.5, 38.3, and 34.4 mg/L C, respectively.

This decrease in nutrients relative to woodchip size suggests that nutrient leaching is dependent on the surface area of the woodchip. The larger woodchips have smaller total surface area per mass and therefore less contact area with the retained water. The decreased surface area due to woodchip size causes less nutrient leaching. As a result, denitrifying microorganisms appear to be slightly limited by the availability of organic carbon. This is reflected by the nitrate mass reduction depicted in Figure 21. While less TKN leached from the larger woodchip columns, the decrease in nitrate reduction caused the total nitrogen mass to increase with increasing woodchip size (Figure 21).

This pattern was also reflected in the rate constants for the varying woodchip sizes. The rate constants for the 5 mm, 9.5 mm, and 13 mm woodchip columns were 11.4, 1.4,
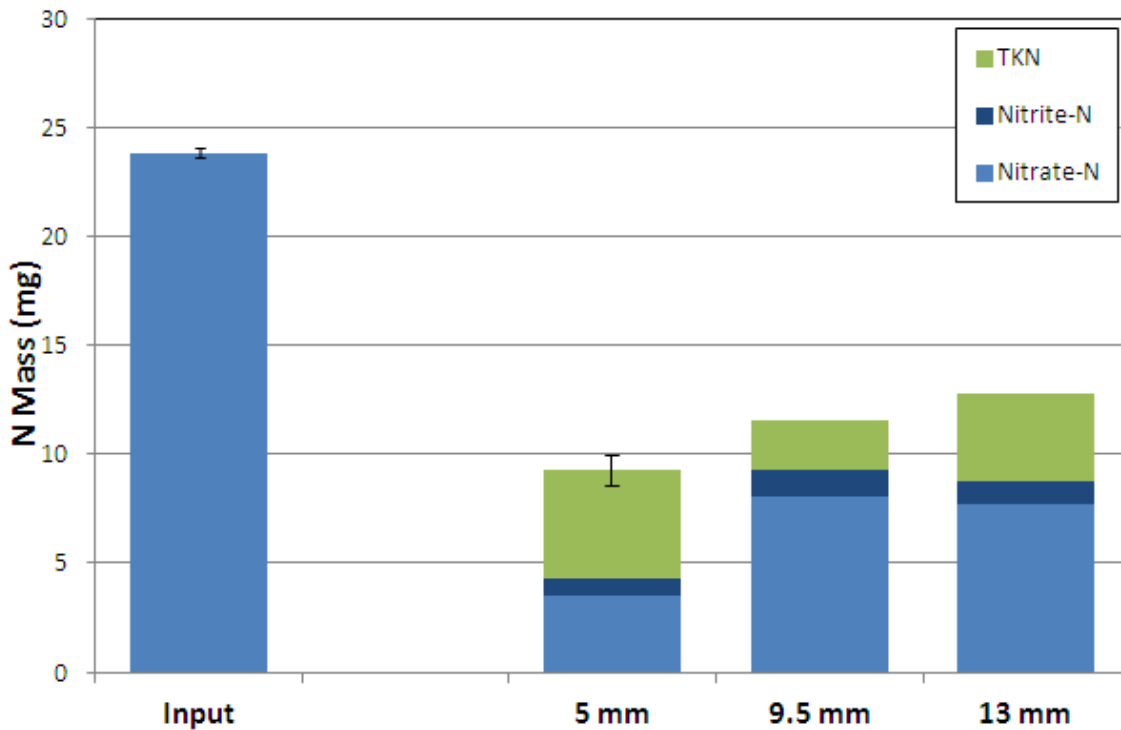
Figure 21: Total nitrogen mass compared for different woodchip sizes of the same species used in the media. The columns are labeled by the chip sizes (mm) used and are compared to the average input nitrogen mass. Each column represents the combined mass of the three successive runs conducted for each size woodchip. The input mass is the average of the three combined masses.

and 1.4 day^{-1}, respectively, for run 3 (Table 7). Again, the smaller woodchips provided for more availability of organic carbon and thus faster denitrification rates. However, while it is notable that the 5 mm woodchip column had a higher rate constant, there was little to no change in the rate constant from the 9.5 to 13 mm columns. Therefore, the 5 mm woodchips provide the best media option but it is difficult to make a distinction between the 9.5 and 13 mm woodchip media.

3.4.3. Woodchip Mass Percentage

Sample pH was unaffected by changing the percentage of woodchip mass in the media as well. In each case the pH of the samples collected remained relatively consistent, between 6.08 and 7.40 throughout the tests. The oxidation/reduction potential in the columns all started between 200 and 300 mV, but the potential decreased less in columns with less organic material. The minimum potentials reached in the 1%, 2.5%, and 4.5% woodchip columns were 236.6, 120.0, and -62.0 mV, respectively. This begins to suggest that as organic material becomes more limited, fewer microorganisms are present to consume dissolved oxygen. This leads to environments that move from oxidizing to reducing much more slowly than those with more available organic material and are therefore not optimum.

Nutrient availability emphasizes the effect of decreasing woodchip mass percentage in the media. The columns with less woodchip mass have less available phosphorus, TKN and organic carbon. The 1%, 2.5%, and 4.5% woodchip columns had average total organic carbon concentrations of 12.7, 27.8, and 40.5 mg/L C, respectively. Total phosphorus and TKN followed the same trend. This emphasizes that the media with less organic material does not provide the optimum environment for denitrification.
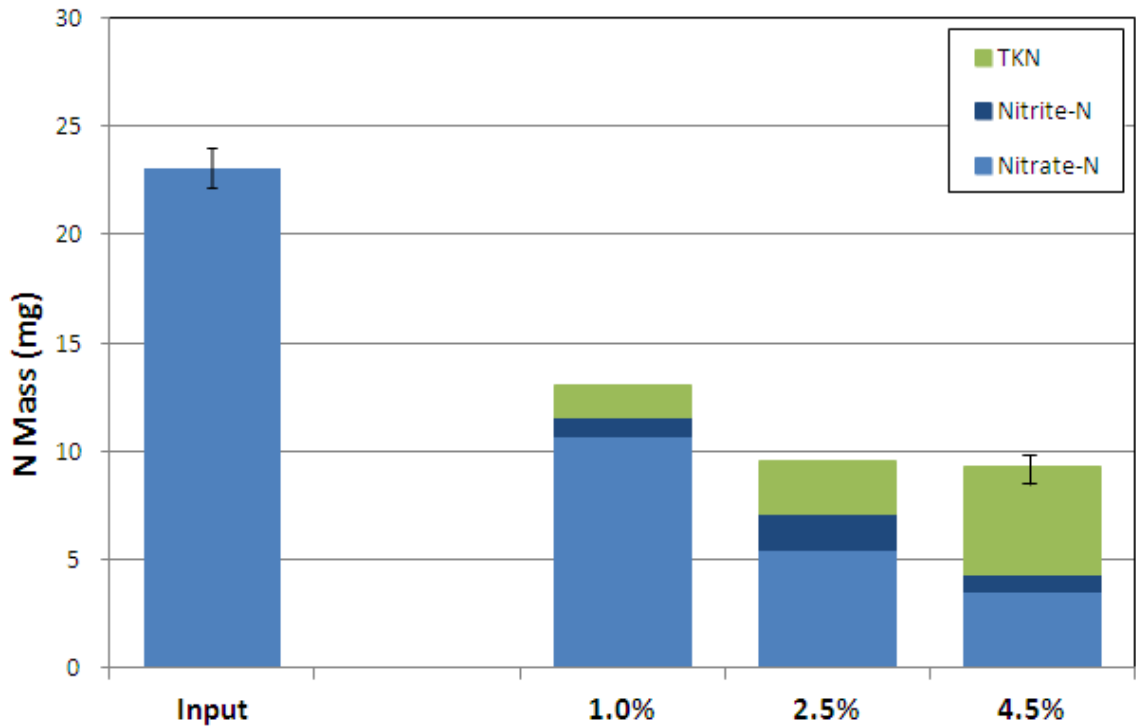
Figure 22: Total nitrogen mass compared for media containing different amounts of woodchips of the same species. The columns are labeled by the percent of woodchips in the media by mass and are compared to the average input nitrogen mass. Each column represents the combined mass of the three successive runs conducted for each percent mass. The input mass is the average of the three combined masses.

Further emphasizing this point, Figure 22 compares the combined total nitrogen

mass in the effluent of all three runs of each column. Figure 22 shows that increased

woodchip mass corresponds to greater decreases in nitrate and total nitrogen mass in the

effluent. The slight increases of TKN in the effluent as a result of more woodchip mass

are negated by decreases of nitrate. Denitrification rate constants also agree with the

effect of changing woodchip mass in the media. The pseudo-first-order rate constants for

the 1%, 2.5%, and 4.5% woodchip columns were 1.5, 7.2, and 11.4 day^{-1}, respectively,

for run 3. The columns with media containing more woodchip mass were able to promote

faster denitrification. This trend may also suggest that even larger woodchip mass

percentages would provide more nitrate removal. However, this assumption is negated by

Robertson (2010). The rate constants found in that study were 2.3 and 2.4 day^{-1}, which are less than those reported in this study (Robertson 2010). Robertson (2010) used a media containing solely woodchips and found very large amounts of organic carbon were leached from the system when nitrate concentrations were rate limiting. While that study does not report the TKN leached, it can be assumed that the high organic carbon corresponds to large amounts of TKN being leached as well. From a total nitrogen perspective, the leached TKN may completely negate the nitrogen being removed through denitrification. The excess organic carbon from Robertson (2010) and similarity in rate constants suggest that further increasing woodchip mass percentages in the media would not significantly increase the nitrate removal efficiency of the media. Instead, nitrate removal would remain constant with increasing woodchip mass percentages while TKN leaching would continue to increase. Therefore, considering the ratios evaluated in this study, 4.5% woodchips by mass in the media provides the optimum environment for denitrification.

3.4.4. Limestone Amendment

The limestone added to the media helped buffer the media and raise the pH of the environment. While the pH of the samples collected increased with the addition of limestone to the media, the pH of the samples did not reach the desired pH of 8.0. The average pH of the collected samples from columns with media containing 0%, 5%, and 10% limestone by mass was 6.29, 7.31, and 7.20 respectively. Note that the difference in pH between the 5% and 10% limestone columns is negligible. This suggests that the addition of more limestone would not further raise the pH. The oxidation/reduction decreased over time to become more reducing. Nutrient availability changed with the
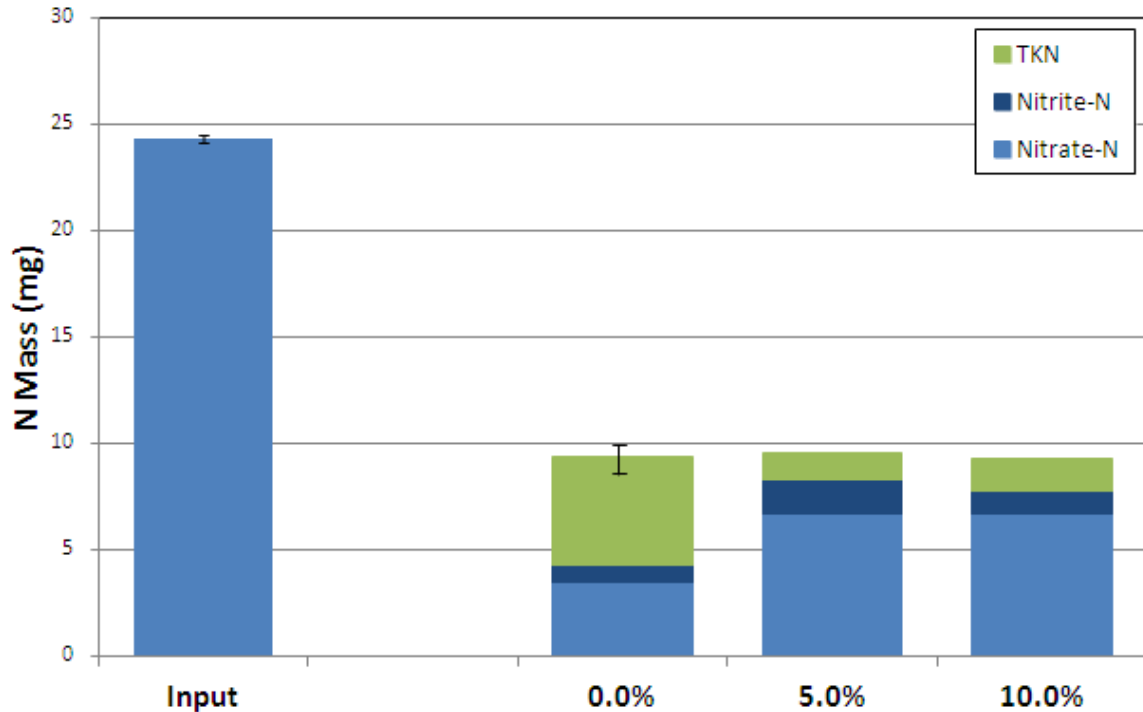
Figure 23: Total nitrogen mass compared for media containing different amounts of limestone. The columns are labeled by the percent of limestone in the media by mass and are compared to the average input nitrogen mass. Each column represents the combined mass of the three successive runs conducted for each percent mass. The input mass is the average of the three combined masses.

percentage of limestone in the media. The increasing limestone percentage corresponded to decreasing nutrient concentrations.

The addition of limestone to the media did not have the desired effect on denitrification. Glass and Silverstein (1998) state the optimum pH for denitrification is near 8.0. The addition of the limestone brought the pH up one full unit from 6.3 to 7.3, but the nitrate removal efficiency decreased. Figure 23 shows the comparison of the combined three runs of total nitrogen mass leaving the columns. The removal of total nitrogen was not greatly affected by increasing limestone content in the media. However, the removal of nitrate decreased with the addition of limestone. The rate constants for the

0%, 5%, and 10% limestone columns were 11.4, 5.9, and 8.9 day^{-1}, respectively. The rate of denitrification seems to be negatively affected by the addition of limestone.

The limestone added to the media may have caused localized pH increase. While the pH of the effluent only increased to 7.3, the pH near the limestone particles may have been much higher. The high pH near the limestone particles may have killed some bacteria which resulted in less nitrate reduction than expected even thought pH increased. Therefore, these data suggest that limestone may be effective at increasing the pH but should be applied differently to the media in order to prevent localized microbial die-off. A different media additive may be able to adequately buffer the environment to a pH of 8.0, without the localized die-off of microbial populations, which may improve the denitrification process.

3.5. Design Factors

The laboratory scale bioretention design successfully removed up to 87.2% of nitrate and 62.4% of total nitrogen in the synthetic stormwater through the denitrification process. The pseudo-first-order rate constants corresponding to the 3rd run for all columns where inflow nitrate concentration and retention time were varied were averaged, along with the WO column replicates (Table 7). In total, 8 runs were averaged together. According to the pseudo-first-order model, the rate constants from these columns should not be affected by these system variations. The average rate constant for these data was 4.1 ± 4.6 day^{-1}.

A design has been developed that would target concentrations of nitrogen in stormwater and treat runoff nitrogen following the nitrogen cycle. The design is a controlled and sustainable system that also requires little to no maintenance. The design

deviates from typical bioretention designs by taking into account a first flush treatment. If a first flush consideration is applied to runoff collected by a bioretention facility, then it can be assumed that treating the first 1.3 mm of runoff could remove up to 84% of the total nitrogen it is carrying (Flint and Davis 2007). Treating the first flush more strictly while allowing whatever remains to be treated normally would effectively optimize the design.

Figure 24: Design alteration to a standard bioretention cell. The cell is split into a treatment train. The first section (Nitrogen Treatment Zone) will remove nitrogen and other pollutants from the first flush of a storm while the second portion filters any overflow that exceeds the storage capacity of the first section.
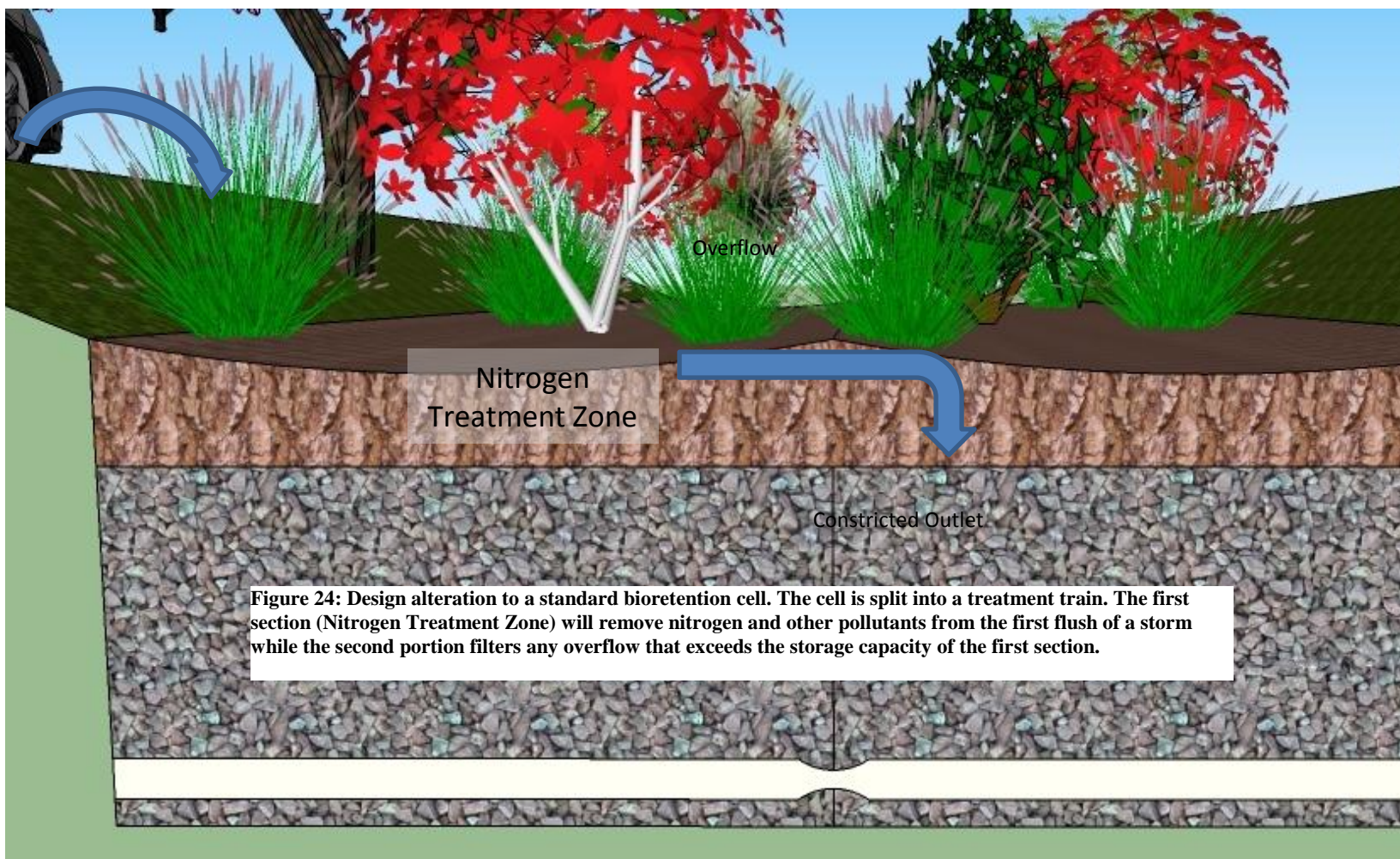
Typical bioretention is considered one homogenous unit. Water runs in and is infiltrated over the entire surface area. Denitrification, being a time sensitive process, can be optimized by increasing the retention time of runoff. By increasing the retention time, however, the volume of water that can be treated by the bioretention is decreased. One

way to achieve large retention times while maintaining the ability to treat large storms is to split the bioretention into two parts or a treatment train. With a split bioretention the first flush of a storm can be treated in a portion of the bioretention cell that is designed to have a large retention time. If a storm is large enough to surpass the available storage volume, overflow would spill into the second portion of the bioretention facility. This portion would filter water quickly and thus allow the entire storm to be treated. Figure 24 shows a design that would facilitate the desired treatment method.

The storm size that can be captured in the denitrification layer of a bioretention treatment train system would vary with the size of the bioretention system. Table 8 shows the largest storm that could be captured by the denitrification layer of the bioretention treatment train. The values assume that all rainfall becomes runoff and the entire watershed is 100% impervious (Table 8). Bioretention system surface area ratios are similar to those defined in Davis et al. (2013), where the bioretention systems ranged from 3% to 7% of the surface area of the corresponding watershed. Table 8 assumes the denitrification layer is 40 cm deep which is a little more than half of the depth of a 70 cm deep bioretention system (Zinger et al. 2013). This media depth increases the retention capacity of the denitrification layer for maximum treatment. Typically denitrification layers in bioretention systems are near 18 cm in depth (Kim et al. 2003, Ergas et al. 2010, Chen et al. 2013). The assumed porosity of the media is 0.5.

Table 8: The maximum storm size that can be captured by the denitrification layer of a bioretention treatment train with varying bioretention sizes and nitrogen treatment layer sizes. This assumes that all rainfall becomes runoff, the entire watershed is impervious, and a denitrification layer media depth of 40 cm.

Percent of Watershed that is bioretention	Percent of bioretention area for nitrogen treatment	Max storm size nitrogen treatment can handle (cm)
3	40	0.24
3	50	0.3
3	60	0.36
5	40	0.4
5	50	0.5
5	60	0.6
7	40	0.56
7	50	0.7
7	60	0.84
10	40	0.8
10	50	1
10	60	1.2

Bioretention designs for treating nitrogen may be constructed in layers to follow the nitrogen cycle (Hsieh et al. 2007; Collins et al. 2010; Ergas et al. 2010). The path that nitrogen will follow through a bioretention system is presented in Figure 25. Organic nitrogen and ammonium are absorbed into the top media layer and later oxidized (Collins et al. 2010). Because oxygen is more available between storm events, nitrification will take place in this top layer when it is not raining (Hsieh et al. 2007). The average amount of time between storm events should be enough to effectively oxidize the organic and ammonium nitrogen to nitrate or nitrite (Hsieh et al. 2007). In a storm, the nitrate and nitrite from the top layer are subsequently carried with the stormwater into the denitrification layer. Because denitrification requires anoxic conditions, the media in the denitrification layer will be fully saturated during a storm event and allowed to drain
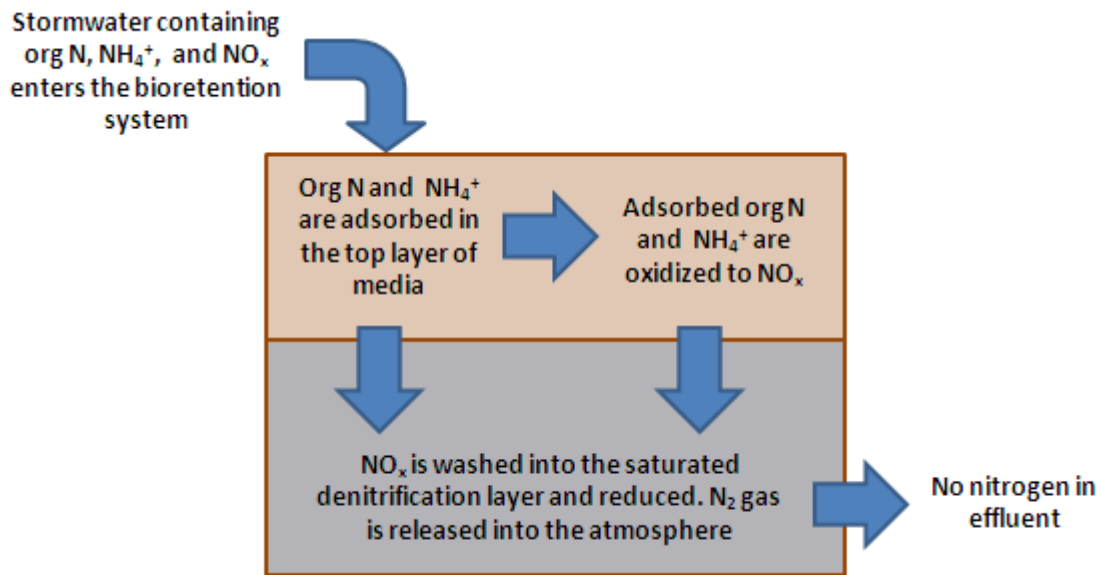
Figure 25: A flow chart of the processes that nitrogen in stormwater runoff undergoes in the bioretention treatment train system.

slowly. Saturation can be accomplished by decreasing the size of the outlet, incorporating

an upturned underdrain, or a combination of the two. This will allow the media to treat

oxidized nitrogen in a large amount of water for a longer duration.

The optimum denitrification layer media contains 4.5% Willow Oak or Red Maple

woodchips that range from 5 mm to 9.5 mm in size and no limestone is added. Assuming

the nitrogen in stormwater entering the denitrification layer (40 cm deep) of a

bioretention treatment train system has been fully converted to nitrate at concentrations of

3 mg/L N (Collins et al. 2010) and stormwater is retained for an average of 1.0 day,

which is the amount of time that microorganisms took to reduce nitrate concentrations to

below detection in the research columns, following pseudo-first-order kinetics and using

the average rate constant stated previously, the stormwater captured by the denitrification

layer would have an average effluent nitrate concentration of 0.05 mg/L N. The result is

62% reduction in the total nitrogen mass in the stormwater. Assuming that 90% of the nitrogen mass is contained in the first flush which is treated in the denitrification layer, 56% of the total nitrogen is removed from the stormwater. These numbers do not account for water loss due to infiltration or plant uptake which would increase the nitrogen mass reduction.

This study did not use plants for possible additional removal of nitrogen. Planting *C. appressa* or *M. ericifolia* in the media has been shown to result in 70% nitrogen removal (Bratieres et al. 2008). While that study was conducted in Australia, vegetation provides a key role in the removal of nitrogen from stormwater in bioretention applications (Bratieres et al. 2008, Lucas and Greenway 2008, Davis et al. 2012, Hunt et al. 2012). Zinger et al. (2013) found that introducing a saturated zone to a media that was not optimized for denitrification improved total nitrogen removal efficiencies. However, vegetation must be harvested after the growing season; otherwise decaying biomass would contribute to the inflow nitrogen concentrations (Davis et al. 2012). This increases maintenance costs. A treatment train with an optimized denitrification process, combined with nitrogen removal by vegetation would provide an environment with optimum nitrogen removal from stormwater runoff.

4. Conclusion

4.1. General Conclusions

Treatment of nitrogen in urban stormwater using bioretention is a technology in its infancy. Modifying typical bioretention designs into a treatment train could improve nitrogen removal efficiencies. This could be done by ensuring that first flush runoff is treated in a denitrification zone while excess runoff is treated traditionally. By creating a system that fully saturates a media containing woodchips as an organic carbon source, available oxygen is depleted and anoxic conditions are created. These conditions, favorable to microbial denitrification, were successfully tested in a laboratory setting. A system where microbial denitrification was inhibited by azide was contrasted with one that was not inhibited. This contrast gave evidence to support the ability of the media to sustain a population of denitrifying microorganisms. This evidence suggests that the treatment train bioretention system would provide the conditions necessary for denitrification and effective removal of nitrate from runoff.

The concentration of nitrate in the influent ranged from 1.5 to 4.5 mg/L N which is considered low in denitrification applications not treating stormwater runoff. Denitrification in systems with low concentrations of nitrate tends to follow first-order kinetics. While the data are not conclusive, it appears that pseudo-first-order kinetics provide the best model for denitrification in this system. A fully established system with optimum media conditions had a denitrification rate constant of 4.1 ± 4.6 day^{-1}.

Retaining stormwater in the denitrification zone for greater amounts of time appears to cause greater reduction of nitrogen concentrations in stormwater runoff. Concentrations of nitrate in stormwater decreased to below 0.2 mg/L in about 1.0 days

(1440 min). Retaining stormwater for this amount of time should remove nitrate from the runoff.

Of the five wood species tested, Willow Oak and Red Maple were found to most substantially reduce the amount of nitrogen in the stormwater. Media with Willow Oak and Red Maple woodchips reduced concentrations of total nitrogen in the runoff by up 60% and 62%, respectively. It is unknown why these two species are able to provide a more suitable environment for denitrification.

Increases in woodchip size decreased the surface area of the woodchips, thereby decreasing the amount of organic carbon available to the denitrifying bacteria. Smaller woodchips corresponded to higher nutrient availability which resulted in greater nitrate reduction. At 4.5% woodchips by mass, media containing 5 mm woodchips removed 82% of nitrate from stormwater runoff while 13 mm woodchips removed 63%. However, in order to preserve the longevity of the system a combination of woodchip sizes may be more effective.

Similarly the percent mass of woodchips in the media directly related to the availability of nutrients and greater reduction of nitrate concentrations. It is expected that greater percentages of woodchips in the media would increase effluent nutrient concentrations resulting in reduced efficiency. Further analysis is needed to determine the percentage of woodchips needed to optimize the media.

While the pH of the system did increase as a result of limestone additions to the media, it did not increase to the desired pH of 8.0. The pH for 5% and 10% limestone columns was 7.3 and 7.2, respectively. The addition of limestone to the media did not raise the efficiency of the system as a result of increased pH. Total nitrogen removal for

media containing 0%, 5% and 10% limestone by mass was 82%, 66%, and 68%, respectively. Another media additive may result in higher pH and greater nitrogen removal.

The optimum environment for microbial denitrification from this study is a saturated media with 4.5% woodchips by mass. The woodchips should be Oak or Maple. The woodchips should vary in size greater than 5 mm in order to provide longevity and prevent clogging the system. Assuming all the nitrogen in runoff containing 3 mg/L N was converted to nitrate and the total volume of a storm was retained in the denitrification layer, this media could effectively reduce nitrate concentrations in urban stormwater runoff by more than 90% and total nitrogen by more than 60%. When incorporated into the treatment train design, first flush runoff would be treated at these efficiencies. This would provide an effective buffer for mitigating the problematic effects of urban runoff on natural water bodies.

4.2. Practical Recommendations

Implementation of a treatment train bioretention system would improve water quality through greater nitrogen reduction in stormwater runoff. The first section of the treatment train would filter water while improving nitrogen mass reduction through denitrification of the first flush runoff. The denitrification layer should be optimized by providing the media described. Overflow from large storms would filter through the second section of the treatment train. With this stepped system, runoff from both large and small storms is treated and the first flush runoff from these storms is targeted for nitrogen removal.

This design can be implemented using different methods for creating a saturated

denitrification layer. While this paper discusses the effect of controlled outlets, upturned underdrains are also a viable option for maintaining saturated media. Reducing the outlet size of the underdrain may also cause saturation of the denitrification layer. However, saturation of other layers when using a reduced outlet size could result in heavy metals leaching. In order to prevent this issue a bypass would be needed above the denitrification layer to allow stormwater to overflow into the second section of the treatment train.

4.3.   Future Research

These design recommendations need to be evaluated in a field scale application. Stormwater inflow and effluent from each section of the treatment train should be monitored for concentrations of nitrogen species. Total, organic, ammonium, nitrate, and nitrite nitrogen should be monitored. Water level in the denitrification layer of the bioretention system should be monitored to ensure that the media is being completely saturated. Stormwater retained in the denitrification layer may infiltrate further and recharge groundwater which would greatly reduce effluent nitrogen mass. Samples should be taken from within the media to ensure that denitrification is taking place before stormwater infiltrates into the groundwater. The rate of denitrification should be monitored over a period of 10 years to ensure the media provides the necessary nutrients for denitrification for a desirable lifespan.

Further evaluation of woodchip species is needed to determine the cause of increased microbial denitrification when certain woodchips are present. Understanding the conditions which cause greater microbial activity could provide further design recommendations. The effect of woodchips surface area should also be further analyzed

for its effect on the availability of organic carbon and the denitrification process. Media additives should be evaluated for their effect on the pH of the system and the denitrification process. Limestone should also be included in this study in different configurations in order to further assess its ability to buffer the system without killing the microbial population.

The denitrification layer may have a more optimum layout. For instance, rather than having a homogeneous media in the denitrification layer, all of the woodchips can be placed in a layer at the bottom and have a porous saturated media above. This may cause the system to operate more like a plug flow system. Denitrification would take place when stormwater reaches the woodchip layer. Implementing a shallow adsorbent media layer below the woodchips may adsorb leached organic material and further reduce the total nitrogen in the effluent. These design adjustments should be evaluated for improved effluent water quality.

Appendix I-A

Woodchip Species:	Willow Oak	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date: Run 1:	5/22/12
Woodchip Mass:	4.5%	Run 2:	5/29/12
Limestone Content:	0.0%	Run 3:	6/5/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.982	2.86	3.10
60	2.982	2.95	2.82
120	3.011	3.16	3.20

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.12	0.14	0.10
60	0.12	0.12	0.10
120	0.11	0.14	0.10

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	4.43	0.10	0.57
712.5	2.28	0.10	0.74
1440	0.10	0.10	0.10
2160	0.10	0.10	0.10
2850	0.10	0.10	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.08	0.06	0.05
712.5	0.63	0.06	0.05
1440	1.08	0.05	0.05
2160	0.06	0.05	0.05
2850	0.06	0.05	0.05

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.68	0.70	0.32
712.5	1.68	0.98	0.43
1440	1.12	0.00	0.58
2160	1.68	0.00	0.56
2850	1.40	0.00	0.70

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.44	0.25	0.22
712.5	0.33	0.20	0.16
1440	0.33	0.17	0.10
2160	-	-	0.14
2850	-	-	0.11

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	253.0	400.7	383.0
180	264.6	392.7	386.1
1200	159.9	133.4	-115.7
1440	82.0	-	-426.3
1650	-51.4	-	-
2640	-482	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	52.82	90.82	31.72
712.5	46.29	32.45	24.73
1440	49.52	20.66	27.94
2160	52.89	22.38	32.20
2850	58.52	29.94	35.18

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.19	0.28	0.25
712.5	0.56	1.58	1.10
1440	0.26	0.50	0.46
2160	0.22	0.24	0.25
2850	0.23	0.12	0.28

pH

Time (min)	Run 1	Run 2	Run 3
172.5	7.05	6.35	6.99
712.5	7.30	6.54	6.70
1440	7.13	6.75	6.87
2160	7.27	6.83	6.71
2850	7.34	7.55	6.87

Temperature (°C)

Time (min)	Run 1	Run 2	Run 3
172.5	24	26	24
712.5	22	23	23
1440	23	24	22
2160	23	23	22
2850	24	22	22

Appendix I-B

Woodchip Species:	Willow Oak	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date:	Run 1: 3/14/13
Woodchip Mass:	4.5%		Run 2: 3/20/26
Limestone Content:	0.0%		Run 3: 3/26/13

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	3.011	3.02	3.02
60	2.994	2.96	3.00
120	2.889	2.94	2.98

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.12	0.10	0.11
60	0.12	0.08	0.11
120	0.10	0.10	0.10

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.89	0.70	0.85
712.5	2.25	0.10	0.10
1440	0.74	0.10	0.10
2160	0.10	0.10	0.10
2850	0.10	0.10	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.01	0.01	0.01
712.5	0.24	0.01	0.01
1440	0.92	0.01	0.01
2160	0.18	0.01	0.01
2850	0.01	0.01	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.84	0.56	1.12
712.5	0.56	0.84	0.56
1440	0.56	0.56	1.12
2160	1.12	0.28	1.96
2850	0.56	0.56	0.56

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.44	0.36	0.12
712.5	0.10	0.14	0.34
1440	0.15	0.14	0.08
2160	0.13	0.13	0.06
2850	0.12	0.08	0.11

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	232.7	247.0	267.1
180	228.6	244.1	261.9
1200	163.0	84.6	15.3
1440	109.4	-38.4	-62.0
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	46.73	81.66	53.68
712.5	44.65	76.58	44.61
1440	50.87	68.84	47.10
2160	69.05	73.51	51.97
2850	83.33	82.60	62.37

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.27	0.27	0.26
712.5	0.77	1.03	1.00
1440	0.28	0.29	0.25
2160	0.33	0.43	0.39
2850	0.26	0.27	0.28

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.34	6.05	6.25
712.5	6.01	5.98	6.53
1440	6.36	6.23	6.60
2160	6.58	6.55	6.72
2850	6.30	5.90	5.96

Temperature (^{o}C)

Time (min)	Run 1	Run 2	Run 3
172.5	26	22	22
712.5	26	22	23
1440	22	21	23
2160	21	21	23
2850	21	21	24

Appendix I-C

Woodchip Species:	Willow Oak	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date:	Run 1: 3/14/13
Woodchip Mass:	4.5%		Run 2: 3/20/13
Limestone Content:	0.0%		Run 3: 3/26/13
			Inhibbited

Inflow Data - Contained 50 mg/L NaN$_3$

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	3.045	2.99	2.91
60	3.014	3.00	3.09
120	3.072	2.99	3.01

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.11	0.13	0.10
60	0.10	0.12	0.10
120	0.10	0.13	0.11

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	3.03	2.97	2.96
712.5	3.04	2.93	3.01
1440	3.07	3.02	2.91
2160	3.05	3.00	3.17
2850	3.00	2.96	3.01

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.01	0.01	0.01
712.5	0.01	0.01	0.01
1440	0.01	0.01	0.01
2160	0.01	0.01	0.01
2850	0.01	0.01	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.96	3.92	2.52
712.5	2.24	2.52	1.96
1440	2.24	2.24	1.68
2160	3.92	2.52	2.24
2850	3.08	2.52	1.96

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.90	0.66	0.82
712.5	0.76	0.94	0.88
1440	0.83	0.82	0.87
2160	0.72	0.84	0.57
2850	0.76	0.89	0.71

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	243.1	232.8	222.2
180	240.2	221.7	225.5
1200	207.4	217.4	215.8
1440	205.4	210.6	221.6
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	76.7	202.1	108.4
712.5	94.8	128.1	67.0
1440	111.2	98.0	54.7
2160	154.9	106.8	58.8
2850	158.9	102.3	63.6

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26	0.28	0.26
712.5	0.79	1.00	0.97
1440	0.25	0.27	0.25
2160	0.39	0.35	0.37
2850	0.27	0.27	0.28

pH

Time (min)	Run 1	Run 2	Run 3
172.5	5.86	6.04	6.19
712.5	6.04	6.20	6.34
1440	6.39	6.38	6.46
2160	6.18	6.40	6.56
2850	6.34	6.39	6.33

Temperature ($^{\circ}$C)

Time (min)	Run 1	Run 2	Run 3
172.5	26	22	22
712.5	26	22	23
1440	22	21	23
2160	21	21	23
2850	21	21	24

Appendix I-D

Woodchip Species:	None
Woodchip Size:	N/A
Woodchip Mass:	N/A
Limestone Content:	0.0%

Avg. Retention Time:	0.8 Days
Start date:	Run 1: 3/30/13
	Run 2: N/A
	Run 3: N/A

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	3.02		
60	3.00		
120	2.98		

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.10		
60	0.10		
120	0.10		

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	3.16		
712.5	3.17		
1440	3.00		
2160	3.04		
2850	2.99		

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.01		
712.5	0.01		
1440	0.01		
2160	0.01		
2850	0.01		

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.00		
712.5	0.00		
1440	0.00		
2160	0.00		
2850	0.00		

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.11		
712.5	0.11		
1440	0.10		
2160	0.10		
2850	0.11		

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	250.7		
180	230.6		
1200	218.5		
1440	200.7		
1650	200.3		
2640	-		

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	ND		
712.5	ND		
1440	ND		
2160	ND		
2850	ND		

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26		
712.5	1.00		
1440	0.25		
2160	0.39		
2850	0.28		

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.66		
712.5	6.98		
1440	6.79		
2160	7.08		
2850	6.97		

Temperature (^{o}C)

Time (min)	Run 1	Run 2	Run 3
172.5	26		
712.5	26		
1440	26		
2160	26		
2850	26		

Appendix I-E

Woodchip Species:	Willow Oak
Woodchip Size:	5mm
Woodchip Mass:	4.5%
Limestone Content:	0.0%

Avg. Retention Time:	0.8 Days	
Start date:	Run 1:	11/12/12
	Run 2:	11/26/12
	Run 3:	12/3/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	1.476	1.48	1.48
60	1.491	1.49	1.49
120	1.527	1.53	1.53

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	-	0.11	0.09
60	-	0.08	0.09
120	-	0.10	0.10

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.27	1.04	1.02
712.5	0.10	0.56	1.03
1440	0.10	0.10	0.15
2160	0.10	0.23	0.24
2850	0.10	0.10	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.21	0.01	0.01
712.5	0.93	0.01	0.01
1440	0.25	0.01	0.01
2160	0.10	0.01	0.01
2850	0.01	0.01	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	5.32	0.28	0.56
712.5	1.12	0.60	0.56
1440	1.96	1.68	0.28
2160	1.40	0.28	0.56
2850	1.12	0.28	0.56

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	-	0.19	0.09
712.5	-	0.13	0.06
1440	-	0.14	0.06
2160	-	0.16	0.05
2850	-	0.11	0.06

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	178.6	209.4	212.7
180	151.9	208.6	203.1
1200	22.0	172.5	156.1
1440	133.2	64.5	184.8
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	35.59	34.73	21.59
712.5	30.22	29.65	18.22
1440	31.54	28.57	17.54
2160	29.71	30.42	21.69
2850	28.62	31.25	25.42

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.23	0.27	0.28
712.5	0.61	1.12	1.15
1440	0.38	0.44	0.27
2160	0.28	0.26	0.39
2850	0.26	0.27	0.27

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.12	6.65	6.48
712.5	6.28	6.49	6.42
1440	5.83	6.34	6.63
2160	5.87	5.90	6.84
2850	6.51	6.21	5.95

Temperature ($^{\circ}$C)

Time (min)	Run 1	Run 2	Run 3
172.5	23	21	22
712.5	20	19	20
1440	19	18	22
2160	19	19	21
2850	15	21	21

Appendix I-F

Woodchip Species:	Willow Oak		Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm		Start date:	Run 1: 11/12/12
Woodchip Mass:	4.5%			Run 2: 11/26/12
Limestone Content:	0.0%			Run 3: 12/3/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	4.073	4.07	4.07
60	4.311	4.31	4.31
120	4.411	4.41	4.41

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	-	0.12	0.14
60	-	0.11	0.10
120	-	0.12	0.12

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.50	4.07	4.34
712.5	1.01	7.46	1.41
1440	0.10	4.31	1.73
2160	0.10	2.58	0.10
2850	0.10	0.81	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.05	0.01	0.01
712.5	1.37	0.03	0.04
1440	1.43	0.70	0.43
2160	0.26	0.55	0.01
2850	0.01	0.27	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.52	0.56	1.12
712.5	2.24	0.56	0.84
1440	2.24	0.00	0.56
2160	1.12	0.28	0.28
2850	0.56	0.00	0.56

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	-	0.20	0.09
712.5	-	0.11	0.10
1440	-	0.09	0.25
2160	-	0.10	0.50
2850	-	0.12	0.06

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	207.1	301.4	233.9
180	181.8	250.1	233.8
1200	73.2	258.8	300.6
1440	-16.5	338.4	310.1
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	33.15	31.06	20.66
712.5	18.61	23.09	14.56
1440	25.13	19.78	14.10
2160	24.75	21.81	16.53
2850	22.52	22.35	18.22

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.24	0.27	0.27
712.5	0.78	1.15	1.15
1440	0.40	0.39	0.28
2160	0.28	0.29	0.32
2850	0.27	0.26	0.25

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.01	6.72	6.78
712.5	6.34	6.50	6.51
1440	6.10	6.15	6.87
2160	6.09	5.75	7.32
2850	6.61	6.12	6.41

Temperature ($^{\circ}$C)

Time (min)	Run 1	Run 2	Run 3
172.5	23	21	22
712.5	20	19	20
1440	19	19	22
2160	19	19	21
2850	15	21	21

Appendix I-G

Woodchip Species:	Willow Oak	Avg. Retention Time:	0.4 Days
Woodchip Size:	5mm	Start date:	Run 1: 4/10/12
Woodchip Mass:	4.5%		Run 2: 4/17/12
Limestone Content:	0.0%		Run 3: 4/24/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.379	3.29	2.91
60	2.526	3.16	2.99
120	2.764	3.18	3.11

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.11	0.11	0.12
60	0.10	0.11	0.11
120	0.10	0.10	0.11

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
140	2.21	2.42	1.72
177.5	2.13	2.05	2.23
432.5	1.19	1.36	1.56
860	0.07	0.75	0.44
1085	0.06	0.06	0.09

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
140	0.08	0.05	0.06
177.5	0.10	0.05	0.05
432.5	0.57	0.05	0.06
860	0.32	0.12	0.11
1085	0.06	0.05	0.05

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
140	0.84	0.84	1.68
177.5	1.16	0.80	1.64
432.5	3.36	0.56	1.40
860	3.36	0.38	0.68
1085	3.36	0.28	0.29

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
140	0.30	0.25	0.31
177.5	-	-	-
432.5	0.10	0.20	0.14
860	-	-	-
1085	-	0.17	0.16

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	194.5	115.0	296.0
180	191.2	120.0	291.0
1200	173.0	70.8	290.5
1440	-	-	-
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
140	106.9	63.37	29.12
177.5	87.21	53.49	23.07
432.5	66.16	48.37	21.06
860	69.27	42.88	24.88
1085	73.54	44.84	26.86

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
140	0.25	0.19	0.28
177.5	0.15	0.27	0.18
432.5	1.54	1.53	1.43
860	0.14	0.26	0.24
1085	0.10	0.22	0.30

pH

Time (min)	Run 1	Run 2	Run 3
140	6.10	6.80	6.51
177.5	5.95	6.43	6.55
432.5	6.54	6.19	6.75
860	7.01	6.65	6.71
1085	7.42	6.92	7.13

Temperature (°C)

Time (min)	Run 1	Run 2	Run 3
140	22	25	24
177.5	23	23	24
432.5	21	22	23
860	21	22	22
1085	22	21	21

Appendix I-H

Woodchip Species:	Willow Oak
Woodchip Size:	5mm
Woodchip Mass:	4.5%
Limestone Content:	0.0%

Avg. Retention Time:	0.6 Days
Start date: Run 1:	5/22/12
Run 2:	5/29/12
Run 3:	6/5/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	3.101	3.05	3.07
60	3.259	3.05	3.08
120	3.339	3.10	3.09

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.11	0.11	0.11
60	0.11	0.11	0.12
120	0.11	0.11	0.11

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
150	3.05	1.68	1.00
300	2.16	2.29	2.06
810	0.10	0.97	1.85
1440	0.10	0.68	0.78
2205	0.10	0.10	0.39

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
150	0.10	0.10	0.10
300	0.76	0.10	0.10
810	2.20	0.10	0.10
1440	1.61	0.55	0.10
2205	1.45	0.10	0.10

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
150	1.68	1.12	0.28
300	1.12	1.12	0.28
810	0.84	0.56	0.28
1440	0.84	0.56	0.00
2205	0.84	0.56	0.28

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
150	0.47	0.18	0.12
300	0.14	0.11	0.08
810	0.14	0.09	0.08
1440	0.11	0.08	0.08
2205	0.14	0.09	0.10

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	265.4	335.2	266.2
180	254.3	328.1	262.0
1200	-43.6	280.7	213.5
1440	-72.7	295.7	219.8
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
150	59.85	33.28	32.34
300	34.86	24.79	21.45
810	36.53	20.60	17.19
1440	34.95	20.66	18.04
2205	35.17	22.19	19.09

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
150	0.27	0.24	0.26
300	0.54	0.54	0.55
810	1.13	1.03	0.87
1440	0.26	0.33	0.24
2205	0.29	0.27	0.27

pH

Time (min)	Run 1	Run 2	Run 3
150	5.92	6.51	6.55
300	5.96	6.31	6.71
810	6.25	6.74	6.80
1440	6.08	6.88	6.92
2205	6.39	6.57	6.45

Temperature (^{o}C)

Time (min)	Run 1	Run 2	Run 3
150	21	23	22
300	21	21	21
810	22	21	21
1440	21	22	21
2205	21	23	21

Appendix I-I

Woodchip Species:	Willow Oak
Woodchip Size:	5mm
Woodchip Mass:	4.5%
Limestone Content:	0.0%

Avg. Retention Time:	1.0 Days
Start date:	Run 1: 5/22/12
	Run 2: 5/29/12
	Run 3: 6/5/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	3.101	3.05	3.07
60	3.259	3.05	3.08
120	3.339	3.10	3.09

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.11	0.11	0.11
60	0.11	0.11	0.12
120	0.11	0.11	0.11

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
195	3.38	1.48	1.19
735	2.10	1.89	1.73
1530	0.10	0.12	0.73
2280	0.10	0.10	0.46
3390	0.10	0.10	0.39

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
195	0.10	0.10	0.10
735	1.04	0.10	0.10
1530	1.90	0.33	0.10
2280	0.53	0.10	0.10
3390	0.10	0.10	0.10

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
195	1.40	0.84	0.56
735	1.12	0.84	0.28
1530	1.40	0.84	0.00
2280	0.00	0.56	0.28
3390	0.84	0.56	0.28

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
195	0.41	0.16	0.12
735	0.18	0.14	0.08
1530	0.13	0.10	0.07
2280	0.18	0.08	0.11
3390	0.15	0.08	0.09

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	225.5	283.3	318.1
180	220.4	285.0	319.6
1200	-54.7	233.5	365.7
1440	-21.9	250.5	367.4
1650	-11.2	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
195	53.26	30.67	30.23
735	33.54	26.57	18.09
1530	31.40	24.39	17.08
2280	41.53	24.68	20.78
3390	38.64	24.70	28.72

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
195	0.28	0.23	0.29
735	0.88	0.88	1.15
1530	0.39	0.42	0.40
2280	0.28	0.30	0.27
3390	0.28	0.27	0.24

pH

Time (min)	Run 1	Run 2	Run 3
195	6.02	6.79	6.63
735	6.12	6.47	6.47
1530	6.16	6.74	6.98
2280	5.95	6.77	6.30
3390	6.62	7.09	6.80

Temperature (°C)

Time (min)	Run 1	Run 2	Run 3
195	21	23	22
735	21	21	21
1530	21	21	21
2280	21	22	21
3390	20	23	22

Appendix I-J

Woodchip Species:	Willow Oak
Woodchip Size:	5mm
Woodchip Mass:	4.5%
Limestone Content:	0.0%

Avg. Retention Time:	1.3 Days
Start date:	Run 1: 8/14/12
	Run 2: 8/21/12
	Run 3: 8/27/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.962	3.09	3.02
60	3.078	3.21	3.09
120	3.105	3.28	3.12

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.12	0.12	0.10
60	0.12	0.10	0.11
120	0.14	0.10	0.07

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
207.5	2.37	2.28	2.17
1000	0.69	2.48	1.92
2170	0.15	0.97	0.72
3355	0.10	0.10	0.10
4345	0.10	0.10	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
207.5	0.11	0.07	0.07
1000	0.82	0.09	0.07
2170	0.11	0.19	0.07
3355	0.07	0.07	0.07
4345	0.07	0.07	0.07

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
207.5	4.48	0.84	0.28
1000	0.56	0.56	0.56
2170	0.84	0.56	0.28
3355	0.28	0.56	0.28
4345	0.28	0.28	0.28

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
207.5	-	0.14	0.11
1000	0.22	0.12	0.07
2170	0.16	0.05	0.16
3355	0.16	0.10	0.07
4345	0.20	0.11	0.09

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	283.8	318.1	274.1
180	276.4	322.5	291.2
1200	124.8	229.9	154.8
1440	98.5	171.6	108.2
1650	-71.6	134.1	86.2
2640	-455	19.2	-408

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
207.5	36.82	18.53	14.48
1000	27.45	17.26	12.34
2170	26.78	-	13.12
3355	28.33	19.78	15.40
4345	32.66	24.04	18.25

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
207.5	0.22	0.28	0.25
1000	0.51	0.83	1.10
2170	0.26	0.41	0.46
3355	0.28	0.28	0.25
4345	0.28	0.28	0.28

pH

Time (min)	Run 1	Run 2	Run 3
207.5	6.14	6.79	6.99
1000	6.48	7.50	6.70
2170	6.45	6.38	6.87
3355	6.27	6.12	6.71
4345	6.79	7.36	6.87

Temperature (^{o}C)

Time (min)	Run 1	Run 2	Run 3
207.5	23	22	24
1000	23	22	23
2170	22	21	22
3355	22	21	22
4345	22	21	22

Appendix I-K

Woodchip Species:	Wild Cherry	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date:	Run 1: 7/3/12
Woodchip Mass:	4.5%		Run 2: 7/10/12
Limestone Content:	0.0%		Run 3: 7/17/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	3.17	3.35	3.05
60	3.145	3.41	3.13
120	3.182	3.42	3.11

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.14	0.10	0.11
60	0.15	0.12	0.12
120	0.14	0.11	0.13

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.98	1.68	1.74
712.5	2.54	1.06	0.92
1440	0.51	0.06	0.09
2160	0.06	0.06	0.13
2850	0.06	0.07	0.11

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.06	0.06	0.05
712.5	0.09	0.05	0.05
1440	0.76	0.05	0.05
2160	0.23	0.05	0.05
2850	0.05	0.05	0.05

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.40	1.12	0.84
712.5	0.84	1.12	1.12
1440	1.12	0.84	0.56
2160	1.68	1.96	1.40
2850	0.84	4.76	3.64

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.30	0.27	0.19
712.5	0.24	0.19	0.18
1440	0.29	0.19	0.19
2160	0.23	0.21	0.19
2850	-	0.22	0.17

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	204.7	310.9	331.8
180	290.7	304.6	318.0
1200	396.8	115.9	408.1
1440	-	-	-
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	173.7	177.9	122.9
712.5	172.8	131.5	89.5
1440	194.3	151.3	113.8
2160	-	164.5	126.0
2850	219.2	178.3	124.5

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.25	0.25	0.27
712.5	0.99	0.90	1.02
1440	0.49	0.37	0.27
2160	0.29	0.26	0.26
2850	0.22	0.27	0.25

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.54	5.76	5.38
712.5	6.20	6.41	5.92
1440	5.77	6.53	5.91
2160	6.00	6.38	5.48
2850	5.99	6.11	6.06

Temperature ($^{\circ}$C)

Time (min)	Run 1	Run 2	Run 3
172.5	24	25	24
712.5	23	22	23
1440	22	22	22
2160	22	22	23
2850	22	22	23

Appendix I-L

Woodchip Species:	Red Maple	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date: Run 1:	8/14/12
Woodchip Mass:	4.5%	Run 2:	8/21/12
Limestone Content:	0.0%	Run 3:	8/28/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.962	3.09	3.02
60	3.078	3.21	3.09
120	3.105	3.28	3.12

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.12	0.12	0.10
60	0.12	0.10	0.12
120	0.14	0.10	0.08

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	3.04	2.05	1.49
712.5	2.71	1.45	1.00
1440	0.29	0.10	0.10
2160	0.10	0.10	0.10
2850	0.10	0.10	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.07	0.07	0.07
712.5	0.13	0.10	0.08
1440	0.43	0.07	0.07
2160	0.08	0.07	0.07
2850	0.07	0.07	0.07

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.68	0.28	0.28
712.5	1.12	0.56	0.00
1440	1.40	0.56	0.00
2160	0.56	0.28	0.00
2850	0.84	0.56	0.00

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.44	0.16	0.14
712.5	0.35	0.13	0.09
1440	0.28	0.14	0.11
2160	0.28	0.17	-
2850	0.27	0.19	0.10

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	265.0	258.1	253.4
180	247.2	275.1	275.1
1200	104.6	163.9	391.2
1440	90.8	-95.7	399.0
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	44.76	31.95	31.23
712.5	43.78	45.95	25.81
1440	49.89	43.80	32.37
2160	53.21	50.66	35.33
2850	55.82	56.25	35.67

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.24	0.24	0.29
712.5	0.56	0.77	1.12
1440	0.29	0.31	0.34
2160	0.29	0.28	0.22
2850	0.28	0.26	0.23

pH

Time (min)	Run 1	Run 2	Run 3
172.5	7.28	6.76	7.01
712.5	6.29	6.08	5.95
1440	6.16	7.00	7.43
2160	6.10	6.31	6.41
2850	6.38	6.21	6.17

Temperature (^{o}C)

Time (min)	Run 1	Run 2	Run 3
172.5	24	22	13
712.5	23	21	22
1440	23	22	22
2160	22	21	22
2850	22	21	21

Appendix I-M

Woodchip Species:	Virginia Pine	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date:	Run 1: 5/22/12
Woodchip Mass:	4.5%		Run 2: 5/29/12
Limestone Content:	0.0%		Run 3: 6/5/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.982	2.86	3.10
60	2.982	2.95	2.82
120	3.011	3.16	3.20

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.12	0.14	0.10
60	0.12	0.12	0.10
120	0.11	0.14	0.10

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.91	0.10	1.17
712.5	2.79	0.39	1.08
1440	1.34	0.11	0.12
2160	0.22	0.08	0.06
2850	0.08	0.07	0.09

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.08	0.06	0.06
712.5	0.36	0.06	0.06
1440	0.78	0.05	0.06
2160	0.71	0.06	0.06
2850	0.05	0.10	0.06

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.68	0.00	0.73
712.5	1.68	1.40	0.98
1440	0.56	3.36	1.82
2160	1.18	0.00	0.70
2850	0.84	0.00	0.00

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.34	0.19	-
712.5	0.24	0.33	0.08
1440	0.25	0.11	0.12
2160	-	-	0.13
2850	-	-	0.13

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	252.2	435.4	426.2
180	245.5	418.2	416.3
1200	173.2	50.4	-48.3
1440	-	-	-
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	108.8	161.6	87.4
712.5	109.2	107.4	71.7
1440	112.2	70.0	77.4
2160	112.4	82.4	82.8
2850	125.5	94.9	91.2

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.17	0.26	0.22
712.5	0.56	1.56	1.00
1440	0.24	0.56	0.36
2160	0.18	0.29	0.26
2850	0.26	0.21	0.26

pH

Time (min)	Run 1	Run 2	Run 3
172.5	7.04	6.28	6.66
712.5	6.54	6.57	6.84
1440	6.75	6.46	6.73
2160	6.86	6.59	6.62
2850	6.79	6.87	6.81

Temperature (°C)

Time (min)	Run 1	Run 2	Run 3
172.5	24	26	24
712.5	22	23	23
1440	23	24	22
2160	23	23	22
2850	24	22	22

Appendix I-N

Woodchip Species:	American Beech	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date:	Run 1: 7/3/12
Woodchip Mass:	4.5%		Run 2: 7/10/12
Limestone Content:	0.0%		Run 3: 7/17/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	3.17	3.35	3.05
60	3.145	3.41	3.13
120	3.182	3.42	3.11

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.14	0.10	0.11
60	0.15	0.12	0.12
120	0.14	0.11	0.13

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.91	1.48	1.44
712.5	0.06	0.71	0.82
1440	0.06	0.09	0.13
2160	0.07	0.08	0.11
2850	0.06	0.06	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.66	0.06	0.06
712.5	0.05	0.05	0.06
1440	0.05	0.05	0.06
2160	0.05	0.05	0.06
2850	0.05	0.05	0.06

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	6.07	2.24	1.68
712.5	3.36	1.40	1.40
1440	3.08	1.12	1.40
2160	3.08	0.56	1.40
2850	2.49	1.68	1.12

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.53	0.33	0.19
712.5	0.48	0.30	0.12
1440	-	0.29	0.12
2160	0.49	0.31	0.12
2850	-	0.29	0.15

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	275.1	364.7	411.8
180	271.2	343.8	402.2
1200	267.2	-337	-168
1440	-	-	-
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	60.81	43.52	23.75
712.5	72.28	27.56	17.60
1440	-	32.26	23.47
2160	76.18	44.58	29.54
2850	93.91	45.82	31.33

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26	0.25	0.29
712.5	1.25	0.86	0.68
1440	0.32	0.27	0.39
2160	0.28	0.27	0.27
2850	0.18	0.23	0.27

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.83	6.55	6.57
712.5	6.99	7.02	6.75
1440	6.38	7.19	6.90
2160	6.64	6.58	6.43
2850	6.21	7.13	7.20

Temperature (°C)

Time (min)	Run 1	Run 2	Run 3
172.5	24	25	24
712.5	23	22	23
1440	22	22	22
2160	22	22	23
2850	22	22	23

Appendix I-O

Woodchip Species:	Willow Oak		Avg. Retention Time: 0.8 Days
Woodchip Size:	9mm		Start date:	Run 1: 5/22/12
Woodchip Mass:	4.5%			Run 2: 5/29/12
Limestone Content:	0.0%			Run 3: 6/5/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.977	2.98	2.89
60	3.007	3.01	2.94
120	3.095	3.10	2.94

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	-	0.09	0.09
60	-	0.10	0.08
120	-	0.09	0.10

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.18	2.96	1.87
712.5	1.27	1.59	2.03
1440	0.32	0.10	0.64
2160	0.10	0.10	0.10
2850	0.59	0.22	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.10	0.10	0.10
712.5	0.49	0.28	0.10
1440	0.25	0.10	0.10
2160	0.10	0.10	0.10
2850	0.10	0.10	0.10

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.28	0.28	0.84
712.5	0.28	0.28	0.28
1440	0.00	0.56	0.56
2160	0.00	0.56	0.56
2850	0.00	0.28	0.56

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	-	0.13	0.12
712.5	-	0.12	0.08
1440	-	0.10	0.06
2160	-	0.10	0.09
2850	-	0.09	0.09

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	247.5	234.3	251.8
180	202.6	226.5	249.3
1200	180.8	221.4	243.5
1440	94.6	223.7	-
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	82.64	40.20	25.18
712.5	50.63	31.66	20.47
1440	49.02	29.96	19.88
2160	63.73	29.04	20.95
2850	55.01	32.52	24.18

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.27	0.27	0.28
712.5	0.94	1.19	1.17
1440	0.40	0.39	0.40
2160	0.27	0.28	0.28
2850	0.28	0.27	0.19

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.02	6.62	6.52
712.5	6.07	6.41	6.32
1440	6.24	6.94	6.36
2160	5.55	6.77	6.21
2850	6.74	6.97	6.46

Temperature (^{o}C)

Time (min)	Run 1	Run 2	Run 3
172.5	19	21	20
712.5	18	18	18
1440	18	17	19
2160	18	17	19
2850	18	18	20

Appendix I-P

Woodchip Species:	Willow Oak	Avg. Retention Time:	0.8 Days
Woodchip Size:	13mm	Start date: Run 1:	5/22/12
Woodchip Mass:	4.5%	Run 2:	5/29/12
Limestone Content:	0.0%	Run 3:	6/5/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.977	2.98	2.89
60	3.007	3.01	2.94
120	3.095	3.10	2.94

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	-	0.09	0.09
60	-	0.10	0.08
120	-	0.09	0.10

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.78	1.74	2.08
712.5	1.85	1.44	2.05
1440	0.39	0.10	0.61
2160	0.30	0.10	0.10
2850	0.10	0.10	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.10	0.10	0.10
712.5	0.27	0.10	0.10
1440	0.29	0.10	0.10
2160	0.10	0.10	0.10
2850	0.10	0.10	0.10

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.84	0.84	0.84
712.5	0.56	0.84	0.84
1440	0.28	0.28	0.56
2160	0.28	0.28	0.56
2850	0.28	0.00	0.84

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	-	0.17	0.13
712.5	-	0.14	0.22
1440	-	0.10	0.04
2160	-	0.10	0.09
2850	-	0.11	0.08

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	271.1	316.1	362.9
180	259.0	320.2	360.1
1200	239.2	315.6	382.8
1440	111.3	331.9	-
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	54.16	34.33	24.38
712.5	33.31	30.73	20.12
1440	47.77	32.53	18.86
2160	55.49	32.79	21.83
2850	51.69	35.04	22.76

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26	0.27	0.27
712.5	0.70	1.12	1.14
1440	0.41	0.38	0.48
2160	0.26	0.28	0.26
2850	0.29	0.28	0.25

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.26	6.57	6.46
712.5	6.51	6.37	6.24
1440	6.37	6.85	6.38
2160	5.77	6.73	6.44
2850	6.67	6.75	6.27

Temperature ($^{\circ}$C)

Time (min)	Run 1	Run 2	Run 3
172.5	19	21	20
712.5	18	18	18
1440	18	17	19
2160	18	17	19
2850	18	18	20

Appendix I-Q

Woodchip Species:	Willow Oak	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date:	Run 1: 1/14/13
Woodchip Mass:	1.0%		Run 2: 1/21/13
Limestone Content:	0.0%		Run 3: 1/28/13

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.836	2.84	2.84
60	3.021	3.02	3.02
120	2.839	2.84	2.84

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.14	0.13	0.13
60	0.11	0.10	0.10
120	0.09	0.08	0.08

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.76	1.46	1.56
712.5	4.25	1.39	1.38
1440	3.95	1.23	1.22
2160	0.84	0.43	0.19
2850	0.30	0.28	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.04	0.04	0.01
712.5	0.05	0.03	0.01
1440	0.48	0.10	0.03
2160	0.60	0.15	0.02
2850	0.69	0.05	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.12	0.14	0.28
712.5	0.28	0.00	0.14
1440	0.84	0.00	0.00
2160	0.56	0.14	0.00
2850	0.56	0.00	0.14

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.12	0.07	0.01
712.5	0.05	0.01	0.01
1440	0.01	0.01	0.01
2160	0.01	0.01	0.01
2850	0.01	0.01	0.01

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	307.8	345.0	245.3
180	296.6	340.9	352.0
1200	238.0	304.0	329.7
1440	236.6	279.5	322.3
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	14.17	12.75	11.12
712.5	14.23	10.40	6.94
1440	15.29	12.55	10.00
2160	16.72	14.51	11.46
2850	16.93	10.19	13.34

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26	0.25	0.27
712.5	0.93	1.01	1.01
1440	0.28	0.27	0.26
2160	0.43	0.28	0.28
2850	0.29	0.28	0.26

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.95	7.20	6.21
712.5	6.95	7.05	6.26
1440	7.14	7.02	6.44
2160	7.40	7.08	6.60
2850	6.81	7.07	6.37

Temperature ($^{\circ}$C)

Time (min)	Run 1	Run 2	Run 3
172.5	21	20	21
712.5	21	19	20
1440	21	19	22
2160	20	20	21
2850	20	20	22

Appendix I-R

Woodchip Species:	Willow Oak	Avg. Retention Time:	0.8 Days
Woodchip Size:	5mm	Start date:	Run 1: 1/14/13
Woodchip Mass:	2.5%		Run 2: 1/21/13
Limestone Content:	0.0%		Run 3: 1/28/13

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.836	2.84	2.84
60	3.021	3.02	3.02
120	2.839	2.84	2.84

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.14	0.13	0.13
60	0.11	0.10	0.10
120	0.09	0.08	0.08

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	2.41	1.42	1.18
712.5	2.65	0.97	0.29
1440	0.51	0.10	0.10
2160	0.10	0.10	0.10
2850	0.10	0.29	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.05	0.01	0.01
712.5	0.55	0.08	0.01
1440	2.58	0.01	0.01
2160	0.68	0.01	0.01
2850	0.01	0.01	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	1.40	0.28	0.84
712.5	0.00	0.28	0.00
1440	0.28	0.00	0.00
2160	0.84	0.28	0.00
2850	0.56	0.28	2.80

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.13	0.09	0.08
712.5	0.06	0.01	0.01
1440	0.01	0.01	0.01
2160	0.01	0.01	0.01
2850	0.06	0.01	0.01

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	235.3	239.3	242.6
180	225.6	237.5	247.1
1200	151.2	194.5	140.1
1440	147.0	208.5	120.0
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	23.49	33.24	24.03
712.5	27.22	24.15	17.18
1440	29.23	29.31	24.28
2160	31.84	32.74	28.18
2850	39.45	20.84	31.70

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26	0.27	0.26
712.5	0.93	1.00	0.99
1440	0.26	0.27	0.26
2160	0.46	0.39	0.36
2850	0.27	0.28	0.26

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.50	6.69	6.25
712.5	6.35	6.59	6.18
1440	6.64	7.00	6.38
2160	6.92	6.98	6.37
2850	6.31	7.11	6.08

Temperature (^{o}C)

Time (min)	Run 1	Run 2	Run 3
172.5	21	20	21
712.5	21	19	20
1440	21	19	22
2160	20	20	21
2850	20	20	22

Appendix I-S

Woodchip Species:	Willow Oak		Avg. Retention Time:	0.8 Days	
Woodchip Size:	5mm		Start date:	Run 1:	11/12/12
Woodchip Mass:	4.5%			Run 2:	11/26/12
Limestone Content:	5.0%			Run 3:	12/3/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.934	2.95	2.86
60	2.963	3.07	2.94
120	3.157	3.09	2.93

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.11	0.11	0.13
60	0.11	0.11	0.13
120	0.11	0.11	0.13

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	3.46	2.86	1.20
712.5	2.62	0.92	0.71
1440	0.46	0.10	0.10
2160	0.10	0.41	0.29
2850	0.38	0.48	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.01	0.03	0.01
712.5	0.29	0.08	0.03
1440	2.16	0.01	0.01
2160	1.62	0.01	0.01
2850	0.01	0.01	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.42	0.42	0.70
712.5	0.14	0.14	0.14
1440	0.14	0.14	0.14
2160	0.14	0.14	0.14
2850	0.14	0.14	0.14

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.21	0.13	0.15
712.5	0.15	0.13	0.11
1440	0.10	0.14	0.11
2160	0.12	0.14	0.10
2850	0.11	0.16	0.12

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	287.1	291.6	327.0
180	265.6	303.5	326.5
1200	139.8	-9.7	12.7
1440	109.7	-87.1	-50.1
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	51.54	29.65	53.21
712.5	47.73	41.30	38.35
1440	58.08	54.35	44.50
2160	59.42	63.09	51.08
2850	85.21	73.35	50.76

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26	0.30	0.30
712.5	0.81	1.03	1.06
1440	0.27	0.29	0.26
2160	0.37	0.53	0.36
2850	0.27	0.28	0.28

pH

Time (min)	Run 1	Run 2	Run 3
172.5	6.99	7.18	7.13
712.5	7.36	7.39	7.26
1440	7.00	7.40	7.50
2160	7.59	7.46	7.79
2850	7.09	7.31	7.24

Temperature (°C)

Time (min)	Run 1	Run 2	Run 3
172.5	20	18	20
712.5	20	19	19
1440	20	19	19
2160	19	19	20
2850	19	19	20

Appendix I-T

Woodchip Species:	Willow Oak
Woodchip Size:	5mm
Woodchip Mass:	4.5%
Limestone Content:	10.0%

Avg. Retention Time:	0.8 Days
Start date:	Run 1: 11/12/12
	Run 2: 11/26/12
	Run 3: 12/3/12

Inflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
5	2.934	2.95	2.86
60	2.963	3.07	2.94
120	3.157	3.09	2.93

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
5	0.11	0.11	0.13
60	0.11	0.11	0.13
120	0.11	0.11	0.13

Outflow Data

Nitrate (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	3.15	2.51	0.93
712.5	2.17	1.79	0.59
1440	0.30	0.10	0.10
2160	0.53	0.41	0.10
2850	0.10	0.38	0.10

Nitrite (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.01	0.01	0.01
712.5	0.54	0.09	0.03
1440	1.91	0.01	0.01
2160	0.01	0.01	0.01
2850	0.01	0.01	0.01

TKN (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	0.14	0.14	0.70
712.5	0.14	0.42	0.28
1440	0.14	0.14	0.28
2160	0.14	0.14	0.14
2850	0.14	0.14	0.14

Total Phosphorus (ppm)

Time (min)	Run 1	Run 2	Run 3
172.5	0.18	0.17	0.13
712.5	0.12	0.15	0.10
1440	0.11	0.16	0.11
2160	0.13	0.16	0.12
2850	0.15	0.16	0.13

Redox Potential (mV)

Time (min)	Run 1	Run 2	Run 3
120	205.3	208.5	219.7
180	193.9	194.1	225.0
1200	160.4	141.7	160.3
1440	147.0	110.3	94.1
1650	-	-	-
2640	-	-	-

Organic Carbon (PPM)

Time (min)	Run 1	Run 2	Run 3
172.5	56.85	39.24	63.65
712.5	58.28	45.09	44.44
1440	67.65	63.31	48.17
2160	87.62	70.46	52.39
2850	112.2	76.91	45.85

Volume (liters)

Time (min)	Run 1	Run 2	Run 3
172.5	0.26	0.27	0.29
712.5	0.78	1.04	1.04
1440	0.27	0.28	0.28
2160	0.36	0.50	0.36
2850	0.26	0.28	0.28

pH

Time (min)	Run 1	Run 2	Run 3
172.5	7.00	7.15	6.99
712.5	7.12	7.35	7.18
1440	7.01	7.48	7.47
2160	6.81	7.40	7.79
2850	6.72	7.34	7.20

Temperature (°C)

Time (min)	Run 1	Run 2	Run 3
172.5	20	18	20
712.5	20	19	19
1440	20	19	19
2160	19	19	20
2850	19	19	20

Appendix II-A

First order Model Derivation

Assume completely mixed
Assume no outflow at t=0
Column full at t=0

$$\frac{dM}{dt} = \cancel{Q_{in} * C_{in}} - Q_{out} * C_{out} - r * V \tag{1}$$

No inflow
Assume first order decay

$$-r = K_1 * C_{out} \tag{2}$$

$$\frac{dM}{dt} = -Q_{out} * C_{out} + K_1 * C_{out} * V \tag{3}$$

$$\frac{dM}{dt} = V \frac{dC}{dt} + C \frac{dV}{dt} \tag{4}$$

Substitute $-Q_{out}$ for dV/dt

$$\frac{dM}{dt} = V \frac{dC}{dt} - C * Q_{out} \tag{5}$$

Set equation 5 and equation 3 equal

$$-\cancel{Q_{out} * C_{out}} + K_1 * C_{out} * \cancel{V} = \cancel{V} \frac{dC}{dt} - \cancel{C * Q_{out}} \tag{6}$$

Effluent and volumes cancel out and we are left with

$$\frac{dC}{dt} = K_1 * C_{out} \tag{7}$$

Integrate

$$\int_{C_0}^{C} \frac{dC}{C_{out}} = \int_{0}^{t} K_1 * dt \tag{8}$$

$$\ln(C) - \ln(C_0) = K_1 * t \tag{9}$$

Final model

$$\boldsymbol{C = C_0 * e^{K_1 * t}} \tag{9}$$

Appendix II-B

Zero order Model Derivation

Assume completely mixed
Assume no outflow at t=0
Column full at t=0

$$\frac{dM}{dt} = \cancel{Q_{in} * C_{in}} - Q_{out} * C_{out} - r * V \tag{1}$$

No inflow
Assume zero order decay

$$-r = K_0 \tag{2}$$

$$\frac{dM}{dt} = -Q_{out} * C_{out} + K_0 * V \tag{3}$$

$$\frac{dM}{dt} = V\frac{dC}{dt} + C\frac{dV}{dt} \tag{4}$$

Substitute $-Q_{out}$ for dV/dt

$$\frac{dM}{dt} = V\frac{dC}{dt} - C * Q_{out} \tag{5}$$

Set equation 5 and equation 3 equal

$$\cancel{-Q_{out} * C_{out}} + K_0 * \cancel{V} = \cancel{V}\frac{dC}{dt} \cancel{- C * Q_{out}} \tag{6}$$

Effluent and volumes cancel out and we are left with

$$\frac{dC}{dt} = K_0 \tag{7}$$

Integrate

$$\int_{C_0}^{C} dC = \int_{0}^{t} K_0 * dt \tag{8}$$

$$C - C_0 = K_0 * t \tag{9}$$

Final model

$$\boldsymbol{C = C_0 + K_0 * t} \tag{10}$$

References

American Public Health Association (APHA), American Water Works Association, Water Environment Federation. (1992). *Standard Methods for the Examination of Water and Wastewater, 18th Ed.*, Washington, DC.

Bach, P. M., McCarthy, D. T., and Deletic, A., (2010). "Redefining the Stormwater First Flush Phenomenon." *Water Research,* 44, 2487-2498.

Blowes, D.W., Robertson, W.D., Ptacek, C.J., Merkley, C., (1994). "Removal of agricultural nitrate from tile-drainage effluent water using in-line bioreactors." *Journal of Contaminant Hydrology,* 15, 207-221.

Bratieres, K., Fletcher, T. D., Deletic, A., Zinger, Y., (1994). "Nutrient and sediment removal by stormwater biofilters: A large-scale design optimization study." *Water Research,* 42, 3930-3940.

Chen, X., Peltier, E., Sturm, B. S. M, Young, C. B., (2013). "Nitrogen Removal and Nitrifying and Denitrifying Bacteria Quantification in a Stormwater Bioretention System." *Water Research,* 47, 1691-1700.

Collins, K. A., Lawrenceb, T. J., Standerc, E. K., Jontosd, R. J., Kaushale, S. S., Newcomerf, T. A., Grimmg, N. B., and Ekbergh, M. L. C., (2010). "Opportunities and Challenges for Managing Nitrogen in Urban Stormwater: A Review and Synthesis." *Ecological Engineering,* 36, 1507-1519.

Davis, A. P., Traver, R. G., Hunt, W. F., Lee, R., Brown, R. A., Olszewski, J. M., (2012). "Hydrologic Performance of Bioretention Storm-Water Control Measures." *Journal of Hydrologic Engineering,* 17(5), 604-614.

Ergas, S. J., Yuan, X., Yao, Y., Pandit, A., Siegel, R., and Sengupta, S., (2010). "Performance of Nitrogen-Removing Bioretention Systems for Control of Agricultural Runoff." *Journal of Environmental Engineering*, 136(10), 1105-1112.

Flint, K. R., Davis A. P., (2007). "Pollutant Mass Flushing Characterization of Highwat Stormwater Runoff from an Ultra-Urban Area." *Journal of Environmental Engineering,* 133(6), 616-626.

Glass, C., Silverstein, J., (1998). "Denitrification Kinetics of High Nitrate Concentration Water: pH effect on Inhibition and Nitrite Accumulation." *Water Research,* 32(3), 831-839.

Hartmann, H., Bohm, T., Jensen, P. D., Temmerman, M., Rabier, F., Golser, M., (2006). "Methods for size classification of wood chips." *Biomass and Engineering,* 30, 944-953.

Hsieh, C. H., Davis, A. P., and Needelman, B. A., (2007). "Nitrogen Removal from Urban Stormwater Runoff through Layered Bioretention Columns." *Water Environment Research,* 79(12), 2404-2411.

Hunt, W. F., Jarrett, A. R., Smith, J. T., Sharkey, L. J., (2006). "Evaluating Bioretention Hydrology and Nutrient Removal at Three Field Sites in North Carolina." *Journal of Drainage and Irrigation Engineering,* 132(6), 600-608.

Hunt, W. F., Davis, A.P., Traver, R.G., (2012). " Meeting Hydrologic and Water Quality Goals through Targeted Bioretention Design." *Journal of Environmental Engineering,* 138(6), 698-707.

Kim, H., Seagren, E. A., and Davis, A. P., (2003). "Engineered Bioretention for Removal of Nitrate from Stormwater Runoff." *Water Environment Federation,* 75(4) 355-67.

Lamholm, S. H., Savidge, R. A., (2003). "A reassessment of carbon content in wood: variation within and between 41 North American species." *Biomass and Engineering*, 25, 281-188.

Lee, P. G., Lea, R.N, Dohmann, E., Predilsky, W., Turk, P.E., Ying, H., Whitson, J.L., (2000). "Denitrification in aquaculture systems: an example of a fuzzy logic control problem." *Biomass and Engineering*, 25, 281-188.

Leverenz, H. L., Haunschildb, K., Hopesa, G., Tchobanoglousa, G., and Darbya, J. L., (2010). "Anoxic Treatment Wetlands for Denitrification." *Ecological Engineering,* 36, 1544-551.

Li, H., Davis, A. P., ASCE F., (2009). "Water Quality Improvement through Reductions of Pollutant Loads Using Bioretention." *Enzyme and Microbial Technology*, 31, 976-985.

Lopez-Fiuza, J., Buys, B., Mosquera-Corral, A., Omil, F., Mendez, R., (2002). "Toxic effects exerted on methanogenic, nitrifying and denitrifying bacteria by chemicals used in a milk analysis laboratory." *Journal of Environmental Engineering*, 139, 567-576.

Lucas, W. C., Greenway, M., (2011a). "Hydraulic Response and Nitrogen Retention in Bioretention Mesocosms with Regulated Outlets: Part 1-Hydraulic Response." *Water Environment Research,* 83.

Maryland Center for Agro-Ecology Inc. (MCAE), (2004), "Forest Production, Industry and Forest Retention Assessment." Queenstown, Maryland.

Morgan II R. P., Kline, K. M., Churchill, J. B., (2012). "Estimating reference nutrient criteria for Maryland ecoregions." *Environmental Monitoring and Assessment*, 185, 2123-2137.

Robertson, W. D., (2010). "Nitrate Removal Rates in Woodchip Media of Varying Age." *Ecological Engineering,* 36, 1581-587.

Son, J., Crowley, C., Goodwin, S., Arabi, M., and Carlson, K. H., (2013). " Relative Phosphorus Load Inputs from Wastewater Treatment Plants in a Northern Colorado Watershed." *Journal of Environmental Quality,* 42, 497-506.

Stumm, W., and Morgan, J. J., (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd. Wiley-Interscience, 1996. Print.

U.S. Fish and Wildlife Service (USFWS), (2001). "Native Plants for Wildlife Habitat and Conservation Landscaping, Maryland: Coastal Plain." Annapolis, Maryland.

Zinger, Y., Blecken, G. T., Fletcher, T. D., Viklander, M., Deletic, A., (2013). " Optimising Nitorgen Removal in Existing Stormwater Biofilters: Benefits and Tradeoffs of a Retrofitted Saturated Zone." *Ecological Engineering,* 51, 75-82.