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The Effect of the Antecedent Dry Conditions on Nitrogen Removal for a Modified Bioretention System

Mackenzie Peterson
University of South Florida, mackenzie.a.peterson@gmail.com

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The Effect of the Antecedent Dry Conditions on Nitrogen Removal for a Modified Bioretention System

by

Mackenzie A. Peterson

A thesis submitted in partial fulfillment
of the requirements for the degree of
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Department of Civil and Environmental Engineering
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University of South Florida

Major Professor: James R. Mihelcic, Ph.D.
Sarina J. Ergas, Ph.D.
Qiong Zhang, Ph.D.

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DEDICATION

To Brian, for being a constant reminder that life does not always go the way you planned, sometimes it goes even better; and to my mom, thank you for always being my rock.

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ABSTRACT

Eutrophication is defined as the ‘over enrichment’ of a water body from nutrients, resulting in uncontrolled growth of primary producers, leading to periods of oxygen depletion from decomposition of the algal organic matter. According to the 2010 Water Infrastructure Needs and Investment (a U.S. Congressional Report), 40% of U.S. water bodies are contaminated with pollutants, including nutrients. Non-point sources of nutrient pollution are a major cause of this reduction in water quality. One way to decrease eutrophication is to manage nutrients found in stormwater runoff, before they reach a receiving water body.

Bioretention cells containing an internal water storage zone (IWSZ) have been shown to remove higher amounts of nitrogen than conventional cells (without an IWSZ). The IWSZ contains an organic carbon substrate, usually derived from wood chips submerged in water, which supports the biochemical process of denitrification. Characteristics of wood chips that affect nitrogen removal include carbon content (%), leaching of dissolved organic carbon (DOC), and wood chip size and type. However, there is limited information on how the intermittent hydraulic loading that is associated with these field systems impacts their performance. Accordingly, the overall goal of this research is to improve understanding of the effect that the antecedent dry conditions (ADC) have on the performance of a field scale bioretention cell modified to contain an IWSZ.

The nine different types of wood chips used in laboratory and field studies identified in the literature were categorized as hardwood and softwood. Literature showed that total

organic carbon (TOC) leached from softwood chips is almost double the TOC measured from the hardwood chips, 138.3 and 70.3 mg/L, respectively. The average observed nitrogen removal for softwood chips was found to be greater than the removal for the average of the hardwood chips (75.2% and 63.0%, respectively). Literature also suggests that larger wood chip size may limit the availability of the carbon for the denitrifying organisms and provides less surface area for the biofilm growth.

A field study conducted for this research compared the performance of a modified bioretention system designed to enhance denitrification, addition of an IWSZ, with a conventional system that does not contain an IWSZ. Fourteen storm events were completed from January 2016 to July 2016 by replicating storm events previously completed in the laboratory using hydraulic loading rates (HLR) of 6.9 cm/h, 13.9 cm/h, and 4.1 cm/h. The goal was to have results from storm events with ADCs of two, four, and eight days, with the varying durations of hydraulic loading of two, four, and six hours. Synthetic stormwater, simulating nitrogen levels common in urban runoff, was used as the system's influent to assist in running a controlled experiment. The resultant ADCs ranged from 0 to 33 days, with the average ADC being 9 days. The fourteen sets of influent samples were averaged to obtain mean influent concentrations for the synthetic stormwater. These values were used when calculating the percent nitrogen removal for the four measured nitrogen species (NO_x – N, NH_4^+– N, organic N, and TN).

The field storm events were separated into three groups based on HLR and duration to eliminate the affects of both variables on nitrogen removal for these results, since the focus is the ADC. For the low HLR (4.1 cm/hr), there were four storm events (ADCs of 4 to 33 days), as the ADC increased, greater percentages of ammonium – nitrogen, organic

nitrogen, and total nitrogen were removed. For nitrate/nitrite – nitrogen, the percent removal was rather consistent for all four storm events, not significantly increasing or decreasing with changes in the ADC. There were five storm events (ADCs of 0 to 28 days) tested with the median HLR (6.9 cm/hr), nitrogen removal for all four species increased as the ADC increased. The increase was significant ($p<0.05$) for ammonium – nitrogen, organic nitrogen, and total nitrogen and not significant ($p>0.05$) for nitrate/nitrite – nitrogen. The third group also contained five storm events (ADCs from 0 to 11 days) that were tested with the highest HLR (13.9 cm/hr). Ammonium – nitrogen, nitrate/nitrite – nitrogen, and total nitrogen all increased with the ADC, and organic nitrogen removal decreased with the increasing ADC. As a result, this research concluded that the difference in HLR affects the nitrogen removal efficiency, but overall increasing the ADC increased nitrogen removal for NO_x – N, NH_4^+ - N, organic N, and TN.

CHAPTER 1: INTRODUCTION

According to the 2010 Water Infrastructure Needs and Investment performed by the Congressional Research Service, 40% of surveyed U.S. water bodies are compromised with pollutants not meeting relevant standards (CRS, 2010). Non-point sources are the major cause of the reduction in water quality, while pollution from point sources is a much smaller percentage (Copeland and Tiemann, 2010). Non-point sources include agricultural and stormwater runoff, precipitation, and drainage (EPA, 2016). In contrast, point sources are defined as a "single identifiable source of pollution" where pollutants are discharged, for example, a pipe, ship, or factory smokestack (NOAA, 2008). Stormwater runoff (a non-point source) is a concern because it can lead to excessive nutrient pollution of water bodies and, in areas such as Tampa Bay, can contribute up to 75% of nitrogen inputs (Wang et al., 2012).

Eutrophication is defined as the 'over enrichment' of a water body from nutrients, causing uncontrolled growth of primary producers (Mihelcic and Zimmerman, 2014), resulting in periods of oxygen depletion from the decomposition of algal organic matter (Ansari, 2014). It may lead to the development of hypoxic zones, areas of the water with low dissolved oxygen concentrations (less than 2 mg/L), causing animal and plant life to suffocate and die (NOAA, 2014). Greening (2014) defines "cultural eutrophication" as a process where human activities in a watershed lead to increased nutrient concentrations in the water body, generating larger amounts of blooms of phytoplankton and microalgae.

This definition includes the impact that humans have on the watershed and the contribution the community makes to the eutrophication of the water body. Eutrophication is a threat to water bodies used for fishing, recreation, industry, and drinking because of the increased growth of bacteria and other organisms (Ansari, 2014). Additionally, the algae growth can prevent sunlight from penetrating the water; blocking the sun's energy that sea grass and other aquatic plants and organisms need to perform photosynthesis. In September of 2013, the Carroll Township near Toledo, Ohio detected dangerously high levels of the algae toxin Microcystin in their drinking water plant's finished water and alerted their residents to stop drinking the water (Kozacek, 2014). Following this detection, the City of Toledo also found high levels of Microcystin in their water and advised the residents served by Toledo Water not to drink it, leaving over 400,000 people in the area without clean drinking water (Kozacek, 2014). Eutrophication has also been a problem in the Tampa Bay since the late 1970's and early 1980's. As of 2009, stormwater accounts for 63% of total nitrogen loadings into the Bay (EPA, 2009).

One way to reduce eutrophication is to manage nutrients found in stormwater runoff before it reaches the water body, resulting in a decrease of nutrients and pollutants in the water. Treating stormwater runoff close to the source of pollution using bioretention systems is a technique for reducing the effects of eutrophication. A bioretention cell combines natural and engineered systems to manage stormwater runoff in developed areas (Lopez et al., 2016a). The cell is made up of layers of sand, gravel, and other media to assist in filtering the runoff. A bioretention cell falls into the category of low impact development (LID) technologies, used to bring the state of a site back to its "predevelopment conditions" or before development occurred in the area. Other examples of LID technologies are green roofs, bioswales, planter boxes, permeable pavement, rainwater harvesting, and green streets and alleys (Locicero, 2015). LID technologies aim to control stormwater runoff volume, peak runoff rate, flow frequency and/or duration, and improving water quality (Ahiablame, 2013). Bioretention cells meet all four of these considerations, along with working to mitigate the impacts urbanization has on water quality. Inherent in the definition of a LID technology, it is important to generate environmentally friendly and effective recommendations for building a bioretention cell.

Literature and research have shown that bioretention cells containing an IWSZ, remove higher amounts of nutrients such as nitrogen and phosphorus (along with total suspended solids (TSS), Cu, and Zn) than standard bioretention cells (Ming-Han 2014; Lopez et al. 2016a) (Figures 1.1 a and b).

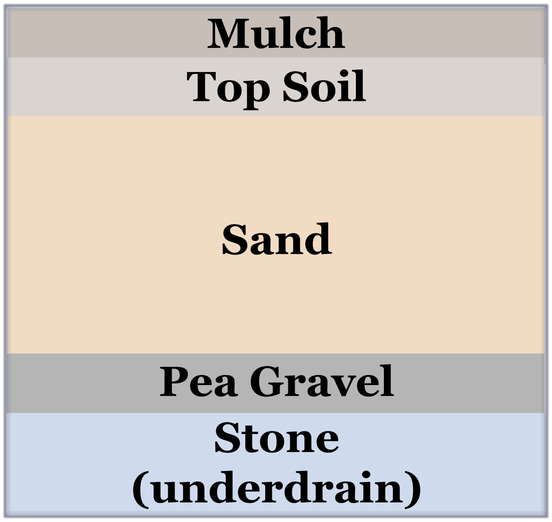

Figure 1.1a. Diagram of a Conventional Bioretention Cell

Figure 1.1b. Diagram of a Modified Bioretention Cell

An IWSZ is an additional layer within the cell that contains a carbon source, such as wood chips, where the water is retained. An anoxic zone is created in the IWSZ to promote denitrification of the water before it drains out of the cell. It has been reported that a bioretention cell with an IWSZ would increase total nitrogen and total phosphorous removal to 60% from around 40% for a conventional cell, for both nutrients (Brown, 2009). The main component of an IWSZ is the carbon source used to support denitrification. The majority of prior studies of bioretention systems with IWSZs have used wood chips as the carbon source (i.e., the wood chips leach DOC into the system which serves as the electron donor for denitrification). These systems have been used to treat stormwater, greywater, agricultural runoff, and wastewater (Ergas et al., 2010; Fowdar et al., 2015; Gilchrist et al., 2014). In order to improve the recommendations for designing a bioretention system that contains an IWSZ, characteristics of wood chips need to be investigated more thoroughly.

A collection of studies and papers reviewed for this thesis outline carbon content (%), TOC leaching, influent and effluent nitrogen concentrations, and percent nitrogen removal. A few of the gaps in this research are the half saturation constant (K_S), ADC or how many days in between water flushing through the system, and size of the wood chips. Examining these topics more closely could generate more information on conditions that effect the operation of a bioretention system, specifically one containing an IWSZ.

1.1 Research Goal, Objectives, and Hypothesis

The overall goal of this research is to improve understanding of the effect that the ADC has on the performance of a modified bioretention cell (containing an IWSZ). There are two objectives and one hypothesis that will guide this research. The first objective is to identify knowledge gaps in the literature surrounding the use, properties, and performance of wood chips in a denitrification bioreactor. The second objective is to look at the difference in nitrogen removal for a modified bioretention system based on variable ADCs. The hypothesis is that storm events with longer ADCs will have lower levels of nitrogen in the effluent water than storm events with shorter ADCs.

CHAPTER 2: LITERATURE REVIEW

Previous studies performed on different types of wood chips were reviewed to understand their potential to remove nitrogen species and promote denitrification, and to identify the biokinetic properties associated with different types of wood chips. The majority of these papers examined the use of wood chips for denitrification and compared them to other sources of organic carbon, such as straw or maize cobs. They were used in various engineering applications, including bioretention cells used to manage stormwater and denitrification beds used to manage agricultural and domestic wastewater. Only two published studies (Peterson et al., 2015 and Lynn et al., 2015a) were identified that reported the values of their ADC in between experiments/storm events. Igielski (2016) (not published at this time) carried out research observing the effect of different influent flow rates and hydraulic retention times (HRTs) on nitrogen removal. In systems that contain anoxic zones, such as discussed later in this literature review, different microbial processes occur to remove nutrients from the influent water. This review will specifically look at the biochemical processes that transform nitrogen in these systems.

2.1 Nitrogen Transformation Processes

Nitrogen occurs in various forms in anthropogenic waste streams and includes inorganic species such as ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) and organic forms such as dissolved organic N and particulate organic N (Collins et al., 2010). Levels of organic and inorganic nitrogen can vary, depending on the land use and hydrologic conditions where the runoff occurs (Collins et al., 2010). In urban areas, organic nitrogen has been reported to be abundant in the "first flush" of stormwater runoff (Flint and Davis, 2007). Typically, influent stormwater entering stormwater control measures, such as bioretention systems, contains nitrogen in the form of NH_4^+, NO_x (NO_3^-/NO_2^-), and/or organic N. In an aqueous system, organic N can undergo ammonification (Equation 2.1) to NH_4^+ (Collins et al., 2010).

$$NH_2COHN_2 + H_2O + 7H^+ \rightarrow 3NH_4{}^+ + CO_2$$

Equation 2.1

A modified bioretention cell contains both an un-submerged and submerged zone (previously depicted in Figure 1b). Within these zones, different microbial processes occur. First, the un-submerged, or unsaturated, zone is where the process of nitrification takes place. Nitrification is a microbial process during which ammonium is oxidized to nitrite and then nitrate (EPA, 2002; Mihelcic and Zimmerman, 2014). This is predominantly done by two different groups of autotrophic bacteria that build organic molecules by consuming energy acquired from an inorganic source; in the case of nitrification the inorganic sources are ammonium or nitrite (EPA, 2002). The first step of nitrification is ammonia-oxidizing bacteria oxidizes the ammonium to nitrite as follows:

$$NH_4{}^+ + 1.5O_2 \rightarrow NO_2{}^- + 2H^+ + 2H_2O$$

Equation 2.2

The second step of nitrification is when the nitrite-oxidizing bacteria oxidize the nitrite to nitrate as follows:

$$NO_2{}^- + H_2O \rightarrow NO_3{}^- + 2H^+ + 2e^-$$

Equation 2.3

The two-step process of nitrification converts nitrogen, but does not remove it. While the stormwater runoff flows through the bioretention system, nitrogen can be removed from the aqueous phase through three different methods: assimilation (nitrogen uptake), adsorption, and denitrification (Collins et al., 2010). Nitrogen assimilation is the process where inorganic nitrogen (ammonium, nitrate, and nitrite) is converted into microbial or plant biomass and temporarily stored as organic N (Collins et al., 2010). Additionally, ammonium can be removed from the aqueous phase by adsorption onto negatively charged particles, such as soil or clay, within the system. Nitrogen uptake through assimilation or adsorption results in temporarily removing the nitrogen from the aqueous phase, but not permanently. Permanent removal of nitrate occurs through microbial denitrification in the aqueous phase of the system. This occurs by converting inorganic nitrogen in an anoxic environment to gaseous forms of nitrogen (N_2O or N_2 gas), which are then released to the atmosphere (Collins et al., 2010).

In a modified bioretention cell, or similar system, the effluent from the layer where the ammonia is nitrified, is the influent into the layer where denitrification occurs. Denitrification occurs when facultative microorganisms respire nitrate under anoxic conditions (i.e., oxygen level is below 0.5 mg DO/L). The denitrifying bacteria can use different electron donors, including both inorganic and organic compounds, such as elemental sulfur and dissolved organic substrates (Lopez et al., 2016b). For applications where a bioretention system is filled with wood chips, the electron donors are the organic substrates, specifically organic carbon leached from wood chips. Denitrification occurs using a carbon substrate to denitrify the nitrate into nitrogen gas and carbon dioxide as follows:

$$2NO_3^- + 2HCOH \rightarrow N_2O + 2CO_2 + H_2O + 2OH^-$$

Equation 2.3

These two transformations occurring consecutively assists in removing total nitrogen from the water. However, if one or both processes are not carried out completely, it could limit total nitrogen removal for a modified bioretention system (Ergas et al., 2009).

2.2 Wood Chip Type

When using wood chips for denitrification in a bioreactor, the type of wood chip used affects the carbon content (%), nitrogen removal, and amounts of organic N, TOC and TKN leached into the system. Previous studies have performed experiments on various materials, including different types of wood chips, to test their denitrification potential (Peterson et al., 2015, Warneke 2011, Gilbert et al., 2008, Healy et al., 2011, Fowdar et al., 2015, Lynn et al., 2015a and b, Ergas et al., 2010). These studies evaluated nitrogen removal in a number of engineered systems which include: bioretention systems, denitrifying biofilters, denitrification beds, permeable reactive barriers, and denitrification bioreactors. Other studies looked at different variables (e.g., wood chip size) that could effect denitrification in a bioreactor (Cameron and Schipper, 2010 and Peterson et al., 2015). This section provides insights to the results that were observed in the studies that evaluated nine different types and seven different sizes of wood chips, and identifies the gaps in the literature for this area of research.

In the seven studies identified for this research (Table 2.1), nine types of wood chips were identified and compared to other wood chips and occasionally to other organic materials used as carbon substrates. This section will solely focus on the different types of wood chips that were tested. The nine different wood chip types are; 1) pine, 2) eucalyptus, 3) maple, 4) wild cherry, 5) oak, 6) beech, 7) coniferous, 8) willow, and 9) red gum. These types of wood chips can be divided into two categories of hardwood and softwood. The hardwood chips are eucalyptus, maple, red gum, oak, wild cherry, and beech, and the softwood chips are pine, coniferous, and willow.

All trees are categorized as either hardwoods or softwoods; however, these terms are deceptive because they do not refer to the hardness of the wood, even though many hardwoods are stronger and tougher in nature (Ma, 2015). A study by Lamlom (2003) assessed the carbon content of 41 species of North American trees, both hardwood and softwood. Out of the nine species in this literature review, six were tested in the Lamlom (2003) study. The average carbon content for hardwood (maple, birch, beech, wild cherry, and oak) was 48.7% +/- 1.3 and the average for softwood (pine) was significantly greater ($p<0.05$) at 51.2% +/- 1.5 (Lamlom, 2003). Hardwood is normally denser than softwood (Ma, 2015); therefore, one can predict that softwoods will promote higher rates of denitrification than hardwoods, due to the ability of water to better penetrate the softwood and leach out the organic carbon.

Table 2.1 outlines the type of study performed, carbon content, TOC leached, influent and effluent nitrogen concentrations, and percent nitrogen removal for each of the wood types and summarizes the averages based on hardwood and softwood groupings. If a wood type was tested in more than one study, it has multiple rows within the table to differentiate the different conditions for each study. The overall carbon content for the hardwood chips reported in Table 2.1 is significantly greater ($p<0.05$) than the softwood, 48.8% and 41.5%, respectively. The amount of leached TOC from the softwood chips was significantly greater ($p<0.05$) and almost double the amount of TOC leached from hardwood chips, 138.3 mg TOC/L and 70.3 mg TOC/L, respectively. The average influent concentration for the softwood chips was significantly higher than the average influent for the hardwood chips; however, this is an experimental parameter and not a property of the woodchip itself. The average nitrogen removal for the softwood chips was about 10% higher than the hardwood chips (not significantly), 75.2% and 63.0%, respectively.

Five out of the nine studies tested pine (softwood) as a carbon source to support denitrification (Peterson et al., 2015, Warneke 2011, Gilbert et al., 2008, Healy et al., 2011, Fowdar et al., 2015). All four reported the carbon content percentage found in pine wood chips, and three of the four values were between 46 and 49% (Peterson et al., 2015, Healy et al., 2011, Fowdar et al., 2015), one of the studies found only 28% carbon content (Gilbert et al., 2008) in the pine wood chips. These values were generally lower than the previously reported carbon content value of 51.2% +/- 1.5 for pine (Lamlom, 2003). The average amount of TOC leached from pine wood chips was 144.4% +/- 39.4 (reported in Gilbert et al., 2008 and Peterson et al., 2015). The average percent removal of nitrogen for pine wood chips was 70.1% +/- 27.2. Four of the influent concentrations for the pine studies varied from 15 mg/L to 57.75 mg/L and one had influent concentrations of 3 mg/L. The variation in both nitrogen removal and influent concentrations are due to the different applications and experimental methodology.

Eucalyptus (hardwood) was tested in two of the eight studies to examine its denitrification potential. Only one study (Lynn et al., 2015b) reported a value for the carbon content (51.2 %) and neither study reported values for leached TOC.

Table 2.1 Collected Data for Nine Different Types of Wood Chips. Type of Study Performed, Carbon Content, TOC Leaching, Influent and Effluent Nitrogen Concentrations, and Nitrogen Removal

	Wood Type	**Type of Study**	**Carbon Content (%)**	**Leached TOC (mg TOC/L)**	**Influent Concentration (mg N/L)**	**Effluent Concentration (mg N/L)**	**N – Removal (%)**	**Reference**
Softwood	Pine	Column	46.6 (0.39)	100.0	3 (0.06)	1.56	48	*Peterson et al., 2015**
	Pine	Column	-	-	15.82 (1.97)	11.09 (0.94)	29.9 (2.5)	*Warneke, 2011*
	Pine	Column	28.11	158	50	< 2.0	96	*Gilbert et al., 2008*
	Pine	Column	28.11	175.3	50	17.7	64.6	*Gilbert et al., 2008*
	Pine	Column	49.6	-	26 (9.2)	1.8	93.08	*Healy et al., 2011*
	Pine	Batch	47.0	-	57.75	6.42	88.88	*Fowdar et al., 2015*
	Coniferous	Batch	44.1	-	32.2	1.61	95.0	*Gilbert et al., 2008*
	Willow	Batch	47.2	120	32.2	4.51	86.0	*Gilbert et al., 2008*
	Average		***41.5 (9.3)***	***138.3 (34.4)***	***33.4 (18.7)***	***5.84 (5.8)***	***75.2 (24.9)***	
Hardwood	Eucalyptus	Column	51.2	-	2.33 (0.12)	BDL	100	*Lynn et al., 2015a,b**
	Eucalyptus	Column	-	-	15.82 (1.97)	9.95 (0.77)	37.1 (1.97)	*Warneke 2011*
	Maple	Column	49.3 (0.5)	42.0	3 (0.06)	1.14	61.8	*Peterson et al., 2015*
	Maple/Birch	Pilot	-	-	7.6 (1.68)	0.9 (0.27)	88.2	*Ergas et al., 2010*
	Red Gum	Batch	44.0	-	55.03	6.99	87.3	*Fowdar et al., 2015*
	Wild Cherry	Column	49.5 (0.2)	153.0	3.0 (0.1)	1.92	36	*Peterson et al., 2015*
	Oak	Column	49.6 (0.2)	41.0	3.0 (0.1)	1.2	61.9	*Peterson et al., 2015*
	Beech	Column	49.7 (0.2)	45.0	3.0 (0.1)	2.04	32	*Peterson et al., 2015*
	Average		***48.8 (2.5)***	***70.3 (55.2)***	***11.6 (18.1)***	***3.45 (3.6)***	***63.0 (26.6)***	

Standard deviation (if applicable) in parenthesis
**Study that reported ADC*

Their influent concentrations varied greatly, 2.33 mg/L and 15.8 mg/L (Lynn et al., 2015b and Warneke, 2011). The nitrogen removal efficiency values ranged from 100% (Lynn et al., 2015b) to 32.6% (Warneke, 2011).

Maple (hardwood) chips were used in two laboratory experiments reviewed for research (Peterson et al., 2015 and combination of maple and birch in Ergas et al., 2010) on bioretention systems, tested with artificial stormwater and agricultural runoff, respectively. Peterson et al. (2015) reported a total carbon content value of 49% for the maple wood chips and 42 mg TOC/L was measured that leached in the effluent; neither value (i.e., carbon content and TOC leaching) was reported in Ergas et al. (2010). The organic carbon content for maple found in Peterson et al. (2015) is similar to the value of 49.2% +/- 0.42 previously reported in Lamlom (2003). The influent total nitrogen values were measured to be 3 mg N/L (Peterson et al., 2015) and 7.6 mg N/L (Ergas et al., 2010), a smaller gap between the two studies compared to the other groups of studies, and resulted in an average nitrogen removal of 75% +/- 18.7.

Peterson et al. (2015) was the only study reviewed here that looked at the denitrification characteristics of wild cherry, oak, and beech wood chips, all categorized as hardwoods. Their organic carbon contents were relatively similar and reported as 49.53, 49.57, and 49.74%, respectively. These results compared well with the carbon content for wild cherry, oak, and beech reported in Lamlom (2003), 49.53% +/- 0.18, 49.6% +/- 0.04, and 46.6% +/- 0.39, respectively. Even though the organic carbon contents were close in percent, the amount of TOC leached from each of these three wood chip types varied greatly. Wild cherry leached the highest concentration of TOC, 153 mg TOC/L, beech leached the second highest concentration at 45 mg TOC/L and oak was the lowest but close to beech at 41 mg TOC/L. The influent total nitrogen concentrations in the water for the studies using these three wood types were the same at 3 mg N/L; however, their effluent total nitrogen values varied. The beech wood chips had the highest measured effluent nitrogen at 2.04 mg N/L (32% removal), wild cherry had the middle amount of nitrogen measured in the effluent at 1.92 mg N/L (36% removal), and oak removed the most nitrogen with an effluent measured as 1.2 mg N/L (61.9% removal).

Gilbert et al. (2008) studied the denitrification potential of seven different organic carbon source substrates, including coniferous and willow wood chips, both softwoods. The organic carbon content values reported for these wood chips were 44.09% and 47.23%, respectively (Gilbert et al., 2008). TOC leaching was only reported for the willow woodchips, 120 mg TOC/L. Their influent total nitrogen concentrations were equal, however, results show that the coniferous wood chips removed higher amounts of nitrogen than the willow chips with effluent values reported for the two systems of 1.61 mg N/L (95% removal) and 4.51 mg N/L (86% removal), respectively.

Fowdar et al. (2015) was the only study that used red gum (hardwood) chips in their column studies in comparison to pine chips and other readily available organic matter. The organic carbon content found for the red gum wood chips was approximately 44%, which is below average for a hardwood chip. There was not a reported value for the amount of TOC leached from the red gum chips. The influent concentration was the highest in the hardwood category and second highest overall, 55.03 mg N/L. The study using red gum wood chips had a nitrogen removal of 87.3%.

Moorman (2010) looked at the performance of various types of lignocellulosic material on the denitrification of agriculture wastewater. The exact wood species tested is not specified, however, it is noted that it was hardwood chips. One of the characteristics examined in this study was the degradation and wood loss of the wood chips inside the bioreactor. The study placed mesh bags filled with wood chips at different depths within the bioreactor and removed the bags to weigh them periodically and calculate the wood loss. The results from Moorman (2010) show that 50% of the wood was lost at the 90-100 cm depth and less than 13% of the wood was lost at the 155-170 cm depth. These results support the technology used in a modified bioretention system or bioreactor where the wood chip denitrification layer is continuously submerged. For portions of the study, the 90-100 cm layer became aerobic due to changes in the water table, where the deeper depths were almost continuously submerged, and there was less wood decay at those levels. The half-life for the continuously submerged wood was predicted to be around 36 years, where the wood that was exposed to oxygen throughout the study was only given a half-life of around 4 years (Moorman 2010). This information is important for denitrification systems that use wood chips as the organic carbon source. In order to elongate the life span of these systems and use less wood chips over the life of the system, the wood chips should remain submerged as much as the system allows. Since hardwood is denser, it will probably decay more slowly than softwood; therefore it is even more imperative that systems using softwood (because of their higher denitrification abilities, as seen in Table 2.1) remain submerged as well.

2.3 Wood Chip Size

Two studies examined the impact of the size of wood chips on denitrification (Cameron and Schipper 2010 and Peterson et al., 2015). The sizes analyzed were: 4, 5, 6, 9.5, 13, 15, and 61 mm and the characteristics identified were amount of TOC leached (Peterson et al., 2015), nitrogen removal (Peterson et al., 2015), and removal rate (Cameron and Schipper, 2010). The results for the different sized wood chips are shown in Table 2.2.

Table 2.2 Collected Data for Seven Different Wood Chip Sizes. Wood Chip Type, TOC Leached, Influent Concentration, and Percent Nitrogen Removal

Size	Wood chip Type	TOC Leached (mg TOC/L)	Influent Concentration (mg N/L)	N Removal (%)	Reference
4 mm (2.0)	Pine (Softwood)	-	150.0 (9)	14.4	*Cameron and Schipper, 2010*
5 mm	Oak (Hardwood)	41	3	85.4	*Peterson et al., 2015*
6 mm (3.3)	Pine (Softwood)	-	150.0 (9)	11.8	*Cameron and Schipper, 2010*
9.5 mm	Oak (Hardwood)	38	3	66.6	*Peterson et al., 2015*
13 mm	Oak (Hardwood)	34	3	68.8	*Peterson et al., 2015*
15 mm (5.3)	Pine (Softwood)	-	150.0 (9)	11.6	*Cameron and Schipper, 2010*
61 mm (19)	Pine (Softwood)	-	150.0 (9)	14.2	*Cameron and Schipper, 2010*

Standard deviation (if applicable) in parenthesis
Performed in the lab as column studies

Only one study (Peterson et al., 2015) was identified that reported the values for leached TOC from different sizes of wood chips. Their results showed that the concentration of TOC leached from the same type of wood chip decreased as the size increased, it was not specified if this increase was significant or not. It is possible that the decrease in leached TOC is due to the decrease in surface area to volume ratio, as the chip size increases. The studies both reported the total nitrogen concentration in the column influent water. Peterson et al. (2015) utilized an influent concentration of 3 mg N/L because they tested nitrogen removal using wood chips for nonpoint sources of stormwater. Cameron and Schipper (2010) had an influent concentration of 150 mg N/L because they were testing a similar application for a waste stream containing higher amounts of nutrients from point source discharges. Due to the variation in influent nitrogen concentration, the nitrogen removal also varied for these two studies. This occurs as an effect of the Monod Model. If the system has high nitrogen concentrations, the specific growth rate approaches its maximum value, and growth is effectively independent of the influent nitrogen concentration (zero-order kinetics) (Mihelcic and Zimmerman, 2014). At low nitrogen concentrations, the specific growth rate is directly proportional to the influent nitrogen concentration (first-order kinetics) (Mihelcic and Zimmerman, 2014). Overall, Peterson et al. (2015) found that columns packed with smaller wood chips had much higher nitrogen percent removal that larger wood chips, 85% compared to 68% removal. Results from Cameron and Schipper (2010) did not show any trend in total nitrogen removal based on the size of the wood chips. This could be due to high influent concentrations or experimental conditions.

One of the studies found that there was no significant difference in nitrogen removal for the different size media (Cameron and Schipper, 2010) while the second study found that the nitrogen removal was higher in the 5 mm wood chips than the larger sized wood chips, 9.5 and 13 mm (Peterson et al., 2015). The increase in the size leads to less effluent TKN and less nitrogen reduction, which resulted in less overall nitrogen removal (Peterson et al., 2015). The larger chips have a smaller total surface area per mass, which leads to less contact with the water and limits the availability of the carbon for the denitrifying organisms and provides less surface area for the biofilm growth (Peterson et al., 2015).

Smaller wood chips have a larger surface area per unit volume, resulting in greater contact between the surface of the wood chip with the water and therefore, potentially greater leaching of DOC which is measured as TOC (Lopez et al., 2016b).

2.4 Literature Summary and Knowledge Gaps

Overall, there are differences in the performance of various wood chips sizes and types when used for denitrification in a system such as a modified bioretention system. While these studies summarized carbon content, amount of TOC leached, influent and effluent nitrogen concentrations, and nitrogen removal, there are gaps in the information being presented in this set of research. None of the studies reviewed in this section reported information about the half saturation constant (K_S), which is an important parameter for denitrification of water with low nitrogen concentrations. Additionally, only two studies (out of nine) discuss the size of wood chips and their effect on denitrification.

Only two of the studies reviewed here reported their ADC value. One study was performed in the laboratory and its primary purpose was not to examine the effects of the ADC on nitrogen removal; therefore, the value of the ADC was the same for each experiment (i.e., ADC of seven days) (Peterson et al., 2015). The second study was also a laboratory column study and it differed from Peterson et al. (2015) because it had a goal of testing different ADC's. Therefore that study (Lynn et al., 2015a) provides us with laboratory data on the effect of varying ADCs for an anoxic zone like designed for an IWSZ (Lynn et al., 2015a). That particular study used eucalyptus wood chips and demonstrated that as the ADC increased from 0 to 4 to 8 to 16 to 30 days, the nitrate removal efficiencies increased (Table 2.3).

Table 2.3 Nitrogen Removals for Differing Antecedent Dry Conditions (Lynn et al., 2015a)

	NO_3^- – N	**TN**
Influent (mg/L)	2.14 (0.51)	2.5 (0.5)
ADC	% Removal	% Removal
0	86	66.5
4	96	75
8	97	76
16	97	79
30	97	75

Igielski (2016) (not published) carried out research that focused on nitrogen removal with variable flow rates and HRTs. That research found that nitrogen removal decreased as the HRT decreased and the influent flow rate increased (Table 2.4).

Table 2.4 Percent Nitrogen Removal with Variable HRTs and Influent Flow Rates (Igielski, 2016)

Influent Flow Rate (mL/min)	HRT (hr)	Average Nitrogen % Removal
11	1.82	41.50
22	0.91	39.29
38.5	0.52	14.50

Kim et al. (2003) states that there are two main purposes of using a lignocellulosic media to promote denitrification; to provide a electron donor and long-lasting carbon source and perform as a base/support for a microbial biofilm. Furthermore, biological denitrification is enhanced with an anoxic zone comprised of water with a dissolved electron donor (DOC leached from the wood chips), the goal is to obtain a long enough contact time so the denitrifying bacteria can respire NO_3^- (Lynn, 2014). The IWSZ layer in a modified bioretention system is designed for this purpose, to help enable the denitrification process. In order to better understand this technology and the factors that influence its performance, these three areas need to be explored further.

CHAPTER 3: MATERIALS AND METHODS

3.1 Field Site and System Description

The field site for this study is located in East Tampa, FL at the Audrey L. Spotford Youth and Family Center, a part of the Corporation to Develop Communities (CDC) of Tampa, Inc. The space around the bioretention cells has a 'mixed urban land use', containing a church, car wash, a laundromat, and residences. Stormwater runoff from the East Tampa region directly drains to a section of Tampa Bay; therefore, bioretention systems located in East Tampa should reduce nutrient loading to the bay (Locicero, 2015).

At the field site there are two full-scale bioretention cells, constructed next to each other in parallel, located in a grassy area between the Spotford building and parking lot (Figures 3.1 and 3.2). The cells were constructed inside a wooden frame and are enclosed by an impermeable liner, to help ensure the consistency of the volume of water entering and leaving the cells; additionally, there are PVC pipes to drain the effluent to the groundwater and that are configured for effluent sampling. Each cell has a surface area of 0.56 m^2, depths that vary by 30 cm (the IWSZ layer in the modified cell), and a ponding volume of 2.54 m^3. Plastic gardening liners were used to outline the top of each cell to allow for ponding to occur.

Figure 3.1 Bioretention Cells at the Corporation to Develop Communities, Audrey L. Spotford Youth and Family Center (Tampa, FL)

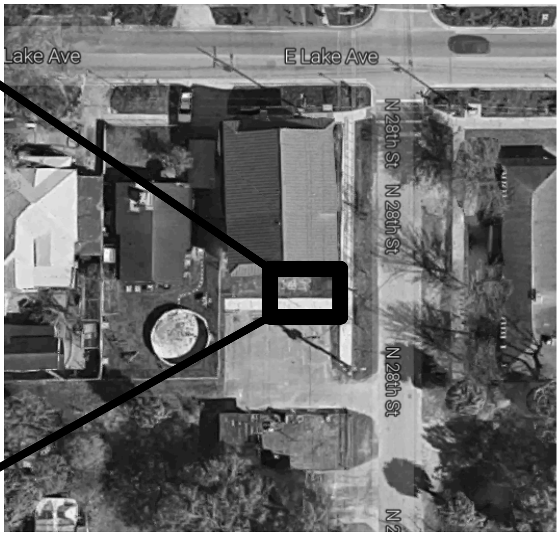

Figure 3.2 Aerial View of Location of Bioretention Cells Near the Audrey L. Spotford Youth and Family Center. (Google Maps)

The deeper cell (modified system) is designed to enhance denitrification by including an IWSZ in the design, compared to the conventional system that does not contain an IWSZ. Both cells (Figures 3.3 and 3.4) have a top layer consisting of 0.3 m of 250 paver sand, a second layer of 0.05 m of pea gravel, and a bottom layer, containing the underdrain, of 0.3 m of #57 limerock. The modified cell has the IWSZ located between the pea gravel and limerock layers. The IWSZ is 0.3 m of a 2:1 (by volume) mixture of pea gravel (0.6 to 1.3 cm in diameter) and eucalyptus (softwood) wood chips (1.3 to 2.5 cm in length) with a porosity of 0.42.

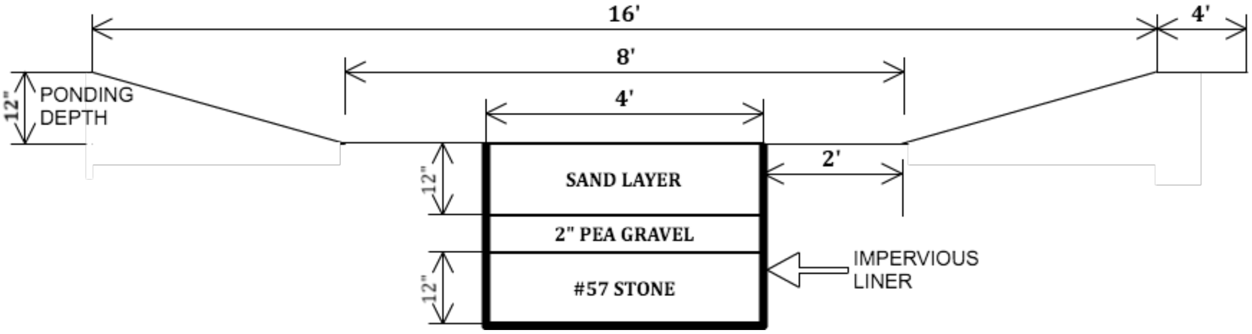

Figure 3.3 Conventional Bioretention Cell Schematic (with permission of Tom Lynn)

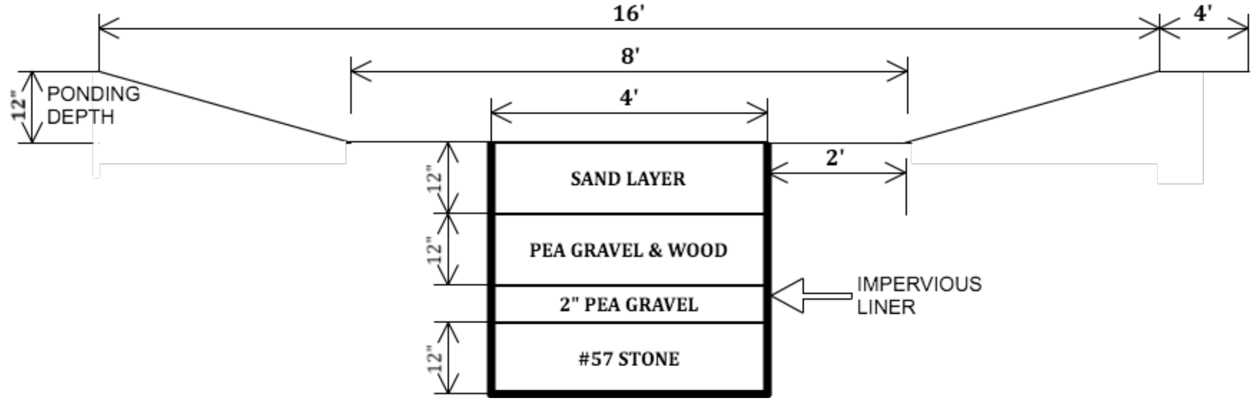

Figure 3.4 Modified Bioretention Cell Schematic (with permission of Tom Lynn)

3.2 Storm Events and ADC Calculations

Fourteen man-made storm events (Table 3.1) were completed over the period of January 2016 to July 2016 using HLRs of 6.9 cm/h, 13.9 cm/h (Lynn, 2014; Lynn et al., 2015b), and 4.1 cm/h HLR (Davis et al., 2006). These HLRs were selected because previous studies (Lynn, 2014; Lynn et al., 2015b, Davis et al., 2006) used the same HLRs in bench scale lab experiments. By using the same HLRs for this field study, the data can later be compared to the lab studies.

Table 3.1 Date, ADC, Duration, and HLR for the Fourteen Storm Events

Date	Storm Event	Duration (hr)	HLR (cm/hr)
1/18/16	1	4	6.9
1/26/16	2	2	13.9
2/2/16	3	2	4.1
2/9/16	4	2	13.9
3/8/16	5	4	6.9
3/17/16	6	6	4.1
3/24/16	7	4	6.9
4/7/16	8	4	6.9
4/19/16	9	4	13.9
4/29/16	10	6	4.1
5/5/16	11	4	13.9
5/19/16	12	4	13.9
6/22/16	13	6	4.1
7/21/16	14	6	6.9

Some storm events were carried out using different HLRs, but with consistent ADCs, while other events had both various loading conditions and ADCs. For this research, the ADC refers to the number of days with less than 1.9 centimeters of rain between storm events. The rainfall data was gathered from USGS gauge 275917082222500, East Lake at Orient Road in Tampa, FL. The rain requirement to calculate the ADC was computed by the amount of water required to flush out 15% of volume of water in the IWSZ. This number was determined after testing different 'flush amounts' (Appendix B, Tables B.1 – B.5). This analysis showed that 10% was too small to count as a storm event and "flush amounts" greater than 20% did not generate clear breaks in the data. The total volume (V_T) and porosity ($\emptyset$) of the IWSZ are 0.17 m^3 and 0.42, respectively, and using these numbers the IWSZ void volume (V_V) was calculated as follows.

$$V_V = \emptyset \times V_T$$

Equation 3.1

The void (pore) volume calculated for the IWSZ was 0.071 m^3, therefore 15% of the pore volume (0.011 m^3) needs to be flushed out of the system to count as a "storm event" for the purpose of this research. Because rainfall data is available in inches, the surface area of the system was used to calculate how many inches of rain would generate the volume of water needed. The surface area of the system (SA) is 0.557 m^2 and 15% of the pore volume (V) is 0.011 m^3. Using this information we can calculate the rainfall (in) required to displace 15% of the water inside the IWSZ as follows.

$$\frac{V}{SA} = h = \frac{0.011\ m^3}{0.557\ m^2} = 0.019\ m = 1.9\ cm$$

Equation 3.2

A limitation of this study is the ADC is determined based on the previous storm event of at least 1.9 cm (displacing 15% of the IWSZ).

3.3 Synthetic Stormwater Composition

Synthetic stormwater, simulating nitrogen levels found in urban runoff, was used as the system's influent to assist in running a controlled experiment. The characteristics of the synthetic stormwater are presented in Table 3.2 and resulted in water quality that is similar to other studies (Davis et al. 2001; Lynn 2014; LeFevre et al. 2014; Lynn et al., 2015b). One stock solution of chemicals was prepared for each rain barrel using deionized (DI) water. Live Oak tree leaves were ground with a Mr. Coffee™ (Model no. IDS55-RB) grinder in the laboratory, for about a minute, until they reached a powder-like consistency. Nine grams of ground tree leaves were measured out and a small tea bag was formed using cheesecloth and string. The leaf tea bag was then placed into 800 mL of DI water overnight; this was to ensure that the leaf particles would not sink to the bottom of the rain barrels when added and that dissolved organic nitrogen would be mixed in with the synthetic stormwater. The bottles with both parts of the synthetic storm water were then brought to the field and mixed with tap water in the 55-gallon rain barrels immediately before running a storm event experiment.

Table 3.2 Synthetic Stormwater Chemical Make-up (adapted from Harper and Baker (2007) and LeFevre et al. (2014)) (Lopez et al., 2016a)

Pollutant	**Target Concentration** (mg/L) (as N)	**Chemical**
Nitrate (NO_3-)	1	Potassium nitrate (KNO_3)
Organic N	1	Ground Live Oak tree leaves*
Ammonium (NH_4+)	1	Ammonium chloride (NH_4Cl)
Total N	3	

**Ground Live Oak tree leaves collected at the University of South Florida (Tampa)*

3.4 Experimental Set–Up

Storm event experiments were conducted between January 2016 and July 2016, with the goal of obtaining results with varying ADCs. The goal was to have results from storm events with ADCs of two, four, and eight days. Additionally, the storm events varied in lengths of two, four, and six hours and in influent flow rates of 381, 641, and 1,291 mL per minute. For each storm event, the weather was checked to obtain the set ideal ADC (initially ADCs of 2, 4, and 8 days were targeted based off of 0.1 in of rainfall to count as a storm event) and to avoid running an experiment on a day where a natural storm event would occur. The synthetic stormwater was made in the laboratory 1-2 days prior to an experiment, stored in clean (acid washed) Nalgene bottles at room temperature, then brought to the field, and mixed in with the tap water in the rain barrel(s), depending on how much water was needed for that specific storm event based on duration and flow rate.

Two pieces of tubing (Masterflex 6404 – 18) ran from inside the rain barrel, through the pump (Cole-Palmer Masterflex L/S, model no. 07528-10 with Easy-load II pump drives, model no. 77200-50) connected to a second set of tubing (Masterflex 3/8"), then a third set of tubing (Masterflex 6424 – 18) containing the valve to take influent samples, and then a third set of tubing (Masterflex – 3/8" inside diameter, vinyl) and out onto the top of each cell (Figure 3.5). The tubing over the cell was perforated with holes one inch apart, using the tip of a hot glue gun (Adhesive Tech™ Model no. 1200) to penetrate the plastic, so the water would be spread out evenly across the top of the cell. Once the desired flow rate was reached for the pump, the second set of tubing was connected to the first so the water would begin to flow from the rain barrel to the tops of both bioretention cells. Throughout the experiment, influent samples were collected from a port in the tube, along with effluent samples pumped (using a Solinst peristaltic pump, model no. 410) from the sample port in both cells (shown in Figure 3.5).

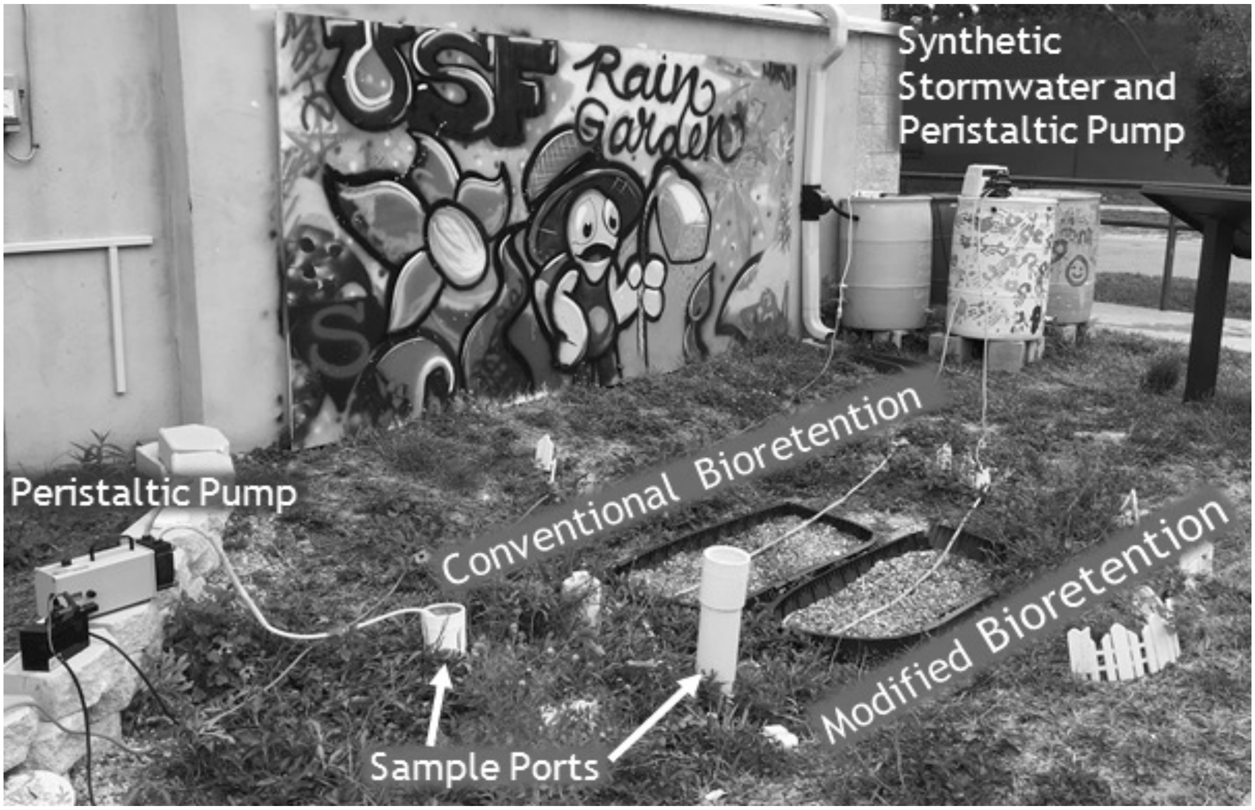

Figure 3.5 Field Site Set-Up (with permission of Emma Lopez)

3.5 Laboratory Methods

100 mL of influent and effluent samples were collected from each bioretention cell at pre-determined time intervals (approximately every 20 or 30 minutes, depending on the experiment) in high-density polyethylene (HDPE) plastic bottles and directly placed in a cooler with ice packs at 5 °C. After the field experiment, the samples were immediately transported to the environmental engineering laboratory at the University of South Florida, where they were then prepared and refrigerated according to Standard Methods (APHA, 2012). NO_x – N and NH_4^+– N were measured by the diffusion conductivity method using a

Timberline Ammonia Analyzer (Ammonia-001, USEPA ATP No. N08-0004). TN was measured for storm events one through seven using the HACH persulfate digestion method (Method 10208). For storm events eight through fourteen TN was measured with a Shimadzu TOC-V CSH Total Organic Carbon / Total Nitrogen Analyzer (Shimadzu Scientific Instruments, Columbia, Maryland). Method detection limits for TN and NO_x – N/NH_4^+– N were 0.03 and 0.014 mg/L, respectively. Organic nitrogen was calculated by subtracting total inorganic nitrogen (TIN) from the TN measurement. All bottles and glassware used for analysis were submerged in an acid bath for a minimum of two hours and triple rinsed with deionized (DI) water prior to use. DI water was used in every washing and testing procedure and a field blank was used in all analyses for each experiment. A set of standard chemicals from the stock of known N species concentration was run along with each set of samples and one was placed after every ten samples analyzed for NO_x – N, NH_4^+ - N, and TN to confirm accuracy of methods and instruments.

3.6 Data Analysis

The results from all fourteen storm events were grouped based on HLR and their durations were made identical for each group. This was done to compare the difference in ADC without influence from the other two variables, which have been known to effect nitrogen removal as well. The nitrogen removals for each grouping of storm events were graphed for each of the four nitrogen species (NO_x – N, NH_4^+ - N, organic N, and TN) to compare the differences in nitrogen removal. Once these groups and percent removals were obtained, statistical analysis was carried out to determine if the results based on the differences in ADC were significant or not. For this experiment the level of significance was

95%, so the p-value was set at 0.05, as traditionally done in scientific experiments (Hypothesis Testing, 2013). This means that results with a p-value below 0.05 were deemed significant and results with a p-value above 0.05 were not significant. The statistical analysis included calculating the standard deviation (S), number of experiments (N), S^2/N, variance, t-score, degrees of freedom, significance level, and p-value (MS Excel). Based on these results, it was determined if a longer or shorter ADC affects nitrogen removal in a modified bioretention system.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Comparison of Conventional and Modified Results

The system containing the conventional bioretention cell, which did not contain an IWSZ (full storm event data for the conventional cell in Appendix A, Table A.4), had lower removals of all five nitrogen species than the modified cell (IWSZ) (Figure 4.1). As shown in this figure, the nitrate/nitrite – nitrogen removal was significantly higher for the modified cell compared to the conventional cell, 78.5% +/- 19.9 and 29.5% +/- 25.2, respectively. Additionally, the modified cell had significantly greater removal of ammonium – nitrogen than the conventional cell, 82.4% +/- 8.7 and 70.1% +/- 18.2, respectively. The difference in organic nitrogen removal was not significant, although the modified cell removed more than the conventional cell, 50.2% +/- 26.4 and 36.3% +/- 34.9, respectively. This is to be expected as the transformation of organic nitrogen is by a hydrolysis reaction (see Equation 2.1 in Chapter 2) and both bioretention systems provide conditions for this reaction. As a sum of the previous nitrogen species, total nitrogen removal efficiency was observed to be significantly higher for the modified cell. The higher levels of nitrate/nitrite – N removal in the modified cell are to be expected due to the IWSZ layer where denitrification occurs because of the anoxic conditions expected in that area and the availability of an organic carbon substrate (TOC leaching from the wood chips) that serves as the electron donor. It is also expected that the ammonium removal levels for both systems would be similar due to the majority of ammonium being converted through nitrification in the sand layer (located in both systems). However, ammonium is also converted through assimilation (nitrogen uptake) and adsorption. Assimilation can occur in both the sand and IWSZ layers because there is microbial biomass growing in both locations, potentially leading to additional removal for the modified system.

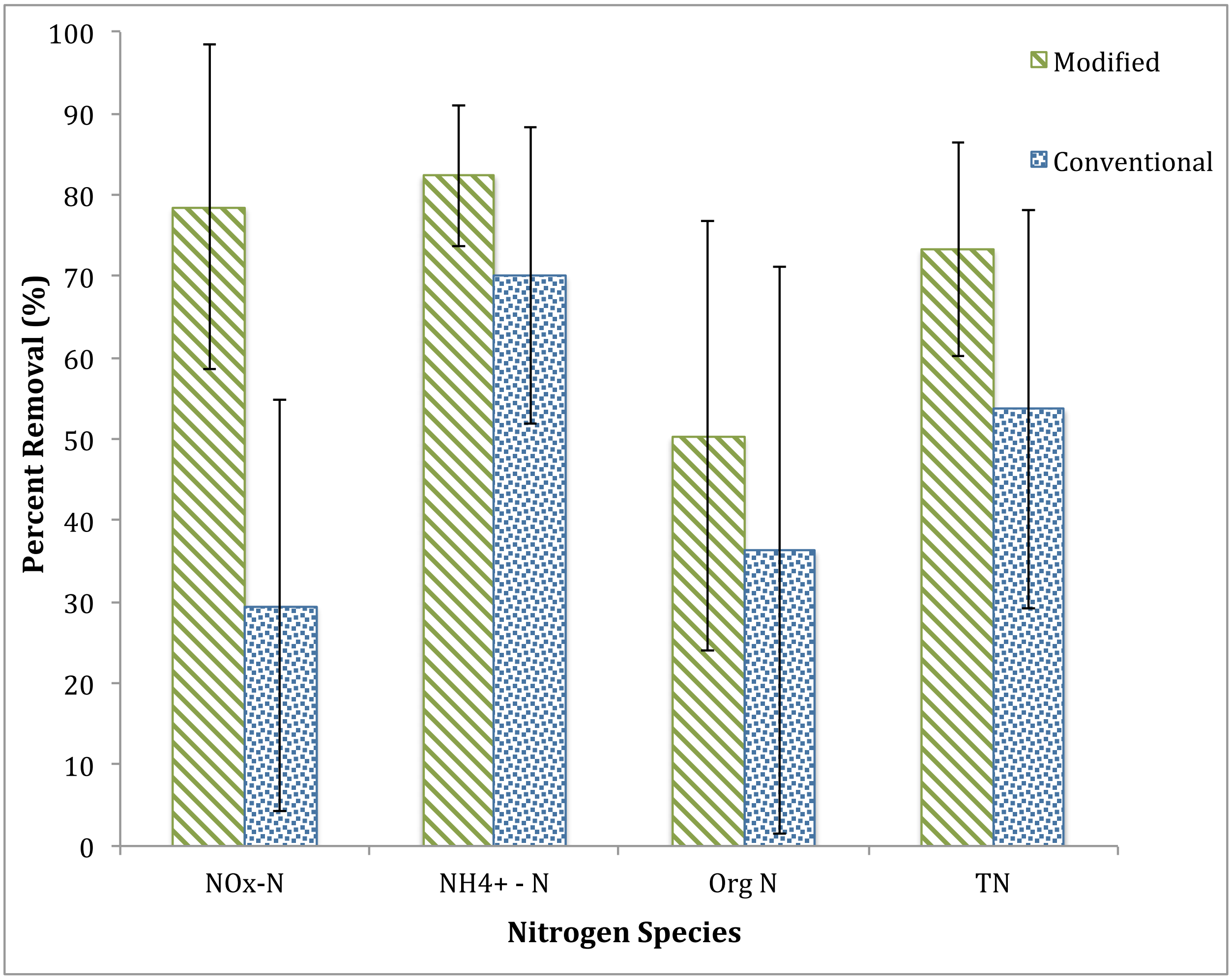

Figure 4.1 Modified and Conventional Nitrogen Percent Removal Results. NO_x – N, NH_4^+ – N, Organic N, and TN

For the conventional cell, none of the storm events removed more than 58% of NO_x – N and two storm events had negative NO_x – N removal, there were higher levels in the effluent than the influent. This may have occurred due to nitrification taking place within the sand layer of the conventional system, ammonium – nitrogen is converted to nitrate/nitrite – nitrogen, and there is no anoxic zone for denitrification which results in greater amounts of nitrate/nitrite – nitrogen in the effluent streams than the influent. The highest amount of nitrogen removal for the conventional cell was in the form of ammonium – nitrogen at 70.1 +/- 18.2%. This is due to the fact that nitrification takes place in the sand layer of a bioretention system and this is the location where it is expected that the majority of ammonium be converted to nitrate. As previously mentioned, ammonium could also be removed through assimilation or adsorption, both of which can occur in the sand layer of the conventional cell. In a conventional system, the chemical species nitrate is not provided appropriate conditions to expect a high amount of denitrification. Based on these results, in was concluded that total nitrogen removal for the modified system is significantly greater than removal in a conventional system, where there is no anoxic zone or supplementary electron donor (carbon substrate) to promote denitrification.

4.2 ADC Calculations and Rainfall Data

Storm event and ADC details are shown in Table 4.1. The ADCs ranged from 0 to 33 days in between storm events and the amount of water replaced in the IWSZ ranged from 35.5% to 100%. All of the storm events with 100% water replacement were man-made. In the previous chapter the antecedent ADC was calculated to displace 15% of the IWSZ water. It was consequently defined as the number of days with less than 1.90 cm of rain between storm events (Lopez et al., 2016a). Precipitation was determined using USGS gauge 275917082222500, which is located 3.43 miles (via Google Maps) northeast of the field site.

Table 4.1 Antecedent Dry Conditions for the Fourteen Storm Events. Conducted at the Field Site in East Tampa

Storm Event	Date of Field Trial	Previous Storm Event	Previous Storm Rain Amount (cm)*	Water Replaced (%)	ADC (days)
1	1/18/16	1/17/16	6.27	49.0	0
2	1/26/16	1/18/16	27.58*	100	7
3	2/2/16	1/28/16	2.87	22.4	4
4	2/9/16	2/2/16	8.20*	64	6
5	3/8/16	2/24/16	4.55	35.5	12
6	3/17/16	3/8/16	27.58*	100	8
7	3/24/16	3/17/16	24.61*	100	6
8	4/7/16	4/2/16	5.08	39.7	4
9	4/19/16	4/7/16	27.58*	100	11
10	4/29/16	4/19/16	55.60*	100	9
11	5/5/16	5/4/16	5.82	45.4	0
12	5/19/16	5/17/16	2.41	18.8	1
13	6/22/16	5/19/16	55.60*	100	33
14	7/21/16	6/22/16	24.61*	100	28

**previous storm event was a human generated storm event*

4.3 Overall Modified System Removal Results

There were four different nitrogen species data sets obtained for both the influent and effluent water samples. The fourteen sets of influent samples were averaged to obtain average influent concentrations for the synthetic stormwater and these values were used when calculating the percent nitrogen removal for all four nitrogen species (NO_x – N, NH_4^+ - N, organic N, and TN). The average influent concentrations, across all fourteen storm events, were 1.07, 1.53, 0.60, and 2.80 mg N/L, respectively. The influent concentrations for each individual storm event can be found in Appendix A, Table A.1.

The results showing the influent and effluent concentrations, and percent removal for the storm events are shown in Table 4.2. Out of the four nitrogen species, ammonium – nitrogen had the highest percent removal at 82.4 % +/- 8.7. There are a few ways that ammonium can be transformed: nitrification, nitrogen uptake, and adsorption. Nitrogen uptake can occur when ammonium is converted into microbial or plant biomass and temporarily stored as organic N. Because there are no plants in the systems for this research, the microorganisms growing inside the cell on the different layers would be the only way that uptake would occur. Second, adsorption can remove ammonium when there are negatively charged particles such as clay or metallic coatings on soil particles, since neither of these materials is believed to be extensively present in the designed system, ammonium is not thought to removed through adsorption in large amounts.

In the bioretention cell, nitrification is expected to occur in the sand layer, and through nitrification, ammonium is converted to nitrite and then nitrate. This is one explanation for why there is good removal of ammonium in both systems and less (not significant) removal of nitrate/nitrite – nitrogen than ammonium – nitrogen in the conventional bioretention system, 78.5 % +/- 19.9. The IWSZ in the bioretention cell is designed to contain an organic carbon (i.e., the wood chips) and be always saturated with water; therefore it is expected to maintain anoxic conditions, which is ideal for denitrification. The denitrification reaction uses a carbon substrate (TOC leached from the wood chips) as the electron donor. The nitrate serves as the electron acceptor and, over the two chemical species, is converted into nitrogen gas and carbon dioxide. This IWSZ is the process where the majority of the nitrate/nitrite is expected to be removed in the system. Because nitrification, adsorption, and assimilation uptake nitrogen but do not remove nitrogen from the system, denitrification is the only process under these conditions that is expected to remove nitrogen from the from the biorentention system.

The lowest percent nitrogen removal observed in both systems (see Figure 4.1) was for organic N, 50.2 % +/- 26.4 in the modified system and much lower in the conventional system. When the influent water enters the bioretention cell, it already contains organic nitrogen that was part of the synthetic stormwater. Organic nitrogen can undergo ammonification, where the organic nitrogen is transformed to ammonium and then resulting ammonium can become nitrified through nitrification. This is the main way that organic nitrogen is removed in the bioretention system; however, there are storm events where the organic nitrogen in the effluent stream was observed to be greater than the influent (Appendix A, Table A.3). This is most likely because the wood chips in the IWSZ leach not only TOC into the system but can also leach organic nitrogen into the system. This can pose a complication for the system, since the carbon substrate is necessary to perform high levels of denitrification, however, these wood chips can contribute extra organic nitrogen to the system. This occurs in the system hydraulically after the layer where ammonification and nitrification are expected to occur; therefore, organic nitrogen leached into the water in the IWSZ may also leave the system in the effluent stream before it has time to be transformed to ammonium.

For the purpose of this analysis, the effluent concentrations used for the percent removal for each storm event are the averages for the effluent over the entire course of the storm event. It is important to know that nitrogen removal (in all forms) does not remain constant over a period of 2, 4 or 6 hours and the removal also differs with the variation in HLR. Figures 4.2 and 4.3 show nitrogen removal over time for two example storm events simulated in the field demonstration with different HLRs of 13.9 and 6.9 cm/hr and durations of 2 and 4 hours.

Table 4.2 Storm Event Results for Modified System: Nitrogen Removal by Species. Percentages calculated using averages of effluent samples throughout storm events (mg N/L)

Storm Event	ADC (d)	NO_x – N % Removal	NH_4^+ – N % Removal	Organic N % Removal	TN % Removal
Influent (mg/L)		1.07 (0.47)	1.53 (0.38)	0.60 (0.29)	2.07 (0.66)
1	0	91.6	89.9	9.3	72.7
2	7	69.3	83.6	43.8	68.9
3	4	99.7	61.3	75.6	73.5
4	6	64.4	78	54.1	64.5
5	12	93.2	93.4	56.6	88.9
6	8	98.6	90.8	50.9	83.8
7	6	92.5	75.7	55.4	76.8
8	4	86.8	86.9	62.7	76.8
9	11	62.9	79.3	64.5	66.9
10	9	98.3	85.1	79	86.8
11	0	27.8	79.4	32.1	46.6
12	1	68.4	72.9	37.3	59.6
13	3	71.7	86.6	-8.3	64.2
14	4	74.1	90.1	89.2	96.5
Average % Removal		*78.5 (19.9)*	*82.4 (8.7)*	*50.2 (26.4)*	*72.5 (9.13)*

Standard deviation (if applicable) in parenthesis

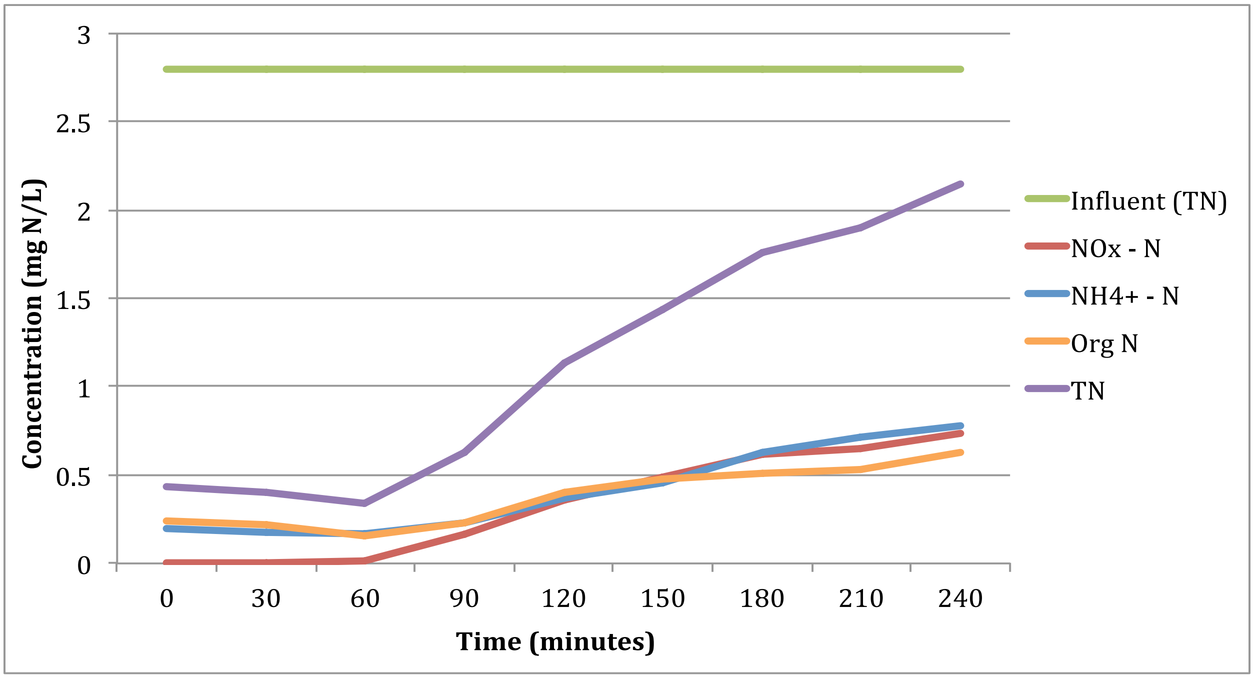

Figure 4.2 Storm Event 12: NO_x – N, NH_4^+ - N, Organic N, and TN Effluent Concentrations Over Time. (ADC: 1 day, HLR: 13.9 cm/hr, Duration: 4 hr)

The most noticeable difference between the two figures is the effluent concentration at the end of the storm event. For the four hour storm event, the effluent total nitrogen concentration was observed greater than 2 mg N/L and was approaching the influent total nitrogen value of 2.79 mg N/L. For the two hour storm event the last effluent sample was still below 0.5 mg N/L, this probably also had to do with the ADC of 12, compared to the ADC of 1 for the four hour storm event. Additionally, the HLR could factor into the amount of nitrogen removed for these two storm events. Figure 4.2 showed a storm event with a HLR of 13.9 cm/hr and Figure 4.3 shows a storm event of 6.9 cm/hr. The lower the HLR is, the longer contact time the stormwater has inside the IWSZ, therefore it is expected there is a greater amount of time in the IWSZ for denitrification to occur.

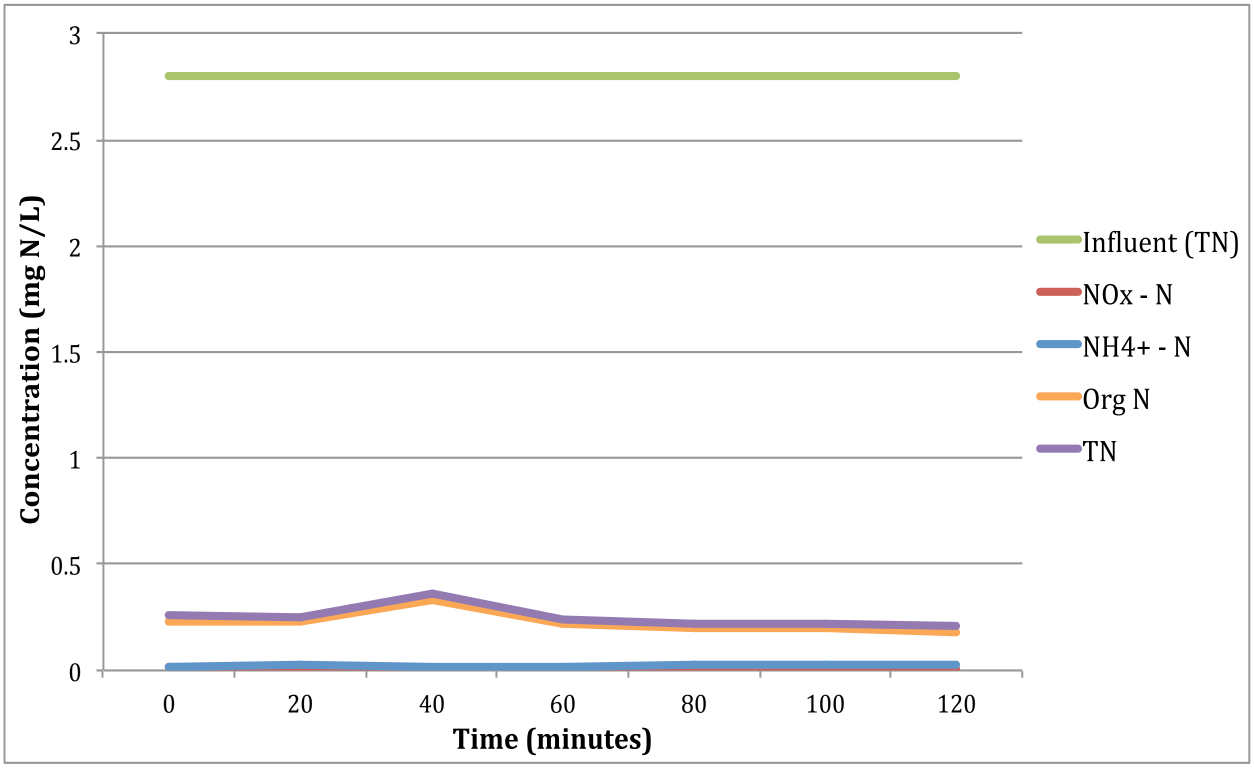

Figure 4.3 Storm Event 5: NO_x – N, NH_4^+ - N, Organic N, and TN Effluent Concentrations Over Time. (ADC: 12 days, HLR: 6.9 cm/hr, Duration: 2 hr)

4.4 Conventional and Modified System Removal Results Based on ADC

The fourteen storm events had varying HLRs and durations. Previous research (Igielski (2016) (not published), Lynn 2014) has shown that both of these variables can affect nitrogen removal in bioretention systems. In order to obtain results that were only dependent on ADC, the storm events were broken up by HLR and the durations were shortened (if necessary) to control both of these additional variables. The same modifications were made to both conventional and modified data in order to look at what could theoretically be entering the IWSZ in the modified cell, based off of the effluent from the conventional cell. Statistical analysis was performed for all three sets of data (Appendix C, Tables C.1 – C.3).

There were four storm events tested using the low HLR (4.1 cm/hr), three of these storm events had a duration of 6 hours while one storm event only lasted for two hours. To keep the data from being skewed by a variable other than the ADC, all four storm events were studied for just the first two hours of the storm event and results were shorted for the three longer events. The four storm events had ADCs of 4, 8, 9, and 33 days. Figure 4.4 illustrates the nitrogen removal results for these four storm events. All four storm events with the HLR of 4.1 cm/hr had high NO_x – N removal, average of 97.7% +/- 0.02, however the ADC did not seem to affect NO_x – N removal for these four storm events. Generally for the other two individual nitrogen species and total nitrogen, the nitrogen removal increased with ADC. The experiment with a four day ADC had a significantly lower NH_4^+ – N removal efficiency than the experiment with a 33 day ADC (61.5% and 93.2%, respectively). Organic nitrogen removal increased for the first three experiments (ADCs: 4, 8, and 9 days) but had a negative removal for the experiment with the longest (33 day)

ADC. Since the ADC was over a month long for this storm event, one possible explanation is that even though there was enough time for denitrification to occur, there was more time for organic N to leach from the wood chips and mix with the water in the IWSZ. The TN results had similar results, consistently showing better removal of TN with increasing ADC, until the storm event with the longest ADC (i.e., 33 days).

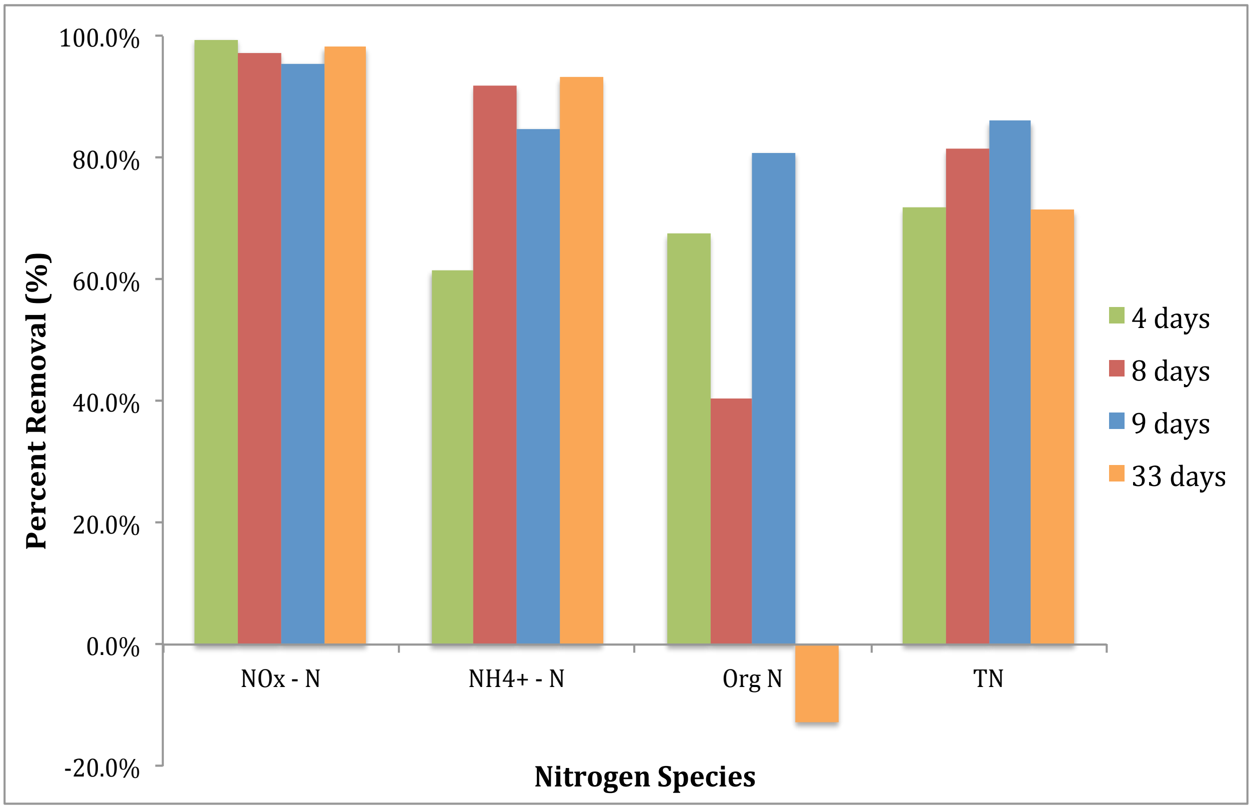

Figure 4.4 Percent Nitrogen Removal for Different ADC for Storm Events with a HLR of 4.1 cm/hr and Two Hour Duration. (ADCs: 4, 8, 9, and 33 days)

Out of the five storm events that were conducted using the midrange HLR (6.9 cm/hr), four of the storm events lasted four hours and one of the storm events lasted six hours. These five storm events can be compared equally by using the first four hours of nitrogen removal data for the fifth storm event, and all of the data from the other four storm events. This was done in order to eliminate the effect of HLR and storm duration on examination of the ADC nitrogen removal data. These storm events had four different

ADCs of 0, 4, 6, and 12 days. Figure 4.5 illustrates the results from these five storm events. The effluent nitrogen was averaged throughout the four hour storm event and percent removal calculated by using the average influent concentrations presented in Table 4.2.

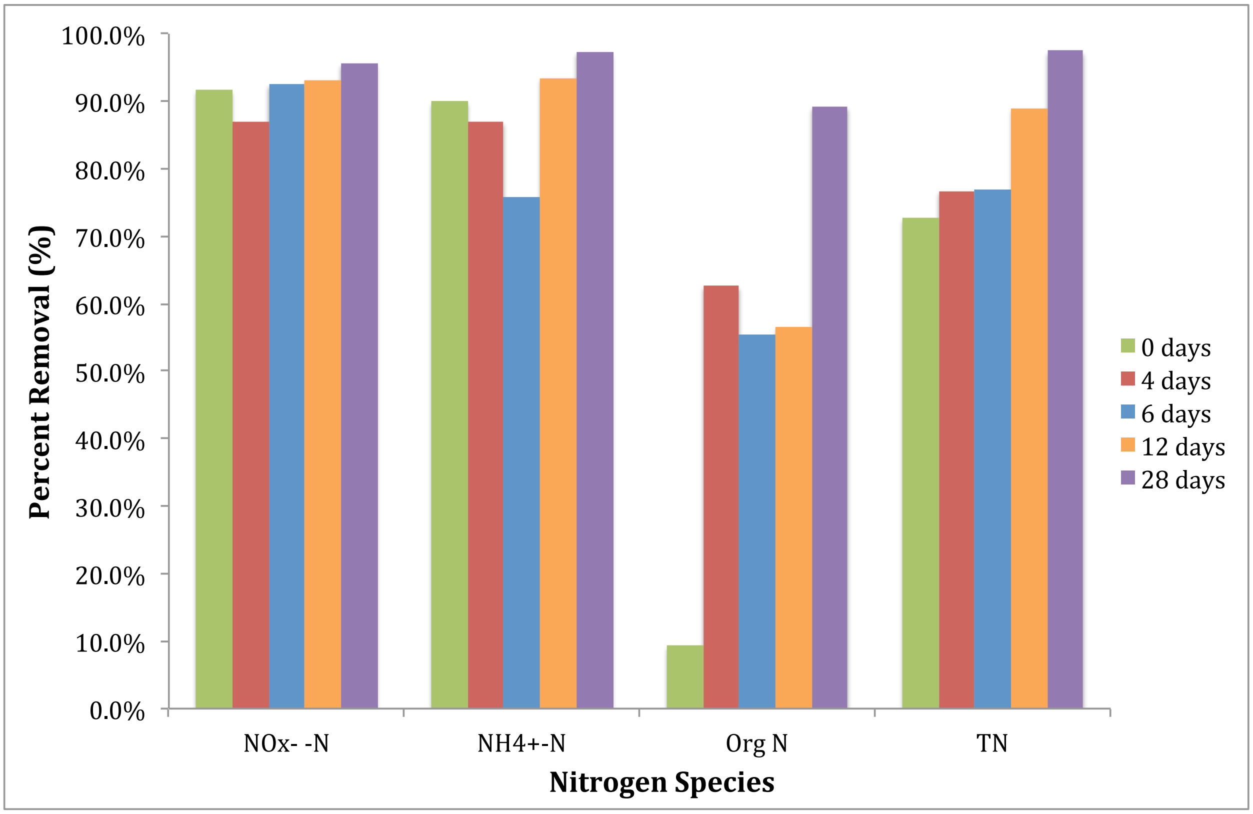

Figure 4.5 Percent Nitrogen Removal for Different ADC for Storm Events with a HLR of 6.9 cm/hr and Four Hour Duration. (ADCs: 0, 4, 6, 12, and 28 days)

The results in Figure 4.5 show that as the ADC increased, the nitrogen removal for all four nitrogen species also increased, though the increase is not large for ammonium – nitrogen and nitrate – nitrogen species. Total nitrogen, although simply a sum of the other three species, shows the most incremental increase as the ADC also increased. The percent nitrogen removal for the storm event with a 28 day ADC was significantly ($p<0.05$) greater than the storm event with a 0 day ADC for NH_4^+– N, Organic N, and TN. The NO_x – N removal results for the 28 day ADC storm event were greater than the removal results for the 0 day ADC storm event, however they were not significant ($p>0.05$). The overall trend for the TN data showed that the ADC increasing for storm events with an HLR of 6.9 cm/hr, also increases the nitrogen removal rate.

There were five storm events conducted at the highest HLR (13.9 cm/hr), three of these storm events were conducted for six hours and two of the storm events were conducted for two hours. As in the previous two cases, the data from the longer storm events was shortened to only include the first two hours to eliminate these variables from the ADC results. These five storm events had ADCs of 0, 1, 6, 7, and 11 days, the percent nitrogen removal results are presented in Figure 4.6.

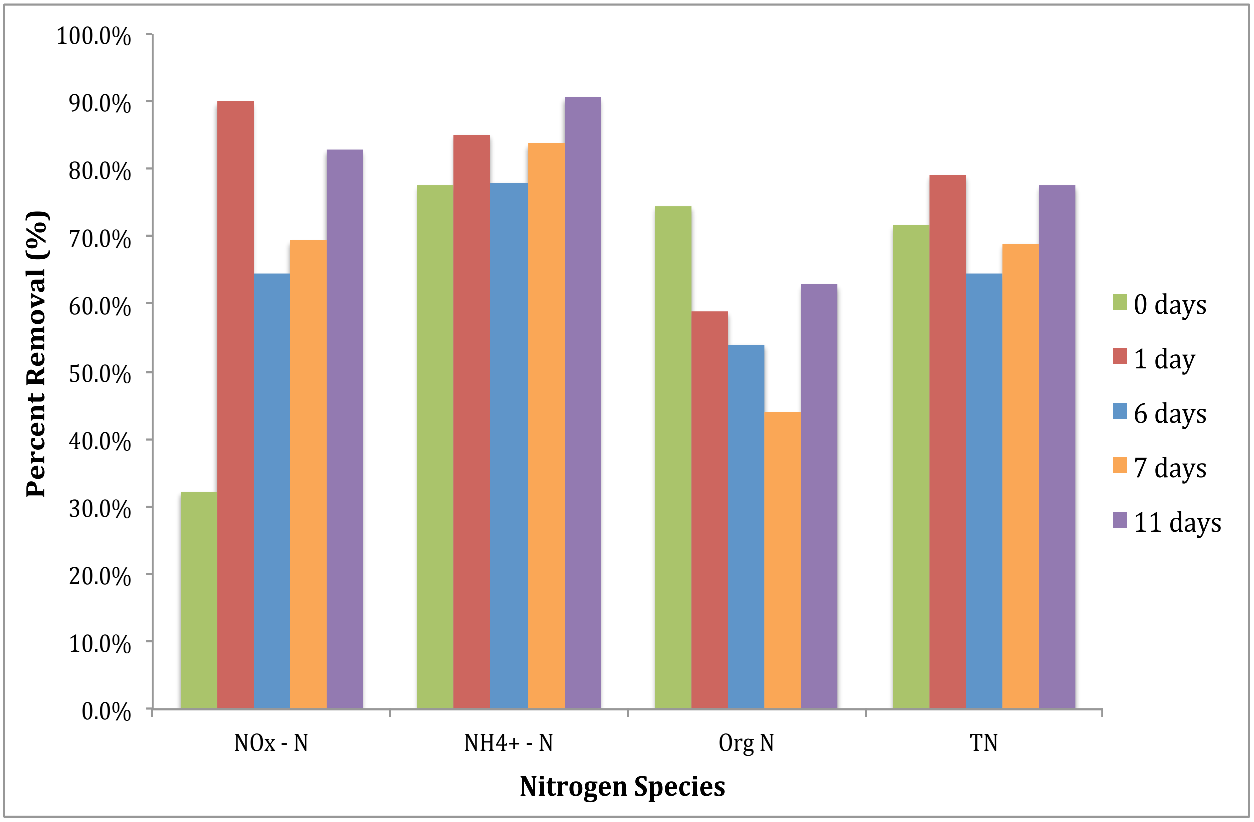

Figure 4.6 Percent Nitrogen Removal for Different ADC for Storm Events with a HLR of 13.9 cm/hr and Four Hour Duration. (ADCs: 0, 1, 6, 7, and 11 days)

Since these five storm events were carried out with the highest HLR, their overall removals differ from the removal efficiencies of the other two groups of storm events. Research (Lynn et al., 2015a) has shown that a greater HLR results in less nitrogen removal (for all forms of nitrogen) than a lower HLR. We can see this from the results that have been presented here (Figures 4.4, 4.5, and 4.6). The greatest amounts of nitrate/nitrite – nitrogen were removed in the first group, Figure 4.4. This is presumably due to the lowest HLR and therefore, the water having a longer contact time inside the IWSZ.

For all three sets of storm events conducted at various HLRs (4.1, 6.9, and 13.9 cm/hr) and lengths (2 and 4 hrs), the data suggested an increasing trend in TN removal as the ADC increased. The data from the three different groups of ADC should be examined further to investigate the effect of HLR on nitrogen removal and ADC. Some of the nitrogen removals increased significantly, such as the group of storm events carried out with a HLR of 6.9 cm/hr. The TN removal increased significantly ($p>0.05$) when the ADC increased from 0 to 28 days. Additionally, the storm events carried out with a 4.1 cm/hr HLR, had significant ($p>0.05$) increases in nitrogen removal from 4 ADC to 9 ADC for ammonium, organic nitrogen, and total nitrogen. These results are supported by the results of Lynn et al. (2015a) who demonstrated that the increase in ADC for consistent HLR and durations of storm events would increase the nitrate – nitrogen removal. Lynn et al. also showed that as the ADC increased from 0 to 16 days, the nitrate – nitrogen removal increased from 86% to 97% and the TN removal increased from 66.5% to 79%.

One advantage of running identical storm events on a conventional and modified system at the same time is to observe what might be happening within the layers of the modified cell. Two storm events were chosen to highlight this data. Storm events 8 and 14 (4 and 28 day ADC, respectively), tested with a HLR of 6.9 cm/hr and a duration of four hours, were chosen because of the middle range HLR and duration for all of the storm events. Table 4.3 outlines the influent and effluent concentrations of different nitrogen species for the conventional cell for these two experiments. The influent concentrations are the same because the average nitrogen concentration was used to determine the percent nitrogen removal for all 14 storm events for the modified cell in Table 4.2.

Table 4.3 Conventional Cell Nitrogen Removal Data: ADCs of 4 and 28 Days

	NO_x – N		NH_4^+– N		Org N		TN	
Influent (mg N/L)	1.067 (0.471)		1.527 (0.384)		0.603 (0.288)		2.797 (1.031)	
ADC (d)	Effluent (mg N/L)	% Removal	Effluent (mg N/L)	% Removal	Effluent (mg N/L)	% Removal	Effluent (mg N/L)	% Removal
4	0.445	58.32	0.191	87.49	0.187	68.98	0.789	71.81
28	0.649	39.17	0.87	43.04	0.065	89.22	0.561	79.95

The next step of this hypothetical analysis is to use the effluent concentrations from the conventional cell (Table 4.3) as the influent data into the IWSZ and the effluent data from the modified cell, to investigate the percent removal from these four nitrogen species, specifically for the IWSZ (Table 4.4).

Table 4.4 Modified Cell Removal Data Under Hypothetical Analysis.
(Influent Concentrations are the Effluent of the conventional system from Table 4.3)

	NO_x – N		NH_4^+– N		Org N		TN	
ADC (d)	Effluent (mg N/L)	% Removal	Effluent (mg N/L)	% Removal	Effluent (mg N/L)	% Removal	Effluent (mg N/L)	% Removal
4	0.1404	68.45%	0.1988	-4.10%	0.2252	-20.45%	0.6497	17.66%
28	0.0471	92.74%	0.0407	95.32%	0.0649	0.15%	0.0719	87.18%

This hypothetical analysis was only performed on two storm events with varying ADC. The data in Table 4.4 suggests that in this analysis there would be close to 0% ammonium – nitrogen removed in the IWSZ for the storm event with an ADC of four days. This is intuitive because as discussed in Chapter 2 (Equations 2.1 – 2.4), the majority of ammonia is expected to be transformed in the sand layer (which is the primary transformation zone of a conventional cell). However, the results for the storm event with a 28 day ADC suggest there was 95% of ammonium – nitrogen removed in the IWSZ during that extended dry period. This result of the hypothetical analysis did not make intuitive sense but could be because the measured effluent concentration was so small which resulted in a larger percent removal. Additionally, this interpretation of data suggested there could be generation of organic nitrogen in the effluent for the storm event with the shorter ADC, this could happen due to organic nitrogen leaching from the wood chips and leaving the system in the effluent. For the longer ADC of 28 days, the hypothetical analysis resulted in basically no removal or addition of organic nitrogen in the IWSZ. This conflicts with the earlier results that the storm event with a 33 ADC had an influx of organic carbon in the effluent. Both of the storm events removed greater than 60% of nitrate/nitrite – nitrogen, however the storm event with a 28 day ADC removed 20% more. This result is most likely because of the longer contact time between the carbon substrate (wood chips) and the stormwater, leading to higher levels of denitrification for the storm event.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1 Summary of Findings

The overall goal of this research was to develop greater understanding of the effect the ADC has on the performance of a modified bioretention cell (containing an IWSZ to better treat nitrogen pollution). There were two objectives and one hypothesis that directed this research. The first objective was to identify knowledge gaps in the literature related to the use, properties, and performance of wood chips that are placed in the IWSZ to promote denitrification. The second objective was to examine the difference in nitrogen removal in a field demonstration for a conventional and modified bioretention system with variable ADCs. The hypothesis was that storm events with longer ADCs would have lower levels of nitrogen in the treated effluent than storm events with a shorter ADC.

The literature review discussed in depth different types of studies performed on denitrification bioreactors with the use of wood chips as the carbon substrate (electron donor). Additionally, values of carbon content (%), TOC leaching, influent and effluent nitrogen concentrations, and nitrogen removal (%) were reported for different types of wood used in different studies. Nine different types of wood chips were tested in the literature through seven different studies and each wood type was categorized as a hardwood or softwood. The literature reported that softwood chips leach significantly ($p<0.05$) more TOC than hardwood chips (138.3% and 70.3%, respectively). Higher amounts of TOC leached into the IWSZ should increase the amount of nitrogen removed for these systems. The literature review did show that systems using softwood chips provided greater total nitrogen removal than systems that used hardwood chips (75.2% and 63.0% removal of total nitrogen, respectively). Lower densities of softwoods (opposed to hardwoods) may provide the ability for the water to more easily penetrate the wood to leach out more bioavailable organic carbon and thus increase nitrogen removal.

The literature review also showed how the removal of individual nitrogen species was impacted by different dry periods (ADCs) between storm events in a bioretention system. Specifically, Lynn et al. (2015a) reported higher amounts of nitrogen removal with increasing ADCs in a (column) laboratory study. The design goal of this scenario is to obtain a long enough contact time between the water and wood chips based IWSZ, so the denitrifying bacteria can convert greater amounts of nitrate and nitrite to nitrogen gas.

This thesis tested the effect of varying ADCs at a field site in East Tampa (Florida) that contained a conventional and modified bioretention cell. Nitrogen removal in the modified system was significantly ($p<0.05$) greater than nitrogen removal in the conventional system for nitrate/nitrite – nitrogen, ammonium – nitrogen, and total nitrogen, and greater (not significantly) for organic nitrogen. In addition, the results demonstrated that the hypothesis was supported; if the ADC before a storm event was increased, the nitrogen removal in the modified bioretention system would also increase. Fourteen storm event experiments were conducted on the two bioretention systems (conventional and modified) to compare the effect of a longer ADC on the nitrogen removal in the system. Three nitrogen species: NO_x – N, NH_4^+ - N, and TN, were tested in the influent and effluent samples throughout each experiment. Organic nitrogen concentrations were then determined using this data. Once the results for all of the storm events were compiled, they were grouped into three groups based on different HLRs (4.1 cm/hr, 6.9 cm/hr, and 13.9 cm/hr) that were tested throughout the research period. Additionally, some of the storm event data were shortened in order to obtain identical lengths of time for all storm events in each group. This was done in order to eliminate the effect on nitrogen removal from two variables (HLR and storm duration) that have been proved to change the nitrogen removal efficiency in a denitrifying system.

For the first group (HLR of 4.1 cm/hr, duration of 2 hrs) the results were generally similar for all four nitrogen species (NO_x – N, NH_4^+ – N, organic N, and TN) due to the low flow. The second group (HLR of 6.9 cm/hr, duration of 4 hrs) showed an increase in nitrogen removal with the increase in ADC. The higher flow rate was able to help move the water through the system faster. The differences in the storm event with an ADC of 0 and the storm event with an ADC of 28 were significant ($p<0.05$) for ammonium – nitrogen, organic N, and TN. The results for nitrate/nitrite – nitrogen did increase with the increase in ADC, but they were not significant ($p>0.05$). The third group with the highest flow (HLR of 13.9 cm/hr, duration of 2 hrs) had removal results that varied as the ADC increased. This is thought to be due to the higher hydraulic loading rate moving water through the system much faster, therefore decreasing the contact time for nitrogen transformation in both the nitrifying and denitrifying zones within the modified system. The TN removal for storm events tested with the highest HLR (13.9 cm/hr) was lower for it's five storm events when compared to the storm events conducted with the other two HLRs (4.1 and 6.9 cm/hr).

In conclusion, softwood chips provide an advantage in the removal of nitrogen in a modified bioretention system as compared to hardwood chips. The modified bioretention cell had higher nitrogen removal efficiencies than the conventional cell. Overall, we can say that the longer ADC does increase nitrogen removal for a modified bioretention system, however there are other variables (HLR and storm duration) that also effect the system and further research should be performed to look at the interaction between all three (ADC, HLR, and storm duration).

5.2 Recommendations for Future Research

This study showed the effect of the ADC on total nitrogen removal efficiency in a field study of a bioretention cell constructed with an IWSZ, using eucalyptus wood chips as the carbon substrate to promote denitrification of nitrogen. Future field demonstrations should be performed on additional bioretention cells located in different parts of the United States to see the effect of climate and the ADC on nitrogen removal. It is also recommended to test the effect of different wood chip types with varying ADCs on nitrogen removal. Another recommendation for future research would be to further examine the effect of the ADC with differing HLRs and durations. The final recommendation from this study would be to add plants into the top of the bioretention cell and determine the effect of adding plants on nitrogen removal with varying ADCs for the system.

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APPENDIX A. STORM EVENT RESULTS

Table A.1 Average Influent Concentrations of NO_x – N, NH_4^+– N, Organic N, and TN

Storm Event	NO_x – N (mg/L)	NH_4^+– N (mg/L)	Org N (mg/L)	TN (mg/L)
1	0.82	1.83	1.17	3.88
2	0.47	1.46	0.29	2.50
3	1.67	1.54	0.50	3.70
4	0.53	1.37	0.57	2.29
5	0.94	1.01	0.69	2.73
6	1.04	2.01	0.86	3.90
7	0.75	1.39	0.62	2.76
8	0.88	0.88	0.20	2.16
9	0.86	0.96	0.28	2.05
10	0.61	1.71	0.83	3.16
11	1.86	1.55	0.41	3.83
12	1.17	2.15	0.83	4.15
13	1.83	1.82		1.02
14	1.50	1.71		1.03
Average	*1.07 (0.47)*	*1.53 (0.38)*	*0.60 (0.29)*	*2.80 (1.03)*

Standard deviation (where applicable) in parenthesis

Table A.2 Modified Cell Nitrogen Removal of NO_x – N and NH_4^+– N

					NO_x– N			NH_4^+– N		
Storm Event	ADC	Duration	HLR	Flow Rate	Effluent	Removal	Removal	Effluent	Removal	Removal
	d	hr	cm/hr	L/min	mg/L	mg/L	%	mg/L	mg/L	%
Influent					1.067 (0.471)			1.527 (0.384)		
1	0	4	6.9	0.64	0.089	0.978	91.64	0.153	1.374	89.95
2	7	2	13.9	1.29	0.327	0.740	69.34	0.250	1.278	83.65
3	4	2	4.1	0.38	0.004	1.064	99.66	0.591	0.937	61.33
4	6	2	13.9	1.29	0.380	0.688	64.44	0.336	1.191	78.00
5	12	4	6.9	0.64	0.073	0.994	93.15	0.099	1.428	93.49
6	8	6	4.1	0.38	0.015	1.053	98.63	0.140	1.387	90.84
7	6	4	6.9	0.64	0.080	0.987	92.49	0.370	1.157	75.78
8	4	4	6.9	0.64	0.140	0.927	86.85	0.199	1.329	86.98
9	11	4	13.9	1.29	0.396	0.671	62.87	0.315	1.212	79.38
10	9	6	4.1	0.38	0.018	1.049	98.28	0.228	1.300	85.10
11	0	4	13.9	1.29	0.771	0.297	27.78	0.314	1.214	79.46
12	1	4	13.9	1.29	0.337	0.730	68.43	0.414	1.114	72.91
13	3	6	4.1	0.38	0.302	0.766	71.72	0.204	1.323	86.65
14	4	6	6.9	0.64	0.277	0.790	74.05	0.150	1.377	90.17

Standard deviation (where applicable) in parenthesis

Table A.3 Modified Cell Nitrogen Removal of Organic N and TN

					Organic N			TN		
Storm Event	ADC	Duration	HLR	Flow Rate	Effluent	Removal	Removal	Effluent	Removal	Removal
	d	hr	cm/hr	L/min	mg/L	mg/L	%	mg/L	mg/L	%
Influent					0.603 (0.288)			2.797 (1.031)		
1	0	4	6.9	0.64	0.547	0.056	9.32	0.763	2.034	72.73
2	7	2	13.9	1.29	0.338	0.265	43.88	0.869	1.928	68.93
3	4	2	4.1	0.38	0.147	0.456	75.58	0.742	2.055	73.49
4	6	2	13.9	1.29	0.277	0.326	54.07	0.993	1.804	64.51
5	12	4	6.9	0.64	0.262	0.341	56.60	0.308	2.489	88.98
6	8	6	4.1	0.38	0.296	0.307	50.89	0.454	2.343	83.76
7	6	4	6.9	0.64	0.269	0.334	55.40	0.650	2.147	76.78
8	4	4	6.9	0.64	0.225	0.378	62.65	0.650	2.147	76.77
9	11	4	13.9	1.29	0.214	0.389	64.49	0.927	1.870	66.86
10	9	6	4.1	0.38	0.127	0.476	79.00	0.370	2.427	86.79
11	0	4	13.9	1.29	0.409	0.194	32.14	1.494	1.303	46.59
12	1	4	13.9	1.29	0.378	0.225	37.29	1.129	1.668	59.63
13	3	6	4.1	0.38	0.653	-0.050	-8.26	1.001	1.795	64.20
14	4	6	6.9	0.64	0.065	0.538	89.22	0.099	2.698	96.47

Standard deviation (where applicable) in parenthesis

Table A.4 Conventional Cell Removal of NO_x – N, NH_4^+– N, Organic N, and TN

				NO_x		NH_4^+		Org N		TN	
Storm Event*	ADC	Length	HLR	Effluent	Removal	Effluent	Removal	Effluent	Removal	Effluent	Removal
	d	hr	cm/hr	mg/L	%	mg/L	%	mg/L	%	mg/L	%
Influent (mg/L)				1.067 (0.471)		1.527 (0.384)		0.603 (0.288)		2.797 (1.031)	
4	6	2	13.9	1.315	-23.16	0.235	84.60	0.246	59.24	1.796	35.79
5	12	4	6.9	0.613	42.56	0.240	84.28	0.542	10.06	1.294	53.72
6	8	6	4.1	0.731	31.48	0.627	58.94	-		-	
7	6	4	6.9	0.642	39.89	0.359	76.48	0.403	33.17	1.291	53.85
8	4	4	6.9	0.445	58.32	0.191	87.49	0.187	68.98	0.789	71.81
9	11	4	13.9	0.733	31.37	0.626	59.00	0.177	70.69	1.660	40.65
10	9	6	4.1	0.723	32.30	0.247	83.84	0.424	29.71	0.424	84.84
11	0	4	13.9	1.202	-12.6	0.562	63.18	0.472	21.69	2.237	20.01
12	1	4	13.9	0.723	32.30	0.923	39.60	0.603	0.03	2.248	19.62
13	3	6	4.1	0.501	53.08	0.141	90.74	0.721	-19.59	0.658	76.47
14	4	6	6.9	0.649	39.17	0.870	43.04	0.065	89.22	0.561	79.95

Standard deviation (where applicable) in parenthesis

**Storm events 1-3 were not included in the conventional results due to experimental error.*

APPENDIX B. ADC CALCULATIONS

Table B.1 ADC Calculations for 10% of the IWSZ Replaced

ADC (days)	NO_x – N % Removal	NH_4^+– N % Removal	Organic N % Removal	TN % Removal
0	91.64	89.95	9.32	72.73
0	27.78	79.46	32.14	46.59
1	68.43	72.91	37.29	59.63
3	71.72	86.65	-	64.20
4	99.66	61.33	75.58	73.49
4	86.85	86.98	62.65	76.77
4	74.05	90.17	89.22	96.47
6	64.44	78.00	54.07	64.51
6	92.49	75.78	55.40	76.78
7	69.34	83.65	43.88	68.93
8	98.63	90.84	50.89	83.76
9	98.28	85.10	79.00	86.79
11	62.87	79.38	64.49	66.86
12	93.15	93.49	56.60	88.98

Table B.2 ADC Calculations for 15% of the IWSZ Replaced

ADC (days)	NO_x – N % Removal	NH_4^+– N % Removal	Organic N % Removal	TN % Removal
0	91.6	89.9	9.3	72.7
0	27.8	79.4	32.1	46.6
1	68.4	72.9	37.3	59.6
4	99.7	61.3	75.6	73.5
4	86.8	86.9	62.7	76.8
6	64.4	78	54.1	64.5
6	92.5	75.7	55.4	76.8
7	69.3	83.6	43.8	68.9
8	98.6	90.8	50.9	83.8
9	98.3	85.1	79	86.8
11	62.9	79.3	64.5	66.9
12	93.2	93.4	56.6	88.9
28	74.1	90.1	89.2	96.5
33	71.7	86.6	-8.3	64.2

Table B.3 ADC Calculations for 20% of the IWSZ Replaced

ADC (days)	NO_x – N % Removal	NH_4^+– N % Removal	Organic N % Removal	TN % Removal
0	91.6	89.9	9.3	72.7
0	27.8	79.4	32.1	46.6
4	99.7	61.3	75.6	73.5
4	86.8	86.9	62.7	76.8
6	64.4	78	54.1	64.5
6	92.5	75.7	55.4	76.8
7	69.3	83.6	43.8	68.9
8	98.6	90.8	50.9	83.8
9	98.3	85.1	79	86.8
11	62.9	79.3	64.5	66.9
12	93.2	93.4	56.6	88.9
13	68.4	72.9	37.3	59.6
28	74.1	90.1	89.2	96.5
33	71.7	86.6	-8.3	64.2

Table B.4 ADC Calculations for 50% of the IWSZ Replaced

ADC (days)	NO_x – N % Removal	NH_4^+– N % Removal	Organic N % Removal	TN % Removal
0	91.6	89.9	9.3	72.7
5	27.8	79.4	32.1	46.6
6	99.7	61.3	75.6	73.5
6	64.4	78	54.1	64.5
6	92.5	75.7	55.4	76.8
7	69.3	83.6	43.8	68.9
7	93.2	93.4	56.6	88.9
8	98.6	90.8	50.9	83.8
9	98.3	85.1	79	86.8
11	62.9	79.3	64.5	66.9
13	86.8	86.9	62.7	76.8
13	68.4	72.9	37.3	59.6
28	74.1	90.1	89.2	96.5
33	71.7	86.6	-8.3	64.2

Table B.5 ADC Calculations for 100% of the IWSZ Replaced

ADC (days)	NO_x – N % Removal	NH_4^+– N % Removal	Organic N % Removal	TN % Removal
5	27.8	79.4	32.1	46.6
6	99.7	61.3	75.6	73.5
6	92.5	75.7	55.4	76.8
7	69.3	83.6	43.8	68.9
7	93.2	93.4	56.6	88.9
8	98.6	90.8	50.9	83.8
9	98.3	85.1	79	86.8
11	62.9	79.3	64.5	66.9
12	64.4	78	54.1	64.5
13	86.8	86.9	62.7	76.8
13	68.4	72.9	37.3	59.6
28	74.1	90.1	89.2	96.5
33	71.7	86.6	-8.3	64.2
220	91.6	89.9	9.3	72.7

APPENDIX C. STATISTICAL ANALYSIS RESULTS FOR STORM EVENTS BASED ON HLR

Table C.1 Low Flow Storm Event Statistical Analysis Results. (4.1 cm/hr)
Standard deviation, number of experiments, variance, t-score, d.f., and p-value

SE	**NO_x – N**	**STDEV**	**N**	**S2/N**	**Var**	**t-score**	**d.f**	**p-value**	**Significant?**
3	99.53%	0.0079	7	0.0000	0.0078	2.75	24	<0.05	Yes
6	97.38%	0.0316	19	0.0001					
3	99.53%	0.0079	7	0.0000	0.0171	2.30	18	<0.05	Yes
10	95.60%	0.0606	13	0.0003					
3	99.53%	0.0079	7	0.0000	0.0879	0.14	18	>0.05	No
13	98.22%	0.3169	13	0.0077					
SE	NH_4^+– N	**STDEV**	**N**	**S2/N**	**Var**	**t-score**	**d.f**	**p-value**	**Significant?**
3	61.50%	0.0119	7	0.0000	0.0096	31.64	24	<0.05	Yes
6	91.82%	0.0369	19	0.0001					
3	61.50%	0.0119	7	0.0000	0.0082	28.54	18	<0.05	Yes
10	84.88%	0.0247	13	0.0000					
3	61.50%	0.0119	7	0.0000	0.0309	10.26	18	<0.05	Yes
13	93.19%	0.1101	13	0.0009					
SE	**Org N**	**STDEV**	**N**	**S2/N**	**Var**	**t-score**	**d.f**	**p-value**	**Significant?**
3	67.50%	0.0838	6	0.0012	0.0515	5.28	13	<0.05	Yes
6	40.31%	0.1153	9	0.0015					
3	67.50%	0.0838	6	0.0012	0.0381	3.52	17	<0.05	Yes
10	80.93%	0.0607	13	0.0003					
3	67.50%	0.0838	6	0.0012	0.0734	10.93	17	<0.05	Yes
13	-12.75%	0.2341	13	0.0042					
SE	**TN**	**STDEV**	**N**	**S2/N**	**Var**	**t-score**	**d.f**	**p-value**	**Significant?**
3	71.79%	0.0788	6	0.0010	0.0572	1.67	13	<0.05	Yes
6	81.37%	0.1419	9	0.0022					
3	71.79%	0.0788	6	0.0010	0.0404	3.52	17	<0.05	Yes
10	86.02%	0.0881	13	0.0006					
3	71.79%	0.0788	6	0.0010	0.0945	0.04	19	>0.05	No
13	71.40%	0.3442	15	0.0079					

SE = storm event
d.f. =degrees of freedom

Table C.2 Median Flow Storm Event Statistical Analysis Results. (6.9 cm/hr)
Standard deviation, number of experiments, variance, t-score, d.f., and p-value

SE	NO_x – N	STDEV	N	S2/N	Var	t-score	d.f	p-value	Significant?
1	91.64%	0.249	10	0.0062	0.0815	0.58	17	>0.05	No
8	86.85%	0.064	9	0.0004					
1	91.64%	0.249	10	0.0062	0.0790	0.10	15	>0.05	No
7	92.49%	0.018	7	0.0000					
1	91.64%	0.249	10	0.0062	0.0942	0.16	21	>0.05	No
5	93.15%	0.187	13	0.0027					
1	91.64%	0.249	10	0.0062	0.1047	0.37	21	>0.05	No
14	95.59%	0.249	13	0.0048					
SE	**NH_4^+– N**	**STDEV**	**N**	**S2/N**	**Var**	**t-score**	**d.f**	**p-value**	**Significant?**
1	89.95%	0.086	10	0.0007	0.0278	1.06	21	>0.05	No
8	86.98%	0.022	13	0.0000					
1	89.95%	0.086	10	0.0007	0.0301	4.71	21	<0.05	Yes
7	75.78%	0.047	13	0.0002					
1	89.95%	0.086	10	0.0007	0.0537	0.65	21	>0.05	No
5	93.49%	0.167	13	0.0022					
1	89.95%	0.086	10	0.0007	0.0360	2.05	21	<0.05	Yes
14	97.35%	0.086	13	0.0006					
SE	**Org N**	**STDEV**	**N**	**S2/N**	**Var**	**t-score**	**d.f**	**p-value**	**Significant?**
1	9.32%	0.075	5	0.0011	0.0793	6.72	8	<0.05	Yes
8	62.65%	0.161	5	0.0052					
1	9.32%	0.075	5	0.0011	0.0605	7.61	9	<0.05	Yes
7	55.40%	0.123	6	0.0025					
1	9.32%	0.075	5	0.0011	0.0557	8.48	10	<0.05	Yes
5	56.60%	0.118	7	0.0020					
1	9.32%	0.075	5	0.0011	0.0503	15.88	7	<0.05	Yes
14	89.24%	0.075	4	0.0014					
SE	**TN**	**STDEV**	**N**	**S2/N**	**Var**	**t-score**	**d.f**	**p-value**	**Significant?**
1	72.73%	0.020	5	0.0001	0.0280	1.44	8	>0.05	No
8	76.77%	0.059	5	0.0007					
1	72.73%	0.020	5	0.0001	0.0194	2.08	9	<0.05	Yes
7	76.78%	0.042	6	0.0003					
1	72.73%	0.020	5	0.0001	0.0171	9.48	10	<0.05	Yes
5	88.98%	0.039	7	0.0002					
1	72.73%	0.020	5	0.0001	0.0105	23.50	16	<0.05	Yes
14	97.43%	0.020	13	0.0000					

SE = storm event
d.f. =degrees of freedom

Table C.3 High Flow Storm Event Statistical Analysis Results. (13.9 cm/hr)
Standard deviation, number of experiments, variance, t-score, d.f., and p-value

SE	NO_x – N	STDEV	N	S2/N	Var	t-score	d.f	p-value	Significant?
11	32.27%	0.62	9	0.0427	0.2294	2.5118	16	$p<0.05$	Yes
12	89.88%	0.30	9	0.0099					
11	32.27%	0.62	9	0.0427	0.2657	1.2109	14	$p>0.05$	No
4	64.44%	0.44	7	0.0279					
11	32.27%	0.62	9	0.0427	0.2788	1.3300	14	$p>0.05$	No
2	69.34%	0.50	7	0.0350					
11	32.27%	0.62	9	0.0427	0.2291	2.2079	16	$p<0.05$	Yes
9	82.86%	0.30	9	0.0098					

SE	NH_4^+– N	STDEV	N	S2/N	Var	t-score	d.f	p-value	Significant?
11	77.54%	0.21	9	0.0048	0.1066	0.7063	16	$p>0.05$	No
12	85.07%	0.24	9	0.0066					
11	77.54%	0.21	9	0.0048	0.0723	0.0636	14	$p>0.05$	No
4	78.00%	0.05	7	0.0004					
11	77.54%	0.21	9	0.0048	0.1239	0.4929	14	$p>0.05$	No
2	83.65%	0.27	7	0.0105					
11	77.54%	0.21	9	0.0048	0.1047	1.2448	16	$p>0.05$	No
9	90.57%	0.24	9	0.0062					

SE	Org N	STDEV	N	S2/N	Var	t-score	d.f	p-value	Significant?
11	74.47%	0.27	9	0.0080	0.1060	1.4700	16	$p>0.05$	No
12	58.88%	0.17	9	0.0032					
11	74.47%	0.27	9	0.0080	0.1420	1.4362	14	$p>0.05$	No
4	54.07%	0.29	7	0.0122					
11	74.47%	0.27	9	0.0080	0.1328	2.3041	13	$p<0.05$	Yes
2	43.88%	0.24	6	0.0096					
11	74.47%	0.27	9	0.0080	0.0955	2.4867	12	$p<0.05$	Yes
9	98.22%	0.08	5	0.0011					

SE	TN	STDEV	N	S2/N	Var	t-score	d.f	p-value	Significant?
11	71.61%	1.00	9	0.1119	0.4093	0.1817	16	$p>0.05$	No
12	79.05%	0.71	9	0.0555					
11	71.61%	1.00	9	0.1119	0.4304	0.1650	14	$p>0.05$	No
4	64.51%	0.72	7	0.0733					
11	71.61%	1.00	9	0.1119	0.4218	0.0636	13	$p>0.05$	No
2	68.93%	0.63	6	0.0659					
11	71.61%	1.00	9	0.1119	0.4189	0.1417	12	$p>0.05$	No
9	77.55%	0.56	5	0.0636					

SE = storm event
d.f. =degrees of freedom