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Denitrifying bioreactors: a solution to groundwater nitrate pollution at the Forge River?

A Thesis Presented

by

Christine Gurdon

to

The Graduate School

In Partial Fulfillment of the

Requirements

For the Degree of

Master of Science

in

Marine and Atmospheric Sciences

Stony Brook University

December 2015

Stony Brook University

The Graduate School

Christine Gurdon

We, the thesis committee for the above candidate for the

Master of Science degree, hereby recommend

acceptance of this thesis.

R. Lawrence Swanson-Thesis Advisor

Associate Dean

School of Marine and Atmospheric Sciences

Stony Brook University

Henry J. Bokuniewicz

Distinguished Service Professor

School of Marine and Atmospheric Sciences

Stony Brook University

Bruce J. Brownawell

Associate Professor

School of Marine and Atmospheric Sciences

Stony Brook University

This thesis is accepted by the Graduate School

Charles Taber

Dean of the Graduate School

Abstract of the Thesis
Denitrifying bioreactors: a solution to groundwater nitrate pollution at the Forge River?

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Christine Gurdon

Master of Science

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Marine and Atmospheric Sciences

Stony Brook University

2015

Denitrifying bioreactors are an approach to remediate groundwater contaminated with nitrate. Their popularity as a remediation system has increased due to their unnecessary maintenance, low cost, and longevity. While field trials on their performance have been conducted, few have been completed in a marine coastal environment. In this study, a denitrification wall was designed to be installed and monitored along the shore of a coastal environment, namely, the Forge River, New York.

Prior to the design phase, a groundwater plume of elevated nitrate-nitrite concentrations needed to be identified. Groundwater nitrate-nitrite concentrations ranged from 0.01-17.68 mg/L along Riviera Drive, a road running parallel to a tributary on the western side of the Forge River. Coarse wood chips were chosen as the carbon source for the denitrifying bioreactor and constant head tests were completed to choose an appropriate proportion of wood chips and sand (background soil), and to calculate the accompanying residence time. Mean hydraulic conductivity measurements were 249.70 cm/day (20% by volume wood chips), 333.50 cm/day (30% by volume wood chips), and 359.42 cm/day (40% by volume of wood chips). As the percent by volume of wood chips increased, the hydraulic conductivity did as well, but none

were statistically higher than the site's soil. The residence time for each medium was calculated with widths of 0.1 m and 0.25 m. The residence times were 3.32 and 8.31 days (20% by volume of wood chips), 2.70 and 6.76 days (30% by volume of wood chips), and 2.51 and 6.27 (40% by volume of wood chips), increasing with width and decreasing with the percent by volume of wood chips. Due to previously observed nitrate removal rates (1.17-3.60 mg/L/day) and the location of elevated groundwater nitrate-nitrite concentrations, a medium consisting of 30% by volume of wood chips and 70% by volume of excavated soil was chosen for the denitrifying bioreactor.

To capture the observed nitrate-nitrite plume, the bioreactor will need to be 47 m in length. Given the range in measured nitrate-nitrite concentrations, and the uncertainty in the nitrate removal rate, the bioreactor should have a width less than 0.25 m, perhaps closer to 0.1 m, to reduce the likelihood of other metabolic processes. At the well location, ideally the bioreactor would be installed as deep as 4.5 m below the surface, with the top residing at 3 m below the surface, to remove the most nitrate-nitrite and to reduce the likelihood of other metabolic processes. Nearer the tide line though, the bioreactor can be installed to shallower depths because the flow lines converge towards the surface. Wells should be installed on the seaward side of the bioreactor to monitor nitrate-nitrite, ammonium, methane, nitrous oxide, and dissolved organic carbon (DOC) concentrations, as well as pH and dissolved oxygen levels.

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Acknowledgements

I want to thank my advisor R. Lawrence Swanson for his guidance and support. He has taught me more things that can be written, but most importantly how to be a great scientist. His great sense of humor and extensive knowledge in physical oceanography are characteristics not many have, so I am grateful to have worked with him. I would also like to thank Henry Bokuniewicz, who, while not my advisor, provided me with that same guidance and support. His patience is duly noted, as well as his invaluable knowledge in hydrogeology. Thank you Bruce Brownawell for your edits and recommendations, David Hirschberg for analyzing my samples, and Steve Abrams for helping with my experiments. Also, a big thank you to the Town of Brookhaven, who funded this project.

I want to thank Bonnie Stephens for editing my thesis and her continual positivity. I will miss our fun conversations. Thank you Molly Graffam for helping me collect groundwater. Your presence definitely made the experience more enjoyable.

Lastly, I want to thank my family for their support, motivation, and positive attitude. You mean the world to me. My biggest thank you goes out to Robert Pagliaro. I could not have completed this project without you. While your expertise in MATLAB coding and analyses enormously helped this project, it was your love, humor, and support that pulled it all together.

Denitrifying bioreactors: a solution to groundwater nitrate pollution at the Forge River?

1.0 Objectives

The objective of this study is to design a denitrifying bioreactor to reduce the amount of nitrate entering the Forge River. Before the design and planning phase, a groundwater plume of elevated nitrate-nitrite concentrations needs to be identified. Aller et al. (2009) observed a high supply of nitrogen via submarine groundwater discharge along the west side of the Forge River, and Swanson et al. (2010b) determined that Wills Creek, a tributary on the west side of the Forge River, exhibited higher total dissolved nitrogen (TDN) concentrations compared to other locations sampled along the river (Figure 1a and 1b). Because of these reasons, Riviera Drive (a road running parallel to Wills Creek) was chosen as the site to collect groundwater samples to locate the plume (Figure 2). Once the location of the plume was identified, soil and hydrological analyses were performed to design a denitrifying bioreactor.

2.0 Introduction

2.1 Sources and Effects of Nitrogen Pollution

Reactive nitrogen compounds, which include all biologically, photochemically, and radiatively active nitrogen compounds in Earth's atmosphere and biosphere (Galloway et al., 2003), are necessary for life. They can be naturally and synthetically produced, by either the decomposition of organic matter or the production of fertilizer, but over the past few decades, synthetic production has been greater (Galloway et al., 2003). While there are benefits to synthetic reactive nitrogen compounds, they are accumulating in the environment because their

production rates are higher than their removal rates (Galloway et al., 2003), promoting environmental consequences such as eutrophication and loss of biodiversity in coastal ecosystems (Howarth et al., 2000).

Ammonium, a compound produced by the decomposition of organic matter and excreted by animals (Powers and Schepers, 1989), has been increasing in concentration in soils due to fertilizer application, and expansion of irrigational and feedlot lands (Power and Schepers, 1989; Wick et al., 2012). Ammonium is an essential element for primary producers, but if not utilized, it will become part of groundwater or surface water. When ammonium is dissolved in a basic solution, ammonia is generated, and unlike ammonium, it cannot be used by primary producers. Therefore, it remains in the groundwater or surface water, or volatilizes and becomes part of the atmosphere. Nitrate is also found in the atmosphere, for reasons such as fossil fuel combustion, where high levels are observed downwind from power plants and major industrial areas (Power and Schepers, 1989). Precipitation transfers ammonia and nitrate from the atmosphere to the ground, consequently integrating these compounds with runoff and groundwater (Power and Schepers, 1989). Groundwater can also contain high concentrations of ammonia due to the effluent from sanitary sewers and septic tanks (Navarro and Carbonell, 2007). When the effluent migrates through the vadose zone into the saturated zone, the ammonia is often nitrified, forming nitrate (Ptacek, 1998).

Nitrogen compounds dissolved in groundwater can enter nearby aquatic bodies via submarine groundwater discharge (SGD). Submarine groundwater discharge, which refers to freshwater discharge below the high tide mark, occurs where an aquifer connects hydraulically with the sea through permeable sediments, and where the hydraulic head driving groundwater

flow is above sea level (Johannes, 1980). Almost all coastal areas meet these conditions, (Corbett et al., 1999) following that SGD is a vehicle for the supply of nitrogen species to coastal waters.

An aquatic body undergoing eutrophication is one where primary production is increasing (Nixon, 1995). There are various causes of eutrophication, such as a change in the hydraulic residence time of the water, a decrease in the turbidity of the water, and a decline in grazer pressure, but the most common cause is nutrient enrichment (Nixon, 1995). While increased primary production can lead to an increase in the production of fishes (Nixon, 1988), serious consequences, such as the increase in size of anoxic or hypoxic areas, fish kills, and loss of biotic diversity, can occur (Galloway et al., 2003; National Research Council, 2000). Furthermore, eutrophication can cause a loss in services that a healthy aquatic environment provides, such as aquatic activities and tourism (Smith et al., 1999).

2.2 Components and Performance of a Permeable Reactive Barrier

A permeable reactive barrier (PRB) is a passive groundwater remediation technology that can treat a variety of contaminants, such as hydrocarbons, chlorinated solvents, metals, pesticides and nutrients (Obiri-Nyarko et al., 2014). It is designed to be more permeable than the surrounding material so that under the influence of the natural hydraulic gradient, the flow of groundwater will not be inhibited, allowing the contaminants to be treated within the PRB (Thiruvengkatachari et al., 2008). Various materials can be used as reactive media, including elemental iron, activated carbon, zeolites, iron oxides/oxyhydrates, phosphates, and clay minerals (Roehl, 2005). Selecting the appropriate reactive media is dependent on the types of contaminants present in the groundwater and the contaminant removal mechanism (Roehl,

2005). Generally speaking, contaminants can be removed from groundwater via three processes (Roehl, 2005): degradation (the decomposition of contaminants to harmless compounds due to chemical or biological reactions), precipitation (the formation of insoluble compounds, resulting in immobilization), and sorption (the adsorption or complex formation of contaminants, resulting in immobilization).

Denitrifying bioreactors, a type of PRB used to remove nitrate from groundwater, utilize inexpensive solid carbon substrates, such as sawdust, leaves, sewage sludge, wood waste, and corn husks (Obiri-Nyarko et al., 2014). This technology promotes a pandemic biological process, specifically, heterotrophic denitrification. Heterotrophic denitrification is a process where nitrate or nitrite is used as the terminal electron acceptor instead of oxygen (Kornaros et al., 1996). Similar to aerobic metabolism, organic substrate is required to act as the electron donor (Kornaros et al., 1996). When a surplus of organic carbon is introduced into an aquifer, aerobic metabolism is stimulated, eventually producing a hypoxic environment (Robertson and Cherry, 1995). Once a hypoxic environment is established, organisms find a replacement for oxygen as an oxidant. Nitrate or nitrite is subsequently selected since it is the next best oxidant that will generate the most energy. Because excess nitrogen via SGD is affecting the habitat health of the Forge River, a denitrifying bioreactor installed along the shore can reduce the amount of nitrate discharged.

2.3 The Kinetics of Denitrification

During heterotrophic denitrification, denitrifying microorganisms, most commonly in the species of *Pseudomonas* for soils, reduce nitrogen oxides (Bremner, 1997):



Denitrifying microorganisms are prevalent in the environment, but their activity is most often limited by the availability of organic material (Bremner, 1997). When enough organic carbon is present, heterotrophic denitrification will reduce nitrate, removing it from the area and subsequently producing N₂ gas.

Numerous experiments have been performed to model and understand the kinetics of denitrification (Kornaros et al., 1996; Körner and Zumft, 1989; Payne and Riley, 1969). Kornaros et al. (1996) investigated the first step of denitrification, that is, the transformation of nitrate to nitrite. They wanted to determine whether nitrate has an inhibitory effect on nitrite reduction, or whether nitrate reduction is essentially faster than nitrite reduction (Kornaros et al., 1996). While performing a batch experiment using *P. denitrificans* grown in a nitrite culture medium, they observed that when 33 mg NO₃-N/L was injected into the medium, the maximum nitrite reduction rate went from 90.6 mg NO₂⁻-N/g cells/hr to 34 mg NO₂⁻-N/g cells/hr, a 62.5% decrease. Interestingly, the nitrite reduction rate was restored back to its original value once all of the nitrate was reduced (Kornaros et al., 1996). Körner and Zumft (1989) observed similar results, where nitrite reduction ceased upon the addition of nitrate to a medium of anoxic nitrate-grown cells.

To determine whether nitrate inhibits the reduction of the other nitrogen oxides involved in denitrification, Kornaros et al. (1996) calculated the growth yield coefficient for both nitrate reduction to nitrogen gas, and nitrite reduction to nitrogen gas, and discovered that a larger

amount of total nitrogen is reduced during nitrite reduction compared to nitrate reduction. Therefore, Kornaros et al. (1996) concluded that the presence of nitrate inhibits each one of the reduction steps from nitrite to nitrogen gas, hindering the overall denitrification process. The results from Payne and Riley (1969) concur with Kornaros et al. (1996), where they observed a slower enzymatic rate for the reduction of NO when nitrate was present. Senbayram et al. (2012) studied denitrification in soils, and while they observed an inhibitory effect of nitrate on the reduction of N₂O, a large concentration of nitrate (10 mM KNO₃⁻) was required. While it is unclear as to what concentration nitrate exerts this inhibitory effect, Kornaros et al. (1996) emphasize the need to incorporate this effect into denitrification models, since the mole fraction of nitrite, and nitric and nitrous oxide increases when nitrate concentrations are high. As will be presented, the highest groundwater nitrate-nitrite concentration recorded along Riviera Drive is 17.6 mg/L. Nitrate's inhibitory effect seems to occur at much higher nitrate concentrations, so it is unlikely that there will be an accumulation and release of nitrous oxide solely due to nitrate's inhibitory effect when the bioreactor is installed.

2.4 Carbon Sources for Denitrifying Bioreactors

Numerous carbon sources for denitrifying bioreactors have been tested (Cameron and Schipper, 2010; Greenan et al., 2006). Cameron and Schipper (2010) tested nine carbon sources and discovered that over a 22-month period, maize cob provided a 3-6.5 fold increase in the rate of nitrate removal compared to varying sizes of wood chips. Greenan et al. (2006) received similar results, where cornstalks provided more rapid and greater total reduction in nitrate compared to wood chips. However, Cameron and Schipper (2010) observed higher leaching of

NH_4^+ and BOD in the maize cob treatment compared to the wood treatment during the first ten months. Also, Greenan et al. (2006) witnessed ammonium production for the cornstalk treatment while no ammonium production for the wood chip treatment. The major difference between the carbon sources is their composition, that is, the ratio of labile carbon to refractory carbon. The higher the ratio, the higher the rate of nitrate removal and degradation of the carbon source. Therefore, selecting the appropriate medium is dependent on the amount of nitrate that needs to be removed, the ease of rejuvenating the medium, and the residence time of the denitrifying bioreactor.

Considering wood as the carbon source, there has been interest in whether hardwood has higher nitrate removal rates than softwood, and whether the size of the wood chip has an effect on the nitrate removal rate. Cameron and Schipper (2010) found that while hardwood had a lower nitrate removal rate than softwood for the first 10 months, there was no statistical difference in nitrate removal rates between softwood and hardwood from the 10th to the 23rd month. With regard to the grain size in the medium, there is not sufficient research on whether grain size has an effect on the nitrate removal rate. Robertson et al. (2005) claimed that denitrification is not restricted to the grain surfaces since they noticed dark-colored rims penetrating several millimeters into the wood particles after completing a 26-month field study. While it is unknown whether grain size in the medium affects nitrate removal rates, it is accepted that it does affect the residence time of the bioreactor. When the grain size in the medium increases, the porosity increases and hence the residence time decreases. This property is very important in the design of the denitrifying bioreactor. A bioreactor with too short of a residence time will not allow sufficient time for nitrate utilization by denitrifying organisms. One with too long of a residence time will result in complete nitrate removal before more nitrate enters the

bioreactor, and so will promote other metabolic pathways such as sulfate reduction and methanogenesis, forming undesirable products such as methane and hydrogen sulfide (Christianson, 2011). Cameron and Schipper (2010) though observed that for a medium containing coarser grains (>10 mm), there was a decrease in the hydraulic conductivity over the 22-month sampling period, while the hydraulic conductivity for a medium containing finer grains remained the same throughout the sampling period. They attribute this observation to the ability of coarser grains to trap gas bubbles. Because the coarser grains in their experiment had a flat surface, it caused the medium to trap gas bubbles more than that of a medium containing finer grains, which are narrower and mesh-like (Cameron and Schipper, 2010). While the hydraulic conductivity of the medium containing coarser grains decreased over the sampling period, it did remain higher than that of the medium containing finer grains (Cameron and Schipper, 2010).

Even though there is a chance of decreasing hydraulic conductivity over time for a medium consisting of coarser grains, a denitrifying bioreactor with a statistically higher hydraulic conductivity than the surrounding soil is beneficial, especially at Riviera Drive, since it affects the flow lines within the entire aquifer system. A hydraulic conductivity contrast between soil layers causes the layer with the higher hydraulic conductivity to focus flow lines and capture groundwater from adjacent zones (H. Bokuniewicz, 2015, Stony Brook University, personal communication) by reason of conserving continuity within the system. Heightened hydraulic conductivity increases the flow rate of groundwater. Continuity needs to be conserved between the heightened hydraulic conductivity layer and the surrounding soil, meaning that the volumetric fluxes need to be equal. For this to happen, a higher volume of water needs to travel through the layer with the higher hydraulic conductivity, which is achieved by the layer drawing

in water from adjacent zones. Robertson et al. (2005) used a model sensitivity analysis to demonstrate how hydraulic conductivity contrast affects streamline gathering capabilities (Figure 3). In their simulation, it was shown that a denitrifying bioreactor 1 m below the surface is able to capture streamlines 4 m below the surface when the denitrifying bioreactor had a hydraulic conductivity contrast factor of 10 (Robertson et al., 2005). Increasing the hydraulic conductivity contrast factor beyond ten continues to increase the depth of capture, but approximately 65% of this effect is achieved with a contrast factor of ten (Robertson et al., 2005). Only a 5% effect on the depth capture is achieved when the contrast hydraulic conductivity factor goes beyond 100 (Robertson et al., 2005). This concept is very important when choosing the medium for the bioreactor at Riviera Drive. As will be demonstrated, consistently higher groundwater nitrate-nitrite concentrations were observed at the deepest wells sampled along the north side of Riviera Drive, specifically at 4.5 m below the surface. Therefore, instead of trenching to 4.5 m, a denitrifying bioreactor with a statistically higher hydraulic conductivity than the surrounding soil can be installed to a shallower depth while still capturing the high nitrate-nitrite concentrations from deeper depths. Also, closer to the tide line, the flow lines would converge closer to the surface, so the bioreactor would be installed to a shallower depth.

2.5 Advantages and Disadvantages of Denitrifying Bioreactors

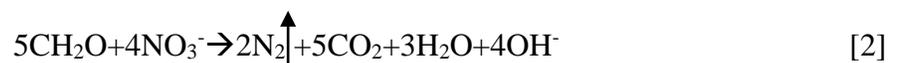
There are numerous advantages to using denitrifying bioreactors over conventional groundwater remediation methods (Thiruvengkatachari et al., 2008). Because denitrifying bioreactors can degrade or immobilize contaminants *in situ*, this technology does not require any additional surface structures or plumbing for storage, treatment, transport or disposal (Robertson

and Cherry, 1995; Thiruvengkatachari et al., 2008). Also, while the land above the denitrifying bioreactor cannot be built on, there will be no indication of its presence. Denitrifying bioreactors do not require an input of energy either since they utilize the natural gradient of groundwater to deliver the contaminants to the reactive zone (Robertson and Cherry, 1995; Thiruvengkatachari et al., 2008).

Maintenance, such as replacement or rejuvenation of the carbon source, may be required, but numerous studies have demonstrated denitrifying bioreactor longevity of at least seven to fourteen years (Robertson et al., 2000; Robertson, 2010; Long et al., 2011). For effective nitrate removal over a prolonged period, the longevity of the organic carbon material is crucial (Robertson and Cherry, 1995). It is expected that during initial operation of denitrifying bioreactors, there will be an excess release of dissolved organic carbon (DOC) (Schipper et al., 2010). Excess leaching will weaken the performance of the bioreactor, and if leachate has sufficient DOC concentrations, it can reduce dissolved oxygen concentrations in receiving waters (Schipper et al., 2010). Robertson and Cherry (1995) observed excess DOC leaching during the initial operation of a denitrification wall they installed in Ontario, over an extended period of time, DOC levels declined and plateaued to much lower levels. Initially, DOC levels in the effluent were approximately 150 mg/L, but 350 days after the barrier was installed, DOC levels declined to approximately 2 mg/L (Robertson and Cherry, 1995). Therefore, it is anticipated to observe high DOC levels in the groundwater leaving the denitrifying bioreactor at Riviera Drive for approximately the first year of its operation.

In addition to DOC leaching, the process of denitrification also consumes carbon.

Consider the equation for denitrification:



For every 1 mole of nitrate converted to N_2 gas, 1.25 moles of carbon are required. Using the total flow volume and the average amount of nitrate attenuated over seven years, Robertson et al. (2000) determined that only 2-3% of the carbon mass present had been consumed since the denitrifying bioreactor was situated. Other factors, such as aerobic respiration, excess DOC leaching, and possibly sulfate reduction, also consume carbon so it was estimated that <10-20% of the initial carbon mass had been consumed (Robertson et al., 2000). This is a small amount of consumption considering that the denitrifying bioreactor had been functioning for seven years. Not only did Robertson et al. (2000) determine that the organic carbon had a slow degradation rate, they also observed that the bioreactor continued to attenuate nitrate, averaging 58-91%, after seven years of operation. Similarly, Long et al. (2011) observed that after 14 years of operation, the denitrification wall continued to remove nitrate from groundwater. The denitrifying enzyme activity rates measured after 14 years of operation were similar to those measured during the first year of operation, indicating that there is still a sufficient amount of total carbon available for the denitrifiers (Long et al., 2011).

While there are numerous benefits to implementing denitrifying bioreactor technology for groundwater remediation, there are some adverse effects. Pollution swapping, which occurs when the reduction in concentration of a pollutant causes an increase in another pollutant (Stevens and Quinton, 2009), has been reported during the use of denitrifying bioreactors (Obiri-Nyarko et al., 2014). Nitrous oxide is an obligatory intermediate during the reduction of nitrate and nitrite to N_2 gas (Bremner, 1997). Environmental conditions, such as high soil oxygen concentrations, low pH levels, and high nitrate concentrations, can terminate the reduction of N_2O to N_2 (Well et al., 2003; Groffman et al., 2000), thereby causing an accumulation and release of this greenhouse gas that is involved in stratospheric ozone destruction. While

Blackmer and Bremner (1978) observed an inhibitory effect that NO_3 has on the reduction of N_2O , they noticed that this effect increases with an increase in NO_3 concentration and a decrease in soil pH (Table 1).

pH of soil	Initial nitrate concentration ($\mu\text{g/g}$ soil)	Inhibition of N_2O reduction by nitrate after 1 hour (%)	Inhibition of N_2O reduction by nitrate after 6 hours (%)
6.8	10	60	36
5.8	10	72	22
5.7	10	88	31

Table 1: The effect pH has on the inhibitory effect of nitrate on N_2O reduction. A lower pH causes nitrate to have more of an inhibitory effect (from Blackmer and Bremner, 1978).

Groffman et al. (2000) observed similar results when performing an experiment using saturated soils from Rhode Island, and calculated a higher ratio of $\text{N}_2\text{O}:\text{N}_2$ in soils with decreasing pH. While there is little documentation on the quantity of N_2O emitted from denitrifying bioreactors, a study by Elgood et al. (2010) is one of the few that measured the amount of N_2O in groundwater that had flowed through a bioreactor. They determined that during the summer months (July to September), the bioreactor acted as a sink of N_2O . During all other months though, the bioreactor did produce N_2O , with the highest production during the winter months (December to March) (Elgood et al., 2010). While a mean of 0.6% of nitrate was removed as N_2O for the entire year, during the winter months, between 1.0 and 1.9% of nitrate was removed as N_2O (Elgood et al., 2010). The higher release of N_2O during winter months is most likely due to the incompleteness of denitrification, that is, nitrate or nitrite was not fully reduced to N_2 . Elgood et al. (2010) attribute this observation to the higher influent O_2 concentrations, with the colder temperatures causing slower reaction rates. Overall, the conditions in the bioreactor during winter months were not reducing enough for nitrate to be completely reduced to N_2 .

Elgood et al. (2010) area-normalized the N₂O flux in the bioreactor effluent (-5.4-14 mg/m²/d) to compare to other environments. Documented N₂O fluxes from agricultural lands, with no added pesticides or fertilizer, ranged from 0.23 mg/m²/d (Mosier et al., 1991) to 0.41 mg/m²/d (Gregorich et al., 2005), whereas land with fertilizer management had fluxes of approximately 0.77 mg/m²/d (Gregorich et al., 2005), and land with manure management had fluxes of approximately 8.21 mg/m²/d (Chang et al., 1998). The N₂O flux in the bioreactor effluent was similar to calculated N₂O fluxes from agricultural lands with and without manure or fertilizer application. More importantly, the N₂O flux range in the bioreactor effluent was significantly less than the N₂O flux from a wastewater treatment plant, calculated to be approximately 1290 mg/m²/d, without tertiary treatment (Czepiel et al., 1995). While there is a likelihood for N₂O release when installing a denitrifying bioreactor, the amount is similar to releases of current practices.

Other compounds that may emanate are carbon dioxide and methane. Denitrifying bioreactors are composed of organic matter, and because of this, carbon dioxide and potentially methane will be emitted due to its eventual decomposition (Schipper et al., 2010). A net increase of atmospheric carbon dioxide will not occur because the organic matter in the bioreactor would have decomposed either way (Schipper et al., 2010). The same can be said for the emission of methane, but because methane is a stronger greenhouse gas than carbon dioxide, it is recommended to be monitored.

Most investigators conducting denitrifying bioreactor field studies install them within a freshwater system (Robertson and Cherry, 1995; Long et al., 2011; Robertson et al., 2010). As will be demonstrated, the groundwater along Riviera Drive is brackish, so it is necessary to understand how denitrifying bioreactors behave when exposed to such environmental conditions.

To evaluate the effect saltwater has on the function of denitrifying bioreactors, Vallino and Foreman (2008) conducted a lab study that involved treating denitrifying bioreactors with freshwater, seawater, and periodic inputs of seawater. Their results demonstrated that seawater did not have an effect on nitrate removal, but the bioreactors exposed to seawater released more ammonium compared to those being treated with freshwater (Vallino and Foreman, 2008). The bioreactors treated with seawater also produced hydrogen sulfide, which can be attributed to the high concentration of sulfate in seawater. Since net ammonium production was not observed when sulfate was absent, such production is likely due to dissimilatory nitrate reduction to ammonium (DNRA) (Vallino and Foreman, 2008), a microbial process where nitrate is transformed to ammonium (Burgin and Hamilton, 2007). Brunet and Garcia-Gil (1996) performed a laboratory study to consider the oxidant effect of nitrate when hydrogen sulfide was present. During sulfide reduction, ammonia was simultaneously produced, suggesting that nitrate reduction to ammonia is related to the presence of hydrogen sulfide (Brunet and Garcia-Gil, 1996). This idea is supported by the observation that nitrite accumulated once hydrogen sulfide was depleted (Brunet and Garcia-Gil, 1996). Other sulfide compounds (FeS and $\text{S}_2\text{O}_3^{2-}$) were tested in conjunction with nitrate, but hydrogen sulfide was the only one that caused an increase in ammonia concentration (Brunet and Garcia-Gil, 1996). Sulfate reduction produces hydrogen sulfide, which then becomes the reductant in DNRA. When installing a bioreactor, ammonia production needs to be limited. Compared to denitrification, sulfate reduction produces significantly less energy. Even though denitrifying bioreactors will be exposed to high concentrations of sulfate when situated in a coastal environment, nitrate will be utilized as an important oxidant, as long as there is approximately 0.5 mg/L of nitrate available (Robertson and Merkely, 1995). After an entire year of sampling, there were no instances where observed

nitrate-nitrite concentrations at the desired location fell below 0.5 mg/L, so it is very unlikely that sulfate reduction will occur. However, considering all of the accessory reactions and chemical species involved during denitrification, it is recommended to monitor the groundwater coming from the bioreactor for DOC, N₂O, methane, hydrogen sulfide, and ammonium once installed.

2.6 Eutrophication in the Forge River

The Forge River, located on the south shore of Long Island, is a major tributary of Moriches Bay (Durand et al., 2011); (Figure 4). It is characterized as a partially mixed estuary, and has relatively low current speeds, causing nutrients and organic matter to accumulate (Swanson et al., 2010a)

In the late 1960s, duck ranching was widespread throughout Suffolk County, and due to the high volume of duck waste, it was considered to be the major factor causing poor water quality in the Forge River (Swanson et al., 2010a). Wastewater coming from duck ranches contained high amounts of nutrients, and at the time, the NYS Department of Health only required removal of settleable solids from the wastewater before the effluent was discharged to receiving waters (Swanson et al., 2010a). Currently, no duck ranches exist in the Forge River watershed, and only one exists on Long Island (D. Davies, Suffolk County Department of Economic Development and Planning, personal communication, 2015), but dissolved nutrients from the duck waste can remain in sediments and groundwater for decades (B. Brownawell, Stony Brook University, personal communication, 2015).

Since 1960, the population in the Forge River watershed has increased by a factor of 5.6 (Swanson et al., 2010a). Because of this increase, the nitrogen load going into the watershed has increased, primarily due to higher septic tank and cesspool usage (Swanson et al., 2010a). Currently, nitrogen loads have been estimated to be approximately 2.7 times greater than those 45 years ago, and the ratio of nitrogen to phosphorus has increased over the past three decades (Swanson et al., 2010a). Aller et al. (2009) studied the cycling of nitrogen in the Forge River, and calculated that 73% of the total external supply of nitrogen to the Forge River is from groundwater, and that the supply is higher on the western side of the watershed. The higher supply on the western side coincides with the denser population (Aller et al., 2009). Durand et al. (2011) observed a similar feature of the Forge River. Using electrical resistivity measurements and seepage meters, they observed a plume of freshwater on the west shore of the Forge River, extending approximately 30 m toward the center of the river and thickness varying between eight and four meters (Durand et al., 2011); (Figure 5a and 5b). Considering these observations and calculations, submarine groundwater discharge is an important source of nitrogen to the Forge River.

The increased supply of nitrogen to the Forge River has substantial consequences. During a water column property study completed during the summer of 2006, dissolved oxygen concentrations were found to be extremely variable at the Brookhaven Town Pier (Wilson et al., 2009). On a particular day in August, surface dissolved oxygen (DO) concentrations ranged from 0 mgO₂/L at sunrise, to 13 mgO₂/L just after noon, with bottom DO concentrations essentially remaining at 0 mgO₂/L throughout the day (Wilson et al., 2009). The Forge River experiences chronic summertime hypoxia, and during the summer of 2006, there was an alarming fish-kill that led to the addition of the Forge River to the 2006 New York State 303(d) List of Impaired

Water Bodies (Durand et al., 2011). Since 2010, there have been persistent fish and crab kills, foul odors, and rotting algal debris during the summer months, and sediments are highly reduced and devoid of macrofaunal organisms as a result of summertime hypoxia (Swanson et al., 2010a). The Forge River remains an important resource for commercial and recreational users (Durand et al., 2011), where approximately 42.7% of the watershed acreage constitutes housing, with much for fishing, boating/canoeing and swimming activities (Swanson et al., 2010a). Therefore, it is important to maintain the health of the Forge River.

3.0 Methods

3.1 Groundwater Sampling

To detect the groundwater plume of elevated nitrate-nitrite concentrations, monitoring wells were installed along the north side of Riviera Drive (Figure 6). Six single wells were first installed on April 28, 2014, and then two multilevel wells (ML-1 and ML-2) and one more single well (MW-7) were installed on June 10, 2014 (Pritt, 2015). All single wells are screened at 3 m, and the two multilevel wells are screened at 1.5, 3, and 4.5 m. Pritt (2015) outlined the process and techniques used to install the wells. Groundwater sampling commenced on September 4, 2014.

Prior to collecting groundwater, the depth to the water table was determined using a tape measure. A peristaltic pump, Thermo Scientific Model 900-1836 with Masterflex precision platinum silicone tubing, was then connected to Teflon tubing in order to withdraw the groundwater. Approximately 530 mL of water were purged from the wells to remove stagnant water, and surface water that may have leaked through the well cap. This is done to obtain a

sample representative of the area's groundwater. After purging, groundwater was collected in a YSI flow chamber, Model MPS 556, and set aside for eight to ten minutes in order for the readings to stabilize. The temperature reading, however, was documented almost immediately. The YSI flow chamber was rinsed with sample water prior to use. Once the YSI readings stabilized, salinity and dissolved oxygen concentrations were documented. Water was then extracted from the YSI flow chamber using a 60 mL syringe, and a PTFE 0.45 µm filter was attached to its end. The filtered water was then placed into a 15 mL Falcon tube, for nitrate-nitrite and ammonium analysis, and a 40 mL clear vial with a septa cap, for total dissolved nitrogen analysis. The samples were frozen to inhibit biological growth and protect the integrity of the sample until analyzed. In May, 2015, pH readings were also recorded using a pH pen, pHep by HANNA.

3.2 Nutrient Analyses

The groundwater samples were analyzed for total dissolved nitrogen (TDN), ammonium, and nitrate-nitrite, and calculations were performed to determine dissolved organic nitrogen (DON). The procedure for nutrient analyses was adopted from the United States Environmental Protection Agency (1983), and the particular methods are for Ammonia 350.1, and Nitrate 353.2. The TDN concentrations were analyzed using a Shimadzu TOC-6000, a high temperature combustion chemofluorescent instrument. Ammonium and nitrate-nitrite concentrations were analyzed using Lachat Instruments Automated Flow Injection Chlorometer, with standard techniques. A phenolate reaction was used for ammonium analyses, and a sulphanilamide reaction was used for nitrate-nitrite analyses, after a Cadmium column reduction was performed.

3.3 HOBO Data Logger Test for Determining the Hydraulic Gradient

The hydraulic gradient, the force behind groundwater flow, is an important feature of saturated soil. According to Darcy's Law, the hydraulic gradient is directly proportional to the volumetric flow rate of water, and the volumetric flow rate serves to determine the residence time of the bioreactor. Because the hydraulic residence time is important when constructing the denitrifying bioreactor, it is necessary to know the hydraulic gradient of the site.

To determine the hydraulic gradient, two HOBO data loggers were situated at the site on the morning of July 30, 2015. One data logger was placed inside well MW-4, and the other was secured to a piling at the end of a pier located directly across from the well (Figure 7). The data loggers measure total pressure in kPa every 30 seconds. The distance from the well to the high tide line (indicated by a wrack line), and the distance from the well to the low tide line was measured. The vertical elevation from the borehole to the bottom of the data logger at well MW-4, in addition to the vertical elevation to the bottom of the data logger at the pier was measured. The vertical elevation of the data logger in the well and that on the pier were also measured using a Nikon Automatic Level AP-7. The data loggers were left in place until the afternoon of July 31, 2015.

The data loggers measure total pressure, which is the summation of atmospheric pressure and the pressure of the water column above the data logger. The pressure of the water column above the data logger is needed to determine the hydraulic gradient, thus the atmospheric pressure needs to be subtracted from the total pressure. The atmospheric pressure during the experimental period was taken from the Southampton weather station data archives provided by Stony Brook University (<http://wx.somassbu.org/pages/dataaccess.php>). The calculated pressures from both data loggers were then converted to meters.

The hydraulic gradient is represented as $dH(t)/L(t)$, where $L(t)$ is the distance between the well and the tide line at time, t , and $H(t)$ is the instantaneous hydraulic head, which is the water level elevation. Traditionally, the hydraulic gradient is determined using two monitoring wells, where $L(t)$ is the distance between the two. It is the difference in hydraulic head between the two locations that drives groundwater flow, but the hydraulic head is zero along the bottom of a water body. Because this site is exposed to a tide, the distance of concern then is that between the well and the tide line, and anything beyond has no effect on groundwater movement.

The point-slope formula was used to compute the horizontal distance between the well and the tide line with respect to time:

$$\eta_p(\text{high tide}) - \eta_p(t) = m(L(\text{high tide}) - L(t)) \quad [3]$$

where

$\eta_p(\text{high tide})$ = the water level elevation at high tide in Wills Creek

$\eta_p(t)$ = the water level elevation in Wills Creek at time t

m = intertidal slope

$L(\text{high tide})$ = the horizontal distance between the well and the high tide line

$L(t)$ = the horizontal distance between the well and the tide line at time t

The intertidal slope, m , was measured by determining the water level elevations in the well and Wills Creek, and using the distance from the well to the fluctuating tide line. Because $H(t)$ represents the water level elevation, $dH(t)$ is computed by taking the difference in water level elevations between the well and Wills Creek. The difference in water level elevation between the MWL in the well and that in the creek was then determined, and used to correct the water level elevations in the well so they are relative to the position of the data logger in Wills Creek. Because the water level elevations in the well and Wills Creek are relative to the same data logger, $dH(t)$ was calculated by subtracting the water level elevation in the well from the water level elevation in Wills Creek. The hydraulic gradient was then plotted over a tidal cycle and averaged.

3.4 Constant Head Test

As Robertson et al. (2005) demonstrated through model sensitivity analysis, the hydraulic conductivity of the denitrifying bioreactor is an important feature of the technology because it allows for shallower installation, while still capturing deep flow lines. Therefore, it is important to know the hydraulic conductivity of the surrounding soil to create a medium that has one substantially higher.

Riviera Drive contains Carver and Plymouth Soils, a type of sand which has a hydraulic conductivity of 379.99 cm/day (Hughes and Porter, 1983). To choose the most appropriate ratio of wood chips to sand for the medium, various wood chip-sand mixtures were tested for hydraulic conductivity. Two types of hydraulic conductivity tests exist, a constant head test and a falling head test. The constant head test method is used for permeable soils ($k > 8.64$ cm/day), while the falling head test method is used for less permeable soils ($k < 8.64$ cm/day). Because Riviera Drive is composed of sand with a hydraulic conductivity greater than 8.64 cm/day, the constant head test method was used.

The constant head test involves the flow of water through a cylindrical soil sample under a constant pressure difference. During the test, the volume of water flowing through the soil column is measured for a given time interval. The following equation is then used to calculate the hydraulic conductivity of the sample:

$$K = \frac{QL}{A\Delta h\Delta t} \quad [4]$$

where Q = volume of water collected

L = length of soil sample

A = cross-sectional area of soil sample

Δh = constant difference in the hydraulic head

Δt = duration of water collection

K = hydraulic conductivity

The soil sample is situated in a chamber, often referred to as a reactor. For the body of the reactor, a cylindrical 10.16 cm diameter PVC pipe was used, and fabric measuring tape was attached to the inside, measuring approximately 60.96 cm. At one end of the PVC pipe (the bottom), a shower drain screen was glued inside, with a window screen placed on top of that. This is done to prevent sand particles from being removed from the reactor as water flows through. Clear vinyl tubing was cut and attached to the top of the reactor, as well as a miniature stopcock. On the side of a sink, two crates were stacked on one another, and a 3.5 gallon plastic bucket, with a hole drilled close to the bottom and a ball valve situated inside, was placed on top of the crates. A piece of tubing was cut, and one end was attached to the faucet sink, and the other clamped to the top of the plastic bucket so that the water level in the bucket was always at the top, practically overflowing. The tubing leading to the top of the reactor was then attached to the plastic bucket, so water could enter the reactor and flow through. The water then discharged from the bottom of the reactor. The tubing attaching the plastic bucket to the top of the reactor was constantly filled with water (Figure 8).

To begin the experiment, the reactor was filled to an arbitrary height, where the only restriction was that the reactor had to be filled to a height that was two times that of the diameter (ASTM D2434-68, 2006). Since the reactor had a 10.16 cm diameter, it had to be filled to at least 20.32 cm. The volume of the cylindrical reactor corresponding to the arbitrary height was calculated, and then multiplied by a percent representing the volume of wood chips in the medium. Using the volume of wood chips, the height corresponding to the wood chips could be determined, which was subtracted from the arbitrary height to determine the height corresponding to the sand. The sand and wood chips were filled to their appropriate heights, and

then put into a bucket so the two materials could be mixed together thoroughly, representing a homogeneous medium. The medium was then placed back inside the reactor.

It is important that air bubbles do not exist within the reactor since they can affect the flow of water through the medium. The entire sample was saturated by pouring water through it slowly, stopping every so often to let the water permeate. It is necessary to note the height of the medium when saturated since it will decrease from what it was prior to saturation. Once the medium was saturated, water continued to be poured into the reactor, filling it to the top. The stopcock valve and the ball valve were opened, and the sink turned on, assuring that the water level in the plastic bucket remained at the top. The height from the water level in the bucket to the outlet was determined using a tape measure, which represented the pressure difference. Next, while the reactor was held upright, a graduated cylinder was placed underneath the outlet. The amount of time required to fill the graduated cylinder to an arbitrary volume was documented. This process was completed three times. One crate was then removed to decrease the hydraulic head, and the same process was completed, acquiring another three sets of measurements. Equation 4 was then used to find the hydraulic conductivity for each trial, and all six trials were averaged to represent the hydraulic conductivity of the medium. This process was completed for three wood chip-sand mixtures.

3.5 Porosity Calculations

The porosity of each wood chip-sand mixture was determined using the following equation:

$$Porosity = \frac{\text{weight of medium saturated} - \text{weight of medium dried}}{\text{total volume of medium}} \quad [5]$$

The weight of the medium saturated was determined by weighing the medium, using an OHAUS scale, after the hydraulic conductivity tests were performed. The saturated medium was then placed in a mechanical convection oven for approximately 8-10 hours at approximately 66°C, and weighed again to determine the weight of the medium dried.

4.0 Results

4.1 Nutrient Concentrations

Total dissolved nitrogen concentrations at the wells ranged from 0.48-27.67 mg/L (Figure 9). Wells ML-1-15, MW-1, ML-2-5, ML-2-10, and ML-2-15 had the highest TDN median concentrations in groundwater, 9.30 mg/L, 11.81 mg/L, 7.21 mg/L, 8.37 mg/L, 6.63 mg/L, indicating the location of a groundwater plume, about 41 m across. For all data analyses, the median, as opposed to the mean, was calculated. Because the residuals for all data sets were not normally distributed, the median is a better parameter to estimate the center of a data set. A relationship between TDN concentrations and season was not apparent. Analyses for specific nitrogen species, namely nitrate-nitrite and ammonium, were also completed, as well as a calculation to determine DON. Ammonium concentrations ranged from 0.00-10.87 mg/L where only three out of thirteen wells exhibited total median ammonium concentrations above 1 mg/L (Figure 10). Nitrate-nitrite concentrations ranged from 0.01-17.68 mg/L, and was more evident

in the groundwater, especially at wells ML-1-10 (5.13 mg/L), ML-1-15 (8.86 mg/L), ML-2-5 (5.07 mg/L), and ML-2-15 (6.19 mg/L); (Figure 11). To confirm that nitrate-nitrite is more pronounced in the groundwater compared to ammonium, a frequency distribution was completed, calculating that 76.88% of the total number of samples had a $\text{NH}_4^+/\text{NO}_3^-$ ratio less than one (Figure 12). The concentration of DON in the groundwater was calculated using the following equation:

$$\text{DON} = \text{TDN} - (\text{ammonium} + \text{nitrate-nitrite}) \quad [6]$$

DON concentrations ranged from 0.00-13.09 mg/L, and similar to ammonium, only two out of thirteen wells exhibited total median DON concentrations above 1 mg/L (Figure 13). Again, to confirm that nitrate-nitrite is more pronounced in the groundwater compared to DON, a frequency distribution was completed, calculating that 79.69% of the total number of samples had a DON/NO_3^- ratio less than one (Figure 14).

Total median oxygen concentrations were fairly low at all of the wells (1.08-3.91 mg/L), but never reached anoxic levels (Figure 15). A relationship exists between oxygen concentrations and season where in the fall/winter months, median oxygen concentrations are higher (1.64-6.22 mg/L) than those in the spring/summer months (0.8-3.5 mg/L). The depth to the water table (DTW) varied from 0.08 m to 0.99 m (Figure 16) and the well water median salinity concentrations ranged from 0.09 to 1.20 (Figure 17) indicating a marine, tidally-influenced site. A relationship was evident between salinity concentrations and season, where in the fall/winter months, median salinity concentrations tended to be higher (0.09-1.76) than those in the spring/summer months (0.09-0.96). This may be due to road salt for ice melt. The median pH measurements, besides that at well MW-5, reflect acidic solutions (4.51-6.69), and interestingly, as the depth increases, the groundwater becomes more acidic (Figure 18). Median pH

measurements for groundwater 4.5 m below the surface ranged from 4.51-5.00, while median pH measurements for groundwater 1.5 m below the surface ranged from 6.23-6.69. The total median temperature of the groundwater ranged from 14.52-20.29°C, where during the fall/winter months median temperatures ranged from 8.28-13.61°C, and during the spring/summer months ranged from 17.66-24.33°C (Figure 19).

4.2 Hydraulic Gradient

Figure 20 illustrates the position of the data loggers with respect to the AP-7, as well as the water level elevation at high tide and at low tide. After determining the intertidal slope (0.09) and applying the point-slope formula, $L(t)$ was calculated, ranging from 13.95 m to 23.32 m. Figure 21 depicts all of the water level elevation data in the well and Wills Creek with respect to the position of the data logger in Wills Creek. The water level elevation at the well ranged from -0.05 m to 0.25 m and the water level elevation in Wills Creek ranged from -0.39 to 0.44 m. The range for $dH(t)$ was -0.35 m to 0.21 m, and the range for the hydraulic gradient was -0.0154 to 0.0148 (Figure 22), with an average of -0.0041. The negative sign signifies a groundwater flow direction from the well towards the creek.

4.3 Hydraulic Conductivity and Porosity for wood chip-sand proportions

The hydraulic conductivity and porosity for the three wood chip-sand media ranged from 249.70 cm/day to 405.22 cm/day and 0.32 to 0.39 (Table 2). The experimental hydraulic conductivity and porosity for the background soil (0% by volume of wood chips) are not

statistically different from the literature value of 379.99 cm/day and 0.4 (Hughes and Porter, 1983).

% by volume of wood chips	Average hydraulic conductivity (cm/day)	Porosity
0%	405.22	0.35
20%	249.70	0.32
30%	333.50	0.37
40%	359.42	0.39

Table 2: The experimental hydraulic conductivity and porosity for media containing different proportions of wood chips.

Changes in the hydraulic conductivity with the addition of wood chips to Riviera Drive’s soil were not well validated in these tests. To determine whether there is a significant difference among the hydraulic conductivity measurements for each of the wood chip-sand proportions, a non-parametric Wilcoxon rank sum statistical test was performed instead of a parametric test because the residuals were not normally distributed. The results of the statistical test can be found in Table 3.

Comparison	p-value
*0% vs. 20%	0.0022
0% vs. 30%	0.0931
0% vs. 40%	0.1797
*20% vs. 40%	0.0022
*20% vs. 30%	0.0022
30% vs. 40%	0.1797

Table 3: Comparison of hydraulic conductivity between experimental media. Media whose hydraulic conductivity are significantly different are marked with an asterisk (*).

Interestingly, there is no significant difference in hydraulic conductivity between the 30% and 40% by volume of wood chips, and those proportions compared to the site soil (sand). However, there is a significant difference in hydraulic conductivity between the 20% and 30% by volume of wood chips, the 20% and 40% by volume of wood chips, and the 20% by volume of wood

chips and sand, where the 20% by volume of wood chips had a statistically lower hydraulic conductivity.

5.0 Discussion

The frequency distributions comparing nitrate-nitrite and ammonium concentrations, and nitrate-nitrite and DON concentrations, confirm that the groundwater along Riviera Drive is contaminated with nitrate-nitrite. The highest median nitrate-nitrite concentrations along the north side of Riviera Drive were between the two multi-level wells, especially at 4.5 m below the surface (6.19-8.86 mg/L). It is possible that high nitrate-nitrite concentrations occur at deeper (unsampled) depths, but a denitrifying bioreactor should capture this nitrate-nitrite plume.

While there is no relationship between nitrate-nitrite concentrations and the nitrate removal rate, there is a temperature dependency for nitrate removal. Robertson and Merkley (2009) observed substantially higher nitrate removal rates at 14°C (220 mg/m²/h) compared to that at 3°C (11 mg/m²/h), and similarly, Cameron and Schipper (2010) reported a statistically greater ($p < 0.001$) nitrate removal rate at 23.5°C than at 14°C for media composed of wood. Along Riviera Drive, the median temperature during the fall/winter months was 11.09°C, while during the spring/summer months it was 18.26°C. Given the results from Robertson and Merkley (2009) and Cameron and Schipper (2010), it is assumed that during the spring/summer months there will be higher nitrate removal rates, but it is uncertain whether the nitrate removal rates will be statistically different between seasons since the median temperatures are relatively similar. Because there is no apparent difference in groundwater nitrate-nitrite concentrations along Riviera Drive between the fall/winter and the spring/summer months, it will be important to

monitor the bioreactor for other metabolic processes, such as methanogenesis, sulfate reduction, and DNRA. Since higher nitrate removal rates are likely to occur during spring/summer months, undesirable compounds may be formed because all of the nitrate may be depleted before more nitrate enters the bioreactor.

The surplus of organic carbon should lower groundwater dissolved oxygen concentrations substantially at Riviera Drive. During a field investigation completed by Elgood et al. (2010), a majority of recorded influent dissolved oxygen concentrations were greater than 5 mg/L and yet a majority of effluent dissolved oxygen concentrations were less than 1 mg/L. There is an apparent difference in groundwater oxygen concentrations between the fall/winter and spring/summer months at Riviera Drive, where during the fall/winter oxygen concentrations are higher. Elgood et al. (2010) observed a similar trend and accredited higher emissions of N_2O during winter months to higher oxygen concentrations. The bioreactor installed along Riviera Drive may not be reducing enough for denitrification to occur during winter months, so it will be important to monitor oxygen concentrations year-round and determine whether denitrification is interrupted.

The groundwater between ML-1 and ML-2 exhibited an acidic (low) median pH measurement of 6.0. Unfortunately, pH measurements were not taken during the fall/winter months, but it is assumed that the pH will not be statistically different from the spring/summer months. While a decreasing pH increases the inhibitory effect NO_3 has on the reduction of N_2O (Blackmer and Bremner, 1978; Groffman et al., 2000; Well et al., 2003), the inhibitory effect does decrease over time as nitrate is transformed into nitrite. In addition, the process of denitrification produces alkalinity, where over time the natural pH of the groundwater in the bioreactor will increase. After three months, Cameron and Schipper (2010) observed a

substantial pH increase (2.5 to 6.6) for a medium containing hardwood. To reduce the likelihood of NO₃ inhibiting the reduction of N₂O during the bioreactor's start-up months, lime should be added to its medium when installed to increase the groundwater's natural pH to approximately 7.0.

On average, the groundwater flow along Riviera Drive is from the well toward Wills Creek (-0.0041). However, instances were observed during the tidal cycle when groundwater moved inland, i.e., when the hydraulic gradient was positive. To determine the distance groundwater moved inland, the following equations were used:

$$v = \frac{K \times \frac{dH(t)}{L(t)}}{\phi} \quad [7]$$

where v = speed of water
 K = hydraulic conductivity
 $\frac{dH(t)}{L(t)}$ = hydraulic gradient
 Φ = porosity

$$d = v \times t \quad [8]$$

where d = distance
 v = speed of water
 t = time

The maximum distance groundwater moved inland was calculated to be 5.13 cm. Considering that these observations were done at the time of spring tide, when the hydraulic head is largest, this distance is an extreme. Also, because the tide lowers within a couple of hours, the effect on the bioreactor should be minimal.

The results from the constant head test were unexpected. I assumed that as the volume of wood chips increased in the medium, the hydraulic conductivity would increase, and that such hydraulic conductivity would be higher than that of the site's soil (sand). When just examining the wood chip-sand proportions, the hydraulic conductivity and porosity both increased, but the

hydraulic conductivity for all three wood chip-sand proportions was not greater than that of the sand. In addition, the 20% by volume of wood chip-sand medium had a statistically lower hydraulic conductivity ($p=0.002$) than that of the sand, while the hydraulic conductivity for the 30% and 40% by volume of wood chips was not statistically different from the hydraulic conductivity of the sand. It may be that the addition of wood chips to the sand caused the medium to trap air bubbles (Cameron and Schipper, 2010), and in terms of water content, these air bubbles behave similarly to solids, therefore reducing the ease by which water can move through the medium. The calculated porosity does not take into account these air bubbles since the medium is dried out, which is why the porosity increased as the percent by volume of wood chips increased, even becoming larger than that of the site's soil (30% and 40% by volume). It is assumed that the medium continues to trap air bubbles as more wood chips are added, but it may be that the increase in porosity is compensating the trapping of air bubbles. This is possibly the reason why the hydraulic conductivity of the medium, with increasing percent by volume of wood chips, approaches that of the sand. It is not likely for this behavior to occur for less permeable soils, like silt, but because the background soil at this site has a relatively high hydraulic conductivity, very coarse particles in mass amounts are required in the medium to result in a statistically higher hydraulic conductivity compared to that of the site. Because neither of the media tested have statistically higher hydraulic conductivities than the site's soil, it is expected that the bioreactor will not capture deeper flow lines. This will not disrupt the function of the bioreactor though. An option that should be considered in the future for soils with a high hydraulic conductivity is mixing coarse wood chips with gravel to significantly heighten the hydraulic conductivity.

6.0 Design and Placement of the Denitrifying Bioreactor

6.1 Selection of Carbon Source

Numerous types of carbon sources have been tested for denitrifying bioreactors. Selecting an appropriate carbon source is based upon influent nitrate concentrations and the ease of rejuvenating the medium. At the desired location along Riviera Drive (between ML-1 and ML-2), median nitrate-nitrite concentrations range between 0.80 mg/L and 8.86 mg/L. For a bioreactor composed of maize cob, Cameron and Schipper (2010) reported nitrate removal rates of 15.0 mg/L/d for a 14°C treatment, and 19.8 mg/L/d for a 23.5°C treatment. Similarly, Greenan et al. (2006) observed a nitrate removal rate of 12.01 mg/L/d when using cornstalks as the carbon source. This type of carbon source has a higher ratio of labile carbon to refractory carbon, allowing organisms to utilize the source more rapidly than if there was a higher ratio of refractory carbon. Carbon sources with a higher ratio of labile carbon to refractory carbon are not appropriate for this site because the high nitrate removal rates will exhaust all of the nitrate before more nitrate enters the bioreactor, causing bacteria to utilize other metabolic processes that yield undesirable compounds. Because of the higher utilization rate, and consequently degradation rate, the bioreactor will not maintain nitrate removal over a prolonged period of time, unless the carbon source was rejuvenated (Cameron and Schipper, 2010). Greenan et al. (2006) observed diminishing nitrate removal rates for a cornstalk medium after 180 days of operation, while the nitrate removal rate for a medium composed of wood chips remained steady. Rejuvenating the carbon source along Riviera Drive would be too difficult, emphasizing the need for a carbon source that demonstrates longevity. Due to the relatively low nitrate-nitrite concentrations along Riviera Drive, the need for a carbon source that demonstrates longevity, and success in the field (Schipper and Vojvodić-Vuković, 2001; Long et al., 2011), wood chips

were chosen as the carbon source for the denitrifying bioreactor along Riviera Drive. In terms of wood chip type, Cameron and Schipper (2010) observed no significant difference in nitrate removal rates between softwood and hardwood, so hardwood wood chips were chosen simply because of availability.

Considering whether to use coarse wood chips or fine wood chips (sawdust), coarse wood chips (2-4 cm) were chosen. The hydraulic conductivity contrast between the bioreactor and the surrounding soil is important along Riviera Drive because higher nitrate-nitrite concentrations exist deeper in the ground. Because wood chips provide a higher porosity compared to sawdust, it was assumed, prior to completing the constant head test, a medium composed of coarse wood chips would result in a higher hydraulic conductivity compared to the surrounding soil.

6.2 Selection of Percent by Volume of Wood Chips

Given the hydraulic conductivity for each of the wood chip-sand proportions, and possible width measurements of the bioreactor, the volume flow rate of water through the bioreactor and the accompanying residence time were calculated (Table 4) using the following equations:

$$q = K \frac{dH(t)}{L(t)} \quad [9]$$

where q = volume flow rate (flux)

K = hydraulic conductivity

$\frac{dH(t)}{L(t)}$ = hydraulic gradient

$$v = \frac{q}{\Phi} \quad [10]$$

where v = speed of water

Φ = porosity

$$\tau = \frac{w}{v} \quad [11]$$

where τ = residence time
 w = width of bioreactor

Volume of woodchips (%)	Width of Bioreactor (m)	Residence Time (days)
20	0.1	3.32
30	0.1	2.70
40	0.1	2.51
20	0.25	8.31
30	0.25	6.76
40	0.25	6.27

Table 4: The calculated residence times concerning two bioreactor widths for experimental media.

The residence time increases with increasing bioreactor width and decreasing percent by volume of wood chips. To choose the appropriate wood chip-sand mixture for the medium and width for the denitrifying bioreactor, it is necessary to apply nitrate removal rates for media consisting of sand and wood. The 20% by volume of wood chip medium was discarded for use because it had a statistically lower hydraulic conductivity than the surrounding soil. While there was no significant difference in hydraulic conductivity between the 40% by volume wood chip medium and the surrounding soil, a nitrate removal rate could not be found. Therefore, a medium consisting of 30% by volume of wood chips was chosen for the bioreactor. Blowes et al. (1994) calculated a nitrate removal rate of 1.17 mg/L/d, while Schipper and Vojvodic-Vukovic (1998) recorded a maximum nitrate removal rate of 3.60 mg/L/d. While there are limited and differing literature values for this medium's nitrate removal rate, it will help in approximating a width for the bioreactor. Given the median nitrate-nitrite concentrations (6.19 and 8.86 mg/L), and the uncertainty in the nitrate removal rate, a residence time between 7.57 and 1.62 days will be required to significantly reduce nitrate-nitrite concentrations (Table 5).

Residence time (days)	Bioreactor width (m)	Nitrate removal rate (mg/L/d)	Median nitrate-nitrite concentrations 4.5 m below the surface (mg/L)
7.57	0.28	1.17	8.86
2.70	0.10	3.60	8.86
5.41	0.20	1.17	6.19
1.62	0.06	3.60	6.19

Table 5: Residence times and bioreactor widths for a medium containing 30% by volume of wood chips and 70% by volume of sand.

Considering the hypothetical amount of nitrate removed before new groundwater enters the bioreactor, a bioreactor width less than 0.25 m, and perhaps 0.1 m, seems appropriate for this site. Nitrate-nitrite concentrations may not be sufficient to support a bioreactor with a width over 0.25 m.

6.3 Placement and Dimensions of Denitrifying Bioreactor

Riviera Drive follows the shoreline of Wills Creek where there is an abundance of vegetation, specifically patches of *Phragmites*. The Town of Brookhaven intends to complete a restoration project along the shoreline of Wills Creek, removing *Phragmites* and replacing it with native vegetation, *Spartina patens* (Veronica King, 2015, Town of Brookhaven, personal communication). *Spartina patens* performs similar functions as *Phragmites*, and being shorter, provides residents with a more aesthetically pleasing view.

The denitrifying bioreactor will be placed approximately two meters seaward from the south side of Riviera Drive (Figure 23). This location was chosen as opposed to underneath the road for various reasons, but primarily because of the location of the water main. As a practical matter, the trenching process will require a couple of days of work, so instead of blocking off the

entire road, one lane can remain open. Lastly, the restoration project will be conducted simultaneously, so activity will be restricted to one area.

In order for the denitrifying bioreactor to capture the nitrate-nitrite plume existing between ML-1 and ML-2, it will need to be approximately 47 m in length. In order to maintain the biological process of denitrification and reduce the likelihood of other metabolic processes, as well as to remove the highest amount of nitrate, it would be ideal for the bioreactor to be installed as deep as 4.5 m below the surface. The rest of the trench can be filled with the excavated soil. The bioreactor will still remove nitrate if installed to a shallower depth, but other metabolic processes may transpire so it is important to monitor the influent and effluent. Because the water table between ML-2 and ML-1 is relatively high (Figure 16), dewatering will need to occur during installation. Many who have situated bioreactors in the field use a frame to assist in the excavation of soil and installation of the bioreactor (Vallino and Foreman, 2008; Robertson and Cherry, 1995).

7.0 Future Work

Monitoring wells need to be installed to determine if the bioreactor is effectively reducing groundwater nitrate-nitrite concentrations. These wells would be positioned on the seaward side of the bioreactor to intercept the groundwater, and the existing monitoring wells on the landward side will document influent groundwater. It would also be beneficial to install one well on each end outside the bioreactor to act as a control (Figure 23).

Various compounds need to be monitored in order to determine whether the denitrifying bioreactor is functioning properly. Nitrate-nitrite concentrations will be measured and compared

at the influent and effluent wells. It is expected to take a couple of weeks for the bacteria to grow and acclimate to the new environmental conditions, and to reduce oxygen concentrations to suboxic levels, so it is not expected to notice differences in nitrate-nitrite concentrations immediately. Blowes et al. (1994) observed differences in influent and effluent nitrate concentrations approximately two weeks after the bioreactor was installed. Ammonium concentrations should also be measured and compared since Vallino and Foreman (2008) observed the production of ammonium in the presence of seawater. Such production is most likely due to DNRA, a process driven by H_2S . As previously mentioned, H_2S is a product of sulfate reduction, and this process should not occur if the bacteria are not removing all of the nitrate within the residence time of the bioreactor. If ammonium concentrations are higher in the effluent compared to the influent, it is possible that the residence time of the bioreactor is too long, causing the bacteria to perform sulfate reduction as their metabolic pathway. For similar reasons, methane concentrations should be measured and compared. If higher methane concentrations are detected in the effluent compared to the influent, the bacteria may be performing methanogenesis as their metabolic pathway since all of the nitrate is being depleted before new groundwater enters the bioreactor.

Because it was observed that high concentrations of DOC leach from the bioreactor during the first year of use (Schipper et al., 2010; Robertson and Cherry, 1995), it is important to monitor such levels. Eventually DOC levels will plateau to a lower level, but the amount of time it takes to do so and the level it plateaus to should be documented. This will help in approximating how much carbon is lost over time. The pH of the effluent should be monitored as well considering that NO_3 has a higher inhibitory effect on the reduction of N_2O at a lower pH. While lime should be added to the medium prior to installing the bioreactor, it would be

necessary to document how the pH changes over time. Nitrous oxide concentrations should also be measured and compared between the influent and effluent wells to confirm that nitrate is being fully reduced to N₂ gas.

The nitrate removal rate will be important to calculate because it will help future investigators select an appropriate medium for their site. This can be easily calculated by measuring the nitrate concentrations at both the influent and effluent wells (mg/L), taking the difference, and then dividing by the residence time of the bioreactor. Lastly, the amount of carbon mass consumed over time should be measured to approximate the longevity of the bioreactor. Robertson et al. (2000) calculated this by estimating the total flow volume going through the bioreactor, multiplying that by the average amount of nitrate attenuated over a certain period of time, and using the mole ratio of 1.25 moles of carbon to 1 mole of nitrate to N₂ gas. The occurrence of other metabolic processes may contribute to carbon loss as well, so their input should be estimated. Measurements for monitoring should be taken at least once or twice a month.

8.0 Conclusions

A denitrifying bioreactor measuring 47 m in length is expected to reduce groundwater nitrate-nitrite concentrations along Riviera Drive. The medium for bioreactor will consist of 70% by volume of excavated soil (sand) and 30% by volume of wood chips, with a hydraulic conductivity of 333.50 cm/day and porosity 0.37. Due to documented nitrate removal rates for this medium, and median nitrate-nitrite concentrations along Riviera Drive (0.80 mg/L-8.86 mg/L), the bioreactor should have a width less than 0.25 m, perhaps closer to 0.1 m, to reduce

the likelihood of other metabolic processes. For conditions along the north side of Riviera Drive, the bioreactor would be installed to a depth of 4.5 m below the surface, with the top residing at 3 m below the surface, to remove the most groundwater nitrate-nitrite and again, to reduce the likelihood of other metabolic processes. If installed to a shallower depth, the bioreactor will reduce nitrate-nitrite concentrations, but there is a chance of more methane, hydrogen sulfide and ammonium production. Closer to the tide line, however, the bioreactor would be placed at a shallower depth because the flow lines converge towards the surface.

There has been great success in the field using denitrifying bioreactors as a groundwater remediation technology. Elgood et al. (2010) reported bioreactor effluent concentrations between <0.01 mg/L and 3.9 mg/L when stream nitrate concentrations ranged between 0.3 and 5.8 mg/L. Robertson and Cherry (1995) also observed a reduction in groundwater nitrate concentrations, where nitrate values up gradient of the denitrifying bioreactor ranged between 5 mg/L and 62 mg/L, and down gradient values ranged between 2 mg/L and 25 mg/L. Considering these results, it is expected that the denitrifying bioreactor installed along Riviera Drive will statistically reduce groundwater nitrate-nitrite concentrations to approximately 1 mg/L or less.

9.0 References

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10.0 Figures

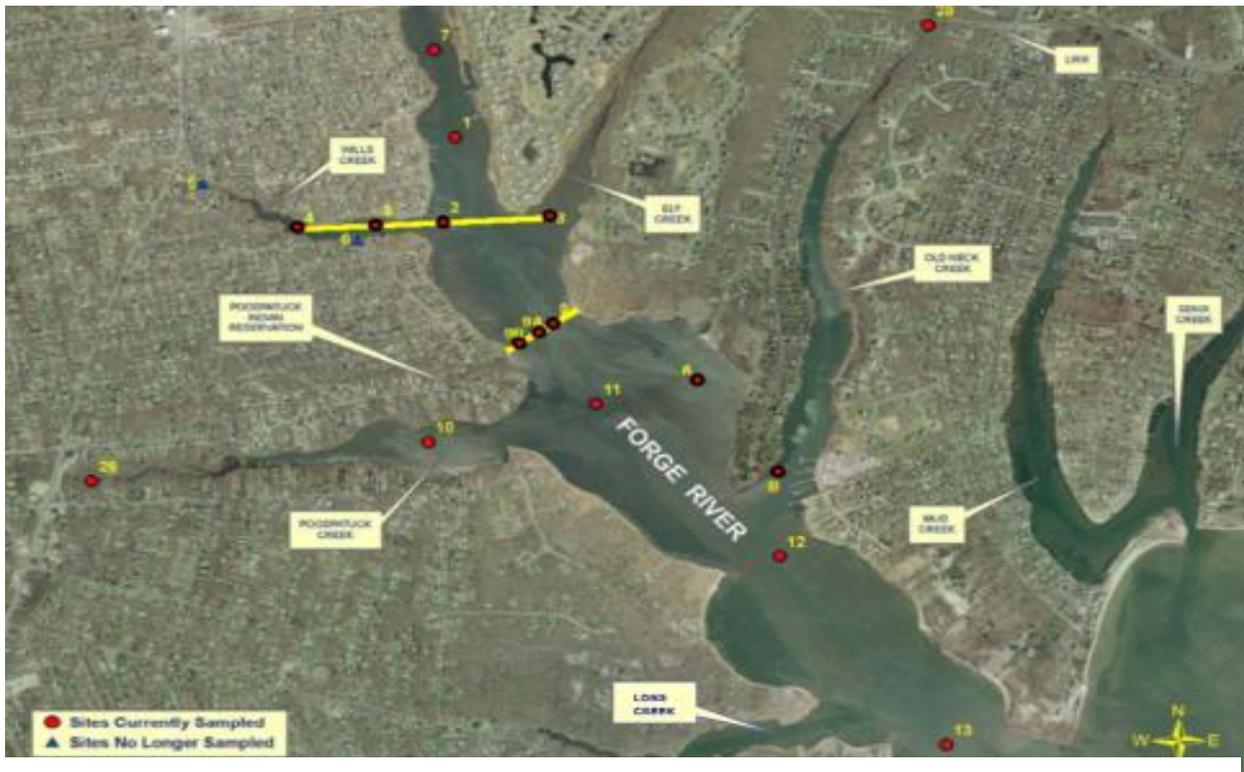


Figure 1a: Map of Forge River showing Suffolk County water quality sampling stations and oceanographic sampling transects (from Swanson et al., 2010b).

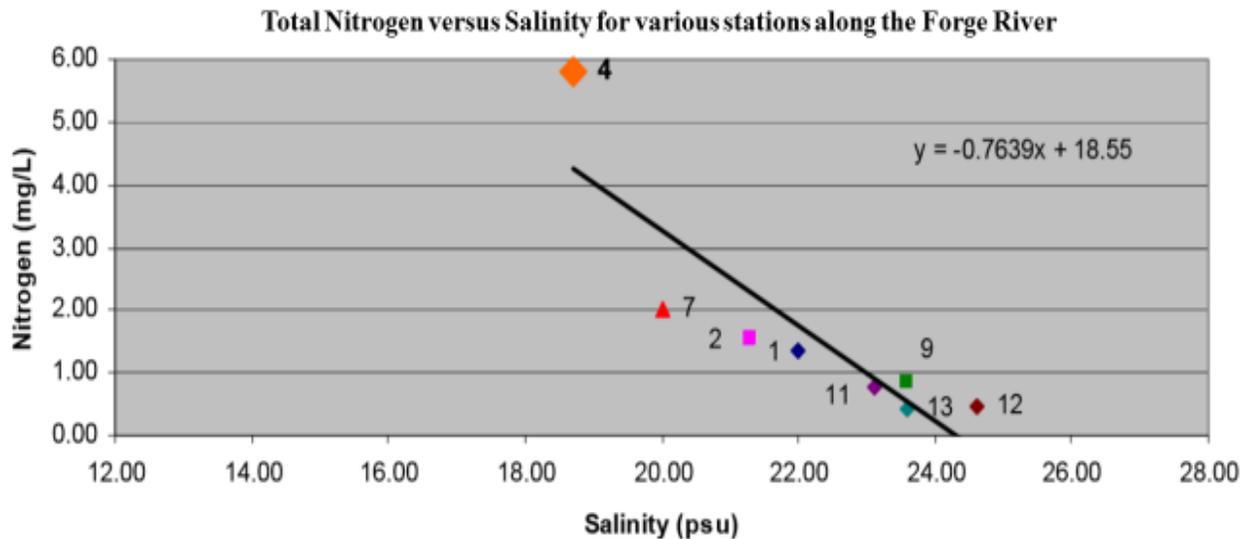


Figure 1b: Total nitrogen concentrations versus salinity for stations (referencing Figure 1a) along the Forge River (from Swanson et al., 2010b). Stations 7, 1, 2, 9, 11, 12, and 13 were sampled on 12 September 2005, 13 October 2005, 10 November 2005, and 5 June 2006. Station 4 (Wills Creek) was sampled on 5 June 2006. Data was taken from Suffolk County Department of Health Services.

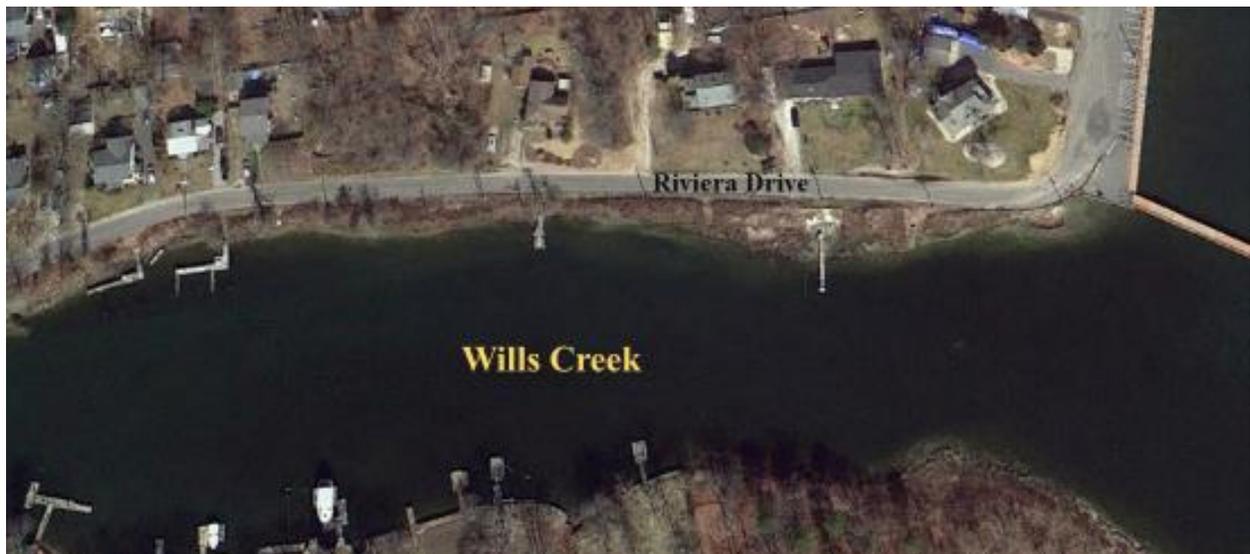


Figure 2: Map of the study site. Located on the western side of the Forge River, Mastic Beach, Town of Brookhaven, New York (from Google Earth 2015).

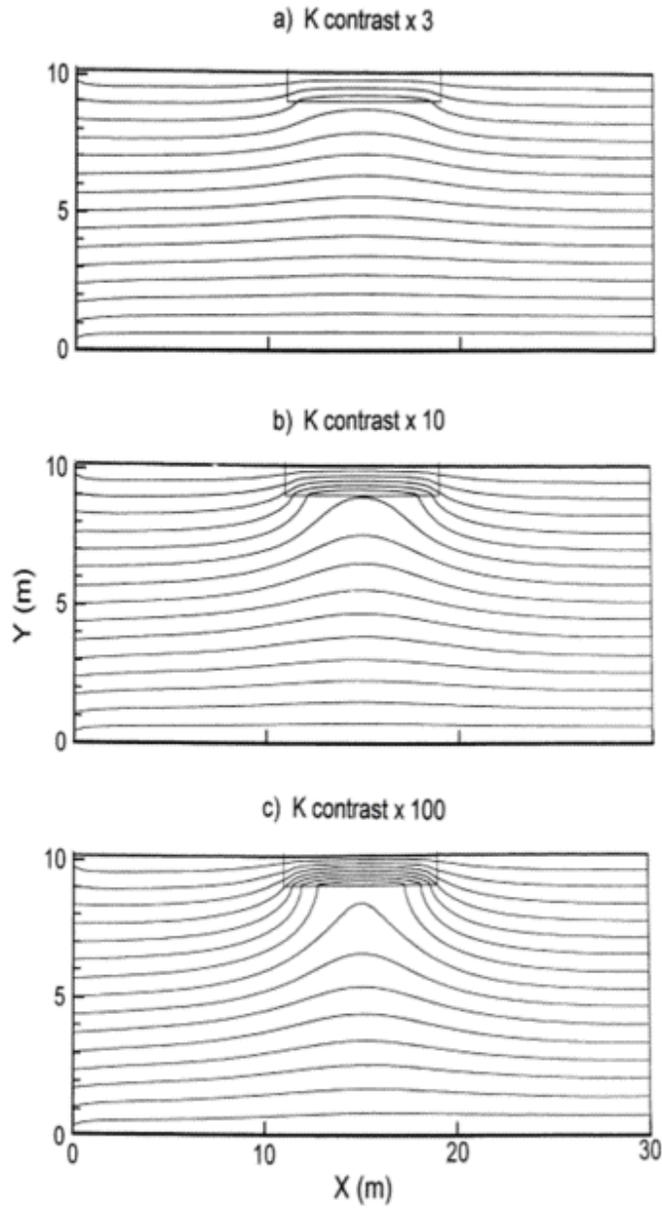


Figure 3: Model sensitivity analysis showing the effect hydraulic conductivity contrast (K) has on the capture of deeper streamlines: (a) layer hydraulic conductivity is three times higher than background layer, (b) layer hydraulic conductivity is 10 times higher, (c) layer hydraulic conductivity is 100 times higher (from Robertson et al., 2005).

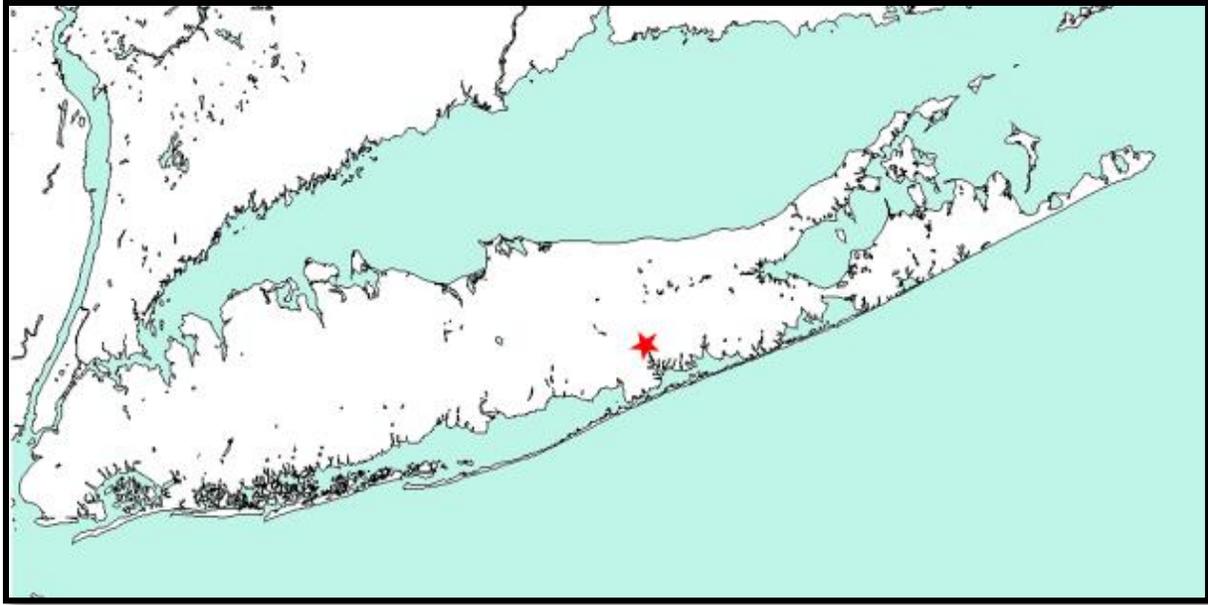


Figure 4: Map of Long Island, with the star indicating the beginning of the Forge River, flowing southward.



Figure 5a: Map of the Forge River indicating transect along which electrical resistivity measurements were completed to determine the extent of a freshwater plume (from Durand et al., 2011).

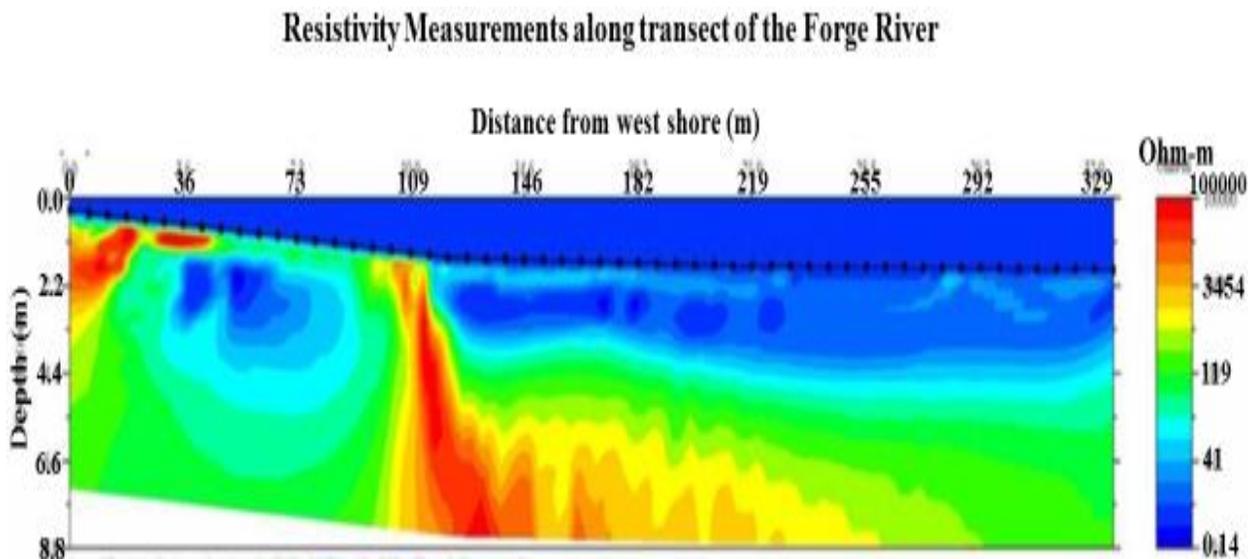


Figure 5b: Water resistivity measurements of transect (referencing Figure 5a) of the Forge River (from Durand et al., 2011). Water resistivity value fixed at 0.285 Ohm.m. Plumes of relatively high resistivity are a proxy for SGD.



Figure 6: Map showing the location of the monitoring wells (MWs) and multilevel wells (MLs) along Riviera Drive. Yellow circles signify the single level wells and red circles signify the multilevel wells (from Pritt, 2015).



Figure 7: Map showing where the HOB0 data loggers were placed for hydraulic gradient test (yellow circles). One placed in well MW-4 and the other attached to a piling at end of pier (from Google Earth 2015).

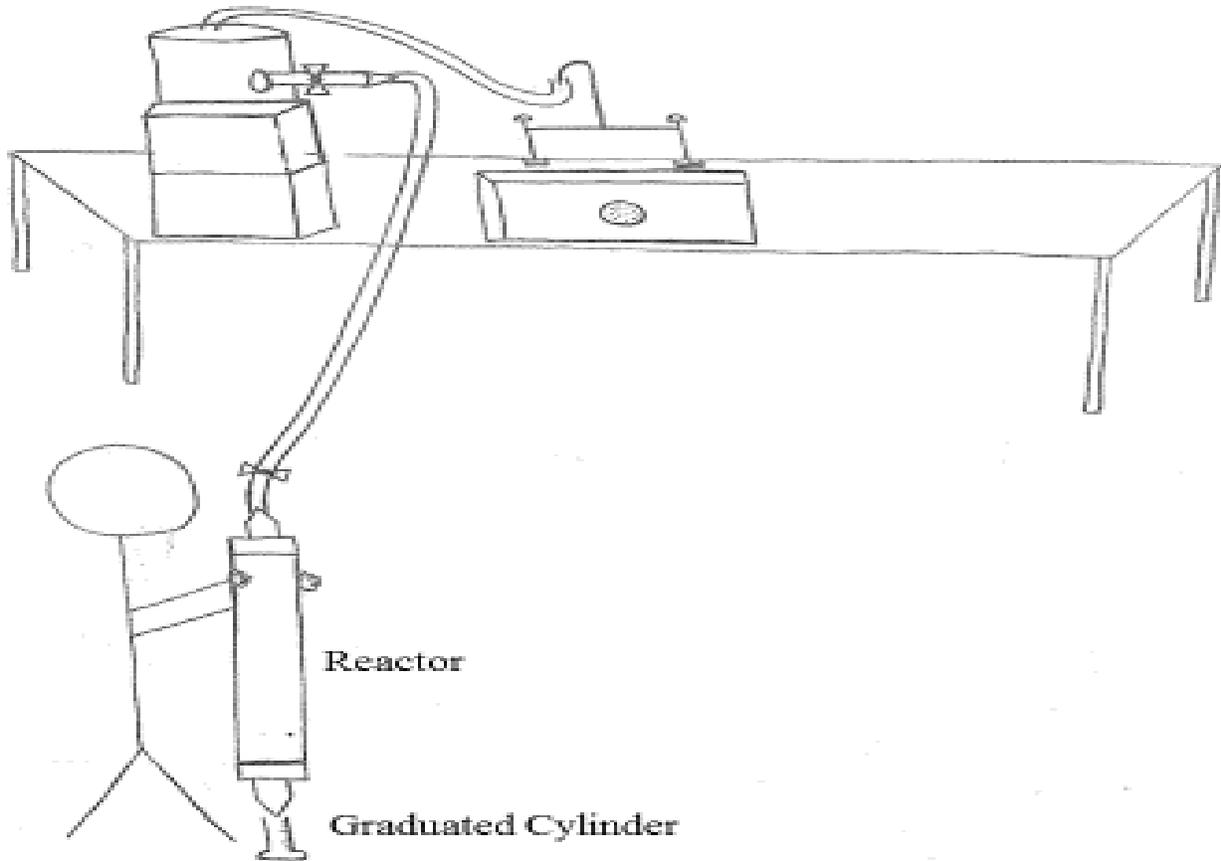


Figure 8: Diagram representing set-up of hydraulic conductivity tests.

Total Dissolved Nitrogen concentrations in groundwater along Wills Creek

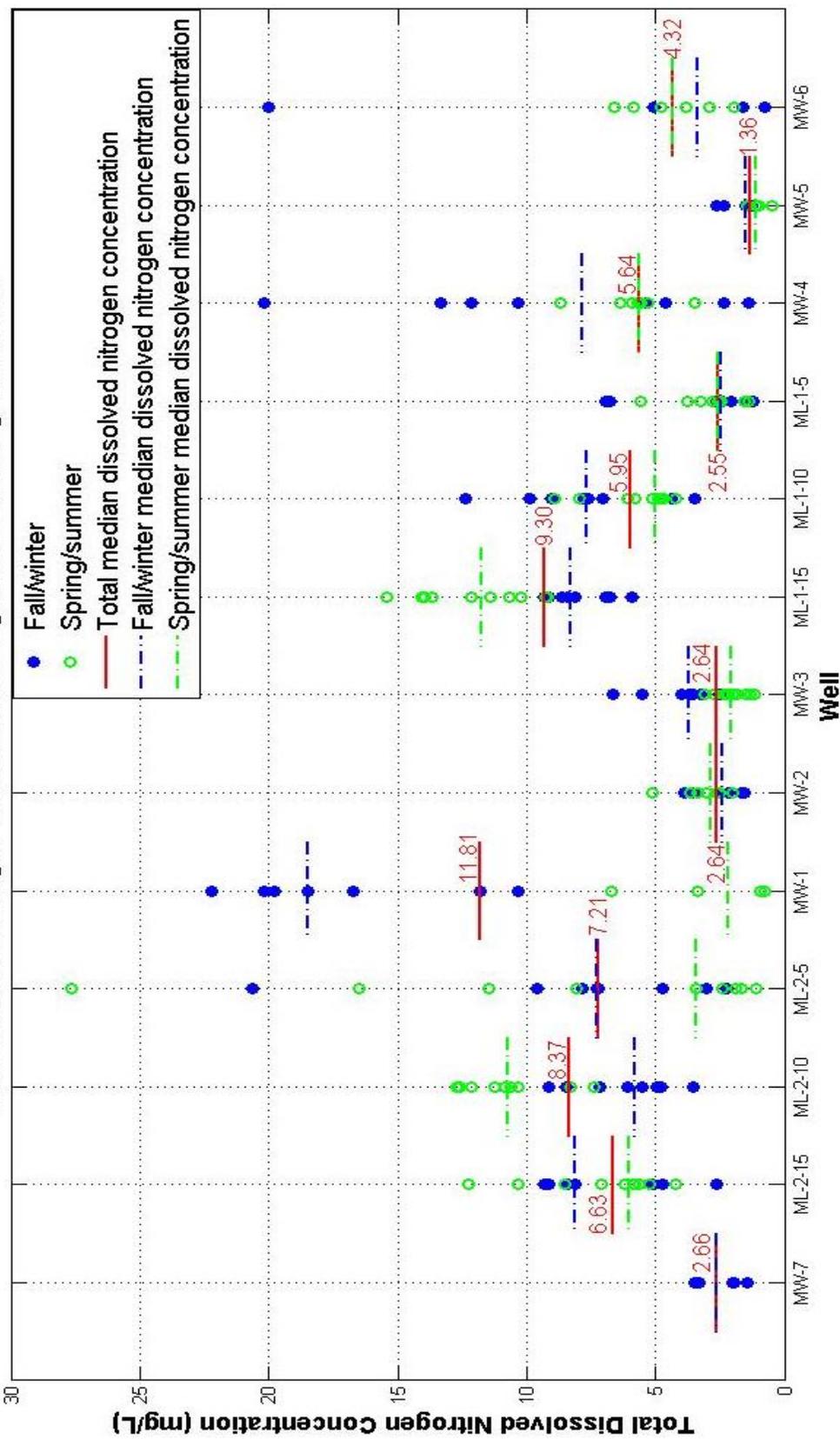


Figure 9: Total dissolved nitrogen concentrations in groundwater along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

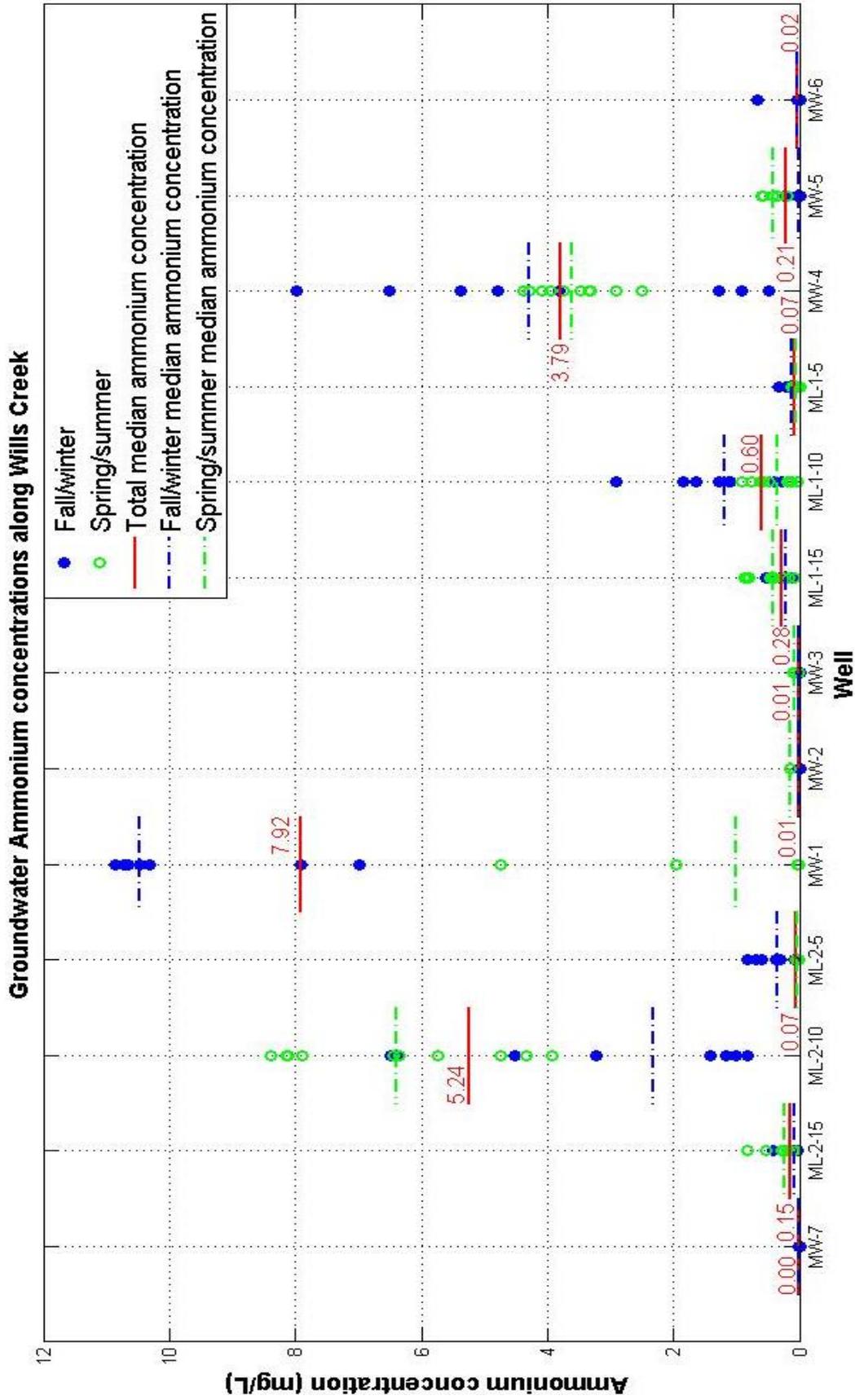


Figure 10: Groundwater ammonium concentrations along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

Groundwater Nitrate-nitrite concentrations along Wills Creek

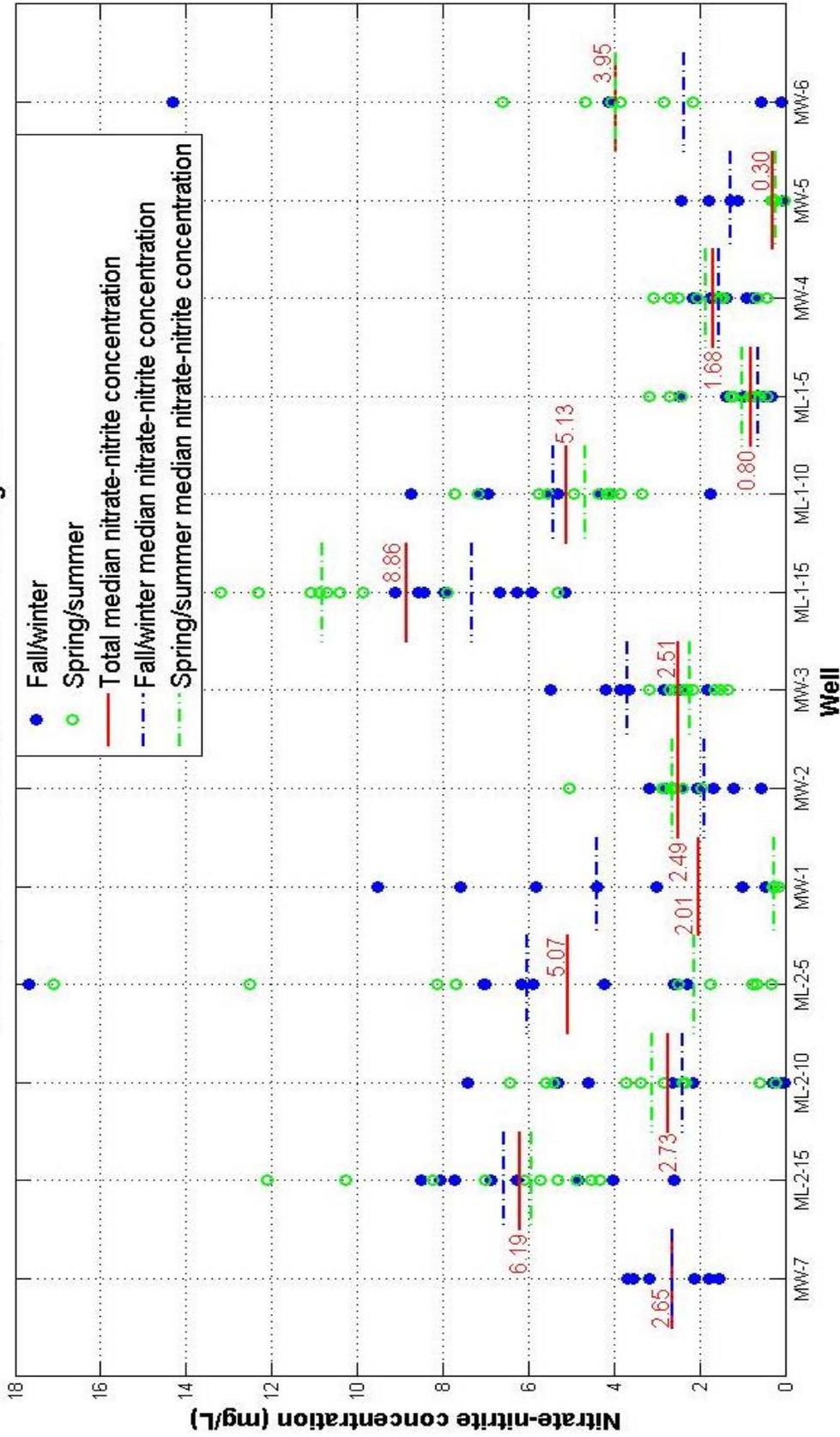


Figure 11: Groundwater nitrate-nitrite concentrations along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

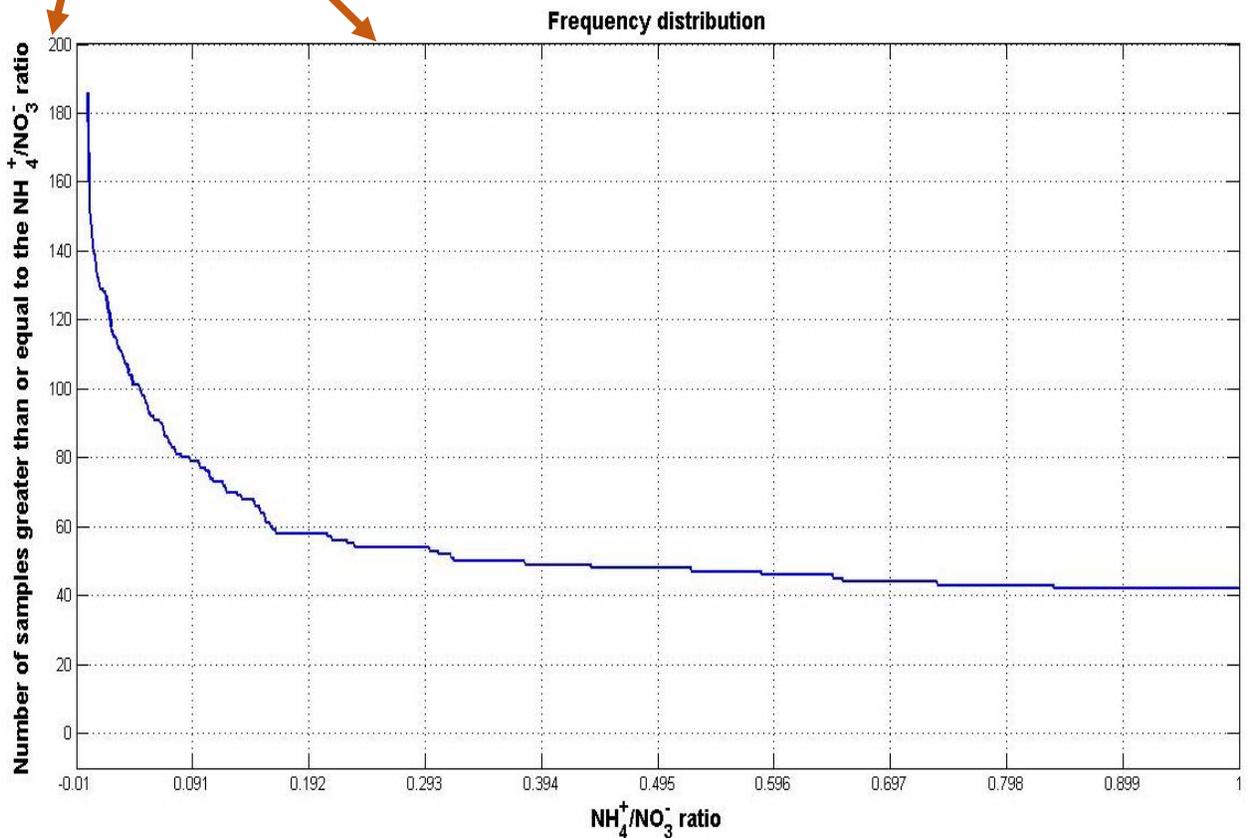
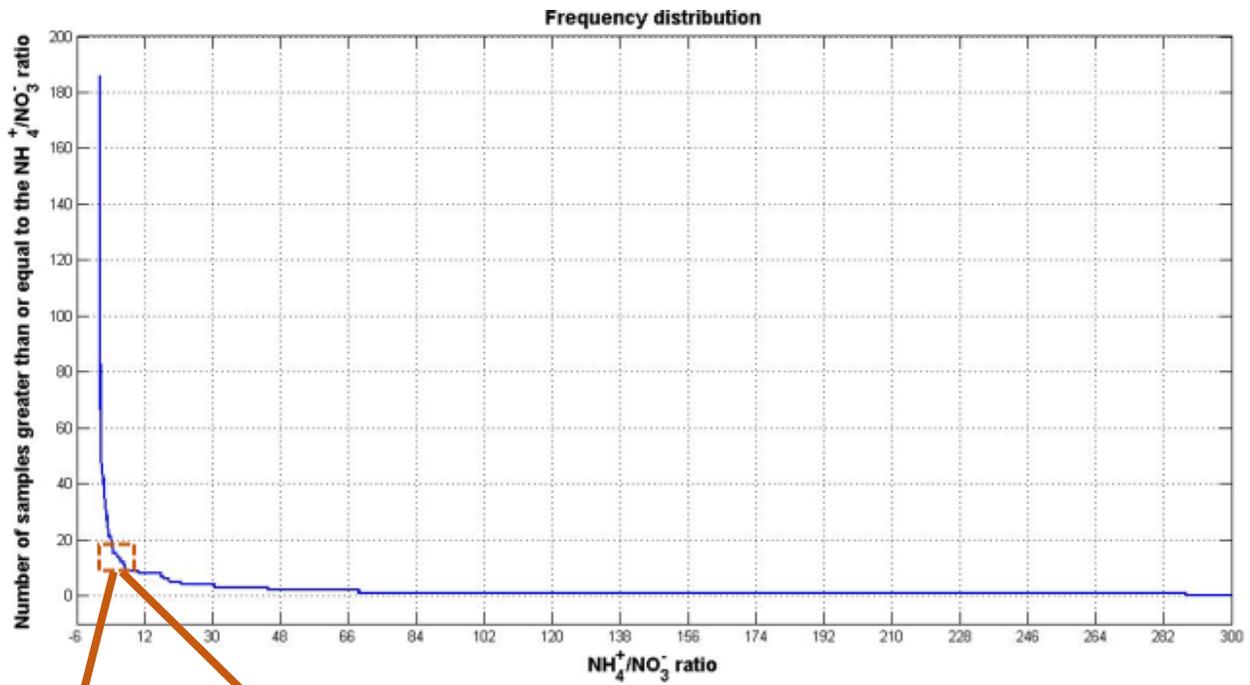


Figure 12: Frequency distribution for $\text{NH}_4^+/\text{NO}_3^-$ ratio, where 76.88% of the total number of samples have a $\text{NH}_4^+/\text{NO}_3^-$ ratio less than one.

Groundwater dissolved organic nitrogen concentrations along Wills Creek

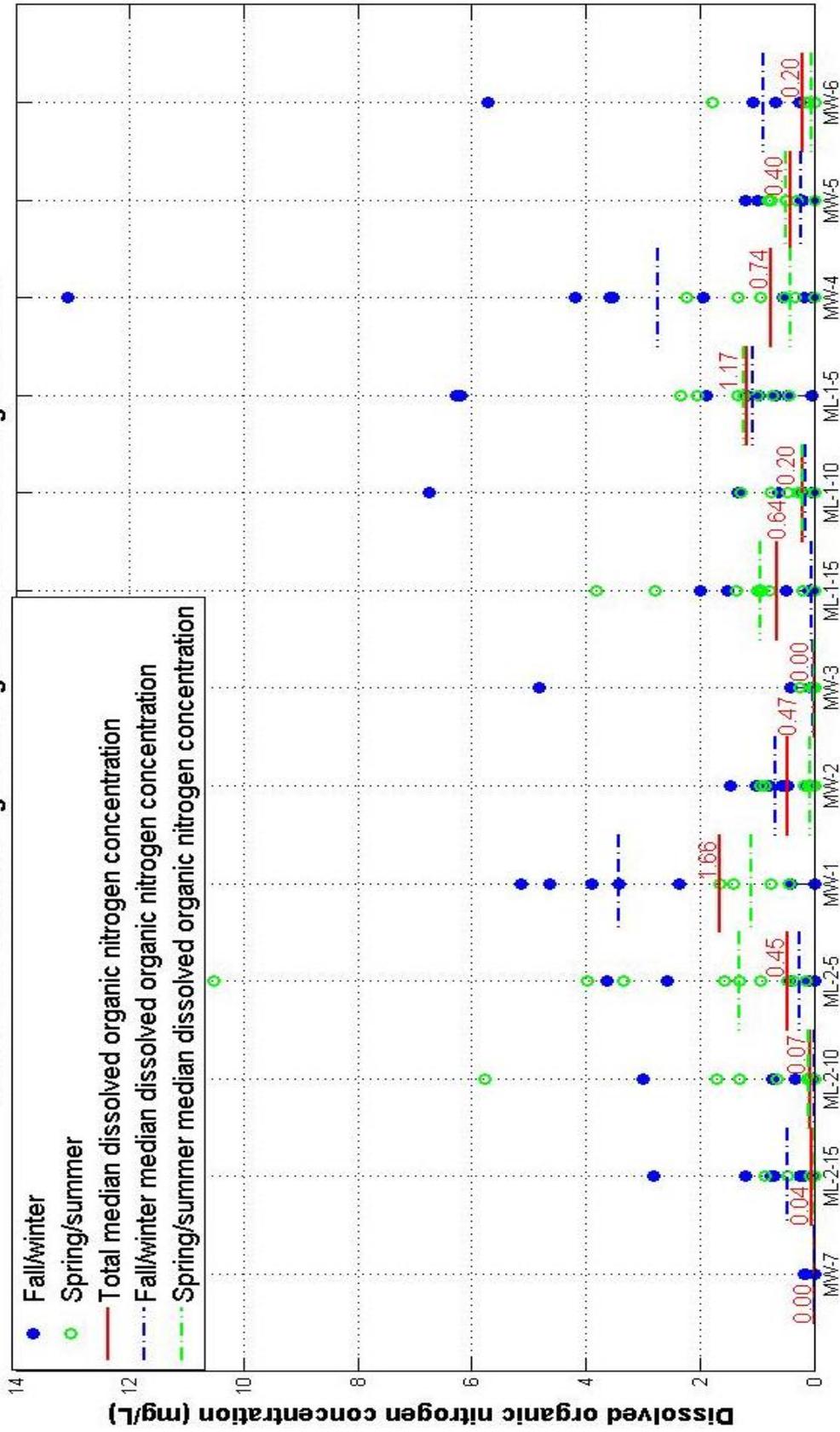


Figure 13: Groundwater dissolved organic nitrogen concentrations along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

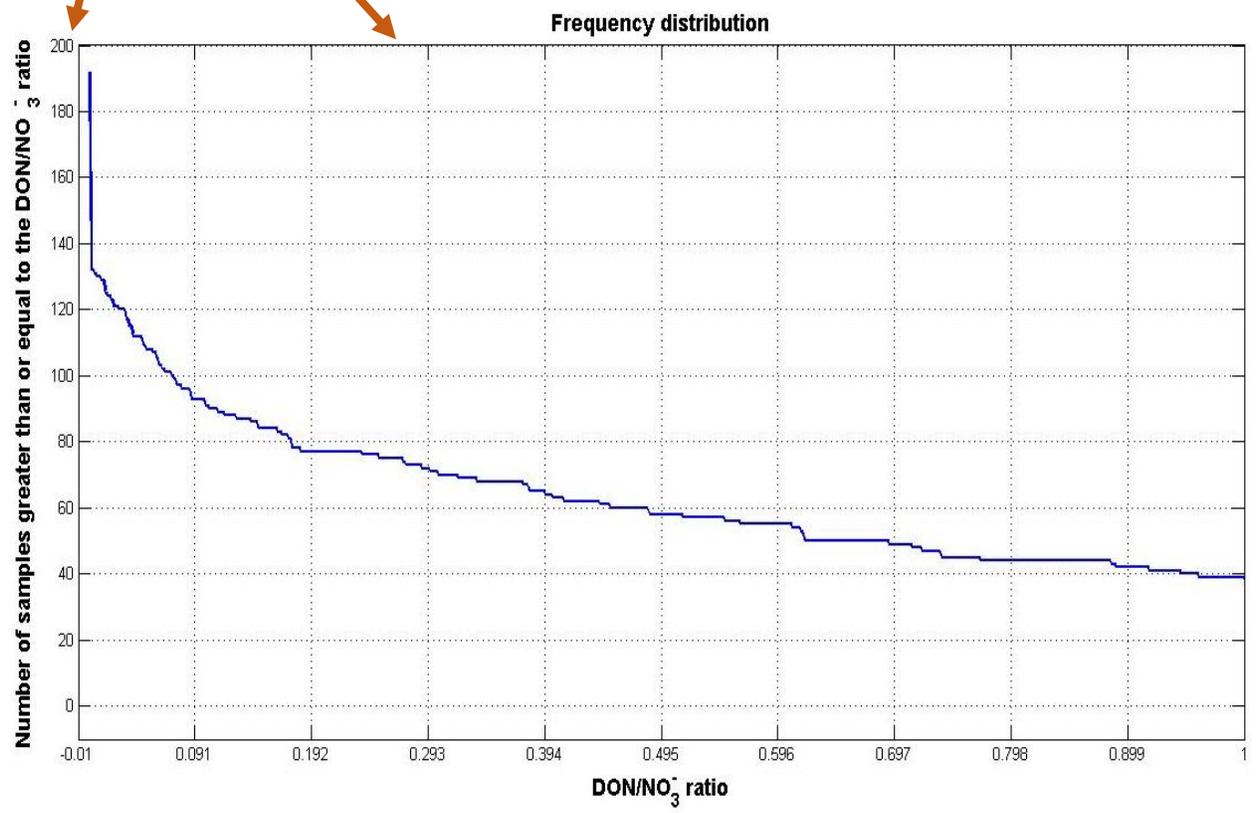
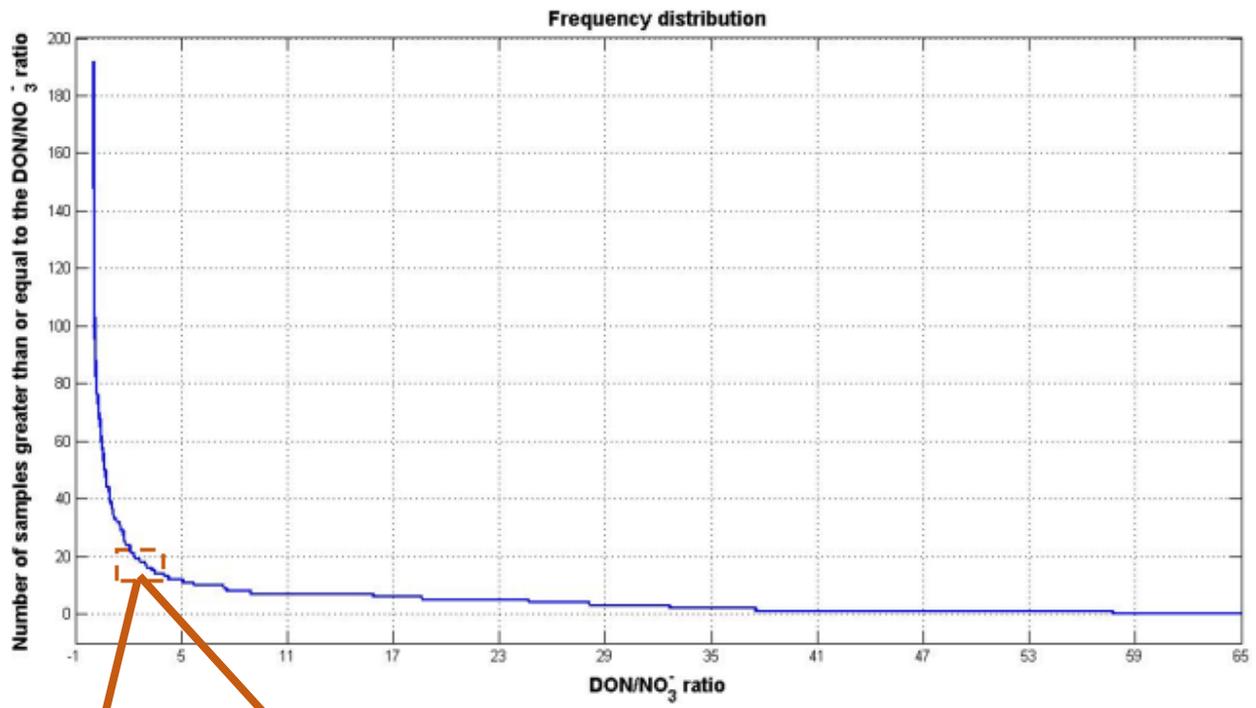


Figure 14: Frequency distribution for DON/NO_3^- ratio, where 79.69% of the total number of samples have a DON/NO_3^- ratio less than one.

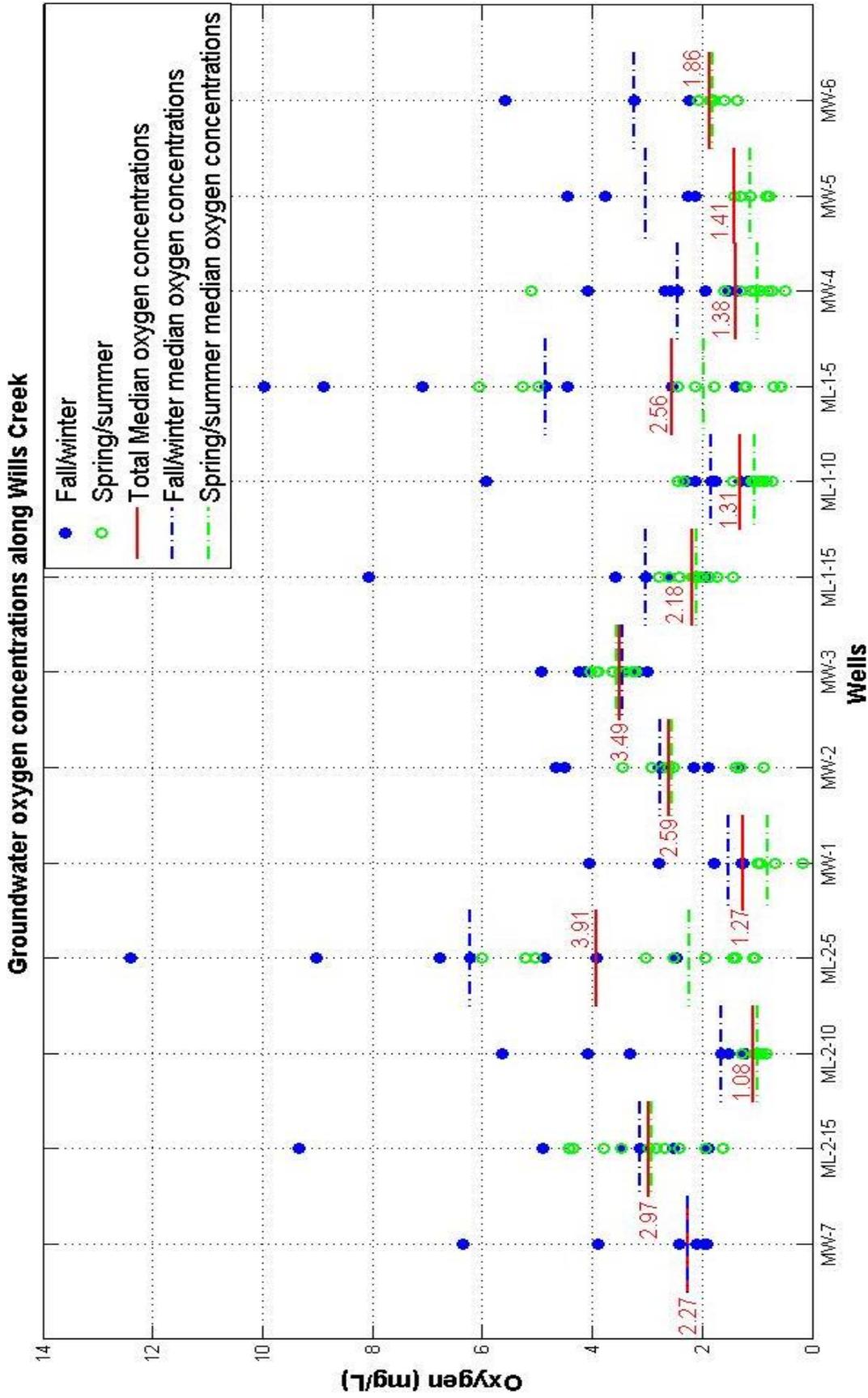


Figure 15: Groundwater oxygen concentrations along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

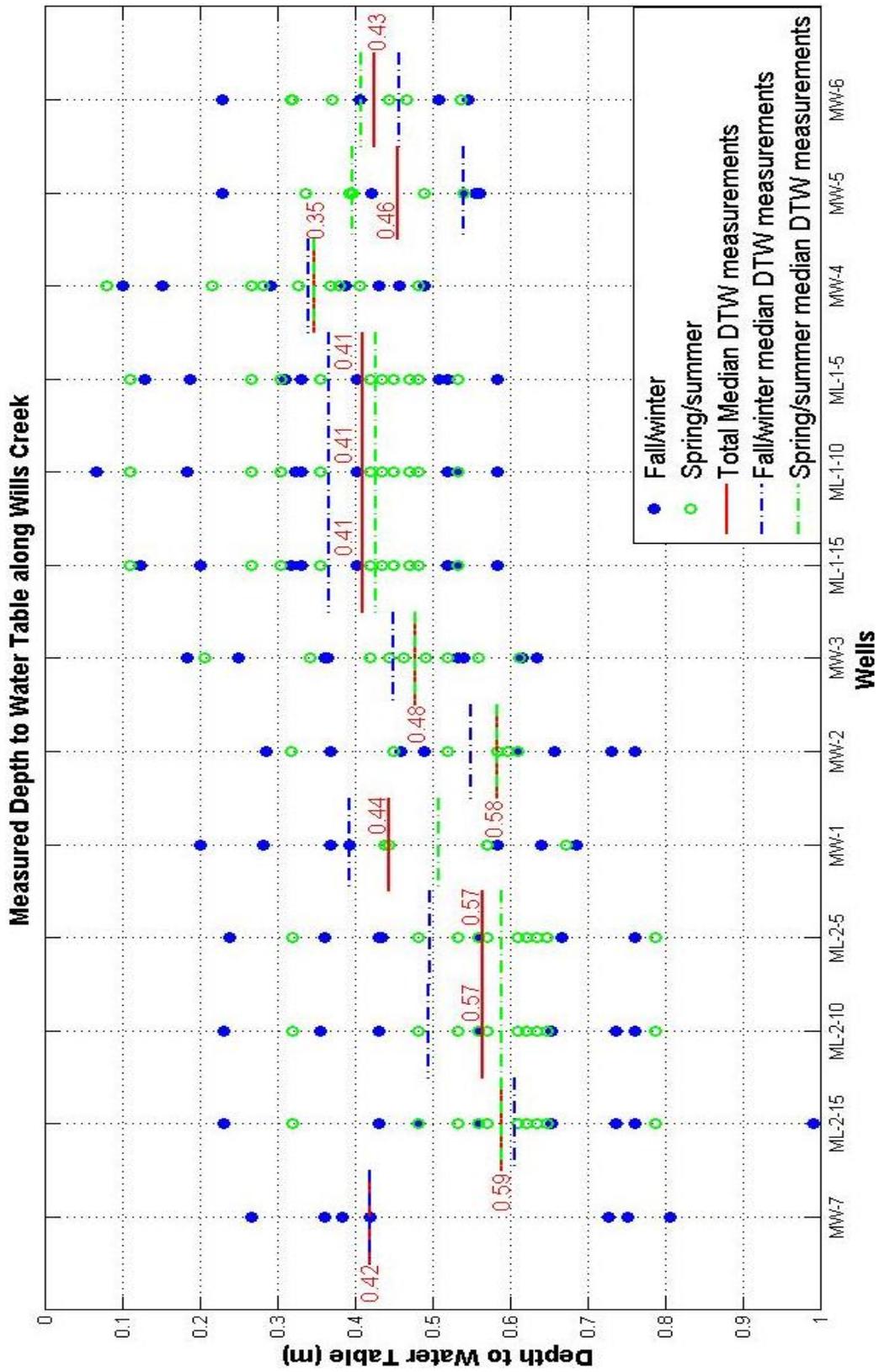


Figure 16: Measured depth to water table along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

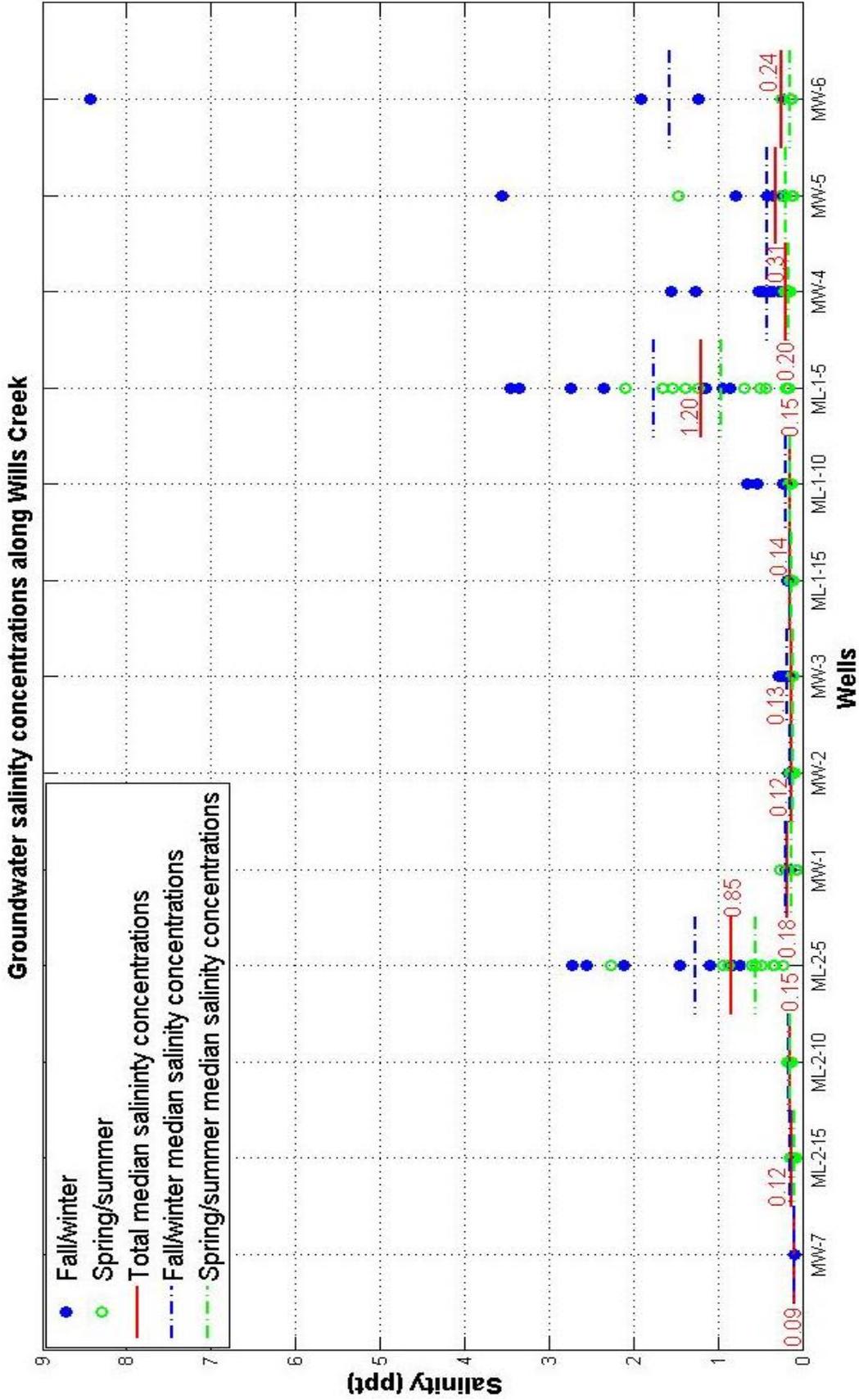


Figure 17: Groundwater salinity measurements along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

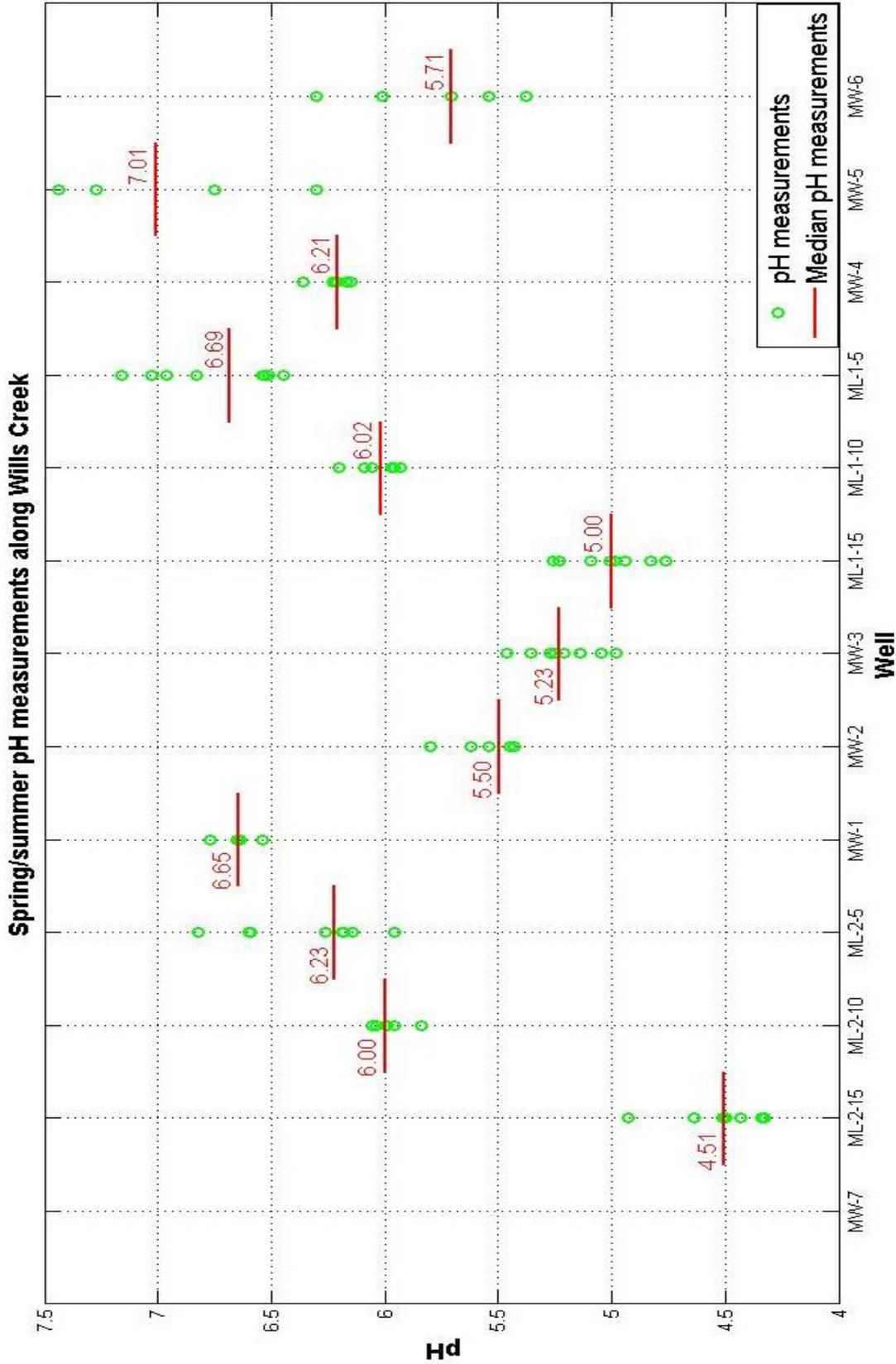


Figure 18: Groundwater pH measurements along Wills Creek. Measurements started in May, 2015 and ended in August, 2015.

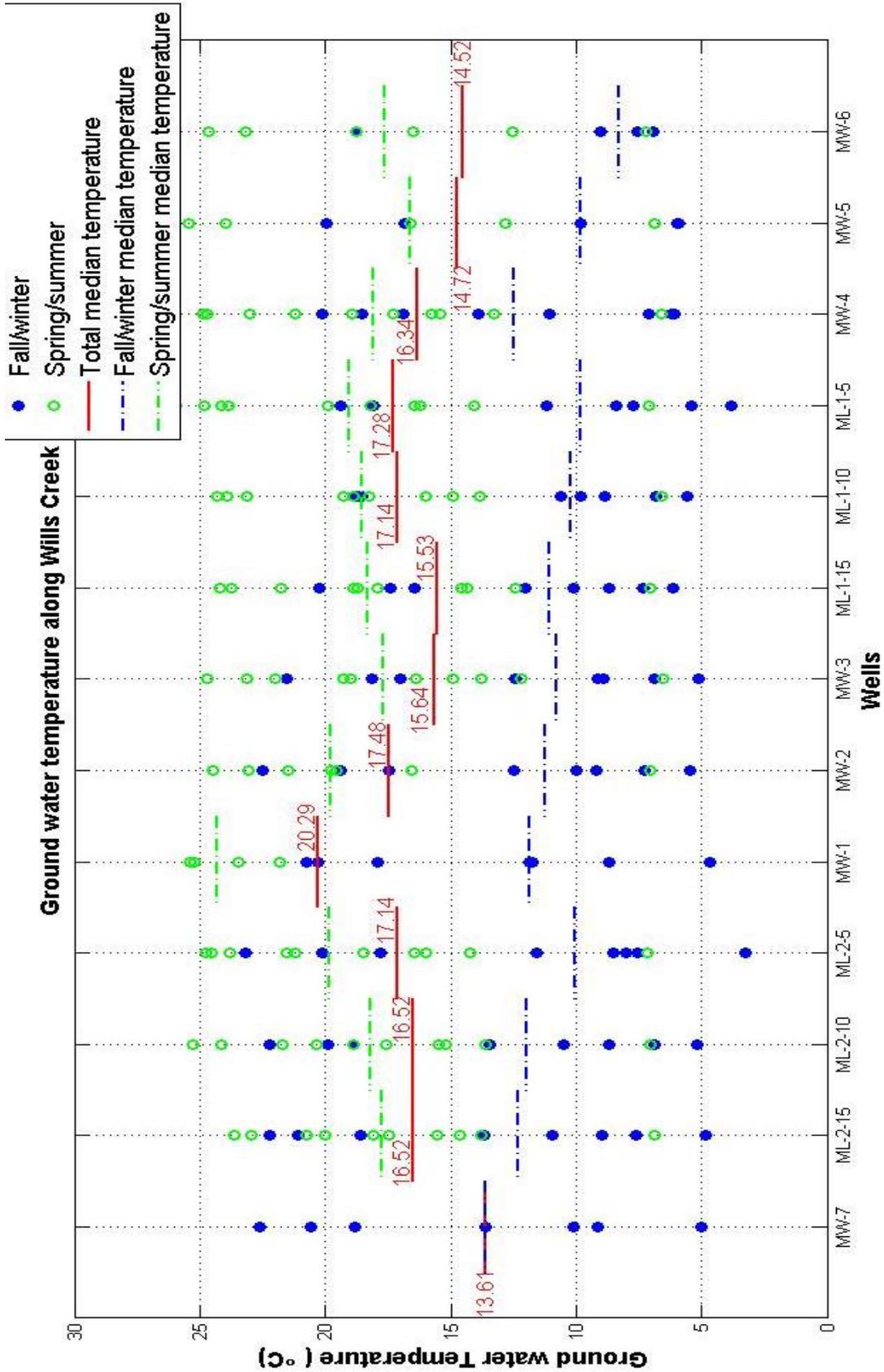


Figure 19: Groundwater temperature measurements along Wills Creek. Fall/winter includes September through March; Spring/summer includes April through August.

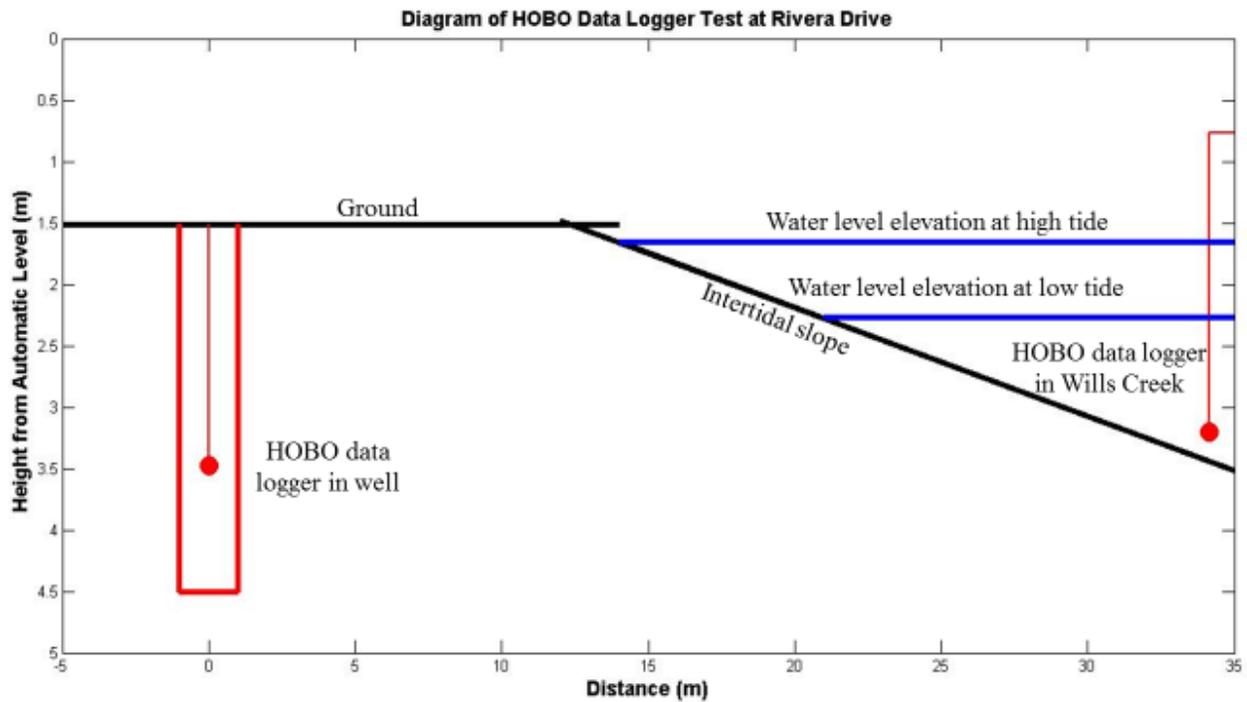


Figure 20: Diagram showing position of HOBO data loggers relative to Automatic Level, with the water level elevation at high tide and at low tide.

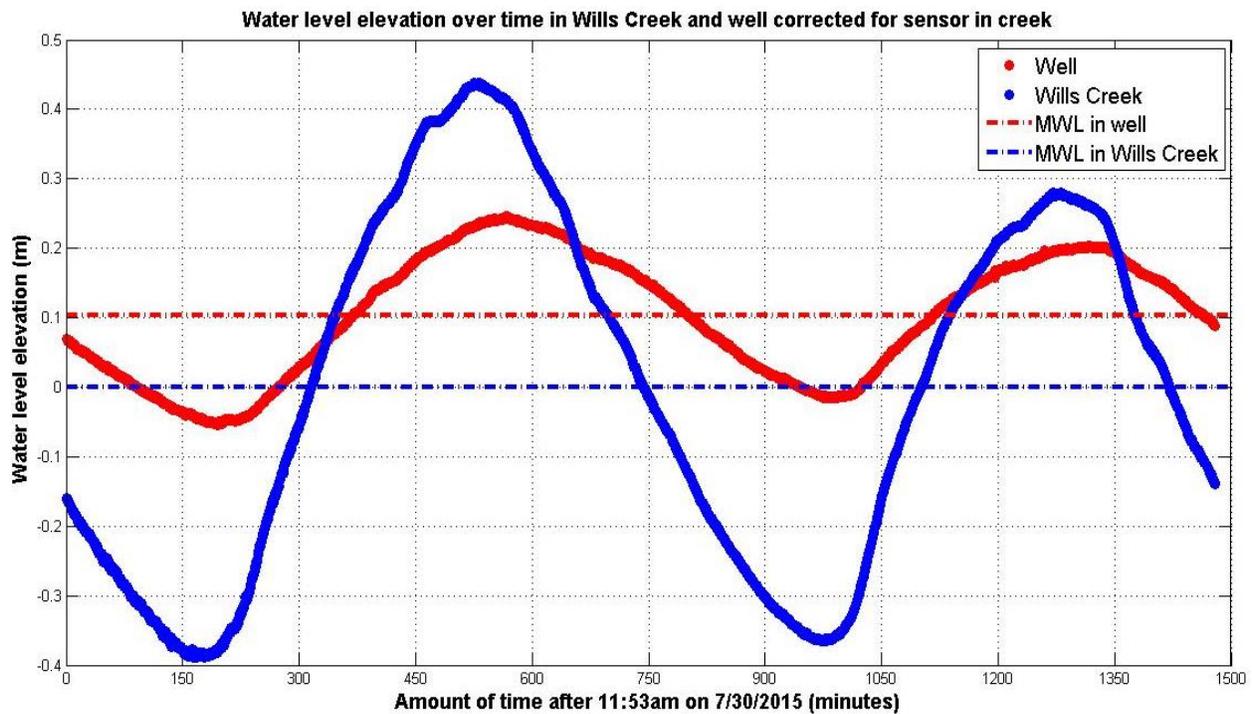


Figure 21: The variation in water level elevation over a tidal cycle at well MW-4 and Wills Creek with respect to the position of the data logger in Wills Creek.

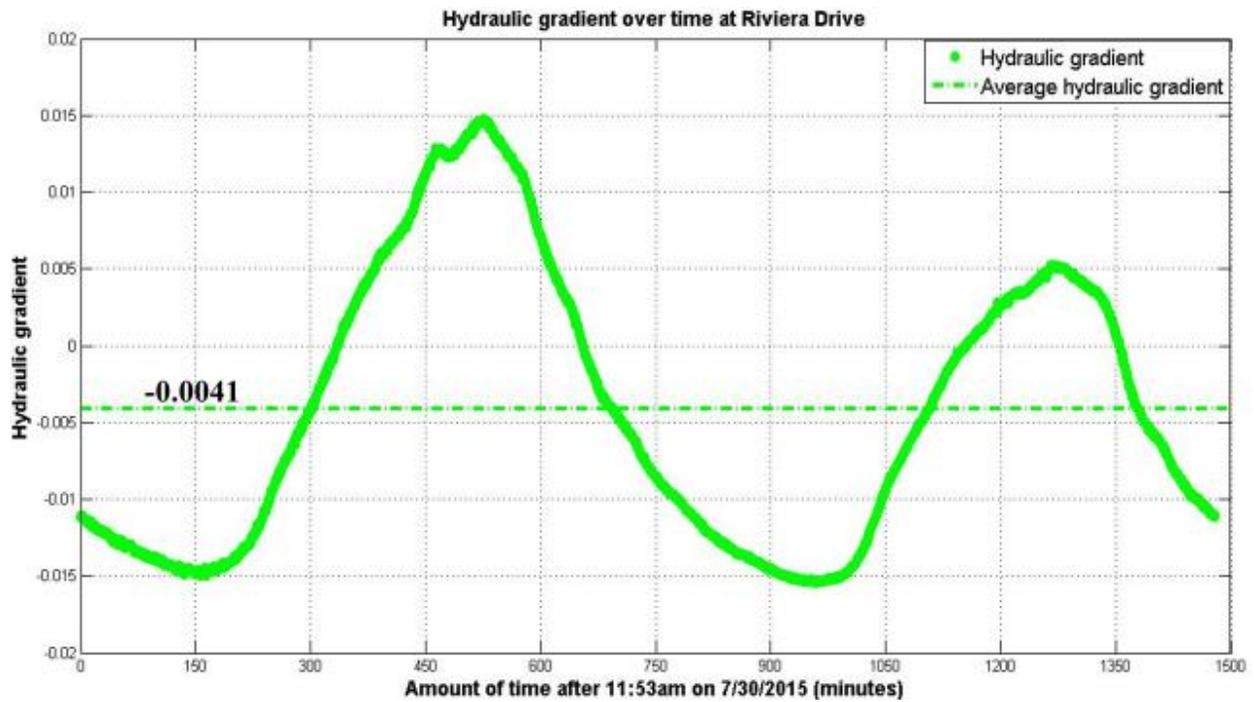


Figure 22: The variation in hydraulic gradient over a tidal cycle at Riviera Drive. The hydraulic gradient varies between -0.0154 and 0.0148, with an average of -0.0041.

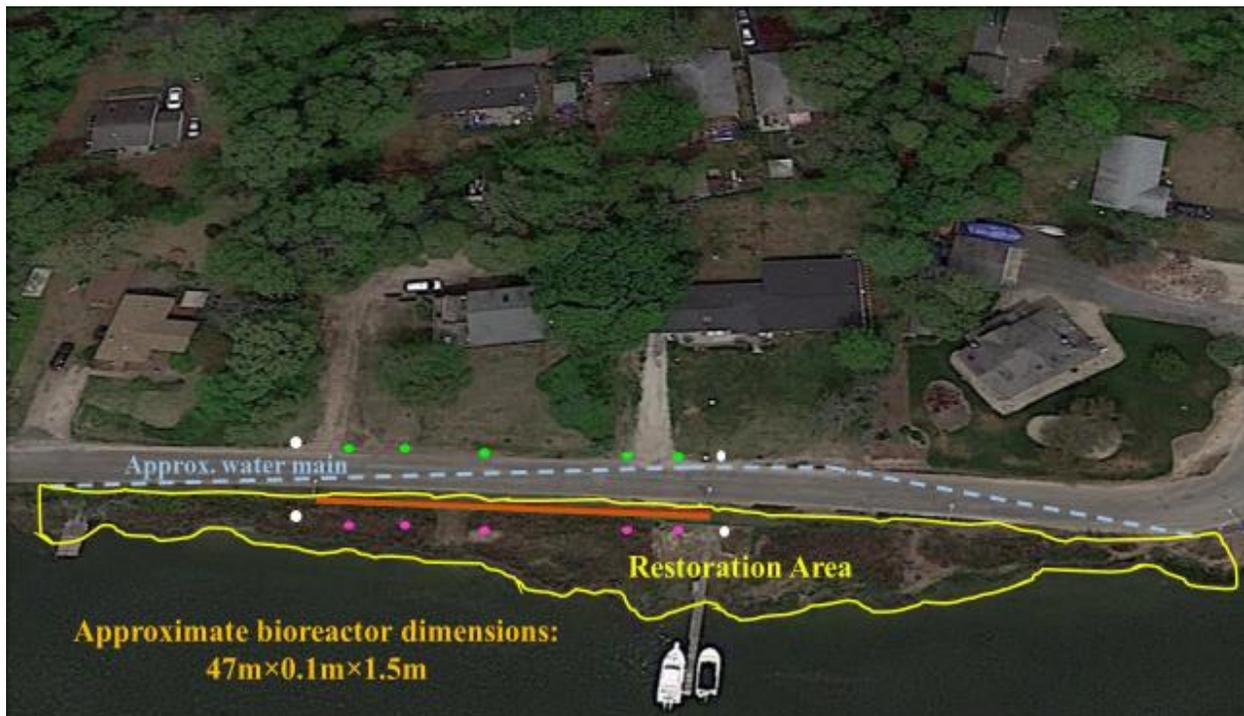


Figure 23: Diagram showing the placement of the denitrifying bioreactor along Riviera Drive (from Google Earth 2015). The green circles represent the influent wells, and the pink circles represent the effluent wells. The control wells are represented by the white circles and the bioreactor is represented by light brown horizontal line.

11.0 Appendix A: Raw data

Date	Site	Salinity	Dissolved Oxygen (mg/L)	Depth to water table (ft)	Temperature (°C)	Time
9/26/2014	MW-6	N/A	N/A	N/A	N/A	N/A
9/26/2014	MW-5	N/A	N/A	N/A	N/A	N/A
9/26/2014	MW-4	0.25	2.69	0.958333	16.9	8:04am
9/26/2014	ML-1-5	3.45	4.84	1.083333	18.08	8:17am
9/26/2014	ML-1-10	0.2	2.12	1.0625	18.51	8:32am
9/26/2014	ML-1-15	0.14	3.58	1.083333	17.43	8:36am
9/26/2014	MW-3	0.15	3.23	1.197917	21.54	9:11am
9/26/2014	MW-2	0.14	2.75	1.510417	22.52	9:41am
9/26/2014	MW-1	0.19	1.78	1.208333	20.75	9:58am
9/26/2014	ML-2-5	2.73	3.91	1.427083	23.16	10:12am
9/26/2014	ML-2-10	0.16	1.64	1.416667	22.24	10:22am
9/26/2014	ML-2-15	0.14	2.51	1.583333	22.24	10:35am
9/26/2014	MW-7	0.09	2.11	1.1875	22.62	10:39am
10/9/2014	MW-6	8.43	2.22	0.75	18.74	8:40am
10/9/2014	MW-5	0.24	3.76	0.75	16.84	8:49am
10/9/2014	MW-4	0.34	1.53	0.5	18.54	8:57am
10/9/2014	ML-1-5	2.75	1.4	0.614583	19.37	9:09am
10/9/2014	ML-1-10	0.23	1.75	0.604167	18.84	9:19am
10/9/2014	ML-1-15	0.15	3.03	0.65625	20.22	9:35am
10/9/2014	MW-3	0.15	4.13	0.822917	18.16	9:55am
10/9/2014	MW-2	0.14	2.79	1.208333	19.38	10:08am
10/9/2014	MW-1	0.19	1.28	0.927083	20.29	10:18am
10/9/2014	ML-2-5	0.88	2.48	1.1875	20.1	10:33am
10/9/2014	ML-2-10	0.15	4.07	1.166667	19.88	10:43am
10/9/2014	ML-2-15	0.14	3.13	3.25	21.11	10:55am
10/9/2014	MW-7	0.09	2.43	1.260417	20.59	11:02am
10/24/2014	MW-6	N/A	N/A	N/A	N/A	N/A
10/24/2014	MW-5	N/A	N/A	N/A	N/A	N/A
10/24/2014	MW-4	0.46	4.08	0.333333	13.92	7:36am
10/24/2014	ML-1-5	3.35	8.88	0.427083	11.2	7:50am
10/24/2014	ML-1-10	0.2	5.94	0.21875	10.62	7:59am
10/24/2014	ML-1-15	0.15	8.06	0.40625	12.04	8:18am
10/24/2014	MW-3	0.16	4.93	0.604167	12.41	8:34am
10/24/2014	MW-2	0.15	4.51	0.9375	12.46	8:48am
10/24/2014	MW-1	0.19	2.79	0.65625	11.86	9:02am
10/24/2014	ML-2-5	2.56	6.77	0.78125	11.57	9:17am
10/24/2014	ML-2-10	0.17	3.32	0.760417	13.46	9:28am
10/24/2014	ML-2-15	0.14	4.89	0.760417	13.65	9:40am
10/24/2014	MW-7	0.1	3.9	0.875	13.61	9:53am
11/4/2014	MW-6	N/A	N/A	N/A	N/A	N/A

11/4/2014	MW-5	0.35	2.13	1.822917	19.94	10:31am
11/4/2014	MW-4	0.52	1.95	1.5	20.13	10:53am
11/4/2014	ML-1-5	2.35	4.45	1.916667	18.11	11:05am
11/4/2014	ML-1-10	0.65	2.28	1.916667	18.65	11:28am
11/4/2014	ML-1-15	0.14	8.06	1.916667	16.46	11:41am
11/4/2014	MW-3	0.24	4.25	2.020833	17.01	11:50am
11/4/2014	MW-2	0.16	4.65	2.395833	17.48	12:02am
11/4/2014	MW-1	0.19	4.06	2.104167	17.92	12:14am
11/4/2014	ML-2-5	2.12	12.4	2.5	17.81	12:31am
11/4/2014	ML-2-10	0.14	5.65	2.416667	18.9	12:40am
11/4/2014	ML-2-15	0.15	9.35	2.416667	18.62	12:56am
11/4/2014	MW-7	0.1	6.35	2.46875	18.82	1:13pm
11/22/2014	MW-6	1.91	86.24	1.333333	9.01	9:18am
11/22/2014	MW-5	0.42	63.8	1.385417	9.81	9:32am
11/22/2014	MW-4	1.56	87.34	1.270833	7.1	9:50am
11/22/2014	ML-1-5	0.85	114.51	1.322917	7.7	10:03am
11/22/2014	ML-1-10	0.53	98.81	1.322917	8.86	10:17am
11/22/2014	ML-1-15	0.16	74.73	1.322917	8.68	10:35am
11/22/2014	MW-3	0.273	60.94	1.770833	8.9	10:53am
11/22/2014	MW-2	0.16	54.2	2.15625	10.01	11:14am
11/22/2014	MW-1	0.18	48.94	1.916667	11.73	11:28am
11/22/2014	ML-2-5	1.09	67.72	2.1875	8.54	11:48am
11/22/2014	ML-2-10	0.14	63	2.145833	10.51	12:19pm
11/22/2014	ML-2-15	0.15	48.19	2.145833	10.94	12:34pm
11/22/2014	MW-7	0.1	80.57	2.385417	10.11	12:39pm
12/17/2014	MW-6	N/A	N/A	N/A	N/A	N/A
12/17/2014	MW-5	N/A	N/A	N/A	N/A	N/A
12/17/2014	MW-4	1.26	2.58	0.958333	11.08	2:01pm
12/17/2014	ML-1-5	1.14	7.08	1.020833	8.41	2:10pm
12/17/2014	ML-1-10	0.2	1.31	1.083333	9.83	2:20pm
12/17/2014	ML-1-15	0.17	2.15	1.041667	10.13	2:31pm
12/17/2014	MW-3	0.19	3.16	1.1875	9.14	2:56pm
12/17/2014	MW-2	0.15	1.88	1.604167	9.18	3:11pm
12/17/2014	MW-1	0.15	1.26	1.291667	8.69	3:25pm
12/17/2014	ML-2-5	0.74	6.22	1.416667	7.53	3:44pm
12/17/2014	ML-2-10	0.17	1.23	1.416667	8.68	4:12pm
12/17/2014	ML-2-15	0.15	1.89	1.416667	8.99	4:15pm
12/17/2014	MW-7	0.09	1.97	1.375	9.15	4:25pm
1/20/2015	MW-6	0.23	5.58	1.791667	6.94	12:53pm
1/20/2015	MW-5	0.79	2.27	1.84375	5.98	1:02pm
1/20/2015	MW-4	0.38	2.44	1.604167	6.19	1:19pm
1/20/2015	ML-1-5	1.16	9.96	1.666667	3.84	1:36pm
1/20/2015	ML-1-10	0.16	1.84	1.75	5.6	1:52pm
1/20/2015	ML-1-15	0.16	1.95	1.75	6.12	1:58pm
1/20/2015	MW-3	0.19	3.46	2.083333	5.14	2:17pm

1/20/2015	MW-2	0.12	1.32	2.5	5.46	2:35pm
1/20/2015	MW-1	0.15	1.27	2.25	4.67	2:49pm
1/20/2015	ML-2-5	0.82	9.03	2.5	3.28	3:07pm
1/20/2015	ML-2-10	0.16	1.2	2.5	5.18	3:19pm
1/20/2015	ML-2-15	0.14	1.89	2.5	4.83	3:34pm
1/20/2015	MW-7	0.09	1.91	2.645833	5.03	3:55pm
3/25/2015	MW-6	1.23	3.23	1.666667	7.55	11:39am
3/25/2015	MW-5	3.56	4.45	1.770833	5.9	11:58am
3/25/2015	MW-4	0.28	1.38	1.416667	6.07	12:06pm
3/25/2015	ML-1-5	0.95	2.56	1.708333	5.41	12:23pm
3/25/2015	ML-1-10	0.15	1.18	1.708333	6.8	12:23pm
3/25/2015	ML-1-15	0.12	2.6	1.708333	7.33	12:23pm
3/25/2015	MW-3	0.13	2.99	1.75	6.9	1:02pm
3/25/2015	MW-2	0.12	2.14	2	7.27	1:34pm
3/25/2015	MW-1	N/A	N/A	N/A	N/A	N/A
3/25/2015	ML-2-5	1.45	4.88	1.833333	7.99	1:57pm
3/25/2015	ML-2-10	0.16	1.52	1.833333	6.88	1:57pm
3/25/2015	ML-2-15	0.12	3.47	1.833333	7.61	1:57pm
3/25/2015	MW-7	N/A	N/A	N/A	N/A	N/A
4/9/2015	MW-6	0.25	1.86	1.052083	7.24	12:45pm
4/9/2015	MW-5	1.47	1.11	1.104167	6.86	12:54pm
4/9/2015	MW-4	0.21	1.05	0.875	6.62	1:06pm
4/9/2015	ML-1-5	0.68	2.13	1	7.13	1:17pm
4/9/2015	ML-1-10	0.15	1.04	1	6.6	1:17pm
4/9/2015	ML-1-15	0.11	2.78	1	7.02	1:17pm
4/9/2015	MW-3	0.13	3.62	1.375	6.53	1:54pm
4/9/2015	MW-2	0.1	1.31	1.708333	7.02	2:21pm
4/9/2015	MW-1	N/A	N/A	N/A	N/A	N/A
4/9/2015	ML-2-5	0.95	3.03	1.75	7.16	2:39pm
4/9/2015	ML-2-10	0.17	1.02	1.75	7.04	2:39pm
4/9/2015	ML-2-15	0.09	2.68	1.75	6.86	2:39pm
4/9/2015	MW-7	N/A	N/A	N/A	N/A	N/A
4/21/2015	MW-6	N/A	N/A	N/A	N/A	N/A
4/21/2015	MW-5	N/A	N/A	N/A	N/A	N/A
4/21/2015	MW-4	0.19	0.81	0.260417	15.43	11:13am
4/21/2015	ML-1-5	1.53	4.99	0.364583	16.2	11:26am
4/21/2015	ML-1-10	0.15	0.97	0.364583	14.94	11:26am
4/21/2015	ML-1-15	0.13	2.18	0.364583	14.33	11:26am
4/21/2015	MW-3	0.12	3.4	0.677083	13.78	11:50am
4/21/2015	MW-2	0.1	0.89	1.041667	16.58	12:07pm
4/21/2015	MW-1	N/A	N/A	N/A	N/A	N/A
4/21/2015	ML-2-5	2.27	5.02	1.052083	15.98	12:23pm
4/21/2015	ML-2-10	0.18	0.97	1.052083	15.46	12:23pm
4/21/2015	ML-2-15	0.08	1.63	1.052083	15.56	12:23pm
4/21/2015	MW-7	N/A	N/A	N/A	N/A	N/A

5/6/2015	MW-6	0.25	1.59	1.458333	12.51	9:55am
5/6/2015	MW-5	0.27	1.41	1.604167	12.81	10:06am
5/6/2015	MW-4	0.19	1.61	1.25	13.27	10:16am
5/6/2015	ML-1-5	0.5	1.19	1.583333	14.06	10:31am
5/6/2015	ML-1-10	0.15	0.83	1.583333	13.86	10:31am
5/6/2015	ML-1-15	0.15	2.07	1.583333	12.4	10:31am
5/6/2015	MW-3	0.13	3.39	1.614583	12.2	11:06am
5/6/2015	MW-2	N/A	N/A	N/A	N/A	N/A
5/6/2015	MW-1	N/A	N/A	N/A	N/A	N/A
5/6/2015	ML-2-5	0.55	1.94	2	14.21	11:27am
5/6/2015	ML-2-10	0.15	0.83	2	13.6	11:27am
5/6/2015	ML-2-15	0.08	1.95	2	13.8	11:27am
5/6/2015	MW-7	N/A	N/A	N/A	N/A	N/A
5/18/2015	MW-6	0.15	1.36	1.760417	16.52	2:00pm
5/18/2015	MW-5	0.19	1.32	1.770833	16.63	2:04pm
5/18/2015	MW-4	0.18	1.11	1.583333	15.78	2:23pm
5/18/2015	ML-1-5	0.44	2.44	1.75	16.47	2:36pm
5/18/2015	ML-1-10	0.15	1.44	1.75	16.01	2:36pm
5/18/2015	ML-1-15	0.14	1.87	1.75	14.59	2:36pm
5/18/2015	MW-3	0.12	3.89	2.010417	14.9	3:03pm
5/18/2015	MW-2	N/A	N/A	N/A	N/A	N/A
5/18/2015	MW-1	N/A	N/A	N/A	N/A	N/A
5/18/2015	ML-2-5	0.56	5.21	2.583333	16.46	3:23pm
5/18/2015	ML-2-10	0.15	1.04	2.583333	15.18	3:23pm
5/18/2015	ML-2-15	0.1	3.47	2.583333	14.66	3:23pm
5/18/2015	MW-7	N/A	N/A	N/A	N/A	N/A
6/3/2015	MW-6	N/A	N/A	N/A	N/A	N/A
6/3/2015	MW-5	N/A	N/A	N/A	N/A	N/A
6/3/2015	MW-4	0.16	0.95	1.333333	18.91	2:48pm
6/3/2015	ML-1-5	2.09	5.28	1.479167	18.19	2:09pm
6/3/2015	ML-1-10	0.16	2.33	1.479167	18.26	2:09pm
6/3/2015	ML-1-15	0.13	2.42	1.479167	18.86	2:09pm
6/3/2015	MW-3	0.12	3.91	1.833333	16.38	2:57pm
6/3/2015	MW-2	0.14	1.38	N/A		
6/3/2015	MW-1	N/A	N/A	N/A	N/A	N/A
6/3/2015	ML-2-5	0.87	6	2.125	18.5	3:33pm
6/3/2015	ML-2-10	0.14	1.05	2.125	17.57	3:33pm
6/3/2015	ML-2-15	0.08	4.43	2.125	17.47	3:33pm
6/3/2015	MW-7	N/A	N/A	N/A	N/A	N/A
6/16/2015	MW-6	N/A	N/A	N/A	N/A	N/A
6/16/2015	MW-5	N/A	N/A	N/A	N/A	N/A
6/16/2015	MW-4	0.16	1.32	0.708333	17.28	9:13am
6/16/2015	ML-1-5	1.65	1.78	0.875	19.88	9:21am
6/16/2015	ML-1-10	0.14	1.09	0.875	18.87	9:21am
6/16/2015	ML-1-15	0.14	1.99	0.875	18.69	9:21am

6/16/2015	MW-3	0.11	3.92	1.125	19.01	10:00am
6/16/2015	MW-2	0.1	2.59	1.479167	19.81	10:15am
6/16/2015	MW-1	N/A	N/A	N/A	N/A	N/A
6/16/2015	ML-2-5	0.49	1.06	1.583333	21.55	10:26am
6/16/2015	ML-2-10	0.14	0.84	1.583333	20.34	10:26am
6/16/2015	ML-2-15	0.08	3.79	1.583333	20.01	10:26am
6/16/2015	MW-7	N/A	N/A	N/A	N/A	N/A
6/29/2015	MW-6	0.15	1.79	1.53125	18.79	1:09pm
6/29/2015	MW-5	N/A	N/A	N/A	N/A	N/A
6/29/2015	MW-4	0.15	5.11	1.333333	21.17	1:20pm
6/29/2015	ML-1-5	1.23	6.07	1.427083	24.13	1:32pm
6/29/2015	ML-1-10	0.15	2.45	1.427083	19.27	1:32pm
6/29/2015	ML-1-15	0.13	2.6	1.427083	17.92	1:32pm
6/29/2015	MW-3	0.11	3.25	1.708333	19.27	2:27pm
6/29/2015	MW-2	0.12	3.45	2	19.55	2:33pm
6/29/2015	MW-1	0.08	0.93	2.208333	21.81	3:35pm
6/29/2015	ML-2-5	0.6	2.52	1.875	21.2	3:05pm
6/29/2015	ML-2-10	0.15	0.96	1.875	18.85	3:05pm
6/29/2015	ML-2-15	0.08	4.35	1.875	18.07	3:05pm
6/29/2015	MW-7	N/A	N/A	N/A	N/A	N/A
7/21/2015	MW-6	0.14	1.81	1.041667	23.2	10:24am
7/21/2015	MW-5	0.13	0.83	1.302083	23.95	10:15am
7/21/2015	MW-4	0.15	0.72	0.927083	23.02	10:03am
7/21/2015	ML-1-5	0.19	0.57	1.166667	23.86	9:21am
7/21/2015	ML-1-10	0.13	1.07	1.166667	23.15	9:21am
7/21/2015	ML-1-15	0.13	1.73	1.166667	21.74	9:21am
7/21/2015	MW-3	0.11	3.2	1.458333	21.98	9:06am
7/21/2015	MW-2	0.11	2.51	1.916667	21.46	8:49am
7/21/2015	MW-1	0.18	0.67	1.458333	23.45	7:49am
7/21/2015	ML-2-5	0.33	1.05	2.083333	23.82	8:00am
7/21/2015	ML-2-10	0.12	1.08	2.083333	21.73	8:00am
7/21/2015	ML-2-15	0.12	2.85	2.083333	20.73	8:00am
7/21/2015	MW-7	N/A	N/A	N/A	N/A	N/A
8/10/2015	MW-6	0.13	2.07	1.21875	24.67	2:31pm
8/10/2015	MW-5	0.11	0.77	1.291667	25.46	2:11pm
8/10/2015	MW-4	0.16	0.72	1.072917	24.69	2:00pm
8/10/2015	ML-1-5	0.16	0.71	1.375	24.8	1:35pm
8/10/2015	ML-1-10	0.13	0.92	1.375	24.31	1:35pm
8/10/2015	ML-1-15	0.12	1.44	1.375	24.19	1:35pm
8/10/2015	MW-3	0.11	4.02	1.520833	24.7	1:23pm
8/10/2015	MW-2	0.11	2.93	1.916667	24.49	1:09pm
8/10/2015	MW-1	0.27	0.18	1.4375	25.38	12:59pm
8/10/2015	ML-2-5	0.23	1.38	1.833333	24.77	12:17pm
8/10/2015	ML-2-10	0.12	0.9	1.833333	25.29	12:17pm
8/10/2015	ML-2-15	0.12	2.97	1.833333	23.61	12:17pm

8/10/2015	MW-7	N/A	N/A	N/A	N/A	N/A
8/22/2015	MW-6	N/A	N/A	N/A	N/A	N/A
8/22/2015	MW-5	N/A	N/A	N/A	N/A	N/A
8/22/2015	MW-4	0.14	0.5	1.208333	24.86	12:00pm
8/22/2015	ML-1-5	1.39	1.22	1.541667	25.95	11:38am
8/22/2015	ML-1-10	0.15	0.72	1.541667	23.92	11:38am
8/22/2015	ML-1-15	0.12	2.14	1.541667	23.76	11:38am
8/22/2015	MW-3	0.11	3.49	1.614583	23.1	11:24am
8/22/2015	MW-2	0.1	2.68	1.958333	23.05	11:10am
8/22/2015	MW-1	0.06	0.98	1.875	25.21	10:39am
8/22/2015	ML-2-5	0.34	1.45	2.041667	24.56	10:25am
8/22/2015	ML-2-10	0.13	1.29	2.041667	24.16	10:25am
8/22/2015	ML-2-15	0.14	2.43	2.041667	22.96	10:25am
8/22/2015	MW-7	N/A	N/A	N/A	N/A	N/A

Site	Date	Total Dissolved Nitrogen (mg/L)	Ammonium (mg/L)	Nitrate-nitrite (mg/L)
MW-6	9/26/2014	N/A	N/A	N/A
MW-5	9/26/2014	N/A	N/A	N/A
MW-4	9/26/2014	13.31	7.98	1.74
ML-1-5	9/26/2014	2.63	0.122	2.477
ML-1-10	9/26/2014	9.88	1.855	8.759
ML-1-15	9/26/2014	9.32	0.39	8.441
MW-3	9/26/2014	5.51	0.012	5.477
MW-2	9/26/2014	3.35	0.009	3.187
MW-1	9/26/2014	19.77	10.314	9.526
ML-2-5	9/26/2014	20.64	0.376	17.678
ML-2-10	9/26/2014	8.45	1.173	7.422
ML-2-15	9/26/2014	8.15	0.062	6.888
MW-7	9/26/2014	2.01	0.007	2.13
MW-6	10/9/2014	5.08	0.676	4.141
MW-5	10/9/2014	2.64	0.01	2.445
MW-4	10/9/2014	12.13	6.513	2.090
ML-1-5	10/9/2014	6.91	0.328	0.391
ML-1-10	10/9/2014	12.35	1.284	4.326
ML-1-15	10/9/2014	8.13	0.158	7.978
MW-3	10/9/2014	6.64	0.008	1.808
MW-2	10/9/2014	3.87	0.020	2.393
MW-1	10/9/2014	22.22	10.715	7.605
ML-2-5	10/9/2014	7.85	0.826	7.047
ML-2-10	10/9/2014	9.14	0.823	5.319
ML-2-15	10/9/2014	2.62	0.101	2.596
MW-7	10/9/2014	3.31	0.014	3.687
MW-6	10/24/2014	N/A	N/A	N/A

MW-5	10/24/2014	N/A	N/A	N/A
MW-4	10/24/2014	10.33	4.780	1.373
ML-1-5	10/24/2014	2.04	0.114	0.760
ML-1-10	10/24/2014	9.01	1.651	7.127
ML-1-15	10/24/2014	6.94	0.181	6.668
MW-3	10/24/2014	3.71	0.006	3.838
MW-2	10/24/2014	3.58	0.004	2.810
MW-1	10/24/2014	16.71	10.465	5.835
ML-2-5	10/24/2014	7.21	0.594	6.171
ML-2-10	10/24/2014	3.55	0.997	2.624
ML-2-15	10/24/2014	5.10	0.084	4.842
MW-7	10/24/2014	N/A	N/A	N/A
MW-6	11/4/2014	N/A	N/A	N/A
MW-5	11/4/2014	1.51	<0.01	1.290
MW-4	11/4/2014	20.189	5.373	1.73
ML-1-5	11/4/2014	1.216	0.07	0.485
ML-1-10	11/4/2014	7.612	2.903	5.54
ML-1-15	11/4/2014	5.936	0.124	6.25
MW-3	11/4/2014	3.553	<0.01	3.65
MW-2	11/4/2014	2.62	<0.01	2.06
MW-1	11/4/2014	20.189	10.655	4.39
ML-2-5	11/4/2014	9.607	0.082	5.89
ML-2-10	11/4/2014	5.509	1.405	4.61
ML-2-15	11/4/2014	9.13	0.038	6.27
MW-7	11/4/2014	3.346	0.002	3.16
MW-6	11/22/2014	20.027	<0.01	14.3
MW-5	11/22/2014	1.334	<0.01	1.77
MW-4	11/22/2014	2.363	0.916	0.894
ML-1-5	11/22/2014	6.749	0.147	0.336
ML-1-10	11/22/2014	7.76	1.112	6.95
ML-1-15	11/22/2014	6.749	0.108	5.13
MW-3	11/22/2014	3.689	<0.01	3.7
MW-2	11/22/2014	1.642	<0.01	1.19
MW-1	11/22/2014	18.499	10.866	3
ML-2-5	11/22/2014	7.287	0.681	7
ML-2-10	11/22/2014	4.802	3.218	2.15
ML-2-15	11/22/2014	9.323	0.062	8.52
MW-7	11/22/2014	3.486	<0.01	3.54
MW-6	12/17/2014	N/A	N/A	N/A
MW-5	12/17/2014	N/A	N/A	N/A
MW-4	12/17/2014	1.414	0.486	0.751
ML-1-5	12/17/2014	1.424	<0.01	0.96
ML-1-10	12/17/2014	7.022	1.107	5.3
ML-1-15	12/17/2014	9.159	0.237	9.13
MW-3	12/17/2014	3.998	<0.01	4.18

MW-2	12/17/2014	1.581	0.011	0.573
MW-1	12/17/2014	11.811	7.922	0.463
ML-2-5	12/17/2014	4.752	0.084	4.24
ML-2-10	12/17/2014	6.092	6.49	0.3
ML-2-15	12/17/2014	4.752	0.041	4.02
MW-7	12/17/2014	1.958	<0.01	1.8
MW-6	1/20/2015	0.79	0.02	0.08
MW-5	1/20/2015	2.33	0.03	1.10
MW-4	1/20/2015	4.61	3.82	0.74
ML-1-5	1/20/2015	2.55	0.20	1.37
ML-1-10	1/20/2015	3.48	0.39	1.74
ML-1-15	1/20/2015	8.62	0.30	8.59
MW-3	1/20/2015	3.25	<.01	2.85
MW-2	1/20/2015	1.60	<.01	0.57
MW-1	1/20/2015	10.35	6.98	1.01
ML-2-5	1/20/2015	3.00	0.31	2.59
ML-2-10	1/20/2015	4.96	4.52	0.10
ML-2-15	1/20/2015	8.41	0.42	8.08
MW-7	1/20/2015	1.42	<.01	1.56
MW-6	3/25/2015	1.64	<.01	0.58
MW-5	3/25/2015	1.25	0.23	0.03
MW-4	3/25/2015	5.37	1.27	2.17
ML-1-5	3/25/2015	2.39	0.03	0.47
ML-1-10	3/25/2015	4.40	0.29	4.06
ML-1-15	3/25/2015	8.43	0.52	5.92
MW-3	3/25/2015	2.52	<.01	2.46
MW-2	3/25/2015	2.16	<.01	1.68
MW-1	3/25/2015	N/A	N/A	N/A
ML-2-5	3/25/2015	2.24	0.02	2.30
ML-2-10	3/25/2015	7.14	6.40	0.02
ML-2-15	3/25/2015	8.10	0.14	7.71
MW-7	3/25/2015	N/A	N/A	N/A
MW-6	4/9/2015	1.94	<.01	2.14
MW-5	4/9/2015	1.08	0.58	0.01
MW-4	4/9/2015	5.56	3.34	2.69
ML-1-5	4/9/2015	1.54	0.13	0.41
ML-1-10	4/9/2015	4.23	0.20	3.86
ML-1-15	4/9/2015	9.22	0.09	5.31
MW-3	4/9/2015	2.33	<.01	2.39
MW-2	4/9/2015	1.99	<.01	1.96
MW-1	4/9/2015	N/A	N/A	N/A
ML-2-5	4/9/2015	1.89	<.01	1.75
ML-2-10	4/9/2015	10.34	4.33	0.23
ML-2-15	4/9/2015	5.24	0.26	4.53
MW-7	4/9/2015	N/A	N/A	N/A

MW-6	4/21/2015	N/A	N/A	N/A
MW-5	4/21/2015	N/A	N/A	N/A
MW-4	4/21/2015	N/A	3.31	3.09
ML-1-5	4/21/2015	3.26	0.12	2.7
ML-1-10	4/21/2015	4.76	0.15	4.37
ML-1-15	4/21/2015	12.12	0.27	10.9
MW-3	4/21/2015	2.27	<0.01	2.56
MW-2	4/21/2015	2.65	<0.01	2.57
MW-1	4/21/2015	N/A	N/A	N/A
ML-2-5	4/21/2015	8.04	<0.01	7.68
ML-2-10	4/21/2015	8.27	6.34	0.61
ML-2-15	4/21/2015	4.19	0.28	4.33
MW-7	4/21/2015	N/A	N/A	N/A
MW-6	5/6/2015	2.92	<0.01	2.83
MW-5	5/6/2015	0.97	0.35	0.31
MW-4	5/6/2015	8.68	3.95	2.51
ML-1-5	5/6/2015	1.38	0.05	0.61
ML-1-10	5/6/2015	4.91	0.12	4.05
ML-1-15	5/6/2015	15.43	0.87	13.2
MW-3	5/6/2015	2.16	<0.01	2.3
MW-2	5/6/2015	N/A	N/A	N/A
MW-1	5/6/2015	N/A	N/A	N/A
ML-2-5	5/6/2015	N/A	<0.01	0.65
ML-2-10	5/6/2015	10.63	8.11	2.41
ML-2-15	5/6/2015	5.65	0.82	5.33
MW-7	5/6/2015	N/A	N/A	N/A
MW-6	5/18/2015	3.83	<0.01	3.85
MW-5	5/18/2015	1.46	0.42	0.23
MW-4	5/18/2015	6.34	4.37	2.05
ML-1-5	5/18/2015	1.57	0.08	0.76
ML-1-10	5/18/2015	4.65	0.04	4.15
ML-1-15	5/18/2015	13.94	0.85	12.3
MW-3	5/18/2015	1.84	<0.01	2.15
MW-2	5/18/2015	N/A	N/A	N/A
MW-1	5/18/2015	N/A	N/A	N/A
ML-2-5	5/18/2015	1.1	<0.01	0.65
ML-2-10	5/18/2015	12.16	8.13	2.32
ML-2-15	5/18/2015	7.09	0.53	7.02
MW-7	5/18/2015	N/A	N/A	N/A
MW-6	6/3/2015	N/A	N/A	N/A
MW-5	6/3/2015	N/A	N/A	N/A
MW-4	6/3/2015	5.58	3.75	2.06
ML-1-5	6/3/2015	3.75	<0.01	2.42
ML-1-10	6/3/2015	4.85	0.15	4.95
ML-1-15	6/3/2015	13.69	0.47	12.3

MW-3	6/3/2015	2	0.11	1.65
MW-2	6/3/2015	5.12	<0.01	5.05
MW-1	6/3/2015	N/A	N/A	N/A
ML-2-5	6/3/2015	27.67	0.04	17.1
ML-2-10	6/3/2015	8.29	5.74	2.83
ML-2-15	6/3/2015	6.17	0.2	6.11
MW-7	6/3/2015	N/A	N/A	N/A
MW-6	6/16/2015	N/A	N/A	N/A
MW-5	6/16/2015	N/A	N/A	N/A
MW-4	6/16/2015	N/A	4.09	1.63
ML-1-5	6/16/2015	2.56	0.05	1.29
ML-1-10	6/16/2015	5.82	0.57	5.56
ML-1-15	6/16/2015	14.05	0.17	11.1
MW-3	6/16/2015	1.33	0.08	1.52
MW-2	6/16/2015	3.67	<0.01	2.82
MW-1	6/16/2015	N/A	N/A	N/A
ML-2-5	6/16/2015	16.52	0.04	12.5
ML-2-10	6/16/2015	12.6	8.38	5.42
ML-2-15	6/16/2015	5.83	0.1	4.88
MW-7	6/16/2015	N/A	N/A	N/A
MW-6	6/29/2015	4.8	<0.01	4.66
MW-5	6/29/2015	N/A	N/A	N/A
MW-4	6/29/2015	5.7	2.92	1.45
ML-1-5	6/29/2015	2.79	0.05	0.69
ML-1-10	6/29/2015	5.13	0.49	3.36
ML-1-15	6/29/2015	10.21	0.45	9.88
MW-3	6/29/2015	1.17	<0.01	1.34
MW-2	6/29/2015	3.36	<0.01	2.41
MW-1	6/29/2015	0.93	0.02	0.15
ML-2-5	6/29/2015	11.49	0.02	8.13
ML-2-10	6/29/2015	12.69	7.9	5.59
ML-2-15	6/29/2015	5.87	0.18	5.72
MW-7	6/29/2015	N/A	N/A	N/A
MW-6	7/21/2015	5.84	<0.01	4.05
MW-5	7/21/2015	1.38	0.61	0.02
MW-4	7/21/2015	5.91	3.48	1.5
ML-1-5	7/21/2015	N/A	0	0.84
ML-1-10	7/21/2015	6.08	0.62	5.74
ML-1-15	7/21/2015	11.41	0.8	10.4
MW-3	7/21/2015	1.49	<0.01	1.52
MW-2	7/21/2015	3.04	<0.01	2.87
MW-1	7/21/2015	3.38	1.96	<0.01
ML-2-5	7/21/2015	2.39	0.05	0.76
ML-2-10	7/21/2015	10.82	6.44	3.73
ML-2-15	7/21/2015	8.5	0.29	8.24

MW-7	7/21/2015	N/A	N/A	N/A
MW-6	8/10/2015	6.58	<0.01	6.61
MW-5	8/10/2015	0.48	0.19	0.29
MW-4	8/10/2015	5.27	4.29	0.66
ML-1-5	8/10/2015	2.44	0.02	1.19
ML-1-10	8/10/2015	7.94	0.76	7.18
ML-1-15	8/10/2015	9.28	0.39	7.89
MW-3	8/10/2015	3.09	<0.01	3.19
MW-2	8/10/2015	2.62	0.14	2.59
MW-1	8/10/2015	6.7	4.75	0.29
ML-2-5	8/10/2015	1.67	0.04	0.31
ML-2-10	8/10/2015	11.23	4.74	6.43
ML-2-15	8/10/2015	10.35	0.17	10.27
MW-7	8/10/2015	N/A	N/A	N/A
MW-6	8/22/2015	N/A	N/A	N/A
MW-5	8/22/2015	N/A	N/A	N/A
MW-4	8/22/2015	3.46	2.51	0.44
ML-1-5	8/22/2015	5.56	0.02	3.19
ML-1-10	8/22/2015	8.91	0.92	7.71
ML-1-15	8/22/2015	10.65	0.07	10.73
MW-3	8/22/2015	2.75	0.01	2.69
MW-2	8/22/2015	2.51	<0.01	2.65
MW-1	8/22/2015	0.74	0.04	0.26
ML-2-5	8/22/2015	3.42	0.01	2.48
ML-2-10	8/22/2015	7.37	3.92	3.38
ML-2-15	8/22/2015	12.27	0.09	12.11
MW-7	8/22/2015	N/A	N/A	N/A