

ABSTRACT

MESSER, TIFFANY LAROSE. Groundwater Nitrate Reductions within Upstream and Downstream Sections of a Riparian Buffer. (Under the direction of Dr. Michael R. Burchell, II).

Riparian buffer systems have gained much interest over the past 25 years for their ability to reduce groundwater nitrate (NO_3^- -N) through the process of denitrification, a process which transforms NO_3^- -N into harmless nitrogen gas. Buffer ability to reduce NO_3^- -N has been found to be variable and does not always work as effectively as desired to meet water quality goals. Therefore research is still needed to identify the causes for variability within these systems to maximize their benefit in conservation programs, such as the North Carolina Conservation Reserve Enhancement Program (NC CREP).

Over the past five years a detailed evaluation of the hydrology and attenuation of groundwater NO_3^- -N was conducted on two sections of buffer enrolled in NC CREP along the same stream. These sections had two distinct widths, but were also in two distinct topographic locations. The research objectives for this site included: 1.) conduct a detailed hydrologic evaluation of the site, 2.) determine changes in NO_3^- -N concentrations through the buffer, 3.) evaluate contributions of denitrification and dilution to observed NO_3^- -N reductions, and 4.) based on research findings, make recommendations for ideal buffer locations for future enrollments in NC CREP, to maximize water quality impacts of the program.

The average buffer widths were 60 m (Section 1) at the upstream location and 43 m (Section 2) at the downstream location. Twenty-one well nests were installed in three

transects within each buffer section to monitor shallow (1.5-2.3 m) and deep (2.7 -3.6 m) groundwater nitrate levels.

NO_3^- -N decreased at the 1.5 m depth through the buffers from Zone 3 (grassed filter strip) to Zone 1 (stream edge) with average NO_3^- -N concentrations of 4.5 to 1.7 mg/L and 12.9 to 1.4 mg/L in Section 1 and Section 2 respectively. Likewise, NO_3^- -N decreased through the buffers from Zone 3 to Zone 1 at the 3 m depth with average NO_3^- -N concentrations of 2.9 to 2.5 mg/L and 12.8 to 6.0 mg/L for Section 1 and Section 2 respectively. Section 2 significantly reduced NO_3^- -N at both the 1.5 m and 3 m depths, while Section 1 only had significant NO_3^- -N reductions at the 1.5 m depth ($\alpha=0.05$). The groundwater NO_3^- -N concentrations entering each section's Zone 3 were significantly different and had an enormous impact on overall nitrate mass in each buffer section. These differences were attributed to contributing groundwater areas from the adjacent field.

Hydrology and water quality results supported denitrification was the predominant NO_3^- -N reduction mechanism in both sections. The relative wetness of Zones 2 and 1, low redox readings and high DOC concentrations during the summer months indicated the sections were suitable for denitrification to proceed. Dilution was most likely minimal as groundwater NO_3^- -N concentrations and NO_3^- -N / Cl^- ratios and a deeper aquifer water quality assessment indicated the waters were separated. Both sections effectively reduced NO_3^- -N concentrations through the buffer. Section 2 appeared to reduce groundwater NO_3^- -N concentrations effectively to meet water quality goals even though it had a smaller width than Section 1. Section 1 most likely had the potential to reduce groundwater NO_3^- -N

concentrations as high as entering Section 2, but was constrained by entering NO_3^- -N concentrations. Although logistically challenging and initially expensive, buffers specifically designed to meet water quality goals, by taking into account critical site attributes, will improve overall water quality leaving agricultural sites, while protecting sensitive streams and estuaries cost effectively.

Groundwater Nitrate Reductions within Upstream and Downstream Sections of a Riparian
Buffer

by
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DEDICATION

I would like to dedicate this to the people who have loved and continue to love me unconditionally and support me through this long and sometimes difficult journey.

To the love of my life Patrick S. Messer

Thank you for always being my inspiration in all aspects of life.

To Mom and Dad

Thank you for teaching me to love and always supporting me to continue my education.

To Tabitha, Bethany, Drew, and Shaina

Thank you for always being there for me and one another.

To my grandparents

Thank you loving our family more than anyone could ever imagine.

BIOGRAPHY

Tiffany Messer was born on September 27, 1986 in Lexington, KY to Drew and Lorra Graham. She is the oldest of three younger siblings Tabitha, Bethany, and Drew. Growing up on a farm outside of Winchester, KY where they raised beef cattle, tobacco, and corn, she soon became aware of the importance of agricultural and water quality. During her high school years she became very active in Calvary Christian Church and learned of her desire to improve water quality conditions in financially limited locations. She graduated from George Rogers Clark High School in 2004.

After graduation she enrolled at the University of Kentucky in Lexington, KY. She received her B.S. in Biosystems and Agricultural Engineering with a specialty in bioenvironmental in 2008. Throughout her undergraduate degree she became involved with several recruitment and leadership roles by serving as an Ambassador for the College of Engineering, and on the College of Agriculture Student Council, the Biosystems and Agricultural Engineering Student Branch, and the ¼ Scale Tractor Team. Three remarkable advisors encouraged and assisted her along the way through her undergraduate program: Dr. Jane Riggs, Dr. Steven Workman, and Dr. Scott Shearer. The opportunities that these three individuals opened for her to participate in, including recruitment, research, and teaching assignments, confirmed her ultimate desire of pursuing a Ph.D. in Biological and Agricultural Engineering and becoming a university professor.

Following her undergraduate graduation she married her high school sweetheart and the love of her life, Patrick Messer. Afterwards they moved immediately to Durham, NC where she

began her M.S. research under the direction of Dr. Michael Burchell in the Biological and Agricultural Engineering Department at North Carolina State University. Her research focus was nitrate reduction in riparian buffers. Despite the long and sometimes heart wrenching process of improving her writing and research techniques, Tiffany ultimately decided to apply to the Ph.D. program at N.

C. State University to take the next step toward her ultimate goal of becoming a professor. Therefore, following the completion of her Master's degree Tiffany plans to continue focusing on water quality treatment systems throughout her Ph.D. and lifelong career.

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CHAPTER 1: INTRODUCTION

Historical Review

The amendment to Section 319 of the Clean Water Act in 1987 focused on nonpoint sources (NPS) of pollution to water quality. NPS pollution has impaired a substantial amount of streams and estuaries in the United States including North Carolina over the past century. All states must now report the progress of restoring impaired water bodies within a set time period using Best Management Practices (BMPs) as required under the Clean Water Act (CWA, 1987).

Concerns of the North Carolina – Department of Environment and Natural Resources (DENR) have elevated over the past 30 years regarding the water quality conditions of the Neuse and Tar-Pamlico River Basins. During the mid-1970's eutrophication became a predominant concern as evidence of these conditions were found in stream surveys of the Neuse River. Eutrophication is a condition caused by excessive nutrient availability resulting in algal blooms that reduce oxygen levels in streams that can result in fish kills. A two year special investigation was completed during the late 1980's and early 1990's for the Neuse River to examine the causes of the algal blooms, leading to reevaluation of regulations (NCDWQ, 2002). Nonpoint source pollution was found to make up a large portion of the nitrogen loading to the Neuse River in North Carolina and majority of this is from agricultural practices (NRDC, 1998).

The Tar-Pamlico Basin in North Carolina was designated nutrient sensitive after a survey discovered that a substantial number of fish kills, diseases in aquatic biota, low oxygen levels,

and harmful algal blooms were occurring in the mid-1980's (NCDWQ, 2007). Therefore, North Carolina – DENR implemented the Tar-Pamlico Nutrient Strategy in 1990 (NCDWQ, 2008). The strategy was comprised of three phases. Phase I (1990-1994) focused on known point source pollution, such as industrial plants, and developed more cost effective ways to reduce nutrient loading (NCDWQ, 2008). Phase II (1994-2004) targeted both point and nonpoint pollution sources. The point source pollution goals for Phase II included keeping phosphorus loading levels measured during 1991 constant depending on estuarine conditions and establishing a 30% reduction in nitrogen loading levels (NCDWQ, 2008). During Phase II, increasing concerns of the impacts of NPS pollution on water quality led to additional regulations being added to the initial phase comprised of voluntary actions. Mandatory rules addressing agriculture, urban stormwater, fertilizer management, and riparian buffer protection were adopted in 2004 (NCDWQ, 2008). Phase III (2004-2014) extends the goals set in Phase II for an additional ten years including the 30% nitrogen reduction.

The reduction of nitrogen has been a critical focus for maintaining acceptable water quality throughout North Carolina for many years and continues today. Nitrate-nitrogen (NO_3^- -N) is a form of nitrogen that adds a considerable amount to the total nitrogen loading in water sources, such as streams. Agricultural NPS pollution is also the leading contributor of NO_3^- -N to rivers in North Carolina (US EPA, 1984; US EPA 2010). North Carolina has therefore implemented the nonpoint rules that are specific to all defined focus areas of NPS pollution stated in Phase II. The nonpoint rules are used to ensure the restoration and protection of waters

throughout the state of North Carolina that are currently, or have the potential to be, impaired due to NPS pollution.

Riparian Buffers

Riparian buffers are one of several focus areas defined in North Carolina that can reduce NPS pollution. The USDA Forest Service defines riparian buffers as (2010):

“An area of trees and other vegetation located in areas adjoining and upgradient from surface water bodies and designed to intercept surface runoff, wastewater, subsurface flow and deeper groundwater flows from upland sources for the purpose of removing or buffering the effects of associated nutrients, sediment, organic matter, pesticides or other pollutants prior to entry into surface waters and groundwater recharge areas.”

Additionally, riparian buffers are defined as follows by leading experts (Lowrance et. al, 1985; Osmond et. al, 2002):

A complex assemblage of plants, organisms, and their environment adjacent to water. Riparian buffers may include wetlands, stream banks, and floodplains since they do not have definitive boundaries. Characterized by laterally flowing water that rises and falls at least once within a growing season and being linear shape, riparian buffers also have a high degree of connectiveness with other ecosystems.

Over the past 25 years extensive research has been conducted examining riparian buffer systems. Acting as natural sinks, riparian buffers also help in the storage of nutrients and therefore, reduce nutrients from reaching surrounding agro-ecosystems (Peterjohn et al., 1984).

Researchers have reported riparian buffers reduce NO_3^- -N concentrations found in surface water and groundwater and improve overall water quality in the adjacent water resources (Evans *et al.*, 2007; Gilliam, 1994; Dukes *et al.*, 2002; Hill, 1996; Schultz *et al.*, 1995).

The United States – Department of Agriculture (USDA) promotes a three zone buffer with distinct vegetation zones to minimize stream contamination (Welsh, 1991). The three vegetation zones work collectively to reduce nutrient runoff (Figure 1.1). Zone 1 includes the area from the edge of the active channel to a minimum 4.6 m (15 ft) perpendicular to the incoming water flow. Vegetation is predominantly hardwoods and should remain undisturbed. Zone 2, with a minimum width of 13.7 m (45 ft), has vegetation that is comprised of that similar to Zone 1, but allows some disturbances. Examples of these disturbances include timber management including harvesting, grading and revegetation, road intrusions into the buffer, and periodic mowing with mitigation (NCDWQ, 2008). Zone 3 has a width of approximately 6.1 m (20 ft). Vegetation in Zone 3 is a grassed filter strip. The area can be used for grazing, but must have some type of grass present at all times (Lowrance *et al.*, 1995).

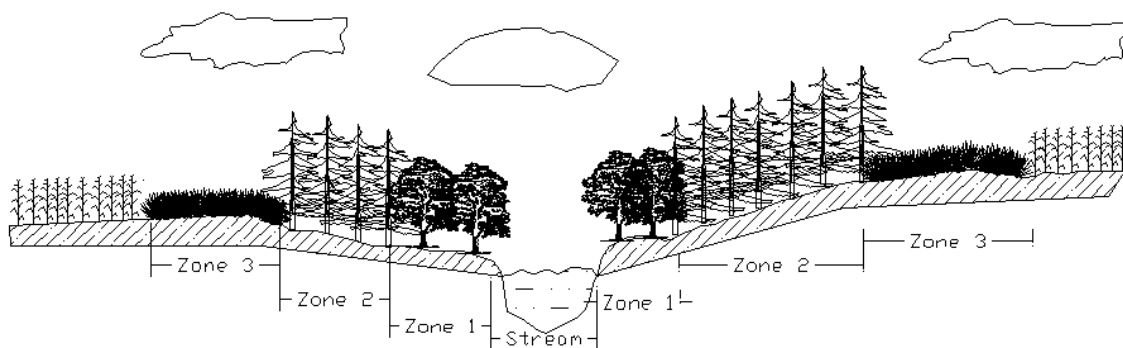


Figure 1.1: Schematic of the riparian buffer zones (adapted from NRCS, 1997)

The three zone design utilizes biogeochemical, physical, and biological mechanisms to reduce pollutants from entering waterways. High water tables and carbon sources from vegetation litter primarily in Zone 1 and 2 provide suitable conditions for biogeochemical processes to occur to reduce subsurface pollutants, such as NO_3^- -N. Physically, riparian zones provide bank stabilization, shading and a reduction in sedimentation. Zone 1 is designed to enhance bank stability and decrease erosion through the root system of the trees around the stream bank (Lowrance *et al.*, 1997). The trees further provide shade over the stream to reduce water temperatures for suitable habitats for stream biota (Tabacchi *et. al*, 1998). Litter cover in all three zones reduces the velocity of runoff. The riparian zones also provide aquatic and wildlife habitat by providing food, (in the form of carbon), cover, and water (Osmond *et al*, 2002).

The state of North Carolina has recognized the potential of riparian buffers to reduce NPS pollution; thus they have implemented nonpoint rules specifically for riparian zones.

Three riparian buffer rules have been mandated by NC-DENR (NCDWQ, 2008):

- 1.) *Protection Rule:* Riparian areas on each side of all intermittent and perennial streams, lakes, ponds and estuarine waters must be no less than 15.2 m (50 ft) and must be protected and maintained. The 9.1 m (30 ft) closest to the stream, Zone 1, is to be undisturbed. Zone 2, the following 6.1 m (20 ft), is to be vegetated and may have some

land activities. (i.e. grading and revegetation, road intrusions into the buffer, and periodic mowing)

2.) *Mitigation Rule*: The rule identifies the process applicants follow to receive approval for activities that are allowed with mitigation and outlines the mitigation measures.

3.) *Delegation Rule*: The rule arranges the requirements and the process for the implementation of buffer rules in local government jurisdictions.

The rules were implemented to increase pollutant reduction opportunities. The protection rule ensures the buffer area will remain undisturbed for biogeochemical and physical processes to proceed, while the mitigation and delegation rules deal with the logistics between the landowner and government. The three rules work collectively to potentially increase pollutant removal efficiency.

Pollutant Removal Processes

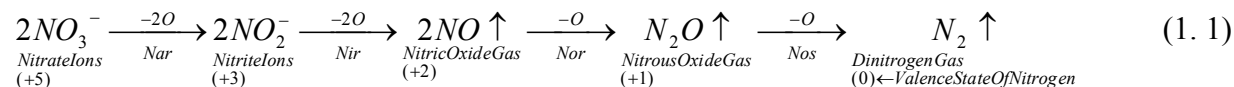
One of the primary goals of using riparian buffers in rural areas is to reduce nutrient losses from fertilizers and other NPS pollutants applied upland of the water source. Surface water and groundwater treatment can occur within riparian buffers. The grass filter strip present in Zone 3 of the riparian buffer slows down and disperses the preferential runoff flow with perpendicular resistance to the grass. Sediment and sediment-bound nutrients, such as phosphorus, become trapped in this zone, which reduces discharge of these pollutants to nearby water bodies (Mankin *et al.*, 2007). Nitrate-N (NO_3^- -N), a subsurface pollutant, can be removed

by a number of mechanisms. These include denitrification, plant immobilization, and microbial immobilization (Hill, 1996). Of these, denitrification is the only process that can completely remove NO_3^- -N from the system. That is why much research has focused on this process.

Enhanced denitrification could be the solution for removing the majority of NO_3^- -N prior to entering waterways (Dukes *et al.*, 2002; Hefting *et al.*, 2005, Spruill, 2004). Denitrification is an anaerobic, microbially mediated process where NO_3^- -N is converted into (harmless) nitrogen gas (N_2) and then released into the atmosphere. If NO_3^- -N is found in the soil pore water, denitrification can occur provided the following conditions are present (Postma *et al.*, 1991; Puckett, 2004; Knowles, 1982; Korom, 1992; Sylvia *et. al.*, 1998):

- 1.) Denitrifying bacteria
- 2.) Anaerobic conditions
- 3.) A carbon source that can act as an electron donor
- 4.) Suitable temperature (35-60° C)
- 5.) Suitable pH conditions (near neutrality)

The following equation displays the chemical process of denitrification (Brady *et al.*, 2008).



The process converts nitrate into dinitrogen, nitric oxide, or nitrous oxide gas by coupling with energy production using oxidative phosphorylation. Denitrifying bacteria use nitrogen in

the form of nitrous oxide instead of oxygen as an electron acceptor. An electron donor in the form of organic carbon is used to reduce nitrogen into oxidized forms. The majority of the bacteria involved in this chemical transfer reaction is heterotrophs and require organic carbon as the electron donor. Predominate types of denitrifying bacteria include *Pseudomonas*, *Alcaligenes*, *Flavobacterium*, and *Bacillus*, with *Pseudomonas* being the most commonly found (Knowles, 1982). Four enzymes correspond with each step of the process: dissimilatory nitrate reductase (Nar), nitrite reductase (Nir), nitric oxide reductase (Nor), and nitric oxide reductase (Nor) (Knowles, 1982; Sylvia *et. al*, 1998).

All of the denitrification enzymes are inhibited by oxygen, which requires submerged conditions in the microsite locations (Sylvia *et. al*, 1998). Therefore, anoxic conditions are crucial for denitrification to occur. Sylvia *et al.* (1998) reported that Nar and Nir become active once oxygen concentrations reach below 10% of the atmospheric concentrations (approximately 0.29 mmol_{O₂}/L_{H₂O} at 20° C). Consequently, variability in water table fluctuation throughout the year considerably affects the rate of denitrification.

Redox potentials have been used to predict biological transformations as well to define if suitable conditions are present for denitrification, such as carbon. Nitrate reduction has been found to begin to occur at Eh values less than 300 mV (Patrick, 1960; Bailey and Beauchamp, 1973). The presence of organic carbon is critical for electron donation and for microbial biomass production. Carbon source availability can vary depending on vegetation and climatic season due to differences in litter on the forest floor (Hefting *et. al*, 2005). Denitrification rates are

highly dependent on temperature and pH conditions in the soil for bacteria to survive and enhance NO_3^- -N reduction. Knowles (1982) cited studies that found denitrification to occur at reduced rates between 10 to 35° C and increase to temperatures of 60 to 75° C then diminish substantially after this point. The pH is critical for denitrification rates as well. Sylvia *et al.* (1998) reported that the denitrifying bacteria functions best near neutrality and low pH inhibits enzyme activity slowing denitrification rates.

Nitrate Removal Effectiveness of Riparian Buffers

Riparian buffers can be ideal for denitrification, but research shows it can be highly variable. Maintaining the ideal conditions in riparian zones for denitrification to occur is critical to increase the efficiency of NO_3^- -N reduction through these systems. Riparian buffers have been found to reduce NO_3^- -N concentrations as much as 90%, while in other cases have been found to have no effect on NO_3^- -N concentrations entering adjacent stream channels (Lowrance *et al.*, 1984; Lowrance, 1992; Dukes *et al.*, 2002; Hunt *et al.*, 2004; Peterjohn *et al.*, 1984; Angier *et al.*, 2008; Spruill, 2004). Therefore, identifying design components which enhance NO_3^- -N removal in these systems is critical for buffers to meet water quality goals.

Hydrology plays a major factor in determining denitrification rates that occur within riparian zones. These hydrologic factors include: groundwater flow direction through the riparian zone, seasonal water table depth in riparian zones, and physical and chemical properties of the soil strata in which groundwater flows (Clément *et al.*, 2002; Hill *et al.*, 2000; Puckett, 2004). Researchers have attempted to identify the combinations of soil type, seasonality,

topography, soil permeability, hydraulic conductivity, and carbon availability that lead to ideal conditions for denitrification to occur in buffer systems.

Groundwater flow along with water table depth is highly dependent on soil types and seasonality. In a study by Spruill (2004), four buffer sites had a range of NO_3^- -N reduction from 95% to 0%. The lack of NO_3^- -N reduction was postulated due to lack of groundwater flow through the buffer area before entering the stream. Groundwater bypass of the active denitrification zones in buffers can occur when, for example, groundwater flow paths do not intercept the buffer due to topographic gradients or restrictive soils, along with high evapotranspiration during the summer along with seasonally deep water table levels that do not allow groundwater to reach active denitrification zones. Dukes *et al* (2002) documented that two of six studied riparian buffers had water table gradients such that water moved from the streams into the buffers. Therefore no NO_3^- -N reduction was provided for the adjacent field by the two buffers. Puckett (2004) completed a study on 13 buffers focusing on groundwater NO_3^- -N fate with respect to the groundwater flow paths. Findings suggested deep groundwater did not reach reduction zones in the buffers due to tile drains, ditches, or flow paths beneath the denitrifying zones. Higher rates of denitrification have been found to occur during warmer months, and higher NO_3^- -N concentrations in the stream were found in cooler months during a buffer study using water quality samples (Böhlke *et al.*, 2007; Lowrance *et al.*, 1995). Both studies results were attributed to water table fluctuations throughout the year preventing water to enter into the reduced marine sediments that would have increased residence time through the buffer.

Residence time is an important factor for NO_3^- -N to reach denitrifying microsites and undergo denitrification. The velocity at which water travels is highly related to the topography and soil permeability in the riparian zone. Vidon *et al.* (2004) examined eight riparian sites to define the effect of topography on NO_3^- -N reduction and water table fluctuations using a model. Topographic qualities in the riparian zones were identified as critical components for decreasing runoff and groundwater velocity within the buffer. Decreased velocities from flatter topographies allow more time for the water to seep through the riparian buffer and possibly denitrify in the soil. Schiff *et. al* (2002) found that deeper water tables were caused by larger hydraulic gradients, increased hydraulic conductivity, and decreased residence times in the riparian zone, resulting in less NO_3^- -N reduction.

Increased buffer width has also been evaluated to observe its effectiveness in increasing residence time and reducing NO_3^- -N. Dukes' *et al.* (2002) study of four riparian buffers with differing widths concluded that the wider plot (15 m) had a 15% greater decrease of NO_3^- -N compared to the thinner plot (8 m). These differences were most likely due to increased residence times through the buffer. Mayer *et. al* (2007) completed a meta-analysis of 89 buffers to estimate buffer NO_3^- -N reduction with widths ranging from 0 to 50 m. The analysis took into account vegetation type and hydrologic flow conditions. NO_3^- -N reduction increased as width increased from 0-25 m, but no additional significant benefit was gained when buffer width was increased to 25-50 m. These findings were attributed to denitrification microsites having higher availability from higher water tables and carbon availability in widths ranging from 0 to 25 m.

Angier's *et al.* (2008) study of a riparian buffer examined widths varying from 60 to 250 m. Groundwater samples indicated that the highest NO_3^- -N concentrations were found in areas with buffer widths greater than 100 m. The study concluded that NO_3^- -N reduction is not only dependent on the component of buffer width, but the flow direction and depth at which groundwater flows through buffer zones was equally, if not more, critical for NO_3^- -N reduction.

Reduction of NO_3^- -N can be dependent on the depth that groundwater flows through the riparian zones during low-flow regimes. In one of many studies, 89% of NO_3^- -N reduction, primarily in the subsurface of the soil, was due to a combination of denitrification and plant uptake (Peterjohn *et al.*, 1984). Further studies were recommended to consider the hydrologic and biogeochemical factors that contributed to each of these mechanisms. Studies completed by Lowrance *et al.* (1995, 1992) using denitrification enzyme activity (DEA) and groundwater monitoring wells have shown that denitrification had highest *potential* rates in soil depths of 0-6 cm, but can occur in saturation zones within 60 cm of the soil surface that are near the stream. The higher *potential* denitrification rates in the upper soil zones could be due to higher organic carbon availability due to tree litter. A study completed in North Carolina completed a DEA analysis within a riparian zone and reported the *potential* rate of denitrification decreased with soil depth (Hunt *et al.*, 2004). Results were attributed to carbon availability in increased soil depths as well. Hill *et. al* (2004) evaluated denitrification potentials (DNP) with soil core samples at depths ranging from 0-400 cm in five riparian buffers. The study found denitrification activity in layers down to 210 cm. Furthermore, Hill *et. al* (2004) reported that

NO_3^- -N concentrations were lower because of increased denitrification rates in coarse sediment layers that was receiving carbon leaching downward from overlying organic rich horizons. Irregular flow patterns and fluctuating water tables decrease anoxic conditions suitable for denitrification at soil depths close to the surface and have also been reported to decrease NO_3^- -N reduction effectiveness during dry regimes (Kellogg *et. al*, 2005).

Soil stratification and conductivity studies have also shown to have an important effect on reduction of NO_3^- -N. Davis *et al.* (2007) completed a study on NO_3^- -N reduction through the A and C soil horizons in shallow groundwater of a riparian buffer with a lateral flow path. Results from well samples were believed to show that the NO_3^- -N concentration in the A horizon experienced dilution from precipitation combined with biological consumption (mostly from plant uptake and denitrification), while the C horizon only showed biological consumption. Again groundwater NO_3^- -N removal correlates to the amount of organic material found on the surface of the buffer. Hefting (2005) reported that biomass production differed significantly in a study of several forested sites between vegetation types. The forested vegetation site had higher organic carbon availability from plant litter on the forest floor and a higher efficiency for NO_3^- -N reduction. Vidon *et al.*, 2004 reported similar results in a study of two riparian zones. Spruill (2004) found higher NO_3^- -N removal efficiencies in soil strata with lower hydraulic conductivities possibly due to longer residence times in the riparian zone.

Several soil studies have been completed using redox potential evaluations to predict occurrences of denitrification biological transformations. Redox potential is a voltage that can

be measured in soil to identify the tendency for a component to accept or donate electrons and predict reduced species in the soil solution (Sylvia *et al.*, 1998; Richardson and Vepraskas, 2001). The potential difference is created as electrons are transferred, becoming more positive (soil oxidized) as a substance loses electrons and more negative (soil waterlogged) as a substance gains electrons (Sylvia *et al.*, 1998). Oxidized soils tend to take electrons from the Pt wire, while reduced soils transfer electrons to the electrode (Richardson and Vepraskas, 2001). Therefore, lower redox potential readings usually exhibit anoxic soils with available carbon sources (Sylvia *et al.*, 1998). The redox potential is measured using a Pt-tipped electrode and a reference electrode creating a standard set of conditions (Richardson and Vepraskas, 2001). The Pt wire is used since it is chemically inert, only conducts electrons, does not generally react with itself, and does not oxidize readily as metals such as Fe, Cu, and Al often do (Richardson and Vepraskas, 2001). In field measurements are completed using a portable Ph/millivolt (mV) and saturated calomel or silver/silver-chloride reference electrode, where the redox potential is measured in millivolts (mV).

Multiple studies have been completed investigating the reliability of redox readings along with occurrences of denitrification. Wafer *et al.* (2004) tested the reliability of redox probes in field work with 240 redox probes. Results showed that 236 probes were found to be long-lasting and dependable over a course of 19 months. Cey *et al.* (1999) used redox potentials to provide evidence that denitrification was occurring through a riparian zone in southern Ontario. Results showed a sharp decline in NO_3^- -N concentrations as redox readings went below 200 mV.

Patrick (1960) showed evidence that NO_3^- -N begins to undergo denitrification at redox potentials as high as 250 mV, with increasing NO_3^- -N concentration reductions correlated with decreasing redox potential.

Difficulties in establishing if denitrification is responsible for observed NO_3^- -N reduction in concentrations are often attributed to the possibility of deeper groundwater mixing within the riparian zones. Discharge and upwelling areas within buffers have been found to have converging flowpaths that could dilute the amount of NO_3^- -N in groundwater, because the deeper groundwater typically contains low NO_3^- -N concentrations (Mengis *et al.*, 1998). Researchers have developed several methods to determine if removal of NO_3^- -N observed is indeed denitrification or dilution. Lowrance (1992) along with other researchers used chloride, from well samples in the riparian zones, to provide evidence that denitrification and not dilution was responsible for observed NO_3^- -N losses. The conservative ion chloride (i.e. having minimal plant uptake and not undergoing microbial transformations in soil) was used to compare changes in the ion relative to NO_3^- -N through the buffer. Results showed that chloride decreased along with NO_3^- -N through the buffer towards the stream, indicating dilution occurring. Mengis *et al.* (1998) used ^{15}N , which is stable and nonradioactive, to evaluate the dynamics of denitrification through riparian buffers. Widory *et al.* (2003) found that ^{15}N enrichment increased as NO_3^- -N decreased. In the event that denitrification occurs the theory is microbes preferentially used N^{14} , leaving the molecularly heavier N^{15} behind. Both studies showed higher concentrations of ^{15}N in

comparison with NO_3^- -N leading to conclusions that microbial denitrification was occurring within the riparian zones.

Studies have shown how denitrification can occur in these systems and the mechanisms that can affect their pollutant reduction efficiencies. Still, designing and establishing the ideal buffer has been debatable as to how to meet all the needed conditions to maximum denitrification efficiency as described above. More research is needed to determine critical design mechanisms that can maximize NO_3^- -N reduction for these systems. Additional studies will add to the progress that has been made and enhance the overall impact of riparian zones.

North Carolina Conservation Reserve Enhancement Program

Research has accomplished enough to justify recommending and funding buffers in conservation programs. However, to maximize their benefit there are still many questions unanswered. Studies are needed to define the most important combinations of these factors to maximize NO_3^- -N removal in these systems. For example riparian buffers are one of the primary BMPs endorsed by the North Carolina Conservation Reserve Enhancement Program (NC CREP) to improve water quality, but enrollments are not always ideal sites.

NC CREP is a voluntary program that promotes producers to restore riparian and wetland areas. The program includes support from the N.C. Division of Soil and Water Conservation, U.S. Department of Agriculture's Farm Service Agency and Natural Resources Conservation Service, N.C. Clean Water Management Trust Fund, and the N.C. Division of Forest Resources (NC CREP, 2008). Targeting nine river basins in North Carolina, the program provides financial

and technical assistance to producers (USDA, 2010). The program's goals are to improve water quality by reducing sediment and nutrient loading in the basins using Best Management Practices (BMPs). As of 2007 NC CREP had 31,794 acres enrolled in the program that protects approximately 873 stream miles. NC CREP hopes to enroll 100,000 acres of environmentally sensitive land through the program.

Producers that choose to take part in the program sign at least a 10 to 15 year contract to convert sensitive cropland and pastureland to conservation practices encouraged by the program (USDA, 2010). A percentage of the soil rental rates and installation costs will be paid to the producers depending on what practice they plan to implement and the length of their contract. The 2007 NC CREP Annual Report proposed paying \$1000 per acre for permanent easements and \$250 per acre for 30-year easements. Eligible BMPs include tree planting of shortleaf pines, hardwood tree planting, filter strips, riparian buffers, wetland restoration, and bottomland timber establishment on wetlands (USDA, 2010). Riparian buffers must have a minimum impact zone of either 50 or 100 feet with limited tree removal. Payments vary depending on county, length of contract, CRP soil rental rates, and tax value of the cropland

The purpose of this study was to evaluate topography, hydrology, biogeochemistry, and geometric factors of what appeared to be an ideally sited riparian buffer enrolled in the NC CREP. Evaluating these factors will help the NC CREP to effectively implement more efficient riparian buffer systems in North Carolina.

Research Objectives

The evaluated research site in this study has been a part of NC CREP since 2004. The location of the site is in Halifax County, North Carolina and part of the Tar-Pamlico River watershed. The site location was chosen by finding an area that appeared to be an ideally functional riparian buffer situated correctly in the landscape. The riparian buffer was receiving a source of nutrients, nitrogen, from an adjacent row crop field. The adjacent field at the research site also enabled data analysis to not be complicated by hydrologic variables such as short circuits by old tile drains or deeply incised qualifying streams/canals. The proposed research will address hydrologic and biogeochemical factors that affects of NO_3^- -N removal in buffers, particularly through denitrification.

Objectives of the research project are:

- 1.) Complete a water quality and hydrologic assessment on riparian buffer effectiveness in reducing groundwater NO_3^- -N through denitrification
- 2.) Determine the effect dilution from deeper groundwater has on reduction of NO_3^- -N through the buffer
- 3.) Determine if differences in buffer width affect NO_3^- -N reductions through the buffer
- 4.) Based on research findings, make recommendations for ideal buffer locations for future enrollments in NC CREP, to maximize water quality impacts of the program

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CHAPTER 2: EFFECTIVENESS OF NITRATE REDUCTION IN A 43 METER WIDE RIPARIAN BUFFER: A HYDOLOGIC AND BIOGEOCHEMICAL EVALUATION

ABSTRACT

Defining ideal landscape and soil conditions for placement of buffers enrolled in conservation programs could maximize stream miles protected, and improve downstream water quality in sensitive streams and estuaries. During the past five years nitrate reduction efficiency of a riparian buffer enrolled in the North Carolina Reserve Enhancement Program (NC CREP) has been evaluated. The average buffer width was 43 m, with a range of 40-45 m. Surficial groundwater monitoring well nests were installed in three transects within the buffer. Each well nest contained a shallow (1.5-2.3 m) and deep (2.7-3.6 m) well. Additional wells were installed in the deeper aquifer to examine interaction with surficial groundwater. Upslope agricultural practices have included soybeans, peanuts, cotton and corn production.

Nitrate concentrations decreased through the buffer from Zone 3 (grassed filter strip) to Zone 1(stream edge) with average concentrations changing from 12.8 to 6.0 mg/L and 12.9 to 1.4 mg/L for deep and shallow wells respectively. Water table measurements, nitrate to chloride ratios, deep aquifer water quality analyses, topography, redox measurements, and dissolved organic carbon (DOC) were used to determine whether the primary mechanism for these

decreases was denitrification or groundwater dilution. The mass removal per year was also calculated to determine the overall impact of the riparian buffer. Results show that both dilution and denitrification contributed to nitrate reductions in the system, but denitrification was the main reducing mechanism. An advanced understanding of the hydrologic and biogeochemical factors in riparian buffers will lead to design recommendations that could possibly enhance pollutant reduction in these treatment systems.

INTRODUCTION

North Carolina, along with other states, has been dealing with major water quality issues over the past 30 years. Eutrophication and associated fish kills have led to increased concerns of the effects of nutrient loads to the Tar Pamlico and Neuse watersheds of North Carolina (NCDWQ, 2002). Excessive loads of nitrate-nitrogen (NO_3^- -N) have been linked to those eutrophic conditions, and a large contributor of these pollutants has been organic and inorganic fertilizers from agricultural production (NRDC, 1998; US EPA, 1984).

Riparian buffers are one type of best management practice (BMP) that has been identified to reduce NO_3^- -N from various pollutant sources, including agricultural practices. Researchers have defined riparian buffers as a complex assemblage of soil, plants, and organisms immediately adjacent to a water course that may include wetlands, stream banks, and floodplains (Lowrance et. al, 1985; Osmond et. al, 2002). The USDA Forest Service (2008) defines riparian buffers as areas of trees and other vegetation that are located in areas adjoining and upgradient from surface water, that intercept surface runoff, wastewater, subsurface flow and deeper groundwater that flows from upland sources. When properly designed and implemented, they can reduce the effects of nutrients, sediment, organic matter, pesticides, and other pollutants prior to their entry into surface water and groundwater recharge areas.

Riparian buffers have been found to reduce NO_3^- -N concentrations in groundwater up to 90% (Peterjohn and Correll, 1984; Lowrance *et al.*, 1984; Lowrance *et al.*, 1985; Lowrance,

1992). The common theme in these studies is the importance of proper buffer placement given site hydrology and biogeochemistry to maximize pollutant removal mechanisms.

Nitrate-N (NO_3^- -N) can be removed by a number of mechanisms. Two predominant removal processes are biological uptake (i.e. plants and microbial communities) and denitrification (Hubbard and Lowrance, 1997; Peterjohn and Correll, 1984; Mayer *et al.*, 2007). While biological uptake allows NO_3^- -N to remain in the buffer system in pools that may be released, denitrification allows for a complete removal of NO_3^- -N from the system through the microbially mediated transformation of NO_3^- -N to N gases (Woodward *et al.*, 2009).

Microbial denitrification within soil requires a source of nitrate, anoxic conditions (indicated by low redox values), a carbon source that can act as an electron donor, suitable temperature, and suitable pH conditions (Postma *et al.*, 1991; Puckett, 2004; Korom, 1992). Groundwater rich in NO_3^- -N must be delivered to soil layers that have these conditions for denitrification to occur. Therefore, a proper hydrologic and biogeochemical regime within buffers is imperative to maximize denitrification potential in riparian buffers.

Over the past 25 years extensive research has been conducted examining riparian buffer effectiveness on groundwater NO_3^- -N reduction (Spruill, 2004; Evans *et. al*, 2007; Gilliam, 1994). Buffer removal of NO_3^- -N is variable and riparian buffers do not always work as effectively as desired (Ocampo *et. al*, 2006). Hydrologic and biogeochemical factors that affect the occurrence and rate of denitrification include: frequency and duration of water table depths in riparian zones, groundwater flow direction through the riparian zone, and biogeochemical

properties of the soil strata in which groundwater flows (i.e. carbon source, nitrate, microbes) (Clément *et. al.*, 2002; Hill *et. al.*, 2000; Puckett, 2004).

Nitrate-N concentration reductions are often attributable to groundwater mixing with and diluting surficial groundwater within the riparian zones (Davis *et al.*, 2007; Altman and Parizek, 1995). Groundwater mixing between surficial and deeper aquifers is dependent on soil profile layering within the buffer, and can ultimately affect NO_3^- -N concentrations in the buffer system. For instance, shallow groundwater with high NO_3^- -N concentrations may be diluted by less concentrated deeper groundwater if the confining layer ends within the riparian buffer.

Buffers can only be effective in reducing NO_3^- -N laden groundwater if soil is ideal for denitrification. To maximize the use of buffers in conservation programs, research is still needed to identify ideal riparian buffer locations with suitable hydrologic and biogeochemical conditions to maximize denitrification occurrences in these systems.

The North Carolina Conservation Reserve Enhancement Program (NC CREP) is a voluntary program that encourages landowners to restore riparian and wetland areas to improve water quality (NC CREP, 2008). Landowners receive rental payments based on the soil rental rate calculated by the Farm Service Agency. Along with rental payments, NC CREP provides up to 50 percent of the expenses to establish the conservation practice (NC CREP, 2008). Since NC CREP provides these payment rates for enrolled areas, the Division of Soil and Water staff who oversee the NC CREP program are interested in defining ideal buffer sites whose contribution to water quality improvement justifies the cost of land acquisition.

A detailed evaluation of the hydrology and attenuation of nitrate in a riparian buffer, that appeared to be in an ideal location, was conducted for NCDENR. The research project objectives were to: conduct a detailed hydrologic evaluation of the site, determine changes in NO_3^- -N concentrations through the buffer, and evaluate contributions of denitrification and dilution to observed NO_3^- -N reductions. Several methods were used to measure hydrologic and biogeochemical factors thought to impact riparian buffer efficiency in removing NO_3^- -N through denitrification such as the frequency and duration of the water table elevation near the soil surface, seasonal flow direction, groundwater chemical properties (NO_3^- -N, Cl^- , Ca^{2+} , and Na^+), and soil redox. The project's original intent was a comparative analysis of two adjacent buffer sections with differing widths. However, the NO_3^- -N pollutant source to both buffer sections was significantly different ($\alpha=0.05$), presumably due to their location in the landscape. Therefore, the performances of the buffers were evaluated individually. Results presented in this paper outline research efforts on the narrower and downstream buffer section. Conclusions from this project will aid in defining ideal hydrologic and biogeochemical regimes for denitrification in riparian buffers to maximize water quality impacts of NC CREP and other conservation programs.

MATERIALS AND METHODS

Site Description

Buffer Description

The study site was located on a row crop farm, north of Enfield, NC, in Halifax County. The farm was situated in the upper coastal plain region of North Carolina and was part of the Tar Pamlico River basin (Figure 2. 1). A NC CREP riparian buffer was installed in 1999 (prior to the initiation of this study), downslope of the agricultural fields and next to an unnamed first-order tributary (Hydrologic Unit 03020102). The buffer was designed to follow NRCS guidelines, which recommended a three-zone design (Figure 2. 2). The tributary flows into nearby Beech Swamp, which drains into the Fishing Creek watershed. The downstream reaches of the tributary became incised and narrowed throughout the study, while the upstream reach had a more natural stream pattern that remained stable. The stream was approximately 1 m (3 ft) wide upstream and approximately 0.5 m (1.5 ft) wide downstream. The 30-year average precipitation in the area was 1153 mm/year (45 in/year) (NC State Climate Office (SCO), 2010).

The site was chosen because it represented a buffer enrolled in the NC CREP program that appeared to be ideally situated in the landscape to provide maximum water quality benefits. Some of its ideal characteristics included an upslope pollutant source and no identified drainage ditches, short-circuiting, or deeply incised stream. Nutrients and sediment from the field adjacent to the buffer were identified as the major pollutant source that would be treated by the

buffer. The primary pollutant source at the site was inorganic fertilizer applied to the adjacent field that produced corn, soybeans, peanuts, and cotton (see fertilization rates in Appendix E).



Figure 2. 1: Research site location.

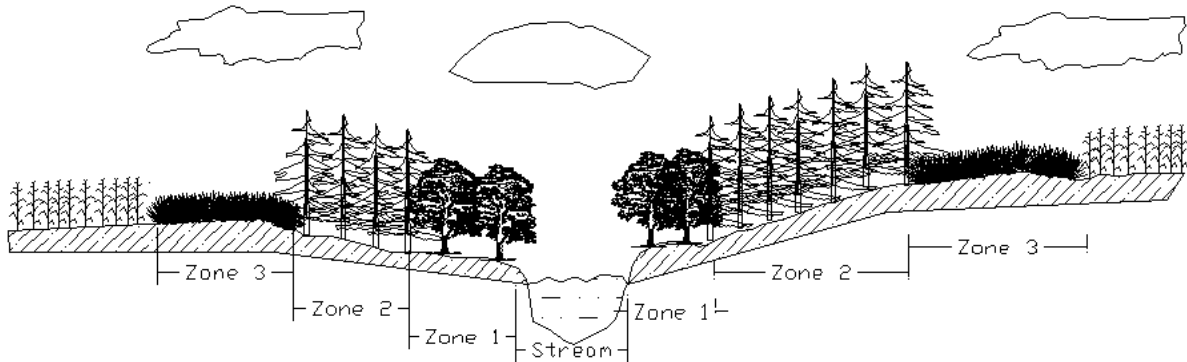


Figure 2. 2: USDA Three Zone Buffer Design – the basis of the design for the research buffer (adapted from NRCS, 1997).

The total length of the analyzed buffer section was approximately 46 m (150 ft) and ranged between 40-45 m in width. (131-148 ft) (Figure 2. 3). The buffer was planted in 1999 with three rows of *Quercus phellos* (willow oak) and *Quercus spp.* (oak) in Zone 1 (near the stream) and *Pinus taeda* (Loblolly pine) throughout Zone 2 (the mid buffer). Predominant vegetation in Zone 3 (a grassed filter strip) consisted of mainly *Trifolium spp.* (clover). A complete vegetation assessment can be found in Appendix A.

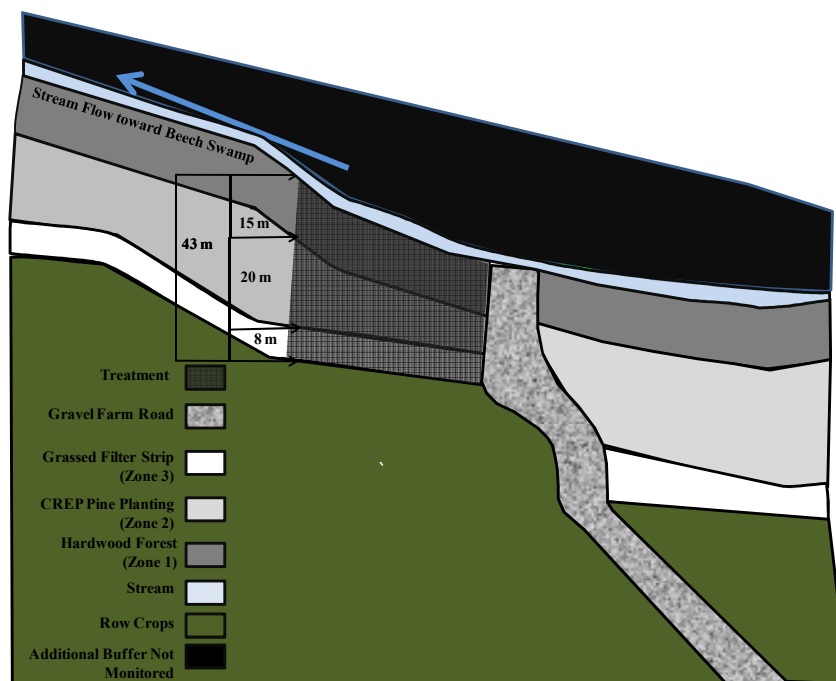


Figure 2. 3: Land cover for research site (Not to Scale).

Site Soils

The NRCS Soil Staff Survey (2006) identifies three dominant soil types at the research site: Marlboro fine sandy loam, Bonneau loamy fine sand, and Gritney fine sandy loam as seen in Figure 2. 4, Table 2.1, and Figure 2. 5. A soil scientist completed an evaluation of the soil profile during instrument installation in December 2004. Upstream of the buffer the stream edge soil was sandy loam that transitioned to sandy clay loam similar to a Lynchburg soil series (Figure 2. 5). The soil assessment also indicated that the buffer's field edge soil had layers of loamy sand transitioning to a shallow clay layer, similar to Gritney, at approximately 0.8 m (33 in) below the soil surface (Figure 2. 5). At 4.6 m (15 ft) below the soil surface a marine clay restrictive layer was identified that was believed to be sufficient for separating the surficial and

deeper aquifer groundwater. A more complete analysis of the field observations can be found in Appendix B.

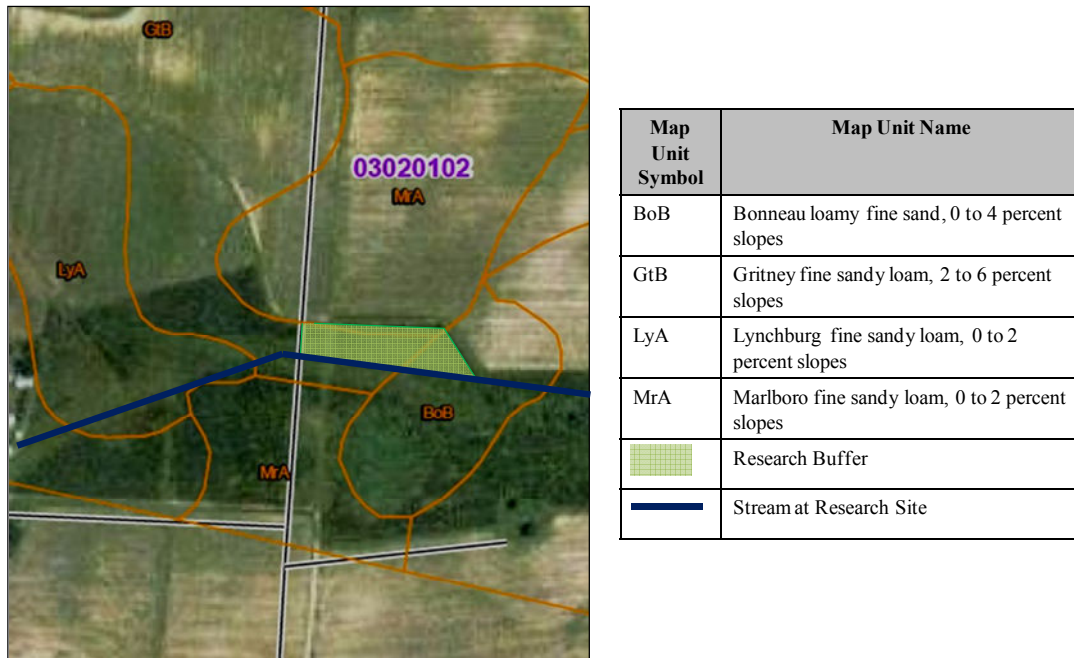


Figure 2. 4: Soil Map of Research Site from USDA-NRCS Soil Survey Staff (2006).

Table 2. 1: Soil classifications within buffer treatment (USDA-NRCS Soil Survey Staff, 2006).

Soil Type	Buffer Zones	Drainage Class	Permeability	Restrictive Layer	Seasonal Water Table
Marlboro fine sandy loam	1 and 2	well drained	moderate	> 2 m	1.2 m to 1.8 m
Bonneau fine loam sand	1, 2, and 3	well drained	moderate	> 2 m	1.0 to 1.5 m
Gritney fine sandy loam	1, 2, and 3	moderately well drained	slow	0.2 m	0.45 to 0.9 m

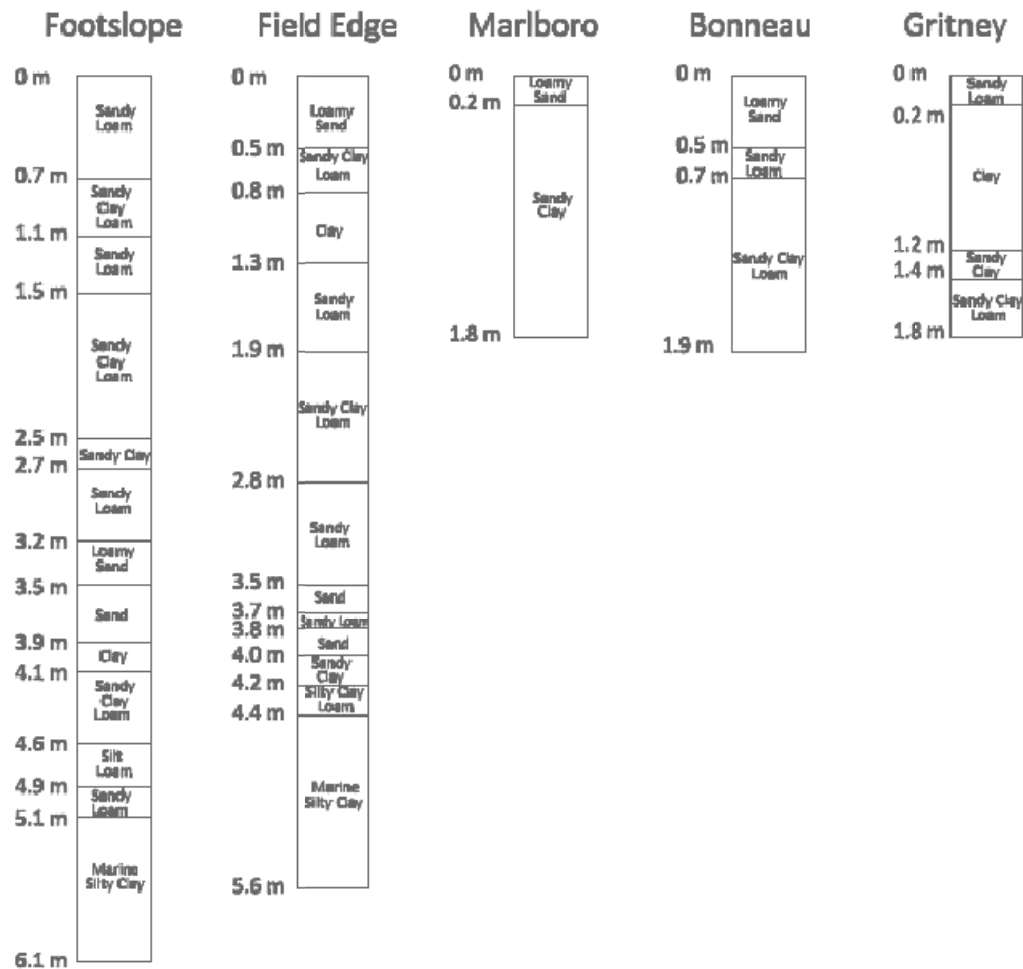


Figure 2. 5: Soil profiles at buffer site and similar soil series (as defined by USDA-NRCS, 2006 and Severson, 2004).

Site Survey

Three site surveys were completed over the study. A topographic and stream survey was done during June of 2004 using a Topcon Electronic Total Station. The second survey evaluated the topography of the field adjacent to the research buffer, monitoring instrumentation, and a stream survey using a Topcon Electronic Total Station. The third survey completed in March

2010 used a Laser Level to determine elevations of instrumentation based on benchmarks established during the initial surveys. Due to the isolated location of the site, an assumed datum elevation of 30.5 m (100 ft) was used to determine relative ground elevation points. AutoCAD Civil 3D Land Desktop Companion 2008 was used for topographic map development for the site.

Site Instrumentation

Groundwater Well Installation

Prior to well installation at the site, the Three Point Method was used to verify groundwater flow through the buffer using temporary piezometer installations (Todd and Mays, 2005). Following this procedure, surficial groundwater monitoring well nests, to be used for both groundwater elevation and water quality measurements, were installed in three transects 15 m (50 ft) apart within the buffer in December 2004 (Figure 2. 6). Each well nest contained a shallow and deep well with maximum depths ranging between 1.5 to 2.3 m (5 to 7 ft) and 2.7 to 3.6 m (9 to 12 ft) from the ground surface respectively. Locations of well nests can be found in Table 2. 2 (distances are relative to the stream edge). Wells were constructed with 5 cm (2 in) diameter PVC. The bottom 0.6 m (2ft) of each well was screened by drilling 1 cm (0.4 in) diameter holes at 15 cm (6 in) spacings. The end of the PVC was capped and covered with a fabric sock to reduce soil intrusion into the well. Wells were installed with a drill rig and an

auger. After the hole was drilled, the well was placed in the hole and then the annular space was immediately backfilled with sand to the top of the well screen, and then sealed with bentonite.

Three water table elevation data loggers (Infinites USA, Inc., Port Orange, FL) with a built in pressure sensor were installed in December of 2004. Water table elevation data loggers were positioned next to well nests in the center transect and were constructed of fully screened 5 cm (2 in) PVC lined with a protective fabric sock. The wells were installed to 3 m (10 ft) depths, backfilled with sand, and the top 30 cm (1 ft) was sealed with bentonite.

In June 2008 four deeper aquifer wells were installed at the site using a geoprobe direct push auger to further monitor deep groundwater to assess any mixing with the surficial groundwater. PVC wells 1.9 cm (1 in nominal) in diameter were placed approximately 1 m below a blue-grey marine sediment layer. Deeper aquifer wells were installed at four locations throughout the site (Figure 2. 6). A 1.5 m (5 ft) pre-packed screen section consisting of a normal slotted PVC screen surrounded by sand and a stainless steel screen were placed at the desired depth of each well. A bentonite pre-packed pipe section with a length of 1.2 m (4 ft) was attached above the screen and the remaining annular space was backfilled with granular bentonite to the surface. A 1 m (3.5 ft) long metal casing was then installed around the well riser for protection. Maximum well depths ranged from 7.6-10.6 m (25-35 ft).

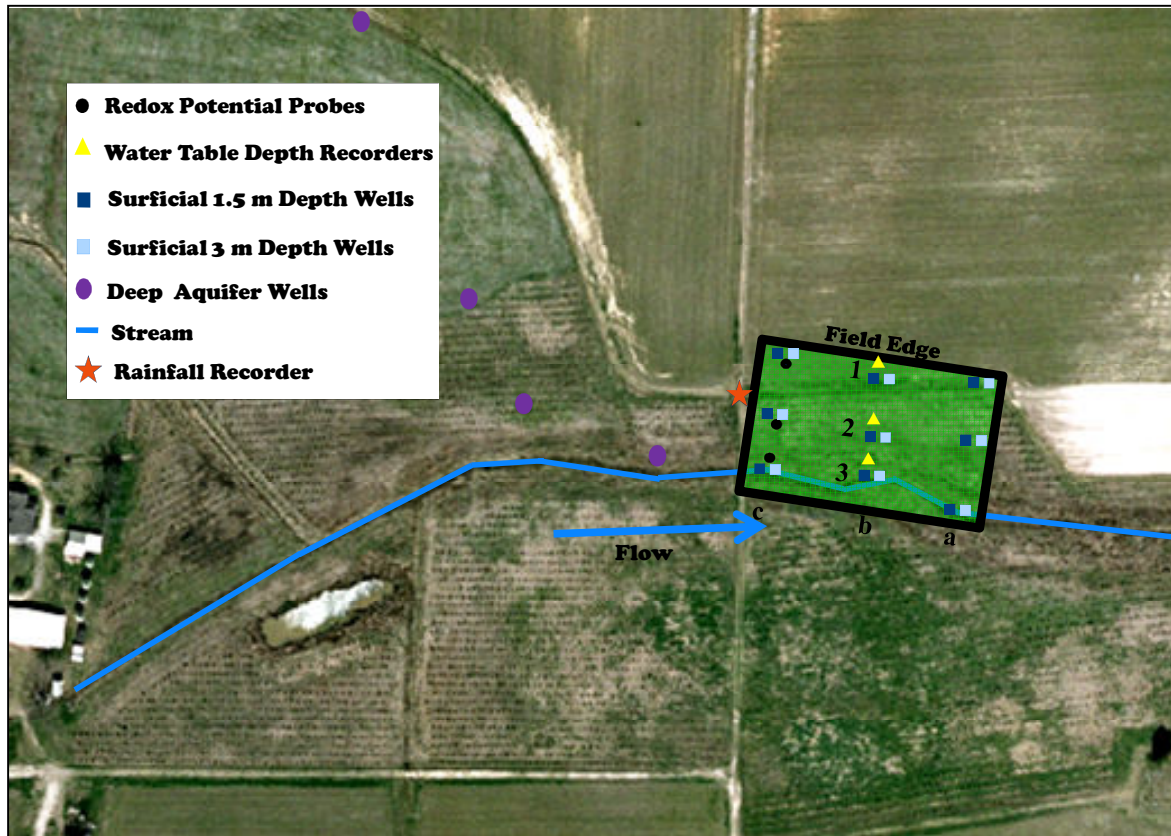


Figure 2. 6: Research site monitoring setup for the study site.

Table 2. 2: Transect layout from Zone 3 to Zone 1. Distances are relative to the stream.

Zone 3 (Grassed Filter Strip)	Zone 2 (Mid Buffer)	Zone 1 (Stream Edge)
40-45 m (131-148 ft)	25-30 m (82- 98 ft)	1.5 m (5 ft)

Rainfall

A tipping bucket and a HOBO (Onset, Bourne, MA) rainfall data logger were installed in December 2004 to continuously monitor precipitation. A manual rain gage was installed next to the data logger to verify accuracy. Due to complications with both the rainfall data logger and

manual rain gage, the NC SCO (2010) data was used for precipitation data in this project for all five monitored years. The monitoring location was 9 miles south of the research site.

Redox Potential Probes

Redox potential probes were installed next to each of the surficial groundwater monitoring wells in the upstream transect, due to excessive wetness of the center transect (Figure 2. 7). The probes were used to measure redox potential readings (Eh) in the buffers. Five platinum-tipped redox probes, constructed as described by Wafer *et. al* (2004) and Faulkner *et al.* (1989), were inserted in 5 cm (2 in) PVC pipe and sealed with a cap. Holes were drilled into the cap allowing each probe to have a port to enter into the soil media. The probes were placed at the same depths as the surficial shallow (1.5-2.3 m) and deep (2.7-3.6 m) water quality well depths. Therefore, there were 5 probes per depth for each location for a total of 30 probes.



Figure 2. 7: Redox potential monitoring nest.

Data Collection

Soil Sampling

In order to estimate seepage flow velocity through the buffer, soil samples were collected at the bottom of each surficial well during installation. A particle size analysis test was then completed by the North Carolina State Soil Science Laboratory and results were used to determine the hydraulic conductivity through each zone of the buffer using SPAW 6.0 (NRCS, Pullman, WA). Results provided soil classifications used to estimate porosity in each zone of the buffer. Porosity estimates along with hydraulic conductivity results were then used for determining groundwater flow velocity from the field to the stream.

Water Table Monitoring

The water table elevation data loggers (Infinites USA, Inc., Port Orange, FL) were used to monitor water table elevation hourly from November 2005 to May 2010. Water table depth datasets were downloaded monthly using a HP 48 G+ handheld calculator (Palo Alto, CA) and monthly manual water table elevation readings were measured in the water table elevation data loggers to account for drifting using a Solinst ® water level meter (Solinst ®, Georgetown, ON). Additionally, monthly water table elevations across the buffer were measured in the surficial groundwater monitoring wells from August 2008 to May 2010 using water level meters.

Water Quality Monitoring

Groundwater samples were collected from the surficial aquifer wells monthly beginning in January 2005 (Figure 2. 8). Each surficial well was purged until dry or until three times the volume of water in the well was removed using a low flow submersible pump. Samples were collected using bailers that were designated to each of the surficial wells to avoid cross contamination.

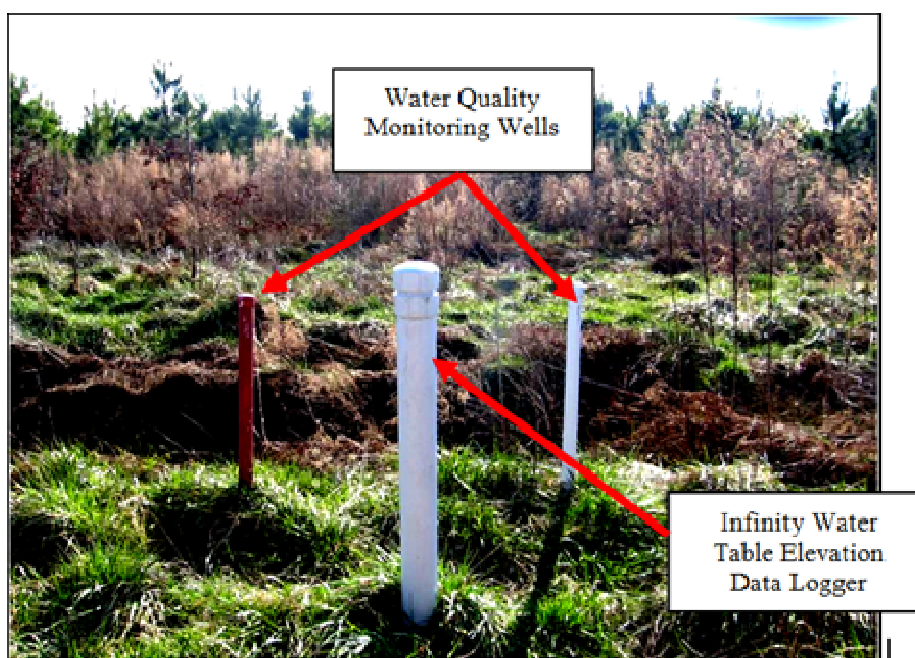


Figure 2. 8: Water table data logger (Infinity USA, Inc., Port Orange, FL) and two surficial aquifer monitoring wells.

Groundwater samples were collected from the deeper aquifer beginning in August 2008. The deeper aquifer wells required the use of an inertial pump (Waterra Groundwater Monitoring Equipment and Supplies, Mississauga, ON) with a SS-13 valve at end of the tubing for purging and sample collection due to the depth of the wells. The wells were purged until dry or evacuated three times the volume of water in the well before samples were taken.

All water quality samples from the surficial and deeper aquifer wells were analyzed for nitrate (NO_3^- -N), chloride (Cl^-), dissolved organic carbon (DOC), ortho-phosphate (O- PO_4), and ammonium (NH_4 -N). Sodium (Na^+) and calcium (Ca^{2+}) analyses began in July 2008. Sample bottles were pre-acidified with H_2SO_4 and iced to a temperature of 4 °C (39 °F) prior to transport to the BAE Environmental Analysis Lab. Sample bottles designated for DOC, Na^+ , and Ca^{2+} evaluations were not pre-acidified. Analyses were conducted by the NCSU-Biological and Agricultural Engineering Environmental Analysis Laboratory. All nutrients measured in the study contributed to understanding nitrogen dynamics within the buffers. Cl^- was used to investigate the possibility of groundwater mixing throughout the buffer. Additionally, Na^{2+} and Ca^{2+} were measured for comparisons of the surficial aquifer groundwater and deeper aquifer groundwater. DOC was examined to validate a carbon source, necessary for denitrification to occur, was present. Methods used in the NCSU-Biological and Agricultural Analysis Lab can be found in Appendix F.

Redox

Redox measurements were taken monthly starting in May of 2006 using a KCl-saturated Ag/AgCl reference electrode (Jensen Instruments, Tacoma, WA) and an Accumet AP63 portable pH/mV meter (Fisher Scientific ®, Pittsburgh, Pa). The five readings at each depth were averaged to represent the redox condition at each location within the buffer and depth in the soil. Measurements were adjusted using a correction factor of 204 mV that was determined using the

assumed soil temperature of 15 °C (59 degrees F) and a measured pH of 5.2 (Richardson and Vepraskas, 2001).

Data Analysis

Water Table Analysis

Water table elevations were determined using the site topographic survey, continuously monitored water table elevation data, and monthly manual water table depth measurements. The average water table elevation and the average water table difference between buffer zones was determined using the following equation.

$$AD = \frac{1}{n} \sum_{i=1}^n (WTE_{upslope_i} - WTE_{downslope_i}) \quad (2.1)$$

Where,

AD = Average Difference (m)

$WTE_{upslope_i}$ = Water table elevation at upslope location

$WTE_{downslope_i}$ = Water table elevation at downslope location

n = Number of daily water table readings collected during study period

Whether the buffer zone met USACE minimum jurisdictional wetland hydrology criteria was determined using continuous water table data. The percentage of consecutive days during the growing season (March 20th thru November 6th) that the water table was within 30 cm of the soil surface consecutively was completed for the three water table monitoring locations.

Groundwater Flow Direction Modeling

During the study, best-fit hydraulic gradients were determined using water table depths of the full scale monitoring system. A groundwater flow Microsoft Excel 2007 spreadsheet was utilized to examine all monitoring wells and model the flow direction change monthly at the research site (Devlin, 2003). Equations 2.2-2.5 were used to define groundwater flow direction.

Equation 2.2 defines the water table (Thangarajan, 2007):

$$Ax + By + Cz = D \quad (2.2)$$

Where, A, B, and C are referenced elevations and coordinate locations of the monitoring wells located on the research site and D is the distance from the origin to the point on the plane which is closest to the origin. The water table coordinates are represented by x and y and the water table elevation is represented by z. The hydraulic gradient was determined using Equation 2.3.

$$gradient = \sqrt{\frac{A^2 + B^2}{C^2}} \quad (2.3)$$

Equation 2.4 was used to calculate the direction of the groundwater flow, where α is measured from the x-axis.

$$\alpha = \arctan \frac{B}{A} \quad (2.4)$$

The hydraulic gradient between two well locations quantified the head loss. Expressed below is the equation for hydraulic gradient.

$$i = \frac{\Delta h}{L} \quad (2.5)$$

Where,

i = Hydraulic gradient (m/m)

Δh = Change in hydraulic heads (m)

L = Flow path length (m)

The flow rate of the groundwater was estimated using Darcy's Equation (Equation 2.6).

$$q = -\bar{v}i \quad (2.6)$$

Where,

q = Flow rate (cm/s)

\bar{v} = Average seepage velocity (cm/s)

i = Hydraulic gradient (m/m)

Determination of the flow velocity required a particle size analysis completed by the North Carolina State Soil Science Laboratory along with porosity values presented in Fangmeier *et al.* (2006). Darcy's equation assumes flow velocity is through the entire cross section of the material and does not take into account that only a fraction of the cross section is able to allow water movement (Todd and Mays, 2005). Therefore, the estimated velocity of a contaminant flowing in groundwater, if no reactions occur with the aquifer soils or other chemicals, can be

determined by using the average seepage velocity. The following equation uses the effective porosity, which is the porosity that is interconnected and available for flow to move through in the soil (Fitts, 2002).

$$\bar{v} = - \frac{K_s i}{n_e} \quad (2.7)$$

Where,

\bar{v} = Average seepage velocity (cm/hr)

i = Hydraulic gradient (m/m)

n_e = Effective porosity

K_s = Hydraulic conductivity (cm/hr)

To determine K_s the Auger Hole Method was conducted in the buffer during the summer of 2009 and winter of 2010 (van Beers, 1958). Measurements were taken at approximately 70 and 100 cm below the soil surface at the stream and mid-buffer locations and 80 and 130 cm below the soil surface at the field edge location to estimate the hydraulic conductivities throughout the treatment. More measurements were attempted, but failed due to low water table conditions. Deeper depths were unattainable due to the length of the auger. Therefore, another K_s was obtained using a particle size assessment from soil collected at the monitoring depths during well installation and SPAW 6.0 (NRCS, Pullman, WA) for greater accuracy. Results supported the K_s from the particle size analysis would be the most suitable for this study since they were at the soil depths being monitored.

Groundwater residence time was then evaluated using the following equation to determine how long a parcel of NO₃⁻-N laden groundwater remained within the buffer:

$$t = v/L \quad (2.8)$$

Where,

t = Residence time (yr)

v = Pore velocity (m/yr)

L = Length of flow through the buffer to the stream (m)

Topographic and water table gradients were modeled using the spreadsheet developed by Devlin (2003) along with Surfer 7 mapping software (Golden Software, Golden, CO). Monthly water table elevations were imported into the modeling software and vectors of the water table gradients were modeled to produce maps that included flow vectors. The angles of groundwater flow relative to the stream were also calculated.

Nitrate-Nitrogen Removal Efficiency

Groundwater NO₃⁻-N removal efficiency was calculated for each zone and transect as well as the overall area of the buffer at the research site. The following equation was used to define the percent removal of groundwater NO₃⁻-N through the buffer system:

$$\% \text{ Removal} = \frac{C_I - C_E}{C_I} * 100\% \quad (2.9)$$

Where,

$\% \text{ Removal}$ = percentage of groundwater NO_3^- -N removed by the buffer (%)

C_I = Concentration (mg/L) of the groundwater entering the buffer

C_E = Concentration (mg/L) of the groundwater discharging to the stream

Nitrate/Chloride Ratios

In an attempt to define whether denitrification or dilution was the cause for groundwater NO_3^- -N concentration reductions observed in the buffer, NO_3^- -N to Cl^- ratios were calculated. Lowrance (1992) along with other researchers have used this conservative ion (i.e. having minimal plant uptake and not undergoing microbial transformations in soil) in riparian zones groundwater to determine if denitrification and not dilution was responsible for observed NO_3^- -N losses. Chloride was used to compare changes in the ion relative to NO_3^- -N through the buffer. Essentially dilution was indicated if ratios remained constant through the buffer towards the stream, while removal by denitrification or other biological activity was supported if ratios decreased through the buffer.

Measured Nitrate-Nitrogen Mass Removal

Several studies have quantified the load of groundwater NO_3^- -N entering and exiting riparian buffers in groundwater using Darcy's Law and the Dupuit-Forchheimer equation (McMahon and Böhlke, 1996; Burns, 1998; Böhlke *et al.*, 2004; Kennedy *et al.*, 2009). The equation assumes a homogenous, isotropic medium. To gain insight as to how groundwater

NO₃⁻-N was changing and/or transforming throughout the buffer, the load was computed to demonstrate the change in the mass of groundwater NO₃⁻-N from the field edge to the stream edge. The load was calculated using field data to define the hydraulic conductivity and hourly monitored water table elevation data along with water quality samples from each well. Figure 2.9 and the Equation 2.10 were used to calculate groundwater NO₃⁻-N load between the field edge and stream edge wells in the buffer through each soil layer within the soil at depths of 1.5 m (5 ft) and 3 m (10 ft) (Birgand *et al.*, 2007; Kennedy *et al.*, 2009, Freeze and Cherry, 1979).

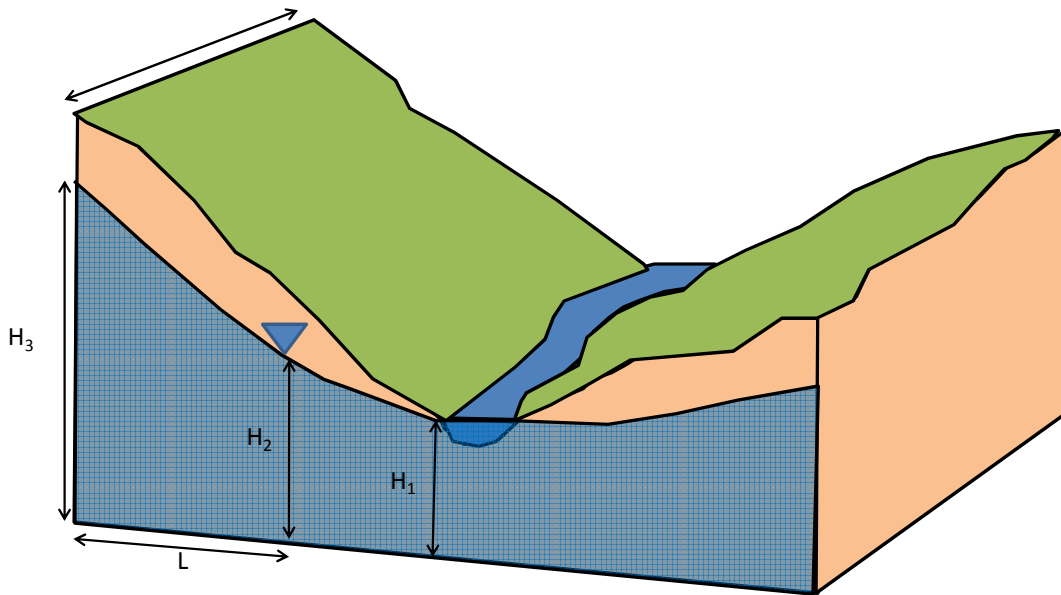


Figure 2. 9: Water table visual for reference for Equation 2.10.

$$Load_{NO3-N} = \frac{2.4 \times 10^{-2} * (H_{Zone3}^2 - H_{Zone2}^2) * K * T * W * C}{2 * L}$$

(2. 10)

Where,

Load_{NO₃-N} = Groundwater NO₃⁻-N flux for each month (kg N)

H = Level of groundwater elevation above datum at position i (m)

K = Hydraulic conductivity at well location (m/hr)

T = Days within each month conversion (days)

C = Influent concentration (mg/L)

W = Length of the buffer (m)

L = Distance between each groundwater well (m)

Statistics

A statistical analysis was completed to define significant differences in groundwater NO₃⁻-N concentrations throughout the buffer treatment system using SAS PROC MIXED ® (SAS Institute, Cary, NC). A log transformation was required to normalize the groundwater NO₃⁻-N concentrations. Random variables included transect and transect depending on well position and the fixed effect was well depth. The model equation can be found below:

$$\text{NO}_3^- \text{-N} = \text{WP} + \text{D} + \text{WP} * \text{D}$$

(2. 11)

Where,

NO₃⁻-N = Groundwater NO₃⁻-N concentrations (mg/L)

WP = Well position through the treatment (1, 2, 3)

Depth = Monitoring well depth (1.5 m or 3 m)

Redox readings, Cl^- , NO_3^- -N/ Cl^- ratios, Na^+ , and Ca^{2+} concentrations were considered individual response variables and evaluated with the same procedure as NO_3^- -N concentrations. Evaluations between deeper aquifer water quality signatures were completed using a mean separation test with NO_3^- -N, Cl^- , NO_3^- -N / Cl^- , Na^+ , and Ca^{2+} concentrations being the individual response variables and the class variables being depth and location (SAS PROC MIXED ®, Cary, NC). Complete results from all statistical analyses can be found in Appendix C.

RESULTS AND DISCUSSION

Groundwater Hydrology Data

Riparian Buffer Relative Wetness

The water table was within 3 m of the soil surface at all locations even during the driest periods of the year and had several wet and dry cycles throughout the study (Figure 2. 10). These conditions enhance groundwater NO_3^- -N reduction according to a hydrologic and NO_3^- -N assessment completed at seven sites by Pinay *et al.* (2007). Findings indicated that an increase in wet and dry cycles near the soil surface allowed nitrification to occur followed by increased denitrification occurrences during wet periods.

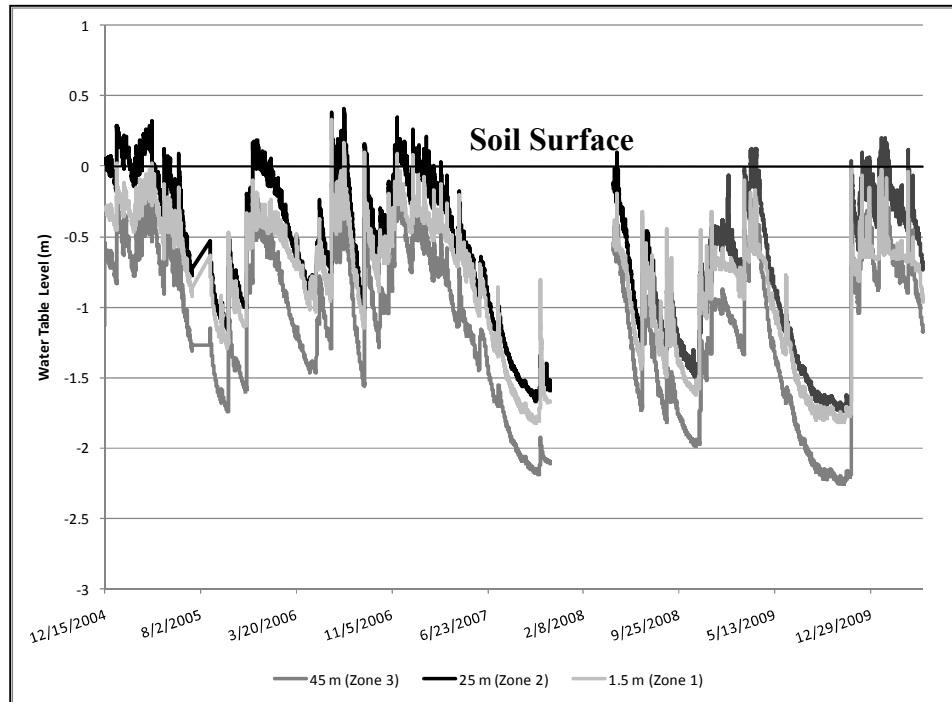


Figure 2. 10: Proximity of the water table to the soil surface within Zones 1-3 in the research buffer. Data unavailable from November 2007 to April 2008 due to equipment malfunction.

Average water table depths relative to the soil surface were 1.16 m, 1.03 m, and 0.88 m with maximum depths below the soil surface of 2.24 m, 2.10 m, and 1.83 m for Zone 3, Zone 2, and Zone 1, respectively (Table 2.3). Zone 3 was found to be the driest zone, as expected. The water table appeared to become deeper beginning in 2007. During 2007-2008, North Carolina had a drought that led to these increases in the water table depths (NCSCO, 2010). Although the water table depths did increase, the water table was within 1.5 m (5 ft) of the soil surface on average each year in all zones within the buffer treatment. These results indicate that the buffer was still relatively wet throughout the year.

Table 2. 3: Average yearly water table depth in Section 2 Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Year	Zone 3 (m)	Zone 2 (m)	Zone 1 (m)
2005	1.16	0.69	0.57
2006	0.86	0.73	0.58
2007	1.37	1.24	1.04
2008	1.39	1.29	1.10
2009	1.40	1.32	1.16
Average (m)	1.16	1.03	0.88

Both pine and oak roots can grow deeper than 85 cm below the soil surface. Depths where these roots are present have been reported as denitrifying hot spots due to decomposing roots and leaching leaf litter if the water table was within these depths (Rotkin-Ellman *et al.*, 2004). Therefore, inundated conditions at various soil depths were examined to identify if the treatment buffer had critical hydrologic conditions for denitrification to take place. Figure 2.11 shows the results of an analysis of the frequency the water table resided at several soil depths in the various buffer zones. These results indicated that all zones had water tables within 60 cm of the soil surface a large portion of the year throughout the study, particularly prior to the 2007-2008 drought.

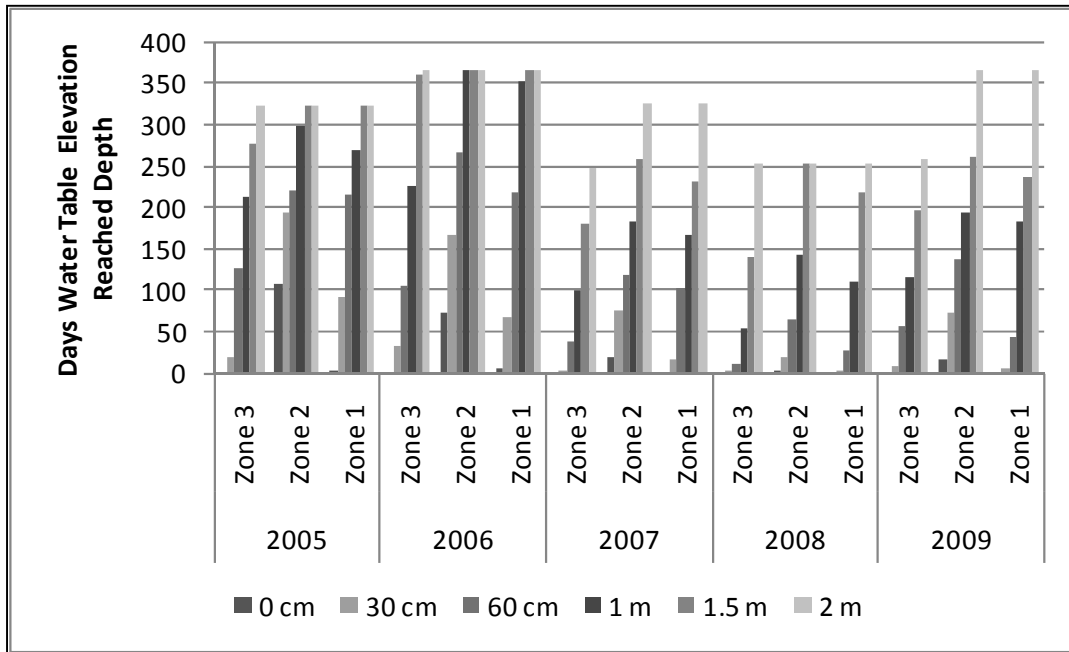


Figure 2. 11: Number of days water table depths were less than 0 cm, 30 cm, 60cm, 1m, 1.5m, and 2m relative to the soil surface. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Riparian areas that are frequently wet can be classified as riparian wetlands. Wetlands have been shown to be effective sinks of groundwater NO_3^- -N (Peterjohn *et al.*, 1984; Humenik *et al.*, 1999; Koskiaho *et al.*, 2003). As such, wetland status of this riparian buffer was used to assess the buffers potential to remove groundwater NO_3^- -N. The wetland hydrology assessment was completed in each zone (Zone 3-grassed filter strip, Zone 2-mid buffer, and Zone-1 stream edge) of the buffer to describe the relative wetness (Figure 2.11). Zone 1 approached minimum jurisdiction criteria, but remained drier after the 2007-2008 drought. Lower water table elevations and stream levels most likely impacted these results. The only location that met minimum jurisdictional wetland hydrology (USACE, 1987) defined as the water table being within 30 cm of the soil surface consecutively more than 5% (11 days) of the growing season

(March 20th thru November 6th) was Zone 2. In fact, the water table was within 30 cm consecutively for 6% to 20% of the growing period four out of five years of the study period (Table 2. 4). This was not surprising, as Zone 2 displayed characteristics of a riparian floodplain marsh wetland, as the soil surface was often wet, planted pine tree survival was low, and herbaceous wetland vegetation was present.

Table 2. 4: Maximum consecutive days water table was within 30 cm of the soil surface during growing season (March 20th thru November 6th). Highlighted cells are years that wetland hydrology was present at monitored zone locations. Data was missing in July through August of 2005 and March through April 2008.

	Zone 3	Zone 2	Zone 1
Depth (cm)	30	30	30
2005 (days)	3	34	22
2006 (days)	5	45	17
2007 (days)	0	2	1
2008 (days)	1	16	1
2009 (days)	0	13	1

Groundwater Gradients

Topography of the buffer did influence the proximity of the water table to the soil surface in this buffer. The buffer had a slope of 4% from Zone 3 to Zone 2 and 0.3% from Zone 2 to Zone 1. The adjacent stream had a slope of 0.7% over the entire research site. Figure 2. 12 shows that the ground elevation decreased substantially between Zones 3 and 2, putting the ground elevation closer to the stream stage between Zones 2 and 1. Therefore, the water table was in close proximity of the soil surface between Zones 2 and 1 since it was closer to the

elevation of the stream channel invert. Additionally the increased relative wetness of Zone 2 compared to Zone 1 was due to the lower topographic elevation of the zone due to a depression between Zones 1 and 2 resulting in water table elevations closer to the soil surface.

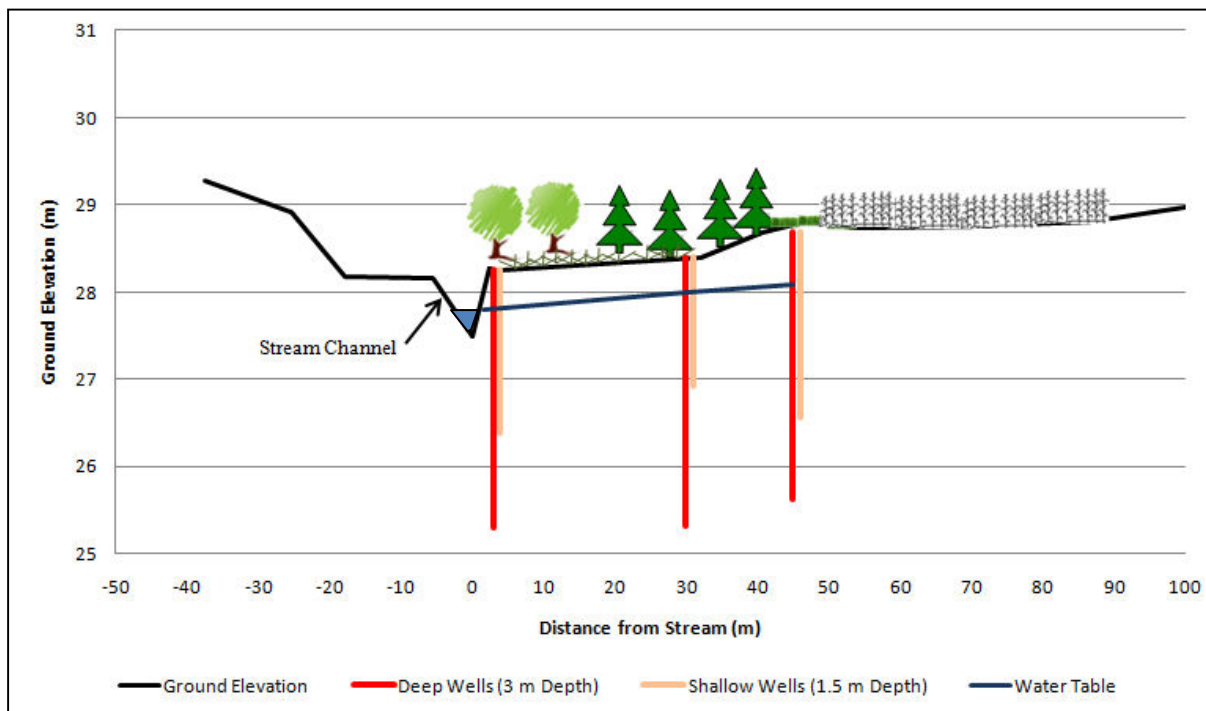


Figure 2. 12: Downstream transect cross section of riparian buffer and surficial monitoring wells.

Water table elevations and gradients were evaluated to investigate the general movement from Zone 3 to Zone 1 throughout the entire buffer study (Figure 2. 13). Since the water table elevations varied year to year as discussed in the prior section, water table elevations were modeled for a wet year (2006) and dry year (2009) to form a better understanding of how the water table elevations changed and how groundwater moved across the site during climatically different years (Figure 2. 14 and Figure 2. 15). As seen in Figure 2. 14 and Figure 2. 15, the wet

and dry years dramatically affected the water table elevations particularly during the summer and fall seasons. During 2006, a considerably wet year at the site, the water tables were highest during the growing season, while during 2009 water tables began to decrease in the spring and continued into the summer and fall seasons. The water table elevation was approximately 29.1 m in all zones in July 2006, while in July 2009 the water tables were approximately 1 m lower (28.3 m). Flow gradients during wetter periods of the year in both 2006 and 2009 indicated water flowing through the buffer from Zone 3 to Zone 1. However, during extremely dry periods in 2009 a small gradient developed where groundwater actually flowed from Zone 1 to Zone 3. The implications of these differences in elevations required a more intensive study as to how these elevation changes affected the groundwater movement in this buffer treatment.

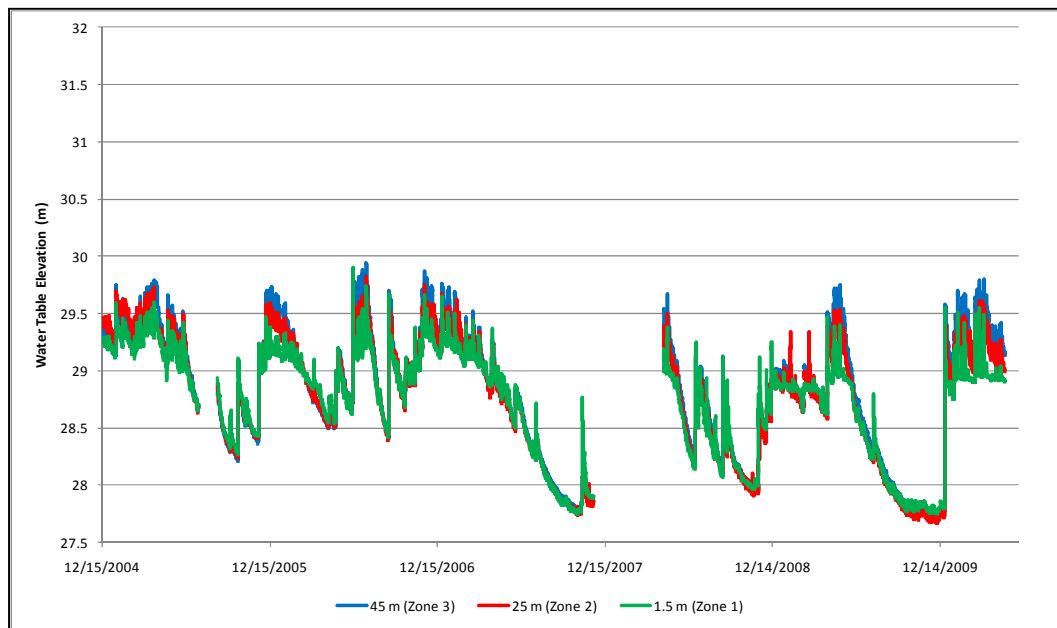


Figure 2. 13: Water table elevations for each zone of the buffer during the study period (December 2004-May 2010).

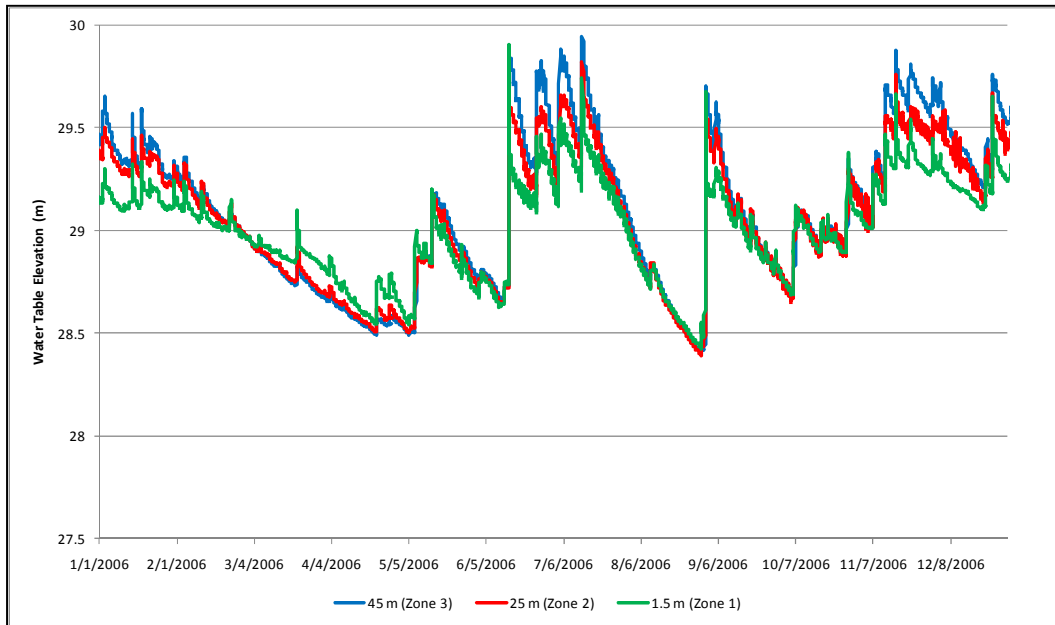


Figure 2. 14: Water table elevations for each zone of the buffer during 2006 (wet year).

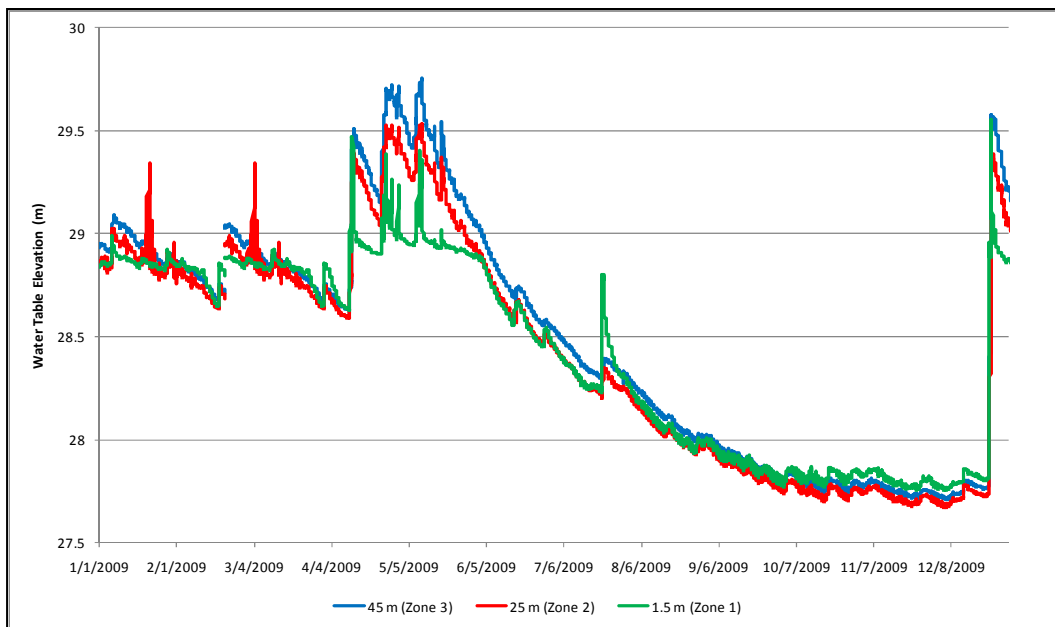


Figure 2. 15: Water table elevations for each zone of the buffer during 2009 (dry year).

The average differences between water table elevations between each zone, were approximately 0.04 m from Zone 3 to Zone 2 and 0.04 m from Zone 2 to Zone 1 throughout the study period, with an overall average difference of 0.08 m through the buffer (Table 2.5). These results supported that groundwater was flowing slowly through the buffer due to the small gradient.

Table 2. 5: Average yearly absolute elevation differences between zones. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Year	Average Absolute Difference (m) (Zone 3 – Zone 2)	Average Absolute Difference (m) (Zone 2 – Zone 1)	Average Absolute Difference (m) (Zone 3 – Zone 1)
2005	0.01	0.09	0.1
2006	0.04	0.05	0.09
2007	0.03	0.00	0.04
2008	0.06	0.01	0.07
2009	0.08	0.04	0.12
Average (m)	0.04	0.04	0.08

Water table gradients from monitored water table elevation readings in surficial groundwater monitoring wells were modeled using mapping software to provide a more detailed study of groundwater movement within the buffer. The models showed that groundwater flow paths did go through the buffer from the adjacent field and that the angle of flow was not always consistent depending on seasonal water table elevations (Figure 2. 16 - Figure 2. 19). The groundwater flowed relatively perpendicular to the buffer during the wettest periods of the study, while during the driest periods the groundwater flowed parallel to the buffer. Groundwater flow

patterns at the research site are displayed for the wettest and driest months, representative of high and low water table elevation periods, in Figure 2. 16 and Figure 2. 17. An evaluation and modeling assessment of each month from August 2008 to May 2010 can be found in Appendix D.

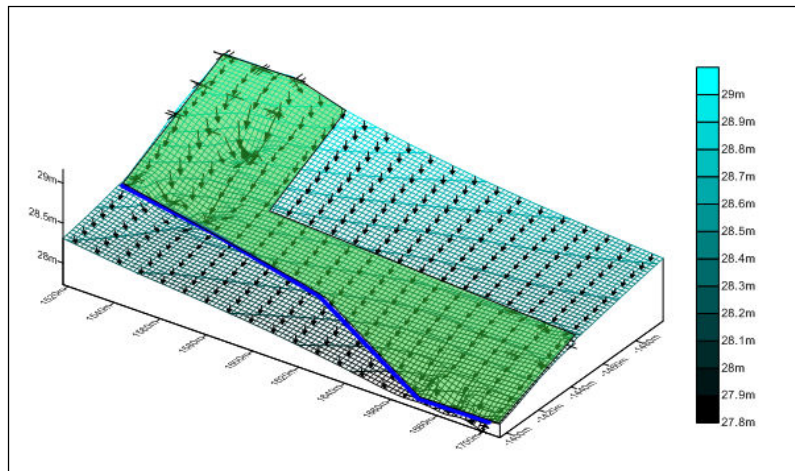


Figure 2. 16: Groundwater flow vectors for April 2009 (wettest period) at the research site. The blue line represents the stream.

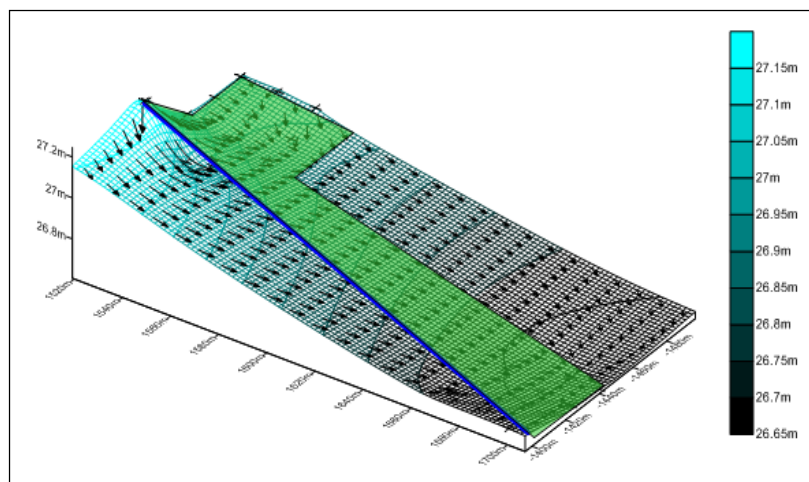


Figure 2. 17: Groundwater flow vectors for November 2009 (driest period) at the research site. The blue line represents the stream.

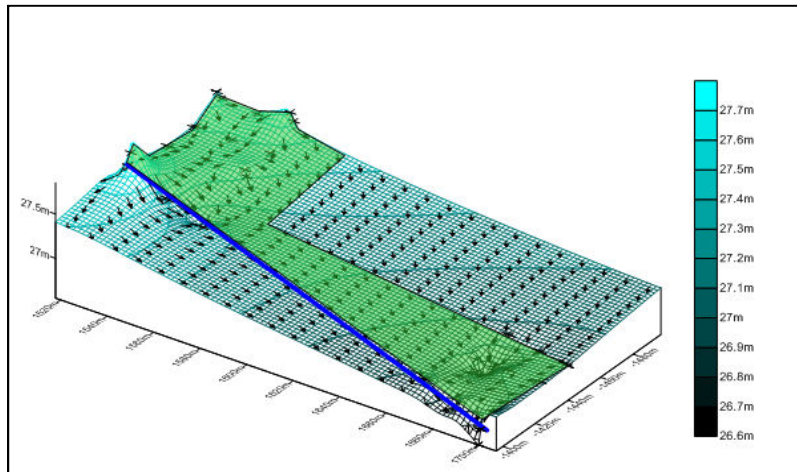


Figure 2. 18: Groundwater flow vectors for July 2009 at the research site. The blue line represents the stream.

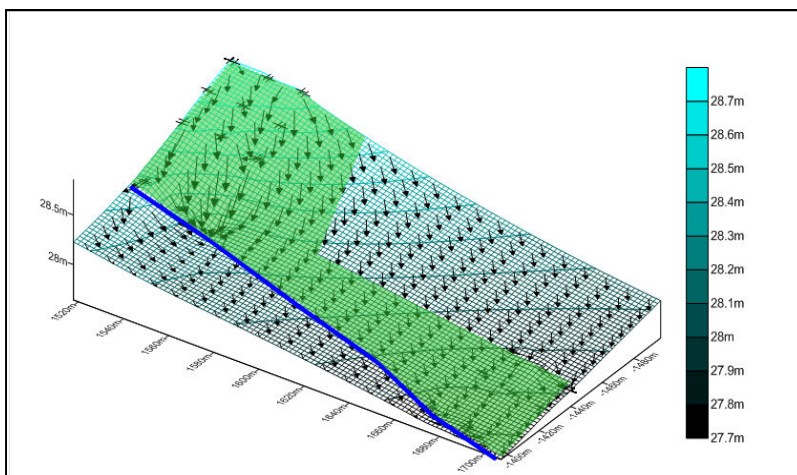


Figure 2. 19: Groundwater flow vectors for January 2009 at the research site. The blue line represents the stream.

The hydraulic gradient was modeled using monthly piezometer readings and a Microsoft Excel 2007 spreadsheet designed by Devlin (2003) beginning in June 2008. Gradients represented water table elevation over distance through the buffer treatment. The gradients through the treatment varied between 0.003-0.010 m/m depending on monthly water table elevations observed in all surficial monitoring wells. Groundwater flow angles estimated using

Devlin (2003) exhibited groundwater direction relative to the stream (parallel to the field) throughout seasonal periods, which were similar to the angles found using the mapping software as seen in Figure 2. 20 - Figure 2. 23.

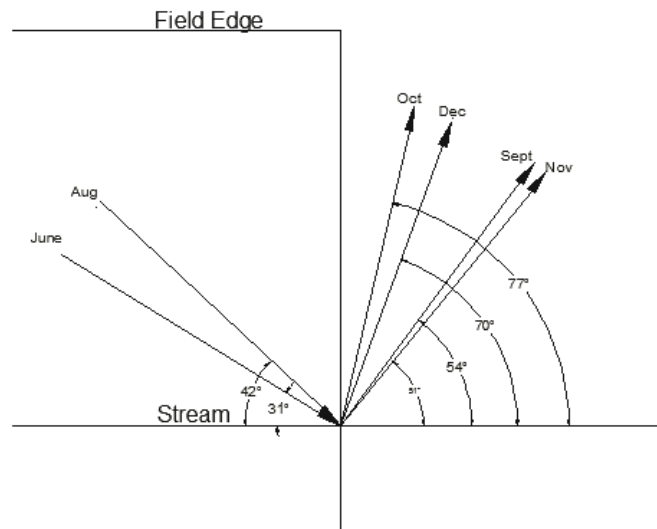


Figure 2. 20: Groundwater flow direction through the buffer relative to the stream for months monitored in 2008.

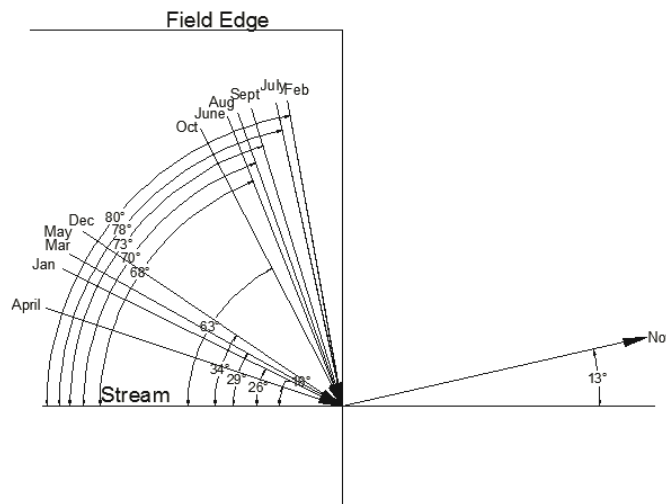


Figure 2. 21: Groundwater flow direction through the buffer relative to the stream for months monitored in 2009.

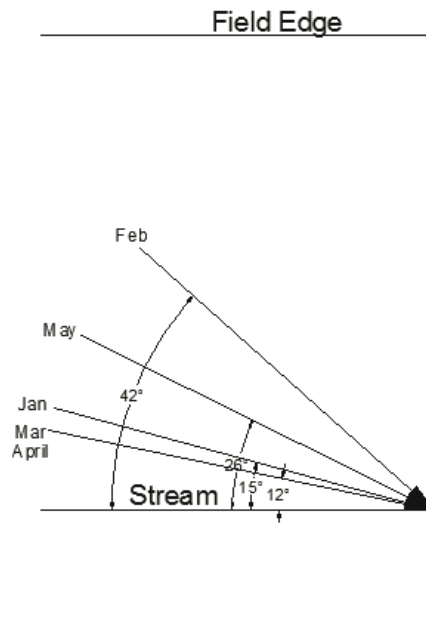


Figure 2. 22: Groundwater flow direction through the buffer relative to the stream for months monitored in 2010.

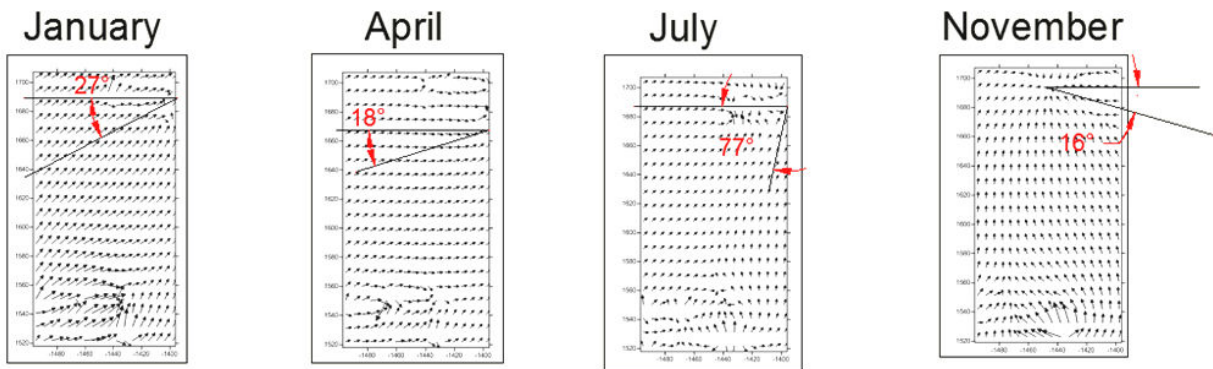


Figure 2. 23: Groundwater angles estimated using Devlin (2003) on contours modeled in Surfer 7 mapping software during 2009 (Golden Software, Golden, CO).

Beech Swamp was located downstream of the buffer zones, parallel to the adjacent field. The data suggests that the groundwater flowed to variable outlet locations depending on water table elevation. Over periods when the water table elevation was closer than 1.5 m below the

soil surface, the groundwater flowed at an angle through the buffer toward a stream discharge area downstream of the buffer. Water table elevations below 1.5 m resulted in groundwater flowing at an angle through the buffer toward Beech Swamp, the lowest topographic elevation in the area. Furthermore, due to the lower topographic location of the buffer location, the contributing groundwater area from the adjacent agricultural field was large (Figure 2. 24 and Figure 2. 25), possibly allowing more concentrated groundwater to easily flow into the system depending on water table elevation gradients.

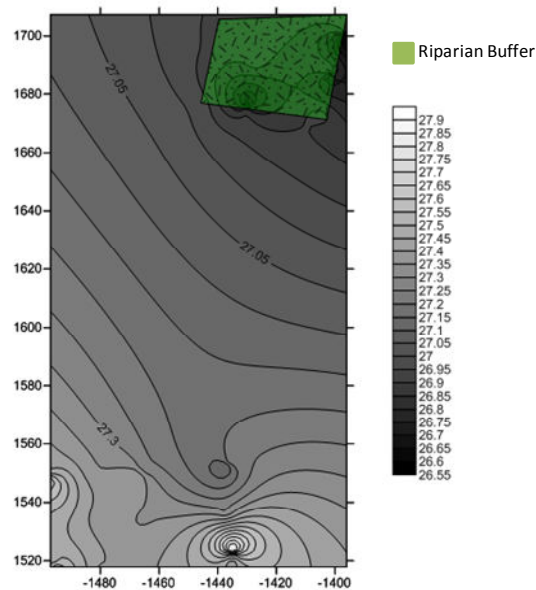


Figure 2. 24: Groundwater contour map of July 2009 (dry period).

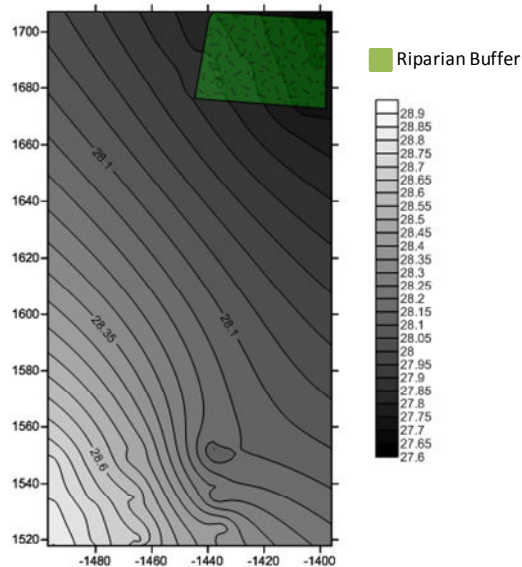


Figure 2. 25: Groundwater contour map of January 2009 (wet period).

Although the groundwater flow direction fluctuated throughout the year, groundwater that was contaminated with NO_3^- -N was continuously within the buffer treatment system, moving slowly in multiple directions throughout the year. Therefore, the determination of how long groundwater resided within the buffer was investigated to determine what residence times within the buffer should be expected at this site.

Saturated Hydraulic Conductivity, Groundwater Velocity, and Residence Time

Soil texture has a major influence on how groundwater passes through riparian buffers. Therefore, a particle size analysis was completed at the depth of the surficial monitoring well screens during equipment installation to identify soil texture at groundwater monitoring depths (1.5 m and 3 m) (Table 2. 6). No major soil texture variations were observed between locations,

although at the 1.5 m depth in Zone 1 the center transect had a higher percentage of silt and a smaller percentage of sand than found in the soil in the upstream transect at the same depth. Variability in the soil between sandy loam and loamy sand was also identified in the soil survey completed at the beginning of the study to determine well depth placement (Figure 2. 5 and Severson, 2004). Therefore, the effective porosity of sand, 0.35, was used as a conservative assumption in calculating travel time (Fangmeier *et al.*, 2006).

Table 2. 6: Particle Size Analysis for Buffer Treatment

Soil ID	Sand	Silt	Clay	USDA	%	%	NRCS Particle Size Model "SPAW Hydrology" hydraulic conductivities (cm/hr)
	%	%	%	Class.	2- 5mm	> 5mm	
1.5 m Depth Center Transect Zone 3	77.3	6.1	16.6	sandy loam	0.0	0.0	3.42
1.5 m Depth Center Transect Zone 2	78.5	7.2	14.3	sandy loam	2.1	0.0	4.21
1.5 m Depth Center Transect Zone 1	65.5	21.3	13.2	sandy loam	15.9	4.6	3.89
1.5 m Depth Upstream Transect Zone 1	78.7	7.5	13.8	sandy loam	17.3	15.9	4.21
3 m Depth Center Transect Zone 3	82.3	8.7	9.0	loamy sand	9.0	1.0	7.02
3 m Depth Center Transect Zone 2	85.4	6.6	8.0	loamy sand	15.1	3.8	7.89
3 m Depth Center Transect Zone 1	79.2	8.8	12.0	sandy loam	9.9	3.7	5.14

The saturated conductivity (K_s) was calculated using the particle size analysis for each zone and the SPAW 6.0 (NRCS, Pullman, CO) modeling program. K_s ranged from 3.4 cm/hr to 4.2 cm/hr at the 1.5 m depth and 5.1 cm/hr to 7.9 cm/hr at the 3 m depth. Groundwater velocities averaged 1.3 cm/day and 2.8 cm/hr at the 1.5 m and 3 m depths. The travel times ranged from 1 to 22 years at the 1.5 m depth with a median of 7 years, while the travel times ranged from 0.45 to 13 years with a median of 4 years at the 3 m depth based on groundwater angle. The 3 m depth was found to have faster moving groundwater due to sandier soil compared to the 1.5 m depth.

Long residence times that allow denitrification to occur are recommended to be greater than 50 years, but denitrification has been found to occur with residence times as small as 1 month (Puckett, 2004; Tesoriero *et al.*, 2005; Dettmann, 2001). The treatment buffer had residence times well within established times for denitrification to occur along with continuous inundated conditions at depths lower than 3 m as discussed in the previous section. Therefore, these conditions would have allowed the riparian zones to provide conditions hydrologically suitable for denitrification to proceed at high rates.

Overall Groundwater Quality NO_3^- -N Results

The hydrology of this buffer appeared very conducive for high groundwater NO_3^- -N removal rates, since Zone 2 appeared to have jurisdictional wetland hydrology and groundwater flowed through the buffer most of the year. NO_3^- -N concentrations from groundwater sampling

in the buffers shallow (1.5 m depth) and deep (3 m depth) surficial wells are shown in Figure 2. 26, Figure 2. 27, and Figure 2. 28. Groundwater mean nitrate levels at the 1.5 m depth from Zone 3 to Zone 1 were 12.9 ± 1.3 mg/L to 1.4 ± 1.3 mg/l respectively, or 89% reduction in the shallow groundwater NO_3^- -N concentration through the buffer. Mean nitrate levels from Zone 3 to Zone 1 at the 3 m depth were 12.8 ± 1.3 mg/L to 6.0 ± 1.3 mg/l respectively, or 54% reduction in the deeper groundwater NO_3^- -N concentration through the buffer. Statistical analysis with SAS PROC MIXED ® (Cary, NC) indicated concentrations at both the 1.5 m and 3m depth groundwater in Zone 1 were significantly lower than in Zone 3 ($\alpha=0.05$). Groundwater NO_3^- -N concentrations results can be seen in Figure 2. 28, which also displays that although average NO_3^- -N concentrations are similar at the 1.5 m and 3 m depths in Zone 3, NO_3^- -N concentrations are much smaller at the 1.5 m depth than the 3 m in Zone 1. A statistical analysis of the water quality using SAS PROC MIXED ® (Cary, NC) also indicated groundwater NO_3^- -N concentrations in Zone 1 were significantly lower at the 1.5 m depth compared to the 3 m depth in the surficial wells ($\alpha=0.05$).

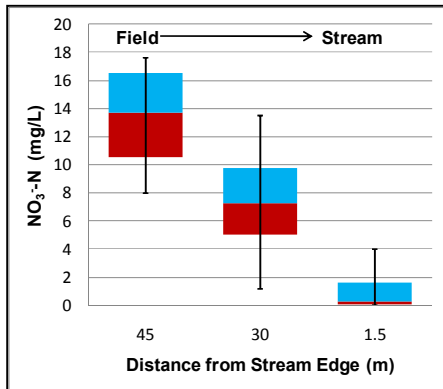


Figure 2.26: The 5%, 25%, median, 75%, and 95% percentiles groundwater NO_3^- -N concentrations over the study for 1.5 m deep surficial wells at differing locations in the riparian buffer (n=165 water quality samples).

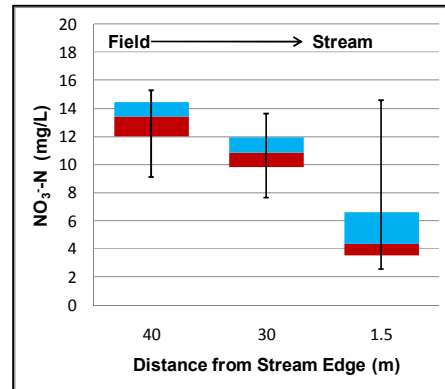


Figure 2.27: The 5%, 25%, median, 75%, and 95% percentiles groundwater NO_3^- -N concentrations over the study for 3 m deep surficial wells at differing locations in the riparian buffer (n=201 water quality samples).

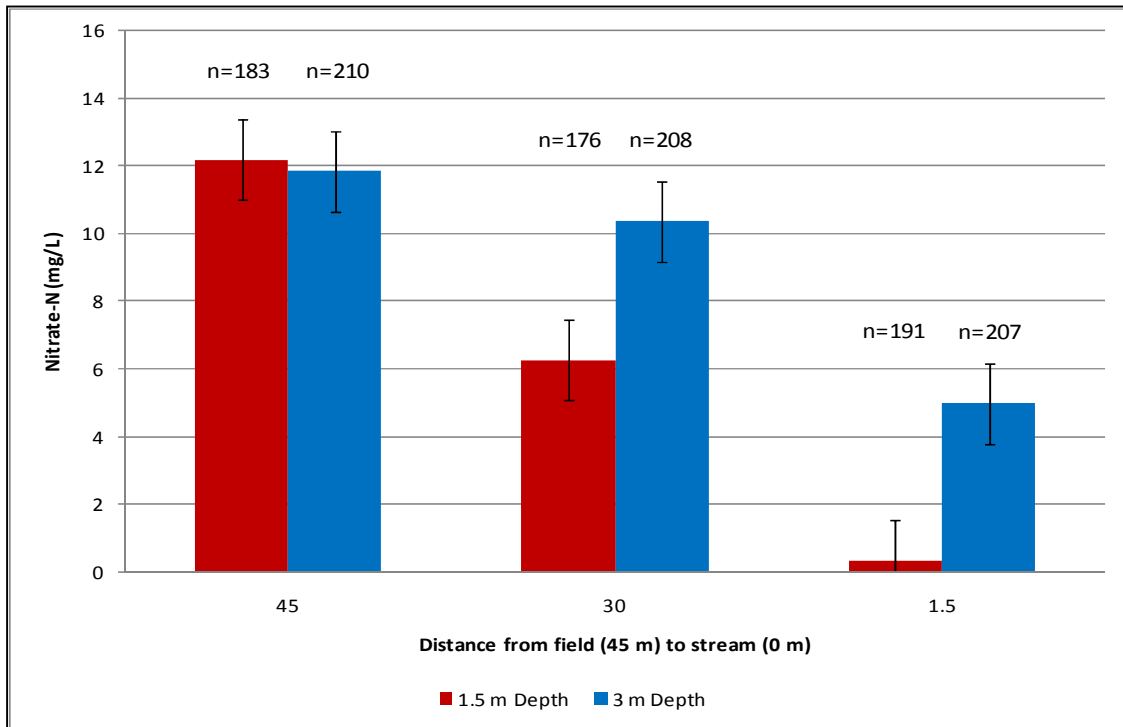


Figure 2.28: Overall mean groundwater NO_3^- -N concentrations at the 1.5 m and 3 m depths ($n_{1.5\text{m}}=550$ and $n_{3\text{m}}=625$ water quality samples). Note – error bars represent standard error.

Beginning in 2007 yearly groundwater NO_3^- -N concentrations at the field edge began to increase and continued to increase throughout the study. This period also began during the 2007-2008 drought during which water tables fell below many shallow groundwater monitoring wells. Although the water table fell during 2007 and never completely recovered before the completion of the study, as the groundwater NO_3^- -N concentrations increased the groundwater NO_3^- -N reduction efficiency also increased. During these periods of deep water table depths, nitrification and mineralization most likely occurred in the soil increasing groundwater NO_3^- -N concentrations and allowing more NO_3^- -N to enter the nitrogen cycle. Additionally higher rates may have been due to lower plant uptake or fertilizer N resulting in more N leaching into the groundwater. Although, these deeper water table depths probably increased groundwater NO_3^- -N concentrations entering the buffer system over the study, groundwater NO_3^- -N concentrations from Zone 3 to Zone 1 decreased to similar and sometimes lower concentrations than observed in previous years (Figure 2. 29). Therefore, the buffer appeared to be reducing entering groundwater NO_3^- -N concentrations efficiently.

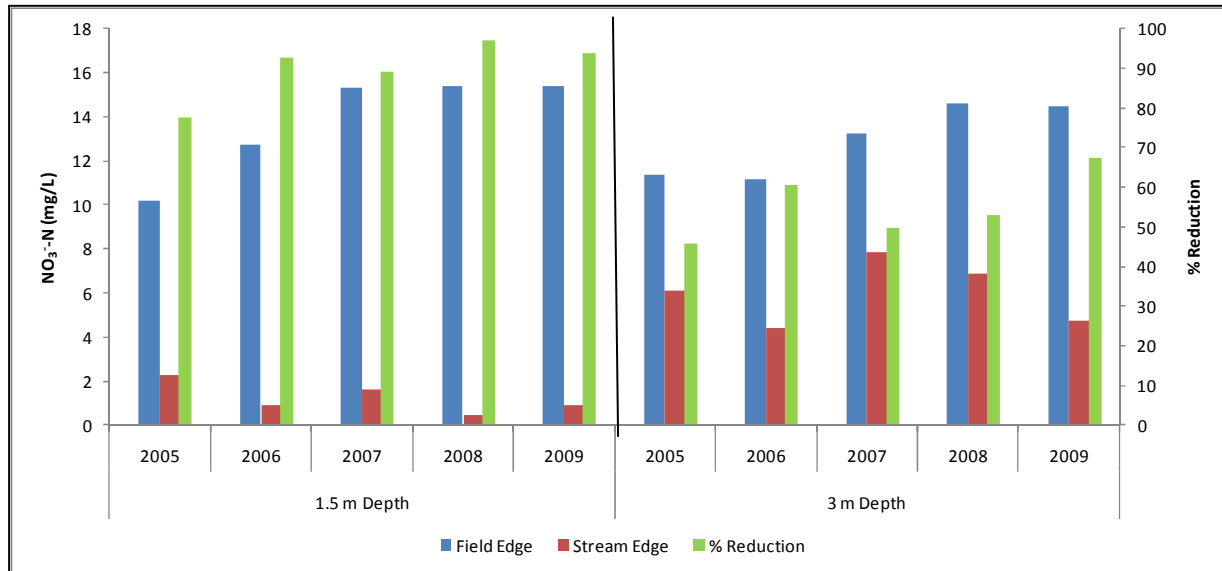


Figure 2. 29: Highest, lowest, and average soil redox readings at the 1.5 and 3 m soil depths at differing distances relative to the stream (June 2005 to April 2010).

Transect and Seasonal NO_3^- -N Trends

A visual evaluation of each transect was used to form a better understanding of the groundwater NO_3^- -N dynamics through the buffer. Limitations of the degrees of freedom in the statistical analysis prevented an overall statistical analysis of each transect. All transects had similar groundwater NO_3^- -N concentrations entering the buffer at the field edge and had a decrease in groundwater NO_3^- -N concentrations from the field edge to the stream at both the 1.5 m and 3 m well depths (Figure 2. 30 and Figure 2. 31). Transect A (downstream transect) and Transect B (center transect) had smaller groundwater NO_3^- -N concentrations at the stream edge than Transect C (upstream transect) at the 1.5 m depth, while Transect B (center transect) and Transect C (upstream transect) had smaller groundwater NO_3^- -N concentrations at the stream edge than Transect A (downstream transect) at the 3 m depth.

The soils heterogeneity seemed to cause these differences observed between transects and well positions. The stream edge 1.5 m depth wells in Transects A and B were found to be located in less sandier soils than Transect C. Therefore, a large portion of the NO_3^- -N laden groundwater could have flowed through the Transect C area and possibly allowed back flow from the stream into the buffer due to the sandier soils. Although Transect A at the 3 m depth had similar soil types to Transects B and C, differences in the tighter overlying soils might have also caused NO_3^- -N concentration differences as well.

Both the 1.5 m and 3 m depth groundwater had NO_3^- -N concentration increases during September to February each year (see Appendix B for application schedules obtained from the landowner). During September to February, vegetation was limited, water table elevations were low, and groundwater occasionally flowed toward Beech Swamp instead of the adjacent stream. All of these possibilities might have affected the concentrations of NO_3^- -N passing within system.

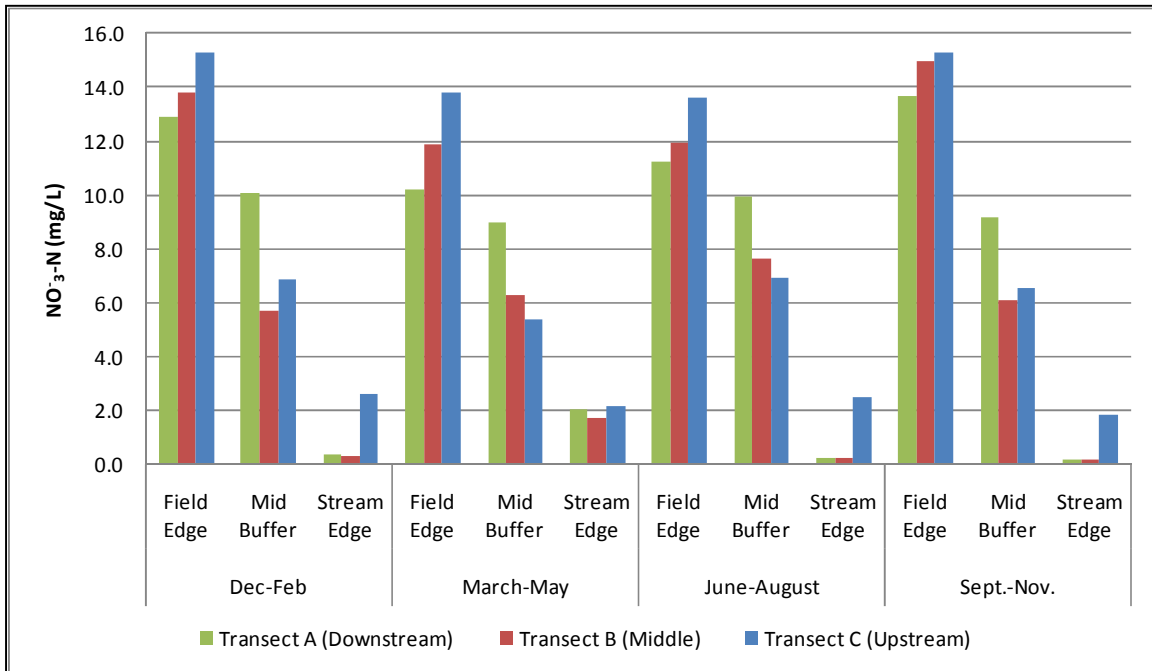


Figure 2. 30: Transect and seasonal NO₃⁻-N evaluation at the 1.5 m depth (n=55 water quality samples)

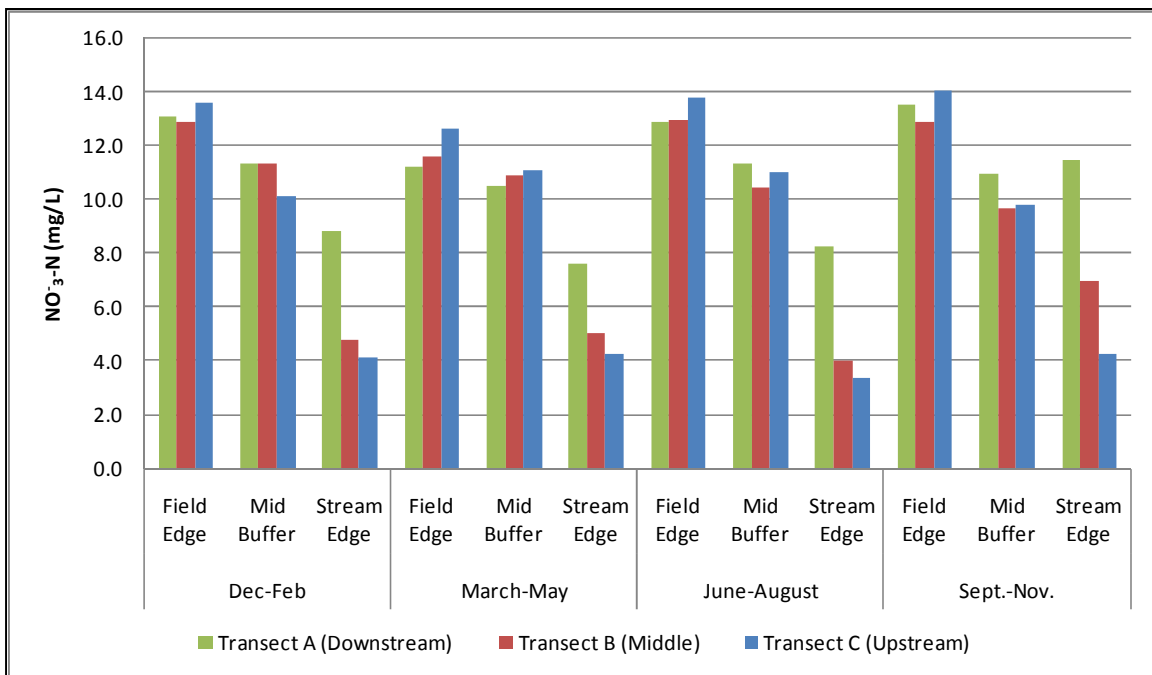


Figure 2. 31: Transect and seasonal NO₃⁻-N evaluation at the 3 m depth (n=65 water quality samples)

NO₃⁻-N Summary

NO₃⁻-N concentrations entering the buffer were high compared to the other nearby buffer locations. This was most likely because the buffer was located at a lower topographic location than both the upland source and the upstream buffer locations and had a larger contributing groundwater area from the adjacent field (Figure 2. 24). At this location the riparian buffer hydrology observations supported that this was a major discharge point for the groundwater originating from the adjacent agricultural field. This resulted in higher concentrations of NO₃⁻-N in the groundwater from a large contributing groundwater area. Therefore, positioning riparian buffers in lower topographic locations not only provides increased opportunities for groundwater to flow into riparian zones from adjacent fields, but more opportunities for higher concentrated groundwater to be treated throughout the year. Based on decreases in concentrations, the NO₃⁻-N treatment efficiency of this buffer appeared to be high, and it was hypothesized that because of the relative wetness of Zone 2, the potential for these reductions to be attributed to denitrification was also high.

Redox Potential

Redox was used to determine denitrification potential in this buffer. Denitrification occurs in soils with low oxidation/reduction (redox) potentials. Reducing conditions have been reported to occur at threshold values ranging between 250-400 mV, with values less than 200 mV being more conducive for denitrification (Patrick, 1960; Bailey and Beauchamp, 1973,

Fielder *et. al*, 2007). Figure 2. 32 displays the overall mean redox potentials recorded for the shallow and deep depths within the upstream transect of the buffer. Mean redox values were almost all below 200 mV indicating overall soil conditions appeared to be favorable for denitrification. The buffer showed a general decrease in redox values from Zone 3 to Zone 1, with the exception of the Zone 2 at the 3 m depth, which at this point remains unexplained. A statistical analysis of the water quality using SAS PROC MIXED ® (Cary, NC) indicated that the 1.5 m and 3 m redox readings were significantly different in Zone 2 and redox readings significantly decreased from Zone 3 to Zone 1 through the buffer at both the 1.5 m and 3 m depths ($\alpha=0.05$).

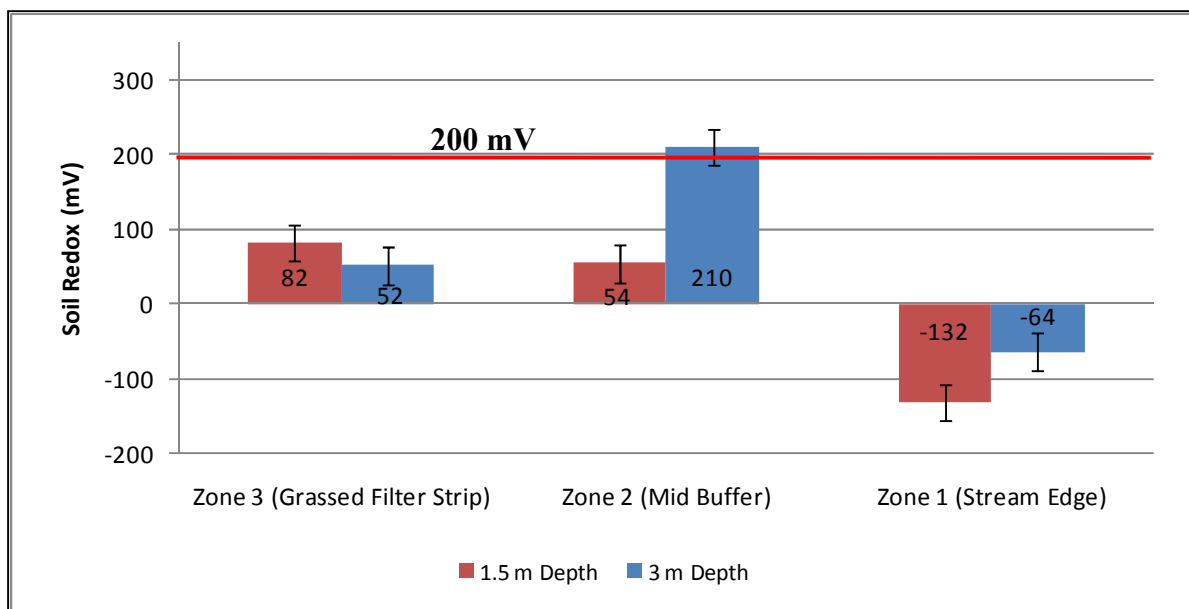


Figure 2. 32: Overall redox reading averages from June 2006 to May 2010. Brackets represent standard error (n=180 samples from each depth and location).

A seasonal analysis was completed to evaluate the combined effects of water table elevation fluctuation and temperatures on redox readings. Redox probes, which were placed equivalent to the depth of the surficial monitoring wells, were below the water table surface during the majority of the year. Overall redox readings decreased from the Zone 3 to Zone 1 throughout the year and were below the threshold indicating possible anoxic conditions in the soil. Despite the fact that Zone 2 was the wettest area (Figure 2. 10), the redox readings were higher and cannot be explained at this time. Regardless of these slight differences in redox readings in the mid-buffer location, the potential for denitrification appeared high throughout the year across the buffer (Figure 2. 33).

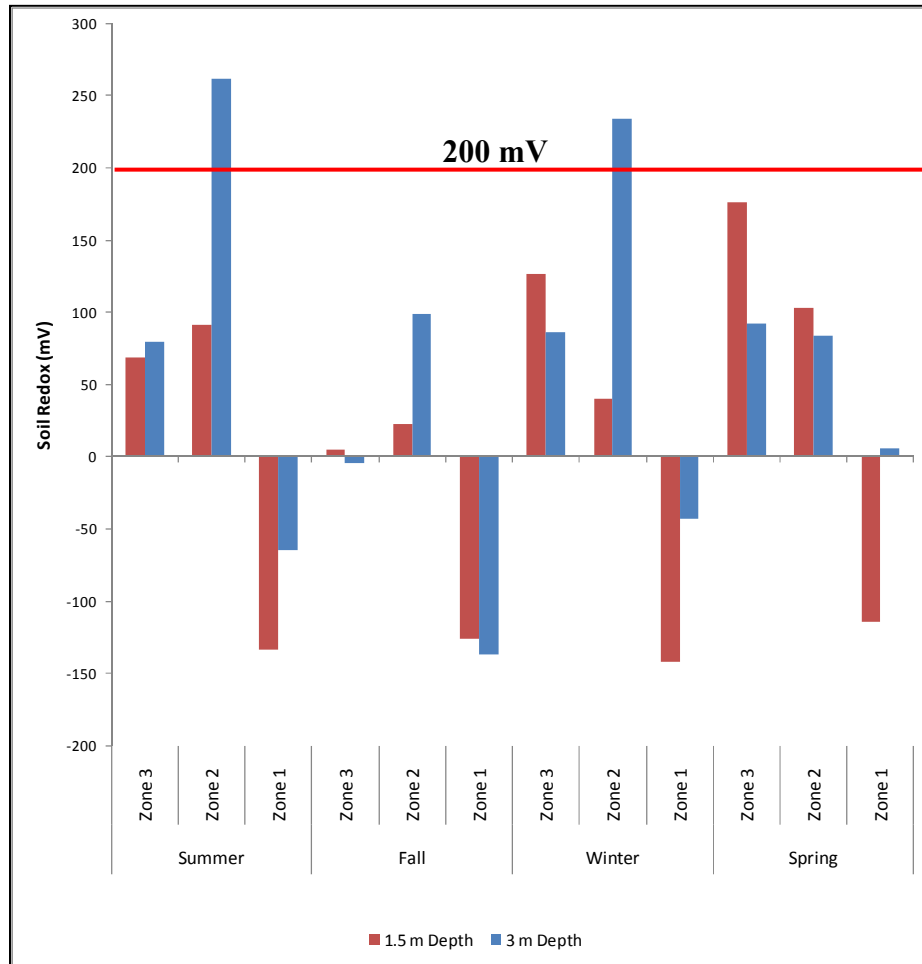


Figure 2. 33: Seasonal evaluation of redox readings in the buffer from Zone 3 to Zone 1 (n=45 during each season).

When NO_3^- -N concentrations and redox potential readings within each zone were plotted, there was no observed relationship due to the high water table elevations and relatively stable soil redox measurements recorded at the site (Figure 2. 34 and Figure 2. 35).

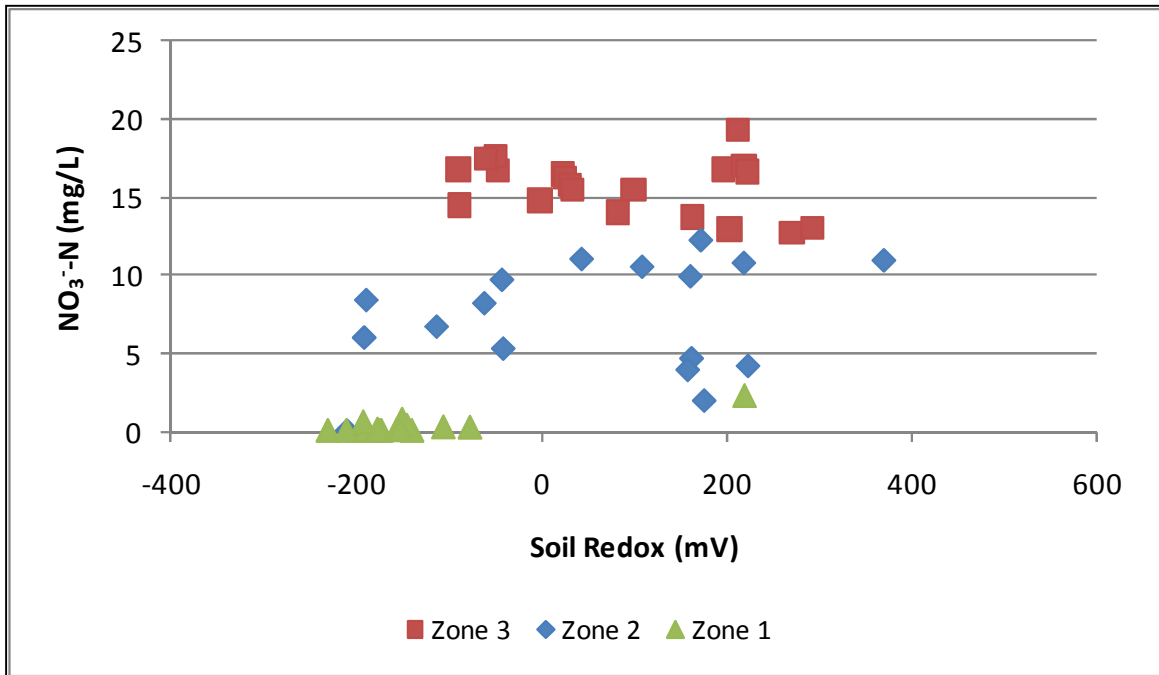


Figure 2. 34: Soil redox compared to NO_3^- -N in center transect at the 1.5 m depth well (June 2005 to April 2010).

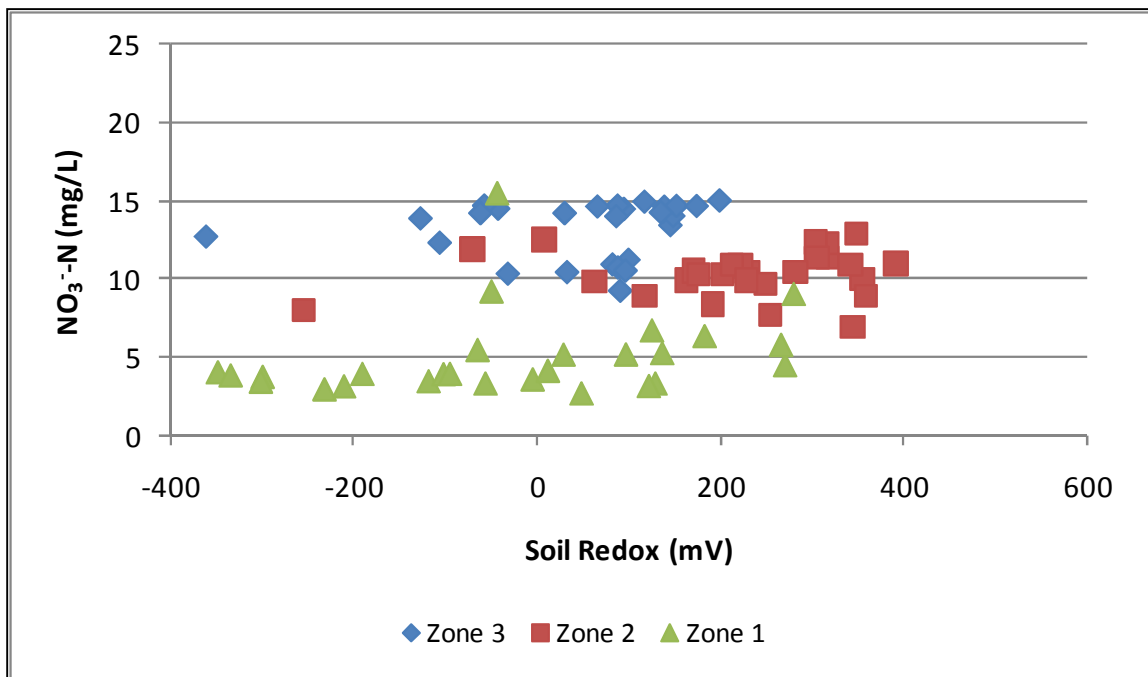


Figure 2. 35: Soil redox compared to NO_3^- -N in center transect at the 3 m depth well (June 2005 to April 2010).

Redox readings had an increasing trend over the course of the study (Figure 2.36-2.38). The trend was most likely due to an extreme drought in 2007-2008, during which the water tables fell dramatically lower than in previously studied years. During the years following the drought, the groundwater hydrology never completely recovered from the drought prior to the end of this study. The highest redox readings, approximately 430 mV (Figure 2. 39), were seen at the stream edge shallow location during the fall of 2008 and 2009 during which the water table elevation fell below the shallow redox probes depths in Zone 2 (mid buffer) and Zone 3 (field edge) (Figure 2.36-2.38). Although, this occurred during the dryer seasons of the year the redox readings were overall low throughout the study, as seen by the averages in Figure 2. 39. Even though the soil redox readings increased over time, the overall yearly average groundwater NO_3^- -N reduction efficiency increased and average redox potential readings remained below the 200 mV threshold with the exception of the Zone 2 at the 3 m depth (Figure 2. 28 and Figure 2.29).

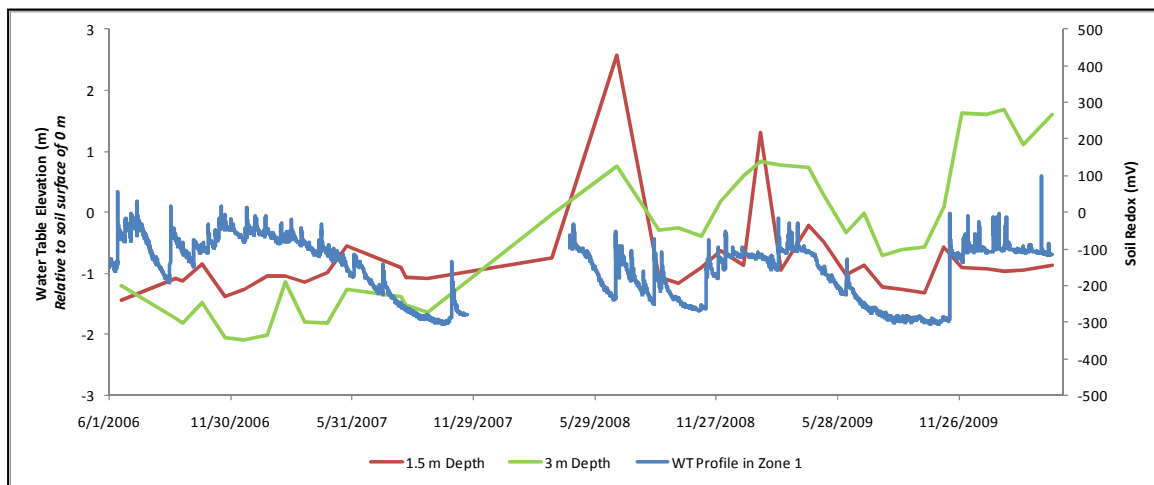


Figure 2. 36: Zone 1 (stream edge) average monthly redox readings with respect to water table elevation at same location (June 2005 to April 2010). Note each redox point is the average of 5 readings.



Figure 2. 37: Zone 2 (mid buffer) average monthly redox readings with respect to water table elevation at same location (June 2005 to April 2010). Note each redox point is the average of 5 readings.

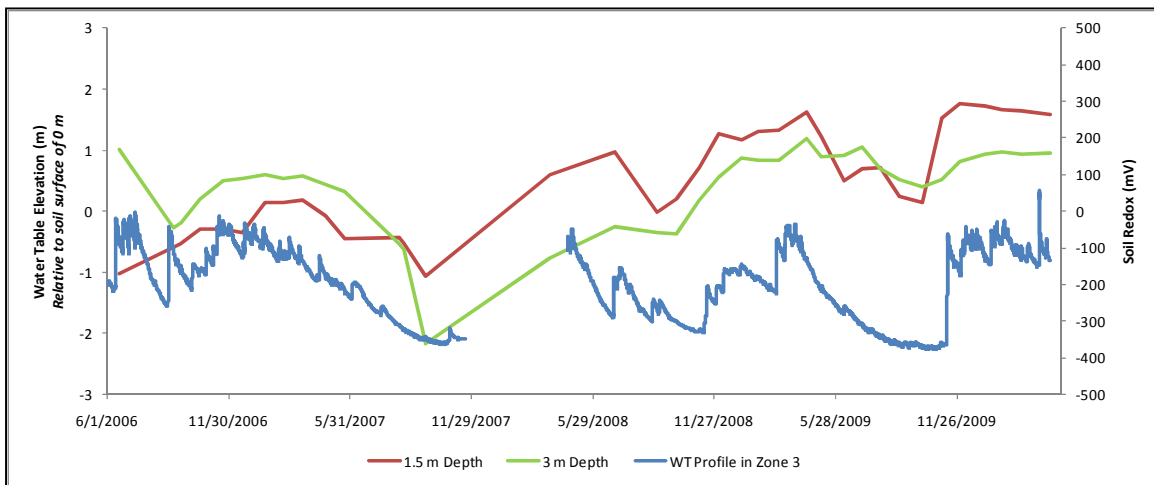


Figure 2. 38: Zone 3 (field edge) average monthly redox readings with respect to water table elevation at same location (June 2005 to April 2010). Note each redox point is the average of 5 readings.

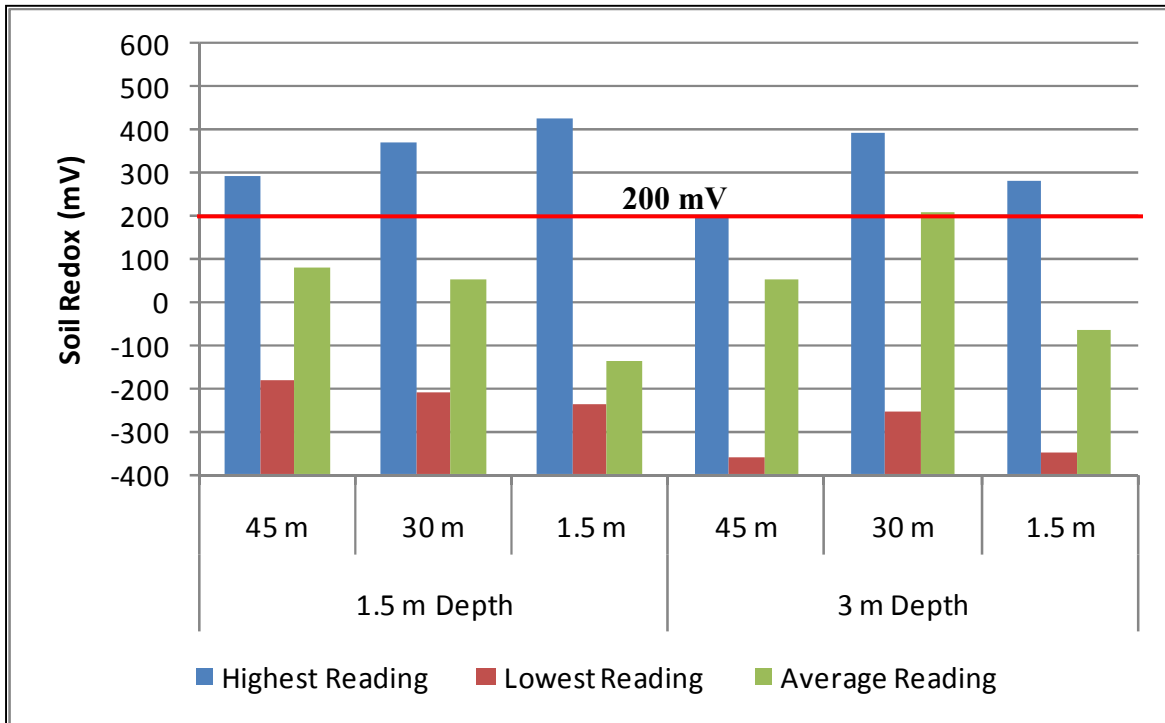


Figure 2. 39: Highest, lowest, and average soil redox readings at the 1.5 and 3 m soil depths at differing distances relative to the stream (June 2005 to April 2010).

Water table elevations were close to the soil surface during the warmest periods and redox measurements during these periods were low. Therefore, it appeared to be ideal conditions for denitrification to occur since microbial activity increases as temperature increases (Knowles, 1982). Carbon source availability can be limiting to the denitrification process depending on vegetation and climatic season due to differences in available litter (Hefting *et. al*, 2005). Since this site had high water table elevations as well as low redox readings throughout the year, available carbon was the final biogeochemical constituent evaluated to support denitrification within this buffer.

Dissolved Organic Carbon (DOC)

A DOC assessment was used to evaluate whether carbon was available in the groundwater to support denitrification. Organic carbon is critical because it serves as an electron donor for microbes during denitrification. Spruill *et. al* (1997) reported in a study completed in eastern North Carolina that water in shallow aquifers with more than 2-3 mg/L of DOC had NO_3^- -N concentrations of less than 2 mg/L, while aquifers with lower DOC had much higher NO_3^- -N concentrations. More recent laboratory studies indicate that DOC concentrations in the 4-8 mg/L range significantly improve denitrification rates (Knies, 2009).

The mean DOC concentrations in the groundwater beneath the buffer at the research site ranged from 2.8-14.5 mg/L. A statistical analysis of the water quality using SAS PROC MIXED[®] (Cary, NC) indicated that the DOC concentrations in Zone 1 were significantly different between the 1.5 m and 3 m well depths ($\alpha=0.05$). Throughout most periods, DOC was higher at the 1.5 m depth than at the 3 m depth. The reduced DOC at the deeper depths may be responsible for the increased groundwater NO_3^- -N concentrations observed at the 3 m depth in Zone 1 (Figure 2. 28 and Figure 2. 29).

The DOC concentrations varied seasonally through the buffer from Zone 3 to Zone 1 (Figure 2. 40 and Figure 2. 41). DOC concentrations were highest in the winter and summer months, while water quality results indicated groundwater NO_3^- -N concentrations to be lowest during the summer at the stream edge (Figure 2. 30 and Figure 2. 31). These values were much higher than the mean DOC samples. High DOC levels along with low redox readings support

that denitrification was not limited during the summer months and was most likely the reason for increased NO_3^- -N reductions within the buffer. DOC samples at the 1.5 m depth were not available during the fall of 2008 or 2009 due to low water table elevations. During these dryer periods higher redox readings were also observed indicating conditions for denitrification were nearer to the threshold values. No additional relationships were observed between groundwater NO_3^- -N concentrations and DOC concentrations most likely due to the DOC concentrations being above 2-3 mg/L throughout the year.

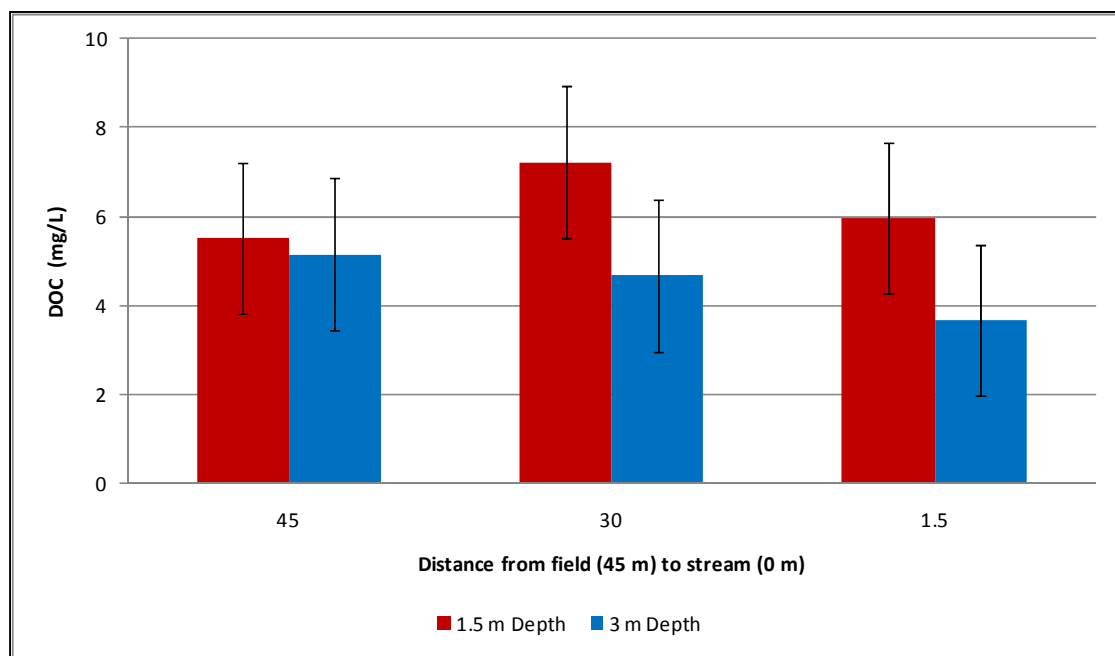


Figure 2. 40: Average DOC concentrations for research site (n=187)

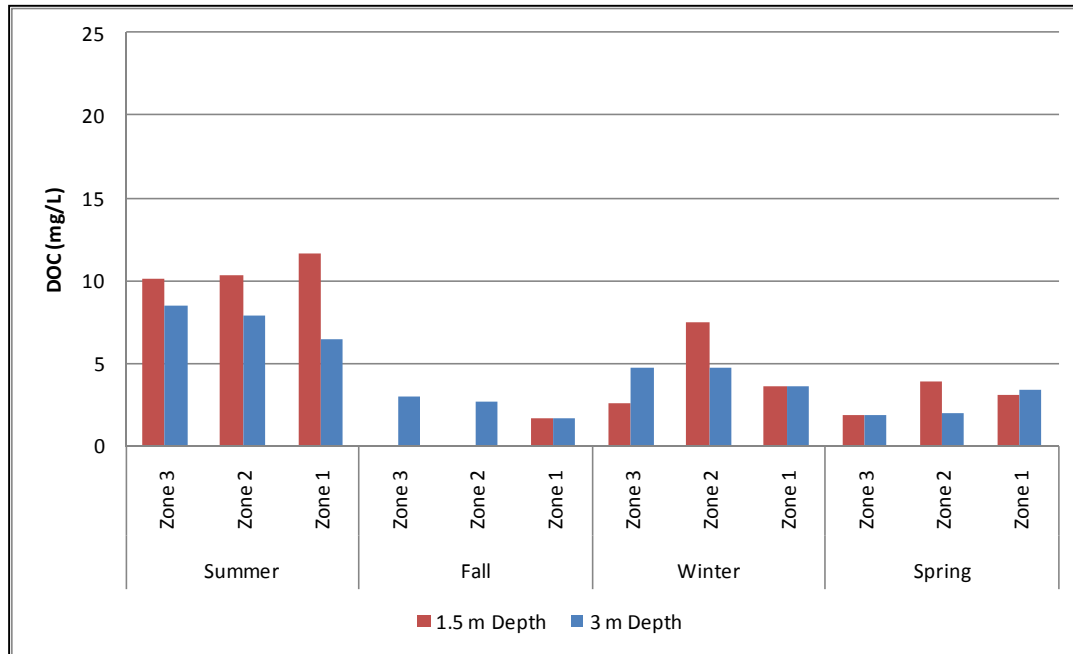


Figure 2. 41: Seasonal evaluation of DOC (n=187) from March 2008-May 2010. Shallow well results for Zone 3 and Zone 2 for fall were unattainable due to low water table elevations at the research site at the time of sampling.

Carbon availability along with low redox readings, high water table elevations, and warm temperatures are the ideal components for denitrification to proceed at high rates. These results support that the buffer had all of the required constituents for denitrification. Although, to confirm that denitrification was the predominant reducing agent the possibility of dilution was investigated.

Denitrification Assessment Using NO_3^- -N to Cl^- Ratios

The evaluation of NO_3^- -N, Cl^- , and NO_3^- -N/ Cl^- ratios in groundwater was used to provide insight as to the process that was responsible for NO_3^- -N differences observed in the riparian buffer treatment (Figure 2. 42 and Figure 2. 43). NO_3^- -N/ Cl^- ratios that decrease through the

buffer is evidence that NO_3^- -N reduction is through biological means, rather than dilution of groundwater with lower concentrations. Mean groundwater NO_3^- -N/ Cl^- ratios from Zone 3 to Zone 1 decreased 84% in the 1.5 m deep groundwater, while mean groundwater NO_3^- -N levels from Zone 3 to Zone 1 decreased by 89%. Mean groundwater NO_3^- -N/ Cl^- ratios from Zone 3 to the Zone 1 dropped 34% in the 3 m groundwater, while mean groundwater NO_3^- -N levels decreased by 54% from Zone 3 to Zone 1. Therefore, mean groundwater NO_3^- -N/ Cl^- ratio percentages were similar at the 1.5 m depth and slightly lower at the 3 m depth compared to the mean groundwater NO_3^- -N concentration reductions found in both the 1.5 m and 3 m surficial wells (Figure 2. 26 and Figure 2. 27). These results alone provide strong evidence that the majority of NO_3^- -N concentration reductions could be attributed to biological activity such as denitrification since the decrease in the groundwater NO_3^- -N/ Cl^- ratios were similar to the decrease in groundwater NO_3^- -N concentrations observed.

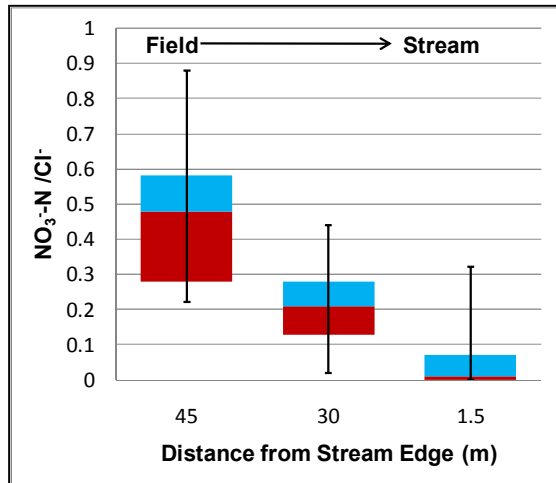


Figure 2. 42. The 5%, 25%, median, 75%, and 95% percentiles of $\text{NO}_3\text{-N}/\text{Cl}^-$ ratio over the study for 1.5 m deep surficial wells at differing locations in the riparian buffer (n=55 water quality samples). Samples were taken from January 2005 – May 2010.

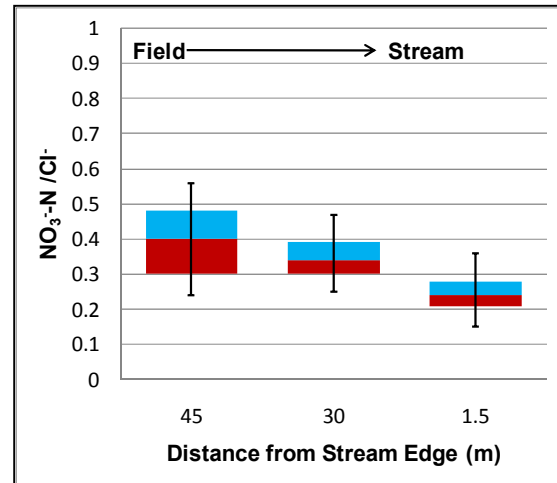


Figure 2. 43. The 5%, 25%, median, 75%, and 95% percentiles of $\text{NO}_3\text{-N}/\text{Cl}^-$ ratio over the study for 3 m deep surficial wells at differing locations in the riparian buffer (n=67 water quality samples). Samples were taken from January 2005 – May 2010.

Realizing that $\text{NO}_3\text{-N}/\text{Cl}^-$ ratios could be influenced by changes in the observed Cl^- concentrations, a more extensive evaluation was completed. Three criteria utilized by Dukes *et al.* (2002) were used in the study to determine the occurrence of groundwater dilution or $\text{NO}_3\text{-N}$ reduction. They included: (1) a decrease in both $\text{NO}_3\text{-N}$ and $\text{NO}_3\text{-N}/\text{Cl}^-$ ratios with an absence of significant changes in Cl^- concentrations indicated that $\text{NO}_3\text{-N}$ was being removed through some other means than groundwater dilution, most likely denitrification below the root zones, (2) a decrease in $\text{NO}_3\text{-N}$ and Cl^- concentrations with relatively constant $\text{NO}_3\text{-N}/\text{Cl}^-$ ratios indicated groundwater dilution from a source below the surficial groundwater, and (3) a decrease in $\text{NO}_3\text{-N}$ concentrations with an increase in Cl^- concentrations resulting in lower $\text{NO}_3\text{-N}/\text{Cl}^-$ ratios was inconclusive for predicting the cause for reduction in $\text{NO}_3\text{-N}$ concentrations within the buffer. A fourth criteria was developed to be used in this study. This criteria was defined as

a decrease in NO_3^- -N concentrations, Cl^- concentrations, and NO_3^- -N/ Cl^- ratios was considered inconclusive for predicting the cause for reduction in NO_3^- -N concentrations within the buffer.

In all four cases, potential dilution was assumed to originate from a deeper groundwater with lower concentrations of NO_3^- -N and Cl^- . Criteria 3 indicated the possibility of groundwater mixing between waters with low NO_3^- -N and high Cl^- concentrations diluting the groundwater NO_3^- -N concentrations, but denitrification could not be ruled out since deeper groundwater was found to have much lower Cl^- concentrations than surficial wells. Likewise, Criteria 4 would lead one to suspect groundwater dilution with decreasing NO_3^- -N and Cl^- concentrations, but due to Cl^- concentrations barely decreasing over the threshold NO_3^- -N/ Cl^- ratios still decreased not allowing denitrification to be ruled out. For this study the threshold for a decrease or increase was defined if a difference existed of more than 10 mg/L in Cl^- concentrations and 0.03 in NO_3^- -N / Cl^- ratios between Zones 3 and 2 and Zones 2 and 1 (Johnson *et. al*, 2007). If differences were smaller than the specified values then concentrations were considered constant between zones during this evaluation.

Evaluation criteria supported means other than dilution (likely denitrification) as the primary mechanism for NO_3^- -N reduction in groundwater moving from Zone 3 to Zone 2 in all 3 m depth and 1.5 m depth areas. The criteria also supported that means other than dilution was responsible for observed NO_3^- -N reduction in one of the six surficial groundwater monitoring areas within Zones 2 and 1 at the 1.5 and 3 m depth (Table 2. 7- Table 2. 12). Dilution of groundwater moving from Zone 2 to Zone 1 could not be ruled out between observation wells

located at 2 of the 3 deep well (3 m depth) areas and 2 of 3 shallow well locations based on Criteria 4. A shallow well location between Zone 2 and Zone 1 was the only location indicating possible groundwater dilution within the buffer treatment (Criteria 2).

Table 2. 7: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for 1.5 m deep wells downstream transect.

*** Constant Cl⁻ concentration between Zone 2 - Zone 1 occurs during March-May.

*** A increase in Cl⁻ concentration between Zone 3 - Zone 2 occurs during Dec.-Feb.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Zone 2	↓	-	↓	Nitrate decrease by other means than dilution
Zone 2 – Zone 1	↓	↓	↓	Inconclusive – possibly groundwater mixing with low Cl ⁻ and NO ₃ ⁻ -N; denitrification cannot be eliminated from these results due to decrease in NO ₃ ⁻ -N/Cl ⁻ ratios

Table 2. 8: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for 1.5 m deep wells center transect.

*** An increase in Cl⁻ concentration between Zone 3 - Zone 2 occurs during Dec. – Feb. and June – Aug.

*** Constant Cl⁻ concentration between Zone 2 - Zone 1 occurs during March-May and Sept.-Nov.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Zone 2	↓	-	↓	Nitrate decrease by other means than dilution
Zone 2 – Zone 1	↓	↓	↓	Inconclusive – possibly groundwater mixing with low Cl ⁻ and NO ₃ ⁻ -N; denitrification cannot be eliminated from these results due to decrease in NO ₃ ⁻ -N/Cl ⁻ ratios.

Table 2. 9: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for 1.5 m deep wells upstream transect.

*** An decrease in NO₃⁻-N/Cl⁻ concentration between Zone 3 – Zone 2 occurs during Sept.-Nov.

*** An increase in Cl⁻ concentrations between Zone 3-Zone 2 occurs during Dec.-Feb.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Zone 2	↓	-	↓	Nitrate decrease by other means than dilution
Zone 2 – Zone 1	↓	↓	-	Groundwater mixing from groundwater with low Cl ⁻ and NO ₃ ⁻ -N concentrations

Table 2. 10: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for 3 m deep wells downstream transect.

***An increase in NO₃⁻-N concentration is constant between Zone 2 – Zone 1 occurs during Sept. – Nov.

***An increase in Cl⁻ concentration is constant between Zone 2 – Zone 1 occurs during Sept. – Nov.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Zone 2	↓	-	↓	Nitrate decrease by other means than dilution
Zone 2 – Zone 1	↓	-	↓	Nitrate decrease by other means than dilution

Table 2. 11: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for 3 m deep wells center transect.

***NO₃⁻-N/Cl⁻ concentration is constant between Zone 2 – Zone 1 during Sept. – Nov.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Zone 2	↓	-	↓	Nitrate decrease by other means than dilution
Zone 2 – Zone 1	↓	↓	↓	Inconclusive – possibly groundwater mixing with low Cl ⁻ and NO ₃ ⁻ -N; denitrification cannot be eliminated from these results due to decrease in NO ₃ ⁻ -N/Cl ⁻ ratios.

Table 2. 12: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for 3 m deep wells in upstream transect.

*** An increase in NO₃⁻-N/Cl⁻ concentration between Zone 3- Zone 2 occurs during June-Aug.

***NO₃⁻-N/Cl⁻ concentration is constant between Zone 2 – Zone 1 during Sept. – Nov.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Zone 2	↓	-	↓	Nitrate decrease by other means than dilution
Zone 2 – Zone 1	↓	↓	↓	Inconclusive – possibly groundwater mixing with low Cl ⁻ and NO ₃ ⁻ -N; denitrification cannot be eliminated from these results due to decrease in NO ₃ ⁻ -N/Cl ⁻ ratios.

It is not apparent why these zones within close proximity to one another would show this variability. The differences that lead to inconclusive results may be explained by soil heterogeneity within the buffer or seasonally variable groundwater flow through the buffer. The

only location indicating possible groundwater dilution was also the location with higher NO_3^- -N concentrations and sandier soils than in other transects. One possible scenario groundwater quality results suggested groundwater dilution could have been due to the sandier soils at this location allowing back flow from the stream to mix with the shallow groundwater. The groundwater and stream water at this location were observed to have similar Cl^- concentrations as well. Seasonal differences were noted in Table 2. 7 - Table 2. 12 and most likely were caused from groundwater direction changes due to fluctuating water table elevations and fertilizer applications.

Utilization of these criteria would be optimal if groundwater Cl^- concentrations remained stable through the buffer. Cl^- concentrations measured within the buffer were significantly different within the buffer at the 1.5 m depth, and ranged from 1.8 to 166.4 mg/L, with averages between 9.0 and 13.0 mg/L dependent on well location and depth ($\alpha=0.05$). The higher concentrations in Cl^- often occurred during the fall and spring months, which may be a result of upland fertilizer applications. Using the groundwater NO_3^- -N/ Cl^- ratio method to determine the primary mechanism for groundwater NO_3^- -N removal was made more complicated due to these variations in Cl^- concentrations.

In summary, groundwater NO_3^- -N along with NO_3^- -N/ Cl^- ratios had similar decreases supporting denitrification was the primary reduction mechanism for groundwater NO_3^- -N reductions. Using Criteria 1-4 described above, groundwater NO_3^- -N/ Cl^- ratios supported that 7 of 12 groundwater monitoring areas had reductions in groundwater NO_3^- -N within the buffer

most likely due to denitrification. Overall, these evaluations support denitrification as the primary reduction mechanism in this buffer. Although these results help in supporting denitrification was the predominant reducing mechanism for groundwater NO_3^- -N reduction, complications due the large range in Cl^- concentrations required further investigations to help determine whether denitrification or dilution was occurring. Therefore, chemical signatures of the surficial and deeper aquifers were examined to identify mixing potential.

Potential Mixing Between Surficial and Deeper Aquifers

Previously, soil borings had indicated a restrictive layer at about 4.6 m (15 ft) below the ground surface that likely separated the surficial and the deeper aquifers. However, the number of deep borings was limited, and was not extensive enough to determine if this layer existed across the entire buffer. Groundwater quality data was compared between surficial and deeper aquifers to identify mixing potential between the two layers to continue the investigation on why groundwater NO_3^- -N loss was observed across the buffer. Na^+ , Ca^{2+} , NO_3^- -N, and Cl^- were the constituents evaluated.

A statistical analysis of the water quality using SAS PROC MIXED ® (Cary, NC) indicated significant chemical differences in NO_3^- -N, Ca^{2+} , and Cl^- concentrations between the surficial and deeper aquifers as shown in Figure 2. 44 - Figure 2. 48 ($\alpha=0.05$). Groundwater in the deeper aquifer (8 and 11 m deep) was much lower in Cl^- and higher in Na^+ than in the surficial aquifer (1.5 and 3 m deep). Figure 2. 44 shows once again how the groundwater NO_3^- -

N concentrations at the 3 m depth were higher than groundwater NO_3^- -N concentrations at the 1.5 m depth, so dilution through upwelling appeared an unlikely major contributor to decreased concentrations at least at the 1.5 m depth (Figure 2. 45).

The difference in groundwater signatures provided strong evidence that mixing was unlikely between waters in the deeper and surficial aquifer. However, the waters in the 1.5 m and 3 m depth did appear to have the same chemistry, since Cl^- , Na^+ , and Ca^{2+} concentrations all appeared similar. Groundwater NO_3^- -N concentrations were the exception – they appeared similar at the field edge Zone 3 only. The concentrations decreased as the groundwater moved through the buffer into Zone 1, while concentrations of the other ions remained within a stable range.

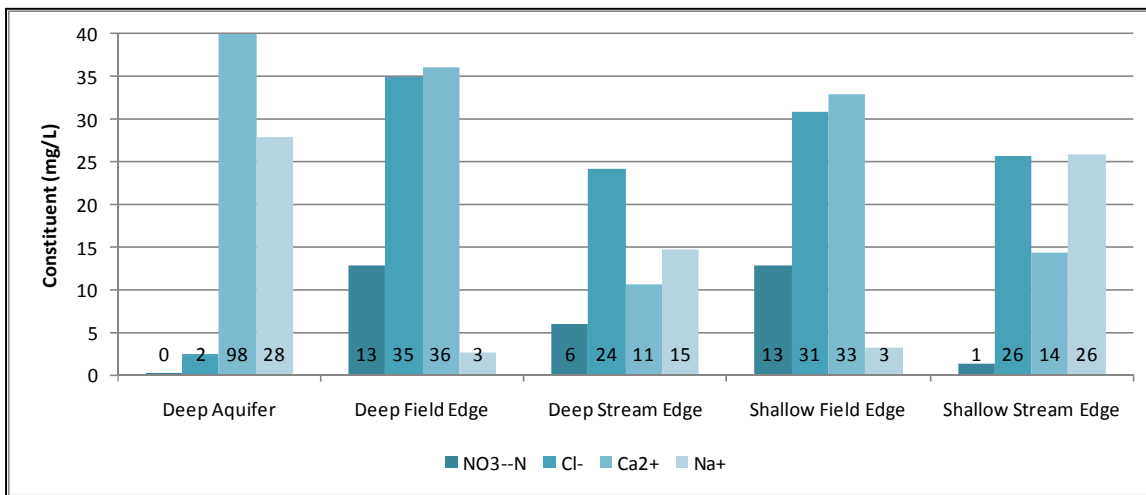


Figure 2. 44: Means of deeper aquifer compared to means of 1.5 m and 3 m depth water quality constituents at the stream and field edge of the riparian buffer treatment system (n values for the 1.5 m, 3 m, 8 m, and 11 m depths were 89, 120, 60, and 20 respectively for NO_3^- -N and chloride; n values for the 1.5 m, 3 m, 8 m, and 11 m depths were 68, 95, 60, and 20 respectively for calcium and sodium). Make note that the calcium quantity in the deep aquifer was cut off for viewing purposes.

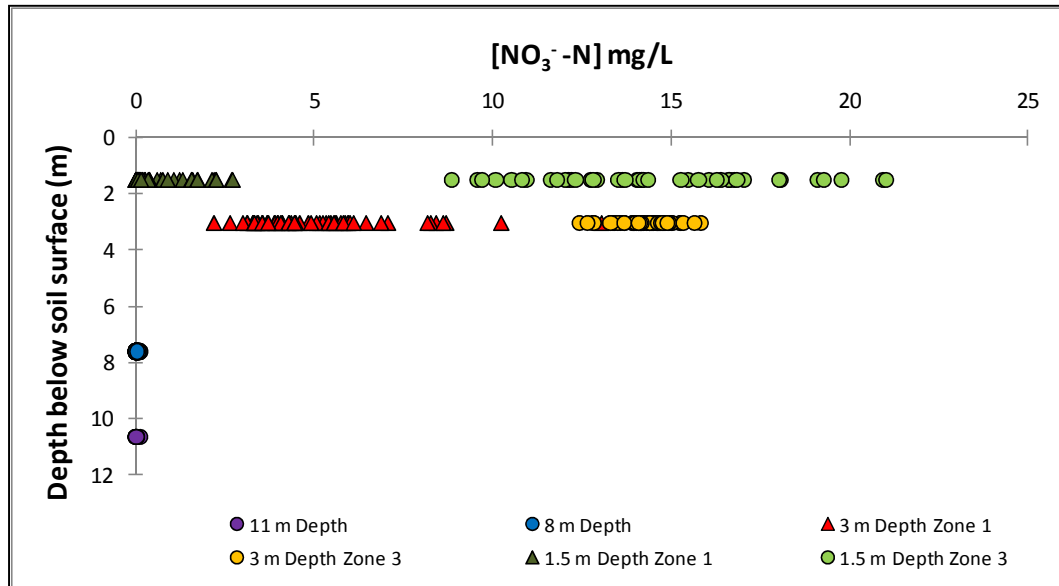


Figure 2. 45: NO_3^- -N concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 89, 120, 60, and 20 respectively.

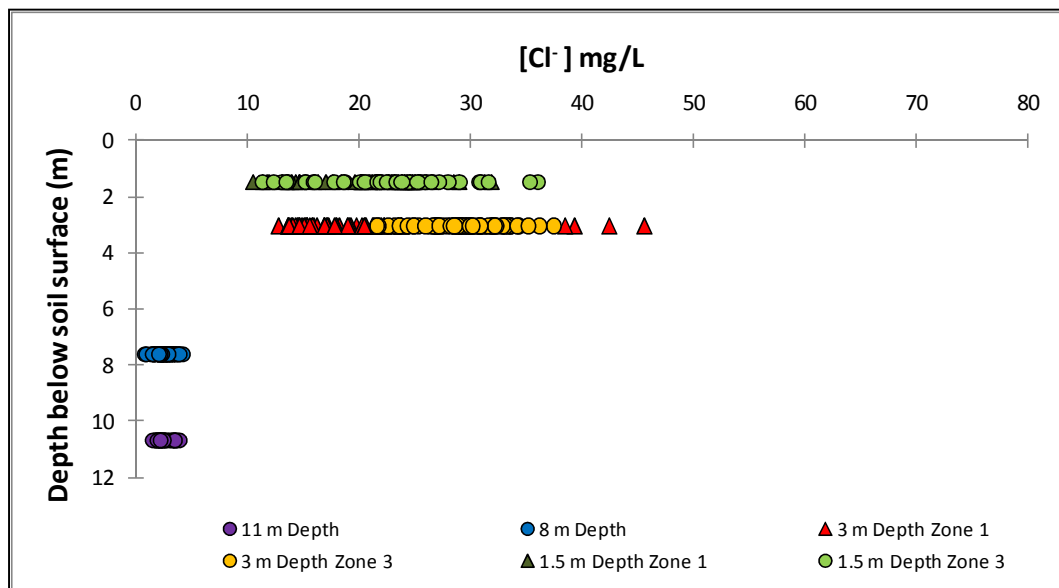


Figure 2. 46: Chloride concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 89, 120, 60, and 20 respectively.

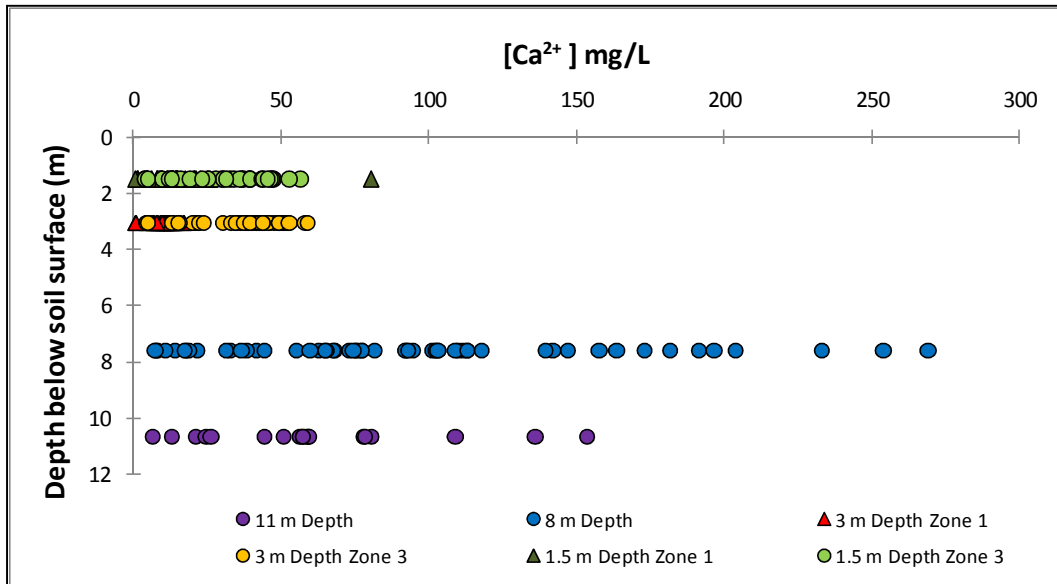


Figure 2. 47: Calcium concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 68, 95, 60, and 20 respectively.

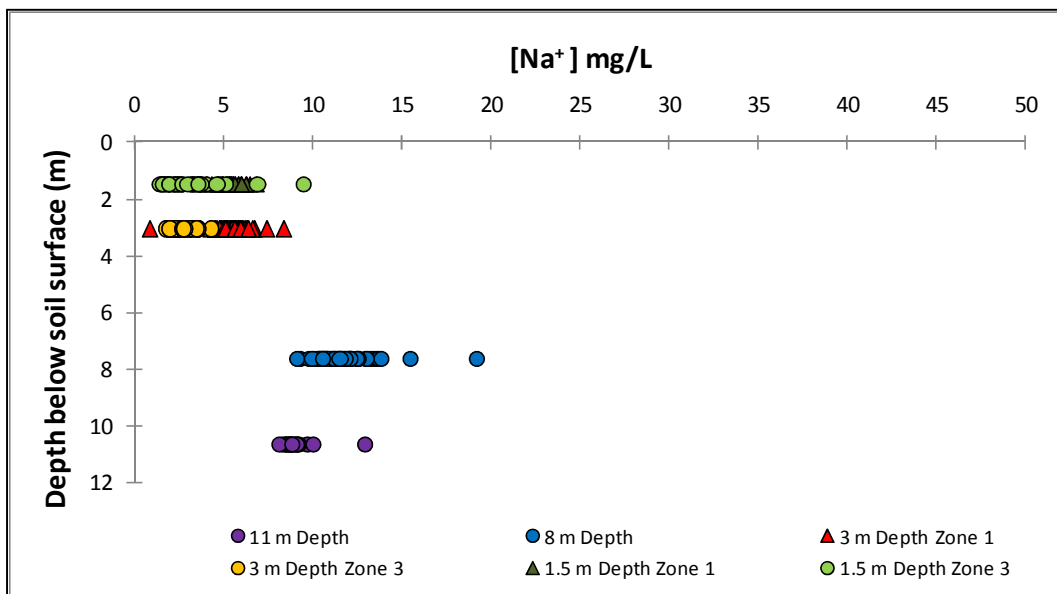


Figure 2. 48: Sodium concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 62, 89, 60, and 20 respectively.

Additional evidence of these waters being separated can be seen in the paired bivariate plots (Figure 2. 49 and Figure 2. 50). The comparison of NO_3^- -N to Ca^{2+} and Na^+ concentrations display that as NO_3^- -N concentrations are decreased through the buffer, the Ca^{2+} and Na^+ remained reasonably constant at both the field edge and stream edge in the surficial aquifer. Calcium concentrations were significantly different between the deeper and surficial aquifers, while the Na^+ concentrations were similar at both the deeper and surficial aquifers and were inconclusive. If dilution due to mixing of groundwater was the predominant reducing mechanism within the riparian buffer system, the Ca^{2+} would have likely increased as approaching the stream. Since the Ca^{2+} remained constant at both the 1.5 m and 3 m depths, dilution appears minimal from these results.

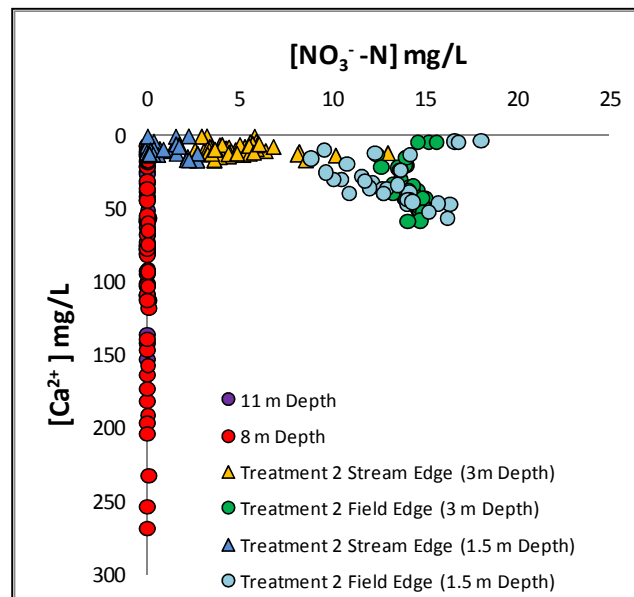


Figure 2. 49: NO_3^- -N concentrations compared to calcium concentrations. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 62, 89, 60, and 20 respectively.

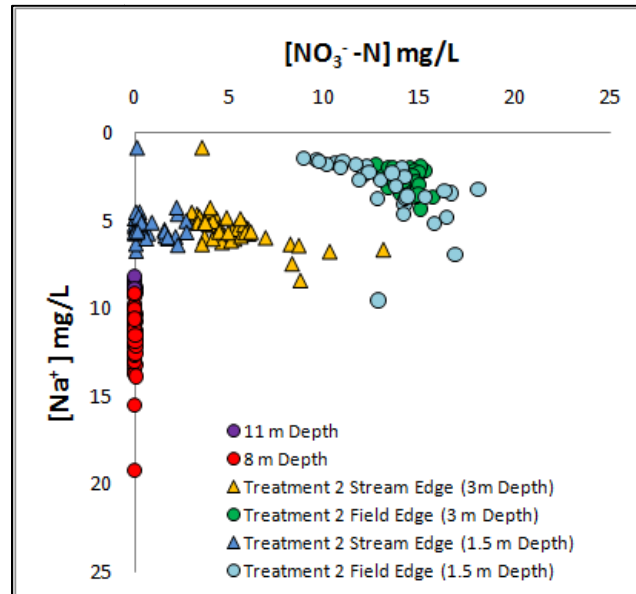


Figure 2. 50: NO₃⁻-N concentrations compared to sodium concentrations. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 62, 89, 60, and 20 respectively.

All water quality observations between the surficial and deeper aquifers supported that the water qualities were ultimately separated. Therefore, groundwater signature observations supported our hypothesis that biological activity, presumably denitrification, was the primary mechanism for groundwater NO₃⁻-N reduction in this buffer, especially at shallower depths. The hydrology assessment, soil redox, and groundwater DOC measurements discussed in the previous sections also supported this hypothesis ultimately supporting that denitrification as the primary groundwater NO₃⁻-N reducing mechanism in this buffer treatment system.

NO₃⁻-N Removal Evaluation through Riparian System

The overall measured NO₃⁻-N mass removal at the 1.5 m and 3 m water quality monitoring depths was calculated using Darcy's Law and the Dupuit-Forchheimer equation to

determine the mass of groundwater NO_3^- -N discharged each year to the stream on a per area basis. Nitrogen was applied to the upland fields at agronomic rates as shown in Table 1 in Appendix E. The total removed groundwater NO_3^- -N mass estimations through Zones 3 through 1 were calculated and can be found in Table 2.13.

Table 2. 13: NO_3^- -N removal per year for varying depths and zones of the studied riparian buffer treatment system.

Depth (cm)	90 cm Soil Layer	240 cm Soil Layer	Total
Total NO_3^--N Removed in Buffer Treatment System (kg N yr⁻¹)	75	150	225
Total NO_3^--N Removed in Buffer Treatment System (kg N yr⁻¹ m²)	0.02	0.04	0.06

Groundwater monitoring water quality samples and Darcy's Law were used to determine the approximate amount of groundwater NO_3^- -N that was removed in the buffer per year at the soil layers at the 90 cm and 240 cm depths (Table 2.13). Groundwater NO_3^- -N entering Zone 3 of the buffer was 80 kg N yr⁻¹ and 176 kg N yr⁻¹ for the 90 to 150 cm and 240 to 300 cm depths, respectively. NO_3^- -N leaving the buffer and discharging into the stream was 5 kg N yr⁻¹ and 25 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. Therefore, the buffer treatment was reducing groundwater NO_3^- -N by 0.02 kg N yr⁻¹ m⁻² (94%) and 0.04 kg N yr⁻¹ m⁻² (86%) for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. These results were similar compared to results that Nelson *et al.* (1995) reported with removal rates of approximately 120 kg N ha⁻¹ yr⁻¹ (0.012 kg N yr⁻¹ m⁻²). Although, the higher removal rates at the

3 m seemed suspicious, the layer had much higher hydraulic conductivities, which allowed more NO_3^- -N to flow through the zones. All of these results indicate the buffer was effectively reducing incoming groundwater NO_3^- -N and removing a substantial amount of NO_3^- -N prior to groundwater entry into the stream.

CONCLUSIONS

Based on evaluations of the hydrology and groundwater quality of this buffer, it appears to be in an ideal landscape position to maximize groundwater NO_3^- -N removal through denitrification. At the 1.5 m depth, mean groundwater NO_3^- -N levels decreased by 89% from Zone 3 to Zone 1 while at the 3 m depth, this decrease was 54%. Hydrologic evaluations supported that NO_3^- -N laden groundwater from the adjacent field was flowing into the riparian buffer the majority of the year due to the topographic location of the buffer. Water table elevations were high (within 3 m of the soil surface) throughout the year, with Zone 2 exhibiting jurisdictional wetland hydrology.

Redox readings were below 200 mV during most of the year indicating reduced conditions critical for denitrification. DOC concentrations during the summer were adequate for denitrification to occur within the monitored surficial soil depths. However, lower DOC concentrations at the 3 m depth may have led to higher groundwater NO_3^- -N concentrations at this depth in Zone 1 throughout the year. Results from water quality data support denitrification the primary NO_3^- -N reduction mechanism. Groundwater NO_3^- -N and NO_3^- -N/ Cl^- ratios had similar decreases from Zone 3 to Zone 1 and NO_3^- -N/ Cl^- ratios indicated that 7 of 12 groundwater monitoring areas had reductions in groundwater NO_3^- -N within the buffer most likely due to denitrification. Dilution was found to be minimal in the surficial and deeper aquifer water quality assessment, with the two waters being found to have significantly different water quality signatures.

Nitrate-N leaving the buffer and discharging into the stream was 5 kg N yr⁻¹ and 25 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively indicating the buffer was reducing NO₃⁻-N by a magnitude of 94% and 86% at the 90 to 150 cm and 240 to 300 cm depths, respectively.

Variable NO₃⁻-N laden groundwater delivery through the buffer could have reduced denitrification efficiency in the system if the riparian buffer did not have high water tables and groundwater flow toward the stream majority of year. High water tables and groundwater flowing toward the stream most of the year likely enhanced denitrification allowing groundwater NO₃⁻-N to reach denitrifying microsites. During dryer periods of the year the change in groundwater flow along with lower water tables elevations reduced these opportunities for NO₃⁻-N laden groundwater to reach these critical microsites. However, groundwater was still flowing through the buffer and likely receiving some treatment. Overall, the water table was relatively close to the soil surface and flowed through the buffer majority of the year making the buffer treatment mostly ideal for enhancing groundwater NO₃⁻-N reduction through denitrification in this system.

High water table elevations along with groundwater NO₃⁻-N concentration reductions, low redox readings, and suitable DOC concentrations during warmer seasons all lead to ideal soil environments for denitrification to occur. To maximize the groundwater NO₃⁻-N removal impact of buffers, conservation programs should enroll lands in landscape positions similar to what is found at this research site since these areas provide more of the required components for high

rates of denitrification (water table depths close to the soil surface, groundwater flow through the buffer majority of the year, high concentrations of groundwater NO_3^- -N entering Zone 3 due to large contributing groundwater area, low redox measurements during warm periods, and high DOC concentrations).

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CHAPTER 3: EFFECTIVENESS OF NITRATE REDUCTION IN A 60 METER RIPARIAN BUFFER: A HYDOLOGIC AND BIOGEOCHEMICAL EVALUATION

ABSTRACT

Maximizing stream miles protected by riparian buffers in conservation programs requires defining ideal landscape and soil conditions for placement of buffers to overall improve downstream water quality in sensitive streams and estuaries. A five year study on the nitrate reduction efficiency of a riparian buffer enrolled in the North Carolina Reserve Enhancement Program (NC CREP) has been evaluated. The studied buffer width was 60 m. Surficial groundwater monitoring well nests were installed in three transects within the buffer, with each well nest containing a shallow (1.5-2.3 m) and deep (2.7-3.6 m) well. Additional wells were installed to measure the quality of water in the deeper aquifer to examine interaction with the surficial groundwater. Upslope agricultural practices have included soybeans, peanuts, cotton and corn production.

Nitrate concentrations decreased through the buffer from Zone 3 (grassed filter strip) to Zone 1 (stream edge) with average concentrations changing from 4.5 to 1.7 mg/l and 2.9 to 2.5

mg/l for shallow and deep wells respectively. Denitrification or groundwater dilution were determined as the primary mechanism for these decreases using water table measurements, nitrate to chloride ratios, deep aquifer water quality analyses, topography, redox measurements, and dissolved organic carbon (DOC). The mass removal per year was also calculated to determine the overall impact of the riparian buffer. Results indicated that denitrification was the primary mechanism contributing to nitrate reductions in the system. However, the topographic location of the buffer made the system nitrate limited, reducing opportunities for denitrification to treat larger quantities of nitrate laden groundwater. Therefore, a clear understanding of the hydrologic and biogeochemical factors in riparian buffers will lead to design recommendations that will possibly enhance pollutant reduction in these treatment systems.

INTRODUCTION

Over the past 30 years North Carolina, along with other states, has been dealing with major water quality issues due to nonpoint source pollution (NPS). The presence of eutrophic conditions in surface water and associated fish kills have increased concerns of the effects of nutrient loads to the Tar Pamlico and Neuse watersheds of North Carolina (NCDWQ, 2002). Excessive loads of nitrate-nitrogen (NO_3^- -N) have been linked as a major contributor to these eutrophic conditions. Organic and inorganic fertilizer from agricultural production has been identified as a large contributor of NO_3^- -N into water systems (NRDC, 1998; US EPA, 1984).

Riparian buffers are one type of best management practice (BMP) recognized by the State of North Carolina to reduce NO_3^- -N from various pollutant sources, including agricultural practices. Riparian buffers have been defined as a complex assemblage of soil, plants, and organisms immediately adjacent to a water course that may include wetlands, stream banks, and floodplains (Lowrance et. al, 1985; Osmond et. al, 2002). These systems can reduce the effects of nutrients, sediment, organic matter, pesticides, and other pollutants prior to entry into surface water and groundwater recharge areas if designed and implemented accurately.

Riparian buffers have been reported to reduce groundwater NO_3^- -N up to 90% (Peterjohn and Correll, 1984; Lowrance *et al.*, 1984; Lowrance *et al.*, 1985; Lowrance, 1992; Dukes *et al.*, 2002; Hunt *et al.*, 2004). Understanding the hydrology and biogeochemistry of these buffer sites to maximize removal mechanisms and pollutant reduction through ideal buffer placement is the common theme throughout all of these studies.

Nitrate-N can be removed by primarily two mechanisms within riparian buffer systems: biological uptake (i.e. plants and microbial communities) and denitrification (Hubbard and Lowrance, 1997; Peterjohn and Correll, 1984; Mayer *et al.*, 2007). Although both of these mechanisms reduce NO_3^- -N in groundwater, biological uptake allows NO_3^- -N to remain in the buffer system in pools that may be released, while denitrification allows for a complete removal of NO_3^- -N from the system through the microbially mediated transformation of NO_3^- -N to N gas (Woodward *et al.*, 2009).

Extensive research has been conducted over the past 25 years to examine the effectiveness of riparian buffer systems on groundwater NO_3^- -N reduction (Spruill, 2004; Evans *et al.*, 2007; Gilliam, 1994). Buffer removal of NO_3^- -N is variable and riparian buffers do not always work as effectively as desired due to hydrologic and biogeochemical conditions within the treatment (Ocampo *et al.*, 2006; Puckett and Hughes, 2005). Defining if denitrification is responsible for observed NO_3^- -N concentration reductions is often made more complicated due to the possibility of deeper groundwater mixing with and diluting surficial groundwater within the riparian zones (Davis *et al.*, 2007; Gu *et al.*, 2008; Altman and Parizek, 1995).

Although the fundamentals of how buffers work is understood well enough for conservation programs to encourage their use, to maximize their benefit in these programs, research is still needed to identify ideal riparian buffer locations with suitable hydrologic and biogeochemical conditions. Identifying these conditions will maximize denitrification occurrences within these systems.

The North Carolina Conservation Reserve Enhancement Program (NC CREP), a voluntary program that encourages buffers to improve water quality by reducing sediment and nutrient loadings into adjacent water basins (NC CREP, 2008). Landowners receive rental payments based on the soil rental rate calculated by the Farm Service Agency. Along with rental payments, NC CREP provides up to 50 percent of the expenses to establish the conservation practice (NC CREP, 2008). Although riparian buffers have been found to reduce both sediment and nutrient loads, unfortunately not all NC CREP enrollments are placed in ideal locations for treatment to thrive. Therefore, the Division of Soil and Water staff who oversee the NC CREP program are interested in defining ideal buffer sites whose contribution to water quality improvement justifies the cost of land acquisition

A comprehensive evaluation of both the hydrology and attenuation of nitrate in a riparian buffer was completed for NC DENR. The research project's primary objectives were to: conduct a detailed hydrologic evaluation of the site, examine the effects of changes in NO_3^- -N concentrations within the buffer, and evaluate contributions of denitrification and dilution to observed NO_3^- -N reductions. Methods used to measure hydrologic and biogeochemical factors thought to impact riparian buffer efficiency in removing NO_3^- -N through denitrification included: the frequency and duration of the water table elevation near the soil surface, seasonal flow direction, soil redox, and groundwater chemical properties (NO_3^- -N, Cl^- , Ca^{2+} , and Na^+). The project's original intent was a comparative analysis of two adjacent buffer treatments with differing widths. However, due to the placement of the buffer treatments, the receiving sources

from the adjacent field were significantly different ($\alpha=0.05$). Therefore, the performances of the buffers were evaluated individually. Results presented in this chapter outline results of the wider and most upstream buffer system. Results from this project will aid in defining both ideal hydrologic and biogeochemical regimes for denitrification in riparian buffers. Findings will lead to recommendations for maximizing water quality impacts of NC CREP and other conservation programs.

MATERIALS AND METHODS

The following sections highlight the methods utilized to collect data and how data was analyzed with a different buffer section at the same site discussed in Chapter 2. Please refer to the MATERIALS and METHODS sections in Chapter 2 for more detailed information on equipment installation, sampling procedures, and data analyses.

Site Description

Buffer Description

The study site was located on the same farm in Halifax County as discussed in Chapter 2. The buffer was a part of a NC CREP enrollment, but was positioned in an upstream, higher elevated location and had a wider width than the buffer section in Chapter 2 (Figure 3. 1 and Figure 3. 2). The total length of the analyzed buffer was approximately 46 m (150 ft). The buffer had an average width of 60 m (197 ft), with a range of 59 to 61 m (193 to 200 ft). The buffer was planted in 1999 with three rows of *Quercus phellos* (willow oak) and *Quercus spp.* (oak) in Zone 1 (near the stream) and *Pinus taeda* (Loblolly pine) throughout Zone 2 (the mid buffer). Predominant vegetation in Zone 3 (a grassed filter strip) consisted of mainly *Trifolium spp.* (clover).

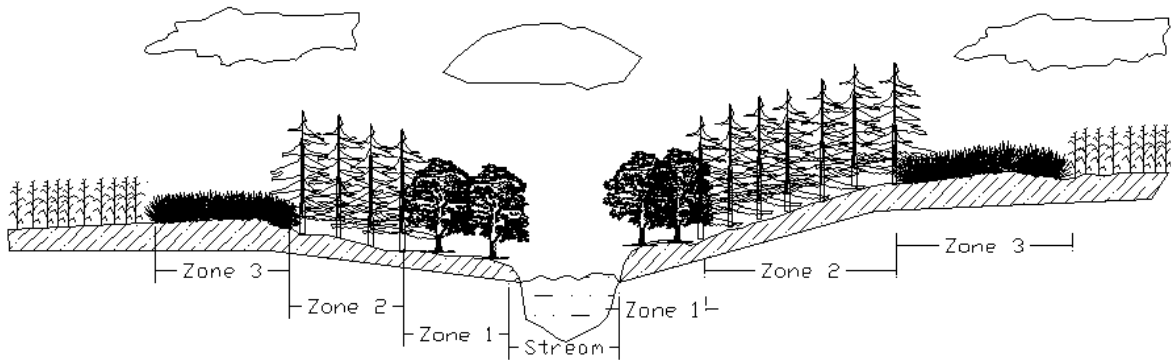


Figure 3. 1: USDA Three Zone Buffer Design – the basis of the design of the buffer studied (adapted from NRCS, 1997).

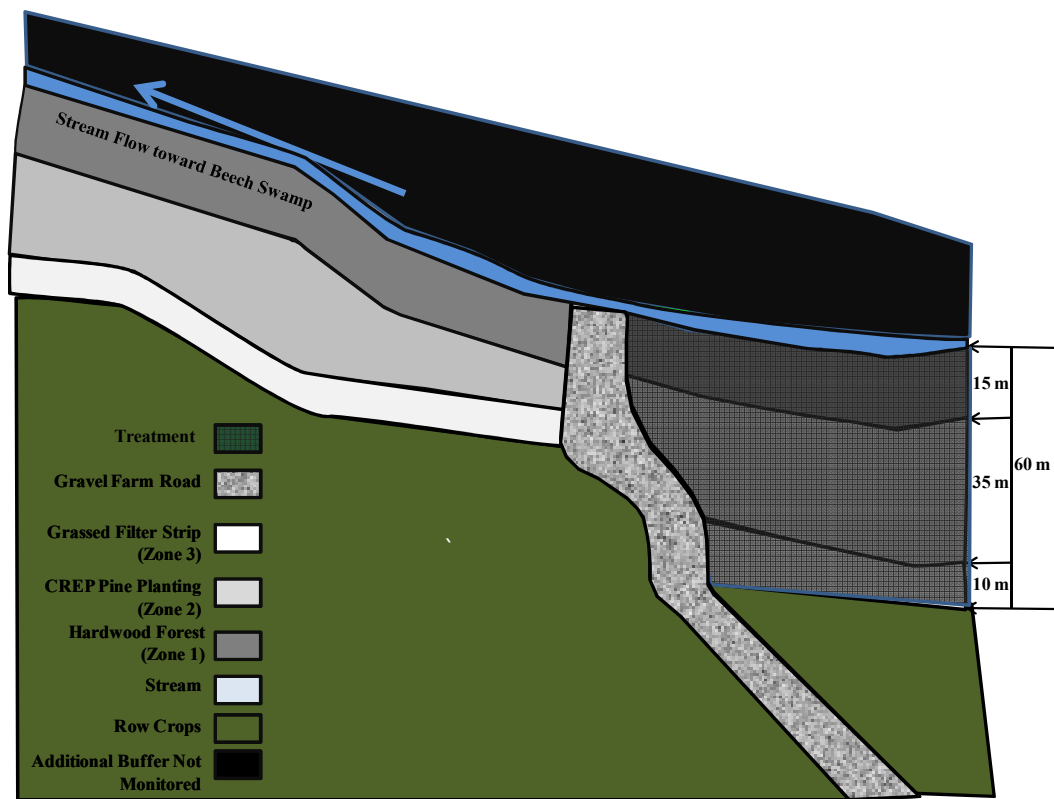


Figure 3. 2: Land cover for research site (Not to Scale).

Site Soils

The NRCS Soil Staff Survey (2006) identifies three dominant soil series at the research site: Marlboro fine sandy loam, Lynchburg fine sandy loam, and Gritney fine sandy loam as seen in Figure 3. 3, Figure 3.4, and Table 3. 1. A soil scientist completed an evaluation of the soil profile during instrument installation in December 2004. The soil assessment also indicated that the field edge soil downstream had layers of loamy sand transitioning to as shallow clay layer at approximately 0.8 m (33 in) below the soil surface similar to Gritney (Figure 3.4). At 4.6 m (15 ft) below the soil surface a marine clay restrictive layer was identified that was believed to be sufficient in separating surficial and deeper aquifer groundwater. A more complete analysis of the field observations can be found in Appendix B.

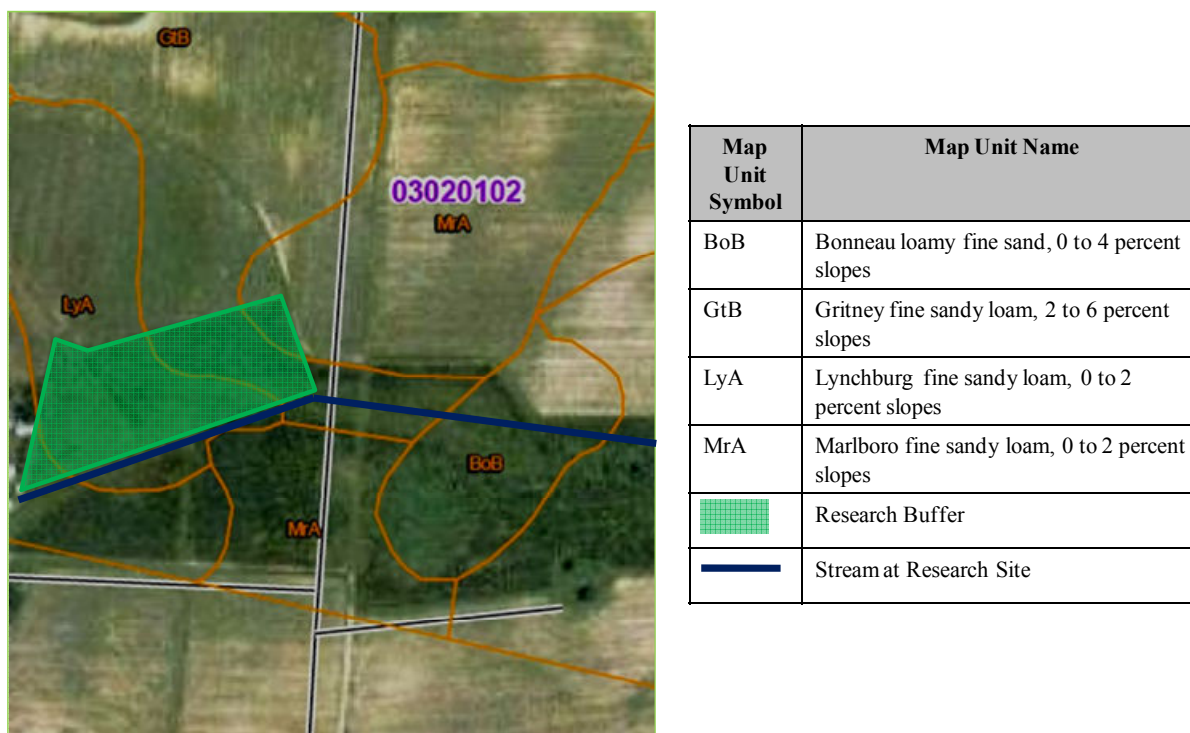


Figure 3. 3: Soil Map of Research Site from USDA-NRCS Soil Survey Staff (2006).

Table 3. 1: Soil classifications within buffer treatment (USDA-NRCS Soil Survey Staff, 2006).

Soil Type	Buffer Zones	Drainage Class	Permeability	Restrictive Layer	Seasonal Water Table
Marlboro fine sandy loam	1 and 2	well drained	moderate	> 2 m	1.2 m to 1.8 m
Lynchburg fine sandy loam	1, 2, and 3	somewhat poorly drained	moderate	1.6 m	0.5 to 1.5 m
Gritney fine sandy loam	1, 2, and 3	moderately well drained	slow	0.2 m	0.45 to 0.9 m

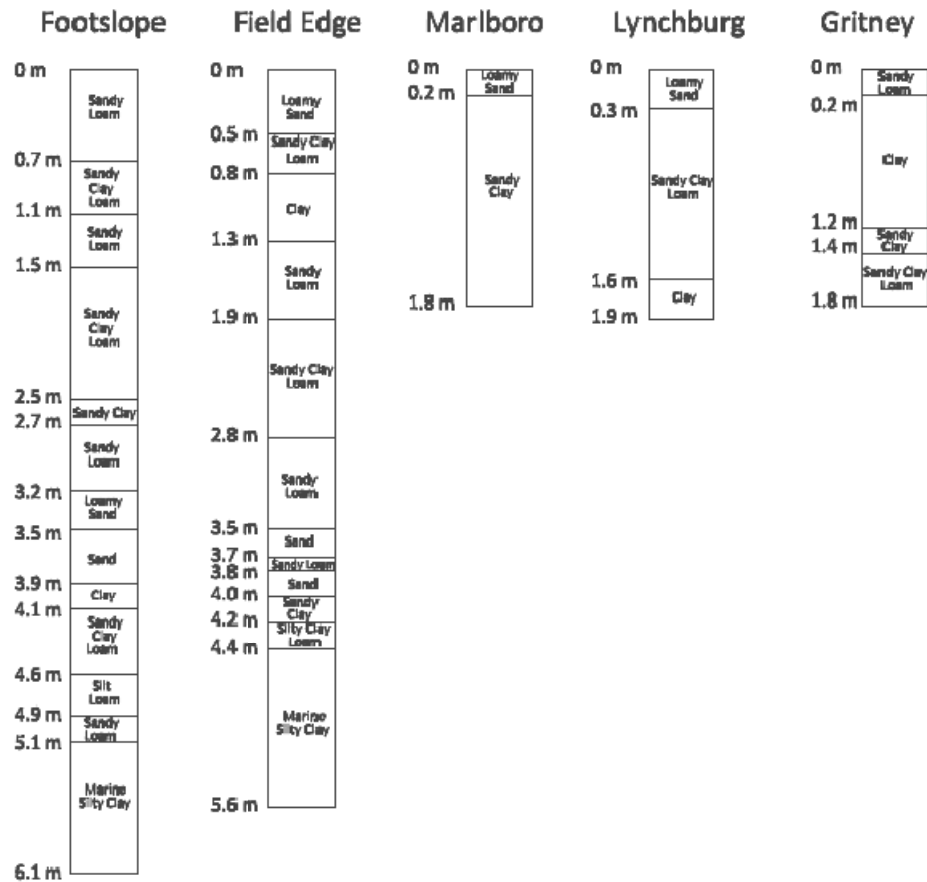


Figure 3. 4: Soil profiles at buffer site and similar soil series (as defined by USDA-NRCS, 2006 and Severson, 2004).

Site Survey

Three site surveys were completed over the study to identify equipment location and topography of the site as described in Chapter 2.

Site Instrumentation

Groundwater Well Installation

Surficial groundwater monitoring wells nests were installed in three transects 15 m (50 ft) apart within the buffer in December 2004 (Figure 3. 5). Each well nest contained a shallow and deep well with maximum depths of 1.5-2.3 m (5-7 ft) and 2.7-3.6 m (9-12 ft) respectively. Locations of well nests can be found in Table 3.2 (distances are relative to the stream). Additionally, four deeper aquifer wells were installed and monitored at the site. The objective of these well installations was to monitor the deeper aquifer groundwater to assess any mixing between the deep and surficial aquifer waters. Well depths ranged from 7.6-10.6 m (25-35 ft).

Three water table elevation data loggers (Infinites USA, Inc., Port Orange, FL) with a built in pressure sensor were installed next to well nests in the center transect in December of 2004 and took hourly water table levels from January 2005 to May 2010.

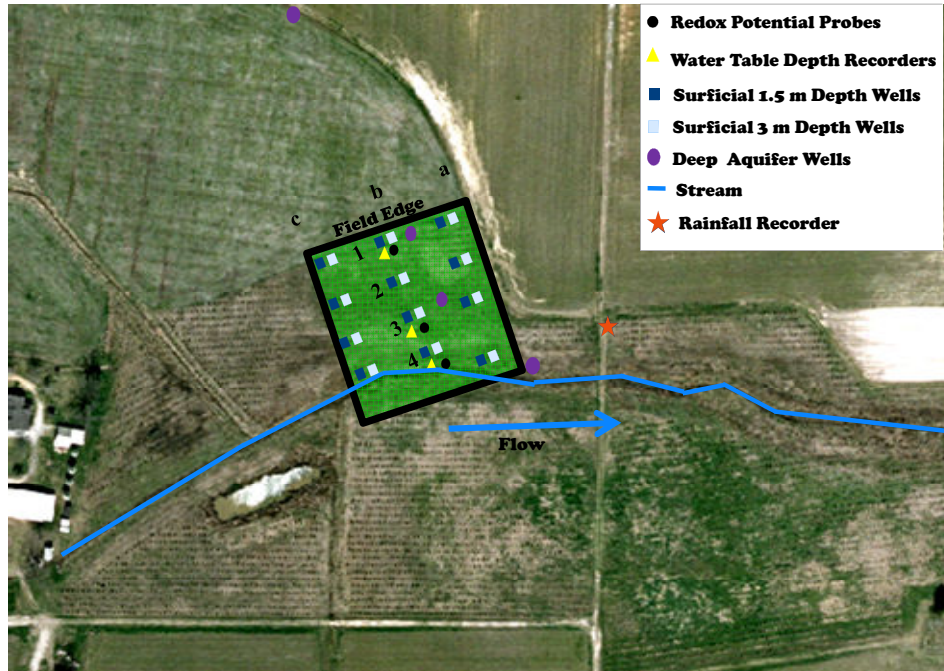


Figure 3. 5: Research site monitoring setup for the study site.

Table 3. 2: Transect layout from Zone 3 to Zone 1. Distances are relative to the stream.

Zone 3 (Grassed Filter Strip)	Zone 2 (Upper Mid Buffer)	Zone 2 (Lower Mid Buffer)	Zone 1 (Stream Edge)
55-60 m (180-197 ft)	45-50 m (148-164 ft)	25-30 m (82- 98 ft)	1.5 m (5 ft)

Rainfall

A tipping bucket, HOBO (Onset, Bourne, MA) data logger, and manual rain gage were installed at the site, but due to complications with both the data logger and manual rain gage, the NC SCO (2010) data was used for precipitation data in this project for all five years.

Redox Potential Probes

Redox potential probes were installed and monitored next to each of the surficial groundwater monitoring wells in the center transect to identify if the soil was suitable for

denitrification. The probes were placed at the same depths as the surficial shallow (1.5-2.3 m) and deep (2.7-3.6 m) water quality well depths. Therefore, there were 5 probes per depth for each location for a total of 40 probes.

Monitoring and Data Collection

Soil Sampling

In order to estimate seepage velocity through the buffer, soil samples were collected at the bottom of each well during installation. A particle size analysis test was then completed by the North Carolina State Soil Science Laboratory and results were used to determine the hydraulic conductivity through each zone of the buffer using SPAW 6.0 (NRCS, 2010). Results provided soil classifications used to estimate porosity in each zone of the buffer. Porosity estimates along with hydraulic conductivity results were then used for determining flow velocity from the field to the stream.

Water Table Monitoring

The water table elevation data loggers were used to monitor water table elevation hourly from November 2005 to May 2010. Water table depth datasets were downloaded monthly using a HP 48 G+ handheld calculator (Palo Alto, CA). Additionally, monthly manual water table elevation readings were completed in the water table elevation data loggers to account for drifting using Solinst ® water level meters (Georgetown, ON). Monthly water table elevation

readings were also completed in the surficial groundwater monitoring wells from August 2008 to May 2010 using water level meters.

Water Quality Monitoring

Groundwater samples were collected from the surficial aquifer monitoring wells monthly beginning in January 2005 to examine differences in water qualities throughout the buffer treatment. Groundwater samples were collected from the deeper aquifer beginning in August 2008. All water quality samples from the surficial and deeper aquifer wells were analyzed for nitrate (NO_3^- -N), chloride (Cl^-), dissolved organic carbon (DOC), ortho-phosphate (O-PO_4), and ammonium (NH_4 -N). Sodium (Na^+) and calcium (Ca^{2+}) analyses began in July 2008. Samples were transported and analyzed by the BAE Environmental Analysis Laboratory at North Carolina State University. All nutrients measured in the study contributed to understanding nitrogen dynamics within the buffers. Cl^- was used to investigate the possibility of groundwater mixing throughout the buffer. Additionally, Na^{2+} and Ca^{2+} were measured for comparisons of the surficial aquifer groundwater and deeper aquifer groundwater. DOC was examined to validate that suitable conditions, a carbon source, was present for denitrification to occur.

Redox

Redox measurements were taken monthly starting in May of 2006 using a KCL-saturated Ag/AgCl (Jensen Instruments, Tacoma, WA) reference electrode and a Fisher Scientific ® accumet AP63 Portable pH/mV meter (Pittsburgh, Pa). The five readings at each depth were

averaged to represent the redox condition at each location within the buffer and depth in the soil. Measurements were adjusted using a correction factor of 204 mV that was determined using the assumed soil temperature of 15 °C (59 degrees F) and a measured pH of 5.2 (Richardson and Vepraskas, 2001).

Data Analysis

Water Table Analysis

Water table elevations were determined using the site topographic survey, continuously monitored water table elevation data, and monthly manual water table depth measurements. The average water table elevation and the average water table difference between buffer zones was determined using the following equation:

$$AD = \frac{1}{n} \sum_{i=1}^n (WTE_{upslope_i} - WTE_{downslope_i}) \quad (3.1)$$

Where,

AD = Average Difference (m)

$WTE_{upslope_i}$ = Water table elevation at upslope location

$WTE_{downslope_i}$ = Water table elevation at downslope location

n = Number of daily water table readings collected during study period

Whether the buffer zone met USACE minimum jurisdictional wetland hydrology criteria was determined using continuous water table data. The percentage of consecutive days during

the growing season (March 20th thru November 6th) that the water table was within 30 cm of the soil surface consecutively was completed for the three water table monitoring locations.

Groundwater Flow Direction Modeling

The hydraulic data analysis and groundwater flow direction modeling were completed using the spreadsheet developed by Devlin (2003) along with Surfer 7 mapping software (Golden Software, Golden, CO). An auger hole hydraulic conductivity test was successful at depths ranging from 78 cm, 135 cm, and 82 cm from Zone 1 to Zone 3 of the buffer respectively to estimate hydraulic conductivities. Although, due to the restrictiveness of the auger height, a particle size analysis completed for the soils at the depth of the surficial monitoring wells during installation and were used to determine the hydraulic conductivity using SPAW 6.0 for better accuracy. Using collected data and hydraulic conductivities, groundwater velocity and residence were calculated within the buffer system.

Nitrate-Nitrogen Removal Efficiency and Nitrate/Chloride Ratios

Groundwater NO₃⁻-N removal efficiency was calculated between each zone and transect as well as the overall area of the buffer at the research site using the following equation:

$$\% \text{ Removal} = \frac{C_I - C_E}{C_I} * 100\%$$

(3.2)

Where,

% Removal = Percentage of groundwater NO_3^- -N removed by the buffer (%)

C_I = Concentration (mg/L) of the groundwater entering the buffer

C_E = Concentration (mg/L) of the groundwater discharging to the stream

In an attempt to define whether denitrification or dilution was the cause for groundwater NO_3^- -N concentration reductions observed in the buffer, NO_3^- -N to Cl^- ratios were calibrated. Lowrance (1992) along with other researchers have used this conservative ion (i.e. having minimal plant uptake and not undergoing microbial transformations in soil) in riparian zones groundwater to determine if denitrification and not dilution was responsible for observed groundwater NO_3^- -N losses. Chloride was used to compare changes in the ion relative to NO_3^- -N through the buffer. Essentially dilution was indicated if ratios remained constant through the buffer towards the stream, while removal by denitrification or other biological activity was supported if ratios decreased through the buffer.

Measured Nitrate-Nitrogen Mass Removal

The groundwater NO_3^- -N loads were estimated to evaluate the change and/or transformations from the field edge to the stream within the buffer. The load was calculated using soil data to estimate the hydraulic conductivity, hourly monitored water table elevation data to estimate the gradient, and water quality samples from each well.

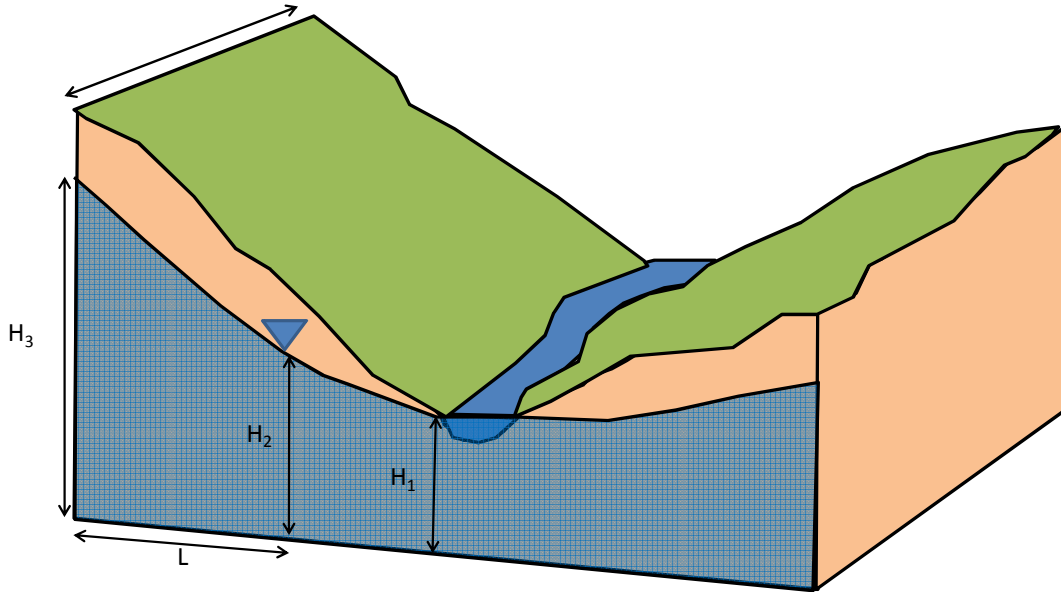


Figure 3. 6: Water table visual for reference for Equation 3.3.

$$Load_{NO_3-N} = \frac{2.4 \times 10^{-2} * (H_{Zone3}^2 - H_{Zone2}^2) * K * T * W * C}{2 * L}$$

(3.3)

Where,

Load_{NO₃-N} = Groundwater NO₃⁻-N flux for each month (kg N)

H = Level of groundwater elevation above datum at position i (m)

K_s = Hydraulic conductivity at well location (m/hr)

T = Days within each month conversion (days)

C = Influent concentration (mg/L)

W = Length of the buffer (m)

L = Distance between each groundwater well (m)

Statistical Analysis

A statistical analysis was completed to define significant differences in groundwater NO_3^- -N concentrations throughout the buffer treatment system using SAS PROC MIXED ® (SAS Institute, Cary, NC). A log transformation was required to normalize the groundwater NO_3^- -N concentrations and a fixed effect of soil depth.

Redox readings, Cl^- , NO_3^- -N/ Cl^- ratios, Na^+ , and Ca^{2+} concentrations were considered individual response variables and evaluated with the same procedure as NO_3^- -N concentrations. Evaluations between the buffer sections and the deeper aquifer water quality signatures were completed using a mean separation tests with NO_3^- -N, Cl^- , NO_3^- -N / Cl^- , Na^+ , and Ca^{2+} concentrations being the individual response variables and the class variable being the depth and well location (SAS PROC MIXED ®, Cary, NC).

RESULTS AND DISCUSSION

Groundwater Hydrology

Riparian Buffer Relative Wetness

The water table was within 3 m of the soil surface at all locations even during the driest periods of the year and had several wet and dry cycles throughout the study (Figure 3. 7). These conditions enhance groundwater NO_3^- -N reduction according to a hydrologic and NO_3^- -N assessment completed at seven sites by Pinay *et al.* (2007). Findings indicated that an increase in wet and dry cycles near the soil surface allowed nitrification to occur followed by increased denitrification occurrences during wet periods.

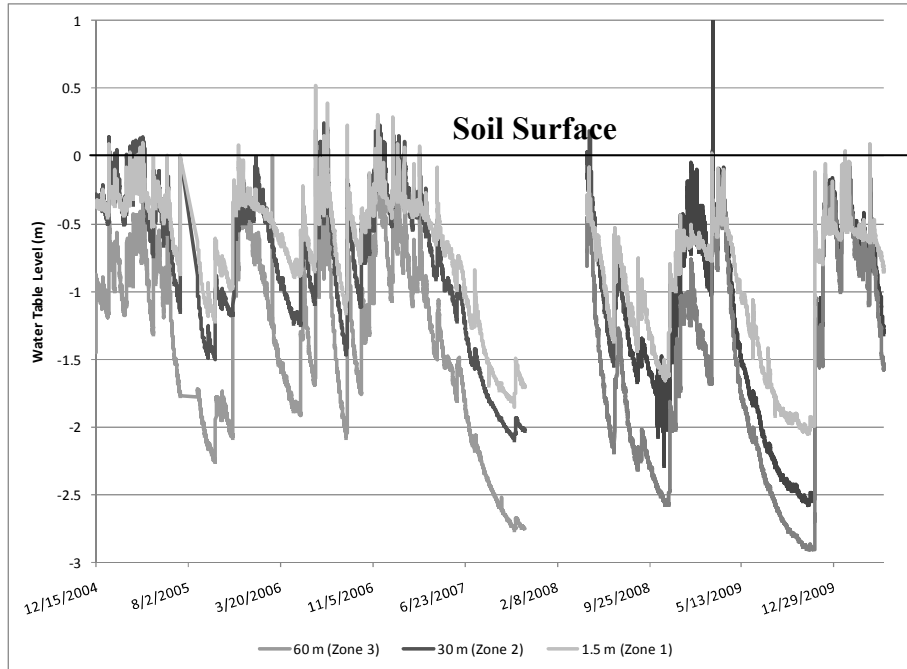


Figure 3. 7: Proximity of the water table to the soil surface within Zones 1-3. Data unavailable from January 2005 to April 2008 due to equipment malfunction.

Average water table depths relative to the soil surface were 1.44 m, 0.99 m, and 0.83 m with maximum depths below the soil surface of 2.8 m, 2.6 m, and 2.1 m for Zone 3, Zone 2, and Zone 1 monitoring locations, respectively (Table 3. 3). The water table appeared to become deeper beginning in 2007. During 2007-2008, North Carolina had a drought that caused these increases in the water table depths (NCSCO, 2010). Although the water table depths did increase from the soil surface the water tables were within 1.5 m (5 ft) of the soil surface on average each year in both Zone 1 and 2 of the buffer treatment. These results indicate that the buffer was still relatively wet in Zones 1 and 2 throughout the year.

Table 3. 3: Average yearly water table depths. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Year	Zone 3 (m)	Zone 2 (m)	Zone 1 (m)
2005	1.09	0.61	0.51
2006	1.06	0.61	0.51
2007	1.69	1.17	0.99
2008	1.75	1.19	1.03
2009	1.70	1.44	1.16
Average (m)	1.44	0.99	0.83

Both pine and oak roots can grow deeper than 85 cm below the soil surface and have been reported as denitrifying hot spots due to decomposing roots and leaching leaf litter (Rotkin-Ellman *et al.*, 2004). Therefore, inundated conditions at various soil depths were examined to identify if the treatment buffer had critical hydrologic conditions for denitrification to take place. Figure 3. 8 shows the results of an analysis of the frequency the water table resided at several soil depths in the various buffer zones. These results indicated that both Zones 1 and 2 had water tables within 60 cm of the soil surface a large portion of the year throughout the study, particularly prior to the 2007-2008 drought.

Riparian areas that are frequently wet can be classified as riparian wetlands. Wetlands have been shown to be effective sinks of groundwater NO_3^- -N (Peterjohn *et al.*, 1984; Humenik *et. al*, 1999; Koskiaho *et. al*, 2003). As such, determining whether this riparian buffer could be classified as a riparian wetland was used to assess the buffers potential to remove groundwater

NO₃⁻-N. Since, the water table elevation was relatively high in Zones 1 and 2 throughout the year a wetland hydrology assessment was completed on each zone in the buffer to evaluate if the riparian buffer could be working as well as a wetland (Figure 3. 8). Zone 2 was the only location that indicated wetland hydrology (Table 3.4). The location barely met the wetland hydrology requirements during 2008 by being within 30 cm of the soil surface consecutively more than 5% (11 days) of the growing season (March 20th thru November 6th) (U.S. ACE, 1987). Furthermore, wetland hydrology was not present during the overall wetter years prior to the drought. A site must meet wetland hydrology criteria 50% of the years evaluated for the location to be stated as a having wetland hydrology, which was not present in this buffer. Therefore, the treatment buffer was not a riparian wetland.

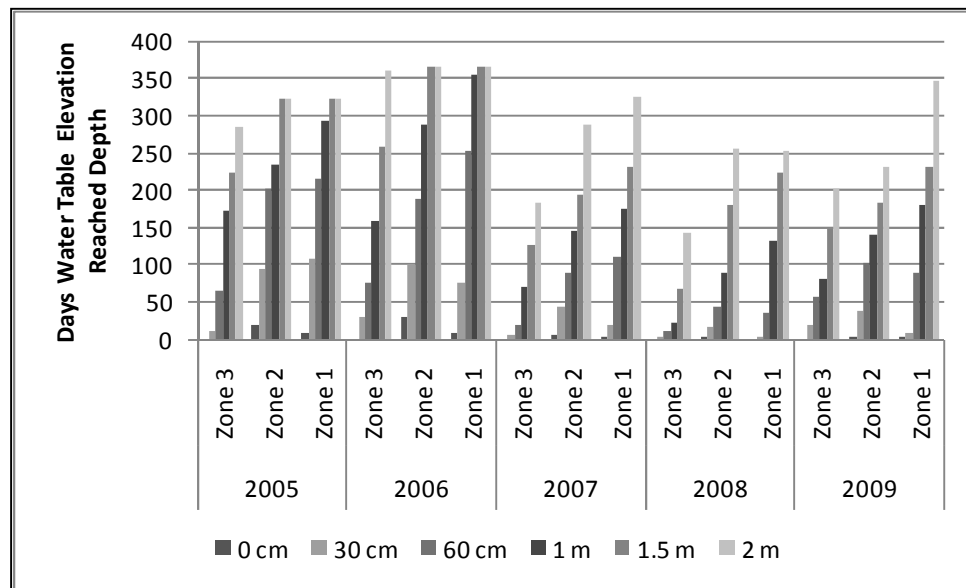


Figure 3. 8: Number of days water table depths were less than 0 cm, 30 cm, 60cm, 1m, 1.5m, and 2m relative to the soil surface. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Table 3. 4: Maximum consecutive days water table was within 30 cm of the soil surface during growing season (March 20th thru November 6th). Highlighted cells are years that wetland hydrology was present at monitored zones. Data was missing in July through August of 2005 and March through April 2008.

	Zone 3	Zone 2	Zone 1
Depth (cm)	30	30	30
2005 (days)	0	10	10
2006 (days)	4	8	7
2007 (days)	0	0	1
2008 (days)	1	14	1
2009 (days)	2	3	0

Groundwater Gradients

Buffer slope and elevation influenced the differences in water table depth and wetland hydrology. Even though the buffer did not meet wetland hydrology criteria, as ground elevation decreased gradually through the buffer towards the stream, the water table became closer to the soil surface (Figure 3. 9). The buffer had a slope from Zone 3 to Zone 1 of 1.67% and the adjacent stream had a slope of 0.7% over the entire research site. Figure 3. 9 displays how the ground elevation gradually decreased from Zone 3 to Zone 1. These results led to further investigations as to how the topography effected the overall movement of groundwater throughout the riparian buffer treatment system.

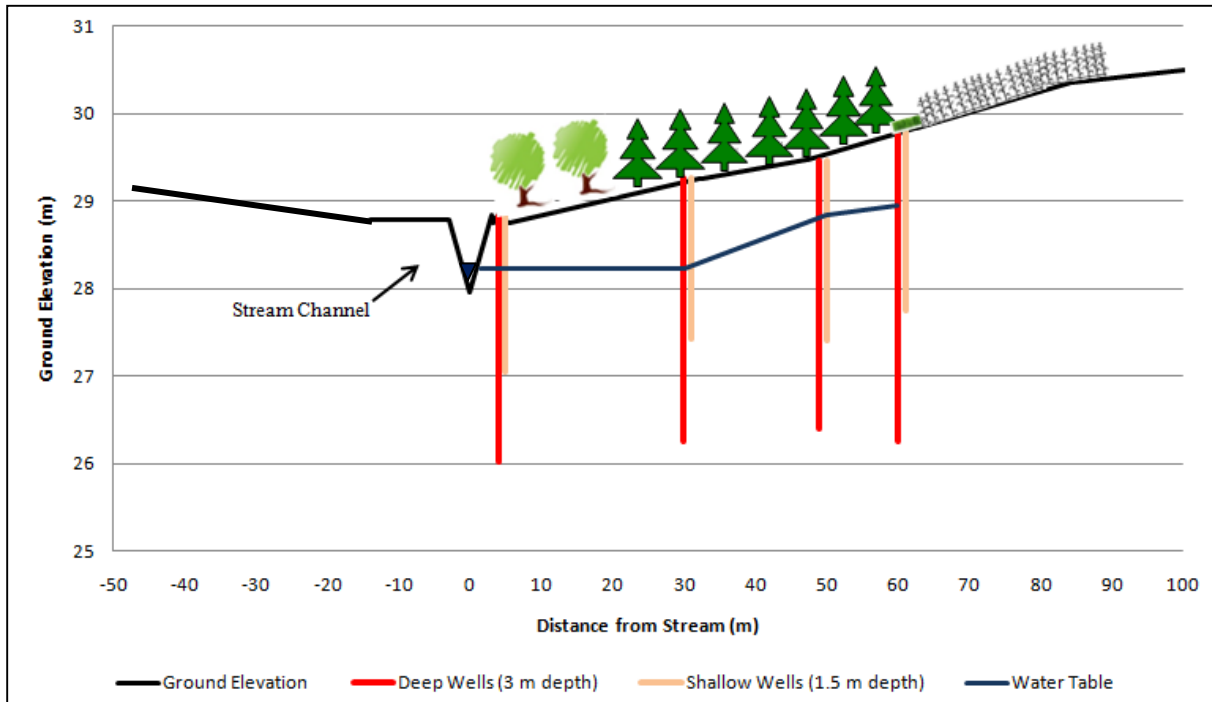


Figure 3. 9: Cross section of center transect of the riparian buffer and surficial monitoring wells.

Water table elevations were evaluated to investigate the general movement from Zone 3 to Zone 1 throughout the entire buffer study (Figure 3. 10). Since the water table elevations varied year to year as discussed in the prior section, water table elevations were modeled for a wet year (2006) and dry year (2009) to form a better understanding of how the water table elevations changed during climatically different years (Figure 3. 11 and Figure 3. 12). As seen in Figure 3. 11 and Figure 3. 12, the wet and dry years dramatically affected the water table elevations particularly during the summer and fall seasons. During 2006, a considerably wet year at the site, the water tables were highest during the growing season, while during 2009 water tables began to decrease in the spring and continued to decrease into the summer and fall

seasons. The water table elevation was approximately 30.5 m in all zones in July 2006, while in July 2009 the water tables were approximately 2 m lower in the soil at 28.5 m. The implications of these differences in elevations required a more intensive study at to how these elevation changes affected the groundwater movement in this buffer treatment across years.

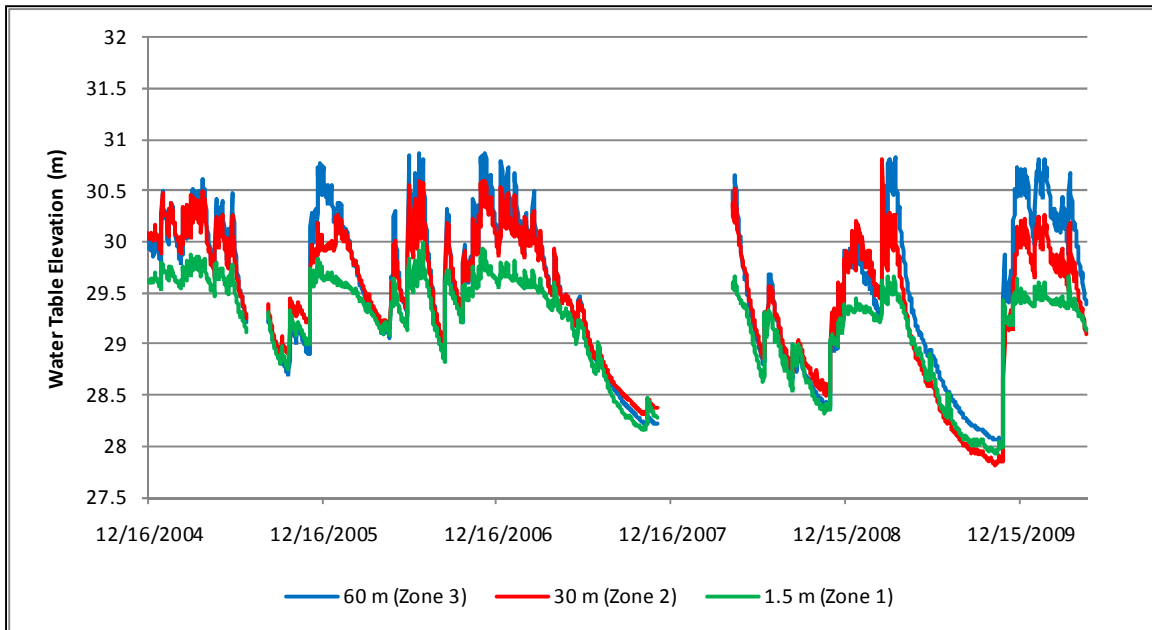


Figure 3. 10: Water table elevations for each zone of the buffer during the study period (December 2004-May 2010).

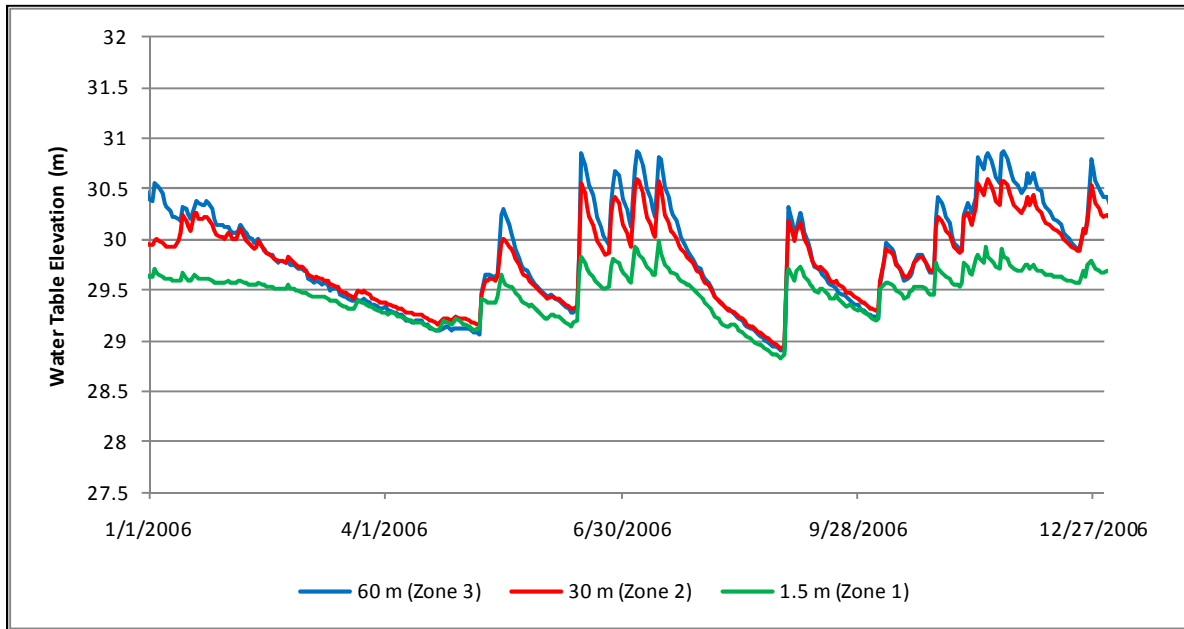


Figure 3. 11: Water table elevations for each zone of the buffer during 2006 (wet year).

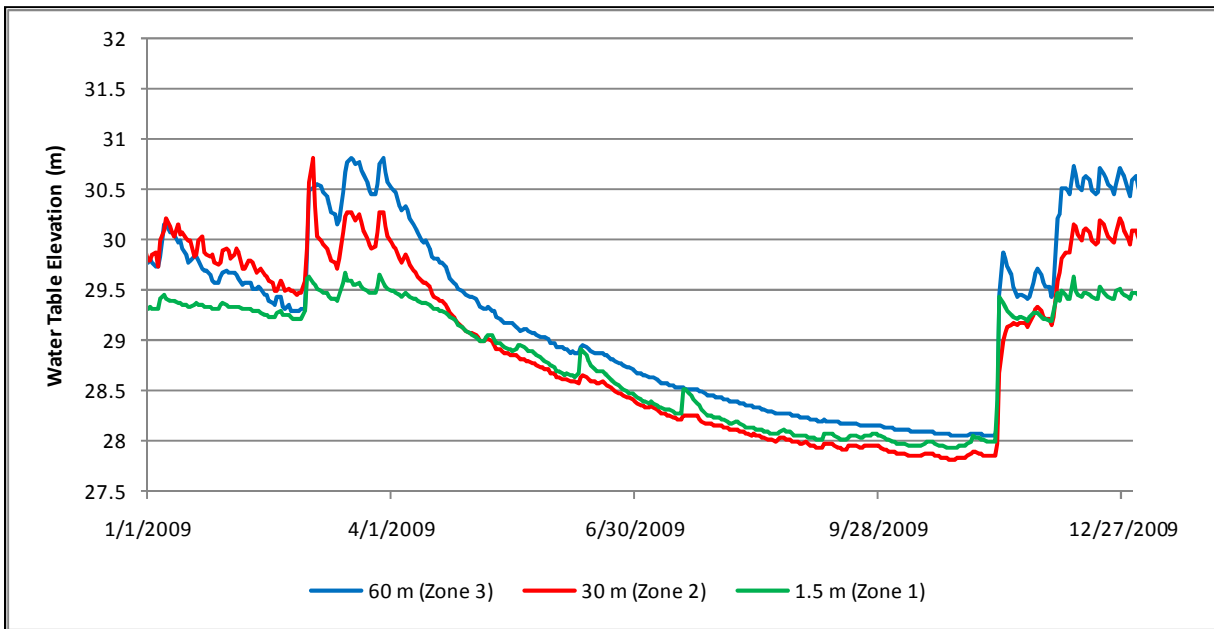


Figure 3. 12: Water table elevations for each zone of the buffer during 2009 (dry year).

The average difference in water table elevations was approximately 0.25 m from Zone 3 to Zone 2 and 0.07 m from Zone 2 to Zone 1 throughout the study period, with an overall average difference of 0.31 m through the buffer (Table 3.5). Negative differences in 2007 and 2008 were during the drought as discussed in the last section. During this period groundwater appeared to flow toward downstream buffer areas and Beech Swamp, which had lower water table elevations.

Table 3. 5: Average yearly elevation differences between zones. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Year	Average Difference (m) (Zone 3 – Zone 2)	Average Difference (m) (Zone 2 – Zone 1)	Average Difference (m) (Zone 3 – Zone 1)
2005	0.03	0.31	0.34
2006	0.06	0.30	0.37
2007	-0.01	0.23	0.22
2008	-0.06	0.24	0.19
2009	0.25	0.13	0.38
Average (m)	0.07	0.25	0.31

Water table gradients from monitored water table elevation readings in surficial groundwater monitoring wells were modeled using Surfer 7 mapping software (Golden Software, 1999). The models showed that groundwater flow paths did go through the buffer from the adjacent field and that the angle of flow was not always consistent depending on seasonal water table elevations (Figure 3. 13 - Figure 3. 16).

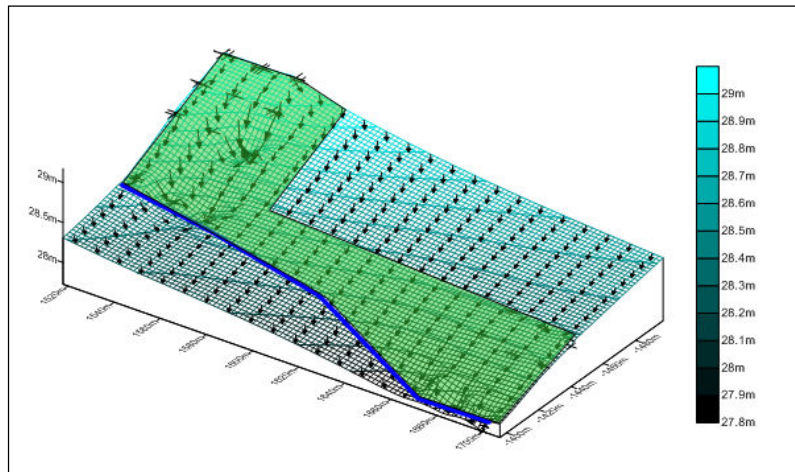


Figure 3. 13: Groundwater flow vectors for April 2009 (wettest period) at the research site. The blue line represents the stream.

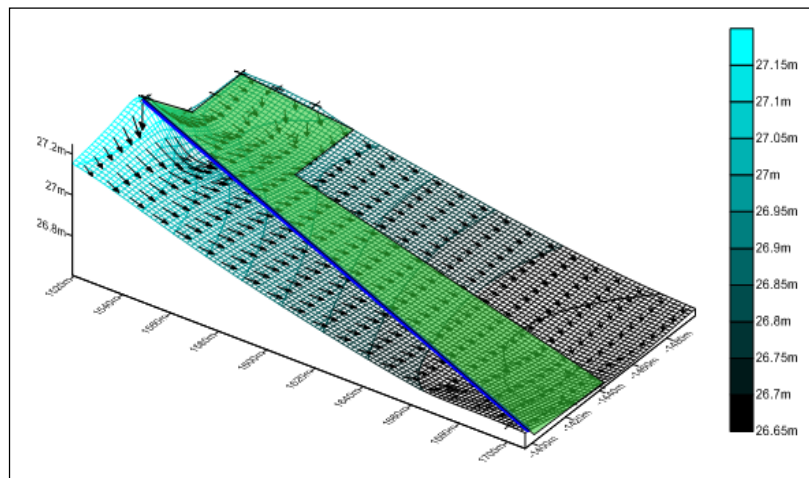


Figure 3. 14: Groundwater flow vectors for November 2009 (driest period) at the research site. The blue line represents the stream.

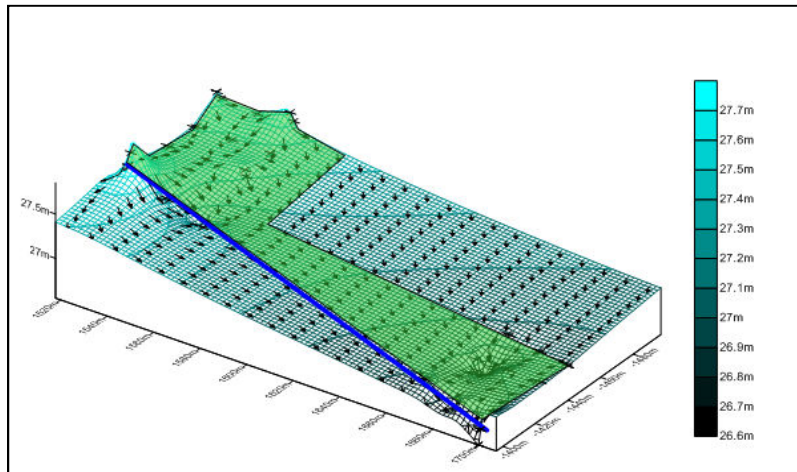


Figure 3. 15: Groundwater flow vectors for July 2009 at the research site. The blue line represents the stream.

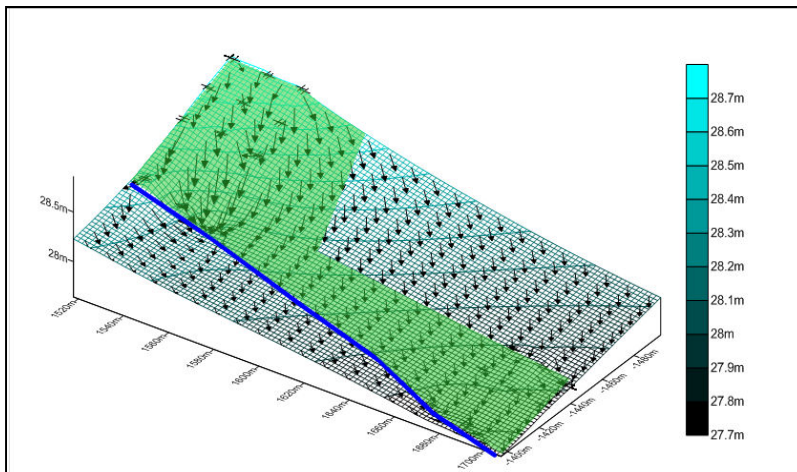


Figure 3. 16: Groundwater flow vectors for January 2009 at the research site. The blue line represents the stream.

The hydraulic gradient was modeled monthly starting in June 2008 using monthly piezometer readings, an excel spreadsheet designed by Devlin (2003), and Surfer modeling software. Gradients represented water table elevation over distance through the buffer treatment. The gradients through the treatment varied between 0.003-0.036 m/m depending on season. Groundwater flow angles estimated using Devlin (2003) exhibited groundwater direction relative

to the stream (parallel to the field) throughout seasonal periods (Figure 3. 17 thru Figure 3.19). The estimated groundwater angles using Devlin (2003) were similar to the angles found using the Surfer 7 mapping software (Golden Software, 1999) as shown in Figure 3. 20.

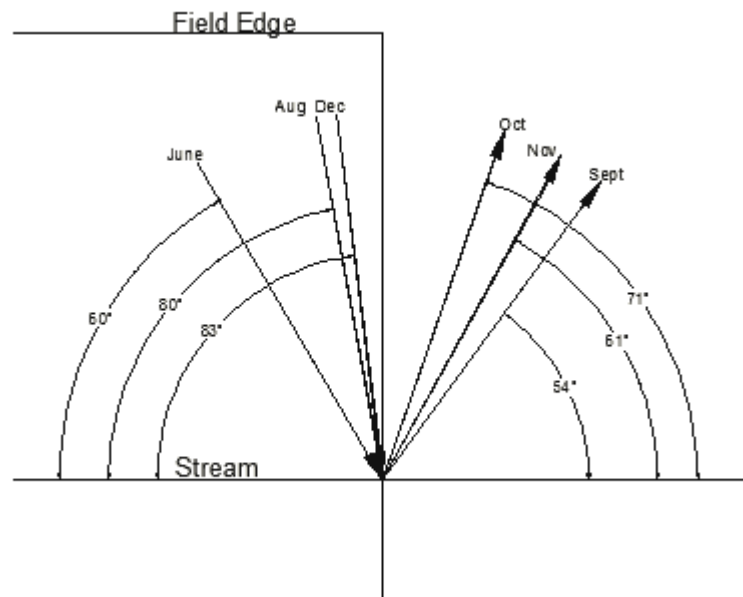


Figure 3. 17: Groundwater flow direction through the buffer relative to the stream for months monitored in 2008.

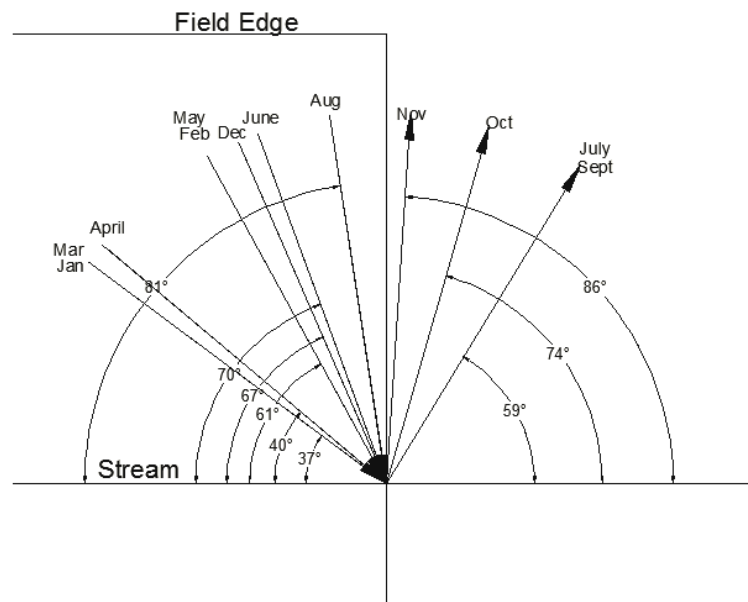


Figure 3. 18: Groundwater flow direction through the buffer relative to the stream for months monitored in 2009.

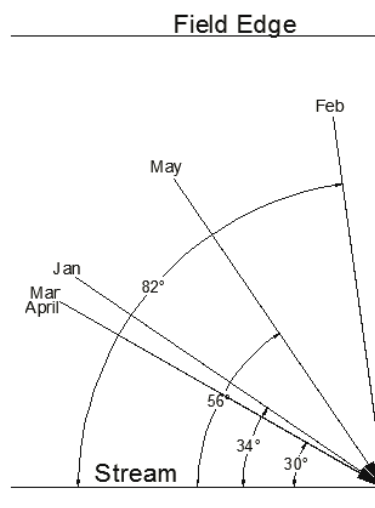


Figure 3. 19: Groundwater flow direction through the buffer relative to the stream for months monitored in 2010.

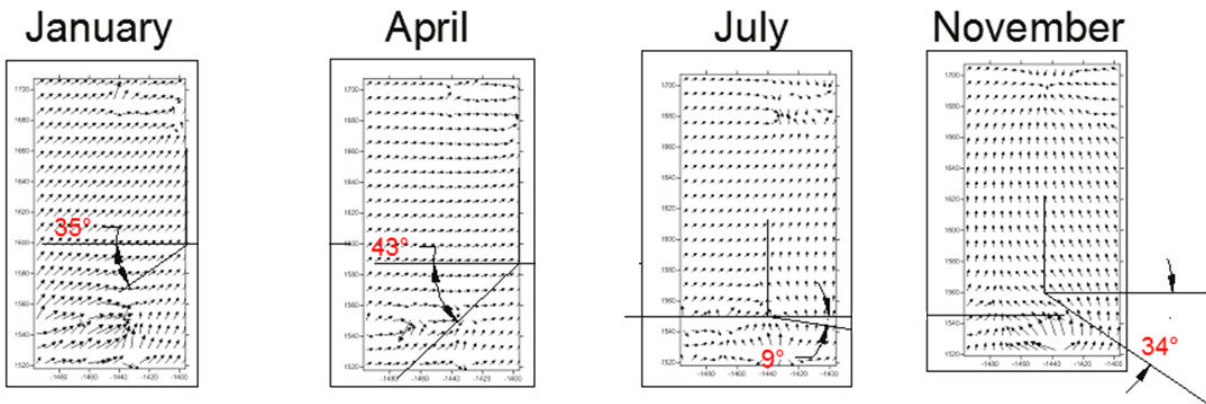


Figure 3. 20: Groundwater angles estimated using Devlin (2003) on contours modeled in Surfer 7 mapping software during 2009 (Golden Software, 1999).

Beech Swamp was located downstream of the buffer zones, parallel to the adjacent field. The data suggests that the groundwater flowed to variable outlet locations depending on water table elevation. Over periods when the water table elevation was closer than 1.5 m to the soil surface the groundwater flowed at an angle through the buffer toward a stream discharge area downstream of the buffer. Water table elevations below 1.5 m resulted in groundwater flowing almost parallel through the buffer toward Beech Swamp, the lowest topographic elevation in the area. Furthermore, the upslope location of this buffer limited the groundwater contributing area entering from the adjacent agricultural field (Figure 3. 21 and Figure 3. 22), possibly allowing less concentrated groundwater from the adjacent field to flow into the buffer.

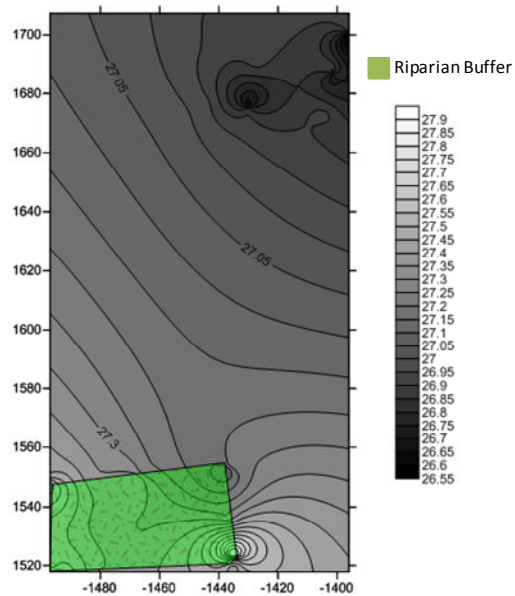


Figure 3. 21: Groundwater contour map of July 2009 (dry period).

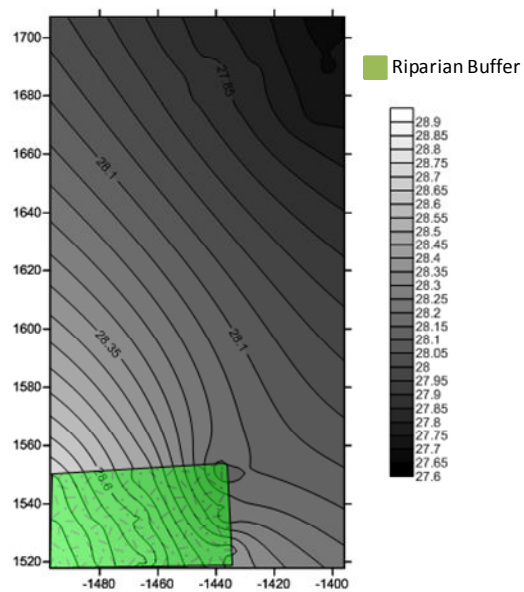


Figure 3. 22: Groundwater contour map of January 2009 (wet period).

Although the groundwater flow direction fluctuated throughout the year, groundwater that was contaminated with NO_3^- -N was continuously within the buffer treatment system, moving slowly in multiple directions throughout the year. Therefore, the determination of the groundwater residence time within the buffer was investigated.

Saturated Hydraulic Conductivity, Groundwater Velocity, and Residence Time

Soil texture has a major influence on how groundwater passes through riparian buffers. Therefore, a particle size analysis was completed at the well depth locations at the beginning of the study to identify any inconsistencies in soil texture at the 1.5 m and 3 m depths within the buffer (Table 3. 6). One major soil texture variation was found at the 1.5 m depth in Zone 1, where the center transect had sandy clay loam and the upstream transect had sandy loam. Variability in the soil between sandy loam and sandy clay loam was also identified in the soil survey completed at the beginning of the study to determine well depth placement (Figure 3.4 and Severson, 2004). The majority of the buffer was classified as sandy loam. Therefore, the effective porosity of the soil was conservatively assumed to be 0.35 and was used in calculating travel time (Fangmeier *et al.*, 2006).

Table 3. 6: Particle Size Analysis for Buffer Treatment

Soil ID	Sand	Silt	Clay	USDA	%	%	NRCS Particle Size Model "SPAW Hydrology" hydraulic conductivities (cm/hr)
	%	%	%	Class.	2-5mm	> 5mm	
1.5 m Depth Center Transect Zone 3	74.6	7.2	18.2	sandy loam	0.0	0.0	2.7
1.5 m Depth Center Transect Upper Zone 2	74.6	5.1	20.3	sandy clay loam	1.1	0.0	1.97
1.5 m Depth Center Transect Lower Zone 2	76.6	5.2	18.2	sandy loam	2.1	0.0	2.76
1.5 m Depth Center Transect Zone 1	73.4	5.4	21.2	sandy clay loam	15.9	4.6	1.94
1.5 m Depth Upstream Transect Zone 1	76.6	7.8	15.6	sandy loam	17.3	15.9	3.42
3 m Depth Center Transect Zone 3	74.6	9.5	15.9	sandy loam	9.0	1.0	3.31
3 m Depth Center Transect Upper Zone 2	84.4	6.6	9.1	loamy sand	4.9	5.3	7.21
3 m Depth Center Transect Lower Zone 2	76.1	6.8	17.1	sandy loam	15.1	3.8	3.06
3 m Depth Center Transect Zone 1	79.8	6.0	14.2	sandy loam	9.9	3.7	4.32

Saturated conductivity (K_s) was calculated using the particle size analysis for each zone and the NRCS SPAW 6.0 modeling program. K_s ranged from 1.94 cm/hr to 3.42 cm/hr at the 1.5 m depth and 3.06 cm/hr to 7.21 cm/hr at the 3 m depth. Groundwater velocity averaged 1.6

cm/day and 3.0 cm/day at the 1.5 m and 3 m depths respectively. The travel times ranged from 1.25 to 16 years at the 1.5 m depth with a median of 11 years, while the travel times ranged from 0.6 to 11 years with a median of 8 years at the 3 m depth based on groundwater angle.

Long residence times (> 50 years) enhance NO_3^- -N removal by denitrification in buffers, but denitrification has been found to occur with residence times as small as 1 month (Puckett, 2004; Tesoriero *et al.*, 2005; Dettmann, 2001). The treatment buffer had residence times within established times for denitrification to proceed, and the soil was continuously inundated at depths above 3 m. These conditions should have allowed this riparian buffer to provide conditions hydrologically suitable for denitrification to proceed at high rates.

Overall Groundwater Quality NO_3^- -N Results

The hydrology of this buffer appeared conducive for high groundwater NO_3^- -N removal rates, since the lower Zone 2 and Zone 1 appeared to have high water tables throughout the study. NO_3^- -N concentrations from groundwater sampling in the buffers 1.5 m and 3 m depths are shown in Figure 3. 23 and Figure 3. 24. 1.5 m depth mean NO_3^- -N levels from Zone 3 to Zone 1 were 4.5 to 1.7 mg/l respectively (63% reduction) in the shallow groundwater. Mean NO_3^- -N levels from Zone 3 to Zone 1 at the 3 m depth were 2.9 to 2.5 mg/l respectively, (15% reduction) in the deeper groundwater. Only at the 1.5 m depth was groundwater NO_3^- -N concentrations found to significantly decrease through the buffer ($\alpha = 0.05$).

Mean groundwater NO_3^- -N results entering this buffer were much lower than NO_3^- -N concentrations in prior middle coastal plain studies, and appeared to be tied the hydrology and groundwater contributing area (Figure 3. 25). Dukes *et. al* (2002) reported entering mean groundwater NO_3^- -N concentrations ranging from 5.6 to 5.8 mg/L at depths ranging from 0.6 m to 3 m, while Jacobs and Gilliam (1985) reported field edge mean groundwater NO_3^- -N concentrations at depths up to 4.25 m to be 8.0 mg/L.

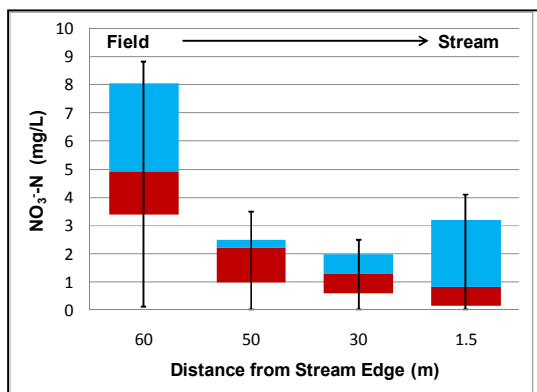


Figure 3. 23: The 5%, 25%, median, 75%, and 95% percentiles of groundwater NO_3^- -N concentrations over the study for 1.5 m deep surficial wells at differing locations in the riparian buffer (n=144 water quality samples).

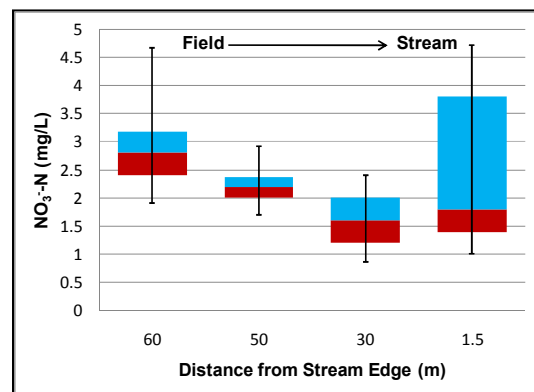


Figure 3. 24: The 5%, 25%, median, 75%, and 95% percentiles of groundwater NO_3^- -N concentrations over the study for 3 m deep surficial wells at differing locations in the riparian buffer (n=202 water quality samples).

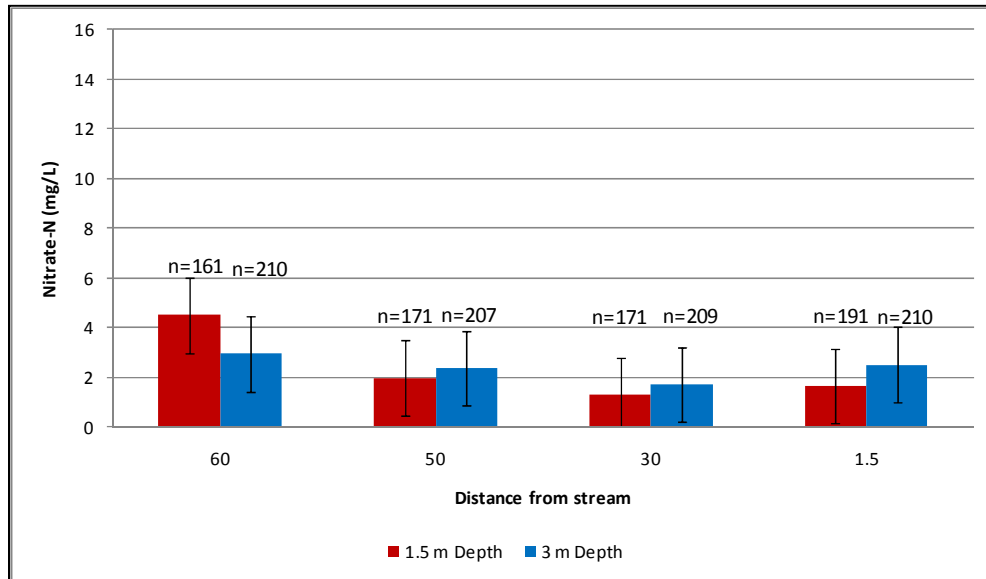


Figure 3. 25: Overall mean groundwater NO_3^- -N concentrations at the 1.5 m and 3 m depths ($n_{1.5\text{m}}=694$ and $n_{3\text{m}}=836$ water quality samples). Note – error bars represent standard error.

A statistical analysis of the water quality using SAS PROC MIXED® (Cary, NC) did not indicate concentrations in Zone 1 being significantly lower than in Zone 3 for the 3 m surficial wells ($\alpha=0.05$), although means showed a general decrease from Zone 3 to lower Zone 2 (30 m from the stream). Inspection of Figure 3. 25 reveals that average groundwater NO_3^- -N concentrations were similar in Zone 3 at both depths. The statistical analysis verified these observations, and further indicated groundwater NO_3^- -N concentrations were significantly smaller at the 1.5 m depth than the 3 m depth surficial monitoring well locations in Zone 1 ($\alpha=0.05$).

Yearly groundwater NO_3^- -N concentrations at the field edge increased throughout the study; the only exception being at the 1.5 m depth in 2009. As discussed in Chapter 2 in 2007 a drought occurred resulting in water table levels that were below many shallow groundwater

monitoring wells. Although in 2007 the water table level fell dramatically and never completely recovered before the completion of the study, as the groundwater NO_3^- -N concentrations increased the groundwater NO_3^- -N reduction efficiency also increased (Figure 3. 26). During these periods of deep water table levels, nitrification and mineralization most likely occurred in the soil increasing groundwater NO_3^- -N concentrations in the system. Additionally higher rates may have been due to lower plant uptake of fertilizer N resulting in more N leached into the groundwater.

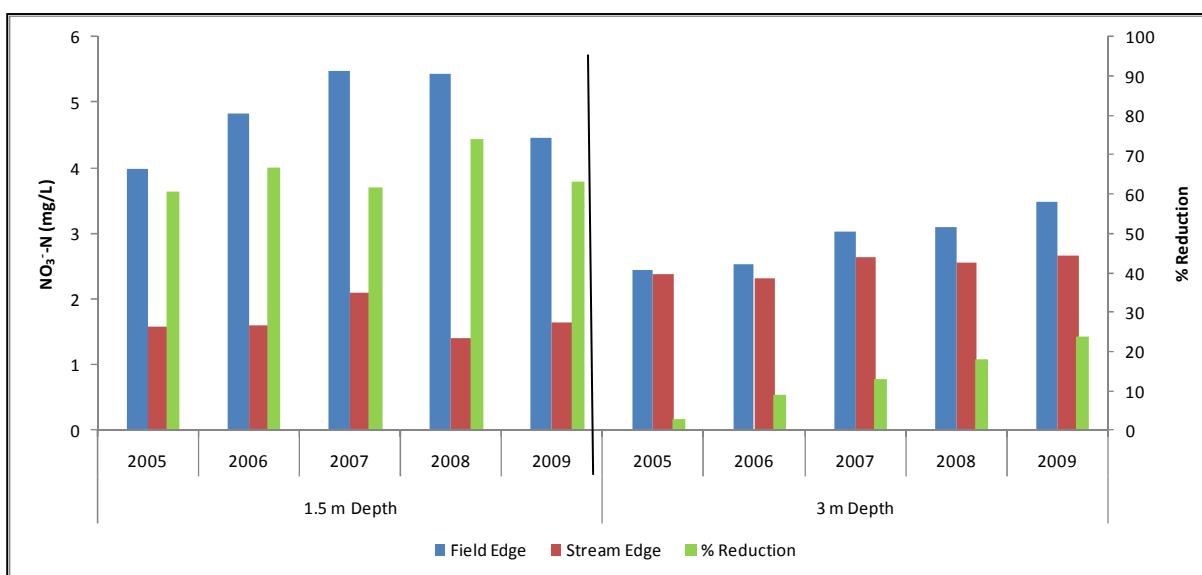


Figure 3. 26: Overall mean groundwater NO_3^- -N concentrations per year at the 1.5 m and 3 m depths ($n_{1.5m}=793$ and $n_{3m}=886$ water quality samples).

Transect and Seasonal Groundwater NO_3^- -N Trends

A visual evaluation of each transect was used to form a better understanding of the groundwater NO_3^- -N dynamics through the buffer due to limitations of the degrees of freedom in the statistical analysis. The center transect had higher groundwater NO_3^- -N concentrations

entering the field edge at the 1.5 m depth, while at the 3 m depth there were no visual differences in groundwater NO_3^- -N concentrations entering the buffer within each transect (Figure 3. 27 and Figure 3. 28). Therefore, the impact of fertilizer applications seemed to decrease with depth. The center transect most likely received the higher concentrations of NO_3^- -N laden groundwater due to the location being in a slight topographic dip at the field edge. Therefore, groundwater and surface water would be routed toward the center transect resulting in increased groundwater NO_3^- -N concentrations.

The soils heterogeneity seemed to cause these differences between other transects and well positions. At both the 1.5 m and 3 m depths the groundwater NO_3^- -N concentrations were higher at the stream edge in Transect C (upstream transect), which often had lower water table elevations relative to other monitoring locations, and was adjacent to a pool in the stream. A particle size analysis identified this monitoring area to contain sandier soils relative to the other monitoring wells at the stream possibly allowing more NO_3^- -N laden groundwater to flow easily through the area. Therefore, a large portion of the NO_3^- -N laden water could have flowed through the Transect C area and possibly allowed surface water to back flow into the buffer due to the sandier soils. The overall mean groundwater NO_3^- -N concentrations at the stream edge at the 1.5 m depth was 1.7 mg/L, while the mean groundwater NO_3^- -N concentrations were 0.3 mg/L, 0.9 mg/L, and 3.6 mg/L for Transects A, B, and C respectively. These differences in transect concentrations demonstrate the complexity of how small differences in soils can have large impacts on overall buffer treatment efficiency.

At both the 1.5 m and 3 m depth groundwater NO_3^- -N concentrations increased during December to May each year. During March to May, fertilizer applications most likely caused the increases in groundwater NO_3^- -N concentrations at the field edge (see Appendix B for application schedules obtained from the landowner). During December to February, vegetation growth was limited, water table elevations were low, and groundwater flowed toward Beech Swamp instead of the adjacent stream possibly allowing increases due to nitrification. All of these possibilities might have affected the concentrations of groundwater NO_3^- -N passing within system.

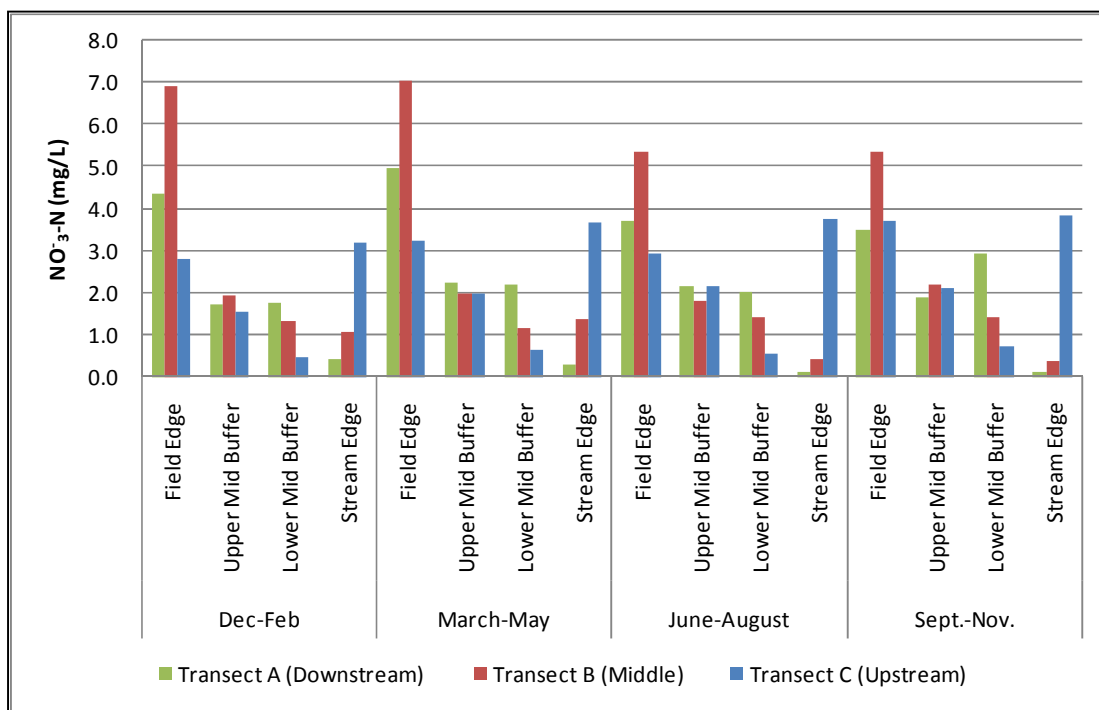


Figure 3. 27: Transect and seasonal groundwater NO_3^- -N evaluation at the 1.5 m depth (n=55 water quality samples).

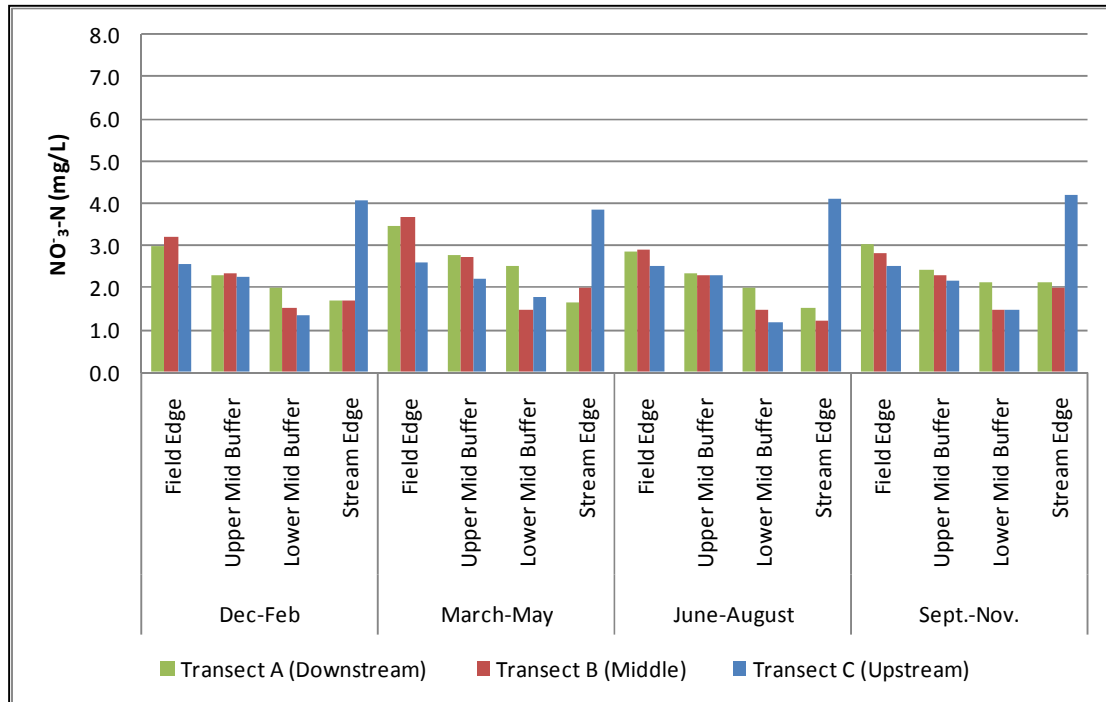


Figure 3. 28: Transect and seasonal groundwater NO₃⁻-N evaluation at the 3 m depth (n=65 water quality samples).

Groundwater NO₃⁻-N Summary

Based on observed decreases in concentrations, the groundwater NO₃⁻-N treatment efficiency of this buffer appeared to be high even with low groundwater NO₃⁻-N concentrations entering the buffer. However, the groundwater NO₃⁻-N concentrations entering the buffer were low compared to the other nearby buffer locations. This was most likely due to the buffer being located at a higher topographic location in relation to the upland source resulting in a smaller groundwater contributing area. Therefore, the width of this buffer might have been oversized for groundwater NO₃⁻-N concentrations entering the buffer. It was hypothesized that because of the relative wetness of lower Zone 2 and Zone 1, the potential for these reductions to be attributed to

denitrification was also high and the system may have been NO_3^- -N limited, but other components that affect denitrification rates were investigated (redox potential and dissolved organic carbon availability).

Redox Potential

Soil redox was used to determine denitrification potential in this buffer. Denitrification occurs in soils with low oxidation/reduction (redox) potentials. Reducing conditions have been reported at threshold values ranging between 250-400 mV, with values less than 200 mV being more conducive for denitrification (Patrick, 1960; Bailey and Beauchamp, 1973, Fielder *et. al*, 2007). Figure 3. 29 displays the overall mean redox potentials recorded for the shallow and deep depths within the center transect of the buffer. Mean redox values were generally below 200 mV indicating that soil conditions appeared to be favorable for denitrification. The buffer showed a general decrease in redox values from Zone 3 to Zone 1, which would be expected, due to the observed increase in relative wetness near the stream. Redox readings significantly decreased through the buffer; the statistical test also indicated the 1.5 m and 3 m redox readings were significantly different in Zone 3 and Zone 2 ($\alpha=0.05$). These results were expected since the water table elevations were periodically below the 1.5 m depth and would allow redox readings to increase when inundated conditions were no longer present.

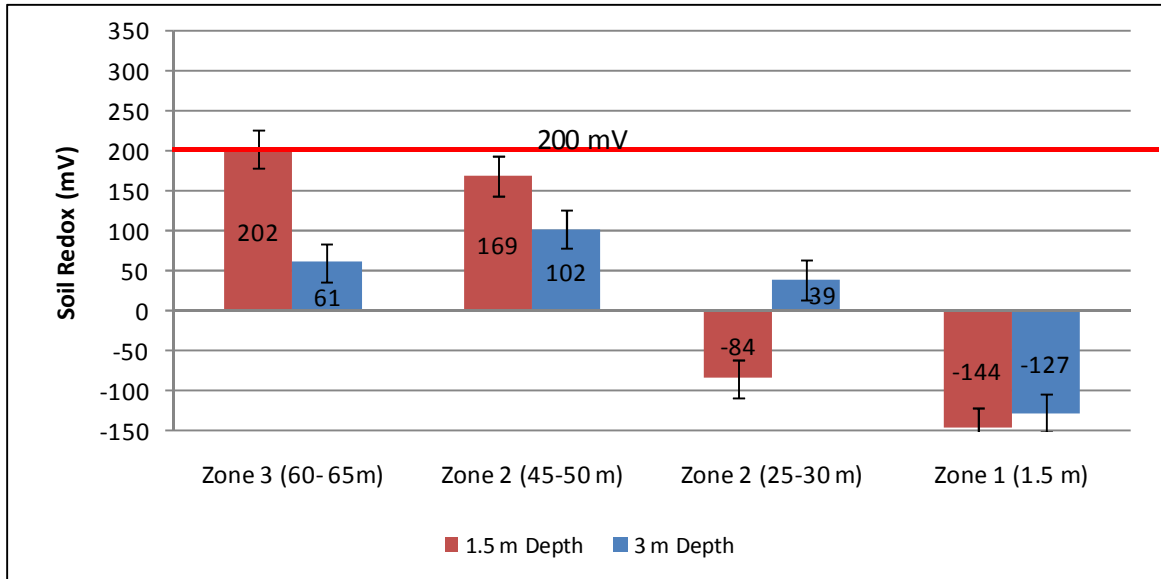


Figure 3. 29: Overall redox reading averages from June 2006 to May 2010 (n=60 total samples from each location). Note – error bars represent standard error.

A seasonal analysis was completed to evaluate the combined effects of water table elevation fluctuation and temperatures on redox readings. Redox probes, which were placed equivalent to the depth of the surficial monitoring wells, were below the water table surface during the majority of the year. Overall redox readings decreased from the Zone 3 to Zone 1 throughout the year and were below the threshold indicating reduced conditions majority of the year, especially in lower Zone 2 (30 m from the stream) and Zone 1 (1.5 m from the stream). Based on redox alone the potential for denitrification appeared high regardless of season in Zones 2 and 1 (Figure 3. 30).

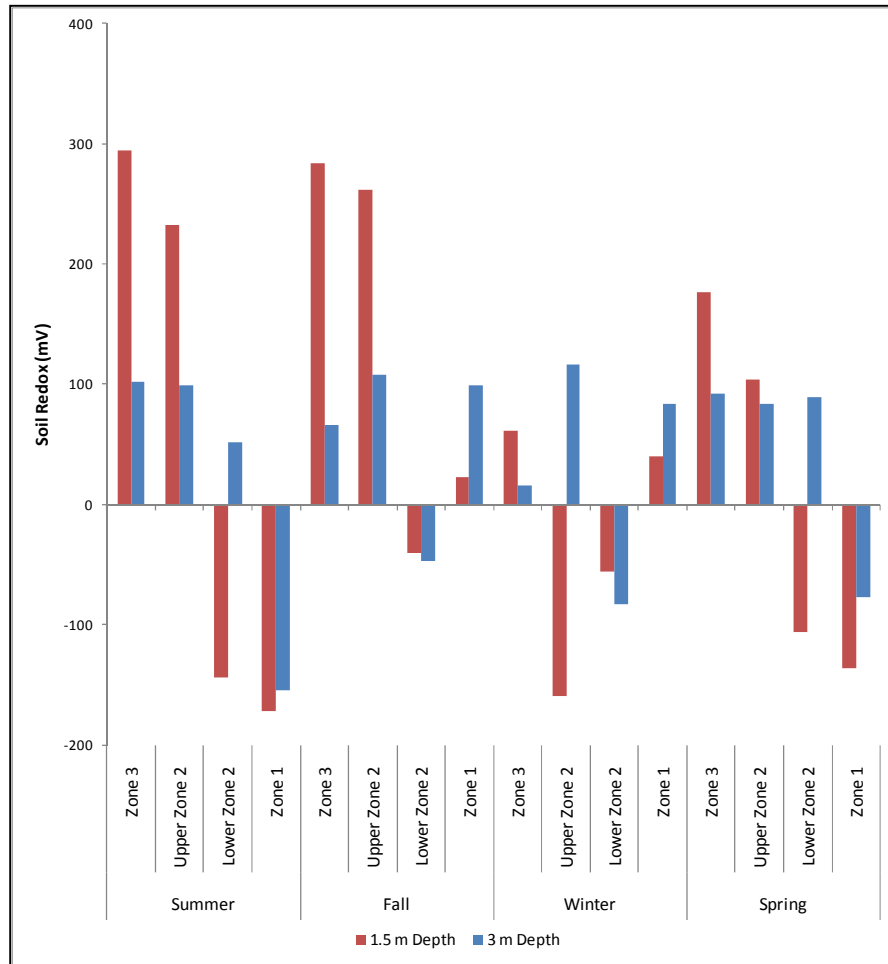


Figure 3. 30: Seasonal evaluation of redox readings in the buffer from Zone 3 to Zone 1 (n=45 during each season).

The highest redox readings, approximately 595 mV (Figure 3. 31), were seen during the summer and fall of 2008 and 2009 during which the water table elevations fell below the shallow redox probes depths in the upper Zone 2 (mid buffer) and Zone 3 (field edge) (Figure 3. 32 - Figure 3. 35). Redox readings had an increasing trend over the study period (Figure 3. 31 - Figure 3. 35). The trend was most likely due to the drop in water table levels during the extreme drought in 2007-2008, which never completely recovered by the end of this study. Although the

redox readings increased over the study period, the groundwater NO_3^- -N concentration reduction efficiency actually increased (Figure 3. 27 and Figure 3. 28). The groundwater NO_3^- -N concentrations most likely did not increase at the stream edge due to the necessary soil conditions for high denitrification rates still being maintained throughout majority of year. Even though the soil redox readings increased over time, the overall yearly average was well below the 200 mV threshold in Zones 2 and 1 (Figure 3. 31).

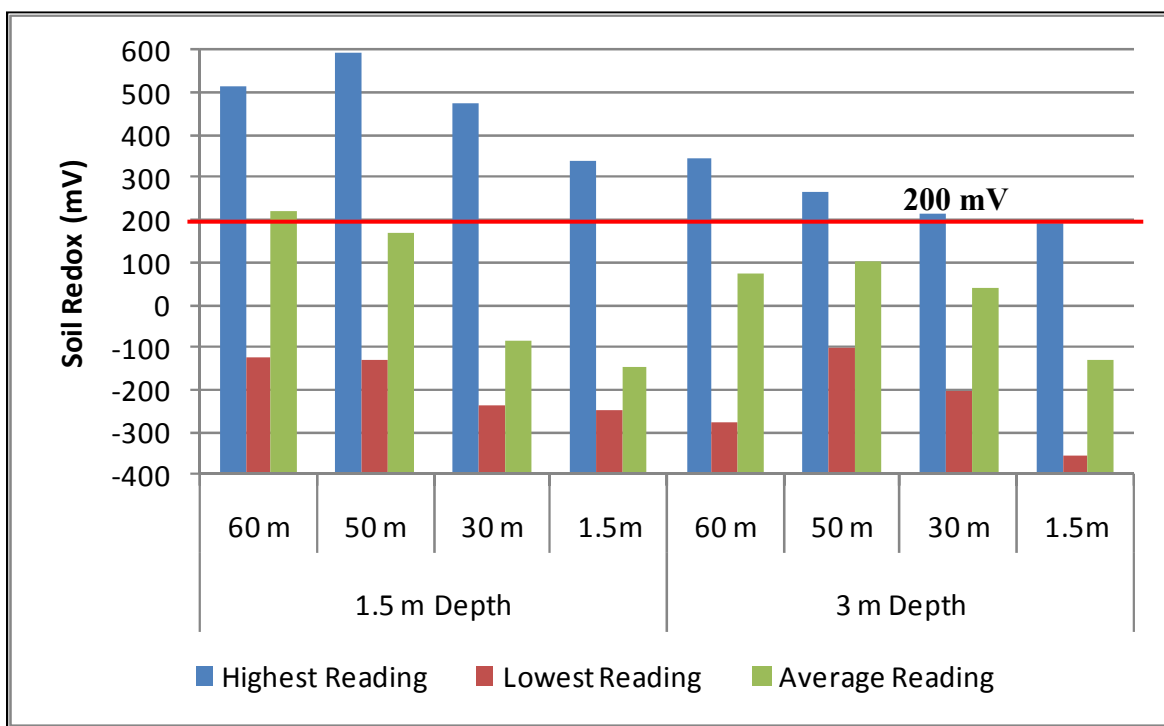


Figure 3. 31 Highest, lowest, and average soil redox readings at the 1.5 and 3 m soil depths at differing distances relative to the stream (June 2005 to April 2010).

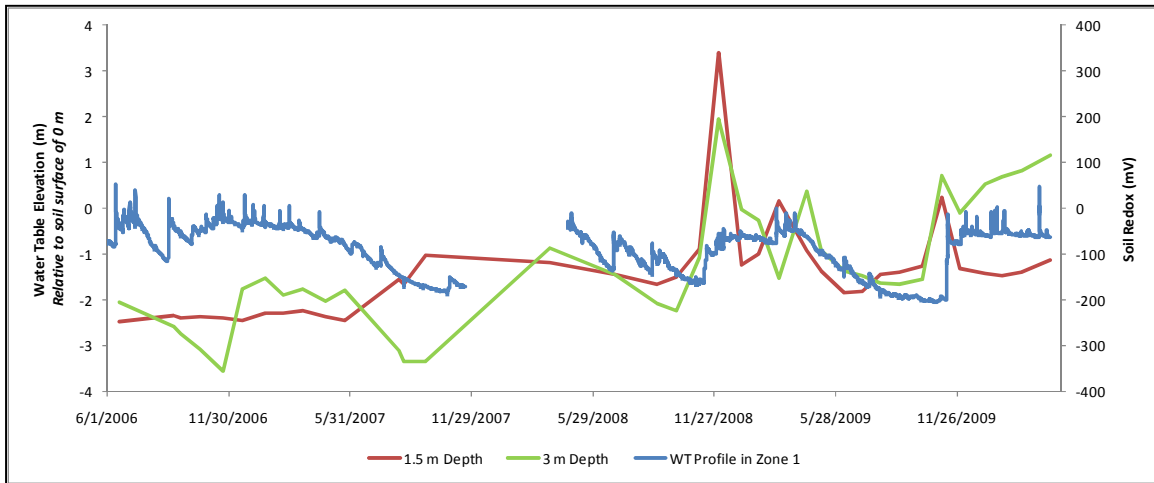


Figure 3.32: Zone 1 (stream edge) 5 averaged monthly redox readings with respect to water table elevation at same location (June 2005 to April 2010).

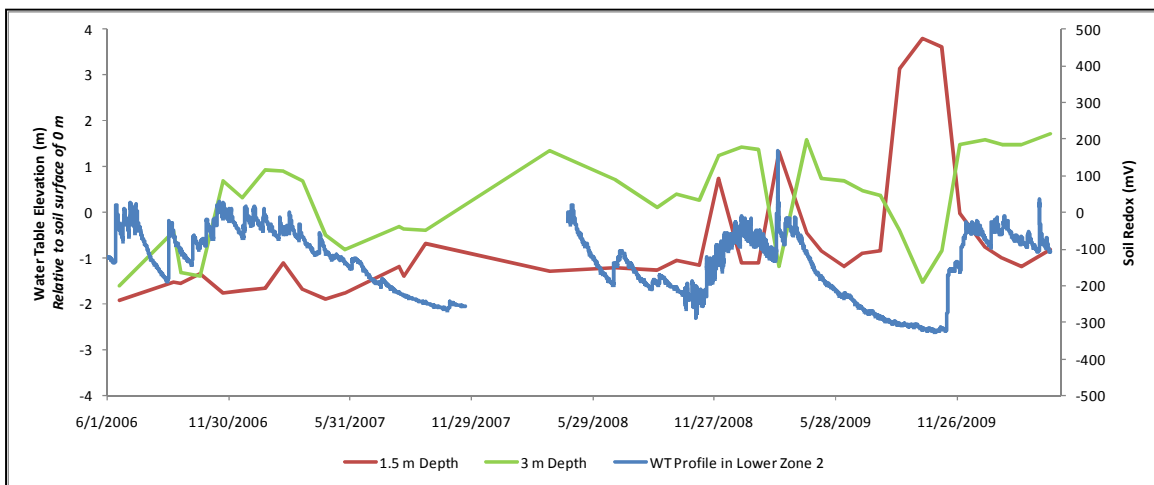


Figure 3.33: Lower Zone 2 (mid buffer) 5 averaged monthly redox readings with respect to water table elevation at same location (June 2005 to April 2010).

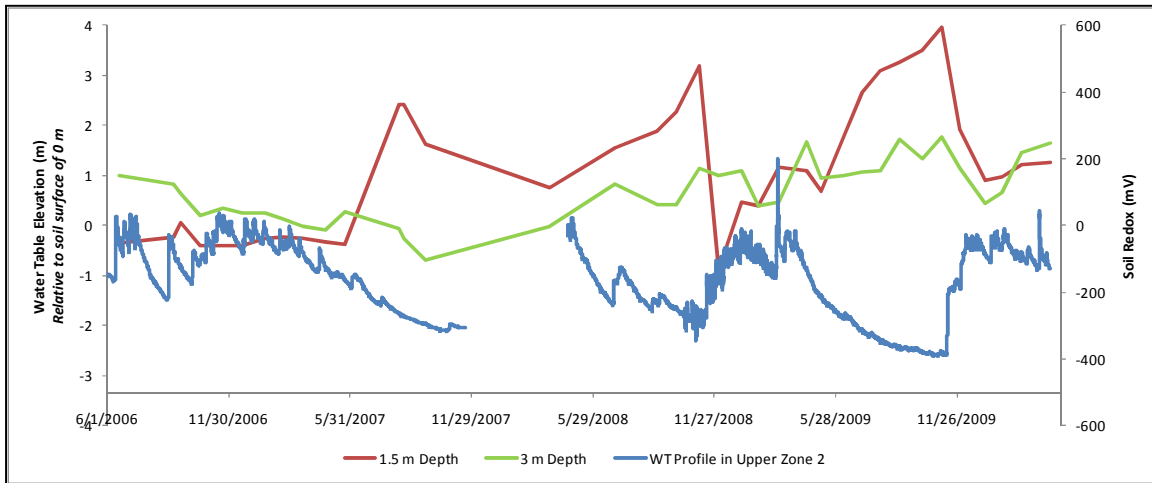


Figure 3.34: Upper Zone 2 (mid buffer) 5 averaged monthly redox readings with respect to water table elevation at same location (June 2005 to April 2010).

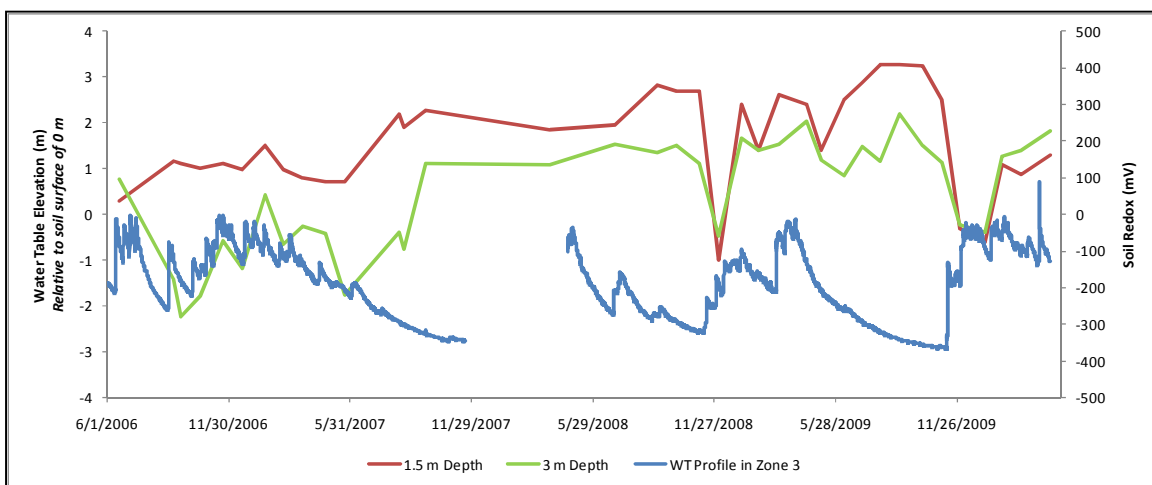


Figure 3.35: Zone 3 (field edge) 5 averaged monthly redox readings with respect to water table elevation at same location (June 2005 to April 2010).

High water tables in lower Zone 2 and Zone 1 during the warmest periods appeared to be ideal for denitrification to occur since microbial activity increases as temperature increases and carbon becomes more available (Knowles, 1982). Carbon source availability can be limiting to the denitrification process depending on vegetation and climatic season due to differences in

available litter (Hefting *et. al*, 2005). Since this site had high water table elevations as well as low redox readings throughout the year, available carbon was the final biogeochemical constituent evaluated to support denitrification within this buffer was only NO_3^- -N limited.

Dissolved Organic Carbon

A dissolved organic carbon (DOC) assessment was used to evaluate whether carbon was available in the groundwater to support denitrification. Organic carbon is critical because it serves as an electron donor for microbes during denitrification. Spruill *et. al* (1997) reported in a study completed in eastern North Carolina that water in shallow aquifers with more than 2-3 mg/L of DOC had groundwater NO_3^- -N concentrations of less than 2 mg/L, while aquifers with lower DOC had much higher groundwater NO_3^- -N concentrations. More recent laboratory studies indicate that DOC concentrations in the 4-8 mg/L range significantly improve denitrification rates (Knies, 2009).

The mean DOC concentrations in the groundwater beneath the buffer at the research site ranged from 2.9-21.2 mg/L. DOC concentrations were significantly different between the 1.5 m and 3 m depths in Zone 2 and 1 of the buffer ($\alpha=0.05$). Throughout most periods, DOC was higher at the 1.5 m depth than at the 3 m depth. The reduced DOC at the deeper depths may be responsible for the increased groundwater NO_3^- -N concentrations at the 3 m depth in Zone 1 (Figure 3. 25 and Figure 3. 26).

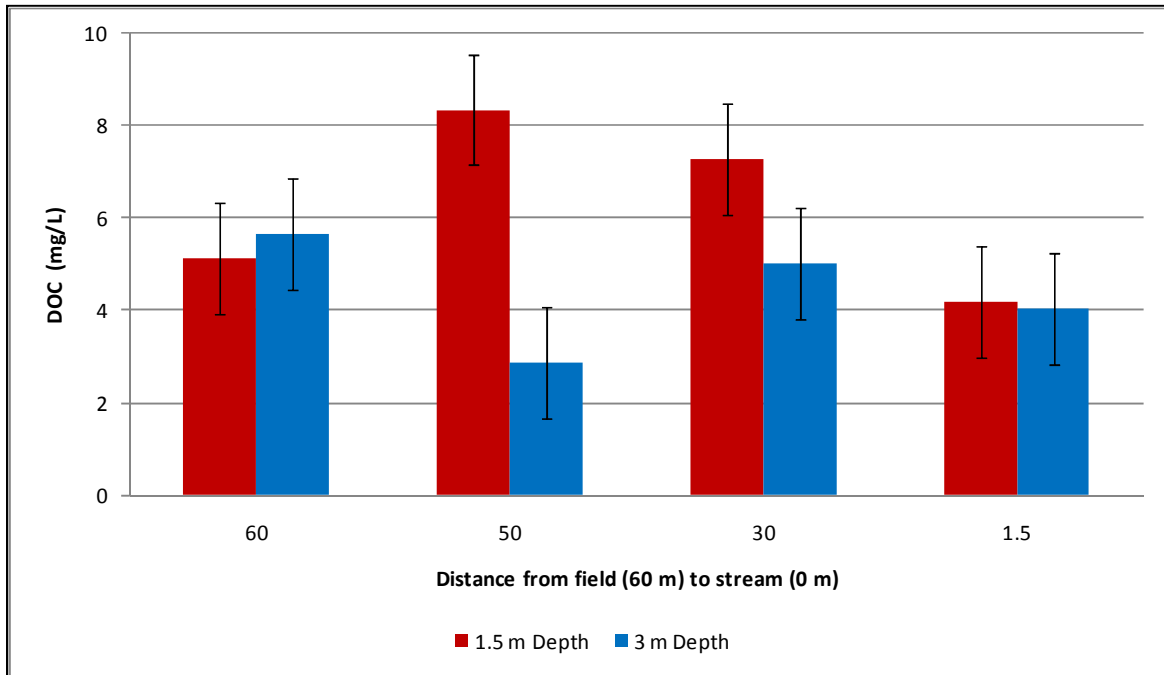


Figure 3. 36: Average DOC concentrations for research site (n=176). Note error bars represent standard error and outliers from suspected well contamination by dead animal or plant material were removed.

The DOC concentrations varied seasonally through the buffer from Zone 3 to Zone 1 (Figure 3. 36). DOC concentrations were highest in the winter and summer months (Figure 3. 36 and Figure 3. 37). Extremely high DOC concentrations along with H_2S gas were observed in water quality samples during the winter months of 2009 in Zone 3 and Zone 2. These high concentrations were believed to be from dead plant material or a dead animal creating a hot spot at the well locations. These samples were removed from the mean DOC calculation due to this suspected contamination (Figure 3. 36).

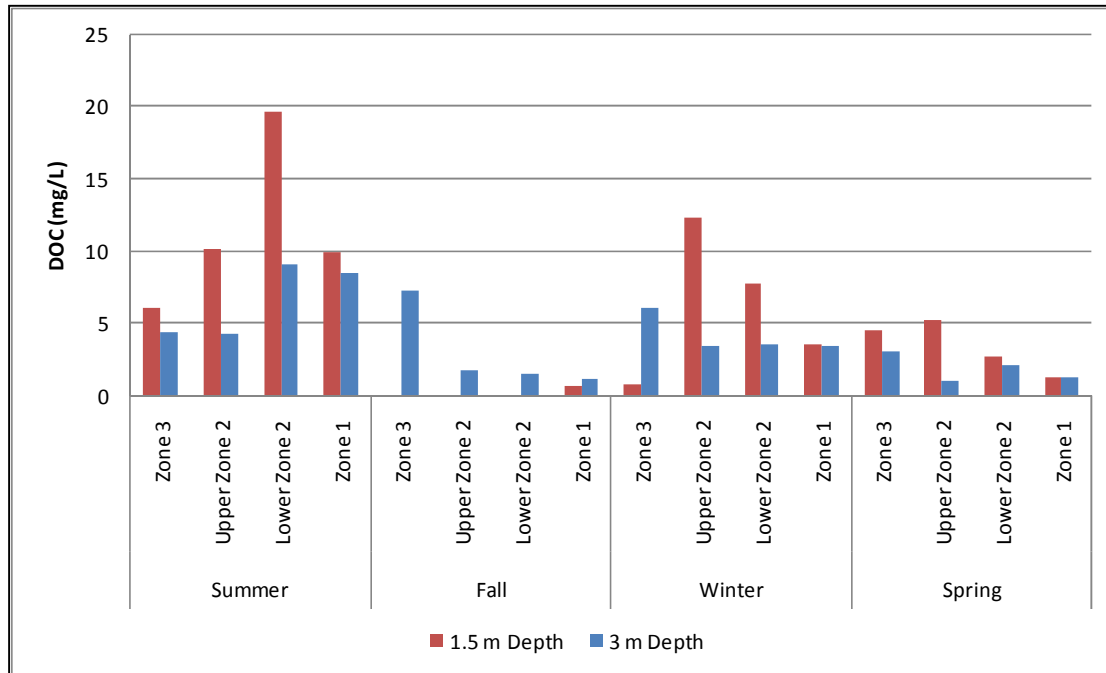


Figure 3. 37: Seasonal evaluation of DOC (n=176) from March 2008-May 2010. 1.5 m depth results for Zone 3 and Zone 2 for fall were unattainable due to low water table elevations at the research site at the time of sampling.

High DOC levels along with low redox readings support that denitrification was not limited during the summer months and was most likely the reason for increased groundwater NO_3^- -N reductions within the buffer. DOC samples at the 1.5 m depth were not available during the fall of 2008 or 2009 due to low water table elevations. During these dryer periods higher redox readings were also observed indicating conditions for denitrification were nearer to the threshold values. A correlation between groundwater NO_3^- -N concentrations and DOC concentrations was not observed most likely due to low groundwater NO_3^- -N concentrations entering the buffer throughout the year and carbon levels being high during the warmer periods.

These results further support that groundwater NO_3^- -N concentrations within the buffer were reduced through the process of denitrification. High water table elevations, low redox readings, and high DOC concentrations all support that the buffer had the required components for high rates of denitrification, but the system was NO_3^- -N limited. Despite these biogeochemical elements appearing available, before it could be established that denitrification was the primary mechanism responsible for groundwater NO_3^- -N reductions, groundwater dilution was investigated.

Denitrification Assessment Using NO_3^- -N to Cl^- Ratios

In an attempt to define whether denitrification or dilution was the cause for NO_3^- -N concentration reductions observed in the buffer, chloride (Cl^-) was also monitored in the groundwater. Lowrance (1992) along with other researchers have used this conservative ion (i.e. having minimal plant uptake and not undergoing microbial transformations in soil) from groundwater samples in riparian zones to provide evidence that denitrification and not dilution was responsible for observed groundwater NO_3^- -N losses. The evaluation of NO_3^- -N, Cl^- , and NO_3^- -N/ Cl^- ratios was therefore used to provide insight as to the process that was responsible for groundwater NO_3^- -N differences observed in the riparian buffer treatment (Figure 3. 38 and Figure 3. 39).

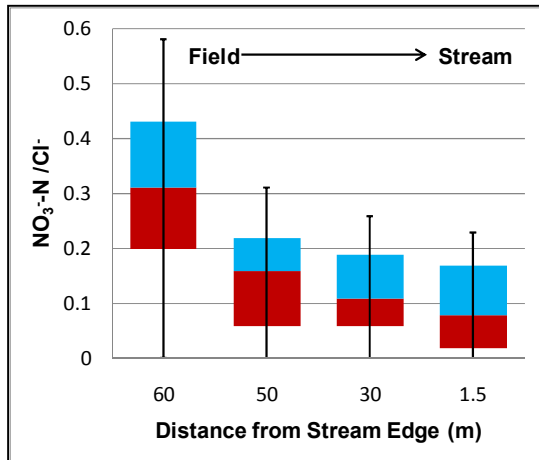


Figure 3. 38: The 25%, The 5%, 25%, median, 75%, and 95% percentiles of $\text{NO}_3^- \text{-N/Cl}^-$ ratio over the study for 1.5 m deep surficial wells at differing locations in the riparian buffer (n=55 water quality samples). Samples were taken from January 2005 – May 2010.

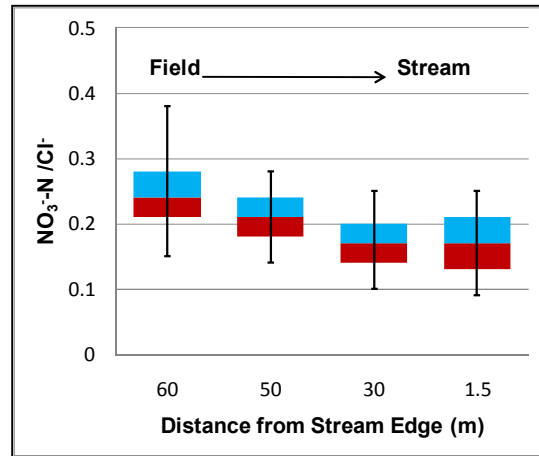


Figure 3. 39: The 25%, The 5%, 25%, median, 75%, and 95% percentiles of $\text{NO}_3^- \text{-N/Cl}^-$ ratio over the study for 3 m deep surficial wells at differing locations in the riparian buffer (n=67 water quality samples). Samples were taken from January 2005 – May 2010.

Mean groundwater $\text{NO}_3^- \text{-N/Cl}^-$ ratios from Zone 3 (field grassed filter strip) to Zone 1 (beside stream) decreased 74% in the 1.5 m deep groundwater, while mean groundwater $\text{NO}_3^- \text{-N}$ levels decreased 63%. Mean groundwater $\text{NO}_3^- \text{-N/Cl}^-$ ratios from Zone 3 (grassed filter strip) to the Zone 1 (beside stream) dropped 36% in the 3 m deep groundwater, while mean groundwater $\text{NO}_3^- \text{-N}$ levels from Zone 3 to Zone 1 decreased 15%. These percentages were greater than the mean groundwater $\text{NO}_3^- \text{-N}$ concentration reductions found in both the 1.5 m and 3 m surficial well depths (Figure 3. 23 and Figure 3. 24). These results alone provide strong evidence that majority of groundwater $\text{NO}_3^- \text{-N}$ concentration reductions could be attributed to denitrification since the decrease in the groundwater $\text{NO}_3^- \text{-N/Cl}^-$ ratios were similar to the decrease in $\text{NO}_3^- \text{-N}$ concentrations observed.

Realizing that groundwater NO_3^- -N/ Cl^- ratios could be influenced by changes in the observed groundwater Cl^- concentrations a more extensive evaluation was completed. Three criteria utilized by Dukes *et. al* (2002) were used in the study to determine the occurrence of groundwater dilution or NO_3^- -N reduction. They included: (1) a decrease in both NO_3^- -N and NO_3^- -N/ Cl^- ratios with an absence of significant changes in Cl^- concentrations indicated that NO_3^- -N was being removed through some other means than groundwater dilution, most likely denitrification below the root zones, (2) a decrease in NO_3^- -N and Cl^- concentrations with relatively constant NO_3^- -N / Cl^- ratios indicated groundwater dilution from a source below the surficial groundwater, and (3) a decrease in NO_3^- -N concentrations with an increase in Cl^- concentrations resulting in lower NO_3^- -N/ Cl^- ratios was inconclusive for predicting the cause for reduction in NO_3^- -N concentrations within the buffer. Two additional criteria were developed to be used in this study. These criteria were defined as: (4) a decrease in NO_3^- -N concentrations with constant Cl^- and NO_3^- -N/ Cl^- ratios, and (5) an increase in NO_3^- -N concentrations and variability in NO_3^- -N/ Cl^- ratios and Cl^- concentrations. Criteria 4 and 5 were all inconclusive for predicting the cause for reduction in NO_3^- -N concentrations within the buffer.

In all cases, potential dilution was assumed to originate from a deeper groundwater with lower concentrations of NO_3^- -N and Cl^- . Criteria 3 indicated the possibility of groundwater mixing between waters with low NO_3^- -N and high Cl^- concentrations diluting the NO_3^- -N concentrations, but denitrification could not be ruled out since deeper groundwater was found to have much lower Cl^- concentrations than surficial wells. Likewise, Criteria 4 would lead one to

suspect the occurrence of groundwater dilution between water with decreasing NO_3^- -N and Cl^- concentrations, but with decreasing NO_3^- -N/ Cl^- ratios denitrification could not be ruled out. Criteria 5 was inconclusive since NO_3^- -N concentrations were increasing. For this study the threshold for a decrease or increase was defined if a difference existed of more than 10 mg/L in Cl^- concentrations and 0.03 in NO_3^- -N / Cl^- ratios between Zones 3 and 2 (grassed filter strip to mid buffer) and Zones 2 and 1 (mid buffer to stream) (Johnson *et. al*, 2007). If differences were smaller than the specified values then concentrations were considered constant between zones during this evaluation. Seasonal differences are noted in Table 3. 7 through Table 3. 12. These differences were most likely caused by groundwater flow direction fluctuations and fertilizer applications.

Table 3. 7: Groundwater mixing conclusions based on NO_3^- -N and Cl^- concentrations, and NO_3^- -N/ Cl^- ratios for shallow groundwater in the downstream transect.

*** An increase in NO_3^- -N concentration between Upper Zone 2 and Lower Zone 2 occurred during Sept.-Feb.

*** An increase in NO_3^- -N / Cl^- concentration between Upper Zone 2 and Lower Zone 2 occurred during Sept.-Nov.

Location	NO_3^- -N	Cl^-	NO_3^- -N/ Cl^-	Conclusions
Zone 3 – Upper Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Upper Zone 2 – Lower Zone 2	↓	-	-	Not interpretable.
Lower Zone 2 – Zone 1	↓	-	↓	Nitrate decrease by other mean than dilution

Table 3. 8: Groundwater mixing conclusions based on NO_3^- -N and Cl^- concentrations, and NO_3^- -N/ Cl^- ratios for shallow groundwater in the center transect.

*** An increase in NO_3^- -N concentration between Lower Zone 2 and Zone 1 occurred during March-May.

*** An decrease in Cl^- concentration between Upper Zone 2 and Lower Zone 2 occurred during Dec.-Feb.

*** NO_3^- -N/ Cl^- concentration was constant between Upper Zone 2 and Lower Zone 2 during Dec.- Feb. and June-Aug.

*** NO_3^- -N/ Cl^- concentration was constant between Lower Zone 2 and Zone 1 during Dec.- Feb.

Location	NO_3^- -N	Cl^-	NO_3^- -N/ Cl^-	Conclusions
Zone 3 – Upper Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Upper Zone 2 – Lower Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Lower Zone 2 – Zone 1	↓	-	↓	Nitrate decrease by other mean than dilution

Table 3. 9: Groundwater mixing conclusions based on NO_3^- -N and Cl^- concentrations, and NO_3^- -N/ Cl^- ratios for shallow groundwater in upstream transect.

*** Does not change seasonally

Location	NO_3^- -N	Cl^-	NO_3^- -N/ Cl^-	Conclusions
Zone 3 – Upper Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Upper Zone 2 – Lower Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Lower Zone 2 – Zone 1	↑	-	↑	Not interpretable.

Table 3. 10: Groundwater mixing conclusions based on NO_3^- -N and Cl^- concentrations, and NO_3^- -N/ Cl^- ratios for deep groundwater in the upstream transect.

*** NO_3^- -N/ Cl^- concentration was constant between Lower Zone 2 and Zone 1 during Sept.-Nov.

Location	NO_3^- -N	Cl^-	NO_3^- -N/ Cl^-	Conclusions
Zone 3 – Upper Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Upper Zone 2 – Lower Zone 2	↓	-	-	Not interpretable.
Lower Zone 2 – Zone 1	↓	-	↓	Nitrate decrease by other mean than dilution

Table 3. 11: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for deep groundwater in the middle transect.

*** A decrease in NO₃⁻-N concentration between Lower Zone 2 and Zone 1 occurs during June – Aug.

*** NO₃⁻-N /Cl⁻ concentration was constant between Lower Zone 2 and Zone 1 during March-May.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Upper Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Upper Zone 2 – Lower Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Lower Zone 2 – Zone 1	↑	-	↓	Not interpretable.

Table 3. 12: Groundwater mixing conclusions based on NO₃⁻-N and Cl⁻ concentrations, and NO₃⁻-N/Cl⁻ ratios for deep groundwater in the upstream transect.

*** NO₃⁻-N /Cl⁻ concentration was constant between Lower Zone 2 and Zone 1 during March-May.

*** NO₃⁻-N /Cl⁻ concentration was constant between Upper Zone 2 and Lower Zone 2 during March-May.

Location	NO ₃ ⁻ -N	Cl ⁻	NO ₃ ⁻ -N/Cl ⁻	Conclusions
Zone 3 – Upper Zone 2	↓	-	-	Not interpretable.
Upper Zone 2 – Lower Zone 2	↓	-	↓	Nitrate decrease by other mean than dilution
Lower Zone 2 – Zone 1	↑	↑	↑	Not interpretable.

Evaluation criteria supported means other than dilution (likely denitrification) as the primary mechanism for groundwater NO₃⁻-N reduction in groundwater moving from Zone 3 to upper Zone 2 in 2 of the 3 deep well (3 m depth) areas and 3 of the 3 shallow (1.5 m depth) well areas. The criteria also supported that means other than dilution was responsible for observed groundwater NO₃⁻-N reductions in 2 of 3 deep well (3 m depth) areas and 2 of 3 shallow well (1.5 m depth) areas in groundwater moving from upper Zone 2 to lower Zone 2. Lastly, the criteria indicated that groundwater traveling from lower Zone 2 to Zone 1 to have groundwater NO₃⁻-N reduction by means other than dilution in 1 of the 3 deep well (3 m depth) areas and 2 of

the 3 shallow (1.5 m depth) areas. All other well locations could not rule out denitrification based on Criteria 4 and 5.

It is not apparent why these zones within close proximity to one another would show this variability. The differences that lead to inconclusive results may be explained by soil heterogeneity within the buffer or seasonally variable groundwater flow through the buffer. Seasonal differences were noted in Table 3.7 - Table 3.12 and most likely were caused from groundwater direction changes due to fluctuating water table elevations and fertilizer applications.

Utilization of these criteria would be optimal if groundwater Cl^- concentrations remained stable through the buffer. Cl^- concentrations measured within the buffer were variable, although not significant, and ranged from 8.05 to 74.86 mg/L, with averages between 9.5 and 16.4 mg/L dependent on well location. The higher concentrations in Cl^- often occurred during the winter and spring months, which may be a result from upland fertilizer applications. Using the NO_3^- -N/ Cl^- ratio method to determine the primary mechanism for groundwater NO_3^- -N removal was made more complicated due to these variations in Cl^- concentrations.

In summary, groundwater NO_3^- -N along with NO_3^- -N/ Cl^- ratios had similar decreases supporting denitrification was the primary groundwater NO_3^- -N reduction mechanism. Using Criteria 1-5 described above, NO_3^- -N/ Cl^- ratios supported that 12 of 18 groundwater monitoring areas had reductions in groundwater NO_3^- -N within the buffer most likely due to denitrification. Although these results support denitrification was the predominant reducing mechanism for

groundwater NO_3^- -N, complications due the large range in Cl^- concentrations required further investigations to confirm whether denitrification or dilution was occurring. Therefore, chemical signatures of the surficial and deeper aquifers were examined to identify mixing potential.

Potential Mixing Between Surficial and Deeper Aquifers

Previously, soil borings had indicated a restrictive layer at about 4.6 m (15 ft) below the ground surface that likely separated the surficial and the deeper aquifers. However, the number of deep borings was limited, and was not extensive enough to determine if this layer existed across the entire buffer. Groundwater quality data was compared between surficial and deeper aquifers to identify mixing potential between the two layers to continue the investigation on why groundwater NO_3^- -N loss was observed across the buffer. Na^+ , Ca^{2+} , NO_3^- -N, and Cl^- were the constituents evaluated.

Significant chemical differences between NO_3^- -N, Ca^{2+} , and Cl^- concentrations occurred in the surficial and deeper aquifers as shown in Figure 3. 40 - Figure 3. 44 ($\alpha=0.05$). Water in the deeper aquifer (8 and 11 m deep) was much lower in Cl^- and higher in Ca^{2+} than in the surficial aquifer (1.5 and 3 m deep) indicating dilution was minimal. However, NO_3^- -N concentrations in the deep surficial wells at 3 m were at higher concentrations than at 1.5 m, so dilution through upwelling appeared an unlikely major contributor to decreased concentrations (Figure 3. 40 and Figure 3. 41).

The difference in groundwater signatures provided strong evidence that mixing was unlikely between waters in the deeper and surficial aquifer. However, the waters in the 1.5 m and 3 m depth did appear to have the same chemistry, since Cl^- , Na^+ , and Ca^{2+} concentrations all appeared similar. Groundwater NO_3^- -N concentrations were the exception – they appeared similar at the field edge Zone 3 only. The concentrations decreased as the groundwater moved through the buffer into Zone 1, while concentrations of the other ions remained within a stable range.

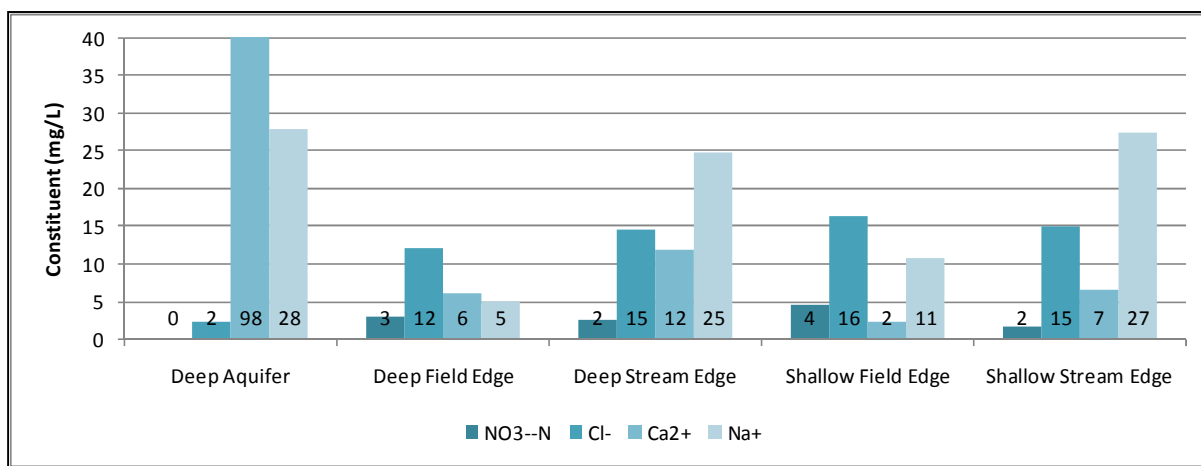


Figure 3. 40: Means deeper aquifer compared to means of shallow, and deep water quality constituents at the stream and field edge of the riparian buffer treatment system (1.5 m, 3 m, 8 m, and 11 m were 78, 120, 60, and 20 respectively for NO_3^- -N and Chloride; 1.5 m, 3 m, 8 m, and 11 m were 53, 87, 60, and 20 respectively for calcium and sodium). Make note that the calcium quantity in the deep aquifer was cut off for viewing purposes.

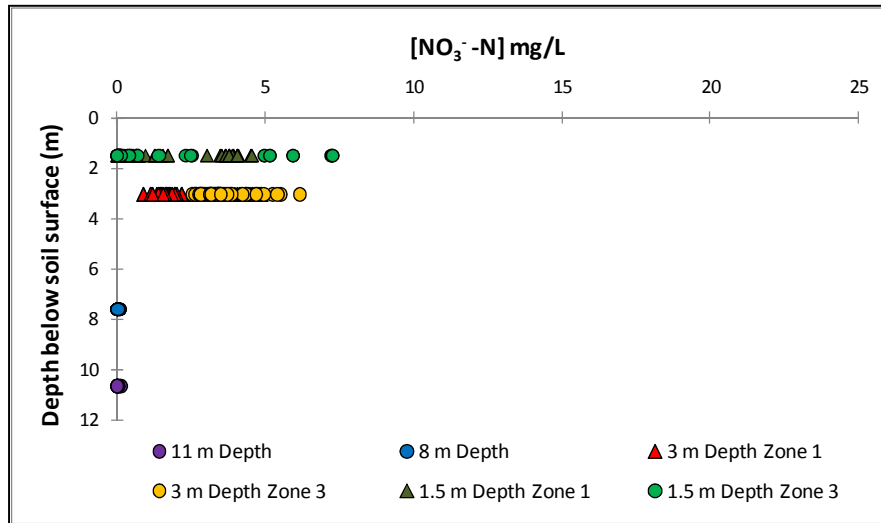


Figure 3. 41: $\text{NO}_3\text{-N}$ concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 78, 120, 60, and 20 respectively.

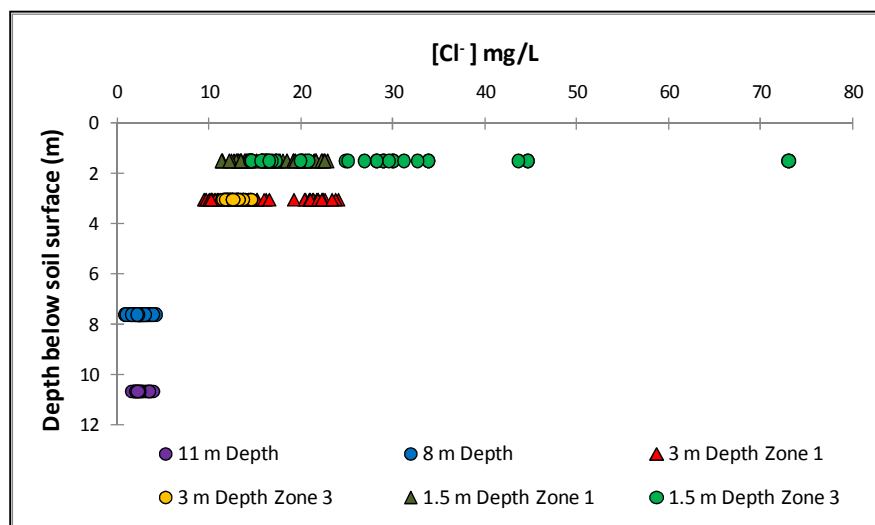


Figure 3. 42: Chloride concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 78, 120, 60, and 20 respectively.

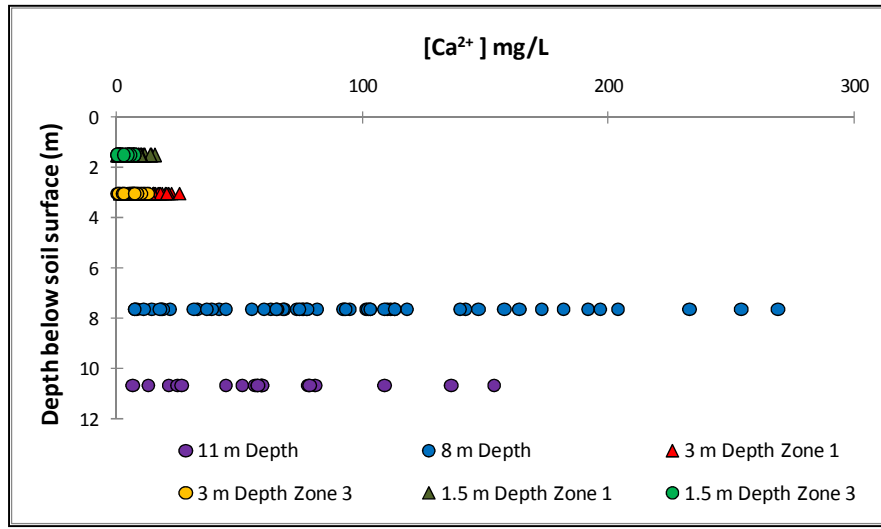


Figure 3. 43: Calcium concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 53, 87, 60, and 20 respectively.

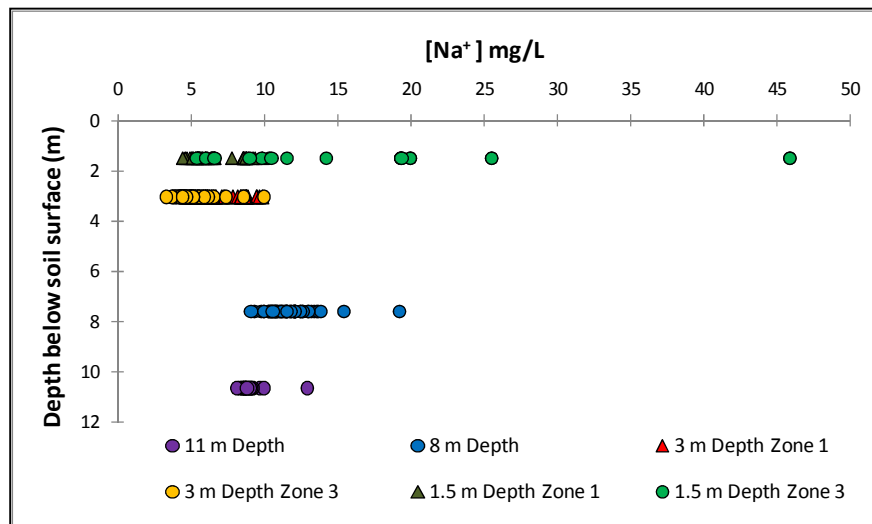


Figure 3. 44: Sodium concentrations at sampled depths. Quantity of samples collected at 1.5 m, 3 m, 8 m, and 11 m were 53, 87, 60, and 20 respectively.

Additional evidence of these waters being separated can be seen in paired bivariate plots (Figure 3. 45 and Figure 3. 46). The comparison of NO_3^- -N to Ca^{2+} and Na^+ concentrations display that as NO_3^- -N concentrations are decreasing the Ca^{2+} and Na^+ remained constant at both

the field edge and stream edge in the surficial aquifer. Ca^{2+} concentrations were significantly different between the deeper and surficial aquifers, while the Na^+ concentrations were inconclusive. However, if dilution would have been the predominant reducing mechanism within the riparian buffer system, the Ca^{2+} would have increased as approaching the stream. Since the Ca^{2+} remained constant at both the 1.5 m and 3 m depths, dilution appears minimal from these results.

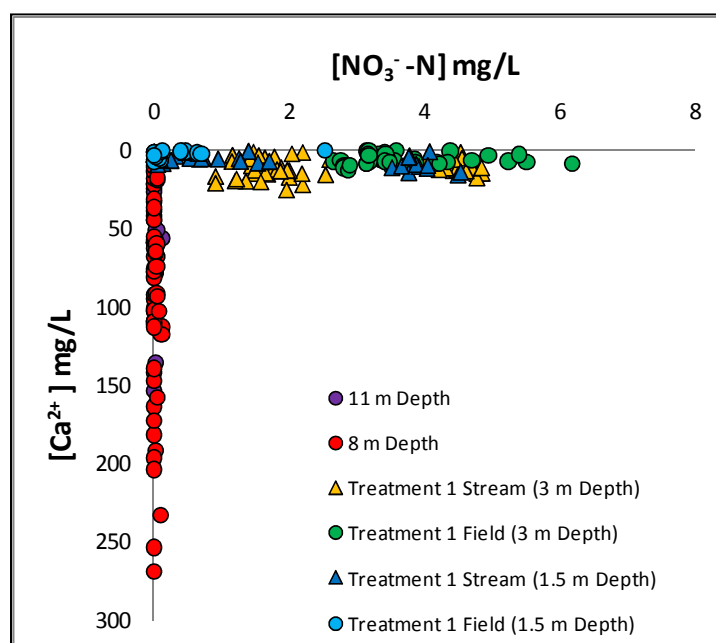


Figure 3. 45: $\text{NO}_3^- - \text{N}$ concentrations compared to calcium concentrations. Quantity of samples collected at 1.5 m, 3 m, and the deeper aquifer were 53, 87, and 80 respectively.

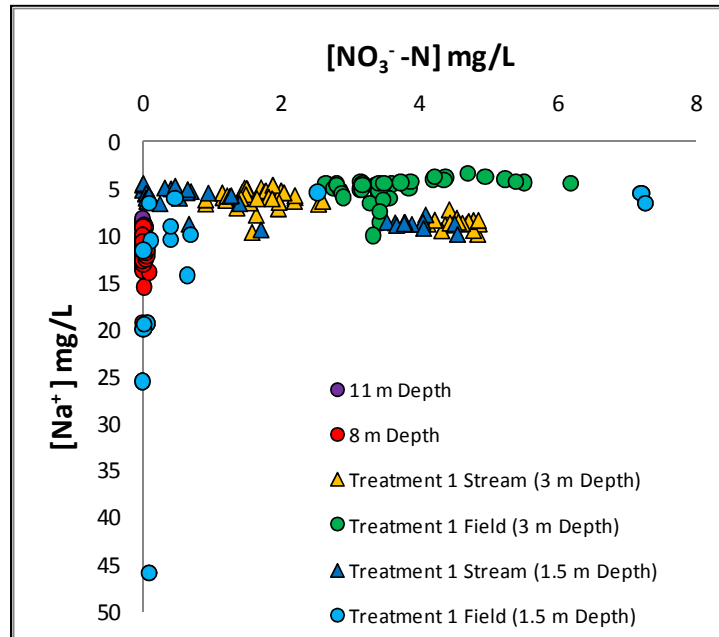


Figure 3. 46: NO_3^- -N concentrations compared to sodium concentrations. Quantity of samples collected at 1.5 m, 3 m, and the deeper aquifer were 53, 87, and 80 respectively.

All water quality observations from the chemical analysis of the surficial and deeper aquifers supported our hypothesis that the two waters are ultimately separated. Therefore, the groundwater signatures further support that biological activity, presumably denitrification, was the primary mechanism for groundwater NO_3^- -N reduction in this buffer. The hydrology assessment, soil redox, and groundwater DOC measurements discussed in the previous sections also support the hypothesis that denitrification was the primary groundwater NO_3^- -N reducing mechanism in this buffer system.

NO₃⁻-N Removal Evaluation through Riparian System

The overall measured groundwater NO₃⁻-N mass removal at the 1.5 m and 3 m water quality monitoring depths was calculated using Darcy's Law and the Dupuit-Forchheimer equation to determine the mass of groundwater NO₃⁻-N discharged each year to the stream on a per area basis. Nitrogen was applied to the upland fields at agronomic rates as shown in Table 1 in Appendix E. The total removed groundwater NO₃⁻-N mass estimations through Zones 3 through 1 were calculated and can be found in Table 3. 13.

Table 3. 13: NO₃⁻-N removal per year for varying depths and zones of the studied riparian buffer treatment system.

Depth (cm)	90 cm Soil Layer	240 cm Soil Layer	Total
Total NO₃⁻-N Removed in Buffer Treatment System (kg N yr⁻¹)	12	-2	10
Total NO₃⁻-N Removed in Buffer Treatment System (kg N yr⁻¹ m²)	0.003	-0.0004	0.0026

Groundwater NO₃⁻-N entering Zone 3 of the buffer was estimated to be 17 kg N yr⁻¹ and 14 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. Groundwater NO₃⁻-N leaving the buffer and discharging into the stream was 4 kg N yr⁻¹ and 15 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. The monitored depths in Section 1 were reducing groundwater NO₃⁻-N by 0.003 kg N yr⁻¹ m⁻² (76 %) for the 90 cm depth soil layer and 240 cm depth soil layer. These results were similar compared to results that Lowrance *et al.* (1995) reported with removal rates of approximately 20 to 39 kg N ha⁻¹ yr⁻¹.

(0.002 - 0.0039 kg N m⁻² yr⁻¹). All of these results indicate the buffer was effectively reducing incoming groundwater NO₃⁻-N and removing NO₃⁻-N prior to groundwater entry into the stream.

CONCLUSIONS

Hydrologic and groundwater quality results of this buffer indicated that the buffer was NO_3^- -N limited, therefore constraining denitrification rates within the system. However, at the 3 m depth, mean groundwater NO_3^- -N levels decreased by 15% from Zone 3 to Zone 1, while at the 1.5 m depth groundwater NO_3^- -N levels decreased by 63% indicating the buffer was reducing groundwater NO_3^- -N. Although these percent differences seemed large, the mass of groundwater NO_3^- -N reduction was low for the size of this buffer due to the low concentrations entering the buffer. Hydrologic evaluations supported that NO_3^- -N laden groundwater from the adjacent field was often bypassing the riparian buffer and flowing to a lower topographic location periods of the year. Water table elevations were high (within 3 m of the soil surface) throughout the year, but wetland hydrology was absent throughout the entire system.

The topographic location of the buffer had a noteworthy effect on the groundwater NO_3^- -N concentrations entering the buffer due to a small groundwater contributing area from the adjacent agricultural field. Since the topographic location was at a higher elevation relative to other buffer locations at the site, the concentrations of NO_3^- -N laden groundwater entering the buffer was lower than expected. Furthermore, the higher topographic location resulted in variability in flow direction of NO_3^- -N laden groundwater allowing groundwater from the adjacent field to intermittently bypass the buffer. Although the groundwater NO_3^- -N concentrations were lower than expected, the buffer did often have high water table elevations

and groundwater flowing toward the stream during other portions of the year allowing groundwater NO_3^- -N to reach denitrifying microsites, particularly in Zones 1 and 2.

Regardless of the low concentrations of NO_3^- -N laden groundwater entering the buffer treatment, water quality data indicated denitrification was the predominant groundwater NO_3^- -N reduction mechanism. Redox readings were found to be below 200 mV in lower Zone 2 and Zone 1 throughout the year indicating reduced conditions critical for denitrification. Residence time and groundwater flow velocity were within suitable ranges for denitrification to occur within the system. DOC concentrations were found to not be limiting during the summer for denitrification to occur within both the 1.5 m and 3 m soil depths. NO_3^- -N and NO_3^- -N/ Cl^- ratios had similar decreases from Zone 3 to Zone 1 and NO_3^- -N/ Cl^- ratios indicated that 12 of 18 groundwater monitoring areas had reductions in groundwater NO_3^- -N within the buffer most likely due to denitrification. The surficial and deeper aquifer water quality assessment indicated dilution to be minimal as well. The two waters were found to have different water quality signatures.

Groundwater NO_3^- -N mass removal in the riparian buffer was estimated to be 10 kgN yr^{-1} ($0.003 \text{ kg N m}^{-2} \text{ yr}^{-1}$). Groundwater NO_3^- -N leaving the buffer and discharging into the stream was estimated to be 4 kg N yr^{-1} and 15 kg N yr^{-1} for the 90 cm depth soil layer and 240 cm depth soil layer, respectively indicating the buffer was reducing groundwater NO_3^- -N by 76 % at the 90 cm depth soil layer and 240 cm depth soil layer.

High water table elevations along with groundwater NO_3^- -N concentration reductions, redox readings, and sufficient DOC concentrations during warmer seasons all lead to ideal soil environments for denitrification to occur. Although all these results indicate groundwater NO_3^- -N was being reduced by denitrification in 1.5 m depth, low groundwater NO_3^- -N concentrations entering the buffer further verified the buffer was NO_3^- -N limited. Therefore, future buffer enrollments in locations receiving low groundwater NO_3^- -N concentrations could be more narrow than this buffer. The buffer had all of the required components to enhance denitrification, but due to the limitation of groundwater NO_3^- -N entering the system, the system most likely could have just as effectively worked at a much smaller width. Assessments must be completed to identify hydrologic and biogeochemical traits of future buffer locations and design buffers to meet water quality goals. Completing these assessments and enrolling and designing buffers to meet water quality goals will maximize the groundwater NO_3^- -N removal impact of buffers enrolled in these conservation programs, while minimizing lands removed from agricultural production.

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CHAPTER 4: GROUNDWATER NITRATE REDUCTIONS WITHIN UPSTREAM AND DOWNSTREAM SECTIONS OF A RIPARIAN BUFFER

ABSTRACT

Defining ideal design and placement of riparian buffers enrolled in conservation programs could maximize stream miles protected and improve downstream water quality in sensitive streams and estuaries. During the past five years, effects on nitrate reduction efficiency of two riparian buffers with differing widths and landscape positions enrolled in the North Carolina Reserve Enhancement Program (NC CREP) have been assessed. The average buffer widths were 60 m (Section 1) and 43 m (Section 2). Well nests were installed in three transects within each buffer to monitor shallow (1.5-2.3 m) and deep (2.7-3.6 m) groundwater nitrate levels. Upslope agricultural practices have included soybeans, peanuts, cotton and corn production.

Nitrate decreased at the 1.5 m depth through the buffers from Zone 3 (grassed filter strip near the field) to Zone 1 (stream edge) with average nitrate concentrations of 4.5 to 1.7 mg/L and 12.9 to 1.4 mg/L in Section 1 and Section 2 respectively. Likewise, nitrate decreased through the buffers from Zone 3 to Zone 1 at the 3 m depth with average nitrate concentrations of 2.9 to 2.5 mg/L and 12.8 to 6.0 mg/L for Section 1 and Section 2 respectively. Water table measurements, topographic surveys, groundwater velocities, residence times, redox measurements, dissolved

organic carbon (DOC), nitrate to chloride ratios, and deep groundwater quality analyses indicated the primary mechanism for these decreases in both sections was likely denitrification rather than groundwater dilution. The nitrate mass removal was also calculated to determine the effectiveness of each section of the riparian buffer.

The groundwater nitrate concentrations entering each section's Zone 3 were significantly different and had a significant impact on overall nitrate mass removal at the 1.5 m and 3 m depths. Therefore, the study provides a comparison of the critical impacts of differences in pollutant source concentrations entering the buffer sections, and provides recommendations as to how to design buffers to account for these differences. The study illustrates that an understanding of local hydrologic and biogeochemical factors are important to buffer design prior to buffer installation for these systems to meet effectively and efficiently water quality goals.

INTRODUCTION

Riparian buffers are important BMPs for protecting streams from pollution by treating surface runoff and shallow groundwater. They can be effective in treating NO_3^- -N laden groundwater only if it slowly moves through buffers at soil depths where conditions are ideal for denitrification. Therefore, designing and implementing buffers at sites with hydrologic and biogeochemical regimes ideal for denitrification is imperative to maximize NO_3^- -N removal potential.

Requirements for denitrification within buffer soils include a source of nitrate, anoxic conditions (indicated by low redox values), a carbon source that can act as an electron donor, suitable temperature, and suitable pH conditions (Postma *et al.*, 1991; Puckett, 2004; Korom, 1992). Optimal NO_3^- -N removal by denitrification in these systems requires groundwater rich in NO_3^- -N flowing through these soil layers with all required components that enhance denitrification. Several studies have investigated the physical, hydrological, and biogeochemical properties that increase reductions of NO_3^- -N through denitrification in these systems (Spruill, 2004; Evans *et. al*, 2007; Gilliam, 1994).

The physical makeup of riparian buffers and the effects of increased buffer widths on NO_3^- -N reduction have been increasingly studied to investigate the benefits of taking these areas out of agricultural production. Dukes' *et al.* (2002) study on four riparian buffers with differing widths concluded that a wider plot (15 m) had a 15% larger reduction of NO_3^- -N concentrations compared to the narrower plot (8 m), with differences attributed to increased residence times

through the buffer. Mayer *et. al* (2007) estimated buffer NO_3^- -N reduction through a meta-analysis of 89 buffers with variable widths. NO_3^- -N reduction was found to significantly increase as widths increased from 0-25 m. However, increasing width from 25-50 m did not significantly increase NO_3^- -N removal. Findings were attributed to higher water tables and carbon availability in buffer portions that were closest to the stream, resulting in more suitable conditions for denitrification to occur. Angier's *et al.* (2008) study of a riparian buffer examined widths varying from 60 to 250 m. Topographic differences along the buffer's field edge allowed one portion of the buffer to receive higher concentrations of NO_3^- -N than upstream portions making comparisons difficult. The study concluded that NO_3^- -N reduction is not only dependent on buffer width, but also groundwater flow direction and depth.

Additional studies have reported that ideal buffer placement is highly dependent on not only the physical dimensions of the buffer, but also on topographic location relative to adjacent pollutant sources, soil zones, water table elevation, and dissolved organic carbon availability (Devito *et al.*, 2000; Hill *et al.*, 2000; Dukes *et. al*, 2002; Clément *et al.*, 2002; Lowrance *et al.*, 1995, 1992; Hefting *et. al*, 2005; Böhlke *et al.*, 2007; Puckett and Hughes, 2005; Vidon *et al.*, 2004; Schiff *et. al*, 2002). The importance of buffer width therefore cannot be assumed the solitary answer to increasing NO_3^- -N reduction efficiency within these systems. Buffer placement in locations that are hydrologically and biogeochemically adequate for denitrification to take place is equally, if not more, critical for NO_3^- -N reduction.

The fundamentals of riparian buffers performance are understood well enough for conservation programs to encourage their use as BMPs to protect water quality. However, research is still needed to identify and study riparian buffer locations that have suitable hydrologic and biogeochemical conditions to maximize denitrification. Once these sites are identified, research is also needed to help determine minimum widths required to provide adequate NO_3^- -N treatment. Site specific NO_3^- -N concentrations, denitrification potential, and water quality goals should determine the widths of riparian buffers, rather than allowing widths to be determined from site conditions alone.

A detailed evaluation of the hydrology and attenuation of groundwater NO_3^- -N was conducted in this study on two sections of buffer along the same stream. These sections had two distinct widths, but were also in two distinct landscape positions. Originally, a comparison of the effects of buffer width on NO_3^- -N reductions within these sections was to be evaluated. However, significant differences in both the hydrology within each buffer section and the groundwater NO_3^- -N concentrations entering the two buffer sections prohibited a direct evaluation of width effects. Therefore, an evaluation of the physical, hydrological, and biogeochemical characteristics influencing the potential for groundwater NO_3^- -N reduction was completed within each of the two buffer sections. This chapter attempts to compare the differences between these buffer sections to provide a clear illustration of the necessity of preliminary evaluations prior to buffer installation. Although often logistically challenging in

conservation programs, initial site evaluations could result in the protection of more stream miles if buffers are designed with respect to current and future incoming pollutant concentrations.

MATERIALS AND METHODS

Comparisons of the two buffer sections are presented with respect to landscape position, width, hydrology (groundwater elevations, direction, and velocity), groundwater NO_3^- -N concentrations entering and leaving, soil biogeochemistry (soil redox, DOC, cations), groundwater mixing/dilution, and NO_3^- -N mass removal estimates. The following sections highlight the methods used to collect data at the site and how the two buffer sections were analyzed. Please refer to the MATERIALS and METHODS sections in Chapters 2 and 3 for more detailed information on equipment installation, sampling procedures, and data analyses for each of the buffer sections.

Site Description

The research buffers were designed and installed in 1999 by members of the North Carolina Division of Soil and Water, who oversee the CREP program, prior to initiation of this study (Figure 4. 1). The total length of the combined buffer sections was approximately 304 m (1000 ft). Section 1 (discussed in Chapter 3) had an average width of 60 m (197 ft), while Section 2 (discussed in Chapter 2) had an average width of 43 m (141 ft). Vegetation and soils within Sections 1 and 2 were relatively similar. However, Zone 2 of Section 2 had poor tree survival and higher quantities of herbaceous wetland vegetation than in Zone 2 of Section 1.

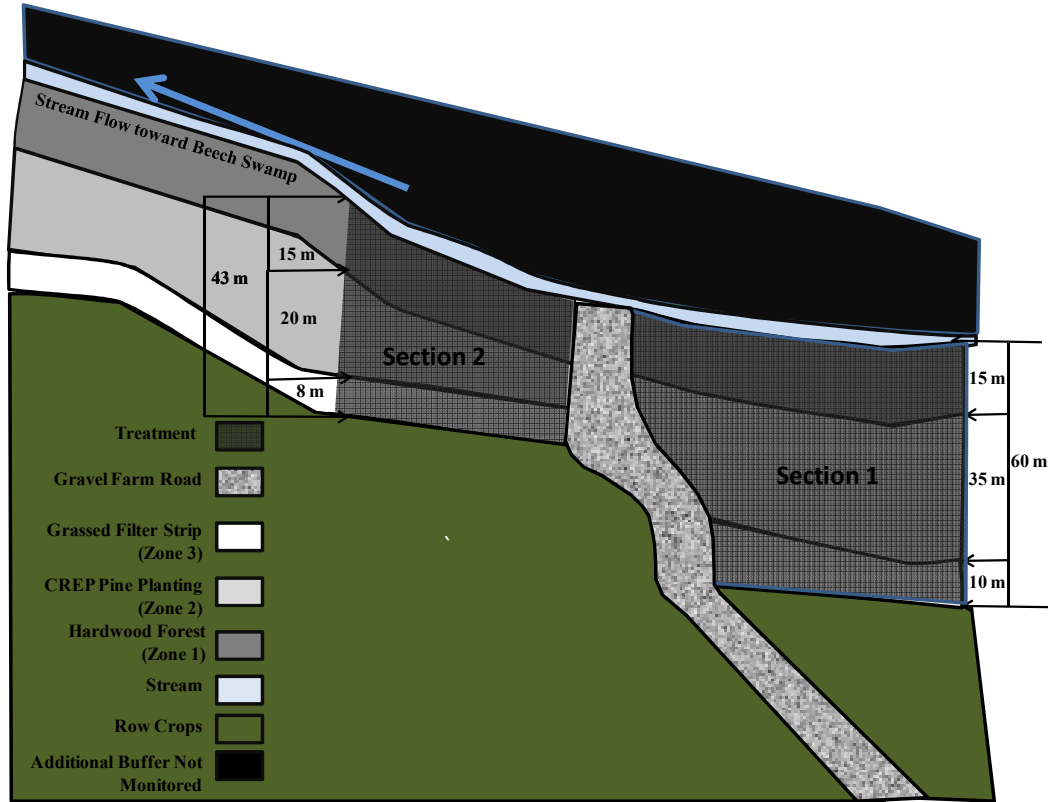


Figure 4. 1: Land cover for research site (Not to Scale).

Instrumentation Installation

Surficial groundwater monitoring well nests (12 in Section 1 and 9 in Section 2) were installed in three transects 15 m (50 ft) apart within each section in December 2004 (Figure 4. 2). Each well nest contained a shallow and deep well with maximum depths ranging between 1.5 to 2.3 m (5 to 7 ft) and 2.7 to 3.6 m (9 to 12 ft) respectively and screened 0.6 m (2ft) above the maximum depth. Section 1 had an upslope additional well nest in each transect to account for its wider width. In June 2008, four deeper aquifer wells were installed at the site to further monitor deep groundwater to assess any mixing with the surficial groundwater in both Section 1 and

Section 2. Three water table elevation data loggers (Infinites USA, Inc., Port Orange, FL) with built in pressure sensors were installed in the center transect of each section next to each water quality well nest. Locations of well nests and the water table elevation data loggers can be found in Table 4. 1 and Table 4. 2 (distances are relative to the stream edge).

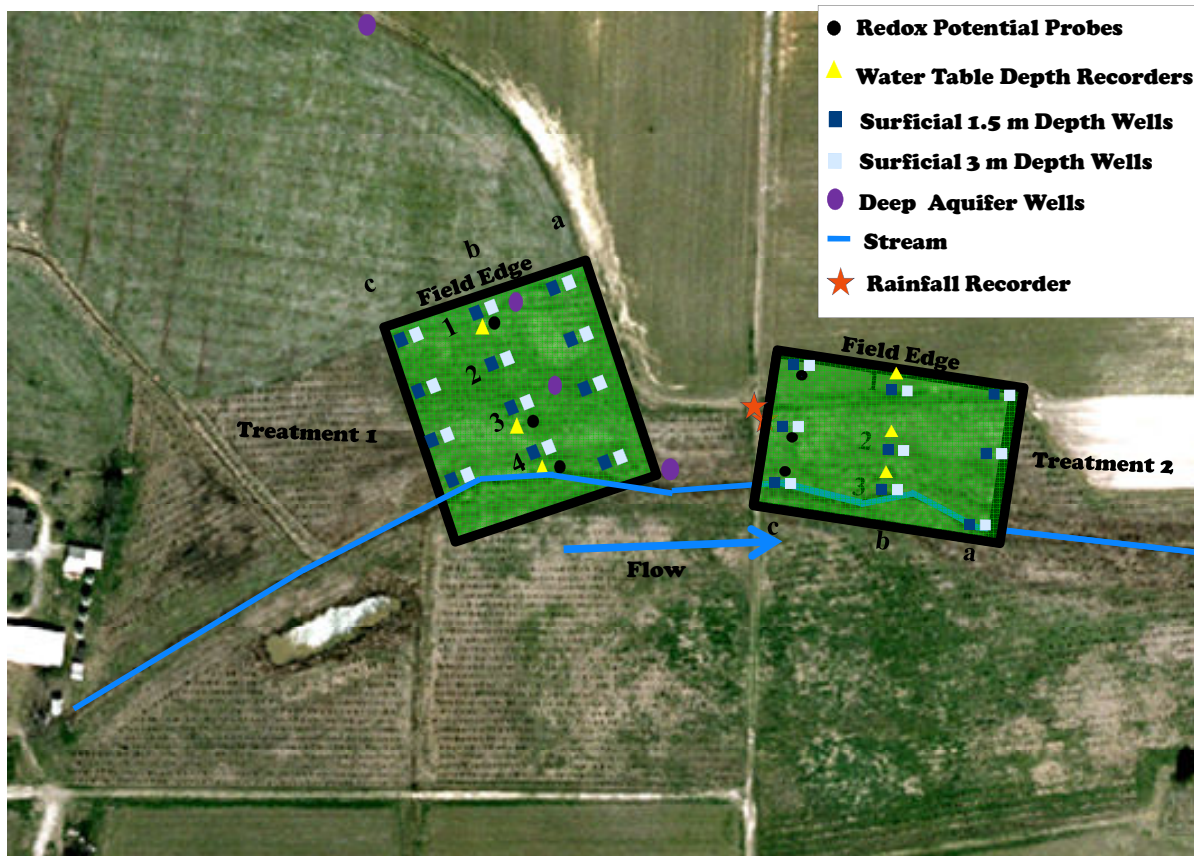


Figure 4. 2: Research site monitoring setup at the study site.

Table 4. 1: Transect layout from Zone 3 to Zone 1 in Section 1. Distances are relative to the stream.				
Zone 3 (Grassed Filter Strip)	Zone 2 (Upper Mid Buffer)	Zone 2 (Lower Mid Buffer)	Zone 1 (Stream Edge)	Transect Spacing
55-60 m (180-197 ft)	45-50 m (148-164 ft)	25-30 m (82- 98 ft)	1.5 m (5 ft)	15 m (50 ft)

Table 4. 2: Transect layout from Zone 3 to Zone 1 in Section 2. Distances are relative to the stream.

Zone 3 (Grassed Filter Strip)	Zone 2 (Mid Buffer)	Zone 1 (Stream Edge)	Transect Spacing
40-45 m (131-148 ft)	25-30 m (82- 98 ft)	1.5 m (5 ft)	15 m (50 ft)

Additionally, redox potential probes were installed next to each of the surficial groundwater monitoring wells in the center transect of Section 1, and the upstream transect of Section 2 (due to the excessive wetness of the center transect). The probes were placed at the same depths as the surficial shallow (1.5-2.3 m) and deep (2.7-3.6 m) water quality wells, so Section 1 had an additional redox monitoring location upslope since it was wider.

Monitoring and Data Collection

Monthly manual water table profiles across the buffer were completed from August 2008 to May 2010 by measuring depth in the surficial groundwater monitoring wells. The water table elevation data loggers were used to monitor water table elevations hourly from November 2005 to May 2010. Soil samples collected at the time of well installation were analyzed for particle size to determine soil hydraulic conductivity at these depths using SPAW 6.0 (NRCS, Pullman, WA). Hydrology and soil data were used for determining groundwater flow direction and residence time within each buffer section.

Groundwater samples were collected monthly from the surficial and deep aquifer wells beginning in January 2005 and August 2008 respectively. All water quality samples from the surficial and deeper aquifer wells were analyzed for nitrate (NO_3^- -N), chloride (Cl^-), ortho-

phosphate (O-PO₄), and ammonium (NH₄-N) monthly, while dissolved organic carbon (DOC) was analyzed from bimonthly samples. Monthly sodium (Na⁺) and calcium (Ca²⁺) analyses began in July 2008. Redox measurements were recorded monthly starting in May of 2006.

Data Analysis

Water Table Analysis

The water table elevations were determined using the site topographic survey, continuously monitored water table elevation data, and monthly manual water table depth measurements. Microsoft Excel 2007 was used for data analysis and to determine the average water table elevation and the average water table difference between buffer zones using the following equation.

$$AD = \frac{1}{n} \sum_{i=1}^n (WTE_{upslope_i} - WTE_{downslope_i}) \quad (4.1)$$

Where,

AD = Average Difference (m)

WTE_{upslope_i} = Water table elevation at upslope location for day i.

WTE_{downslope_i} = Water table elevation at downslope location for day i.

n = Number of daily water table readings collected during study period

The USACE minimum jurisdictional wetland hydrology criteria, in association with continuous water table data, were used to determine the buffers status. The percentage of

consecutive days during the growing season (March 20th thru November 6th) that the water table was within 30 cm of the soil surface at the three water table monitoring locations was computed to test for jurisdictional status.

Groundwater Flow Direction Modeling

The hydraulic data analysis and groundwater flow direction model were completed using spreadsheet methods developed by Devlin (2003) along with Golden Surfer 7 mapping software (Golden, CO). Particle size analysis was used to estimate hydraulic conductivities through the buffer sections for determination of residence times and flow velocities using Darcy's Law.

Nitrate-Nitrogen Removal Efficiency and Nitrate/Chloride Ratios

Groundwater NO₃⁻-N removal efficiency was calculated between each zone and transect as well as the overall area of the buffer at the research site using the following equation.

$$\% \text{ Removal} = \frac{C_I - C_E}{C_I} * 100\%$$

(4. 2)

Where,

% Removal = percentage of groundwater NO₃⁻-N removed through the buffer (%)

C_I = Concentration (mg/L) of the groundwater entering the buffer

C_E = Concentration (mg/L) of the groundwater discharging to the stream

In an attempt to define whether denitrification or dilution was the cause for groundwater NO₃⁻-N concentration reductions observed in the buffer, NO₃⁻-N to Cl⁻ ratios were also

monitored in the groundwater. Lowrance (1992) along with other researchers have used Cl^- a conservative ion (i.e. having minimal plant uptake and not undergoing microbial transformations in soil), to provide evidence that denitrification and not dilution was responsible for observed groundwater NO_3^- -N losses. Essentially dilution was indicated if NO_3^- -N decreased and ratios remained constant through the buffer towards the stream, while removal by denitrification or other biological activity was supported if NO_3^- -N and ratios decreased through the buffer.

Measured Nitrate-Nitrogen Mass Removal

The groundwater NO_3^- -N loads were estimated to evaluate the change and/or transformations of groundwater NO_3^- -N from the field edge to the stream within the buffer. Monthly NO_3^- -N load was calculated using hydraulic conductivities estimated from soil data, hydraulic gradients estimated from hourly monitored water table elevation data, and NO_3^- -N concentrations from water quality samples from each well.

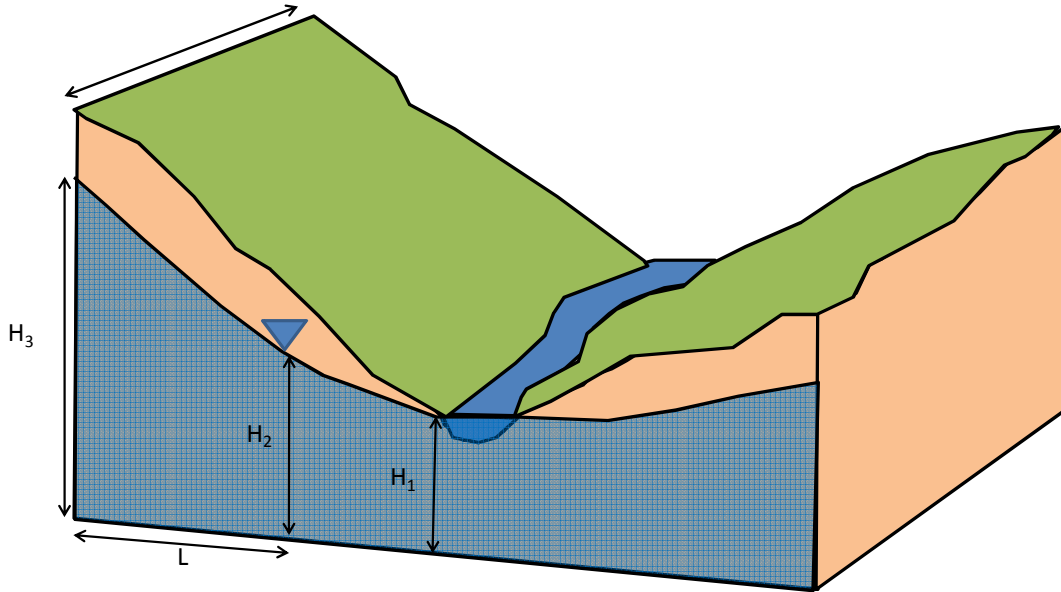


Figure 4. 3: Water table visual for reference for Equation 4.3.

$$Load_{NO_3-N} = \frac{2.4 \times 10^{-2} * (H_{Zone3}^2 - H_{Zone2}^2) * K * T * W * C}{2 * L}$$

(4. 3)

Where,

Load_{NO₃-N} = Groundwater NO₃⁻-N flux for each month (kg N)

H = Level of groundwater elevation above datum at position i (m)

K_s = Hydraulic conductivity at well location (m/hr)

T = Days within each month conversion (days)

C = Influent concentration (mg/L)

W = Length of the buffer (m)

L = Distance between each groundwater well (m)

Statistical Analysis

A statistical analysis was completed to define significant differences in NO_3^- -N concentrations throughout the buffer treatment system using SAS PROC MIXED ® (SAS Institute, Cary, NC). A log transformation was required to normalize the groundwater NO_3^- -N concentrations and the fixed effect was depth.

Redox readings, Cl^- , NO_3^- -N/ Cl^- ratios, Na^+ , and Ca^{2+} concentrations were considered individual response variables and evaluated with the same procedure as NO_3^- -N concentrations. Evaluations between the buffer sections and the deeper aquifer water quality signatures were completed using a mean separation SAS T-test with NO_3^- -N, Cl^- , NO_3^- -N / Cl^- , Na^+ , and Ca^{2+} concentrations being the individual response variables and the class variable being the depth and well position (SAS PROC MIXED ®, Cary, NC).

RESULTS AND DISCUSSION

Overall Summary of Results

NO_3^- -N removal and factors that may have influenced that removal are summarized in Table 4. 3 for both buffer sections. The greatest differences between the two sections appeared to be in groundwater NO_3^- -N concentrations entering the buffer and in contouring. Section 2 appeared to be a wetter buffer section overall, and received high concentrations of NO_3^- -N laden groundwater compared to Section 1. Results also indicated that highly concentrated NO_3^- -N

laden groundwater moved more slowly through Section 2 than through the wider buffer section, Section 1. Variations of components that may enhance denitrification between the two buffer sections were investigated to develop recommendations as to how to account for these differences in buffer designs prior to installation. Results from this analysis will be discussed in detail throughout the following sections.

Table 4. 3: Overall comparisons of Section 1 and Section 2

Section	Section 1		Section 2	
Depth	1.5 m	3 m	1.5 m	3 m
Width	55-60 m		40-45 m	
Mean Nitrate Entering	4.5 mg/L	2.9 mg/L	12.9 mg/L	12.8 mg/L
Mean Nitrate Leaving	1.7 mg/L	2.5 mg/L	1.4 mg/L	6.0 mg/L
Nitrate Reduction Efficiency	63%	15%	89%	54%
Minimum Wetland Hydrology Criteria Met	Absent in Zones 3 and 1 Present 1 of 5 years in Zone 2		Present 2 of 5 years in Zone 1 Present 4 of 5 years in Zone 2 Absent in Zone 3	
Meets Jurisdictional Wetland Criteria	Absent in all zones		Present in Zone 2	
Field Edge Average Elevation (relative to 30 m Benchmark)	30.1 m		28.8 m	
Groundwater Gradients	0.003 – 0.036 m/m		0.003 – 0.010 m/m	
Average Groundwater Velocity	1.6 cm/day	3.0 cm/day	1.3 cm/day	2.8 cm/day
Median Residence Time	11 years	8 years	7 years	4 years
Mean Redox	Average close or below 200 mV at all locations		Average close or below 200 mV at all locations	
Mean DOC	2.9 - 12.2 mg/L		2.8 - 14.5 mg/L	
Nitrate/Chloride Ratios Reduction Efficiency	74%	36%	84%	34%
Measured Nitrate Removed per year (soil layer at monitored depth)	10 kgN year ⁻¹		225 kgN year ⁻¹	
Measured Nitrate Removed per year over area (soil layer at monitored depth)	0.0026 kgN year ⁻¹ m ⁻²		0.06 kgN year ⁻¹ m ⁻²	

Overall Groundwater Quality NO_3^- -N Results

Mean groundwater NO_3^- -N concentrations entering the field edge of Section 1 and 2 at both depths were significantly different ($\alpha=0.05$). Groundwater NO_3^- -N concentrations entering Section 2 were approximately 3 times higher than concentrations entering Section 1 (Figure 4. 4 and Figure 4. 5). Additionally the mean groundwater NO_3^- -N concentrations at the 1.5 m depth entering the stream from Sections 1 and 2 were not significantly different ($\alpha=0.05$).

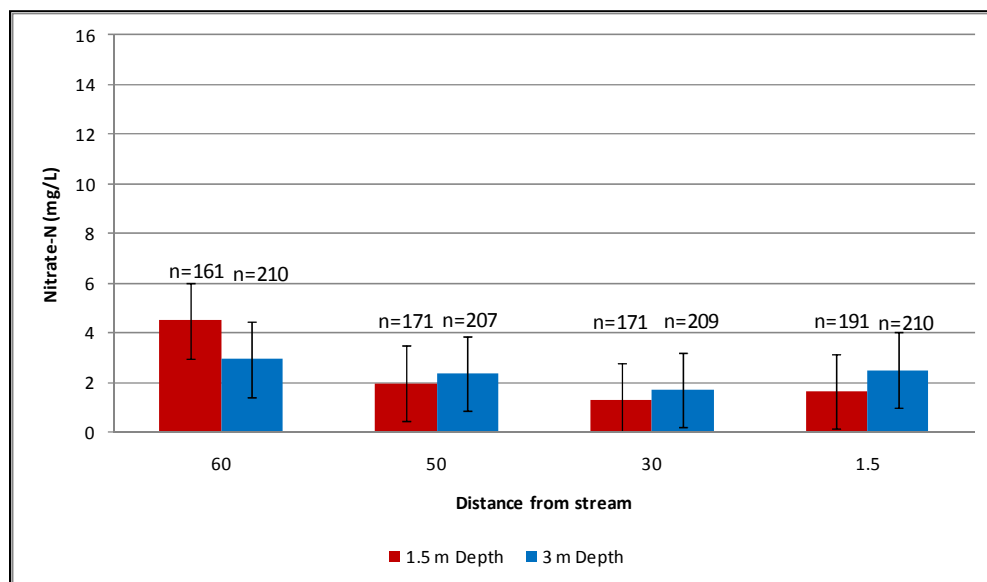


Figure 4. 4: Section 1 overall mean groundwater NO_3^- -N concentrations at the 1.5 m and 3 m depths ($n_{1.5m}=694$ and $n_{3m}=836$ water quality samples). Note – error bars represent standard error.

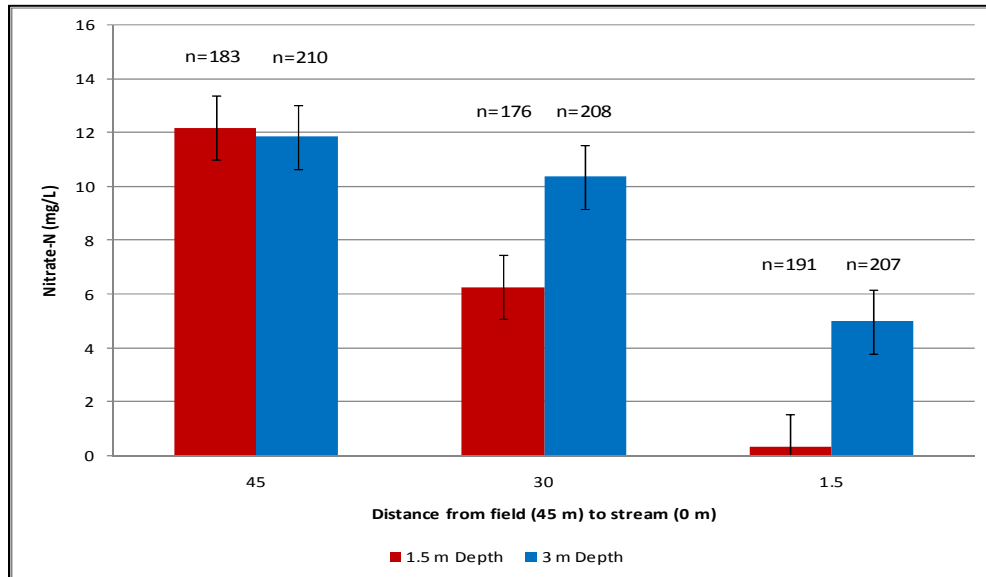


Figure 4. 5: Section 2 overall mean groundwater NO_3^- -N concentrations at the 1.5 m and 3 m depths ($n_{1.5\text{m}}=550$ and $n_{3\text{m}}=625$ water quality samples). Note – error bars represent standard error.

Statistically, groundwater NO_3^- -N at the 1.5 m depth in Section 1 and the 1.5 m and 3 m depths in Section 2 were significantly reduced through the buffer ($\alpha=0.05$). The percent NO_3^- -N reductions observed in each buffer section were related to incoming groundwater NO_3^- -N concentrations (Table 4. 3). Since the groundwater NO_3^- -N concentrations entering Section 1 were low, the observed percent NO_3^- -N reductions were also lower than in Section 2. The mean groundwater NO_3^- -N concentrations in Section 1 at the 1.5 m depth in Zone 3 and Zone 1 were 4.5 and 1.7 mg/l respectively (63% reduction). Mean groundwater NO_3^- -N concentrations at the 1.5 m depth in Section 2 in Zone 3 and Zone 1 were 12.9 and 1.4 mg/l respectively (89% reduction). Of note are the similar Zone 1 concentrations in each section, which may imply some sort of biogeochemical limitation for NO_3^- -N reduction as approaching the stream. Mean groundwater NO_3^- -N concentrations in Zone 3 to Zone 1 in the 3 m depth groundwater in Section

1 decreased from 2.9 to 2.5 mg/l respectively (15% reduction), while NO_3^- -N concentrations in the same zones in Section 2 decreased from 12.8 and 6.0 mg/l respectively (54% reduction).

Significant differences in NO_3^- -N concentrations at the field edge of both buffers made it difficult to make performance comparisons with respect to the widths. However, the other factors such as landscape setting (i.e. position of each section with respect to the stream and upland source), hydrology (i.e. groundwater flow and direction), and biogeochemistry of the buffer soils were evaluated to access factors that may have influenced entering groundwater NO_3^- -N concentrations and groundwater NO_3^- -N reductions through buffer sections.

Groundwater Hydrology

Riparian Buffer Relative Wetness

The water table was closer to the soil surface in Section 2 on average (Figure 4. 6 and Figure 4. 7). Average water table distances from the soil surface were approximately 0.25 m closer in Zone 3 in Section 2 compared to Section 1, while Zone 2 and 1 in Section 1 and 2 had similar average water table depths (Table 4. 4).

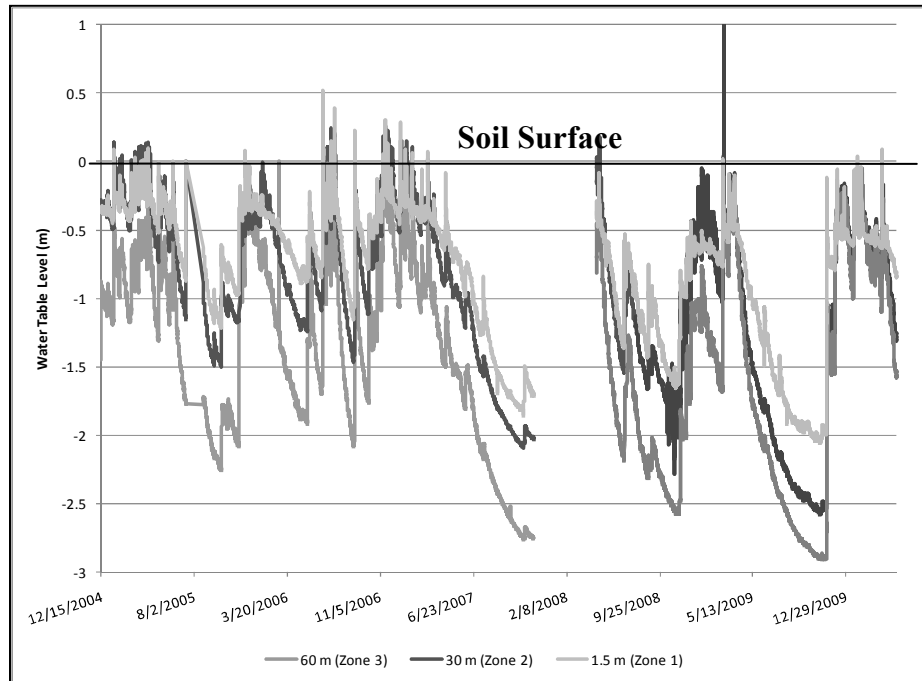


Figure 4.6: Proximity of the water table to the soil surface within Zones 1-3 in Section 1. Data unavailable from January 2005 to April 2008 due to equipment malfunction.

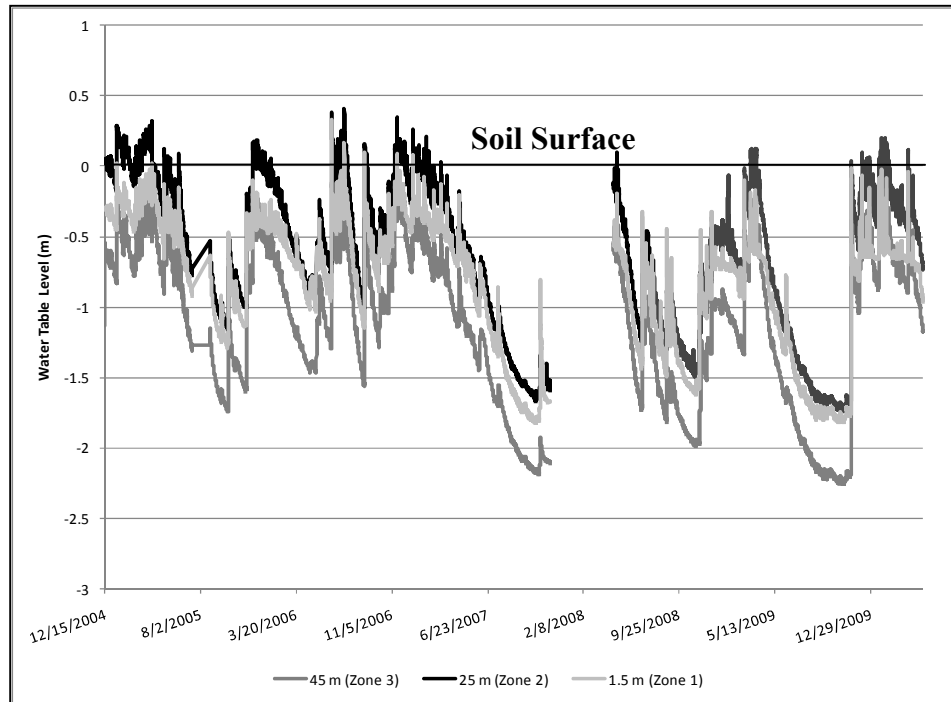


Figure 4. 7: Proximity of the water table to the soil surface within Zones 1-3 in Section 2. Data unavailable from November 2007 to April 2008 due to equipment malfunction.

Table 4. 4: a.) Average annual water table depths in Section 1. b.) Average annual water table depths in Section 2. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

a.)

Year	Zone 3 (m)	Zone 2 (m)	Zone 1 (m)
2005	1.09	0.61	0.51
2006	1.06	0.61	0.51
2007	1.69	1.17	0.99
2008	1.75	1.19	1.03
2009	1.70	1.44	1.16
Average (m)	1.44	0.99	0.83

b.)

Year	Zone 3 (m)	Zone 2 (m)	Zone 1 (m)
2005	1.16	0.69	0.57
2006	0.86	0.73	0.58
2007	1.37	1.24	1.04
2008	1.39	1.29	1.10
2009	1.40	1.32	1.16
Average (m)	1.16	1.03	0.88

The water tables levels became lower beginning in 2007 in both Sections 1 and 2, because North Carolina experienced a major drought during 2007 and 2008 (NCSCO, 2010). Despite this drought, water table levels on average were within 1.5 m (5 ft) of the soil surface each year in Zone 2 (30 m from the stream) and Zone 1 (1.5 m from the stream) of Section 1, and in all zones in Section 2. The Zone 2 monitoring location (30 m from the stream) to the stream edge of Section 1 and entire Section 2 were approximately the same width, so the similarities between the water tables relative to the soil surface of these zones were not surprising.

Riparian areas that have water tables near the soil surface for extended durations can often be classified as riparian wetlands. Wetlands, in general, have been shown to be effective sinks of NO_3^- -N (Peterjohn *et al.*, 1984; Humenik *et. al*, 1999; Koskiaho *et. al*, 2002). A wetland hydrology assessment was completed on each zone (Zone 3-grassed filter strip, Zone 2-mid buffer, and Zone-1 stream edge) at the monitoring locations of the buffer sections to determine which portions of these buffers could be considered riparian wetlands, in order to assess the potential of these buffers to remove groundwater NO_3^- -N.

Minimum jurisdictional wetland hydrology is defined as the water table being within 30 cm of the soil surface consecutively more than 5% (11 days) of the growing season (March 20th thru November 6th for Halifax County, NC) in 50% of the years evaluated (USACE, 1987). Section 1 did not meet the criteria because Zone 2 only met jurisdictional wetland hydrology in one out of five years (Table 4. 5). Section 2 met the jurisdictional wetland hydrology criteria in Zone 2 in four out of five years and Zone 1 was close, as it met jurisdictional wetland hydrology

in two out of five years (Table 4. 5). This was not surprising, as Zone 2 displayed characteristics of a riparian floodplain marsh, as the soil surface was often wet, planted pine tree survival was low, and herbaceous wetland vegetation was present (Figure 4. 8 and Figure 4. 9). These results suggested that Section 2 was overall hydrologically better suited for denitrification since the system was wetter more frequently and for longer periods of time, supporting the high groundwater NO_3^- -N removal rates observed.

Table 4. 5: Maximum consecutive days water table was within 30 cm of the soil surface during growing season (March 20th thru November 6th). Highlighted cells are years that wetland hydrology was present at monitored zones. Data was missing in July through August of 2005 and March through April 2008.

	Section 1			Section 2		
	Zone 3	Zone 2	Zone 1	Zone 3	Zone 2	Zone 1
2005 (days)	0	10	10	3	34	22
2006 (days)	4	8	7	5	45	17
2007 (days)	0	0	1	0	2	1
2008 (days)	1	14	1	1	16	1
2009 (days)	2	3	0	0	13	1



Figure 4. 8: Vegetation in Section 1 Zones 1 and 2 (higher pine tree survival).



Figure 4. 9: Vegetation in Section 2 Zones 1 and 2 (lower pine tree survival and more herbaceous wetland plants present).

Despite the wetter conditions observed in Section 2, the area was not mapped as a hydric area on the GIS hydric map (NRCS, 2010; NCSU Library Geodata Server, 2010), while areas in Section 1 were indicated as partially hydric locations. Inconsistencies between the GIS hydric map and site evaluations further exhibit the critical need for site evaluations to determine

accurate buffer placement and dimensions prior to buffer installation on these hydrologically sensitive sites (Figure 4. 10).

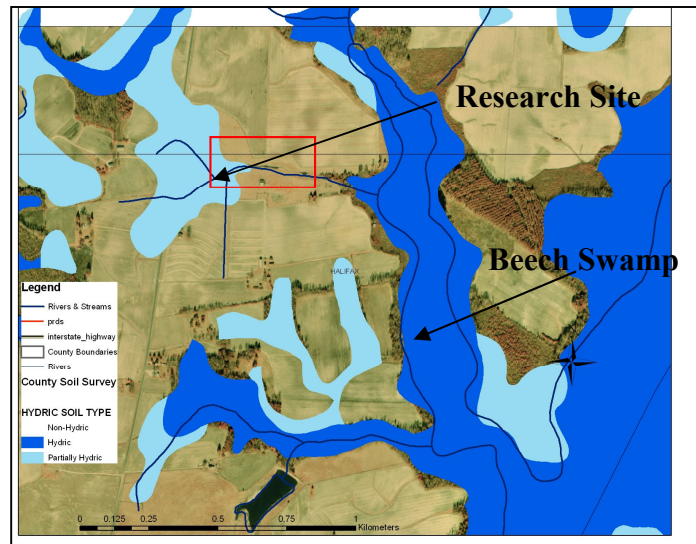


Figure 4. 10: GIS hydric soil map for Halifax County (NRCS, 2010 and NSCU Library Geodata server, 2010).

Groundwater Gradients

Buffer slope and elevation influenced the differences in water table depth and wetland hydrology between the two buffer sections. Figure 4. 10 shows the ground elevation decreased monotonically with a slope of 1.67% through Section 1, while Figure 4. 12 shows that the ground elevation in Section 2 decreased substantially to a 4% slope between Zones 3 to 2 and flattened out with a 0.3% slope between Zones 2 to 1. The slope variations in Section 2, at a lower surface elevation relative to Section 1, resulted in ground surface elevation being closer to the water table.

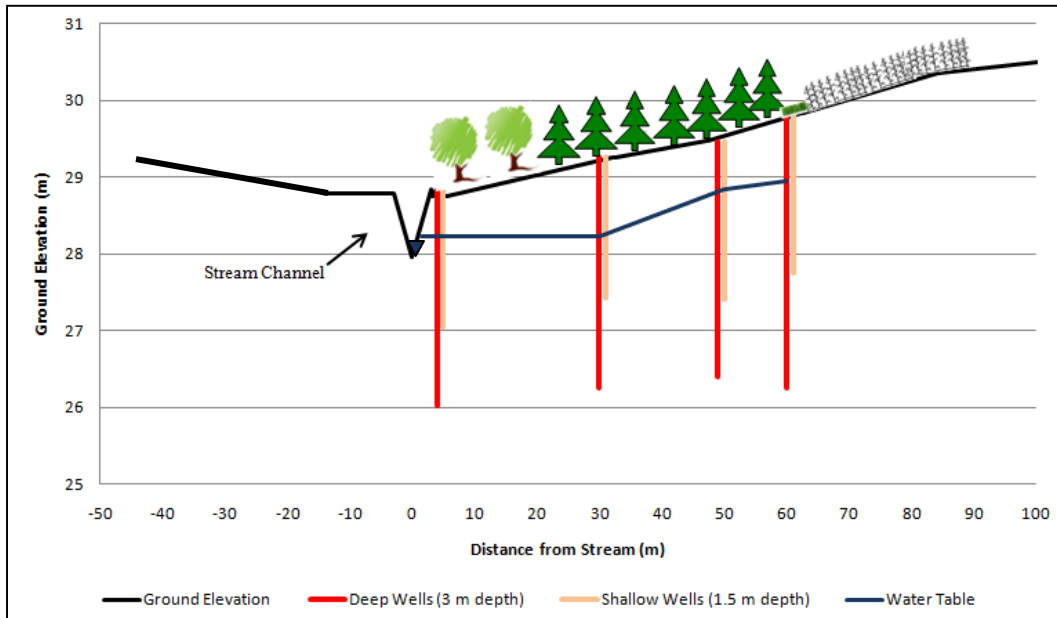


Figure 4.11: Center transect cross section of Section 1 and surficial monitoring wells.

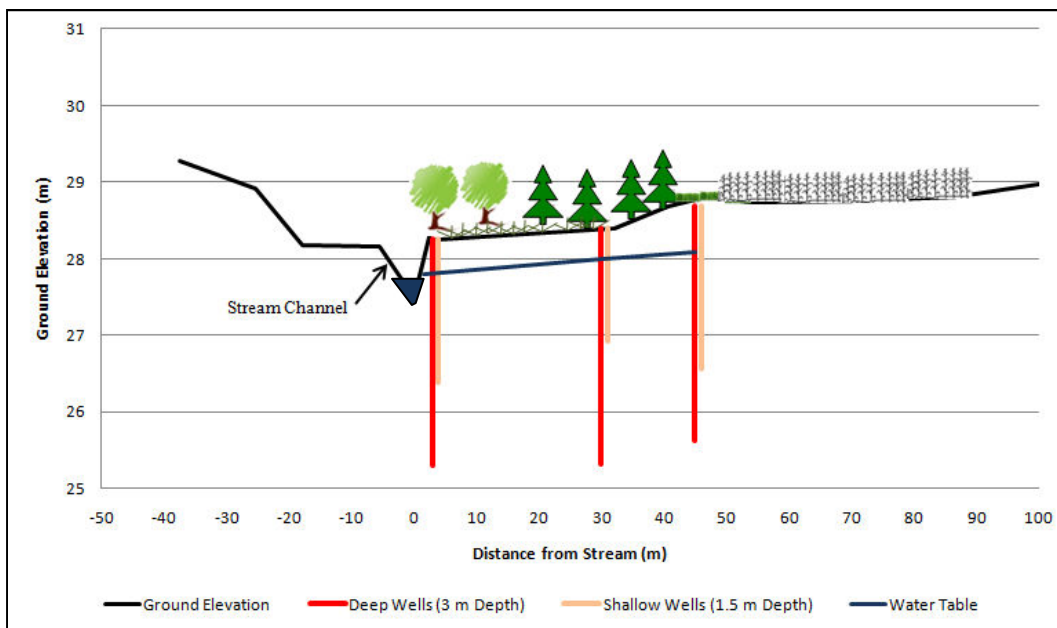


Figure 4.12: Downstream transect cross section of Section 2 and surficial monitoring wells.

Water table elevations and gradients were evaluated to investigate the general groundwater movement from Zone 3 to Zone 1 in Sections 1 and 2. Average water table elevations were higher in Section 1 than in Section 2 during wetter years, while during dryer years the water table elevations were much more similar (Figure 4. 13 and Figure 4. 14). Lower water table elevations in Section 2 indicated local groundwater flow downstream of the buffer. During 2006, a considerably wet year at the site, the water table elevations were highest during the growing season, while during 2009 water table elevations began to decrease in the spring and continued into the summer and fall seasons in both buffer sections. During July 2006 the water table elevation had an average of approximately 30.5 m across all zones, while in July 2009 water tables were approximately 2 m lower (28.5 m) in Section 1. The water table elevation was approximately 29.1 m in Section 2 in July 2006, while in July 2009 the water tables were approximately 1 m lower (28.3 m). These results indicate that the water table elevations in Section 2 were not as dramatically influenced by dry periods as in Section 1.

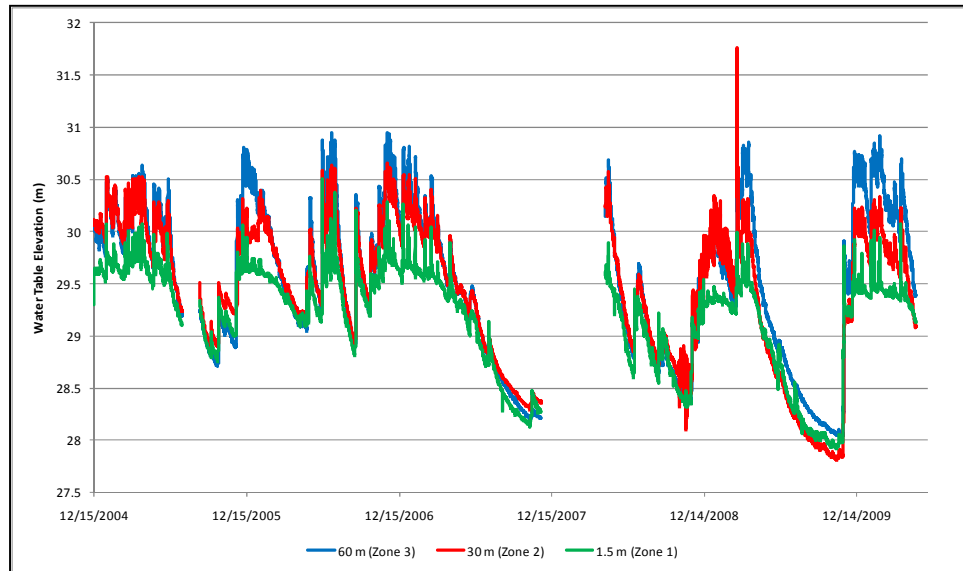


Figure 4. 13: Water table elevations for each zone of Section 1 during the study period (December 2004-May 2010).

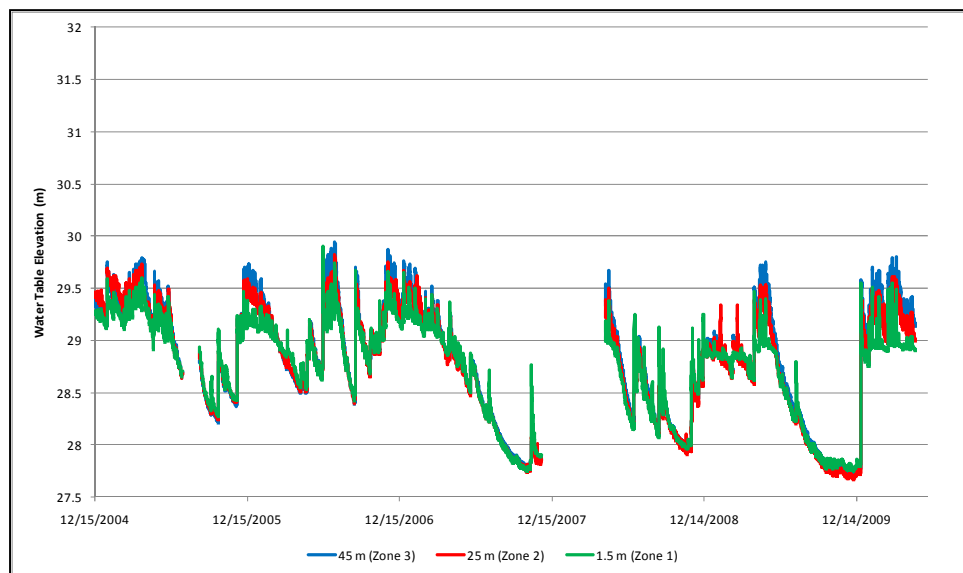


Figure 4. 14: Water table elevations for each zone of Section 2 during the study period (December 2004-May 2010).

The average difference in water table elevations was smaller in Section 2 from Zones 2 to 1 compared to Section 1, while Zones 2 to 3 were similar in Section 2 compared to Section 1. The average water table difference from the field edge to the stream was 0.2 m lower in Section

2, suggesting smaller flow gradients between zones through the buffer. Possible causes for these differences could be attributed to Sections 2's lower topographic placement and flatness. Negative groundwater elevation differences between Zones 3 and 2 in Section 1 were during the drought as discussed in the last section. During this period groundwater appeared to flow to downstream buffer areas and Beech Swamp, both of which were at lower elevations and therefore had lower water table elevations.

Table 4. 6: Average yearly groundwater elevation differences between zones in Section 1. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Year	Average Difference (m) (Zone 3 – Zone 2)	Average Difference (m) (Zone 2 – Zone 1)	Average Difference (m) (Zone 3 – Zone 1)
2005	0.03	0.31	0.34
2006	0.06	0.30	0.37
2007	-0.01	0.23	0.22
2008	-0.06	0.24	0.19
2009	0.25	0.13	0.38
Average (m)	0.07	0.25	0.31

Table 4. 7: Average yearly groundwater elevation differences between zones in Section 2. Note data was unavailable from November 2007 to April 2008 due to equipment malfunction.

Year	Average Difference (m) (Zone 3 – Zone 2)	Average Difference (m) (Zone 2 – Zone 1)	Average Difference (m) (Zone 3 – Zone 1)
2005	0.01	0.09	0.1
2006	0.04	0.05	0.09
2007	0.03	0.00	0.04
2008	0.06	0.01	0.07
2009	0.08	0.04	0.12
Average (m)	0.04	0.04	0.08

Groundwater contours indicated Section 2 as a major discharge area. Furthermore, the overall site map and groundwater contour maps clearly show that the downstream Section 2 had a larger groundwater contributing area from the adjacent field than Section 1, as majority of the groundwater was flowing toward the lower topographic location (Section 2), regardless of season (Figure 4. 15 and Figure 4. 17). The implications of this larger contributing groundwater area was that more farmland was draining towards Section 2 than Section 1. This resulted in groundwater with high NO_3^- -N concentrations being routed to Section 2, as was observed in the field edge groundwater samples.

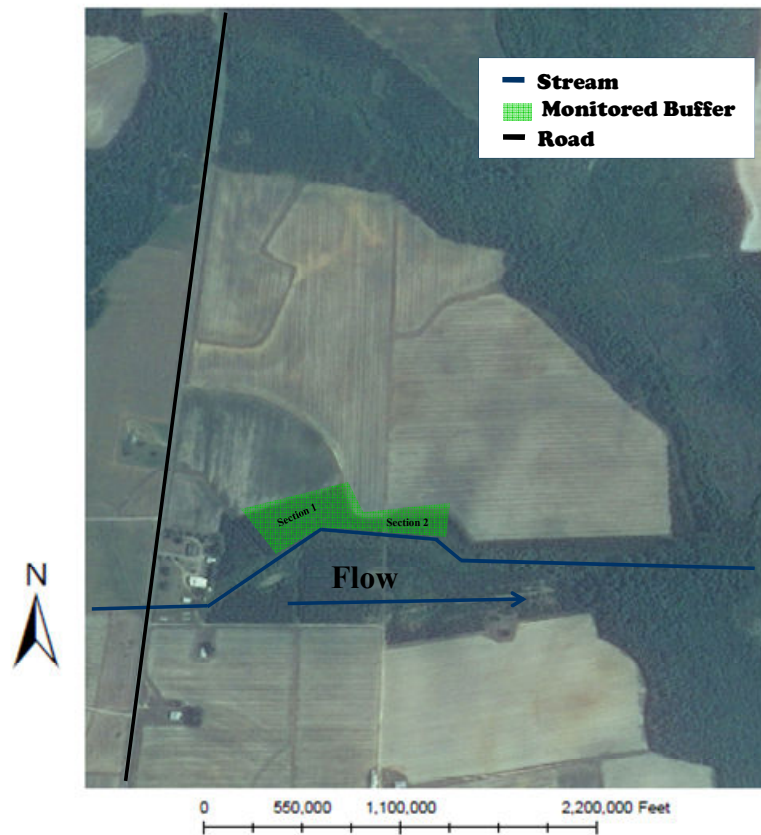


Figure 4. 15: Overall site map.

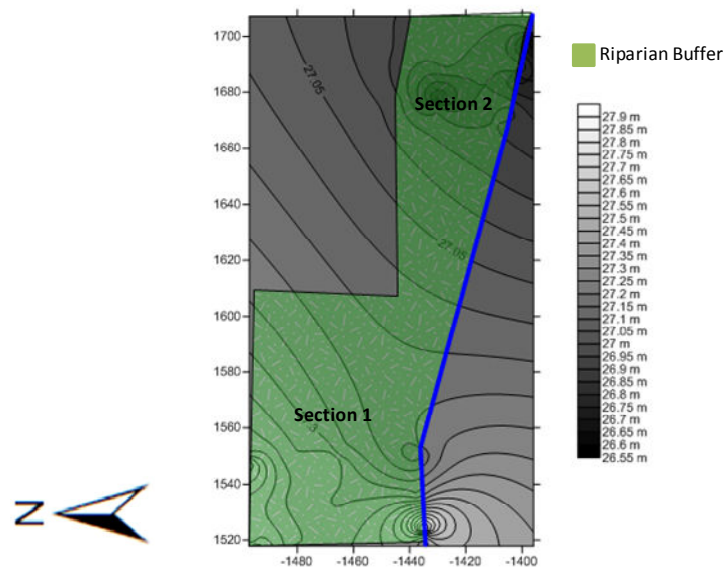


Figure 4. 16: Groundwater contour map of July 2009 (dry period).

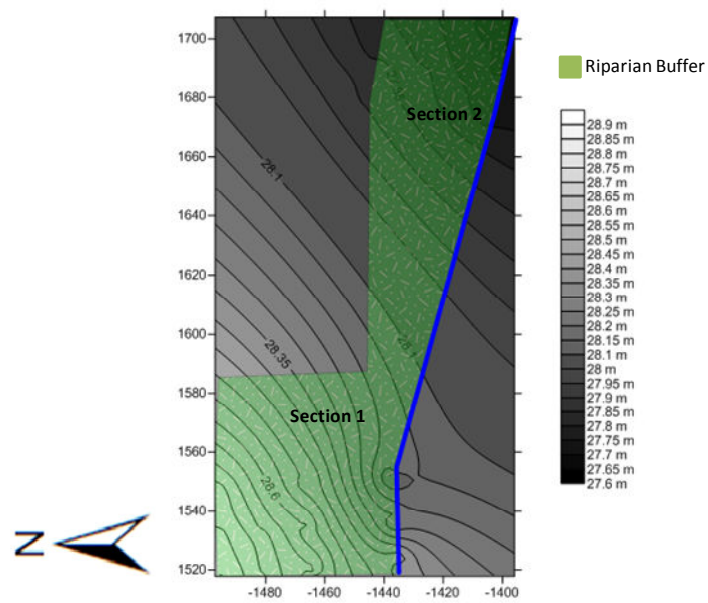


Figure 4. 17: Groundwater contour map of January 2009 (wet period).

The hydraulic gradient was modeled monthly starting in June 2008 using monthly piezometric readings from the water quality wells, a spreadsheet analysis designed by Devlin (2003), and mapping software. Gradients represented water table elevation differences over horizontal distance through the buffer sections. Section 1 had higher gradients than Section 2; gradients varied between 0.003-0.036 m/m in Section 1 and 0.003-0.010 m/m in Section 2 depending on month. Lower gradients in Section 2 generally caused water to move slower through the buffer, increasing opportunities for NO_3^- -N laden groundwater to reach denitrifying sites. Therefore, Section 1, although a wider buffer section, appeared to have the potential for groundwater to move faster through the system than Section 2, the narrower buffer section.

This was verified when groundwater seepage velocities were estimated for the buffers. The larger gradients in Section 1 allowed groundwater velocities to be higher at both the 1.5 m and 3 m depths. K_s in Section 1 ranged from 1.94 cm/hr to 3.42 cm/hr at the 1.5 m depth and 3.06 cm/hr to 7.21 cm/hr at the 3 m depth, while K_s ranged in Section 2 from 3.4 cm/hr to 4.2 cm/hr at the 1.5 m depth and 5.1 cm/hr to 7.9 cm/hr at the 3 m depth. Groundwater velocity averaged 1.6 cm d^{-1} and 3.0 cm d^{-1} in Section 1 at the 1.5 m and 3 m depths respectively. Groundwater velocities averaged 1.3 cm d^{-1} and 2.8 cm d^{-1} in Section 2 at the 1.5 m and 3 m depths. The velocities were higher at the deeper depths due to a decrease in effective porosity.

Median travel times were similar between the sections even though Section 1 was wider. Section 1 had travel times of 11 years at the 1.5 m depth and 8 years at the 3 m depth over an average length of 60 m. The median travel times of Section 2 were 7 and 4 years at the 1.5 m

and 3 m depths, respectively. These similar values were due to higher groundwater gradients allowing groundwater to move faster in the wider Section 1, compared to the more narrow Section 2. Additionally groundwater spent more time moving from Zone 2 to Zone 1 in Section 2 than found in Section 1 at the 3 m depth, which is the area denitrification proceeds at its highest rates (Table 4. 8). Due to these difference NO_3^- -N laden groundwater had more time per unit area in Section 2 to find denitrifying sites compared to Section 1.

Table 4. 8: Travel times using the Devlin (2003) and Dupuit-Forchheimer methods between each monitoring location in the buffer zones for Sections 1 and 2 based on groundwater angle.

Section	Section 1		Section 2	
	1.5 m depth	3 m Depth	1.5 m depth	3 m Depth
Travel time of groundwater from Zone 3 to 2 (years)	0.5 to 7	0.3 to 4.5	0.3 to 12	0.25 to 8
Travel time of groundwater from Zone 2 to 1 (years)	0.75 to 9	0.3 to 6.5	0.7 to 10	0.2 to 7
Travel time of groundwater from Zone 3 to 1 (years)	1.25 to 16	0.6 to 11	1.0 to 22	0.45 to 13

Redox Potential and Dissolved Organic Carbon

Denitrification occurs in soils with low oxidation/reduction (redox) potentials and high dissolved organic carbon (DOC) concentrations. Both sections had low average redox readings and suitable DOC concentrations for denitrification, as described below.

Mean redox values for the study period were predominately below 200 mV in Section 1 and Section 2 indicating soil conditions favorable for denitrification for most periods (Patrick,

1960; Bailey and Beauchamp, 1973, Fielder *et. al*, 2007) and therefore potential for NO_3^- -N reductions in both sections was also high (Figure 4. 18 and Figure 4. 19).

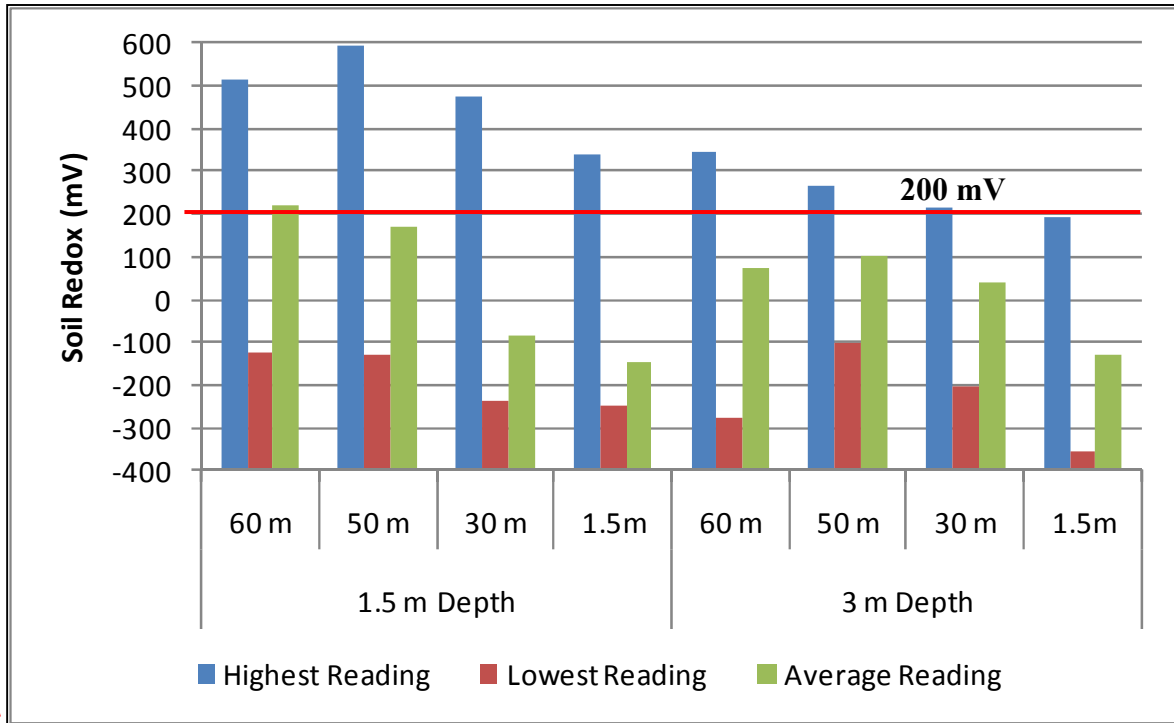


Figure 4. 18: Section 1 highest, lowest, and average soil redox readings at the 1.5 and 3 m soil depths at differing distances relative to the stream from June 2005 to April 2010 (n=60 total samples from each location).

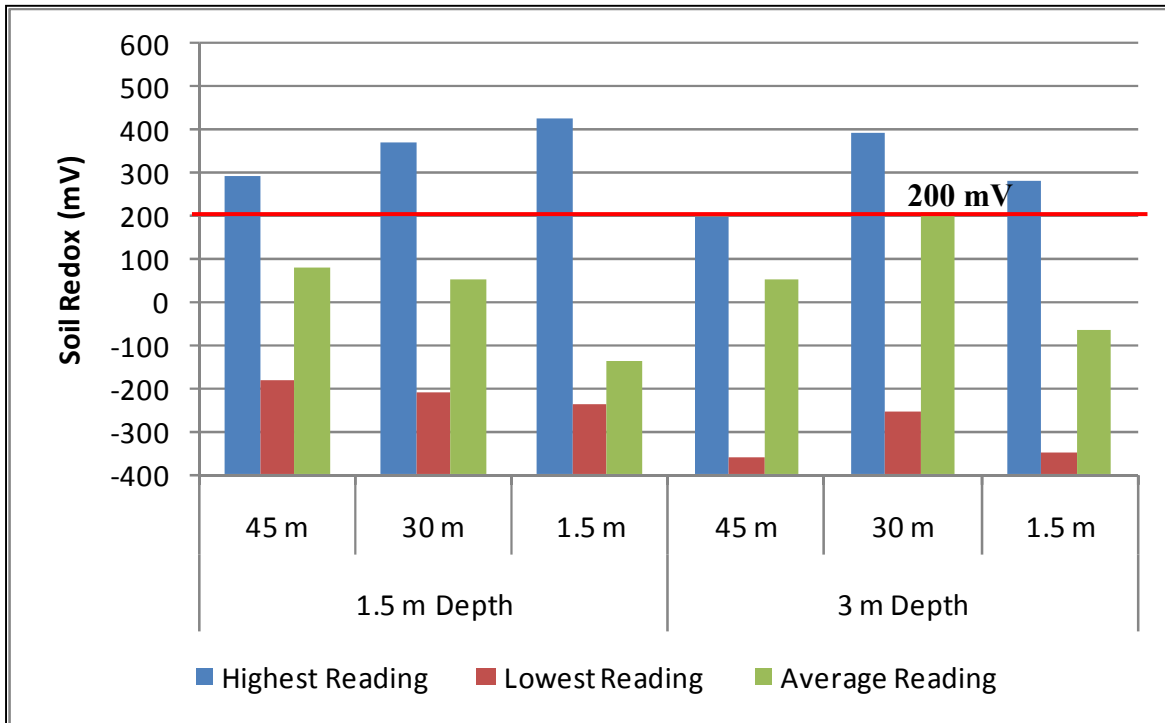


Figure 4. 19: Section 2 highest, lowest, and average soil redox readings at the 1.5 and 3 m soil depths at differing distances relative to the stream from June 2005 to April 2010 (n=60 total samples from each location).

Redox readings were comparable in Sections 1 and 2. Zone 1 (1.5 m) at both depths did not show significant differences in mean redox readings between the two sections ($\alpha=0.05$). The 1.5 m depth had a significant difference in mean redox readings at the field edge (60 m for Section 1 and 45 m for Section 2 from the stream) ($\alpha=0.05$), while Section 2 had lower mean redox readings because the water table was nearer to the soil surface. Section 1 had significantly lower mean redox values at both the 1.5 m and 3 m depths at the lower Zone 2 monitoring location (30 m from the stream) of Section 1 compared to Zone 2 in Section 2, despite the wetter conditions observed in Section 2. The cause for these differences remains unexplained.

Regardless of these differences, redox readings were low indicating the soil was not limited for denitrification to proceed if other required conditions were met.

A DOC assessment was used to evaluate whether carbon availability in the groundwater differed between Sections 1 and 2 (Figure 4. 20 -Figure 4. 23). Mean DOC concentrations were found to not be statistically different between the two buffer sections in all zones. DOC concentrations were found to vary seasonally through both buffer sections with both sections showing the highest concentrations during the summer and winter seasons.

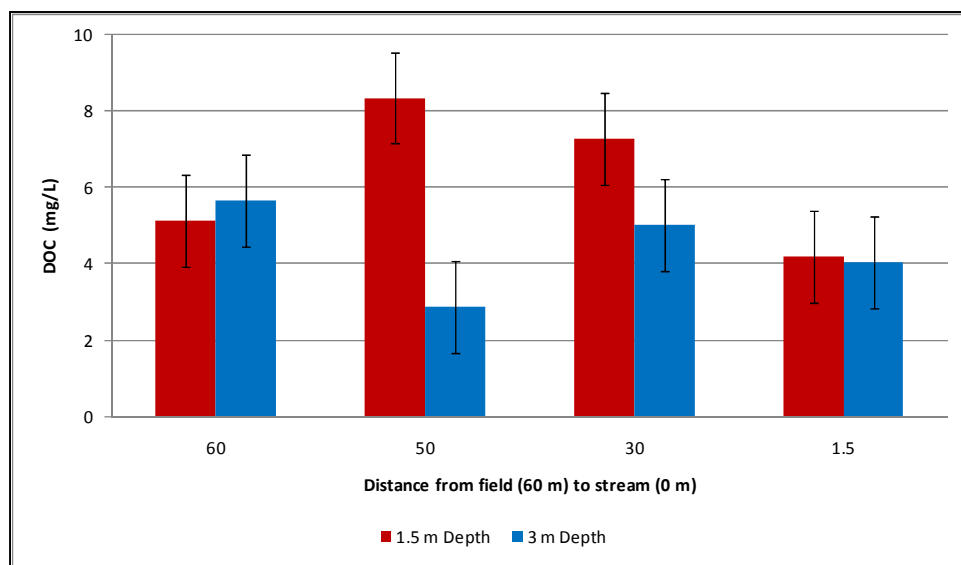


Figure 4. 20: Section 1 average DOC concentrations for research site (n=176). Note error bars represent standard error and outliers from suspected well contamination by dead animal or plant material were removed.

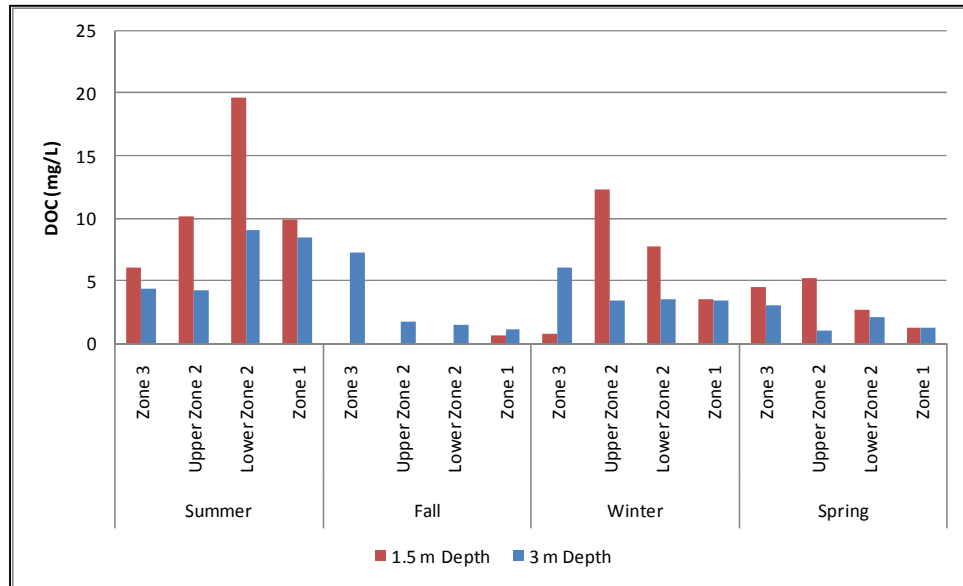


Figure 4. 21: Section 1 seasonal evaluation of DOC (n=176) from March 2008-May 2010. 1.5 m depth results for Zone 3 and Zone 2 for fall were unattainable due to low water table elevations at the research site at the time of sampling. Note outliers removed.

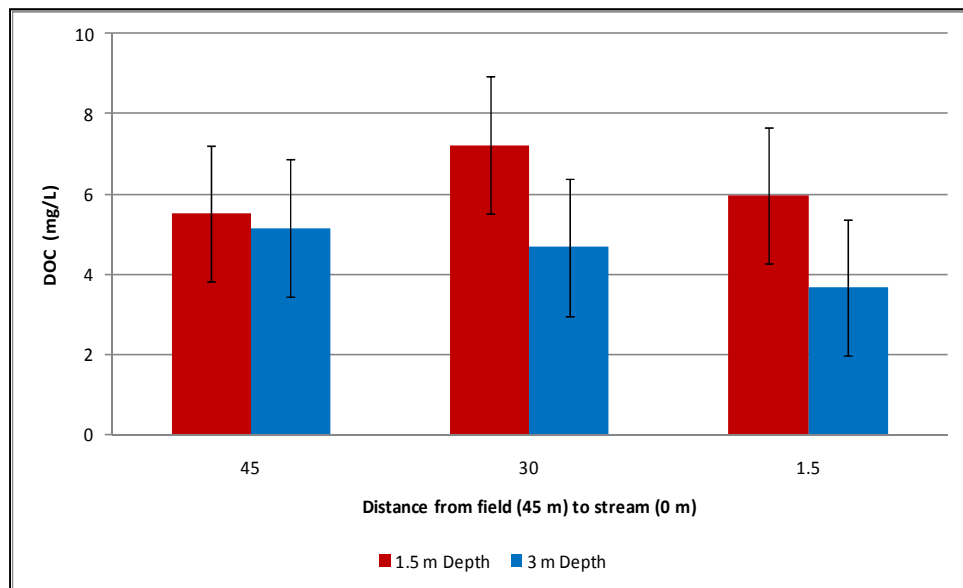


Figure 4. 22: Section 2 average DOC concentrations for research site (n=187). Note: error bars represent standard error.

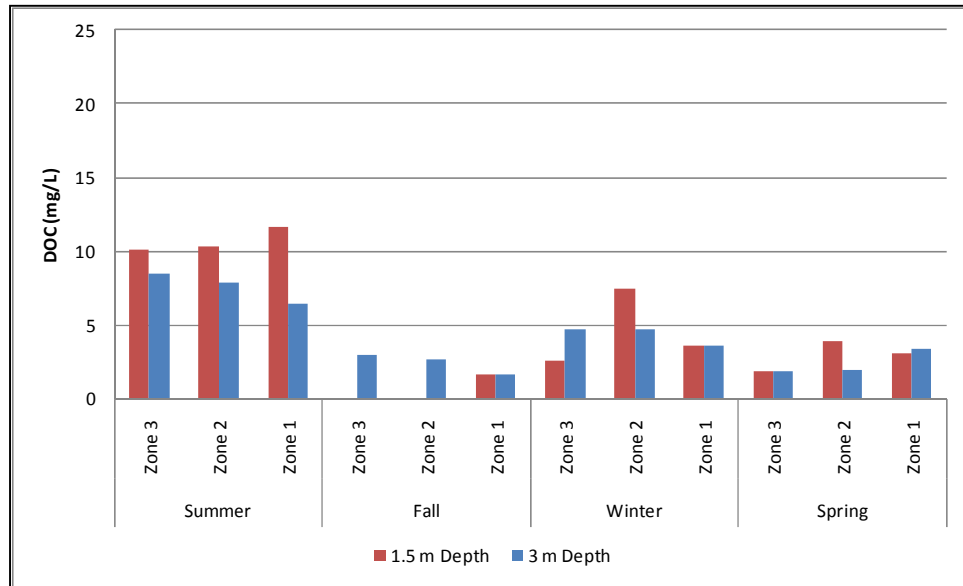


Figure 4. 23: Section 2 seasonal evaluation of DOC (n=187) from March 2008-May 2010. 1.5 m and 3 m results for Zone 3 and Zone 2 for fall were unattainable due to low water table elevations at the research site at the time of sampling.

Both sections had high DOC concentrations, higher than 4-8 mg/L, during the warm seasons, which was sufficient to support denitrification (Knies, 2009; Spruill *et. al*, 1997). DOC concentrations in the 1.5 m depths were higher than in 3 m depths in both sections at most locations. These differences may have caused the higher NO_3^- -N concentrations at the 3 m depth.

Overall, both sections had all the needed components for denitrification to proceed at high rates, including high water tables, low redox readings, and suitable DOC concentrations. The one exception was incoming groundwater NO_3^- -N entering Section 1 that appeared to limit denitrification of that buffer section.

Denitrification / Dilution Assessment

Soil borings indicated a restrictive layer at about 4.6 m (15 ft) below the ground surface that likely separated the surficial and the deeper aquifers. However, since restrictive layers can be non-homogeneous the effect of dilution was examined. Nitrate-N/Cl⁻ ratios were monitored in the groundwater as discussed in Chapters 2 and 3.

Section 1 had higher percent differences in mean NO₃⁻-N/Cl⁻ ratios from Zone 3 to Zone 1 than NO₃⁻-N percent differences, while Section 2 had similar percent differences in mean NO₃⁻-N/Cl⁻ ratios from Zone 3 to Zone 1 as mean NO₃⁻-N percent differences (Table 4. 3). Mean NO₃⁻-N/Cl⁻ ratios in Section 1 from Zone 3 to Zone 1 had a 74% reduction at the 1.5 m depth and a 36% reduction at the 3 m depth. Mean NO₃⁻-N/Cl⁻ ratios in Section 2 decreased by 84% at the 1.5 m depth and 34% at the 3 m depth. Mean groundwater NO₃⁻-N concentration percent reductions along with similar mean NO₃⁻-N/Cl⁻ ratio percent reductions support denitrification as the primary reduction mechanism for NO₃⁻-N reductions in both buffer sections.

Additional evidence of minimum groundwater mixing was completed through a groundwater quality investigation of the surficial and deeper aquifers to identify mixing potential between the two layers. The chemical analysis of the waters indicated significant differences between the surficial and deeper aquifers. Water in the deeper aquifer (monitored 8-11 m deep) was significantly lower in Cl⁻ and higher in Ca²⁺ than in the surficial aquifer (1.5 and 3 m deep) in Section 1 and Section 2 ($\alpha = 0.05$). Therefore, the low Cl⁻ concentrations further support that biological activity, presumably denitrification, was the predominant reducing mechanism since

NO_3^- -N/ Cl^- decreased while Cl^- concentrations remained relatively constant. These differences in groundwater signatures provided additional strong evidence that mixing was unlikely between waters in the deeper and surficial aquifers.

However, groundwater within 1.5 m and 3 m of the surface in each section appeared to have the same chemistry, because Cl^- , Na^+ , and Ca^{2+} concentrations were similar particularly in Zone 1. The 3 m depths in Sections 1 and 2 were found to have sandier soils that could have allowed for mixing with both the 1.5 m depth and the stream. Stream water quality results indicated an increase in mean NO_3^- -N concentrations from 1.2 mg/L upstream to 5.9 mg/L downstream. These concentrations were similar to groundwater NO_3^- -N concentrations in Zone 1 in Section 1 (upstream) and Section 2 (downstream) at the 3 m depth. Therefore, mixing between the 1.5 m and 3 m depth groundwater and the stream appeared possible.

Groundwater quality data suggests that the groundwater NO_3^- -N reductions through the buffer were presumably due to denitrification, and with some potential mixing of the shallow groundwater near the stream in Zone 1. Groundwater quality results, along with high water tables, low redox readings, and high DOC concentrations all supported the hypothesis that biological activity, presumably denitrification, was the primary mechanism for NO_3^- -N reduction in both buffer sections. Differences in the NO_3^- -N reduction performance between the two buffer sections were due to differences in groundwater entering Zone 3 of each section, delivering more highly concentrated NO_3^- -N groundwater to Section 2 - the more downstream buffer section.

NO₃⁻-N Removal Evaluation through Riparian System

Mean groundwater NO₃⁻-N concentrations, Darcy's Law, groundwater gradients, and porosity were used to estimate the overall NO₃⁻-N mass removal at the 90 cm depth soil layer and 240 cm depth soil layer (Table 4.9). NO₃⁻-N entering Zone 3 of Section 1 was estimated to be 17 kg N yr⁻¹ and 14 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. NO₃⁻-N leaving Section 1 and discharging into the stream was 4 kg N yr⁻¹ and 15 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. Groundwater NO₃⁻-N concentrations were elevated near the stream at the 3 m depth compared to upslope groundwater NO₃⁻-N concentrations in Section 1, thus resulting overall increases of NO₃⁻-N within the buffer. NO₃⁻-N entering Zone 3 of Section 2 was 80 kg N yr⁻¹ and 176 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. NO₃⁻-N leaving Section 2 and discharging into the stream was 5 kg N yr⁻¹ and 25 kg N yr⁻¹ for the 90 cm depth soil layer and 240 cm depth soil layer, respectively.

Table 4. 9: Potential NO₃⁻-N removal per year for varying depths and zones of the studied riparian buffer section system.

Section	Depth (cm)	90 cm Soil Layer	240 cm Soil Layer	Total
1	Total NO₃⁻-N Removed in Buffer Treatment System (kgN yr⁻¹)	12	-2	10
	Total NO₃⁻-N Removed in Buffer Treatment System (kgN yr⁻¹m⁻²)	0.003	-0.0004	0.0026
2	Total NO₃⁻-N Removed in Buffer Treatment System (kgN yr⁻¹)	75	150	225
	Total NO₃⁻-N Removed in Buffer Treatment System (kgN yr⁻¹m⁻²)	0.02	0.04	0.06

The monitored depths in Section 1 was reducing groundwater NO₃⁻-N by 0.003 kg N yr⁻¹ m⁻² (76 %) for the 90 cm depth soil layer and no change in the 240 depth soil layer, while Section 2 was reducing groundwater NO₃⁻-N by 0.02 kg N yr⁻¹ m⁻² (94 %) and 0.04 kg N yr⁻¹ m⁻² (86%) for the 90 cm depth soil layer and 240 cm depth soil layer, respectively. Percent reductions were higher at the 1.5 m depth in Section 1 and the 1.5 m and 3 m depths in Section 2 compared to the percent reductions found in measured groundwater NO₃⁻-N concentration samples. These differences can be attributed to taking into account the hydraulic conductivity and gradient differences in the two buffer sections. Section 2 results were similar compared to results that Nelson *et al.* (1995) reported with removal rates of approximately 120 kg N ha⁻¹ yr⁻¹

(0.012 kg N m⁻² yr⁻¹). Lowrance *et al.* (1995) estimated removal rates similar to Section 1 ranging from 20 to 39 kg N ha⁻¹ yr⁻¹ (0.002 – 0.0039 kg N m⁻² yr⁻¹) in an analysis that included removal of NO₃⁻-N through all mechanisms, not only denitrification.

The mass of groundwater NO₃⁻-N leaving the system in Sections 1 and 2 were similar at the 1.5 m depths possibly indicating an irreducible concentration due to mineralization and nitrification that may contribute NO₃⁻-N to the system. Section 2 exhibited larger magnitudes of NO₃⁻-N reduction from Zone 3 to Zone 1 on a per area basis most likely due to having a larger groundwater contributing area from the adjacent field producing a larger mass of NO₃⁻-N entering the section. Most importantly, these results indicate that Section 2, although thinner than Section 1, was effectively reducing NO₃⁻-N concentrations through the system. Although Section 1 was a wider buffer, low NO₃⁻-N concentrations entering the section due to a smaller groundwater contributing area from the adjacent field relative to Section 2, most likely constrained the buffer from its maximum removal potential. Due to these limitations, Section 1 might have removed more NO₃⁻-N if higher NO₃⁻-N concentrations were entering the system. As such, it is likely that less width could have been used in the design for the buffer in Section 1, taking less farmland out of production, while allowing payments by NC CREP for this additional acreage to be used elsewhere at another site.

CONCLUSIONS

Discerning the exact buffer width for future installations must be determined dependent on the incoming groundwater NO_3^- -N concentrations and research is still needed to determine these designs. Section 2 appeared to reduce groundwater NO_3^- -N concentrations effectively even though it had a smaller width than Section 1, and appeared to be designed adequately to meet NO_3^- -N reduction goals. Based on observed decreases in concentrations, the groundwater NO_3^- -N treatment efficiency of both buffer sections appeared to be high even with low groundwater NO_3^- -N concentrations entering Section 1. Most likely Section 1 had the potential to reduce groundwater NO_3^- -N concentrations as high as entering Section 2, but due to limited NO_3^- -N concentrations entering the system this evaluation could not be completed. Additionally, Section 1 appeared to be oversized relative to the groundwater NO_3^- -N concentrations entering the buffer section.

Results from hydrology and water quality data supported denitrification as the predominant NO_3^- -N reduction mechanism in both sections. The relative wetness of Zone 2 and Zone 1 in both sections indicated the potential for denitrification was high. Furthermore, low redox readings and high DOC concentrations during the summer months indicated the buffer was not carbon limited. A confining layer at 4.6 m below the soil surface within the buffers indicated dilution was at most minimal. Dilution was further determined to be minimal as NO_3^- -N and NO_3^- -N/ Cl^- ratios had similar decreases from Zone 3 to Zone 1 and the surficial and deeper aquifer water quality assessment found the water quality signatures to be significantly different

in both sections. Therefore, high water table elevations along with NO_3^- -N concentration reductions, redox readings, and DOC concentrations during warmer seasons all lead to ideal soil environments for denitrification.

The groundwater contributing areas entering the buffer sections from the adjacent field had an evident influence on the NO_3^- -N concentrations entering the two sections. Results indicate that the buffer section placed in the lower topographic location received groundwater from a larger contributing area from adjacent agricultural practices resulting in higher NO_3^- -N concentrations. Furthermore, Section 2 had smaller groundwater gradients resulting in groundwater moving slower through the buffer system and having more time to encounter denitrifying sites.

The overall estimated groundwater NO_3^- -N mass removal from hydrology and groundwater monitoring data was higher in Section 2 than Section 1. However, Section 1 was constrained from its maximum removal potential due to low NO_3^- -N concentrations entering the buffer.

Many buffer widths and placements are dependent on the landowner and the allowable buffer width supported by conservation programs, as found at this site. Therefore, installed buffer width is rarely a function of meeting NO_3^- -N reduction goals for groundwater entering the buffer. During this study, the buffer section located at the lower elevation (Section 2) was receiving higher concentrations of groundwater NO_3^- -N, while the wider buffer was receiving significantly lower NO_3^- -N concentrations. One recommendation, based on findings of this

study, would be to place narrow buffers in areas having smaller groundwater contributing areas from agricultural practices, as concentrations of groundwater NO_3^- -N enter systems are likely lower.

All results further indicate the importance of site evaluations prior to buffer installations. To maximize the groundwater NO_3^- -N removal impact of buffers enrolled in conservation programs, hydrologic and groundwater quality evaluations could be completed prior to land enrollment. Designing riparian buffers relative to groundwater contributing areas, available denitrification enhancing conditions (water table depths close to the soil surface, low redox readings, and available DOC), and entering groundwater NO_3^- -N concentrations will improve NO_3^- -N removal within the systems, while preserving valuable land for agricultural practices instead of unnecessarily taking it out of production. Although logistically challenging and initially expensive, buffers specifically designed to meet water quality goals, by taking into account these critical site attributes, will improve overall water quality leaving agricultural sites, while protecting sensitive streams and estuaries cost effectively.

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APPENDICES

APPENDIX A: Vegetation Assessment

Vegetation Overview

A vegetation assessment was completed in November 2009 to assess the species and health of the trees and plants at the riparian buffer site. Zone 3 (filter strip) in Section 1 consisted of *Panicum clandestinum* (deertongue) and *Trifolium spp.* (clover). Section 1 had a clear understory in Zone 2 with prevalent *Ligustrum sinense* (Chinese privet), *Rubus argustus* (blackberry), and *Microstegium*. Section 1 had *Pinus taeda* (loblolly pine) as the dominant tree in Zone 2. Zone 1 consisted of *Quercus phellos* (willow oak), *Salix nigra* (black willow), and *Quercus spp.* (oak). Ground vegetation in Zone 1 was *Festuca spp.* (fescue) on the banks and *Rubus argustus* (blackberry).

Section 2 had a similar Zone 3 (filter strip) as seen in Section 1. The *Pinus taeda* (loblolly pines) in Zone 2 was thinner and were not growing as well as seen in Section 1. The Zone 2 canopy had closed and *Rubus argustus* (blackberry) and *Sambucus nigra ssp. Canadensis* (common elderberry) were identified in the canopy as well. Zone 1 consisted of *Sambucus nigra ssp. canadensis* (elderberry), *Juglans nigra* (black walnut), *Salix nigra* (black willow), *Quercus phellos* (willow oak), and *Quercus spp.* (oak). There was evidence of deer rubbing on the trees, which hinders the health of the trees. The *Quercus spp.* (oak) grew closer together in Section 2 than in Section 1. The area indicated swampy vegetated features. Additional plant species identified in Section 2 included *Solidago spp.* (goldenrod) and *Solanum carolinense* (horse

nettle). The *Pinus taeda* (loblolly pines) in Section 1 and Section 2 were similar even though visually Section 1's *Pinus taeda* (loblolly pines) looked healthier. The average diameter and average height for Section 1 and 2 were 7.6 m and 7.74 m and 16.9 cm and 17.0 cm respectively. Additional plant species identified by a plant specialist from the NCSU Biological and Agricultural Engineering Department can be found in Table A. 1.

Table A. 1: Plant species for Sections 1 and 2 at the research buffer site

Scientific Name	Common Name	Form	Type
<i>Allium vineale</i>	wild garlic	forb	exotic
<i>Daucus carota</i>	wild carrot	forb	exotic
<i>Festuca</i> spp.	fescue	grass	exotic
<i>Ilex opaca</i>	American holly	tree	native
<i>Juglans nigra</i>	black walnut	tree	native
<i>Ligustrum sinense</i>	Chinese privet	shrub	exotic
<i>Liquidambar styraciflua</i>	sweetgum	tree	native
	Japanese		
<i>Lonicera japonica</i>	honeysuckle	vine	exotic
<i>Panicum clandestinum</i>	deertongue	grass	native
<i>Panicum virgatum</i>	switchgrass	grass	native
<i>Phytolacca americana</i>	pokeweed	shrub	native
<i>Pinus taeda</i>	loblolly pine	tree	native
<i>Prunus serotina</i>	black cherry	tree	native
<i>Quercus phellos</i>	willow oak	tree	native
<i>Quercus</i> spp.	oak	tree	native
<i>Rubus argustus</i>	blackberry	shrub	native
<i>Salix nigra</i>	black willow	tree	native
<i>Sambucus nigra</i> ssp.			
<i>canadensis</i>	common elderberry	shrub	native
<i>Solanum carolinense</i>	horsenettle	forb	native
<i>Solidago</i> spp.	goldenrod	forb	native
<i>Trifolium</i> spp.	clover	forb	exotic
<i>Vitis</i> spp.	grape	vine	native

APPENDIX B: Soil Analysis

Section 1 Soil Chemical Analysis

A soil chemical analysis was completed to determine if the soil layers had an effect on NO_3^- -N reduction within the buffer due to carbon availability. Results showed trends in NO_3^- -N. The highest NO_3^- -N concentrations were found in the top layer of soil. Carbon percentages were highest in the top layer as well. Carbon availability increased through the buffer most likely due to vegetation providing increased carbon availability from leaf litter.

Table B. 1: Section 1 soil chemical analysis completed in the BAE Environmental Analysis Laboratory for the three soil layers closest to the soil surface.

Depth Beneath Soil Surface (cm)	Location	TKN (mg/L)	TP (mg/L)	NH ₃ -H (mg/L)	NO ₃ -N (mg/L)	PH	Bulk Density	% C	% N
15	Field	319.13	68.74	1.88	4.01	4.99	1.01	0.29	0.03
23.4	Field	252.48	59.45	0.98	2.39	5.14	1.05	0.23	0.02
29	Field	312.87	68.54	1.28	2.37	5.12	1.05	0.25	0.03
13	Field Edge	410.36	74.84	1.48	5.11	5.2	1	0.44	0.04
21	Field Edge	275.61	50.42	2.16	2.03	5.62	1.05	0.28	0.03
26	Field Edge	259.71	64.29	2.13	0.79	5.45	0.94	0.22	0.02
11.4	Mid Buffer	462.47	78.15	1.31	4.52	5.55	1.01	0.76	0.04
20	Mid Buffer	254.75	27.43	0.87	1.35	5.8	1.06	0.29	0.02
28	Mid Buffer	250.3	34.89	1.18	0.6	5.29	1.03	0.20	0.02
11.4	Stream Edge	644.46	172.92	3.44	1.78	5.36	1.01	0.87	0.06
20	Stream Edge	367.75	62.91	1.75	0.87	5.49	0.99	0.73	0.04

Section 2 Soil Chemical Analysis

A soil chemical analysis was completed to determine if the soil layers had an effect on NO_3^- -N reduction within the buffer due to carbon availability. Results showed that the chemical composition of soil did not show any observed trends in NO_3^- -N. The results indicated that NO_3^- -N was present in all soil zones along with carbon. Carbon was highest within the buffer most likely due to vegetation providing increased carbon availability from leaf litter decomposition.

Table B. 2: Section 2 soil chemical analysis completed in the BAE Environmental Analysis Laboratory for the three soil layers closest to the soil surface.

Depth Beneath Soil Surface (cm)	Location	TKN (mg/L)	TP (mg/L)	NH ₃ -H (mg/L)	NO ₃ -N (mg/L)	PH	Bulk Densiy	% C	% N
11	Field	191.04	140.04	0.37	1.95	5.53	1.14	0.22	0.02
18	Field	63.6	74.53	0.6	1.14	5.26	1.13	0.08	0.01
25	Field	54.1	62.37	0.18	1.49	4.8	1.02	0.06	0.01
15	Field Edge	69.75	46.99	0.93	2.95	5.12	1.16	0.12	0.01
20	Field Edge	151.09	63.91	1.32	3.44	4.9	1.2	0.14	0.02
30	Field Edge	190.62	57	1.57	4.3	4.8	1.16	0.15	0.02
10	Mid Buffer	417.12	101.81	2.14	1.47	4.96	1.03	0.69	0.04
20	Mid Buffer	192.99	72.8	1.14	1.08	4.92	1.16	0.23	0.02
28	Mid Buffer	122.34	46.3	1.09	1.09	4.92	1.03	0.20	0.02
11	Stream Edge	225.04	116.4	0.64	1.59	5.12	1.05	0.37	0.03
15	Stream Edge	411.25	220.79	0.52	2.49	5.23	1.15	0.67	0.05
32	Stream Edge	556.17	111.58	1.42	0.95	5.15	1.11	0.86	0.05

DEA Procedures (Provided by Amey Tilak, NCSU 2009)

DENITRIFICATION PROCEDURES

May, 2009

Note: These have been edited to reflect changes in DEA measurements, but not to reflect changes for the new GC or new standards methods

Steps in making up nitrous oxide standards

General: Standards can be made up in either air or nitrogen. If standards are to be used for slurries which are incubated under nitrogen atmosphere, make up standards in nitrogen. If standards are to be used for cores incubated under air atmosphere, make up in air. If standards to be used for both cores and slurries, make up in air.

1. Make up a 5000 ppm stock standard: Evacuate round flask three times, refill with air or N₂, withdraw 15 mL from flask, add 15 mL pure nitrous oxide. Mix by hand 1 min with beads swirling.
2. Make up 5, 10, 25, 50 ppm standards from stock standard. Evacuate flasks three times, refill with air or N₂, withdraw 3, 6, 15, 30 mL from the flasks. Add 3, 6, 15, and 30 mL of 5000ppm standard. One (1) PPM standard is in gas bottle.
3. If you need complete sets of higher standards (125 ppm, 250 ppm, etc) start with 10000 ppm stock by using 30 mL of pure nitrous oxide.
4. If you just need a few higher standards, you can make them up by carefully doing dilutions in the crimp top vials. Always use the glass syringe (marked standards only) to do these. All dilutions are based on (vol of standard or sample)/total volume of standard or sample plus diluent).
5. When making standards, be very careful not to leave the nitrous oxide tank on and let the gas escape into the room. This can contaminate the room air for a number of hours and make good standards difficult to obtain.
6. Fill vials with standards after checking one set to see if you have a good linear standardization.

Standardization of Gas Chromatograph

General: These GC standards tend to have a good bit of what seems like random variation. In general, we have used the means of all standards to calculate the line segments used for standardization. The lowest line segment goes through the origin.

1. Compile all standards for a run
2. Calculate mean area for each standard. Discard ones that are more than 10% different from the mean.
3. Determine line segments for calculation of unknowns. These are generally 0, air (0.3) 1, 5, 10 ppm then 10, 25 50 ppm, then 50, 125, 250 ppm, etc.
4. When you have the conc vs area relationships, calculate PPM of unknowns using line segments.

Gas sampling for nitrous oxide analysis

1. Generally, you will want to store mL samples in the crimp top vials. If you use a 5 mL sample, use 5 mL of standard. Make sure the sample volume and standard volume are the same.
2. For either cores or slurries, there will generally be two gas samples per incubation. The nitrous oxide production rate will be figured by the change in concentration over the time period between samples.
3. When taking samples from cores, pump the head space three times with the sampling syringe before sampling. Do not pull enough vacuum so that the core is sucked up into the top of the incubation syringe. Flush the syringe by pumping some room air between pumping the incubation syringes.

Core and slurry incubations

Cores

1. Before going to the field, number all incubation syringes and store in boxes in order that they will be taken. Core samples will come in from the field in the incubation syringe. Adjust the headspace on each one to 30 mL by either pushing the core up from the bottom or removing soil from the bottom and letting the core move down.
2. Place small red serum stopper firmly on tip of incubation syringe. Withdraw 3 mL from headspace, add mL acetylene. This should be done with the glass "acetylene only" syringe - three at a time can be done. Whenever you are injecting through these small serum stoppers, use a 23 G 1 inch needle.

3. Using 21 G 1 inch needle, pump each core three times with 50 mL syringe labeled pump. Be careful not to pull the core up so only pull about 10 mL.
4. Incubate for four hours, taking samples at 1 hour and four hours. Incubate at 25 C or room temp if incubator not available.
5. After incubation, measure the length (L) and headspace (HS) of each core and then store cores in freezer.

Slurries

1. Soils should be well mixed in the field, stored in whirlpak or ziplock bags with minimal headspace (squeeze air out). Store soil on ice from field and refrigerate in lab.
 2. Before experiment starts, number and weigh all serum bottles you will use. Weigh bottles with grey serum stopper. Record weights on data sheets.
 3. Place approximately 20 or 40 g of soil in the tared serum bottle. For soils expected to be high DEA, use 20g. For low DEA use 40 g. Either scoop soil into the bottle with a scoopula or use the 5 mL cutoff syringes (15mL = approx 20 g, 30mL = 40g). Get approximately 20 or 40 g in each bottle. Place grey serum stopper into serum bottle after soil is added to avoid drying.
 4. Re-weigh bottle plus soil with serum stopper. Record weight on data sheets
 5. Add 20 mL (or 40mL) of solution to each bottle from repipet. Slurries will be made with 20 mL (or 40 mL) of one or more of the following solutions:
 - a) solution 1 - 1 g/L chloramphenicol (chl)
 - b) solution 2 - 1 g/L chl and 200 mg NO₃-N/L (1.444 g KNO₃/L)
 - c) solution 3 - 1 g/L chl and 2 g glucose-C/L (5.505 g Glucose/L)
 - d) solution 4 - 1 g/L chl, 200 mg NO₃-N/L, 2 g Glucose-C/L - DEA**
- Solution 4 is used to measure actual denitrification potential or denitrifier enzyme assay.
6. Crimp top onto bottle. They are now ready to evacuate and gas.

7. Evacuate and gas in sets of twelve. Evacuate and add N₂ twice. Evacuate third time and add N₂/acetylene mixture. To take off bottles follow these steps: 1) turn three way valve back to the N₂ tank; 2) relieve overpressure by taking off bottle #1 leaving needle in the bottle; 3) take off other bottles; 4) turn valve to vacuum and turn vacuum off. DO NOT TURN VACUUM OFF WHILE IT IS PULLING A VACUUM.
8. Slurries should be incubated in the orbital shaker so that the slurry will remain well mixed. Incubate at room temp and record temp in your lab notebook.
9. Take samples at 1 hour and 4 hours after start of incubation. Record start and end times for a sampling in your lab notebook.
10. After gas sampling is done, weigh bottle, measure headspace in bottles by filling with water and re-weighing

Processing cores

When ready to process, allow to thaw, put entire core into weighed soil moisture can and then weigh entire core plus can. The core is now ready for subsampling for nitrate/ammonium extraction, gravimetric soil moisture determination, and any other measurements that will be done on the soil. Check with Dr. Mbuya to see what he wants you to do besides the KCl extract for nitrate/ammonium determination and the gravimetric soil moisture. This is how we would do these things: From the entire thawed core, weigh 12 grams of soil into bottle that can be placed on a shaker. Add 20 mL of a 2 M KCl solution and shake for one hour. Filter the solution into 20 mL scintillation vials and analyze the filtrate for nitrate and ammonium by standard colorimetric techniques. Take the remaining thawed soil and dry for three days at 105 C to a constant weight. Record the dry weight. This will allow calculation of gravimetric soil moisture. Please note, if total C or N needs to be determined on the soil, it needs to be done on an air-dried soil.

Processing bagged soils after they are used for slurries

Processing the bagged soils is similar to the cores except that the total weight of the bag of soil is not needed. After slurries are started, store bags in freezer. When ready to process, allow to thaw. From the thawed bag of soil, weigh 12 grams of soil into bottle that can be placed on a shaker. Add 20 mL of a 2 M KCl solution and shake for one hour. Filter the solution into 20mL scintillation vials and analyze the filtrate for nitrate and ammonium by standard colorimetric techniques. Take about 50 g (49-50 g) of the remaining thawed soil and dry for three days at 105 C to a constant weight. Record the dry weight. This will allow calculation of gravimetric soil moisture (SM). Please note, if total C or N needs to be determined on the soil, it needs to be done on an air-dried soil.

Calculations for cores

Determine bulk density of cores based on the total mass of dried soil (including the portion removed for KCl extraction) and the volume of the core ($V = \pi \cdot r^2 \cdot L$). Bulk Density (BD) = mass (g)/volume (cubic centimeters). Total porosity (TP) is:

$$TP = (1 - (\text{bulk density} / \text{particle density}))$$

$$\% \text{Water Filled pore space} = [SM / (TP \cdot V)] \cdot 100$$

See Lowrance and Smittle (1988) paper for proper equations.

The denitrification calculations are shown here:

Need gravimetric soil moisture (SM), Headspace (HS); Total weight of core (TWC) incubation bottle.

$$\text{Time 2} - \text{Time 1} = \Delta T \text{ (DT)}$$

$$\text{SoilWater} = SM \cdot TWC$$

$$\text{SoilDry} = TWC - \text{SoilWater};$$

$$\text{Concentration Change (CC)} = N_2O(\text{Time2}) - N_2O(\text{Time1});$$

$$\text{Volume } N_2O = CC \cdot HS + CC \cdot \text{Soilwater} \cdot 0.667 \quad \text{- this converts concentration to volume and accounts for dissolved } N_2O$$

$$\text{Mass } N_2O \text{ (ng)} = \text{Volume } N_2O \cdot 1.842 \quad \text{- converts volume to mass.}$$

$$\text{Rate} = (\text{Mass } N_2O / \text{SoilDry}) \cdot (24 / DT) \quad \text{- This converts to a daily rate. Can also express as hourly rate}$$

Calculations for denitrification potential

Determine fraction gravimetric soil moisture (SM);

Determine Headspace (HS) - usually = 130 ml for 20g samples and 100mL for 40g samples;

Record Soil Wet Weight (SoilWet) - the amount put into the incubation bottle.

$$\text{Time 2} - \text{Time 1} = \Delta T \text{ (DT)}$$

$$\text{SoilWater} = SM \cdot \text{SoilWet}$$

$$\text{TotalWater} = \text{SoilWater} + 20 \text{ (volume of solution added);}$$

$$\text{SoilDry} = \text{SoilWet} - \text{SoilWater};$$

$$\text{Concentration Change (CC)} = N_2O(\text{Time2}) - N_2O(\text{Time1});$$

$$\text{Volume } N_2O = CC \cdot HS + CC \cdot \text{TotalWater} \cdot 0.667 \quad \text{- this converts concentration to volume and accounts for dissolved } N_2O$$

$$\text{Mass } N_2O \text{ (ng)} = \text{Volume } N_2O \cdot 1.842 \quad \text{- converts volume to mass.}$$

Rate = (MassN₂O/SoilDry)*(24/DT) - This converts to a daily rate. Can also express as hourly rate

Calculations for denitrification potential

Determine fraction gravimetric soil moisture (SM);

Determine Headspace (HS) - usually = 140 mL;

Record Soil Wet Weight (SoilWet) - the amount put into the incubation bottle.

Time 2 - Time 1 = delta T (DT)

SoilWater = SM*SoilWet

TotalWater = SoilWater + 20 (volume of solution added);

SoilDry = SoilWet - SoilWater;

Concentration Change (CC) = N₂O(Time2) - N₂O(Time1);

Volume N₂O = CC*HS + CC*TotalWater*0.667 - this converts concentration to volume and accounts for dissolved N₂O

MassN₂O (ng) = Volume N₂O*1.842 - converts volume to mass.

Rate = (MassN₂O/SoilDry)*(24/DT) - This converts to a daily rate. Can also express as hourly rate

NC CREP Boring Log Evaluations (NC DENR Div. of Water Quality)


	NC DENR Division of Water Quality - Aquifer Protection Section	Page <u>1</u> of <u> </u> Boring # <u>L2</u> County <u>Halifax</u>
BORING LOG		

Project CREP JC Wiley Region RRO Hydro/Tech Milosh
 Drill Equipment & Method Geoprobe Start Date 5/21/08 Completion Date 5/21/08
 Sample Method Boring Diameter 2" Total Depth 24 Screen Interval 19-24
 Land Elevation TOC Elevation Groundwater (ft btoc) 0 Hours 24 Hours

Ele v.	De pth (ft. bls)	Lithology Description	Notes/Well Description
	1	Tan/brown silty sand	
		Tan/orange fine to med sandy silt – water table	0-17 ft
		Gray, orange and red silty fine sandy clay - mottled	0.75" pvc
			Casing
	5		
		Same as above with 3" layer of slightly rounded quartz gravels	
		Same as above with 6" layer of light gray coarse sandy clay	17-19 ft
		3" layers of orange and beige fine to coarse sandy clayey silt with many rounded gravels	bentonite
	10	Same as above with decreasing clay and decreasing gravels	
		White and orange silty fine gravelly coarse sand in 3" layers	19-24
			screen
		Tan fine to medium sand	
		Same as above but becoming coarser	
	15	Tan and black and orange and red clayey silt in very fine horiz bands	
		Hard contact with dark gray micaceous clayey silt	
	20		
		Same as above, but becoming more clayey and more shells and tighter	
	25		


Form GW-2 (B)

Revised 5/4/2004

	NC DENR Division of Water Quality - Aquifer Protection Section	Page 1 of Boring # F1
BORING LOG		County Halifax

Project CREP JC Wiley Region RRO Hydro/Tech Milosh
 Drill Equipment & Method Geoprobe Start Date 5/21/08 Completion Date 5/21/08
 Sample Method _____ Boring Diameter 2" Total Depth 32 Screen Interval 27-32
 Land Elevation _____ TOC Elevation _____ Groundwater (ft btoc) 0 Hours _____ 24 Hours _____

Elev.	Depth (ft. bls)	Lithology Description	Notes/Well Description
	1	Beige silty fine sand	0-21 ft casing 21-27 ft Bentonite 27-32 ft Screen Used .75" pvc well
		Light brown very fine sandy silt	
		Brown/gray and orange mottled fine sandy silty clay	
	5		
		6" of pale yellow and orange silty clay	
		Light gray silty clay	
	10	Light gray sandy silty clay	
		6" of black and white sand - water table at 10 ft bls	
		Black, white, orange and tan fine sandy clay in thin horiz layers	
	15	Brown, orange, off white and dark red silty fine to medium sand	
		Hard contact with tan light gray and orange silty clay in fine horiz layers	
		Light gray silty clay	
		Orange, tan and off white medium to coarse sand with many rounded gravels	
	20	Hard contact with tan/orange clayey silt	
		Dark orange silty sand	
		White silt in gravelly coarse sand	
		2" black and white and orange silt in fine horiz layers	
	25	Dark gray clayey silt	
	30	Dark gray clayey silt until 32 feet deep	

	NC DENR Division of Water Quality - Aquifer Protection Section	Page <u>1</u> of <u> </u> Boring # <u>HI</u> County <u>Halifax</u>
BORING LOG		

Project CREP JC Wiley Region RRO Hydro/Tech Milosh
 Drill Equipment & Method Geoprobe Start Date 5/20/08 Completion Date 5/20/08
 Sample Method Boring Diameter 2" Total Depth 24 Screen Interval 19-24
 Land Elevation TOC Elevation Groundwater (ft btoc) 0 Hours 24 Hours

Ele v.	De pth	Lithology Description	Notes/Well Description
	1	Dark tan silty fine sand with organic material	
			0-17 ft
		Orange sandy clayey silt	0.75" pvc
		Red and orange and gray mottled very fine sandy clayey silt	Casing
	5		
		Same as above with distinct bands of color and coarser sand	17-19 ft
			bentonite
		Pink and tan fine fine to coarse sandy silt – wet	
	10	Light orange and tan coarse sandy silt with rounded quartz gravels – water table	19-24
		Fine gravelly white silty coarse sand in fine horiz layers with coarse gravels	screen
		Same as above with distinct horiz bands of black sand	
		Black and white and orange clayey silt in fine horizontal layers	
	15	Hard contact with dark gray silty clay with very fine sand and mica	
	20		
		Dark gray silty clay with marine shells	
	25		
		Began to collect 2 ft cores with discrete sampler due to sloughing in	
	30		

Boring# _____



NC DENR Division of Water Quality -
Aquifer Protection Section
BORING LOG

Page 1 of 1
Boring # M-1
County Halifax

Project CREP-RG Willey Region _____ Hydro/Tech R Bolich
Drill Equipment & Method GeoProbe Start Date 5/22/08 Completion Date 5/22/08
Sample Method _____ Boring Diameter 2.1 Total Depth 24' Screen Interval 19-24'
Land Elevation _____ TOC Elevation _____ Groundwater (ft btoc) 0 Hours _____ 24 Hours _____

Elev.	Depth (ft. b/s)	Sample #	Lithology Description	Well Diagram	Notes/Well Description
	1		Direct push with no samples until 22 feet.		Well set with 5 feet of prepacked ¾" 10 slot screen from 19 to 24 feet; bentonite from 0 – 19 feet.
	5				
			Softer material from 9 to 12 feet.		
	10				
			Harder from 12 to 15 feet.		
	15		Softer from 15 to 24 feet (Yorktown?).		
	20				
		S-1	Dark grey clayey SILT & shell fragments; nearly horizontal laminations; slightly dense; water around shell frags; no odor; moist to wet.		
	25				
	30				

Survey Completed by Soil Surveyor (Erik Severson)

1. Field edge

A—0-10 inches; very dark grayish brown (10YR 3/2) loamy sand, loose consistency.

E—10-19 inches; very pale brown (10YR 7/4) loamy sand, friable.

Bt1—19-33 inches; light olive brown (2.5Y 5/6) sandy clay loam; 5% brownish yellow (10YR 5/8) Fe concentrations.

Bt2—33-50 inches; light olive brown (2.5Y 5/6) clay; 10% strong brown (7.5YR 5/6) concentrations, 10% gray (5Y 6/1) depletions.

C1—50-73 inches; reddish yellow (7.5YR 6/6) sticky sandy loam, medium to coarse sand grains evident.

C2—73-87 inches; olive yellow (2.5Y 6/6) light (~21% clay) sandy clay loam; 15% light bluish gray (8/5PB), and 5% yellowish red (5YR 5/8) concentrations.

C3—87-110 inches, variegated sandy clay loam; 40% light bluish gray (8/5PB), 30% pale brown (10YR 6/3), 20 % light olive brown (2.5Y 5/6), and 10% yellowish red (5YR 5/8) concentrations (color looks overall duller than previous horizon).

C4—110-131 inches; very pale brown (10YR 7/4) sandy loam; 30% grayish brown (2.5Y 5/2) faint organic bodies surrounded by a pale yellow (5Y 7/4) Fe depleted rim.

C5—131-136 inches; olive (2.5Y 5/4) sandy loam.

Cg1—136-144 inches; gray (10YR 6/1) sand.

Cg2—144-150 inches; gray (5Y 6/1) clay lenses surrounded by 30% pale yellow (5Y 8/4) relatively thick Fe depleted rims, and olive yellow (2.5Y 6/8) sandy loam.

2C1—150-158 inches; light yellowish brown (10YR 6/4) sand.

2C2—158-166 inches; yellowish brown (10YR 5/4) sandy clay; 10% gray (5Y 6/1) clay lenses, 5% dark yellowish brown (10YR 3/4) organic streaks; 10% gravel.

3C—166-173 inches; yellowish brown (10YR 5/6) silty clay loam; 10% strong brown (7.5YR 5/6) Fe conc.

4C—173-228 inches; bluish gray (5/10B) and greenish gray (4/10BG) soft marine silty clay.

Recommended Monitoring Well Depths: Shallow: 6-8 feet Deep: 10-14 feet

2. Footslope

A—0-15 inches; brown (10YR 3/3) sandy loam.

E—15-26 inches; very pale brown (10YR 7/4) sandy loam.

Bt—26-43 inches; olive yellow (2.5Y 6/6) sandy clay loam; yellowish brown (10YR 5/8) concentrations, 10% gray (2.5Y 7/1) depletions.

BC—43-60 inches; light yellowish brown (10YR 6/4) sandy loam; 7% light gray (2.5Y 7/2) depletions, 5% brownish yellow (10YR 5/8) concentrations.

C1—60-80 inches; yellowish brown (10YR 5/4) sticky sandy clay loam; saturated.

2C2—80-98 inches; light brown (7.5YR 6/4) sandy clay loam; 15% brownish yellow (10YR 5/8) concentrations; 10% bluish gray (5/BP) depletions; 2% gravel.

2C3—98-107 inches; reddish yellow (7.5YR 6/6) tight sandy clay; 12% rounded gravel.

2Cg4—107-127 inches; white (2.5Y 8/1) gravelly sandy loam, 15% .5 cm diameter gravels. (Fe depleted zone, same depositional event is likely).

2C5—127-136 inches; strong brown (7.5YR 5/8) coarse loamy sand.

3C6—136-155 inches; pale yellow (2.5 7/4) gravelly coarse sand; 25% bluish gray (5/BP) depletions.

3C7—155-160 inches; gray (5Y 6/1) clay lenses surrounded by 30% pale brown (10YR 6/3) and 20% strong brown (7.5YR 4/6) concentrations.

3C8—160-180 inches; pale yellow (2.5Y 7/4) sandy clay loam; 35% gray (5Y 6/1) depletions, 10% gravel.

4C9—180-192 inches; yellowish brown (10YR 5/6) and reddish yellow (7.5YR 6/6) silt loam.

5C10—192-200 inches; yellowish brown (10YR 4/4)sandy loam.

6C11—200-240 inches; greenish gray (5/5G) marine silty clay, 5% gravels.

Recommended Monitoring Well Depths: Shallow: 4-6 feet Deep: 10-13 feet

APPENDIX C: Statistical Evaluation Results

Code for Statistical Evaluations

NO₃-N Evaluation Example Code (adapted from Grabow, 2010)

```
options ls=85 nodate nocenter formdlm="+";

data one;
  infile "C:\Users\Tiffany Messer\Desktop\Stats2\Treatment1.csv"
  firstobs=2 dlm="," dsd;
  input SampleID $ Date : mmddyy10. Treatment Transect WellPosition Depth $ NO3 Cl NCl Na Ca DOC;
  week=week(date);
  day=day(date);
  lno3=log(no3+.01);
run;

data two;
  infile "C:\Users\Tiffany Messer\Desktop\Stats2\Treatment2.csv"
  firstobs=2 dlm="," dsd;
  input SampleID $ Date : mmddyy10. Treatment Transect WellPosition Depth $ NO3 Cl NCl Na Ca DOC;
  week=week(date);
  day=day(date);
  lno3=log(no3+.01);
run;

data both;
  set one two;
run;

proc sort data=both;
  by treatment depth;
run;

data sorttime;
  set both;
run;

proc sort data=sorttime;
  by treatment SampleID Date;
run;

proc print data=sorttime;
run;

proc sort;
  by treatment depth;
run;
```

```

data one;
  set one;
  if treatment > . ;
  if depth < "T" and depth > " " ;
run;
proc sort;
  by depth;
run;
proc mixed data=both method=type3;

  by treatment;
  class depth wellposition transect week treatment day date ;
  model lno3=wellposition|depth / outp=two;
  random transect transect*wellposition date;

  lsmeans wellposition|depth/slice=(wellposition depth);
run;

proc gplot data=both;
by treatment;
plot lno3*wellposition=depth;
run;
proc mixed data=sorttime COVTEST;
  by treatment;
  class SampleID depth wellposition transect week treatment day date ;
  model lno3=wellposition|depth / outp=two;
  random transect transect*wellposition date;
  repeated/subject=SampleID type=ar(1);
  lsmeans wellposition|depth/slice=(wellposition depth);
run;
proc gplot data=two;
by treatment;
plot resid*Date;
by SampleID;
run;

```

Redox Evaluation Example Code

```

options ls=85 nodate nocenter formdlm="+";

data one;
  infile "C:\Users\Tiffany Messer\Desktop\Stats2\redox1.csv"
  firstobs=2 dlm="," dsd;
  input Treatment Location Date : mmddyy10. depth $ redox;
  week=week(date);
  day=day(date);

```

```

    lredox=log(redox+400);
run;
data two;
  infile "C:\Users\Tiffany Messer\Desktop\Stats2\redox2.csv"
  firstobs=2 dlm="," dsd;
  input Treatment Location Date : mmddyy10. depth $ redox;
  week=week(date);
  day=day(date);
  lredox=log(redox+400);
run;
data both;
  set one two;
run;

proc sort data=both;
  by treatment depth;
run;
data sorttime;
  set both;
run;
proc sort data=sorttime;
  by treatment location;
run;
proc print data=sorttime;
run;

proc sort data=both;
  by treatment depth;
run;
data one;
  set one;
  if treatment > . ;
  if depth < "T" and depth > " ";
run;
proc sort;
  by depth;
run;
proc mixed data=both method=type3;
  by treatment;
  class location depth treatment;
  model lredox=location|depth / outp=two;
  lsmeans location|depth/slice=(location depth);
run;

```

NO₃⁻-N Statistical Analysis Results using PROC MIXED

Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	1.0955	0.3510	6	3.12	0.0206
WellPosition		2	0.5169	0.3510	6	1.47	0.1913
WellPosition		3	0.1173	0.3510	6	0.33	0.7495
WellPosition		4	0.1487	0.3508	6	0.42	0.6864
Depth	D		0.7703	0.06131	1424	12.56	<.0001
Depth	S		0.1690	0.06334	1424	2.67	0.0077
Depth*WellPosition	D	1	1.0314	0.3531	1424	2.92	0.0035
Depth*WellPosition	D	2	0.8267	0.3532	1424	2.34	0.0194
Depth*WellPosition	D	3	0.4515	0.3531	1424	1.28	0.2013
Depth*WellPosition	D	4	0.7715	0.3531	1424	2.18	0.0291
Depth*WellPosition	S	1	1.1596	0.3546	1424	3.27	0.0011
Depth*WellPosition	S	2	0.2071	0.3544	1424	0.58	0.5590
Depth*WellPosition	S	3	-0.2168	0.3544	1424	-0.61	0.5407
Depth*WellPosition	S	4	-0.4741	0.3537	1424	-1.34	0.1803

The SAS System 74

Treatment=1

The Mixed Procedure

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	1424	2.05	0.1522
Depth*WellPosition		2	1	1424	48.89	<.0001
Depth*WellPosition		3	1	1424	57.15	<.0001
Depth*WellPosition		4	1	1424	212.16	<.0001
Depth*WellPosition	D		3	1424	0.36	0.7836
Depth*WellPosition	S		3	1424	3.18	0.0233

Figure C. 1: Treatment 1 NO₃⁻-N statistical analysis results

Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
Depth	S		1.0798	0.09997	1077	10.80	<.0001
Depth*WellPosition	D	1	2.4713	0.1699	1077	14.55	<.0001
Depth*WellPosition	D	2	2.3393	0.1700	1077	13.76	<.0001
Depth*WellPosition	D	3	1.6055	0.1700	1077	9.44	<.0001
Depth*WellPosition	S	1	2.4934	0.1715	1077	14.54	<.0001
Depth*WellPosition	S	2	1.8339	0.1720	1077	10.66	<.0001
Depth*WellPosition	S	3	-1.0879	0.1709	1077	-6.37	<.0001

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	1077	0.06	0.8008
Depth*WellPosition		2	1	1077	32.55	<.0001
Depth*WellPosition		3	1	1077	966.81	<.0001
Depth*WellPosition	D		2	1077	7.60	0.0005
Depth*WellPosition	S		2	1077	125.28	<.0001

Figure C. 2: Treatment 2 NO₃⁻-N statistical analysis results

CI Statistical Analysis Results using PROC MIXED

Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	2.5865	0.1056	6	24.49	<.0001
WellPosition		2	2.5371	0.1056	6	24.02	<.0001
WellPosition		3	2.3296	0.1056	6	22.06	<.0001
WellPosition		4	2.5947	0.1056	6	24.58	<.0001
Depth	D		2.4237	0.04887	1309	49.59	<.0001
Depth	S		2.6002	0.04915	1309	52.91	<.0001
Depth*WellPosition	D	1	2.4615	0.1062	1309	23.18	<.0001
Depth*WellPosition	D	2	2.4226	0.1062	1309	22.81	<.0001
Depth*WellPosition	D	3	2.2256	0.1062	1309	20.96	<.0001
Depth*WellPosition	D	4	2.5851	0.1062	1309	24.35	<.0001
Depth*WellPosition	S	1	2.7115	0.1067	1309	25.42	<.0001
Depth*WellPosition	S	2	2.6515	0.1066	1309	24.88	<.0001
Depth*WellPosition	S	3	2.4335	0.1066	1309	22.83	<.0001
Depth*WellPosition	S	4	2.6043	0.1064	1309	24.49	<.0001

The SAS System 159

Treatment=1

The Mixed Procedure

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	1309	93.10	<.0001
Depth*WellPosition		2	1	1309	79.74	<.0001
Depth*WellPosition		3	1	1309	66.17	<.0001
Depth*WellPosition		4	1	1309	0.61	0.4348
Depth*WellPosition	D		3	1309	1.88	0.1316
Depth*WellPosition	S		3	1309	1.20	0.3097

Figure C. 3: Treatment 1 CI statistical analysis results

Treatment=2							
The Mixed Procedure							
Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
Depth	S		3.3013	0.03865	993	85.42	<.0001
Depth*WellPosition	D	1	3.5292	0.1185	993	29.79	<.0001
Depth*WellPosition	D	2	3.4175	0.1185	993	28.85	<.0001
Depth*WellPosition	D	3	3.0262	0.1185	993	25.54	<.0001
Depth*WellPosition	S	1	3.3393	0.1190	993	28.07	<.0001
Depth*WellPosition	S	2	3.6220	0.1191	993	30.41	<.0001
Depth*WellPosition	S	3	2.9425	0.1188	993	24.78	<.0001

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	993	26.43	<.0001
Depth*WellPosition		2	1	993	29.89	<.0001
Depth*WellPosition		3	1	993	5.29	0.0216
Depth*WellPosition	D		2	993	3.70	0.0252
Depth*WellPosition	S		2	993	6.14	0.0022

Figure C. 4: Treatment 2 CI statistical analysis results

NO₃⁻-N/Cl⁻ Statistical Analysis Results using PROC MIXED

Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	-1.3823	0.2127	6	-6.50	0.0006
WellPosition		2	-1.8730	0.2127	6	-8.81	0.0001
WellPosition		3	-2.0523	0.2127	6	-9.65	<.0001
WellPosition		4	-2.2459	0.2125	6	-10.57	<.0001
Depth	D		-1.6068	0.03980	1309	-40.38	<.0001
Depth	S		-2.1700	0.04194	1309	-51.74	<.0001
Depth*WellPosition	D	1	-1.3780	0.2147	1309	-6.42	<.0001
Depth*WellPosition	D	2	-1.5571	0.2148	1309	-7.25	<.0001
Depth*WellPosition	D	3	-1.7293	0.2147	1309	-8.05	<.0001
Depth*WellPosition	D	4	-1.7627	0.2147	1309	-8.21	<.0001
Depth*WellPosition	S	1	-1.3867	0.2164	1309	-6.41	<.0001
Depth*WellPosition	S	2	-2.1888	0.2161	1309	-10.13	<.0001
Depth*WellPosition	S	3	-2.3754	0.2160	1309	-10.99	<.0001
Depth*WellPosition	S	4	-2.7291	0.2153	1309	-12.68	<.0001

The SAS System 245

Treatment=1

The Mixed Procedure

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	1309	0.02	0.9003
Depth*WellPosition		2	1	1309	85.53	<.0001
Depth*WellPosition		3	1	1309	89.92	<.0001
Depth*WellPosition		4	1	1309	216.83	<.0001
Depth*WellPosition	D		3	1309	0.53	0.6626
Depth*WellPosition	S		3	1309	5.39	0.0011

Figure C. 5: Treatment 1 NO₃⁻-N/Cl⁻ Statistical Analysis Results

Treatment=2							
The Mixed Procedure							
Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
Depth	S		-1.9448	0.06517	993	-29.84	<.0001
Depth*WellPosition	D	1	-0.9776	0.1525	993	-6.41	<.0001
Depth*WellPosition	D	2	-1.0474	0.1525	993	-6.87	<.0001
Depth*WellPosition	D	3	-1.3896	0.1526	993	-9.11	<.0001
Depth*WellPosition	S	1	-0.8084	0.1537	993	-5.26	<.0001
Depth*WellPosition	S	2	-1.6760	0.1540	993	-10.88	<.0001
Depth*WellPosition	S	3	-3.3500	0.1532	993	-21.86	<.0001

■

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	993	6.45	0.0112
Depth*WellPosition		2	1	993	86.92	<.0001
Depth*WellPosition		3	1	993	889.66	<.0001
Depth*WellPosition	D		2	993	1.69	0.1846
Depth*WellPosition	S		2	993	57.61	<.0001

Figure C. 6: Treatment 2 NO₃⁻-N/Cl⁻ Statistical Analysis Results

DOC Statistical Analysis Results using PROC MIXED

Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	0.2913	0.1740	6	1.67	0.1451
WellPosition		2	0.2037	0.1740	6	1.17	0.2861
WellPosition		3	0.1105	0.1740	6	0.64	0.5488
WellPosition		4	0.07035	0.1734	6	0.41	0.6990
Depth	D		-0.06324	0.1392	1013	-0.45	0.6497
Depth	S		0.4012	0.1401	1013	2.86	0.0043
Depth*WellPosition	D	1	0.1386	0.1784	1013	0.78	0.4372
Depth*WellPosition	D	2	-0.06719	0.1786	1013	-0.38	0.7068
Depth*WellPosition	D	3	-0.1278	0.1784	1013	-0.72	0.4741
Depth*WellPosition	D	4	-0.1966	0.1781	1013	-1.10	0.2698
Depth*WellPosition	S	1	0.4440	0.1814	1013	2.45	0.0145
Depth*WellPosition	S	2	0.4746	0.1809	1013	2.62	0.0088
Depth*WellPosition	S	3	0.3488	0.1811	1013	1.93	0.0544
Depth*WellPosition	S	4	0.3373	0.1791	1013	1.88	0.0600

The SAS System 331

Treatment=1

The Mixed Procedure

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	1013	11.24	0.0008
Depth*WellPosition		2	1	1013	36.31	<.0001
Depth*WellPosition		3	1	1013	27.97	<.0001
Depth*WellPosition		4	1	1013	38.80	<.0001
Depth*WellPosition	D		3	1013	1.26	0.2858
Depth*WellPosition	S		3	1013	0.27	0.8460

Figure C. 7: Treatment 1 DOC Statistical Analysis Results

The SAS System							
Treatment=2							
The Mixed Procedure							
Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
Depth	S		1.0488	0.5201	134	2.02	0.0457
Depth*WellPosition	D	1	0.8076	0.5447	134	1.48	0.1405
Depth*WellPosition	D	2	0.5928	0.5436	134	1.09	0.2774
Depth*WellPosition	D	3	0.02821	0.5396	134	0.05	0.9584
Depth*WellPosition	S	1	0.6689	0.5617	134	1.19	0.2358
Depth*WellPosition	S	2	1.3151	0.5670	134	2.32	0.0219
Depth*WellPosition	S	3	1.1624	0.5489	134	2.12	0.0360

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	134	0.23	0.6349
Depth*WellPosition		2	1	134	5.78	0.0176
Depth*WellPosition		3	1	134	18.84	<.0001
Depth*WellPosition	D		2	134	3.42	0.0357
Depth*WellPosition	S		2	134	1.75	0.1775

Figure C. 8: Treatment 2 DOC Statistical Analysis Results

Na⁺ Statistical Analysis Results using PROC MIXED

The SAS System

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Treatment=1

The Mixed Procedure

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	140	137.15	<.0001
Depth*WellPosition		2	0	.	.	.
Depth*WellPosition		3	0	.	.	.
Depth*WellPosition		4	1	140	0.43	0.5141
Depth*WellPosition	D		3	140	0.68	0.5672
Depth*WellPosition	S		1	140	1.94	0.1662

Figure C. 9: Treatment 1 Na⁺ Statistical Analysis Results

Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
Depth*WellPosition	D	1	1.1402	0.2127	144	5.36	<.0001
Depth*WellPosition	D	3	1.8718	0.2116	144	8.85	<.0001
Depth*WellPosition	S	1	1.2326	0.2145	144	5.75	<.0001
Depth*WellPosition	S	3	1.8534	0.2127	144	8.71	<.0001

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	144	2.62	0.1079
Depth*WellPosition		3	1	144	0.14	0.7113
Depth*WellPosition	D		1	144	13.79	0.0003
Depth*WellPosition	S		1	144	9.68	0.0022

Figure C. 10: Treatment 2 Na⁺ Statistical Analysis Results

Ca²⁺ Statistical Analysis Results using PROC MIXED

Treatment=1

The Mixed Procedure

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	137	79.53	<.0001
Depth*WellPosition		2	0	.	.	.
Depth*WellPosition		3	0	.	.	.
Depth*WellPosition		4	1	137	52.10	<.0001
Depth*WellPosition	D		2	137	5.30	0.0061
Depth*WellPosition	S		1	137	17.26	<.0001

Figure C. 11: Treatment 1 Ca²⁺ Statistical Analysis Results

Treatment=2

The Mixed Procedure

Least Squares Means

Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
Depth*WellPosition	D	1	3.5151	0.1599	142	21.98	<.0001
Depth*WellPosition	D	3	2.2307	0.1584	142	14.08	<.0001
Depth*WellPosition	S	1	3.4226	0.1624	142	21.07	<.0001
Depth*WellPosition	S	3	2.5130	0.1601	142	15.70	<.0001

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	142	2.48	0.1172
Depth*WellPosition		3	1	142	30.09	<.0001
Depth*WellPosition	D		1	142	774.53	<.0001
Depth*WellPosition	S		1	142	258.89	<.0001

Figure C. 12: Treatment 2 Ca²⁺ Statistical Analysis Results

T-tests for Difference in NO₃⁻-N Concentrations at the Field Edge

NO₃⁻-N differences depending on treatment

meanz 166

The TTEST Procedure

Variable: NO3

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
1	101	3.6568	2.3478	0.2336	0	9.1400
2	116	10.2762	6.0336	0.5602	0	21.0200
Diff (1-2)		-6.6194	4.6942	0.6389		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
1		3.6568	3.1933 4.1203	2.3478	2.0626 2.7252
2		10.2762	9.1666 11.3859	6.0336	5.3444 6.9284
Diff (1-2)	Pooled	-6.6194	-7.8786 -5.3602	4.6942	4.2893 5.1841
Diff (1-2)	Satterthwaite	-6.6194	-7.8185 -5.4203		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	215	-10.36	<.0001
Satterthwaite	Unequal	153.15	-10.91	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	115	100	6.60	<.0001

Figure C. 13: NO₃⁻-N differences between Treatments 1 and 2

meanz 167

The TTEST Procedure

Variable: NO3

Depth	N	Mean	Std Dev	Std Err	Minimum	Maximum
D	64	3.4797	0.7656	0.0957	2.5400	6.1800
S	37	3.9632	3.7595	0.6181	0	9.1400
Diff (1-2)		-0.4836	2.3479	0.4849		

Depth	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
D		3.4797	3.2884 3.6709	0.7656	0.6522 0.9273
S		3.9632	2.7098 5.2167	3.7595	3.0572 4.8834
Diff (1-2)	Pooled	-0.4836	-1.4457 0.4786	2.3479	2.0614 2.7275
Diff (1-2)	Satterthwaite	-0.4836	-1.7499 0.7828		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	99	-1.00	0.3211
Satterthwaite	Unequal	37.735	-0.77	0.4442

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	36	63	24.11	<.0001

Figure C. 14: Nitrate differences depending on well depth for Treatment 1

meanz

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The TTEST Procedure

Variable: NO3

Depth	N	Mean	Std Dev	Std Err	Minimum	Maximum
D	64	10.7714	4.9872	0.6234	2.1900	15.8400
S	52	9.6667	7.1187	0.9872	0	21.0200
Diff (1-2)		1.1047	6.0346	1.1266		

Depth	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
D		10.7714	9.5256 12.0172	4.9872	4.2481 6.0401
S		9.6667	7.6849 11.6486	7.1187	5.9658 8.8281
Diff (1-2)	Pooled	1.1047	-1.1272 3.3365	6.0346	5.3426 6.9340
Diff (1-2)	Satterthwaite	1.1047	-1.2154 3.4248		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	114	0.98	0.3289
Satterthwaite	Unequal	88.405	0.95	0.3467

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	51	63	2.04	0.0075

Figure C. 15: Nitrate differences depending on well depth for Treatment 2

Evaluation of Treatment 1 and 2 Depth and Deep Aquifer Interactions using PROC MIXED

*****							25	
meanz								
The TTEST Procedure								
Variable: NO3								
Treatment		N	Mean	Std Dev	Std Err	Minimum	Maximum	
1		1506	2.3543	1.7241	0.0444	0	14.7000	
3		82	0.0163	0.0272	0.00300	0	0.1200	
Diff (1-2)			2.3380	1.6795	0.1905			
Treatment		Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev		
1			2.3543	2.2672 2.4415	1.7241	1.6646 1.7880		
3			0.0163	0.0104 0.0223	0.0272	0.0236 0.0321		
Diff (1-2)		Pooled	2.3380	1.9644 2.7116	1.6795	1.6230 1.7401		
Diff (1-2)		Satterthwaite	2.3380	2.2507 2.4253				
Method		Variances	DF	t Value	Pr > t			
Pooled		Equal	1586	12.28	<.0001			
Satterthwaite		Unequal	1518.2	52.51	<.0001			
Equality of Variances								
Method		Num DF	Den DF	F Value	Pr > F			
Folded F		1505	81	4019.35	<.0001			

Figure C. 16: T-test of the NO₃-N concentrations between Treatment 1 surficial and confined aquifers

meanz 35

The TTEST Procedure

Variable: NO3

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
2	1156	8.5707	5.1604	0.1518	0	31.5000
3	82	0.0163	0.0272	0.00300	0	0.1200
Diff (1-2)		8.5543	4.9884	0.5701		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
2		8.5707	8.2729 8.8685	5.1604	4.9583 5.3798
3		0.0163	0.0104 0.0223	0.0272	0.0236 0.0321
Diff (1-2)	Pooled	8.5543	7.4359 9.6728	4.9884	4.7993 5.1932
Diff (1-2)	Satterthwaite	8.5543	8.2565 8.8522		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	1236	15.01	<.0001
Satterthwaite	Unequal	1155.9	56.35	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	1155	81	36008.2	<.0001

Figure C. 17: T-test of the NO₃-N concentrations between Treatment 2 surficial and confined aquifers

meanz 40

The TTEST Procedure

Variable: Ca

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
1	166	7.6702	5.3870	0.4181	0	25.7000
3	73	87.6060	59.5675	6.9719	7.4600	269.0
Diff (1-2)		-79.9358	33.1386	4.6539		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
1		7.6702	6.8446 8.4957	5.3870	4.8632 6.0383
3		87.6060	73.7079 101.5	59.5675	51.2273 71.1771
Diff (1-2)	Pooled	-79.9358	-89.1041 -70.7675	33.1386	30.4049 36.4166
Diff (1-2)	Satterthwaite	-79.9358	-93.8573 -66.0144		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	237	-17.18	<.0001
Satterthwaite	Unequal	72.518	-11.44	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	72	165	122.27	<.0001

Figure C. 18: T-test of the Ca²⁺ concentrations between Treatment 1 surficial and confined aquifers

meanz 3

The TTEST Procedure

Variable: Ca

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
2	169	21.7231	16.0804	1.2370	0.8600	80.7000
3	73	87.6060	59.5675	6.9719	7.4600	269.0
Diff (1-2)		-65.8829	35.2915	4.9428		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
2		21.7231	19.2812 24.1651	16.0804	14.5294 18.0050
3		87.6060	73.7079 101.5	59.5675	51.2273 71.1771
Diff (1-2)	Pooled	-65.8829	-75.6197 -56.1461	35.2915	32.3970 38.7585
Diff (1-2)	Satterthwaite	-65.8829	-79.9837 -51.7821		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	240	-13.33	<.0001
Satterthwaite	Unequal	76.572	-9.30	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	72	168	13.72	<.0001

Figure C. 19: T-test of the Ca^{2+} concentrations between Treatment 2 surficial and confined aquifers

meanz 44

The TTEST Procedure

Variable: Na

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
1	169	18.8556	62.7442	4.8265	3.3200	415.0
3	73	21.0684	47.1394	5.5172	8.1100	348.0
Diff (1-2)		-2.2127	58.5015	8.1935		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
1		18.8556	9.3273 28.3840	62.7442	56.6924 70.2539
3		21.0684	10.0699 32.0668	47.1394	40.5392 56.3268
Diff (1-2)	Pooled	-2.2127	-18.3531 13.9276	58.5015	53.7032 64.2486
Diff (1-2)	Satterthwaite	-2.2127	-16.6777 12.2522		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	240	-0.27	0.7873
Satterthwaite	Unequal	179.35	-0.30	0.7631

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	168	72	1.77	0.0066

Figure C. 20: T-test of the Na^+ concentrations between Treatment 1 surficial and confined aquifers

meanz

45

The TTEST Procedure

Variable: Na

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
2	171	13.7561	50.2501	3.8427	0.8400	298.0
3	73	21.0684	47.1394	5.5172	8.1100	348.0
Diff (1-2)		-7.3122	49.3451	6.8989		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
2		13.7561	6.1705 21.3417	50.2501	45.4291 56.2248
3		21.0684	10.0699 32.0668	47.1394	40.5392 56.3268
Diff (1-2)	Pooled	-7.3122	-20.9018 6.2773	49.3451	45.3132 54.1707
Diff (1-2)	Satterthwaite	-7.3122	-20.6016 5.9771		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	242	-1.06	0.2902
Satterthwaite	Unequal	144.41	-1.09	0.2786

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	170	72	1.14	0.5427

Figure C. 21: T-test of the Na⁺ concentrations between Treatment 2 surficial and confined aquifers

Redox Interactions using PROC MIXED

Treatment=1

The Mixed Procedure

Least Squares Means

Effect	depth	Location	Estimate	Standard Error	DF	t Value	Pr > t
Location		1	6.2141	0.04541	280	136.86	<.0001
Location		2	6.2409	0.04541	280	137.45	<.0001
Location		3	5.8395	0.04541	280	128.61	<.0001
Location		4	5.4644	0.04541	280	120.34	<.0001
depth	D		5.9350	0.03211	280	184.85	<.0001
depth	S		5.9444	0.03211	280	185.14	<.0001
Location*depth	D	1	6.0573	0.06421	280	94.33	<.0001
Location*depth	S	1	6.3708	0.06421	280	99.21	<.0001
Location*depth	D	2	6.2014	0.06421	280	96.57	<.0001
Location*depth	S	2	6.2805	0.06421	280	97.81	<.0001
Location*depth	D	3	6.0350	0.06421	280	93.98	<.0001
Location*depth	S	3	5.6441	0.06421	280	87.90	<.0001
Location*depth	D	4	5.4465	0.06421	280	84.82	<.0001
Location*depth	S	4	5.4822	0.06421	280	85.37	<.0001

Tests of Effect Slices

Effect	depth	Location	Num DF	Den DF	F Value	Pr > F
Location*depth		1	1	280	11.92	0.0006
Location*depth		2	1	280	0.76	0.3845
Location*depth		3	1	280	18.52	<.0001
Location*depth		4	1	280	0.15	0.6947
Location*depth	D		3	280	27.04	<.0001
Location*depth	S		3	280	48.39	<.0001

Figure C. 22: Treatment 1 redox statistical analysis results

Treatment=2							
The Mixed Procedure							
Least Squares Means							
Effect	depth	Location	Estimate	Standard Error	DF	t Value	Pr > t
Location		1	6.0995	0.05341	210	114.20	<.0001
Location		2	6.2125	0.05341	210	116.32	<.0001
Location		3	5.5529	0.05341	210	103.97	<.0001
depth	D		6.0070	0.04361	210	137.75	<.0001
depth	S		5.9028	0.04361	210	135.36	<.0001
Location*depth	D	1	6.0710	0.07553	210	80.38	<.0001
Location*depth	S	1	6.1279	0.07553	210	81.13	<.0001
Location*depth	D	2	6.3686	0.07553	210	84.32	<.0001
Location*depth	S	2	6.0563	0.07553	210	80.18	<.0001
Location*depth	D	3	5.5815	0.07553	210	73.89	<.0001
Location*depth	S	3	5.5243	0.07553	210	73.14	<.0001
Tests of Effect Slices							
Effect	depth	Location	Num DF	Den DF	F Value	Pr > F	
Location*depth		1	1	210	0.28	0.5950	
Location*depth		2	1	210	8.55	0.0038	
Location*depth		3	1	210	0.29	0.5931	
Location*depth	D		2	210	27.69	<.0001	
Location*depth	S		2	210	19.06	<.0001	

Figure C. 23: Treatment 2 redox statistical analysis results

Code for statistical evaluations using means to take into account day to day variations (Not used in this study)

NO₃⁻N Evaluation Example Code

```
options ls=85 nodate nocenter formdlm="+";

data one;
  infile "Treatment1.csv" firstobs=4 dlm="," dsd;
  input SampleID $ Date : mmddyy10. Treatment Transect WellPosition Depth $
NO3 Cl NCl Na Ca DOC;
  week=week(date);
  day=day(date);
  lno3=log(no3+.01);
run;
data two;
  infile "Treatment2.csv" firstobs=4 dlm="," dsd;
```

```

    input SampleID $ Date : mmddyy10. Treatment Transect WellPosition Depth $
NO3 Cl NCl Na Ca DOC;
    week=week(date);
    day=day(date);
    lno3=log(no3+.01);
run;
data both;
    set one two;
run;
proc means data=both noprint nway;
    class treatment wellposition transect depth;
    var no3 lno3;
    output out=meanz mean=no3mean lno3mean;
run;
proc print data=meanz;
    title "meanz";
run;

proc sort data=both;
    by treatment depth;
run;

symbol value=dot i=r1;

proc sort;
    by treatment depth;
run;
data one;
    set one;
    if treatment > . ;
    if depth < "T" and depth > " ";
run;
proc sort;
    by depth;
run;
proc mixed data=meanz method=type3;
    by treatment;
    class depth wellposition transect treatment ;
    model lno3mean=wellposition|depth / outp=two;
    random transect transect*wellposition ;
    lsmeans wellposition|depth/slice=(wellposition depth);
run;

proc gplot data=meanz;
    by treatment;
    plot lno3mean*wellposition=depth;
run;

```


Redox Evaluation Example Code

```
options ls=85 nodate nocenter formdlim="+";

data one;
  infile "redox1.csv" firstobs=4 dlm="," dsd;
  input Treatment Location Date : mmddyy10. Depth $ redox;
  week=week(date);
  day=day(date);
  lredox=log(redox+400);
run;

data two;
  infile "redox2.csv" firstobs=4 dlm="," dsd;
  input Treatment Location Date : mmddyy10. Depth $ redox;
  week=week(date);
  day=day(date);
  lredox=log(redox+400);
run;

data both;
  set one two;
run;

proc means data=both noprint nway;
  class treatment location depth date;
  var redox lredox;
  output out=meanz mean=redoxmean lredoxmean;
run;

proc print data=meanz;
  title "meanz";
run;

proc sort;
  by treatment location;
run;

symbol value=dot i=r1;
proc gplot data=meanz;
  by treatment location;
  plot lredoxmean*date=depth;
run;

proc sort data=both;
  by treatment depth;
run;

data both;
  set one;
```

```

    if treatment > . ;
    if depth < "T" and depth > " ";
run;

proc sort;
    by depth;
run;

proc mixed data=meanz method=type3;
    by treatment;
    class location depth treatment;
    model lredoxmean=location|depth / outp=two;
    lsmeans location|depth/slice=(location depth);
run;

```

Confined and Surficial Aquifer Evaluation Example Code

```

options ls=85 nodate nocenter formdlm="+";

data one;
    infile "Treatment1.csv" firstobs=4 dlm="," dsd;
    input SampleID $ Date : mmddyy10. Treatment Transect WellPosition Depth $
NO3 Cl NCl Na Ca DOC;
    week=week(date);
    day=day(date);
    lno3=log(no3+.01);
run;

data two;
    infile "Deepl.csv" firstobs=4 dlm="," dsd;
    input SampleID $ Date : mmddyy10. Treatment Transect WellPosition Depth $
NO3 Cl NCl Na Ca DOC;
    week=week(date);
    day=day(date);
    lno3=log(no3+.01);
run;

data both;
    set one two;
run;

proc ttest data=both;
    class treatment;
    var NO3;
run;

```

NO₃⁻-N Statistical Analysis Results using PROC MIXED

Effect	DF	DF	F Value	Pr > F
WellPosition	3	6	1.25	0.3722
Depth	1	8	7.91	0.0227
Depth*WellPosition	3	8	1.86	0.2141

Least Squares Means

Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	1.1010	0.3559	6	3.09	0.0213
WellPosition		2	0.5166	0.3559	6	1.45	0.1969
WellPosition		3	0.1388	0.3559	6	0.39	0.7100
WellPosition		4	0.1383	0.3559	6	0.39	0.7110
Depth	D		0.7697	0.1169	8	6.59	0.0002
Depth	S		0.1776	0.1169	8	1.52	0.1670
Depth*WellPosition	D	1	1.0314	0.4135	8	2.49	0.0373
Depth*WellPosition	D	2	0.8271	0.4135	8	2.00	0.0805
Depth*WellPosition	D	3	0.4490	0.4135	8	1.09	0.3092
Depth*WellPosition	D	4	0.7715	0.4135	8	1.87	0.0991
Depth*WellPosition	S	1	1.1706	0.4135	8	2.83	0.0221
Depth*WellPosition	S	2	0.2061	0.4135	8	0.50	0.6315
Depth*WellPosition	S	3	-0.1714	0.4135	8	-0.41	0.6894
Depth*WellPosition	S	4	-0.4948	0.4135	8	-1.20	0.2657

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	8	0.11	0.7495
Depth*WellPosition		2	1	8	2.18	0.1785
Depth*WellPosition		3	1	8	2.17	0.1788
Depth*WellPosition		4	1	8	9.05	0.0169
Depth*WellPosition	D		3	8	0.28	0.8402
Depth*WellPosition	S		3	8	2.48	0.1354

Figure C. 24: Section 1 NO₃⁻-N statistical analysis results

The Mixed Procedure

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
WellPosition	2	4	46.99	0.0017
Depth	1	6	14.59	0.0088
Depth*WellPosition	2	6	9.01	0.0156

Least Squares Means

Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	2.4843	0.1740	4	14.28	0.0001
WellPosition		2	2.0845	0.1740	4	11.98	0.0003
WellPosition		3	0.2481	0.1740	4	1.43	0.2269
Depth	D		2.1367	0.1715	6	12.46	<.0001
Depth	S		1.0745	0.1715	6	6.26	0.0008
Depth*WellPosition	D	1	2.4716	0.2971	6	8.32	0.0002
Depth*WellPosition	D	2	2.3390	0.2971	6	7.87	0.0002
Depth*WellPosition	D	3	1.5996	0.2971	6	5.38	0.0017
Depth*WellPosition	S	1	2.4969	0.2971	6	8.40	0.0002
Depth*WellPosition	S	2	1.8301	0.2971	6	6.16	0.0008
Depth*WellPosition	S	3	-1.1034	0.2971	6	-3.71	0.0099

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	6	0.00	0.9599
Depth*WellPosition		2	1	6	1.12	0.3314
Depth*WellPosition		3	1	6	31.50	0.0014
Depth*WellPosition	D		2	6	2.50	0.1621
Depth*WellPosition	S		2	6	41.57	0.0003

Figure C. 25: Section 2 NO₃⁻-N statistical analysis results

CI Statistical Analysis Results using PROC MIXED

Effect	Num DF	Den DF	F Value	Pr > F
WellPosition	3	6	1.42	0.3265
Depth	1	8	58.55	<.0001
Depth*WellPosition	3	8	5.32	0.0262

Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	2.5874	0.09969	6	25.95	<.0001
WellPosition		2	2.5394	0.09969	6	25.47	<.0001
WellPosition		3	2.3275	0.09969	6	23.35	<.0001
WellPosition		4	2.5948	0.09969	6	26.03	<.0001
Depth	D		2.4243	0.04157	8	58.32	<.0001
Depth	S		2.6003	0.04157	8	62.56	<.0001
Depth*WellPosition	D	1	2.4615	0.1023	8	24.06	<.0001
Depth*WellPosition	D	2	2.4250	0.1023	8	23.70	<.0001
Depth*WellPosition	D	3	2.2255	0.1023	8	21.75	<.0001
Depth*WellPosition	D	4	2.5851	0.1023	8	25.27	<.0001
Depth*WellPosition	S	1	2.7133	0.1023	8	26.52	<.0001
Depth*WellPosition	S	2	2.6538	0.1023	8	25.94	<.0001
Depth*WellPosition	S	3	2.4295	0.1023	8	23.75	<.0001
Depth*WellPosition	S	4	2.6046	0.1023	8	25.46	<.0001

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	8	29.94	0.0006
Depth*WellPosition		2	1	8	24.73	0.0011
Depth*WellPosition		3	1	8	19.66	0.0022
Depth*WellPosition		4	1	8	0.18	0.6821
Depth*WellPosition	D		3	8	1.91	0.2065
Depth*WellPosition	S		3	8	1.28	0.3447

Figure C. 26: Section 1 CI statistical analysis results

The Mixed Procedure

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
WellPosition	2	4	4.66	0.0902
Depth	1	6	0.12	0.7442
Depth*WellPosition	2	6	3.71	0.0892

Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	3.4356	0.1125	4	30.53	<.0001
WellPosition		2	3.5225	0.1125	4	31.31	<.0001
WellPosition		3	2.9839	0.1125	4	26.52	<.0001
Depth	D		3.3245	0.04063	6	81.82	<.0001
Depth	S		3.3035	0.04063	6	81.30	<.0001
Depth*WellPosition	D	1	3.5298	0.1246	6	28.34	<.0001
Depth*WellPosition	D	2	3.4180	0.1246	6	27.44	<.0001
Depth*WellPosition	D	3	3.0258	0.1246	6	24.29	<.0001
Depth*WellPosition	S	1	3.3414	0.1246	6	26.82	<.0001
Depth*WellPosition	S	2	3.6269	0.1246	6	29.12	<.0001
Depth*WellPosition	S	3	2.9421	0.1246	6	23.62	<.0001

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	6	3.11	0.1283
Depth*WellPosition		2	1	6	3.82	0.0984
Depth*WellPosition		3	1	6	0.61	0.4632
Depth*WellPosition	D		2	6	3.37	0.1045
Depth*WellPosition	S		2	6	5.69	0.0411

Figure C. 27: Section 2 CI statistical analysis results

NO₃⁻-N/Cl⁻ Statistical Analysis Results using PROC MIXED

Effect	Num DF	Den DF	F Value	Pr > F
WellPosition	3	6	2.20	0.1893
Depth	1	8	11.63	0.0092
Depth*WellPosition	3	8	1.54	0.2778

Least Squares Means						
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value Pr > t
WellPosition		1	-1.3796	0.2187	6	-6.31 0.0007
WellPosition		2	-1.8783	0.2187	6	-8.59 0.0001
WellPosition		3	-2.0421	0.2187	6	-9.34 <.0001
WellPosition		4	-2.2565	0.2187	6	-10.32 <.0001
Depth	D		-1.6078	0.08398	8	-19.14 <.0001
Depth	S		-2.1704	0.08398	8	-25.84 <.0001
Depth*WellPosition	D	1	-1.3780	0.2739	8	-5.03 0.0010
Depth*WellPosition	D	2	-1.5592	0.2739	8	-5.69 0.0005
Depth*WellPosition	D	3	-1.7313	0.2739	8	-6.32 0.0002
Depth*WellPosition	D	4	-1.7627	0.2739	8	-6.44 0.0002
Depth*WellPosition	S	1	-1.3812	0.2739	8	-5.04 0.0010
Depth*WellPosition	S	2	-2.1973	0.2739	8	-8.02 <.0001
Depth*WellPosition	S	3	-2.3530	0.2739	8	-8.59 <.0001
Depth*WellPosition	S	4	-2.7502	0.2739	8	-10.04 <.0001

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	8	0.00	0.9926
Depth*WellPosition		2	1	8	3.74	0.0892
Depth*WellPosition		3	1	8	3.55	0.0963
Depth*WellPosition		4	1	8	8.96	0.0173
Depth*WellPosition	D		3	8	0.35	0.7924
Depth*WellPosition	S		3	8	3.65	0.0635

Figure C. 28: Section 1 NO₃⁻-N/Cl⁻ Statistical Analysis Results

The Mixed Procedure						
Type 3 Tests of Fixed Effects						
Effect	Num DF	Den DF	F Value	Pr > F		
WellPosition	2	4	18.63	0.0094		
Depth	1	6	20.00	0.0042		
Depth*WellPosition	2	6	11.68	0.0085		
Least Squares Means						
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value Pr > t
WellPosition		1	-0.8960	0.1566	4	-5.72 0.0046
WellPosition		2	-1.3662	0.1566	4	-8.73 0.0010
WellPosition		3	-2.3764	0.1566	4	-15.18 0.0001
Depth	D		-1.1387	0.1111	6	-10.25 <.0001
Depth	S		-1.9537	0.1111	6	-17.59 <.0001
Depth*WellPosition	D	1	-0.9775	0.2223	6	-4.40 0.0046
Depth*WellPosition	D	2	-1.0482	0.2223	6	-4.71 0.0033
Depth*WellPosition	D	3	-1.3903	0.2223	6	-6.25 0.0008
Depth*WellPosition	S	1	-0.8144	0.2223	6	-3.66 0.0105
Depth*WellPosition	S	2	-1.6842	0.2223	6	-7.58 0.0003
Depth*WellPosition	S	3	-3.3625	0.2223	6	-15.12 <.0001
Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	6	0.27	0.6238
Depth*WellPosition		2	1	6	4.06	0.0305
Depth*WellPosition		3	1	6	39.03	0.0008
Depth*WellPosition	D		2	6	0.88	0.4636
Depth*WellPosition	S		2	6	30.16	0.0007

Figure C. 29: Section 2 NO₃⁻-N/Cl⁻ Statistical Analysis Results

DOC Statistical Analysis Results using PROC MIXED

Effect		Num DF	Den DF	F Value	Pr > F
WellPosition		3	6	0.74	0.5653
Depth		1	8	17.42	0.0031
Depth*WellPosition		3	8	0.70	0.5757

Least Squares Means

Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	0.2856	0.1200	6	2.38	0.0548
WellPosition		2	0.2140	0.1200	6	1.78	0.1248
WellPosition		3	0.08101	0.1200	6	0.68	0.5248
WellPosition		4	0.04044	0.1200	6	0.34	0.7476
Depth	D		-0.02418	0.05513	8	-0.44	0.6725
Depth	S		0.3347	0.05513	8	6.07	0.0003
Depth*WellPosition	D	1	0.1951	0.1476	8	1.32	0.2229
Depth*WellPosition	D	2	-0.01481	0.1476	8	-0.10	0.9226
Depth*WellPosition	D	3	-0.07082	0.1476	8	-0.48	0.6443
Depth*WellPosition	D	4	-0.2062	0.1476	8	-1.40	0.2000
Depth*WellPosition	S	1	0.3762	0.1476	8	2.55	0.0343
Depth*WellPosition	S	2	0.4429	0.1476	8	3.00	0.0171
Depth*WellPosition	S	3	0.2328	0.1476	8	1.58	0.1534
Depth*WellPosition	S	4	0.2871	0.1476	8	1.94	0.0877

Tests of Effect Slices

Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	8	1.11	0.3232
Depth*WellPosition		2	1	8	7.08	0.0288
Depth*WellPosition		3	1	8	3.12	0.1154
Depth*WellPosition		4	1	8	8.23	0.0209
Depth*WellPosition	D		3	8	1.11	0.3993
Depth*WellPosition	S		3	8	0.35	0.7922

Figure C. 30: Section 1 DOC Statistical Analysis Results

Type 3 Tests of Fixed Effects					
Effect	Num DF	Den DF	F Value	Pr > F	
WellPosition	2	4	0.88	0.4814	
Depth	1	6	5.88	0.0514	
Depth*WellPosition	2	6	7.35	0.0244	

Least Squares Means							
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value	Pr > t
WellPosition		1	0.7445	0.2148	4	3.47	0.0257
WellPosition		2	0.8691	0.2148	4	4.05	0.0155
WellPosition		3	0.5175	0.2148	4	2.41	0.0736
Depth	D		0.5421	0.1641	6	3.30	0.0163
Depth	S		0.8786	0.1641	6	5.35	0.0017
Depth*WellPosition	D	1	0.9062	0.2461	6	3.68	0.0103
Depth*WellPosition	D	2	0.6919	0.2461	6	2.81	0.0307
Depth*WellPosition	D	3	0.02821	0.2461	6	0.11	0.9125
Depth*WellPosition	S	1	0.5827	0.2461	6	2.37	0.0557
Depth*WellPosition	S	2	1.0464	0.2461	6	4.25	0.0054
Depth*WellPosition	S	3	1.0068	0.2461	6	4.09	0.0064

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	6	1.81	0.2268
Depth*WellPosition		2	1	6	2.18	0.1905
Depth*WellPosition		3	1	6	16.59	0.0066
Depth*WellPosition	D		2	6	4.15	0.0738
Depth*WellPosition	S		2	6	1.31	0.3373

Figure C. 31: Section 2 DOC Statistical Analysis Results

Na⁺ Statistical Analysis Results using PROC MIXED

Type 3 Tests of Fixed Effects						
Effect		Num DF	Den DF	F Value	Pr > F	
WellPosition		3	2	0.28	0.8379	
Depth		1	4	11.83	0.0263	
Depth*WellPosition		1	4	10.37	0.0323	

Least Squares Means						
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value Pr > t
WellPosition		1	1.9134	0.1720	2	11.13 0.0080
WellPosition		2	Non-est	.	.	.
WellPosition		3	Non-est	.	.	.
WellPosition		4	2.1400	0.1720	2	12.45 0.0064
Depth	D		1.8098	0.1123	4	16.12 <.0001
Depth	S		Non-est	.	.	.
Depth*WellPosition	D	1	1.5842	0.1856	4	8.54 0.0010
Depth*WellPosition	D	2	1.7311	0.3094	4	5.60 0.0050
Depth*WellPosition	D	3	1.7947	0.3094	4	5.80 0.0044
Depth*WellPosition	D	4	2.1292	0.1856	4	11.47 0.0003
Depth*WellPosition	S	1	2.2425	0.1856	4	12.08 0.0003
Depth*WellPosition	S	4	2.1508	0.1856	4	11.53 0.0003

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	4	22.18	0.0092
Depth*WellPosition		2	0	.	.	.
Depth*WellPosition		3	0	.	.	.
Depth*WellPosition		4	1	4	0.02	0.8849
Depth*WellPosition	D		3	4	1.25	0.4027
Depth*WellPosition	S		1	4	0.10	0.7649

Figure C. 32: Section 1 Na⁺ Statistical Analysis Results

Treatment=2						
The Mixed Procedure						
Type 3 Tests of Fixed Effects						
Effect		Num DF	Den DF	F Value	Pr > F	
WellPosition		1	2	21.01	0.0444	
Depth		1	4	0.36	0.5796	
Depth*WellPosition		1	4	0.03	0.8662	

Least Squares Means						
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value Pr > t
WellPosition		1	0.9708	0.1368	2	7.10 0.0193
WellPosition		3	1.9052	0.1368	2	13.93 0.0051
Depth	D		1.4142	0.09940	4	14.23 0.0001
Depth	S		1.4617	0.09940	4	14.71 0.0001
Depth*WellPosition	D	1	0.9399	0.1477	4	6.36 0.0031
Depth*WellPosition	D	3	1.8885	0.1477	4	12.78 0.0002
Depth*WellPosition	S	1	1.0016	0.1477	4	6.78 0.0025
Depth*WellPosition	S	3	1.9219	0.1477	4	13.01 0.0002

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	4	0.31	0.6099
Depth*WellPosition		3	1	4	0.09	0.7800
Depth*WellPosition	D		1	4	18.83	0.0123
Depth*WellPosition	S		1	4	17.72	0.0136

Figure C. 33: Section 2 Na⁺ Statistical Analysis Results

Ca²⁺ Statistical Analysis Results using PROC MIXED

Type 3 Tests of Fixed Effects						
Effect	Num DF	Den DF	F Value	Pr > F		
WellPosition	1	2	8.15	0.1039		
Depth	1	4	8.97	0.0401		
Depth*WellPosition	1	4	0.53	0.5063		

Least Squares Means						
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value Pr > t
WellPosition		1	0.9884	0.1667	2	5.93 0.0273
WellPosition		2	Non-est	.	.	.
WellPosition		3	Non-est	.	.	.
WellPosition		4	1.9267	0.1667	2	11.56 0.0074
Depth	D		2.3869	0	4	Infnty <.0001
Depth	S		Non-est	.	.	.
Depth*WellPosition	D	1	1.5953	0.2844	4	5.61 0.0050
Depth*WellPosition	D	2	2.0992	0	4	Infnty <.0001
Depth*WellPosition	D	3	3.5573	0	4	Infnty <.0001
Depth*WellPosition	D	4	2.2959	0.2844	4	8.07 0.0013
Depth*WellPosition	S	1	0.3815	0.2844	4	1.34 0.2509
Depth*WellPosition	S	4	1.5574	0.2844	4	5.48 0.0054

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	4	6.93	0.0580
Depth*WellPosition		2	0	.	.	.
Depth*WellPosition		3	0	.	.	.
Depth*WellPosition		4	1	4	2.57	0.1844
Depth*WellPosition	D		1	4	2.29	0.2046
Depth*WellPosition	S		1	4	6.46	0.0639

Figure C. 34: Section 1 Ca²⁺ Statistical Analysis Results

Treatment=2						
The Mixed Procedure						
Type 3 Tests of Fixed Effects						
Effect	Num DF	Den DF	F Value	Pr > F		
WellPosition	1	2	724.82	0.0014		
Depth	1	4	0.29	0.6169		
Depth*WellPosition	1	4	23.38	0.0084		

Least Squares Means						
Effect	Depth	Well Position	Estimate	Standard Error	DF	t Value Pr > t
WellPosition		1	3.3444	0.07555	2	44.27 0.0005
WellPosition		3	2.3043	0.07555	2	30.50 0.0011
Depth	D		2.8363	0.07629	4	37.18 <.0001
Depth	S		2.8124	0.07629	4	36.87 <.0001
Depth*WellPosition	D	1	3.4628	0.08172	4	42.38 <.0001
Depth*WellPosition	D	3	2.2097	0.08172	4	27.04 <.0001
Depth*WellPosition	S	1	3.2261	0.08172	4	39.48 <.0001
Depth*WellPosition	S	3	2.3988	0.08172	4	29.36 <.0001

Tests of Effect Slices						
Effect	Depth	Well Position	Num DF	Den DF	F Value	Pr > F
Depth*WellPosition		1	1	4	14.45	0.0191
Depth*WellPosition		3	1	4	9.22	0.0385
Depth*WellPosition	D		1	4	457.62	<.0001
Depth*WellPosition	S		1	4	199.47	0.0001

Figure C. 35: Section 2 Ca²⁺ Statistical Analysis Results

T-tests for Difference in NO₃⁻-N Concentrations at the Field Edge

Effect	Num DF	Den DF	F Value	Pr > F
Depth	1	190	0.15	0.6971
Treatment	1	190	134.49	<.0001
Depth*Treatment	1	190	1.97	0.1624

Least Squares Means

Effect	Depth	Treatment	Estimate	Standard Error	DF	t Value	Pr > t
Depth	D		7.8798	1.3921	190	5.66	<.0001
Depth	S		7.6429	1.4189	190	5.39	<.0001
Treatment		1	3.8104	1.4031	190	2.72	0.0072
Treatment		2	11.7124	1.4248	190	8.22	<.0001
Depth*Treatment	D	1	3.5027	1.4363	190	2.44	0.0157
Depth*Treatment	D	2	12.2569	1.4702	190	8.34	<.0001
Depth*Treatment	S	1	4.1180	1.5102	190	2.73	0.0070
Depth*Treatment	S	2	11.1678	1.4936	190	7.48	<.0001

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The Mixed Procedure

Tests of Effect Slices

Effect	Depth	Treatment	Num DF	Den DF	F Value	Pr > F
Depth*Treatment	D		1	190	109.99	<.0001
Depth*Treatment	S		1	190	51.23	<.0001
Depth*Treatment		1	1	190	0.47	0.4958
Depth*Treatment		2	1	190	1.79	0.1829

Figure C. 36: T test of NO₃⁻-N Concentration differences at the field edge of Section 1 and Section 2

NO₃⁻-N, Ca²⁺, and Na⁺ differences depending on aquifer

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The TTEST Procedure

Variable: NO3

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
1	1506	2.3543	1.7241	0.0444	0	14.7000
3	82	0.0163	0.0272	0.00300	0	0.1200
Diff (1-2)		2.3380	1.6795	0.1905		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
1		2.3543	2.2672 2.4415	1.7241	1.6646 1.7880
3		0.0163	0.0104 0.0223	0.0272	0.0236 0.0321
Diff (1-2)	Pooled	2.3380	1.9644 2.7116	1.6795	1.6230 1.7401
Diff (1-2)	Satterthwaite	2.3380	2.2507 2.4253		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	1586	12.28	<.0001
Satterthwaite	Unequal	1518.2	52.51	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	1505	81	4019.35	<.0001

Figure C. 37: T-test of the NO₃⁻-N concentrations between Section 1 surficial and confined aquifers

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The TTEST Procedure

Variable: NO3

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
2	1156	8.5707	5.1604	0.1518	0	31.5000
3	82	0.0163	0.0272	0.00300	0	0.1200
Diff (1-2)		8.5543	4.9884	0.5701		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
2		8.5707	8.2729 8.8685	5.1604	4.9583 5.3798
3		0.0163	0.0104 0.0223	0.0272	0.0236 0.0321
Diff (1-2)	Pooled	8.5543	7.4359 9.6728	4.9884	4.7993 5.1932
Diff (1-2)	Satterthwaite	8.5543	8.2565 8.8522		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	1236	15.01	<.0001
Satterthwaite	Unequal	1155.9	56.35	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	1155	81	36008.2	<.0001

Figure C. 38: T-test of the NO₃⁻-N concentrations between Section 2 surficial and confined aquifers

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The TTEST Procedure

Variable: Ca

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
1	166	7.6702	5.3870	0.4181	0	25.7000
3	73	87.6060	59.5675	6.9719	7.4600	269.0
Diff (1-2)		-79.9358	33.1386	4.6539		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
1		7.6702	6.8446 8.4957	5.3870	4.8632 6.0383
3		87.6060	73.7079 101.5	59.5675	51.2273 71.1771
Diff (1-2)	Pooled	-79.9358	-89.1041 -70.7675	33.1386	30.4049 36.4166
Diff (1-2)	Satterthwaite	-79.9358	-93.8573 -66.0144		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	237	-17.18	<.0001
Satterthwaite	Unequal	72.518	-11.44	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	72	165	122.27	<.0001

Figure C. 39: T-test of the Ca^{2+} concentrations between Section 1 surficial and confined aquifers

meanz

3:

The TTEST Procedure

Variable: Ca

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
2	169	21.7231	16.0804	1.2370	0.8600	80.7000
3	73	87.6060	59.5675	6.9719	7.4600	269.0
Diff (1-2)		-65.8829	35.2915	4.9428		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
2		21.7231	19.2812 24.1651	16.0804	14.5294 18.0050
3		87.6060	73.7079 101.5	59.5675	51.2273 71.1771
Diff (1-2)	Pooled	-65.8829	-75.6197 -56.1461	35.2915	32.3970 38.7585
Diff (1-2)	Satterthwaite	-65.8829	-79.9837 -51.7821		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	240	-13.33	<.0001
Satterthwaite	Unequal	76.572	-9.30	<.0001

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	72	168	13.72	<.0001

Figure C. 40: T-test of the Ca^{2+} concentrations between Section 2 surficial and confined aquifers

meanz

44

The TTEST Procedure

Variable: Na

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
1	169	18.8556	62.7442	4.8265	3.3200	415.0
3	73	21.0684	47.1394	5.5172	8.1100	348.0
Diff (1-2)		-2.2127	58.5015	8.1935		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
1		18.8556	9.3273 28.3840	62.7442	56.6924 70.2539
3		21.0684	10.0699 32.0668	47.1394	40.5392 56.3268
Diff (1-2)	Pooled	-2.2127	-18.3531 13.9276	58.5015	53.7032 64.2486
Diff (1-2)	Satterthwaite	-2.2127	-16.6777 12.2522		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	240	-0.27	0.7873
Satterthwaite	Unequal	179.35	-0.30	0.7631

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	168	72	1.77	0.0066

Figure C. 41: T-test of the Na⁺ concentrations between Section 1 surficial and confined aquifers

meanz

45

The TTEST Procedure

Variable: Na

Treatment	N	Mean	Std Dev	Std Err	Minimum	Maximum
2	171	13.7561	50.2501	3.8427	0.8400	298.0
3	73	21.0684	47.1394	5.5172	8.1100	348.0
Diff (1-2)		-7.3122	49.3451	6.8989		

Treatment	Method	Mean	95% CL Mean	Std Dev	95% CL Std Dev
2		13.7561	6.1705 21.3417	50.2501	45.4291 56.2248
3		21.0684	10.0699 32.0668	47.1394	40.5392 56.3268
Diff (1-2)	Pooled	-7.3122	-20.9018 6.2773	49.3451	45.3132 54.1707
Diff (1-2)	Satterthwaite	-7.3122	-20.6016 5.9771		

Method	Variances	DF	t Value	Pr > t
Pooled	Equal	242	-1.06	0.2902
Satterthwaite	Unequal	144.41	-1.09	0.2786

Equality of Variances

Method	Num DF	Den DF	F Value	Pr > F
Folded F	170	72	1.14	0.5427

Figure C. 42: T-test of the Na⁺ concentrations between Section 2 surficial and confined aquifers

Redox Interactions using PROC MIXED

Treatment=1

The Mixed Procedure

Least Squares Means							
Effect	Depth	Location	Estimate	Standard Error	DF	t Value	Pr > t
Location		1	6.2214	0.04598	278	135.30	<.0001
Location		2	6.2409	0.04532	278	137.70	<.0001
Location		3	5.8395	0.04532	278	128.85	<.0001
Location		4	5.4644	0.04532	278	120.57	<.0001
Depth	D		5.3387	0.03228	278	183.96	<.0001
Depth	S		5.3444	0.03205	278	185.49	<.0001
Location*Depth	D	1	6.0720	0.06595	278	92.07	<.0001
Location*Depth	S	1	6.3708	0.06410	278	99.40	<.0001
Location*Depth	D	2	6.2014	0.06410	278	96.75	<.0001
Location*Depth	S	2	6.2805	0.06410	278	97.99	<.0001
Location*Depth	D	3	6.0350	0.06410	278	94.16	<.0001
Location*Depth	S	3	5.6441	0.06410	278	88.06	<.0001
Location*Depth	D	4	5.4465	0.06410	278	84.98	<.0001
Location*Depth	S	4	5.4822	0.06410	278	85.53	<.0001

Tests of Effect Slices						
Effect	Depth	Location	Num DF	Den DF	F Value	Pr > F
Location*Depth		1	1	278	10.56	0.0013
Location*Depth		2	1	278	0.76	0.3836
Location*Depth		3	1	278	18.59	<.0001
Location*Depth		4	1	278	0.15	0.6942
Location*Depth	D		3	278	27.37	<.0001
Location*Depth	S		3	278	48.57	<.0001

Figure C. 43: Proc mixed of redox interactions in Section 1

Treatment=2

The Mixed Procedure

Least Squares Means							
Effect	Depth	Location	Estimate	Standard Error	DF	t Value	Pr > t
Location		1	6.0984	0.05438	208	112.15	<.0001
Location		2	6.2125	0.05360	208	115.91	<.0001
Location		3	5.5529	0.05360	208	103.61	<.0001
Depth	D		6.0063	0.04419	208	135.93	<.0001
Depth	S		5.9028	0.04376	208	134.89	<.0001
Location*Depth	D	1	6.0689	0.07799	208	77.81	<.0001
Location*Depth	S	1	6.1279	0.07580	208	80.85	<.0001
Location*Depth	D	2	6.3686	0.07580	208	84.02	<.0001
Location*Depth	S	2	6.0563	0.07580	208	79.90	<.0001
Location*Depth	D	3	5.5815	0.07580	208	73.64	<.0001
Location*Depth	S	3	5.5243	0.07580	208	72.88	<.0001

Tests of Effect Slices						
Effect	Depth	Location	Num DF	Den DF	F Value	Pr > F
Location*Depth		1	1	208	0.29	0.5879
Location*Depth		2	1	208	8.49	0.0040
Location*Depth		3	1	208	0.28	0.5944
Location*Depth	D		2	208	27.45	<.0001
Location*Depth	S		2	208	18.93	<.0001

Figure C. 44: Proc mixed of redox interactions in Section 2

APPENDIX D: Hydraulic Gradient and Flow Direction Modeling and Calculations

Table D. 1: Calculated hydraulic gradient and flow direction angle for each month water table elevation was monitored in monitoring wells.

Section 1			Section 2		
Date	Gradient	Angle	Date	Gradient	Angle
6/10/2008	0.006	-60.0	6/10/2008	0.004	-31.8
8/6/2008	0.006	-79.4	8/6/2008	0.003	-42.9
9/3/2008	0.007	54.0	9/3/2008	0.004	54.1
10/1/2008	0.007	71.3	10/1/2008	0.001	77.2
11/5/2008	0.008	61.6	11/5/2008	0.002	51.1
12/3/2008	0.009	-83.6	12/3/2008	0.003	70.4
1/13/2009	0.011	-37.2	1/13/2009	0.004	-26.7
2/3/2009	0.008	-61.4	2/3/2009	0.003	-80.4
3/3/2009	0.015	-37.8	3/3/2009	0.010	-29.3
4/7/2009	0.015	-40.7	4/7/2009	0.010	-18.3
5/6/2009	0.006	-61.3	5/6/2009	0.002	-30.3
6/9/2009	0.006	-70.2	6/9/2009	0.003	-68.1
7/7/2009	0.011	86.3	7/7/2009	0.005	-78.7
8/4/2009	0.003	-81.6	8/4/2009	0.005	-70.1
9/1/2009	0.013	86.3	9/1/2009	0.004	-73.4
10/6/2009	0.018	74.1	10/6/2009	0.003	-63.1
11/3/2009	0.007	59.2	11/3/2009	0.002	13.0
12/1/2009	0.006	-67.1	12/1/2009	0.005	-34.2
1/7/2010	0.013	-34.4	1/7/2010	0.007	-15.7
2/2/2010	0.036	-82.2	2/2/2010	0.013	-42.3
3/2/2010	0.012	-30.8	3/2/2010	0.006	-12.6
4/15/2010	0.010	-29.5	4/15/2010	0.006	-12.4
5/4/2010	0.004	-56.9	5/4/2010	0.004	-26.7

Flow Velocity and Residence Time Calculations

Table D. 2: Section 1 1.5 m depth flow velocity and residence time calculations water table elevation data. Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond. 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
8/1/2008	0.08	1.30	0.31	30.00	0.67	0.12	1.00	0.33	0.62	470.03	1.29
9/1/2008	0.08	1.30	0.29	30.00	0.72	0.09	1.00	0.26	0.78	548.10	1.50
10/1/2008	0.07	1.30	0.26	30.00	0.79	0.09	1.00	0.25	0.81	583.91	1.60
11/1/2008	0.07	1.30	0.27	30.00	0.75	0.08	1.00	0.24	0.85	586.16	1.61
12/1/2008	0.11	1.30	0.42	30.00	0.49	0.09	1.00	0.27	0.78	463.16	1.27
1/1/2009	0.10	1.30	0.37	30.00	0.55	0.15	1.00	0.42	0.48	377.33	1.03
2/1/2009	0.09	1.30	0.32	30.00	0.65	0.17	1.00	0.49	0.42	389.37	1.07
3/1/2009	0.20	1.30	0.73	30.00	0.28	0.14	1.00	0.40	0.51	289.45	0.79
4/1/2009	0.17	1.30	0.63	30.00	0.33	0.18	1.00	0.52	0.40	264.26	0.72
5/1/2009	0.13	1.30	0.48	30.00	0.43	0.12	1.00	0.35	0.59	373.43	1.02
6/1/2009	0.12	1.30	0.43	30.00	0.48	0.08	1.00	0.23	0.91	506.50	1.39
7/1/2009	0.10	1.30	0.39	30.00	0.53	0.07	1.00	0.19	1.07	586.64	1.61
8/1/2009	0.09	1.30	0.35	30.00	0.59	0.06	1.00	0.16	1.26	672.64	1.84
9/1/2009	0.09	1.30	0.32	30.00	0.64	0.05	1.00	0.15	1.40	745.20	2.04
10/1/2009	0.08	1.30	0.31	30.00	0.66	0.05	1.00	0.13	1.53	799.92	2.19
11/1/2009	0.13	1.30	0.47	30.00	0.43	0.04	1.00	0.12	1.64	758.45	2.08
12/1/2009	0.21	1.30	0.76	30.00	0.27	0.07	1.00	0.20	1.01	467.63	1.28
1/1/2010	0.19	1.30	0.72	30.00	0.28	0.17	1.00	0.48	0.42	258.75	0.71
2/1/2010	0.20	1.30	0.75	30.00	0.27	0.17	1.00	0.48	0.43	255.96	0.70
3/1/2010	0.18	1.30	0.69	30.00	0.30	0.17	1.00	0.48	0.42	264.00	0.72
4/1/2010	0.17	1.30	0.63	30.00	0.33	0.15	1.00	0.42	0.49	298.01	0.82
5/1/2010	0.14	1.30	0.51	30.00	0.40	0.12	1.00	0.36	0.58	357.86	0.98

Table D. 3: Section 1 1.5 m depth flow velocity and residence time calculations using Devlin (2003). Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond. 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
6/1/2008	0.01	1.30	0.02	30.00	9.21	0.01	1.00	0.02	11.98	7733.32	21.19
8/1/2008	0.01	1.30	0.02	30.00	9.75	0.01	1.00	0.02	12.67	8184.73	22.42
9/1/2008	0.01	1.30	0.03	30.00	7.74	0.01	1.00	0.02	10.06	6499.06	17.81
10/1/2008	0.01	1.30	0.03	30.00	7.73	0.01	1.00	0.02	10.05	6487.33	17.77
11/1/2008	0.01	1.30	0.03	30.00	7.26	0.01	1.00	0.02	9.44	6096.16	16.70
12/1/2008	0.01	1.30	0.03	30.00	6.23	0.01	1.00	0.03	8.10	5231.72	14.33
1/1/2009	0.01	1.30	0.04	30.00	5.18	0.01	1.00	0.03	6.74	4349.81	11.92
2/1/2009	0.01	1.30	0.03	30.00	7.11	0.01	1.00	0.02	9.25	5970.32	16.36
3/1/2009	0.02	1.30	0.06	30.00	3.62	0.02	1.00	0.04	4.70	3035.20	8.32
4/1/2009	0.01	1.30	0.05	30.00	3.80	0.01	1.00	0.04	4.94	3192.01	8.75
5/1/2009	0.01	1.30	0.02	30.00	9.90	0.01	1.00	0.02	12.87	8309.53	22.77
6/1/2009	0.01	1.30	0.02	30.00	9.78	0.01	1.00	0.02	12.72	8214.42	22.51
7/1/2009	0.01	1.30	0.04	30.00	4.96	0.01	1.00	0.03	6.45	4164.88	11.41
8/1/2009	0.00	1.30	0.01	30.00	16.65	0.00	1.00	0.01	21.64	13973.67	38.28
9/1/2009	0.01	1.30	0.05	30.00	4.25	0.01	1.00	0.04	5.52	3566.34	9.77
10/1/2009	0.02	1.30	0.07	30.00	3.12	0.02	1.00	0.05	4.06	2619.10	7.18
11/1/2009	0.01	1.30	0.02	30.00	8.35	0.01	1.00	0.02	10.86	7011.63	19.21
12/1/2009	0.01	1.30	0.02	30.00	9.93	0.01	1.00	0.02	12.91	8334.05	22.83
1/1/2010	0.01	1.30	0.05	30.00	4.22	0.01	1.00	0.04	5.49	3543.27	9.71
2/1/2010	0.04	1.30	0.13	30.00	1.55	0.04	1.00	0.10	2.01	1300.02	3.56
3/1/2010	0.01	1.30	0.04	30.00	4.71	0.01	1.00	0.03	6.12	3951.53	10.83
4/1/2010	0.01	1.30	0.04	30.00	5.75	0.01	1.00	0.03	7.48	4830.06	13.23
5/1/2010	0.00	1.30	0.01	30.00	13.87	0.00	1.00	0.01	18.04	11647.38	31.91

Table D. 4: Section1 3m depth flow velocity and residence time calculations using water table elevation data. Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond. 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
6/1/2008	0.09	2.00	0.51	30.00	0.40	0.15	2.35	1.02	0.20	220.47	0.60
7/1/2008	0.11	2.00	0.61	30.00	0.34	0.11	2.35	0.71	0.29	229.49	0.63
8/1/2008	0.08	2.00	0.47	30.00	0.44	0.12	2.35	0.78	0.26	255.08	0.70
9/1/2008	0.08	2.00	0.44	30.00	0.47	0.09	2.35	0.62	0.33	292.15	0.80
10/1/2008	0.07	2.00	0.40	30.00	0.51	0.09	2.35	0.60	0.34	313.15	0.86
11/1/2008	0.07	2.00	0.42	30.00	0.49	0.08	2.35	0.57	0.36	311.16	0.85
12/1/2008	0.11	2.00	0.64	30.00	0.32	0.09	2.35	0.62	0.33	237.56	0.65
1/1/2009	0.10	2.00	0.57	30.00	0.36	0.15	2.35	1.00	0.21	205.62	0.56
2/1/2009	0.09	2.00	0.49	30.00	0.42	0.17	2.35	1.16	0.18	218.91	0.60
3/1/2009	0.20	2.00	1.12	30.00	0.18	0.14	2.35	0.94	0.22	146.25	0.40
4/1/2009	0.17	2.00	0.97	30.00	0.21	0.18	2.35	1.21	0.17	139.20	0.38
5/1/2009	0.13	2.00	0.74	30.00	0.28	0.12	2.35	0.81	0.25	194.08	0.53
6/1/2009	0.12	2.00	0.66	30.00	0.31	0.08	2.35	0.53	0.39	254.84	0.70
7/1/2009	0.10	2.00	0.59	30.00	0.35	0.07	2.35	0.45	0.46	293.27	0.80
8/1/2009	0.09	2.00	0.54	30.00	0.38	0.06	2.35	0.38	0.53	334.34	0.92
9/1/2009	0.09	2.00	0.49	30.00	0.42	0.05	2.35	0.34	0.60	369.53	1.01
10/1/2009	0.08	2.00	0.48	30.00	0.43	0.05	2.35	0.32	0.65	394.87	1.08
11/1/2009	0.13	2.00	0.73	30.00	0.28	0.04	2.35	0.29	0.70	358.30	0.98
12/1/2009	0.21	2.00	1.17	30.00	0.18	0.07	2.35	0.48	0.43	221.10	0.61
1/1/2010	0.19	2.00	1.11	30.00	0.18	0.17	2.35	1.14	0.18	133.40	0.37
2/1/2010	0.20	2.00	1.15	30.00	0.18	0.17	2.35	1.13	0.18	131.39	0.36
3/1/2010	0.18	2.00	1.06	30.00	0.19	0.17	2.35	1.14	0.18	136.89	0.38
4/1/2010	0.17	2.00	0.97	30.00	0.21	0.15	2.35	0.99	0.21	153.56	0.42
5/1/2010	0.14	2.00	0.78	30.00	0.26	0.12	2.35	0.84	0.25	185.35	0.51

Table D. 5: Section1 3m depth flow velocity and residence time calculations using Devlin (2003). Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond/ 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
8/1/2008	0.01	2.00	0.03	30.00	6.34	0.01	2.35	0.04	8.99	5594.03	15.33
9/1/2008	0.01	2.00	0.04	30.00	5.03	0.01	2.35	0.05	7.14	4441.93	12.17
10/1/2008	0.01	2.00	0.04	30.00	5.02	0.01	2.35	0.05	7.12	4433.91	12.15
11/1/2008	0.01	2.00	0.04	30.00	4.72	0.01	2.35	0.05	6.70	4166.56	11.42
12/1/2008	0.01	2.00	0.05	30.00	4.05	0.01	2.35	0.06	5.75	3575.74	9.80
1/1/2009	0.01	2.00	0.06	30.00	3.37	0.01	2.35	0.07	4.78	2972.98	8.15
2/1/2009	0.01	2.00	0.04	30.00	4.62	0.01	2.35	0.05	6.56	4080.55	11.18
3/1/2009	0.02	2.00	0.09	30.00	2.35	0.02	2.35	0.10	3.33	2074.47	5.68
4/1/2009	0.01	2.00	0.08	30.00	2.47	0.01	2.35	0.10	3.51	2181.65	5.98
5/1/2009	0.01	2.00	0.03	30.00	6.43	0.01	2.35	0.04	9.13	5679.33	15.56
6/1/2009	0.01	2.00	0.03	30.00	6.36	0.01	2.35	0.04	9.02	5614.33	15.38
7/1/2009	0.01	2.00	0.06	30.00	3.22	0.01	2.35	0.07	4.57	2846.58	7.80
8/1/2009	0.00	2.00	0.02	30.00	10.82	0.00	2.35	0.02	15.35	9550.62	26.17
9/1/2009	0.01	2.00	0.07	30.00	2.76	0.01	2.35	0.09	3.92	2437.50	6.68
10/1/2009	0.02	2.00	0.10	30.00	2.03	0.02	2.35	0.12	2.88	1790.08	4.90
11/1/2009	0.01	2.00	0.04	30.00	5.43	0.01	2.35	0.04	7.70	4792.26	13.13
12/1/2009	0.01	2.00	0.03	30.00	6.45	0.01	2.35	0.04	9.15	5696.09	15.61
1/1/2010	0.01	2.00	0.07	30.00	2.74	0.01	2.35	0.09	3.89	2421.73	6.63
2/1/2010	0.04	2.00	0.20	30.00	1.01	0.04	2.35	0.24	1.43	888.52	2.43
3/1/2010	0.01	2.00	0.07	30.00	3.06	0.01	2.35	0.08	4.34	2700.76	7.40
4/1/2010	0.01	2.00	0.05	30.00	3.74	0.01	2.35	0.06	5.30	3301.21	9.04
5/1/2010	0.00	2.00	0.02	30.00	9.02	0.00	2.35	0.03	12.79	7960.66	21.81

Table D. 6: Section2 1.5m depth flow velocity and residence time calculations using water table elevation data. Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond. 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
6/10/2008	0.13	1.80	0.67	30.00	0.31	0.05	2.02	0.30	0.68	358.66	0.98
8/6/2008	0.12	1.80	0.62	30.00	0.33	0.05	2.02	0.27	0.77	401.17	1.10
9/3/2008	0.12	1.80	0.61	30.00	0.34	0.04	2.02	0.25	0.81	420.80	1.15
10/1/2008	0.11	1.80	0.55	30.00	0.38	0.04	2.02	0.24	0.87	455.57	1.25
11/5/2008	0.12	1.80	0.61	30.00	0.34	0.04	2.02	0.24	0.86	436.94	1.20
12/3/2008	0.15	1.80	0.78	30.00	0.26	0.06	2.02	0.36	0.57	304.91	0.84
1/13/2009	0.15	1.80	0.79	30.00	0.26	0.07	2.02	0.39	0.53	286.60	0.79
2/3/2009	0.14	1.80	0.73	30.00	0.28	0.06	2.02	0.32	0.64	337.81	0.93
3/3/2009	0.20	1.80	1.03	30.00	0.20	0.11	2.02	0.61	0.34	196.16	0.54
4/7/2009	0.18	1.80	0.92	30.00	0.22	0.08	2.02	0.46	0.45	245.35	0.67
5/6/2009	0.14	1.80	0.73	30.00	0.28	0.05	2.02	0.31	0.66	343.40	0.94
6/9/2009	0.12	1.80	0.64	30.00	0.32	0.04	2.02	0.25	0.84	422.66	1.16
7/7/2009	0.11	1.80	0.56	30.00	0.37	0.04	2.02	0.22	0.93	475.03	1.30
8/4/2009	0.10	1.80	0.50	30.00	0.41	0.03	2.02	0.19	1.09	546.70	1.50
9/1/2009	0.09	1.80	0.48	30.00	0.43	0.03	2.02	0.17	1.19	591.70	1.62
10/6/2009	0.09	1.80	0.47	30.00	0.44	0.03	2.02	0.17	1.23	610.34	1.67
11/3/2009	0.15	1.80	0.78	30.00	0.26	0.06	2.02	0.36	0.57	303.43	0.83
12/1/2009	0.20	1.80	1.03	30.00	0.20	0.10	2.02	0.58	0.36	202.95	0.56
1/7/2010	0.20	1.80	1.00	30.00	0.20	0.10	2.02	0.56	0.37	209.57	0.57
2/2/2010	0.20	1.80	1.04	30.00	0.20	0.10	2.02	0.60	0.34	197.77	0.54
3/2/2010	0.19	1.80	0.95	30.00	0.22	0.09	2.02	0.49	0.42	231.66	0.63
4/15/2010	0.18	1.80	0.93	30.00	0.22	0.08	2.02	0.46	0.44	242.35	0.66
5/4/2010	0.16	1.80	0.81	30.00	0.25	0.06	2.02	0.37	0.55	295.00	0.81

Table D. 7: Section2 1.5m depth flow velocity and residence time calculations using Devlin (2003). Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond. 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
6/10/2008	0.00	1.80	0.02	30.00	10.23	0.00	2.02	0.02	9.11	7057.90	19.34
8/6/2008	0.00	1.80	0.01	30.00	15.03	0.00	2.02	0.02	13.39	10373.25	28.42
9/3/2008	0.00	1.80	0.02	30.00	9.26	0.00	2.02	0.02	8.25	6393.10	17.52
10/1/2008	0.00	1.80	0.01	30.00	32.08	0.00	2.02	0.01	28.59	22144.61	60.67
11/5/2008	0.00	1.80	0.01	30.00	19.66	0.00	2.02	0.01	17.52	13567.55	37.17
12/3/2008	0.00	1.80	0.02	30.00	11.73	0.00	2.02	0.02	10.45	8096.53	22.18
1/13/2009	0.00	1.80	0.02	30.00	10.02	0.00	2.02	0.02	8.93	6916.20	18.95
2/3/2009	0.00	1.80	0.01	30.00	15.16	0.00	2.02	0.02	13.51	10463.39	28.67
3/3/2009	0.01	1.80	0.05	30.00	3.90	0.01	2.02	0.06	3.47	2690.61	7.37
4/7/2009	0.01	1.80	0.05	30.00	4.13	0.01	2.02	0.06	3.68	2852.36	7.81
5/6/2009	0.00	1.80	0.01	30.00	18.47	0.00	2.02	0.01	16.46	12751.96	34.94
6/9/2009	0.00	1.80	0.02	30.00	13.49	0.00	2.02	0.02	12.02	9312.99	25.52
7/7/2009	0.01	1.80	0.03	30.00	7.62	0.01	2.02	0.03	6.79	5257.76	14.40
8/4/2009	0.01	1.80	0.03	30.00	7.98	0.01	2.02	0.03	7.11	5506.82	15.09
9/1/2009	0.00	1.80	0.02	30.00	10.48	0.00	2.02	0.02	9.34	7236.49	19.83
10/6/2009	0.00	1.80	0.02	30.00	13.30	0.00	2.02	0.02	11.85	9178.21	25.15
11/3/2009	0.00	1.80	0.01	30.00	26.33	0.00	2.02	0.01	23.47	18176.58	49.80
12/1/2009	0.00	1.80	0.02	30.00	8.22	0.00	2.02	0.03	7.33	5675.29	15.55
1/7/2010	0.01	1.80	0.04	30.00	5.61	0.01	2.02	0.04	5.00	3873.41	10.61
2/2/2010	0.01	1.80	0.07	30.00	2.99	0.01	2.02	0.08	2.66	2060.62	5.65
3/2/2010	0.01	1.80	0.03	30.00	6.96	0.01	2.02	0.03	6.21	4806.57	13.17
4/15/2010	0.01	1.80	0.03	30.00	6.46	0.01	2.02	0.04	5.76	4459.90	12.22
5/4/2010	0.00	1.80	0.02	30.00	10.33	0.00	2.02	0.02	9.21	7131.74	19.54

Table D. 8: Section 2 3m depth flow velocity and residence time calculations using water table elevation data. Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond. 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
8/6/2008	0.12	3.70	1.28	30.00	0.27	0.05	3.10	0.41	0.25	189.12	0.52
9/3/2008	0.12	3.70	1.25	30.00	0.27	0.04	3.10	0.39	0.27	196.92	0.54
10/1/2008	0.11	3.70	1.12	30.00	0.31	0.04	3.10	0.36	0.28	215.06	0.59
11/5/2008	0.12	3.70	1.25	30.00	0.27	0.04	3.10	0.37	0.28	202.03	0.55
12/3/2008	0.15	3.70	1.61	30.00	0.21	0.06	3.10	0.55	0.19	145.92	0.40
1/13/2009	0.15	3.70	1.62	30.00	0.21	0.07	3.10	0.60	0.17	139.39	0.38
2/3/2009	0.14	3.70	1.50	30.00	0.23	0.06	3.10	0.49	0.21	160.00	0.44
3/3/2009	0.20	3.70	2.11	30.00	0.16	0.11	3.10	0.93	0.11	99.34	0.27
4/7/2009	0.18	3.70	1.90	30.00	0.18	0.08	3.10	0.70	0.15	119.38	0.33
5/6/2009	0.14	3.70	1.49	30.00	0.23	0.05	3.10	0.48	0.21	161.90	0.44
6/9/2009	0.12	3.70	1.31	30.00	0.26	0.04	3.10	0.38	0.27	194.63	0.53
7/7/2009	0.11	3.70	1.14	30.00	0.30	0.04	3.10	0.34	0.30	220.18	0.60
8/4/2009	0.10	3.70	1.03	30.00	0.33	0.03	3.10	0.29	0.35	250.46	0.69
9/1/2009	0.09	3.70	0.99	30.00	0.35	0.03	3.10	0.26	0.39	268.67	0.74
10/6/2009	0.09	3.70	0.96	30.00	0.36	0.03	3.10	0.26	0.40	276.84	0.76
11/3/2009	0.15	3.70	1.60	30.00	0.21	0.06	3.10	0.56	0.18	145.72	0.40
12/1/2009	0.20	3.70	2.12	30.00	0.16	0.10	3.10	0.88	0.12	101.44	0.28
1/7/2010	0.20	3.70	2.06	30.00	0.17	0.10	3.10	0.85	0.12	104.53	0.29
2/2/2010	0.20	3.70	2.14	30.00	0.16	0.10	3.10	0.91	0.11	99.32	0.27
3/2/2010	0.19	3.70	1.96	30.00	0.18	0.09	3.10	0.75	0.14	113.69	0.31
4/15/2010	0.18	3.70	1.91	30.00	0.18	0.08	3.10	0.71	0.14	118.04	0.32
5/4/2010	0.16	3.70	1.67	30.00	0.21	0.06	3.10	0.57	0.18	140.98	0.39

Table D. 9: Section 2 3m depth flow velocity and residence time calculations using Devlin (2003). Soil type was assumed sandy loam based on soil samples and a porosity of 0.35 was therefore used.

Date	Gradient 3-2 (m ² /m)	Cond. 3-2 (cm/hr)	Seepage Velocity (m*cm/hr)	Area to Stream (m ²)	Time (3-2) (years)	Gradient 1-2 (m ² /m)	Cond. 2-1 (cm/hr)	Seepage Velocity (m*cm/hr)	Time 1-2 (years)	Time (days)	Time 1-3 (years)
8/6/2008	0.00	3.70	0.03	30.00	7.31	0.00	3.10	0.02	8.73	5853.57	16.04
9/3/2008	0.00	3.70	0.05	30.00	4.51	0.00	3.10	0.04	5.38	3607.60	9.88
10/1/2008	0.00	3.70	0.01	30.00	15.87	0.00	3.10	0.01	18.63	12591.03	34.50
11/5/2008	0.00	3.70	0.02	30.00	9.56	0.00	3.10	0.02	11.41	7656.10	20.98
12/3/2008	0.00	3.70	0.04	30.00	5.71	0.00	3.10	0.03	6.81	4568.83	12.52
1/13/2009	0.00	3.70	0.04	30.00	4.87	0.00	3.10	0.04	5.82	3902.78	10.69
2/3/2009	0.00	3.70	0.03	30.00	7.37	0.00	3.10	0.02	8.80	5904.44	16.18
3/3/2009	0.01	3.70	0.11	30.00	1.90	0.01	3.10	0.09	2.26	1518.30	4.16
4/7/2009	0.01	3.70	0.10	30.00	2.01	0.01	3.10	0.09	2.40	1609.57	4.41
5/6/2009	0.00	3.70	0.02	30.00	8.99	0.00	3.10	0.02	10.73	7195.86	19.71
6/9/2009	0.00	3.70	0.03	30.00	6.56	0.00	3.10	0.03	7.83	5255.27	14.40
7/7/2009	0.01	3.70	0.06	30.00	3.71	0.01	3.10	0.05	4.42	2966.92	8.13
8/4/2009	0.01	3.70	0.05	30.00	3.88	0.01	3.10	0.04	4.63	3107.47	8.51
9/1/2009	0.00	3.70	0.04	30.00	5.10	0.00	3.10	0.03	6.09	4083.51	11.19
10/6/2009	0.00	3.70	0.03	30.00	6.47	0.00	3.10	0.03	7.72	5179.21	14.19
11/3/2009	0.00	3.70	0.02	30.00	12.81	0.00	3.10	0.01	15.29	10256.95	28.10
12/1/2009	0.00	3.70	0.05	30.00	4.00	0.00	3.10	0.04	4.77	3202.54	8.77
1/7/2010	0.01	3.70	0.08	30.00	2.73	0.01	3.10	0.06	3.26	2185.74	5.99
2/2/2010	0.01	3.70	0.14	30.00	1.45	0.01	3.10	0.12	1.73	1162.80	3.19
3/2/2010	0.01	3.70	0.06	30.00	3.39	0.01	3.10	0.05	4.04	2712.32	7.43
4/15/2010	0.01	3.70	0.07	30.00	3.14	0.01	3.10	0.05	3.75	2516.70	6.90
5/4/2010	0.00	3.70	0.04	30.00	5.03	0.00	3.10	0.03	6.00	4024.40	11.03

Table D. 10: Example sheet of Devlin (2003) for determining groundwater flow angles and gradient

#	[X] matrix			[D] matrix	
	x	y	z	D	
2A1D	4725.7	5601.3	90.4	1	27.55
2A1S	4726.3	5596.1	90.5	1	27.59
2A2D	4677.2	5595.2	90.2	1	27.51
2A2S	4676.9	5590.3	90.1	1	27.49
2A3D	4579.4	5579.1	90.0	1	27.45
2A3S	4579.5	5576.1	89.8	1	27.39
2B1D	4732.9	5556.1	90.5	1	27.59
2B1S	4734.2	5552.6	90.6	1	27.62
2B2D	4682.4	5550.1	90.3	1	27.53
2B2S	4682.6	5544.1	90.2	1	27.49
2B3D	4599.8	5536.5	90.2	1	27.50
2B3S	4600.5	5531.9	89.9	1	27.42
2C1D	4741.0	5508.1	90.6	1	27.63
2C1S	4741.0	5504.5	90.6	1	27.63
2C2D	4691.8	5499.0	90.5	1	27.59
2C2S	4690.7	5495.1	90.3	1	27.53
2C3D	4609.9	5483.9	90.3	1	27.52
2C3S	4610.1	5479.4	90.1	1	27.47

Table D. 11: Additional example sheet of Devlin (2003) for determining groundwater flow angles and gradient

{[P]t[P]}																	
392830935	466103463																
466103463	553146154																
7595585	9013359																
{[P]t[P]}																	
2.52E-05	3.34E-06																
3.34E-06	2.87E-05																
-0.0015	-0.0019																
{[P]t[P]}																	
0.0014	0.001	0.000	0.0005	-0.001	-0.001	0.0012	0.0011	0.0003	0.0004	-0.0016	-0.001	0.001	0.001	8.1E-5	0.0003	-0.001	-0.001
0.0016	0.001	0.001	0.0016	0.001	0.001	0.0001	0	0.0002	0.0002	0	0.0001	-0.001	-0.001	-0.002	-0.001	-0.001	-0.001
-0.18	-0.14	-0.12	-0.13	-0.02	-0.01	-0.076	-0.053	-0.029	-0.042	0.1023	0.0608	0.028	0.037	0.0929	0.0648	0.202	0.181
Pt																	
4725.70	4726.31	4677	4676.93	4579.4	4579.5	4732.9	4734.2	4682.4	4682.6	4599.8	4600.5	4741.0	4741.0	4691.8	4690.7	4609.9	4610.1
5601.30	5596.19	5595	5590.30	5579.1	5576.1	5556.1	5552.6	5550.1	5544.1	5536.5	5531.9	5508.1	5504.5	5499.0	5495.1	5483.9	5479.4
90.41	90.54	90.3	90.19	90.06	89.89	90.54	90.63	90.33	90.21	90.23	89.983	90.66	90.673	90.52	90.33	90.30	90.15

$$\{[P]t[P]\}'[P]t[D] = [A] \text{ matrix}$$

A -4.12411E-05
 B 2.06981E-05
 C 0.011932718

gradient 0.00386 m/m
 angle off x axis -26.6512011 degrees

Groundwater Flow Vectors Modeled in Surfer 9 (Golden Software, 2010)

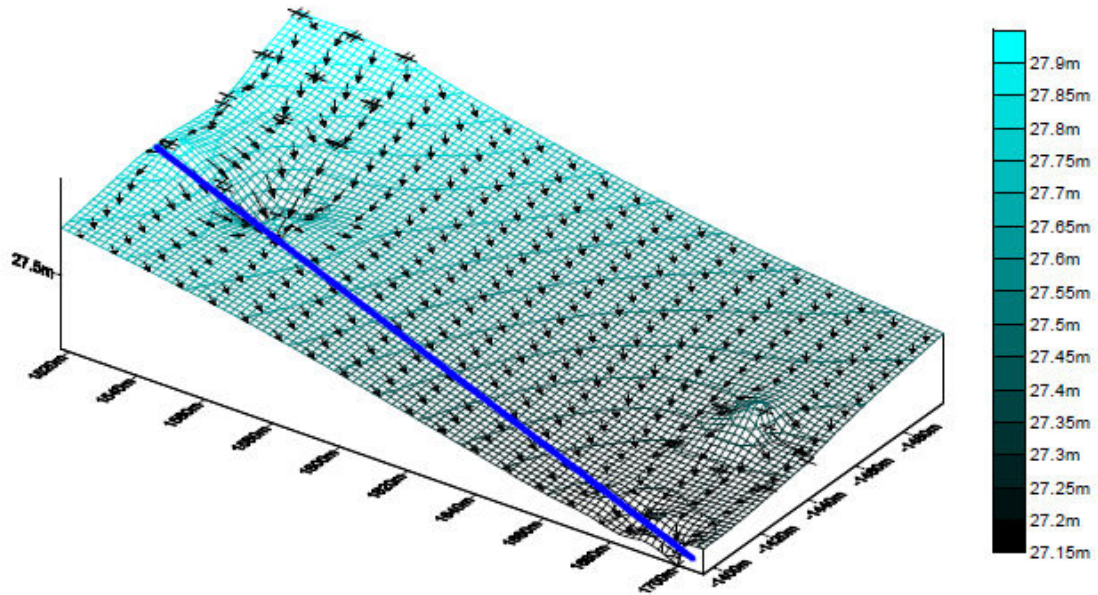


Figure D. 1: Groundwater flow vectors during June 2008

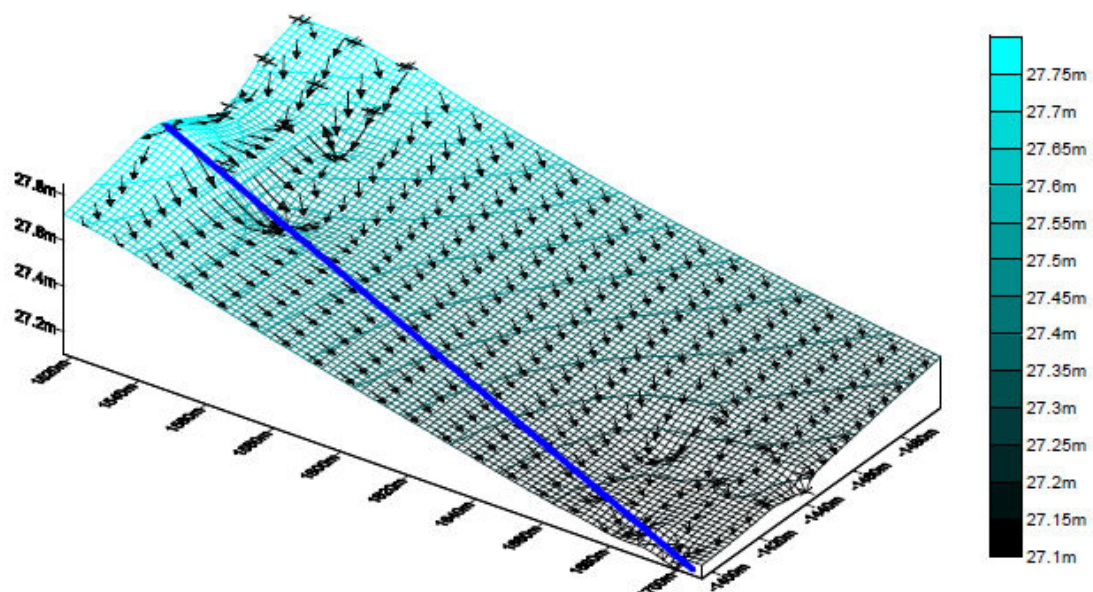


Figure D. 2: Groundwater flow vectors during August 2008

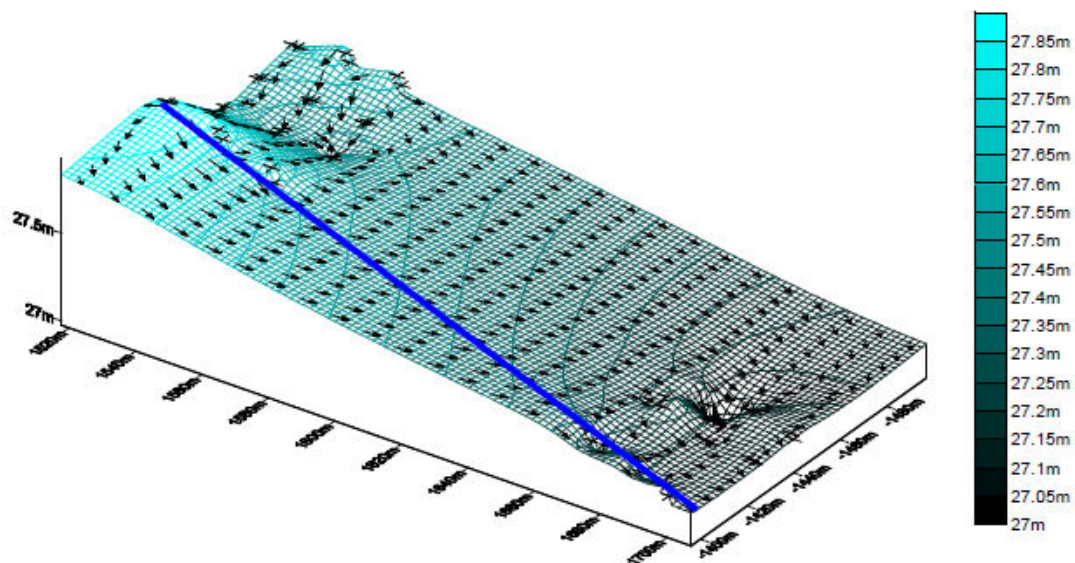


Figure D. 3: Groundwater flow vectors during September 2008

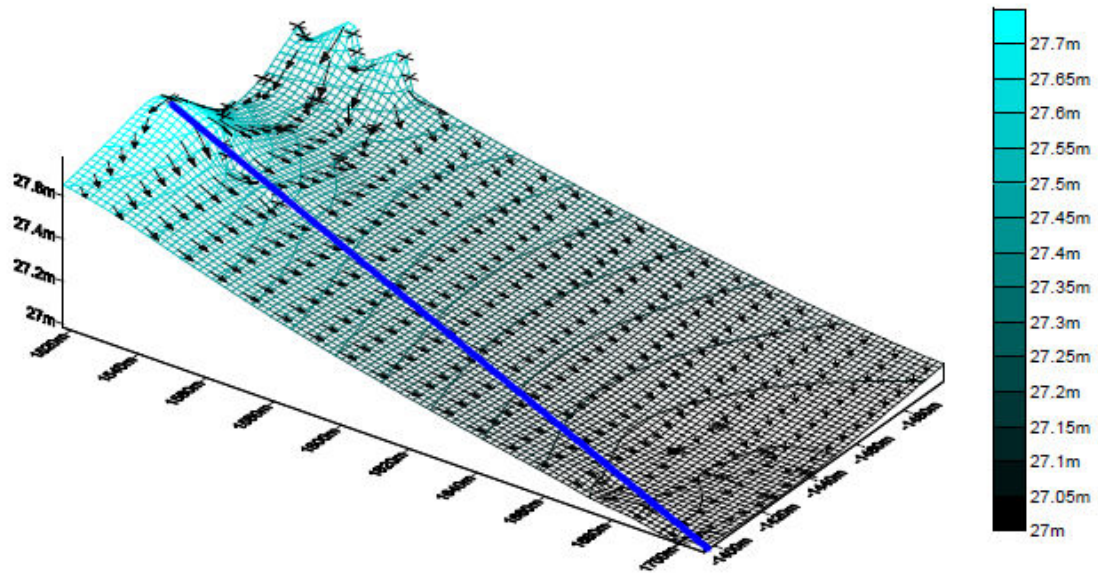


Figure D. 4: Groundwater flow vectors during October 2008

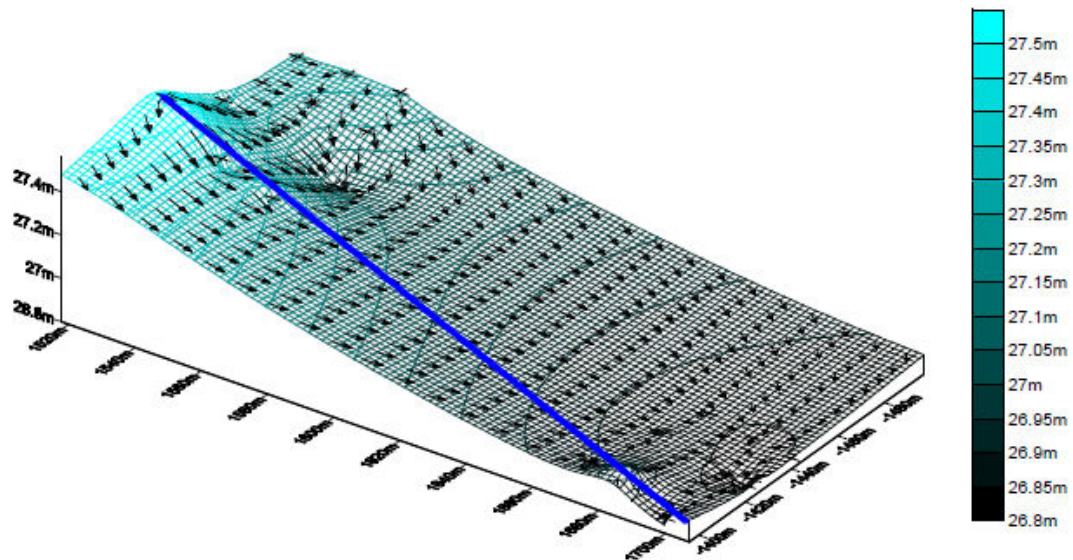


Figure D. 5: Groundwater flow vectors during November 2008

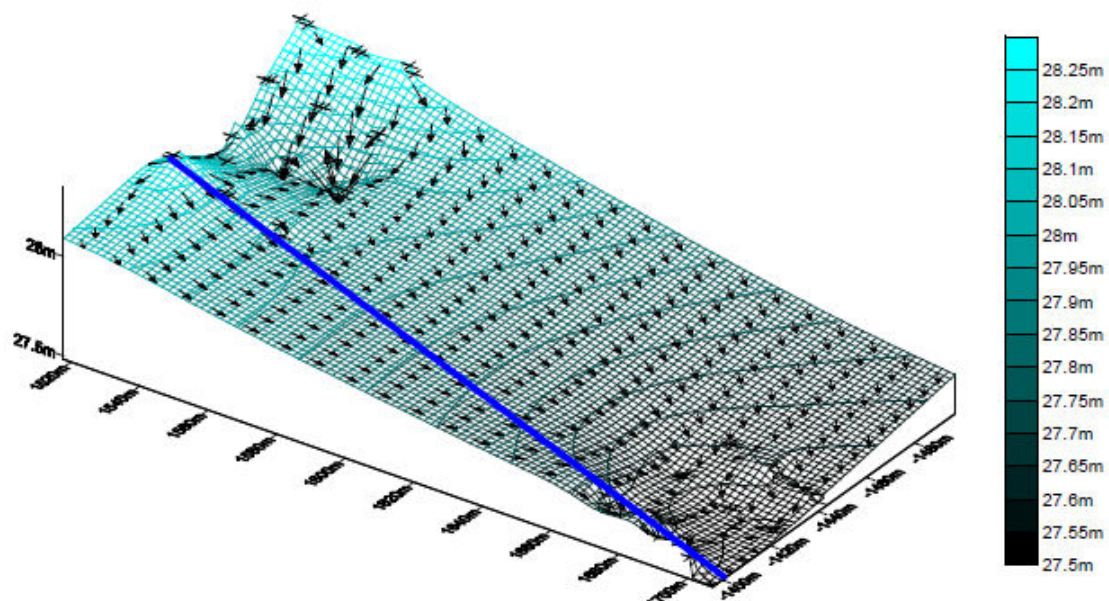


Figure D. 6: Groundwater flow vectors during December 2008

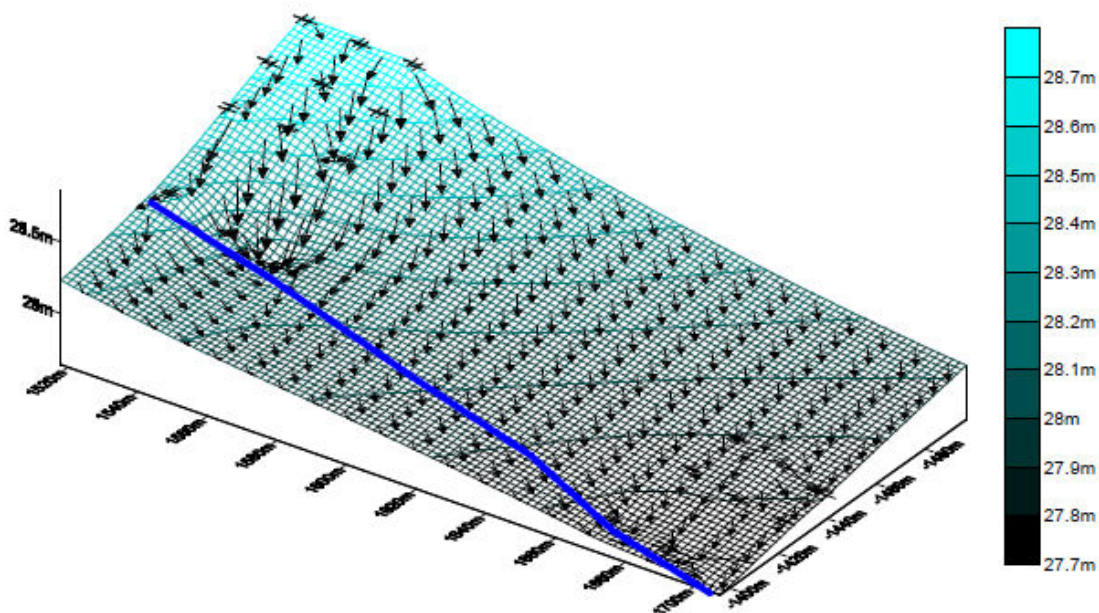


Figure D. 7: Groundwater flow vectors during January 2009

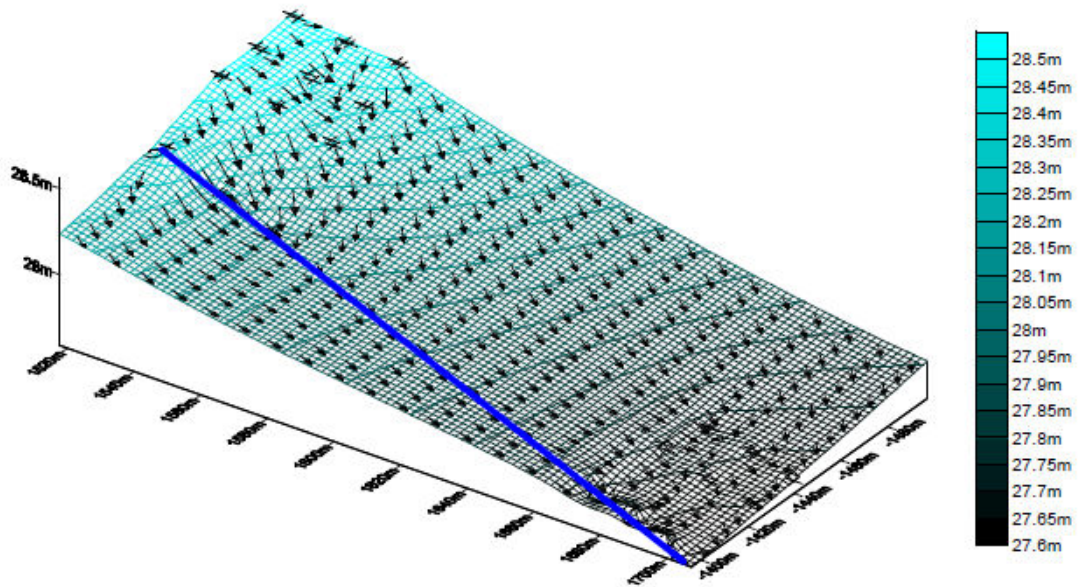


Figure D. 8: Groundwater flow vectors during February 2009

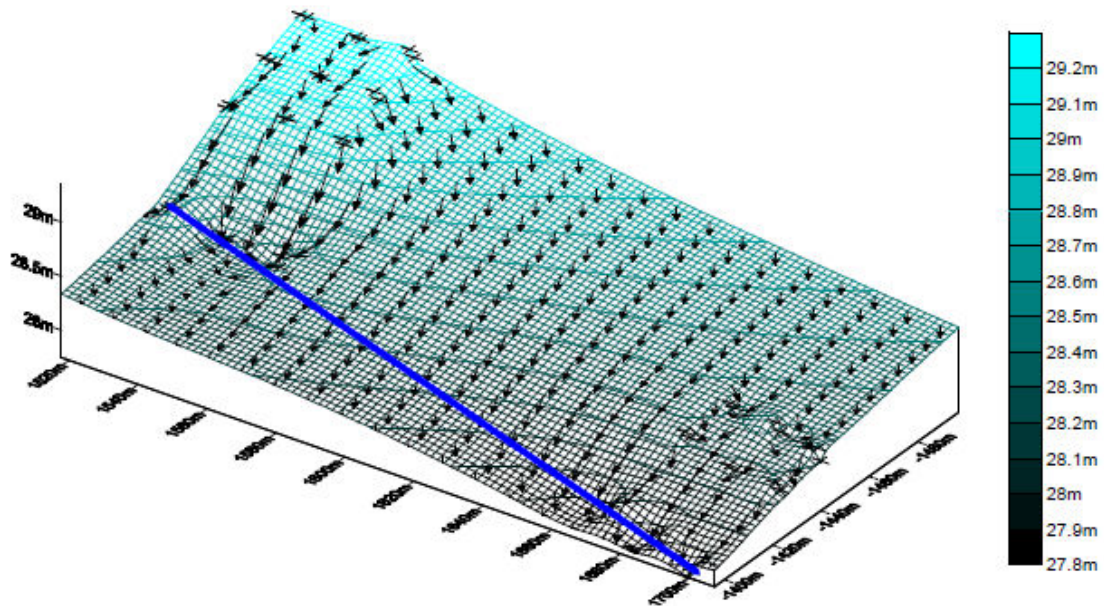


Figure D. 9: Groundwater flow vectors during March 2009

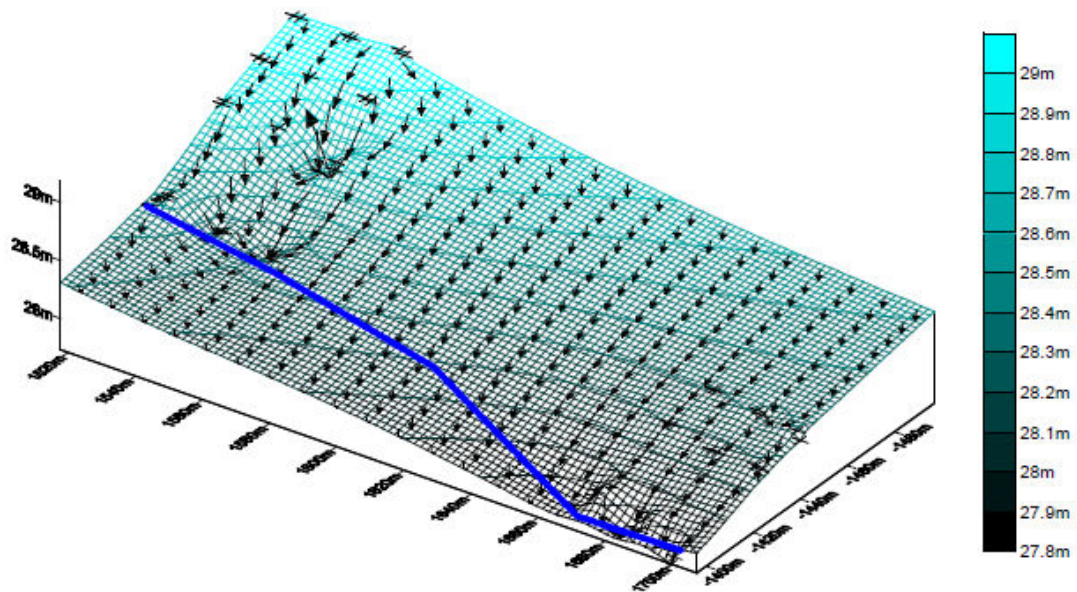


Figure D. 10: Groundwater flow vectors during April 2009

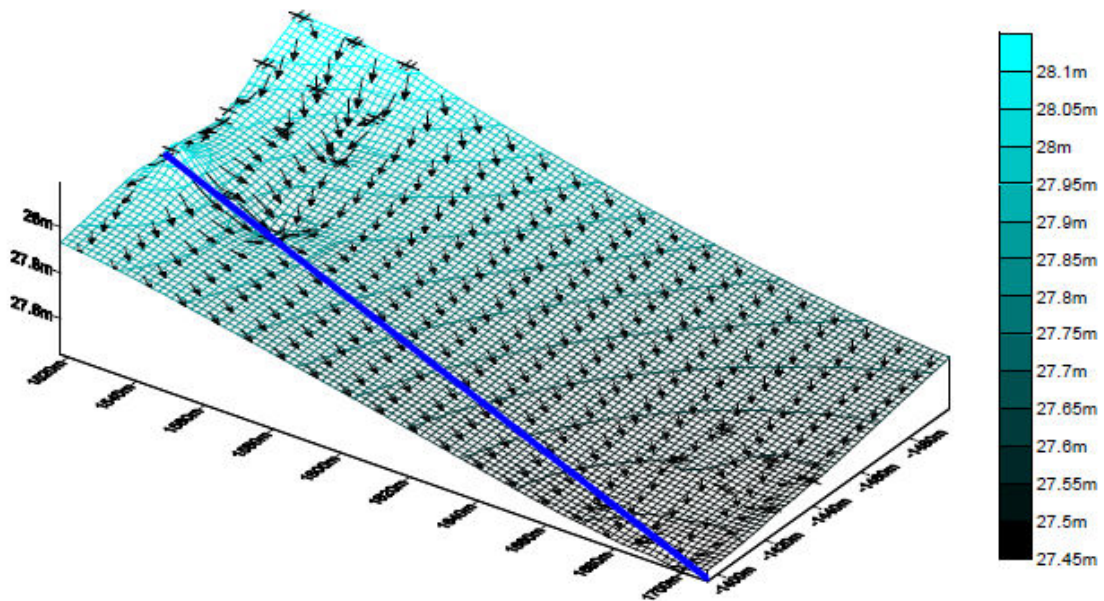


Figure D. 11: Groundwater flow vectors during May 2009

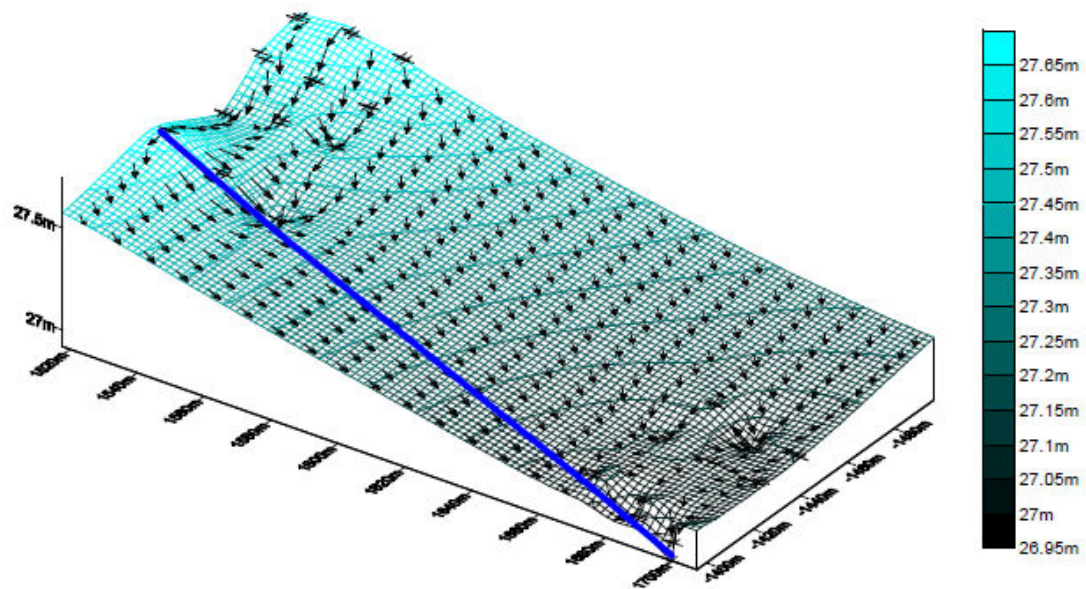


Figure D. 12: Groundwater flow vectors during June 2009

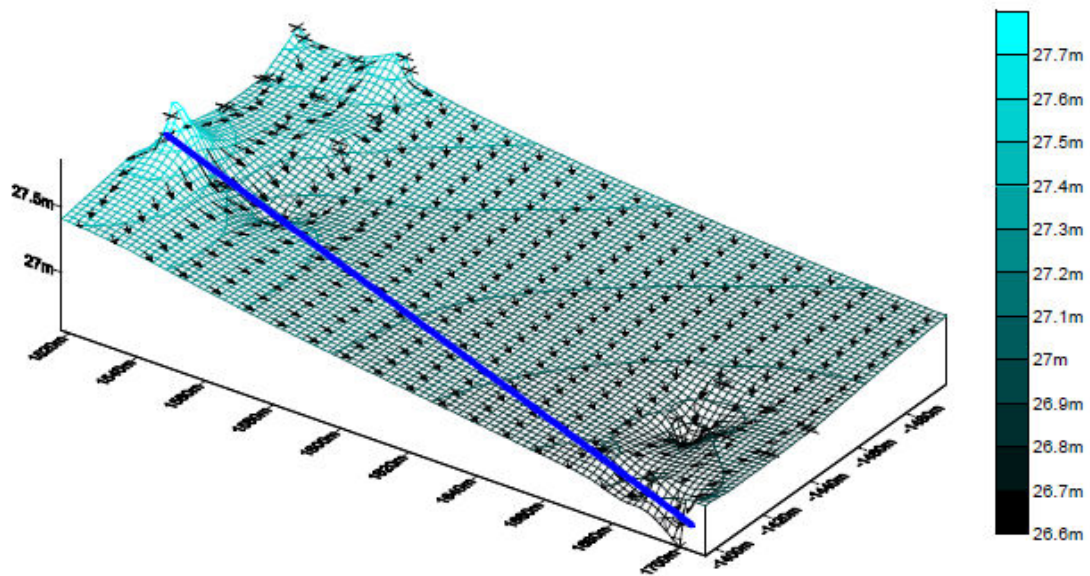


Figure D. 13: Groundwater flow vectors during July 2009

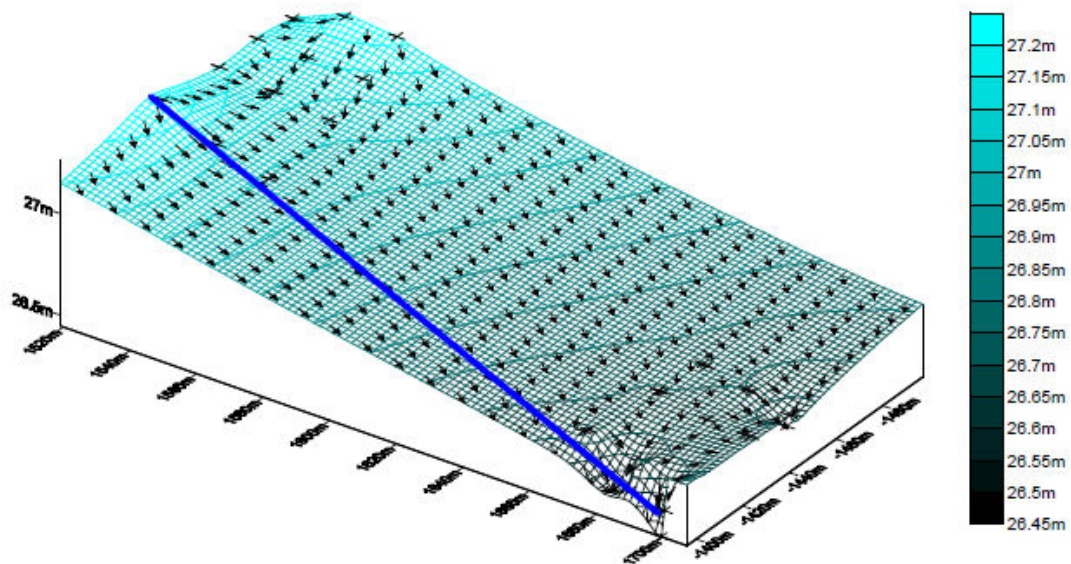


Figure D. 14: Groundwater flow vectors during August 2009

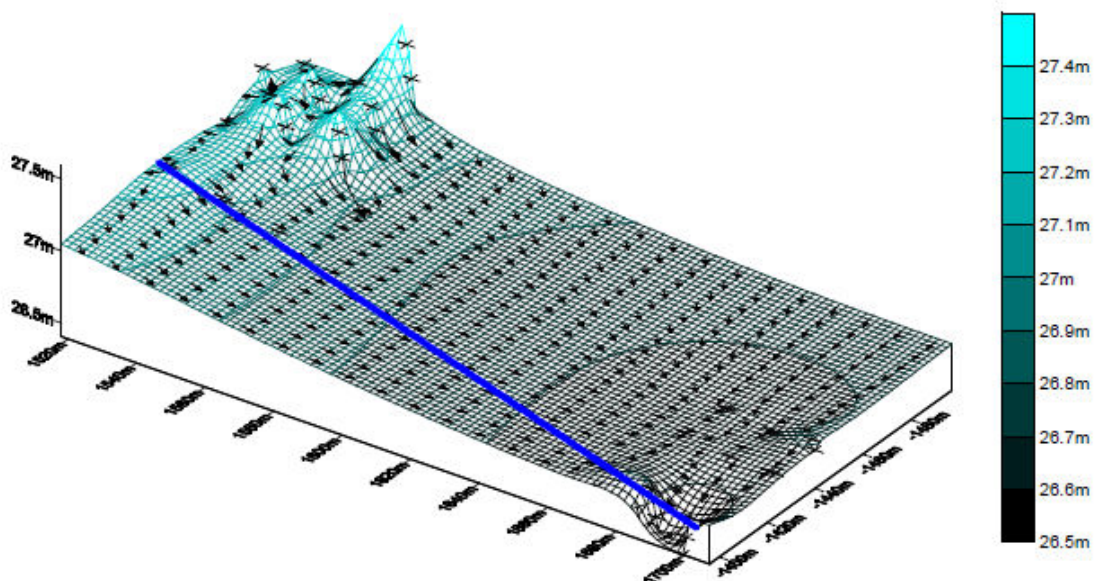


Figure D. 15: Groundwater flow vectors during September 2009

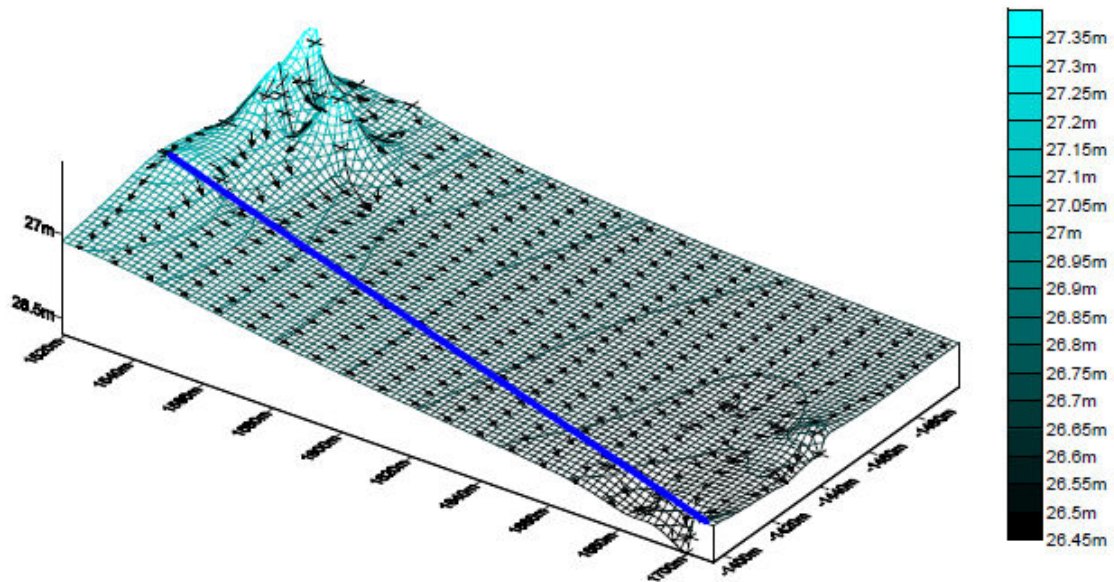


Figure D. 16: Groundwater flow vectors during October 2009

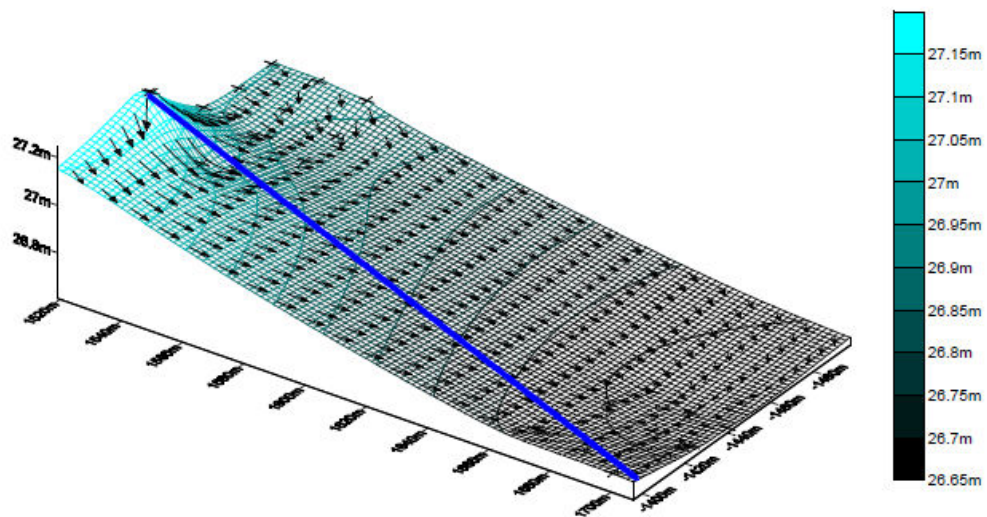


Figure D. 17: Groundwater flow vectors during November 2009

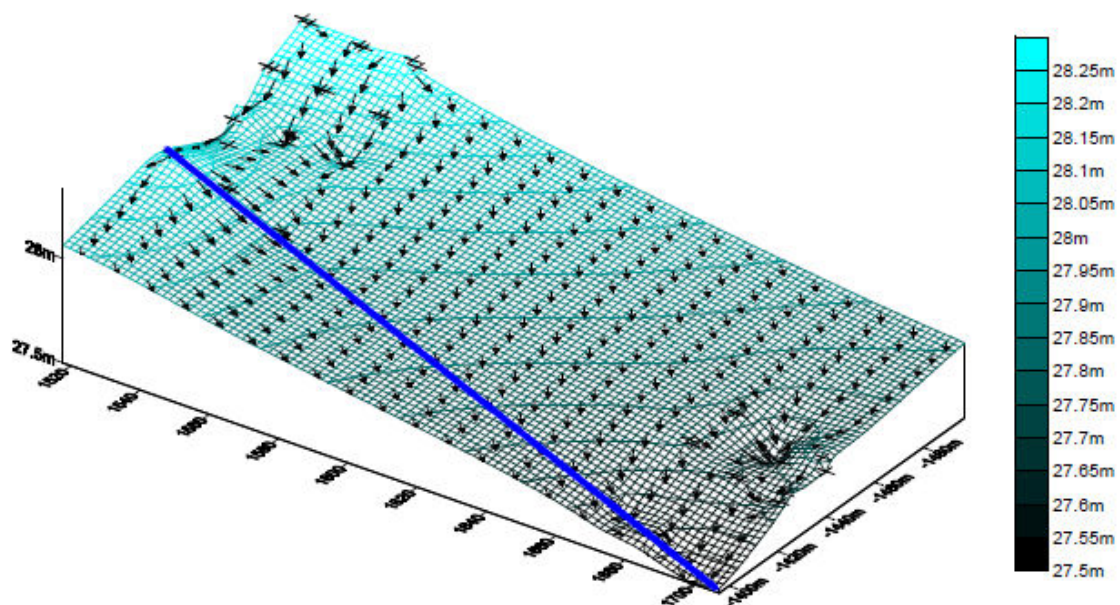


Figure D. 18: Groundwater flow vectors during December 2009

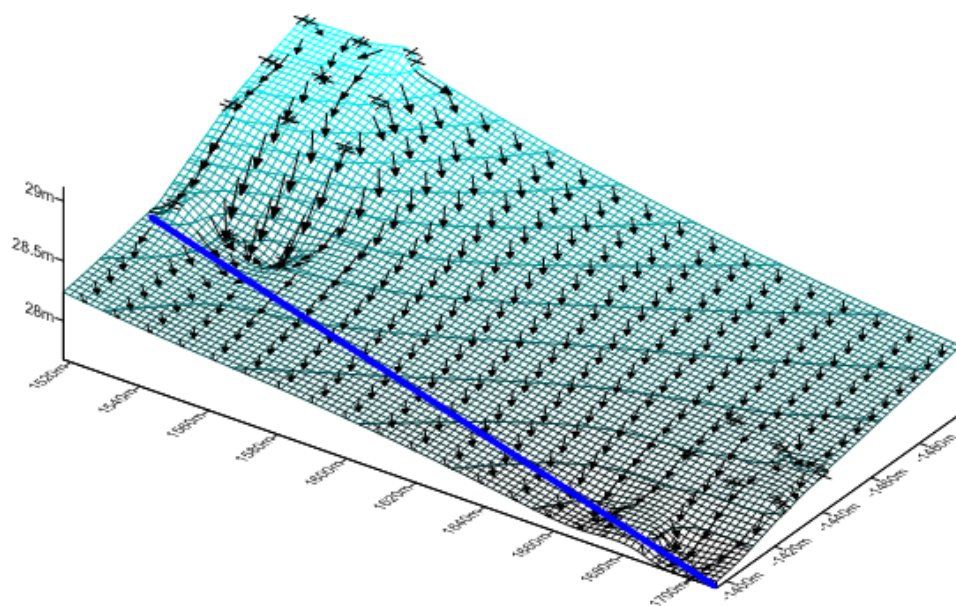


Figure D. 19: Groundwater flow vectors during January 2010

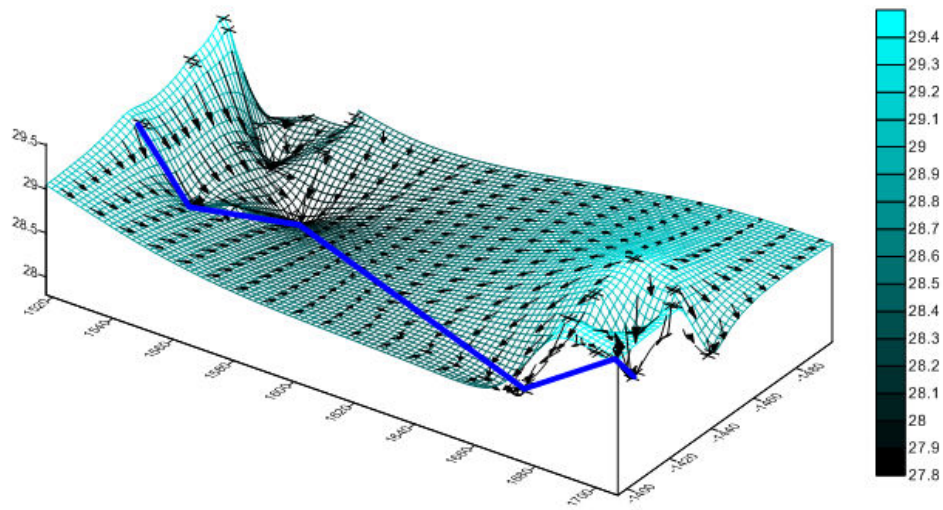


Figure D. 20: Groundwater flow vectors during February 2010

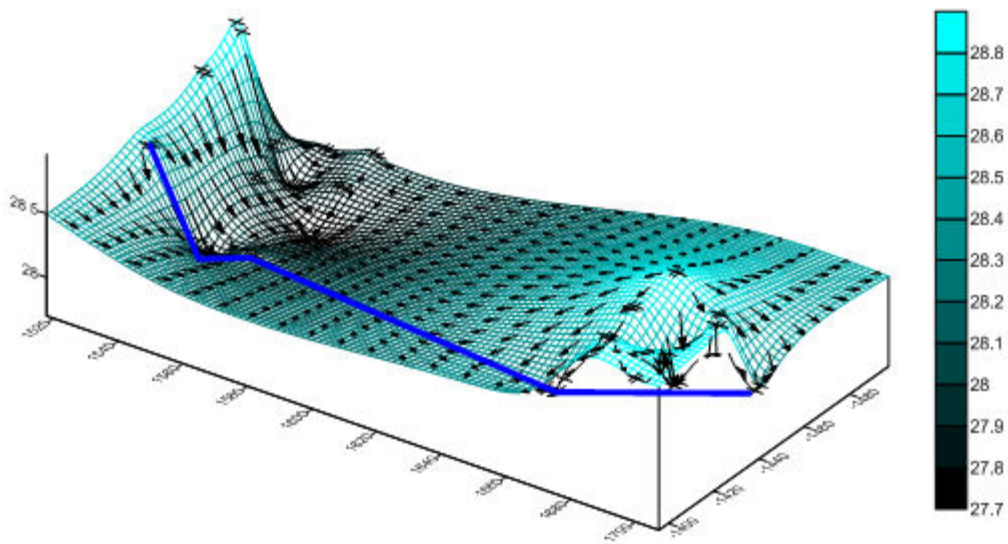


Figure D. 21: Groundwater flow vectors during March 2010

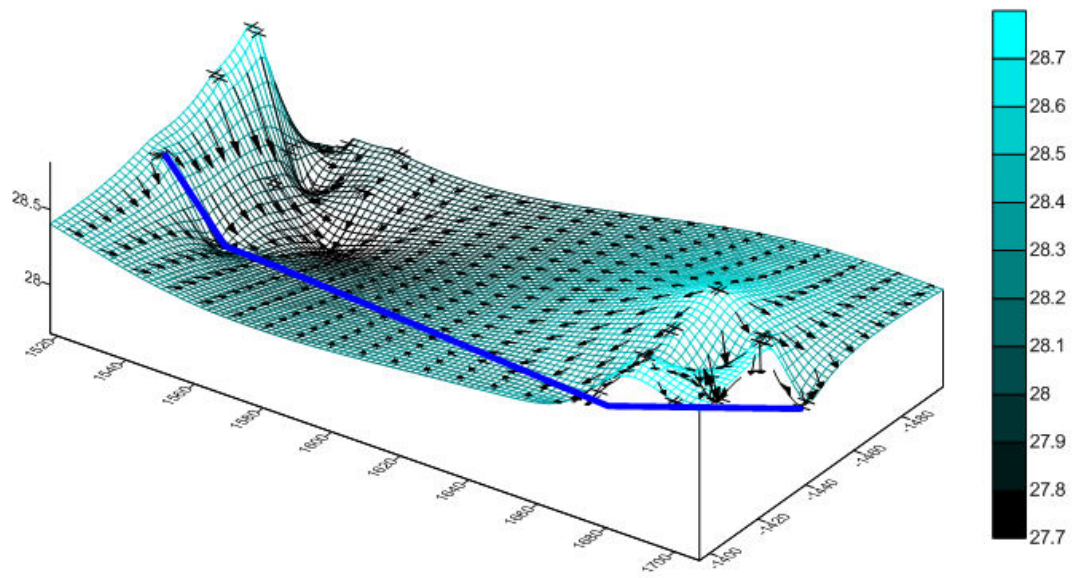


Figure D. 22: Groundwater flow vectors during April 2010

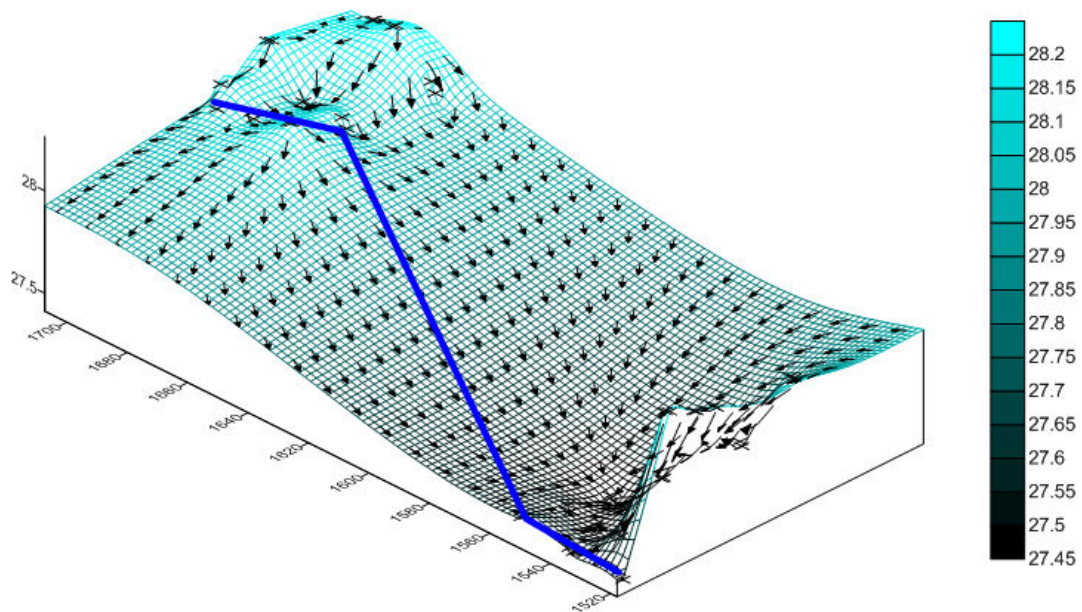


Figure D. 23: Groundwater flow vectors during May 2010

APPENDIX E: Nitrogen Application and Removal Calculations

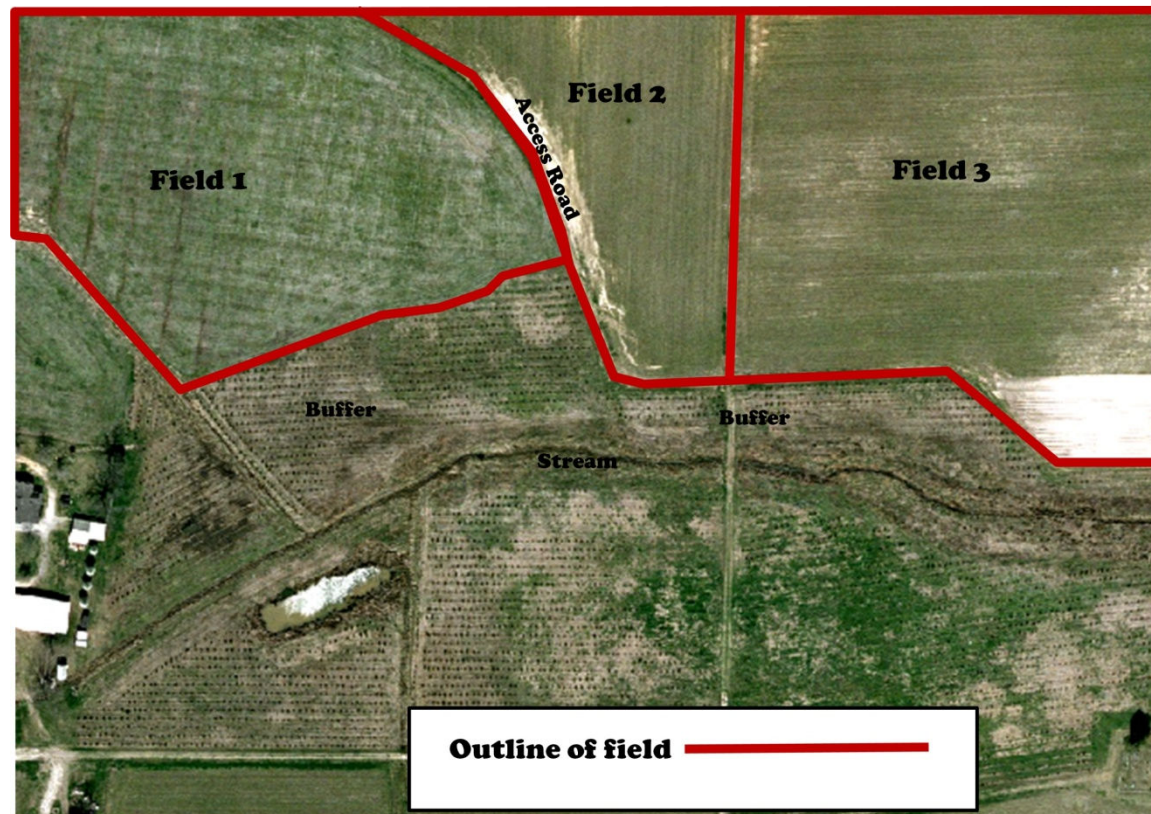


Figure E. 1: Layout of applications to adjacent field.

Table E. 1: Nitrogen Application each year on the research study site's field 1.

Year	Crop(s)	Dates Fertilizer Applied	Type of Fertilizer Applied	Amount of Fertilizer Applied
2007	1.strip till corn	1.4/3/07	1.4-11-32	1.300lb. per acre
	2.	2.4/2/07	2.10-34-0	2.10 gal. per acre
	3.	3.4/2/07	3.anhydrous	3.120 units
2008	1.strip till corn	1.4/4/08	1.4-11-32	1.300lbs.
	2.	2.4/3/08	2.10-34-0	2.10 gal. per acre
	3.	3.4/3/08	3.anhydrous	3.120 units
2009	1.no till soybeans	1.5/26/09	1.4-11-32	1.300lbs. per acre
	2.	2.	2.	2.
	3.	3.	3.	3.
2010	1.plans to plant cotton	1.	1.	1.
	2.	2.	2.	2.
	3.	3.	3.	3.

Table E. 2: Nitrogen Application each year on the research study site's field 2.

Year	Crop(s)	Dates Fertilizer Applied	Type of Fertilizer Applied	Amount of Fertilizer Applied
2007	1.striptill cotton	1.4/24/07	1.potash	1.200 lbs.
	2.”	2.4/26/07	2.anhydrous	2. 80 units
	3.	3.4/26/07	3.10-34-0	3.10 gal. per acre
2008	1.striptill cotton	1.4/21/08	1.potash	1.200lbs.
	2.”	2.4/22/08	2.10-34-0	2.10 gal. per acre
	3.	3.6/6/08	3.27%	3.300 lbs per acre
2009	1.striptill cotton	1.4/29/09	1. potash	1.200lbs.
	2.”	2.4/30/09	2.10-34-0	2.10 gal. per acre
	3.	3.6/10/09	3.27%	3.300lbs
2010	1.plan to plant strip till cotton	1.	1.	1.
	2.	2.	2.	2.
	3.	3.	3.	3.

Table E. 3: Nitrogen Application each year on the research study site's field 3.

Year	Crop(s)	Dates Fertilizer Applied	Type of Fertilizer Applied	Amount of Fertilizer Applied
2007	1.striptill cotton	1.same as field 2 2007	1.	1.
	2.	2.	2.	2.
	3.	3.	3.	3.
2008	1.striptill cotton	1.4/21/08	1.potash	1.200 lbs per acre
	2."	2.4/22/08	2.10-34-0	2.10 gal per acre
	3.	3.6/06/08	3.27%	3.300 lbs.
2009	1.striptill cotton	1.4/30/09	1.10-34-0	1.10 gal per acre
	2.	2.6/10/09	2.27%	2.300 lbs. per acre
	3.	3.4/29/09	3.potash	3.200 lbs. per acre
2010	1.plan to plant peanuts	1.	1.potash	1.200lbs. per acre
	2.	2.	2.	2.
	3.	3.	3.	3.

Potential Nitrate-Nitrogen Mass Removal

Highest rates of denitrification have been reported to occur at the soil surface where root density, organic matter, and microbial activity are highest and reduce quickly with depth (Lowrance *et al.*, 1995; Lowrance, 1992; Hunt *et al.*, 2004). Therefore, to report a complete estimate of the overall *potential* capacity of groundwater NO_3^- -N being reduced through denitrification within the riparian zone the denitrifying removal capacity was estimated for higher soil layers.

A denitrification enzyme activity (DEA) analysis was completed within each buffer section to estimate the *potential* groundwater NO_3^- -N that could be reduced in higher soil layers within the buffer treatment by the method proposed by Maître *et. al* (2005). DEA is the denitrification rates that occurs in an incubated slurry and is used to predict the *potential* of denitrification occurring within soils. Soil from the three soil layers closest to the soil surface in each zone of Sections 1 and 2 and adjacent field was collected during February 2009 to evaluate denitrification enzyme activity (DEA) through the buffer site. Samples were taken at depths ranging from 38 to 74 cm, 29 to 71 cm, 51 to 71 cm, and 33 to 67 cm from the adjacent field to Zone 1 respectively in Sections 1, while samples were taken at depths ranging from 21 to 69 cm, 18 to 69 cm, 17 to 80 cm, and 19 to 75 cm from the adjacent field to Zone 1 respectively in Section 2. Soil was sampled using an auger and approximately 20-40 mL soil cores were placed in a plastic bag, iced, and shipped to USDA-ARS in Tifton, GA for processing.

Maitre *et al.* (2005) estimated the denitrifying removal capacity using soil properties, water table elevation monitoring, and DEA soil analyses. The following equation was used from Maitre *et al.* (2005) to determine the denitrifying removal capacity in the higher soils layers of the studied riparian buffer. The DRC was then converted to a per area basis (m²) based on the area of the buffer section.

$$DRC = Vol_{Soil\ layer} * \%_{Interaction} * \rho * DEA * (365 \times 10^{-6} \text{ days/year})$$

(E. 1)

Where,

DRC = Denitrifying removal capacity (kg N/yr)

Vol_{Soil Layer} = Volume in soil horizon interacting with groundwater (m³)

%_{Interaction} = Percentage of volume of soil interacting with the water table

ρ = Bulk density of soil (Mg/m³)

DEA = Denitrification enzyme activity for investigated soil layer (μgN/kgday)

A denitrification enzyme activity (DEA) analysis was completed center transect to estimate the *potential* mass of possible groundwater NO₃⁻-N reduction in higher soil layers within Section 1. DEA is the measured amount of denitrification rates that occur in an incubated slurry and is used to predict the potential of denitrification occurring within soils. The highest rates of DEA were found in the top soil zone locations (Figure E. 2 and Figure E. 30). These results were lower than compared to results found in Maitre *et. al* (2005) who had evaluated wetlands. DEA results during the winter in the highest soil layer of the Maitre *et. al* (2005) study

had mean values of 604, 212, and 24 ng N g⁻¹ h⁻¹ over a one hour incubation period for the 3 soil horizons beginning with the top soil horizon respectively. The DEA rates increased as incubation time increases and anoxic conditions become present (Figure E.2 and Figure E.3).

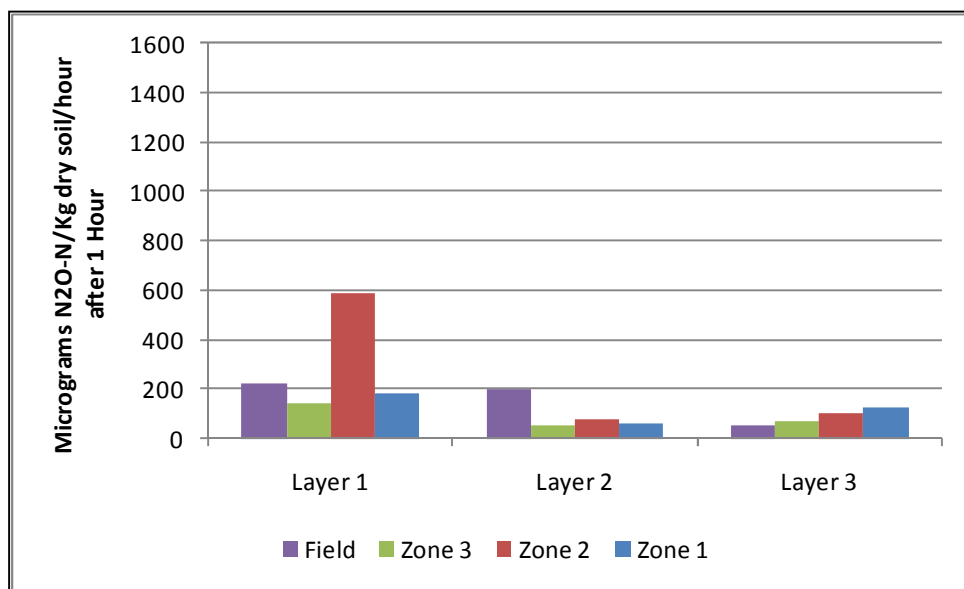


Figure E. 2: DEA after one hour of incubation.

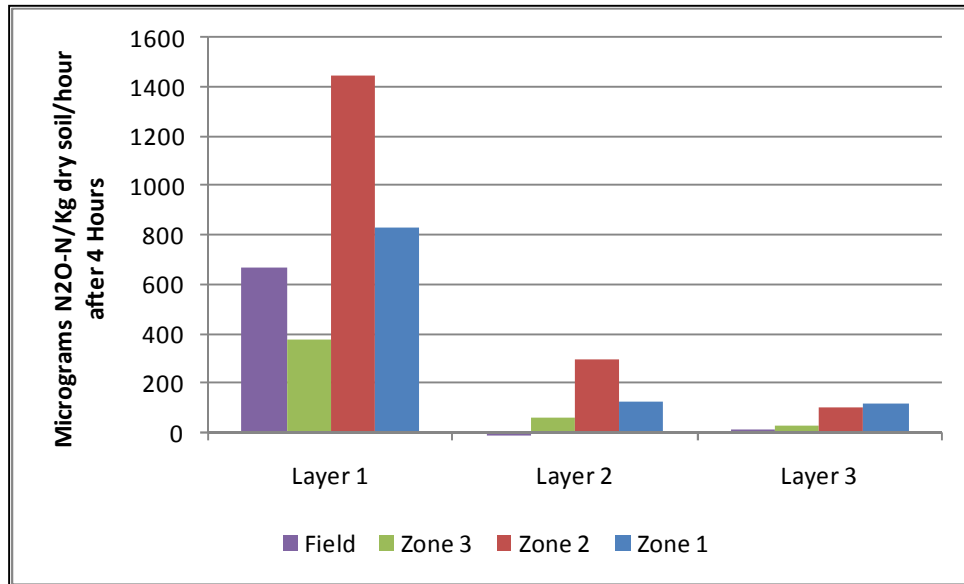


Figure E. 3: DEA after four hours of incubation.

A denitrification enzyme activity (DEA) analysis was completed in the upstream and downstream transects of Section 2 to estimate the *potential* mass of possible NO_3^- -N reduction in higher soil layers within the buffer treatment. The highest rates of DEA were found in the top soil zone locations (Figure E. 4 - Figure E. 7), and rates were measured slightly lower in the downstream transect (Transect A) than measured in the upstream transect (Transect C), indicating high potential for denitrification near the soil surface. These results were lower than compared to results found in Maître *et. al* (2005) who had evaluated wetlands. DEA results during the winter in the highest soil layer of the Maître *et. al* (2005) study had mean values of 604, 212, and 24 $\text{ng N g}^{-1} \text{ h}^{-1}$ over a one hour incubation period for the 3 soil horizons beginning with the top soil horizon respectively. The DEA rates increase as incubation time increases and anoxic conditions become present as seen in Figure E.4 thru Figure E.7.

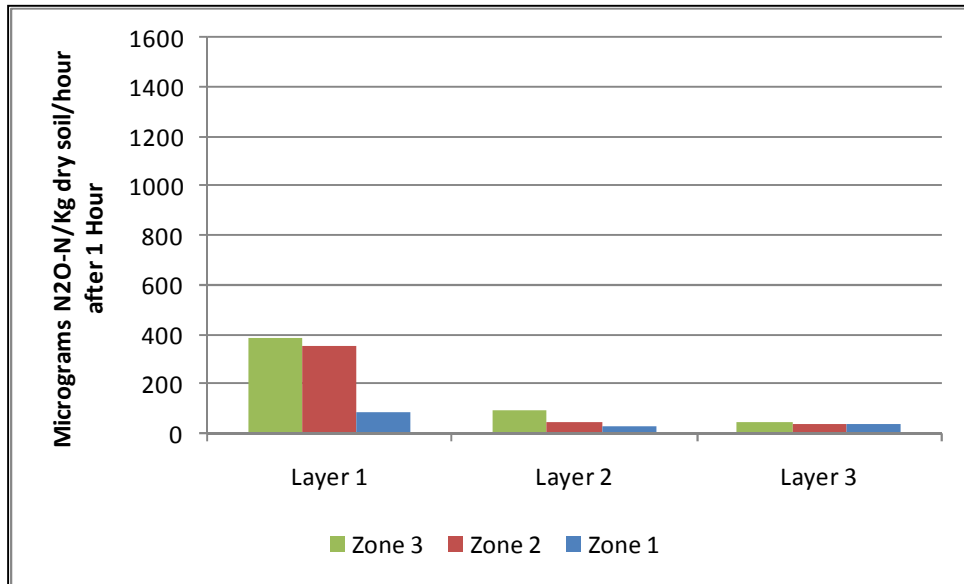


Figure E. 4: DEA for Transect A after one hour of incubation.

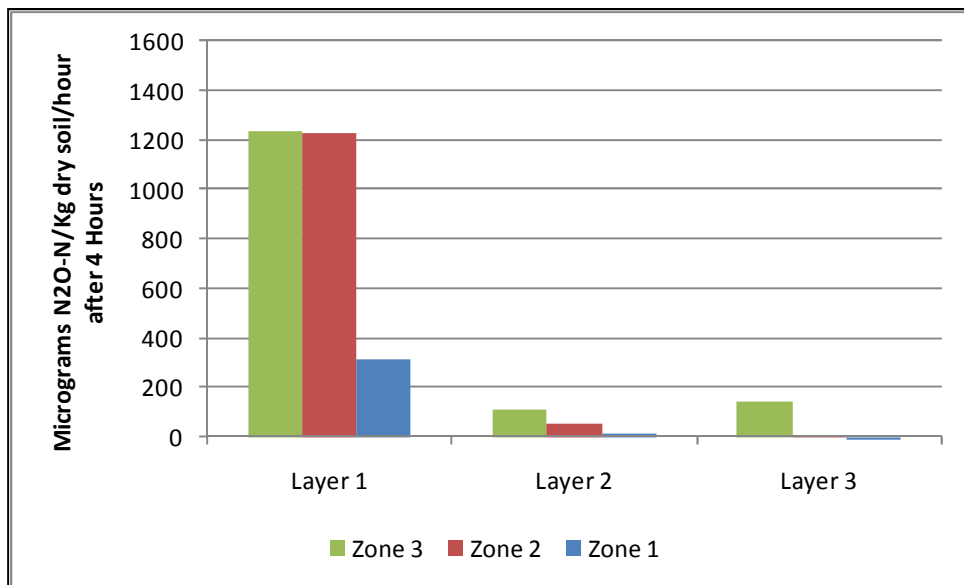


Figure E. 5: DEA for Transect A after four hours of incubation.

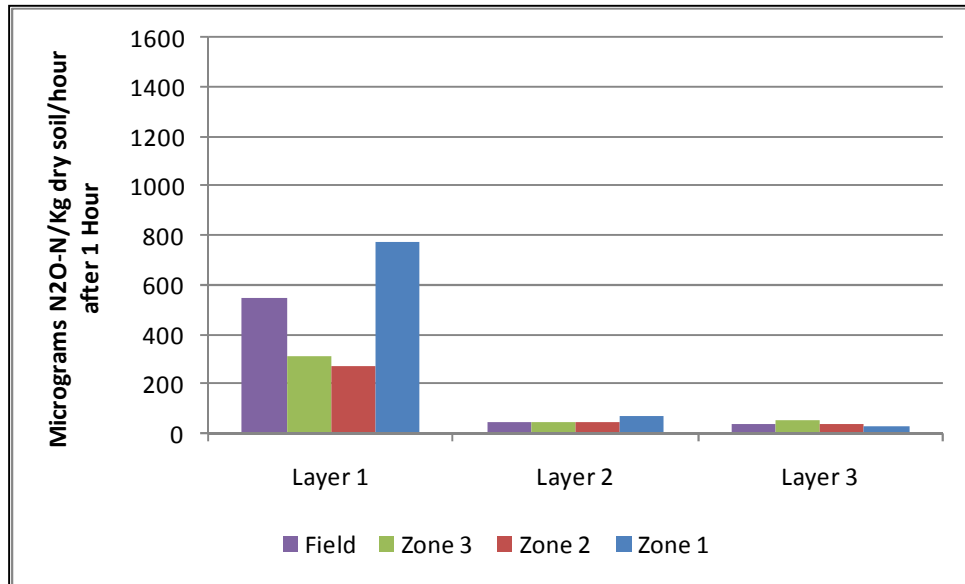


Figure E. 6: DEA for Transect C after one hour of incubation.

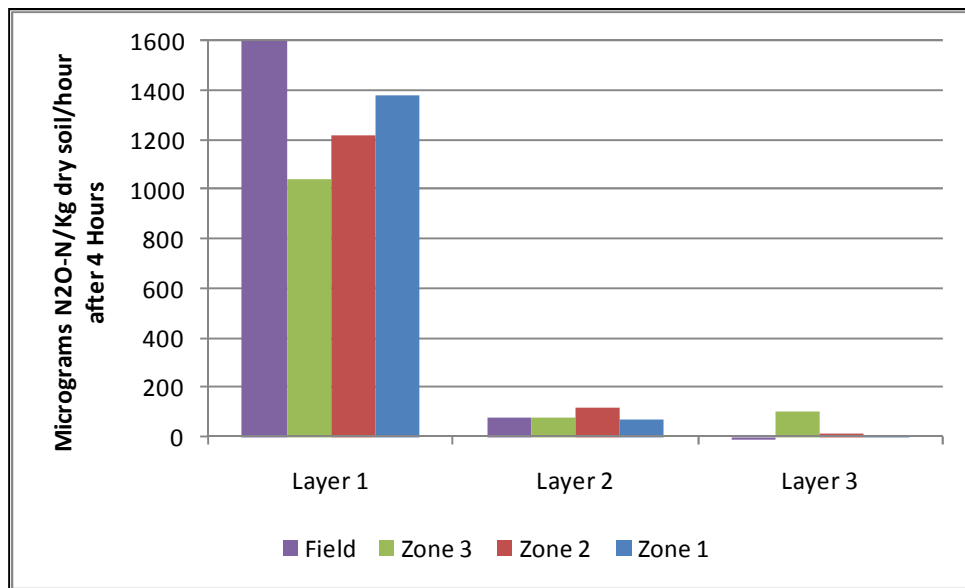


Figure E. 7: DEA for Transect C after four hours of incubation

Section 1 was estimated to *potentially* remove more NO_3^- -N than Section 2 (Table E.4). Section 1 was estimated to *potentially* remove $2690 \text{ kg N yr}^{-1}$, while Section 2 was estimated to

potentially remove 2210 kg N yr⁻¹ in the upper 70 cm of the soil. Therefore, Section 1 had the *potential* to remove approximately 0.04 to 0.16 kg N yr⁻¹m⁻², while Section 2 had the *potential* to remove 0.03 to 0.18 kg N yr⁻¹ m⁻³ dependent on soil depth. These estimates were the maximum possible NO₃⁻-N removal at the 0 -70 cm depths of the two buffer sections based on hydrology and that the system was not NO₃⁻-N or carbon limited. Higher *potential* removal rates were found in Section 1 due to higher DEA measurements in the soil samples.

Table E. 4: Potential NO₃⁻-N removal based on DEA analysis

Section	Depth (cm)	Potential NO ₃ ⁻ -N removal		
		0 – 30 cm	30 – 50 cm	50 – 70 cm
1	Total NO ₃ ⁻ -N Removed in Buffer Treatment System (kgN yr ⁻¹)	1480	390	820
	Total NO ₃ ⁻ -N Removed in Buffer Treatment System (kgN yr ⁻¹ m ²)	0.16	0.04	0.09
2	Total NO ₃ ⁻ -N Removed in Buffer Treatment System (kgN yr ⁻¹)	1670	265	275
	Total NO ₃ ⁻ -N Removed in Buffer Treatment System (kgN yr ⁻¹ m ²)	0.18	0.03	0.03

APPENDIX F: Installation Procedures and Laboratory Procedures

BAE Environmental Analysis Laboratory at NCSU Analytical Procedures

Table F. 1: Analytical Procedures followed by the BAE Environmental Analysis Laboratory

Pollutant	Analysis	References
NO ₃ ⁻ -N + NO ₂ -N (Nitrate Nitrogen)	Ammonia-salicylate method for automated analysis. Emerald green color formed by reaction with ammonia, sodium salicylate, sodium hypochlorite in a buffered alkaline medium.	EPA Method 351.2 (1979) or Standard Method 4500-NH ₃ G (1998), with slight modifications including dialysis.
Cl ⁻ (Chloride)	Ferricyanide method for automated analysis.	EPA Method 325.2 (1979) or Standard Method 4500-Cl-E (1998) with slight modifications including dialysis.
O-PO ₄ -P (Orthophosphate Phosphorus)	Ascorbic acid method for automated analysis.	EPA Method 365.1 (1979) or Standard Method 4500-P F (1998) with slight modifications including dialysis.
TP (Total Phosphorus)	Persulfate digestion, and ascorbic acid method for automated analysis.	EPA Method (1979) or Stand Method 4500-P F (1998) with slight modifications including dialysis.
TKN (Total Kjeldahl Nitrogen)	Persulfate Digestion, and ammonia salicylate method for automated analysis.	EPA Manual 351.2 (1979) with slight modifications including dialysis or Stand Methods 4500N _{org} B (1998).
FSS (Total Suspended Solids)	Gravimetric Method.	EPA Methods 160.1 – 160.4 (1979) or Standard Methods 2540 (1998).
Metals: Calcium and Sodium (Ca ²⁺ and Na ⁺)	Nitric acid digestion for total metals followed by direct aspiration atomic absorption spectroscopy, Na and K by emission spectroscopy.	EPA (1979) or Standard Methods 3111-B (1998).

Water Quality Monitoring Well Installation Procedure

Prior to the installation of water quality monitoring wells, the Three Point Method verified the groundwater flow progressing through the future buffer location was acceptable for the study (Todd and Mays, 2005; Schwartz and Zhang, 2003; Kashef, 1986). Completion of the

evaluation required measuring the hydraulic head following the installation of three piezometers in 2004 and measuring the distance between each of the piezometers. The calculations for the hydraulic gradient used the measurements to verify ground water flow proceeded through the proposed buffer location as completed in past studies (Todd and Mays, 2005). The installation of the full-scale monitoring well design followed the verification of groundwater flow direction (Figure F. 1).

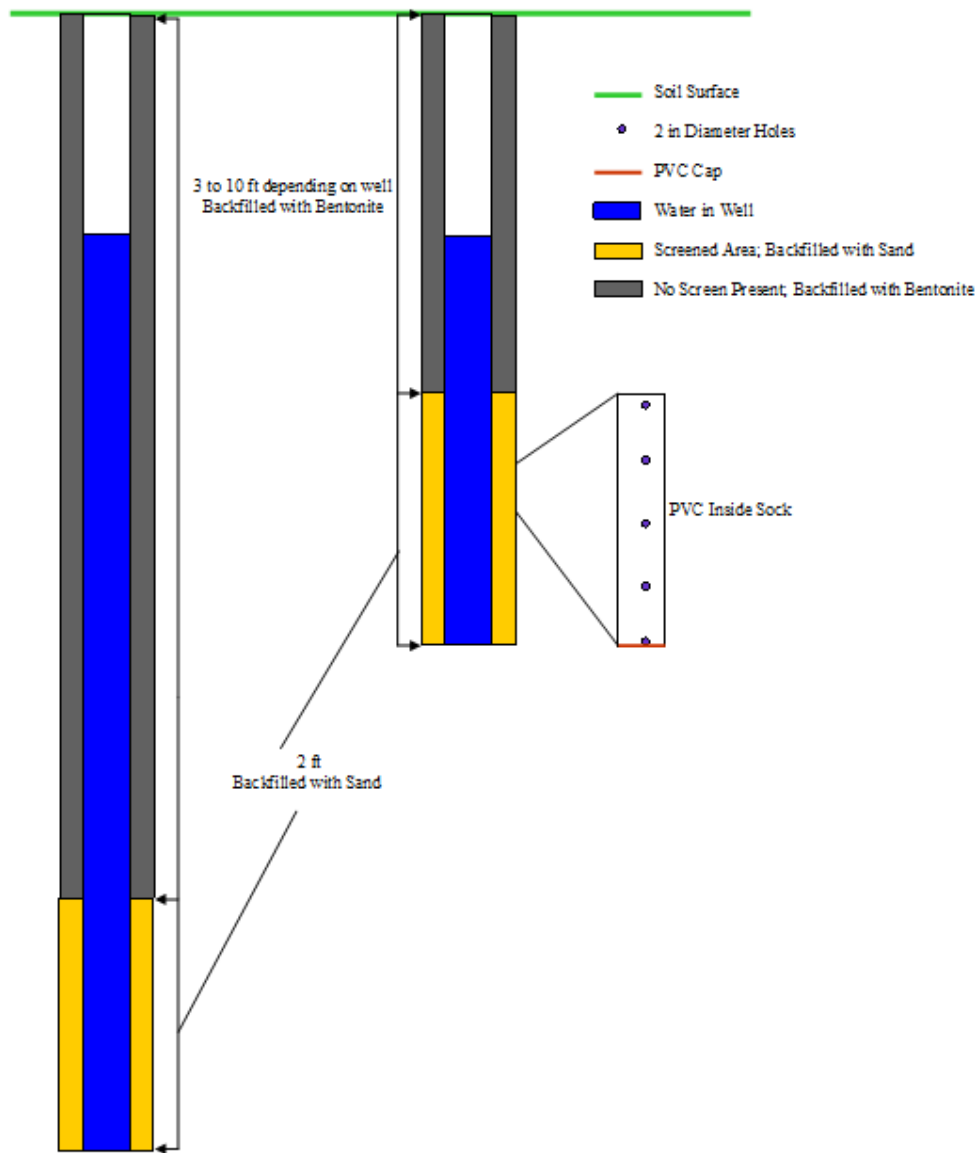


Figure F. 1: Well Installation

APPENDIX G: Other Water Quality Constituents

Section 1 NH₄-N and O-PO₄

NH₄-N and O-PO₄ were compared to NO₃⁻-N to define any correlations that may have existed during the study period. Averages were taken within each buffer section for the 1.5 m and 3 m depths and were modeled. No significant relationships were seen. The NH₄-N and O-PO₄ concentrations were relatively low. There were some outliers as seen in the figures below (Figure G.1 and Figure G.2).

The low NH₄-N concentrations exhibit nitrification had transformed most NH₄-N into NO₃⁻-N relatively quickly, which could then undergo the process of denitrification. In addition, most of the nitrogen found in the groundwater was in the form of NO₃⁻-N. Furthermore, the investigation exhibited that the concentrations of both NH₄-N and O-PO₄ were both similar in the 1.5 m and 3 m depths at the field edge and stream. These results once again indicate that groundwater dilution was minimal.

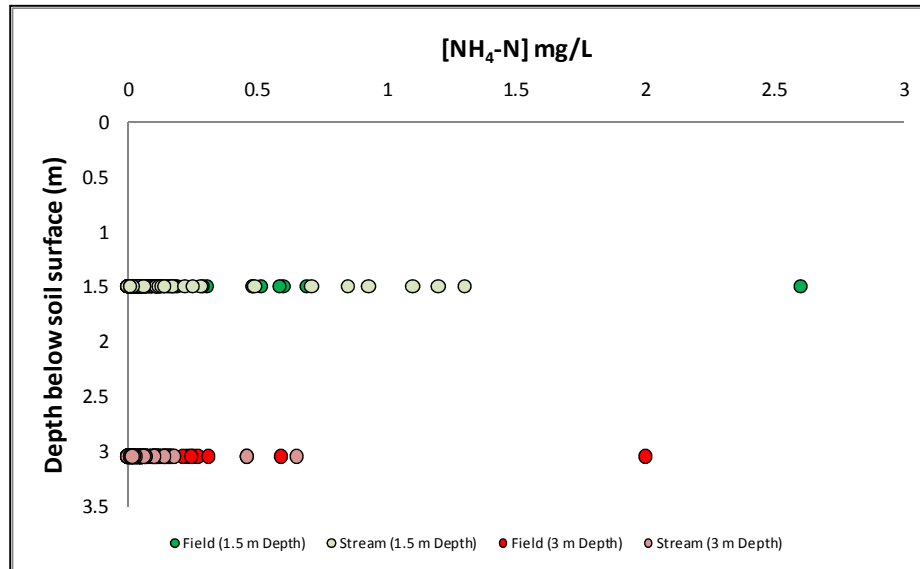


Figure G. 1: $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ at water quality monitoring depths 1.5 m and 3m ($n_{\text{shallow}} = 50$ and $n_{\text{deep}} = 64$)

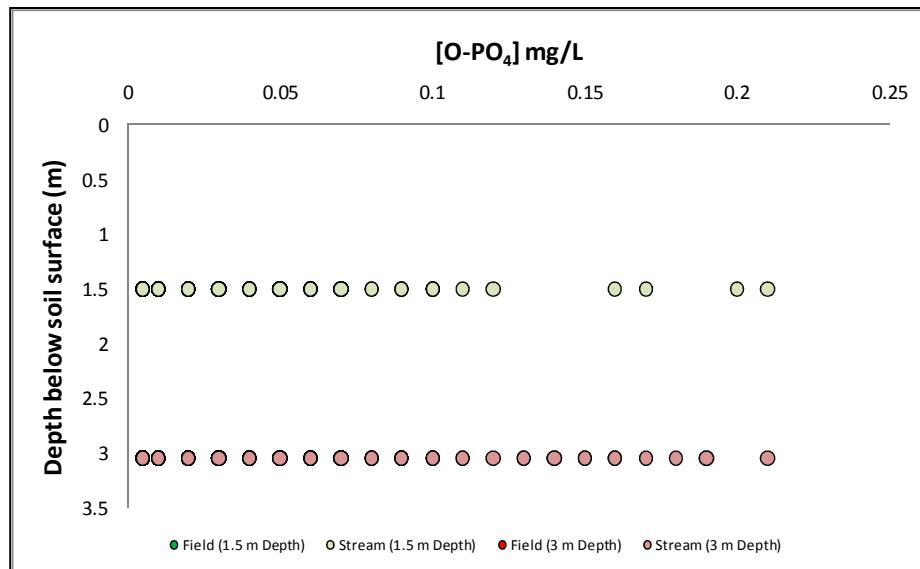


Figure G. 2: $\text{O-PO}_4\text{NO}_3\text{-N}$ at water quality monitoring depths 1.5 m and 3m ($n_{\text{shallow}} = 50$ and $n_{\text{deep}} = 64$)

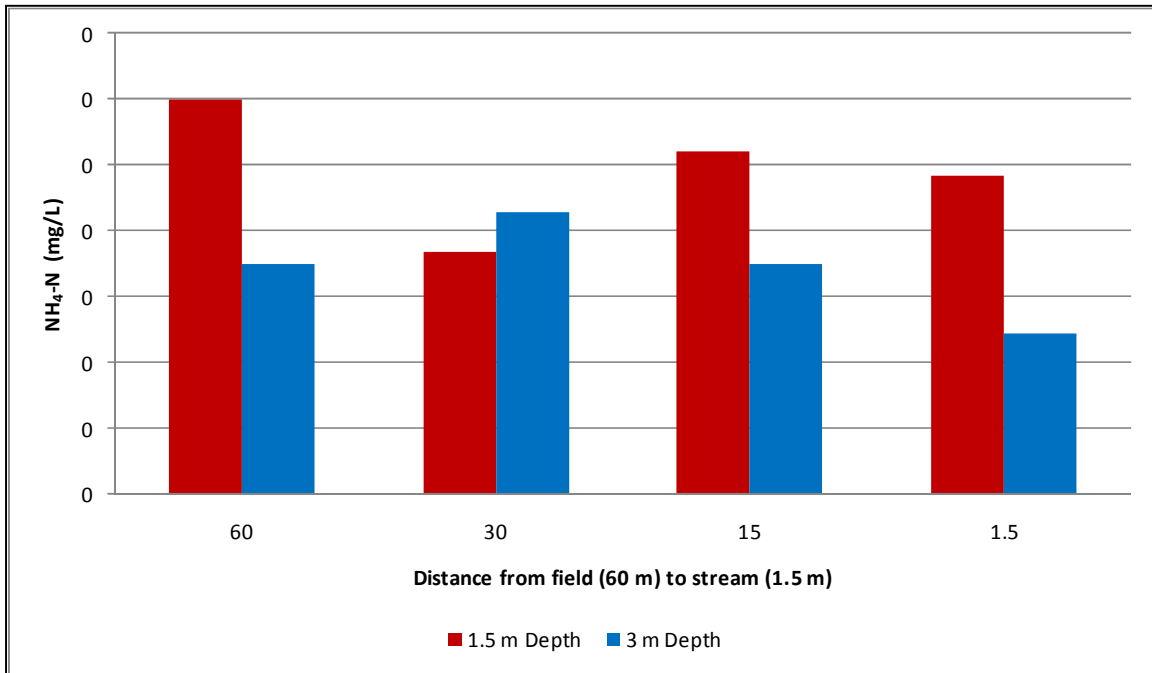


Figure G. 3: Section 1 average $\text{NH}_4\text{-N}$ at the 1.5 m and 3 m monitoring depths ($n_{\text{shallow}} = 50$ and $n_{\text{deep}} = 64$)

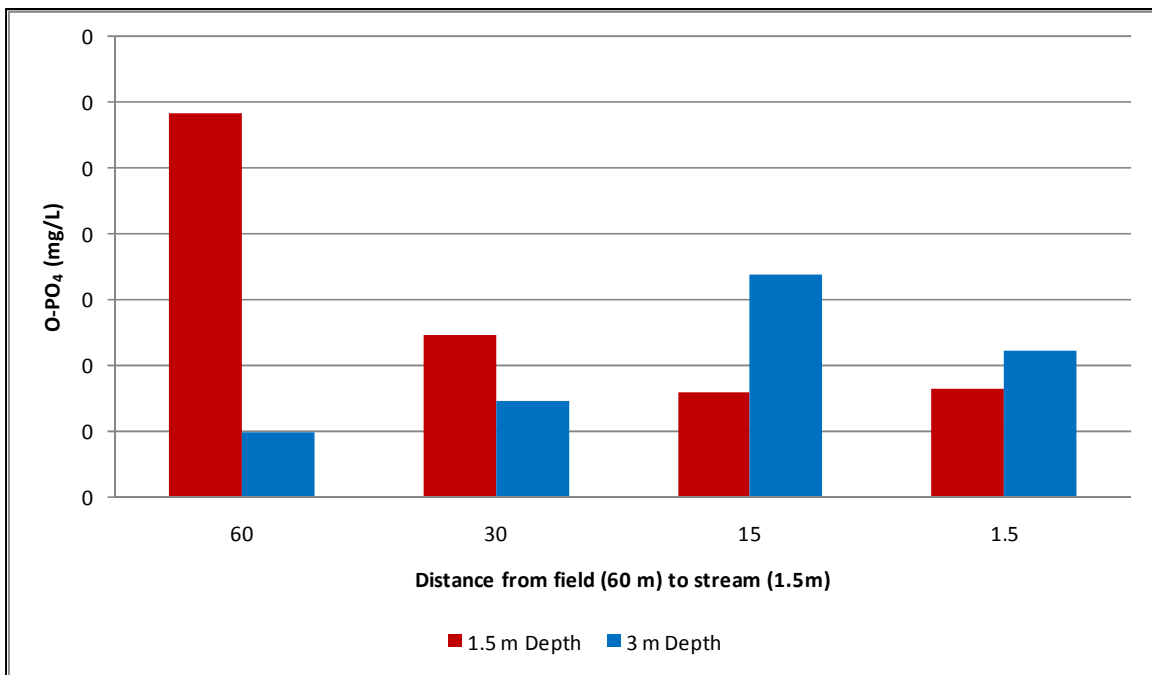


Figure G. 4: Section 1 average O-PO_4 at the 1.5 m and 3 m monitoring depths ($n_{\text{shallow}} = 50$ and $n_{\text{deep}} = 64$)

Section 2 NH₄-N and O-PO₄

NH₄-N and O-PO₄ were compared to NO₃⁻-N to define any correlations that may have existed during the study period. Averages were taken within each buffer section for the 1.5 m and 3 m depths and were modeled (Figure G. 5 and Figure G. 6). No significant relationships were seen. The NH₄-N and O-PO₄ concentrations were relatively low. There were some outliers as seen in the figures below (Figure G. 7 and Figure G. 8).

The low NH₄-N concentrations exhibit nitrification had transformed most NH₄-N into NO₃⁻-N relatively quickly, which could then undergo the process of denitrification. In addition, most of the nitrogen found in the groundwater was in the form of NO₃⁻-N. Furthermore, the NH₄-N and O-PO₄ being similar in both the shallow and deep wells at the field and stream edge indicates once again that the water chemistries are not being diluted by ground water dilution.

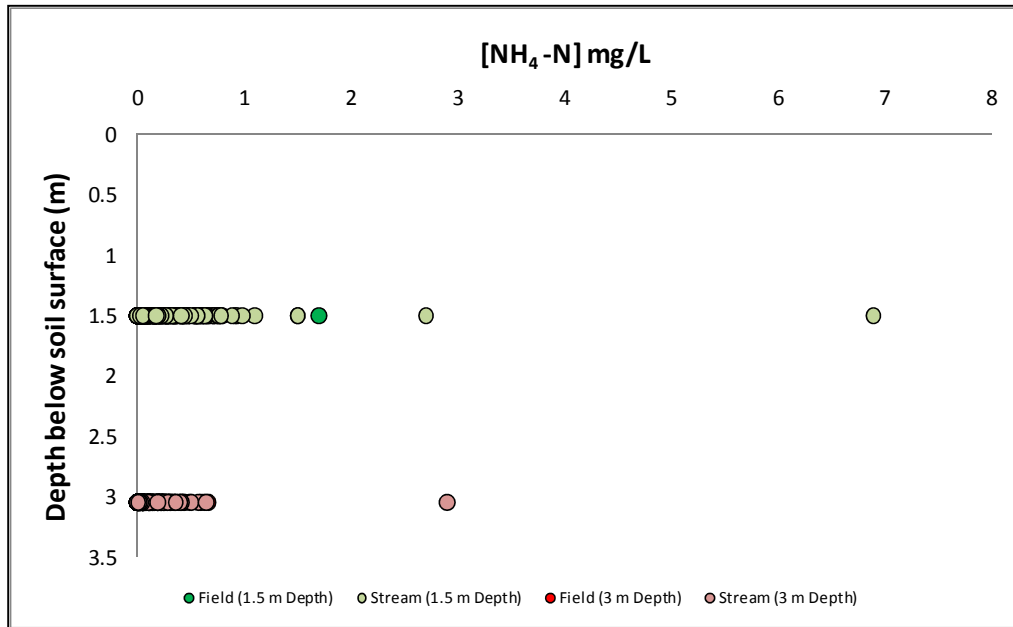


Figure G. 5: $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ concentrations at the 1.5 m and 3 m monitoring depths ($n_{1.5\text{ m}}=50$ and $n_{3\text{ m}}=64$)

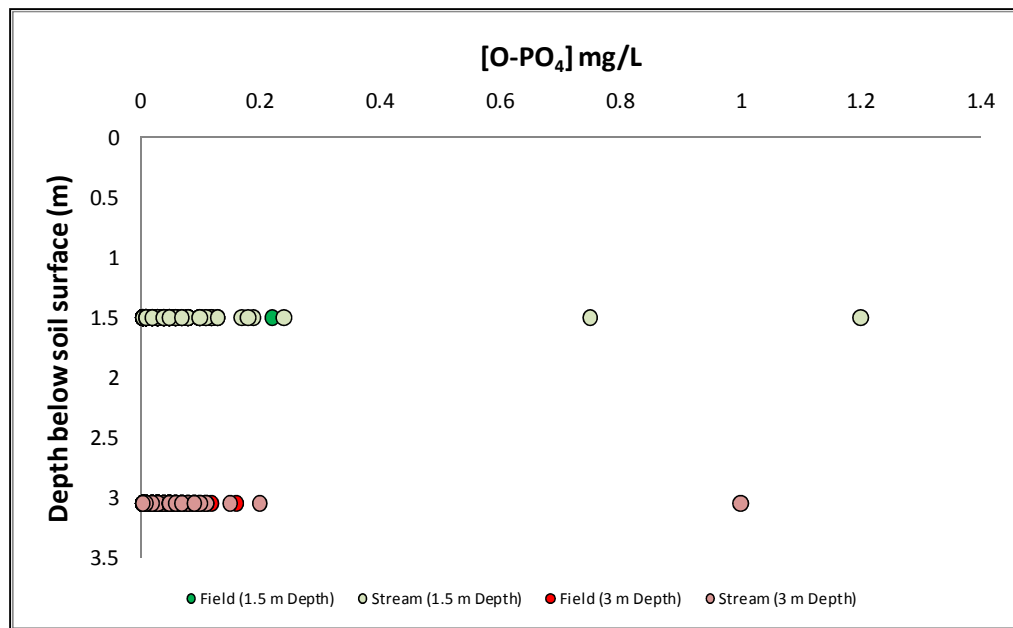


Figure G. 6: O-PO_4 to $\text{NO}_3\text{-N}$ concentrations at the 1.5 m and 3 m monitoring depths ($n_{1.5\text{ m}}=50$ and $n_{3\text{ m}}=64$)

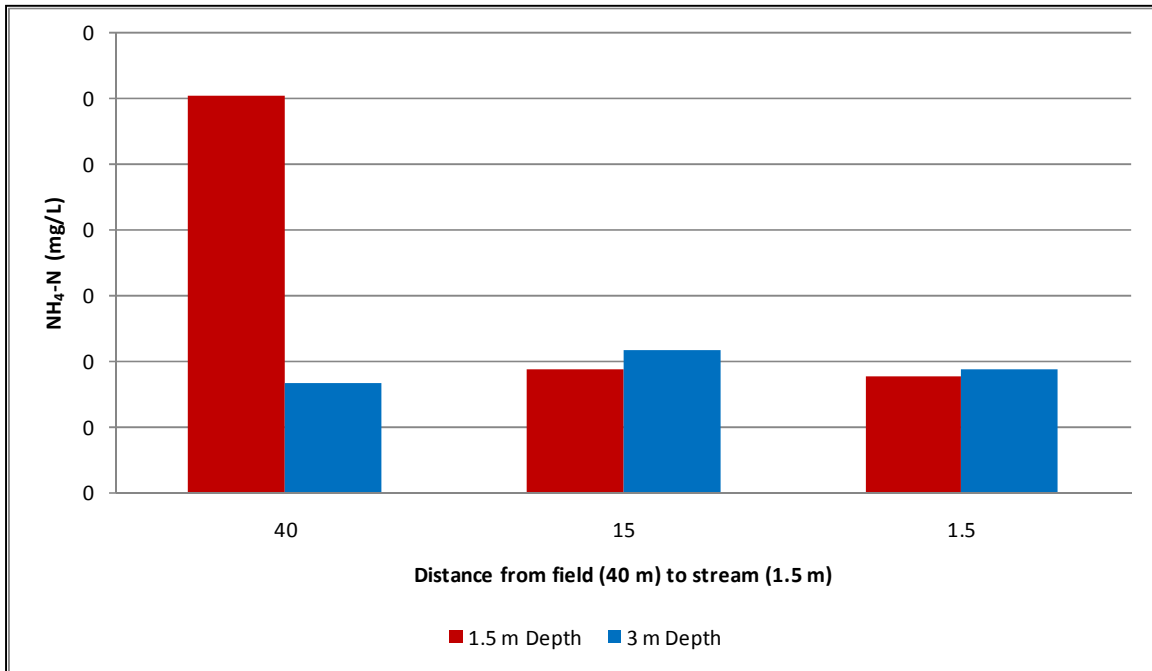


Figure G. 7: Section 2 average $\text{NH}_4\text{-N}$ at the 1.5 m and 3 m monitoring depths ($n_{1.5\text{ m}}=50$ and $n_{3\text{ m}}=64$)

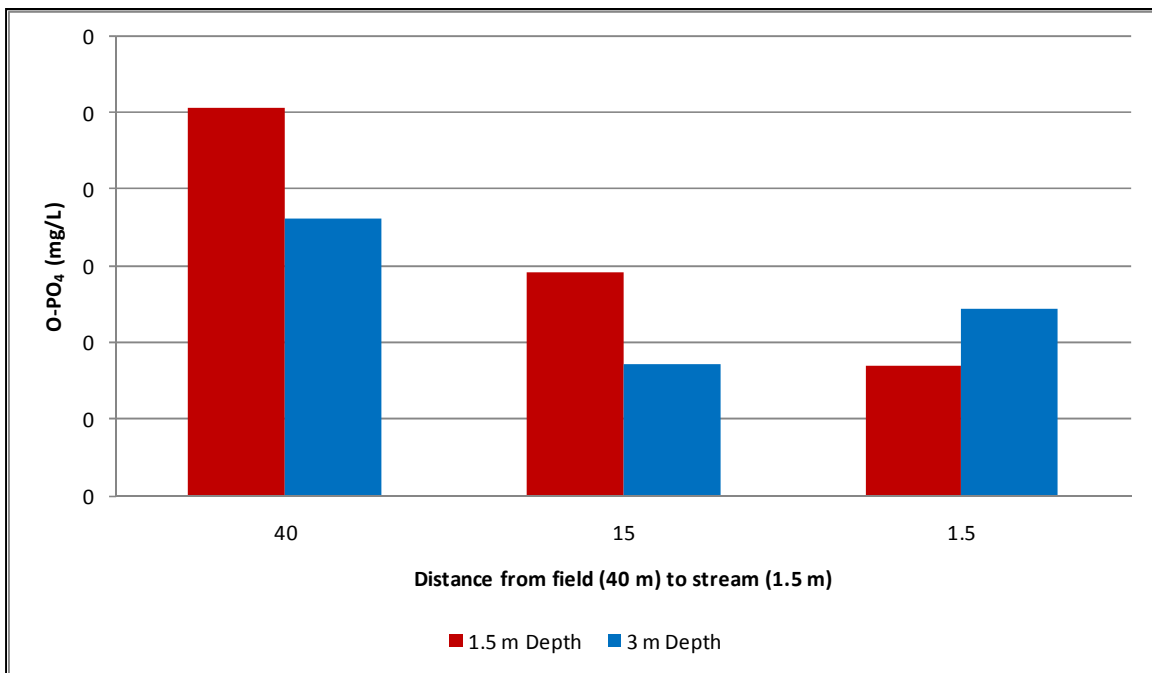


Figure G. 8: Section 2 average O-PO_4 at the 1.5 m and 3 m monitoring depths ($n_{1.5\text{ m}}=50$ and $n_{3\text{ m}}=64$)

NO₃⁻-N concentrations to DOC and DOC over Time

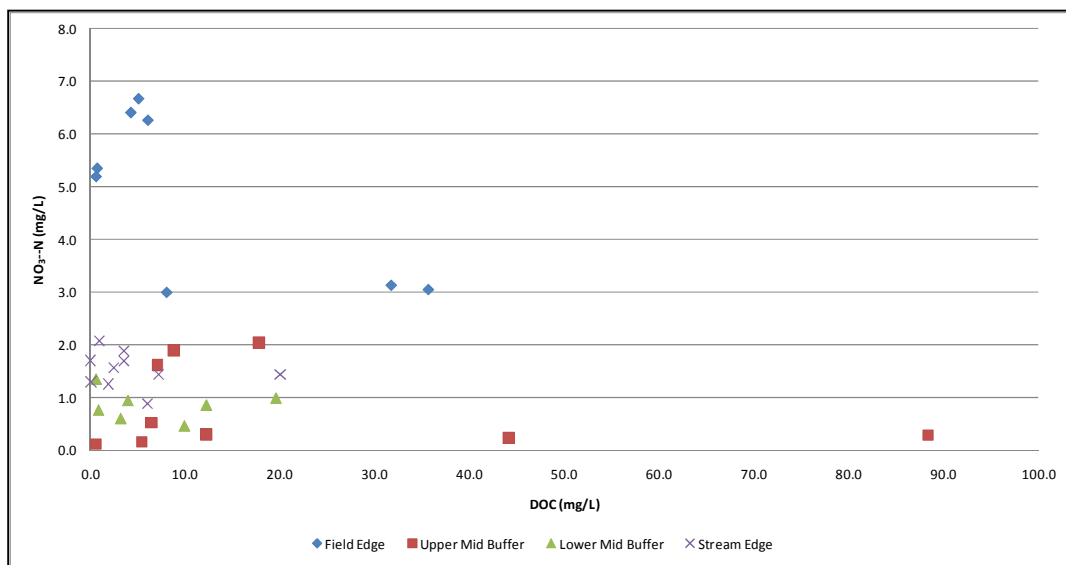


Figure G. 9: Section 1 NO₃⁻-N concentrations to DOC at 1.5 m below the soil surface.

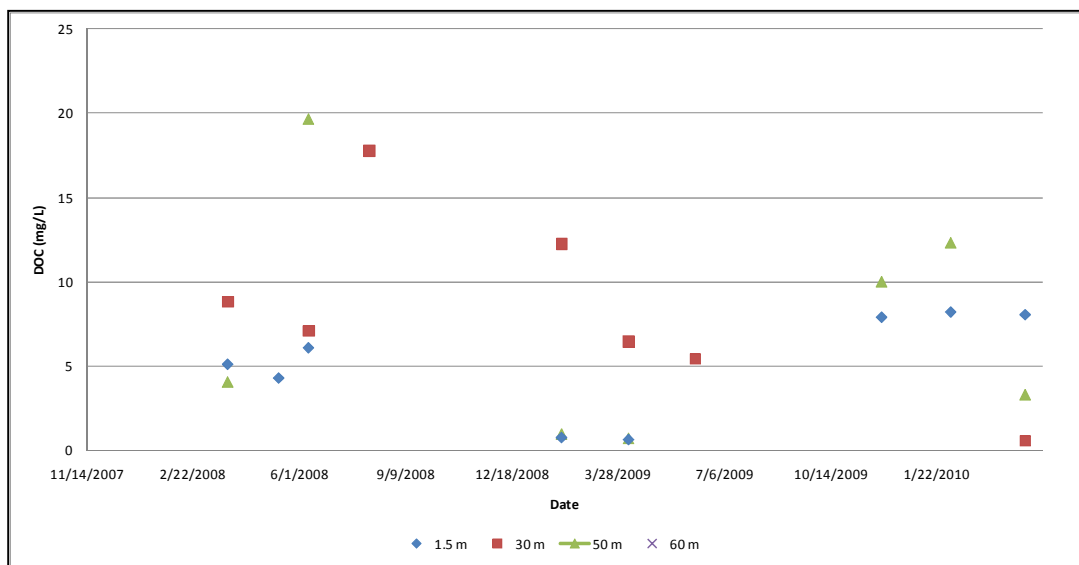


Figure G. 10: Section 1 DOC at 1.5 m below the soil surface.

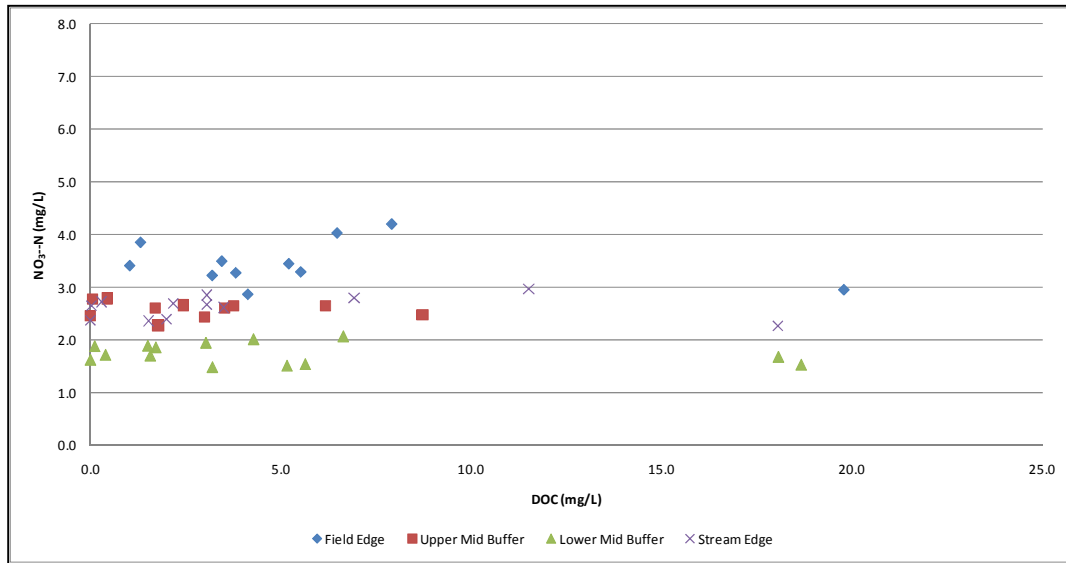
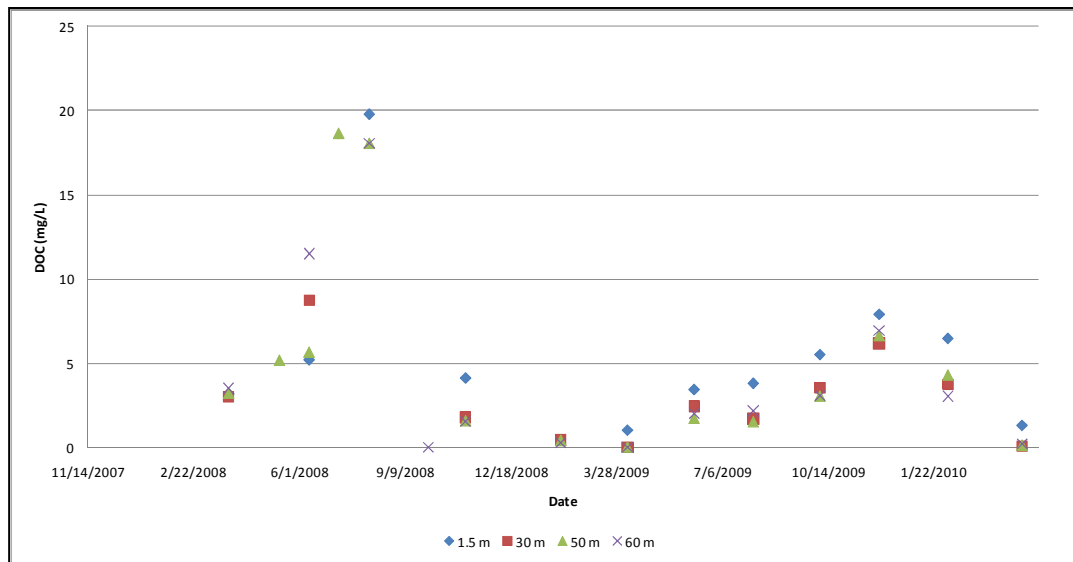


Figure G. 11: Section 1 NO₃⁻-N concentrations to DOC at 3 m below soil surface



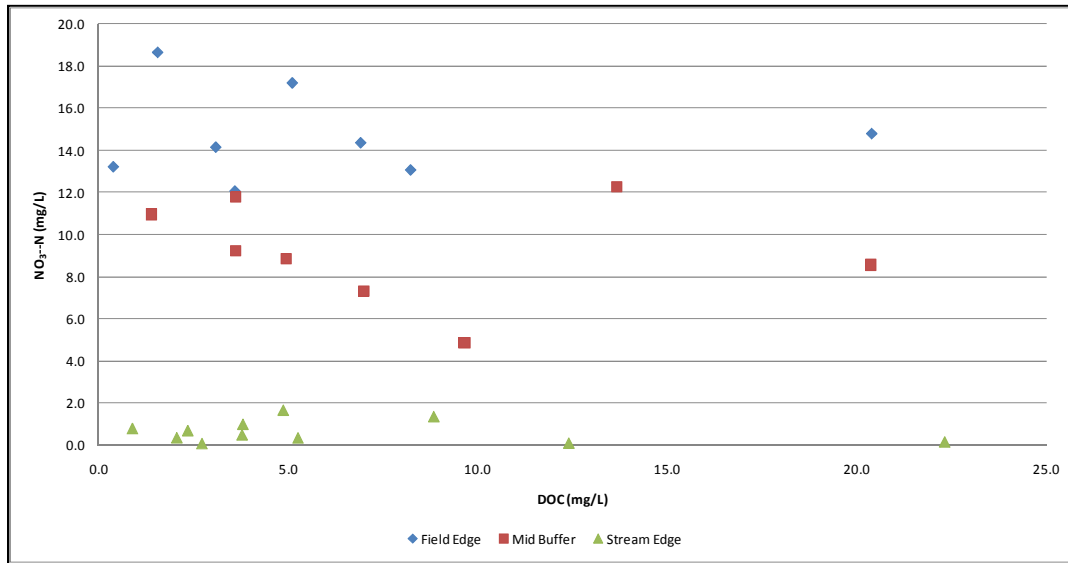


Figure G. 13: Section 2 NO_3^- -N concentrations to DOC at 1.5 m below the soil surface.

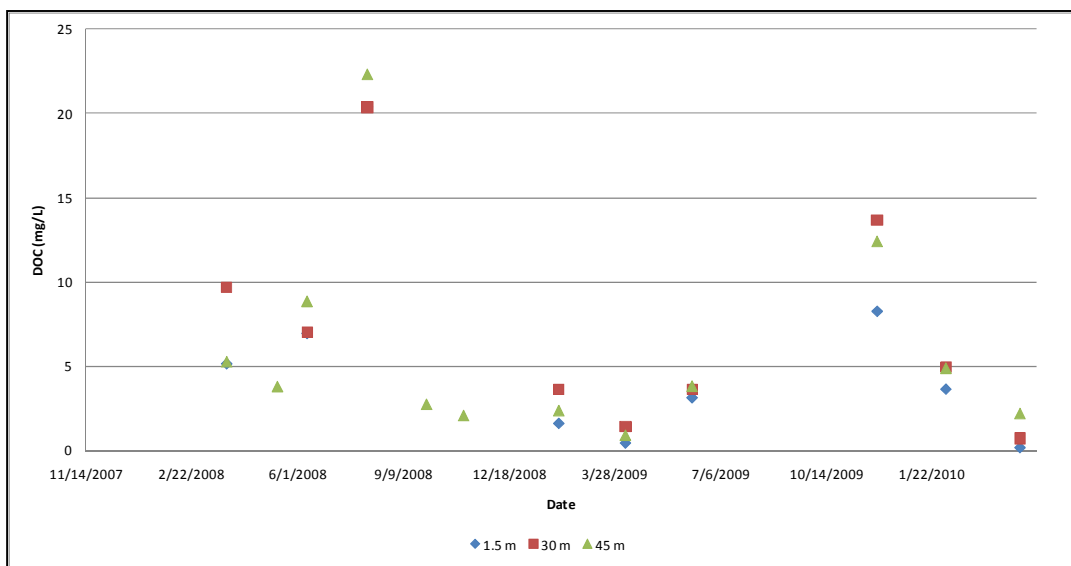


Figure G. 14: Section 2 DOC at 1.5 m below the soil surface.

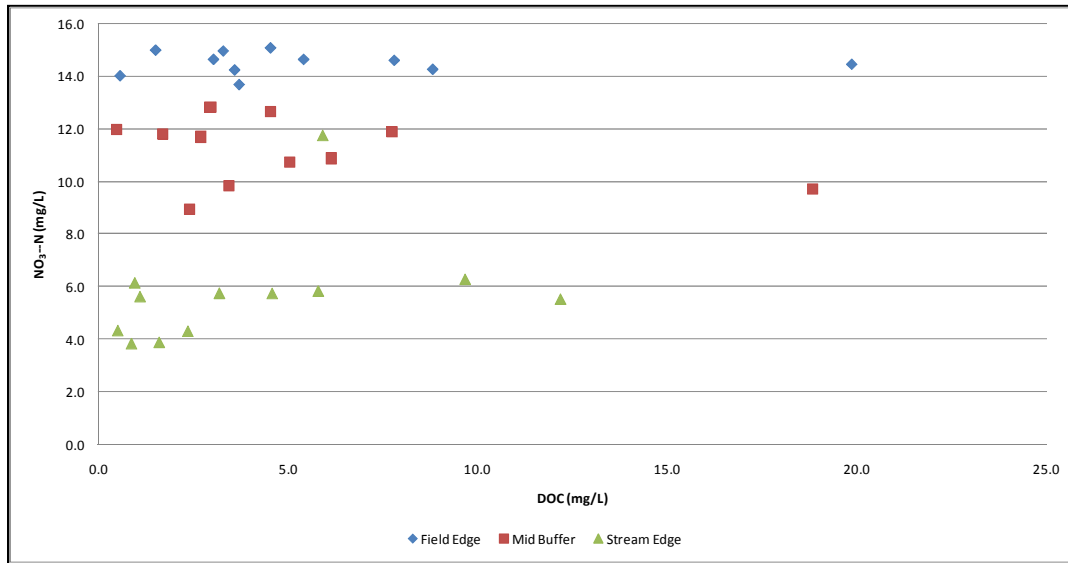


Figure G. 15: Section 2 NO₃⁻-N concentrations to DOC at 3 m below soil surface

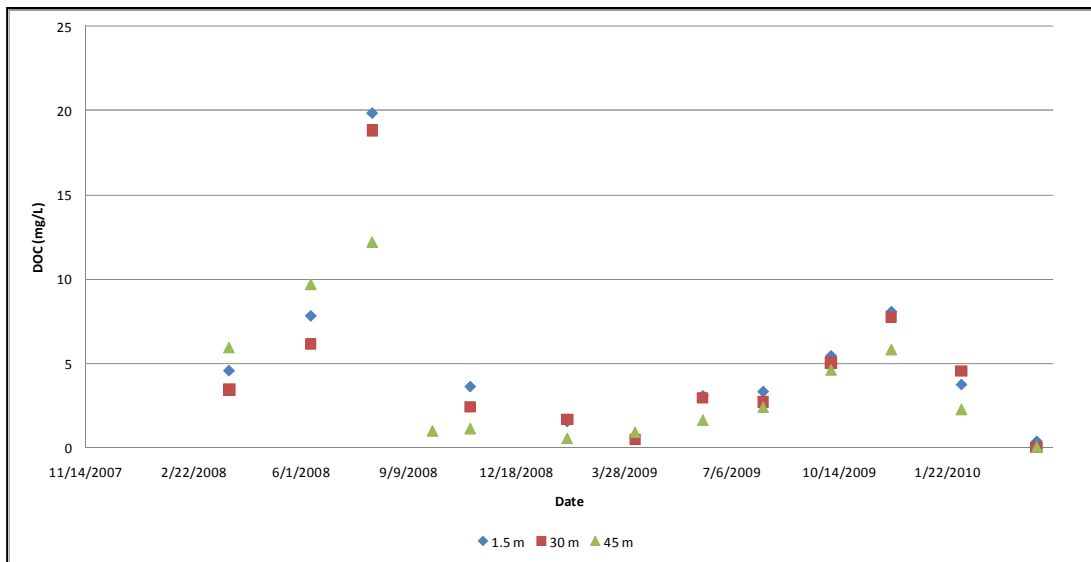


Figure G. 16: Section 2 NO₃⁻-N concentrations to DOC at 3 m depth below soil surface

APPENDIX H: Water Table Elevation and Rainfall Evaluations

Section 1 Evaluations

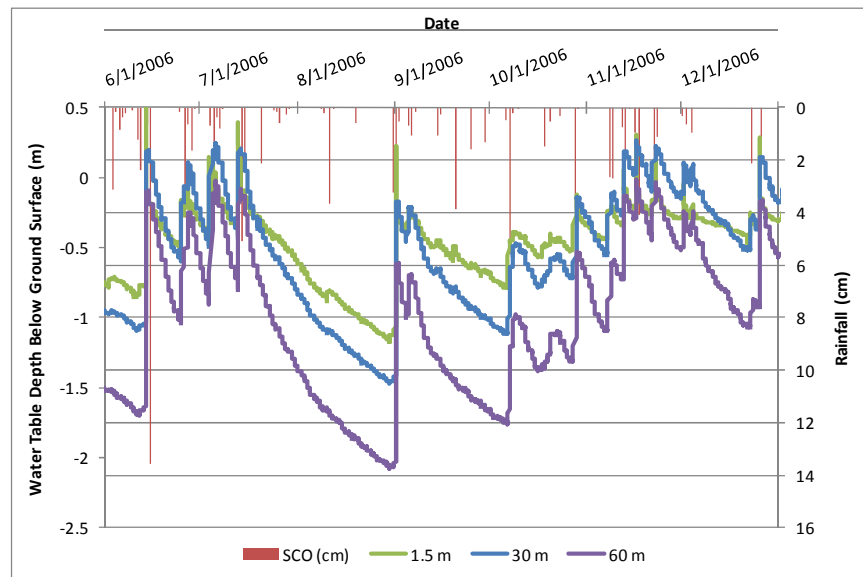


Figure H. 1: Rainfall and water table elevations during 2006

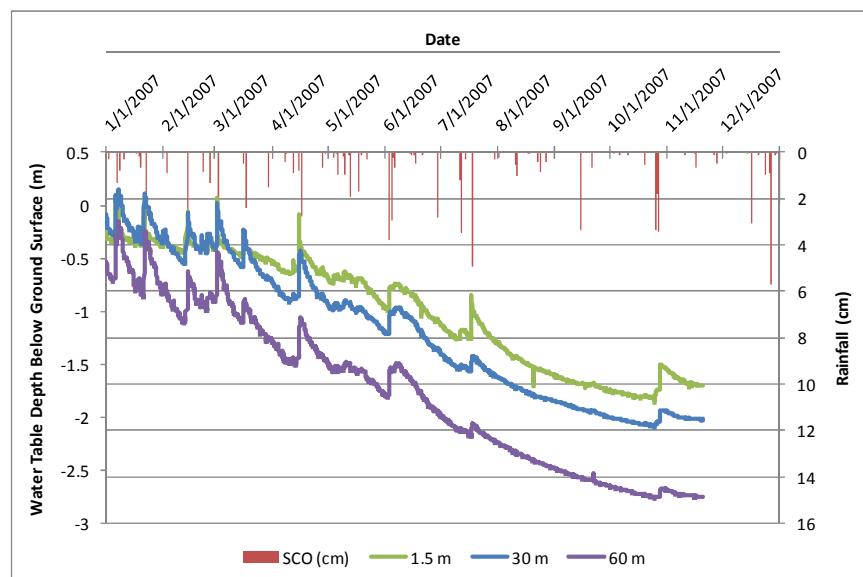


Figure H. 2: Rainfall and water table elevations during 2007

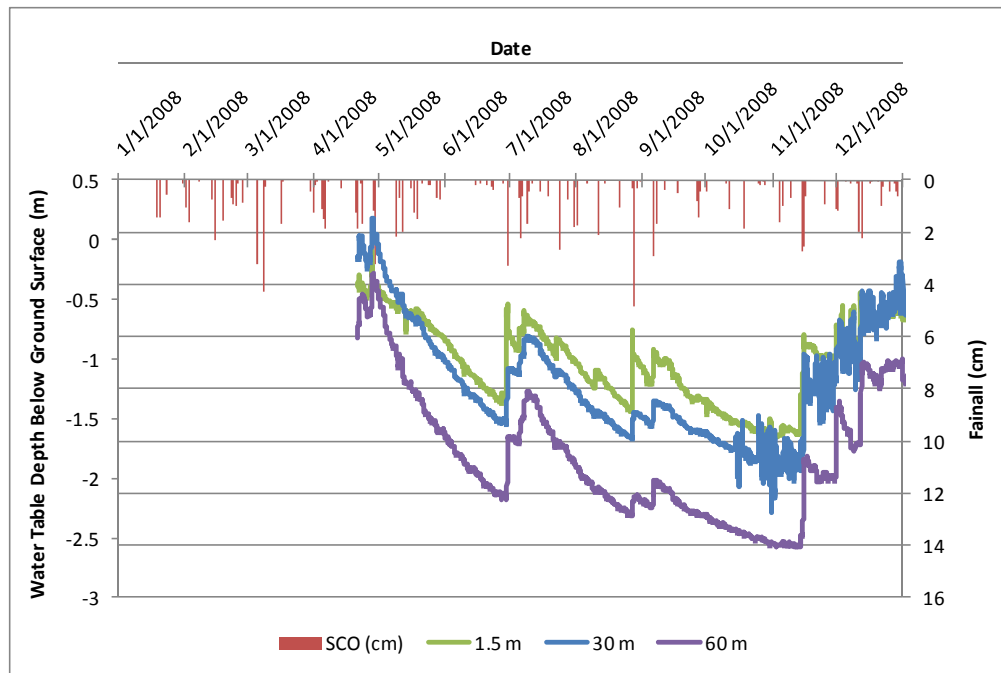


Figure H. 3: Rainfall and water table elevations during 2008

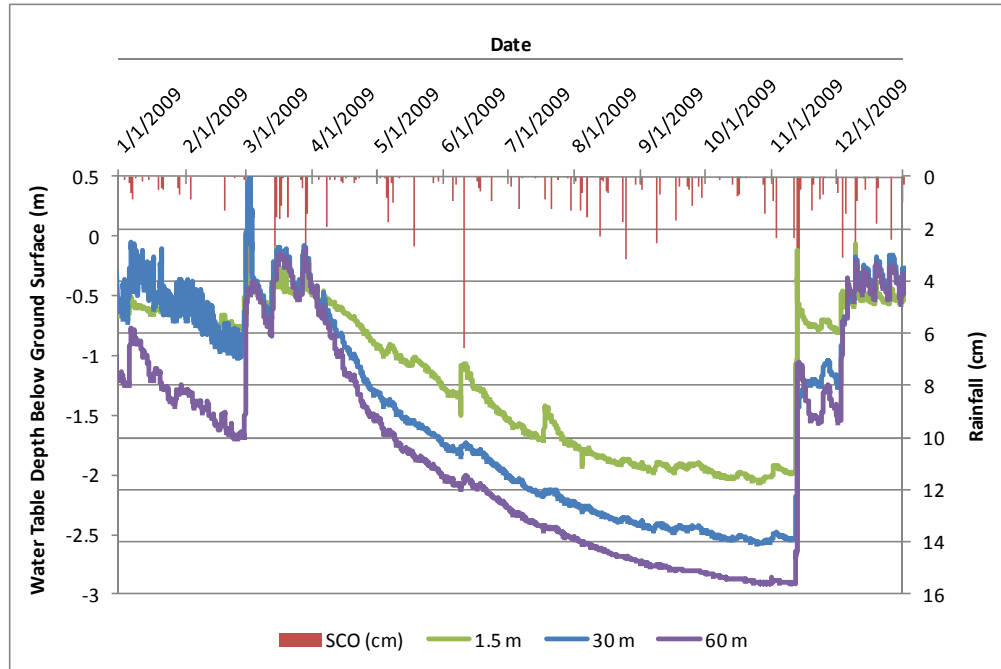


Figure H. 4: Rainfall and water table elevations during 2009

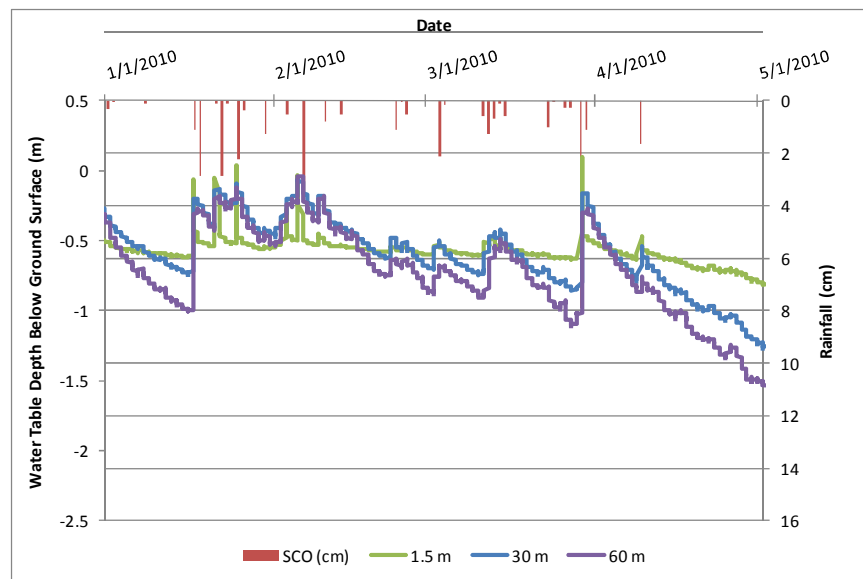


Figure H. 5: Rainfall and water table elevations during 2010

Section 2 Evaluations

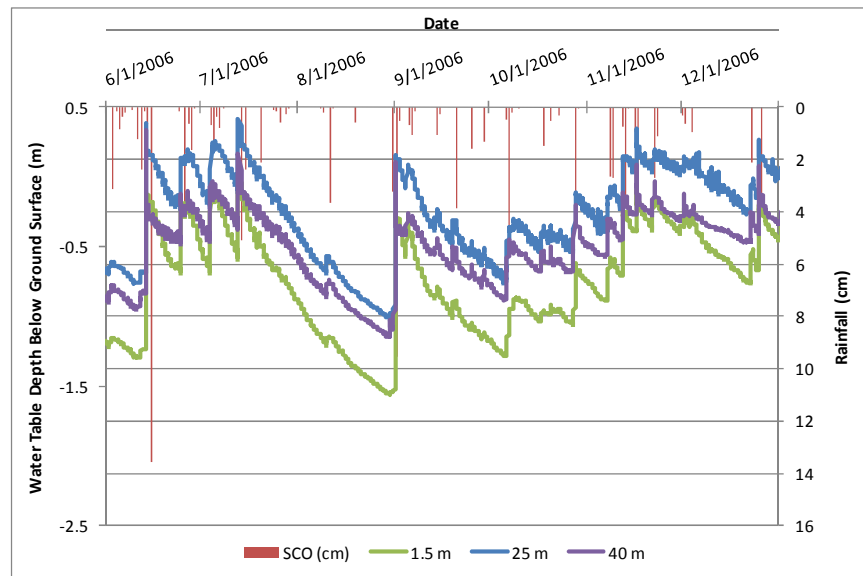


Figure H. 6: Rainfall and water table elevations during 2006

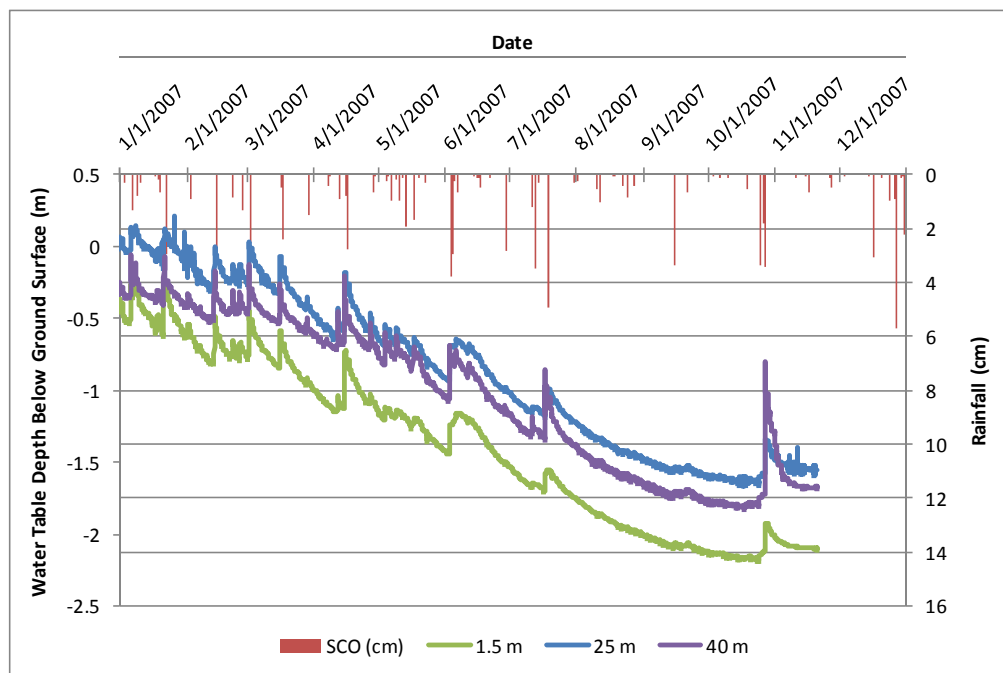


Figure H. 7: Rainfall and water table elevations during 2007

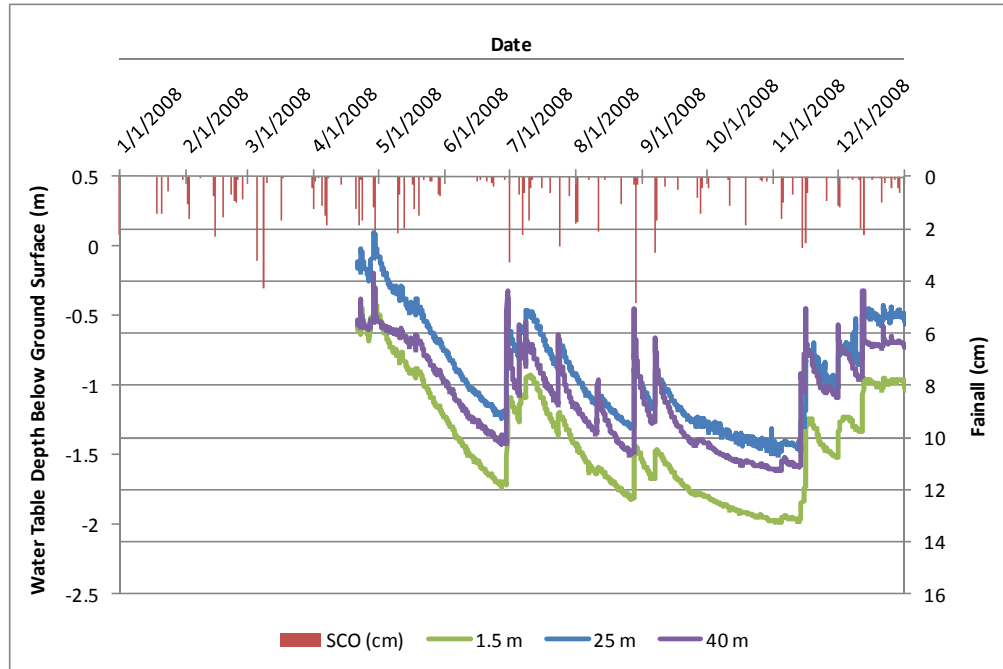


Figure H. 8: Rainfall and water table elevations during 2008

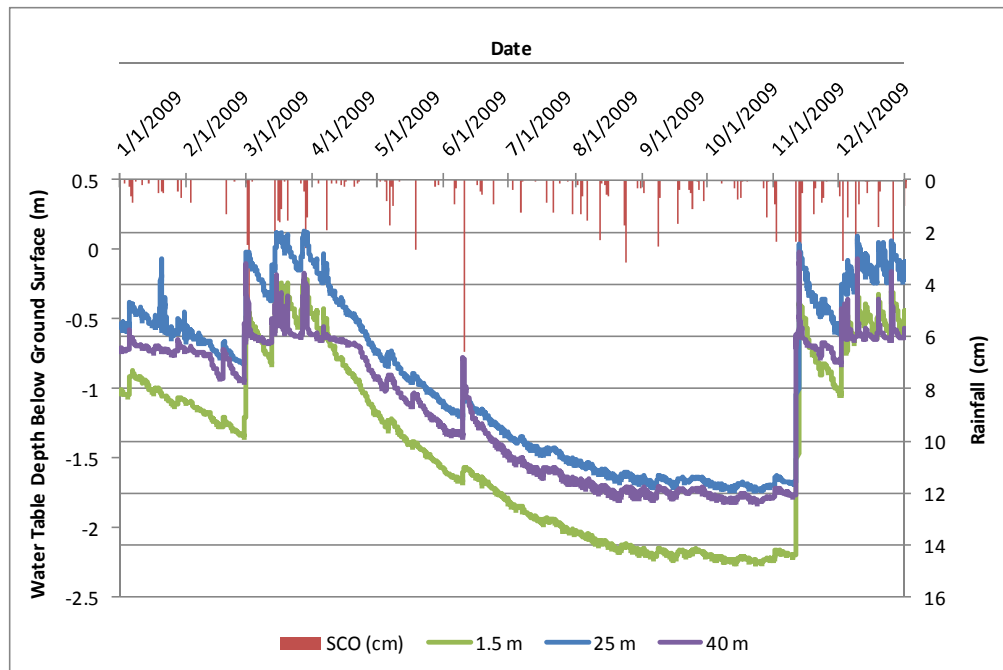


Figure H. 9: Rainfall and water table elevations during 2009

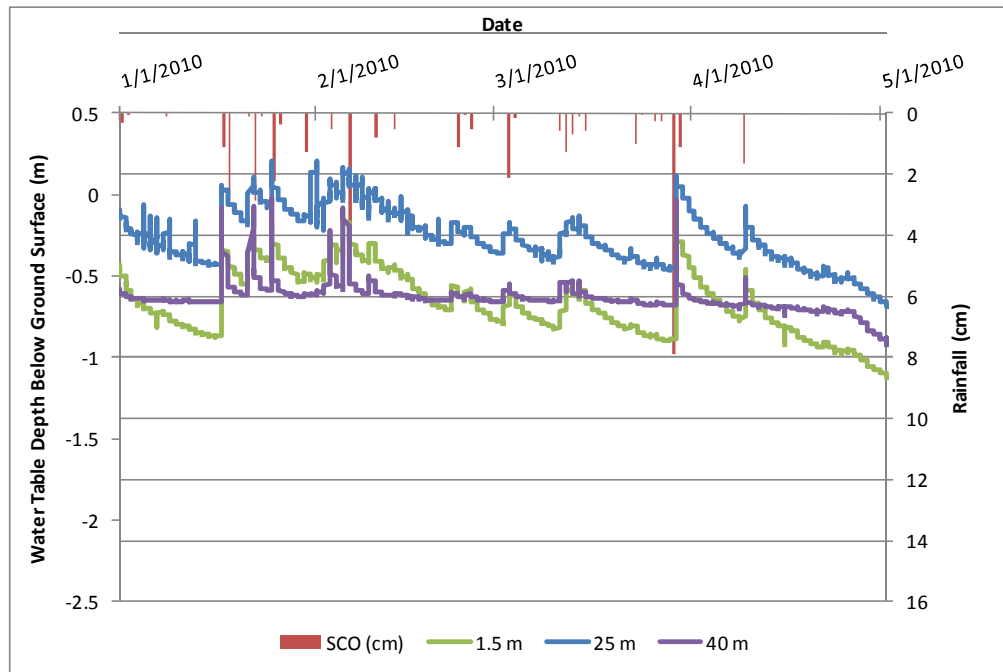


Figure H. 10: Rainfall and water table elevations during 2010

APPENDIX I: Surface Water Analysis

Surface water sampling was completed using an upstream and downstream design. The flow at the upstream station was less than the downstream station. The upstream station had a Doppler velocity meter installed in a culvert approximately 75 m (250 ft) downstream of the station, while the downstream station had a weir installed. The Doppler velocity meter was removed once the data collected was used to develop the stage-discharge curves for upstream and downstream of the buffer. Stage was then used to determine the discharge using bubblers at each surface water sampling location. 6712 Portable Teledyne ISCO automated samplers with integrated 730 Bubbler Flow Modules (Teledyne ISCO, Lincoln, NE) were installed at the upstream and downstream stations to take flow-proportional surface water samples.

NO_3^- -N, Cl^- , O-PO_4 , and FSS were investigated to determine if relationships existed between groundwater and upstream and downstream surface water. NO_3^- -N concentrations increased by 380% from the upstream to downstream monitoring locations (Figure H.1). This was most likely due to majority of the NO_3^- -N laden groundwater flowing toward the downstream discharge locations in Section 2 throughout majority of the year. NO_3^- -N concentrations tended to be higher during the drier periods of the year when groundwater was flowing parallel to the stream toward Beech Swamp and most likely came from unknown upstream pollutant sources. Furthermore, NO_3^- -N concentrations were similar to concentrations found at the stream edge (Zone 1) of Section 1 location indicating the possibility of the surface water mixing with the groundwater.

Likewise, Cl^- concentrations in the surface water at the upstream monitoring location were similar to the groundwater at the stream edge (Zone 1) in Section 1 further indicating surface water mixing with groundwater within Section 1. Cl^- concentrations did not show significant variability in the water qualities upstream and downstream and were overall similar throughout the year (Figure H.2). O-PO_4 concentrations were higher at the upstream locations compared to the downstream locations. This indicated that the buffers were intercepting surface water runoff from adjacent fields (Figure H.3). O-PO_4 pollutants enter streams through surface runoff attached to soil particles; therefore, the filter strip of the buffer was working appropriately and reducing the O-PO_4 pollutants entering the stream.

FSS did not show significant variability between the upstream and downstream locations throughout the year, except during the fall (Figure H.4). This period was the driest period of the year and often the upstream location would go dry not allowing water quality samples to be taken. These periods were during hurricane season as well. Heavy rains after long dry periods allowed large amounts of sediment to enter the stream and go quickly to the downstream location. Therefore, the increase was most likely due to heavy rains after long dry periods causing significant volumes of runoff to flow quickly into the stream.

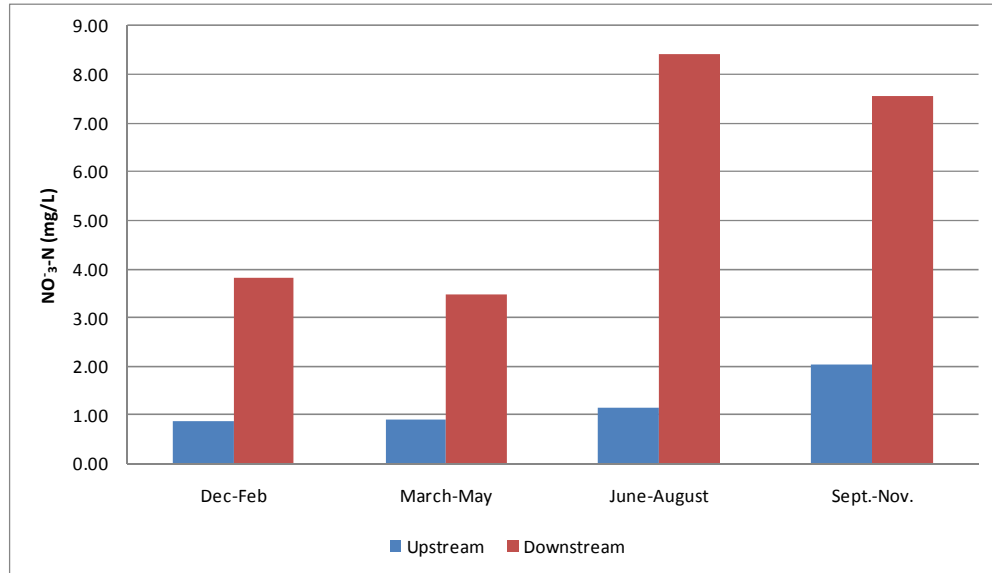


Figure I. 1: NO_3^- -N seasonality in upstream to downstream surface water evaluation

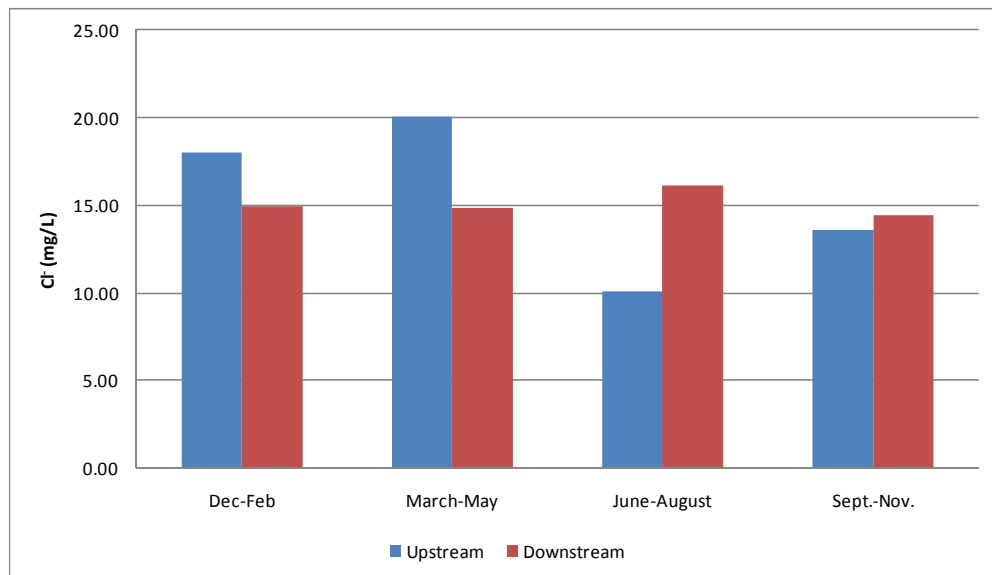


Figure I. 2: Cl^- seasonality in upstream to downstream surface water evaluation

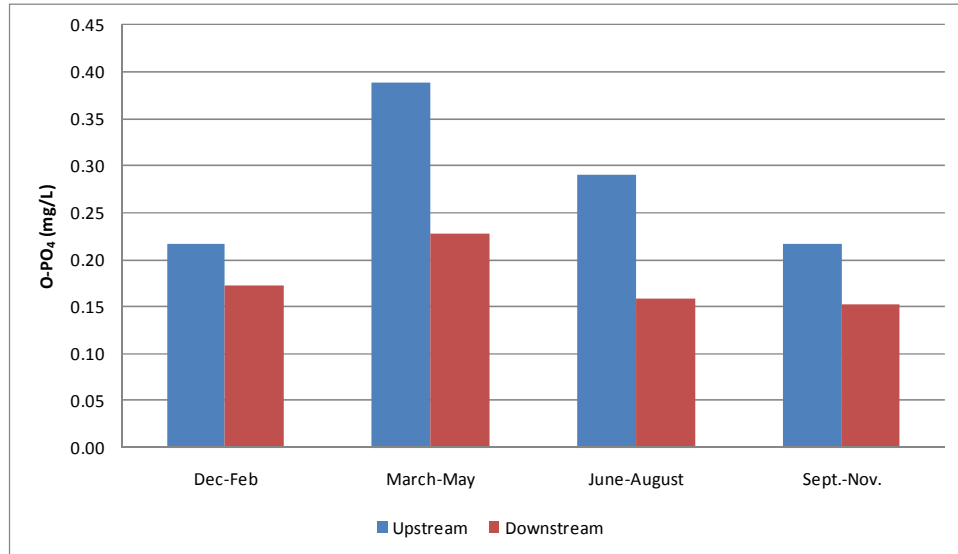


Figure I. 3: O-PO₄ seasonality in upstream to downstream surface water evaluation

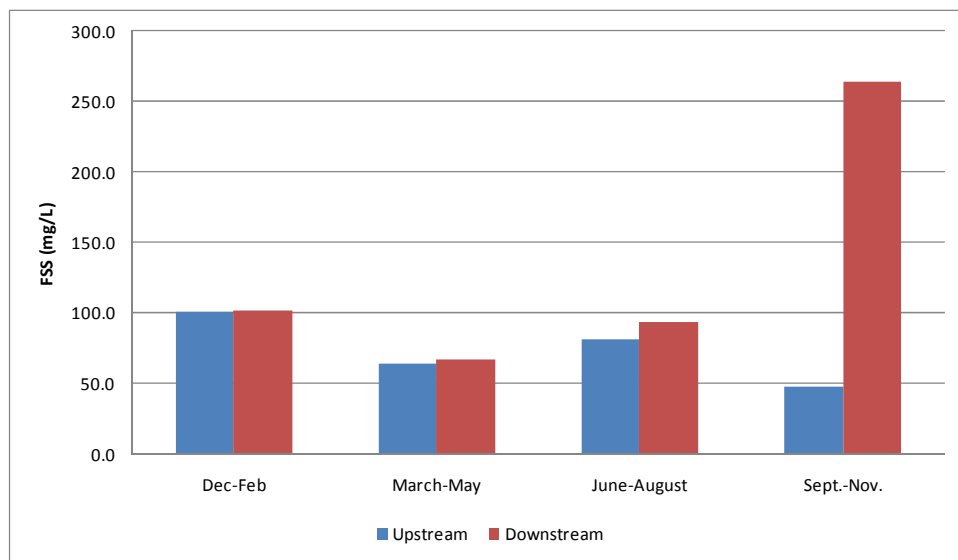


Figure I. 4: FSS seasonality in upstream to downstream surface water evaluation

A visual evaluation indicated a possible correlation between groundwater NO₃⁻-N concentrations and redox potential readings in Zone 3 at both the 1.5 and 3 m depth. Zones 1 and 2 did not appear to have correlations to (Figure H.5 and Figure H.6). These correlations

were observed most likely due to the deeper water table depths in Zone 3 allowing aerobic conditions to be present more often than found in other zones where the water tables were closer to the soil surface throughout the year.

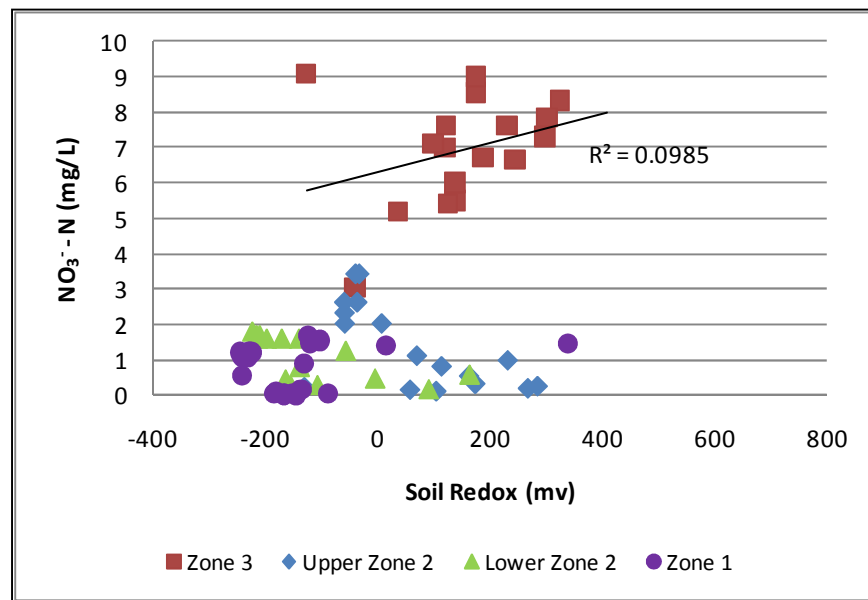


Figure I. 5: Soil redox compared to groundwater NO_3^- -N in center transect at the 1.5 m depth wells (June 2005 to April 2010).

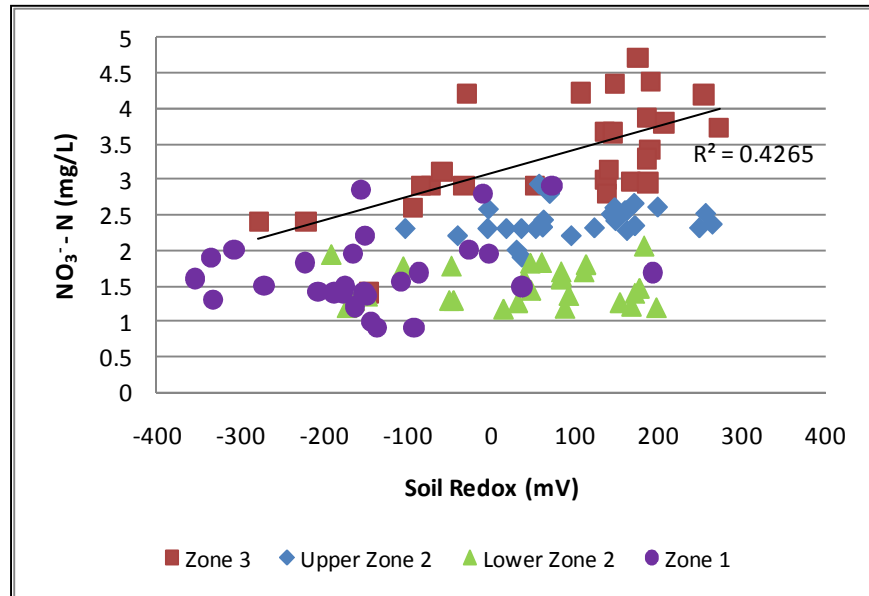


Figure I. 6: Soil redox compared to groundwater NO₃⁻-N in center transect at the 3 m depth well (June 2005 to April 2010).