

## **Abstract**

Ricks, Staci Nichole Effect of Riparian Buffers on Soil Redox Potential. (Under the direction of Dr. Robert O. Evans)

Excess pollution in Eastern North Carolina has led to unprecedented regulations to reduce the nitrogen loading to the Neuse River by thirty-percent by the year 2003. The primary culprit of excess nutrients is nonpoint sources. Agricultural processes have been identified as the prime perpetrator for the nonpoint source pollution. Interception of this pollution must be accomplished before it reaches groundwater and eventually surface water supplies. Denitrification reduces the nitrate into nitrogen gas, thus atmospheric nitrogen. One indicator of denitrifying conditions is soil redox potential.

This study evaluates the soil redox potentials at depths greater than 1.5m. The effect and interaction of buffer width and vegetation type on groundwater nitrate concentration was evaluated. Lower concentrations of nitrate-nitrogen were correlated to soil redox potentials at depths greater than 1.5m.

The Center for Environmental Farming Systems in Goldsboro, North Carolina had an ongoing riparian buffers study implemented five channelized streams. Three of these riparian buffers were instrumented with soil redox electrodes. Each replicate had two widths of buffers, 8m and 15m. There were five different vegetations: fescue (cool season grass), switch grass (deep rooted grass), forest (pine and mixed hardwoods), native vegetation, and no buffer (i.e., row crop or pasture). Redox electrodes were constructed and installed along the stream and buffer/field edge at depths of 1.5m and 3.0m. These depths corresponded to the depths of the existing ground water quality monitoring wells on each buffer. These wells and redox electrodes were monitored for a period sixteen months.

Redox values were usually lower at the deeper depth, and lower near the ditch than at the field/buffer edge. The deep electrodes along the ditch exhibited reducing conditions in every replicate. Buffer width affected redox readings in one replicate, buffer width affected nitrate-nitrogen concentrations in all replicates. Vegetation affected the redox readings with switchgrass generally exhibiting the lowest redox values of all vegetation types. Vegetation had little effect on the nitrate-nitrogen concentrations.

Low nitrate-nitrogen concentrations were related to low soil redox potentials in specific area of a given well. Where soil redox was low, there was a presence of organic carbon and the soil was saturated it was concluded that denitrification was occurring. Buffer width, location relative to the stream, and soil redox potential had an affect on the concentrations of nitrate-nitrogen. After three years of evaluation vegetation type has not shown an impact on nitrate-nitrogen concentrations.

**Effect of Riparian Buffers on Soil Redox Potential**

By

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A thesis submitted to the Graduate Faculty of  
North Carolina State University  
in partial fulfillment of the requirements for the Degree of  
Master of Science

**Biological and Agricultural Engineering**

Raleigh, North Carolina

2002

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## **Biography**

Staci Nichole Ricks was born on June 13, 1978 in Smithfield, North Carolina. She moved to Wilmington, North Carolina when she was twelve years old. After graduating from John T. Hoggard High School in 1996, she attended North Carolina State University. There she pursued a Bachelor of Science degree in Textile Chemistry. Upon graduating in the spring of 1999, she decided to change her direction of study to engineering. She enrolled in the graduate program in the Department of Biological and Agricultural Engineering under the direction of Dr. Robert Evans. Her research focused on the effects of riparian buffers on soil redox and water quality. She accepted a position with Stantec Consulting in Raleigh, NC.

## Acknowledgments

First and foremost, I would like to thank God, for without His strength and encouragement this degree would have never materialized. I have learned throughout this process that a masters degree is a solitary arduous task that tests your independence as well as determination. Along the way I received enormous help from friends, family, and coworkers.

I would like to thank to Dr. Robert Evans for providing the opportunity for me to pursue and obtain a masters degree in engineering and assisting my research. Also for always challenging me academically so that I would never settle, and in turn I learned more about myself as an individual than I thought possible.

Special thanks to L.T. Woodlief, Michael Adcock, and Jonathan Smith for assisting me with the field installation of the redox electrodes and equipment, I would have never been able to do all of it without you guys. The statistical analysis would not have been completed if it were not for the patience and knowledge of Andy Hale. I would also like to thank Melanie Carter who diligently helped with the construction of the redox electrodes and salt bridges.

And lastly, my parents and sister for always being just a phone call away and having an ear to listen. Thanks for always being my source of encouragement and motivation.

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# Chapter 1 – Background Information

## Introduction

North Carolina's water quality in streams and estuaries has slowly declined. Increased nutrient levels in surface streams and eutrophication of some Coastal Plain waters has led to studies about nitrate losses from agricultural fields (Jacobs and Gilliam 1985). High contaminant levels of nitrogen degrade drinking water quality. Nitrate can be toxic to humans and aquatic organisms; fecal bacteria and other microbes in animal wastes can cause disease. Excess nitrogen as well as phosphorus can degrade surface and groundwater by promoting algae blooms, which may suffocate fish and other aquatic organisms. Groundwater quality is important in North Carolina because many of the state's rural residents rely on groundwater for their primary source of drinking water.

There are numerous culprits in the degradation of water quality. The primary source of nitrogen and phosphorus is reported to be agricultural nonpoint sources. A nonpoint source is an activity that takes place over a broad area and results in the diffuse release of pollutants from numerous locations (Gale et al., 1995). The North Carolina Division of Water Quality estimates nonpoint sources account for approximately three-quarters of nitrogen loading to the Neuse River (NCDWQ, 1996a). Agricultural nonpoint sources have been identified as being one of the largest contributors of excess nutrients.

Excess nutrients, particularly nitrogen and phosphorus, in surface water result in nuisance algae blooms that are unsightly, disrupt the food chain and can lead to fish kills. Fish kills are a recurring problem in the Neuse and Tar-Pamlico Rivers and estuaries. These fish kills and the presence of algae blooms have led to the Neuse River being classified as nutrient sensitive by the North Carolina Division of Water Quality (NCDWQ, 1996a).

Elevated levels of nitrogen in the water aggravate these problems. The Environmental Management Commission of North Carolina adopted rules to reduce inputs of nitrogen and phosphorus to the Neuse and Tar-Pamlico River basins. The Neuse River Rules target a thirty percent reduction in nitrogen loading to the Neuse River basin by 2003.

To achieve the thirty percent nitrogen reduction, the agricultural community must utilize one or more best management practices, (BMPs). One BMP that is being highly encouraged is establishment of permanent vegetative cover along side streams, known as riparian buffers. Riparian or vegetative buffers are one BMP that can be implemented to control the nitrogen loading to streams.

### **Vegetated Buffers**

Vegetated or riparian buffers are areas next to water bodies such as streams, lakes, or rivers that can be used to intercept and reduce sediment, nitrogen and other contaminants to streams from nonpoint source pollution. Vegetated buffers can also provide bank stabilization and aquatic and wildlife habitat (Gilliam et. al., 1994). Figure 1.1 illustrates a natural riparian buffer area along a stream in an agricultural field. Natural vegetative buffers have been reported to remove eighty to ninety percent of shallow groundwater nitrate (Gilliam et al., 1979; Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Pinay and Decamps, 1988; Lowrance, 1992; Haycock and Pinay 1993; Jordan et al., 1993).

Nitrate is an element commonly required for crop production. Crops are not one-hundred percent efficient at using this element and nitrate that is not used by the crop or soil organisms continues to move through the soil profile into the shallow groundwater and

eventually feeds surface water (Osmond and Gilliam, 1999). Since nitrate is very mobile in the soil, it needs to be intercepted before it reaches the shallow groundwater or surface water.

The nitrogen cycle is illustrated in Figure 1.2, which shows the four biological processes that remove nitrogen from groundwater: vegetative uptake (vegetative immobilization), microbial immobilization, storage in soil as organic nitrogen, and denitrification. Denitrification is the permanent microbial conversion of nitrate nitrogen to a gaseous form of nitrogen that is lost to the atmosphere (Weller et al., 1994). The major removal mechanism of nitrate in groundwater in riparian buffers is hypothesized to be denitrification (Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985 and Weller et al., 1994). To remove the nitrate before it reaches surface water, the groundwater must pass through a carbon rich, anaerobic zone. Decaying plant roots or other organic material provide a source of carbon needed to provide the energy source for bacteria that convert nitrate-nitrogen to harmless nitrogen gas (Osmond and Gilliam, 1994).

### **Functionality of Riparian Buffers**

Hydrology (how water moves) is an important factor influencing the effectiveness of a riparian buffer (Gilliam et al., 1997; Correll, 1997). The hydrologic cycle is illustrated in Figure 1.3. Water falls on agricultural cropland via rainfall and either infiltrates the soil or runs off the land in overland flow. The surface runoff carries sediment and sediment-associated pollutants, such as phosphorous (Osmond and Gilliam 1999). Vegetative buffers can retain about fifty percent of surface water phosphorus (Gilliam 1994). It does this by intercepting the surface runoff and decreasing its velocity. This allows the sediment and the sediment born nutrients to settle in the buffer and not pollute the water body.

The water that infiltrates the soil feeds the groundwater. This water carries nitrate-nitrogen from the root zone into the soil. This nitrate-nitrogen must be treated before it discharges into surface waters, such as rivers or lakes. For treatment of shallow groundwater, buffers are reported to be more effective where a shallow aquitard or impermeable layer exists, (Figure 1.3). The restrictive layer forces flow to become lateral rather than continue vertically to deep groundwater. This layer drives the flow of water through the root zone and causes the upper soil horizons to become saturated. This creates an anaerobic zone. The absence of oxygen allows for the electrons produced by the decomposition of organic matter to start the process of denitrification (Gilliam 2000).

### **Denitrification**

Denitrification involves biological and chemical processes that convert nitrate-nitrogen to nitrous oxide and then to di-nitrogen gas ( $N_2$ ). The reaction is controlled by the amount of organic material (carbon, energy source) available to the microbes, the supply of nitrate, and the lack of oxygen (Vepraskas 2000). All three things must be present in order for the reaction to be carried out (Peterjohn and Correll 1984; Correll and Weller 1989; Lowrance and Pionke, 1989; Weller, 1994). It is also dependent on the pH and electrical potential in the soil system (Bailey and Beauchamp 1971).

Figure 1.4 illustrates the chemistry of denitrification. The bacteria in the soil produce electrons and protons from the carbon source. The electrons and protons are needed in the reaction to convert the nitrate to di-nitrogen gas (Bohn 1971).

## **Reduction- Oxidation**

The effect of riparian buffers on soil redox has been assessed by measuring redox potential of the soil (Quispel 1947; Gambrell et al., 1975). Redox potential occurs in soils as a result of the presence of oxidized and reduced forms of organic and inorganic material (Bailey and Beauchamp 1971). Redox potential measurements have been associated with losses of nitrogen from soils due to denitrification (Meek et al., 1969; Patrick 1960; Bell 1969).

Soil redox is a measurement of electrical potential, or a systems capacity to oxidize a material. Redox is an abbreviation for reduction-oxidation. Redox potential (Eh) is the value defining a system's capacity for gaining or losing electrons. Redox potential is the voltage measured between a platinum wire and reference electrode that is in contact with the soil solution. Voltage is an expression for electric potential or potential difference and is measured with a voltmeter. The voltmeter measures potential rather than current so that a constant current flow between the electrodes is not established. A constant current would cause chemical changes to occur in the soil that would affect the voltage reading.

The Nernst equation is used to calculate oxidation-reduction potentials (ORP). ORPs vary as a function of: standard reduction potential,  $E^0$  (electrical potential of each half reaction), the relative ion activity, temperature, and number of electrons transferred in the half reactions (Sparks, 1995).

$$E = E^0 - (0.0257/n) * \ln(Q)$$

Oxidation is the acceptance of electrons and reduction is the loss of electrons. These two reactions are coupled. The reactions influence: soil colors, organic matter contents, and the amounts of O<sub>2</sub>, NO<sub>3</sub>, and SO<sub>4</sub><sup>4-</sup> in the soil water.

When an element accepts an electron its valence state is reduced. The most common reduction reaction in soils is the reduction of molecular oxygen to water (Vepraskas 2000). In well-aerated soils, electrons produced by organic matter decomposition are removed by O<sub>2</sub> to make water. In waterlogged soils, O<sub>2</sub> (air) enters soil very slowly because soil pores are filled with water. As organic matter decomposes in waterlogged soils, electrons are consumed in order by: O<sub>2</sub>, NO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>3</sub>, SO<sub>4</sub><sup>4-</sup>, or CO<sub>2</sub><sup>-</sup>.

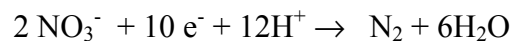
Oxidation-reduction reactions occur in a sequence based on the tendency of the oxidized species to be reduced. The electrons follow an outlined path for the reduction of elements in the soil. This path is listed below and is characterized by the chemical properties of the elements listed below. (Ponnamperuma, F.N., 1972; Mitsch et al., 1993).

- Aerobic oxidation with oxygen as the terminal electron acceptor

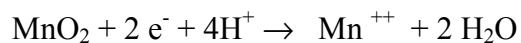


- The reduction of nitrate (NO<sub>3</sub><sup>-</sup>) to nitrous oxide (N<sub>2</sub>O) or di-nitrogen (N<sub>2</sub>)

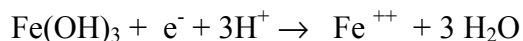
(This is referred to as denitrification)



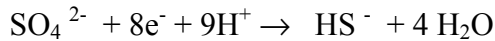
- The transformation of manganic to manganous compounds



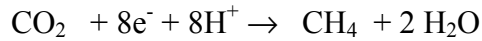
- The reduction of ferric iron to ferrous iron



- The reduction of sulfates to sulfides



- Organic matter becomes an electron acceptor for the production of methane gas



It is commonly accepted that a redox potential value of 350 mV is the critical level for denitrification for pH's under 10 (McBride, 1994), however the Eh values at which nitrate is reduced has been debated throughout the literature (Kunickis, 2000). Nitrate was reported to be stable at 200 mV at pH 7 from Ponamperuma's study (1972). Fluhler reported a range from 270 mV to 350 mV for biological reduction of nitrate and nitrite (Fluhler et al. 1976).

Recent research conducted with redox electrodes has assessed denitrification at relatively shallow depths. These depths are predominantly concentrated in the upper thirty centimeters of the soil, where the most biological activity is likely to occur.

The chemical and biological processes at depths approaching three meters have not been well documented. Organic carbon generally decreases with depth, which causes a lack of energy sources for microorganisms to feed upon to produce the essential electrons and protons, needed for denitrification. As a result, it is generally believed that most denitrification occurs at shallow depths defined by the root zone of locally growing plants.

## **Objectives**

The overall objective of this study was to evaluate the potential for denitrification below the root zone in riparian buffers. Specific objectives were to:

- Determine the effect riparian buffers have on soil redox potential at depths greater than 1.5m to decide if conditions are favorable for denitrification.

- Correlate redox values at the deeper depth with water quality samples to determine if the nitrate-nitrogen concentrations were lower where the redox value was indicative of reducing conditions.

- Determine if there was a relationship between vegetation type or buffer width and nitrate-nitrogen concentrations.

## Chapter 1 Figures



Figure 1.1 Natural riparian buffers along agricultural ditches

# Process of Denitrification

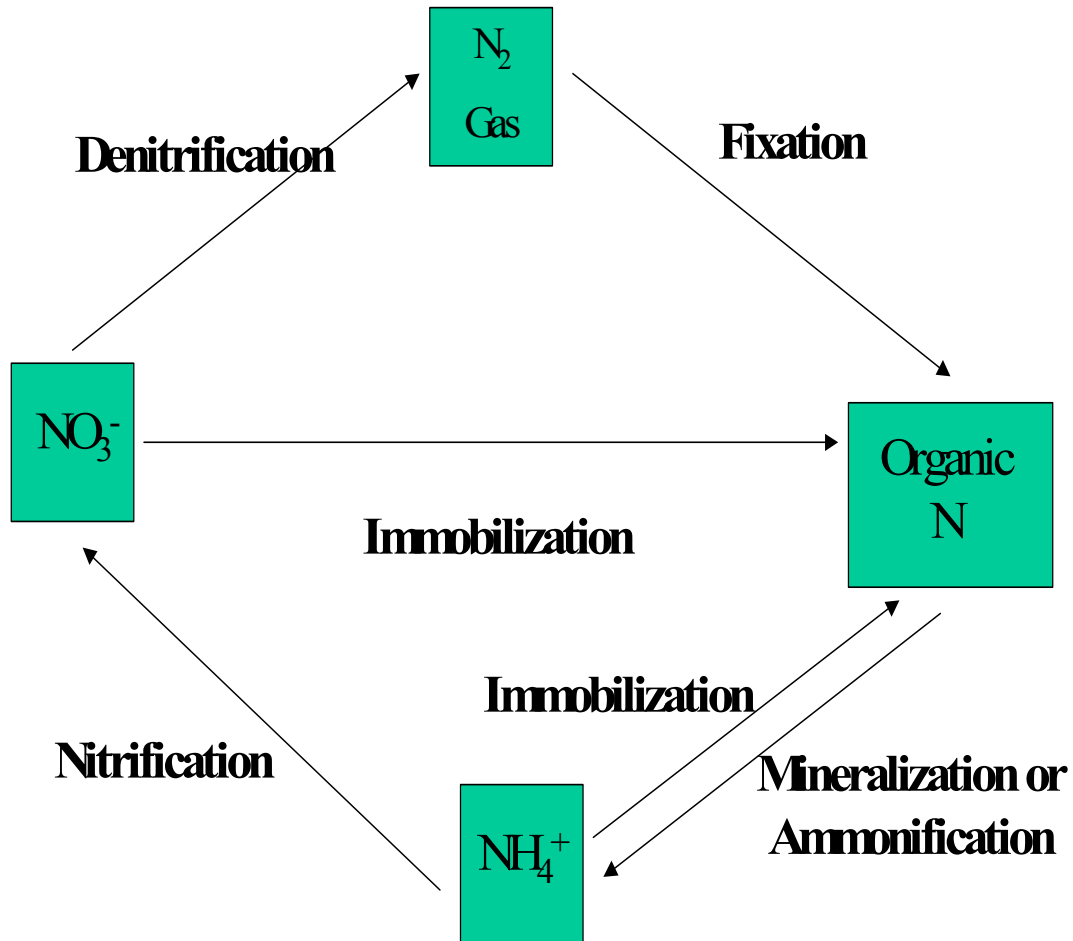


Figure 1.2 Nitrogen Cycle

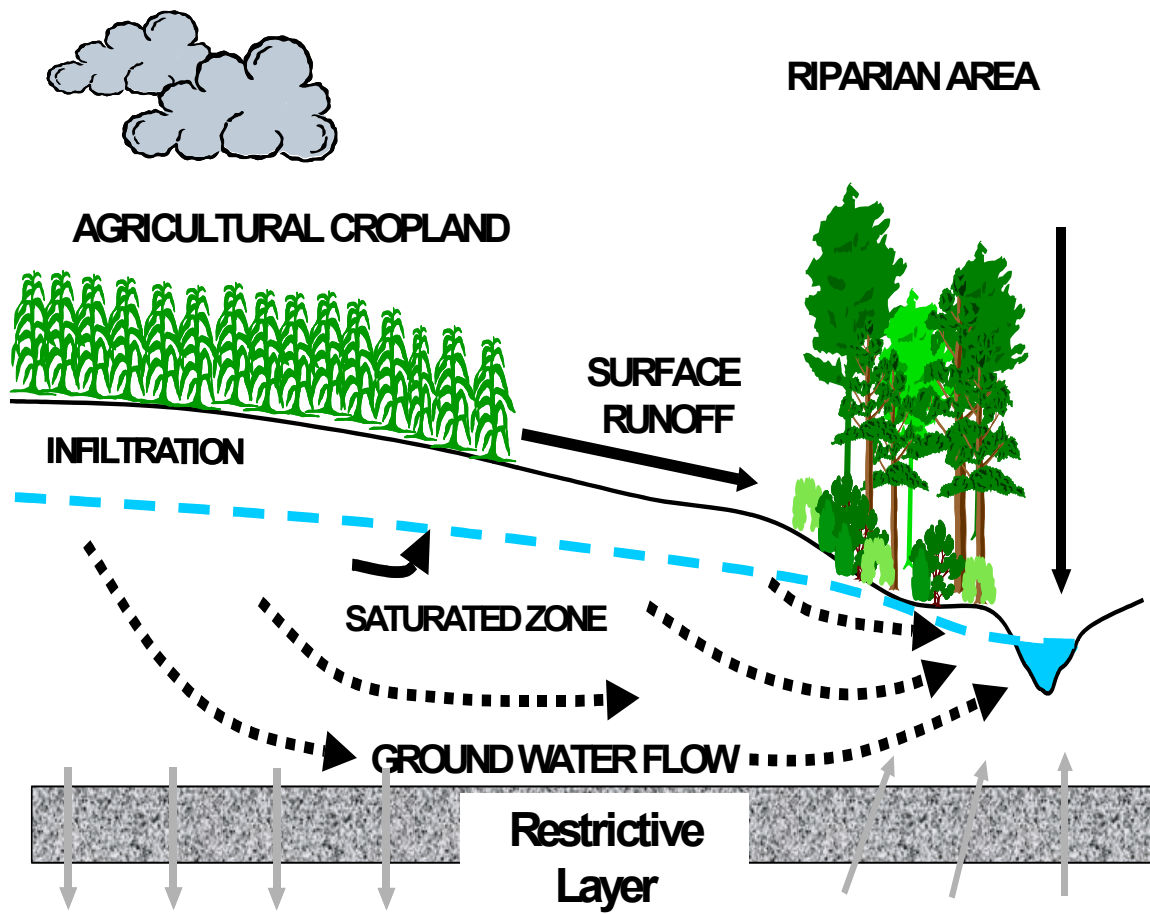


Figure 1.3 Schematic of Riparian Buffer

# Chemistry

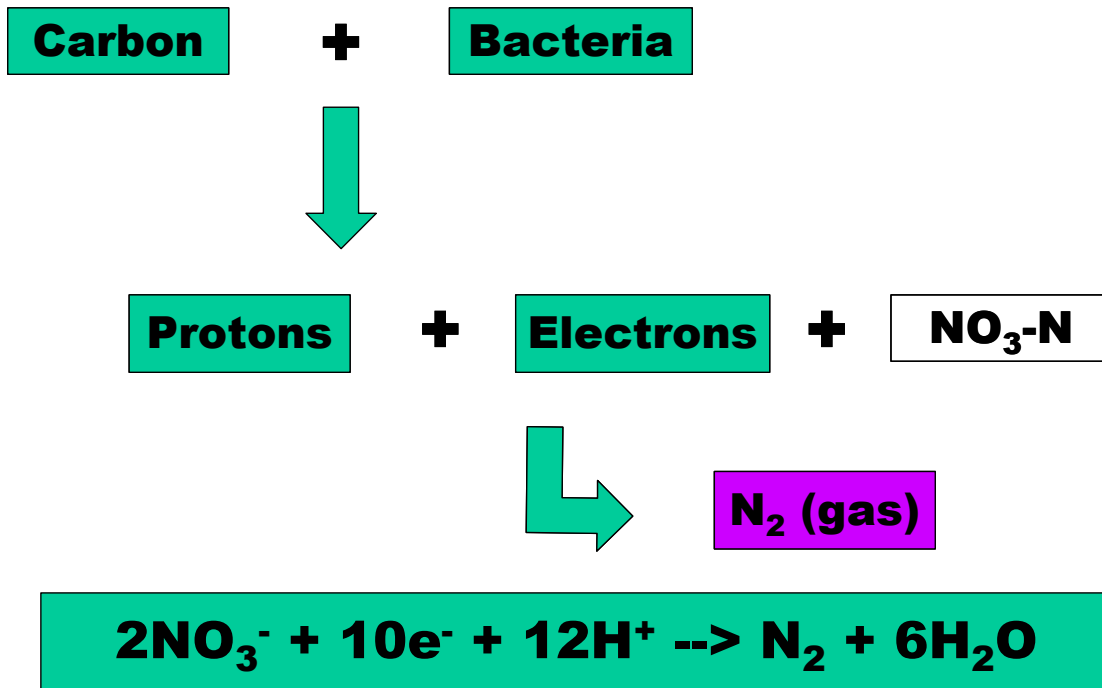


Figure 1.4 Process of Denitrification

## **Chapter 2- Research Methods**

### **Site Description**

The study site is located near Goldsboro, North Carolina at the Center for Environmental Farming Systems (CEFS). Goldsboro is located in the middle coastal plain physiographic region that is characterized by gently sloping hills with broad, relatively flat fields used for intensive agriculture (refer to Figure 2.1). The soils on the site are terrace and floodplain soils. Soil mappings identified the soils of great importance as Roanoke (fine, mixed, Typic Endoaquults), Tomotley (fine-loamy, Typic Endoaquults), Tarboro (Typic Udipsamments), and Wickham (fine-loamy, Typic Hapludults). Randomly spaced ditches and channelized streams are used to drain low-lying areas. Ditches and channelized streams at CEFS discharge directly into the Neuse River. Row crops, beef, dairy and swine production have existed at CEFS for several decades so there is a long history of nutrient addition, particularly nitrogen and phosphorus, to most fields. Nitrate nitrogen concentrations in shallow groundwater beneath most agricultural fields exceed 10 mg NO<sub>3</sub>-N/L (Kunickis, 2000, Dukes, 2000).

### **Prior Studies**

A riparian buffer study was initiated in 1997 to evaluate the influence of buffer width and vegetation type on nitrate transformation through the buffer. Buffer widths were 8 and 15 m and vegetation types included fescue (cool season grass), switch grass (deep rooted grass), forest (pine and mixed hardwoods), native vegetation, and no buffer (i.e., row crop or pasture). Each plot was 24 m in length parallel to the drainage ditch or channelized stream. A

group of ten plots (2 widths X 5 vegetation types) comprised a landscape replicate. The system of 10 plots was installed at 6 different landscape locations resulting in a total of 60 buffer plots across the farm. Land uses upslope of the buffers included: row crops (R1, R2S and R2N), beef pasture (R4W) and dairy pasture (R4E and R5). An overview of the study site is shown in Figure 2.2. Vegetation treatments were established in the spring of 1998. Severe flooding in September, 1999 damaged or destroyed most vegetation such that replanting was required which was completed in the spring of 2000. Figures 2.3-2.5 illustrate the vegetation layout per replicate.

Shallow groundwater monitoring wells were installed as a nest of three wells with one nest located at the buffer/agricultural field interface and another nest along the edge of the drainage ditch (buffer/ditch interface). It was assumed that the ditch well nest was the lower gradient such that shallow ground water flowed from the field towards the ditch (Dukes, 2000). Each nest consisted of three monitoring depths denoted as deep (just above the first aquitard), medium (just below the seasonal low water table) and shallow (near the top of the seasonal high water table). Well depths were determined from soil investigations that determined the depths to the restrictive layers and the expected depth to the water table (Kunickis, 2000). The deep wells were typically screened at 3 m, medium wells screened at 2.1 m, and shallow wells screened at 0.6 m as measured from the soil surface. The screened section was typically 0.5 m in length. Groundwater monitoring began in July of 1998 and proceeded monthly until June, 2000.

Redox electrodes were installed in 13 plots along a portion of two landscape replicates (R1 and R2N) to establish whether or not the buffers established conditions conducive for denitrification (Kunickis, 2000). Redox electrodes were installed in a nest at two depths, 76

and 152 cm, and placed near the well nests in each of the 13 plots. The shallow nest consisted of 5 electrodes spaced about 15 cm apart. Only 3 electrodes comprised the deeper nest. Redox measurements were made weekly for a period of one year by measuring the voltage difference between each platinum electrode and a Ag/AgCl reference electrode. Results of the initial monitoring period (Kunickis, 2000) are summarized in the following section.

### **Redox Results for the Period February, 1999 to February, 2000**

Early redox measurements were difficult to interpret (Kunickis, 2000). It was expected that more reduced conditions would be found at deeper depths. There were reduced conditions near the ditches at deeper depths but generally oxidized conditions at the field/buffer interface at all depths. Along the ditch, reduced conditions appeared to be related to soil texture with more reduced conditions associated with finer textured soil regardless of depth. In some locations, reduced conditions were observed at the shallow depth while oxidized conditions were observed at the deeper depth. Plot to plot differences along the ditch were also related to soil texture. It was difficult to directly link nitrate reduction to redox measurements because soil water sampling depths did not match depth of redox measurements. There was significant reduction in nitrate concentrations in the deepest wells, but no redox measurements were made at this depth to confirm denitrification. If the decrease in nitrate-nitrogen concentration resulted from denitrification, the relatively low concentration of carbon at the deeper depths indicated a long resident time would be required. There was also no consistent trend between redox measurements and buffer width. The inclusiveness of the initial study pointed to the need to expand the measurement of redox to more plots and deeper depths to better match exact locations with soil water measurements.

## **Expansion of the Oxidation-Reduction Study**

The focus of the study reported herein was to expand the oxidation-reduction measurements to better link redox measurements to nitrate-nitrogen concentration measured in the groundwater wells. The expansion included the addition of redox electrodes at the 3 m depth in all plots in R1, R2N, and R4W. In addition, redox probes were installed at the 1.5 m depth in R4W and the remaining plots not previously instrumented in R1 and R2N. As a result, all plots in R1, R2N, and R4W were instrumented to measure redox at the 1.5 and 3 m depths along the ditch and at the field/buffer interface. In three of the five 50 ft buffer plots of R2N, electrodes were installed in the middle of the plot. This was to determine if the redox reading changed incrementally from the field to the ditch. This provided a comparison of redox measurements between the 8 m plots with the equivalent landscape portion of the 15 m plots. In other words, in the 8 m plots, 8 m corresponded to the field/buffer edge whereas in the 15 m plots, 8 meters corresponded to the plot center. For the purposes of this paper the 1.5m electrodes are referred to as the medium depth and the 3.0m electrodes are referred to as the deep depth.

## **Redox Electrode Fabrication**

Redox electrodes were constructed from the following materials:

Brass brazing rods: 2.4mm diameter and 914mm long

Platinum wire: 99.95%, pure, 20 gauge cut in 15 mm lengths

Brazing paste

Heat-Shrink Tubing: 3/8 inch and 1/4 inch diameters in 48-inch lengths

Marine Tex epoxy

Brazing fuel propylene torch

Multi-purpose Heat Gun

Insulated Stranded Copper Wire: 14 gauge

Soldering iron and Solder

Brass rods were cut into 15.2cm sections. Holes were drilled parallel to the length of the rod in the center of one end of each brass rod. The holes were 1mm wide by 5mm deep. Soldering paste (brazing paste) was inserted into the drilled hole. A piece of 1mm by 15mm platinum wire was inserted into the hole in the rod (Figure 2.8). The two metals were brazed with a kerosene torch until the brass metal was red and glowing, close to melting, which fused the two metals together. Care was taken not to let the platinum pop out due to the heat and the expansion of the brass. The rods were allowed to cool, upon cooling each connection was tested. The platinum was gently pulled on to determine if the two metals were fused together, if not the brazing process was repeated until they were fused together.

Marine-tex epoxy was ribboned around the interface of the platinum and brass rod and allowed to cool and dry for 48 hours. After drying, the excess was sanded off using an electric sander with care taken not to sand or damage the platinum. The Marine tex was sanded down to 6.4mm leaving enough area to be covered with heat shrink tape.

The opposite end of brass rod was sanded about 25mm to create a good electrical contact with the copper wire. The 14-gauge copper-stranded wire was cut in 4.6m lengths. One end of the wire was stripped about 25-51mm. The exposed wire was then wrapped around the sanded end of the rod and soldered. It was important to achieve a solid electrical contact between the copper wire and the rod since this is the place the electrons will be traveling. Electrical tape was wrapped around the solder to prevent any sharp metal pieces from puncturing the heat shrink material.

The heat shrink (6.4mm) was cut into 63-75mm sections. Two sections were shrunk onto the electrode. One section was placed at the marine tex epoxy and brass rod interface and the other was at the copper wire brass rod interface (Figure 2.9). The two were heated and shrunk making sure no air bubbles were trapped. If air got trapped in the heat shrink, it was stripped off using a knife. The larger heat shrink (9.5mm) was cut into 450mm pieces. This piece was slid over the entire probe ensuring coverage of the marine tex and the wire. The heat shrink was shrunk onto the length of the brass rod shaft, again avoiding trapping air (Figure 2.10). Electrical tape was used to seal the end interface between the wire and the heat shrink to keep out water and organisms.

### **Testing the Redox Electrodes**

The constructed redox electrodes were tested for accuracy using a standard Ferrous-Ferric Solution for Oxidation-Reduction Potential (ORP) measurements (Light 1973). The solution contained ferrous ammonium sulfate, ferric ammonium sulfate, and sulfuric acid. The test was performed using an Ag, AgCl, KCl saturated reference electrode. The testing solution was placed into a beaker and the platinum tip of the electrode was cleaned lightly using steel wool. The platinum tip on the electrode was inserted into the solution along with the reference electrode. These two were hooked up to the voltmeter. The standard solution was 457 mV; any electrode that deviated by more than 10 mV was discarded.

### **Salt Bridge Formulation**

A salt bridge was constructed for each location of the redox electrodes. They were made according to a recipe given by Dr. Michael Vepraskas in the North Carolina Department of Soil Science. The recipe consisted of 25 - 30 g Agar and 250 mg KCl (tech grade or lower). One liter of water was brought to a boil and the agar and KCl were dissolved in it. The liquid was poured into 25.4mm diameter PVC pipe with the bottom capped and allowed to set. The pipe was taken to the field and holes were drilled in the PVC to allow for the KCl to interact with the soil solution.

### **Redox Electrode Protection**

The electrodes were encased in 13 mm PVC pipe. This was to protect the probes as well as give them stability. The 13mm PVC caps were drilled with two holes, one was 1.6 mm and the other was 8mm. These two holes were in the same place with the larger drill bit

not piercing the cap and the smaller drill bit actually piercing a hole into the cap. This hole was large enough to allow for the platinum tip to protrude through the cap and then there was an area in the cap for the electrode to rest (Figure 2.11). If only one hole was drilled the platinum would be easily bent rendering the electrode useless.

The caps were glued to 153 mm pieces of 6mm PVC pipe. The electrodes were inserted into the pipe and cradled in the cap. 10 mL of epoxy was injected into the pipe to stabilize the electrode in a vertical direction. Once the epoxy had dried a PVC couple was added to the 153 mm pipe and either 184 cm or 367 cm pipe was added. The end of the pipe was capped with another 13mm cap in which a hole was drilled for the wire to pass through. The interface of the wire and the PVC cap was sealed with silicone. The electrodes were ready for installation.

## **Installation**

A drill rig with a hollow stemmed auger that had a 229 mm outside diameter was used to bore the holes. A cluster of three electrodes was placed into this hole in a triangular design to maximize the distance between each electrode. The hole was backfilled with native soil, sand, and the last 30 cm –45cm to the soil surface was backfilled with bentonite clay pellets. The shallow probes were placed adjacent to the groundwater wells, and the deeper probes were installed parallel to the ditch next to the shallow probes. The wire from each of the electrodes was attached to a wooden stand (see Figure 2.3), which was called a station. The station was the area where all of the data was collected using a voltmeter.

On R1, the deep electrodes (305cm) were installed on 16 sites, eight along the field and eight along the ditch. The switchgrass replica was not monitored due to the poor stand.

Electrodes were installed on every plot on R2N. Every plot on R1 and R2N had medium (152cm) and deep (305cm) electrodes.

Three plots on R2N had electrodes installed in the middle of the 15m buffers. These electrodes were installed to study the variability within the buffer. Through previous studies it was determined that the nitrogen concentration decreased through these vegetation plots and it was thought the dramatic change in soil type could be the reason. They were installed in the trees, native, and switchgrass. Sixteen sites were outfitted with medium and deep electrodes on R4W. The pasture replicates were not instrumented due to the difficulty of protecting the electrodes due to the destructive nature of the cattle.

The recommended number of replicates of the electrodes was five. Five electrodes are needed for statistical and variability reasons (Vepraskas 2000). The replication of five electrodes is typically used in wetlands where the upper 30 cm of the soil profile has a tremendous amount of variability and biological activity (Vepraskas 2000). At the deeper depths there is less variability due to the decreasing amount of organic matter and microbial activity. Due to the deep depth in this study and the anticipated decrease in biological activity at this depth only three replicates of these electrodes were installed. At each station in the plot there are six electrodes, a cluster of three at 152 cm and three at 305 cm. There are a total of ninety-six (96) electrodes on R1, one hundred and thirty-eight (138) on R2N, and ninety-six (96) on R4W. There are a total of three hundred and thirty (330) electrodes in this study.

### **Groundwater Monitoring**

To establish the effectiveness of the riparian buffers at shallow groundwater nitrate removal, groundwater-monitoring wells were installed. Wells were installed in nests of three.

Each well nest consisted of three different depths to determine the effect of the buffers at varying depth in the soil profile. The depth of the deep well was 2.1 – 3.5 m (7-11.5 ft) refer to figure 2.7. The depth of the wells was measured from the soil surface to the top of the 0.6 m (2ft) well screen (Dukes 2000). The medium wells were 1.5 – 2.1 m (5-7 ft) and the shallow wells were 0.6 – 1.0 m (2-3 ft) deep. Wells were installed in the center of each 24 m (80 ft) vegetation plot. A well nest was installed along the buffer/ditch edge along with the buffer/field edge. The direction of groundwater flow on these replicates is from the field to the ditch (Dukes 2000).

### **Groundwater Monitoring Well Installation**

The groundwater monitoring wells were installed in the summer of 1998. The wells were constructed from 32 mm (1.25 in) polyvinyl chloride (PVC) pipes. Numerous small holes were drilled into the lower 61 cm and screening fabric was placed over the bottom 61 cm of the PVC pipe and secured with tape (Kunickis 2000). Wells were installed with a mobile drill rig along with a high-pressure jet of water that was used to jet down a temporary solid casing of 100 mm (4 in) PVC pipe. Bentonite clay was placed above the screened zone to 0.6m (1ft) of the soil surface, concrete was then poured around the base of the wells to prevent infiltration of surface water.

Well depths were determined from soil investigations that determined the depths to the restrictive layers within the profile and the expected depth to the water table. The wells were screened within the most transmissive zones. These zones were usually 0.6 to 1.2 m for the shallow wells, 1.8 to 2.4 m for the medium depth wells, and 3.0 to 3.7 m for the deep wells

(Kunickis 2000). The depth and thickness of the transmissive zones was documented in a previous study as well as noted during the installation of the redox electrodes.

### **Groundwater Quality Sampling**

The sampling of the groundwater monitoring wells began in July of 1998 and proceeded monthly until June 2000. After June 2000 the wells were sampled bi-monthly until October 2001. Two portable pumping units were designed using three peristaltic pumps that ran off of a marine 12-volt battery. The wells were purged using the suction tubes attached to the pumps for two wells volumes before a 50mL sample was taken. The samples were collected in an acid washed high-density polyethylene bottles. The samples were placed in coolers with ice and transported to the Soil Science Lab at North Carolina State University in Raleigh, North Carolina and stored at 4 C until the analyses were completed.

The samples were analyzed for  $\text{NO}_3\text{-N}$ , Cl,  $\text{NH}_4$ ,  $\text{PO}_4$  and dissolved organic carbon content (DOC). The samples were filtered through filter paper and 5 mL volumes were pipetted into sample cuvettes. The samples were then run through a Lachat Quickchem 8000 slow injection auto analyzer for the  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ , and  $\text{PO}_4$  analysis. The Lachat was run according to Standard Methods 4500 (Greenberg et al. 1992). The Haack-Buckler Digital Chloridometer was used to measure the dissolved chloride (Gilliam 1971). Standard Method 5310 B – Combustion –Infrared Method was used to analyze the dissolved organic carbon content (APHA 1992).

## **Redox Data Analysis**

Redox data was collected bi-weekly throughout a sixteen-month period. There were three readings for the three electrodes at each site. These three readings were averaged to get a single value for the particular location and depth. None of the values were dismissed, even in cases where one value was abnormally high or low. They were all taken into account with the idea that the conditions that each probe was in could vary tremendously.

A variety of graphs were generated of the redox data. The average of the three electrodes at each depth was calculated for each date. This average redox data for each vegetation plot was graphed over the time period of the data collection. This was done for each replicate by width and vegetation. The mean redox value for each vegetation by width for all the replicates was determined. The average redox value for the field and the ditch locations was calculated.

All of the replicates were grouped together in a randomized block design to determine if there was a significant difference between the three replicates at  $\alpha=0.05$ . The null hypothesis was that the two means were equal. There were 6682 observations that were used.

The SAS software was used to statistically analyze the redox data. The PROC GLM procedure was used. The GLM procedure uses the method of least squares to fit general linear models. Among the statistical methods available in PROC GLM are regression, analysis of variance, analysis of covariance, multivariate analysis of variance, and partial correlation (SAS 1985). PROC GLM analyzes data within the framework of General linear models. PROC GLM handles models relating one or several continuous dependent variables to one or several independent variables. The independent variables may be either

*classification* variables, which divide the observations into discrete groups, or *continuous* variables. Thus, the GLM procedure can be used for many different analyses.

The classification variable, or class variable, were as follows: width, vegetation, depth, location, and depth (SAS 1985). The width had two levels 8m or 15m, the vegetation varied by replication. R2N had five levels of vegetation, fescue, no buffer, switchgrass, trees, and native vegetation. R1 has four levels that were no buffer, native, trees, and fescue. The switchgrass was not included since that stand was poor. R4W has four levels also. They were switchgrass, native, fescue, and trees. The no buffer vegetation for this replication was pasture, and this plot was not instrumented for redox. The depth had two levels, deep and medium. Location also had two levels that were ditch and field.

The Bonferroni *t* test was run on the redox data. Bonferroni *t* tests for differences between means for all main effect means in the MEANS statement.

The model statement modeled redox with respect to these class variables. The LSMEANS was calculated for the depth, width, vegetation and location. Least-squares means (LS-means) are computed for each *effect* listed in the LSMEANS statement. Only classification effects in the LSMEANS statement may be used. These effects must contain only classification variables. In contrast to the MEANS statement, the LSMEANS statement performs multiple comparisons on interactions as well as main effects (SAS 1985).

### **Groundwater Statistical Analysis**

The water quality data was analyzed using the SAS statistical package to determine differences in groundwater quality due to vegetation, width, depth, and date. In SAS, PROC

MIXED was used for the analysis because there is a dependence of the response variable on the classification factor of interest; these factors are known as covariates.

PROC MIXED was used due to the unequal sample sizes and randomly missing values for each of the replicates. This was due to the difference in vegetation plots, (there were five vegetations on R2N and only four on R1 and R4W), and some redox electrode data was not collected on certain dates due to errors with equipment. PROC MIXED estimated the least square means for all the wells regardless of the randomly missing values.

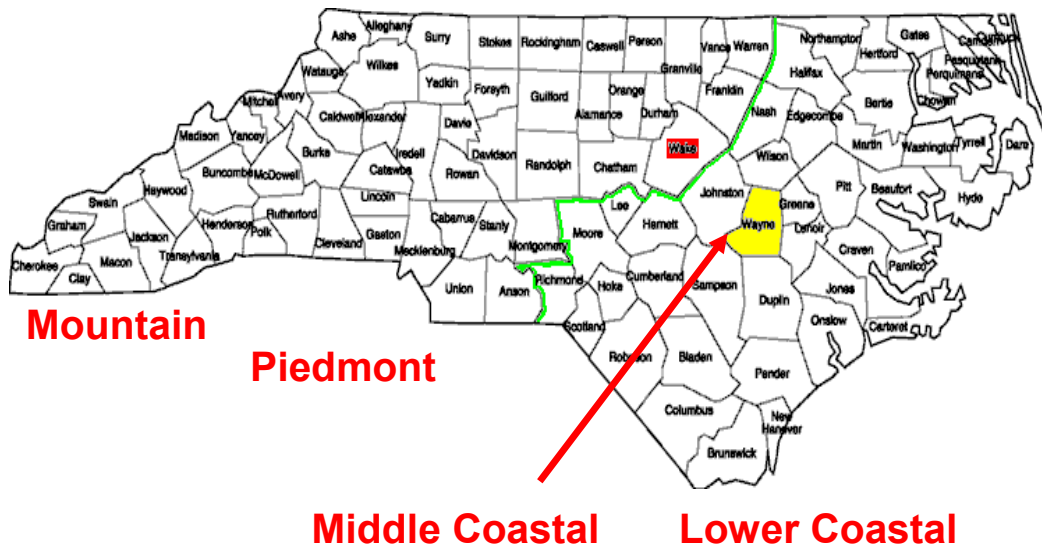
The data was classified as either upstream (field location) or downstream (ditch location). The water quality data was determined to be paired data because the downstream concentrations of nitrate were considered to be dependent on the upstream concentrations. If the field concentration is high then the ditch concentration will be proportional to this value. Thus, the statistical analysis was performed using a covariate, with the ditch being the dependent variable. Width, vegetation, depth, and date were the independent variables. The PROC MIX procedure uses a covariant that adjusts the ditch values to a common reference point. The reference point is the average value for the field data. This value is 5.2 for the deep wells and 7.0 for the medium wells. The difference between the two values usually the same. Thus they are just adjusted values based on the effect the covariant has on the data.

PROC GLM was also used to analyze the water chemistry data in the same manner as the redox data. A variety of graphs were generated of the water quality data. The average change in nitrate-nitrogen from the field to the ditch in each of the wells, medium and deep, was graphed for all three replicates. The average nitrate concentrations for each buffer width for the location and depth were compared. The nitrate nitrogen for each date was graphed for

all the vegetation plots for each replicate. The mean nitrate nitrogen for the 8m buffer and the 15m buffer was graphed.

## Chapter 2 Figures

### Site Location – Goldsboro, NC Center for Environmental Farming Systems



- **Predominance of moderately well drained soils**
- **Intensive agricultural region in state**
- **Most streams channelized or deeply incised**

Figure 2.1 Location of research site

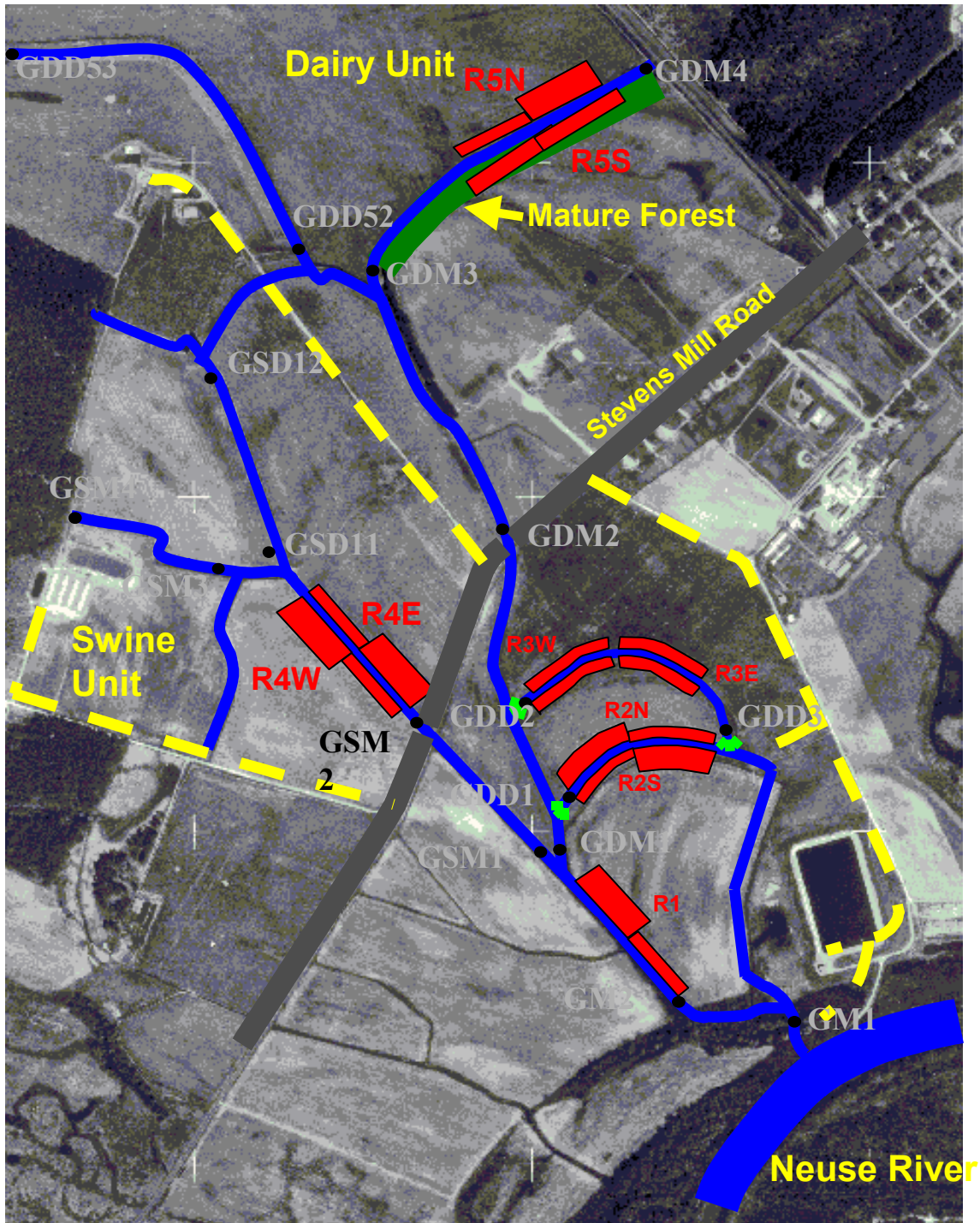


Figure 2.2 Layout of Research Site (Adapted from Dukes, 2000)

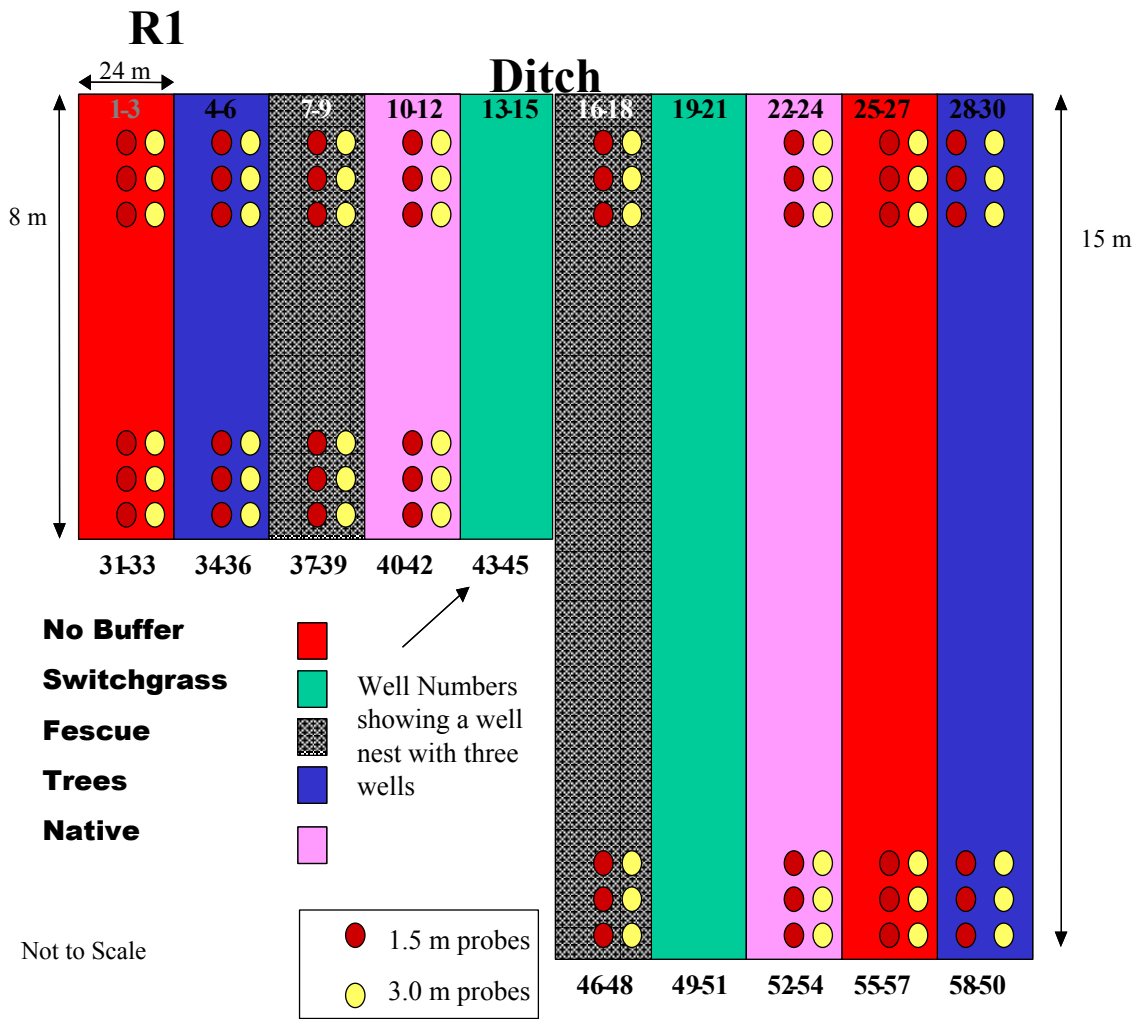
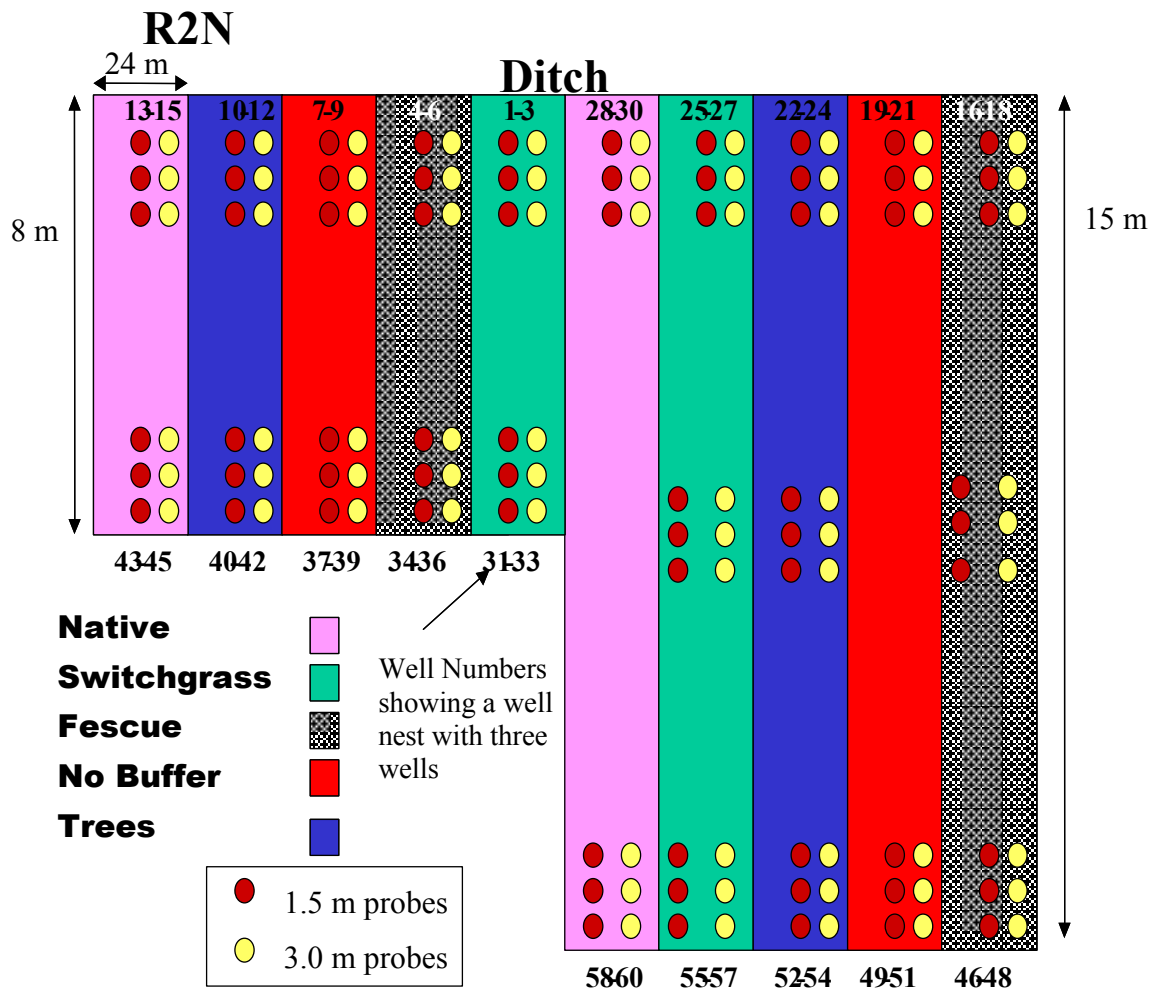


Figure 2.3 R1- Schematic of buffers (Adapted from Dukes, 2000)



Not to Scale

Figure 2.4 R2N Schematic of buffers (Adapted from Dukes, 2000)

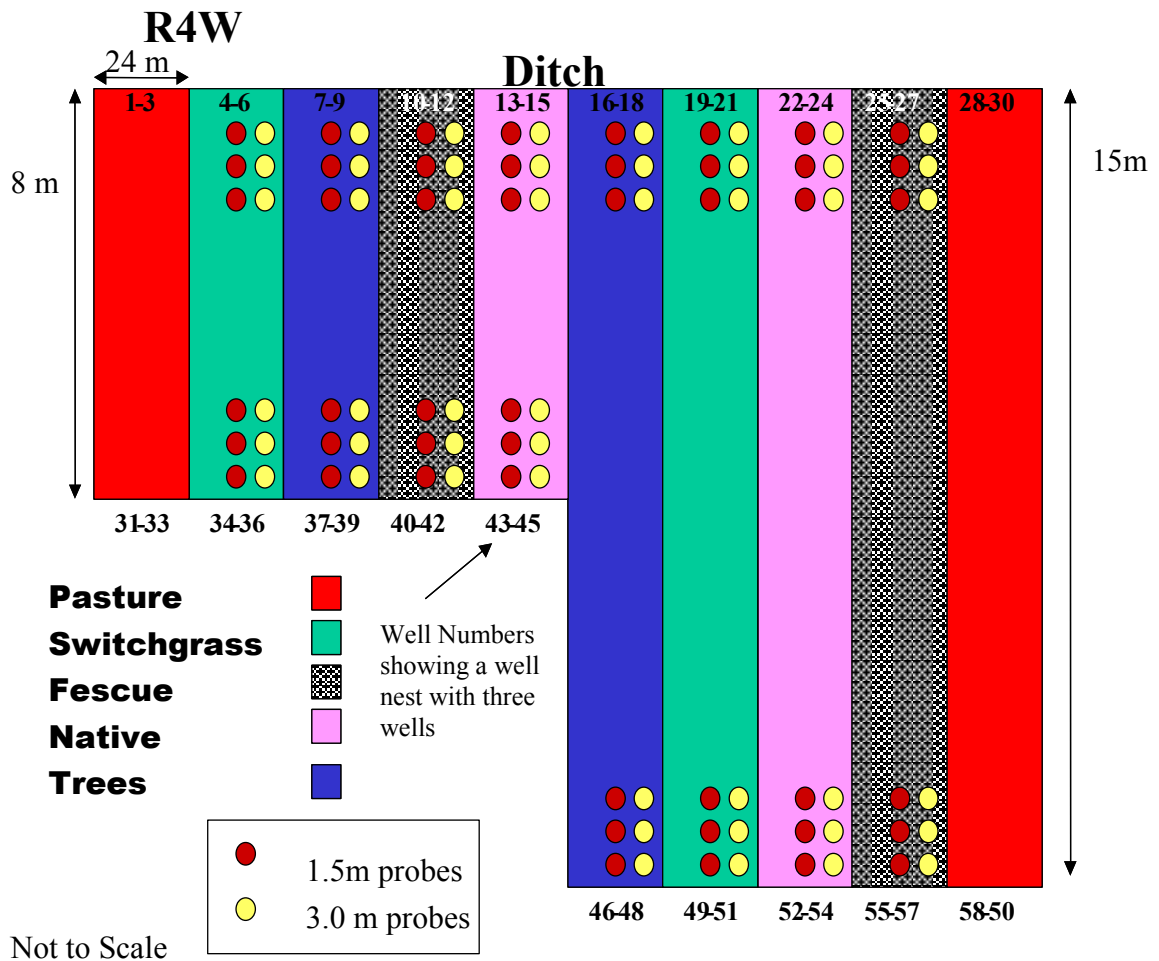
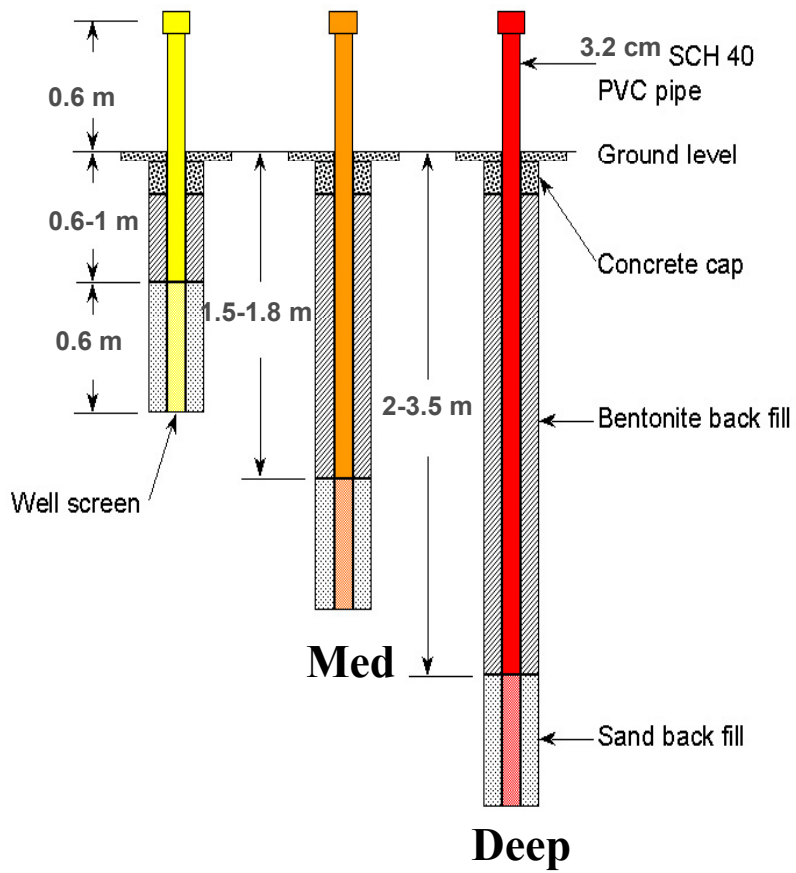


Figure 2.5 R4W Schematic of Buffers (Adapted from Dukes, 2000)



Figure 2.6 Redox electrode station for collecting data



# Well Nest Detail

Figure 2.7 Well Nest Detail (Adapted from Dukes, 2000)

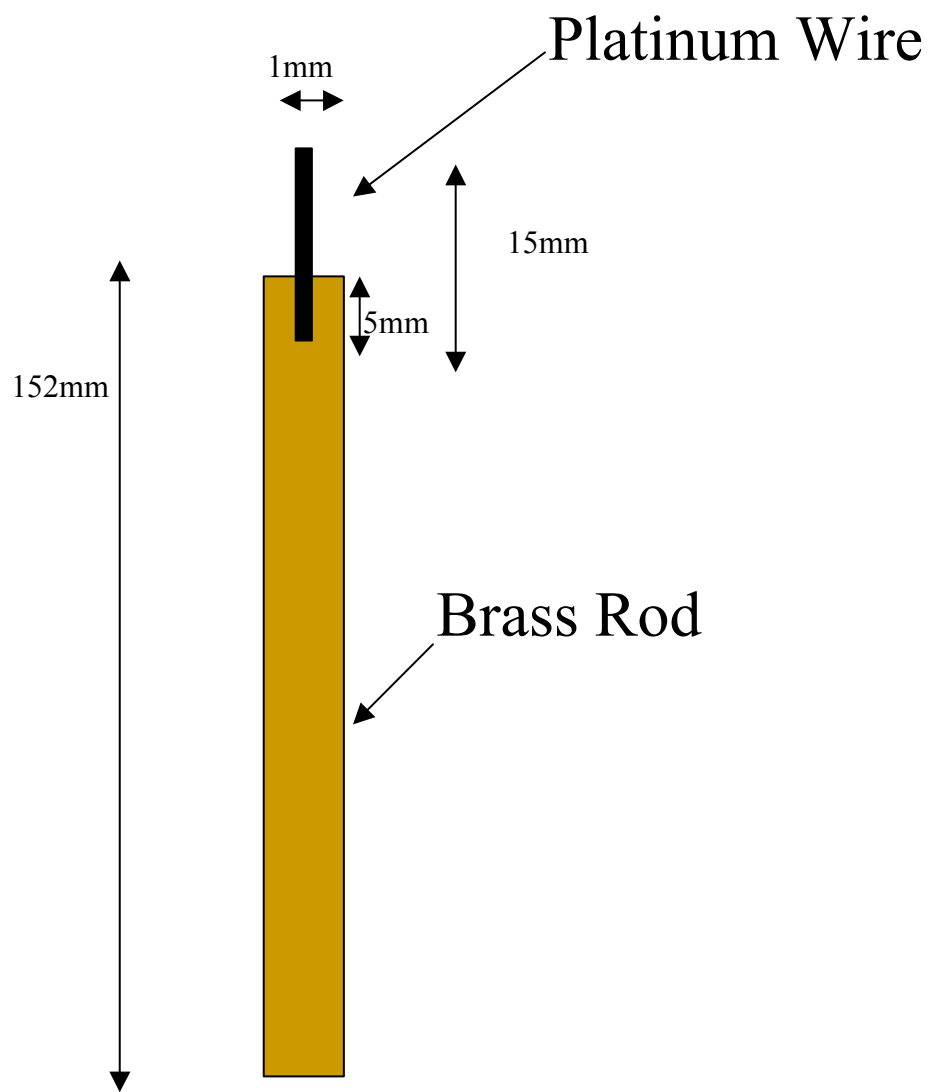


Figure 2.8 Schematic of Redox Electrode

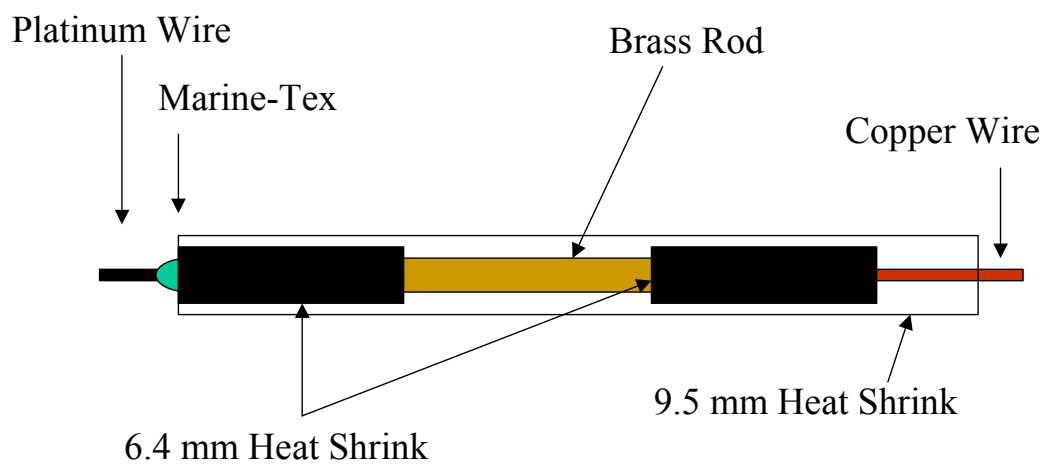


Figure 2.9 Schematic of electrodes covered in heat shrink



Figure 2.10 Picture of redox electrode



Figure 2.11 Protection of redox electrode

## **Chapter 3 – Influence of Location, Depth, Width and Vegetation on Soil Redox Values**

### **General Trends**

Redox values were generally lower (more reduced) at the deeper depth (Figure 3.1) and lower near the ditch than at the field/buffer edge, Figure 3.2. A redox value of roughly 350 mV, for a pH under 10, is the threshold where nitrate nitrogen starts to be reduced thus signaling conditions for denitrification (McBride, 1994). Deep values were below the threshold level where denitrification occurs, Figure 3.1. Conditions were highly reduced near the ditch (deep mean ~ 125 mV), Figure 3.4a,b,c and marginally reduced at the field/buffer edge (deep mean ~ 350 mV), refer to Figure 3.4a,b,c. Conditions at the medium depth were well oxidized and generally above 400 mV, Figures 3.1 and 3.3a.b.c. When averaged across all plots, redox was significantly lower at the deep depth, Table 3.1. Redox conditions were relatively constant over time at all depths and locations. Similar trends were observed for all plots (Appendix Figures 1-6). There were no seasonal variations; and differences between sampling dates were not significant, (Appendix Figure 1-6).

In the 8m buffers, medium depth redox values on R1 (mean 630 mV) were higher than R2N (mean 493 mV) or R4W (mean 476 mV) Table 3.1, and none of the values were below the threshold value for nitrate reduction. At the deep depth, R4W (mean 235 mV) had higher values than R1 or R2N, but all values were well below the nitrate reduction threshold.

Redox values for the 15m buffers were generally lower than the 8m buffers Figure 3.5, although differences at the deep depth were not significantly lower than for the 8m width.

Values at the medium depth were significantly lower on the 15 m buffers (mean ~400 mV) than the 8 m buffers (mean 643 mV) Table 3.2, although mean values at the mid depth were generally slightly oxidized (above 350 mV). Redox conditions were reduced at the deep depth and conducive for denitrification.

**Table 3.1 -Variations in overall redox values as influenced by landscape position**

	R1	R2N	R4W	ALL
Depth	(mV)	(mV)	(mV)	(mV)
Medium	630a	493a	476a	532a
Deep	208b	231b	235b	225b
Mean	419	362	356	379
Difference	422	262	241	307
Width				
8m	538a	467a	375a	467a
15m	308b	275b	333a	299b
Mean	423	371	354	373
Difference	230	192	42	168
Location				
Field	469a	481a	448a	469a
Ditch	398b	270b	264b	308b
Mean	434	378	356	389
Difference	71	211	184	161
Vegetation				
Fescue	423ab	318c	382a	370c
Switchgrass	----	283c	215b	252d
Trees	383b	321c	406a	365c
Native	452a	426c	419a	433b
No Buffer	473a	509a	-----	493a
Mean	433	371	356	317

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison Test

## **Depth**

Depth was determined to significantly affect redox values. Across all plots, there was a difference of 307 mV between the mean redox values of the deep and medium depths, Table 3.1.

## **Depth-Width Interaction**

Redox differences between the medium and deep depths were greater on the 8m buffers (395 mV) than the 15 m buffers (210 mV), Table 3.2. There was no significant effect of width at the deep depth (15 m mean = 195 mV, 8 m mean = 220 mV) for Replicate 1, but there was considerable difference at the medium depth where the 8m buffers were more oxidized (mean = 784 mV) than the 15m buffers (mean = 420 mV), Table 3.2. The mean water table on R1 and R2N was slightly below the medium depth electrodes so anaerobic conditions may not be met (Table 3.3). Anaerobic conditions typically caused by saturation are required for denitrification to occur and this could be the reason the medium depth electrode redox values are high. R2N and R4W exhibited significant differences across both widths for each depth.

Overall, conditions were slightly reduced on the 15m buffers for all replicates (mean = 299 mV) but oxidized conditions were generally observed on the 8m buffers (mean = 467 mV) Table 3.2. There was little difference in mean values between landscape replication, although R1 tended to be more oxidized, particularly at the medium depth. The seasonal water table along the ditch is located at 1.5m, which is just at the depth of the medium electrodes (Figure 3.14). However the water table drops lower along the field/buffer edge, thus anaerobic conditions might not always be met. The field values of R2N were around 600 mV (Figure 3.3b), which is highly oxidized. The high redox values can be explained by the

lower water table on this replicate at the field/buffer edge (Figure 3.15). There was more redox variation between depth and buffer width on the narrower buffers.

Simply comparing redox means can be misleading as a highly oxidized value averaged with a slightly reduced value could indicate an overall oxidized condition, yet, denitrification could be occurring under the slightly reduced condition. For example, a value of 300 mV is adequate for denitrification; yet, there is not much difference in the oxidizing conditions at 400 mV versus 600 mV. When averaged with a 300 mV value, there is a significant difference between the interpretation of the mean of these values, 350 being suitable for denitrification and 450 representing an oxidized state. Furthermore, mean values can be skewed by a very high or low value. For example, average redox values on the 8m buffers generally indicate oxidized conditions, yet reduced conditions were prevalent at the deep depth, Figure 3.6. The redox values at the medium depth for the 8m buffer on R1 were 300 mV higher than any other values. When averaged with other values within the comparison groups, the high value on R1 for the 8m plots tends to bias the mean towards an oxidized condition. Similarly, comparing buffer width means in Table 3.2, it appears that conditions are more reduced and conducive for denitrification on the 15m buffers than the 8m buffers (15m mean 299 mV, 8m mean 467 mV). However, there is little difference between widths at the deep depth (i.e., all values at the deep depth are reduced, regardless of buffer width, Figures 3.6 and 3.7), so the overall mean is biased by the high value from the R1 8m plots.

**Table 3.2. Relationship between buffer width and depth of electrode on redox conditions.**

Width-Depth Interaction	R1	R2N	R4W	Mean
8m medium	784a	571a	573a	643a
8m deep	220b	339b	173b	248b
Depth Difference 8m	564	232	400	395
15m medium	420a	408a	360a	400a
15m deep	195b	116b	306b	190b
Depth Difference 15m	225	292	53	210
Means by buffer width				
Mean 8m	538a	467a	375a	467a
Mean 15m	308b	275b	333b	299b
Means by depth				
Mean medium	630a	493a	476a	532a
Mean deep	208b	231b	235b	225b
Medium				
8m	784a	571a	573a	643a
15m	420b	407b	360b	400b
Deep				
8m	220a	339a	307a	257a
15m	195a	116b	173b	190b
Mean landscape replicate	419	362	356	379

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison Test

### Depth-Location Interaction

As used here, location refers to the relative location of the electrodes relative to the stream or ditch. Two relative locations were evaluated: one approximately 1 m up slope of the stream, referred to as the ditch location; and the other immediately up slope of the buffer at the interface between the field and buffer, referred to as the field location.

At the medium depth, there was no significant difference between the field and ditch redox values on R1, Figure 3.3a. These values at the medium depth on R1 were oxidized and can be attributed to the water table depth at this location (Figure 3.14). The water table was

generally below the 1.5m redox electrodes on most occasions, so saturated conditions were unlikely at the medium depth.

On R2N and R4W, the ditch values were significantly lower than the field values, Figure 3.3 b,c and Figure 3.4 b,c, although neither the field or ditch values were in the reducing range. Redox values at the medium depth along the field edge were highly oxidized on all three landscape replicates at approximately 600 mV, Figure 3.3, and again the depth to the water table is located just at the depth of the medium electrodes, thus the area may not have anaerobic conditions.

At the deep depth, redox conditions were highly reduced along the ditch and moderately reduced conditions at the field/buffer edge on all three-landscape replicates, Table 3.4. Mean values along the ditch were lower than the field values and their differences were significant. The water table was well over the electrodes at the deep depth of 3.0m, thus the area was saturated and anaerobic (Table 3.3). The probability of encountering reducing conditions clearly increased with depth, Figures 3.8 and 3.10.

**Table 3.3. Mean depth to water table for each replicate**

Replicate	R1	R2N	R4W
Ditch Location			
8m	1.5	1.6	0.9
15m	1.6	1.4	0.8
Field Location			
8m	1.8	1.9	1.3
15m	2.0	2.2	1.2

**Table 3.4. Relationship between redox electrode depth and location relative to ditch on redox conditions.**

Depth-Location Interaction	R1	R2N	R4W	Mean
Ditch Location				
Medium depth	590a	451a	397a	479a
Deep depth	137b	160b	112b	136b
Difference	453	291	285	343
Field Location				
Medium depth	616a	733a	537a	629a
Deep depth	279b	405b	365b	350b
Difference	337	328	172	279
Means by Location				
Ditch	364a	306a	255a	308
Field	448b	569b	451b	489
Mean landscape replicate	406	438	353	399

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison Test

### Buffer Width

The relationship between buffer width and redox is shown in Figure 3.8, 3.11, and 3.12. Average redox values were 467 mV for the 8m buffer compared to 299 mV for the 15m buffer, Table 3.2. Redox values associated with the 15m buffer were significantly lower than the 8m buffer, this was consistent for all three landscape replications, Table 3.2. It would seem that redox conditions would be independent of buffer width, except to the extent that the width of the buffer resulted in the electrodes being installed in different soil or at different landscape elevations. The soil tends to be better drained and the depth to the water table increases at greater distances from the ditch.

The land surface slopes towards the ditches/streams, so surface elevation increases at greater distances from the streams. Since all medium or deep electrodes were the same

length, the installed depth followed the contour of the land. As a result, the electrodes at the field/buffer edge were installed at a higher elevation. As noted in the previous section, the probability of reduced conditions increased with depth, so it follows that elevation differences should have resulted in conditions that were less reduced along the field/buffer edge of the 15m buffers compared to the 8m buffers. But, as seen in Figure 3.11-3.12, redox conditions were generally more rather than less reduced at the field/buffer edge for the 15m buffers compared to the 8m buffer. Average Eh values were about 100 mV lower along the field edge and over 200 mV lower next to the ditch on the 15m buffers compared to the 8m buffers.

Soil texture differences could affect redox values with more reduced conditions expected to be associated with finer textured soils. The smaller the soil particle (i.e. clay) the more tightly it can hold water and thus create an anaerobic area. Sand particles are much larger and have more voids, and thus more water is able to flow through sand than clay. Therefore the finer the texture of soil particles, the higher the water content of the soil.

Kunickis (2000) observed that the soils associated with the 8m buffers along R2N were sandier than the soils associated with the 15m buffer. This was consistent with the relative slope of the stream. The 8m buffers were located along the higher elevation of the stream and the 15m buffers at the lower elevation. It would follow that more oxidized conditions would be associated with the 8m buffers along this landscape replication. Comparing Figures 3.11b and 3.12b, this was the case on R2N. However, on R1 and R4W, the 15m buffers are located along the higher elevation of the stream and the soils along the 8m buffers tend to be finer textured. Following the above logic, more reduced conditions would be expected on the 8m buffers along landscape replicates R1 and R4W. Comparing Figure

3.11a to Figure 3.12a and Figure 3.11c to Figure 3.12c, this was not observed. Average redox values were lower on the 15m buffers at both the field and stream locations. This seems contrary to both the relative landscape position where the buffers are located and associated soil texture. However, the redox values were consistently related to water table depth, Figure 3.14, 3.15. On R1, the water table was below the 1.5m electrodes for both buffer widths. On R2N and R4W, the water table was above the electrodes on the 15m buffers and at or below the electrodes on the 8m buffers. Where the water table was above the electrodes, redox conditions were generally in the reducing range regardless of buffer width.

To further evaluate the interaction between buffer width and redox values, additional redox electrodes were installed in the middle of three of the 15m buffers on R2N. These midpoint electrodes were the equivalent distance from the stream as the field/buffer electrodes associated with the 8m buffers. The redox gradient from the ditch to the midpoint electrodes was 35.9 mV per meter compared to 16.8 mV per meter from the midpoint to the field edge (Figure 3.13). The redox gradient on the 15m plots from the ditch to the midpoint was higher than the gradient on the 8m buffer for the corresponding distance. The dramatic difference in unit change of redox on the 15m plots was likely the result of the finer textured soil near the ditch. The soil in the middle of the 15m plots is sandy, but not as sandy as the field/buffer edge. The soil changes rapidly from sandy at the midpoint to tight marine clay along the ditch, a distance of 8m, and this could be the cause of the large change in redox values from the field to the ditch in these three 15m buffers.

## **Vegetation Interaction**

The influence of vegetation on redox values is summarized in Table 3.1 and 3.6. There were statistically significant differences between types of vegetation, Table 3.1. This result might lead to the conclusion that vegetation is an important factor in determining redox conditions and ultimately influencing rates of denitrification. However, the differences between vegetation were not consistent across all landscape replicates. For example, on R1, tree plots were significantly lower than native vegetation or row crops (no buffer); while on R2N switchgrass had the lowest redox value, although not significantly different from trees, fescue, or native. On R4W, switchgrass was significantly lower than the other vegetation types. When averaged across all landscape locations, the no buffer treatment had significantly higher redox than the other vegetation types, Table 3.1 while the switchgrass had the lowest redox values. There was no significant difference between fescue or trees. Overall the only vegetation that exhibited a consistent difference over the two replicates in which it was planted was switchgrass. This is reasonable due to the mature stand of switchgrass on both these replicates compared to the other vegetations on the replicates.

Vegetation was not expected to impact the deeper redox values due to the fact the roots do not reach the depth of 3.0m. Over time the degradation of the roots of this vegetation could be transported through the soil profile to the depths of 3.0m and then it could impact the redox values by creating conditions conducive for denitrification.

**Table 3.5. Dissolved Organic Carbon Content**

Replicate	R1	R2N	R4W
Ditch Location	(mg/L)	(mg/L)	(mg/L)
Medium	1.6	2.6	1.9
Deep	2.0	2.1	1.4
Field Location			
Medium-8m	1.1	1.8	1.5
Deep-8m	1.6	1.6	1.8
Medium-15m	1.1	1.8	2.1
Deep-15m	1.1	1.0	1.9

Table 3.5 summarizes the dissolved organic carbon content in the groundwater samples. All of the locations had some degree of organic carbon present. It would be customary to have higher organic carbon at the medium depth than at the deep depth, due to the presence of vegetation, i.e., roots at the medium depth. However this is not the case in all replicates. For example, R1 deep wells along the ditch had higher organic carbon than the medium wells. The vegetation growing along the ditch bank in which the roots grow inward could possibly reach the deep well depth providing a source of carbon and could explain the higher organic content at the deep depth.

The field location for the deep wells on the 8m buffers on R1 and R4W both exhibited higher organic carbon content than the medium wells. The existing vegetation cannot be credited with this anomaly. However over a period of time the previous vegetation could have been broken down and the water at these sites could transport the organic carbon through the soil profile to these depths. Due to the fact there was a presence of organic carbon at the deep depth, this is not the limiting factor for denitrification. At the deep depths there was organic carbon, along with anaerobic conditions thus the low redox values for the deep depth most likely lead to denitrification.

The redox differences associated with vegetation were likely due to anomalies due to soil and relative landscape position rather than the vegetation itself. For example, on R1, trees tested to be significantly lower (Table 3.1) yet the tree stand and tree size on R1 was the poorest of the three landscape replicates. On R2N, the lower values observed for the switchgrass, trees and fescue were likely associated with the interaction of the tighter soil (discussed in the previous section) on the 15m buffers, Table 3.6. The lower values for the switchgrass plots on R4W might be representative of the vegetation. Switchgrass stand and growth on R4W far exceeded the other types of vegetation on R4W and the switchgrass on the other replicates. Overall, there continues to be major differences in cover and growth of the different types of vegetation from plot to plot. Several more years of establishment will be required for consistent trends to develop.

**Table 3.6 Influence of vegetation on redox values**

Vegetation interactions	R1	R2N	R4W	Mean
Ditch				
Fescue	445a	146c	321ab	293b
Switchgrass	--	79c	79c	80c
Trees	295b	311b	276b	296b
Native vegetation	334b	357ab	372a	353b
No buffer	516a	421a	--	465a
Field				
Fescue	402b	486b	442b	447b
Switchgrass	--	479b	346c	419b
Trees	473b	330c	536a	436b
Native vegetation	570a	503b	467ab	517a
No buffer	4311b	593a	--	519a
Medium depth				
Fescue	620b	499b	416b	518a
Switchgrass	--	308c	425b	362c
Trees	545c	421b	623a	514b
Native vegetation	644b	483b	439b	528b
No buffer	704a	688a	--	695a
Deep depth				
Fescue	203a	75a	347a	198bc
Switchgrass	--	259b	-3c	146c
Trees	204a	200b	189b	198bc
Native vegetation	224a	356c	398a	324a
No buffer	200a	265b	--	234b
8m buffer				
Fescue	635a	461b	447ab	516a
Switchgrass	--	386c	183c	292b
Trees	498b	543a	374b	478a
Native vegetation	620a	389c	490a	499a
No buffer	410c	538a	--	476a
15m buffer				
Fescue	175c	167b	305bc	206c
Switchgrass	--	178b	252c	210c
Trees	261b	67c	444a	234c
Native vegetation	243bc	467a	338b	356b
No buffer	552a	478a	--	511a

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison Test

## **Redox Summary**

Redox values were usually lower at the deeper depth, and lower near the ditch than at the field/buffer edge. The deep electrodes along with the ditch exhibited reducing conditions in every replicate. The water table was higher along the ditch and the electrodes at the deep depth were always well below the water table. The medium electrodes were highly oxidized in R1 and fairly oxidized in R2N and R4W. These oxidized conditions could be attributed to the water table being located just at the depth of 1.5m of the electrodes.

Width was not a factor on R4W, but did influence the redox values in the other two replicates. This could possibly be due to the upslope land use of pasture, compared to the other replicates where row crops predominate. R1 had the greatest difference in width overall. Saturation did not occur at the medium depth on R1 and it did occur at the deep depth, one of the key components for denitrification to occur was not been met; therefore, the redox value were in the oxic range of around 600 mV. Differences among width were greater among the 15m buffers. This could be due to the water table depth being lower at the field and the dissolved organic carbon content being lower at the field also. Organic carbon in addition to anaerobic conditions is necessary for denitrification to occur.

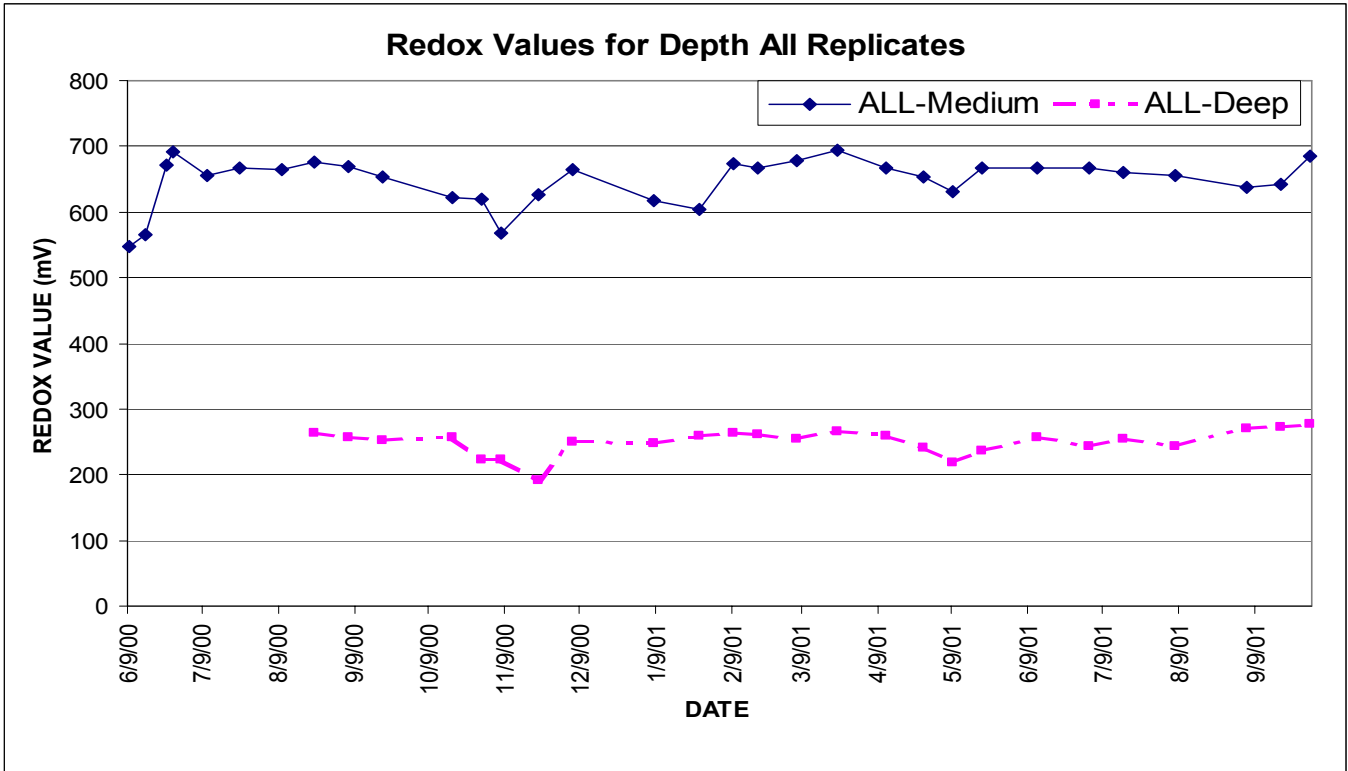
Depth of the electrodes was an important factor relating to redox values. The water table along the ditch was around 1.5m for replicate R1 and R2N, however it was higher in R4W, around 1.0m. The electrodes were located at 1.5m, so there were periods of time where the water table was below the electrodes, thus providing periods of aerobic conditions which were not conducive for denitrification to occur.

Location of the electrodes was an important factor in redox values. The ditch values were lower than the field redox values. The organic carbon measurements were usually

higher near the ditch than the field. The flow of water through the buffers could move some of the organic carbon from the field to the ditch, thus increasing the probability of denitrification.

Across all vegetation types, switchgrass had consistently lower redox values. Switchgrass was the most mature stand of vegetation, so it is reasonable that switchgrass would have the lowest values for redox. The availability of organic carbon in the soil is greater where there is a mature stand of vegetation. Statistically there were differences in vegetation type, however vegetation stand and maturity did not support this conclusion. Statistical differences were observed for some plots with poor stands. These plots were not different from the no buffer and native plots. The vegetation effects are believed to be due to the differences in soil type and landscape positioning rather than the vegetation itself.

### Chapter 3 Figures



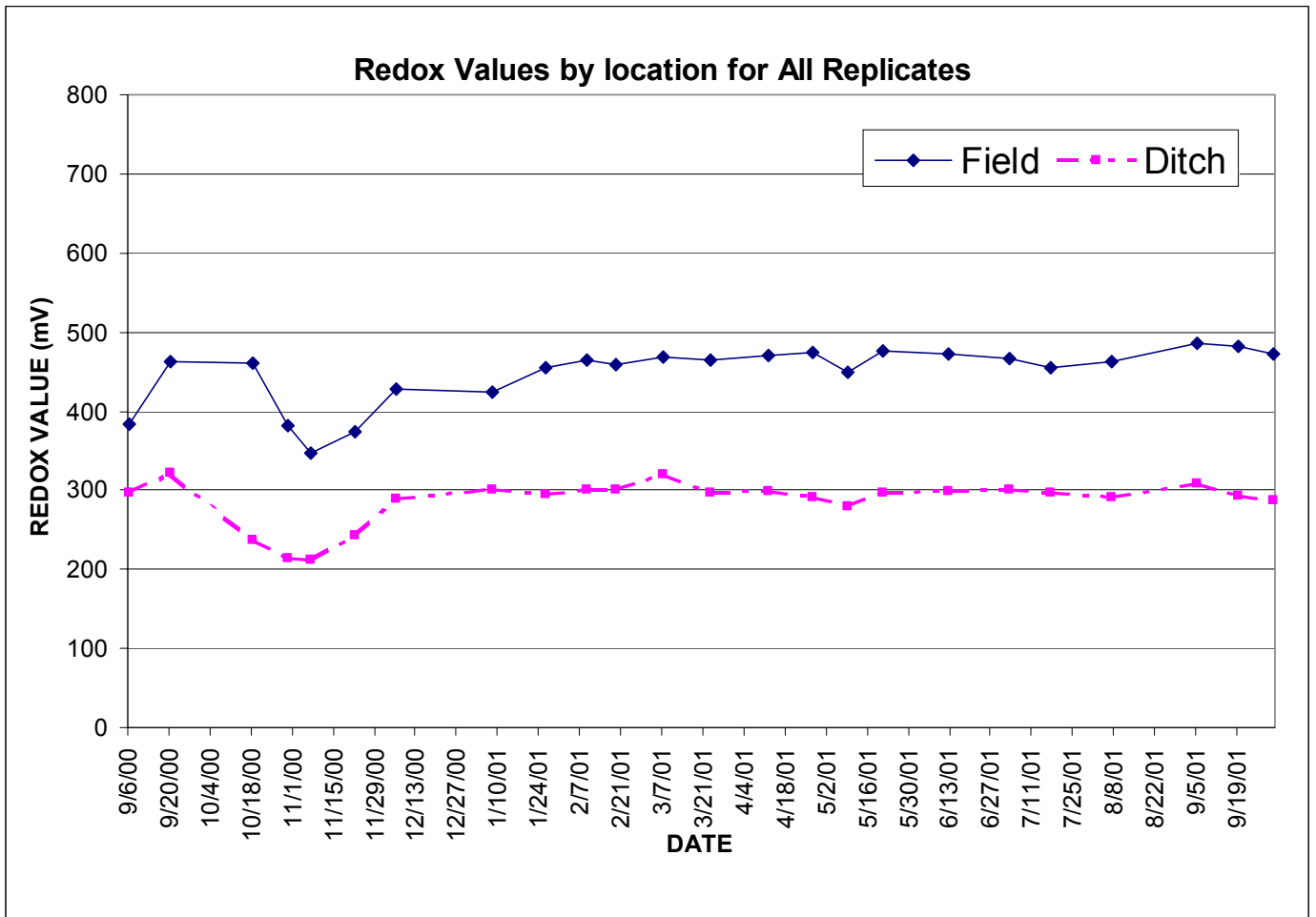


Figure 3.2 All replicates over time for field and ditch locations

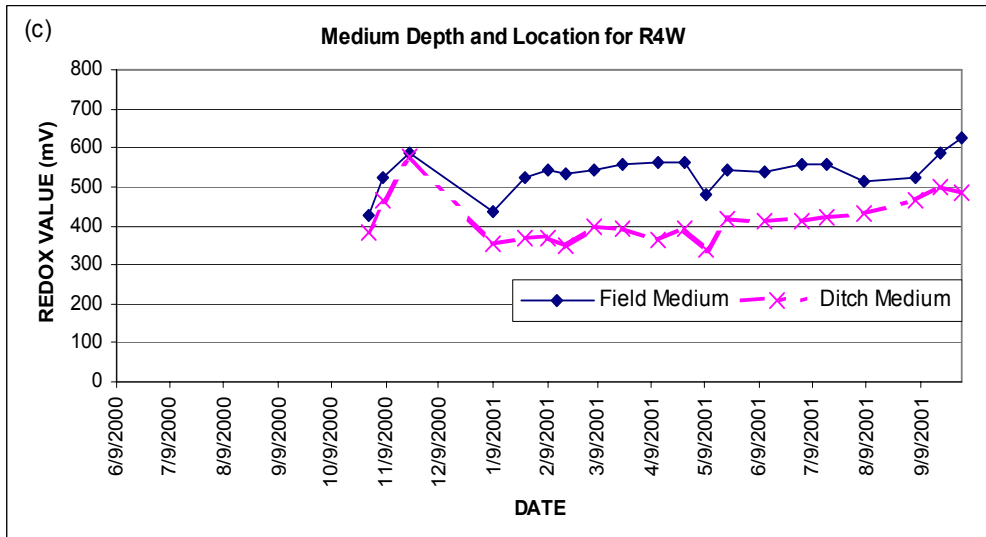
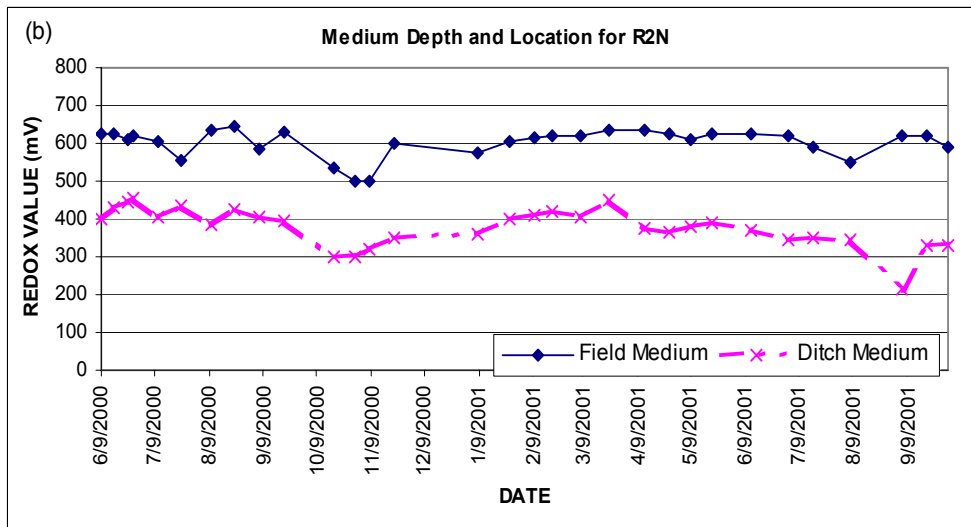
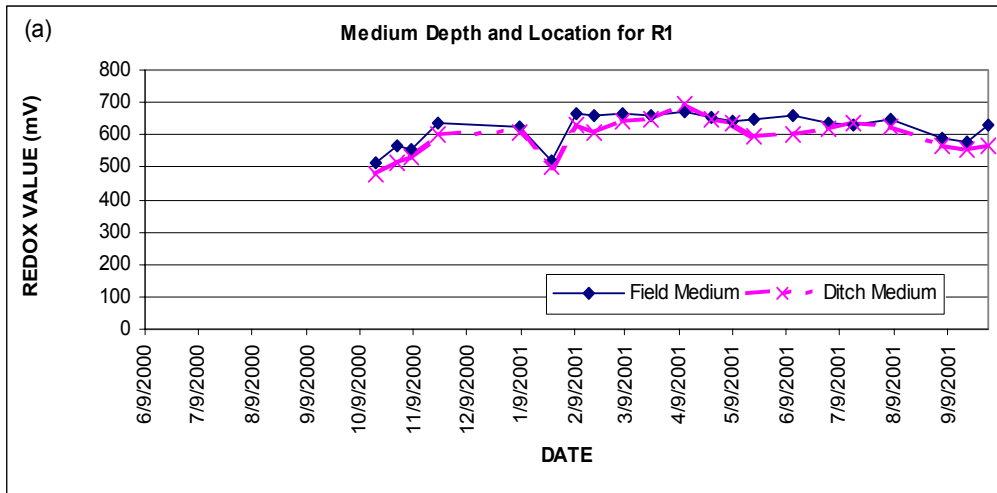


Figure 3.3 a,b,c The effect of medium depth on redox values over time

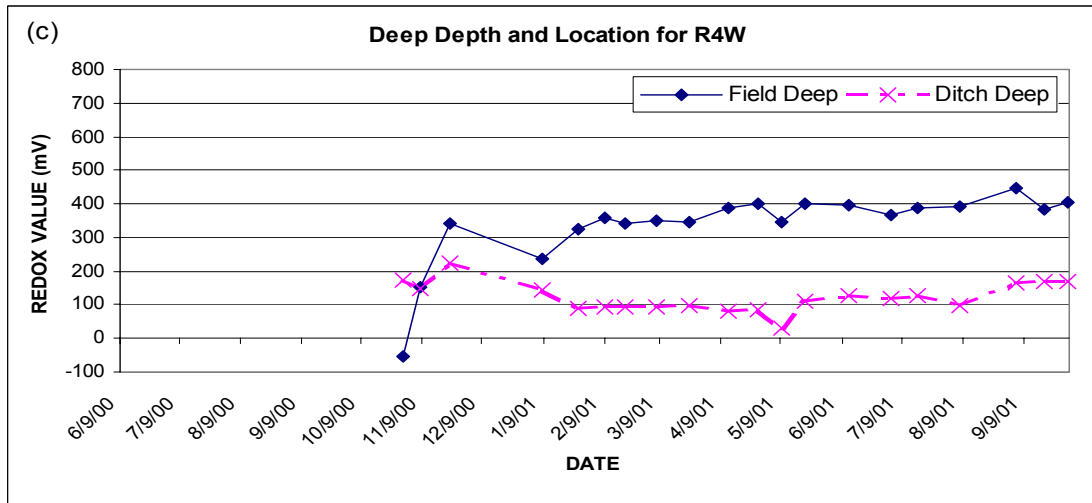
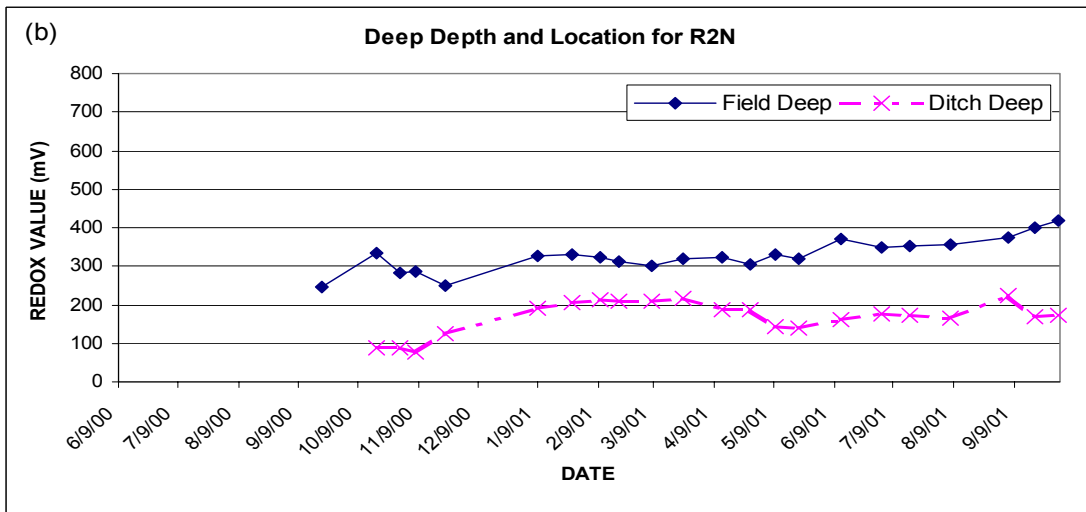
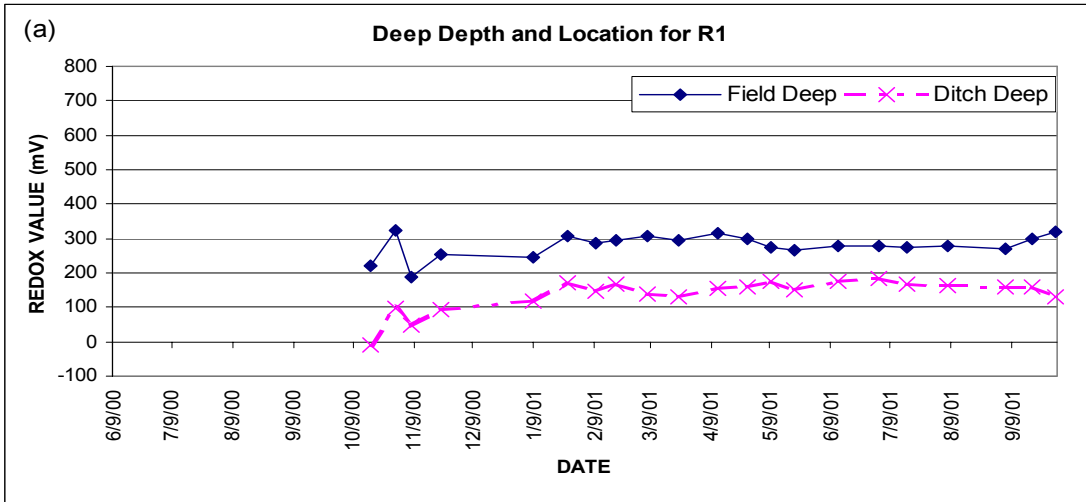


Figure 3.4 a,b,c The effect of deep depth on redox values over time

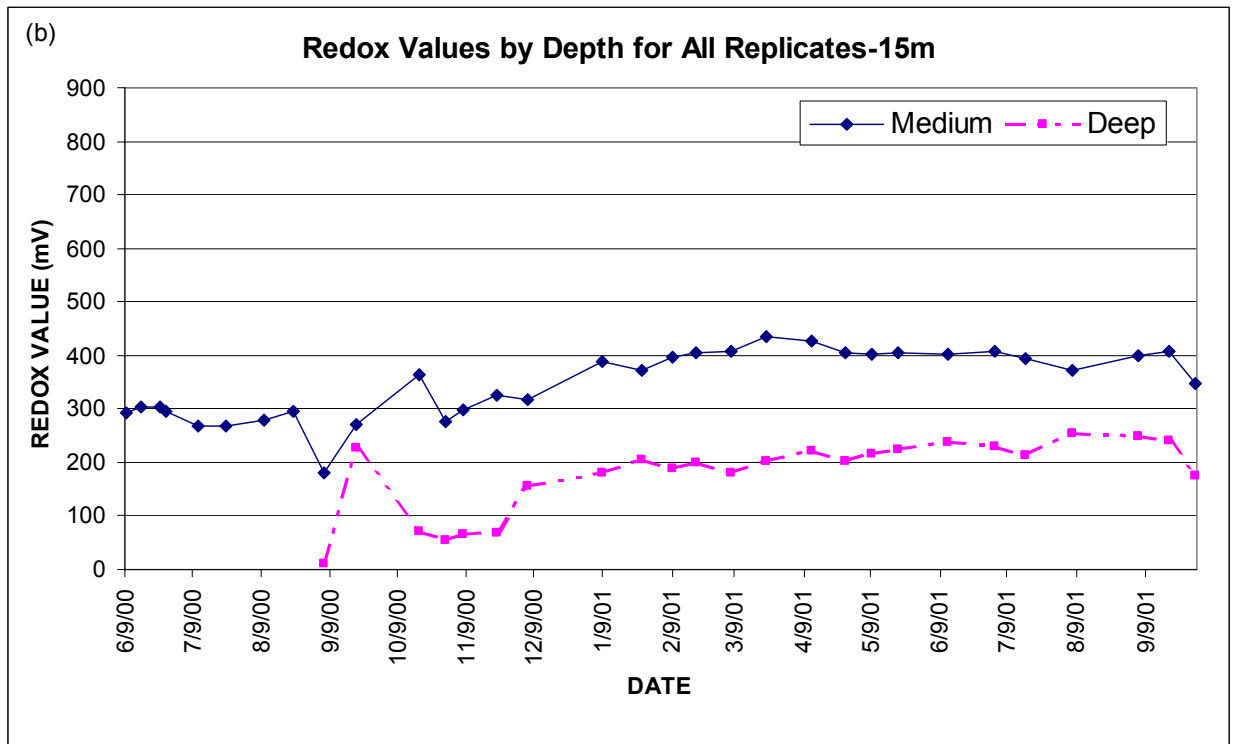
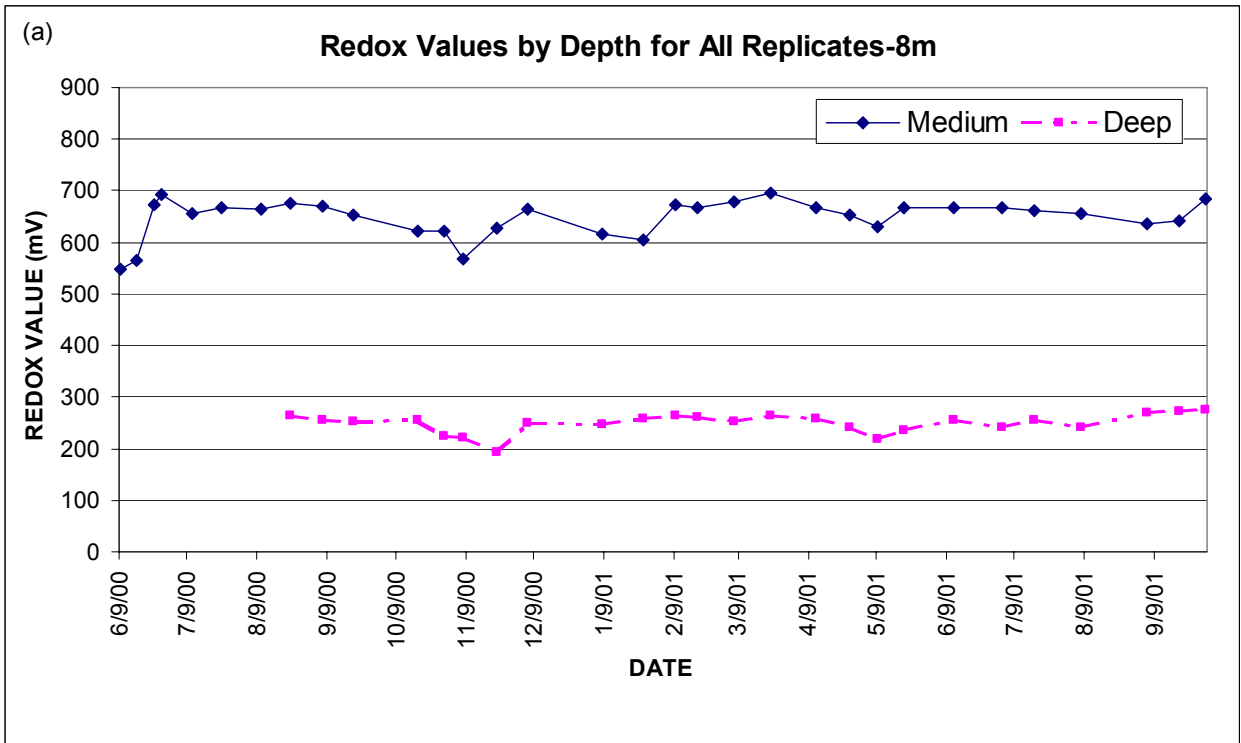


Figure 3.5 a,b Redox values over time for medium and deep depth for all replicates by buffer width

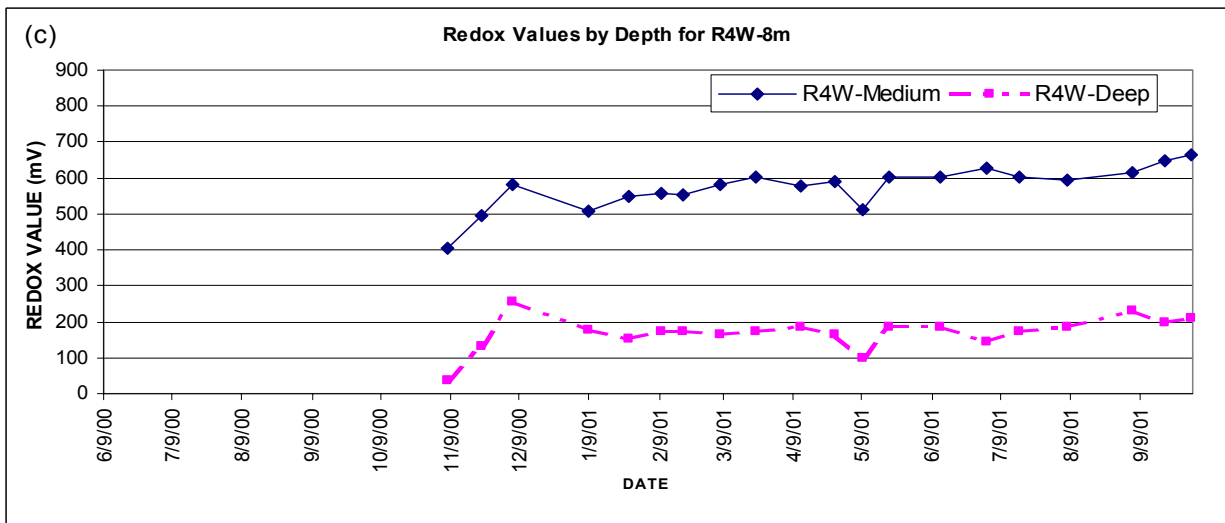
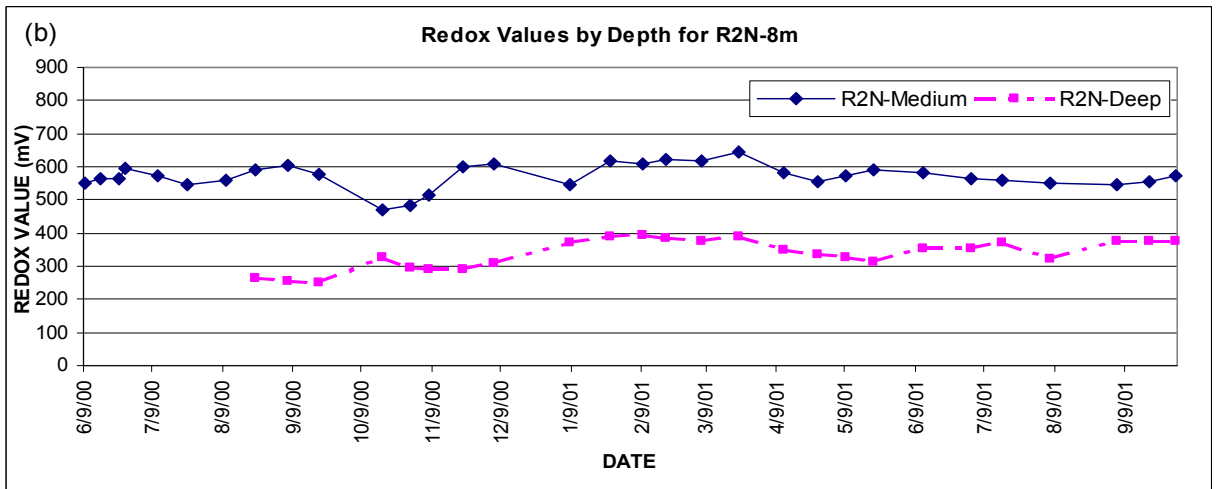
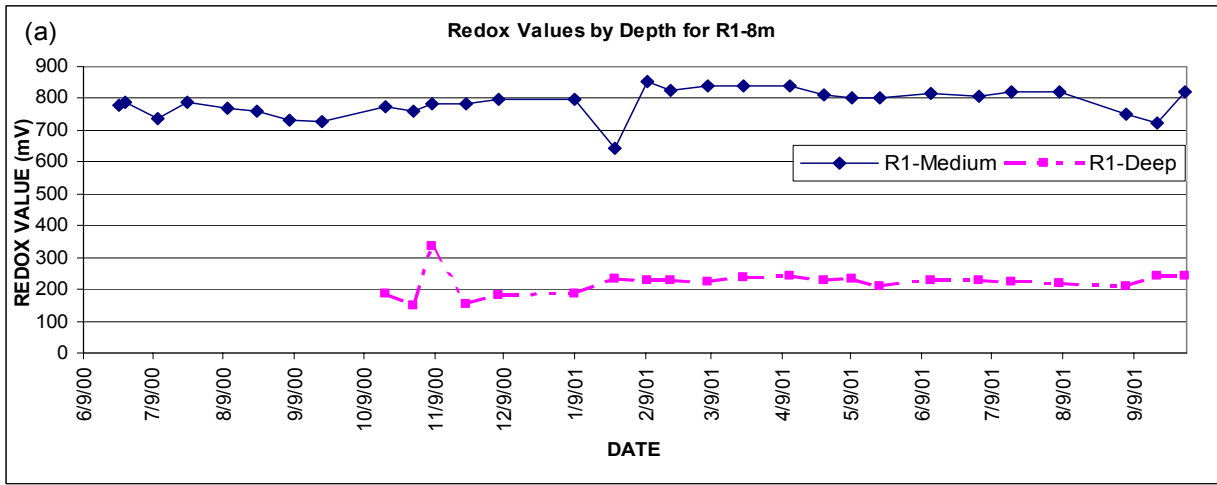


Figure 3.6 a,b,c Redox values over time for each 8m replicate by depth

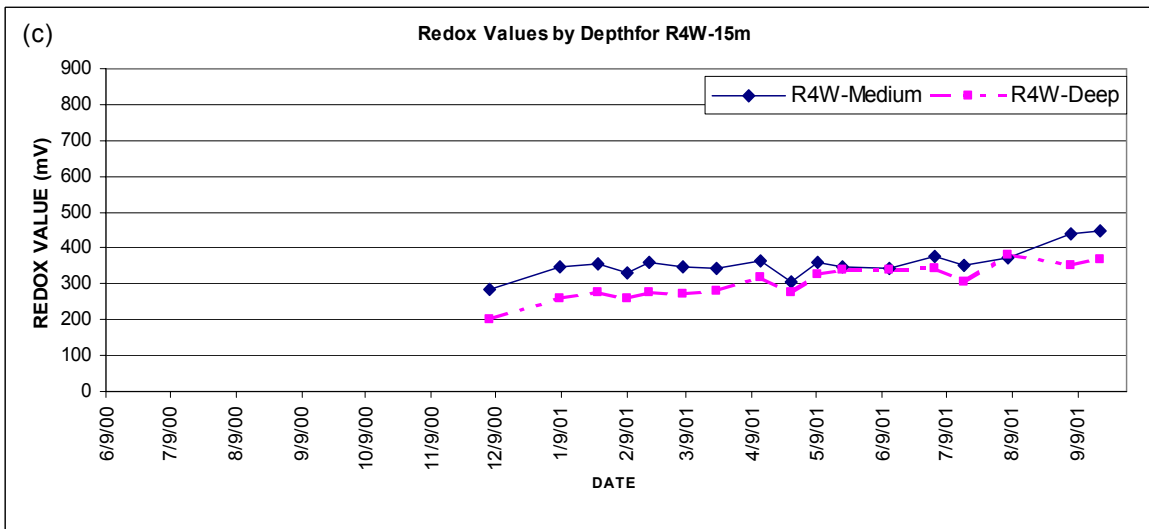
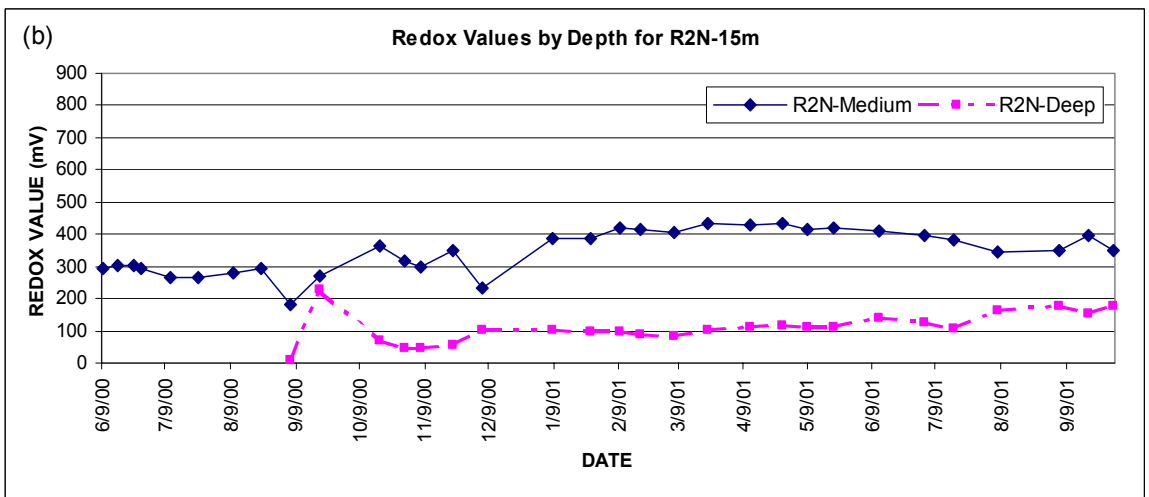
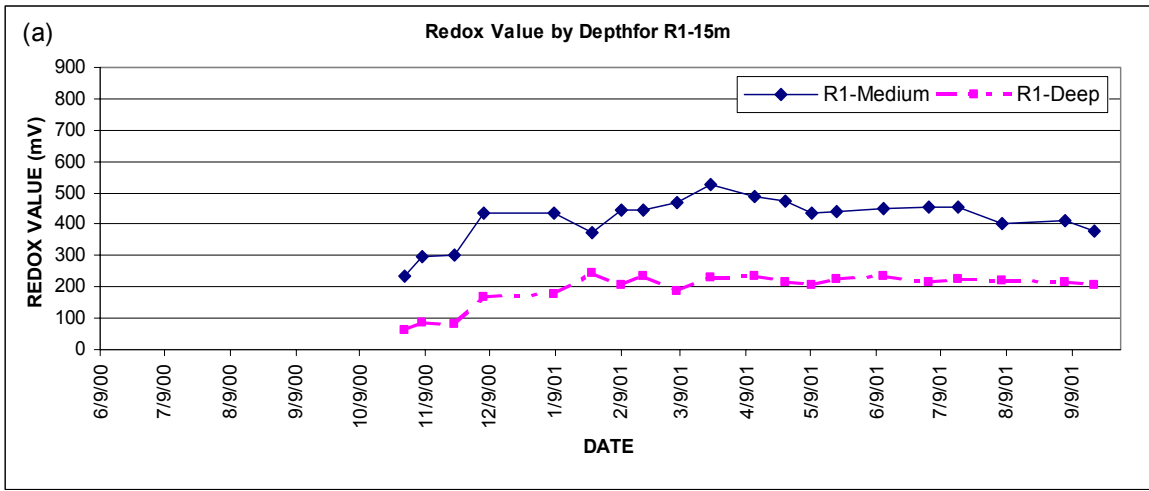


Figure 3.7 a,b,c Redox values over time for each 15m replicate by depth

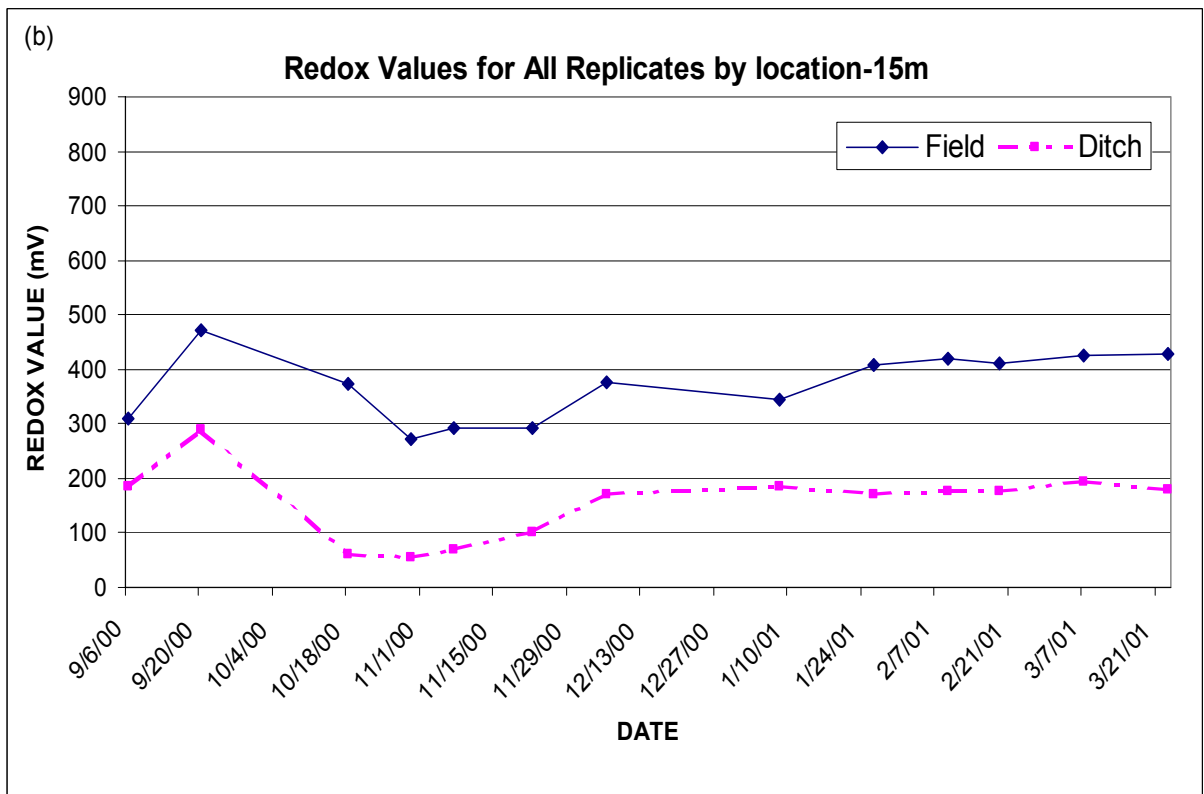
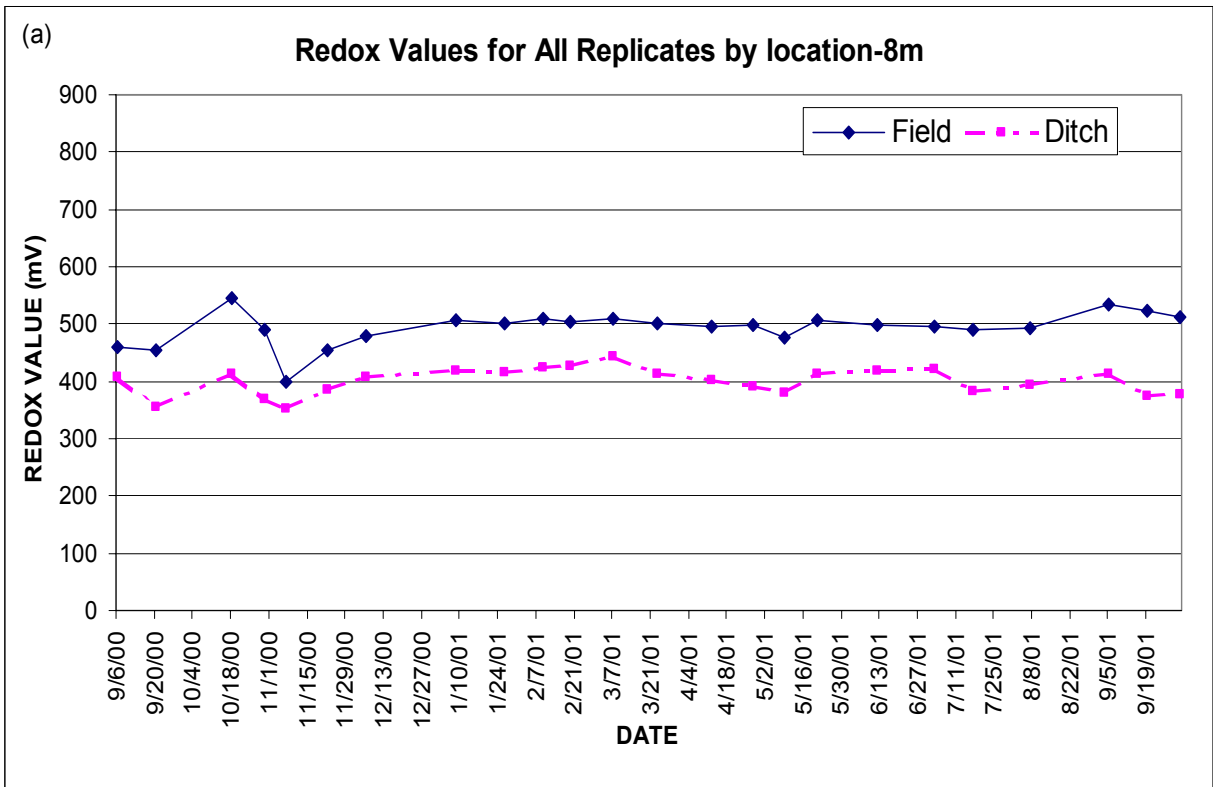


Figure 3.8 a,b Redox values over time for all replicates by location for each buffer width

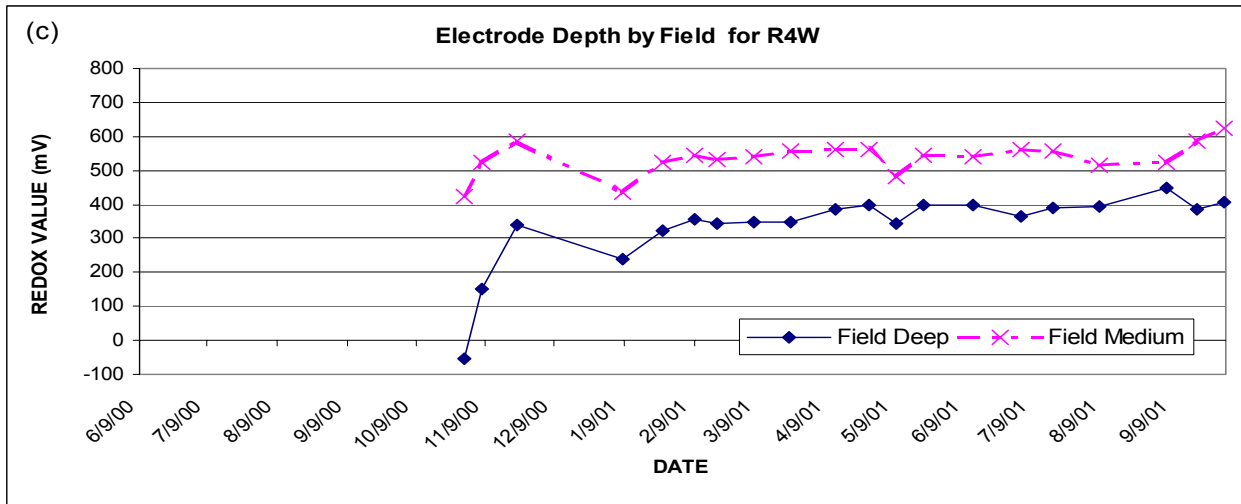
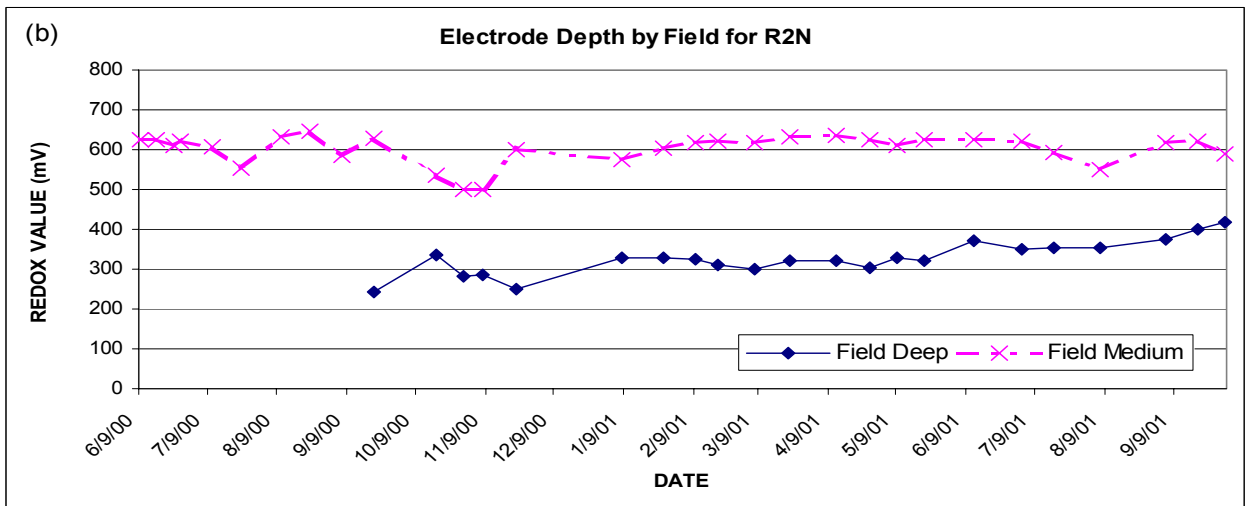
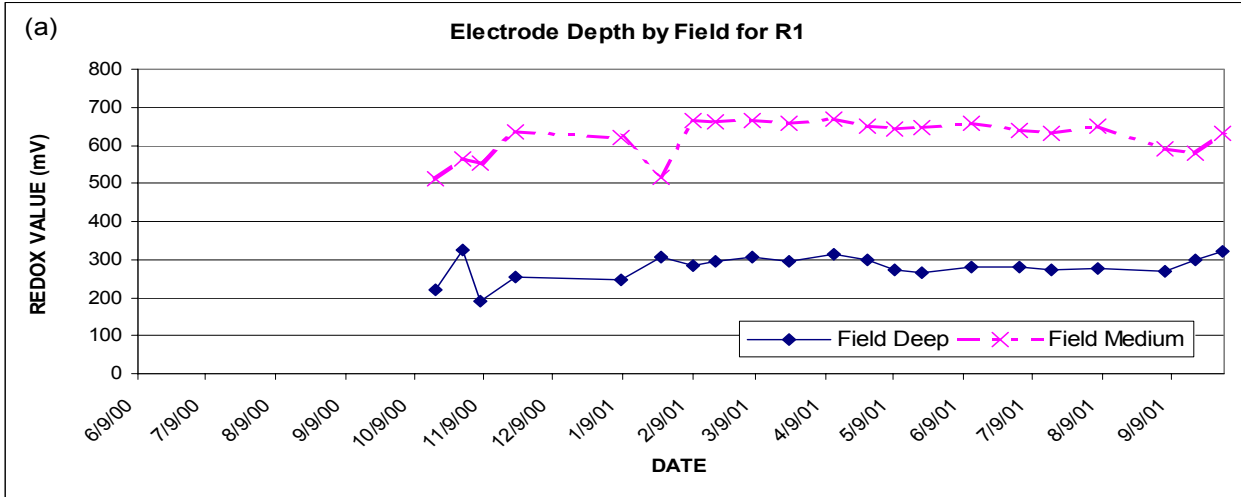


Figure 3.9 a,b,c Redox values over time for each replicate by field location

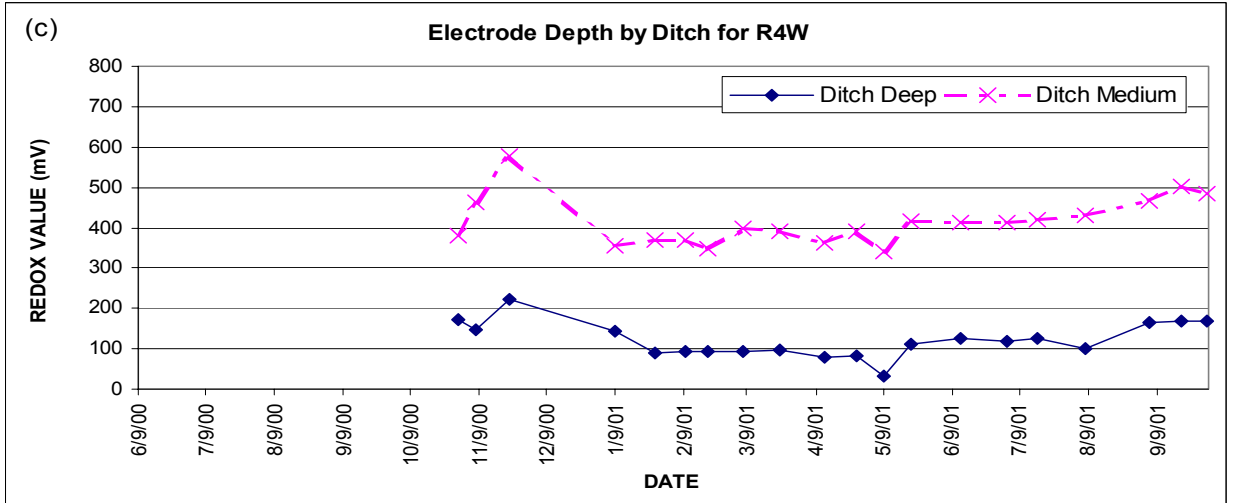
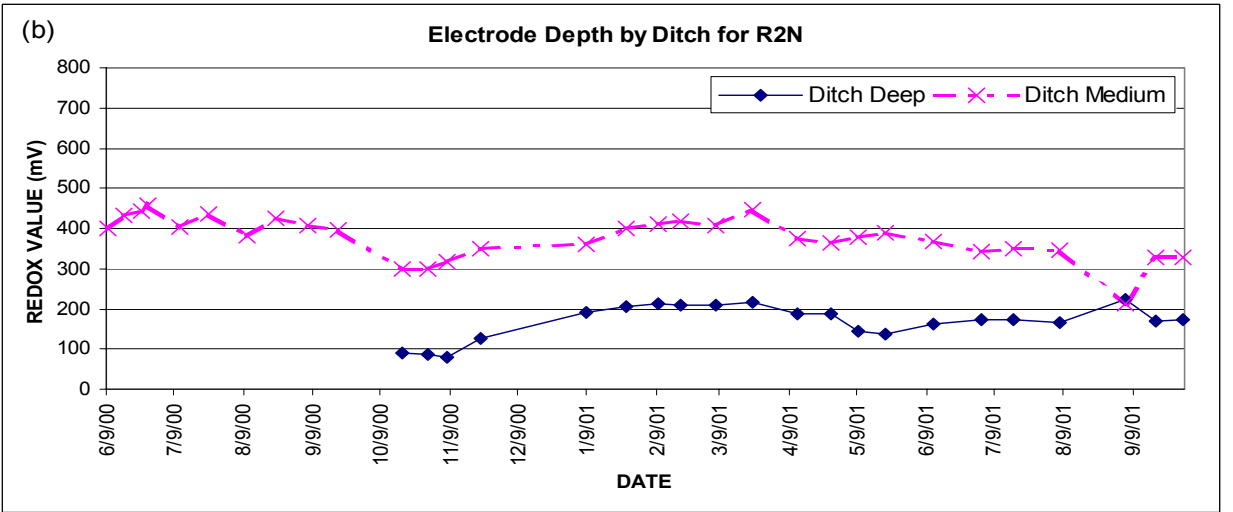
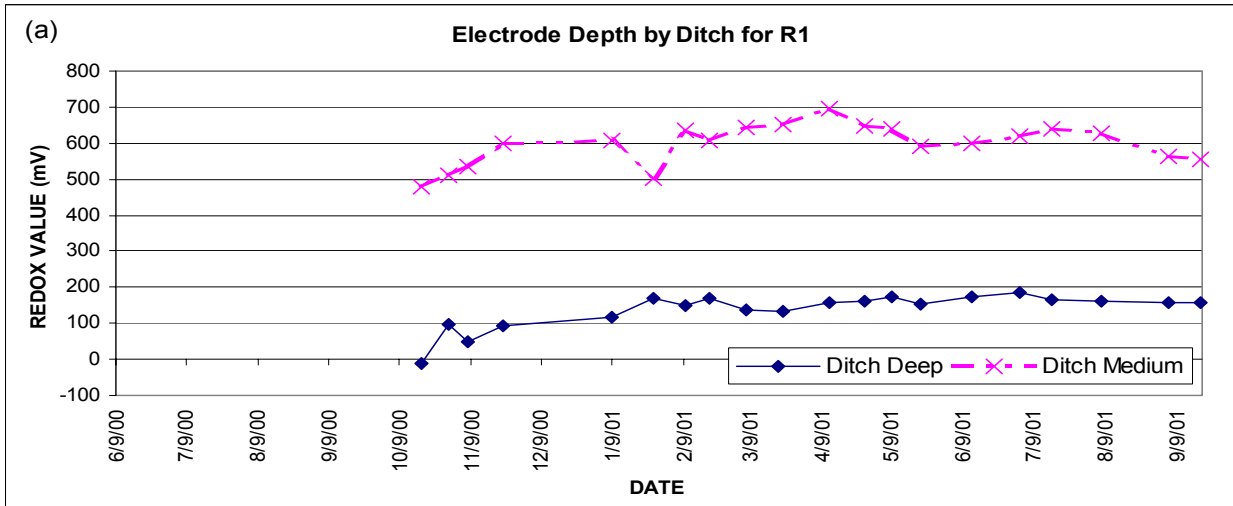


Figure 3.10 a,b,c Redox values over time for each replicates by ditch location

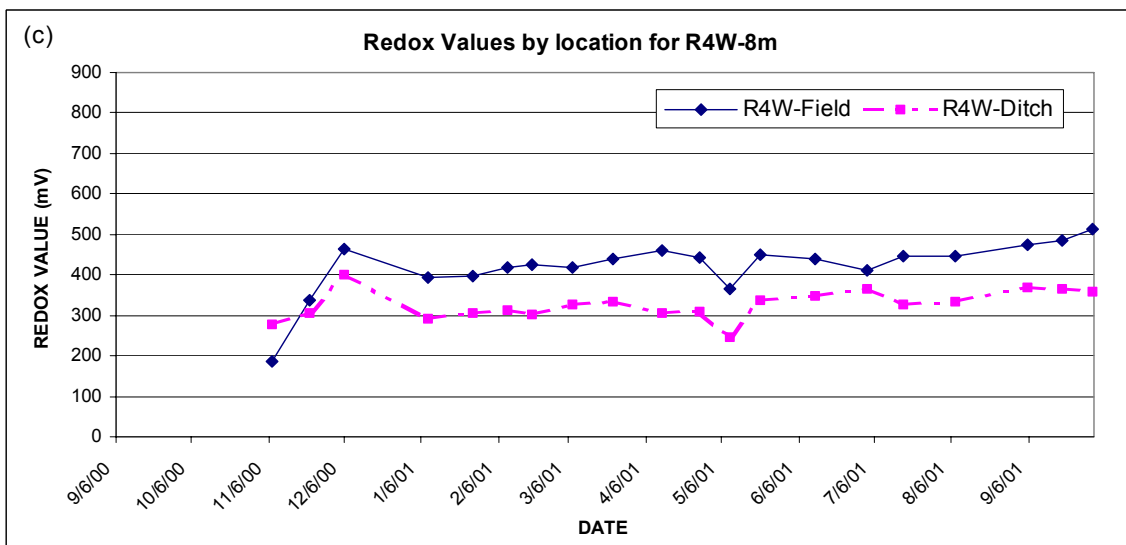
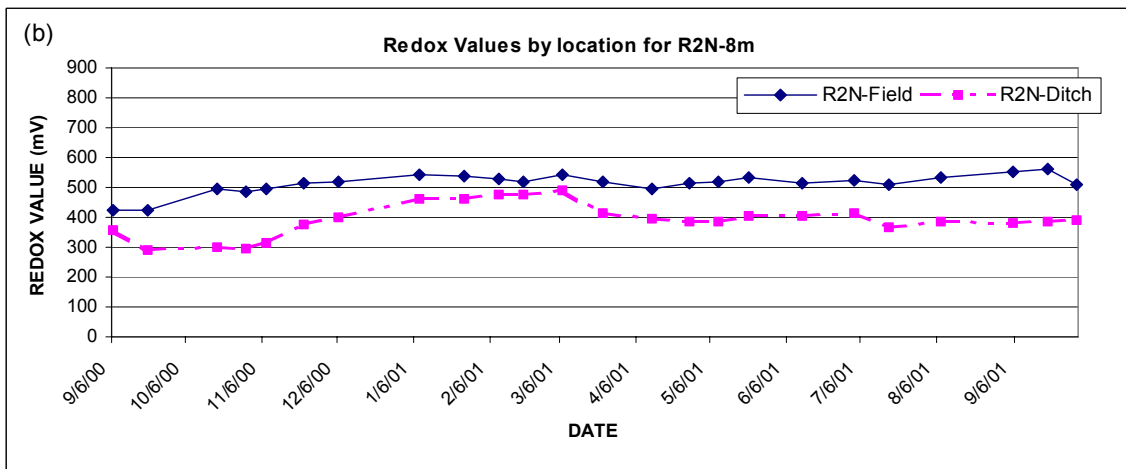
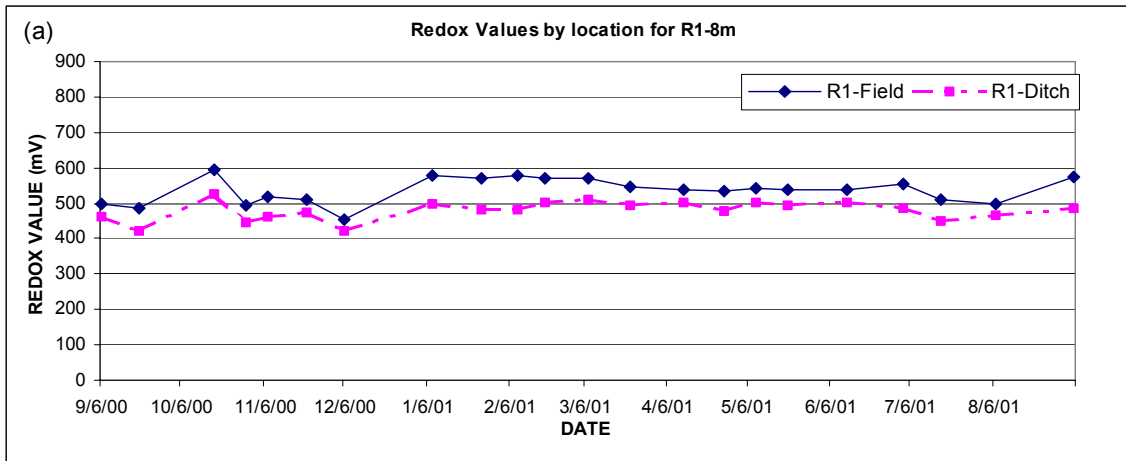


Figure 3.11 a,b,c Redox values over time for each 8m replicates by location

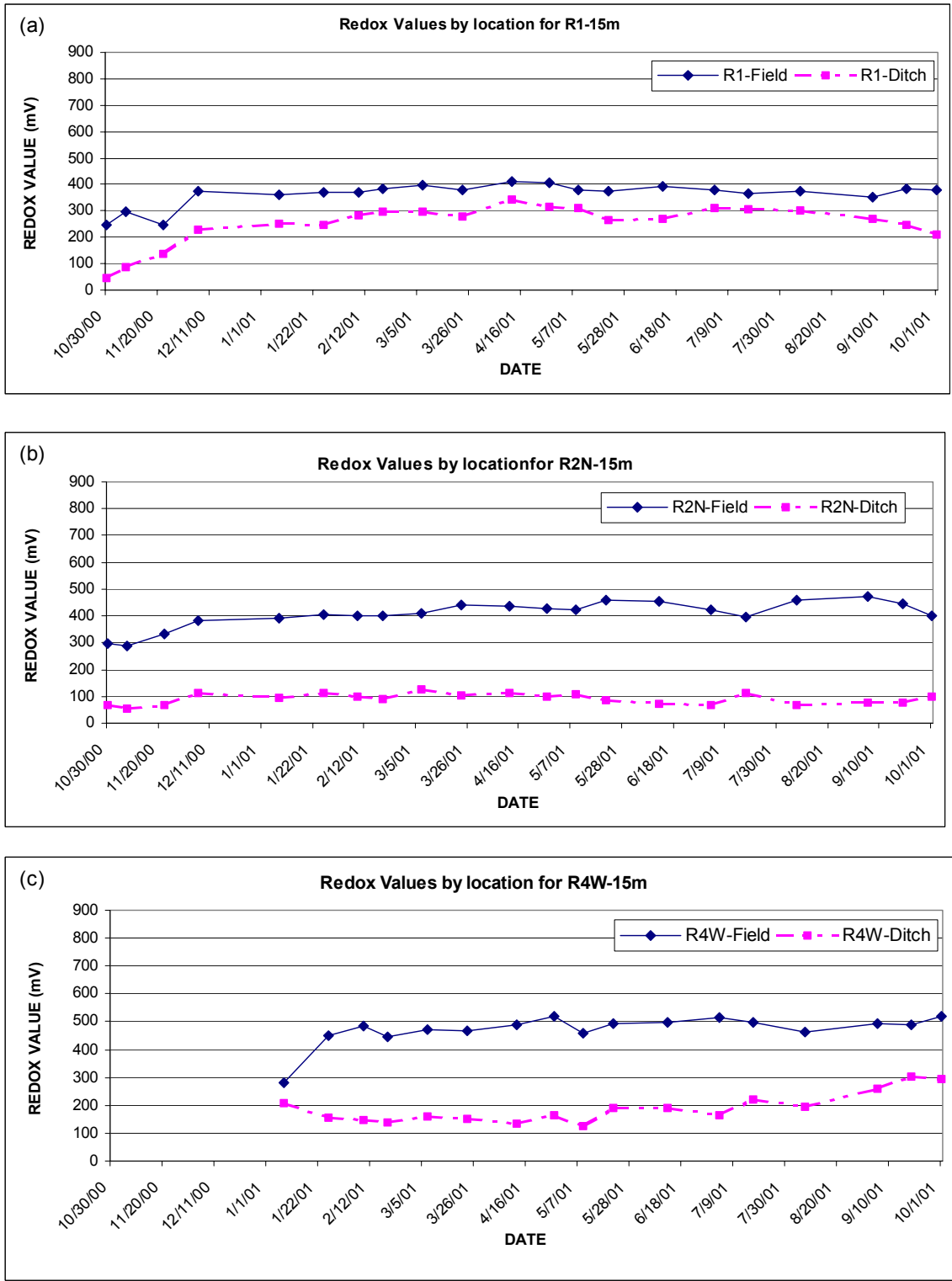


Figure 3.12 a,b,c Redox values over time for each 15m replicates by location

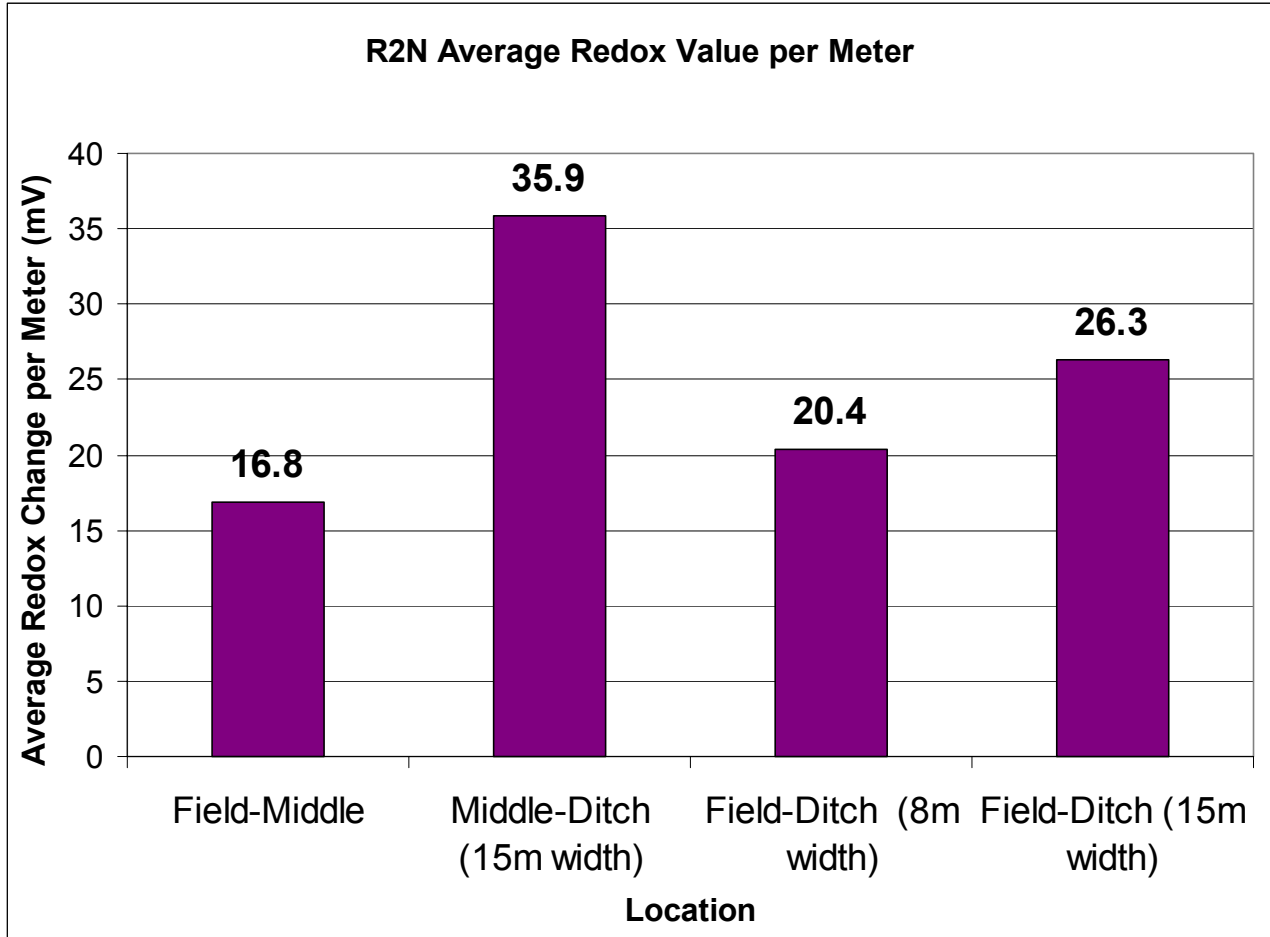


Figure 3.13 Average redox value per meter for R2N

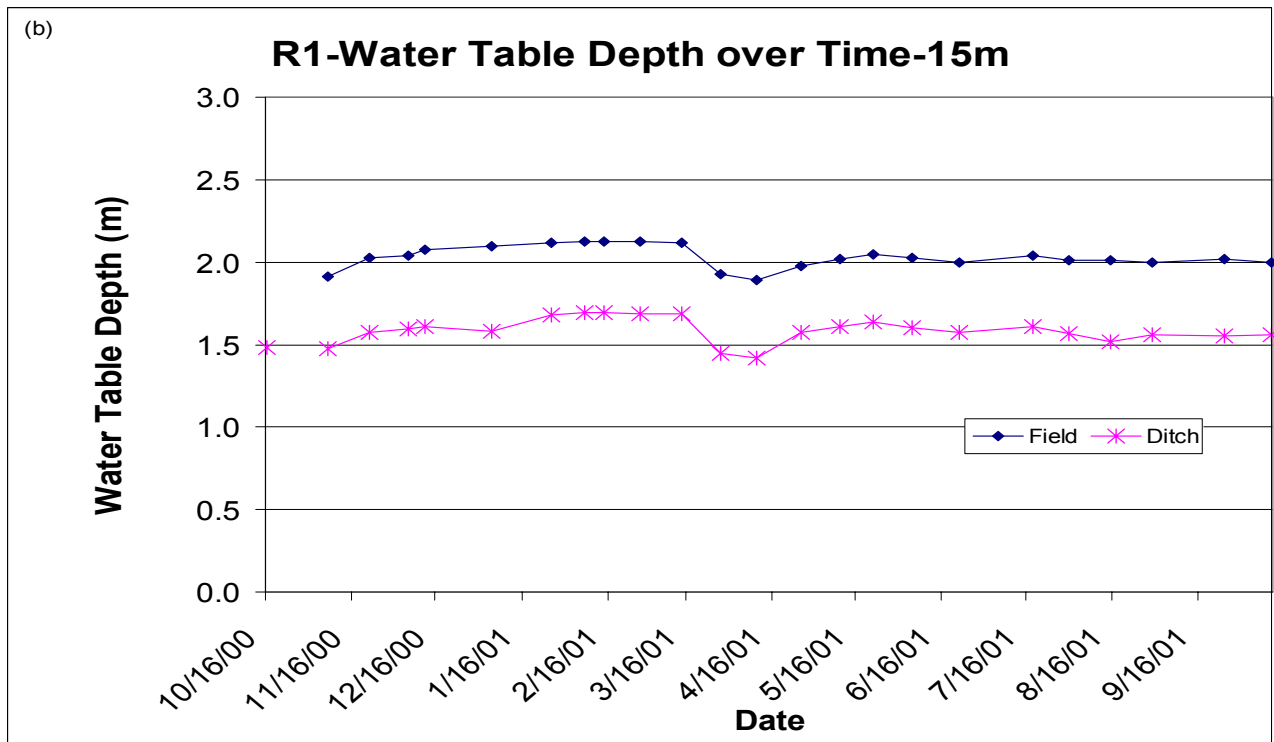
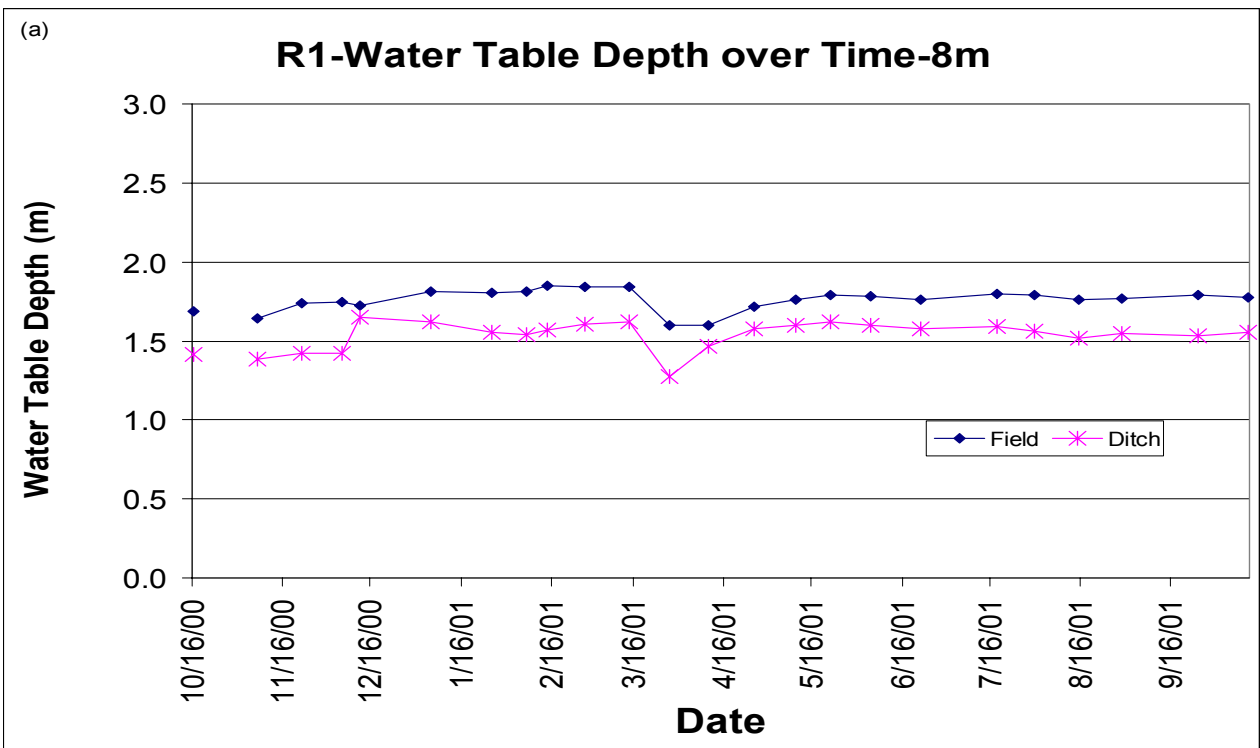


Figure 3.14a,b R1-Depth to the Water Table

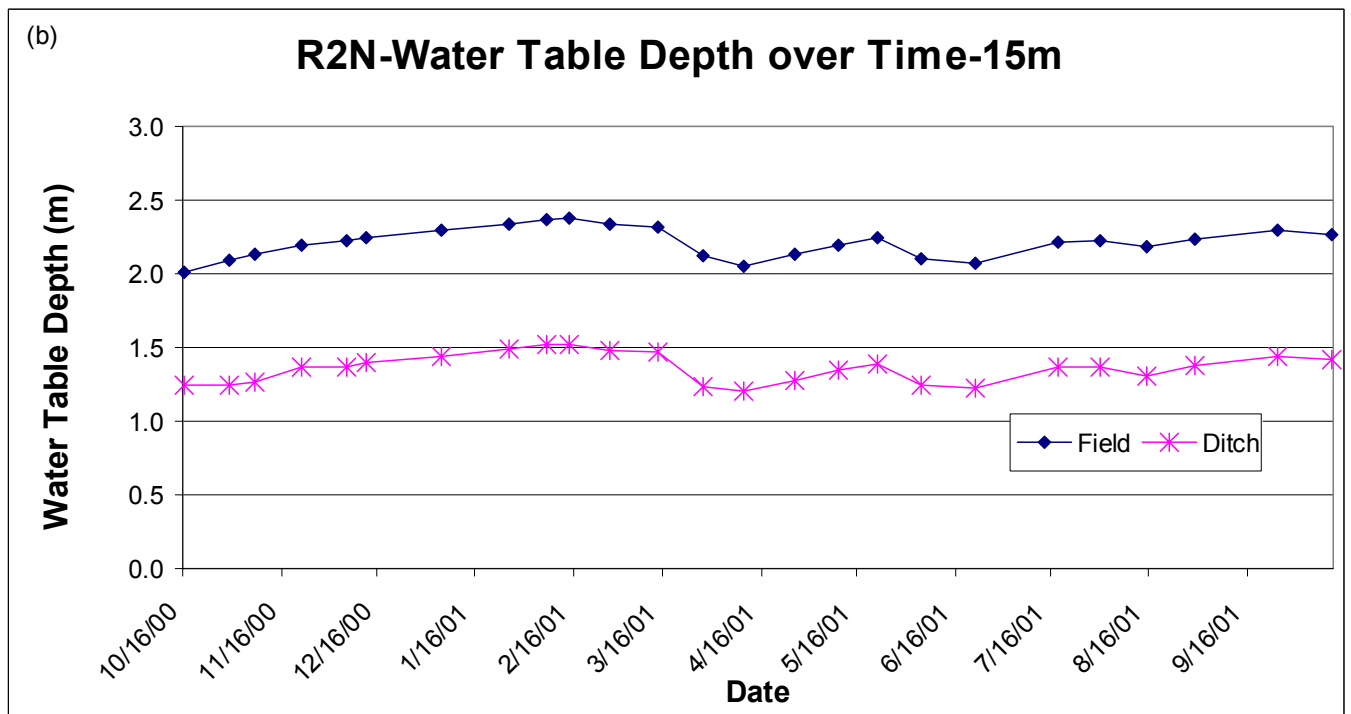
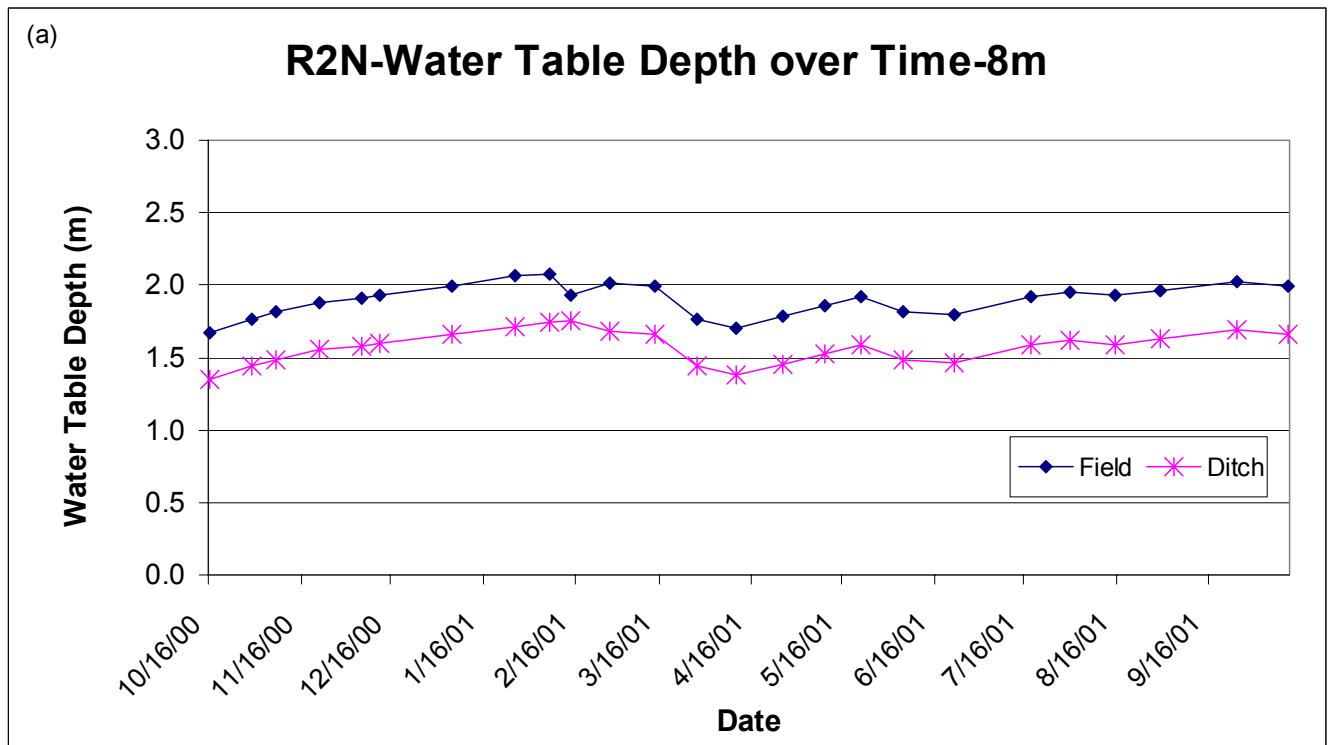


Figure 3.15 a,b R2N- Depth to the water table

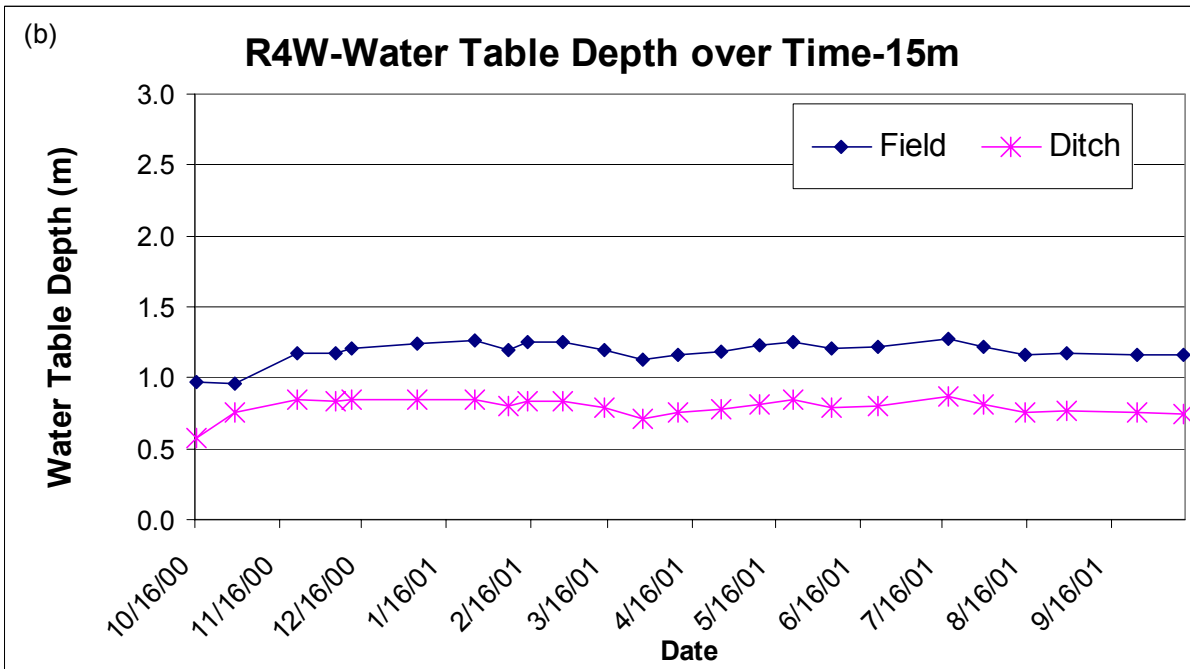
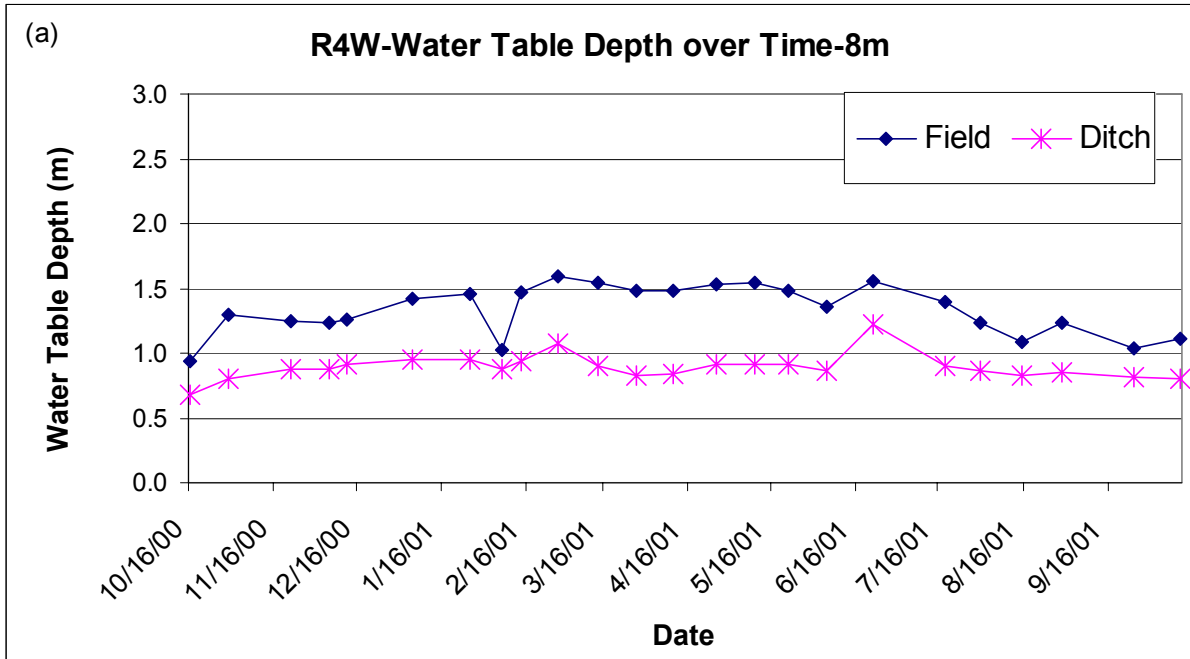


Figure 3.16 a, b R4W- Depth to the water table

## **Chapter 4 – Influence of Location, Depth, Width and Vegetation on Nitrate-Nitrogen Concentrations**

### **General Trends**

Nitrate-nitrogen concentrations are summarized in Table 4.1. The deeper wells had lower concentrations of nitrate-nitrogen relative to the medium depth wells, Figure 4.1. The water traveling to the deep wells has longer time with a higher chance for the nitrate-nitrogen to be intercepted and treated before reaching the groundwater or surface water. The redox values were also reduced at the deep depth, which would suggest denitrification, Figure 3.1.

The concentrations were lower along the ditch than at the field/buffer edge for both widths, Figure 4.2. Similar trends were observed for all plots (Appendix Figures 7, 8, 13, and 19). There were no seasonal variations; and differences between sampling dates were not significant (Appendix Figure 7). Vegetation was not significant when averaged over the entire replicate, Table 4.1, however a significance arose when broken down into individual landscape replicates Table 4.4.

**Table 4.1 -Variations in overall nitrate-nitrogen values as influenced by landscape position**

	R1	R2N	R4W	ALL
Depth				
Medium	5.3a	4.4a	8.4a	6.0a
Deep	3.0b	3.1b	4.7b	3.5b
Difference	2.3	1.3	4.3	2.5
Width				
8m	4.7a	4.2a	6.8a	4.8a
15m	3.5b	3.3b	6.4a	4.7a
Difference	1.2	0.9	0.4	0.1
Location				
Field	5.0a	4.9a	8.4a	6.0a
Ditch	3.2b	2.6b	4.8b	3.5b
Difference	1.8	2.3	3.6	2.5
Vegetation				
Fescue	4.0a	3.5a	6.0a	4.5ab
Switchgrass	--	3.9a	6.0a	4.9a
Trees	4.2a	3.8a	7.4a	5.1a
Native	4.5a	3.8a	7.0a	5.1a
No Buffer	4.0a	3.8a	--	3.7b

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison

### Nitrate Reduction

Figures 4.3 through 4.6 show nitrate concentration and percent decrease through the buffer for each replicate as a function of buffer width. Percent decrease was calculated by taking the difference in nitrate concentration between the field/buffer wells and the ditch wells; then dividing by the field/buffer well concentration and multiplying the result by 100. Figure 4.3 illustrates the percent decrease through the buffers for all replicates. Overall there was higher percent reduction in the deep wells than in the medium wells, and the largest decrease was in the deep wells of the 15m buffer.

Nitrate concentrations were highest on R4W, then R1, and lowest on R2N, and this was congruent to the previous study done by M. Dukes. R4W is located in a field that was used for pasture, as well as for swine lagoon effluent applications. Row crops were predominantly planted on R2N and R1. The field values for nitrate nitrogen for all replicates on the 15m buffer were higher than the field values of the 8m buffers. Even though the field/buffer edge was higher at the 15m buffer, the ditch concentration of nitrate-nitrogen was lowest for the 15m buffers in all cases. The 15m buffer had more nitrogen entering the buffer, and the concentration of the nitrate was reduced to lower than the 8m buffer at the ditch.

In general, nitrate concentrations were expected to decrease as shallow groundwater flowed through the buffers from the field/buffer edge to the ditch or stream. Nitrate concentrations decreased on R1, R2N medium wells and R4W as expected, Figure 4.4a,b, 4.5a and 4.6a,b, but the concentration in the deep wells on R2N in the 8m buffer increased at the ditch, Figure 4.2b. Redox values in the 8m buffer at the deep depth along the ditch on R2N were reduced which would suggest the ditch nitrate concentrations should be lower than the field concentrations Table 3.1. Higher nitrate-nitrogen concentrations near the ditch suggest that the nitrate maybe reaching the ditch wells through some means other than conventional shallow groundwater flow, Table 4.1.

## **Depth**

The average concentration of the deep wells was 3.5 mg/L and the concentration of the medium depth wells was 6.0 mg/L, Table 4.2, 4.3. This can be explained due to the longer flow paths and the increased time the water was in the saturated zone. Figures 4.3-4.6 show the deeper wells having higher percent decrease of nitrate-nitrogen than the medium wells.

The deep wells along the ditch exhibited lower concentrations than the corresponding wells in the field, Table 4.3. Redox values indicated reducing conditions along the ditch and at the deep depth for all replicates. R2N and R4W had redox values that were well below the threshold value for reduction to occur, while R1 had marginally reduced conditions.

**Table 4.2. Relationship between well depth and location relative to ditch on nitrate-nitrogen concentrations.**

Depth-Location Interaction	R1	R2N	R4W	Mean
Ditch Location				
Medium depth	5.0a	3.2a	7.1a	5.0a
Deep depth	1.3b	2.1b	2.5b	2.0b
Difference	3.7	1.1	4.6	3.0
Field Location				
Medium depth	5.6a	5.6a	9.8a	7.0a
Deep depth	4.6b	4.1b	7.0b	5.1b
Difference	1.0	1.5	2.8	1.9
Means by Location				
Ditch	3.2a	2.6a	4.8a	3.5a
Field	5.0b	4.8b	8.4b	6.0b
Mean landscape replicate	4.1	3.7	6.6	4.8

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison Test

### Width

Nitrate concentrations were significantly lower on R1 and R2N for the 15m buffers compared to the 8m buffers. This was consistent with redox values, which also indicated more reduced conditions in the 15m buffer. R4W did not exhibit significance between the 8m and 15m widths for the nitrate data Table 4.1 or the redox values, Table 3.1. Nitrate concentrations were further evaluated to determine buffer width and depth interactions, Table 4.5. The 15m width exhibited a significant difference at both depths, but the 8m width

did not. A greater percent decrease was found in the 15m buffers, relative to the 8m buffers Figures 4.3-4.6. Width was a factor affecting nitrate decreases through the buffer.

**Table 4.3. Relationship between well depth and buffer width relative to the location of wells on nitrate-nitrogen concentrations.**

	R1	R2N	R4W	Mean
Medium Depth				
Width = 8m				
Field	5.0a	4.8a	9.4a	6.3a
Ditch	4.5a	4.5a	8.7b	5.8b
Width = 15m				
Field	6.6a	6.5a	10.3a	7.5a
Ditch	5.6b	1.9b	5.6b	4.2b
Deep Depth				
Width = 8m				
Field	3.2a	3.9a	6.7a	4.4a
Ditch	1.3b	3.5a	2.5b	2.7b
Width = 15m				
Field	6.1a	4.8a	7.3a	5.9a
Ditch	1.3b	0.3b	2.6b	1.3b

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison Test

### Redox-Nitrate Trends

Figures 4.7-4.9 illustrate trends between redox values and nitrate-nitrogen concentrations by depth for each replicate. Depth to the water table on R1 was about 1.9m in the field and about 1.5m next to the ditch. The electrodes at the medium depth of 1.5m barely reach the water table Figure 4.10a. Because the electrodes barely reach the water table at the ditch and they do not reach the water table at the field, anaerobic conditions seldom occur. High redox values on R1 at the medium depth are evidence that anaerobic conditions did not develop, Figure 4.7a. The redox values were highly oxidic; around 800 mV, and the nitrate-

nitrogen concentrations were around 6.0 mg/L. The deep depth of the wells and the redox electrodes penetrate the water table and are about 1.0m below the water table at this site. Since the electrodes are saturated by water, anaerobic conditions are created at the deep depth facilitating denitrification conditions.

The effect of the water table is clearly shown in Figure 4.7b. The redox values are significantly lower, (~ 200 mV) and the nitrate-nitrogen concentrations were also lower (~2.0 mg/L) compared to the medium depth. R2N had a water table similar to R1, (Figure 4.10 b). The medium depth wells and electrodes did not penetrate the water table, except for along the ditch at the 15m buffer. The values of redox were high in the medium depth electrodes compared to the deep depth electrodes. The same trend of higher nitrate-nitrogen concentrations in the medium depth wells than in the deep depth wells was seen in R2N.

R4W had the highest water table of all three replicates. The electrodes and wells both penetrated the water table on this site. Thus, anaerobic conditions and saturation were likely. The redox values were high (~550 mV) even though the water table was above the electrodes. The explanation could be that the other factors affecting redox may not have been present, i.e., a lack of microbial activity or organic carbon at this particular site. However, at the deep depth, the redox values were around 200 mV and the nitrate-nitrogen concentrations decreased (Figure 4.9a,b).

## **Vegetation**

Vegetation did not significantly impact shallow groundwater nitrate-nitrogen concentrations. Mean nitrate concentrations for all replicates by width, depth, and vegetation are in Appendix Figure 4.1-4.16. Table 4.4 illustrates the interactions the vegetation had on

nitrate-nitrogen concentrations. Overall there was little difference between vegetation, but some statistical differences arose at the deep depth. The vegetation was not expected to impact the water quality at the deep depth since the roots of the plants had not likely reached this depth. Thus the statistical interactions noted in Table 4.4 are likely due to differences in soil properties and not vegetation type.

Redox values, nitrate-nitrogen concentrations, and water table depth are graphed for each 8m and 15m buffer replicate in Figures 4.11-4.16. There was relatively no change in nitrate concentrations for the medium wells on the 8m buffer on R1. The constant  $\text{NO}_3\text{-N}$  concentrations were consistent with the high redox values (between 700-850mV) for the medium depth. The water table was usually lower than the 1.5 m electrodes, thus anaerobic conditions were not likely met which is consistent with high redox values and nitrate concentrations. There was no distinguishable difference in concentration or redox between the no buffer plots and the other vegetation plots, although this replicate had relatively poor stands for some vegetation types so this observation is not surprising.

Contrary to the medium wells and electrodes, the deep electrodes and wells exhibited variability between the vegetation types, Figure 4.11. On this buffer, the no buffer exhibited the lowest nitrate concentrations as well as low redox values. There was a minute amount of nitrate on this plot, thus even if there were permanent vegetation on this buffer, its impact would be negligible since there was little nitrate at the field edge. Overall, nitrate concentrations were consistent with redox values except for the fescue plot where nitrate declined substantially although redox values were above the threshold. Generally, now nitrate concentrations were associated with low redox values.

On R1, there were modest declines in nitrate concentration through the 15m buffer at the medium depth. The redox values were at or above the reducing threshold, so nitrate concentrations were generally consistent with redox with one exception. Redox values for the tree plot were below the reducing threshold while nitrate concentrations were high. There were no significant differences among vegetation types.

The deep wells and electrodes in the 15m buffers exhibited greater differences among vegetation types than in the 8m buffers, Figure 4.12. The electrodes and wells penetrated the water table at roughly 2m below the surface. All four plots had high nitrate concentrations at the field and lower nitrate concentrations at the ditch. On three plots (native, fescue, and trees), the lower nitrate concentrations were consistent with reducing conditions observed at the ditch. On the no buffer, the decline in nitrate was accompanied by redox values above 600 mV at the ditch, thus denitrification was not likely the cause for the nitrate decline.

The medium depth electrodes and wells in the 8m buffers on R2N barely penetrated the water table at the ditch, and they did not reach the water table at the field/buffer edge, Figure 4.13. The redox values were high by the ditch, except for the native vegetation, which was under 100 mV. There was little difference in the percent decrease across all vegetation types in this 8m buffer. Overall, results were consistent with constant NO<sub>3</sub>-N concentrations associated with high redox values and a lack of reducing conditions.

At the deep depth, the 8m buffer on R2N wells and redox electrodes were approximately 1m below the top of the water table and thus within a saturated zone. There was little variability in the nitrate concentrations across vegetation types except for the switchgrass, which had low nitrate at the field. The redox values on all plots, except fescue, were in the marginal range for denitrification. Even though the electrodes were in the

saturated zone, reduced conditions had not developed in these plots and as a result, nitrate concentrations did not decline from field to ditch.

The 15m buffers on R2N all exhibited nitrate nitrogen concentration decreases across the buffers except for the native vegetation, Figure 4.14. The small decrease for the native vegetation at the medium depth was consistent with the high redox values above the threshold for denitrification. Nitrate concentrations were consistent with redox values at 8 of the 10 well locations. There was no significant difference in vegetation except for the native plot. The no buffer plot also performed as well as the vegetated plots in terms of nitrate concentration decline. The electrode depth was not saturated at the field but was saturated at the ditch. Three plots were reduced at the ditch while two (native and no buffer) were not. There was no obvious explanation for these differences other than possibly localized soil variability. The low redox values at the ditch were associated with finer textured soil, (Kunickis, 2000).

The deep electrodes and wells along the 15m buffer on R2N all exhibited high percent decreases in nitrate concentrations through the buffer (Figure 4.14). The redox values at the ditch were all well below the value needed for denitrification to occur. The high percent reduction in nitrate concentrations can be linked to denitrification due to the low redox values, presence of organic carbon at this depth, and the electrodes were well into the saturated zone.

The water table on replicate R4W was the closest to the soil surface of the replicates (Figure 4.15). The redox electrodes and the wells were routinely saturated, except for a short period of time at the field location of the 8m buffers. Redox electrodes were not installed in the “no buffer” treatment due to the destructive nature of the cattle, but there were wells installed in the “no buffer” plots.

The redox values for R4W 8m buffer plots at the medium depth were oxic with redox values approximately 500-750 mV, Figure 4.15. There was little change in nitrate concentrations through the buffers at the medium depth Figure 4.15. Infact nitrate concentrations increased slightly on three of the five treatments. Vegetation had little effect on nitrate concentrations since the concentrations of nitrate on the no buffer plots were not different than on the other vegetation types.

Nitrate concentrations decreased from the field to the ditch for the 8m buffers at the deep depth except for the no buffer plot (Figure 4.15). The redox values at the ditch on fescue, trees, and switchgrass were well below the threshold value for denitrification. The nitrate concentrations for the corresponding locations decreased dramatically, usually around 80%. Although nitrate concentrations increased from the field to the ditch on then o buffer plot, concentrations were relatively low at both locations and were not significantly different from the other vegetation types.

The 15m buffer plots on R4W all exhibited decreases in nitrate concentrations at the medium depth (Figure 4.16). The wells and electrodes were well in the saturated zone for both the medium and deep locations (Figure 4.16). The redox values for the ditch location for native, fescue, and switchgrass were below the threshold value where denitrification occurs. Nitrate concentrations dropped at all five ditch locations including the tree treatment where redox values were above the denitrification threshold and the no buffer treatment.

Nitrate concentrations decreased from the field to the ditch on the 15m buffers on R4W (Figure 4.16). The highest decrease was in the switchgrass plot, which corresponded to the lowest redox value at the ditch. Plot to plot differences in nitrate concentrations were consistent with difference in redox values. Again the no buffer plot was not different from the

other vegetation plots (Figure 4.16). This suggests that vegetation did not affect nitrate reductions in R4W.

**Table 4.4. Influence of vegetation on nitrate-nitrogen concentrations**

Vegetation interactions	R1	R2N	R4W	Mean
Ditch				
Fescue	3.2a	2.2a	3.9a	3.1a
Switchgrass	--	2.8a	4.6a	3.7a
Trees	2.7a	2.6a	5.2a	3.5a
Native vegetation	3.5a	3.1a	5.6a	4.1a
No buffer	3.5a	2.5a	--	3.0a
Field				
Fescue	4.8ab	4.9a	8.2a	6.0ab
Switchgrass	--	4.9a	7.4a	6.1a
Trees	5.8a	5.1a	9.7a	6.8a
Native vegetation	5.7a	4.4a	8.4a	6.3a
No buffer	3.7b	5.1a	--	4.5b
Medium depth				
Fescue	4.9a	4.3a	7.4a	5.5ab
Switchgrass	--	4.8a	8.6a	6.7a
Trees	6.0a	4.0a	10.3a	6.7a
Native vegetation	5.2a	4.7a	7.6a	5.9ab
No buffer	5.0a	4.3a	--	4.6b
Deep depth				
Fescue	3.1ab	2.7a	4.6ab	3.4ab
Switchgrass	--	3.0a	3.2b	3.1b
Trees	2.5b	3.7a	4.6ab	3.6ab
Native vegetation	3.9a	3.0a	6.5a	4.4a
No buffer	2.3b	3.3a	--	2.8b
8m buffer				
Fescue	3.8ab	4.4a	7.5ab	5.3ab
Switchgrass	--	3.6b	5.0b	4.3bc
Trees	3.4b	4.6a	6.0b	4.6ab
Native vegetation	4.6a	4.2ab	8.8a	5.8a
No buffer	2.2c	4.2ab	--	3.2c
15m buffer				
Fescue	4.1a	2.7a	4.5b	3.8b
Switchgrass	--	4.1a	6.8ab	5.5a
Trees	5.0a	3.1a	8.9a	5.6a
Native vegetation	4.4a	3.3a	5.3b	4.4ab
No buffer	5.5a	3.4a	--	4.3ab

Values within groups (depth, width, location, vegetation) followed by the same lower case letter vertically are not significantly different at the 5% level by the Tukey Multiple Comparison Test

## Nitrate Trends Over Time

Nitrate-nitrogen concentrations for the period July 1998 to June 2000 (Dukes 2000) were compared to the values reported herein to evaluate trends over time, Figure 4.17 a,b,c. Nitrate-nitrogen concentrations on R1 remained fairly consistent over the 3.5-year period since buffers were established. Land use upslope of the buffers on R1 has remained fairly constant, so after more than 3-years, the buffers have not affected nitrate concentrations on this replicate. Nitrate concentrations on R2N, Figure 4.17b, dropped from 12 mg/L for the medium wells and 6 mg/L for the deep wells and approximately 4 mg/L and 3 mg/L for the medium and deep wells respectively over the 3.5-year period. This decrease in nitrate-nitrogen concentration may be influenced by the presence of the buffer at this location. However, land use on half of R2N also changed resulting in less nitrogen being applied to fields upslope of the buffer which might also explain the lower concentrations through the buffer.

A decrease in nitrate-nitrogen concentration was also observed on R4W, Figure 4.17c. The medium depth well decreased from approximately 13mg/L to 7 mg/L and the deep wells had a decrease from around 9 mg/L to 4 mg/L. This change in concentration is gradual over the three-year time period, which again could be attributed to the effect of the buffer. Land use and nitrogen fertilization upslope of R4W remained fairly constant over the period. The vegetation is better established on this replicate and thus the effect the vegetation has on water quality could be starting to show in this replicate. But in order to better quantify the effect of the buffer and vegetation on water quality data collection needs to continue.

## Nitrate Summary

Nitrate nitrogen concentrations decreased with increasing depth and generally decreased from the field to the ditch. The decrease in concentration with increasing depth can be attributed to denitrification since the redox values were well below the reducing range for nitrate at the deeper depths. The redox values were an indication of where denitrifying conditions existed. Denitrification would be indicative of the primary mechanism of lower concentration of nitrate-nitrogen when low redox values occurred in the same area where low nitrate concentrations were measured.

In general, variations in nitrate-nitrogen concentration were consistent with redox measurements. There were a total of 104 pairs of observations (26 vegetative plots X 2 depths X 2 locations) across the three landscape replicates. Nitrate nitrogen concentrations were correlated to redox values for approximately 85% (88 or 104) of the paired values. Where redox values were above 350 mV, nitrate concentrations remained fairly constant across a given plot at a given depth. Where redox values dropped below 350 mV, nitrate concentrations tended to decrease. While the expected relationship between nitrate concentration and redox was observed 85% of the time, exceptions were observed in 15% of the cases. For some of these, nitrate concentrations remained constant although redox values were well below 350 mV. In other cases, nitrate concentrations dropped while redox values were above the threshold for denitrification. Overall, there was strong evidence that declines in nitrate concentration were correlated to denitrification; however, there were cases where declines in nitrate concentration were due to some other mechanism, most likely dilution (Dukes, 2000).

Nitrate nitrogen concentration reductions were generally higher on the 15m buffers compared to the 8m buffers. This suggests the 15m buffers were more effective at reducing nitrate nitrogen concentrations. The wider buffer allows for longer residency time for the shallow groundwater in the soil profile where it has a higher chance of being intercepted and treated.

Overall, vegetation type had little impact on nitrate-nitrogen concentrations. This was not surprising since the vegetation is relatively young and has not had an opportunity to establish rooting at the deeper depths where denitrification appears to be occurring. The vegetation would not likely be a factor at the deep depths, since the roots do not reach the depth of 3.0m. Over a period of time, the vegetation may have a greater impact on the water quality, due to the increase in organic carbon that would be carried to the deeper depths by water movement through the soil profile. After 3.5-years of study, the vegetation has not had a significant effect on nitrate concentrations. The effect of the buffers over the three-year period may be becoming clearer, but more data collection is needed in order to fully assess the effectiveness of the riparian buffers at this site.

## Chapter 4 Figures

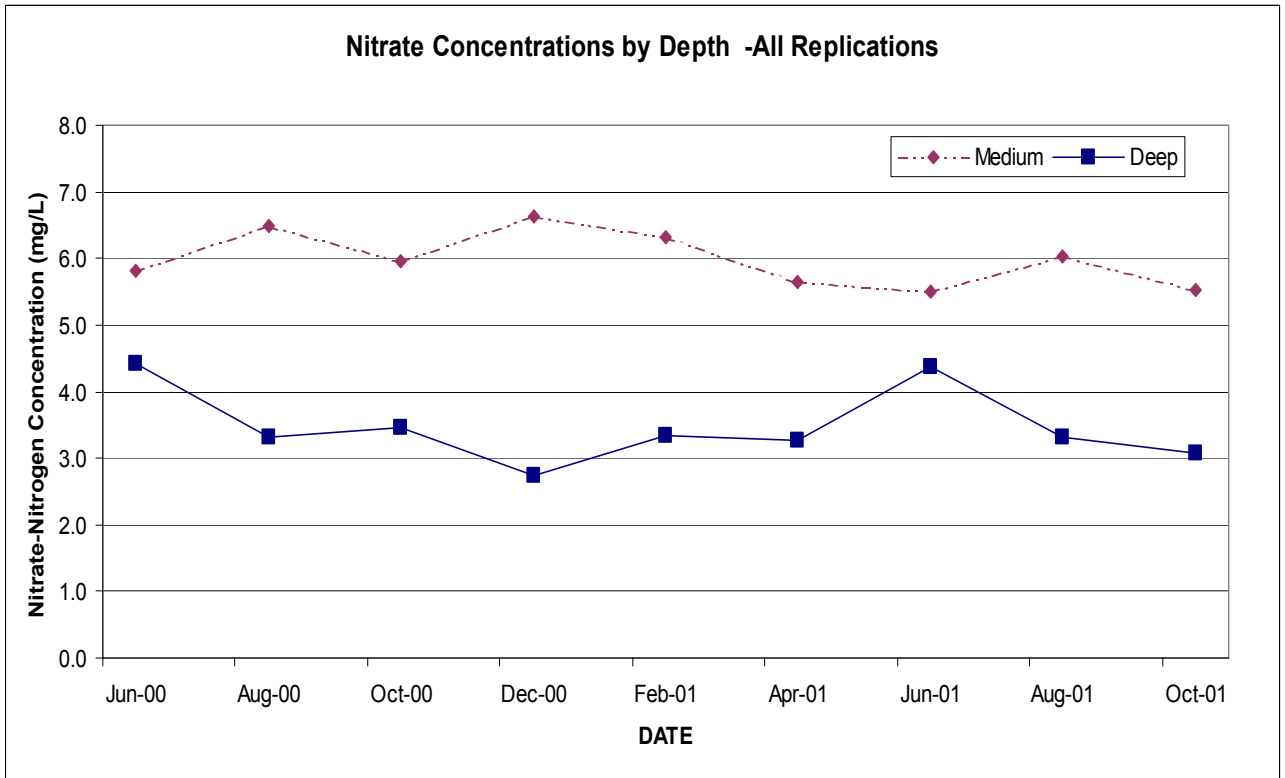


Figure 4.1 Nitrate concentrations for all replicates by depth of well

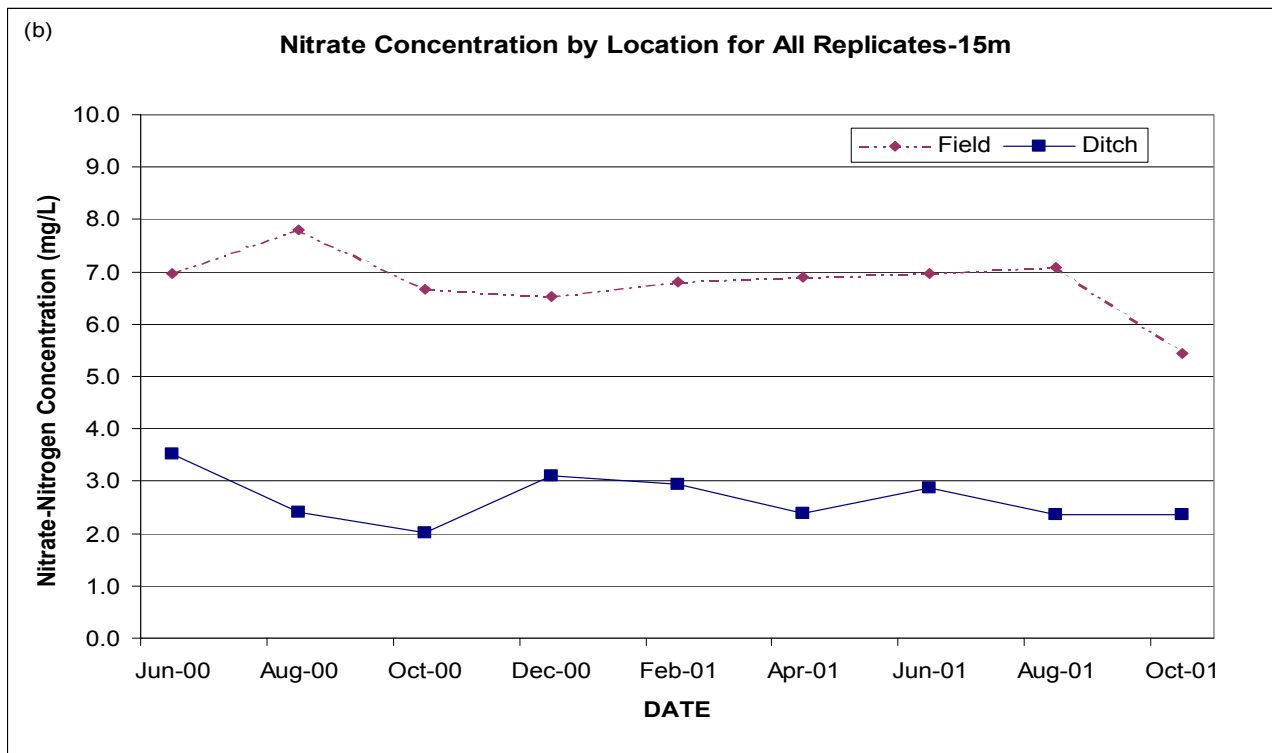
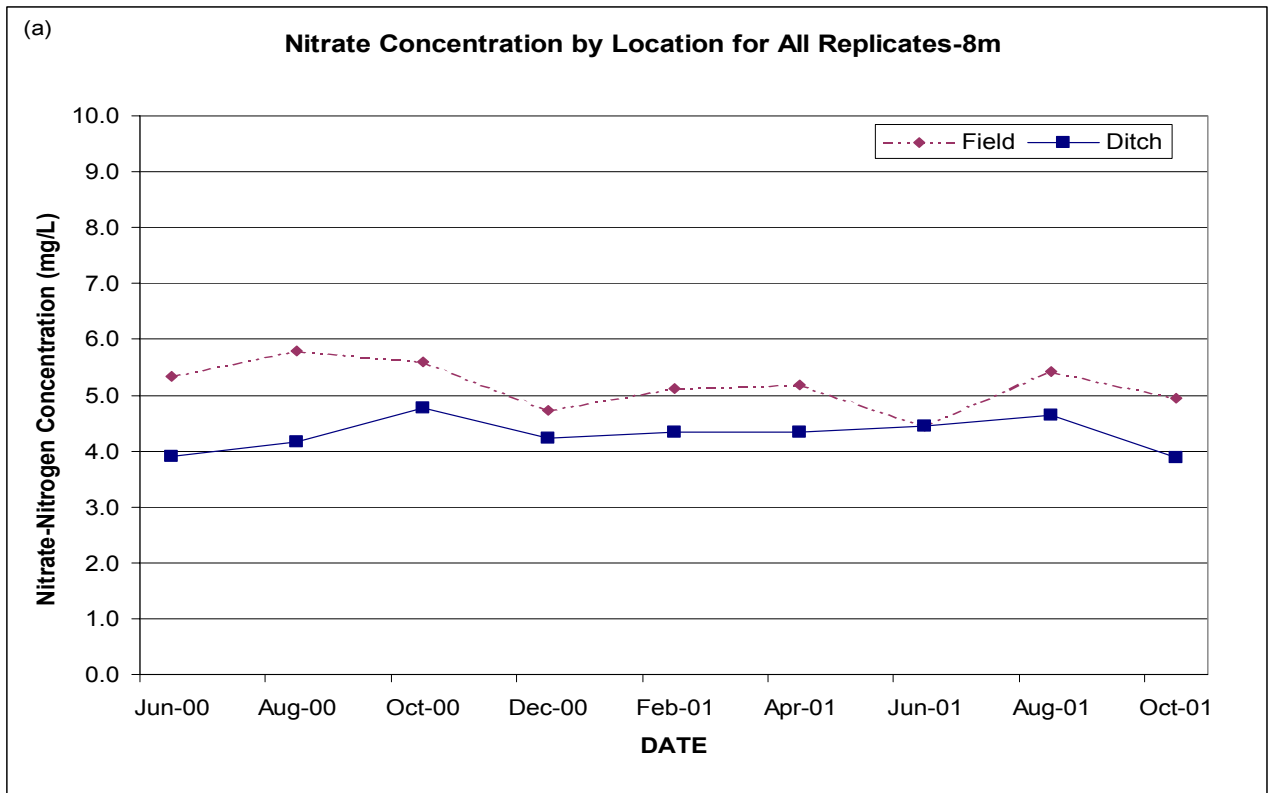


Figure 4.2 a, b Nitrate concentrations for all replicates by location

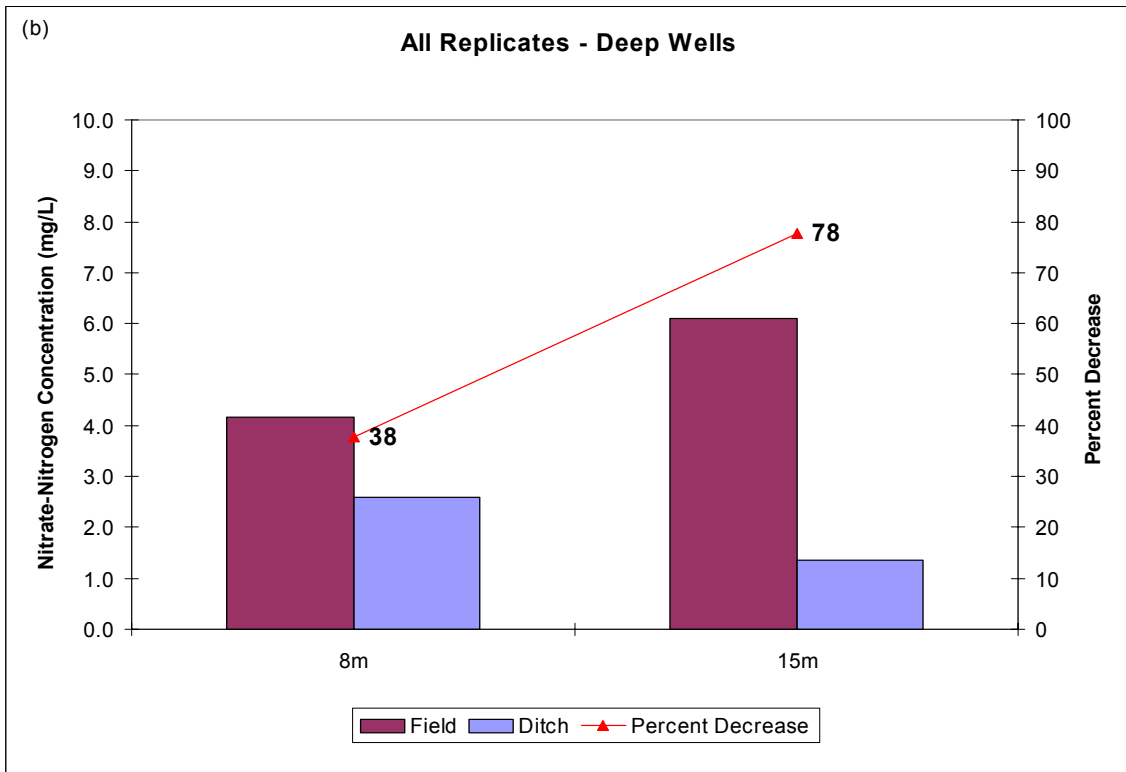
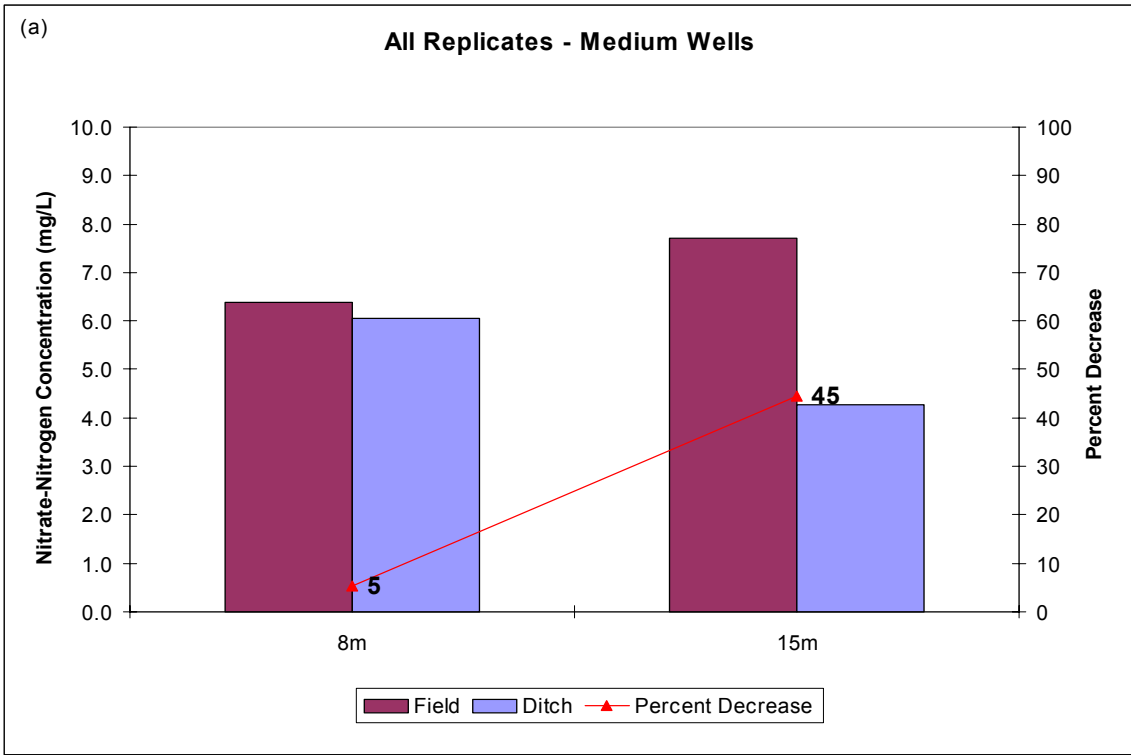


Figure 4.3 Percent decrease across buffers for all replicates

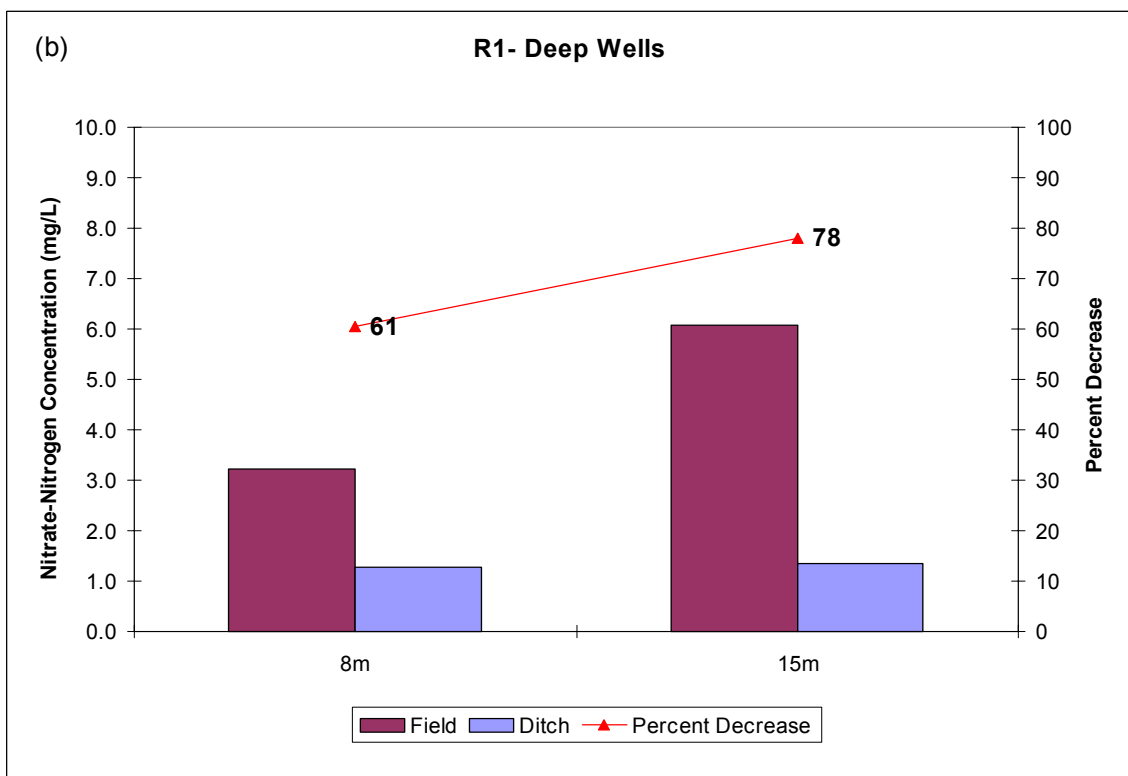
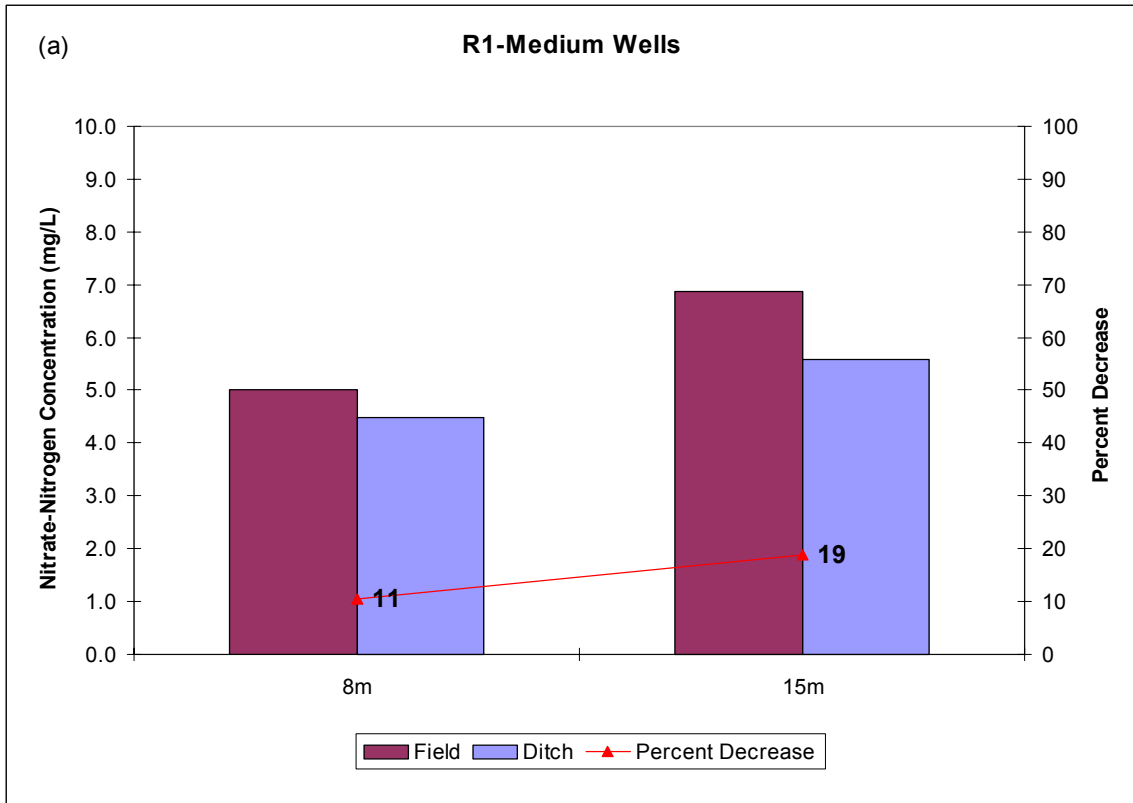


Figure 4.4 Percent decrease across buffers for replicate 1

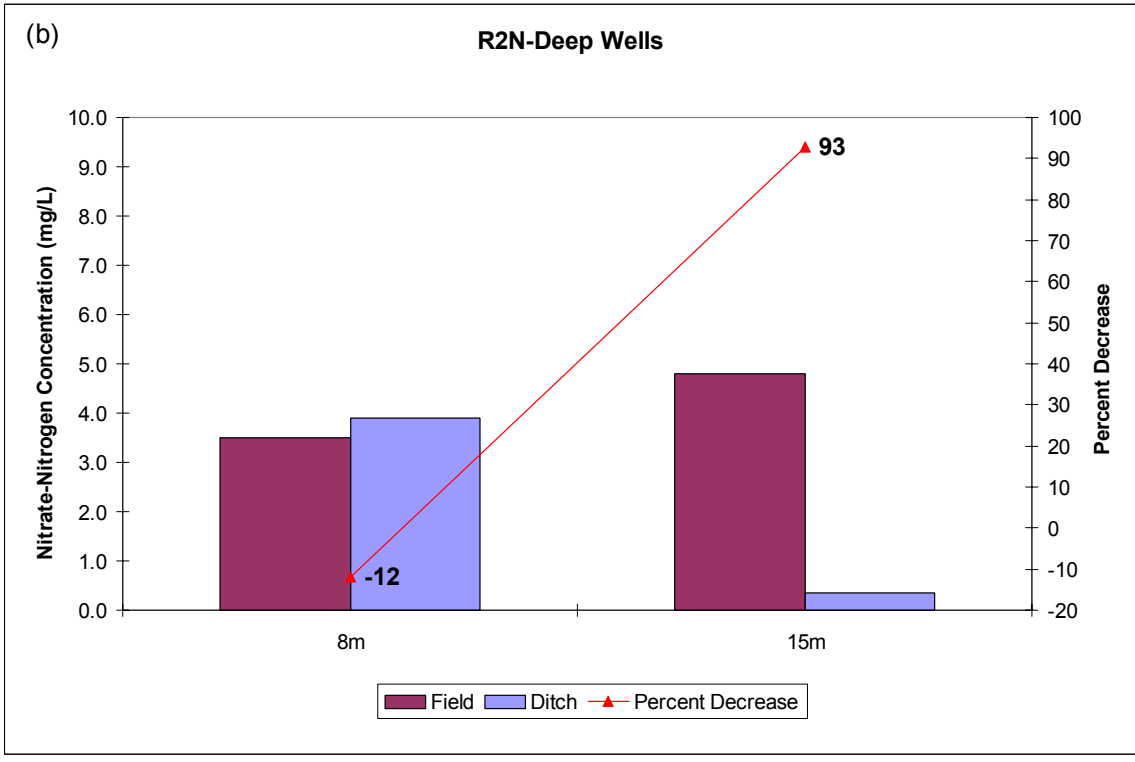
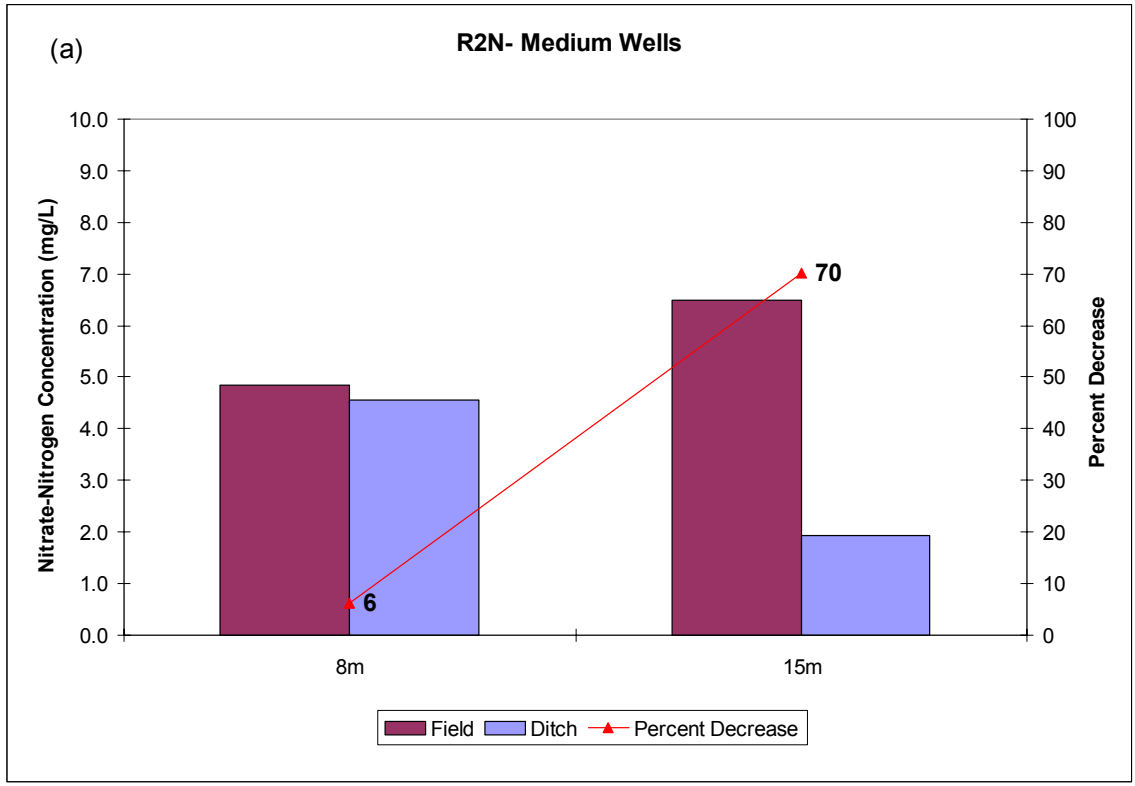


Figure 4.5 Percent decrease across buffers for replicate 2N

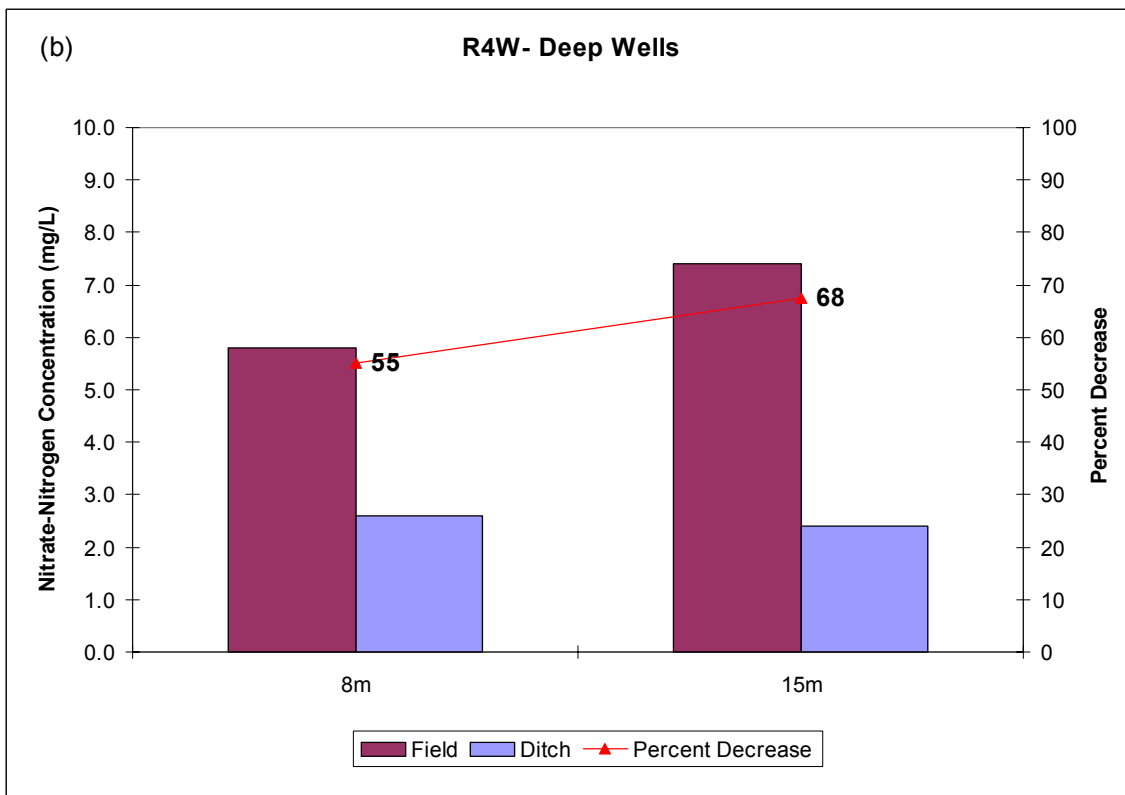
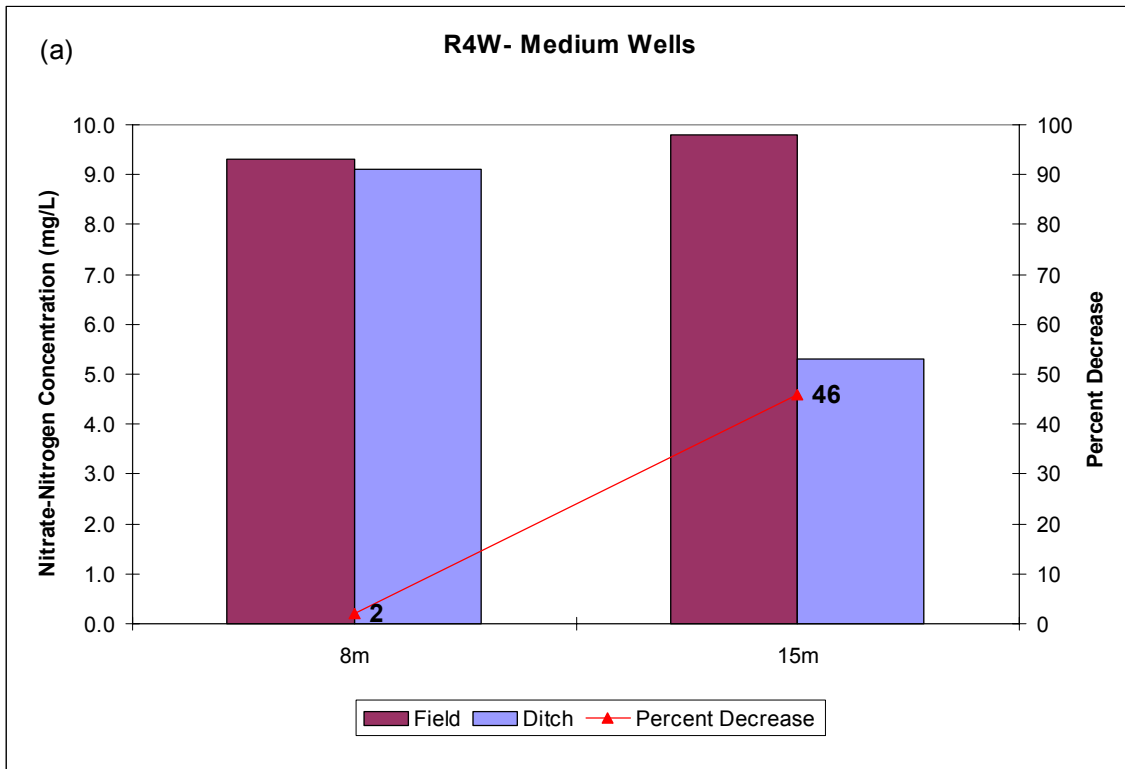


Figure 4.6 Percent decrease across buffers for replicate 4W

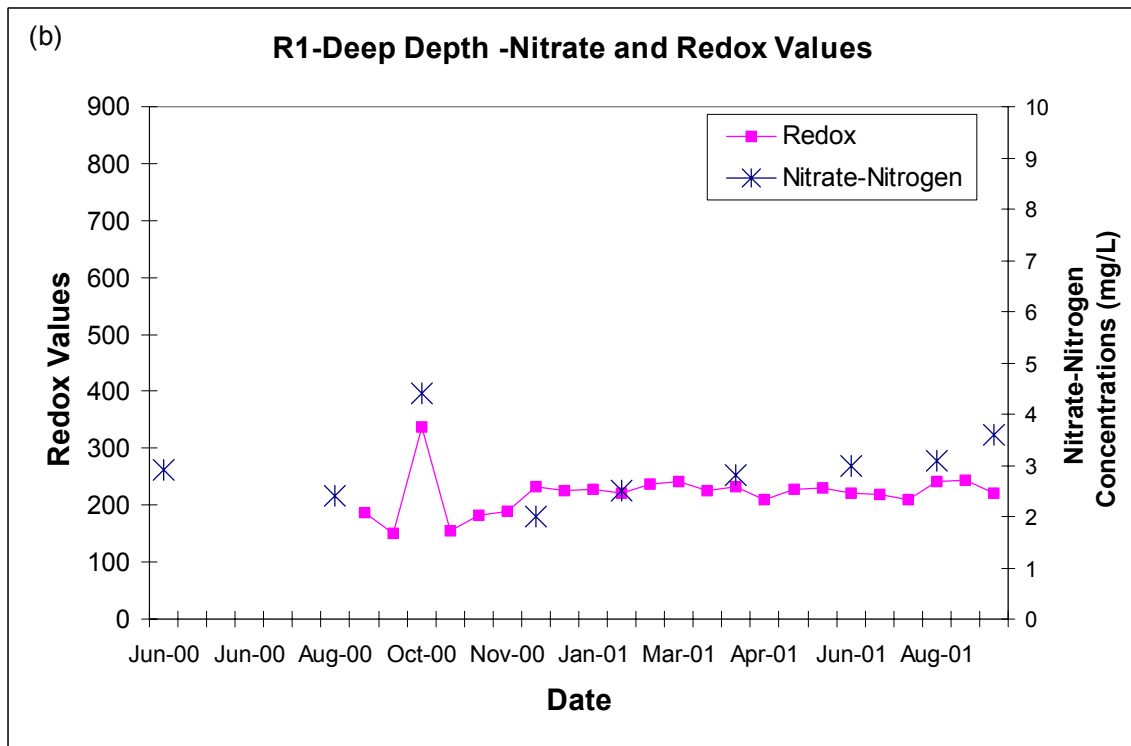
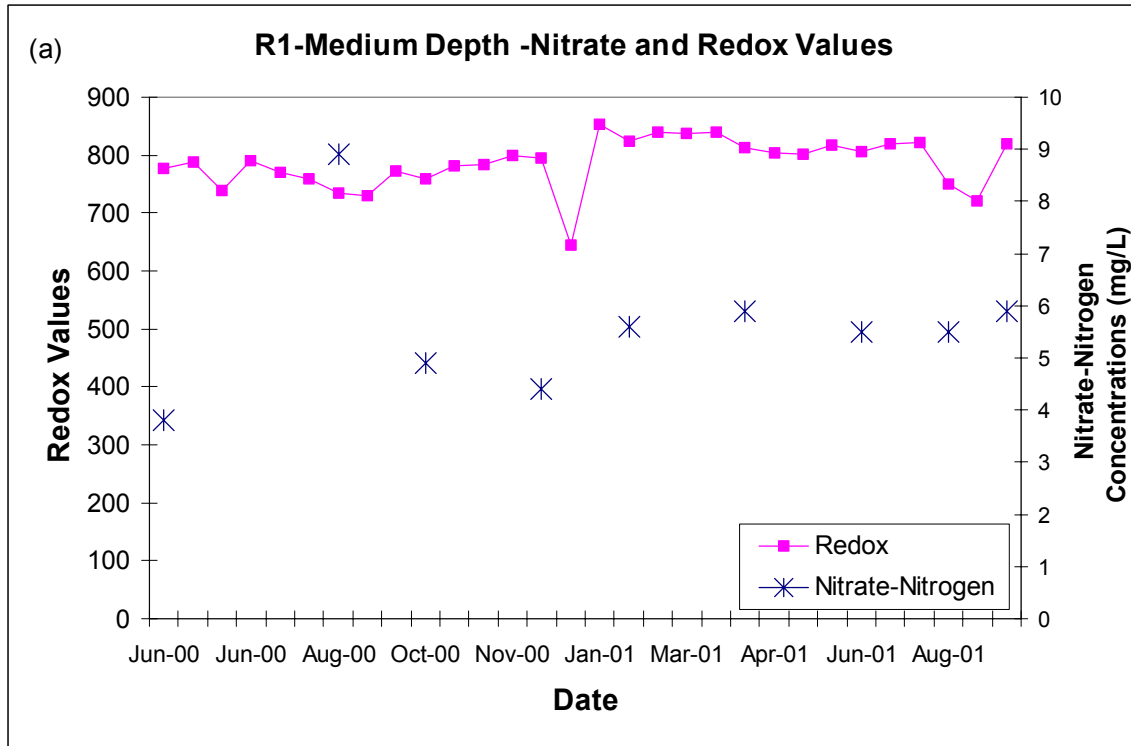


Figure 4.7 Redox values along with nitrate-nitrogen concentrations for R1

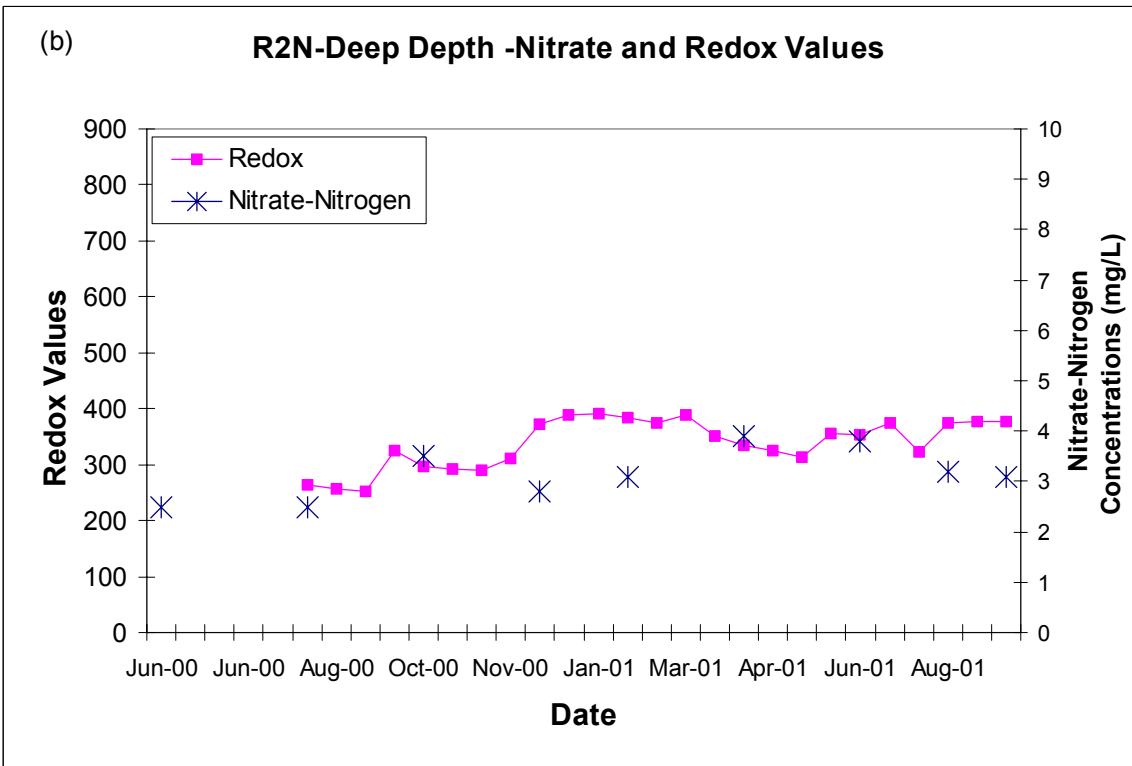
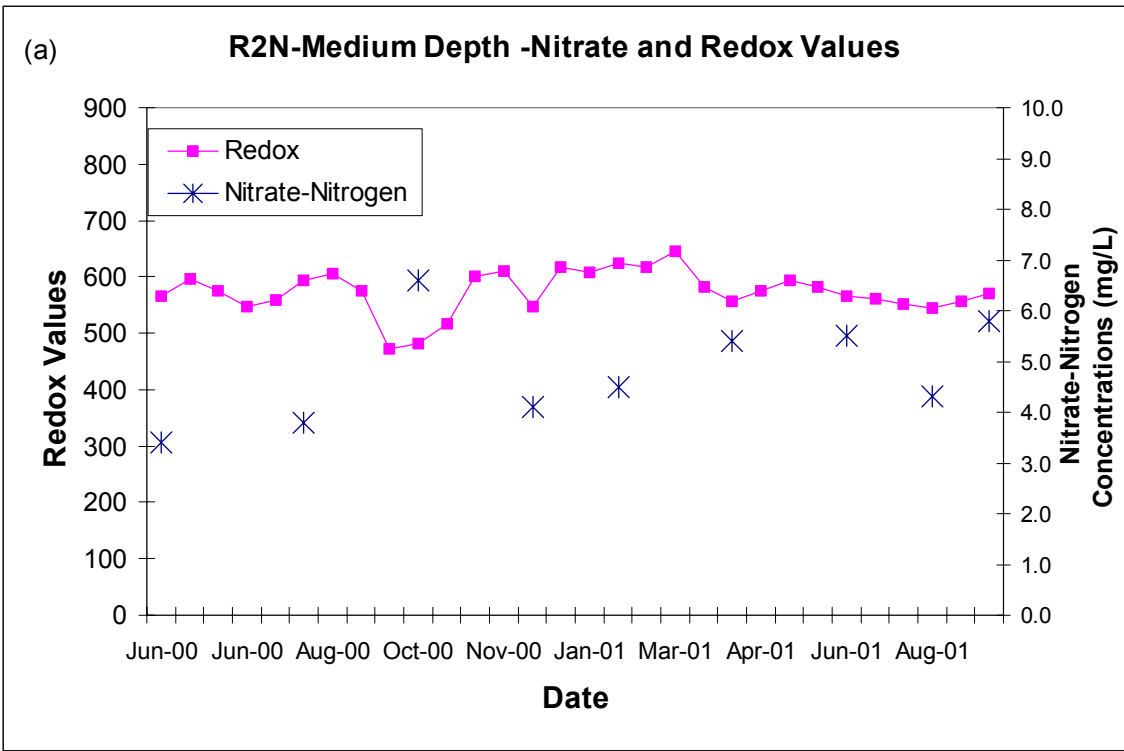


Figure 4.8 Redox values along with nitrate-nitrogen concentrations for R2N

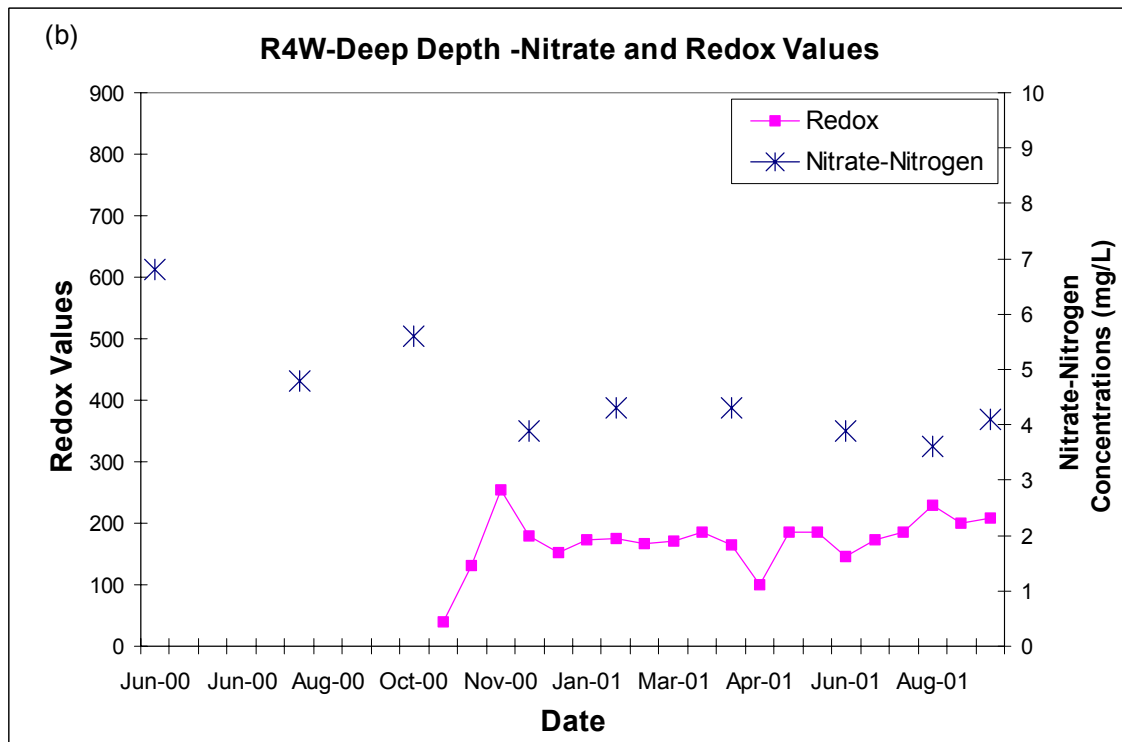
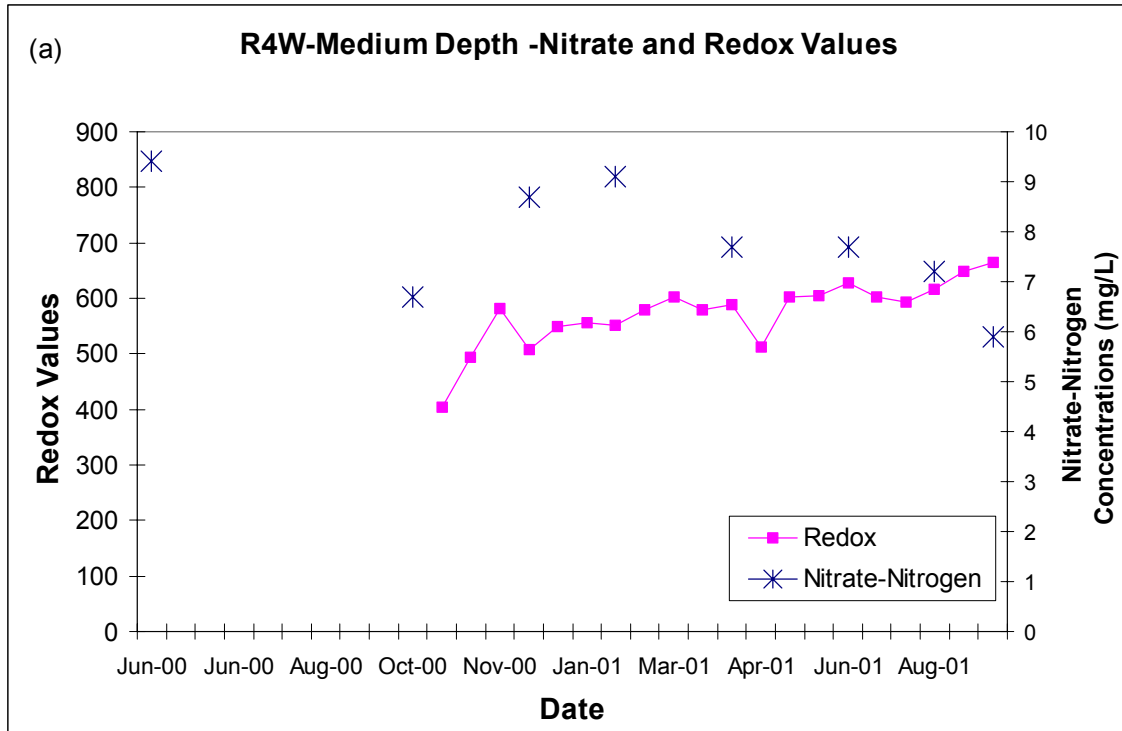


Figure 4.9 Redox values along with nitrate-nitrogen concentrations for R4W

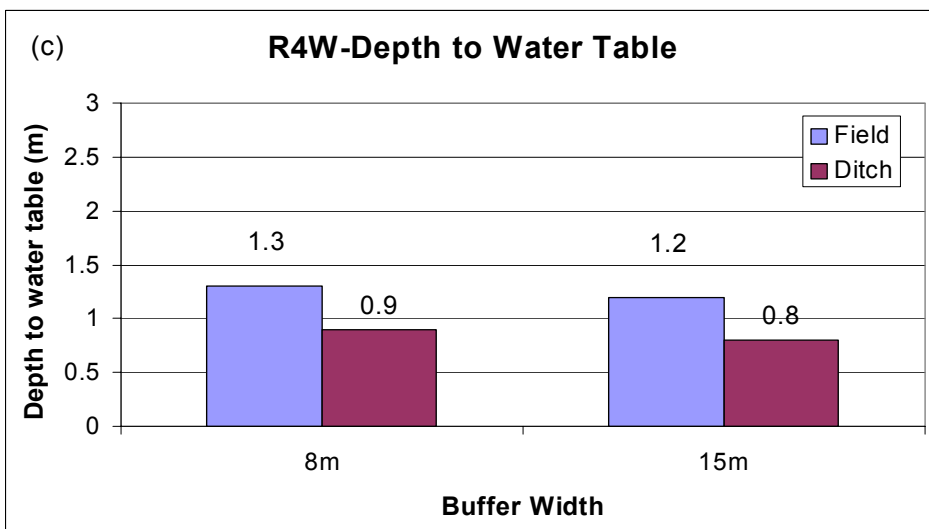
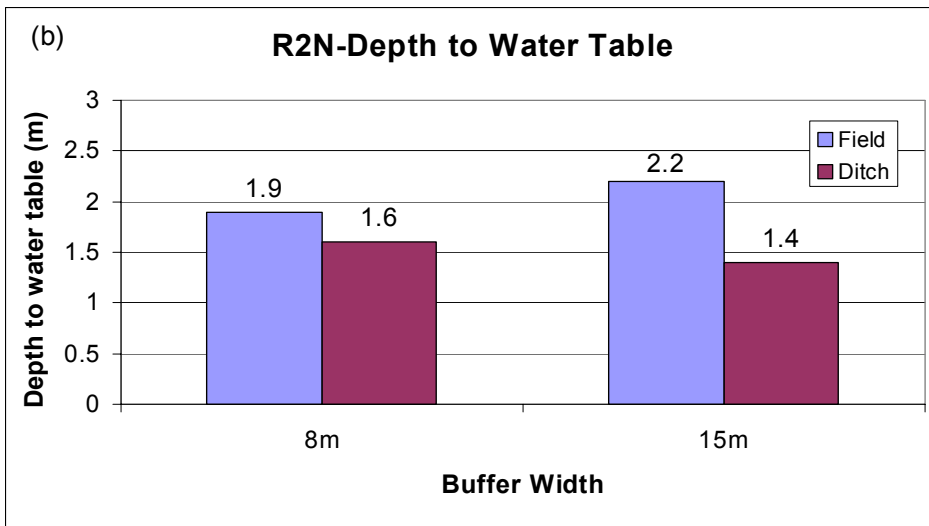
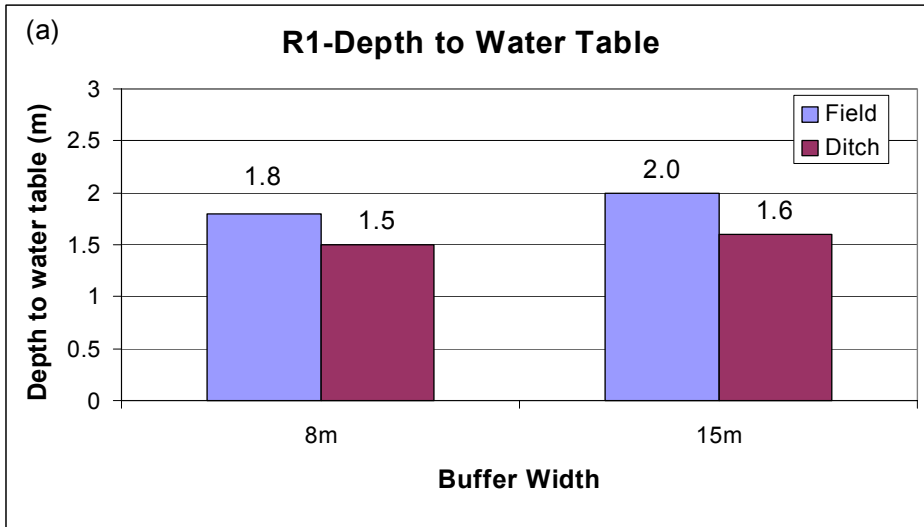


Figure 4.10 Depth to water table for each replicate

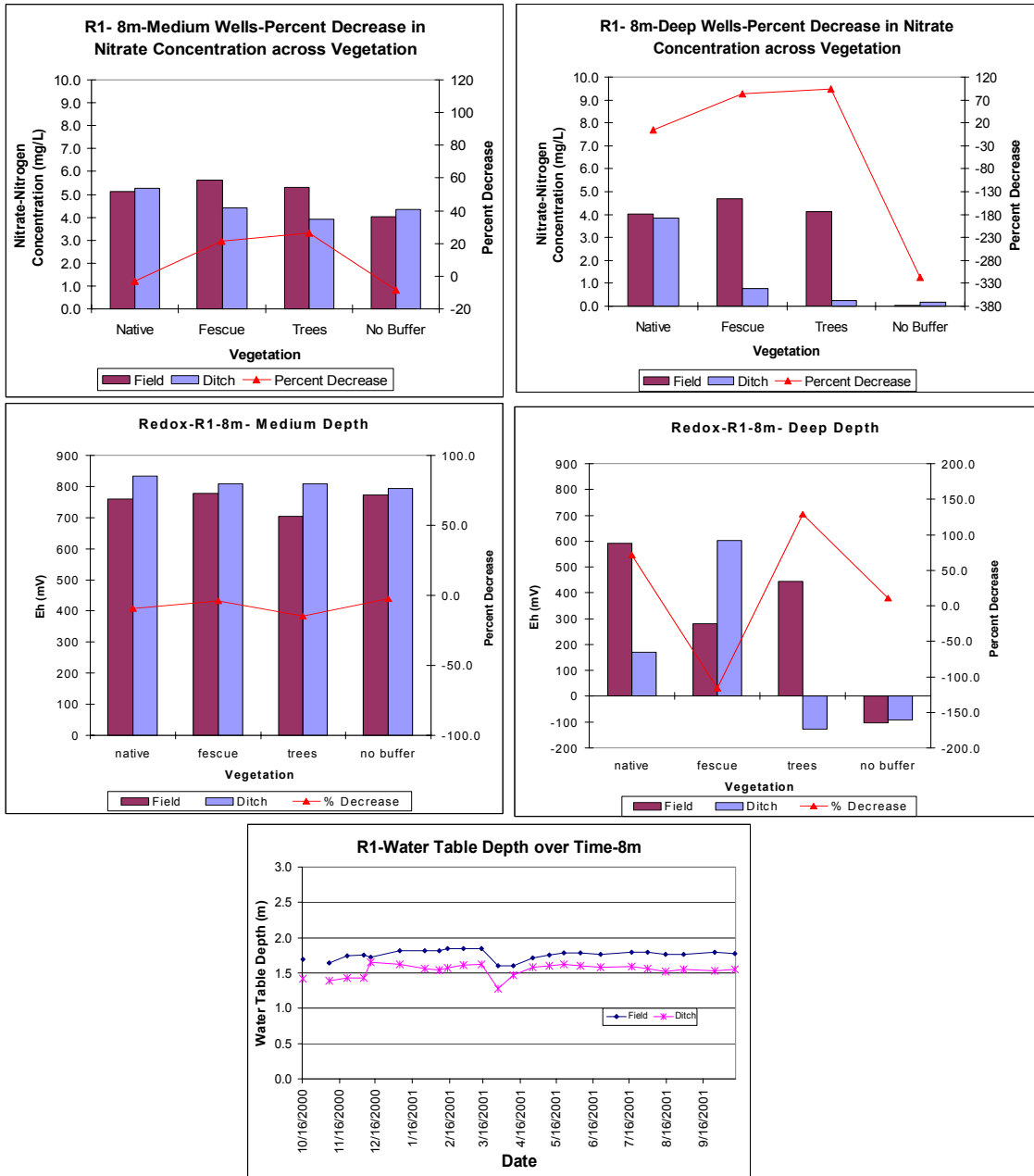


Figure 4.11 Nitrate, Redox, and Water Table information on R1-8m

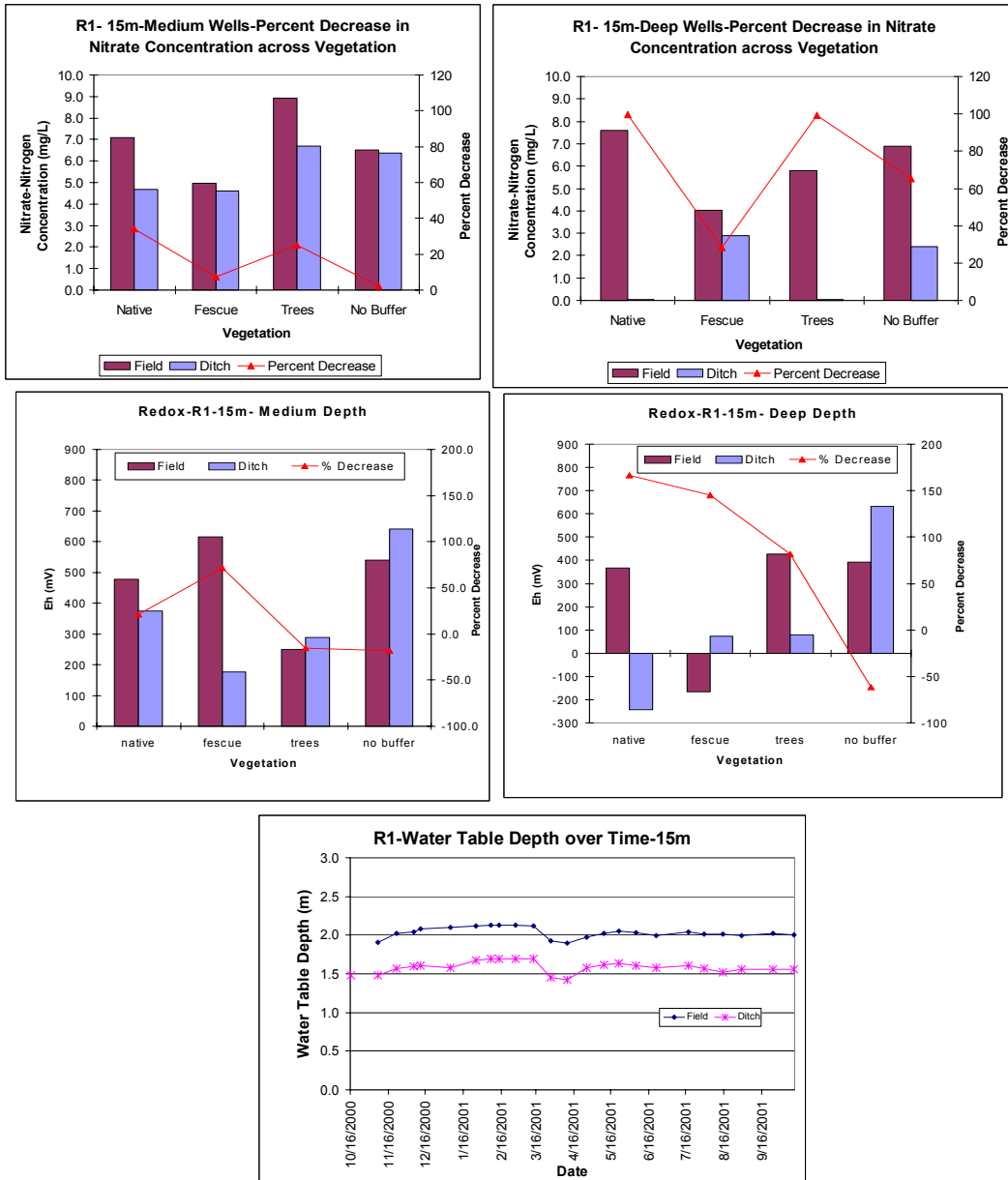


Figure 4.12 Nitrate, Redox, and Water Table information on R1-15m

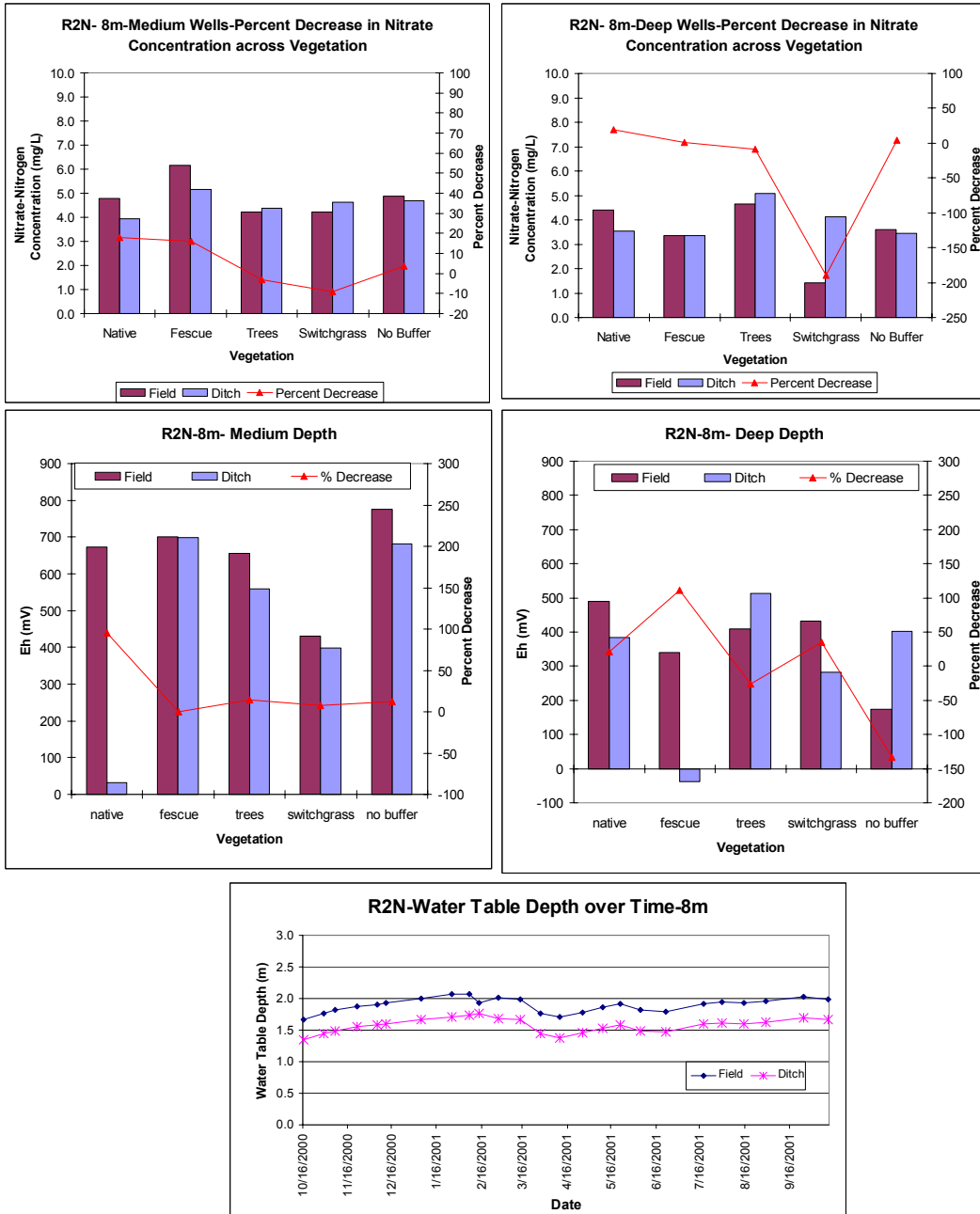


Figure 4.13 Nitrate, Redox, and Water Table information on R2N-8m

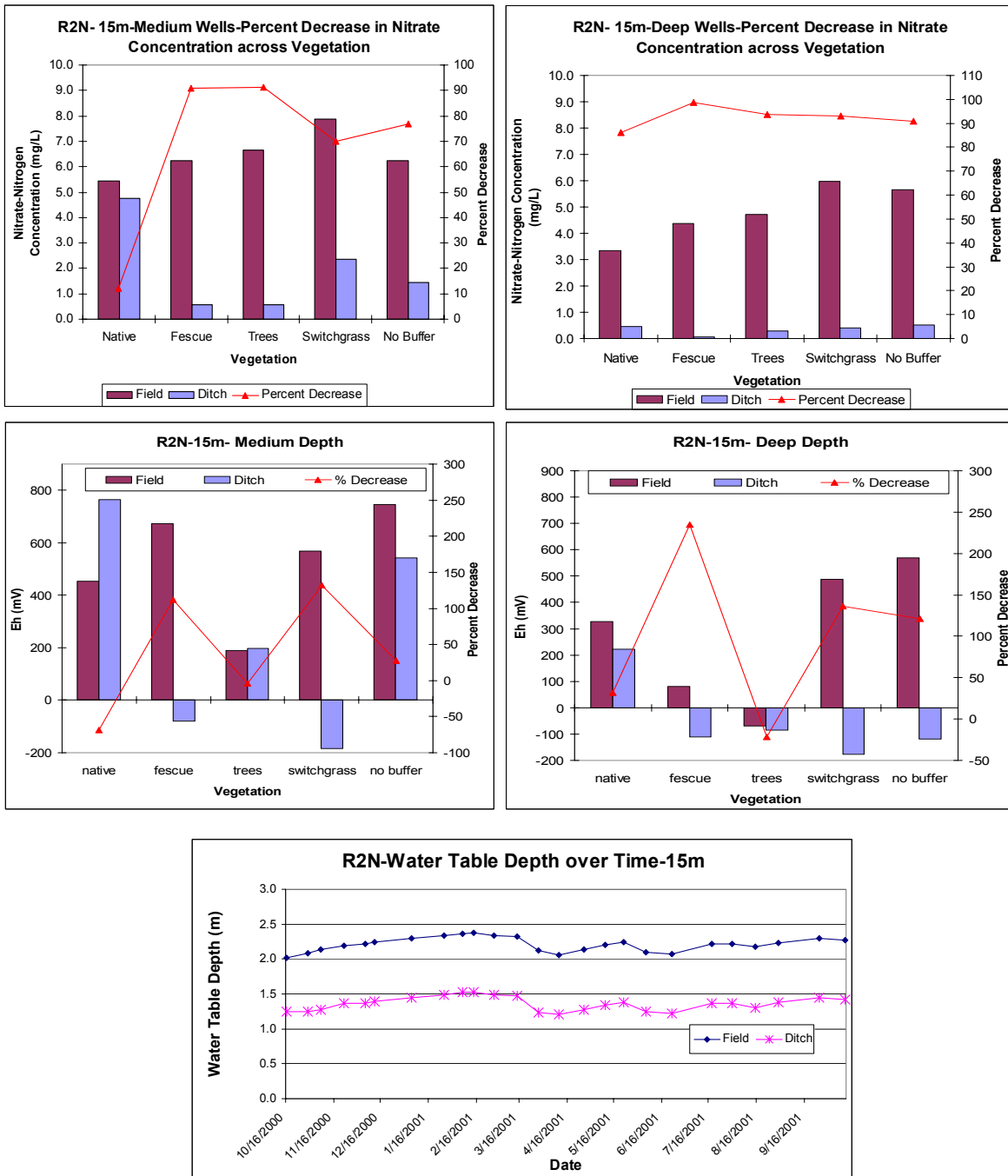


Figure 4.14 Nitrate, Redox, and Water Table information on R2N-15m

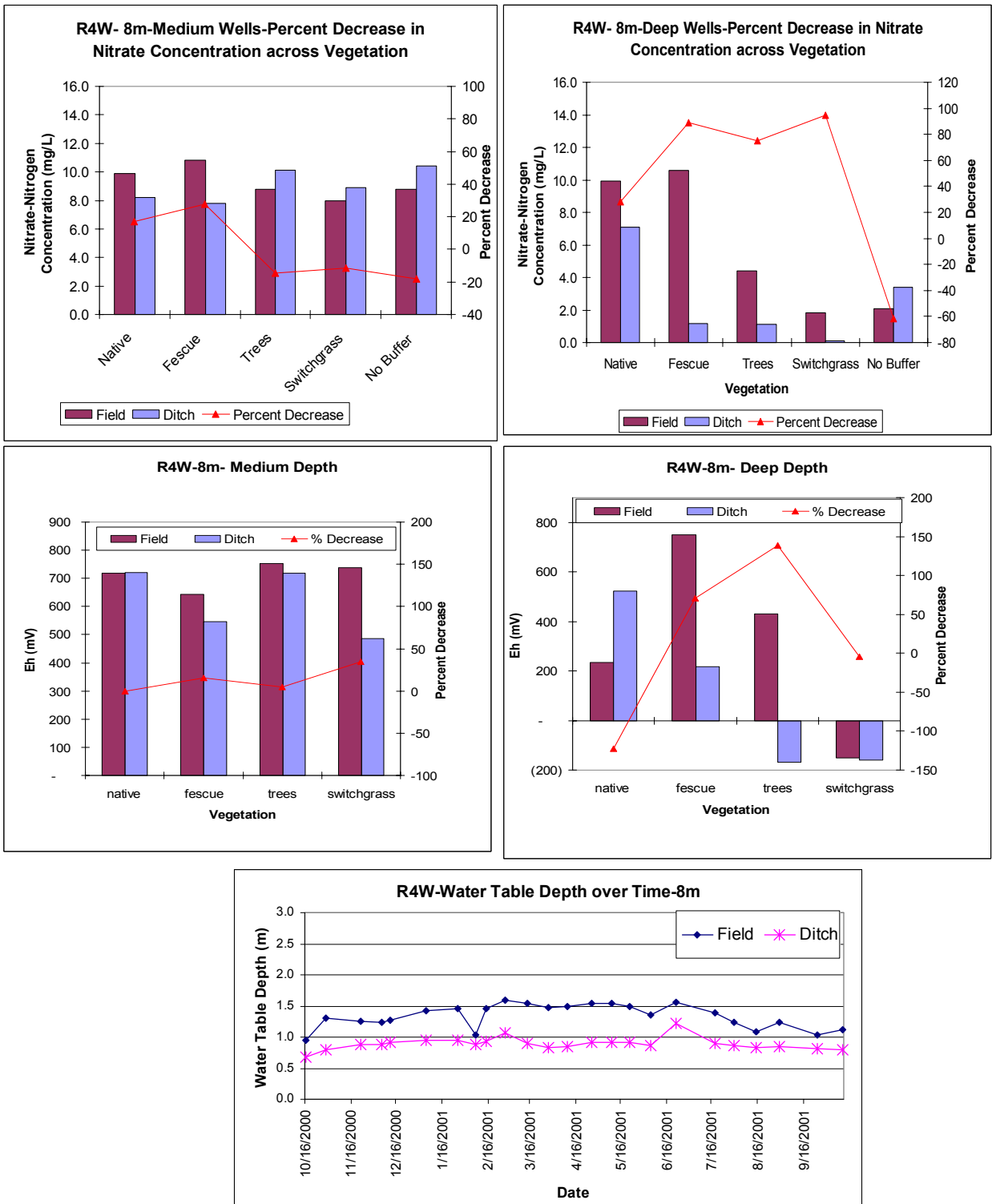


Figure 4.15 Nitrate, Redox, and Water Table information on R4W-8m

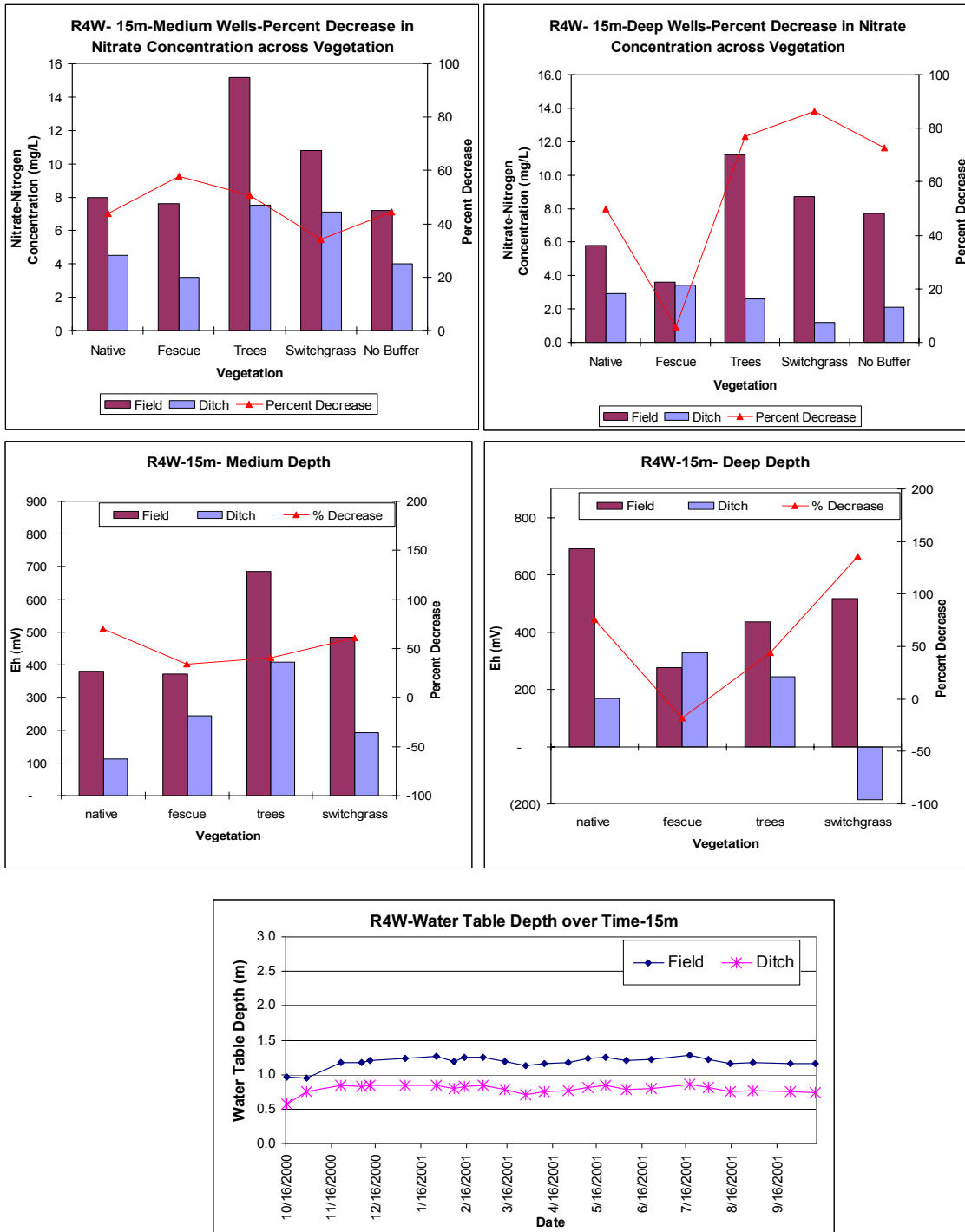


Figure 4.16 Nitrate, Redox, and Water Table information on R4W-15m

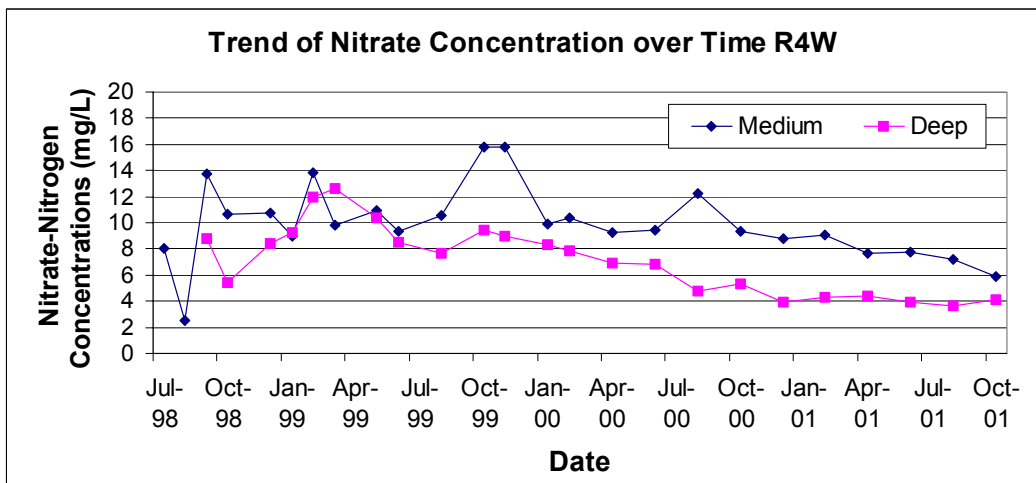
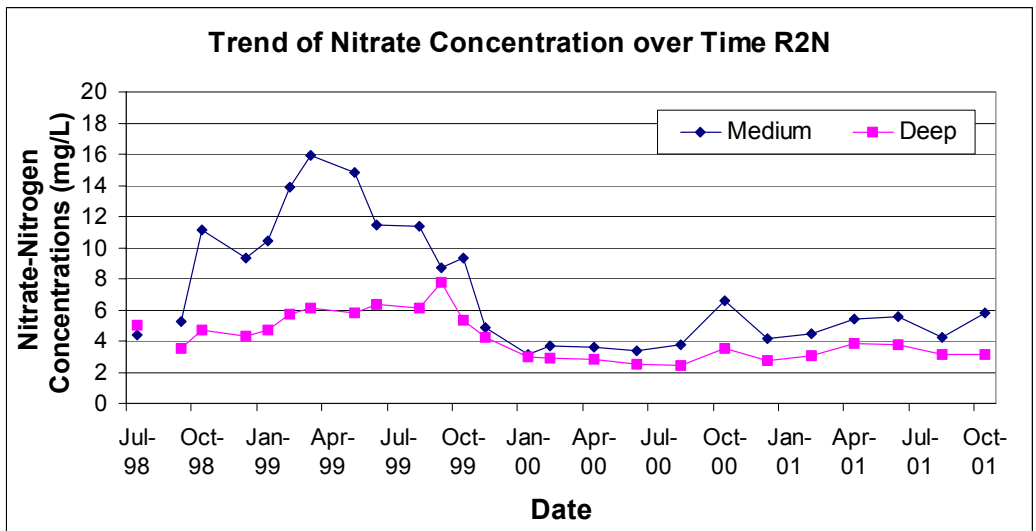
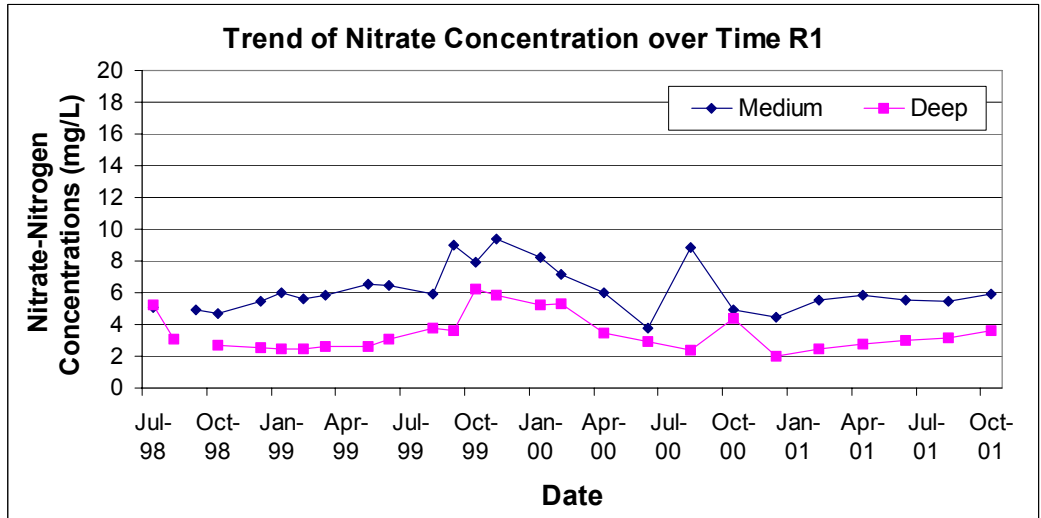


Figure 4.17 Trend of nitrate concentrations over a three-year period

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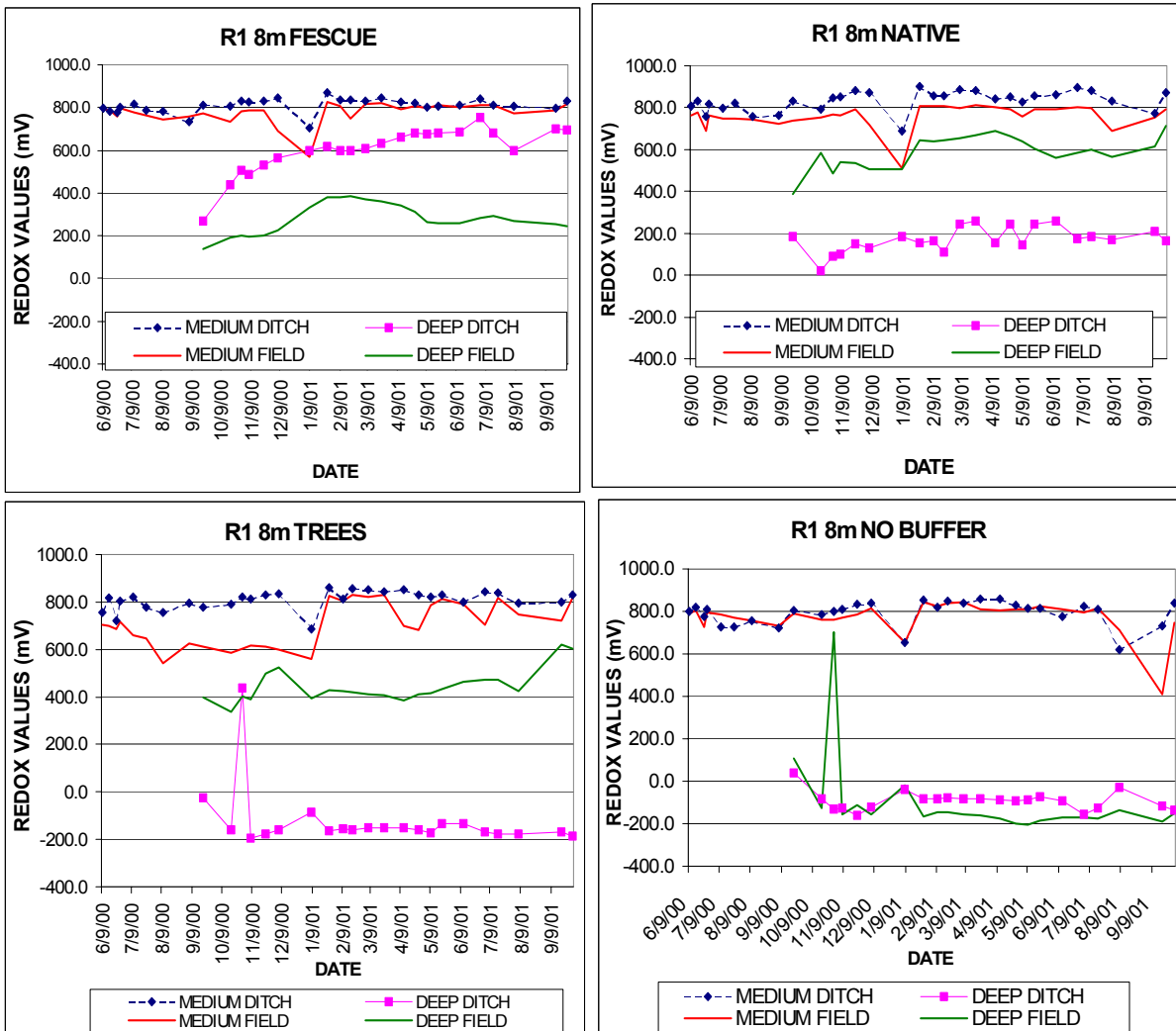
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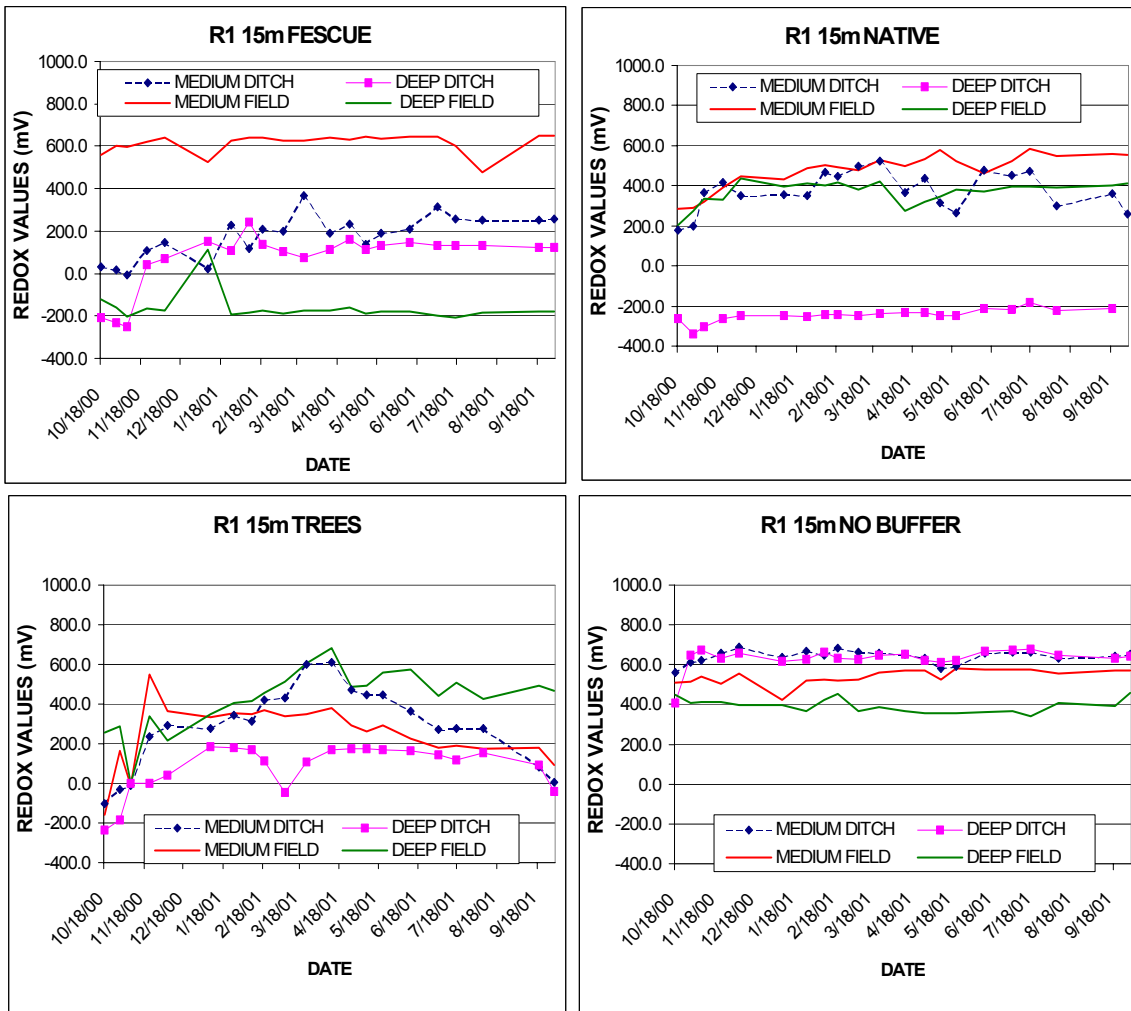
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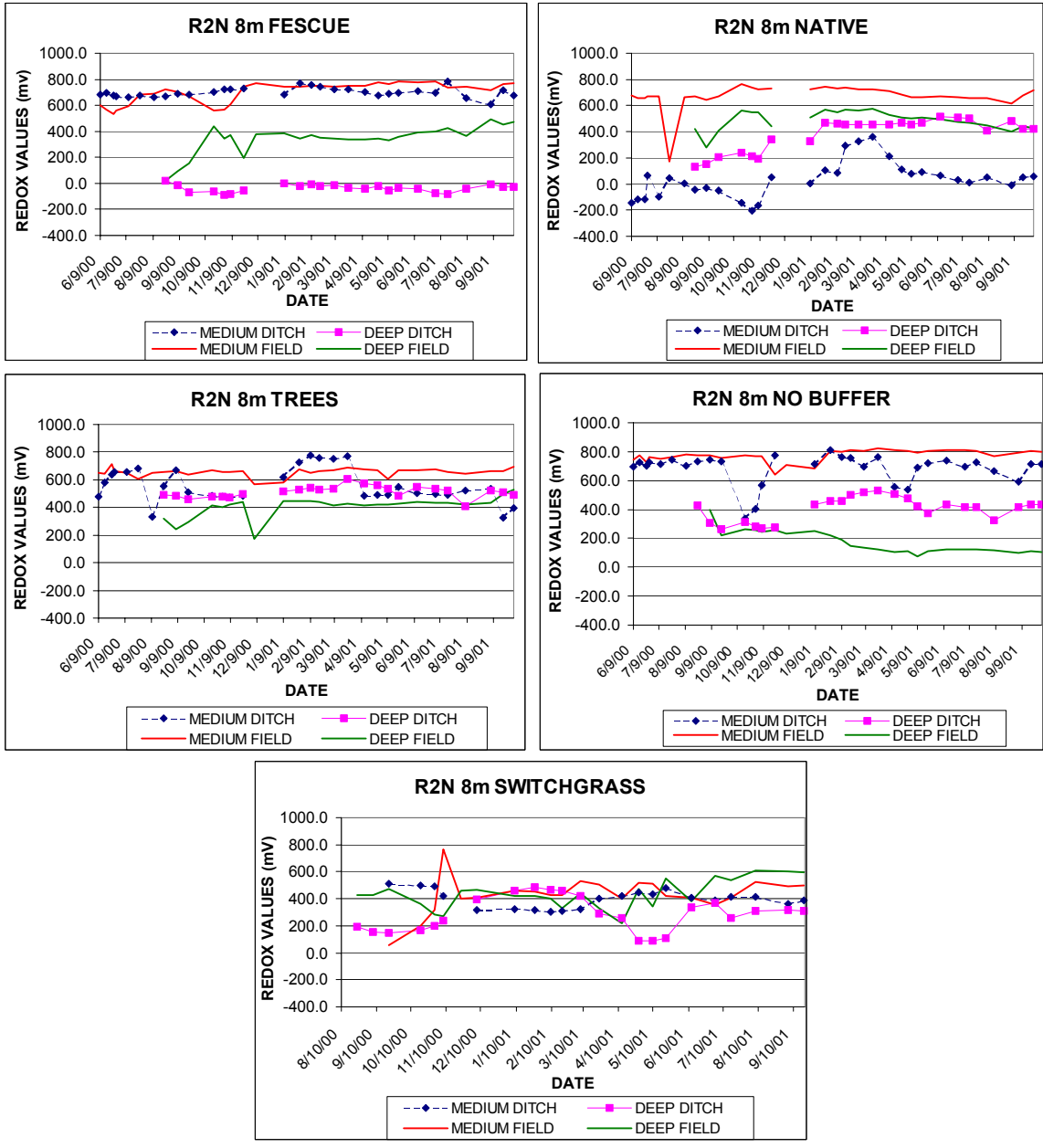
# Appendix



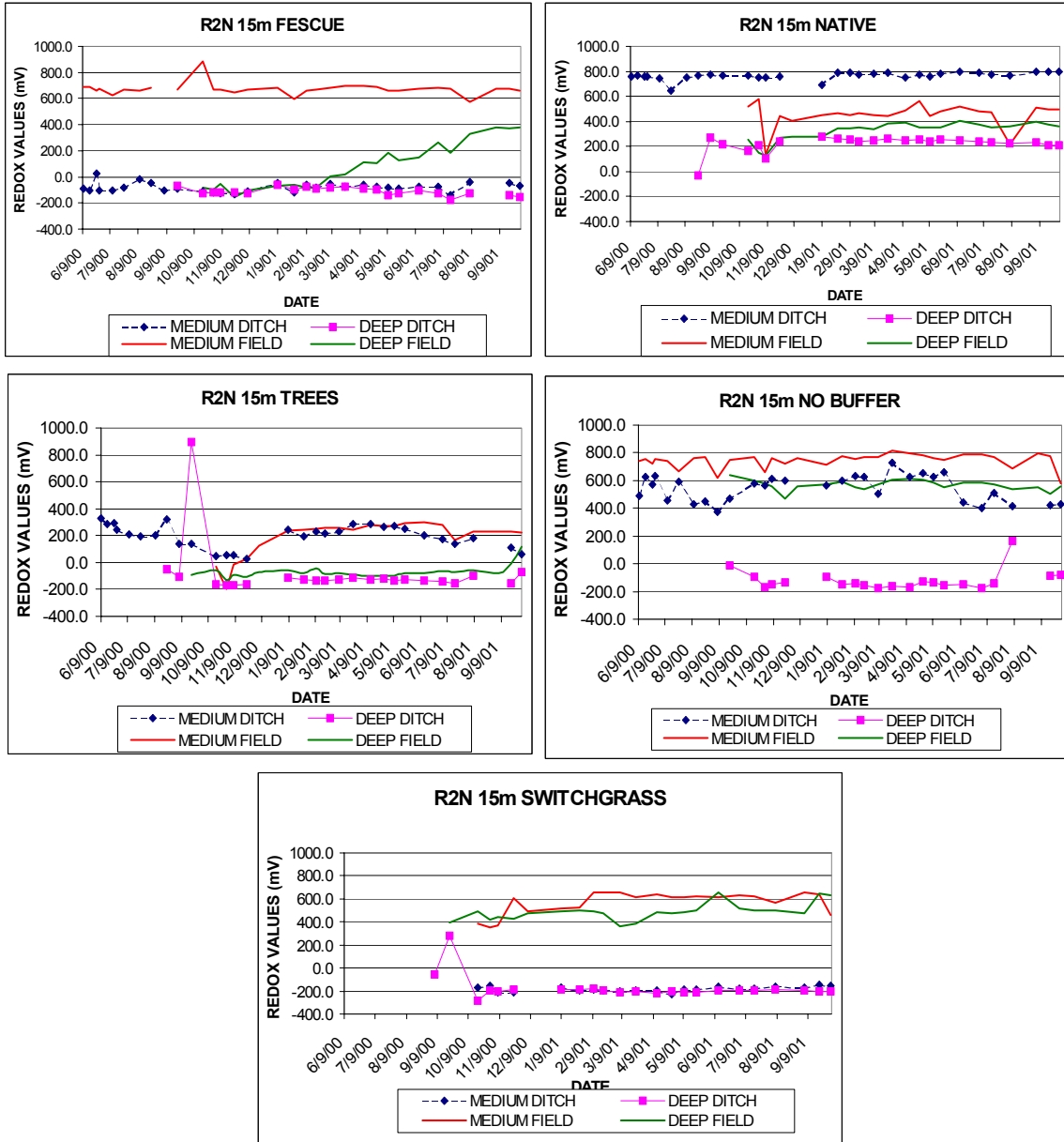
Appendix Figure 1 Redox Trends over time for each vegetation R1-8m



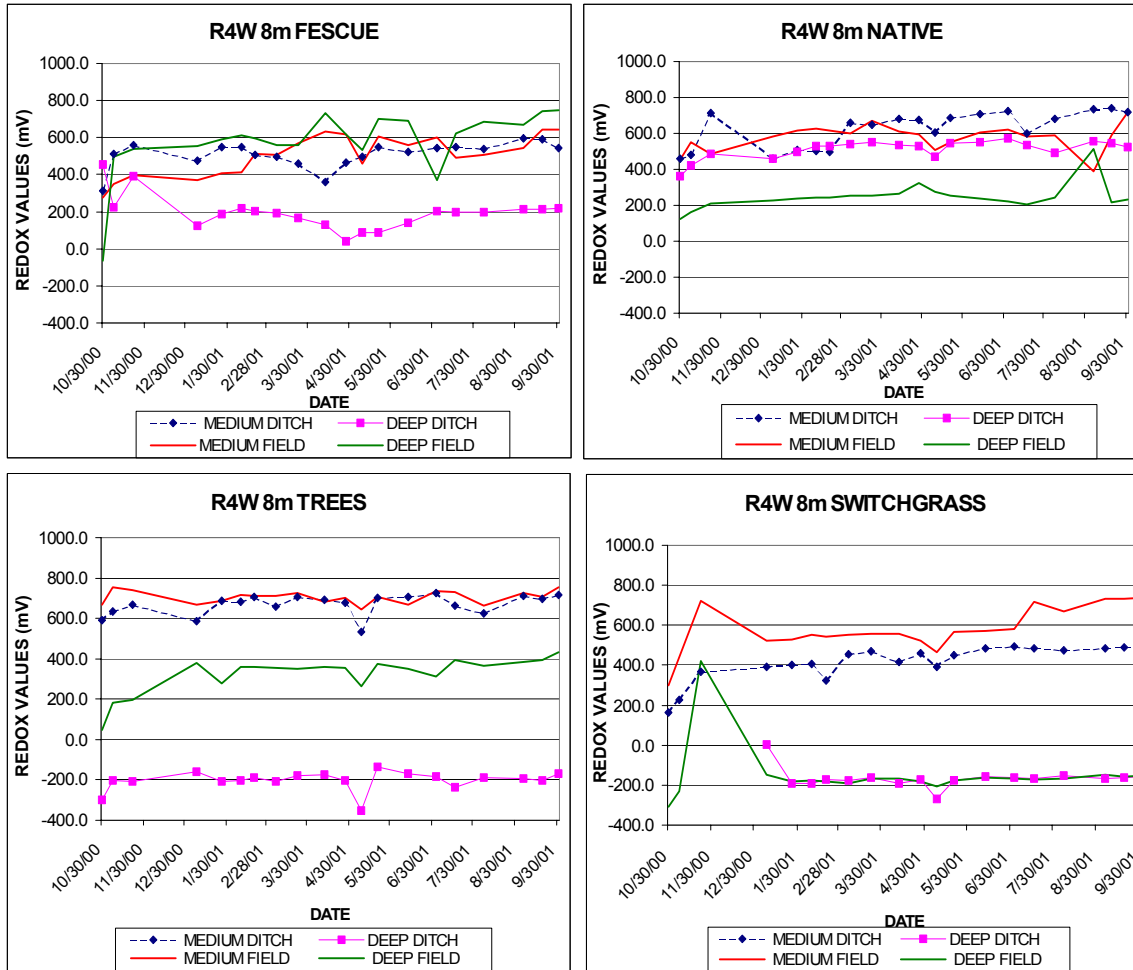
Appendix Figure 2 Redox Trends over time for each vegetation- R1-15m



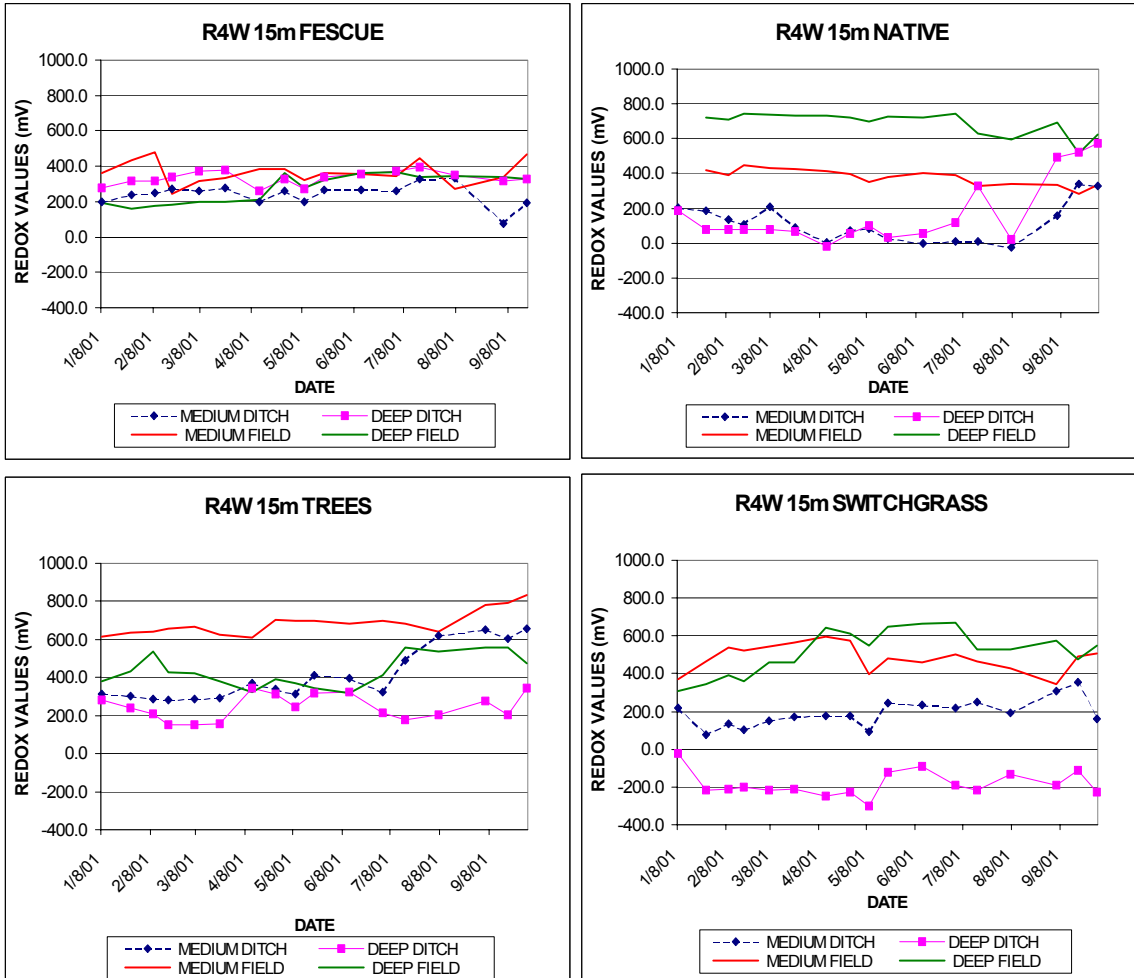
Appendix Figure 3 Redox Trends over time for each vegetation- R2N-8m



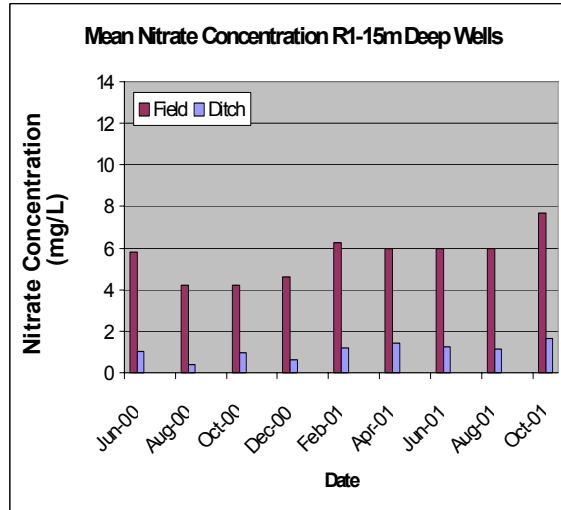
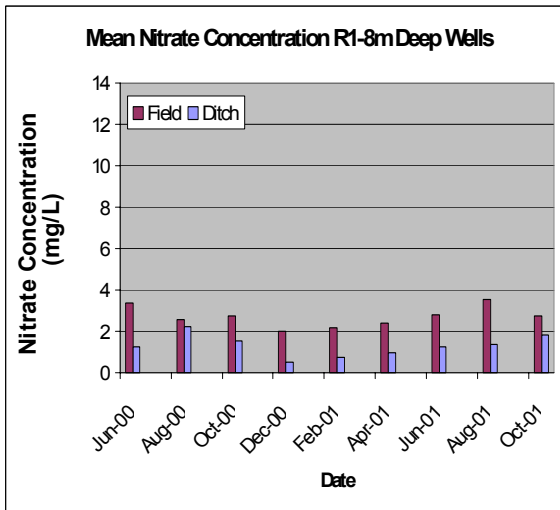
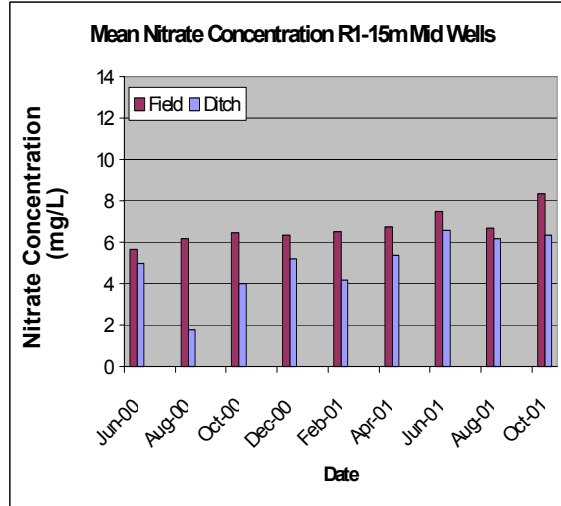
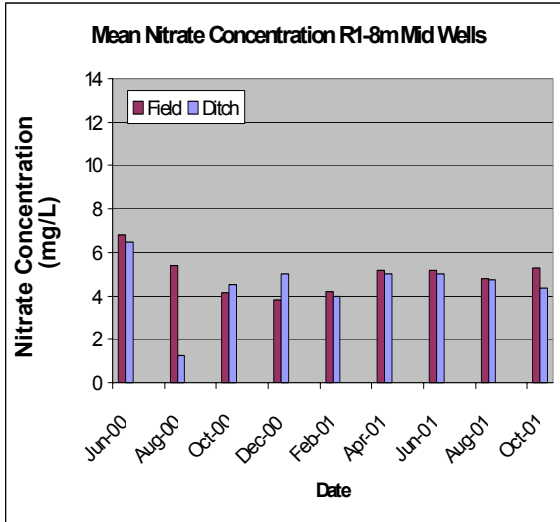
Appendix Figure 4 Redox Trends over time for each vegetation- R2N-15m



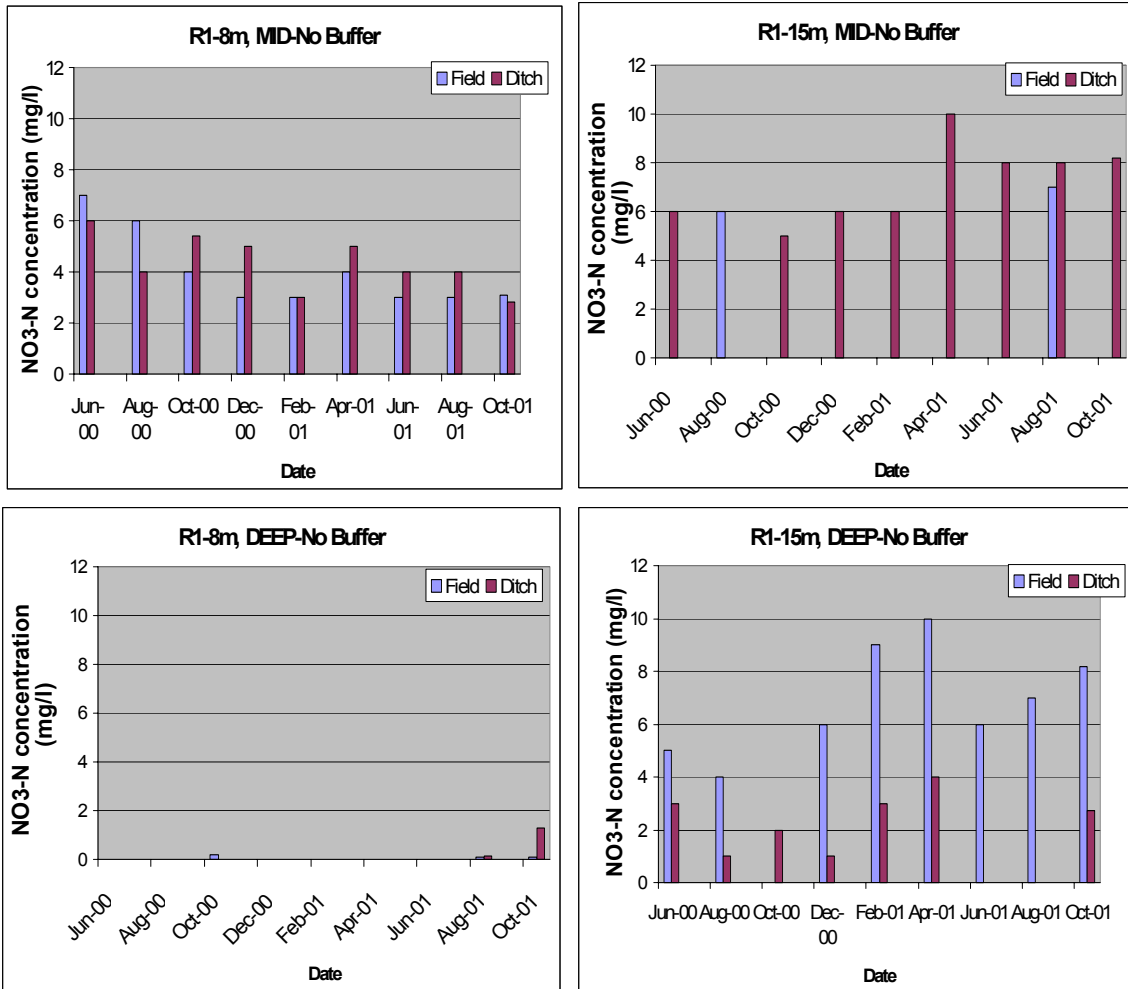
Appendix Figure 5 Redox Trends over time for each vegetation- R4W-8m



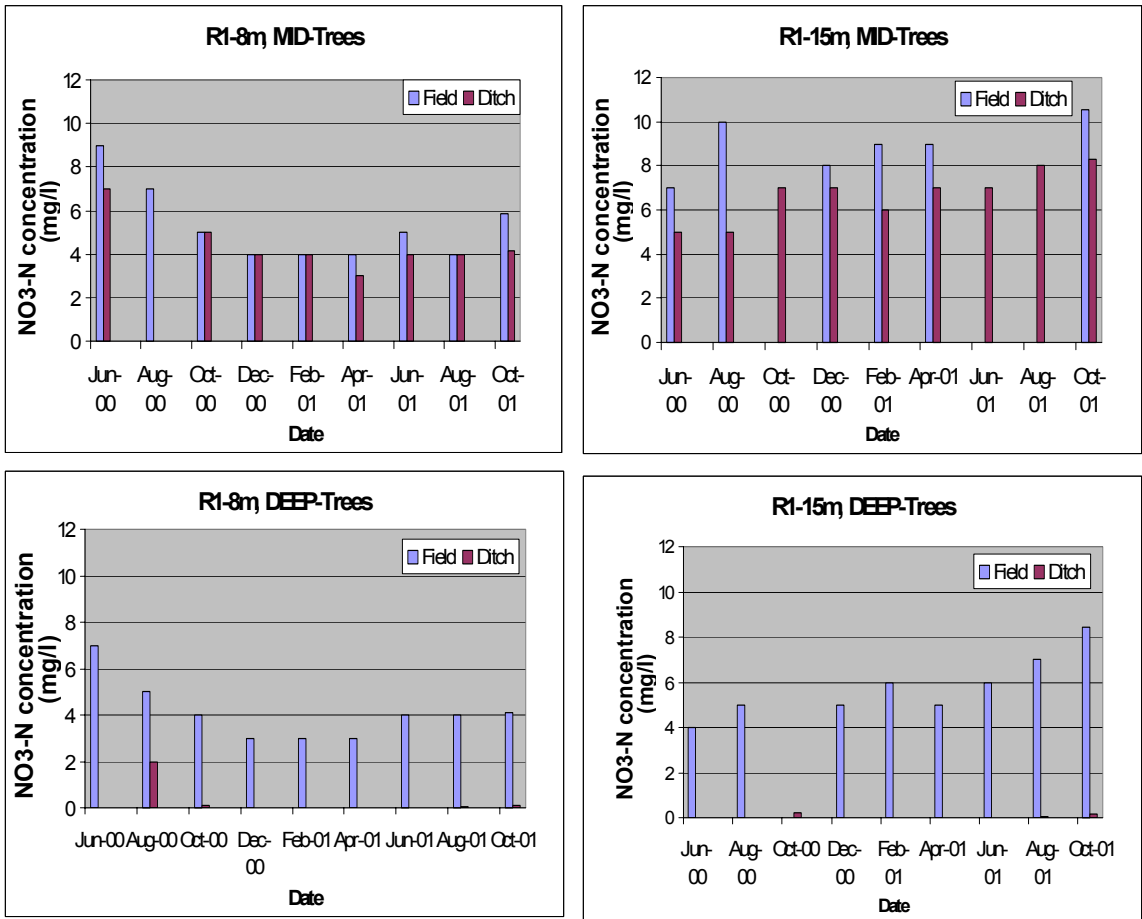
Appendix Figure 6 Redox Trends over time for each vegetation- R4W-15m



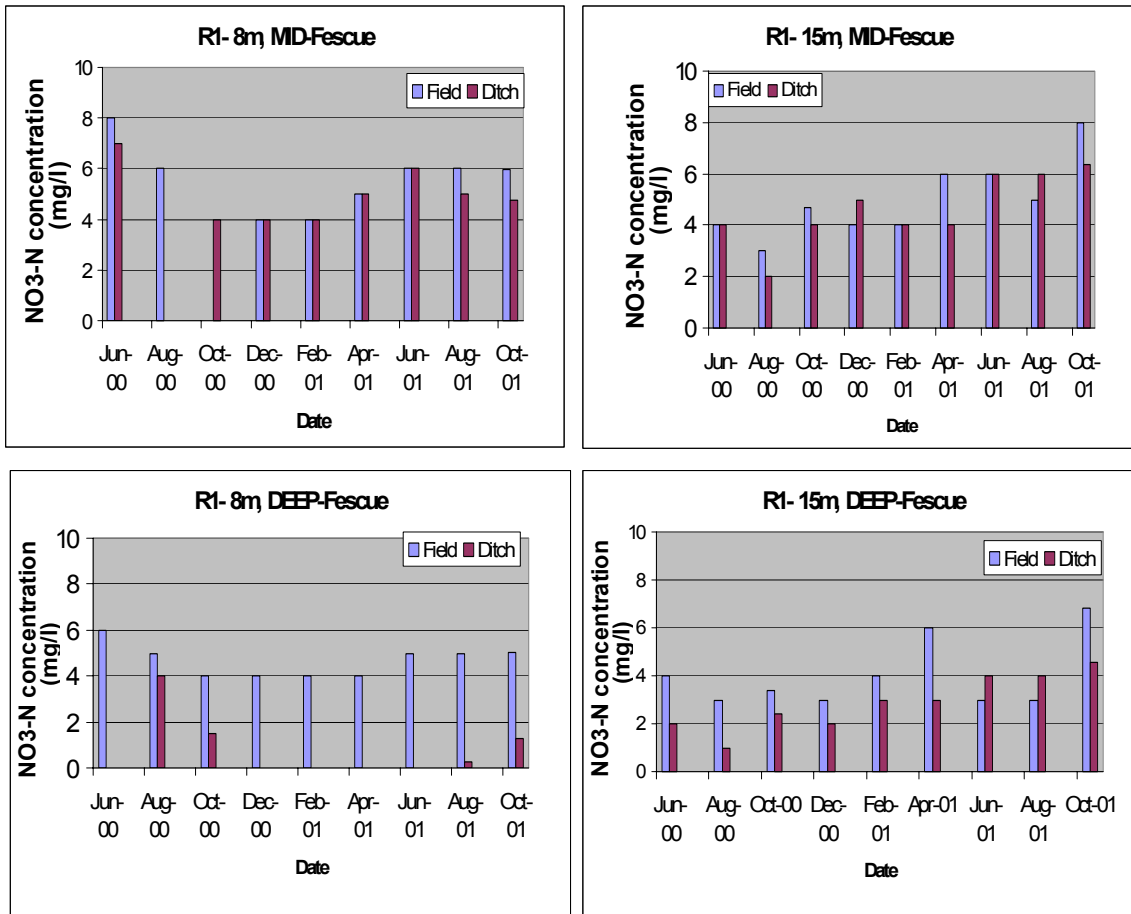
Appendix Figure 7 Mean Nitrate Concentrations for R1



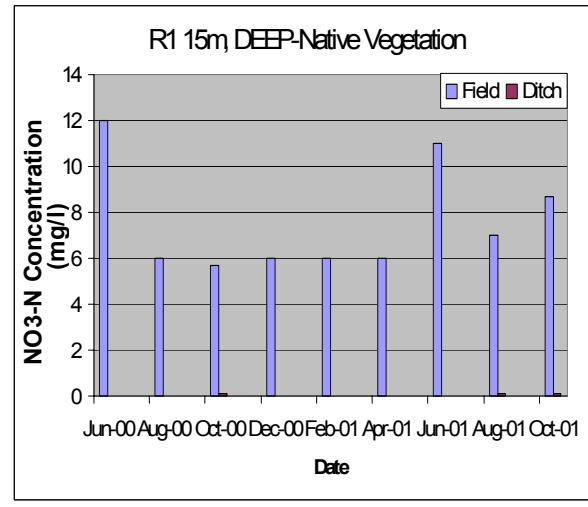
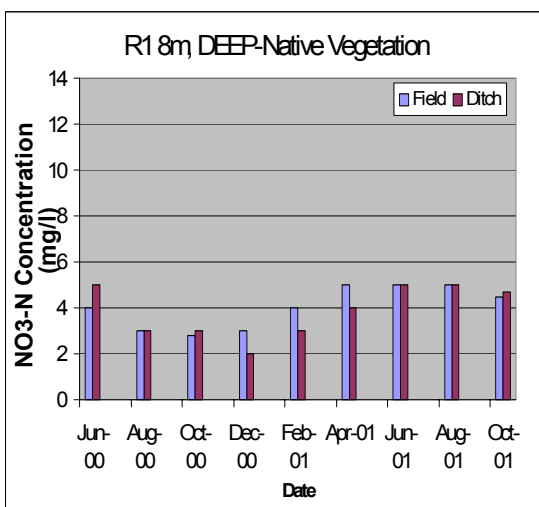
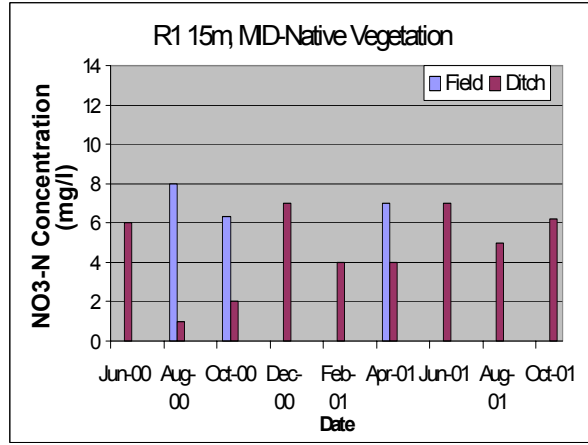
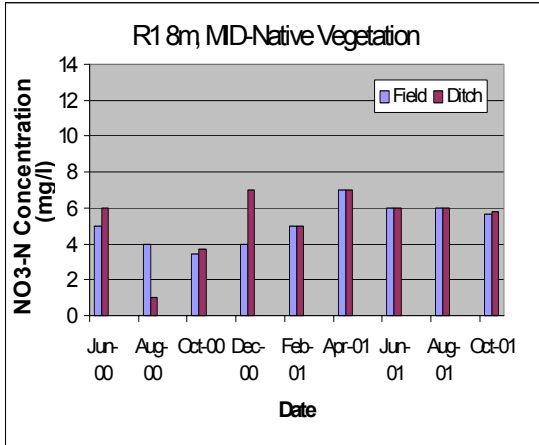
Appendix Figure 8 Nitrate Concentrations for R1-No buffer



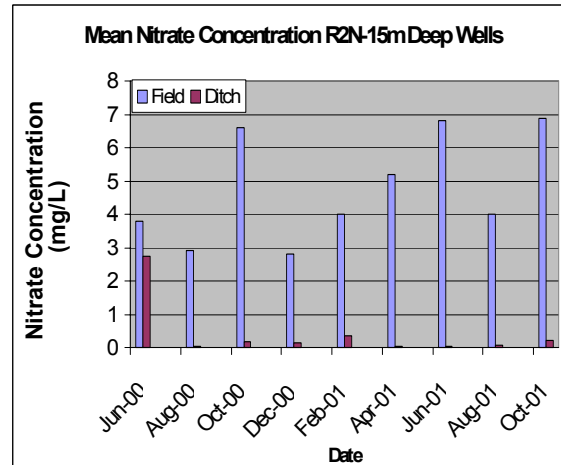
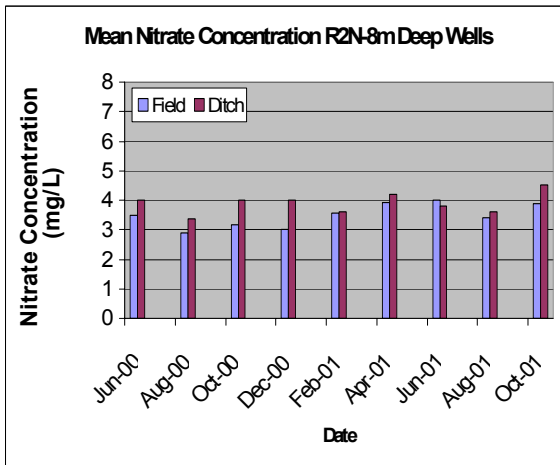
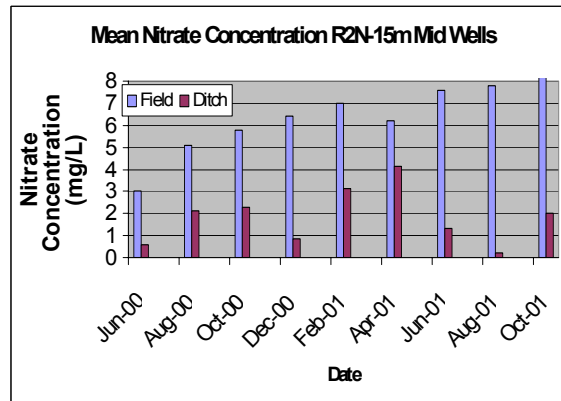
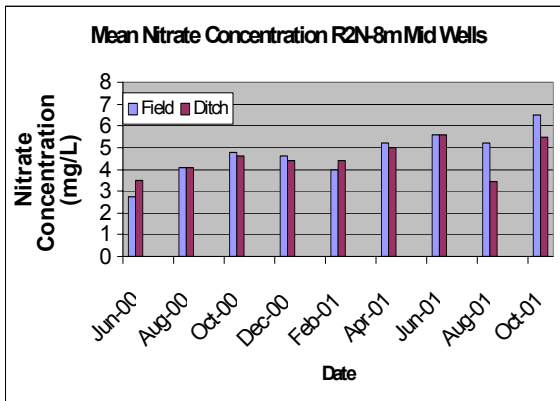
Appendix Figure 9 Nitrate Concentrations for R1-Trees



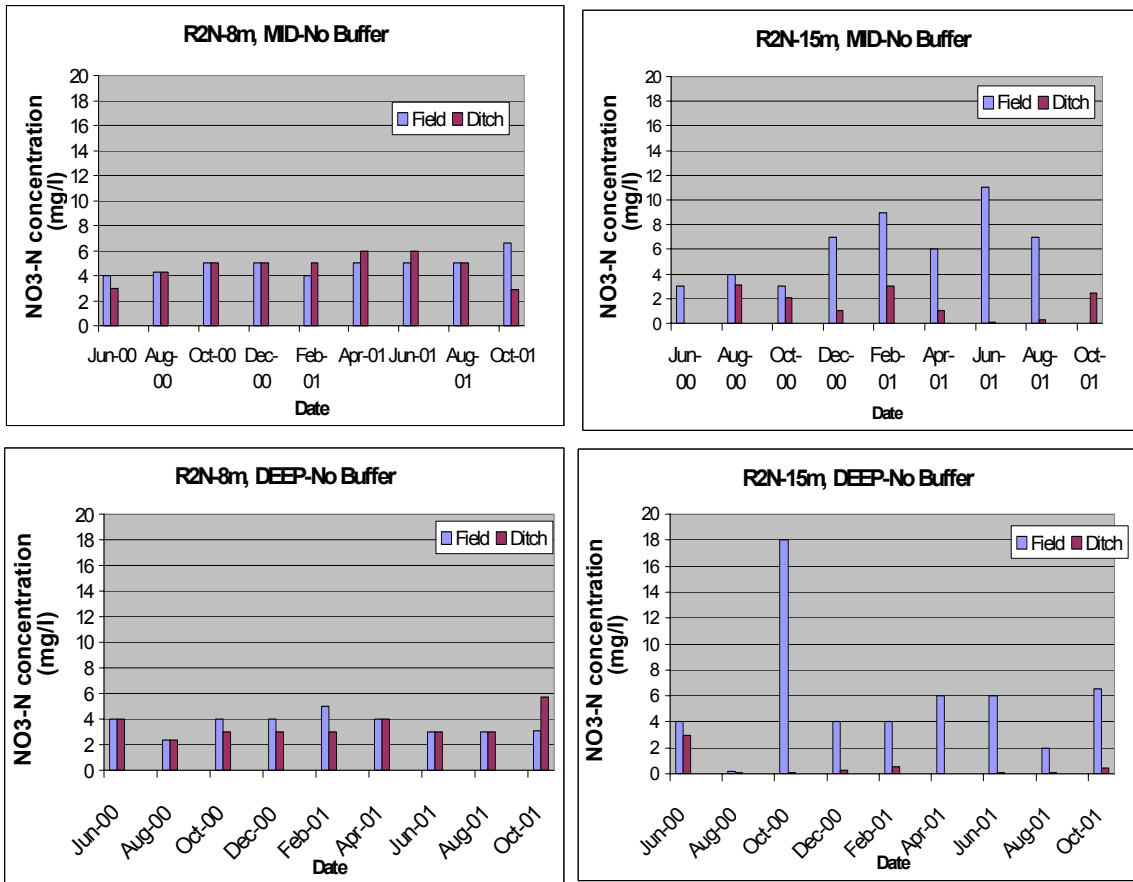
Appendix Figure 10 Nitrate Concentrations for R1-Fescue



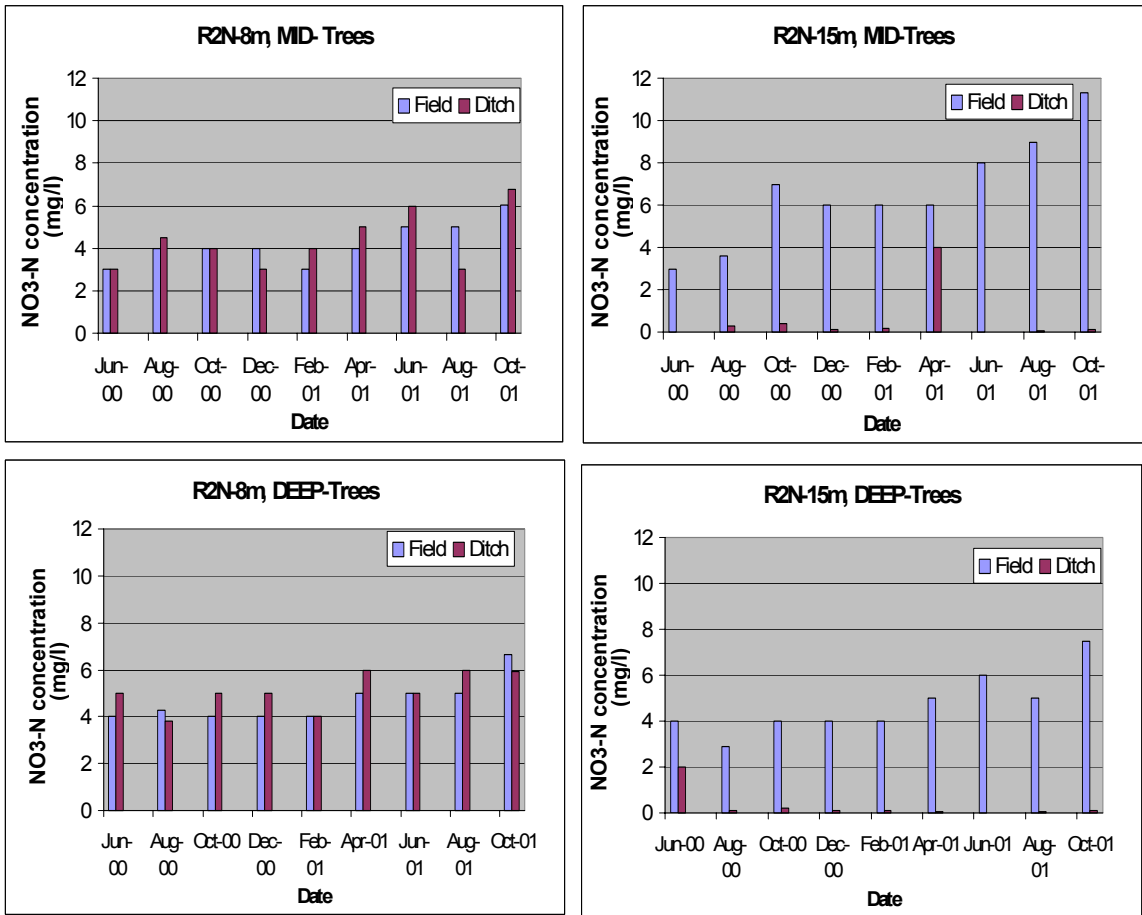
Appendix Figure 11 Nitrate Concentrations for R1-Native Vegetation



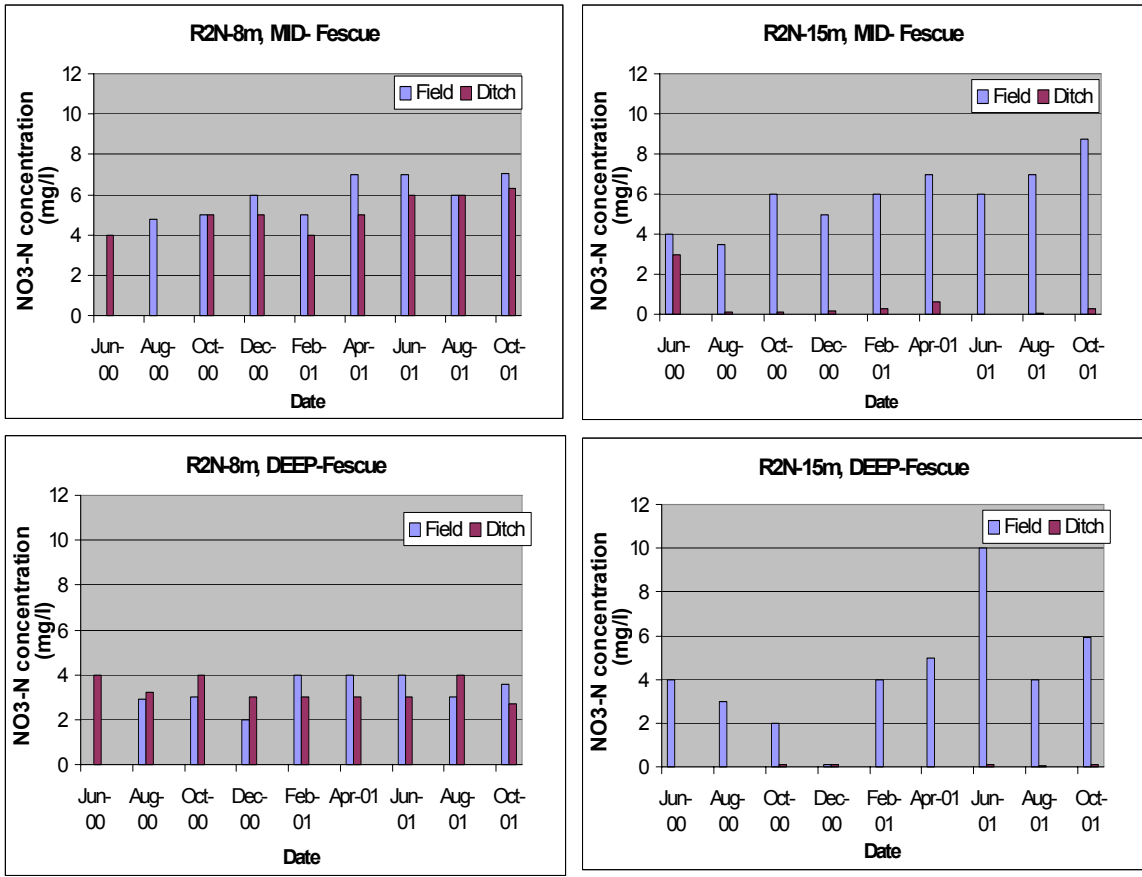
Appendix Figure 12 Mean Nitrate Concentrations for R2N



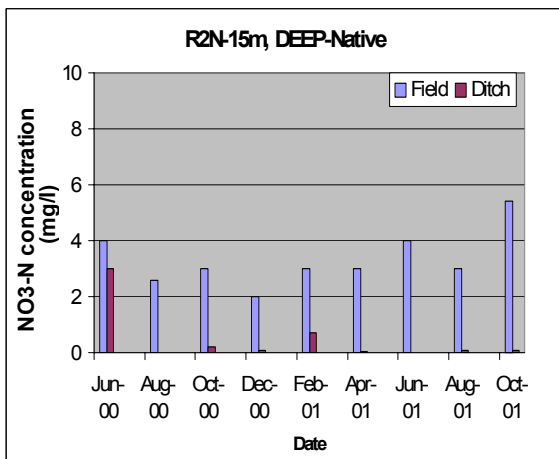
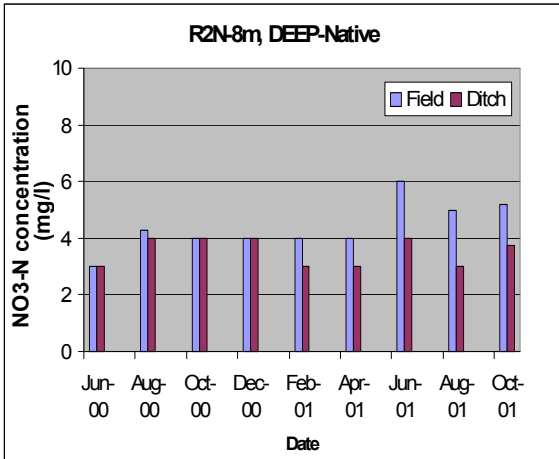
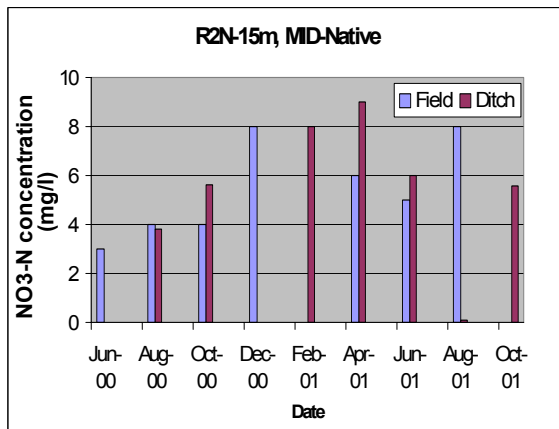
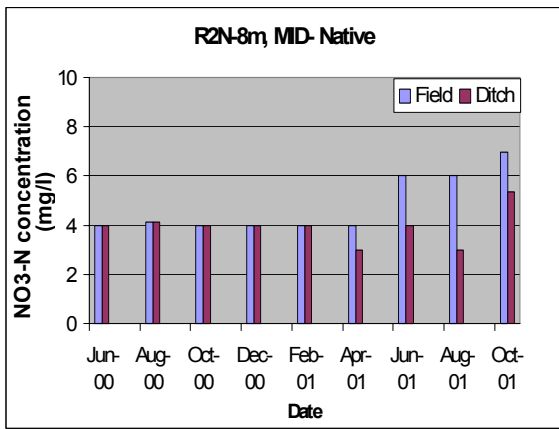
Appendix Figure 13 Nitrate Concentrations for R2N-No Buffer



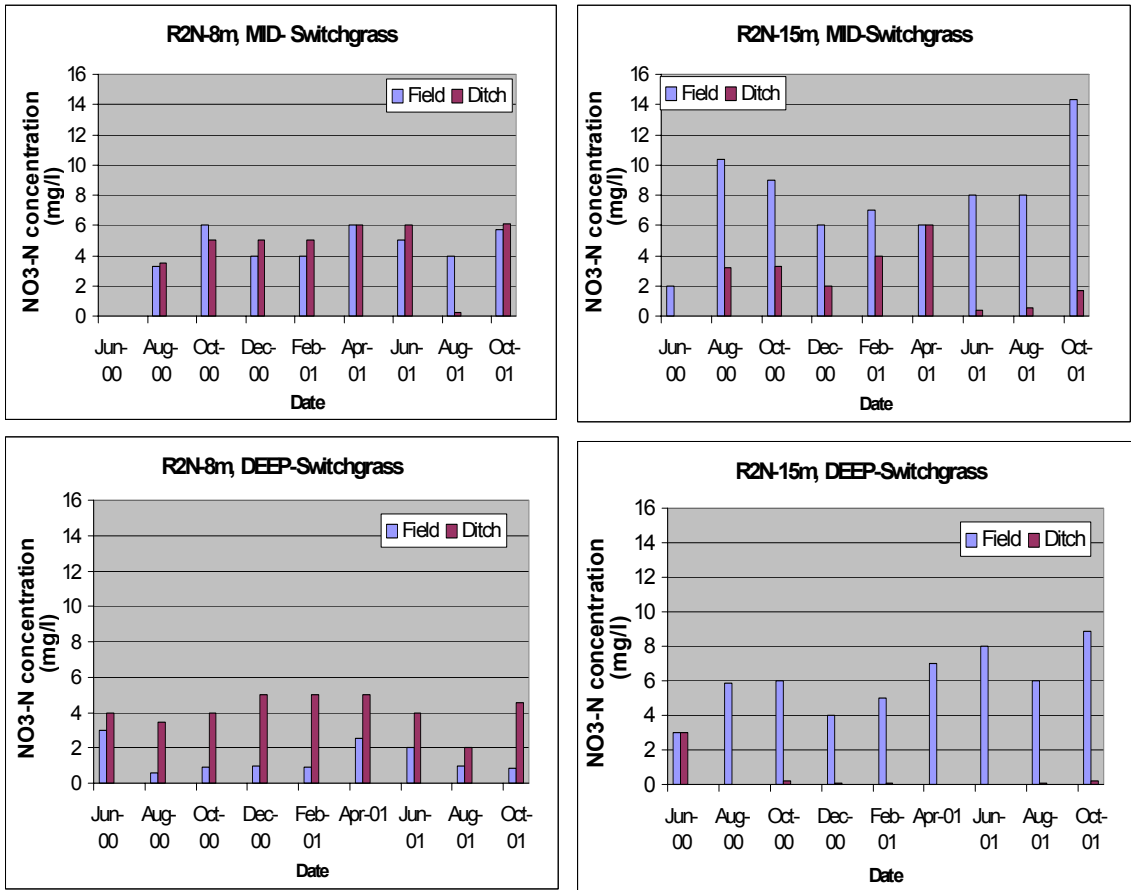
Appendix Figure 14 Nitrate Concentrations for R2N-Trees



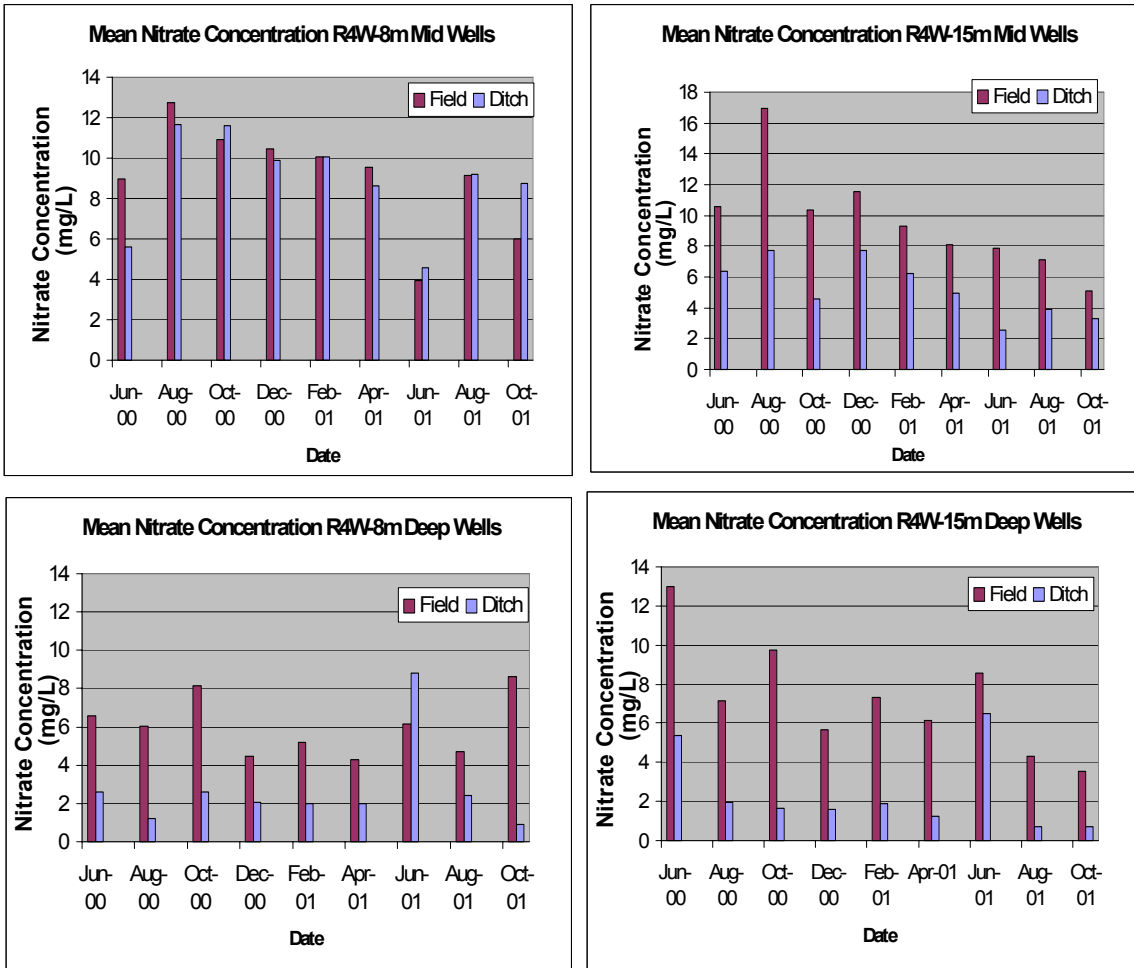
Appendix Figure 15 Nitrate Concentrations for R2N-Fescue



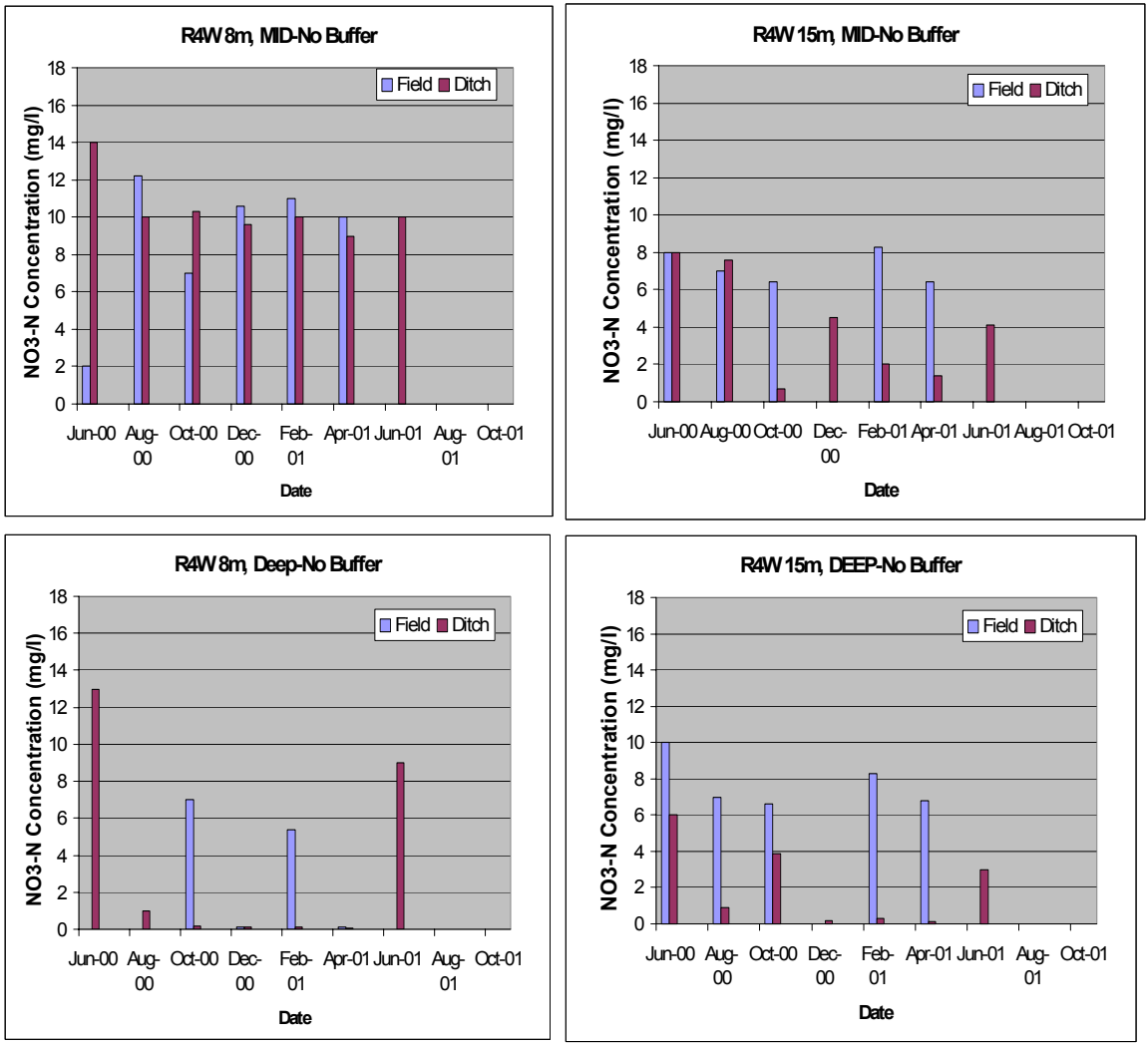
Appendix Figure 16 Nitrate Concentrations for R2N-Native



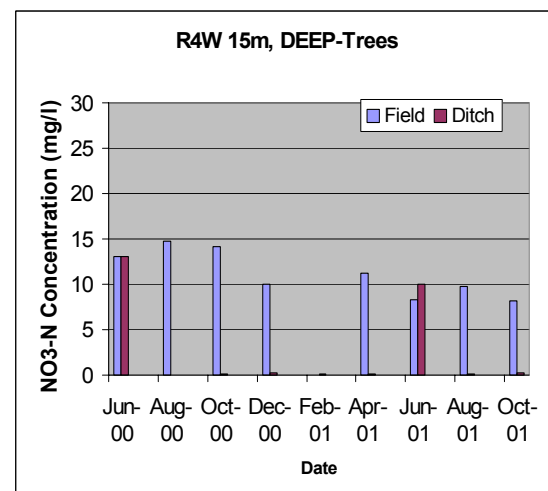
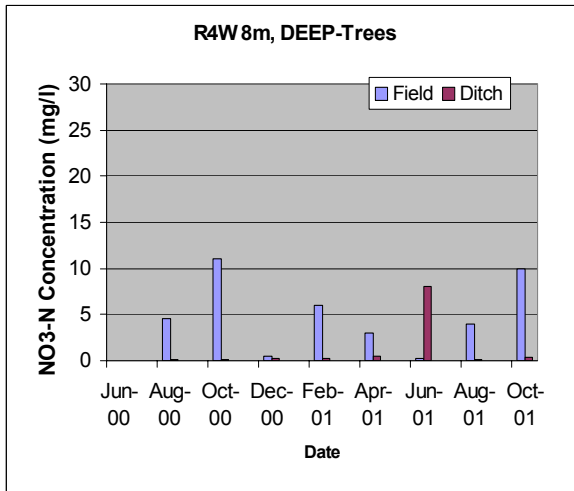
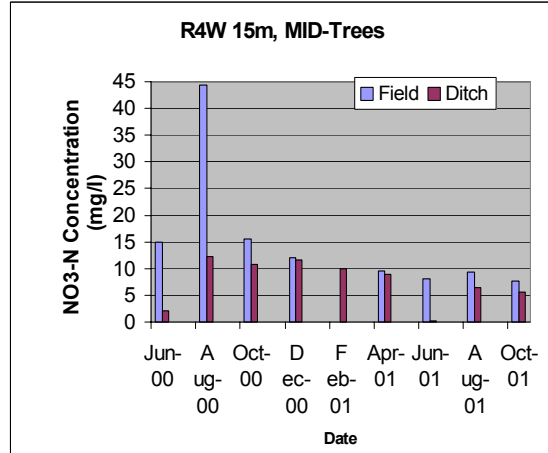
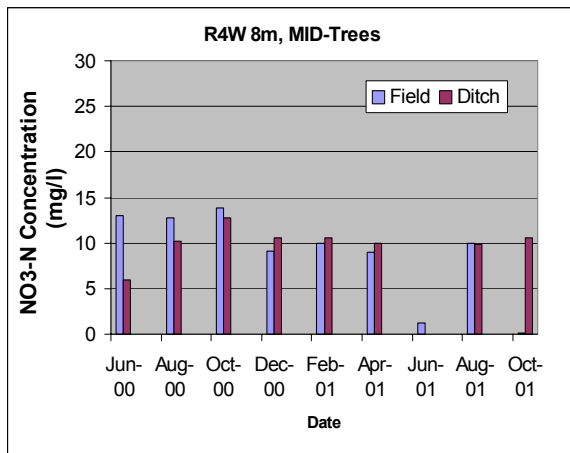
Appendix Figure 17 Nitrate Concentrations for R2N-Switchgrass



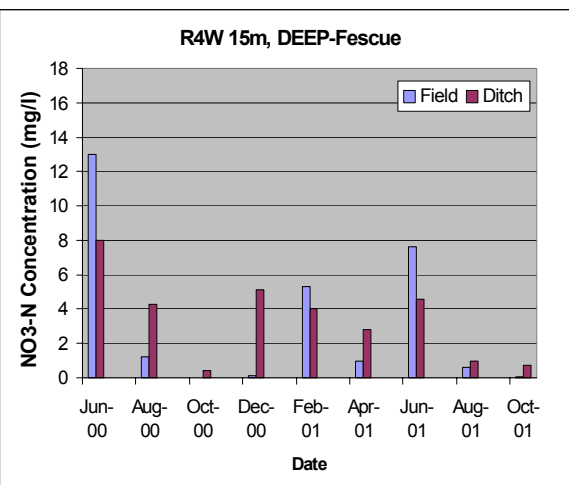
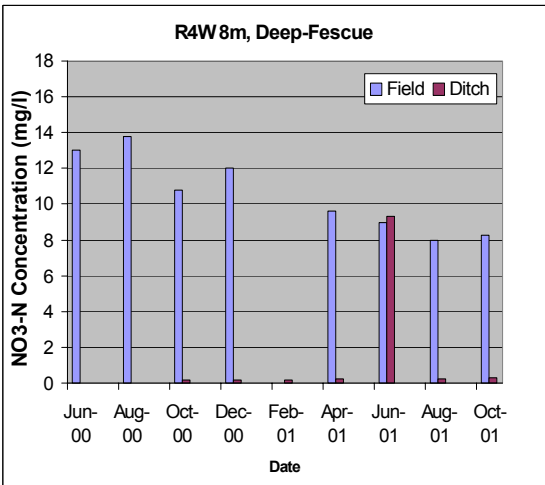
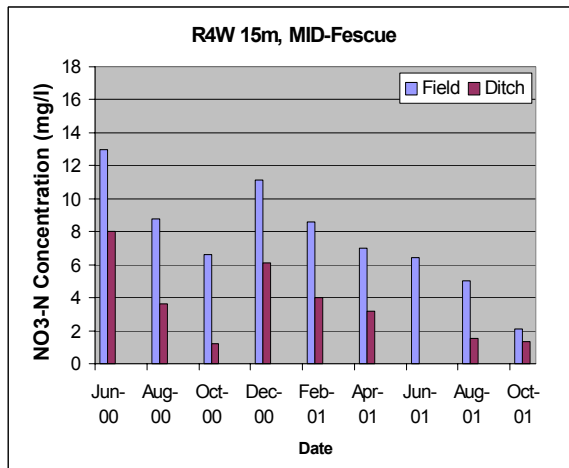
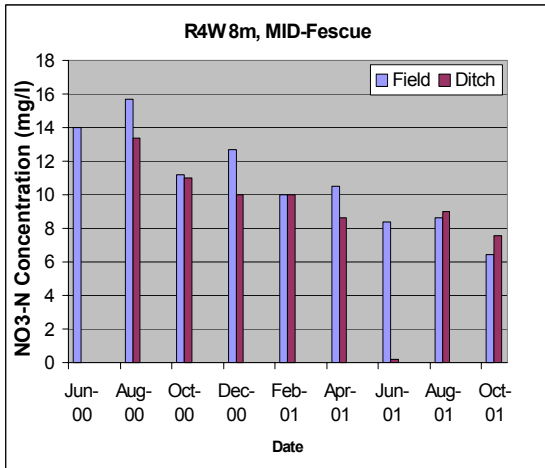
Appendix Figure 18 Mean Nitrate Concentrations for R4W



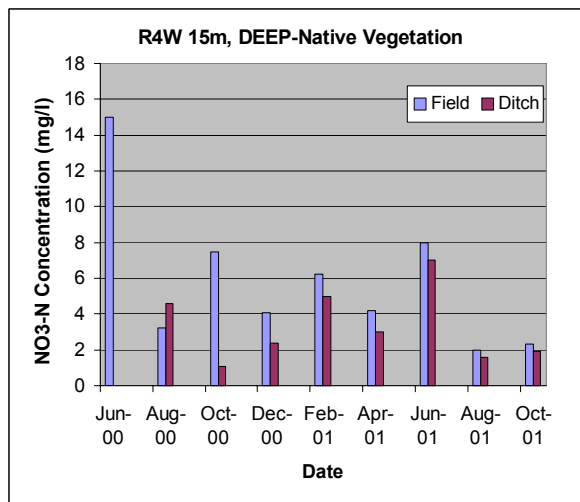
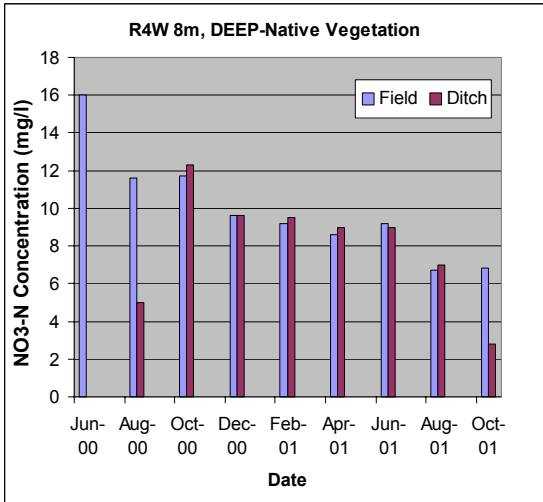
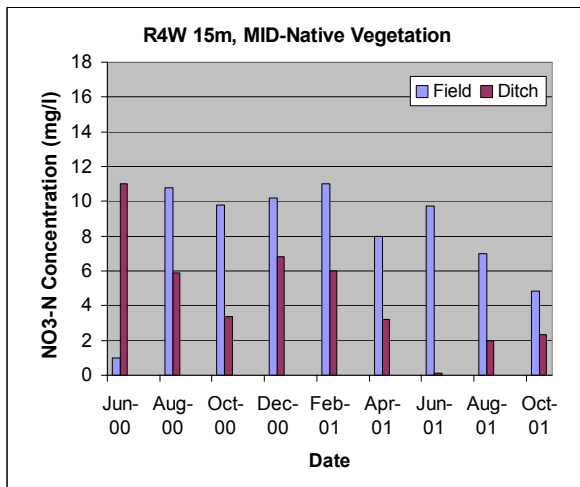
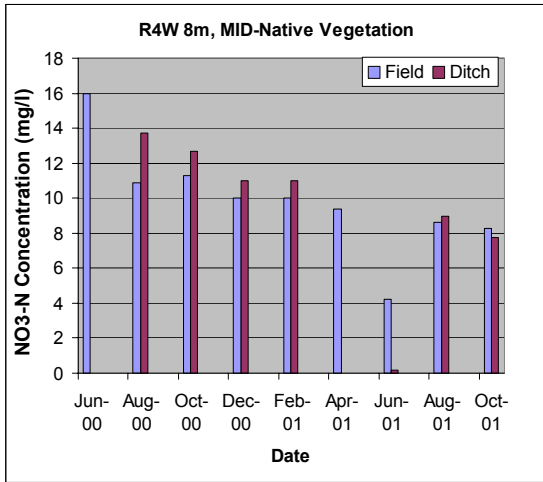
Appendix Figure 19 Nitrate Concentrations for R4W-No Buffer



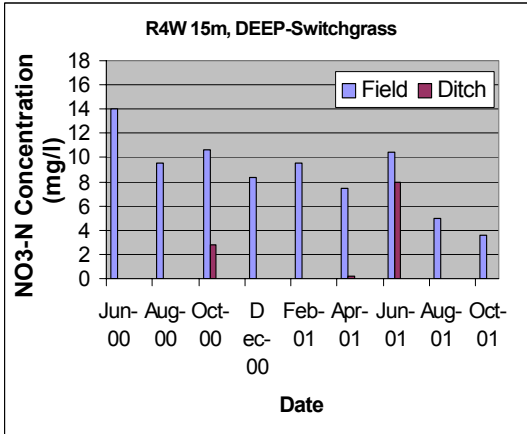
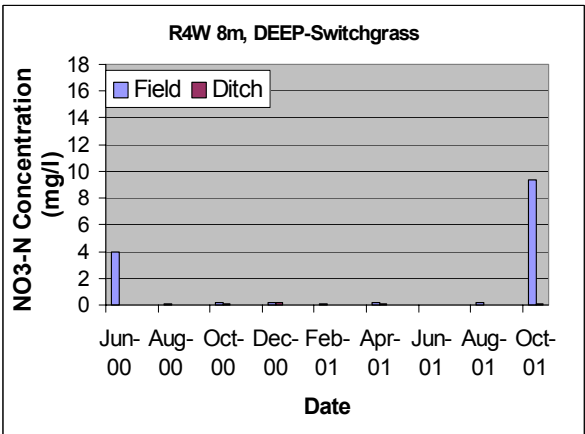
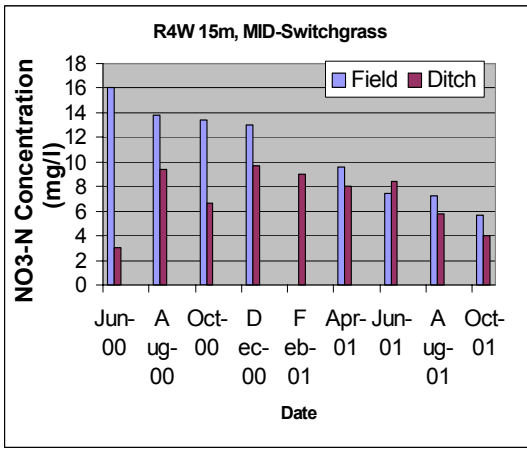
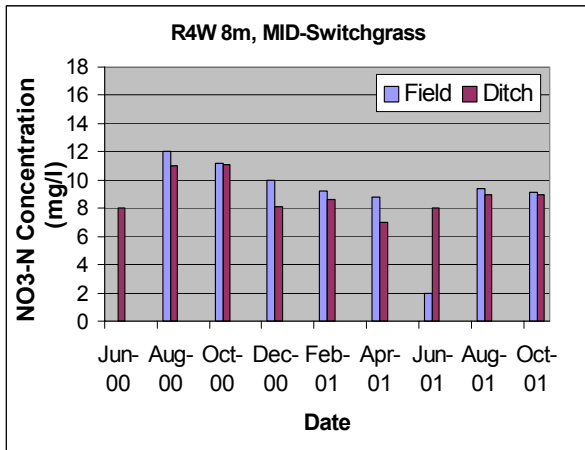
Appendix Figure 20 Nitrate Concentrations for R4W-Trees



Appendix Figure 21 Nitrate Concentrations for R4W-Fescue



Appendix Figure 22 Nitrate Concentrations for R4W-Native Vegetation



Appendix Figure 23 Nitrate Concentrations for R4W-Switchgrass