THESIS

NITRATE REMOVAL FROM GROUNDWATER USING A REACTIVE STREAM STABILIZATION STRUCTURE

Submitted by

Christina M. Mitchell

Department of Civil and Environmental Engineering

In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Spring 2010

COLORADO STATE UNIVERSITY

March 12, 2010

WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY CHRISTINA M. MITCHELL ENTITLED NITRATE REMOVAL FROM GROUNDWATER USING A REACTIVE STREAM STABILIZATION STRUCTURE BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

Committee on Graduate Work

Chester Watson

Mary Stromberger

Advisor: Kenneth Carlson

Department Head: Luis Garcia

ABSTRACT OF THESIS

NITRATE REMOVAL FROM GROUNDWATER USING A REACTIVE STREAM STABILIZATION STRUCTURE

Riparian zones that remove nitrate (NO_3^-) from groundwater play a significant role in protecting and improving the quality of receiving surface waters. Denitrification, the microbial conversion of NO_3 to gaseous forms of nitrogen (N) is an important removal mechanism in these systems. For this process to occur there must be a supply of organic carbon (C). High levels of organic C may be found in the subsurface of relatively undisturbed riparian zones. However, in areas where streambank erosion has resulted in the loss of riparian vegetation (C source) and organic-rich sediments, the amount of C available for denitrification is likely to be low. Vegetation may become established in these areas soon after the banks are stabilized using standard structural and/or bioengineering techniques. However, it will take time for organic C to accumulate in the soil. Thus, significant NO_3 removal via denitrification will not be immediately observed following the completion of bank stabilization work.

This study examined the potential for improving existing streambank stabilization designs to accelerate and maximize groundwater NO_3 removal benefits. A simple, cost-effective structure, called the reactive stream stabilization (RS2) structure, was designed for the purpose of this study. The RS2 structure combines a permeable reactive barrier composed of solid-phase organic C (sawdust) with a common bank stabilization technique (longitudinal peaked stone toe protection). A small field-scale RS2 structure and a control (no organic C amendment) were constructed along a stream in July 2003. The two systems were monitored from August to

December 2003 and from May to September 2004. During the initial monitoring period, NO_3 removal in the reactive barrier averaged 93% (7.27 mg N L^{-1} along the upslope edge, versus 0.48 mg N L^{-1} along the downslope edge). In comparison, NO_3 removal in the control averaged 30% (12.3 mg N L^{-1} along the upslope edge, versus 8.65 mg N L^{-1} along the downslope edge). It was not possible to measure NO_3 removal in the control the following spring and summer because the artificially generated plume of NO_3 was not intercepted by the monitoring wells in the system. The plume was, however, intercepted by the wells located in the reactive barrier. Nitrate loss in the reactive barrier was high and averaged 97% (17.9 mg N L^{-1} along the upslope edge, versus 0.51 mg N L^{-1} along the downslope edge) during this period. The results of this study suggest that RS2 structures can enhance groundwater NO_3 removal along streams. Additional field testing needs to be completed to verify these results, but it appears that the RS2 structure could be an effective tool for reducing NO_3 loading to waterways.

Christina M. Mitchell
Department of Civil and Environmental Engineering
Colorado State University
Fort Collins, CO 80523
Spring 2010

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1. INTRODUCTION

Nitrate contamination of shallow groundwater supplies is a problem in many agricultural regions that is often linked to crop fertilization practices (USEPA, 2000; Nolan and Stoner, 2000). Large amounts of NO_3 can accumulate in the soil profile when commercial fertilizers and animal manure are applied in excess of crop requirements. Nitrate, a soluble form of N, moves easily with surface water (precipitation and irrigation) through the unsaturated zone, particularly in areas with well-drained soils (Nolan and Stoner, 2000). Nitrate that leaches below the root zone can enter shallow aquifers, and then be transported via groundwater flow to nearby streams.

Healthy, undisturbed riparian zones are known to be effective at reducing the amount of NO_3 delivered to streams in subsurface flows. Studies have shown that riparian zones can reduce NO_3 concentrations in shallow groundwater by more than 90% (Jacobs and Gilliam, 1985; Cooper, 1990; Vidon and Hill, 2004a). Denitrification, the microbial reduction of NO_3 to N gases, was identified as the principal NO_3 removal mechanism in these studies. For denitrification to occur organic C must be available and oxygen must be absent or limiting. These conditions are found in the subsurface below the water table at some, but not all, sites. For example, in areas where streambank erosion has resulted in the loss of riparian vegetation and organic-rich sediments, the amount of C available for denitrification is likely to be low. One would expect most of the NO_3 in shallow groundwater to reach the stream at these sites.

Nitrate contamination of streams and rivers is a concern for two reasons. First, high concentrations of NO_3 (>10 mg N L^{-1}) in surface waters used for drinking can cause infant methemoglobinemia, a serious condition, which can be fatal if left untreated (National Research Council, 1995; Knobeloch et al., 2000; Knobeloch and Proctor, 2001). Second, excess NO_3 in

rivers can adversely affect downstream coastal areas. For example, NO_3 from the Mississippi-Atchafalaya River system is one of the main causes of severe bottom-water hypoxia (dissolved oxygen concentrations at or below 2 mg L^{-1}) in the northern Gulf of Mexico (Committee on Environment and Natural Resources, 2000; Rabalais et al., 2002). The size of the Gulf of Mexico's hypoxic zone averaged 15,670 km^2 (6,000 mi^2) during the 5-yr period 2005–2009 (Louisiana Universities Marine Consortium, 2009). As stated in the *Gulf Hypoxia Action Plan 2008 for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico and Improving Water Quality in the Mississippi River Basin*, the goal is "to reduce or make significant progress toward reducing the five-year running average areal extent of the Gulf of Mexico hypoxic zone to less than 5,000 square kilometers by the year 2015" (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008, p. 9). A 45% or more reduction in N loading to the Gulf may be needed to reach this goal (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008). Riparian restoration is one of the strategies recommended for reducing discharges of N, particularly NO_3, to streams and rivers, and eventually the Gulf (Committee on Environment and Natural Resources, 2000; Mitsch et al., 2001).

The first step towards improving the condition of riparian zones along some streams is to stabilize the bank. This can be accomplished using structural methods, which incorporate the use of stone or some other hard material, and/or bioengineering techniques (Johnson and Stypula, 1993; Biedenharn et al., 1997). Vegetation may become established on the bank soon after these techniques are applied if conditions are favorable. However, it will take time for organic C to accumulate in the soil. Thus, significant reduction of NO_3 via denitrification will not be immediately observed after the bank is stabilized using standard techniques.

Permeable reactive barriers (PRBs) composed of organic material (sawdust) have been used to accelerate or enhance denitrification in groundwater (Robertson et al., 2000, 2008; Schipper and Vojvodić-Vuković, 2001). Reductions in groundwater NO_3 concentrations were observed shortly after these systems were installed, as well as over the long term (5 to 14 yr). In

this study, a permeable reactive barrier containing sawdust was combined with a common bank stabilization technique (longitudinal peaked stone toe protection) to enhance NO_3 removal near a stream. The design concept is shown in Fig. 1.1.

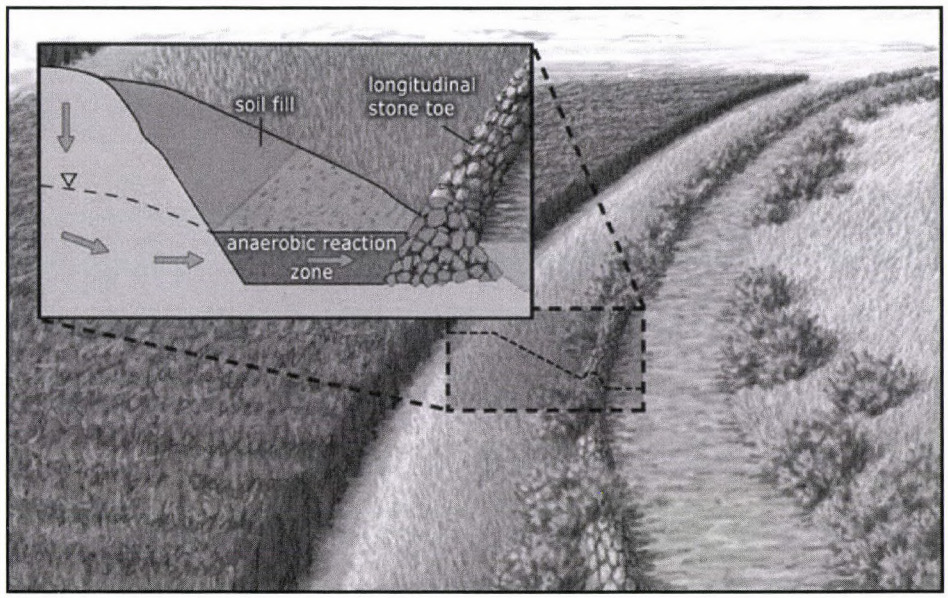

Fig. 1.1. Reactive stream stabilization (RS2) structure. The anaerobic reaction zone represents the permeable reactive barrier composed of sawdust. The blue arrows indicate the direction of groundwater flow.

A small field-scale RS2 structure and a control (no organic C amendment) were constructed along a stream at Colorado State University's Engineering Research Center in Fort Collins, CO. Field studies were conducted during the first year of operation to assess the difference in treatment performance between the two systems. Treatment performance was evaluated by monitoring the change in the concentration of NO_3 in groundwater as it flowed through each system. It was predicted that the RS2 structure would be more effective at reducing NO_3 concentrations in groundwater than the control. This thesis documents the design and construction of the RS2 structure, and the results of the field studies.

CHAPTER 2. LITERATURE REVIEW

2.1 Nitrate and Health

Nitrate contamination of surface water systems used for drinking is a public health concern. High concentrations of NO_3 in drinking water can cause infant methemoglobinemia, a condition characterized by elevated levels of methemoglobin in the blood. After NO_3 is ingested, it is reduced to nitrite in the digestive tract. Nitrite and hemoglobin then react to produce methemoglobin (National Research Council, 1995; Nelson and Hostetler, 2003). Methemoglobin can accumulate in the infant's blood because only a small amount of enzyme is available to convert methemoglobin back to hemoglobin (Knobeloch et al., 2000; Knobeloch and Proctor, 2001; Nelson and Hostetler, 2003). Unlike hemoglobin, methemoglobin is not able to carry oxygen. Thus, as methemoglobin levels increase, the blood's oxygen-carrying capacity decreases (Knobeloch and Proctor, 2001). Cyanosis (gray or bluish discoloration of the skin) becomes visible when methemoglobin levels reach 10 to 20% (Nelson and Hostetler, 2003). Other symptoms of methemoglobinemia, such as rapid heart rate and rapid breathing, appear at higher concentrations (National Research Council, 1995; Nelson and Hostetler, 2003). Death can occur when levels exceed 50% if the infant does not receive treatment (National Research Council, 1995; Knobeloch et al., 2000).

To protect infants, the EPA set the maximum contaminant level (MCL) for NO_3 in drinking water at 10 mg N L^{-1} (National Research Council, 1995). Concentrations exceeding this limit have been measured in some streams and rivers that are used as drinking water sources. In Iowa, for example, NO_3 has been detected at levels above the MCL in the Des Moines River (McIsaac and Libra, 2003) and Raccoon River (Shilling and Lutz, 2004), both of which are

sources of drinking water for Des Moines area residents. To address this problem, Des Moines Water Works constructed a $3.7 million ion-exchange NO_3 removal facility. The system is used when NO_3 concentrations in the river water reach 9 mg N L^{-1} at a cost of $3000 per day (Woolson, 2002; Des Moines Water Works, 2003). During the period 1992 to 2006, the system was operated 42 days a year on average (D. Graham, personal communication, 2006). Management practices that minimize NO_3 loads to the Des Moines and Raccoon Rivers could potentially lead to a reduction in facility usage and thus drinking water treatment costs. Such efforts could also reduce the amount of NO_3 transported downstream to the Mississippi River, which drains into the Gulf of Mexico. Negative impacts associated with the delivery of excess NO_3 to the Gulf and other coastal systems are discussed below.

2.2 Nitrate in Coastal Systems

Nitrogen limits primary production in many temperate-zone coastal systems (National Research Council, 2000; Howarth and Marino, 2006). Consequently, an increase in NO_3 inputs to these systems can lead to an increase in algal biomass. This "increase in the supply of organic carbon" (Nixon, 1995, p. 202) is referred to as eutrophication. One of the negative impacts associated with eutrophication is the loss of bottom-dwelling plants such as seagrasses. This loss is primarily caused by a reduction in light availability due to excessive growth of phytoplankton in the upper portion of the water column, epiphytic algae on the leaves, and/or macroalgae on or near the bottom of the seafloor (Bricker et al., 1999; Hemminga and Duarte, 2000; Hauxwell et al., 2003). The loss of seagrass beds is a concern because they provide food and refuge for many fish and crustaceans, some of which are economically valuable. In addition, they improve water quality by taking up and sequestering nutrients, and trapping sediment (Hemminga and Duarte, 2000).

An increase in algal production can also lead to severe bottom water oxygen depletion in some coastal systems. Algae eventually die and sink to the bottom along with other particulate

organic matter. Bacteria degrade this organic matter. During this process, oxygen is consumed. In water bodies that experience stratification, much of the oxygen that is lost is not replenished because water at the bottom is not able to mix with surface waters that are oxygen-rich. Oxygen levels in these systems can decrease "beyond the point that sustains most animal life" (Diaz, 2001, p. 276). When this occurs, the term hypoxic is used to describe the bottom water (Committee on Environment and Natural Resources, 2000; Diaz, 2001). Fish and other mobile animals respond to hypoxic conditions by leaving the affected area. Animals that are not able to escape, however, show signs of stress and/or die (Committee on Environment and Natural Resources, 2000; Rabalais et al., 2001; Breitburg, 2002).

Hypoxia is a problem in many coastal systems (Bricker et al., 1999; Diaz, 2001). The hypoxic zone (dissolved oxygen concentrations at or below 2 mg L^{-1}) that forms annually in the northern Gulf of Mexico is one of the largest in the world (Rabalais et al., 2002). In July 2009, the hypoxic zone covered 8,000 km^2 (3,089 mi^2) (Louisiana Universities Marine Consortium, 2009). The key factors contributing to the formation of this massive hypoxic zone are water column stratification and excessive phytoplankton growth due to N enrichment (Committee on Environment and Natural Resources, 2000; Rabalais et al., 2002).

Research indicates that algal production increased and hypoxia became more severe in the northern Gulf of Mexico during the second half of the last century (Committee on Environment and Natural Resources, 2000; Rabalais et al., 2002). The amount of NO_3 delivered to the Gulf also increased considerably over that time period (Goolsby et al., 1999; Committee on Environment and Natural Resources, 2000; Goolsby and Battaglin, 2000; Rabalais et al., 2002). The average flux of NO_3 from the Mississippi River Basin to the Gulf was 328,000 t yr^{-1} between 1955 and 1970, and 969,000 t yr^{-1} between 1980 and 1999 (Goolsby and Battaglin, 2000). Most of the increase in NO_3 loading was attributed to an increase in commercial fertilizer use, precipitation, and river discharge (Goolsby et al., 1999; Goolsby and Battaglin, 2000). Other

factors that contributed to the increase were the artificial drainage of agricultural lands and the loss of riparian zones and wetlands (Rabalais et al., 2002).

In 1997, the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force was established in response to increased concern about water quality problems in the Mississippi River Basin and hypoxia in the northern Gulf of Mexico (USEPA, 2000). Over the course of several years, members of the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force worked on developing a plan of action to address these issues (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2001; Rabalais et al., 2002). In January 2001, the *Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico* (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2001) was submitted to Congress in accordance with The Harmful Algal Bloom and Hypoxia Research and Control Act of 1998 (Public Law 105-383). In June 2008, the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force issued a revised plan (the *Gulf Hypoxia Action Plan 2008 for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico and Improving Water Quality in the Mississippi River Basin*). As stated in the 2008 Action Plan, the goal is "to reduce or make significant progress toward reducing the five-year running average areal extent of the Gulf of Mexico hypoxic zone to less than 5,000 square kilometers by the year 2015" (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008, p. 9). A 45% or more reduction in N loading to the Gulf may be needed to reach this goal (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008). Strategies recommended for reducing discharges of N, particularly NO_3, to streams and rivers, and eventually the Gulf, include the implementation of best management practices (BMPs) on farms, and the creation and restoration of riparian zones (Committee on Environment and Natural Resources, 2000; Mitsch et al., 2001).

2.3 Nitrate Removal in Stream Riparian Zones

Healthy, undisturbed riparian zones in agricultural areas are known to be effective at reducing the amount of NO_3 delivered to streams in subsurface flows. Studies have shown that forested riparian zones can reduce NO_3 concentrations in shallow groundwater from agricultural fields by more than 90% (Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Lowrance, 1992; Haycock and Pinay, 1993; Jordan et al., 1993; Vidon and Hill, 2004a). Large declines in shallow groundwater NO_3 concentrations have also been measured in grass-vegetated riparian zones (Cooper, 1990; Haycock and Pinay, 1993; Clément et al., 2002). It is important to note, however, that not all riparian zones effectively attenuate NO_3 (Hill, 1996). As discussed later, the extent to which NO_3 removal occurs in these systems depends on many factors.

Groundwater NO_3 removal in riparian areas may be the result of several processes including plant uptake, microbial assimilation, dissimilatory NO_3 reduction to NH_4 (DNRA), and denitrification (Hill, 1996). Nitrate that is taken up by plant roots and microorganisms is reduced to NH_4, which is used to make amino acids. The amino acids are then utilized to form other N-containing compounds (Heritage et al., 1999; Myrold, 1999). This N will be released back to the soil following the decomposition of plant residues and dead bacterial cells.

Dissimilatory NO_3 reduction to NH_4 is another mechanism that does not result in the loss of N from the system. It is a process that is mediated by certain fermentative bacteria under anaerobic conditions (Tiedje, 1988). It is expected to occur in environments where Eh is very low (< 0 mV) and the supply of organic C is high relative to that of NO_3 (Tiedje, 1988; Reddy and DeLaune, 2008). The process involves two steps, the first being the reduction of NO_3^- to NO_2^-, and the second, the reduction of NO_2^- to NH_4^+. Most bacteria obtain energy from the first reaction, but not the second (Tiedje, 1988). The NH_4 generated in the second step is released to the soil solution.

Denitrification is a respiratory process in which NO_3, the terminal electron acceptor, is reduced to N_2O and/or N_2. These gases are released to the atmosphere. Thus, denitrification

results in the loss of N. The process is carried out by a large number of bacteria including, for example, species belonging to the genera *Pseudomonas*, *Alcaligenes*, *Flavobacterium,* and *Bacillus*. These bacteria use oxygen as the terminal electron acceptor when it is available. After the oxygen has been consumed, they utilize NO_3 and reduce it to N_2 as follows (Tiedje, 1994; Myrold, 1999; Rittmann and McCarty, 2001):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO(g) \rightarrow N_2O(g) \rightarrow N_2(g)$$

A specific enzyme catalyzes each reduction step (Tiedje, 1994; Myrold, 1999; Rittmann and McCarty, 2001). The four reduction reactions and corresponding enzymes are (Rittmann and McCarty, 2001):

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \quad \text{(Nitrate Reductase)} \quad [1]$$

$$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O \quad \text{(Nitrite Reductase)} \quad [2]$$

$$2NO + 2e^- + 2H^+ \rightarrow N_2O + H_2O \quad \text{(Nitric Oxide Reductase)} \quad [3]$$

$$N_2O + 2e^- + 2H^+ \rightarrow N_2 + H_2O \quad \text{(Nitrous Oxide Reductase)} \quad [4]$$

Electron transport to each N oxide results in the formation of a proton motive force, which drives the synthesis of the high-energy compound, adenosine triphosphate (ATP) (Tiedje, 1994; Rittmann and McCarty, 2001). The electrons originate from the substance that undergoes oxidation (electron donor). Some bacteria can use reduced forms of Fe and S as electron donors (Korom, 1992; Straub et al., 1996). Most soil denitrifiers, however, use organic compounds (Myrold, 1999). The overall reaction when a simple carbohydrate (CH_2O) serves as the electron donor is (Delwiche, 1981):

$$5CH_2O + 4NO_3^- \rightarrow 5CO_2 + 2N_2 + 3H_2O + 4OH^- \quad [5]$$

This reaction has been identified as the principal mechanism of NO_3 removal at many riparian study sites (Jacobs and Gilliam, 1985; Cooper, 1990; Verchot et al., 1997; Hill et al., 2000; Clément et al., 2002; Vidon and Hill, 2004b).

2.4 Factors Affecting Denitrification in Stream Riparian Zones

Vegetation is one factor that affects denitrification in stream riparian zones. Vegetation provides denitrifiers with a supply of organic C (e.g., root exudates). In addition, plant-derived organic C stimulates aerobic respiration, which contributes to the development of anaerobic conditions. Parkin (1987) measured high denitrification activity within anaerobic microsites surrounding decomposing plant material in surface soils at a field site in Maryland. Similarly, Jacinthe et al. (1998) found that denitrification activity was concentrated around patches of organic material (decaying roots) in the subsurface (0.6 m below the soil surface) of a forested riparian zone in Rhode Island. These patches were found below the water table during the dormant season. High rates of NO_3 removal were measured at this study site (Nelson et al., 1995; Gold et al., 1998). In another study, Addy et al. (1999) found that patches of organic matter in poorly drained forested and herbaceous riparian subsurface soils stimulated denitrification. Patches and roots were observed up to 90 cm below the soil surface at both the forested and herbaceous sites. These results and those reported by Clément et al. (2002) indicate that significant NO_3 removal by denitrification can occur in areas where incoming NO_3-contaminated shallow groundwater interacts with plant-derived organic matter in the top 2 to 3 ft of soil. It is important to remember that these studies were conducted in areas with dense vegetation cover. In riparian zones where bank erosion has resulted in the loss of vegetation, NO_3 removal from shallow groundwater via denitrification would likely be limited by organic C availability.

It should be noted that many streams requiring bank stabilization work are incised (C. Watson, personal communication, 2004). As stated by Simon and Darby (1999, p. 3), "the defining characteristic of incised channels is that they have, at some point in their history undergone, or are undergoing, bed-level lowering." Incision or bed degradation can lower riparian water tables (Bravard et al., 1999; Schilling et al., 2004). In areas where this has occurred, groundwater may flow at depths of 1 to several meters below the soil surface. Some researchers have found denitrification activity to be low or absent at such depths due to a shortage

of organic C (McCarty and Bremner, 1992; Starr and Gillham, 1993). This is in contrast to findings reported by others. For example, Hill et al. (2000) measured high rates of denitrification 1.5 to 3.7 m below the soil surface near C-rich buried channel deposits in a forested riparian zone in southern Ontario, Canada. In another study, Kellogg et al. (2005) measured significant denitrification activity 1.5 and 2.6 m below the soil surface close to a stream. Buried organic deposits were found up to 3 m below the soil surface near the sampling locations at this study site. These results suggest that significant denitrification can occur deep in the subsurface if buried organic deposits are present. It is unlikely, however, that such deposits would be present near the stream in areas where banks are actively eroding.

2.5 Streambank Stabilization and Riparian Zone Restoration

As mentioned previously, the restoration of riparian zones has been proposed as an approach for reducing the amount of NO_3 transported via groundwater flow from agricultural fields to streams and ultimately downstream coastal waters. It is recommended that degraded riparian zones bordering small (first- and second-order) streams be repaired before those bordering larger, higher-order channels since "most of the flow in high-order streams comes from low-order stream channels, and only a small portion of the flow in high-order streams actually crosses the riparian areas associated with the high-order stream segment" (National Research Council, 2002, p. 76). The first step towards improving the condition of riparian areas along some small streams is to stabilize the bank. This can be accomplished using structural methods and/or bioengineering techniques. Structural methods, which incorporate the use of stone (e.g., longitudinal peaked stone toe protection) or some other hard material, are typically used to protect the toe or base of the bank from erosive flows. Vegetative/bioengineering techniques are often used to stabilize the upper portion of the bank (Johnson and Stypula, 1993; Biedenharn et al., 1997). Vegetation may become established on the bank soon after these techniques are applied if conditions are favorable. However, it takes time for organic matter to accumulate in the soil. Thus, significant

loss of NO_3 via denitrification will not be immediately observed after the bank is stabilized using standard techniques.

2.6 Optimizing Nitrate Removal in Areas Targeted for Streambank Stabilization

The objective of this study was to determine if NO_3 removal could be accelerated and optimized by modifying bank stabilization designs to include permeable reactive barrier technology. Permeable reactive barriers have been used to remove NO_3 from groundwater. In 1992, Robertson and Cherry (1995) constructed a permeable reactive barrier (1.2 m wide by 0.6 m thick) to treat septic system NO_3. Installation of the reactive barrier involved digging a trench and then backfilling it with a soil mixture containing 20% sawdust by volume as a source of C for denitrifiers. Following construction activities, a groundwater-monitoring program was initiated to evaluate system performance. During the first year of operation (September 1992 to September 1993), NO_3 levels declined from 57–62 to 2–25 mg N L^{-1} as groundwater flowed through the reactive barrier. Significant NO_3 removal was measured in this system over the next 14 years (Robertson et al., 2000, 2008).

Schipper and Vojvodić-Vuković (1998) installed a reactive barrier to treat NO_3-contaminated groundwater emanating from an area that was irrigated with dairy effluent. The reactive barrier (35 m long, 1.5 m deep, and 1.5 m wide) contained approximately 30% sawdust by volume. The system was monitored over a 5-yr period, during which time no decline in performance was observed. During the study, NO_3 concentrations in groundwater upslope of the reactive barrier ranged from 5 to 15 mg N L^{-1}. Groundwater NO_3 concentrations in the reactive barrier were typically less than 2 mg N L^{-1} (Schipper and Vojvodić-Vuković, 2001). Laboratory studies confirmed that denitrification was responsible for the observed decline in NO_3 concentration (Schipper and Vojvodić-Vuković, 2000, 2001).

Fahrner (2002) constructed a reactive barrier (170 m long, 1.5 m deep, and 1.5 m wide) composed of sawdust (30% by volume) downgradient of a cattle feedlot in Australia. Nitrate

removal in this system averaged 71% (62 mg N L^{-1} upgradient, versus 18 mg N L^{-1} downgradient) during the first year of operation. The author concluded that denitrification was responsible for the observed NO_3 loss; however, this was not confirmed by direct measurement. Information on the long-term performance of this system has not been published to date.

Permeable reactive barrier technology has been incorporated into the design of subsurface tile drainage systems. Jaynes et al. (2008) installed reactive barriers composed of oak woodchips parallel to a drainage tile under a cropped field in Iowa. Nitrate was removed from water as it flowed through the woodchip filled trench on each side of the tile. Nitrate concentrations in drainage from this system averaged 8.8 mg N L^{-1} during the 5-yr study period (2001-2005). In comparison, NO_3 concentrations in drainage from the conventional system (control) averaged 22.1 mg N L^{-1}.

CHAPTER 3. DEVELOPMENT AND PRELIMINARY ASSESSMENT OF REACTIVE STREAM STABILIZATION STRUCTURE

3.1 Introduction

During the summer of 2003, an experimental field structure was constructed along a stream behind the Engineering Research Center at Colorado State University in Fort Collins, CO. The field structure consisted of three isolated research cells, identified as Cells A, B, and C (Fig. 3.1). Reactive stream stabilization structures were constructed in Cells A and C. The RS2 structure combined a permeable reactive barrier with longitudinal peaked stone toe protection. The reactive barrier was installed adjacent to the stone toe in Cells A and C. The RS2 structure in Cell C was designed and constructed for a separate study to evaluate the potential for improving streambank stabilization techniques to maximize P removal benefits. The RS2 structure in Cell A was built specifically for this study; the system was designed to intercept and treat incoming NO_3-contaminated groundwater. Solid-phase organic C (sawdust) was included in the reactive barrier mixture in Cell A to stimulate denitrification. Sawdust was selected as the C source for the following reasons:

- Column studies performed at Colorado State University's Environmental Engineering Laboratory to assess the denitrification potential of three solid C sources (sawdust, compost, and leaves) demonstrated that sawdust was the most effective material for promoting denitrification.
- Field studies have demonstrated that reactive barriers composed of sawdust are very effective at removing NO_3 from groundwater (Robertson and Cherry, 1995; Schipper and Vojvodić-Vuković, 1998, 2000, 2001; Robertson et al., 2000, 2008; Fahrner, 2002).

- It decomposes slowly. Thus, it is suitable for use in long-term treatment applications.
- It is readily available and inexpensive.

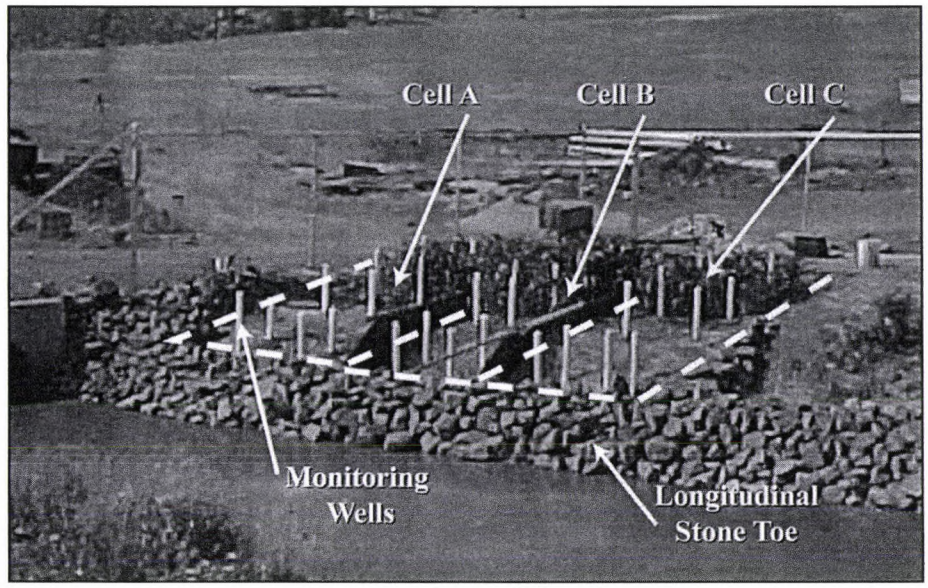

Fig. 3.1. Experimental field structure.

Cell B was the control cell (Fig. 3.1). A permeable reactive barrier was not installed adjacent to the stone toe in this cell. The section adjacent to the stone toe was constructed using only native soil. Native soil was also used to construct the field plot upslope of the bank in each cell (Fig. 3.1). The field plots were planted to corn and fertilizer was applied shortly thereafter to generate NO_3-contaminated groundwater. A network of monitoring wells was installed to examine changes in the chemistry of groundwater as it moved from the field plot to the stone toe in each cell. The wells were located along two transects perpendicular to the stream in each cell (Fig. 3.1). A fence was installed to exclude animals from the study site.

A cross-section of the research cell and a plan view of the field structure are shown in Fig. 3.2. Each cell was lined with a 45 mil impermeable rubber liner. The cells were constructed at a slope of 4% to promote flow towards the stream. The slope of the stone toe was lined with filter fabric to prevent the loss of material and provide a flow path in and out of the system. Cell A was 5.9 m (19.5 ft) long, 2.0 m (6.5 ft) wide, and 1.1 m (3.5 ft) deep. Control Cell B was 5.9 m (19.5 ft) long, 1.5 m (5 ft) wide, and 1.1 m (3.5 ft) deep. The installed reactive barrier in Cell A

was approximately 1.5 m (5.0 ft) long, 1.7 m (5.6 ft) wide, and 0.6 m (2 ft) deep (measured at the center). Construction details are provided in section 3.2.

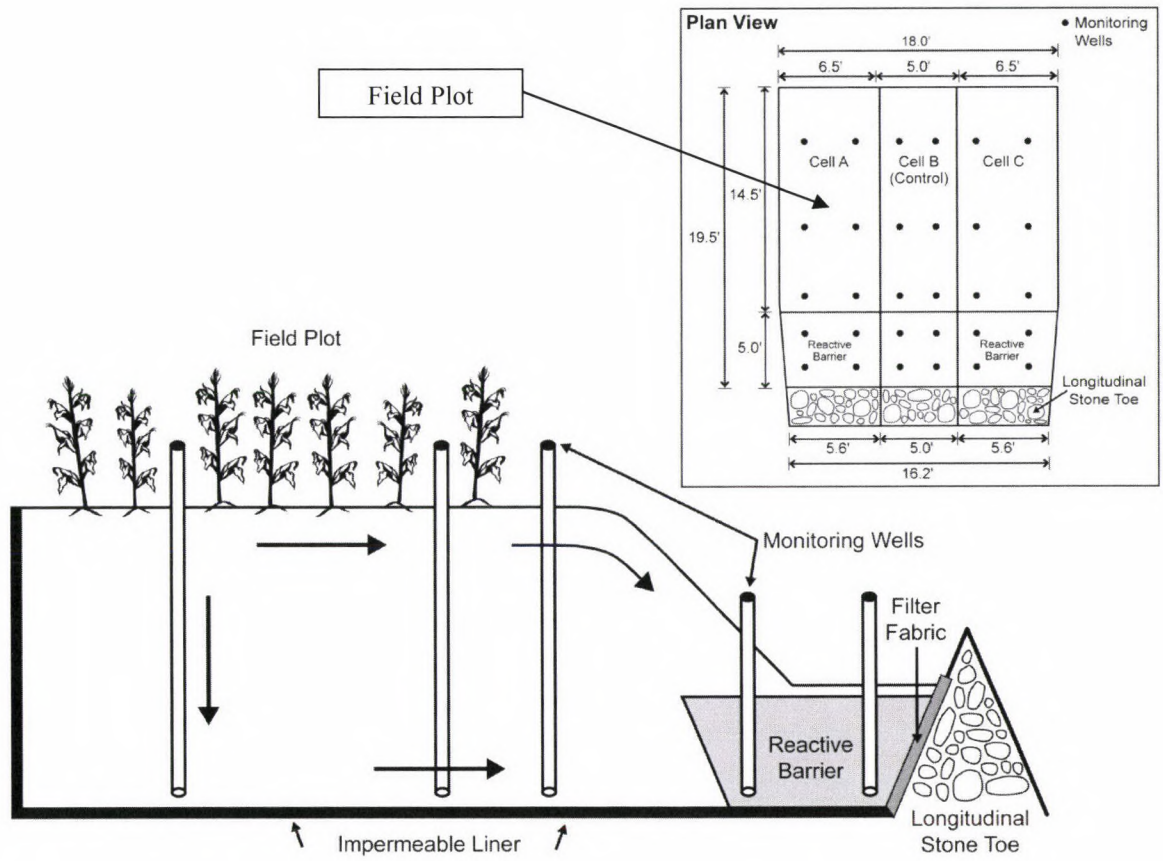

Fig. 3.2. Cross section of research cell and plan view of field structure.

Construction of the experimental field structure was completed in July 2003. This study was conducted from August to December 2003 to evaluate the initial difference in treatment performance between the RS2 structure (Cell A) and the bank in Cell B (control). It was predicted that the RS2 structure would be more effective at reducing NO_3 concentrations in groundwater than the control.

3.2 Materials and Methods

3.2.1 Study Site and Construction

The experimental field structure shown in Fig. 3.1 was constructed at the Engineering Research Center along a stream, which flows through the property. The Engineering Research Center features both indoor and outdoor laboratories for conducting large-scale model and full-scale prototype hydraulic studies, and environmental engineering laboratories equipped with advanced analytical instrumentation for water quality research. The U.S. Bureau of Reclamation's Horsetooth Reservoir, which is located west of the facility, is utilized as a water supply for both indoor and outdoor hydraulic investigations. A testing flume, with a discharge capacity of 80 cfs, is located near the study site (Fig. 3.3). Operation of the flume caused high streamflows, which occasionally resulted in flooding of the lower bank in the field structure.

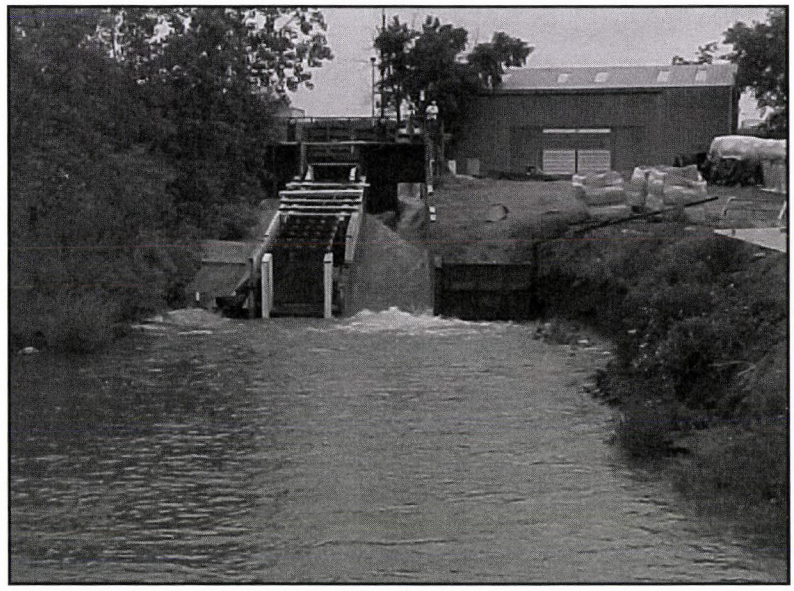

Fig. 3.3. Testing flume at study site.

Design and construction of the field structure began in May 2003. The first phase of construction involved excavating an 18-ft section of the right bank and part of the adjacent terrace with a backhoe. This resulted in an opening, approximately 5.5 m (18 ft) long, 6.1 m (20 ft) wide, and 1.4 m (4.5 ft) deep, parallel to the stream (Fig. 3.4). The depth of the excavation coincided with the level of the current floodplain.

Fig. 3.4. Excavation of streambank and adjacent terrace.

Steel frames or walls were fabricated and used in conjunction with impermeable liners to divide the area into three separate research cells (Fig. 3.5 and 3.6). Two frames were constructed using 1-in square steel tubing. The frames were positioned a distance apart equivalent to the width of the middle cell (Cell B), and welded together with pieces of steel tubing. The steel tubing connections provided stability, eliminating the need to dig trenches to anchor the two walls (frames). The steel frames were installed following preparation of the surface soil. Stones and roots were removed and native soil mixed with sand was added to fill in low areas and create a slope (4%) to promote flow towards the stream. A gas-powered, vibratory roller was used to compact the soil. A level was used to verify that the slope across the bottom was uniform. Filter fabric (Mirafi® Filterweave® 700) was then installed on the bottom and side slopes for liner protection.

The next phase of construction involved isolating the three research cells and backfilling to reconstruct the upland area (field plots). After the filter fabric was installed, the steel frames described above were lowered into the excavation (Fig. 3.5). A Firestone® EPDM 45 mil rubber liner (20 x 30 ft) was then placed in each research cell (Fig. 3.6). The liner draped over the side slopes and the steel frames. Clamps were used to secure the liner to the steel frames. The native

soil removed was used as fill after being passed through a 4 in square screen. Disturbance to the soil at the study site resulted in the formation of large clods. The screening process was performed to remove these large clods and minimize the degree of short-circuiting.

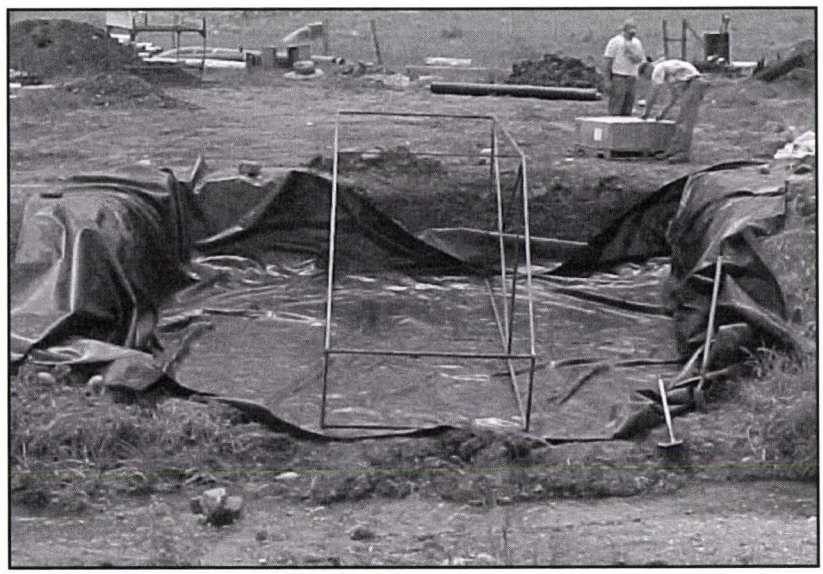

Fig. 3.5. Placement of filter fabric and steel frames.

Fig. 3.6. Placement of impermeable liner in research cell.

A systematic approach was employed to reconstruct the upland area (field plot) in each cell. A small quantity of soil fill, approximately 1 yd, was added to each cell and spread across a section of the bottom with a shovel or rake (Fig. 3.6). This resulted in a relatively uniform soil layer in each cell. Layers of soil were added to each cell simultaneously in the same manner to a

depth that corresponded to the adjacent land surface elevation (Fig. 3.7). Since the soil fill was distributed evenly, the tension on the liner along the steel frame(s) in each cell was similar. This minimized slipping and kept the liner from protruding through the openings in the frame and into the adjacent cell. A shallow trench was dug around the perimeter to secure the liner and underlying filter fabric.

Fig. 3.7. Reconstruction of upland area (field plots).

Longitudinal peaked stone toe protection was the bank stabilization technique used in this study. This technique was selected because it is a proven method of bank stabilization commonly used by the U.S. Army Corps of Engineers (C. Watson, personal communication, 2010). It is important to note though that other techniques (e.g., stacked coir geotextile rolls) could be used in conjunction with reactive barrier technology. In this study, the stone toe was constructed using well-graded, angular granite. The stone was lowered into the stream using a bobcat. The stone was then hand placed at a rate of 1 ton per linear foot along the toe of the streambank adjacent to the study site. This resulted in a triangular section of stone (34 linear ft) with a crown elevation 3 ft above the streambed (Fig. 3.8). To protect the structure from high flows associated with flume operations, toe protection was extended an additional 16 ft upstream and a tieback was incorporated into the design. A shallow trench was excavated into the bank slope to facilitate the

placement of the tieback stone. The stream shown in Fig. 3.8 is running at the typical flow rate but as mentioned, when the testing flume upstream was running, the flow rate could increase by as much as 80 cfs resulting in flooding of the lower bank in the field structure.

Fig. 3.8. Longitudinal peaked stone toe protection with tieback.

Before the reactive barrier was installed in Cell A, excess liner extending beyond the base of the stone toe was removed. Strips of filter fabric were cut and placed along the slope of the toe structure. The filter fabric was tucked under the liner along the base to secure its position. Some of the stone forming the peak was moved and then repositioned on top of the filter fabric to hold the material in place. The slope of the stone toe was lined with filter fabric to prevent the loss of reactive barrier material and provide a flow path in and out of the system (Fig. 3.9).

Untreated pine sawdust was mixed with native soil, coarse sand, and silty sand (silt-sand mixture) to construct the reactive barrier in Cell A. Only a small amount of native soil (10% by volume) was included in the mixture. During construction, the excavated soil was piled on the ground surface where it dried while the research cells were being constructed. Cohesive (clay) soils tend to form large, firm clumps when dry. As mentioned previously, a screening process was performed to remove large clods from the soil. Most of the screened soil was used to construct the field plots and the bank in Cell B (control). Only a small amount of the remaining soil was

suitable for mixing with the pine sawdust. Other soils (coarse and silty sands) were used to increase the volume of reactive barrier material. The reactive barrier in Cell A contained 20% sawdust, 35% coarse sand, 35% silty sand, and 10% native soil by volume.

Fig. 3.9. Placement of filter fabric along slope of stone toe.

Spatial variations in hydraulic conductivity (K) within the reactive barrier can result in channeling of flow, and consequently a decrease in treatment performance (Benner et al., 2001). Steps were taken in this study to ensure that the reactive barrier mixture was homogeneous (uniform K). Small piles containing the appropriate volume of each material were formed and mixed individually on the ground surface using a bobcat. The well-mixed piles were then combined into a single pile. Reactive barrier installation involved backfilling the section along the base, adjacent to the stone toe, with the uniform mixture (Fig. 3.10). Cell A contained approximately 40 ft^3 of reactive barrier material. The installed reactive barrier was approximately 1.5 m (5.0 ft) long, 1.7 m (5.6 ft) wide, and 0.6 m (2 ft) deep (measured at the center).

In an actual field application, the reactive barrier component of the RS2 structure would simply be covered with soil. In this study, a high permeability sand layer was installed on the bank slope in Cell A to divert surface runoff generated from fertilizer and irrigation practices through the reactive barrier (Fig. 3.11). Native soil was then added to cover the coarse sand layer

and the exposed section of the reactive barrier adjacent to the stone toe (Fig. 3.12). The bank in Cell B (control) was constructed using only native soil. Grass seed was planted on the bank in each cell.

Fig. 3.10. Reactive stream stabilization (RS2) structure in Cell A.

Fig. 3.11. Coarse sand layer on bank slope in Cell A.

Fig. 3.12. Native soil covering sand layer and reactive barrier.

3.2.2 Operating Conditions

The field plots were planted to sweet corn and a drip irrigation system was installed, with a valve manifold to isolate each cell. Drip lines were positioned along the rows of corn planted in each cell. Liquid fertilizer and irrigation water were applied separately to the field plots through the drip system. Irrigation and fertilization practices began in July 2003 following the completion of construction activities.

The N application rate for sweet corn is 250 lb $acre^{-1}$ for a soil with low NO_3-N (< 9 ppm) and organic matter in the 0 to 1% range (Ells, 1993). Based on this recommendation, the suggested N rate for the field plots in Cells A and B combined (3.8×10^{-3} acres) was about 1 lb per season. If fertilizer rates were based on crop demand, 1 lb of N would have been applied on the field plots in Cells A and B. However, the purpose of this study was to evaluate the effectiveness of the RS2 structure in Cell A in terms of NO_3 removal. Fertilizer was applied at a rate (see below), which exceeded the suggested rate, to ensure a detectable concentration of NO_3 in the groundwater. The water-soluble fertilizer used in this study contained 20% total N (4% ammoniacal N, 6% NO_3-N, and 10% urea N) and 20% total P by weight. Fertilizer solution was prepared by dissolving 1 lb of dry fertilizer in 200 gallons of water. The concentration of N and P

in the liquid fertilizer was 120 mg L^{-1}. Bulk liquid fertilizer was pumped from a storage tank through the drip irrigation system.

The field plots in Cells A and B were irrigated and fertilized from July to December 2003. Two hundred gallons of liquid fertilizer (0.2 lb N) were applied to each field plot once a week for the first 6 weeks. Fertilizer application rates were then reduced near the end of the crop cycle. From mid-August to November, 133 gallons of liquid fertilizer (0.133 lb N) were applied to each field plot weekly. The field plots were fertilized once in November. On this date, 133 gallons of liquid fertilizer (0.133 lb N) were applied to each field plot. During the initial phase of the study, each field plot was irrigated 3 days per week (288 gallons per day). At the end of August, irrigation was reduced to 144 gallons per day, 3 times per week. In November, irrigation was applied when the weather permitted.

3.2.3 Sampling, Analysis, and Instrumentation

A network of monitoring wells was installed to examine changes in the chemistry of groundwater as it moved from the field plots through the reactive barrier in Cell A and the bank in Cell B. The monitoring wells were installed along two transects perpendicular to the stream in each cell (Fig. 3.13). Five monitoring wells were located in each transect. Monitoring wells in rows 1 and 2 were located in the reactive barrier in Cell A, and in the bank in Cell B. Rows 1 and 2 were 1.5 ft and 3.5 ft from the stone toe, respectively. Monitoring wells in the field plots were 6.75 ft (row 3), 11.0 ft (row 4), and 16 ft (row 5) from the stone toe.

The monitoring wells were constructed of nominal 2-in diameter, Boart Longyear schedule 40 polyvinyl chloride (PVC) casing and slotted pipe screen (0.010-in slot width). Wells in the field plots (rows 3 through 5) were installed by hand auguring to the desired depth, inserting the well casing and screen, backfilling with filter-pack material (silica sand) to 5 in above the top of the well screen, and filling the remaining borehole with bentonite pellets. The wells in rows 1 and 2 were constructed by placing the well casings and screens in hand-augured

holes that were the same size as the outside diameter of the wells. Native clay soil was packed around the wells at the soil surface to prevent movement of surface water down the well casing. The top and bottom of the wells were capped. The wells in the field plots were screened at a depth of 1.5 to 3.5 ft (cell bottom) below the soil surface. The wells in rows 1 and 2 were screened at a depth of 1.0 to 2.0 ft (cell bottom) below the soil surface.

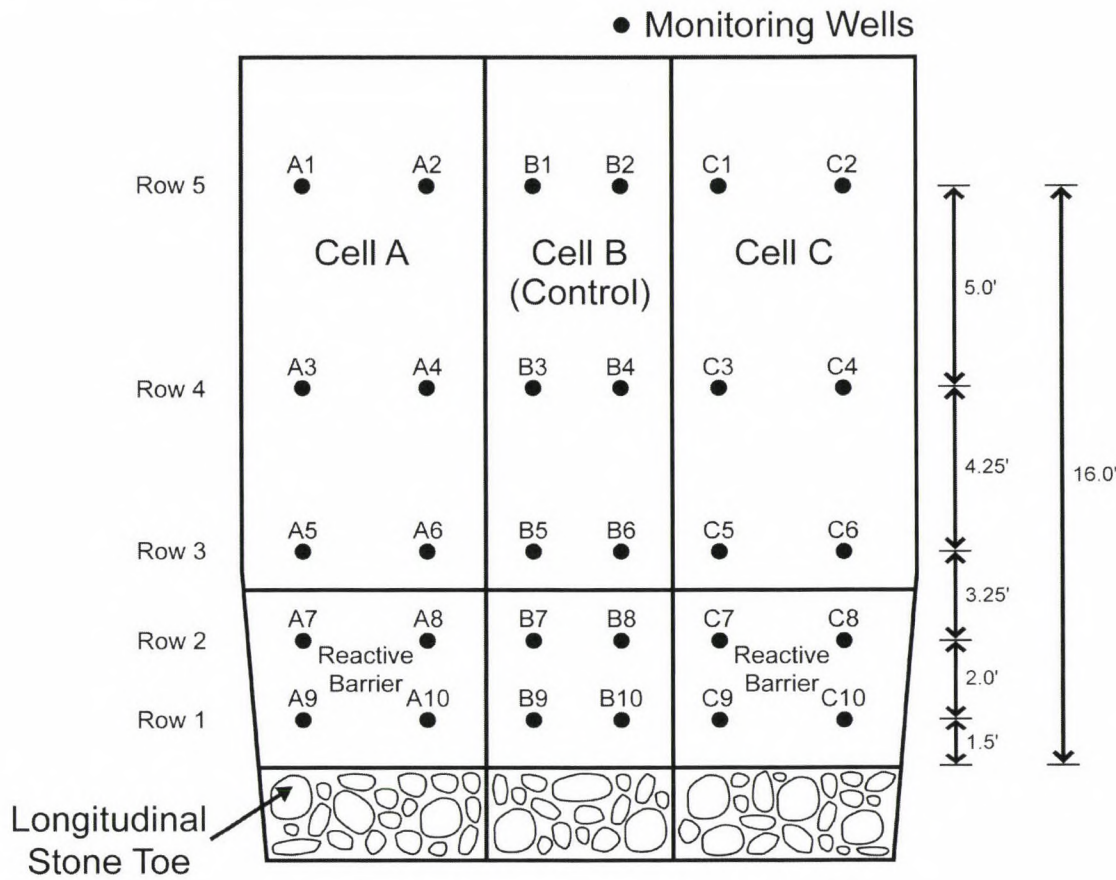

Fig. 3.13. Monitoring well network.

Groundwater sampling was conducted approximately every two weeks from 7 Aug. to 2 Dec. 2003. The depth to water in each well was measured from the top of the well casing using a Solinst Model 101 water level meter (Solinst Canada Ltd., Georgetown, ON, Canada) before sampling was initiated. The water table elevation at each well was determined by subtracting the measured depth to groundwater from the surveyed elevation of the top of the well casing. Water table elevations are provided in Table C.1 in Appendix C.

The monitoring wells were purged before samples were collected. One case volume of water was removed from each well with a peristaltic pump. Samples were collected on the following day when the wells contained sufficient sample volume. To prevent cross-contamination between wells, field equipment was rinsed with deionized water after each use. Groundwater samples were transported to the laboratory immediately after collection. A portion of each sample was filtered through a 0.45-μm membrane filter for the determination of dissolved analytes (NO_3 and NH_4). The remaining unfiltered water was saved for total organic carbon (TOC) and alkalinity measurements. Both filtered and unfiltered samples were stored at 4°C until analyses were performed.

All of the groundwater samples were analyzed for NO_3 on a Dionex 2000i/SP Ion Chromatograph (Dionex Corporation, Sunnyvale, CA). Nitrate concentrations, reported by the laboratory as less than the method detection limit (0.1 mg N L^{-1}), were replaced by a value equal to half the detection limit. Groundwater samples collected only on certain sampling dates were analyzed for NH_4, alkalinity, and TOC. Ammonium was measured using a Thermo Orion Model 95-12 Ammonia Electrode (Thermo Orion, Beverly, MA). Total organic carbon was measured using a Hach astroTOC UV Analyzer (Hach Company, Loveland, CO). Alkalinity was determined by titration with standardized sulfuric acid (H_2SO_4) using a Hach Digital Titrator (Hach Company, Loveland, CO). Quality-assurance measures included routine use of duplicate samples, blanks, and quality control check standards.

The following water quality parameters were measured in the field before the wells were sampled: oxidation-reduction potential (ORP), dissolved oxygen (DO), pH, specific conductance, and temperature. All of these parameters were measured simultaneously using a multi-parameter water quality instrument, the Hydrolab MiniSonde 4a (Hydrolab-Hach Company, Loveland, CO). The Hydrolab MiniSonde 4a was calibrated before each sampling event in accordance with manufacturer's recommendations. The instrument was slowly lowered into the well and readings

were recorded when they stabilized. The instrument was thoroughly rinsed with deionized water after each use.

The Hydrolab ORP sensor combines a platinum (Pt) electrode and a silver/silver chloride (Ag/AgCl) reference electrode in one body. Oxidation-reduction potential readings recorded in the field were converted to Eh values using the following equation (American Public Health Association, American Water Works Association, and Water Environment Federation, 1998):

$$Eh = ORP(mV) + Eh_{reference\ solution}\,(mV) - ORP_{reference\ solution}\,(mV) \qquad [6]$$

where

ORP	=	sample potential relative to the Ag/AgCl reference electrode
$Eh_{\text{reference solution}}$	=	theoretical Eh of reference solution
$ORP_{\text{reference solution}}$	=	potential of reference solution relative to the Ag/AgCl reference electrode

The difference between the last two terms in the equation is 200 mV at 25°C. Thus, if the temperature of the groundwater and the reference solution (ZoBell's solution) is 25°C, the Eh of the sample would simply be equal to the ORP reading measured in the field plus 200 mV. Corrections were made for groundwater temperatures.

In this study, analyses were performed to characterize the physical, chemical and hydrogeologic properties of the soil and reactive barrier material in the research cells. Samples of soil and reactive barrier material were collected during monitoring well installation in July 2003. In the field plots, soil samples were collected at different depths (0 to 6 in, 6 to 12 in, and 12 to 42 in) using an auger. This sampling technique was used to characterize the near surface soils, which were amended with compost material to stimulate plant growth, as well as soils at depth beneath the surface. Undisturbed core samples were collected for determining K. These samples were retrieved by driving thin-walled metal cylinders into the soil to a depth, which coincided with the location of the well screen. Core and bulk samples were also collected near the stone toe. The samples were sent to Colorado State University's Soil and Plant Testing Laboratory for

analysis. Table 3.1 lists the parameters measured in the laboratory and corresponding analytical methods.

Precipitation was measured at the study site with a Productive Alternatives All Weather Rain Gauge (Productive Alternatives, Inc., Fergus Falls, MN). The rain gauge was checked and emptied daily. Stream stage was measured once a day using a staff gauge mounted to a bridge near the field structure.

3.3 Results and Discussion

Raw groundwater quality data can be found in Appendix A. Hydraulic conductivity values of soil and reactive barrier material are shown in Table E.1, Appendix E. Other physical as well as chemical properties of the soil and reactive barrier material are summarized in Appendix B.

3.3.1 Groundwater Nitrate Removal in Cells A and B

Nitrate removal from groundwater was measured from row 2 to row 1 in each cell (see Fig. 3.13). Nitrate removal could not be determined on the first sampling event (August 7) in Cell A because the monitoring wells located in row 1 at the end of the reactive barrier were dry. For the remainder of the study, the wells located in row 1 contained sufficient sample volume. Nitrate removal from groundwater in Cells A and B from 19 Aug. to 2 Dec. 2003 is summarized in Table 3.2.

Table 3.1. Soil properties and testing methods.

Property	Methods†	Reference
Chemical		
pH	Determined from saturated soil paste (method 21a)	U.S. Salinity Laboratory Staff (1954)
Electrical conductivity	Determined from saturation extract (method 4b)	U.S. Salinity Laboratory Staff (1954)
Organic matter	Modified Walkley-Black method	Nelson and Sommers (1996)
NO_3-N	AB-DTPA extraction followed by Cd reduction flow injection analysis	Kuo (1996) Mulvaney (1996)
P	AB-DTPA extraction followed by colorimetric analysis	Kuo (1996)
K, Zn, Fe, Cu, and Mn	AB-DTPA extraction. Soil extract analyzed using ICP spectroscopy	Soltanpour et al. (1996)
Lime estimate	Qualitative fizz test with dilute acid (method 6E2a)	Soil Survey Staff (1996)
Exchangeable Al	Potassium chloride extraction followed by ICP analysis	Barnhisel and Bertsch (1982)
Physical		
Particle size distribution	Hydrometer method	Gee and Bauder (1986)
Hydraulic conductivity	Constant head method	Klute and Dirksen (1986)
Total porosity	Calculation from particle and bulk densities	Danielson and Sutherland (1986)

†AB-DTPA, ammonium bicarbonate-diethylenetriaminepentaacetic acid; ICP, inductively coupled plasma.

Table 3.2. Groundwater nitrate removal in Cells A and B during 2003 study.

	Cell A (Reactive Barrier)			Cell B (Control)		
Date	NO_3-N		Removal	NO_3-N		Removal
	mg L^{-1}		%	mg L^{-1}		%
	Row 2	Row 1		Row 2	Row 1	
19 Aug.	6.01	1.94	68	24.5	11.3	54
3 Sept.	2.54	1.15	55	11.5	2.87	75
16 Sept.	4.87	0.13	97	13.3	11.6	12
30 Sept.	10.8	0.05	100	13.7	11.0	19
14 Oct.	12.1	0.05	100	12.7	9.48	25
4 Nov.	11.8	0.21	98	10.2	10.9	0
20 Nov.	5.84	0.21	96	5.08	6.14	0
2 Dec.	4.17	0.08	98	7.43	5.96	20
Mean	7.27	0.48	93	12.3	8.65	30

As shown in Table 3.2, the reactive barrier in Cell A removed NO_3 from groundwater throughout the study, even in the colder months when the temperature of the groundwater was between 3 and 7°C. Nitrate concentrations in the reactive barrier near the upslope edge (row 2) ranged from 2.54 to 12.1 mg N L^{-1}. Concentrations of NO_3 in groundwater at the end of the reactive barrier (row 1) were less than 2.0 mg N L^{-1}. On average, NO_3 concentrations decreased 93% from 7.27 to 0.48 mg N L^{-1} as groundwater flowed through the system. In comparison, NO_3 removal in the control (Cell B) averaged 30% (12.3 mg N L^{-1} in row 2, versus 8.65 mg N L^{-1} in row 1).

Nitrate removal in the reactive barrier varied early in the study, but was consistently high (>95%) from mid-September to December (Table 3.2). It was anticipated that treatment performance would fluctuate during the initial period following reactive barrier installation. Construction activities, and the installation of the reactive barrier and monitoring wells, resulted in significant soil disturbance. Stabilization of the groundwater system and re-establishment of the microbial community occur over time. Thus, the initial results may not reflect actual performance (Powell et al., 1998). Rainfall may have also influenced the results during this period, particularly in the beginning of September. A significant storm event (2.2 in of

precipitation) occurred just before sampling was conducted on September 3. Rainfall transported across the surface of the field plot in Cell A may have been diverted through the high permeability coarse sand layer installed on the bank. The reactive barrier wells in row 2 were positioned to intercept both incoming groundwater and surface runoff that infiltrated through the sand. Thus, the low NO_3 concentration (2.54 mg N L^{-1}) measured in row 2 on September 3 may be due to the mixing of overland flow with shallow groundwater (dilution). This could explain the low percentage of NO_3 removal (55%) observed on that date.

Groundwater NO_3 removal in Cell B (control) varied from 0 to 75% (Table 3.2). The high NO_3 removal (75%) measured on September 3, shortly after the storm event, may be attributed to dilution. Overland flow generated during the rainstorm flowed over the bank (low permeability soil) and collected at the bottom of the bank slope between the wells positioned in rows 1 and 2. Some of this water likely infiltrated into the soil and entered the shallow groundwater. This would have resulted in lower than expected NO_3 concentrations near the stone toe (row 1) and consequently higher percentages of NO_3 removal.

Streamflow may have affected groundwater chemistry near the soil-stream interface in Cell A, as well in Cell B, during the study. Operation of the testing flume on August 18 resulted in higher than normal streamflow and stage (water-surface elevation of the stream). It is possible that water from the stream entered the bank in both cells and mixed with groundwater near the stone toe (row 1). Hence, a fraction of the decrease in NO_3 from row 2 to row 1 in Cells A and B on August 19 may be due to dilution. High streamflows were not observed before the other sampling dates. Thus, dilution of groundwater by stream water cannot account for the high NO_3 removal observed in Cell A during most of the study.

3.3.2 Organic Carbon in Soil and Groundwater

Organic matter (sawdust) was mixed with soil adjacent to the stone toe in Cell A to enhance NO_3 removal via denitrification. The organic matter content of the reactive barrier material in Cell A,

however, was lower than that of the unamended soil along the stone toe in Cell B (2.2 versus 4.2%). It is important to note that these results were obtained by analyzing only one soil sample from each cell. This one sample may not have been representative of the system.

Samples were collected from groundwater wells for TOC analysis on six occasions during the study period. It was anticipated that groundwater TOC concentrations would be higher in Cell A (reactive barrier) than in Cell B (control). As shown in Table 3.3, TOC concentrations were actually slightly lower on average in Cell A than in Cell B. Total organic carbon concentrations in row 2 averaged 7.61 mg L^{-1} in Cell A and 9.52 mg L^{-1} in Cell B. Total organic carbon concentrations near the stone toe in row 1 averaged 11.0 and 12.1 mg L^{-1} in Cells A and B, respectively. There is no apparent explanation for the difference in groundwater TOC concentrations between the two cells.

Table 3.3. Groundwater total organic carbon (TOC) concentrations in Cells A and B.

Location	Row	TOC†
		mg L^{-1}
Cell A	3	20.3 ± 1.90
	2	7.61 ± 0.81
	1	11.0 ± 1.92
Cell B	3	11.9 ± 1.95
	2	9.52 ± 1.50
	1	12.1 ± 2.28

†Values are means ± standard error (n=6).

When interpreting TOC results, it is important to remember that only a fraction of the TOC is microbially available. Thus, even though TOC concentrations were slightly lower in Cell A, the amount of C available to denitrifiers may have actually been higher in this cell than in Cell B. This theory is supported by the higher NO_3 removal observed in Cell A than in Cell B.

3.3.3 Physico-chemical Parameters

Organic compounds derived from the decomposing sawdust are a source of C and electron donors (energy) for denitrifiers. In addition, these compounds stimulate aerobic respiration, which contributes to the development of anaerobic or low Eh conditions. Denitrification occurs when Eh values (at pH=7) are between +200 and +300 mV (Reddy and DeLaune, 2008). In this study, groundwater Eh was measured using a Hydrolab ORP sensor. The sensor was lowered into the wells and readings were recorded after allowing 5 minutes for equilibration. Field readings were higher than actual Eh values because the water column in the well was exposed to the atmosphere. Nevertheless, Eh values in the reactive barrier where most of the NO_3 removal occurred (near the wells positioned in row 1) were around +200 mV or less during most of the study (Table 3.4). Values were lower in the reactive barrier (Table 3.4) than in the control (Table 3.5). The high Eh values measured in both systems at the end of the study may be due to increased concentrations of DO in the groundwater at the lower temperatures (Tables 3.4 and 3.5).

Table 3.4. Temperature, dissolved oxygen (DO), and Eh measurements in the reactive barrier (Cell A).

Date	Temperature		DO		Eh	
	°C		mg L^{-1}		mV	
	Row 2	Row 1	Row 2	Row 1	Row 2	Row 1
3 Sept.	17.4	18.1	3.6	1.7	174	27
16 Sept.	no data	no data	4.2	no data	226	207
30 Sept.	13.2	12.3	1.1	0.9	178	142
14 Oct.	11.6	10.4	2.2	1.4	205	163
4 Nov.	9.8	8.3	1.9	3.0	363	233
20 Nov.	7.0	6.1	6.6	3.2	394	354
2 Dec.	5.1	3.8	6.4	3.6	483	436
Mean (SE)	11.7 (1.8)	10.9 (2.1)	3.7 (0.8)	2.3 (0.5)	289 (47)	223 (51)

Table 3.5. Temperature, dissolved oxygen (DO), and Eh measurements in the control.

Date	Temperature		DO		Eh	
	°C		mg L^{-1}		mV	
	Row 2	Row 1	Row 2	Row 1	Row 2	Row 1
3 Sept.	17.0	17.1	3.6	3.2	200	171
16 Sept.	no data	no data	3.6	3.6	224	227
30 Sept.	13.2	12.0	2.1	2.0	236	240
14 Oct.	12.1	10.5	2.5	2.8	294	298
4 Nov.	9.8	8.5	1.7	0.8	390	391
20 Nov.	7.3	6.4	4.2	4.7	514	525
2 Dec.	5.5	4.1	6.5	6.4	545	548
Mean (SE)	10.8(1.7)	9.8 (1.9)	3.5 (0.6)	3.4 (0.7)	343 (54)	343 (56)

Temperature affects the solubility of oxygen in water and rates of microbial processes (Myrold, 1999). Stanford et al. (1975) examined the effects of temperature on denitrification rates and found that rates approximately doubled for every 10°C increase in temperature between 15 and 35°C. They also observed a large decrease in the denitrification rate when temperatures dropped from 15 to 5°C. Groundwater temperatures in the reactive barrier decreased from about 17°C in early September to 4-5°C in December (Table 3.4). Denitrification rates likely decreased during this period; however, rates may have been high enough in the colder months to account for NO_3 loss.

Denitrification is an alkalinity generating process. Based on Eq. [5], 3.57 mg of alkalinity as calcium carbonate ($CaCO_3$) is generated for every mg of NO_3-N reduced. Alkalinity did increase from row 2 to row 1 in the reactive barrier (Table 3.6). The increase, however, was more than expected based on the change in NO_3 concentration. Other reactions that may have contributed to the alkalinity increase include manganese (Mn^{4+}), ferric iron (Fe^{3+}), and sulfate (SO_4^{2-}) reduction. After NO_3 has been depleted, anaerobic bacteria oxidize organic C using Mn^{4+}, Fe^{3+}, and then SO_4^{2-} as terminal electron acceptors. The reduction of Mn^{4+} to manganous manganese (Mn^{2+}) can occur when Eh is between +200 and +300 mV at pH=7. The reduction of Fe^{3+} to ferrous iron (Fe^{2+}) and SO_4^{2-} to hydrogen sulfide (H_2S) can occur when Eh values (at

pH=7) are between +100 and –100 mV, and < -100 mV, respectively (Reddy and DeLaune, 2008). Iron and SO_4^{2-} reduction may have occurred, even though Eh values in the reactive barrier were typically greater than 100 mV (Table 3.4). It is important to remember that Eh measurements were likely higher than actual in situ values due to aeration of the well samples. Another important thing to keep in mind is that these measurements, in general, are not considered a reliable indicator of redox processes (Sigg, 2000). Additional insight could be obtained by measuring the concentration of Mn^{2+}, Fe^{2+}, and sulfide in groundwater. An increase in these reduced species from row 2 to row 1 would be indicative of Mn^{4+}, Fe^{3+}, and SO_4^{2-} reduction. It should be noted that an increase in specific conductance would be expected if insoluble Mn^{4+} and Fe^{3+} were transformed to soluble Mn^{2+} and Fe^{2+}. Specific conductance did increase in the reactive barrier from row 2 to row 1 (Table 3.6).

Table 3.6. Alkalinity, pH, and specific conductance measurements in Cells A and B. Values are means ± standard error (n).

Location	Row	Alkalinity†	pH	Specific Conductance
		mg L^{-1} as $CaCO_3$		µS cm^{-1}
Cell A	3	785 ± 19.3 (6)	6.82 ± 0.08 (7)	1568 ± 74 (7)
	2	216 ± 28.0 (6)	6.81 ± 0.10 (7)	579 ± 103 (7)
	1	375 ± 33.4 (6)	6.90 ± 0.07 (7)	689 ± 36 (7)
Cell B	3	582 ± 17.6 (6)	6.72 ± 0.16 (7)	1273 ± 121 (7)
	2	311 ± 22.8 (6)	6.88 ± 0.11 (7)	711 ± 51 (7)
	1	306 ± 29.5 (6)	7.03 ± 0.08 (7)	626 ± 30 (7)

†$CaCO_3$, calcium carbonate.

3.3.4 Nitrate Removal Mechanisms Other Than Denitrification

There are processes besides denitrification that can result in the removal of NO_3 from groundwater. These processes include plant uptake, microbial assimilation, and DNRA. Plants and microorganisms need N to make amino acids and other compounds. They take up and reduce

NO_3 to NH_4 for this purpose (Heritage et al., 1999; Myrold, 1999). Studies were not conducted to determine how much NO_3 was removed via plant and microbial assimilation. However, it can be assumed that the amount taken up by plants was very small since vegetation was sparse on the bank during the growing season.

Dissimilatory NO_3 reduction to NH_4 is a microbially mediated process that is expected to occur in environments where Eh is very low (< 0 mV) and the supply of organic C is high relative to that of NO_3 (Tiedje, 1988; Reddy and DeLaune, 2008). In this process, NO_3 is reduced to NO_2, which is then reduced to NH_4. The NH_4 is released to the environment. Ammonium concentrations were measured, in addition to NO_3, in samples collected from the wells on five occasions during the study period. As shown in Table 3.7., the increase in NH_4 from row 2 to row 1 in the reactive barrier was very small compared to the decrease in NO_3. These results, combined with Eh measurements (Table 3.4), suggest that DNRA accounted for only a small percentage of the observed removal.

Table 3.7. Groundwater nitrate and ammonium concentrations in Cells A and B during 2003 study. Values are means ± standard error (n).

Location	Row	NH_4-N	NO_3-N
		mg L^{-1}	
Cell A	3	0.51 ± 0.11 (5)	2.02 ± 0.41 (9)
	2	0.05 ± 0.02 (5)	6.48 ± 1.41 (9)
	1	0.18 ± 0.06 (5)	0.48 ± 0.25 (8)
Cell B	3	0.15 ± 0.11 (5)	14.2 ± 1.96 (9)
	2	0.03 ± 0.01 (5)	11.9 ± 1.83 (9)
	1	0.11 ± 0.06 (5)	8.88 ± 1.04 (9)

3.3.5 Groundwater Chemistry in Cell A (Row 3 to Row 2)

During the study, groundwater NO_3 concentrations increased from row 3 to row 2 in Cell A (Table 3.7). The change in NO_3 concentration was accompanied by a decrease in NH_4 (Table 3.7) and alkalinity (Table 3.6). This pattern is indicative of nitrification. Nitrification is a two-step process, whereby NH_4 is oxidized to NO_3 when oxygen is available. First, NH_4 is oxidized to NO_2 by ammonia-oxidizing bacteria (e.g., Nitrosomonas). In the second step, NO_2 is converted to NO_3 by nitrite-oxidizing bacteria (e.g., Nitrobacter) (Water Environment Federation, 1998; Myrold, 1999). The total reaction is (Water Environment Federation, 1998):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad [7]$$

This reaction may have occurred; however, since the decrease in NH_4 was small (0.46 mg N L^{-1}) compared to the increase in NO_3 (4.46 mg N L^{-1}) (Table 3.7), it cannot account for most of the change in NO_3 concentration from row 3 to row 2.

Nitrification also contributed very little to the decrease in alkalinity from row 3 to Row 2 in Cell A (Table 3.6). Suppose that 1.0 mg NH_4-N was oxidized to NO_3-N. Based on Eq. [7], oxidation of 1.0 mg NH_4-N results in the production of 1.43 x 10^{-4} mol of H^+ (strong acid), which will destroy 1.43 x 10^{-4} mol of bicarbonate (HCO_3^-) alkalinity or 7.14 mg of alkalinity expressed as $CaCO_3$. On average, NH_4 concentrations decreased by less than 1.0 mg N L^{-1} (Table 3.7) and alkalinity decreased by 569 mg L^{-1} (as $CaCO_3$) (Table 3.6).

The change in groundwater chemistry from row 3 to row 2 in Cell A may be attributed to operating conditions and bank composition. During the study, liquid fertilizer and water were applied separately to the field plot through the drip irrigation system. The field plot was irrigated frequently (three times per week) to promote NO_3 leaching. It is likely that a considerable amount of water delivered to the plot flowed downslope across or just beneath the ground surface, and then through the coarse sand layer on the bank. Nitrate, which accumulated in the soil profile due to excess fertilizer application, would have been transported downslope with the irrigation

water. As mentioned previously, the reactive barrier wells in row 2 were positioned to intercept not only groundwater, but also surface runoff and shallow unsaturated flow that infiltrated through the coarse sand layer. This would explain why NO_3 concentrations were higher in samples retrieved from the wells located in row 2 than in row 3. The mixing of irrigation water with shallow groundwater in the wells positioned in row 2 would also explain the sharp decline in alkalinity (Table 3.6), TOC (Table 3.3), and specific conductance (Table 3.6) from row 3 to row 2.

3.4 Summary and Conclusions

In this study, a small RS2 structure was designed and then constructed along a stream. The RS2 structure combined a permeable reactive barrier with longitudinal peaked stone toe protection. The reactive barrier was positioned adjacent to the stone toe in the path of groundwater flow. Sawdust was included in the reactive barrier mixture to enhance NO_3 removal from groundwater via denitrification. The sawdust provided denitrifying bacteria with a source of C and energy. In addition, it stimulated microbial activity which contributed to the development of anaerobic or low Eh conditions in the system.

A control was constructed that contained only native soil adjacent to the stone toe. After construction was completed, a field study was conducted to evaluate the initial difference in treatment performance between the control and the RS2 structure. Fertilizer and irrigation water were applied to field plots located upslope of the structures to generate NO_3-contaminated groundwater for the study. Treatment performance was evaluated by monitoring the change in the concentration of NO_3 in groundwater as it flowed through each system.

A significant decline in NO_3 was observed as groundwater flowed through the reactive barrier during the study, even in the colder months when the temperature of the groundwater was between 3 and 7°C. Dilution may explain some of this decrease; however, it is evident that NO_3

was removed from groundwater because large reductions in NO_3 concentrations were observed during dry periods when streamflow was low. Some of the NO_3 may have been assimilated by plants and microorganisms, and/or converted to NH_4 by DNRA bacteria. A large fraction of the incoming NO_3 was likely removed via denitrification since conditions were favorable for the process in the reactive barrier (e.g., Eh was low and organic C was available).

The control was not as effective as the RS2 structure at reducing NO_3 concentrations in groundwater. Nitrate removal in the control averaged only 30% (12.3 mg N L^{-1} along the upslope edge, versus 8.65 mg N L^{-1} along the downslope edge). In comparison, NO_3 removal in the reactive barrier averaged 93% (7.27 mg N L^{-1} along the upslope edge, versus 0.48 mg N L^{-1} along the downslope edge). These preliminary results suggest that RS2 structures can accelerate and maximize groundwater NO_3 removal along streams.

CHAPTER 4. PERFORMANCE ASSESSMENT AND MONITORING OF REACTIVE STREAM STABILIZATION STRUCTURE IN 2004

4.1 Introduction

During the summer of 2003, a small RS2 structure was constructed along a stream behind the Engineering Research Center at Colorado State University in Fort Collins, CO. The RS2 structure combined a permeable reactive barrier with longitudinal peaked stone toe protection. The reactive barrier was positioned adjacent to the stone toe in the path of groundwater flow. Sawdust (solid-phase organic C) was included in the reactive barrier mixture to enhance NO_3 removal from groundwater via denitrification. A control was also constructed at the study site. The control contained only native soil adjacent to the stone toe. The control and RS2 structure were located in Cells B and A, respectively (see Fig. 3.1).

A field study was conducted from August to December 2003 to evaluate the initial difference in treatment performance between the RS2 structure and the control (Chapter 3). In that study, the field plots were irrigated frequently to promote NO_3 leaching. Some of the irrigation water applied infiltrated into the soil and reached the water table, and some of the water flowed across or just beneath the surface of the field plot towards the bank in each cell. A high permeability coarse sand layer was installed on the bank in Cell A to divert surface runoff and lateral unsaturated flow through the reactive barrier. As discussed in Chapter 3, irrigation water that infiltrated through the coarse sand layer likely affected groundwater chemistry in the reactive barrier near the upslope edge. In March 2004, operating conditions were modified to promote flow at depth from the upslope edge of the field plot to the stone toe in each cell. A tracer study was conducted after modifications were made to evaluate flow patterns in Cells A and B.

Procedural and structural modifications that were made in the spring and the results of the tracer study are discussed in this chapter.

A field study was conducted from May to September 2004 to (1) evaluate the difference in performance (NO_3 removal) between the RS2 structure (Cell A) and the control (Cell B), and (2) gain insight into NO_3 removal processes. It was anticipated that the RS2 structure would be more effective at reducing NO_3 concentrations in groundwater than the control. The results are presented and discussed in this chapter.

4.2 Materials and Methods

4.2.1 Procedural and Structural Modifications

In March 2004, a trench (2.0 ft deep and 1.0 ft wide) was dug just upslope of the field plot wells located in row 5 (Fig. 3.13) in each cell. The trenches were then backfilled with pea gravel up to the soil surface. Three drip lines were placed on the surface of the gravel to distribute flow across the entire length of each trench. A solution of sodium nitrate ($NaNO_3$) (30 mg N L^{-1}) was continuously applied to each trench beginning in May 2004. The $NaNO_3$ solution was stored in a 1500-gal tank located on a raised platform. Sodium nitrate solution flowed by gravity from the tank, through the piping system, to the trench in each cell. Flow rates fluctuated during the study because a constant level of solution was not maintained in the tank. To minimize variations in flow, flow control valves located before the in-line flow meters were adjusted daily, such that solution was delivered to each trench at a rate of about 5 gallons per hour.

4.2.2 Sampling, Analysis, and Instrumentation

Groundwater sampling was conducted approximately every two weeks from May to September 2004. The depth to water in each well was measured from the top of the well casing using a Solinst Model 101 water level meter (Solinst Canada Ltd., Georgetown, ON, Canada) before samples were collected. The water table elevation at each well was determined by subtracting the

measured depth to groundwater from the surveyed elevation of the top of the well casing. Water table elevations are provided in Table C.2 in Appendix C.

A peristaltic pump was used to collect samples from the wells. To minimize disturbance in the well (mixing within the water column) and the surrounding formation, the sample line (pump tubing) was slowly lowered into the well to a depth, which coincided with location of the well screen, and water was pumped from the well at a low flow rate. Only a small amount of water ($\leq$ 250 ml) was collected from each well. To prevent cross-contamination between wells, field equipment was decontaminated after each use by rinsing with deionized water. Equipment and field blanks were collected for quality control before each sampling event. The equipment blank was prepared by passing deionized water through the pump tubing (sample lines). A sample of the deionized water used for equipment decontamination was collected and labeled "field blank". Dilute hydrochloric (HCl) acid solution was used to clean the pump tubing between sampling events.

Groundwater samples were transported to the laboratory immediately after collection. Samples were filtered through 0.45-µm membrane filters and stored at 4°C until analyses were performed. All of the groundwater samples were analyzed for NO_3 on a Dionex 2000i/SP Ion Chromatograph (Dionex Corporation, Sunnyvale, CA). Nitrate concentrations, reported by the laboratory as less than the method detection limit (0.01 mg N L^{-1}), were assigned a value equal to half the detection limit. Samples collected from the wells on certain sampling dates were also analyzed for NH_4. Ammonium was measured using a Thermo Orion Model 95-12 Ammonia Electrode (Thermo Orion, Beverly, MA). Quality-assurance measures included routine use of duplicate samples, blanks, and quality control check standards.

The following parameters were measured in the field every two weeks, but not on the same day groundwater samples were collected: DO, ORP, pH, temperature, and specific conductance. Field parameters were measured using a multi-parameter water quality instrument, the Hydrolab MiniSonde 4a (Hydrolab-Hach Company, Loveland, CO). The Hydrolab

MiniSonde 4a was calibrated before each sampling event in accordance with manufacturer's recommendations. The instrument was slowly lowered into the well and readings were recorded when they stabilized. The instrument was thoroughly rinsed with deionized water after each use.

The Hydrolab ORP sensor combines a Pt electrode and an Ag/AgCl reference electrode in one body. Oxidation-reduction potential readings recorded in the field were converted to Eh values using Eq. [6]. Since the difference between the last two terms in Eq. [6] is 205 mV at 17° C (the average temperature of groundwater in Cells A and B during the study), the Eh of the sample was simply equal to the ORP reading measured in the field plus 205 mV.

Precipitation was measured at the study site with a Productive Alternatives All Weather Rain Gauge (Productive Alternatives, Inc., Fergus Falls, MN). The rain gauge was checked and emptied daily. Stream stage was measured once a day using a staff gauge mounted to a bridge near the field structure. In the previous experiment, operation of the testing flume located near the site occasionally resulted in flooding of the lower bank in the field structure. The flume was not operated during this study.

Groundwater flow velocity through the reactive barrier in Cell A and the bank in Cell B (control) was calculated using hydrologic measurements and Darcy's Law as described in Appendix D. Slug tests were conducted to determine K of the soils and reactive barrier material. The slug test procedure and results are summarized in Appendix E. Slug tests were performed in wells A3, A10, B4, and B8. Wells A3 and B4 are located in field plots A and B, respectively (Fig. 3.13). Well A10 is located in the reactive barrier in Cell A, and well B8 is located in the bank in Cell B (Fig. 3.13). Soil samples were collected near these wells, at depths corresponding to the location of the well screens, for porosity analysis in July 2004. Total porosity was calculated using particle and bulk densities (Danielson and Sutherland, 1986).

Bromide has been used as a tracer in field studies to (1) determine if NO_3 loss was due to physical processes (e.g., dilution) (Nelson et al., 1995; Verchot et al., 1997; Hill et al., 2000), (2) evaluate flow patterns (Jordan et al., 1993; Nelson et al., 1995; Verchot et al., 1997; Hedin et al.,

1998), and (3) estimate flow velocity (Nelson et al., 1995; Hedin et al., 1998). In this study, sodium bromide (NaBr) was added to the $NaNO_3$ solution to trace the path of groundwater flow through Cells A and B. Groundwater samples were collected and analyzed for Br before the tracer test was conducted to determine background concentrations. Background Br concentrations ranged from <0.01 to 0.53 mg L^{-1} in Cell A, and from <0.01 to 0.63 mg L^{-1} in Cell B (Table F.9, Appendix F). A solution containing 160 mg L^{-1} of Br and 133 mg L^{-1} of NO_3 was applied to the trench in each cell continuously for one week (July 15 to July 22) at a rate of about 3.3 gallons per hour. Samples were collected from the monitoring wells in Cell A once a day beginning on July 16. The wells in Cell B were sampled only on the last day of the study (July 22). Disposable bailers were used to collect samples from the wells. Groundwater samples were analyzed for Br on a Dionex 2000i/SP Ion Chromatograph (Dionex Corporation, Sunnyvale, CA). Bromide concentrations, reported by the laboratory as less than the method detection limit (0.01 mg L^{-1}), were assigned a value equal to half the detection limit.

4.3 Results and Discussion

Raw groundwater quality data can be found in Appendix F.

4.3.1 Nitrate Concentrations and Subsurface Flow Patterns in Cells A and B

In this study, $NaNO_3$ solution (30 mg N L^{-1}) was continuously applied to a trench that was located just upslope of the field plot wells in row 5 (Fig. 3.13) in each cell. Samples were collected from the monitoring wells in Cells A and B for NO_3 analysis on eight occasions during the study period. Mean groundwater NO_3 concentrations in Cells A and B are presented in Table 4.1. As can be seen in this table, most of the $NaNO_3$ solution applied to the trench in Cell B was not intercepted by the wells during the study. Nitrate concentrations were consistently low in all of the wells located in the field plot (rows 3 through 5), as well as in the bank (rows 1 and 2). In Cell A, NO_3 concentrations were very low in the field plot wells. However, high NO_3

concentrations were observed in the reactive barrier near the upslope edge (row 2). Nitrate concentrations in the reactive barrier wells located in row 2 ranged from about 9.0 to 25.0 mg N L^{-1} (Table 4.3) and averaged 17.9 mg N L^{-1}. High NO_3 concentrations in row 2 were reduced to low levels (< 1.0 mg N L^{-1}) at the end of the reactive barrier (row 1). Nitrate removal from groundwater in the reactive barrier is discussed in detail in sections 4.3.3 and 4.3.4.

Table 4.1. Groundwater nitrate concentrations in Cells A and B from May to September 2004. Values are means ± standard error (n=8).

Location	Row	NO_3-N	Location	Row	NO_3-N
		mg L^{-1}			mg L^{-1}
Cell A			Cell B		
Field Plot	5	0.77 ± 0.23	Field Plot B	5	2.10 ± 0.25
	4	0.39 ± 0.16		4	0.21 ± 0.09
	3	0.15 ± 0.12		3	0.07 ± 0.03
Reactive	2	17.9 ± 1.92		2	0.24 ± 0.08
Barrier	1	0.51 ± 0.34	Streambank	1	0.31 ± 0.29

Low permeability clay and clay loam soils (native soil) were used to construct the field plots in Cells A and B, and the bank in Cell B. When clay soils dry, they contract or shrink. Shrinkage results in the formation of large, often deep, cracks. These cracks influence the movement of water and contaminants through the subsurface. During the study, large cracks were visible on the surface of the field plots and the bank in Cell B. It is believed that the majority of solution applied to the trench in each cell flowed laterally through cracks or channels (preferential flow paths) in the saturated or unsaturated zone, rather than through the bulk soil. This would explain why NO_3 concentrations were consistently low in all of the wells located in Cell B and in the field plot in Cell A during the study.

The high concentrations of NO_3 observed in the reactive barrier wells located in row 2 may be attributed to bank composition. As mentioned previously, a high permeability coarse sand layer was installed on the bank slope in Cell A. The reactive barrier wells in row 2 were positioned to intercept both incoming groundwater and solution that flowed through the coarse

sand. Nitrate concentrations in the wells located in row 2 were similar, which suggests that the sand layer distributed incoming flows uniformly across the reactive barrier. Coarse sand was also included in the reactive barrier mixture to promote uniform flow.

4.3.2 Tracer Experiment

In July, a tracer experiment was conducted using Br to investigate subsurface flow patterns in Cells A and B. A solution containing NO_3 (30 mg N L^{-1}) and Br (160 mg L^{-1}) was applied to the trench in each cell at a rate of about 3.3 gallons per hour continuously from July 15 to July 22. The trench was located just upslope of the field plot wells in row 5 (Fig. 3.13) in each cell. Groundwater samples were collected and analyzed for Br on the last day of the experiment (July 22) in Cell B. As expected, Br levels were low (0.01–6.0 mg L^{-1}) in all of the wells in Cell B (Table F.9, Appendix F). In Cell A, samples were collected from the wells for Br analysis once a day beginning on July 16. The raw data can be found in Appendix F, Table F.9. Bromide concentrations by row in Cell A from July 16 to July 22 are presented in Table 4.2.

Table 4.2. Groundwater bromide concentrations in Cell A.

		Br						
Location	Row	16 July	17 July	18 July	19 July	20 July	21 July	22 July
		mg L^{-1}						
Field Plot	5	1.97	0.25	2.93	2.79	40.5	2.21	5.21
	4	0.01	0.15	0.40	0.49	1.60	0.57	1.45
	3	0.35	0.01	0.22	2.23	1.02	1.47	1.28
Reactive Barrier	2	17.2	69.0	99.6	118	150	155	157
	1	4.25	46.1	86.5	29.6	69.6	78.3	73.7

As shown in Table 4.2, Br levels in the field plot wells were relatively low compared to the concentration in the solution (160 mg L^{-1}). High concentrations of Br, however, were detected in the reactive barrier wells located in row 2 soon after the solution was applied to the trench. The rapid transport of Br through the low permeability field soils confirms that solution

flowed along preferential pathways in the field plot. Bromide concentrations in the reactive barrier wells positioned within each row were similar. This suggests that flow was relatively uniform through the reactive barrier.

Bromide concentrations were lower in row 1 than in row 2 (Table 4.2). In other words, not all of the Br was recovered. Plants growing on the bank may have taken up some of the Br. Research has shown that various plants can remove Br from soil water (Owens et al., 1985; Kung, 1990). Some of the Br loss may also be attributed to dilution. Streamflow was higher than normal on two occasions during the tracer experiment. It is possible that water from the stream channel entered the bank and mixed with groundwater near the stone toe in row 1. Another explanation for the low Br concentration in row 1 is the short test duration. Since Br levels comparable to the concentration in the solution (160 mg L^{-1}) were not detected until the end of the test period in row 2 (Table 4.2), levels higher than those measured during the study may have been detected in row 1 at a later date.

4.3.3 Nitrate Removal in the Reactive Barrier

The performance of the RS2 structure in Cell A was evaluated by examining the change in NO_3 concentration from row 2 to row 1 (Fig. 3.13). One of the monitoring wells located in row 1 (well A9) at the end of the reactive barrier was often dry or contained very little water (insufficient sample volume). Samples were collected from this well and analyzed for NO_3 only on three occasions during the study (June 9, June 22, and August 3). On all other sampling dates, end-of-barrier NO_3 concentrations were determined from samples retrieved from well A10. Groundwater NO_3 concentrations and removal in the reactive barrier on each sampling date are presented in Table 4.3.

Table 4.3. Nitrate concentrations and removal in the reactive barrier during 2004 study.

Date	NO_3-N		Removal
	mg L^{-1}		%
	Row 2	Row 1	
24 May	19.1	0.02	100
8 June	22.2	0.31	99
22 June	22.2	0.80	96
6 July	15.7	0.02	100
22 July	24.8	0.01	100
3 Aug.	18.5	0.09	100
17 Aug.	12.2	2.81	77
1 Sept.	8.8	0.04	100

The results in Table 4.3 show that most of the NO_3 was removed from groundwater as it flowed through the reactive barrier. Nitrate concentrations in the reactive barrier near the upslope edge (row 2) ranged from about 9.0 to 25.0 mg N L^{-1}. Concentrations of NO_3 in groundwater at the end of the reactive barrier (row 1) were usually less than 1.0 mg N L^{-1}. On average, NO_3 concentrations declined 97% from 17.9 mg N L^{-1} in row 2 to 0.51 mg N L^{-1} in row 1 (Table 4.1).

Groundwater velocity through the reactive barrier from row 2 to row 1 was calculated on each sampling date using Darcy's Law equation, water-level measurements, and estimates of porosity and K. Flow rates varied during the study in response to fluctuations in the water table. Groundwater velocities ranged from 0.07 to 0.37 ft d^{-1}, which corresponded to residence times of about 14 to 72 days (Table D.1, Appendix D). Nitrate removal was consistently high despite variations in residence time.

4.3.4 Nitrate Removal Mechanisms

The reactive barrier component of the RS2 structure in Cell A was designed to enhance NO_3 removal via denitrification. As mentioned previously, this reaction occurs under anaerobic or low Eh conditions (Reddy and DeLaune, 2008; +200 to +300 mV). Groundwater Eh was measured in the reactive barrier using a Hydrolab ORP sensor. The sensor was lowered into the wells and readings were recorded after allowing 5 min for equilibration. Field readings were higher than

expected because the water column in the well was exposed to air. Nevertheless, Eh was low enough to support denitrification. Values in the reactive barrier near the downgradient edge (row 1) where most of the NO_3 removal occurred were between 60 and 100 mV (Table F3, Appendix F) and averaged 87.1 mV (Table 4.4).

Table 4.4. Summary of field measurements in the reactive barrier in 2004. Values are means ± standard error (n=7).

Row	Temperature	DO†	Eh	pH	Specific Conductance
	°C	mg L^{-1}	mV		µS cm^{-1}
2	16.4 ± 0.41	1.00 ± 0.31	121 ± 8.65	7.14 ± 0.03	428 ± 33.9
1	16.1 ± 0.49	0.32 ± 0.04	87.1 ± 3.39	6.89 ± 0.04	579 ± 39.5

†DO, dissolved oxygen

Processes other than denitrification that may explain some of the decline in NO_3 observed as groundwater flowed through the reactive barrier in Cell A include DNRA, plant uptake, and microbial assimilation. Dissimilatory NO_3 reduction to NH_4 is a microbially mediated process that is expected to occur in environments where Eh is very low (< 0 mV) and the supply of organic C is high relative to that of NO_3 (Tiedje, 1988; Reddy and DeLaune, 2008). The NH_4 produced via this process is released to the environment. Ammonium concentrations increased from row 2 to row 1 in the reactive barrier during the study (Table 4.5). However, the increase in NH_4 was very small compared to the decrease in NO_3 (Tables 4.1 and 4.5). These results, combined with Eh measurements (Table 4.4), suggest that DNRA accounted for only a small percentage of the observed removal.

An increase in NH_4 was observed over time in the reactive barrier from the 2003 field study to this study (Tables 3.7 and 4.5). This increase may be the result of DNRA, and possibly ammonification (mineralization of organic N). Ammonium produced via these processes can accumulate in anaerobic environments since nitrification is inhibited. It is important to note that NH_4 production may have been slightly higher than that indicated by the data since some of the

NH_4 could have been adsorbed onto negatively charged soil particles (clay and organic matter), fixed within the clay lattice, and/or taken up by plants and microorganisms (Hartel, 1999; Myrold, 1999).

Table 4.5. Groundwater ammonium concentrations in the reactive barrier (Cell A) during the 2004 field study.

Location	Row	NH_4-N†
		mg L^{-1}
Reactive Barrier	2	1.09 ± 0.60
	1	1.19 ± 0.25

†Values are means ± standard error (n=5).

Microorganisms and plants can assimilate both NH_4 and NO_3. However, as demonstrated by Rice and Tiedje (1989), the amount of NO_3 assimilated by soil microorganisms may be reduced when NH_4, the preferred N source, is available. These researchers found that NO_3 uptake was partially inhibited by NH_4 concentrations that were lower than those measured in the reactive barrier. It is therefore possible that microorganisms in the reactive barrier assimilated only a small fraction of the incoming NO_3. Results of other studies (e.g., Schipper and Vojvodić-Vuković, 2000; Greenan et al., 2006) further support the theory that microbial assimilation accounted for only a small percentage of the removal.

It was assumed that very little NO_3 was removed from groundwater by plants in the previous study. This assumption was based on the fact that there was not much vegetation on the bank in Cell A. In this study, plant uptake may have been an important NO_3 removal mechanism, since dense vegetation (grass and weeds) covered the bank, and the water table was close to the surface. Further investigation is needed to determine the extent to which plant uptake contributed to the observed decline in NO_3.

Some of the decrease in NO_3 measured on certain sampling dates may be attributed to dilution. This is supported by tracer study results. Heavy precipitation was observed before sampling was conducted on June 22 and September 1. Hence, rain infiltration may have been the cause of lower NO_3 concentrations in the reactive barrier on these two sampling dates. The low

NO_3 concentrations measured at the end of the reactive barrier on June 8 and July 22 may be the result of groundwater mixing with water from the stream, since high streamflows were observed before these two dates. Dilution effects could be evaluated in future studies by continuously monitoring the change in concentration of a suitable tracer along groundwater flow paths.

4.4 Summary and Conclusions

In the spring of 2004, a dosing trench was installed along the upslope edge of the field plot in each cell. The trenches were installed to remedy problems associated with the use of the fertilizer and water delivery system in the previous study. After the trenches were installed, a field study was conducted to evaluate the difference in treatment performance (NO_3 removal) between the RS2 structure (Cell A) and the control (Cell B). Unfortunately, it was not possible to compare the two systems in this study because most of the NO_3 solution delivered to the trench in Cell B was not intercepted by the monitoring wells. Nitrate solution was also not intercepted by the field plot wells in Cell A. The field plot in Cell A and the bank and field plot in Cell B were constructed using native clay and clay loam soils. When this soil dried, it contracted and cracked. Large cracks were observed on the surface of Cell B and the field plot in Cell A. It is believed that most of the solution flowed laterally through cracks or channels rather than through the bulk soil in Cell B and the field plot in Cell A.

The NO_3 plume was intercepted by the reactive barrier and flow through the system appeared to be rather uniform. This was likely due to its composition. Groundwater NO_3 concentrations were high (8.8 to 25 mg N L^{-1}) in the reactive barrier near the upslope edge during the study. These high NO_3 concentrations were typically reduced to less than 1 mg N L^{-1} near the downgradient edge. Dilution may explain some of this decrease; however, it is evident that NO_3 was removed from groundwater because large reductions in NO_3 concentrations were observed during dry periods when streamflow was low. Some of the NO_3 may have been assimilated by plants and microorganisms, and/or converted to NH_4 by DNRA bacteria. A large fraction of the

incoming NO_3 was likely removed via denitrification since conditions were favorable for the process in the reactive barrier (e.g., Eh was low and organic C was available). The high NO_3 removal measured in the reactive barrier during this study, combined with the results of the previous study (Chapter 3), suggest that the RS2 structure could be an effective tool for reducing NO_3 loading to waterways.

CHAPTER 5. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

This study examined the potential for improving current streambank stabilization designs to accelerate and maximize NO_3 removal benefits. A structure, which combined a permeable reactive barrier composed of solid-phase organic C (sawdust) with longitudinal peaked stone toe protection, was designed and constructed to enhance the potential for groundwater denitrification near a stream. The reactive barrier was positioned just upslope of the stone toe in the path of groundwater flow. Field experiments were conducted to evaluate the difference in treatment performance between this system (Cell A) and a control (bank in Cell B). The first experiment was conducted over a four-month period in 2003 following the completion of construction activities. Fertilizer and irrigation water were applied to field plots located upslope of the structures to generate NO_3-contaminated groundwater for the study. The field plots were not irrigated and fertilized during the second experiment in 2004; instead, NO_3 solution was continuously applied to a trench that was installed upslope of the field plot in each cell. Treatment performance was assessed in both experiments by monitoring the change in the concentration of NO_3 in groundwater as it flowed through each system.

A significant decline in NO_3 was observed as groundwater flowed through the reactive barrier in Cell A during both studies, even in the colder months when the temperature of the groundwater was between 3 and 7°C. Dilution may explain some of this decrease; however, it is evident that NO_3 was removed from groundwater because large reductions in NO_3 concentrations were observed during dry periods when streamflow was low. Some of the NO_3 may have been assimilated by plants and microorganisms, and/or converted to NH_4 by DNRA bacteria. A large fraction of the incoming NO_3 was likely removed via denitrification since conditions were

favorable for the process in the reactive barrier (e.g., Eh was low and organic C was available). Further research is needed to verify that denitrification was the primary mechanism of NO_3 removal in the system.

It was predicted that the reactive barrier would be more effective than the control at reducing NO_3 concentrations in groundwater. The difference in performance between the two systems in the first experiment (reactive barrier: 93% removal, control: 30% removal) supports this prediction. It was not possible to compare the two in the second experiment because most of the NO_3 solution delivered to the trench was not intercepted by the monitoring wells in the control (bank in Cell B). Nitrate solution was also not intercepted by the field plot wells in Cells A and B. The field plot in Cell A and the bank and field plot in Cell B were constructed using native clay and clay loam soils, which shrink and crack when dry. It is believed that most of the solution flowed laterally through shrinkage cracks (preferential pathways) rather than through the bulk soil in Cell B and the field plot in Cell A. A possible solution to this problem would have been to install the dosing trench immediately upslope of the bank in each cell, and to build the bank in Cell B using the same materials that were used to construct the reactive barrier in Cell A (minus the sawdust). A large percentage of coarse and silty sand was incorporated into the reactive barrier mixture. This may explain why flow was more uniformly distributed in the reactive barrier than in the control.

The RS2 structure was designed not only to intercept and treat NO_3-contaminated groundwater, but also to collect surface runoff. Some of the incoming surface water flowed down the bank slope and then pooled on the ground surface just upslope of the stone toe. It is likely that sediment and particulate nutrients (sediment-bound P and N) in the surface runoff settled out and accumulated on the soil surface. Presumably, NO_3 was removed from this water as it moved downward through the reactive barrier mixture. Research is needed to determine the extent to which the system reduced the amount of sediment and nutrients delivered to the stream in surface runoff.

While there are benefits associated with the use of RS2 structures, there are also some potential concerns. For instance, a considerable amount of N_2O (denitrification end product) may be released from the system. This is a concern since N_2O contributes to global warming as well as stratospheric ozone depletion. Another potential concern is that aquatic life in surface waters downstream of the structure may be adversely affected by the reactive barrier effluent since in contains low concentrations of dissolved oxygen. It is important to note that water exiting the reactive barrier also contained elevated levels of organic C. Decomposition of this material can further reduce oxygen concentrations in the receiving surface water system. It is recommended that studies be conducted to investigate these potential environmental impacts.

Although problems were encountered with the design and operation of the research cells, it can be said that this study was a success, since it demonstrated how permeable reactive barrier technology could be combined with a common bank stabilization technique to enhance NO_3 removal along streams. It is recommended that a full-scale system be constructed and tested to (1) verify the results of this experiment and (2) assess long-term performance. There are a few factors that can affect system performance over time. These include a reduction in permeability due to gas and microbial biomass accumulation (Soares et al., 1989), and a decrease in available C. Sawdust-derived labile C will be consumed in denitrification and other microbially mediated reactions. In addition, some of the C will be transported out of the system with groundwater and stream water. Even though eventually there will be little sawdust-derived C in the reactive barrier to support denitrification, a decrease in performance will not likely be observed since C inputs from the bank vegetation will offset the loss of sawdust-derived C. A decline in performance due to excessive biomass and gas production is also not expected since it has not been observed in similar systems (Robertson et al., 2000, 2008; Schipper and Vojvodić-Vuković, 2001). It is likely then, that high NO_3 removal, similar to that measured in this short-term study, will be measured in a full-scale system over the long term.

The installation of RS2 structures, particularly in areas where NO_3 loading to streams is very high, could lead to a marked improvement in downstream water quality. The impact of a particular system on downstream water quality will depend in part on the placement of the reactive barrier. It is important to note that although the reactive barrier was positioned adjacent to the stone toe in this study, it could be installed upslope in the upper bank region. At some sites, it may be easier and/or necessary to install the system in the upper bank region. Prior to installing a system at a particular site, information about the local groundwater system (e.g., direction and rate of groundwater flow, aquifer permeability, and depth to impermeable layer) will need to be obtained. This information is needed to ensure that the reactive barrier is positioned to intercept incoming NO_3-contaminated groundwater. It is also needed for design purposes. Ideally, the reactive barrier should be designed and constructed to intercept most if not all of the NO_3 plume. In areas where groundwater flows in a horizontal direction and an impermeable layer is present at a shallow depth, the vertical extent of the plume could be easily captured by installing the reactive barrier down to the impermeable layer. This would be relatively inexpensive, since extensive excavation would not be required. In other areas, for example, where an impermeable layer is not present at a shallow depth, and groundwater flows deep beneath the surface and upward as it approaches the stream, constructing a system that intercepts most of the NO_3-contaminated groundwater may not be feasible. In this case, the best approach would be to design a reasonably sized system that intercepts a portion of the NO_3 plume. If the system is designed properly, a significant reduction in NO_3 loading to the stream could potentially be achieved at a low cost.

REFERENCES

Addy, K.L., A.J. Gold, P.M. Groffman, and P.A. Jacinthe. 1999. Ground water nitrate removal in subsoil of forested and mowed riparian buffer zones. J. Environ. Qual. 28:962-970.

American Public Health Association, American Water Works Association, and Water Environment Federation. 1998. 2580 B. Oxidation-reduction potential measurement in clean water. p. 2-76. *In* Standard methods for the examination of water and wastewater. 20th ed. APHA, AWWA, and WEF, Washington, DC.

Barnhisel, R., and P.M. Bertsch. 1982. Aluminum. p. 275-300. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Benner, S.G., D.W. Blowes, and J.W.H. Molson. 2001. Modeling preferential flow in reactive barriers: Implications for performance and design. Ground Water 39:371-379.

Biedenharn, D.S., D. Derrick, C.M. Elliott, and C.C. Watson. 1997. The WES stream investigation and streambank stabilization handbook. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Bravard, J.P., G.M. Kondolf, and H. Piēgay. 1999. Environmental and societal effects of channel incision and remedial strategies. p. 303-342. *In* S.E. Darby and A. Simon (ed.) Incised river channels: Processes, forms, engineering, and management. John Wiley & Sons, Chichester, UK.

Breitburg, D. 2002. Effects of hypoxia, and the balance between hypoxia and enrichment, on coastal fishes and fisheries. Estuaries 25:767-781.

Bricker, S.B., C.G. Clement, D.E. Pirhalla, S.P. Orlando, and D.R.G. Farrow. 1999. National estuarine eutrophication assessment: Effects of nutrient enrichment in the nation's estuaries. NOAA, National Ocean Service Special Projects Office, and National Centers for Coastal Ocean Science, Silver Spring, MD.

Clément, J.C., G. Pinay, and P. Marmonier. 2002. Seasonal dynamics of denitrification along topohydrosequences in three different riparian wetlands. J. Environ. Qual. 31:1025-1037.

Committee on Environment and Natural Resources. 2000. Integrated assessment of hypoxia in the northern Gulf of Mexico. National Science and Technology Council Committee on Environment and Natural Resources, Washington, DC.

Cooper, A.B. 1990. Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. Hydrobiologia 202:13-26.

Danielson, R.E., and P.L. Sutherland. 1986. Porosity. p. 443-461. In A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Delwiche, C.C. 1981. The nitrogen cycle and nitrous oxide. p. 1-15. *In* C.C. Delwiche (ed.) Denitrification, nitrification, and atmospheric nitrous oxide. John Wiley & Sons, New York.

Des Moines Water Works. 2003. Consumer confidence report. Available at http://www.dmww.com/CCR/DMWWCCR2003.pdf (verified 24 Aug. 2009). Des Moines Water Works, Des Moines, IA.

Diaz, R.J. 2001. Overview of hypoxia around the world. J. Environ. Qual. 30:275-281.

Ells, J.E. 1993. Vegetable fertilizer guide. No. 0.509. Colorado State University Cooperative Extension, Fort Collins, CO.

Fahrner, S. 2002. Groundwater nitrate removal using a bioremediation trench. Honours thesis. Univ. of Western Australia, Perth.

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. p. 383-411. In A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Gold, A.J., P.A. Jacinthe, P.M. Groffman, W.R. Wright, and R.H. Puffer. 1998. Patchiness in groundwater nitrate removal in a riparian forest. J. Environ. Qual. 27:146-155.

Goolsby, D.A., and W.A. Battaglin. 2000. Nitrogen in the Mississippi Basin-Estimating sources and predicting flux to the Gulf of Mexico. U.S. Geological Survey Fact Sheet 135-00. USGS, Reston, VA.

Goolsby, D.A., W.A. Battaglin, G.B. Lawrence, R.S. Artz, B.T. Aulenbach, R.P. Hooper, D.R. Keeney, and G.J. Stensland. 1999. Flux and sources of nutrients in the Mississippi-Atchafalaya River Basin: Topic 3 report for the integrated assessment on hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Ser. No. 17. NOAA Coastal Ocean Program, Silver Spring, MD.

Greenan, C.M., T.B. Moorman, T.C. Kaspar, T.B. Parkin, and D.B. Jaynes. 2006. Comparing carbon substrates for denitrification of subsurface drainage water. J. Environ. Qual. 35:824-829.

Hartel, P.G. 1999. The soil habitat. p. 21-43. *In* D.M. Sylvia et al. (ed.) Principles and applications of soil microbiology. Prentice Hall, New Jersey.

Hauxwell, J., J. Cebrian, and I. Valiela. 2003. Eelgrass Zostera marina loss in temperate estuaries: Relationship to land-derived nitrogen loads and effect of light limitation imposed by algae. Mar. Ecol. Prog. Ser. 247:59-73.

Haycock, N.E., and G. Pinay. 1993. Groundwater nitrate dynamics in grass and poplar vegetated riparian buffer strips during the winter. J. Environ. Qual. 22:273-278.

Hedin, L.O., J.C. von Fischer, N.E. Ostrom, B.P. Kennedy, M.G. Brown, and G. P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology 79:684-703.

Hemminga, M.A., and C.M. Duarte. 2000. Seagrasses in the human environment. p. 248-291. *In* Seagrass ecology. Cambridge Univ. Press, Cambridge.

Heritage, J., E.G.V. Evans, and R.A. Killington. 1999. The microbiology of soil and of nutrient cycling. p. 1-15. *In* Microbiology in action. Cambridge Univ. Press, Cambridge.

Hill, A.R. 1996. Nitrate removal in stream riparian zones. J. Environ. Qual. 25:743-755.

Hill, A.R., K.J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51:193-223.

Howarth, R.W., and R. Marino. 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. Limnol. Oceanogr. 51:364-376.

Hvorslev, M.J. 1951. Time lag and soil permeability in ground-water observations. Bull. No. 36. U.S. Army Corps of Eng., Waterways Exp. Stn., Vicksburg, MS.

Jacinthe, P.A., P.M. Groffman, A.J. Gold, and A. Mosier. 1998. Patchiness in microbial nitrogen transformations in groundwater in a riparian forest. J. Environ. Qual. 27:156-164.

Jacobs, T.C., and J.W. Gilliam. 1985. Riparian losses of nitrate from agricultural drainage waters. J. Environ. Qual. 14:472-478.

Jaynes, D.B., T.C. Kaspar, T.B. Moorman, and T.B. Parkin. 2008. In situ bioreactors and deep drain-pipe installation to reduce nitrate losses in artificially drained fields. J. Environ. Qual. 37:429-436.

Johnson, A.W., and J.M. Stypula (ed.) 1993. Guidelines for bank stabilization projects in the riverine environments of King County. King County Department of Public Works, Surface Water Management Division, Seattle, WA.

Jordan, T.E., D.L. Correll, and D.E. Weller. 1993. Nutrient interception by a riparian forest receiving inputs from adjacent cropland. J. Environ. Qual. 22:467-473.

Kellogg, D.Q., A.J. Gold, P.M. Groffman, K. Addy, N.H. Stolt, and G. Blazejewski. 2005. In situ ground water denitrification in stratified, permeable soils underlying riparian wetlands. J. Environ. Qual. 34:524-533.

Klute, A., and C. Dirksen. 1986. Hydraulic conductivity and diffusivity: Laboratory methods. p. 687-734. In A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Knobeloch, L., and M. Proctor. 2001. Eight blue babies. WMJ 100:43-47.

Knobeloch, L., B. Salna, A. Hogan, J. Postle, and H. Anderson. 2000. Blue babies and nitrate-contaminated well water. Environ. Health Perspect. 108:675-678.

Korom, S.F. 1992. Natural denitrification in the saturated zone: A review. Water Resour. Res. 28: 1657-1668.

Kung, K.-J. S. 1990. Influence of plant uptake on the performance of bromide tracer. Soil Sci. Soc. Am. J. 54:975-979.

Kuo, S. 1996. Phosphorus. p. 869-920. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. 5. SSSA, Madison, WI.

Louisiana Universities Marine Consortium. 2009. Gulf of Mexico dead zone surprisingly small in area, but severe. Available at http://www.gulfhypoxia.net/Research/ShelfwideCruises/2009/Files/Press_Release.pdf (verified 1 Mar. 2010). LUMCON, Chauvin, LA.

Lowrance, R. 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. J. Environ. Qual. 21:401-405.

McCarty, G.W., and J.M. Bremner. 1992. Availability of organic carbon for denitrification of nitrate in subsoils. Biol. Fertil. Soils 14:219-222.

McIsaac, G.F., and R.D. Libra. 2003. Revisiting nitrate concentrations in the Des Moines River: 1945 and 1976-2001. J. Environ. Qual. 32:2280-2289.

Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. 2001. Action plan for reducing, mitigating, and controlling hypoxia in the northern Gulf of Mexico. USEPA, Office of Wetlands, Oceans, and Watersheds, Washington, DC.

Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. 2008. Gulf hypoxia action plan 2008 for reducing, mitigating, and controlling hypoxia in the northern Gulf of Mexico and improving water quality in the Mississippi River Basin. USEPA, Office of Wetlands, Oceans, and Watersheds, Washington, DC.

Mitsch, W.J., J.W. Day, Jr., J.W. Gilliam, P.M. Groffman, D.L. Hey, G.W. Randall, and N. Wang. 2001. Reducing nitrogen loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to counter a persistent ecological problem. BioScience 51:373-388.

Mulvaney, R.L. 1996. Nitrogen – inorganic forms. p. 1123-1184. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. 5. SSSA, Madison, WI.

Myrold, D.D. 1999. Transformations of nitrogen. p. 259-294. *In* D.M. Sylvia et al. (ed.) Principles and applications of soil microbiology. Prentice Hall, New Jersey.

National Research Council. 1995. Nitrate and nitrite in drinking water. National Academy of Science Press, Washington, DC.

National Research Council. 2000. Clean coastal waters: Understanding and reducing the effects of nutrient pollution. National Academy Press, Washington, DC.

National Research Council. 2002. Riparian areas: Functions and strategies for management. National Academy Press, Washington, DC.

Nelson, W.M., A.J. Gold, and P.M. Groffman. 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. J. Environ. Qual. 24:691-699.

Nelson, K.A., and M.A. Hostetler. 2003. An infant with methemoglobinemia. Hospital Physician 39:31-38.

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961-1010. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. 5. SSSA, Madison, WI.

Nixon, S.W. 1995. Coastal marine eutrophication: A definition, social causes, and future concerns. Ophelia 41:199-219.

Nolan, B.T., and J. D. Stoner. 2000. Nutrients in groundwaters of the conterminous United States, 1992-1995. Environ. Sci. Technol. 34:1156-1165.

Owens, L.B., R.W. Van Keuren, and W. M. Edwards. 1985. Groundwater quality changes resulting from a surface bromide application to a pasture. J. Environ. Qual. 14:543-548.

Parkin, T.B. 1987. Soil microsites as a source of denitrification variability. Soil Sci. Soc. Am. J 51:1194-1199.

Peterjohn, W.T., and D.L. Correll. 1984. Nutrient dynamics in an agricultural watershed: Observations on the role of a riparian forest. Ecology 65:1466-1475.

Powell, R.M., D.W. Blowes, R.W. Gillham, D. Schultz, T. Sivavec, R.W. Puls, J.L. Vogan, P.D. Powell, and R. Landis. 1998. Permeable reactive barrier technologies for contaminant remediation. EPA/600/R-98/125. USEPA, Office of Research and Development, Washington, DC.

Rabalais, N.N., D.E. Harper, Jr., and R.E. Turner. 2001. Responses of nekton and demersal and benthic fauna to decreasing oxygen concentrations. p. 115-128. *In* N.N. Rabalais and R.E. Turner (ed.) Coastal hypoxia: Consequences for living resources and ecosystems. American Geophysical Union, Washington, DC.

Rabalais, N. N., R.E. Turner, and D. Scavia. 2002. Beyond science into policy: Gulf of Mexico hypoxia and the Mississippi River. BioScience 52:129-142.

Reddy, K.R., and R.D. DeLaune. 2008. Biogeochemistry of wetlands. CRC Press, Boca Raton, FL.

Rice, C.W., and J.M. Tiedje. 1989. Regulation of nitrate assimilation by ammonium in soils and in isolated soil microorganisms. Soil Biol. Biochem. 21:597-602.

Rittmann, B.E., and P.L. McCarty. 2001. Environmental biotechnology: Principles and applications. McGraw-Hill, New York.

Roberston, W.D., D.W. Blowes, C.J. Ptacek, and J.A. Cherry. 2000. Long-term performance of in situ reactive barriers for nitrate remediation. Ground Water 38:689-695.

Robertson, W.D., and J.A. Cherry. 1995. In situ denitrification of septic-system nitrate using reactive porous media barriers: Field trials. Ground Water 33:99-111.

Robertson, W.D., J.L. Vogan, and P.S. Lombardo. 2008. Nitrate removal rates in a 15-year-old permeable reactive barrier treating septic system nitrate. Ground Water Monitoring and Remediation. 28:65-72.

Schilling, K.E., and D.S. Lutz. 2004. Relation of nitrate concentrations to baseflow in the Raccoon River, Iowa. J. Am. Water Resour. Assoc. 40:889-900.

Schilling, K.E., Y.K. Zhang, and P. Drobney. 2004. Water table fluctuations near an incised stream, Walnut Creek, Iowa. J. Hydrol. 286:236-248.

Schipper, L., and M. Vojvodić-Vuković . 1998. Nitrate removal from groundwater using a denitrification wall amended with sawdust: Field trial. J. Environ. Qual. 27:664-668.

Schipper, L.A., and M. Vojvodić-Vuković. 2000. Nitrate removal from groundwater and denitrification rates in a porous treatment wall amended with sawdust. Ecol. Eng. 14:269-278.

Schipper, L.A., and M. Vojvodić-Vuković. 2001. Five years of nitrate removal, denitrification and carbon dynamics in a denitrification wall. Water Res. 35:3473-3477.

Sigg, L. 2000. Redox potential measurements in natural waters: Significance, concepts and problems. p. 1-12. *In* J. Schuring et al. (ed.) Redox: Fundamentals, processes and applications. Springer Press, Berlin.

Simon, A., and S.E. Darby. 1999. The nature and significance of incised river channels. p. 3-18. *In* S.E. Darby and A. Simon (ed.) Incised river channels: Processes, forms, engineering, and management. John Wiley & Sons, Chichester, UK.

Soares, M.I.M., S. Belkin, and A. Abeliovich. 1989. Clogging of microbial denitrification sand columns: Gas bubbles or biomass accumulation? Z. Wasser-Abwasser-Forsch 22: 20-24.

Soil Survey Staff. 1996. Soil survey laboratory methods manual. Soil Survey Investigations Rep. No. 42. Version 3.0. U.S. Gov. Print. Office, Washington, DC.

Soltanpour, P.N., G.W. Johnson, S.M. Workman, J.B. Jones, Jr., and R.O. Miller. 1996. Inductively coupled plasma emission spectrometry and inductively coupled plasma – mass spectroscopy. p. 91-140. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. 5. SSSA, Madison, WI.

Stanford, G., S. Dzienia, and R.A. Vander Pol. 1975. Effect of temperature on denitrification rate in soils. Soil Sci. Soc. Am. Proc. 39:867-870.

Starr, R.C., and R.W. Gillham. 1993. Denitrification and organic carbon availability in two aquifers. Ground Water 31:934-947.

Straub, K.L., M. Benz, B. Schink, and F. Widdel. 1996. Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. Appl. Environ. Microbiol. 62:1458-1460.

Tiedje, J.M. 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. p. 179-244. *In* A.J.B. Zehnder (ed.) Biology of anaerobic microorganisms. John Wiley & Sons, New York.

Tiedje, J.M. 1994. Denitrifiers. p. 245-268. *In* R.W. Weaver et al. (ed.) Methods of soil analysis. Part 2. Microbiological and biochemical properties. SSSA Book Ser. 5. SSSA, Madison, WI.

USEPA. 2000. National water quality inventory: 1998 report to Congress. EPA-841-R-00-001. Office of Water, Washington, DC.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. USDA Handb. 60. U.S. Gov. Print. Office, Washington, DC.

Verchot, L.V., E.C. Franklin, and J.W. Gilliam. 1997. Nitrogen cycling in piedmont vegetated filter zones: II. Subsurface nitrate removal. J. Environ. Qual. 26:337-347.

Vidon, P.G.F., and A.R. Hill. 2004a. Landscape controls on nitrate removal in stream riparian zones. Water. Resour. Res. 40:W03201.

Vidon, P., and A. R. Hill. 2004b. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. Biogeochemistry 71:259-283.

Water Environment Federation. 1998. Principles of biological nitrogen removal. p. 59-87. *In* Biological and chemical systems for nutrient removal. Water Environment Federation, Alexandria, VA.

Watson, I., and A.D. Burnett. 1993. Hydrology: An environmental approach. Buchanan Books Cambridge, Ft. Lauderdale, FL.

Woolson, E. 2002. Raccoon River watershed project. Stormwater. July-August. Available at http://www.stormh20.com/july-august-2002/river-watershed-project.aspx (verified 24 Aug. 2009).

APPENDIX A:

2003 GROUNDWATER QUALITY DATA

Table A.1. Groundwater nitrate concentrations in Cells A and B during 2003 study.

Location	Well ID	NO_3-N								
		7 Aug.	19 Aug.	3 Sept.	16 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
		mg L^{-1}								
Cell A	A1	11.3	2.60	0.74	1.00	31.2	28.2	39.5	22.5	13.3
	A2	30.8	6.07	0.92	5.81	17.5	14.2	25.7	14.1	8.54
	A3	6.80	0.23	0.05	2.99	6.9	3.36	6.72	10.4	6.69
	A4	1.19	6.03	2.06	16.0	17.2	18.9	24.9	10.9	5.03
	A5	0.92	0.47	0.52	1.19	1.2	2.74	2.76	2.66	2.20
	A6	3.02	10.0	2.71	2.52	no data	0.44	0.62	0.15	0.94
	A7	no data	6.87	no data	1.87	6.70	6.79	no data	4.52	3.68
	A8	0.19	5.15	2.54	7.87	14.8	17.5	11.8	7.16	4.65
	A9	no data	3.72	2.26	0.17	0.05	0.05	0.26	0.37	0.11
	A10	no data	0.16	0.05	0.10	0.05	0.05	0.15	0.05	0.05
Cell B	B1	27.8	10.5	2.10	6.80	8.70	15.1	35.9	28.1	21.3
	B2	5.86	7.09	1.82	12.9	22.3	29.2	32.4	12.8	6.86
	B3	2.34	4.50	2.35	7.70	12.8	20.8	18.0	18.2	14.6
	B4	5.03	6.16	1.75	15.1	15.9	23.5	38.0	4.38	9.45
	B6	16.3	16.5	10.8	15.1	15.4	25.1	12.5	13.5	2.78
	B7	no data	34.1	3.96	10.8	12.1	11.9	9.35	6.86	6.24
	B8	8.88	14.9	19.1	15.7	15.2	13.4	11.1	3.29	8.61
	B9	8.76	12.1	2.77	12.3	13.0	11.4	20.4	7.38	7.87
	B10	12.6	10.5	2.98	10.9	9.00	7.55	1.38	4.89	4.04

Table A.2. Groundwater total organic carbon (TOC) concentrations in Cells A and B during 2003 study.

Location	Well ID	TOC					
		19 Aug.	16 Sept.	30 Sept.	14 Oct.	20 Nov.	2 Dec.
		mg L^{-1}					
Cell A	A1	23.1	13.8	no data	11.7	7.4	8.9
	A2	30.3	17.0	18.5	11.3	9.7	9.5
	A3	40.5	24.4	20.7	17.7	5.6	9.7
	A4	14.1	8.2	9.1	6.2	5.1	6.4
	A5	27.6	21.0	24.5	15.0	11.3	14.9
	A6	14.6	19.6	33.3	19.3	20.3	22.0
	A7	8.6	7.2	7.1	7.0	3.4	5.9
	A8	8.6	10.4	9.7	7.4	4.1	11.9
	A9	12.4	9.5	12.2	7.1	4.6	9.0
	A10	24.6	17.8	10.7	9.6	5.1	9.7
Cell B	B1	25.2	11.7	21.4	18.5	8.5	11.2
	B2	16.2	13.5	9.0	8.2	4.8	6.4
	B3	30.5	21.3	21.5	16.1	16.5	16.9
	B4	15.8	11.1	9.3	10.4	4.1	11.7
	B6	17.7	15.8	14.9	6.8	8.2	7.8
	B7	16.8	10.3	7.6	6.7	6.7	8.1
	B8	15.2	11.3	8.2	6.9	5.0	11.6
	B9	16.8	8.0	7.7	7.6	3.9	12.6
	B10	24.3	15.8	12.3	11.9	5.0	19.4

Table A.3. Oxidation-reduction potential (ORP) of groundwater in Cells A and B during 2003 study.

Location	Well ID	ORP						
		3 Sept.	16 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
		mV						
Cell A	A1	-130	-24	7	212	222	269	365
	A2	-26	-1	36	224	220	278	361
	A3	-193	-11	-106	-58	104	199	363
	A4	-57	14	-70	-12	184	242	360
	A5	-52	15	-79	-41	194	208	260
	A6	-54	6	-95	-77	16	111	157
	A7	-43	22	-33	-18	141	169	243
	A8	-20	19	-25	13	164	195	295
	A9	no data	5	-51	-13	no data	173	275
	A10	-178	-2	-79	-75	23	110	168
Cell B	B1	-35	-23	23	2	150	196	271
	B2	-35	10	42	31	167	223	308
	B3	-123	no data	1	70	174	262	326
	B4	19	15	1	78	178	274	319
	B6	2	16	23	85	180	291	332
	B7	-3	17	25	85	178	299	328
	B8	-8	20	32	89	181	305	334
	B9	-26	20	32	89	181	310	333
	B10	-42	24	34	92	180	316	335

Table A.4. Eh of groundwater in Cells A and B during 2003 study.

Location	Well ID	Eh						
		3 Sept.	16 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
		mV						
Cell A	A1	75	181	214	419	432	481	579
	A2	179	204	243	431	430	490	575
	A3	12	194	101	149	314	411	577
	A4	148	219	137	195	394	454	574
	A5	153	220	128	166	404	420	474
	A6	151	211	112	130	226	323	371
	A7	162	227	174	189	351	381	457
	A8	185	224	182	220	374	407	509
	A9	no data	210	156	194	no data	385	489
	A10	27	203	128	132	233	322	382
Cell B	B1	170	182	230	209	360	408	485
	B2	170	215	249	238	377	435	522
	B3	82	no data	208	277	384	474	540
	B4	224	220	208	285	388	486	533
	B6	207	221	230	292	390	503	546
	B7	202	222	232	292	388	511	542
	B8	197	225	239	296	391	517	548
	B9	179	225	239	296	391	522	547
	B10	163	229	241	299	390	528	549

Table A.5. Groundwater temperatures in Cells A and B during 2003 study.

Location	Well ID	Temperature					
		3 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
		°C					
Cell A	A1	18.4	16.3	15.2	14.5	9.1	8.8
	A2	17.7	15.5	14.7	12.8	9.4	7.7
	A3	17.7	15.2	14.3	12.3	8.9	7.3
	A4	17.2	14.6	13.9	12.0	9.0	7.2
	A5	17.7	14.3	13.4	11.6	8.2	6.5
	A6	17.4	14.3	13.5	11.4	8.8	6.5
	A7	17.5	13.3	11.8	10.1	6.9	4.9
	A8	17.3	13.1	11.5	9.6	7.1	5.3
	A9	no data	12.2	10.2	no data	6.0	3.6
	A10	18.1	12.3	10.6	8.3	6.2	4.0
Cell B	B1	17.3	15.4	13.6	10.9	8.6	6.6
	B2	17.1	15.2	14.2	11.2	8.8	6.9
	B3	16.8	14.1	13.7	11.2	8.9	7.1
	B4	16.8	14.2	13.5	11.2	8.8	7.0
	B6	17.0	13.2	13.1	10.7	8.5	6.6
	B7	17.0	13.2	12.2	10.0	7.4	5.6
	B8	17.1	13.2	12.0	9.6	7.2	5.3
	B9	17.0	12.1	10.6	8.7	6.4	4.1
	B10	17.2	11.9	10.4	8.3	6.4	4.1

Table A.6. Groundwater dissolved oxygen (DO) concentrations in Cells A and B during 2003 study.

		DO						
Location	Well ID	3 Sept.	16 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
		mg L^{-1}						
Cell A	A1	1.92	2.25	1.36	3.63	1.17	5.85	4.91
	A2	2.78	2.94	1.21	2.50	1.65	6.78	4.73
	A3	0.28	2.20	0.32	2.75	0.81	5.50	2.24
	A4	1.39	5.05	1.10	2.97	1.00	5.08	4.76
	A5	2.19	4.89	0.21	0.97	1.19	4.22	2.73
	A6	2.56	4.01	0.48	1.60	0.77	5.06	3.32
	A7	4.14	4.65	1.64	2.65	2.45	6.87	5.52
	A8	3.03	3.70	0.58	1.72	1.41	6.40	7.32
	A9	no data	no data	1.27	2.01	no data	3.22	4.07
	A10	1.70	no data	0.62	0.70	3.00	no data	3.20
Cell B	B1	1.59	3.34	1.48	2.21	1.43	3.42	4.12
	B2	3.08	2.58	1.73	1.82	1.21	4.15	4.60
	B3	1.42	no data	1.03	1.75	0.78	1.72	2.28
	B4	5.04	2.51	1.79	2.31	1.28	6.39	6.41
	B6	1.49	3.54	2.06	2.06	1.25	2.71	4.07
	B7	4.15	3.91	2.02	2.53	1.74	4.22	6.58
	B8	3.02	3.23	2.27	2.41	1.56	4.22	6.51
	B9	3.87	3.83	2.77	2.77	0.71	4.64	6.64
	B10	2.50	3.43	1.31	2.89	0.86	4.84	6.13

Table A.7. Groundwater pH values in Cells A and B during 2003 study.

		pH						
Location	Well ID	3 Sept.	16 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
Cell A	A1	6.68	6.76	6.58	6.62	6.63	6.96	6.89
	A2	6.74	6.59	6.69	6.71	6.66	6.99	6.93
	A3	6.72	6.76	6.75	6.67	6.72	6.98	7.04
	A4	6.65	6.46	6.66	6.66	6.62	6.99	7.00
	A5	6.76	6.41	6.82	6.82	6.84	7.06	7.06
	A6	6.61	6.52	6.77	6.82	6.82	7.08	7.09
	A7	6.61	6.44	6.70	6.66	6.76	7.11	7.05
	A8	6.60	6.47	6.82	6.72	6.98	7.20	7.23
	A9	no data	6.37	6.97	6.92	no data	7.20	7.12
	A10	6.66	7.01	6.91	6.89	6.85	7.13	7.08
Cell B	B1	6.85	6.31	6.77	6.78	6.67	6.89	6.93
	B2	6.84	5.98	6.74	6.73	6.69	6.84	6.94
	B3	6.73	no data	6.76	6.77	6.79	6.96	6.97
	B4	6.66	5.78	6.80	6.69	6.60	6.96	6.97
	B6	6.73	5.78	6.89	6.83	6.78	7.03	6.98
	B7	6.76	6.07	6.88	6.95	6.96	7.16	7.24
	B8	6.77	6.63	6.84	6.90	6.90	7.11	7.21
	B9	6.97	6.65	7.00	7.12	6.89	7.20	7.27
	B10	7.02	6.63	7.00	7.15	6.95	7.26	7.24

Table A.8. Specific conductance of groundwater in Cells A and B during 2003 study.

Location	Well ID	Specific Conductance						
		3 Sept.	16 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
		$\mu S\ cm^{-1}$						
Cell A	A1	1486	1579	1353	1230	1184	848	853
	A2	1223	1377	1154	1024	947	849	829
	A3	1979	1379	2171	1855	1409	668	825
	A4	1194	551	1064	923	731	571	534
	A5	1943	1578	1954	1792	1558	1316	1240
	A6	1451	1434	1748	1558	1621	1444	1320
	A7	587	407	489	450	1626	253	341
	A8	763	559	663	622	622	340	382
	A9	no data	692	707	668	no data	502	522
	A10	783	737	836	800	705	589	612
Cell B	B1	2086	1856	1791	1691	1330	1291	1111
	B2	1296	1303	1150	1203	1210	962	658
	B3	2266	no data	1949	1698	1808	1785	1728
	B4	677	1126	1235	1140	1100	463	397
	B6	1521	1721	706	1304	1337	1149	1171
	B7	740	681	707	606	742	543	485
	B8	1163	900	722	639	732	527	764
	B9	599	657	542	538	652	510	483
	B10	851	741	710	613	715	537	621

Table A.9. Groundwater alkalinity in Cells A and B during 2003 study.

Location	Well ID	Alkalinity†						
		7 Aug.	19 Aug.	3 Sept.	16 Sept.	30 Sept.	14 Oct.	20 Nov.
		mg L^{-1} as $CaCO_3$						
Cell A	A1	446	526	485	489	479	409	310
	A2	421	400	241	422	377	303	314
	A3	568	784	850	840	726	613	272
	A4	447	438	428	360	326	211	240
	A5	727	914	940	917	928	741	723
	A6	736	617	741	775	829	791	793
	A7	351	250	no data	158	no data	100	190
	A8	325	175	240	224	no data	186	151
	A9	no data	298	no data	326	no data	346	260
	A10	522	424	380	402	no data	356	281
Cell B	B1	536	554	560	623	516	530	385
	B2	478	358	368	390	275	409	280
	B3	709	701	609	587	620	672	546
	B4	503	346	235	255	295	515	150
	B6	615	562	602	634	580	558	518
	B7	360	265	303	310	284	341	200
	B8	no data	310	388	408	274	255	233
	B9	400	311	288	282	229	261	198
	B10	411	348	389	322	342	276	184

†$CaCO_3$, calcium carbonate.

Table A.10. Groundwater ammonium concentrations in Cells A and B during 2003 study.

Location	Well ID	NH_4-N				
		16 Sept.	30 Sept.	14 Oct.	20 Nov.	2 Dec.
		mg L^{-1}				
Cell A	A1	0.15	0.07	4.72	0.10	0.09
	A2	0.12	0.09	1.03	0.06	0.10
	A3	1.31	1.23	1.31	0.18	0.60
	A4	0.32	0.01	0.09	0.06	0.06
	A5	0.35	0.48	0.58	0.16	0.16
	A6	0.58	1.00	0.90	0.75	0.11
	A7	0.01	0.02	0.05	0.17	0.03
	A8	0.01	0.01	0.02	0.11	0.04
	A9	0.08	0.02	0.12	0.26	0.17
	A10	0.01	0.79	0.02	0.21	0.10
Cell B	B1	0.36	0.02	0.23	0.15	0.12
	B2	0.12	0.01	0.04	0.11	0.04
	B3	0.09	0.01	0.07	0.14	0.08
	B4	0.10	0.01	0.07	0.01	0.11
	B6	0.57	0.01	0.03	0.11	0.04
	B7	0.02	0.02	0.01	0.01	0.02
	B8	0.08	0.03	0.01	0.01	0.05
	B9	0.03	0.01	0.02	0.02	0.24
	B10	0.12	0.01	0.12	0.14	0.44

APPENDIX B:

2003 LABORATORY SOIL TESTING RESULTS

Table B.1. Chemical properties of soil and reactive barrier material in Cell A.

Location	Well Id	Depth	pH	Electrical Conductivity	Lime Estimate	Organic Matter	NO_3-N	P	K	Zn	Fe	Mn	Cu	Al
		in		mmhos cm^{-1}		%	ppm							mg kg^{-1}
Field	A1	0-6	7.7	4.9	Medium	5.5	41.2	85.0	2336	9.6	30.3	9.7	39.1	14.4
		6-12	7.6	3.7	Medium	4.3	61.4	52.0	651	4.9	15.9	7.5	14.4	14.4
		12-42	7.7	2.0	Medium	4.9	21.5	20.4	310	3.1	11.6	4.7	9.1	<0.1
	A5	0-6	7.6	1.6	Medium	3.8	42.2	11.0	274	2.8	13.9	6.9	6.6	<0.1
		6-12	7.5	1.1	Medium	3.5	16.5	4.2	235	1.7	11.6	8.5	2.9	<0.1
		12-42	7.5	1.0	Medium	3.9	6.7	1.8	225	1.6	12.8	8.5	2.7	1.3
Barrier	A10	10-22	7.4	1.3	Medium	2.2	3.0	7.0	174	1.1	30.0	31.0	2.2	<0.1

Table B.2. Chemical properties of soil and bank material in Cell B.

Location	Well Id	Depth	pH	Electrical Conductivity	Lime Estimate	Organic Matter	NO_3-N	P	K	Zn	Fe	Mn	Cu	Al
		In		mmhos cm^{-1}		%	ppm							mg kg^{-1}
Field	B1	0-6	7.6	7.5	High	5.6	152.0	110.0	2161	9.4	22.3	12.2	35.7	<0.1
		6-12	7.5	6.0	High	4.2	127.0	21.0	617	2.9	12.9	10.3	9.1	0.4
		12-42	7.6	3.4	Medium	3.9	78.0	23.0	423	3.2	14.5	9.4	9.8	2.6
	B5	0-6	7.4	1.3	High	4.0	21.7	5.6	294	1.8	13.4	12.4	3.1	<0.1
		6-12	7.6	1.3	High	4.7	30.0	4.0	255	1.7	10.5	6.1	2.7	<0.1
		12-42	7.1	1.7	Low	4.1	20.4	50.0	1047	4.5	31.4	11.0	14.6	<0.1
Bank	B9	10-22	7.3	1.1	High	4.2	1.9	2.7	257	1.5	30.0	31.6	3.3	3.1

Table B.3. Physical properties of soil and reactive barrier material in Cell A.

Location	Well Id	Depth	Porosity	Sand	Silt	Clay	Texture
		in			%		
Field	A1	0-6	no data	38	24	38	Clay Loam
		6-12	no data	34	25	41	Clay
		12-42	0.555	36	24	40	Clay/Clay Loam
	A5	0-6	no data	44	22	34	Clay Loam
		6-12	no data	42	22	36	Clay Loam
		12-42	0.563	39	19	42	Clay
Barrier	A10	10-22	0.515	64	14	22	Sandy Clay Loam

Table B.4. Physical properties of soil and bank material in Cell B.

Location	Well Id	Depth	Porosity	Sand	Silt	Clay	Texture
		In		%			
Field	B1	0-6		38	24	38	Clay Loam
		6-12		38	24	38	Clay Loam
		12-42	0.550	34	24	42	Clay
	B5	0-6		36	24	40	Clay/Clay Loam
		6-12		42	20	38	Clay Loam
		12-42	0.508	41	22	37	Clay Loam
Bank	B9	10-22	0.517	44	20	36	Clay Loam

APPENDIX C:

WATER TABLE ELEVATION

Table C.1. Water table elevation at each well on sampling dates in 2003.

Location	Well ID	Water Table Elevation								
		7 Aug.	19 Aug.	3 Sept.	16 Sept.	30 Sept.	14 Oct.	4 Nov.	20 Nov.	2 Dec.
		ft								
Cell A	A1	91.49	92.72	92.54	92.53	92.71	92.91	91.68	92.54	92.65
	A2	91.55	92.69	93.04	92.60	92.72	93.14	91.92	91.80	92.96
	A3	91.32	92.49	91.96	91.97	91.97	92.16	91.42	92.52	92.52
	A4	91.35	92.84	91.92	92.63	91.83	92.81	91.53	92.20	92.61
	A5	91.31	92.40	92.21	91.65	92.41	92.28	91.06	91.91	91.95
	A6	91.08	91.23	91.21	91.20	91.15	91.11	91.01	90.98	91.45
	A7	91.09	91.11	92.12	92.01	92.35	92.28	91.02	91.92	91.86
	A8	91.11	91.80	91.18	92.10	92.41	92.38	91.07	92.03	91.94
	A9	no data	91.63	91.53	91.45	91.44	91.37	no data	91.24	91.27
	A10	91.03	91.33	91.55	91.28	91.44	91.37	90.96	91.31	91.27
Cell B	B1	91.68	92.63	92.40	92.61	92.25	92.58	92.15	92.83	92.74
	B2	91.76	93.18	93.06	92.83	93.14	92.51	92.07	92.98	93.13
	B3	91.51	91.71	91.90	91.91	91.64	92.02	91.61	91.73	91.81
	B4	91.61	93.01	92.81	92.92	93.01	92.99	91.81	92.67	92.54
	B6	91.02	91.76	91.20	91.32	91.37	91.30	91.15	91.33	91.53
	B7	90.88	92.06	91.91	91.89	92.00	92.00	90.90	91.96	91.90
	B8	90.90	92.05	91.87	91.89	91.98	91.91	91.17	91.90	91.87
	B9	90.71	91.17	91.60	91.75	92.02	92.03	90.97	91.88	91.88
	B10	90.61	90.99	91.54	91.60	91.94	91.87	91.02	91.58	91.51

Table C.2. Water table elevation at each well on sampling dates in 2004.

Location	Well ID	Water Table Elevation							
		24 May	8 June	22 June	6 July	22 July	3 Aug.	17 Aug.	1 Sept.
		ft							
Cell A	A1	92.84	92.99	92.71	92.67	92.86	92.99	92.93	92.31
	A2	92.89	92.89	93.06	92.94	92.42	92.82	92.91	92.57
	A3	92.69	92.92	92.75	92.69	92.79	92.83	92.32	92.13
	A4	92.71	92.88	92.90	92.41	92.82	92.89	92.45	92.18
	A5	92.60	92.73	92.50	92.01	92.55	92.51	92.29	91.50
	A6	92.52	92.77	92.50	92.45	92.62	92.59	91.99	92.10
	A7	92.36	92.55	92.47	92.49	92.49	92.46	91.99	91.27
	A8	92.48	91.69	92.45	92.02	92.56	92.53	92.12	91.20
	A9	91.28	91.24	91.25	90.97	91.03	no data	no data	91.00
	A10	91.29	91.30	91.30	91.10	91.28	91.23	91.13	90.95
Cell B	B1	93.12	93.22	93.09	92.82	93.22	93.26	93.15	92.46
	B2	93.03	93.04	92.91	92.88	93.16	93.14	92.98	92.60
	B3	92.66	92.53	92.65	92.36	92.71	92.67	92.17	91.96
	B4	92.71	92.69	92.51	92.51	92.86	92.83	92.28	92.03
	B6	91.76	91.73	92.05	91.98	91.95	92.06	91.65	91.40
	B7	91.88	92.18	92.28	91.46	91.95	91.70	91.06	91.03
	B8	91.76	92.05	91.90	91.40	91.84	91.70	91.11	91.05
	B9	91.39	91.30	91.49	91.05	91.31	91.30	90.75	90.75
	B10	90.95	90.92	91.20	90.85	90.92	90.94	90.51	90.60

APPENDIX D:

GROUNDWATER VELOCITY AND RESIDENCE TIME

Groundwater velocity was estimated using Darcy's Law equation:

$$v_x = -\frac{K(dh/dl)}{n_e} \quad [8]$$

where

v_x	=	average linear velocity
K	=	saturated hydraulic conductivity
dh/dl	=	hydraulic gradient
n_e	=	effective porosity

Slug tests were performed as described in Appendix E to determine K of the bank and reactive barrier material. Total porosity was calculated using particle and bulk densities (Danielson and Sutherland, 1986). Total porosity was used as an estimate of n_e. Hydraulic gradient, which is the change in head over a certain distance, was estimated using water table elevations (Table C.2, Appendix C).

Residence time was calculated as follows:

$$t = \frac{w}{v_x} \quad [9]$$

where

t	=	residence time
w	=	width of the reactive barrier or bank
v_x	=	average linear velocity

Groundwater flow rates through the reactive barrier, and the residence time of groundwater in the system, were calculated using data collected in 2004. On 24 May, the change in head from row 2 (well pair A7-A8) to row 1 (well pair A9-A10) in the reactive barrier was 92.42 – 91.29 ft. The distance from row 2 to row 1 was 2.0 ft. The hydraulic gradient was (92.42 - 91.29 ft) / (2.0 ft) or 0.565. Total porosity of the reactive barrier material was 0.375. Saturated hydraulic conductivity of the reactive barrier material was 0.20 ft d^{-1}. The average linear velocity of groundwater from row 2 to row 1 in the reactive barrier on this date was calculated as follows:

$$v_x = -\frac{(0.20\,ft/day)\times(0.565)}{0.375} = 0.301\,ft/day$$

Residence time was calculated by dividing the width of the reactive barrier by the average linear velocity. The width of the reactive barrier was 5.0 ft. Using the velocity calculated in the example above, the residence time of groundwater in the reactive barrier was estimated to be 16.6 days.

Table D.1 shows groundwater velocity and residence time estimates for each sampling date in 2004. Velocity was determined using a K value of 0.20 ft d^{-1} and a n_e value of 0.375. Residence time was estimated by dividing 5ft (the width of the reactive barrier) by the velocity.

Table D.1. Groundwater velocity and residence time in the reactive barrier during 2004 study.

Date	Hydraulic Gradient (Row 2 to Row 1)	Average Linear Velocity ft d^{-1}	Residence Time d
24 May	0.565	0.30	16.6
8 June	0.425	0.23	22.1
22 June	0.593	0.32	15.8
6 July	0.610	0.33	15.4
22 July	0.685	0.37	13.7
3 Aug.	0.633	0.34	14.8
17 Aug.	0.463	0.25	20.3
1 Sept.	0.130	0.07	72.1

Table D.2 shows groundwater velocity and residence time in the control (bank in Cell B) during the 2004 study. Velocity was determined using a K value of 0.0142 ft d^{-1} and a n_e value of 0.4011. Residence time was estimated by dividing 5ft (the width of the bank in Cell B) by the velocity.

Table D.2. Groundwater velocity and residence time in the control during 2004 study.

Date	Hydraulic Gradient (Row 2 to Row 1)	Average Linear Velocity ft d^{-1}	Residence Time d
24 May	0.325	0.012	435
8 June	0.502	0.018	281
22 June	0.373	0.013	379
6 July	0.240	0.008	589
22 July	0.390	0.014	362
3 Aug.	0.290	0.010	487
17 Aug.	0.228	0.008	621
1 Sept.	0.182	0.006	774

APPENDIX E:

HYDRAULIC CONDUCTIVITY MEASUREMENTS

E.1 Laboratory Hydraulic Conductivity Measurements

Shortly after the research cells were constructed in 2003, core samples were collected from the field plots, the reactive barrier, and the control (bank in Cell B). These samples were retrieved by driving thin-walled metal cylinders into the soil to a depth, which coincided with the location of the well screen. Saturated hydraulic conductivity (K) was measured on the cores using the constant head method (Klute and Dirksen, 1986). As shown in Table E.1, the K values of the control and field plot materials were higher than the K value of the reactive barrier material.

Table E.1. Hydraulic conductivity (K) of soil and reactive barrier material (laboratory determinations).

Location	Well ID	K
		ft d^{-1}
Cell A field plot	A1	26.0
	A5	88.3
Cell A reactive barrier	A10	2.8
Cell B field plot	B1	4.0
	B5	13.9
Cell B control	B9	83.8

These results were unexpected since the reactive barrier was constructed using materials that were more permeable than those used to construct the control and field plots.

E.2 Slug Test Data Collection and Analysis

Saturated hydraulic conductivity can be measured in the field by conducting slug tests. In July 2004, slug tests were performed in four monitoring wells (wells A3, A10, B4, and B8) to obtain a better estimate of K. The slug test was conducted as described by Watson and Burnett (1993). The method developed by Hvorslev (1951) was used to calculate K from the slug test data.

The static water level in each well was measured from the top of the casing. Then, a slug of water was removed from each well using a disposable bailer. The water level was measured in each well immediately after the slug of water was removed and over time as the water level rose and approached its initial (static) level. The change in water level noted immediately after the slug of water was removed was expressed as H_o. The change in water level (from the initial level) at some time, t, after the slug was removed was expressed as H. The ratio H/H_o was computed and plotted against time on semilogarithmic paper. The time for the water level to rise to 37% of the initial change was determined by examining the plots. This value was expressed as T_o. After T_o was determined, the following equation was used to calculate hydraulic conductivity:

$$K = \frac{r^2 \ln(L/R)}{2LT_o} \qquad [10]$$

where

K	=	hydraulic conductivity
R	=	radius of augured hole
L	=	length of gravel pack
r	=	radius of well casing
T_o	=	time for water level to reach 37% of initial change

This equation is valid if L/R is greater than 8. The ratio L/R for each well was 14.

E.3 Slug Test Data and Results

A slug test was performed in well A3. The results of the test are shown in Table E.2 and the data are plotted in Fig. E.1.

Table E.2. Well A3 slug test data.

Elapsed Time	Depth to Water	Change in Water Level (H)	H/H_o
min	ft	ft	
Static Level	3.30		
0	3.68	0.38 (H_o)	1.00
2	3.60	0.30	0.79
4	3.57	0.27	0.71
6	3.56	0.26	0.68
8	3.56	0.26	0.68
10	3.55	0.25	0.66
12	3.54	0.24	0.63
14	3.54	0.24	0.63
16	3.54	0.24	0.63
28	3.51	0.21	0.55
30	3.51	0.21	0.55
32	3.51	0.21	0.55
34	3.50	0.20	0.53
36	3.50	0.20	0.53
38	3.50	0.20	0.53
40	3.50	0.20	0.53
42	3.50	0.20	0.53
44	3.50	0.20	0.53
46	3.49	0.19	0.50
48	3.49	0.19	0.50
50	3.49	0.19	0.50
52	3.49	0.19	0.50
54	3.49	0.19	0.49
56	3.49	0.19	0.49
58	3.48	0.18	0.47
60	3.48	0.18	0.47
62	3.48	0.18	0.47
64	3.47	0.17	0.45
66	3.47	0.17	0.45
70	3.47	0.17	0.45
74	3.46	0.16	0.42
78	3.46	0.16	0.42
80	3.46	0.16	0.42
82	3.46	0.16	0.42
88	3.46	0.16	0.42
96	3.45	0.15	0.39
98	3.45	0.15	0.39
102	3.44	0.14	0.37
104	3.44	0.14	0.37

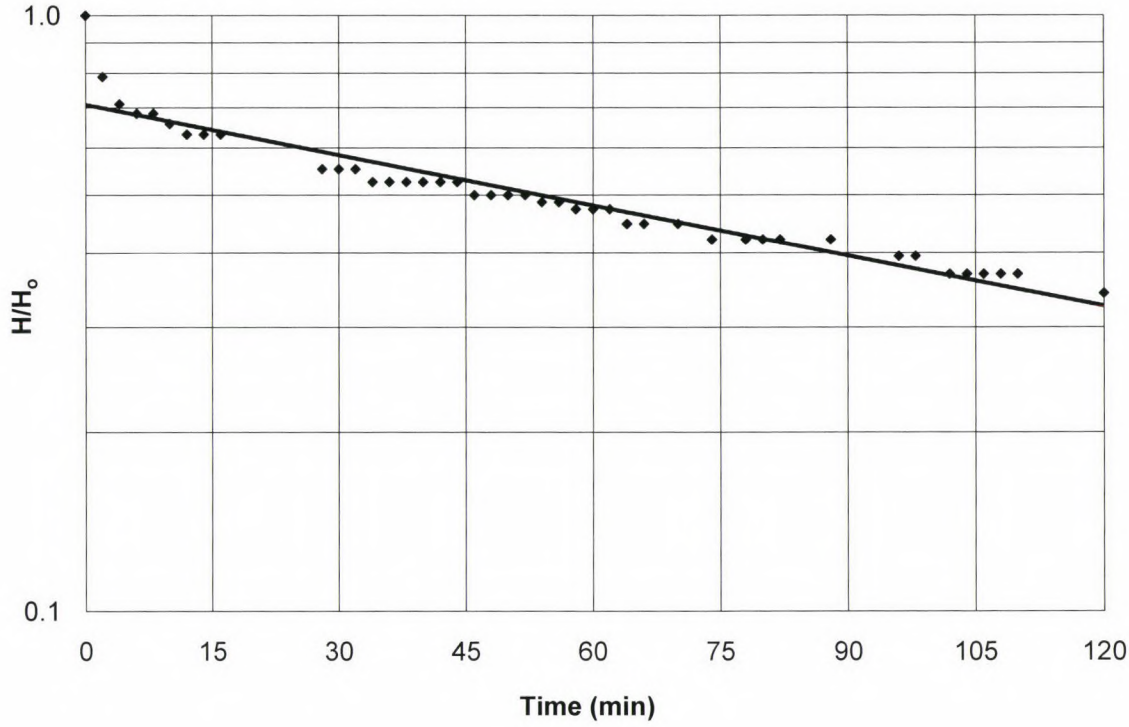

Fig. E.1. Plot of head ratio (H/H_o) versus time for well A3.

Eq. [10] was used to calculate K, where:

T_o = 103 min (obtained from Fig. E.1), R = 0.167 ft, L = 2.333 ft, r = 0.086 ft

$$K = \frac{(0.086\,\text{ft})^2 \times \ln(2.333\,\text{ft} / 0.167\,\text{ft})}{2 \times 2.333\,\text{ft} \times 103\,\text{min}}$$

$$= 4.06 \times 10^{-5}\,\text{ft/min} \times 1440\,\text{min/day}$$

$$= 5.85 \times 10^{-2}\,\text{ft/day}$$

A slug test was performed in well A10. The results of the test are shown in Table E.3 and the data are plotted in Fig. E.2.

Table E.3. Well A10 slug test data.

Elapsed Time	Depth to Water	Change in Water Level (H)	H/H_o
min	ft	ft	
Static Level	3.26		
0	3.67	0.41 (H_o)	1.00
0.8	3.66	0.40	0.98
0.9	3.66	0.40	0.98
1.0	3.65	0.39	0.95
1.1	3.65	0.39	0.95
1.2	3.65	0.39	0.95
1.8	3.64	0.38	0.93
2.4	3.63	0.37	0.90
3.3	3.62	0.36	0.88
4.5	3.61	0.35	0.85
5.7	3.60	0.34	0.83
6.5	3.59	0.33	0.80
8.0	3.58	0.32	0.78
9.3	3.57	0.31	0.76
10.6	3.56	0.30	0.73
11.9	3.55	0.29	0.71
13.5	3.54	0.28	0.68
14.7	3.53	0.27	0.66
16.1	3.52	0.26	0.63
17.5	3.51	0.25	0.61
18.9	3.50	0.24	0.59
20.9	3.49	0.23	0.56
23.0	3.48	0.22	0.54
24.8	3.47	0.21	0.51
27.0	3.46	0.20	0.49
30.3	3.45	0.19	0.46
32.5	3.44	0.18	0.44
34.8	3.43	0.17	0.41
37.0	3.42	0.16	0.39
40.0	3.41	0.15	0.37
43.5	3.40	0.14	0.34
47.0	3.39	0.13	0.32
50.5	3.38	0.12	0.29
52.0	3.37	0.11	0.27
55.5	3.36	0.10	0.24
60.0	3.35	0.09	0.22

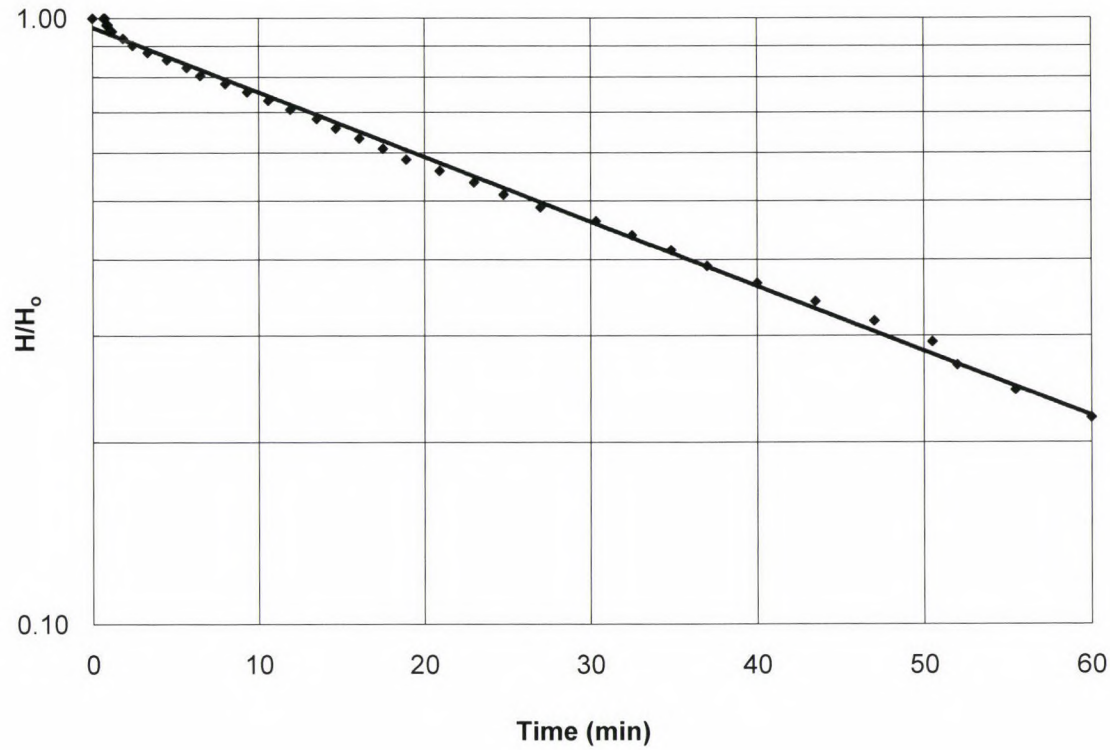

Fig. E.2. Plot of head ratio (H/H_o) versus time for well A10.

Eq. [10] was used to calculate K, where:

T_o = 40 min (obtained from Fig. E.2), R = 0.125 ft, L = 1.75 ft, r = 0.086 ft

$$K = \frac{(0.086\,\text{ft})^2 \times \ln(1.75\,\text{ft} / 0.125\,\text{ft})}{2 \times 1.75\,\text{ft} \times 40\,\text{min}}$$

$$= 1.39 \times 10^{-4}\,\text{ft/min} \times 1440\,\text{min/day}$$

$$= 0.20\,\text{ft/day}$$

A slug test was performed in well B4. The results of the test are shown in Table E.4 and the data are plotted in Fig. E.3.

Table E.4. Well B4 slug test data.

Elapsed Time	Depth to Water	Change in Water Level (H)	H/H_o
min	ft	ft	
Static Level	3.15		
0	3.61	0.46 (H_o)	1.00
1	3.55	0.40	0.87
2	3.53	0.38	0.83
3	3.52	0.37	0.80
4	3.51	0.36	0.78
5	3.51	0.36	0.78
7	3.50	0.35	0.76
8	3.50	0.35	0.76
9	3.50	0.35	0.76
10	3.50	0.35	0.76
15	3.49	0.34	0.74
20	3.48	0.33	0.72
25	3.48	0.33	0.72
30	3.48	0.33	0.72
35	3.48	0.33	0.72
40	3.47	0.32	0.70
50	3.46	0.31	0.67
55	3.45	0.30	0.65
60	3.45	0.30	0.65
65	3.45	0.30	0.65
70	3.44	0.29	0.63
75	3.44	0.29	0.63
80	3.44	0.29	0.63
90	3.43	0.28	0.61
95	3.43	0.28	0.61
100	3.43	0.28	0.61
110	3.42	0.27	0.59
120	3.41	0.26	0.57
125	3.41	0.26	0.57
136	3.40	0.25	0.54
142	3.39	0.24	0.52
147	3.39	0.24	0.52
152	3.39	0.24	0.52
157	3.38	0.23	0.50
162	3.38	0.23	0.50
197	3.37	0.22	0.48
215	3.36	0.21	0.46
220	3.36	0.21	0.46
225	3.36	0.21	0.46
230	3.35	0.20	0.43
235	3.35	0.20	0.43
245	3.35	0.20	0.43
256	3.34	0.19	0.41
266	3.33	0.18	0.39
276	3.32	0.17	0.37
286	3.32	0.17	0.37
296	3.31	0.16	0.35

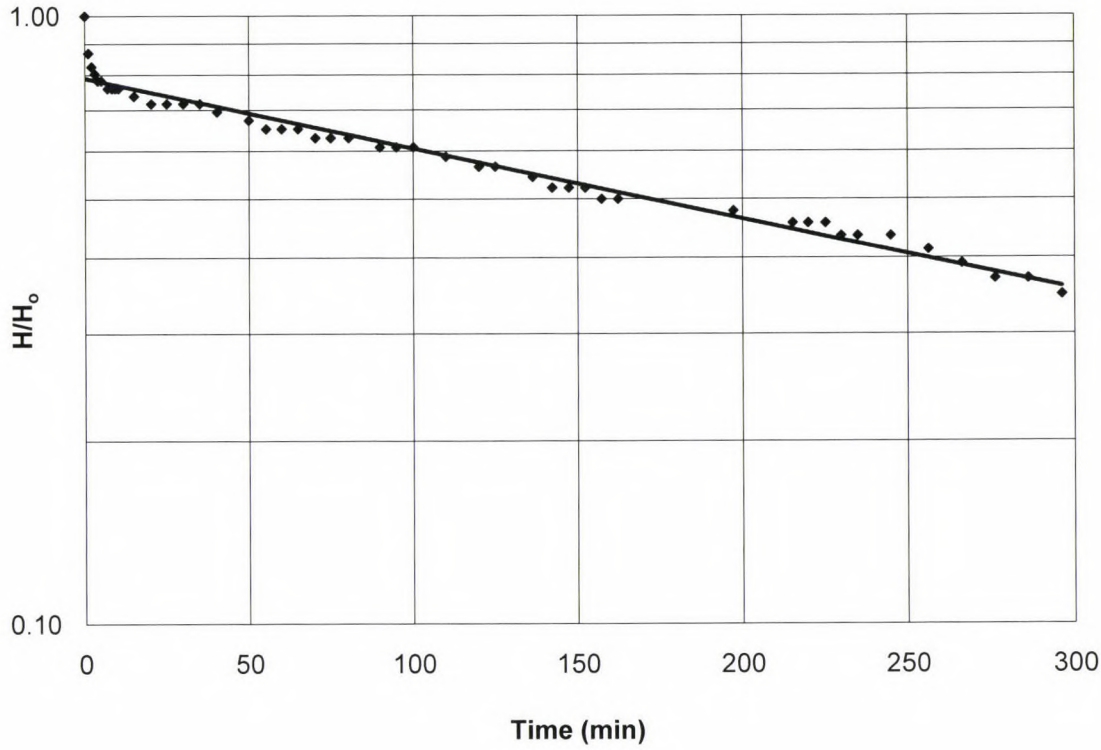

Fig. E.3. Plot of head ratio (H/H_o) versus time for well B4.

Eq. [10] was used to calculate K, where:

T_o = 287 min (obtained from Fig. E.3), R = 0.167 ft, L = 2.333 ft, r = 0.086 ft

$$K = \frac{(0.086\,\text{ft})^2 \times \ln(2.333\,\text{ft}/0.167\,\text{ft})}{2 \times 2.333\,\text{ft} \times 287\,\text{min}}$$

$$= 1.46 \times 10^{-5}\,\text{ft/min} \times 1440\,\text{min/day}$$

$$= 2.10 \times 10^{-2}\,\text{ft/day}$$

A slug test was performed in well B8. The results of the test are shown in Table E.5 and the data are plotted in Fig. E.4.

Table E.5. Well B8 slug test data.

Elapsed Time	Depth to Water	Change in Water Level (H)	H/H_o
min	ft	ft	
Static Level	3.28		
0	3.62	0.34 (H_o)	1.00
1	3.59	0.31	0.91
5	3.59	0.31	0.91
10	3.58	0.30	0.88
15	3.58	0.30	0.88
20	3.58	0.30	0.88
25	3.58	0.30	0.88
30	3.58	0.30	0.88
40	3.57	0.29	0.85
45	3.57	0.29	0.85
50	3.57	0.29	0.85
55	3.57	0.29	0.85
60	3.57	0.29	0.85
65	3.57	0.29	0.85
70	3.57	0.29	0.85
87	3.56	0.28	0.82
95	3.55	0.27	0.79
100	3.55	0.27	0.79
105	3.55	0.27	0.79
110	3.55	0.27	0.79
115	3.55	0.27	0.79
120	3.55	0.27	0.79
125	3.55	0.27	0.79
130	3.55	0.27	0.79
135	3.55	0.27	0.79
143	3.54	0.26	0.76
155	3.53	0.25	0.74
160	3.53	0.25	0.74
165	3.53	0.25	0.74
170	3.53	0.25	0.74
177	3.52	0.24	0.71
180	3.52	0.24	0.71
190	3.52	0.24	0.71
195	3.52	0.24	0.71
233	3.51	0.23	0.68
255	3.50	0.22	0.65
263	3.49	0.21	0.62
270	3.49	0.21	0.62
275	3.49	0.21	0.62
288	3.48	0.20	0.59
298	3.48	0.20	0.59
308	3.46	0.18	0.53
318	3.46	0.18	0.53
321	3.45	0.17	0.50
339	3.43	0.15	0.44
349	3.43	0.15	0.44
359	3.42	0.14	0.41
369	3.42	0.14	0.41
389	3.40	0.12	0.35
419	3.37	0.09	0.26

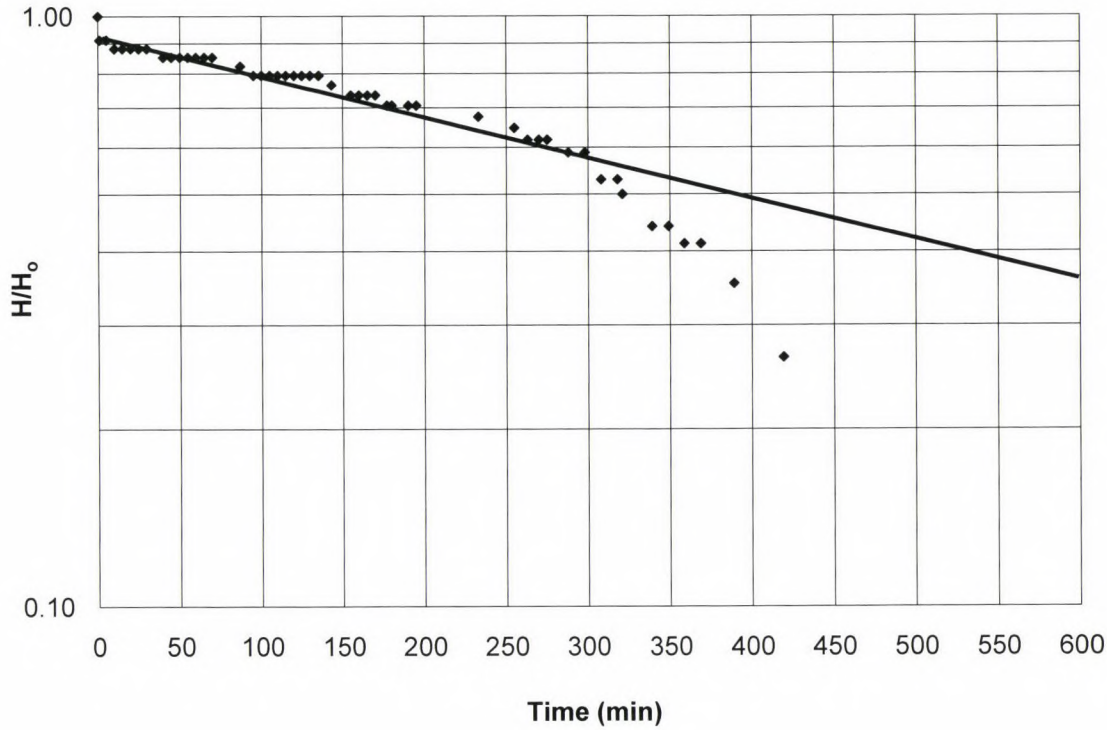

Fig. E.4. Plot of head ratio (H/H_o) versus time for well B8.

Eq. [10] was used to calculate K, where:

T_o = 567 min (obtained from Fig. E.4), R = 0.125 ft, L = 1.75 ft, r = 0.086 ft

$$K = \frac{(0.086\,\text{ft})^2 \times \ln(1.75\,\text{ft} / 0.125\,\text{ft})}{2 \times 1.75\,\text{ft} \times 567\,\text{min}}$$

$$= 9.83 \times 10^{-6}\,\text{ft/min} \times 1440\,\text{min/day}$$

$$= 1.42 \times 10^{-2}\,\text{ft/day}$$

APPENDIX F:

2004 GROUNDWATER QUALITY DATA

Table F.1. Groundwater nitrate concentrations in Cells and B during 2004 study.

Location	Well ID	NO_3-N							
		24 May	8 June	22 June	6 July	22 July	3 Aug.	17 Aug.	1 Sept.
		mg L^{-1}							
Cell A	A1	0.03	0.30	1.42	0.47	3.97	1.04	0.81	2.45
	A2	0.27	0.15	0.34	0.08	0.05	0.10	0.50	0.26
	A3	0.16	0.03	0.01	0.02	1.31	0.02	1.32	0.03
	A4	2.28	0.53	0.14	0.02	0.005	0.04	0.36	0.03
	A5	0.01	0.08	0.01	0.01	0.005	0.03	0.43	0.21
	A6	0.005	0.07	0.005	0.02	0.005	0.01	1.47	0.03
	A7	20.0	19.6	19.6	11.4	24.4	16.9	4.84	6.17
	A8	18.3	24.8	24.9	20.0	25.2	20.0	19.6	11.4
	A9	no data	0.58	0.005	no data	no data	0.14	no data	no data
	A10	0.02	0.04	1.60	0.02	0.005	0.04	2.81	0.04
Cell B	B1	2.09	2.06	5.87	4.26	5.82	3.72	3.17	3.36
	B2	1.00	0.66	0.79	0.25	0.07	0.17	0.005	0.22
	B3	0.20	0.09	0.005	0.02	0.005	0.02	0.33	0.01
	B4	0.32	0.19	0.005	0.31	0.005	1.54	0.24	0.05
	B6	0.06	0.17	0.005	0.02	0.02	0.02	0.27	0.01
	B7	0.03	0.28	1.21	0.31	0.06	0.07	0.14	0.09
	B8	0.17	0.84	0.11	0.05	0.04	0.07	0.31	0.06
	B9	0.01	0.02	0.005	0.02	0.005	0.04	no data	0.04
	B10	0.01	0.03	0.005	0.02	0.005	0.03	2.33	0.03

Table F.2. Oxidation-reduction potential (ORP) of groundwater in Cells A and B during 2004 study.

Location	Well ID	ORP						
		27 May	10 June	24 June	8 July	29 July	5 Aug.	20 Aug.
		mV						
Cell A	A1	-122	-116	-157	-5	-126	-115	-75
	A2	-70	-99	-84	-13	-115	-78	-54
	A3	-62	-128	-145	-105	-151	-123	-143
	A4	8	-87	-143	-91	-138	-97	-128
	A5	-152	-138	-122	-120	-140	-109	-128
	A6	-157	-145	-144	-125	-136	-135	-138
	A7	-116	-123	-107	-71	-93	-81	-64
	A8	-104	-100	-78	-63	-84	-58	-37
	A9	-111	-143	no data	no data	no data	no data	no data
	A10	-120	-121	-120	-113	-111	-127	-107
Cell B	B1	-119	-50	-44	-19	-96	-33	-82
	B2	-124	-43	-27	-69	-105	-94	-107
	B3	-116	-86	-124	-100	-122	-112	-130
	B4	-139	-99	-117	-93	-111	-70	-111
	B6	-68	-95	-118	-104	-122	-116	-120
	B7	-123	-81	-57	-63	-118	-103	-111
	B8	-104	-76	-97	-56	-129	-113	-103
	B9	-172	-137	-158	-117	-146	-143	-125
	B10	-204	-126	-201	-105	-144	no data	-115

Table F.3. Eh of groundwater in Cells A and B during 2004 study.

Location	Well ID	Eh						
		27 May	10 June	24 June	8 July	29 July	5 Aug.	20 Aug.
		mV						
Cell A	A1	83	89	48	200	79	90	130
	A2	135	106	121	192	90	127	151
	A3	143	77	60	100	54	82	62
	A4	213	118	62	114	67	108	77
	A5	53	67	83	85	65	96	77
	A6	48	60	61	80	69	70	67
	A7	89	82	98	134	112	124	141
	A8	101	105	127	142	121	147	168
	A9	94	62	no data	no data	no data	no data	no data
	A10	85	84	85	92	94	78	98
Cell B	B1	86	155	161	186	109	172	123
	B2	81	162	178	136	100	111	98
	B3	89	119	81	105	83	93	75
	B4	66	106	88	112	94	135	94
	B6	137	110	87	101	83	89	85
	B7	82	124	148	142	87	102	94
	B8	101	129	108	149	76	92	102
	B9	33	68	47	88	59	62	80
	B10	1	79	4	100	61	no data	90

Table F.4. Groundwater temperature in Cells A and B during 2004 study.

Location	Well ID	Temperature						
		27 May	10 June	24 June	8 July	29 July	5 Aug.	20 Aug.
		°C						
Cell A	A1	16.5	19.2	17.0	18.4	19.3	20.0	18.9
	A2	15.5	18.6	16.0	18.6	18.3	19.5	18.5
	A3	14.4	16.5	15.6	16.9	17.9	18.0	17.8
	A4	14.5	16.7	15.3	16.9	17.6	17.8	17.7
	A5	14.0	15.9	15.3	16.6	17.4	17.6	17.5
	A6	14.4	16.8	15.1	16.9	17.5	17.8	17.4
	A7	14.7	16.8	15.6	17.3	16.6	17.9	16.7
	A8	14.5	16.7	15.2	16.9	16.6	17.7	16.5
	A9	15.0	17.0	no data	no data	no data	no data	no data
	A10	12.6	16.4	15.5	17.3	15.9	17.7	15.9
Cell B	B1	14.9	18.4	15.4	18.0	17.8	18.8	18.1
	B2	15.1	18.5	15.3	18.0	17.9	18.9	18.3
	B3	14.6	17.3	15.2	17.3	17.8	18.2	17.8
	B4	14.5	17.1	15.0	17.1	17.7	18.1	17.8
	B6	14.3	16.3	14.9	16.7	17.5	17.7	17.4
	B7	14.4	16.4	14.9	16.9	16.7	17.6	16.8
	B8	14.2	16.3	14.9	16.9	16.8	17.7	16.8
	B9	14.0	16.1	15.2	17.3	15.9	18.0	16.1
	B10	13.2	15.9	15.0	17.2	15.7	no data	16.0

Table F.5. Groundwater dissolved oxygen (DO) concentrations in Cells A and B during 2004 study.

		DO						
Location	Well ID	27 May	10 June	24 June	8 July	29 July	5 Aug.	20 Aug.
		mg L^{-1}						
Cell A	A1	0.95	0.80	0.67	0.59	1.36	0.86	0.56
	A2	1.27	0.80	1.18	0.73	0.97	0.77	0.77
	A3	0.37	0.63	0.44	0.36	0.59	0.33	0.39
	A4	1.05	0.95	0.77	0.62	1.08	0.39	0.77
	A5	0.71	0.42	0.41	0.33	0.50	0.26	0.38
	A6	0.63	0.53	0.41	0.37	0.76	0.28	0.31
	A7	0.37	0.68	0.52	0.50	0.46	0.80	3.23
	A8	1.12	0.73	0.41	0.31	0.58	0.66	3.62
	A9	0.33	no data	no data	no data	no data	no data	no data
	A10	0.49	0.38	0.17	0.20	0.41	0.41	0.25
Cell B	B1	0.65	0.47	0.32	0.33	0.85	0.57	0.50
	B2	0.73	0.75	0.99	0.55	1.17	0.38	0.54
	B3	0.68	0.80	0.52	0.68	0.49	0.43	0.33
	B4	0.82	0.57	0.72	0.57	0.62	0.44	0.76
	B6	1.31	0.79	0.61	0.44	0.66	0.31	0.46
	B7	1.19	0.76	1.31	1.09	0.93	0.41	1.57
	B8	1.32	1.39	1.05	2.75	1.16	0.54	1.73
	B9	0.32	0.45	0.28	0.89	0.37	0.40	0.36
	B10	0.22	0.97	0.29	0.69	0.48	no data	0.35

Table F.6. Groundwater pH values in Cells A and B during 2004 study.

Location	Well ID	pH						
		27 May	10 June	24 June	8 July	29 July	5 Aug.	20 Aug.
Cell A	A1	6.81	6.64	6.57	6.75	6.78	6.75	6.79
	A2	6.82	6.70	6.53	6.82	6.78	6.74	6.77
	A3	6.82	6.66	6.46	6.76	6.80	6.73	6.79
	A4	6.91	6.80	6.61	6.82	6.86	6.70	6.82
	A5	6.97	6.85	6.76	6.88	6.91	6.76	6.90
	A6	6.94	6.88	6.70	6.90	6.91	6.81	6.88
	A7	7.17	7.19	7.08	7.07	7.12	7.13	7.08
	A8	7.22	7.30	7.02	7.22	7.23	7.05	7.10
	A9	7.20	6.94	no data	no data	no data	no data	no data
	A10	6.85	6.84	6.71	6.93	6.92	6.86	6.91
Cell B	B1	6.71	6.73	6.46	6.67	6.70	6.70	6.71
	B2	6.77	6.82	6.57	6.72	6.77	6.71	6.78
	B3	6.86	6.83	6.63	6.78	6.81	6.77	6.82
	B4	6.81	6.77	6.61	6.79	6.83	6.80	6.85
	B6	6.90	6.82	6.68	6.80	6.84	6.75	6.84
	B7	6.99	6.90	6.83	6.91	6.94	6.84	6.98
	B8	7.02	6.97	6.85	7.06	7.01	6.95	7.07
	B9	6.60	6.85	6.77	6.89	7.00	6.94	7.05
	B10	7.01	6.91	6.81	6.92	7.09	no data	7.16

Table F.7. Specific conductance of groundwater in Cells A and B during 2004 study.

Location	Well ID	Specific Conductance						
		27 May	10 June	24 June	8 July	29 July	5 Aug.	20 Aug.
		$\mu S\ cm^{-1}$						
Cell A	A1	1020	939	954	911	1083	1115	1057
	A2	1311	1243	1195	1264	1277	1299	1293
	A3	1291	1239	1252	1252	1271	1304	1369
	A4	1020	993	901	940	1038	1085	1159
	A5	789	912	1047	1079	1089	1127	1119
	A6	1387	1237	1225	1231	1260	1275	1366
	A7	399	348	395	366	581	390	618
	A8	395	347	365	364	524	394	505
	A9	397	no data	no data	no data	no data	no data	no data
	A10	500	507	497	546	671	710	678
Cell B	B1	1052	926	926	960	1027	941	975
	B2	1163	1070	1061	1191	1179	1227	1221
	B3	1523	1342	1351	1449	1426	1376	1457
	B4	1882	1639	1329	1552	1238	864	1331
	B6	1570	1557	1491	1574	1540	1539	1591
	B7	967	755	820	907	986	1024	1003
	B8	893	809	791	878	984	1028	1045
	B9	932	916	884	969	960	1102	840
	B10	1123	941	794	982	777	no data	650

Table F.8. Groundwater ammonium concentrations in Cells A and B during 2004 study.

Location	Well ID	NH_4-N				
		24 May	8 June	22 June	22 July	17 Aug.
		mg L^{-1}				
Cell A	A1	0.76	1.26	0.72	0.18	1.04
	A2	0.46	1.00	0.36	0.28	0.75
	A3	1.31	1.36	1.46	1.21	2.19
	A4	0.58	1.32	0.04	0.36	1.25
	A5	0.99	1.35	0.34	0.95	0.91
	A6	1.54	1.68	1.56	0.99	1.81
	A7	3.19	1.64	0.29	0.19	0.23
	A8	3.31	1.48	0.11	0.32	0.11
	A9	no data	0.84	0.27	no data	no data
	A10	2.03	1.00	1.04	0.90	1.44
Cell B	B1	1.86	1.52	0.38	0.40	1.10
	B2	0.35	0.29	0.23	0.54	0.43
	B3	0.99	1.36	0.47	0.59	0.88
	B4	0.57	1.17	0.36	0.43	0.47
	B6	0.72	0.38	0.62	0.67	0.73
	B7	0.37	0.35	0.38	0.54	0.76
	B8	0.17	0.51	0.29	0.59	1.05
	B9	1.26	2.46	0.73	1.10	2.15
	B10	0.24	0.36	0.36	0.21	no data

Table F.9. Groundwater bromide concentrations before and during tracer study.

Location	Well ID	Br							
		Background Concentration	16 July	17 July	18 July	19 July	20 July	21 July	22 July
		mg L^{-1}							
Cell A	A1	0.48	3.23	0.01	5.31	3.20	55.5	3.62	9.70
	A2	0.51	0.70	0.50	0.55	2.38	25.5	0.80	0.72
	A3	0.53	0.01	0.30	0.80	0.68	2.15	0.62	2.60
	A4	<0.01	0.01	0.01	0.01	0.29	1.05	0.51	0.29
	A5	<0.01	0.21	0.01	0.44	3.51	1.29	2.08	2.40
	A6	0.42	0.49	0.01	0.01	0.94	0.74	0.85	0.15
	A7	<0.01	15.6	60.1	99.4	116.4	157.3	160.6	160.0
	A8	<0.01	18.7	77.9	99.7	119.0	141.9	148.8	154.0
	A9	no data	1.14	44.1	82.2	no data	no data	no data	no data
	A10	<0.01	7.35	48.1	90.8	29.6	69.6	78.3	73.7
Cell B	B1	<0.01							5.70
	B2	0.56							0.66
	B3	0.54							0.01
	B4	<0.01							0.35
	B6	0.63							2.70
	B7	<0.01							0.29
	B8	<0.01							0.01
	B9	<0.01							0.58
	B10	<0.01							0.96