CONTROLS ON NITRATE DEGRADATION IN TWO ADJACENT WETLAND STREAMS WITH DIFFERENT GEOCHEMISTRY AND FLOW-SOURCE TERMS, WATKINSVILLE, GA

by

KATHERINE L. SCHROER

(Under the Direction of Valentine Nzengung)

ABSTRACT

A two-year sampling program was conducted to elucidate controls on nitrate N removal and retention in two small wetland streams that drain portions of a 10ha cattle pasture and crop field. Cow manure and synthetic fertilizer were the main sources of nitrate N to the wetland. A man-made earthen berm prevented surface runoff from entering the Protected Stream (63m long), whereas the adjacent Runoff Stream (70m) received surface runoff from the pasture. The Protected Stream had been dredged and had a perennial spring flowing from its headcut; the Runoff Stream did not. The two streams are 14m apart at headcut. Four seasonal tracer injection tests (Chapter 3) were conducted to evaluate wetland stream response to a pulse of high but realistic concentration of [NO_3^--N]. In addition, samples were collected ~monthly for two years at 8-10 sampling stations and samples were analyzed for the several redox parameters using field probes, laboratory instruments and wet chemistry methods. Residence time exerted a primary control on N removal processes. Denitrification and/or nitrate reduction to ammonia were enhanced when residence times were longer. Organic carbon was the main electron donor in both streams. Sulfide may be an important secondary reductant. Temperature exerted control on stream redox processes above 18-20°C . Stream baseflow exerted less control than baseflow-plus-runoff on the wetland's capacity to remove nitrate N. These results constrain processes that affect nitrate N removal efficiency in agricultural wetland streams.

INDEX WORDS: Nitrogen, flow-source term, redox chemistry, nutrient loads, tracer injection

CONTROLS ON NITRATE DEGRADATION IN TWO ADJACENT WETLAND STREAMS WITH DIFFERENT GEOCHEMISTRY AND FLOW-SOURCE TERMS, WATKINSVILLE, GA

by

KATHERINE L. SCHROER

B.A., University of Illinois at Chicago, 1981

A Dissertation Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2011

CONTROLS ON NITRATE DEGRADATION IN TWO ADJACENT WETLAND STREAMS WITH DIFFERENT GEOCHEMISTRY AND FLOW-SOURCE TERMS, WATKINSVILLE, GA

by

KATHERINE L. SCHROER

Major Professor:	Valentine Nzengung
Committee:	Roger Burke Paul Schroeder John Washington David Wenner

Electronic Version Approved:

Maureen Grasso
Dean of the Graduate School
The University of Georgia
August 2011

DEDICATION

This dissertation is dedicated to Martha Schroer (1932-2010).

ACKNOWLEDGEMENTS

I thank my advisor, Dr. Valentine Nzengung, for his advice and friendship. He and my committee members, Drs. John Washington, David Wenner, Paul Schroeder, and Roger Burke, all gave me the scientific tools and support - directly and by each of their examples – that I needed to conduct this research.

My profound thanks go to USDA for allowing me to conduct my research at their site. Dr. Dinku Endale and Mr. Stephen Norris kindly provided much logistical support and helpful suggestions.

The UGA Geology Department provided with me with financial support, including several grants and teaching assistantships. Ms. Beatriz Stephens, Ms. Pat Hancock and Ms. Mary Crowe helped me navigate the departmental and graduate school waters. My fellow graduate student, Dr. Lina Wayo, often helped in the field and encouraged me with her friendship.

I want to extend special thanks to the USEPA ORD-ERD-NERL in Athens, GA. Dr. John Washington and Dr. Mac Long provided me with unlimited access to the nutrients laboratory, all instruments and supplies therein for analysis of all of my samples, and office space to support my research. Dr. Washington, Ms. Lidia Samarkina and Dr. B.T. Thomas graciously shared their considerable combined scientific experience in the field and in the laboratory. Dr. Caroline Stevens assisted with all four tracer injection experiments and provided useful suggestions for data analysis. I am very grateful to all of my above mentors at EPA.

I especially thank Jeff Clippard for his unwavering support on this journey.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Nitrogen (N) is present in many compounds and is part of a complex cycle in the bio-, hydro-, litho- and atmospheres. The ubiquitous cycling is due to many intrinsic properties of N. 1) All living things require nitrogen as a fundamental building block of life. 2) Although N_2 gas (elemental nitrogen) is about 78% of the air we breathe, only a few specialized organisms and natural high-energy phenomena can break the strong triple chemical bonds between the two N atoms. These nitrogen "fixing" processes render N both bioavailable and chemically reactive, and the resulting compounds or species collectively are referred to as reactive N (Nr). 3) Depending on local conditions, Nr gains and loses electrons – up to 3 and 5, respectively, from its elemental state. This property increases Nr's reactivity with many other species, resulting in a complex, interdependent relationship between the nitrogen cycle and other global biogeochemical cycles, such as those of oxygen, hydrogen, carbon and sulfur. 4) Nr is physically transported to, chemically transformed between, and stored in atmospheric, biological, mineral, amorphous solid, and aquatic sinks at a variety of time and space scales. Some of the reactive pathways within and between these sinks transform Nr back to N_2 gas, whereas many species of Nr are not so benign.

Natural sources of Nr include N-fixing bacteria, some of which are aquatic and many of which live symbiotically in the root zones of legumes and a few plant species (more in Chapter 2). Lightning (Evangelou, 1998) and volcanic energy (Huebert et al., 1999) also provide enough energy to break the strong triple bond between the two N atoms of N_2. In addition to natural sources, early 20th century advances in laboratory chemistry and changes in crop management have led to a dramatic increase in the application of Nr to stimulate crop growth. Nitrogen fertilizer often has been applied in amounts, forms, locations and seasons exceeding target crops' capacity for uptake (Nangia et al., 2010; Poor and McDonnell, 2007). Depending on reaction pathways, excess Nr either volatilizes, sorbs to soil minerals, is leached through the soil to ground water, or is introduced to surface waters via ground water discharge, surface runoff, precipitation or atmospheric deposition. Aqueous environments thus receive reactive nitrogen from many sources and via many flowpaths. For example, about two thirds of nitrogen in the Mississippi River Basin is from agricultural runoff and the remaining third is from urban runoff, atmospheric deposition and point sources (Kadlec, 2010). Of the latter, Nr is a component of several manufactured products, including explosives, resins, glues, and animal and fish food supplements (Galloway et al., 2008).

Population growth drives and, to a large extent, is made possible by increased production of Nr. Use of synthetic fertilizer started to increase sharply after 1950 to support a growing world population (Bashkin et al., 2002). Between 1970 and 2008, production of N fertilizer increased by 120% while world population increased by 78% (Galloway et al., 2008). Population increase and poor management also have caused more Nr to be released from municipal waste and septic systems (Meile, et al., 2010) and concentrated animal feeding operations (USEPA, 2009). Exacerbating the situation, consumption of fossil fuels, which commonly contain Nr, increased about 240% in the latter half of the 20th century (Mosier, 2002). Consequently, the distribution of gaseous nitrogen loadings in the atmosphere has shifted, and now includes more fixed oxides of nitrogen (Groffman, 2000; Moomaw, 2002).

The striking increase in Nr has led to unintended and, in many places, dire environmental consequences. For example, nitrate (NO_3^-) concentrations greater than about 20 mg/L in drinking water causes blue baby syndrome (methomoglobinemia) and has been correlated to certain cancers at lower concentrations (Nolan, 1999; Groffman, 2000). In aquatic systems, excess nitrate creates eutrophic (well nourished) conditions, causing rapid growth of algae. As some algae die while more continue to grow, organic carbon in the dead algae is oxidized by bacteria, which consume oxygen dissolved in the water. As hypoxic (low oxygen) conditions develop and degrade toward anoxia (no oxygen), the water body increasingly cannot support oxygen-respiring aquatic life, ultimately leading to dead zones. The areas of some dead zones, such as the one in the Gulf of Mexico, are quite large (seasonally as large as 21,000 km^2) (Rivera-Monroy et al., 2010), and averaging 15,500 km^2 between 2004 - 2009 (Marine Science Today, 2009). In addition to grievous consequences for aquatic life, dead zones adversely affect local fisheries, which weaken local economies (Rivera-Monroy et al., 2010). A recent study documented more than 400 dead zones covering a quarter of a million square miles in coastal areas worldwide (UNEP, 2010). Conspicuous examples, in addition to the Gulf of Mexico, are the partly enclosed waters between Japan and Korea, the Baltic Sea and Northern Adriatic Sea (UNEP, 2010), and countless small lakes and ponds (USEPA, 2009). Furthermore, some nutrient-rich coastal waters also experience a marked increase in the growth of phytoplankton, which increases turbidity. The resulting decrease in light penetration limits growth of submerged aquatic vegetation such as eelgrass (Johnes and Butterfield, 2002), which in turn robs fish and invertebrates of important habitat, including nursery and refuge (Rabalais, 2002). Nitrate also has been implicated in causing toxic “red tides” in the Gulf of Mexico and blooms of *Pfiesteria pisicida* along the mid-Atlantic coast (Showstack, 2000). In addition to problems due to excess Nr in the environment, there are secondary consequences as well. For example, ammonia (NH_4^+)-based fertilizers increase mobility of the herbicide atrizine by initially increasing soil pH, thereby inhibiting atrazine sorption and increasing its desorption from soils (Liu et al., 1995).

Gaseous species of Nr that accumulate in the atmosphere also are harmful. Nitrous oxide (N_2O) has about 320 times more global-warming potential than carbon dioxide (Holland et al., 2005), although N_2O is only about 6% of all anthropogenic greenhouse gas sources (Del Grosso et al., 2008). However, nitrous oxide also contributes to destruction of the stratospheric ozone layer (Moomaw, 2002). Nitric oxide (NO) and nitrogen dioxide (NO_2), collectively referred to as NO_x, react with O_2 to form ozone (O_3) in the troposphere (Moomaw, 2002; Stark et al., 2002), which is a greenhouse gas, is toxic to plants and animals, and which may reduce efficiency of terrestrial CO_2 sequestration (Holland et al., 2005). NO_x also reacts with atmospheric water vapor, producing nitric and nitrous acids in water droplets. Subsequent rain delivers Nr to terrestrial and aquatic systems, which acidifies soil and water (Mosier, 2002). Note that NO_x is the only major air pollutant that has not decreased since passage of the Clean Air Act in 1963 (Howarth et al., 2002).

The above-mentioned environmental and human health problems attributed to Nr increasingly are recognized as critical issues of national and international scope. In the most recent bi-annual water quality report to Congress, states cite nutrients such as nitrate among the highest priority pollutants in streams, lakes, ponds, reservoirs, bays and estuaries (USEPA, 2009). In 2004, the United States ratified the United Nations' Gothenburg Protocol to Abate Acidification, Eutrophication and Ground Level Ozone, which aims to strengthen objectives of the 1979 Long Range Transport of Air Pollutants Treaty (LRTAP), largely due to worsening Nr-related environmental problems (Sliggers and Kakebeeke, 2004).

Research published to date focuses on many aspects of the N cycle, such as releases to the environment (e.g., Howarth et al., 2002), transport pathways (e.g., Galloway et al., 2008), loads to receiving basins (e.g., Mitsch et al.; 2005), and environmental and human health consequences (e.g., USEPA, 2009). However, questions remain concerning the net climate effects of increasing Nr, how tropical regions will respond to increased inputs of Nr, the effects of biofuel development on the N cycle, and a better understanding of the risks posed to human health by increasing Nr (Galloway et al., 2008). In addition to these large-scale questions, many process-level aspects of Nr cycling are poorly understood. These include 1) lack of tools for estimating how watershed-scale conditions (e.g., land use/land cover, local soils, topography, climate) and changes therein influence nitrate concentrations in downstream waters (Poor and McDonnell, 2007; Kaushal et al., 2010; Yang and Jin, 2010); 2) difficulties in quantifying nitrate export from wetlands and headwater streams due to poor understanding of N cycling processes across multiple spatial and temporal scales (Ocampo et al., 2006); 3) internal processes that allow constructed or restored wetlands to remove pulse or periodic releases of non-point source nitrate (Kadlec, 2010); 4) specific factors that *limit* nitrate removal in wetlands (Bastviken et al., 2009); 5) the influence of different environmental variables on nitrous oxide emissions during nitrate reduction in river sediments (Laverman et al., 2010); 6) extent to which denitrification gas products in shallow wetland streams are entrapped in sediments and/or in plant aerenchyma (low-resistance channels and cavities in plants that allow exchange of gases at the root zone) (Matheson and Sukias, 2010); and 7) continued lack of consistency in characterizing redox settings, making it difficult to determine local conditions driving redox reactions in natural waters (Washington et al., 2004, 2006).

This study investigates the causes for dissimilar distributions of Nr and other redox species in two small wetland streams that are adjacent to each other but have different source terms. The two streams, only 14m apart at headcut, drain a cow pasture and portions of a small cropped area (primarily cotton, sorghum, rye) near the summit of the catchment. There are three main differences in stream configuration and hydrology: 1) a man-made berm prevents most surface water runoff to one of the streams (Protected Stream), but the other stream (Runoff Stream) is open to surface runoff from the cow pasture; 2) the Protected Stream has a spring flowing from its headcut whereas the Runoff stream does not have a conspicuous spring at its headcut; and 3) the Protected Stream is 65.3 (from cage) meters long from the flume spillway of the headcut spring to its confluence with the Runoff Stream, whereas the more meandering Runoff Stream is 78.4 meters long.

The central objective of this research was to identify the dominant variables affecting denitrification rates in the studied streams and, from this, elucidate controls on denitrification in headwater streams of the Southern Piedmont.

This research is divided into two manuscripts:

1) Chapter 3 provides results and analysis of four seasonal tracer injection tests, which will constrain processes contributing to observed loss of nitrate concentration in the two wetland streams.
2) Chapter 4 investigates concentrations, based on approximately monthly sampling, of several redox species and field parameters in the two streams. These chemical distributions change along each of the two flow paths. The magnitude and direction of the downstream change in each parameter varies between the two streams. In addition, species distributions vary seasonally at each sampling location, but again not in the same manner at each location, and with differing seasonal trends in each stream. Statistical analyses of these differences will help clarify controls on the evolution of species distributions and establish functionality between different hydrological and geochemical process operating in each stream, along the flow paths of both streams, and seasonally.

Chapter 5 is an executive summary of the hypotheses, methods, results and broad implications of this reasearch.

This project is part of a larger research effort at the USDA Agricultural Research Station in Watkinsville GA, where researchers from several disciplines have studied pathogen transport, sustainable crop production, cattle management, hill slope hydrology, and vadose water and ground water geochemistry. Research results from this dissertation project will further contribute to our understanding of redox processes in general and nitrogen speciation in particular in a field-scale research location where climate, precipitation, and soil type are the same and where up-gradient ground water levels and downstream wetland discharge have been well documented over the past several years.

References

Bashkin, V.N., S.U. Park, M.S. Choi and C.B. Lee (2002) Nitrogen budgets for the Republic of Korea and the Yellow Sea region. Biogeochemistry 57/58: 387-403.

Bastviken, S.K., P.G. Eriksson, I. Martins, J.M. Neto, L. Leonardson and K. Tonderski (2003) Wetlands and aquatic processes: Potential nitrification and denitrification on different surfaces in a constructed treatment wetland. J. Environ. Qual. 32:2414-2420.

Del Grosso, S.J., T. Wirth, S.M. Ogle and W.J. Parton (2008) Estimating agricultural nitrous oxide emissions. Eos 89(51): 529.

Evangelou, W.P. (1998) Environmental Soil and Water Chemistry: Principles and Applications. John Wiley and Sons, Inc.

Galloway, J.N., A.R. Townsend, J.W. Erisman, M. Bekunda, Z. Cai, J.R. Freney, L.A. Martinelli, S.P. Seitzinger, M.A. Sutton (2008) Transformation of the nitrogen cycle: Recent trends, questions and potential solutions. Science 320:889-892.

Holland, E.A., S.B. Bertram, M.A. Carroll, A.B. Guenther, P.B. Shepson, J.P. Sparks and J. Lee-Taylor (2005) U.S. nitrogen science plan focuses collaborative efforts. EOS 86(27):253,256.

Howarth, R.W., E.W. Boyer, W.J. Pabich and J.N. Galloway (2002) Nitrogen use in the United States from 1961-2000 and potential future trends. Ambio 31(2):88-96.

Huebert, B., P. Vitousek, J. Sutton, T. Elias, J. Heath, S. Coeppicus, S. Howell, and B. Blomquist (1999) Volcano fixes nitrogen into plant-available forms. Biogeochemistry 47:111-118.

Kaushal, S.S., M.L. Pace, P.M. Groffman, L.E. Band, K.T. Belt, P.M. Mayer, and C. Welty (2010) Land use and climate variability amplify contaminant pulses. Eos 91(25):221.

Johnes P.J. and D. Butterfield (2002) Landscape, regional and global estimates of nitrogen from land to sea: Errors and uncertainties. Biogeochemistry 57/58: 429-476.

Kadlec, R.H. (2010) Nitrate dynamics in event-driven wetlands. Ecological Engineering 36:503-516.

Laverman, A.M., J.A. Garnier, E.M. Mounier, and C.L. Roose-Amsaleg (2010) Nitrous oxide production kinetics during nitrate reduction in river sediments. Water Research 44:1753-1764.

Liu, Z., S.A. Clay, D.E. Clay and S.S. Harper (1995) Ammonia impacts on Atrazine leaching through undisturbed soil columns. J. Environ. Qual. 24:1170-1173.

http://marinesciencetoday.com/2009/08/05/gulf-of-mexico-dead-zone-smaller-than-predicted-but-deeper/

Matheson, F.E., M.L. Nguyen, A.B. Cooper, T.P. Burt and D.C. Bull (2002) Fate of ^{15}N-nitrate in uplanted, planted and harvested riparian wetland soil microcosms. Ecol Eng. 19:249-264.

Meile, C., W.P. Porubsky, R.L. Walker, and K. Payne (2010) Natural attenuation of nitrogen loadings from septic effluents: Spatial and environmental controls. Water Research 44:1399-1408.

Mitsch, W.J., J.W. Day, L. Zhang, and R.R. Lane (2005) Nitrate-nitrogen retention in wetlands in the Mississippi River Basin. Ecological Engineering 24:267-278.

Mosier, A.R. (2002) Environmental challenges associated with needed increases in global nitrogen fixation. Nutrient Cycling in Agroecosystems 63:101-116.

Moomaw, W.R. (2002) Energy, industry and nitrogen: Strategies of decreasing reactive nitrogen emissions. Ambio 31(2):184-189.

Nangia, V., P.H. Gowda, and D.J. Mulla (2010) Effects of changes in N-fertilizer management on water quality trends at the watershed scale. Agricultural Water Management:97:1855-1860.

Nolan, B.T. (1999) Nitrate behavior in ground waters of the Southeastern USA. Journal of Environmental Quality 28: 1518-1527.

Poor, C., and J.J. McDonnell (2007) The effects of land use on stream nitrate dynamics. J. Hydrology 332:54-68.

Rabalais, N. Nitrogen in aquatic ecosystems (2002) Ambio 31(2):102-112.

Rivera-Monroy, V.H., P. Lenaker, R.R. Twilley, R.D. Delaune, C.W. Lindau, W. Nuttle, E. Habib, R.W. Fulweiler, E. Castañeda-Moya (2010) Denitrification in coastal Louisiana: A spatial assessment and research needs. Journal of Sea Research 63: 157-172.

Showstack, R. (2000) Nutrient over-enrichment implicated in multiple problems in U.S. waterways. EOS 81(43):497-499.

Sliggers, J. and W. Kakebeeke, eds. (2004) Clearing the Air: 25 years of the Convention on Long-range Transboundary Air Pollution. United Nations , 180p.

Stark, J.M., D.R. Smart, S.C. Hart, and K. A. Haubensack (2002) Regulation of nitric oxide emissions from forest and rangeland soils of western North America. Ecology 83(8): 2278-2292.

UNEP (2010) UNEP Year Book: New Science and Developments in our Changing Environment 2010. United Nations Environmental Programme. 66p.

USEPA (2009) Natural Water Quality Inventory: Report: to Congress, 2004 Reporting Cycle. Office of Water EPA-841-R-08-001, 37p.

Washington, J.W., D.M. Endale, L.P. Samarkina and K.E. Chappell (2004) Kinetic control of oxidation state at thermodynamically buffered potentials in subsurface waters. Geochimica et Cosmochimica Acta 68, 4831-4842.

Washington, J.W., R.C. Thomas, D.M. Endale, K.L. Schroer, and L.P. Samarkina (2006) Groundwater N speciation and redox control of organic N mineralization by O_2 reduction to H_2O_2. Geochimica et Cosmochimica Acta 70:3533-3548.

Yang, X. and W. Jin (2010) GIS-based spatial regression and prediction of water quality in river networks: A case study in Iowa. J. Environ. Management 91:1943-1951.

CHAPTER 2

LITERATURE REVIEW

2.1 Redox Chemistry

Any understanding of reactions between reactive nitrogen (Nr) with other chemical species begins with familiarity with oxidation-reduction (redox) chemistry. Along with acid-base chemistry, redox chemistry is considered a “master” variable in the distribution of chemical species in natural waters. Acid-base chemistry focuses on the transfer of hydrogen ions (H^+), which are protons, whereas redox chemistry tracks the movement of electrons (e^-). Since water is naturally charge-neutral, redox and acid-base reactions are highly interdependent.

In aqueous solutions, electron activity indicates the relative tendency of a solution to accept electrons (Stumm and Morgan, 1996). Electron activity is expressed in pe units and is analogous to pH, which is the negative log of H^+ activity in mol/L. In contrast to electrons, hydrogen ions (H^+) in solutions are hydrated to form the hydronium ion (H_3O^+). H_3O^+ is measurable in terms of concentration or activity (see below). Electrons do not remain in aqueous solution due to their extremely large charge-to-mass ratio.

Electron activities in natural aqueous environments vary depending on several local conditions including relative species concentrations, presence of soluble solids, pH buffer capacity and gas exchange with the atmosphere. Half reactions typically are written as a reduction (Stumm and Morgan, 1976). Table 2.1 depicts several aqueous redox species in order of declining pe for the stated conditions.

Table 2.1. Example electron activities in neutral water. pe^0 (W) for unit reductions (one electron exchanged) in pH 7 water at 25°C for 1M concentrations (except HCO_3^-, for which 10^{-3}M is used) (from Stumm and Morgan, 1996).

Redox Couple	Reduction Half-Reaction	pe^0 (W)
O_2/H_2O	$1/4O_{2(g)} + H^+ + e^- = ½H_2O$	+13.75
$NO_3^-/N_{2(g)}$	$1/5NO_3^- + 6/5H^+ + e^- = 1/10N_2(g) + 3/5H_2O$	+12.65
NO_3^-/NO_2^-	$1/2NO_3^- + H^+ + e^- = 1/2NO_2^- + 1/2H_2O$	+7.15
NO_3^-/NH_4^+	$1/8NO_3^- + 5/4H^+ + e^- = 1/8NH_4^+ + 3/8H_2O$	+6.15
NO_2^-/NH_4^+	$1/6NO_2^- + 4/3H^+ + e^- = 1/6NH_4^+ + 1/3H_2O$	+5.82
$CH_2O/CH_4(g)$	$1/4CH_2O + H^+ + e^+ = 1/4CH_4(g) + 1/4H_2O$	-0.06
$FeOOH_{(s)}/FeCO_{3(s)}$	$FeOOH(s) + HCO_3^-(10^{-3}) + 2H^+ + e^- = FeCO_3(s) + 2H_2O$	-0.8
$SO_4^{2-}/S_{(s)}$	$1/6SO_4^{2-} + 4/3H^+ + e^- = 1/6S(s) + 2/3H_2O$	-3.30
$SO_4^{2-}/H_2S_{(g)}$	$1/8SO_4^{2-} + 5/4H^+ + e^- = 1/8H_2S(g) + 1/2H_2O$	-3.50
SO_4^{2-}/HS^-	$1/8SO_4^{2-} + 9/8H^+ + e^= = 1/8HS^- + 1/2H_2O$	-3.75
$S^0/H_2S_{(g)}$	$1/2S(s) + H^+ + e^- = ½H_2S(g)$	-4.11
$CO_2(g)/CH_4(g)$	$1/8CO_2(g) + H^+ + e^- = 1/8CH_4(g) + 1/4H_2O$	-4.13
N_2/NH_4^+	$1/6N_2(g) + 4/3H^+ + e^- = 1/3NH_4^+$	-4.68
H^+/H_2	$H+ + e^- = 1/2H_2(g)$	-7.00
$CO_2(g)/C_{org}$	$1/4CO_2(g) + H^+ + e^- = 1/4CH_2O + 1/4H_2O$	-8.2

Note that calculated potentials and field measurements strongly suggest that O_2 is reduced to H_2O through H_2O_2, which is then reduced to H_2O (Washington et al., 2006). Trace concentrations of many other species such as chromium, manganese, copper and arsenic participate in redox reactions and the redox states of these species affects their mobility in water and their toxicities. However, they usually are present in small concentrations that are not sufficient to affect the concentrations of the species listed (Stumm and Morgan, 1996).

The oxidized species of a given redox pair tends to oxidize equimolar concentrations of the reduced species of a redox pair having a lower pe^0(W) value (Stumm and Morgan, 1996). Stumm and Morgan (1996) report a classic, biologically-mediated reduction sequence in ground waters in which oxygen and then nitrate (high potential oxidants) are the initial electron acceptors from lower-potential species, followed by iron and sulfate reduction, followed by methanogenesis. In this scenario, the higher potential species are reduced first because greater differences in potential between reduced electron donors and oxidized electron acceptors yield more energy and thus more efficient microbial growth (Tiedje et al., 1981). Some case studies (e.g., Puckett et al., 2002) have reported this sequence along ground water flow paths. However, caution must be used in making assumptions about any strict ordering in the sequence of redox reactions. For example, dissolved O_2 often reacts relatively slowly with some reductants because of kinetic limitations. Consequently, reduced species such as Fe^{2+} and Mn^{2+} often are in solution with dissolved oxygen, reflecting nonequilibrium redox conditions (McBride, 1994).

Although every redox reaction must have a balance between reducing and oxidizing equivalents, water bodies often are characterized as “oxidizing” or “reducing.” Some aquatic environments are dominated by an effectively infinite source of either low or high potential redox sensitive species that buffer or poise the system toward a more reducing or more oxidizing environment relative to the concentrations and potentials of other species present. For example, local environments become “strongly reducing” when bottom sediments contain a large pool of electron donors such as H_2 and organic carbon. When relatively low concentrations of a high potential species such as nitrate are introduced, reduction of nitrate may not deplete the large pool of reductants in the system. On the other extreme, a strongly oxidizing environment occurs, for example, in streams with sandy or rocky bottoms flowing through landscapes that release high loads of nitrate from agricultural, urban and/or point sources. In this setting, nitrate is a high potential oxidant that can oxidize relatively low concentrations of lower potential species dissolved in the water without the pool of nitrate becoming significantly depleted. In general, species of dissolved Nr are very sensitive to shifts in redox environment (McClain et al., 1994).

Redox reactions often result in products that are in a different phase than the reactants due to precipitation and/or dissolution of minerals, and the production of gases. For example, sulfate reduction in ground water, with organic C as the electron donor, results in precipitation of iron sulfide minerals (e.g., mackinawite, pyrite). Many redox reactions thus are limited in their reversibility due to insoluble or volatile end products and/or changing pH as the redox environment changes (Correll, 1997).

2.2 Nitrogen Cycle

Nitrogen exists in a total of 9, but commonly 7, oxidation states from –3 to +5 (Whitten and Gailey ,1981; Zumdahl, 2000). Major N compounds in the environment (Figure 2.1) include nitrate (NO_3^-, +5), nitrogen dioxide gas (NO_2, +4), nitrite (NO_2^-, +3), nitric oxide gas (NO, +2), and nitrous oxide gas (N_2O, +1). Nitrogen in organic N (R- NH_2, generally -3), ammonia gas (NH_3, -3) and ammonium ion

(NH_4^+, -3) all are in the –3 oxidation state (Madigan et al., 2003, Stumm and Morgan, 1996). Elemental (valence state = 0) nitrogen is in the form of dinitrogen (N_2), which is a gas at atmospheric pressures.

Dinitrogen gas, which makes up about 78% of the atmosphere (Fetter, 1992), requires much energy (22 kcal/mol, Groffman, 2000) to break the triple N_2 bond. Reactions that break the strong N_2 bond, called "fixing" the nitrogen, yield reactive nitrogen products (Nr) that are bioavailable and/or much more chemically reactive than N_2 gas.

There are several processes that provide this energy. For example, N_2 gas can be oxidized through combustion of fossil fuels such as in vehicle engines and thermal power plants (Groffman, 2000, Moomaw, 2002).

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \tag{2.1}$$

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \tag{2.2}$$

Some organic N in the fuel (up to 2% in petroleum and in coal) also is converted to NO_2 during combustion (Moomaw, 2002). These reactions also can be achieved in the atmosphere by the ionizing effects of lightning and cosmic radiation (Evangelou, 1998). For microorganisms, the most efficient way to convert N_2 gas into a usable form is through reduction to ammonia gas. A few specialized organisms can expend the energy required to fix nitrogen with hydrogen gas as the electron donor. These include some species of cyanobacteria ("blue-green algae") and several species of bacteria that symbiotically live in the root zones of legumes (e.g., soy, peas, clover) and other plant species such as alder and sweet fern (Madigan et al., 2003). Reactions depend on specific N-fixing organisms and usually require molybdenum-based enzymes (nitrogenase) and simple organic substrate such as acetylene (C_2H_2) (Madigan et al., 2003). The half reaction is:

$$8H^+ + 8e^- + N_2 \rightarrow 2NH_3 + H_2 \tag{2.3}$$

Until the early 20th century, natural biotic and abiotic processes provided all of the fixed nitrogen. In 1909, Fritz Haber succeeded in breaking the N_2 bond in the laboratory by reacting nitrogen with hydrogen gases to form synthetic ammonia (Zumdahl, 2000). Carl Bosch modified Haber's process for larger scale production by 1913. However, it wasn't until after the two world wars that nitrogen fertilizer was produced in mass quantities, and commercial consumption increased dramatically (from less than 5 to more than 85 megatons between 1950 and 2000 (Smil, 2002). It is estimated that, as of 2002, about 40% of the world's population was sustained by food grown with synthetic fertilizers made possible by Haber-Bosch process (Smil, 2002).

The redox state of nitrogen, whether naturally or anthropogenically fixed, is important for biological uptake. The two forms of Nr most widely used by plants and mircoorganisms, ammonium and nitrate N, have complete outer electron shell configurations (1s2 2s2 2p6 and 1s2 respectively). Most bacteria use ammonia as a sole nitrogen source (Mariotti et al., 1988), although many also can use nitrate (Madigan et al., 2003). Likewise, ammonium is easier to assimilate and preferred by most plants, especially trees (Verchot et al., 1997). However, ammonium can cause toxicity in some plants, whereas most plants can both assimilate and tolerate nitrate (Garnica et al., 2010). Once assimilated, organisms transform the ammonium- or nitrate- N to amino acids and other organic molecules (McClain et al., 1998), which are available to other organisms in the food chain. Note that in some ecosystems that are strongly limited in Nr (e.g., arctic and alpine tundra), native plants can take up dissolved organic nitrogen in the form of amino acids, which bypasses the microbial mineralization step necessary for most plants to exploit organic N pools (Harrison et al., 2007). Organic N is released back into the environment at various rates from animal waste and dead organisms. Ammoniafying bacteria mineralize (convert to inorganic form) organic N to ammonia (Hedin et al., 1998; Madigan et al., 2003).

Ammonia is the first inorganic form of N released when organic forms of N such as urea are mineralized under both aerobic and anaerobic conditions (Nolan, 1999):

$$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{2.4}$$

Some of the ammonia may not dissolve into solution but instead can be lost to the atmosphere through volatilization (Casciotti et al., 2003). However, in waters with $pH < 9.25$, NH_3 is protonated to form the ammonium ion, NH_4^+:

$$NH_3 + H^+ \Leftrightarrow NH_4^+ \tag{2.5}$$

or

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \tag{2.6}$$

The hydroxyl ion produced by hydrolysis of ammonia in the above reaction commonly is converted to bicarbonate in natural waters in this pH range, with a net reaction:

$$NH_3 + H_2O + CO_2 \Leftrightarrow NH_4^+ + HCO_3^- \qquad (2.7)$$

Equilibrium between NH_3 and NH_4^+ is established quickly relative to NH_3 oxidation rates (Casciotti et al., 2003).

2.2.1 Nitrification

In the presence of O_2, nitrogen is oxidized to nitrous oxide, nitrite and nitrate, the major oxidized aqueous species of Nr. Both biotic and abiotic processes regulate the concentrations and distributions of dissolved Nr (Triska et al., 1993).

Under aerobic conditions, ammonium is converted by bacteria to nitrite and then nitrate:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \qquad (2.8)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad (2.9)$$

In freshwater environments, the first step is mediated by the genus *Nitrosomonas* and the second by *Nitrobacter* (Madigan et al., 2003). Nitrification is a significant sink for ammonium in streams (Mulholland et al., 2000). Excess ammonia nitrogen in soil also is oxidized to nitrate according to the above net reactions, a process that takes about 1-3 weeks (Evangelou, 1998).

In ammonia-rich waters such as animal sewage and municipal wastewaters, ammonia can be oxidized anaerobically to N_2 with nitrite as the electron acceptor, a process called anoxic ammonia oxidation, or anammox (Madigan et al., 2003):

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad (2.10)$$

This reaction is carried out by *Brocadia Anammoxidans*. A requirement for this reaction is that there be oxic zones in the water where some ammonia is converted to nitrite aerobically so that there will be enough nitrite to act as the electron acceptor in the anammox reaction. However, high levels of oxygen inhibit the anammox reaction (Madigan et al., 2003).

2.2.2 Denitrification, Nitrate Reduction

Denitrification is the reduction of nitrate along a pathway to N_2 gas. Denitrification proceeds when Eh is below 300mV (Jordan et al., 1993). This can be carried out abioitically (described below) or by nitrate reducing bacteria, which use nitrate as the terminal electron acceptor. Biological denitrification generally requires C_{org} for cell growth and as electron donor to maintain a low Eh (Smith and Tiedje, 1979). When organic matter serves directly as the electron donor, complete denitrification is represented by:

$$4NO_3 + 5CH_2O \rightarrow 2N_2 + 5HCO_3^- + H^+ + 2H_2O \qquad (2.11)$$

This is a net reaction, as nitrate usually is reduced through steps to nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O). Each of these species can be end products depending on local conditions such as pH, temperature, trace metals (Fe, Cu, Mo) for enzymes, dissolved oxygen concentration and the presence of other species that may inhibit some steps of denitrification (Rivera-Monroy et al., 2010).

Although denitrifying bacteria are present in stream waters (Kellman and Hillaire-Marcel 1998), the presence of dissolved O_2 generally inhibits microbial denitrification due to repression of synthesis of nitrate reductase (Madigan et al., 2003). Instead, microbial denitrification is thought to occur where NO_3^- diffuses into organic-carbon rich bottom sediments (Kellman and Hillaire-Marcel 1998). However, tolerance to oxygen is variable. For example, *P. denitrificans* requires hypoxic or anoxic conditions, whereas other denitrifiers such as *T. pantotropha,* can tolerate substantial oxygen (Kaplan and Wofsy, 1985; Ferguson, 1994,). Nitrate and nitrite reductases are inhibited when the dissolved oxygen concentration exceeds about 7% of water in equilibrium with air, whereas nitrous oxide reductase can only be expressed at lower levels of oxygen (Ferguson, 1994). Another consideration is organic carbon distribution. For example, in very shallow streams with nearby, continual sources of organic carbon (e.g., algal mats, other decaying plant matter and/or upland cow pasture): particulate and dissolved C_{org} may be vertically distributed in the water column, which enhances in-stream biological denitrification (Bastviken et al., 2003).

Hydrogen gas is a product of organic fermentation and is an important electron source for respiration with nitrate as the electron acceptor (Postma and Jacobson, 1996):

$$5H_2 + 2NO_3^- + 2H^+ \rightarrow N_2 + 6H_2O \qquad (2.12)$$

Concentration of dissolved H_2 has been proposed as a major control on redox environments (more below).

Inorganic species such as Mn^{2+}, Fe^{2+}, and HS^- also serve as electron donors in nitrate reduction (Korom, 1992; Kappor, 1997). For example, Cheng et al. (1997) observed almost complete aerobic reduction of nitrate to ammonia in the presence of zero-valent iron and either HCl or a pH buffer for ammonia production. In natural settings, nitrate reduction by Mn^{2+}, Fe^{2+}, or HS^- often is mediated by chemolithoautotrophic bacteria in the bottom sediments of wetlands and other fresh water bodies (Rivera-Monroy et al., 2010). For example, ferrous iron may be incorporated structurally in minerals such as pyrite and siderite, or adsorbed to glauconite, chlorite, biotite, illite, or other local clay minerals (Böhlke and Denver, 1995; Ernstsen, 1996; Puckett and Cowdery, 2002). Ferrous iron available from clay minerals and amorphous iron solids probably is the most important mechanism for nitrate reduction in organic-poor sediments (Ernstsen, 1996). For example, Endale et al. (2003) determined that denitrification in a Georgia Piedmont shallow aquifer was coupled to $Fe(OH)_3$ production. This results in the chemical reduction of nitrate, oxidation of ferrous iron, and precipitation of ferric iron as relatively insoluble oxides and oxyhydroxides. A net reaction is:

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow N_2 + 10FeOOH + 18H^+ \qquad (2.13)$$

Boettcher et al. (1990) observed a decrease in nitrate with depth in ground water, which they attribute to denitrification using reduced sulfur in pyrite as the electron donor, facilitated by the bacterium *Thiobacillus denitrificans*. Oxidative dissolution of pyrite leads to autotrophic denitrification (Molénat and Gascuel-Odoux, 2002):

$$14NO_3^- + 5FeS_2 + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \qquad (2.14)$$

The above reaction also can proceed abiotically in oxic conditions (Jorgensen et al., 2009). Ferrous iron released in this reaction can further reduce nitrate:

$$5Fe^{2} + NO_3^- + 7H_2O \rightarrow 5FeOOH + 1/2\,N_2 + 9H^+ \qquad (2.15)$$

Yielding the net reaction (Aravena and Robertson, 1998):

$$5FeS_2 + 15NO_3^- + 5H_2O \rightarrow 10SO_4^{2-} + 7.5N_2 + 5FeOOH + 5H^+ \quad (2.16)$$

This reaction leads to an increase in sulfate concentrations corresponding to the decrease in $[NO_3^-]$. For example, Molénat and Gascuel-Odeux (2002) found decreased nitrate and increased sulfate concentrations in a weathered shale, which they attributed to denitrification coupled with oxidative dissolution of pyrite in the shale.

Nitrate is reduced to ammonia for energy (dissimilatory nitrate reduction) or for cell growth (assimilatory nitrate reduction) (Maître et al., 2003). Nitrate reduction also can proceed abiotically using reductants such as "green rust" compounds ($Fe^{2+}{}_4Fe^{3+}{}_2(OH)_{12}SO_4{\bullet}yH_2O$), whereby nitrate is reduced to ammonium with the formation of magnetite (Fe_3O_4) (Hansen et al. 1996). Dissimilatory nitrate reduction is similar to denitrification in that both processes use the high redox potential nitrate as an electron acceptor (Tiedje et al., 1981). Local control on whether nitrate undergoes denitrification or dissimilatory reduction to ammonia has been related to the ratio of nitrate concentration to percent organic carbon concentration (Schipper et al., 1994). In this study, dissimilatory nitrate reduction to ammonia occurred in sediments where the ratio of nitrate to organic carbon was low (0.4 or less), and denitrification is the dominant reduction pathway where the ratio of nitrate-to-carbon was higher (Schipper et al., 1994).

Assimilatory nitrate reduction generally occurs in settings that lack sufficient concentrations of reduced nitrogen for growth. In these environments, nitrate can provide nitrogen for cell growth but microbes first must reduce nitrate N to ammonia, which is more bioavailable (Tiedje et al., 1981). Also there can be assimilative nitrate reduction followed by ammonification of organic N upon death of the organism (Evangelou, 1998, Madigan et al., 2003). Nitrifying bacteria can oxidize the ammonia through nitrite back to nitrate (Casciotti et al., 2003), completing a cycle nested within the overall N cycle.

Some species such as NO_2^-, N_2O, and NO are products both of nitrification and denitrification (Del Grosso et al., 2008). After nitrate reduction to nitrite, for example, changes in soil aeration affect the reductases and influence whether NO or N_2O is the dominant gaseous product of denitrification (Conrad, 1996). Dissimilatory reduction of nitrate/nitrite to NH_4^+ also is accompanied by some N_2O production. Further complexities arise as, for example, one reduction pathway of N_2O involves N_2 fixation, since N_2O is one of the substrates of the N-fixing enzyme, nitrogenase (Kaplan and Wofsy, 1985).

The ultimate sink for N_2O is the last step of denitrification: $N_2O \rightarrow N_2$

$$N_2O + H_2 \rightarrow N_2 + HOH \qquad (2.17)$$

(Kaplan and Wofsy, 1985). In anaerobic soils with accumulated N_2O and depleted NO_3^-, reduction of N_2O to N_2 is enhanced by a small addition of NO_3^-, and the rate of this process increases rapidly with decreasing pH. In this case, nitrate is thought to stimulate *production* of N_2O reductase but too much nitrate inhibits the *activity* of the enzyme (Blackmer and Bremner, 1979). Note that excess dissolved N_2 below the root zone strongly indicates that denitrification is occurring because N_2 is the ultimate denitrification product and equilibrium with atmospheric N_2 is difficult to achieve (Böhlke and Denver, 1995).

In aerobic environments, chemoautotrophic oxidation of ammonia can proceed through NO and N_2O gases, which exsolve according to their partition coefficients (Casciotti et al. 2003). Nitrification zones usually show a decrease in $[NH_4^+]$ that was initially present, because ammonium is the most reduced N species and thus prone to oxididation (Ostrom et al., 2002). However, as mentioned above, there are other causes for decrease in ammonium concentration, such as sorption, biological uptake, or, at high pH, ammonia volatilization.

The above nitrification, denitrification and nitrate reduction reactions illustrate the complex interdependence between the N cycle, cycles of Nr reductants (e.g., carbon, sulfur and iron), and oxidants (mainly the oxygen cycle). As discussed above, the presence of specific redox species do not by themselves indicate whether an environment is oxidizing or reducing. Most redox species, including those of Nr, undergo phase changes and partitioning between solid, dissolved and gas phases. Nitrate thus can be chemically reduced and/or denitrified upon oxidation of any of several reductants, depending largely on which reduced species are present in sufficient concentrations to serve as the electron donor (more about the importance of concentration below). As denitrification proceeds, bulk water chemistry changes accordingly. Many of these reactions are not reversible due to volatile products and/or changing pH (Correll, 1997).

2.3 Characterizing Redox Environment

Characterizing the redox environment is important for understanding and comparing aquatic environments and ultimately predicting the extent to which they transport, transform and/or alter the toxicity of several redox-sensitive components, including major redox species (O_2/H_2O_2; $NO_3^-/N_2/NH_4^+$; SO_4^{2-}/HS^-; Mn(III)/(IV); Fe(II)/(III)), organic contaminants (TCE/PCE) and trace elements (As(II)/(V); Cr(III)/(VI). In spite of this importance, redox potential remains very difficult to measure or model (Sigg, 2000, Washington et al., 2004). In general, as redox reactions proceed in a non-buffered system, the overall Eh changes as the ratio of electron acceptors to reduced complimentary species changes (Correll, 1997).

The redox electrode is easy to use but does not yield reliable results in most settings. In order to be accurate, inert platinum electrodes used for measuring redox potential must represent the net effective electric potential contributed by all redox species present. However, redox reactions with the Pt-electrode surface proceed at different rates, resulting in an unstable exchange current at the electrode (Sigg, 2000). In addition, Peiffer et al (1992a, as reported in Peiffer, 2000) determined that a single redox couple controls the electrode voltage if either its standard reaction rate constant and/or its concentration are two orders of magnitude higher than that of other redox couples present. Thus, equilibrium often is not established at the electrode, yielding inaccurate and/or imprecise measurements.

Redox potential for individual couples can be measured using the Nernst equation, which is (in terms of electron activity, pe):

$$pe = \log K/n + 1/n \log (\Pi a_i^v \{\textit{oxidized}\}/\Pi a_i^v \{\textit{reduced}\}) \quad (2.18)$$

where the brackets {} denote ion activity in solution, which is expressed in units of concentration but usually is less than the measured concentration in environmental systems. The main disadvantage of calculating pe based on the Nernst equation is that it is a thermodynamic relationship, i.e., it assumes equilibrium conditions (Snoeyink and Jenkins, 1980). Equilibrium among all redox couples rarely are achieved in natural waters (e.g., Lindberg and Runnells, 1984).

There have been several studies in recent years promoting dihydrogen gas (H_2) as an important redox indicator. H_2 is a product of fermentation, which is a bacterially mediated process under anaerobic conditions (Hoehler et al., 1998):

$$CH_2O + H_2O \rightarrow CO_2 + 2H_2 \qquad (2.19)$$

where CH_2O represents carbohydrate organic matter. This approach is based on the assumption that biologically mediated oxidation of H_2 donates electrons and reduces terminal electron acceptors in a mutually reinforcing series. Briefly, microorganisms that reduce higher potential terminal electron acceptors (O_2, NO_3^-) are thought both to cause and tolerate a lower [H_2] because they derive more energy reducing the higher potential oxidant. By keeping [H_2] at low levels, these organisms may out-compete species that reduce terminal electron acceptors (TEAs) of lower potential, because the latter organisms require a higher concentration of H_2 to thrive (Lovley and Goodwin, 1988). Conclusions drawn from this approach are not always reliable, because there are many important biotic and abiotic redox reactions in which reductants besides H_2 are oxidized (Washington et al., 2004, and others cited above). Analysis of [H_2] has been useful in some settings such as anoxic zones in ground water (Lovley and Goodwin, 1998) and may be useful to discriminate between reduction of higher potential reductions (nitrate, Mn(IV) or Fe(III)) from lower-potential processes such as sulfate reduction and methanogenesis (Hoehler et al., 1998; Washington et al., 2004).

The "local partial equilibrium" (LPE) approach recognizes that products of slow fermentative degradation of organic matter become reactants in relatively rapid secondary and tertiary redox reactions. In the LPE approach, the segregation in many natural settings of electron acceptors into distinct zones (e.g., O_2 -reducing, NO_3^- -reducing, Fe^{3+} -reducing) reflects equilibrium between two or more redox pairs in each zone rather than as a net energy yield of all redox species in the system (Postma and Jakobsen, 1996). Washington et al. (2004) further demonstrated that a bimodal clustering of redox potentials (calculated from activities of redox-sensitive species in water samples) exists in settings where there are sources both of high-potential oxidants (dissolved O_2, NO_3^-) and low potential reductants (C_{org}). The pe of a redox couple is in one or the other of the two clusters depending on whether the more oxidized or more reduced form of that couple is more concentrated (i.e., if the more oxidized species in a redox couple has a higher concentration than the reduced species, the calculated pe of that couple will plot in the higher cluster). These data suggest that reaction rates are driven more by concentration than previously thought, rather than exclusively due to the magnitude of the voltage potential differences between redox couples. Phrased differently, higher concentration e^- acceptors are more accessible regardless of their potentials. This interpretation retains the assumption that oxidants react with reductants of lower potential and reductants react with oxidants of higher potential. Thus, although the maximum difference in potential yields the greatest transfer of *energy*, differences in potential may not neatly translate to the *rates* of reactions. To investigate this, Washington et al. (2004) plotted concentrations of several redox species (for example, the reduced form of a couple) versus deviation from equilibrium with each species' dominant complimentary reactant (a higher potential oxidant). Results showed that deviation from equilibrium increased as concentration decreased, confirming that concentration exerts significant control on redox reaction rates.

As explained above regarding intermediate products of both nitrification and denitrification reactions, but stressed again here, the bi- and sometimes multi-directional pathways of Nr and other redox reactions is another complicating factor in characterizing redox environments. These include dissolved species (e.g., NH_4^+, NO_3^-), precipitation and dissolution of minerals and other solids (e.g., FeS_2, organic carbon and organic nitrogen in water) and atmospheric gases (e.g., O_2 and N_2 partitioning between gas and water phases) (Chapelle et al., 1995). For example, Triska et al. (1993) reported that the proportion of nitrate to ammonium in the upper and middle reaches of a tropical swamp reflected local oxidizing conditions: $[NH_4^+]$ decreased from groundwater to spring water to channel water, whereas $[NO_3^-]$

increased along these zones. However, a nearby source of ammonium (e.g., animal waste or ammonia-based fertilizer) to the stream during runoff would result in nearby [NH_4^+] and [NO_3^-] that are not coupled to each other making it imprudent to characterize the redox setting based on their concentrations at a given time. Statistical analyses such as Pearsons's R coefficients are useful to establish possible cause and effect relationships between time- (including inter-seasonal) and space-trends.

Evans (2006) proposed the term "redox decoupling," defining it as an influx of enough redox sensitive species to change the capacities of local environments to oxidize or reduce, and "electrochemical differentiation" as the extent to which one or more redox decoupling processes cause changes in existing *gradients* in redox potential.

The extent to which researchers use the above approaches and terms is partly based on different disciplines (e.g., geological or biological) and research environments (e.g., laboratory or field; ground- or surface water; background or polluted conditions).

2.4 N Mobility and Transport

As discussed above, Nr is transformed via multi-step reaction pathways to the other aqueous, gaseous, organic and inorganic Nr species depending on local conditions. This leads to short- and long-term, small- and large-scale cycling of nitrogen between the hydrosphere, biosphere and atmosphere (Van Breemen et al., 2002). Cycling of N superimposed on advective transport is called nitrogen spiraling (Bisson and Bilby 2001). Another conceptual model is that of cascading (e.g., Galloway et al., 2008; Galloway and Cowling, 2002), which recognizes the transfer of Nr between the terra-, bio-, hydro, and atmospheres, different species within each sphere, and biogeochemical cycling between each sphere. The degree to which a given reaction will proceed in a specific hydrological setting also depends on the rates of chemical reactions and biological processes relative to flow velocity (Botter et al, 2010). Transport rates of nitrogen in different forms leads to local cycling and storage at different time scales for some of the N pool and varying rates of transport downstream for the remainder. In aqueous environments, nitrogen removal effectiveness is defined as the ratio of N removed to the total N moving through the system. This effectiveness depends on specific pathways of water through the system (Maître et al., 2003).

Local controls on N releases to the environment include, but are not limited to, land use practices, the geometric relationship between recharge and discharge areas, and the extent and effectiveness of natural remediation zones (e.g., organic C, reduced minerals) (Böhlke and Denver, 1995). Warmer water decreases O_2 solubility, which further enhances the efficiency of most nitrate-reducing bacteria (Hemond and Duran, 1989). Nitrate removal rates are assumed to be higher during spring and summer growing seasons, due both to faster denitrification rates and to uptake as plants grow (Burns and Nguyen, 2002). Denitrification often is a proportionally greater nitrate removal mechanism in winter when local vegetation is dormant (Hill et al., 2004). In addition, if enough organic carbon is present during the growing season, denitrification can still be a dominant nitrate removal mechanism in riparian ground water (Hill et al., 2004).

In addition to biological uptake described above, ammonium N accumulates in many soils (Meuleman et al., 2003) by adsorbing to net negative charges on and/or exchange structural cations with 2:1 clay minerals (e.g., the smectites, illite and vermiculite) (Juang et al., 2001), and less so to 1:1 clays such as kaolinite. Ammonium also adsorbs to peat and to other organic matter (Abbès et al., 1993). As such, NH_4^+ is much less mobile in the environment than the negatively charged NO_3^- ion (McBride, 1994). Indeed, one of the ways in which wetlands and other vegetated buffer zones retain nitrogen is soil retention of ammonium and organic nitrogen (Correll, 1997; Meuleman et al., 2003).

Nitrate flows through the vadose zone and into ground water. From there, nitrate follows natural hydraulic gradients or is pumped into private or municipal drinking water wells. In some aquifers, denitrification can be significant along deep ground water flow paths in the presence of reduced minerals such as glauconite (Böhlke and Denver, 1995). Often, though, down-gradient mixing of ground waters from different recharge areas dilutes nitrate concentrations. In addition to denitrification and dilution, ground water that follows deeper, longer flow paths may have lower nitrate concentrations simply because less N fertilizer was applied at the time and place of recharge (Puckett et al., 2002). For ground water flowing toward streams, the most active region for denitrification usually is in riparian zones (the interface between upland areas and streams) and stream-bottom sediments (Hedin et al., 1998).

In shallow streams or near the riparian zone, some stream nitrate may be taken up by plants (Maître et al., 2003). As in ground water, lower downstream nitrate concentrations can be diluted due to mixing of waters from different sources, which is often misinterpreted as nitrate loss (Maître et al., 2003). Hydrological retention occurs in areas of a stream channel where velocity decreases, where flow is physically obstructed or where there are recirculation pools at stream margins (Edwards, 1998; Triska et al., 1989). Stream water also can continually flow into and out of the hyporheic zone, a shallow layer of stream bottom sediment at the interface between stream and ground water to induce redox-driven transformation of N. This is mainly due to advection caused by irregularities on the stream-bottom surface (Jonsson et al., 2003; Rutherford and Nguyen, 2004). The depth of exchange with the hyporheic zone is determined by the morphology of the stream channel, roughness of the stream bed and permeability of the bottom sediments (Triska et al., 1989). Stream chemical processes depend both on the magnitude of the reaction rate constant and on the residence time in a particular environment (Kimball et al., 1994). Higher discharge, which often is accompanied by increase in velocity, may lead to residence times that are shorter than one or more nitrate removal processes (Cooper, 1990). On the other hand, lower stream discharge improves the efficiency of nitrate removal by increasing the residence time and hence contact with reducing stream-bottom sediments (Cooper, 1990) and also more time for uptake by plants and filter feeders (Edwards et al, 1998). In short reaches, longer retention times due to exchange with the hyporheic zone and other storage areas play a significant role in denitrification, especially those high in dissolved organic C (Triska et al., 1989). Dentrifying bacteria are present in streams but become most active in stream bottom sediments due to the more reducing environment and to longer nitrate residence times (Kellman and Hillaire-Marcel, 1998). Biological uptake and denitrification rates increase with increasing [NO_3^-]. However, a threshold is reached above which biological pools become saturated and/or denitrification rates remain constant with increasing [NO_3^-]. At this point, removal efficiency – the proportion of [NO_3^-] removed to that introduced - declines. Nitrate subsequently travels to the next stream reach, which may be receiving nitrate from other low order streams. Low order streams are very important for nitrate removal both because of their high bed area to water volume ratio, and also because they represent most of the stream length within a given watershed (Mulholland et al., 2008). In general, denitrification is the main pathway for removal of nitrate from streams and other surface water bodies such as lakes and estuaries (Peterson et al., 2001; Rivera-Monroy et al., 2010). In the United States, more than 70% of anthropogenic N is stored, denitrified or volatilized in watersheds, with less than 30% reaching the oceans (Howarth et al., 1996, Boyer et al., 2002 in Mayer et al., 2002).

2.5 Wetlands

Wetlands are an interface or transition zone between terrestrial and aquatic environments, and are defined by their hydrology, vegetation type and soil type (USEPA, 2007). Wetlands receive water from precipitation, surface flow and ground water discharge. Wetlands soils, also called hydric soils, are saturated or flooded long enough during the growing season to allow for anaerobic conditions to develop, which in turn allows organic matter to accumulate (USEPA, 2007). As a setting for release, cycling and/or transport of nitrogen, many of the processes described above come together in wetlands

Wetlands perform valuable functions, such as providing habitat for many diverse species of plants and animals, filtering contaminants, and buffering land from marine storm surges. Natural and man-made or enhanced riparian wetlands can significantly retard the flow of streamwater, introduce bio/chemical reductants and/or encourage plant uptake (Burns and Nguyen, 2002). In addition to retarding or recycling nutrients, wetlands are useful in bioremediation of organic pesticides and heavy metals (Suthersan, 1996). Because of the extremely valuable role they play as habitat, hydrological buffer and pollution abatement, wetlands are protected under the Clean Water Act (USEPA, 2007).

Denitrification and N assimilation can occur in wetlands (Böhlke and Denver, 1995). Denitrifying bacteria are associated with the surfaces of some submersed wetland plants and wood matter (Bastviken et al., 2003). In addition to bacteria, fungi are capable of reducing nitrate. For example, Seo and DeLaune (2010) observed that denitrification by wetland fungi were optimal in aerobic or weakly reducing conditons, whereas bacteria reduced nitrate in strongly reducing conditions. Vegetation helps maintain organic matter in wetland soils, which in turn maintains low redox conditions and promotes denitrification (Correll, 1997). Wetland soils contain very little dissolved oxygen starting at depths as low as 2 cm below the soil surface (Matheson et al., 2002). Organic-rich wetlands are very effective at removing nitrate from wastewaters (Meuleman et al., 2003). The type of vegetation present appears to affect both N uptake rates and denitrification rates and different wetland plants supply different amounts of usable carbon. (Cooper, 1994).

Seasonal and other climate variations play a large role in the efficacy of wetlands to remove nitrate. For example, Puckett et al. (2002) attributed relatively high [NO_3^-] and [NH_4^+] during the winter months to slow rate of plant. However, many wetlands reach a steady-state with respect to N assimilation due to plant uptake, at which point N removal is due mainly to denitrification (Cooper, 1994). This leads to a complicated relationship between C and N, where N is required for the plants, which, after death, provide the C for further reduction and/or denitrification of excess N. The redox environment in wetlands can alter between nitrification and denitrification corresponding to alternating wet and dry periods in wetland soils (Meuleman et al., 2003). This is due not only to precipitation, but also to non-uniform flow and preferential flow paths, which are common features of wetland streams (Cooper, 1994).

Wetland N budgets include a full range of end-member N cycling processes such as ammonia volatilization (output), which occurs at pH > 8, and nitrogen fixation (input) (Meuleman et al., 2003). Thus, wetlands cycle nitrogen at various rates, depending on several interacting factors including initial nitrate and ammonium concentrations discharging to the wetland, total organic carbon, C:N ratio, decomposition rate of organic matter (which in turn depends also on climate), plant uptake rates of nitrate and ammonium, and water flow velocity (Burns and Nguyen, 2002). Denitrification is also accomplished in the presence of organic matter and other chemical reductants such as iron sulfides, the latter of which react with nitrate to form dinitrogen gas and sulfate (Correll, 1997).

Wetlands often are constructed, and existing wetlands enhanced, to maximize their capacities to store and/or chemically transform pollutants. Mitsch et al. (2005) calculated, based on field data, that construction of about 22,000 km^2 of new wetlands in the Mississippi River basin (< 1% of the basin) is necessary to remove 40% of the nitrogen delivered to the Gulf of Mexico, based on relationships they observed between loading and wetland retention rates, and on estimates of annual N loads to the Gulf of Mexico. This could be done in conjunction with or as an alternative to major reductions in fertilizer use (Mitcsh et al., 2005). However, decomposition of wetland organic matter is relatively slow, so it takes time for a wetland to become fully established (Meuleman et al., 2003). Design variables in constructed wetlands include addition of substrate, alteration of channel configuration, dams, and introduction of specific plant species to maximize optimum wetland viability and health. Constructed wetlands sometimes include vertical flow systems to maximize contact time with substrate (Meuleman et al., 2003). There are several forms of DOC that can be added to wetlands. For example, beds of hay or wood, stabilized with vegetation, become a continuous, gradual source of organic C to wetland channels (Hedin et al., 1998).

2.6 Tracer Injection Experiments

Tracer injection experiments are useful for examining hydrological, physical and chemical characteristics along a flow path (Field 2002). For example, dye tracers are useful for determining flow paths and travel times through karst terrain and fractured bedrock (Field 2002). Tracer experiments also have been used to model hyporheic exchange of stream solutes (Jonsson et al., 2003) and to characterize transient storage in different stream reaches (Manson, 2000). Co-injection of stable and chemically reactive tracers distinguishes between processes, such as dilution, that affect both tracers and processes that affect only the concentration of the reactive tracer (Triska et al., 1993).

In streams, there are four main transport processes that affect both reactive and conservative tracers: 1) advection, or the rate at which the tracer plumes move downstream; 2) dispersion, which is the in-stream mixing processes that cause the plumes to spread laterally, longitudinally and vertically; 3) ground water discharge, which both increases stream discharge and dilutes the tracers; and 4) storage-zone exchange, which is the movement of tracers into and out of temporary storage or slower-moving zones such as riparian debris or the hyporheic zone (Wagner and Harvey, 1997).

Common conservative tracers include dye (e.g, Rhodamine WT, Florescein) and bromide. Each of the conservative tracers has advantages and disadvantages, depending on the particular setting and/or duration of the tracer experiment. For example, Florescein photodegrades with a half-life of about 3 days (Martin et al., 1999) and Rhodamine WT sorbs to sediments. Bromide is non-conservative in sediments high in iron oxide solids (Seaman et al., 1996). Conservative tracers help establish minimum, average and maximum travel times between the point of injection and downstream collection points, and thus are useful for estimating stream velocities (Triska et al., 1993).

Reactive tracers are the chemical species being studied to determine their partitioning and reactions in specific settings. Tracer studies with nitrate and a conservative tracer allow one to distinguish between dilution and hydrologic storage (which affects both tracers) from the sum of all transformation processes such as denitrification, microbial immobilization and plant uptake (Triska et al., 1993; Verchot et al., 1997; Burns and Nguyen, 2002; Jonsson et al., 2003). Studies that examine $\delta^{15}N$, or $((({}^{15}N/{}^{14}N)_{sample} \div ({}^{15}N/{}^{14}N)_{std}) - 1) \times 1000$, along the flowpath are used to distinguish further between local cycling processes that cause isotope partitioning (e.g., nitrification, denitrification) from those that do not (e.g., plant uptake) (Abu Bakar et al., 1994, Casciotti et al., 2003).

Tracer experiment design depends on study objectives and local conditions, and there are major trade-offs when choosing one injection or sampling strategy over another (Wagner and Harvey, 1997). In some cases, a preliminary tracer test may be necessary in order to obtain the transport properties that are necessary to design a robust tracer experiment (Field 2002). Major considerations include desired concentration at the point of injection, injection rate and duration, volume of injectate, number and locations of down-gradient sampling points, and sampling frequency at each sampling point. Synoptic sampling usually is conducted when there is more than one down-stream sampling location (Triska et al., 1993). When both reactive and conservative tracers are used, they are injected simultaneously (Jonsson et al., 2003).

Injection durations vary, depending on several factors such as travel time, distance from injection to collection points, anticipated reaction times and study objectives. For example, tracers can be introduced as an instantaneous dose or pulse (Burns and Nguyen, 2002), as short duration (rise-plateau-fall) in small streams (Field, 2002; Triska et al., 1993), or as a longer-term, constant-rate injection (Kilpatrick and Cobb, 1985). Wagner and Harvey (1997) found that sampling throughout the rise, plateau and fall after a short duration injection provided more reliable estimates of stream parameters such as stream area, dispersion coefficient, ground water inflow and storage area than a single pulse or constant stream injection.

To interpret the results of a stream tracer injection experiment, one must compare the downstream concentrations of conservative to reactive tracers. If downstream reactive and conservative tracer concentrations in the stream have the same ratios as their concentrations in the injectate (minus background concentrations) (Verchot et al., 1997), then the reactive tracer was not affected by removal processes (i.e., did not react) (Burns and Nguyen, 2002). To estimate tracer loss, the masses (area under curve in time vs concentration curve) at each downstream sampling location are compared to the masses of reactive and conservative tracer added to the stream (Jonsson et al., 2003). Loss of conservative tracer indicates storage or loss through the streambed. A greater loss of reactive tracer such as nitrate indicates that removal processes have been active along the stream reach, but does by itself not distinguish between removal processes (i.e., biological assimilation, plant uptake or denitrification). Note that incomplete mixing of tracer with stream water at the point of sample collection yields artificially low or high sample concentrations of tracer species.

Upstream concentration versus time curves characteristically are steep-sided and symmetrical, with maximum concentrations becoming lower and the limbs progressively less steep further downstream due to longitudinal dispersion (Kirchner et al., 2001). This retardation and spread of the downstream breakthrough curve, in turn, must be considered when determining sampling initiation and frequency at the downstream site (Field,2002). Downstream breakthrough curves also may have a steeper rising than falling limb due to temporary storage (e.g., Burns and Nguyen (2002).

Conservative tracers sometimes are present in reliably consistent background concentrations that are useful for certain applications. For example, agricultural runoff often contains high chloride (Böhlke and Denver, 1995), which is an effective conservative tracer because it does not react in most conditions (Kirchner et al., 2001). In low flow streams, where discharge is difficult to measure, background chloride can be used to establish mass conservation, which then can be used to calculate background nitrate loads and, from that, discharge (Ribolzi et al., 2000).

One last, but important consideration when designing a tracer injection experiments is the potential environmental consequences of any chemicals (conservative or reactive) added to a stream. Concentrated dyes may be stressful to wildlife and also cause public concern. As stated above, bromide can react with chemicals added to public water supply systems and cause potentially harmful byproducts in drinking water. The many environmental problems caused by nitrate have already been discussed in Chapter 1. Therefore, care should be given in choosing the mass of each tracer that will provide optimal experimental value without causing unnecessary harm to the environment.

2.7 Management Practices

Efforts to control release of Nr have been difficult because fertilizer N is associated with food and energy production, and also because Nr is transported long distances in air or water (Mosier et a., 2002). However, Some management practices reduce the introduction of reactive nitrogen to the environment. These include careful assessment of the amount and timing of crop fertilization and irrigation to ensure maximum uptake by crops (Casey et al., 2002; Mosier et al., 2002).

Physical modifications have been proposed and/or tested over the past few years. Rivera-Monroy et al. (2010) propose diverting nitrate-laden water from the Mississippi to areas where wetlands have been lost or stressed, in order to supply soil and nutrients necessary for wetlands to become re-established. In areas where rice and other semi-aquatic crops are grown, nitrate-rich stream water can be diverted through the paddy fields, which have a high capacity for nitrate removal (Ichino and Kasuya, 1998).

Improved management is required in both urban and areas of lower population density. Minimizing impervious surfaces in residential areas will help reduce direct runoff of nutrients and other pollutants (Poor and McDonnell, 2007). Septic systems also are an important source of Nr and need improved management strategies. Increasing the distance between the septic system and streams or other surface water bodies is one of the most effective ways to control discharge, as natural attenuation may be sufficient to remove Nr leaked from septic systems to ground water (Azadpour-Keeley et al., 1999). The best minimum setback distance depends on many factors such as depth to water table, hydraulic conductivity and gradient, and background chemistry of the surface water being recharged (e.g., freshwater vs. saltwater and other considerations) (Meile et al., 2010).

Adding amendments such as organic carbon (Bastviken et al., 2003) or zero-valent iron (Cheng et al., 1997) to aqueous systems can lead to enhanced denitrification but also lower the Eh of the entire system. This can lead to dissolution/precipitation reactions (ITRC, 2000), which may mobilize metals in some settings. It is also possible to optimize the surfaces preferred by denitrifying bacteria, which are site- and season-specific (Bastviken et al., 2003). However, many questions still remain regarding environmental factors that limit nitrate transformation rates (Jorgensen et al., 2009). Specific questions addressed in this research are summarized in Chapter 1.

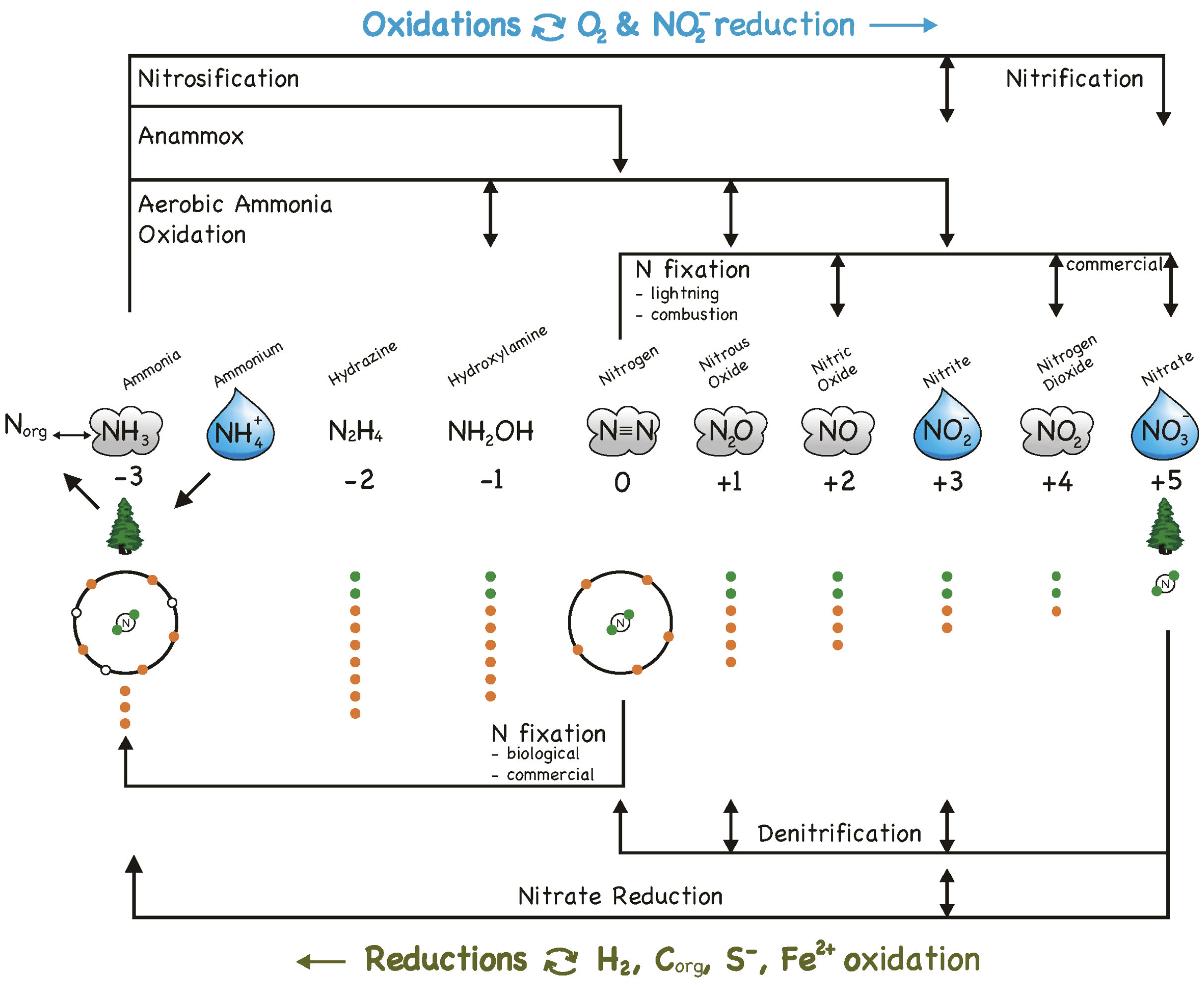

Figure 2.1. The nitrogen cycle. Nitrogen species are arranged from the most reduced (left) to the most oxidized (right). Ammonia (N in -3 oxidation state) and nitrate (N in +5 oxidation state) both have full outer electron shells and are the N species taken up by plants and microorganisms. Common oxidation pathways are shown on the top and reduction pathways along the bottom.

References

Abbès, C., L.E. Parent and A. Karam (1993) Ammonia sorption by peat and N fractionation in some peat-ammonia systems. Fertilizer Research 36:249-257.

Abu Bakar, R., K.W.T. Goulding, C.P. Webster, RP.R. Poulton and D.S. Powlson (1994) Estimating nitrate leaching and denitrification by simultaneous use of Br and ^{15}N tracers. J. Sci. Food Agric. 66:509-519.

Aravena, R. and W.D. Robertson (1998) Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic plume. Ground Water 36(6):975-982.

Azadpour-Keeley, A., H.H. Russell and G.W. Sewell (1999) Microbial processes affecting monitored narutral attenuation of contaminants in the subsurface. USEPA Office of Research and Development, Office of Solid Waste and Emergency Response. EPA/540/S-99/001. 18p.

Bashkin, V.N., S.U. Park, M.S. Choi and C.B. Lee (2002) Nitrogen budgets for the Republic of Korea and the Yellow Sea region. Biogeochemistry 57/58: 387-403.

Bastviken, S.K., P.G. Eriksson, I. Martins, J.M. Neto, L. Leonardson and K. Tonderski (2003) Wetlands and aquatic processes: Potential nitrification and denitrification on different surfaces in a constructed treatment wetland. J. Environ. Qual. 32:2414-2420.

Bastviken, S.K., S.E.B. Weisener, G. Thiere, J.M. Svensson, P.M. Ehde, K.S. Tonderski (2009) Effects of vegetation and hydraulic load on seasonal nitrate removal in treatment wetlands. Ecological Engineering 35:946-952.

Bisson, P.A. and R.E. Bilby (2001) Organic matter and trophic dynamics. *In* Naiman, R.J. and R.E. Bilby, eds. River Ecology and Management: Lessons from the Pacific Coastal Region. Springer, 705p.

Blackmer, A.M. and J.M. Bremner (1979) Stimulatory effect of nitrate on reduction of N_2O to N_2 by soil microorganisms. Soil Biol. Biochem. 11:313-315.

Böhlke, J.K. and J.M. Denver (1995) Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. Water Resources Research 31(9): 2319-2339.

Boettcher, J., O. Strebel, S. Voerkelius and H.-L. Schmidt (1990) Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. Journal of Hydrology 114: 413-424.

Botter, G., N.B. Basu, S. Zanardo, P.S.C. Rao, and A. Rinaldo (2010) Stochastic modeling of nutrient losses in streams: Interactions of climatic, hydrologic, and biogeochemical controls. Water Resources Research 46(W08509), 14p.

Brown, C.J., J.D. Coates, and M.A.A. Schoonen (1999) Localized sulfate reducing zones in a coastal plain aquifer. Ground Water 37(4): 505-516.

Burns, D.A. amd L. Nguyen (2002) Nitrate movement and removal along a shallow groundwater flow path in a riparian wetland within a sheep-grazed pastoral catchment: Results of a tracer study. New Zealand Journal of Marine and Freshwater Research 36: 371-385.

Casciotti, K.L., D.M. Sigman, B.B. Ward (2003) Linking diversity and stable isotope fractionation in ammonia-oxidizing bacteria. Geomicrobiology Journal 20: 335-353.

Casey, F.X.M., N. Derby, R.E. Knighton, D.D. Steele and E.C. Stegman (2002) Initiation of irrigation effects on temporal nitrate leaching. Vadose Zone Journal 1:300-309.

Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford and D.A. Vroblesky (1995) Deducing the distribution of terminal electron-accepting processes in hydrological diverse groundwater systems. Water Resources Research 31: 359-371.

Cheng, I.F., R. Muftikian, Q. Fernando, and N. Korte (1997) Reduction of nitrate to ammonia by zero-valent iron. Chemosphere 35(11):2689-2695.

Conrad, R. (1996) Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O and NO. Microbiological Reviews 60(4):609-640.

Cooper, A.B. (1994) Coupling wetland treatment to land treatment: An innovative method for nitrogen stripping? Water Science and Technology 29: 141-149.

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

Correll, D.L. (1997) Buffer zones and water quality protection: general principles. Pgs 7-20 in Buffer Zones: Their Processes and Potential in Water Protection – The Proceedings of the International Conference on Buffer Zones, September 1996. Haycock, N.E., T.P. Burt, K.W.T. Goulding, and G. Pinay (eds). Quest Environmental, Herfordshire, UK.

Del Grosso, S.J., T. Wirth, S.M. Ogle and W.J. Parton (2008) Estimating agricultural nitrous oxide emissions. EOS 89(51): 529.

Edwards, R.T. (1998) The Hyporheic Zone. *In* Naiman, R.J. and R.E. Bilby, eds. River Ecology and Management: Lessons from the Pacific Coastal Ecoregion. Springer –Verlag, 705p.

Endale, D.M., J.W. Washington, and L. Samarkina (2003) Role of iron-rich Georgia soils in controlling nitrate contamination of ground water. Proceedings of the 2003 Georgia Water Resources Conference, held April 23-24, 2003 at the University of Georgia. Karen J. Hatcher, editor, Institute of Ecology, The University of Georgia, Athens, Georgia.

Ernstsen, V. (1996) Reduction of nitrate by Fe^{2+} in clay minerals. Clays and Clay Minerals 44(5):599-608.

Evangelou, W.P. (1998) Environmental Soil and Water Chemistry: Principles and Applications. John Wiley and Sons, Inc.

Evans, K.A. (2006) Redox decoupling and redox budgets: Conceptual tools for the study of earth systems. Geology 34(6): 489-492.
Ferguson, S.J. (1994) Denitrification and its control. Antonie van Leeuwenhoek 66:89-110.

Fetter, C.W. (1992) Contaminant Hydrology. Macmillan Publishing Company.
Field, M.S. (2002) Efficient hydrologic tracer-test design for tracer-mass estimation and sample-collection frequency, 2. Experimental Results. Environmental Geology 42: 839-850.

Galloway, J.N. and E.B. Cowling (2002) Reactive nitrogen and the world: 200 years of change. Ambio 31(2):64-71.

Galloway, J.N., A.R. Townsend, J.W. Erisman, M. Bekunda, Z. Cai, J.R. Freney, L.A. Martinelli, S.P. Seitzinger, M.A. Sutton (2008) Transformation of the nitrogen cycle: Recent trends, questions and potential solutions. Science 320:889-892.

Garnica, M., F. Houdusse, A.M. Zamerreño, J.M. Garcia-Mina (2010) The signal effect of nitrate supply enhances active forms of cytokinins and indole acetic content and reduces abscisic acid in wheat plants grown with ammonium. J. Plant Physioloby 167:1264-1272.

Groffman, P.M. (2000) Nitrogen in the environment. In Malcom E. Sumner (ed.) Handbook of Soil Science. CRC Press: C-190 – C-200.

Harrison, K.A., R. Bol, and R.D. Bardgett (2007) Preferences for different nitrogen forms by coexisting plant species and soil microbes. Ecology 88(4): 989-999.

Hansen, H.Chr.B., Koch, C.B., Nancke-Krogh, H.N., Borggaard, O.K., and Sorensen, J. (1996) Abiotic nitrate reduction to ammonium: Key role of green rust. Environ Sci. Technol. 30:2053-2056.

Hedin, L.O., J.C. von Fischer, N.E. Ostrom, B.P. Kenney, M.G. Brown and G.P. Robertson (1998) Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology 79(2): 684-703.

Hemond, H.F. and A.P. Duran (1989) Fluxes of N_2O at the sediment-water and water-atmosphere boundaries of a nitrogen-rich river. Water Resources Research 25(5):839-846.

Hill, A.R., P.G.F. Vidon, and J. Langat (2004) Denitrification potential in relation to lithology in five headwater riparian zones. J. Envrion. Qual. 33:911-919.

Hoehler, T.M., M.J. Alperin, D.B. Albert and C.S. Martens (1998) Thermodynamic control on hydrogen concentrations in anoxic sediments. Geochimica et Cosmochimica Acta 62: 1745-1756.

Holland, E.A., S.B. Bertram, M.A. Carroll, A.B. Guenther, P.B. Shepson, J.P. Sparks and J. Lee-Taylor (2005) U.S. nitrogen science plan focuses collaborative efforts. EOS 86(27):253,256.

Hooper, R.P. (2001) Applying the scientific method to small catchment studies: a review of the Panola Mountain experience. Hydrological Processes 15:2039-2050.

Howarth, R.W., E.W. Boyer, W.J. Pabich and J.N. Galloway (2002) Nitrogen use in the United States from 1961-2000 and potential future trends. Ambio 31(2):88-96.

Huebert, B., P. Vitousek, J. Sutton, T. Elias, J. Heath, S. Coeppicus, S. Howell, and B. Blomquist (1999) Volcano fixes nitrogen into plant-available forms. Biogeochemistry 47:111-118.

ITRC (Interstate Technology and Regulatory Cooperation Work Group) (2000) Emerging Technologies for Enhanced In Situ Biodenitrification (EISBD) of Nitrate-Contaminated Ground Water: Technology Overview. 47p.

Ichino, K. and M. Kasuya (1998) Nitrogen removal in paddy fields: An option for water quality improvement in rivers. Ecological Engineering 10:159-164.

James, B.R. and R.J. Bartlett (2000) Redox Phenomena *in* Sumner, M.E. (ed) Handbook of Soil Science, CRC Press.

Johnes P.J. and D. Butterfield (2002) Landscape, regional and global estimates of nitrogen from land to sea: Errors and uncertainties. Biogeochemistry 57/58: 429-476.

Jonsson, K., H. Johansson, A. Wörman (2003) Hyporheic exchange of reactive and conservative solutes in streams – tracer methodology and model interpretation. Journal of Hydrology 278:153-171.

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.

Jorgensen, C.J., O.S. Jacobsen, B. Elberling, and J. Aamand (2009) Microbial oxidation of pyrite coupled to nitrate reduction in anoxic groundwater sediment. Environ. Sci. Technol. 43(13):4851-4857.

Juang, T.C., M.K. Wang. H.J. Chen, and C.C. Tan (2001) Ammonium fixation by surface soils and clays. Soil Science 166(5):345-352.

Kadlec, R.H. (2010) Nitrate dynamics in event-driven wetlands. Ecological Engineering 36:503-516.

Kaplan, W.A. and S.C. Wofsy (1985) The biogeochemistry of nitrous oxide: a review. Advances in Aquatic Microbiology, Vol. 3:181-206.

Kappor, A., (1997) Nitrate removal from drinking water – review. Jour. Environmental Engineering 123(4).

Kaushal, S.S., M.L. Pace, P.M. Groffman, L.E. Band, K.T. Belt, P.M. Mayer, and C. Welty (2010) Land use and climate variability amplify contaminant pulses. Eos 91(25):221.

Kellman, L. and C. Hillaire-Marcel (1998) Nitrate cycling in streams: using natural abundances of NO_3^- - δ-^{15}N to measure *in-situ* denitrification. Biogeochemistry 43: 273-292.

Kilpatrick, F.A. and E.D. Cobb (1985) Measurement of discharge using tracers: Techniques of water-resources investigations of the United States Geological Survey Book 3, Chapter A16.

Kimball B.A., R.E. Broshears, K.E. Bencala, D.M. McKnight (1994) Coupling of hydrologic transport and chemical reactions in a stream affected by acid mine drainage. Environmental Science and Technology 28: 2065-2073.

Kirchner, J.W., X. Feng, C. Neal (2001) Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations. Journal of Hydrology 254:82-101.

Korom, S. (1992) Natural denitrification in the saturated zone: A review. Water Resources Research 28(6):1657-1668.

Laverman, A.M., J.A. Garnier, E.M. Mounier, and C.L. Roose-Amsaleg (2010) Nitrous oxide production kinetics during nitrate reduction in river sediments. Water Research 44:1753-1764.

Lewis, G.N. and M. Randall (1921) The activity coefficient of strong electrolytes. J. Am. Chem. Soc. 43(5):1112-1154.

Lin, A.Y.-C., J.F. Debroux, J.A. Cunningham, M. Reinhard (2003) Comparison of rhodamine WT and bromide in the determination of hydraulic characteristics of constructed wetlands. Ecological Engineering 20: 75-88.

Lindberg, R.D. and D.D. Runnells (1984) Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. Science 255:925-927.

Liu, Z., S.A. Clay, D.E. Clay and S.S. Harper (1995) Ammonia impacts on Atrazine leaching through undisturbed soil columns. J. Environ. Qual. 24:1170-1173.

Lovley, D.R. and S. Goodwin (1988) Hydrogen concentrations as an indicator of the predominant terminal electron-accepting processes. Geochimica et Cosmochimica Acta 52: 2993-3003.

Madigan, M.T., J.M. Martinko and J. Parker (2003) Brock Biology of Microorganisms, Tenth Edition. Prentice Hall, 1005 p.

Maître, V., A.-C. Cosandey, E. Desagher, A. Parriaux (2003) Effectiveness of groundwater nitrate removal in a river riparian area: the importance of hydrogeological conditions. Journal of Hydrology 278:76-93.

Manson, J.R. (2000) Predicting stream transient storage zone characteristics from tracer data. Water Resources Research 36(2): 629-631.

Marine Science Today (2009)
http://marinesciencetoday.com/2009/08/05/gulf-of-mexico-dead-zone-smaller-than-predicted-but-deeper/

Mariotti, A. (1986) Denitrification in groundwaters, principles and methods for its measurement: A review. Journal of Hydrology 88(172): 1-23.

Mariotti, A., A. Landreau, and B. Simon (1988) ^{15}N isotope biogeochemistry and natural denitrification processes in ground water: Application to the chalk aquifer of northern France. Geochimica et Cosmochimica Acta 52, no. 7: 1869-1878.

Martin, J.L., S.C. McCutcheon and R.W. Schottman (1999) Hydrodynamics and Transport for Water Quality Monitoring. CRC Press, 795p.

Matheson, F.E., M.L. Nguyen, A.B. Cooper, T.P. Burt and D.C. Bull (2002) Fate of ^{15}N-nitrate in unplanted, planted and harvested riparian wetland soil microcosms. Ecol Eng. 19:249-264.

Matheson, F.E. and J.P. Sukias (2010) Nitrate removal processes in a constructed wetland treating drainage from dairy pasture. Ecological Engineering 36:1260-1265.

Mayer B., E.W. Boyer, C. Goodale, N.A. Jawarski, N. Van Breemen, R.W. Howarth, S. Seitsinger, G. Billen, K. Lajtha, K. Nadelhoffer, D. Van Dam, L.J. Heitling, M. Nosal, K. Paustian (2002) Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints. Biogeochemistry 57/58: 171-197.

McBride, M.B. (1994) Environmental Chemistry of Soils. Oxford University Press, 406p.

McClain, M.E., J.E. Richey and T.P. Pimentel (1994) Groundwater nitrogen dynamics at the terrestrial-lotic interface of a small catchment in the Central Amazon Basin. Biogeochemistry 27: 113-127.

McClain, M.E., R.E. Bilby and F.J. Triska (1998) Nutrient cycles and responses to disturbance. *In* Naiman and Bilby, eds, River Ecology and Management: Lessons from the Pacific Coastal Ecoregion. Springer, 750p.

Meile, C., W.P. Porubsky, R.L. Walker, and K. Payne (2010) Natural attenuation of nitrogen loadings from septic effluents: Spatial and environmental controls. Water Research 44:1399-1408.

Meuleman, A.F.M., R. van Logtestijn, G.B.J. Rijs, J.T.A. Verhoeven (2003) Water and mass budgets of a vertical-flow constructed wetland used for wastewater treatment. Ecological Engineering 20:31-44.

Mitsch, W.J., J.W. Day, L. Zhang, and R.R. Lane (2005) Nitrate-nitrogen retention in wetlands in the Mississippi River Basin. Ecological Engineering 24:267-278.

Molénat, J. and Gascuel-Odoux, C. (2002) Modelling flow and nitrate transport in groundwater for the prediction of water travel times and of consequences of land use evolution on water quality. Hydrological Processes 16: 479-492.

Moomaw, W.R. (2002) Energy, industry and nitrogen: Strategies of decreasing reactive nitrogen emissions. Ambio 31(2):184-189.

Mosier, A.R. (2002) Environmental challenges associated with needed increases in global nitrogen fixation. Nutrient Cycling in Agroecosystems 63:101-116.

Mosier, A.R., M.A. Bleken, P. Chaiwanakupt, E.C. Ellis, J.R. Freney, R.B. Howarth, P.A. Matson, K. Minami, R. Naylor, K.N. Weeks and Z.-L. Zhu (2002) Policy implications of human-accelerated nitrogen cycling. Biogeochemistry 57/58: 477-516.

Mulholland, P.J., A.M. Helton, G.C. Poole, R.O. Hall Jr., S.K. Hamilton, B.J. Peterson, J.L.Tank, L.R. Ashkenas, L.W. Cooper, C.N. Dahm, W.K. Dodds, S.E.G. Findlay, S.V. Gregory, N.B. Grimm, S.L. Johnson,W.H. McDowell, J.L. Meyer, H.M. Valett, J.R. Webster, C.P. Arango, J.J. Beaulieu, M.J. Bernot, A.J. Burgin, C.L. Crenshaw, L.T. Johnson, B.R. Niederlehner, J.M. O'Brien, J.D. Potter, R.W. Sheibley, D.J. Sobota, and S.M. Thomas (2008) Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452:202-204.

Mulholland, P.J., J.L. Tank, D.M. Sanzone, W.M. Wollheim, B.J. Peterson, J.R. Webster, and J.L. Meyer (2000) Nitrogen cycling in a forest stream determined by a ^{15}N tracer addition. Ecological Monographs 70(3): 471-493.

Nangia, V., P.H. Gowda, and D.J. Mulla (2010) Effects of changes in N-fertilizer management on water quality trends at the watershed scale. Agricultural Water Management 97:1855-1860.
Nolan, B.T. (1999) Nitrate behavior in ground waters of the Southeastern USA. Journal of Environmental Quality 28: 1518-1527.

Ocampo, C.J., C.E. Oldham, and M. Sivapalan (2006) Nitrate attenuation in agricultural catchments: Shifting balances between transport and reaction. Water Resources Research 42, WO1408: 16 p.

Ostrom, N.E., L.O. Hedin, J.C. von Fischer, and G.P. Robertson (2002) Nitrogen transformations and NO_3^- removal at a soil-stream interface: A stable isotope approach. Ecological Applications 12(4): 1027-1043.

Peiffer, S. (2000) Characteristics of the redox state of aqueous systems: Towards a problem-oriented approach. In Schuering, J., H.D. Schulz, W.R. Fischer, J. Boettcher, W.H.M. Duijnisveld (Eds.) Redox: Fundamentals, processes and applications. Springer-Verlag, p. 24-41.

Peterson, B.J., W.M. Wolheim, P.J. Mulholland, J.R. Webster, J.L. Meyer, J.L. Tank, E. Marti, W.B. Bowden, H.M. Valett, A.E. Hershey, W.H. McDowell, W.K. Dodds, S.K. Hamilton, S. Gregory, D.D. Morrall (2001) Control of nitrogen export from watersheds by headwater streams. Science 292: 86-90.

Poor, C., and J.J. McDonnell (2007) The effects of land use on stream nitrate dynamics. J. Hydrology 332:54-68.

Postma, D. and R. Jakobsen (1996) Redox zonation: Equilibrium constraints on the Fe(III)/SO_4^{-3} reduction interface. Geochimica et Cosmichimica Acta 60(17) 3169-3175.

Puckett, L.J. and T.K. Cowdery (2002) Transport and fate of nitrate in a glacial outwash aquifer in relation to ground water age, land use practices, and redox processes. Journal of Environmental Quality 31: 782-796.

Puckett, L.J., T.K. Cowdery, P.B. McMahon, L.H. Tornes, and J.D. Stoner (2002) Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system, Water Resour. Res. 38:1-20.

Rabalais, N. Nitrogen in aquatic ecosystems (2002) Ambio 31(2):102-112.

Ribolzi, O., P. Andrieux, V. Valles, R. Bouzigues, T. Bariac, M. Voltz (2000) Contribution of groundwater and overland flows to storm flow generation in a cultivated Mediterranean catchment. Quantification by natural chemical tracing. Journal of Hydrology 233:241-257.

Rivera-Monroy, V.H., P. Lenaker, R.R. Twilley, R.D. Delaune, C.W. Lindau, W. Nuttle, E. Habib, R.W. Fulweiler, E. Castañeda-Moya (2010) Denitrification in coastal Louisiana: A spatial assessment and research needs. Journal of Sea Research 63: 157-172.

Rutherford, J.C. (1994) River Mixing. John Wiley, New York. 362p.

Rutherford, J.C., and M.AL. Nguyen (2004) Nitrate removal in riparian wetlands: Interactions between surface flow and soils. J. Environ. Qual. 33:1133-1143.

Schipper, L.A., A.B. Cooper, C.G. Harfoot, and W.J. Dyck (1994) An inverse relationship between nitrate and ammonium in an organic riparian soil. Soil Biol. Biochem. 26:799-800.

Seaman, J. C., P.M. Bertsch, S.F. Korom and W.P. Miller (1996) Physicochemical controls on nonconservative anioin migration in coarse-textured alluvial sediments. Ground Water 34(5):778-783.

Seo, D.C., and R.D. DeLaune (2010) Fungal and bacterial mediated denitrification in wetlands: Influence of sediment redox condition. Water Research 44: 2441-2450.

Showstack, R. (2000) Nutrient over-enrichment implicated in multiple problems in U.S. waterways. EOS 81(43): 497-499.

Sigg, L. (2000) Relevance of redox potential measurements. In Schuering, J., H.D. Schulz, W.R. Fischer, J. Boettcher, W.H.M. Duijnisveld (Eds.) Redox: Fundamentals, processes and applications. Springer-Verlag, p. 1-12.

Sliggers, J. and W. Kakebeeke, eds. (2004) Clearing the Air: 25 years of the Convention on Long-range Transboundary Air Pollution. United Nations , 180p.

Smil, V. (2002) Nitrogen and food production: Proteins for human diets. Ambio 31(2):126-131.

Smith, M.S.. and J.M. Tiedje (1979) Phases of denitrification following oxygen depletion in soil. Soil Biol. Biochem. 11:261-267.

Snoeyink, V.L. and D. Jenkins (1980) Water Chemistry. John Wiley & Sons, 463p.

Stark, J.M., D.R. Smart, S.C. Hart, and K. A. Haubensack (2002) Regulation of nitric oxide emissions from forest and rangeland soils of western North America. Ecology 83(8): 2278-2292.

Stumm, W. and J.J. Morgan (1996) Aquatic chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd Edition. John Wiley and Sons, Inc.

Suthersan, S. (1996) Remediation Engineering: Design Concepts. Lewis Publishers, 362 p.

Tiedje, J. M., J. Sorensen and Y.-Y.L. Chang (1981) Assimilatory and dissimilatory nitrate reduction: Perspectives and methodology for simultaneous measurement of several nitrogen cycle processes. Ecol. Bull. (Stockholm) 33: 331-342.

Triska, F.J., V.C. Kennedy, R.J. Avanzino, G.W. Zellweger, and K.E. Bencala (1989) Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes. Ecology 70(6): 1893-1905.

Triska, F. J., Pringle, C.M., Zellweger, G.W., Duff, J.H., and Avanzino, R.J. (1993) Dissolved inorganic nitrogen composition, transformation, retention and transport in naturally phosphate-rich and phosphate-poor environments. Canadian Journal of Fisheries and Aquatic Science 50: 665-675.

UNEP (2010) UNEP Year Book: New Science and Developments in our Changing Environment 2010. United Nations Environmental Programme. 66p.

USEPA (2007) Nutrient Criteria Technical Guidance Manual: Wetlands. EPA-822-R-07-004.

USEPA (2009) Natural Water Quality Inventory: Report: to Congress, 2004 Reporting Cycle. Office of Water EPA-841-R-08-001, 37p.
Van Breemen N., E.W. Boyer, C.L. Goodale, N.A. Jaworski, K. Paustian, S.P. Seitzinger, K. Lajtha, B. Mayer, D. Van Dam, R.W. Howarth, K. Nadelhofer, M. Eve and G. Billen (2002) Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern U.S.A. Biogeochemistry 57/58: 267-293.

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.

Wagner, B.J. and J.W. Harvey (1997) Experimental design for estimating parameters of rate-limited mass transfer: Analysis of stream tracer studies. Water Resources Research 33:1731-1741.

Washington, J.W., D.M. Endale, L.P. Samarkina and K.E. Chappell (2004) Kinetic control of oxidation state at thermodynamically buffered potentials in subsurface waters. Geochimica et Cosmochimica Acta 68, 4831-4842.

Washington, J.W., R.C. Thomas, D.M. Endale, K.L. Schroer, and L.P. Samarkina (2006) Groundwater N speciation and redox control of organic N mineralization by O_2 reduction to H_2O_2. Geochimica et Cosmochimica Acta 70:3533-3548.

Weber, R. and J. Fripp (2010) Understanding fluvial systems: Wetlands, streams and floodplains. USDA/NRCS Technical Note No. 4, 26p.

Whitten, K.W. and K.D. Gailey (1981) General Chemistry. Saunders College Publishing, 621 pgs.

Yang, X. and W. Jin (2010) GIS-based spatial regression and prediction of water quality in river networks: A case study in Iowa. J. Environ. Management 91:1943-1951.

Zumdahl, S.S. and S.A. Zumdahl (2000) Chemistry. Houghton Mifflin Company, 1143p.

[1]CHAPTER 3

EVALUATING DENITRIFICATION IN TWO SMALL, ADJACENT WETLAND STREAMS WITH TRACER INJECTION TESTS IN THE GEORIGA PEIDMONT

---

[1] Schroer, K.L., D.M. Endale, J.W. Washington, R.C. Thomas and V. Nzengung. To be submitted to *Water Resources Research*.

Abstract

A small wetland has been modified to study the effect of different flow-source terms on N cycling. Two adjacent shallow streams flow through a small wetland draining a cattle pasture. Surface runoff is prevented from flowing to the Protected Stream by a man-made earthen berm, the stream channel had been dredged, and there is a flowing spring at its headcut. The adjacent Runoff Stream (14m apart at headcut) accepts water and soil runoff from the up-gradient pasture. Four seasonal tracer injection tests were conducted to evaluate wetland stream response to a pulse of high but realistic concentration of [NO_3^--N] (50mg/L at the point of mixing). Mixed nitrate and bromide tracer were pumped at a steady rate for 30 minutes into the Protected Stream during the spring, fall, winter and summer tracer tests, and simultaneously into both streams during the summer test. Downstream samples were collected during the rise, plateau and fall of the tracer breakthrough curves and analyzed for field parameters (DO, SpC, pH, T and discharge); reduced N ions, ([NO_2^--N], [NH_4^+-N]); [Br^-]; [Fe^{2+}]; [Fe_{total}]; [SO_4^{2-}]; [DOC]; [Cl^-]; and dissolved gases [N_2O], [$H_2CO_3^*$], [CH_4] and [H_2]. Tracer [N]/[Br^-] and mass recoveries, electron mass balances, and stream N removal efficiencies (with/without tracer) were also calculated. The hypothesis, which cannot be rejected, was that residence time exerts a primary control on nitrate removal. Denitrification and/or nitrate reduction to ammonia were important tracer N removal processes during the Runoff Stream summer and Protected Stream fall tracer tests. Addition of tracer spike did not cause a disproportionately large increase in N removal rates from the Protected Stream. Organic carbon was the main electron donor in both streams. However, sulfide and ferrous iron may have been important secondary reductants. These results constrain processes that affect nitrate N removal efficiency in agricultural wetland streams.

Introduction

Nitrogen (N) cycle research focuses on anthropogenic releases to the environment (e.g., Howarth et al., 2002), transport pathways (e.g., Galloway et al., 2008), loads to receiving basins (e.g., Mitsch et al.; 2005), and human health consequences (e.g., USEPA, 2009). Many process-level aspects of N cycling are not well understood. Examples include: 1) difficulties in quantifying nitrate export from wetlands and headwater streams due to multiple oxidative, spatial and temporal scales over which N-cycling takes place (Ocampo et al., 2006); 2) internal processes that allow constructed or restored wetlands to remove periodic releases of non-point source nitrate (Kadlec, 2010); 3) processes that *limit* nitrate removal in wetlands (Bastviken et al., 2009); and 4) the relative influence of environmental variables on nitrous oxide emissions during nitrate reduction in river sediments (Laverman et al., 2010). Understanding environmental controls on denitrification and its end products in natural settings, as well as the best methods to study them, still needs refinement (Inwood et al., 2007).

Based on a 2-year monthly, dry-weather sampling program, (data reported in Chapter 4) NO_3^- -N concentrations in two short (60-70m) mutually proximal (14m apart at headcut) agricultural wetland streams decreased from 6-9mg/L at the headwaters to 2-4mg/L at their confluence. The two streams have different flow-source terms, as described below. One of the streams, the Runoff Stream, often had higher initial nitrate concentration and greater loss along the flow path than the Protected Stream. However, it was not clear to what extent the lower nitrate concentration was due to ground water flux through the streambed, temporary storage in the system (e.g., uptake by plants, hydrologic retention), or loss of N to the atmosphere as N_2O or N_2 gas. During the study period, dissolved O_2 concentrations were about the same in the two streams. In contrast, alkalinity, NO_2^- -N, NH_4^+-N, and Fe^{2+} were higher - and dissolved CH_4 and organic C (DOC) significantly higher - in the Runoff than in the Protected Stream.

In 3 seasonal tracer injection experiments (spring, winter, fall), a collaborating team consisting of USDA-NRCS, USEPA and University of Georgia scientists pumped nitrate (about 50mg/L at point of mixing in the stream) and bromide (about 10mg/L at point of mixing) dissolved in 10L of water at a constant rate for 30 minutes into the headwaters of the Protected Stream. In a summer experiment, we injected tracer simultaneously into both the Protected and Runoff Streams. We collected samples at mid- and, more intensively, downstream sampling stations for about 6 hours. The purpose of these experiments was to establish stream hydrologic characteristics, determine extent of N loss, and evaluate which dominant processes explain the observed nitrate loss along each of the two wetland streams. This was accomplished by 1) evaluating four seasonal tracer injection breakthrough curves at three (upstream, midstream, downstream) sampling locations in each of the two wetland streams; 2) calculating nitrate/bromide recoveries, to infer the extent to which uptake and/or transformation caused the observed downstream decrease in nitrate concentrations; and 3) for the dual-stream, summer experiment, evaluate downstream changes in concentrations of reduced N and other redox-sensitive species during the course of the experiments. Answers to these case-study questions contribute to our understanding of how site-specific conditions (hydrology and biogeochemistry) across relatively short times and distances affect transformation of nitrate into potentially less harmful species before entering first-order streams.

Background and Setting

Role of Wetland Streams in N Storage and Removal

Manure and anthropogenic N fertilizer has been applied in varied amounts, locations and seasons, which often exceeds target crops' capacity for uptake (Poor and McDonnell, 2007; Nangia et al., 2010). Population increase and poor management also have caused more reactive nitrogen to be released from municipal waste and septic systems (Meile, et al., 2010) and through concentrated animal feeding operations (USEPA, 2009). Along coastal regions, covering a quarter of a million square miles, more than 400 dead zones have been documented and attributed to eutrophication and consequent anoxia/hypoxia, (UNEP, 2010). Additionally, countless eutrophic small lakes and ponds in the U.S. are thought to be similarly affected (USEPA, 2009). In the U.S., more than 70% of anthropogenic N is stored, denitrified or volatilized in watersheds, with less than 30% reaching the oceans (Howarth et al., 2002, Mayer et al., 2002).

A major role of treatment wetlands is to reduce nitrate loadings from upland sources to higher-order streams (Kadlec, 2010). Controls on rates of nutrient losses are known to include the complex interactions between several inter-dependent factors, including climate, hydrology, and the local bio-geochemical environment (Botter et al., 2010). In shallow streams or near the riparian zone, some stream nitrate may be taken up by plants (Maître et al., 2003). Wetlands become seasonally established with respect to N assimilation due to plant uptake. Under these conditions, N removal is due mainly to denitrification (Cooper, 1994).

In non-wetland streams and other surface water bodies such as lakes and estuaries, denitrification generally is the main pathway for removal of nitrate (Peterson et al., 2001; Rivera-Monroy et al., 2010). Depending on local conditions, higher nitrate loading to streams increases the rate of dentrification, although removal *efficiency* decreases as nitrate loads continue to increase (Silvennoinen et al., 2008).

Denitrifying bacteria are present in stream waters, although the presence of dissolved O_2 inhibits denitrification due to repression of synthesis of nitrate reductase (Madigan et al., 2003). Some microbes can denitrify in the presence of oxygen, such as *P. denitrificans.* Other denitrifiers (e.g., *T. pantotropha)* can tolerate substantial oxygen (Kaplan and Wofsy, 1985; Ferguson, 1994,). Fungi also are capable of reducing nitrate. Seo and DeLaune (2010) observed that denitrification by wetland fungi was optimal in aerobic or weakly reducing conditions, whereas bacteria reduced nitrate in strongly reducing conditions. For many bacteria, nitrate and nitrite reductases are inhibited when oxygen concentration exceeds about 7% saturation, whereas nitrous-oxide reductase can be expressed at lower levels of oxygen (Ferguson, 1994).

Denitrification reaction rates and directions may vary over short distances. Many studies (e.g., Kellman and Hillaire-Marcel 1998, Bastviken et al., 2003) have shown that wetland denitrification rates were highest in organic-rich bottom sediments. As much as 30-40% of nitrate nitrogen can be denitrified in stream-bottom sediments and in riparian zones (Thieu et al., 2009). Denitrifying bacteria also are associated with the surfaces of some submersed wetland plants and wood matter (Bastviken et al., 2003). Particulate and dissolved organic C may be vertically distributed in the water column in some settings, which enhances in-stream biological denitrification (Bastviken et al., 2003).

A related driver for dentrification is the availability of potential electron donors. Biological denitrification requires organic C for cell growth (Smith and Tiedje, 1979). When organic matter serves directly as the electron donor, complete denitrification can be represented by:

$$5CH_2O + 4\,NO_3^- + 4\,H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O \qquad (3.1)$$

This is a net reaction, as nitrate usually is reduced through steps to nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O) (Aravena and Robertson, 1998, Rivera-Monroy et al., 2010).

Inorganic species such as Mn^{2+}, Fe^{2+}, and S^- also serve as electron donors in the chemical reduction of N (Korom, 1992; Kappor, 1997). Reduced lake-bottom sulfide species (e.g., amorphous iron monosulfides, mackinawite and pyrite) are a source of sulfate when electron acceptors such as nitrate are present (Holmer and Storkholm, 2001). For pyrite, the reaction is:

$$14NO_3^- + 5FeS_2 + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \qquad (3.2)$$

The above reaction can be facilitated by autotrophs (Molénat and Gascuel-Odoux, 2002) or abiotically in oxic conditions (Jorgensen et al., 2009). Ferrous iron released in this reaction can provide electrons for further nitrate reduction:

$$5Fe^2 + NO_3^- + 7H_2O \rightarrow 5FeOOH + 1/2\,N_2 + 9H^+ \qquad (3.3)$$

Yielding the overall reaction (Aravena and Robertson, 1998):

$$5FeS_2 + 15NO_3^- + 5H_2O \rightarrow 10SO_4^{2-} + 7.5N_2 + 5FeOOH + 5H^+ \qquad (3.4)$$

The above reactions have been reported in ground water studies under anaerobic conditions, where nitrate-rich water is in contact with soil pyrite longer than in streams. In aerobic conditions, denitrification with sulfide as the electron donor is facilitated by lithoautotrophic bacteria as (Beristain-Cardoso, 2009):

$$S^{2-} + 1.6NO_3^- + 1.6H^+ \rightarrow SO_4^{2-} + 0.8N_2 + 0.8H_2O \qquad (3.5)$$

Ferrous iron also may be available from clay minerals and amorphous iron hydroxides (Ernstsen, 1996). For example, Endale et al. (2003) determined that denitrification at the headcut spring in this current study was coupled to oxidation of ferrous iron (in the up-gradient, shallow, iron-rich saprolite aquifer) and to $Fe(OH)_3$ production.

Stream hydrological processes exert an additional control on a wetland's capacity to remove nitrate N. Hydrological retention occurs in areas of a stream channel where velocity decreases or where flow is physically obstructed by rocks, fallen logs, abundant leaf litter or beaver dams, or where there are recirculation pools at stream margins (Triska et al., 1989; Edwards, 1998). Hydraulic storage of nitrate and other solutes retards transport in some streams (e.g., Triska et al., 1989). Stream water also can continually flow into and out of the hyporheic zone (i.e., a shallow layer of stream-bottom sediment at the interface between stream and ground water). This is mainly due to pressure-driven advection caused by irregularities on the stream-bottom surface (Jonsson et al., 2003; Rutherford and Nguyen, 2004). The depth of exchange with the hyporheic zone is determined by the morphology of the stream channel, roughness of the stream bed and permeability of the bottom sediments (Triska et al., 1989).

Tracer Injection Experiments

Tracer injection experiments are useful for examining physical and chemical characteristics along a flow path (Field 2002). For example, tracer experiments have been used to model hyporheic exchange of stream solutes (Jonsson et al., 2003) and to characterize transient N storage in different stream reaches (Manson, 2000). Co-injection of stable and chemically reactive tracers distinguishes between processes that affect both tracers, such as dilution, and processes that affect only the concentration of the reactive tracer (Triska et al., 1993). Common conservative tracers include dye (e.g, Rhodamine WT, florescein) and bromide. Each "conservative' tracer has advantages and disadvantages, depending on the setting and/or duration of the tracer experiment. For example, florescein photodegrades with a half-life of about 3 days (Martin et al., 1999), Rhodamine WT sorbs to sediments, and bromide is a potential precursor to disinfection by-products in drinking water (Lin et al., 2003). Also, bromide is non-conservative in sediments high in iron oxide solids (Seaman et al., 1996). Conservative tracers also help establish travel times between the point of injection and downstream collection points, and thus are useful for estimating stream velocities (Triska et al., 1993).

Reactive tracers are the chemical species being studied to determine their fate in specific settings. For example, nitrate tracer studies distinguish the effects of physical processes such as dilution and hydrologic storage (which affects both tracers) from the sum of all transformation processes such as denitrification, microbial immobilization and plant uptake (Triska et al., 1993; Verchot et al., 1997; Burns and Nguyen, 2002; Jonsson et al., 2003). Tracer experiment design depends on study objectives and local conditions, and there are major trade-offs when choosing one injection or sampling strategy over another (Wagner and Harvey, 1997). In some cases, a preliminary tracer test may be necessary in order to obtain the transport properties that are necessary to design a robust tracer experiment (Field 2002). Major considerations include desired concentration at the point of injection, injection rate and duration, volume of injectate, number and locations of down-gradient sampling points, sampling frequency at each sampling point, and lower detection limits of the tracers. Synoptic sampling usually is conducted when there is more than one down-stream sampling location (Triska et al., 1993). When both reactive and conservative tracers are used, they are injected simultaneously (Jonsson et al., 2003).

Injection durations may vary depending on factors such as travel time, distance from injection to collection points, and anticipated reaction times. Tracers can be introduced via: 1) an instantaneous dose or pulse (Burns and Nguyen, 2002); 2) a constant-rate injection (Kilpatrick and Cobb, 1985); or 3) a short duration rise-plateau-fall design in small streams (Field, 2002; Triska et al., 1993). Wagner and Harvey (1997) found that sampling throughout the rise, plateau and fall after a short duration injection provided more reliable estimates of stream parameters such as dispersion coefficients, ground-water inflow, and storage times than either single pulse or constant-stream injections.

A reactive tracer has not been bio/chemically transformed if downstream reactive and conservative tracer concentrations in the stream have the same ratios as their concentrations in the injectate (Burns and Nguyen, 2002), minus stream background concentrations (Verchot et al., 1997). A greater loss of reactive tracer such as nitrate indicates that nitrate has been removed along the stream reach, but does not distinguish between removal processes (i.e., biological assimilation, plant uptake or denitrification). To estimate tracer loss, the mass (area under load vs time curve) at each downstream sampling location is compared to the mass of reactive and conservative tracer added to the stream (Jonsson et al., 2003). Loss of conservative tracer indicates either storage or loss through the streambed or loss by photo-oxidation. Note that conservation of mass can only be calculated if cross-stream mixing imparts little variability above or at the sample collection point (Rutherford, 1994).

Conservative tracers sometimes are present in reliably consistent background concentrations that are useful for conservation of mass calculations. For example, agricultural runoff often contains high chloride, which is an effective conservative tracer because it does not react under most conditions (Kirchner et al., 2001).

Field Setting

The study site is at the U.S. Department of Agriculture (USDA) J. Phil Campbell Sr., Natural Resources Conservation Center in Watkinsville, GA. All of the laboratory work was conducted at the U.S. Environmental Protection Agency (USEPA) Office of Research and Development, National Exposure Research Laboratory, Ecosystems Research Division in Athens, Georgia, about 10 km from the field site. The field site is in the Oconee River Watershed, Southern Piedmont Physiographic Province between the Southern Appalachian Mountains and the Georgia Coastal Plain. Local soil type is Cecil and Pacolet series, clayey, koalinitic, thermic, Typic Kanhapludult. A saprolite layer, <8 to >21 meters depth and developed on the Athens Gneiss, which also forms an unconfined aquifer through which shallow ground water flows to the wetland (Washington et al, 2004).

The research area (Figure 3.1) is a small (92m long, 40m wide) vegetated depression at the base of USDA's Watershed 2, which is about 10ha. Most of this area was in cow pasture and vegetated buffer around the wetland. A small portion of the watershed draining to the wetland was in rotating crop (e.g., cotton, sorghum, pearl millet, barley, clover, rye (D. Endale, pers. comm.)). The cropped area was slightly below grade, inhibiting most surface runoff toward the wetland. However, the wetland likely is hydrologically connected to a portion of the cropped area via shallow ground water flow through the saprolite and/or underlying fractured bedrock. During the study period (2003-2005), the upgradient pasture was fertilized once or twice per year at a rate of 57-114 kgN/ha (Muckler, 2010). At varying intervals, averaging about one week in every six, 80-100 cows were rotated into the pasture immediately up-gradient and beyond the catchment of the study wetland. Cattle waste is high both in N and available organic C (van Groenigen et al., 2004). Local climate is seasonally variable with hot, humid summers and cool winters with frequent sub-freezing temperatures at night. The study period, 2003-2005 had annual rainfalls of 52, 48 and 61 cm, respectively (Georgia Forestry Commission, 2011), which were the rainiest years between 1998 and 2008. Vegetation in the depression includes both forest (e.g., oak, privet) and wetland species (e.g., duckweed, other prevalent grasses, and willow).

There are three main differences between the Protected Stream located to the north and the Runoff Stream to the south. Firstly, a man-made berm prevents most surface water runoff to the Protected Stream, whereas the Runoff Stream is open to the cow pasture. Secondly, the Protected Stream has a perennial spring flowing from its headcut whereas the Runoff Stream has no conspicuous spring at its headcut. A few years prior to the beginning of this study, a small H-flume was built into the headcut just below the spring. Water discharged from the spring flows across the flume and over the spillway, ~37cm above the stream surface. A wooden vertical barrier 6cm high and 1.6m wide - the full width of the stream at this point - facilitates horizontal mixing of the spring water upon discharge to the Protected Stream. Discharge at the spring is measured at the spillway with a bucket and stopwatch. Rates ranged from 7-31 L/min, with an average of 23 L/min. For the four tracer injection experiments, discharge at the spring ranged from 14-29 L/min (Table 1). Discharge in the Protected Stream generally is higher, approximately 2-5 times that in the Runoff Stream. Finally, the Protected Stream is 63 meters long from headcut to its confluence with the Runoff Stream, whereas the more meandering Runoff Stream is 70 meters long. Distance between points of injection to the downstream sample locations were 58m in the Protected Stream and 52m in the Runoff Stream. Both streams are shallow (5 - 20 cm deep), narrow (0.1 – 1.2m wide) and slow (velocity ranged from 0.6 – 0.9 m/min during tracer experiments). Soil between the two streams was at or near saturation during most of the study period, based on water-logging in the wake of footprints and the presence of numerous small (0.08 – 0.5m^2) pools, especially in down-gradient, inter-stream areas of the depression. During the two-year study period, Station 4 (Protected Stream) average field parameters were: temperature 17.4°C with a standard deviation (+/-) of 3.9; dissolved oxygen 5.2mg/L (+/- 2.3); pH 6.0 (+/- 0.3); and specific conductance was 80.2µS/cm (+/- 7.2). Average field parameters at Station 3 (Runoff Stream) were: temperature 15.9°C (+/- 6.0); pH 6.4 (+/- 0.3); dissolved O_2 5.0mg/L (+/- 2.4) and specific conductance 114.5µS/cm (+/- 10.6). Background stream conditions are discussed further in Chapter 4.

Methodology

Ten sampling stations were established at the head-cut spring (Station 8), an upstream location in the Runoff Stream (Station 5) at mid- (Stations 6 and 10) and downstream (Stations 3 and 4) locations of both streams, at a point about 12 meters downstream of their confluence (Station 2), and at the large downstream flume (Station 1) (Figure 1). Samples were collected approximately monthly for two years and analyzed for several N and other redox-sensitive species (results are discussed in Chapter 4).

Based on stream residence time determined by preliminary dye tracer results, a 30 minute injection was selected for the tracer tests. This made it possible to capture the breakthrough curves as they passed each of the three sampling locations and for tracking the changes in other downstream chemical parameters during the rise and fall of the tracer plume. Bromide was chosen as the conservative tracer because studies have shown that it is conservative for at least 10 days in wetland sediments (Cooper 1994). We determined optimal concentrations at the point of mixing at 50mg/L (3.57mM) NO_3^--N and 10 mg/L (0.12mM) Br. Nitrate target concentration was based on the highest measured nitrate concentration at the spring, which was about 47 mg/L NO_3^- -N (D. Endale, pers. comm.). Thus, a target of 50 mg/L NO_3^--N at the point of mixing would provide tracer decay data of a substantial but realistic concentration. Tracer masses added to achieve the target concentration increased the 24-hour NO_3^--N load delivered at the spring by only about 10%, and were lower than some maximum background loads recorded at the site. The target concentration for bromide was 10 mg/L (0.12mM) at the point of mixing, which provided sufficient [Br^-] for analysis.

The full calculation for mass of calcium nitrate that was injected at a constant rate over a 30 minute period is:

([Q at spring] L/min) (30 min) ([50-BG] mg N/L) (236.15g $Ca(NO_3)_2{\bullet}4H_2O$ / 28gN) (1g/1000mg)
= Xg $Ca(NO_3)_2{\bullet}4H_2O$ (3.6)

where BG is the background NO_3^--N concentration at the point of mixing.
The calculation for bromide is similar except that the target concentration at the point of mixing is 10 mg/L (0.12mM) and the negligible background concentration was not subtracted.

To capture tracer breakthrough curves at each station efficiently, the study design included more frequent sampling at each sampling station prior to the tracer plume arrival, with a decrease in sampling frequency at upstream stations as [NO_3^{-}N] decreased to background levels.

Field Methods

One week before the first tracer test, a preliminary florescein dye tracer test was conducted. Although the green dye was difficult to track against the wetland vegetation, it provided data on the velocity of the leading front of the dye plume at about 15 locations with an average distance of 4m apart. Results (not included) of this preliminary dye test indicated that the front of the dye plume passed the downstream sampling location (Station 4) at t=90 minutes and that the main body of the dye plume passed at about t=100 minutes. The day before each of the four tracer tests, grab samples from the spring were analyzed for NO_3^- -N using a Hach DR 2800 Spectrophotometer and Hach NitraVer Accuvac ampules (Cadmium Reduction Method 8039, wavelength 500nm, range 0-30.0 mg/L NO_3^- -N).

Tracer $Ca(NO_3)_2 \bullet 4H_2O$ and NaBr were weighed and brought to 10L with deinoized water in a 20L capacity Nalgene polypropylene (PP) carboy and mixed slowly on a stir plate overnight. At the onset of each test (9:45 – 10:30am), the tracer was pumped from the carboy through Tygon tubing using a MasterFlex E/S Portable Sampler peristaltic pump for 30 minutes, at a constant rate of 0.33L/min. The point of injection was about 1m downstream of the headcut flume in Protected Stream and 2m upstream of Station 5 in the Runoff Stream. During and after injection, samples were collected every 10 minutes (15 for the Spring 2004 experiment) during the rising and falling limbs of the tracer breakthrough curves. The plume movement in the creek was followed by visually tracking Rhodamine WT dye injected during the first tracer test. During subsequent (no dye) experiments, the plume was tracked using the portable Hach Spectrophotometer and NitraVer Accuvac ampules, which have a 1- minute mixing and 5-minute reaction time. Nitrate concentrations obtained using the field spectrophotometer also provided a range of concentrations to expect from subsequent quantitative analysis using ion chromatography. The stream-water samples were collected at up-, mid- and downstream locations based on a combination of a sampling schedule and tracking of the plume using the portable spectrophotometer.

Sampling at the downstream stations (Station 4 in the Protected Stream (all experiments) and Station 3 in the Runoff Stream (summer tracer test only)) included conventional field parameters, and sampling for iron and dissolved gas analysis in addition to the water samples collected at up- and mid-stream locations (fig 3-1). Field parameters were measured with portable probes: pH, T (Orion Model 250A+), Dissolved Oxygen, T (YSI Model 55), Specific Conductance, T (YSI Model 30). The stream samples were collected in 125mL Nalgene high-density polyethylene (HDPE) bottles, rinsed 3 times with sample and submerged approximately to the midpoint of stream depth or, where depth was very shallow, held horizontally to allow flow to enter the bottle. Bottles were kept in coolers and put in freezers upon return from the field. Samples for iron analysis were collected in 50mL glass serum bottles. The morning of each test, the serum bottles were prepared by adding 10μL of 12.35M HCl, capped with a septum, crimp-sealed and purged using two needles (one for delivery, one for outflow) of N_2 gas for one minute at a flow rate of 115-120mL/min. In the field, samples for iron analysis were collected with a glass syringe. The syringe and stainless steel needle were pre-rinsed 3 times with sample and injected into the prepared serum bottles through 0.22 um filters, then rinsed 3 times with dionized water. Samples for gases were collected at Station 4 (and Station 3 for the summer experiment) with the peristaltic pump in custom-made 1 L glass jars with lower inflow and upper outflow ports. The morning of each tracer test, gas sample bottles were purged with ultra-high purity N_2 gas for 20 minutes. Gas sample bottles were placed in coolers and, after 2 sampling rounds from each stream, driven to the USEPA laboratory for immediate analysis, washed, air-dried, and returned to the field, while remaining bottles were on hand to continue sampling.

Analytical Methods

Samples were analyzed in the laboratory for NO_3^-, Br^-, Cl^-, SO_4^{--} (Dionex Anion Ion Chromatograph (IC) with a specific-conductivity dectector (SpCD) for the Spring 2004 tracer test; Metrohm Peak dual-channel (cation/anion) IC (SpCD) for the three subsequent tracer tests) dissolved NO_2^- (Diazotization, Hach DR 2010 Spectrophotometer). Ammonia was analyzed using the Phenate method (Washington et al., 2004 after Clesceri et al., 1998). Dissolved gases (N_2O, H_2 CH_4, CO_2) were analyzed with Agilent 6890 Gas Chromatograph (ECD/TCD, Washington et al., 2004). Iron (II, III and total) was analyzed using the Ferrozine/spectrophotometer method (Washington et al., 2004, after Viollier et al., 2000). Finally, dissolved organic carbon (DOC) was analyzed on a Shimadzu 5050A Total Organic Carbon Analyzer.

Data Analysis

1) Instantaneous N Recovery:

Instantaneous nitrate-N recovery for samples collected at the downstream sampling locations were calculated as (modified from Valett et al. (1996) and Triska et al. 1993).

$$\text{N Recovery} = [NO^-_3 - N]_t \,/\, {}_{,}f[Br]_t \qquad (3.7)$$

where subscript t designates an instantaneous sample at time t.

$$f[Br]_t = [NO^-_3 - N]_{BG} + (([NO^-_3]/[Br^-])_{inject} \times [Br^-]_t) \qquad (3.8)$$

where BG is background, inject is tracer injectate prepared at the laboratory, and t is measured from samples for each sampling time.

Note that $[Br^-]_t$ is the only measured and temporally changing variable on the right side in equation 3.8; $f[Br]_t$ takes into account both different N and Br^- tracer masses in the injectate, and background (pre-injection) $[NO^-_3 - N]$ at the downstream sampling location. The $[NO^-_3 - N]/[Br^-]$ ratio in the injectate was about 4.5:1 as measured in mg/L (25:1 in molar concentrations). However, this ratio varies between the tracer tests because $[NO^-_3 - N]_{BG}$ at the point of injection was different for each tacer test (Table 3.1).

$[NO^-_3]_t$ equaled $f[Br^-]_t$ and N Recovery was 1 where nitrate behaved as conservatively as bromide along the stream flow paths. When $[NO^-_3]_t < f[Br^-]_t$, nitrate has been transformed and/or assimilated in the wetland. Background stream bromide was below detection (no peaks) (Dionex IC) for the spring, 2004 study. For the remaining tracer tests (Metrohm Peak IC), background bromide concentrations ranged from below detection to 0.27μM, with an average of 0.049 μM. The very low background concentration of bromide is modeled as 0mM in N Recovery calculations.

2) Estimating Flow in Protected and Runoff Streams:

Agricultural runoff often contains high chloride, which is an effective conservative tracer because it does not react in most conditions (Kirchner et al., 2001). In the study wetland for this project, $[Cl^-]$ in the Runoff Stream was consistently twice that in the Protected Stream. Stream velocity at Stations 3 and

4 is too low, and the streams too shallow, to measure discharge using velocity/transect profiles. In low flow streams such as these, where discharge is difficult to measure, background chloride can be used to establish mass conservation, which then can be used to calculate background nitrate loads and, from that, discharge (Ribolzi et al., 2000). Discharge was calculated using the consistent difference in background chloride concentrations in the two streams and assuming that $[Cl^-]$ at Station 1, where discharge can be measured at the downstream flume, is due to mixing of waters from the two wetland streams. Equations relating chloride concentrations to discharge at Stations 3 and 4 are (Triska et al., 1989; Schroer et al., 2007):

$$Q_1 = Q_3 + Q_4 \tag{3.9}$$

$$Q_1 [Cl^-]_1 = Q_3[Cl^-]_3 + Q_4 [Cl^-]_4 \tag{3.10}$$

where Q_1 was measured in the field and $[Cl^-]_1$, $[Cl^-]_3$ and $[Cl^-]_4$ were quantified in the laboratory using ion chromatography. Combination and rearrangement of terms in Eq 3.10 provides estimates of the discharge in the two wetland streams at the time of data collection:

$$Q_3 = Q_1 (([Cl^-]_1 - [Cl^-]_4) / ([Cl^-]_3 - [Cl^-]_4) \tag{3.11}$$

$$Q_4 = Q_1 - Q_3 \tag{3.12}$$

Loads at different sampling locations are additive (Ostrom et al., 2002). Thus, downstream tracer loads equal the sum of upstream loads minus storage, loss and/or transformation.

Addressing uncertainty of the values we report, one field sample was collected at each time/location during the tracer tests; error is calculated from two or more repeated laboratory analyses. An exception to this is ammonia, for which two samples were taken at some sampling times during the summer tracer test. Two variables may be added or subtracted (e.g., nitrate concentration minus background). In this case, standard deviation is the square root of the sum of the squared standard deviations for each variable (Rose et al., 1979). When two or more variables are multiplied (e.g., discharge multiplied by concentration=load), the standard deviation equals the product multiplied by the square root of the sum of all squared coefficients of variation (Bennett et al., 1954).

3) Calculating Breatkthrough Curve Decay Constants

Decay constants (λ) were calculated using natural rate of decay equations (Faure, 1998):

$$dC/dt = -\lambda C \tag{3.13}$$

$$\int dC_t / C_{0,\text{ falling limb}} = -\lambda \int dt \tag{3.14}$$

$$\ln C_t - \ln C_{0,\text{ falling limb}} = -\lambda t \tag{3.15}$$

$$\ln C_t = -\lambda t + \ln C_{0,\text{ falling limb}} \tag{3.16}$$

$$\ln C_t / C_{0,\text{ falling limb}} = -\lambda t \tag{3.17}$$

where $C_{0,\text{ falling limb}}$ is a concentration on the falling limb after peak concentration, t is time after onset of sample collection (min), (e.g., t=300 (Protected Stream) and t=250 (Runoff Stream) and λ is the slope.

4) Calculating Loads

Tracer Loads were calculated as areas under the Load vs. Time curves. For concentration curves that did not return to background, estimated concentrations were modeled for $[NO_3^- \text{-N}]_t$ at 10 minute intervals between t=330 and t=1440 using calculated decay constants (Eq 3.13 – 3.17) and solving for

$$\ln[NO_3^- \text{-N}]_t = -\lambda t + \ln[NO_3^- \text{-N}]_{0,\text{ falling limb}} \tag{3.18}$$

where $\ln C_{0,\text{ falling limb}}$ was a concentration along the measured falling limb after which natural log nitrate concentrations yielded a consistent slope between measured values on the falling limb and the measured value at t=1440 min. For example, the slope for Station 4, Protected Sream $\ln[NO_3^- \text{-N}]_t$ was -0.001. Modeled $\ln[NO_3^- \text{-N}]_t$ converts to modeled concentrations as

$$[NO_3^- \text{-N}]_{t\,t} = [NO_3^- \text{-N}]_{t\,0,\text{ falling limb}} e^{-_{\lambda} t} \tag{3.19}$$

Results

The upstream tracer breakthrough curves (Figure 3.2) had the highest concentrations of tracer NO_3^- N and Br^- and the steepest rising and falling limbs. Maximum $[NO^-_3 \text{–N}]$ at the upstream sampling location (3m downstream of Station 8 in the Protected Stream; Station 5 in the Runoff Stream) were 2.95mM (41.3 mg/L) in the spring tracer test, 4.78mM (66.9mg/L) in the fall, 4.21mM (59.0mg/L) in the winter, 3.46mM (48.0mg/L) in the summer Protected Stream and 6.86mM (96.1mg/L) in the summer Runoff Stream (Table 3.3). At the mid-stream sampling location (Station 6 in the Protected Stream, Station 10 in the Runoff Stream), the ratios between maximum midstream and maximum upstream concentrations average 0.35 (+/- 0.17) and between maximum downstream (Station 4 in the Protected Stream and Station 3 in the Runoff Stream) and maximum upstream concentrations average 0.12 (+/- 0.06). Mid- and downstream curves are progressively wider and also steeper on the rising relative to the falling limb.

<u>Seasonal Comparison</u>

As stated above, all four of the tracer tests were conducted in the Protected Stream, whereas the summer test was conducted simultaneously in both the Protected and Runoff Streams.

Field parameters (Table 3.2) were measured only at the downstream sampling stations, and time coverage was poor in the Summer test, Runoff Stream.

Data from Table 3.4 (Figure 3.5) show: a) significant rise and fall in Runoff Stream (RS) [NO_2^- -N] corresponding to arrival of tracer breakthrough curve, with stable [NO_2^- -N] in the Protected Stream (PS); b) highest [NH_4^+ -N] in fall PS and lowest in winter PS; highest c) [Fe^{2+}] and d) [Fe^{2+}]:[Fe_{total}] in summer PS and fall RS; e) increasing [SO_4^{2-}] in the Runoff Stream only; and f) 2.5- to 3-fold higher concentration and apparent dip and recovery of [DOC] in the Runoff Stream.

For the three experiments (winter, fall and summer) in which dissolved gases were measured (Table 3.5, Figure 3.6), comparison of dissolved [N_2O-N] at Station 4 (Protected Stream) shows higher and increasing dissolved [N_2O –N] in summer than in winter or fall. There was virtually no change in [N_2O-N] during the winter experiment, with steady concentrations between 0.041 - 0.044μM (0.57 - 0.62μg/L). During the fall experiment, concentrations fluctuated between 0.075 and 0.089μM (1.05 – 1.25μg/L) between t=40min and t=200min, after which concentrations increased to 0.096μM at t=230min, 0.103μM at t=250 and 280, and decreasing to 0.101 and 0.100μM at t=340 and 370 min, respectively. In contrast, Protected Stream dissolved [N_2O-N] in the summer experiment increased from 0.056μM at t=70min to 0.090μM at t=285min. Dissolved [CO_2] was highest in the fall and lowest in winter Protected Stream, and increased in the Runoff Stream during the summer test. Runoff Stream [CH_4] was highest, and [H_2] was somewhat higher in both summer PS and RS.

Summer Tracer Test

Results for the only dual-stream injection – the summer experiment – are compared side-by-side (Table 3.3, Figure 3.3). Initial downstream [NO_3^--N]$_t$ in the Protected Stream was 226.8μM and in the Runoff Stream was 53.6 μM. On the rising limb in each stream f[Br-]t and [NO_3^--N]$_t$ were approximately the same. After peak concentrations, f[Br-]t was higher than [NO_3^--N]$_t$ in both streams for the remainder of the test. In the Protected Stream, there was a maximum difference of about 70μM between f[Br-]t and [NO_3^--N]$_t$ at peak concentration (between t=100 and t=120 min), after which the difference between the two concentrations decreased until t=170 min. For all sampling times after t=170 min, f[Br-]t was 25-40μM higher than [NO_3^--N]$_t$ for the remainder of the test. In the Runoff Stream, peak concentrations were at t=90 min, when the difference between f[Br-]t and [NO_3^--N]$_t$ was 108.5μM. However, the difference between f[Br-]t and [NO_3^--N]$_t$ in the Runoff Stream became increasingly greater with increasing time, until a maximum difference of 230.2 μM at 330 minutes.

Instantaneous (concentration-based) N recovery at the downstream sampling locations during the summer tracer test fluctuated between 0.9-1.1 in the Protected Stream and 0.3-1.0 in the Runoff Stream (Table 3.3, Figure 3.5). The initial decrease in Runoff Stream Recovery corresponded to the arrival of the tracer plume at Station 3 and Recovery continued to decrease to 0.3 at t=330 min. Recovery in the Protected Stream remained at 1.1 at t=1440 min, and in the Runoff Stream returned to 0.9 at t=1440.

Several redox-sensitive species were measured during the experiments, and, for the summer experiment at the downstream sampling locations, many of these vary between the Protected and Runoff Streams (Table 3.4). Nitrite [NO_2^- N] concentrations (Table 3.4, Figure 3.6) in the Protected Stream remained virtually constant, ranging from 0.11 – 0.21μM at Station 3. At Station 4 in the Runoff Stream, however, background [NO_2^- -N] was 0.28μM, rose steadily and reached a peak of 1.15 μM at 140min and returned to near background (0.30μM) the next morning at t=1440 minutes.

Ammonium [NH_4^+ -N] concentrations (Table 3.4, Figure 3.6) were very irregular in the Protected Stream (0.55 – 1.02μM) until t=160 min, after which concentrations remained below 0.53μM, lower than that in the Runoff Stream, and decreased unsteadily to a low of 0.33μM at t=270min, then rose to 0.58μM at t= 330min. Ammonium N in the Runoff Stream was more consistent (0.71 – 0.82μM) before t=150 and increased unsteadily to 1.06μM at t=240. The highest concentrations in both streams were in bottles collected the next morning at t=1440 min: 1.15μM in the Protected and 1.39μM in the Runoff Stream.

Both total and ferrous (Fe^{2+}) iron concentrations (Table 3.4, Figure 3.6) fluctuated in both streams, with significantly higher initial concentrations and greater net loss in the Runoff Stream. Specifically, at t=0min, ferrous and total iron were 8.48μM and 11.15μM, respectively, in the Protected Stream, and 63.4μM and 75.0μM in the Runoff Stream. In the last samples taken for iron analysis, ferrous and total iron concentrations were 3.05μM and 4.58μM in the Protected Stream (t=280min) and 28.5μM and 33.6μM (t=270 min) in the Runoff Stream. The ratios of Fe^{2+}/Fe^{total} iron in the Protected Stream varied between 0.76 at t=0min and 0.39 at t=220min, with a subsequent increase to 0.64 and 0.66 for the last two iron samples at t=250min and t=280 min. In the Runoff Stream, Fe^{2+}/Fe^{total} fluctuated between 0.84 – 0.88 for the first three samples, decreased to 0.72 at t=150min, and increased to 0.84 for the last sample at t=270min.

Initial sulfate (SO_4^{2-}) concentration (Table 3.4, Figure 3.6) was lower in the Protected Stream (11.9μM) than in the Runoff Stream (14.1uM). Concentrations remained relatively constant in both streams until 120min, after concentrations fluctuated near background in the Protected Stream but rose more or less steadily in the Runoff Stream, to 20.5μM at t=270min. Sulfate concentration reached its peak in both the Runoff Stream (21.2μM) and in the Protected Stream (17.8μM) in the sample collected the following morning at t=1440min.

Dissolved organic C concentrations (Table 3.4, Figure 3.6) in the Protected Stream were about 0.33 those in the Runoff Stream, with a shallow trough-shaped trend in both streams. Initial concentration (t=0min) was 45.1µM in the Protected Stream and 134.6µM in the Runoff Stream. Minimum [DOC] in the Protected Stream was 21.0µM at t=250min and in the Runoff Stream was 94.3µM in t=200min. Final [DOC] in the Protected Stream was 47.9µM and in the Runoff Stream was 151.6µM in t=1440min.

Dissolved gases concentrations and trends also differed between the two streams. Nitrous oxide [N_2O –N] concentrations (Table 3.5, Figure 3.7) were the same (0.22µM) in the first samples of both streams at t=70 min. Thereafter, [N_2O-N] in the Protected Stream rose only slightly to 0.36µM at t=185 min, decreased to 0.33µM at t=215 min, and increased back to 0.36µM at t=185 min. In contrast, [N_2O-N] rose steeply in the Runoff Stream to a maximum concentration of 4.13µM at t=200min and decreased to 2.89µM in the last dissolved gas sample at t=280 min. Maximum Runoff Stream [N_2O -N], which corresponded with the peak time of the tracer breakthrough curve, was 19 times higher than the initial concentration, whereas maximum [N_2O -N] in the Protected Stream was only 1.6 times the initial measured concentration.

Dissolved carbon dioxide [CO_2] (Table 3.5, Figure 3.7) had initial concentrations of 512µM at t=70min in the Protected and 620µM at t=70min in the Runoff Stream. Concentrations fluctuated slightly with a net decrease to 473µM at t=285min in the Protected Stream. In the Runoff Stream, the second sample of dissolved [CO_2^-] (t=90min) increased to 788µM, continued to increase gradually to 806µM for the next three samples, and increased again to 963µM for the final gas sample at t=280min.

Dissolved methane (Table 3.5, Figure 3.7) in the Protected Stream was 0.83µM at t=70min, increased to 1.27µM at t=100min, and decreased steadily to 0.27 at t=285. In the Runoff Stream, dissolved methane concentration was 28 to 41 times higher than that in the Protected Stream, but did not have a time trend. Maximum Runoff Stream [CH_4] was 34.2 µM in the first sample at t=67min and the lowest was 13.8µM at t=205min.

Dissolved hydrogen (Table 3.5, Figure 3.7) were < 2nM in both streams except for one anomalously high (5.40nM at t=215min) in the Protected Stream. Concentrations varied, and there was not a consistent pattern. Concentrations in the Runoff Stream were within a narrow range, 1.05 and 1.42nM, after a concentration minimum of 0.35nM for the first sample at 67min.

Natural background chloride concentrations (Table 3.6, Figure 3.8) were used to calculate stream discharge at Stations 3 and 4 using the mass conservation equations (Eq. 3.9 – 3.12) and discharge at Station 1 (Table 3.1). Based on these calculations, discharge at Station 4 (Protected Stream) was 40.5 L/min and at Station 3 (Runoff Stream) was 8.5 L/min. Maximum $NO_3^-{}_t$ load (Table 3.6, Figure 3.9) was 21.1mmol/min and maximum fBr^-_t load was 23.9mmol/min, both at t=110. In the Runoff Stream, maximum $NO_3^-{}_t$ load was 4.3mmol/min at t=90 min and maximum fBr^-_t load was 5.2mmol/min at t=90, 100 min. Total downstream masses of N, Br^-, and f Br^- recovered (Table 3.6) were determined geometrically, in increments of each successive data point, as the area under the measured and modeled load vs. time curves (Figure 3.9) and above background of 8.6mmol/min at Station 4 (Protected Stream) and 0.0mmol/min at Station 3 (Runoff Stream). In the Protected Stream, total NO_3^--N mass recovered based on samples collected at Station 4 was 2578.1 (+/- 43.6)mmol and total fBr^- mass was 2524.5 (+/- 50.8)mmol, 97% and 92%, respectively, compared to the 2751.7mmol mass introduced in the tracer. In the Runoff Stream, recovered masses at Station 4 was 860.3 (+/- 14.0)mmol of NO_3^--N and 1978.0 (+/- 18.8)mmol of fBr^-, 31% and 72%, respectively, compared to the same mass of injectate (2751.7mmol) as in the Protected Stream.

Discussion

The evolution from steep-sided and symmetrical breakthrough curves at the upstream location to progressively lower maximum concentrations with asymmetrical, wider limbs is attributed to longitudinal dispersion (Kirchner et al., 2001). This is caused by a combination of: 1) vertical and transverse velocity shear, namely that the shallow stream water and tracer travel more slowly along the stream bed and banks than in the middle of the channel (Rutherford, 1994); and 2) hydrologic storage (Burns and Nguyen (2002).

Average stream velocities were similar (based on arrival of the plume fronts) and tracer stream-reach length in the Runoff Stream was 15% shorter than in the Protected Stream. The 30% loss in bromide mass recovery indicates temporary hydrologic storage in the Runoff Stream. Longer contact with organic rich sediments yielded even lower nitrate-N Recovery due to denitrification. in the organic- and iron-rich stream bed.

Abundant leaf litter in the Protected Stream during the fall tracer test likely contributed to high concentrations of reduced species by providing solid organic substrate and/or causing retardation of flow. However, based N/Br recovery, nitrate likely was a minor oxidant, as it was in other seasons in the Protected Stream.

The slight dip and subsequent steady increase in N Recovery for the summer tracer tests in the Protected Stream suggests that N removal processes were operating in the Protected Stream. Denitrification is supported by the steadily increasing Protected Stream nitrous oxide production in the summer, but not in winter or fall. In contrast, the sharp, steady decline in Runoff Stream N Recovery – which returned to unity by the next morning – indicates much more efficient N removal compared to the Protected Stream.

Summer tracer masses recovered, arrived at using calculated loads, were similar for NO_3^--N and adjusted bromide in the Protected Stream, and dissimilar – lower NO_3^--N than fBr^- mass recovered- in the Runoff Stream, consistent with N Recovery trends. That bromide mass recovered was much lower in the Runoff than in the Protected Stream is attributed to hydrologic storage. The 72% fBr^- mass recovered indicates that about 28% (100% - 72%) of the N loss was due to storage and 41% (72% - 31%) due to N removal processes. The remaining 31% of tracer N mass in the Runoff Stream was recovered.

During the two year study period, Station 3 consistently had higher concentrations than Station 4 for methane, DOC, ammonium, dissolved H_2 and dissolved CO_2, and lower concentrations of dissolved oxygen and nitrate (discussed further in Chapter 4). This suggests that conditions at Station 3 are more reducing than those at Station 4, which is necessary but not sufficient to support that denitrification is greater in the Runoff Stream.

Chemical reduction of nitrate proceeds as (Rivera-Monroy et al., 2010):

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \qquad (3.20)$$

Thus, two moles of NO_3^--N or nitrite N are required to produce one mole of nitrous oxide or di-nitrogen gas. Background concentrations of both nitrite- and nitrous oxide-N species were about the same in each of the two streams but both increased sharply only in the Runoff Stream, which is consistent with dentrification. In a study of 12 headwater streams, Beaulieu et al. (2009) found a strong correlation between peak N_2O production rates from stream-bottom sediments and peak water-column nitrate concentration. Thus, the higher concentration of tracer [NO_3^- N] at the head of the Runoff Stream may partially account for the higher concentrations of nitrite- and N_2O –N upon arrival of the tracer plume in the Runoff Stream. However, during introduction of the same tracer mass to both streams, the ratio of Runoff-to-Protected stream concentrations was about 2:1 for [NO_3^- -N] near the points of injection. At the downstream collection points, the ratio was 1:1 for [NO_3^- -N], 5:1 for [NO_2^- -N] and 11:1 for [N_2O –N]. Thus, although higher concentrations of nitrate may stimulate denitrifying activity, there must be sufficient reducing equivalents. This is consistent with the findings of Inwood et al., (2007), who determined that stream sediment denitrification rates in 9 headwater streams were limited *either* by nitrate or organic C concentrations.

There is a complex relationship between many variables that control the distributions and denitrification end-products of the gaseous N species NO_2, NO, N_2O and, ultimately, N_2. These include pH, temperature, trace metals (Fe, Cu, Mo) for enzymes, dissolved oxygen concentration and the presence and/or concentrations of other species that may inhibit some steps of denitrification (Rivera-Monroy et al., 2010)**.** For example, using stream-bottom sediments from a tributary of the River Seine and a combination of flow-through reactor and batch/slurry experiments (both kept under anoxic conditions), Laverman et al. (2010) determined that the addition of carbon increased production of NO_2 gas and decreased production of N_2O in this setting. employed continuous-flow experiments to analyze intact sediment cores from the beds of eutrophic rivers in Finland for N_2O and N_2 emissions. Although the ratio N_2O:N_2 in Silvennoinen et al. (2008) increased with increasing nitrate load, the ratio remained below

0.04, with N_2 clearly being the dominant end-product of these denitrification reactions. In addition to removal via partitioning to the atmosphere, denitrification gas products in shallow wetland streams also can be entrapped in sediments and/or in plant aerenchyma (low-resistance channels and cavities in plants that allow exchange of gases at the root zone) (Matheson and Sukias, 2010). Finally, only one denitrification gas product (N_2O) was measured in this study. Thus, it is impossible to determine how much of the tracer nitrate was completely denitrified in either stream.

In the summer experiment, the concentration of Runoff Stream ferrous iron is initially 6-fold that in the Protected Stream and both streams exhibit a net decrease of about 60%. The ratio of ferrous-to-total iron also decreases and recovers in both streams, indicating that ferrous iron is being oxidized to ferric iron at a faster rate in the tracer injection plume. Although initial $[Fe^{2+}]:[Fe_{total}]$ is similar (0.76 in the Protected Stream and 0.84 in the Runoff Stream) the Protected Stream ratio decreases by 50% before increasing toward initial values. The Runoff Stream ratio has more fluctuation, with an 18% decrease between the highest and lowest values. These results indicate that ferrous iron may play a relatively more important role in Protected Stream denitrification.

Reduced sulfur species (e.g., amorphous iron monosulfides, mackinawite and pyrite) are a source of sulfate from lake bottom sediments when electron acceptors such as nitrate are present (Holmer and Storkholm, 2001). In aerobic conditions, denitrification with sulfide as the electron donor is facilitated by lithoautotrophic bacteria as (Beristain-Cardoso, 2009; Sher et al., 2008):

$$5H_2S + 8NO_3^- \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O + 2H^+ \quad (3.21)$$

Some of the $[SO_4^2]$ observed during the Runoff Stream summer experiment may have been due to replacement of of SO_4^2 by excess tracer Br^- and.or NO_3^--N. However, exchangeable sorption sites on iron oxides and hydroxides are in the order $Cl^- < NO_3^- < H_2BO_3^- < MoO_4^{2-} < SO_4^{2-} < PO_4^{3-} < SiO_4^{4-}$. (Solecki, 2010). This indicates that monovalent anions such as NO_3^- and Br^- ar not likely to cause significant desorption of SO_4^{-2-} as the tracer plume moves flows past the downstream sampling location. Finally, from the summer tracer test, $[SO_4^{2-}]$ remained stable at about 14 uM with decreasing Runoff Stream N/Br Recovery from 1.0 to 0.8, then increased to 20uM as N/Br recovery decreased to about 0.5, and remained at 20uM as Recovery decreased to 0.3. This may have been caused by desorption of sulfate ions as the tracer plume moved past Station 3. However, the threshold changes in slope may also indicate rapid secondary oxidation of sulfate between these [N]/[Br^-].

Several studies have shown that contact time between nitrate-rich stream waters and carbon-rich bottom sediments may be an important limiting factor in NO_3^- reduction in streams (e.g., Kellman and Hillaire-Marcel, 1998; Beaulieu, 2009) and organic carbon has been identified as the main electron donor in denitrification mass balance studies (Aravena and Robertson 1997).

There is decrease and return to background of [DOC] in both streams, although this is more pronounced in the Runoff Stream. This supports denitrification in both streams with organic C among electron donors. Note that the consumption of dissolved organic C can be replenished by dissolution of abundant particulate organic C (Jordan et al., 1993), masking the total mass of C consumed. The concentration in the Runoff Stream of dissolved carbon dioxide, a product of carbon oxidation and initially similar to that in the Protected Stream, increased during the experiment, indicating faster rates of denitrification in the Runoff Stream.

Conclusions:

Residence time exerted a primary control on N removal processes during the tracer tests. Thirty-one per cent of Runoff Stream tracer NO_3^- -N mass was recovered after 24 hours compared to 72% bromide mass recovery. Thus, about 28% of tracer bromide and 41% (72-31%) of summer Runoff Stream NO_3^- -N mass were retained in the wetland. Nintety-four per cent of the Protected Stream tracer NO_3^- -N and 92% of tracer bromide were recovered. Runoff Stream Station 3 NO_3^- -N loads were consistently one-third or less those at Station 4 during the two-year project period.

Denitrification and/or nitrate reduction to ammonia was an important tracer N removal process during the Runoff Stream summer tracer test and Protected Stream fall test. The 30% of tracer NO_3^- -N that was neither stored nor recovered was chemically reduced or removed by other wetland removal processes such as plant uptake. Increased concentrations of NO_3^- -N reduction products ([NO_2^- -N], [N_2O]) and increased concentrations in oxidized species of possible reductants ([SO_4^{2-}], [$H_2CO_3^*$])

reflected dentrification. Electron mass balance indicated that there were more than enough electrons donated by sulfide and organic C to reduce NO_3^- -N lost from the tracer plume to N_2; however, this does not take kinetic controls into consideration. Plant uptake was not measured but may have accounted for some of the nitrate N removed during the summer test.

Fall tracer [NH_4^+ -N] is 5 times higher, [$H_2CO_3^*$] 2-3 times higher, [DOC] 1.5-2 times higher and [CH_4] 10-30 times higher than either summer or winter Protected Stream values. This suggests that some NO_3^- -N may have been reduced to ammonia. Peak [NO_3^- -N] was attained 10-30 minutes later at Station 6 and 35-60 minutes later at Station 4 during the fall than during the spring, winter or summer Protected Stream tests, indicating that leaf litter caused both increased residence time and more reducing conditions in the fall than during the other Protected Stream tests.

Addition of tracer spike did not cause a disproportionately large increase in N removal rates from the Protected Stream. Protected Stream tracer NO_3^- -N mass (tracer + background, which was the total area under the NO_3^- -N load vs. Time) was compared to background "low end" (percent increase between Stations 8 and 4 using actual background nitrate N loads) and "high end" (percent increase between Station and 8 and Station 4 if Station 4 load was calculated using Station 8 background concentrations). For example, during the spring tracer test, 28% of tracer-plus-background NO_3^- -N was lost between Stations 8 and 4. However, between 19% (actual background loads) and 30% (if there had been no removal processes between Stations 8 and 4) background NO_3^- -N would have been removed from the wetland. Only the winter stream Protected Stream test yielded a greater % loss in tracer mass than the background "low end" and "high end" ranges.

Organic carbon was the main electron donor in both streams. Electron mass balance calculations indicated that reducing equivalents available from organic C to reduce nitrate N were 2 orders of magnitude higher than reducing equivalents that would be available via sulfide oxidation to sulfate. However, sulfide consumption was not measured directly but inferred only by sulfate production, which may not represent all sulfide oxidation. Also, during the summer tracer test, [SO_4^{2-}] remained stable at about 14 uM with decreasing Runoff Stream [N]/[fBr^-] Recovery from 1.0 to 0.8, then increased to 20uM

Recovery decreased to about 0.5, and remained at 20uM as Recovery decreased to 0.3. The threshold changes in slope may also indicate rapid secondary oxidation of sulfide. These results constrain processes that affect nitrate N removal efficiency in agricultural wetland streams.

Table 3.1. Background conditions and mass of injectate. Background [NO_3^-N] was measured the day before each test using a Hach DR 2800 Spectrophotometer and Hach NitraVer Accuvac ampules. Prior-day discharge also was measured at the wetland downstream flume (Station 1) to provide information on overall wetland flow conditions. [NO_3^- -N] values reported in this table were used only to calculate mass of calcium nitrate tracer and are not included in test results (Table 3.3).

	Background			Inject							
	St. 8 Q	St. 1 Q	[NO_3^-N]	$Ca(NO_3)_2$	N		NaBr	Br^-		N/Br	
Date	(L/min)	(L/min)	(mg/L)	• $4H_2O$ (g)	(g)	(mmol)	(g)	(g)	(mmol)	(g)	(mmol)
25-Mar-04	22.3	37.8	5.0	253.9	30.1	2150.4	8.6	6.7	83.7	4.5	25.7
21-Oct-04	14.2	25.9	6.2	157.4	18.7	1332.8	5.5	4.3	53.3	4.4	25.0
08-Feb-05	28	52.3	8.0	297.5	35.3	2520.0	10.8	8.4	105.1	4.2	24.0
17-Aug-05	28.6	48.9	5.1	324.9	38.5	2751.7	11.0	8.6	107.3	4.5	25.6

Table 3.2. Field Parameters. Ph, temperature (T) and dissolved oxygen (DO) remained relatively constant or exhibited trendless fluctuations. Specific conductance (SpC) increased and decreased corresponding with passing of the tracer plume.

25 March 2004

Time	pH	T (C)	DO(mg/L)	SpC(uS/cm)
0	6.14	14.9	10.56	80.4
30	6.2	16.5	10.47	77.6
45	6.19	16.9	10.18	77.8
60	6.21	17.4	10.51	77.9
75	6.21	17.9	10.26	83.2
90	6.17	18.2	10.1	103.8
105	6.13	18.6	10.25	119.1
120	6.12	18.9	10.41	125.9
135	6.11	19.4	10.01	128
150	6.13	19.8	9.38	123.9
180	6.11	20.6	9.16	110
225	6.12	20.8	8.84	97.1
330	6.06	20	6.86	88.2
390	6.04	19	6.44	87.3

21 Oct 2004

Time	pH	T (C)	DO(mg/L)	SpC(uS/cm)
40	5.51	18.6	3.79	82.1
90	5.49	18.7	3.16	87.1
120	5.49	18.7	3.01	93.6
160	5.46	18.8	3.31	96.4
200	5.43	18.9	3.52	95.1
230	5.46	18.9	3.56	94.4
250	5.53	18.9	3.83	93.7
280	5.5	18.9	3.70	93.4
340	5.52	19	3.77	92
370	5.54	19.1	3.74	92

Table 3.2 (continued)
8 Feb 2005

Time	pH	T (C)	DO(mg/L)	SpC(uS/cm)
60	6.39	12	7.89	89.9
90	6.1	12.6	7.77	109.3
110	6.03	12.7	7.51	137.8
140	6.06	12.8	7.42	135
170	6.11	13	7.36	118.2
200	6.15	13.6	7.62	106.5
220	6.17	13.9	7.59	102.6
240	6.13	14.5	7.58	98.3
270	6.18	14.6	7.00	96.2
300	6.17	14.4	6.65	95.7
330	6.27	14.2	6.37	95.3
360	6.18	13.9	6.07	95.3

17 Aug 2005
Protected Stream (Station 4)

Time	pH	T (C)	DO(mg/L)	SpC(uS/cm)
0	6.06	20.8		
30	6.08	20.7	3.68	70.9
60	6.07	20.9	3.65	70.5
130	5.98	21.2	3.41	98.1
220	6.01	21.8	3.48	83.6
285	6.05	22.6	3.24	81.9

Runoff Stream (Station 3)

0	6.6	22.9	3.05	120.2
130	6.63	23.5	3.02	142
285	6.62	23.6	3.10	127.6

Table 3.3. Breakthrough curve concentration and N Recovery data. For the summer experiment, values presented in gray-scale between t=430min and t=1330min were estimated by applying the rate of decay equation to values measured on the receding limb of the breakthrough curves and a final measurement taken at t-1440min. Natural log tracer concentration quotients at each time t, after peak (p) concentration are used to calculate the decay constant, $\lambda_{t,}$. Decay slopes between successive times t become more consistent at the downstream stations (except for Fall test, Protected Stream), indicating that the downstream breakthrough curves more closely follow a natural decay pattern. Standard deviation, where listed, was calculated from results of two or more laboratory sample runs from a single field sample.

25-Mar-2004	Time (min)	[NO3$^-$ N] (uM)	SD	ln([NO$_3^-$ N]$_t$ /[NO$_3^-$ N]$_p$)	λ_t	[Br-] (uM)	SD	f[Br-]$_t$ (uM)	SD	ln(f[Br$^-$]$_t$ /f[Br$^-$]$_p$)	λ_t	N Recovery	SD
Upstream	0	333.3				0.00		333.3				1.00	
(Station 8)	15	2948.5		0.0		100.5		2916.3		0.0		1.01	
	30	725.1		-1.4	-0.094	14.5		705.2		-1.4	-0.095	1.03	
	45	373.3		-2.1	-0.069	0.00		333.3		-2.2	-0.072	1.12	
	60	356.5		-2.1	-0.047	0.94		357.6		-2.1	-0.047	1.00	
	75	345.5		-2.1	-0.036	0.72		351.8		-2.1	-0.035	0.98	
Midstream	0	294.0				0.00		294.0				1.00	
(Station 6)	30	356.1				2.07		347.3				1.03	
	45	395.8				8.50		512.5				0.77	
	60	707.4				31.9		1113.4		0.0		0.64	
	75	915.2		0.0		25.1		939.4		-0.2	-0.011	0.97	
	90	825.4		-0.1	-0.007	17.3		739.9		-0.4	-0.014	1.12	
	135	492.9		-0.6	-0.010	6.37		457.7		-0.9	-0.012	1.08	
	180	359.8		-0.9	-0.009	2.85		367.3		-1.1	-0.009	0.98	
	240	337.3		-1.0	-0.006	1.48		332.0		-1.2	-0.007	1.02	
Downstream	0	233.8				0.00		233.8				1.00	
(Station 4)	45	250.4				0.00		233.8				1.07	
	90	368.1				3.63		327.1				1.13	
	100	456.4				6.43		399.2				1.14	
	110	513.1				7.87		436.2				1.18	
	115	591.2				12.7		559.1				1.06	
	120	635.2				15.4		629.6		0.0		1.01	
	125	650.6		0.0		13.0		568.8		-0.1	-0.020	1.14	
	140	639.3		-0.02	-0.001	14.4		604.6		0.0	-0.002	1.06	
	145	636.3		-0.02	-0.001	13.2		572.2		-0.1	-0.004	1.11	
	150	616.4		-0.05	-0.002	13.6		583.2		-0.1	-0.003	1.06	
	155	600.7		-0.08	-0.003	10.2		496.5		-0.2	-0.007	1.21	
	165	553.3		-0.16	-0.004	8.70		457.4		-0.3	-0.007	1.21	
	170	524.8		-0.21	-0.005	8.08		441.5		-0.4	-0.007	1.19	
	175	491.5		-0.28	-0.006	7.88		436.4		-0.4	-0.007	1.13	
	180	469.4		-0.33	-0.006	7.28		420.9		-0.4	-0.007	1.12	
	185	440.6		-0.39	-0.006	6.84		409.5		-0.4	-0.007	1.08	
	225	357.6		-0.60	-0.006	4.45		348.3		-0.6	-0.006	1.03	
	240	356.5		-0.60	-0.005	3.88		333.6		-0.6	-0.005	1.07	
	255	287.3		-0.82	-0.006	4.48		348.9		-0.6	-0.004	0.82	
	330	316.7		-0.72	-0.004	1.97		284.4		-0.8	-0.004	1.11	
	390	234.2		-1.02	-0.004	0.00		233.8		-1.0	-0.004	1.00	
	1260	233.5		-1.02	-0.001	0.00		233.8		-1.0	-0.001	1.00	

Table 3.3 (continued)

21-Oct-2004	Time (min)	[NO3$^-$ N] (uM)	SD	ln([NO$_3^-$ N]$_t$ /[NO$_3^-$ N]$_p$)	λ_τ	[Br-] (uM)	SD	f[Br-]$_t$ (uM)	SD	ln(f[Br$^-$]$_t$ /f[Br$^-$]$_p$)	λ_τ	N Recovery	SD
Upstream	0	367.1				0.00		367.1				1.00	
(Station 8)	10	4776.3				173.0		4695.8		0.0		1.02	
	20	1063.7		0.00		31.6		1158.1		-1.4	-0.140	0.92	
	40	517.8		-0.72	-0.036	5.16		496.1		-2.2	-0.075	1.04	
	60	386.6		-1.01	-0.025	1.30		399.6		-2.5	-0.049	0.97	
	90	387.0		-1.01	-0.014	0.80		387.0		-2.5	-0.031	1.00	
	180	431.3		-0.90	-0.006	0.49		379.4		-2.5	-0.015	1.14	
	240	364.7	13.0	-1.07	-0.005	0.17	0.24	371.4		-2.5	-0.011	0.98	0.04
	310	361.6	11.2	-1.08	-0.004	0.17	0.24	371.4		-2.5	-0.008	0.97	0.03
	360	343.7		-1.13	-0.003	0.00		367.1		-2.5	-0.007	0.94	
Midstream	0	278.4				0.00		278.4				1.00	
(Station 6)	20	328.4				0.00		278.4				1.18	
	40	290.1				0.00		278.4				1.04	
	50	480.2				10.2		532.6				0.90	
	70	579.9				14.4		638.0				0.91	
	80	920.4		0.00		21.3		811.5		0.0		1.13	
	90	691.6		-0.29	-0.029	13.9		626.2		-0.3	-0.026	1.10	
	100	564.5		-0.49	-0.024	9.35		512.3		-0.5	-0.023	1.10	
	110	489.3		-0.63	-0.021	6.99		453.3		-0.6	-0.019	1.08	
	130	415.6		-0.80	-0.016	4.61		393.6		-0.7	-0.014	1.06	
	150	378.5		-0.89	-0.013	3.48		365.4		-0.8	-0.011	1.04	
	180	339.1		-1.00	-0.010	2.97		352.7		-0.8	-0.008	0.96	
	210	340.3		-1.00	-0.008	2.32		336.4		-0.9	-0.007	1.01	
	240	331.0		-1.02	-0.006	1.98		327.8		-0.9	-0.006	1.01	
	310	319.8		-1.06	-0.005	1.54		317.0		-0.9	-0.004	1.01	
	360	292.5	11.2	-1.15	-0.004	1.30	0.30	311.0		-1.0	-0.003	0.94	0.04
Downstream	30	157.7				0.00		157.7				1.00	
(Station 4)	40	181.2	2.67			0.00	0.17	157.7				1.15	0.03
	60	169.1	15.0			0.00	0.29	157.7				1.07	0.11
	90	193.9	2.73			0.30	0.00	165.3				1.17	0.02
	100	192.3				0.82		178.1				1.08	
	110	214.4				1.42		193.2				1.11	
	120	243.1	10.1			2.59	0.23	222.5				1.09	0.05
	130	248.2				2.66		224.3				1.11	
	140	253.0		0.00		2.75		226.5				1.12	
	150	251.8		0.00	0.000	2.75		226.5				1.11	
	160	255.4	16.6	0.01	0.000	2.86	0.27	229.4		0.0		1.11	0.08
	170	252.2		0.00	0.000	2.65		223.9		0.0	-0.002	1.13	
	180	232.8		-0.08	-0.002	2.44		218.8		0.0	-0.002	1.06	
	190	252.0		0.00	0.000	2.60		222.7		0.0	-0.001	1.13	
	200	238.5	6.13	-0.06	-0.001	2.84	0.03	228.8		0.0	0.000	1.04	0.03
	220	231.3		-0.09	-0.001	2.37		216.9		-0.1	-0.001	1.07	
	230	237.0	8.73	-0.07	-0.001	2.61	0.11	223.0		0.0	0.000	1.06	0.04
	240	243.2		-0.04	0.000	2.42		218.3		0.0	-0.001	1.11	
	250	236.7	7.43	-0.07	-0.001	2.58	0.12	222.3		0.0	0.000	1.06	0.04
	260	240.5		-0.05	0.000	2.36		216.8		-0.1	-0.001	1.11	
	270	240.1		-0.05	0.000	2.29		215.1		-0.1	-0.001	1.12	
	280	232.1	6.79	-0.09	-0.001	2.43	0.12	218.5		0.0	0.000	1.06	0.03
	290	232.7		-0.08	-0.001	2.18		212.2		-0.1	-0.001	1.10	
	300	236.1		-0.07	0.000	2.21		213.1		-0.1	-0.001	1.11	
	310	230.2	1.04	-0.09	-0.001	2.36	0.04	216.7		-0.1	0.000	1.06	0.01
	320	225.7	8.21	-0.11	-0.001	2.33	0.02	215.9		-0.1	0.000	1.05	0.04
	340	226.6	3.94	-0.11	-0.001	2.15	0.07	211.6		-0.1	0.000	1.07	0.02
	370	223.8	1.92	-0.12	-0.001	2.13	0.10	210.9		-0.1	0.000	1.06	0.02

Table 3.3 (continued)

	Time	$[NO3^{-}\ N]$		$\ln([NO_3^{-}\ N]_t$		[Br-]		$f[Br-]_t$		$\ln(f[Br^{-}]_t$		N	
8-Feb-2005	(min)	(uM)	SD	$/[NO_3^{-}\ N]_p)$	λ_τ	(uM)	SD	(uM)	SD	$/f[Br^{-}]_p)$	λ_τ	Recovery	SD
	0	393.4	19.3			0.02	0.31	390.8				1.01	0.05
Upstream	10	2954.3	171.1			106.4	1.46	2943.2				1.00	0.06
(Station 8)	20	4184.5				157.8		4175.7		0.0		1.00	
	25	4214.0		0.00		156.6		4148.0		0.0	-0.001	1.02	
	30	3974.3		-0.06	-0.012	149.5		3977.2		0.0	-0.005	1.00	
	35	3906.8		-0.08	-0.008	147.1		3919.0		-0.1	-0.004	1.00	
	40	716.7		-1.77	-0.118	11.9		678.5		-1.8	-0.091	1.06	
	50	430.1	23.0	-2.28	-0.091	2.05	0.04	442.5		-2.2	-0.075	0.97	0.05
	63	369.7		-2.43	-0.064	0.88		414.6		-2.3	-0.054	0.89	
	80	435.0	24.2	-2.27	-0.041	1.38	0.27	426.5		-2.3	-0.038	1.02	0.06
	140	406.8		-2.34	-0.020	0.31		401.0		-2.3	-0.020	1.01	
	190	390.4		-2.38	-0.014	0.27		399.8		-2.3	-0.014	0.98	
	200	420.3		-2.31	-0.013	0.21		398.5		-2.3	-0.013	1.05	
	300	392.5		-2.37	-0.009	0.37		402.4		-2.3	-0.008	0.98	
	330	414.0	16.8	-2.32	-0.008	0.79	0.30	412.4		-2.3	-0.007	1.00	0.04
	1450	398.6		-2.36	-0.002	-0.40		383.7		-2.4	-0.002	1.04	
Midstream	0	340.4				-0.09		338.2				1.01	
(Station 6)	20	348.4	16.0			0.05	0.27	341.6				1.02	0.05
	30	357.7				0.73		357.8				1.00	
	40	654.2				14.5		687.0				0.95	
	50	1063.2				25.0		940.5				1.13	
	60	1490.0				34.0		1156.1				1.29	
	70	1522.6		0.00		34.7		1173.3				1.30	
	80	1214.7		-0.23	-0.023	35.4		1188.4		0.0		1.02	
	100	638.5		-0.87	-0.029	13.9		673.5		-0.6	-0.028	0.95	
	110	589.6		-0.95	-0.024	8.46		543.3		-0.8	-0.026	1.09	
	120	485.8		-1.14	-0.023	6.83		504.1		-0.9	-0.021	0.96	
	130	491.0		-1.13	-0.019	4.93		458.6		-1.0	-0.019	1.07	
	140	423.5		-1.28	-0.018	4.03		437.1		-1.0	-0.017	0.97	
	150	442.9		-1.23	-0.015	3.11		415.0		-1.05	-0.015	1.07	
	170	417.8		-1.29	-0.013	2.28		395.0		-1.10	-0.012	1.06	
	191	402.2		-1.33	-0.011	1.79		383.3		-1.13	-0.010	1.05	
	210	344.0		-1.49	-0.011	4.15		439.8		-0.99	-0.008	0.78	
	260	303.6		-1.61	-0.008	2.77		406.8		-1.07	-0.006	0.75	
	300	433.1		-1.26	-0.005	0.84		360.5		-1.19	-0.005	1.20	
	330	380.1		-1.39	-0.005	0.85		360.9		-1.2	-0.005	1.05	
	350	387.4		-1.37	-0.005	1.37		373.2		-1.2	-0.004	1.04	
	360	348.6	2.14	-1.47	-0.005	0.43	0.05	350.7		-1.2	-0.004	0.99	0.01
	1414	360.2		-1.44	-0.001	1.03		365.1		-1.2	-0.001	0.99	
Downstream	0	349.2	4.50			0.00	0.00	349.2				1.00	0.01
(Station 4)	30	323.2	10.9			0.00	0.36	349.2				0.93	0.04
	60	355.0	30.0			1.33	2.34	381.0				0.93	0.16
	70	329.0	1.19			0.57	0.32	362.9				0.91	0.02
	80	365.6				2.75		415.2				0.88	
	90	469.4	19.8			6.94	0.17	515.5				0.91	0.04
	100	556.4	0.40			10.8	0.81	608.9				0.91	0.03
	110	684.5	37.9			16.3	0.50	739.2				0.93	0.05
	120	735.9		0.00		17.8		776.7		0.0		0.95	
	130	707.2	40.7	-0.04	-0.004	17.2	0.53	762.1		0.0	-0.002	0.93	0.06
	140	668.2	33.5	-0.10	-0.005	15.6	0.39	722.2		-0.1	-0.004	0.93	0.05
	160	593.4	69.4	-0.22	-0.005	11.1	0.88	615.6		-0.2	-0.006	0.96	0.12
	170	555.7		-0.28	-0.006	10.1		590.7		-0.3	-0.005	0.94	
	180	515.1	7.59	-0.36	-0.006	7.78	0.72	535.8		-0.4	-0.006	0.96	0.03
	190	486.6	1.25	-0.41	-0.006	6.64	0.61	508.4		-0.4	-0.006	0.96	0.03
	200	454.9	23.6	-0.48	-0.006	6.08	0.24	494.9		-0.5	-0.006	0.92	0.05
	210	455.8	1.06	-0.48	-0.005	5.52	0.00	481.6		-0.5	-0.005	0.95	0.00
	220	422.0	23.2	-0.56	-0.006	4.67	0.18	461.1		-0.5	-0.005	0.92	0.05
	230	334.6	52.8	-0.79	-0.007	3.20	0.67	425.9		-0.6	-0.005	0.79	0.13
	240	406.2	20.8	-0.59	-0.005	3.88	0.06	442.3		-0.6	-0.005	0.92	0.05
	250	401.2		-0.61	-0.005	3.20		425.9		-0.6	-0.005	0.94	
	260	396.8	6.84	-0.62	-0.004	2.99	0.02	421.0		-0.6	-0.004	0.94	0.02
	270	380.1	12.8	-0.66	-0.004	2.85	0.08	417.5		-0.6	-0.004	0.91	0.03

Table 3.3 (continued)

	Time	[NO3^{-} N]		ln([NO$_3^-$ N]$_t$		[Br-]		f[Br-]$_t$		ln(f[Br$^-$]$_t$		N	
	(min)	(uM)	SD	/[NO$_3^-$ N]$_p$)	λ_τ	(uM)	SD	(uM)	SD	/f[Br$^-$]$_p$)	λ_τ	Recovery	SD
	280	408.5		-0.59	-0.004	2.25		403.0		-0.7	-0.004	1.01	
	290	386.8	1.15	-0.64	-0.004	2.49	0.00	408.9		-0.6	-0.004	0.95	0.00
	300	359.8		-0.72	-0.004	2.36		405.8		-0.6	-0.004	0.89	
	310	377.9	3.55	-0.67	-0.004	2.11	0.11	399.7		-0.7	-0.003	0.95	0.01
	320	375.9	2.94	-0.67	-0.003	1.98	0.18	396.6		-0.7	-0.003	0.95	0.01
	330	363.9	19.5	-0.70	-0.003	1.88	0.13	394.3		-0.7	-0.003	0.92	0.05
	340	382.8	18.4	-0.65	-0.003	1.66	0.03	388.9		-0.7	-0.003	0.98	0.05
	350	373.5		-0.68	-0.003	1.82		392.7		-0.7	-0.003	0.95	
	360	373.0	3.56	-0.68	-0.003	2.28	1.23	403.8		-0.7	-0.003	0.92	0.07
17-Aug-2005	0	362.2	1.93			BDL	0.45	359.1				1.01	0.03
Upstream	10	3428.8	216.5	0.00		78.3	9.96	2369.9		0.0		1.45	0.18
(Station 8)	20	942.3	64.4	-1.29	-0.129	14.5		734.8		-1.2	-0.117	1.28	0.09
	30	507.6		-1.91	-0.096	6.65		532.9		-1.5	-0.075	0.95	
	40	367.1	30.5	-2.23	-0.074	0.91	0.72	385.5		-1.8	-0.061	0.95	0.09
	50	363.1		-2.25	-0.056	0.34		370.9		-1.9	-0.046	0.98	
	60	374.2		-2.22	-0.044	0.82		383.2		-1.8	-0.036	0.98	
	90	361.3		-2.25	-0.028	0.19		367.0		-1.9	-0.023	0.98	
	185	361.0		-2.25	-0.013	0.27		369.2		-1.9	-0.011	0.98	
	210	376.6		-2.21	-0.011	0.73		381.0		-1.8	-0.009	0.99	
	240	350.5		-2.28	-0.010	0.23		368.2		-1.9	-0.008	0.95	
	270	357.7		-2.26	-0.009	0.21		367.7		-1.9	-0.007	0.97	
	330	359.8	2.54	-2.25	-0.007	0.19	0.02	367.1		-1.9	-0.006	0.98	0.01
	1425	383.0		-2.19	-0.002	0.19		367.1		-1.9	-0.001	1.04	
Midstream	0	295.8				0.18		300.4				0.98	
(Station 6)	10	301.9				0.20		301.0				1.00	
	20	304.8				0.16		299.8				1.02	
	30	353.0				2.13		350.4				1.01	
	50	1412.1				45.9		1474.1				0.96	
	60	1631.3		0.00		53.0		1656.2		0.0		0.98	
	80	768.6		-0.75	-0.038	20.2		814.4		-0.7	-0.035	0.94	
	90	575.1		-1.04	-0.035	12.0		604.7		-1.0	-0.034	0.95	
	120	412.3		-1.38	-0.023	5.07		425.9		-1.4	-0.023	0.97	
	150	376.6		-1.47	-0.016	3.37		382.1		-1.5	-0.016	0.99	
	210	343.3		-1.56	-0.010	2.11		350.0		-1.6	-0.010	0.98	
	270	331.7		-1.59	-0.008	1.64		337.8		-1.6	-0.008	0.98	
	270	331.6		-1.59	-0.008	1.65		338.1		-1.6	-0.008	0.98	
	300	324.3		-1.62	-0.007	1.47		333.6		-1.6	-0.007	0.97	
	330	324.7		-1.61	-0.006	1.33		330.0		-1.6	-0.006	0.98	
	1430	327.9		-1.60	-0.001	0.25		302.3		-1.7	-0.001	1.08	
Downstream	0	226.8	6.07			0.00		226.8				1.00	0.06
(Station 4)	30	222.5	0.37			0.00	0.42	226.8				0.98	0.05
	60	227.1	6.72			0.00	0.44	226.8				1.00	0.06
	90	377.4	8.55			7.99		431.7				0.87	0.02
	100	486.4				12.9		558.6				0.87	0.00
	110	520.5	9.79	0.00		14.2	0.54	589.8		0.0		0.88	0.03
	120	512.3	2.25	-0.02	-0.002	13.8	0.47	579.7		0.0	-0.002	0.88	0.02
	130	477.4	18.7	-0.09	-0.004	12.3	0.40	542.8		-0.1	-0.004	0.88	0.04
	140	447.9	5.15	-0.15	-0.005	10.7	0.32	502.2		-0.2	-0.005	0.89	0.02
	150	409.8	10.1	-0.24	-0.006	9.05	0.07	458.9		-0.3	-0.006	0.89	0.02
	160	393.3	8.80	-0.28	-0.006	8.27	0.12	439.0		-0.3	-0.006	0.90	0.02
	170	373.7	2.50	-0.33	-0.006	7.25	0.13	412.8		-0.4	-0.006	0.91	0.01
	180	355.6	2.37	-0.38	-0.005	6.35	0.13	389.7		-0.4	-0.006	0.91	0.01
	190	337.9	12.6	-0.43	-0.005	5.76	0.11	374.5		-0.5	-0.006	0.90	0.03
	200	337.5	7.17	-0.43	-0.005	5.54	0.17	368.8		-0.5	-0.005	0.92	0.02
	220	306.2	10.3	-0.53	-0.005	4.52	0.17	342.7		-0.5	-0.005	0.89	0.03
	230	314.2	0.56	-0.50	-0.004	4.37	0.01	338.8		-0.6	-0.005	0.93	0.00
	240	302.0		-0.54	-0.004	4.10		331.9		-0.6	-0.004	0.91	
	250	289.5	10.4	-0.59	-0.004	3.90	0.05	326.9		-0.6	-0.004	0.89	0.03
	270	281.8	10.6	-0.61	-0.004	3.53	0.00	317.3		-0.6	-0.004	0.89	0.03
	280	271.9	0.42	-0.65	-0.004	3.39	0.00	313.8		-0.6	-0.004	0.87	0.00
	300	275.9	8.79	-0.63	-0.003	3.09	0.01	306.0		-0.7	-0.003	0.90	0.03
	330	271.5	8.39	-0.65	-0.003	2.83	0.07	299.4		-0.7	-0.003	0.91	0.03

Table 3.3 (continued)

	Time (min)	[NO3$^-$ N] (uM)	SD	ln([NO$_3^-$ N]$_t$ /[NO$_3^-$ N]$_p$)	λ_τ	[Br-] (uM)	SD	f[Br-]$_t$ (uM)	SD	ln(f[Br$^-$]$_t$ /f[Br$^-$]$_p$)	λ_τ	N Recovery	SD
	430	265.5		-0.67	-0.002	1.91		275.8		-0.8	-0.002	0.96	
	530	262.9		-0.68	-0.002	1.32		260.7		-0.8	-0.002	1.01	
	630	260.2		-0.69	-0.001	0.91		250.2		-0.9	-0.002	1.04	
	730	257.6		-0.70	-0.001	0.63		243.0		-0.9	-0.001	1.06	
	830	255.1		-0.71	-0.001	0.44		238.0		-0.9	-0.001	1.07	
	930	252.5		-0.72	-0.001	0.30		234.5		-0.9	-0.001	1.08	
	1030	250.0		-0.73	-0.001	0.21		232.1		-0.9	-0.001	1.08	
	1130	247.5		-0.74	-0.001	0.14		230.5		-0.9	-0.001	1.07	
	1230	245.1		-0.75	-0.001	0.10		229.3		-0.9	-0.001	1.07	
	1330	242.6		-0.76	-0.001	0.07		228.6		-0.9	-0.001	1.06	
	1440	259.5	4.00	-0.70	-0.001	0.05	0.27	228.1		-0.9	-0.001	1.14	0.04
Runoff Stream	0	201.4				0.27		208.3				0.97	
Upstream	10	5686.4				202.0		5382.3				1.06	
(Station 5)	20	6858.6		0.00		232.3		6159.1				1.11	
	30	6769.5		-0.01	-0.001	245.6		6500.2		0.0		1.04	
	40	3332.8		-0.72	-0.036	136.9		3713.6		-0.6	-0.056	0.90	
	50	642.8	20.5	-2.37	-0.079	20.6	0.04	730.3		-2.2	-0.109	0.88	0.03
	60	423.3		-2.79	-0.070	10.6		472.0		-2.6	-0.087	0.90	
	90	268.0		-3.24	-0.046	3.25		284.8		-3.1	-0.052	0.94	
	120	237.6	2.41	-3.36	-0.034	1.92	0.03	250.5		-3.3	-0.036	0.95	0.01
	180	224.4		-3.42	-0.021	1.03		227.9		-3.4	-0.022	0.98	
	210	217.0		-3.45	-0.018	0.76		220.9		-3.4	-0.019	0.98	
	240	231.5		-3.39	-0.015	1.41		237.5		-3.3	-0.016	0.97	
	270	215.5		-3.46	-0.014	0.58		216.2		-3.4	-0.014	1.00	
	300	221.7		-3.43	-0.012	0.55		215.5		-3.4	-0.013	1.03	
	330	217.9		-3.45	-0.011	0.50		214.2		-3.4	-0.011	1.02	
	1433	205.8		-3.51	-0.002	0.36		210.6		-3.4	-0.002	0.98	
Midstream	0	123.3				0.25		129.7				0.95	
(Station 10)	10	122.5				0.27		130.2				0.94	
	20	363.0				8.72		347.1				1.05	
	40	2537.8				87.8		2375.0				1.07	
	50	2878.0				109.6		2935.3		0.0		0.98	
	60	3104.2		0.00		94.4		2544.1		-0.1	-0.014	1.22	
	70	2285.0		-0.31	-0.031	86.4		2339.5		-0.2	-0.011	0.98	
	80	1691.2		-0.61	-0.030	64.0		1765.3		-0.5	-0.017	0.96	
	90	1289.1		-0.88	-0.029	48.9		1377.6		-0.8	-0.019	0.94	
	210	297.7		-2.34	-0.016	8.26		335.2		-2.2	-0.014	0.89	
	240	257.0		-2.49	-0.014	6.51		290.4		-2.3	-0.012	0.89	
	270	229.5		-2.60	-0.012	5.36		260.7		-2.4	-0.011	0.88	
	300	212.3		-2.68	-0.011	4.51		238.9		-2.5	-0.010	0.89	
	330	201.4		-2.74	-0.010	3.88		222.8		-2.6	-0.009	0.90	
Downstream	0	53.6				0.00		53.6				1.00	
(Station 3)	30	53.1				0.00		53.6				0.99	
	60	215.5				6.93		231.2				0.93	
	90	506.4	15.9	0.00		21.9	0.71	614.3				0.82	0.04
	110	494.8		-0.02	-0.001	22.0		617.8		0.0		0.80	
	120	480.7	4.91	-0.05	-0.002	21.6	0.24	607.8		0.0	-0.0016	0.79	0.01
	140	430.2		-0.16	-0.003	20.1		567.9		-0.1	-0.0028	0.76	
	150	401.9		-0.23	-0.004	19.0		542.1		-0.1	-0.0033	0.74	
	170	355.8		-0.35	-0.004	17.6		505.8		-0.2	-0.0033	0.70	
	180	315.3	8.65	-0.47	-0.005	16.1	0.32	466.8		-0.3	-0.0040	0.68	0.02
	190	274.7	3.52	-0.61	-0.006	14.8	0.15	432.7		-0.4	-0.0045	0.63	0.01
	200	232.9	0.02	-0.78	-0.007	13.3	0.04	393.6		-0.5	-0.0050	0.59	0.00
	210	263.9	3.59	-0.65	-0.005	14.9	0.17	436.1		-0.3	-0.0035	0.61	0.01
	220	231.7	0.41	-0.78	-0.006	13.7	0.08	405.2		-0.4	-0.0038	0.57	0.00

Table 3.3 (continued)

Time (min)	[NO3$^-$ N] (uM)	SD	ln([NO$_3^-$ N]$_t$ /[NO$_3^-$ N]$_p$)	λ_τ	[Br-] (uM)	SD	f[Br-]$_t$ (uM)	SD	ln(f[Br$^-$]$_t$ /f[Br$^-$]$_p$)	λ_τ	N Recovery	SD
230	236.3		-0.76	-0.005	14.1		416.2		-0.4	-0.0033	0.57	
240	219.1	9.43	-0.84	-0.006	13.6	0.36	401.9		-0.4	-0.0033	0.55	0.03
250	211.0		-0.88	-0.005	13.4		398.1		-0.4	-0.0031	0.53	
270	183.6		-1.01	-0.006	12.7		378.2		-0.5	-0.0031	0.49	
280	173.6		-1.07	-0.006	12.3		370.2		-0.5	-0.0030	0.47	
300	129.9	1.54	-1.36	-0.006	11.7	0.10	353.1		-0.6	-0.0029	0.37	0.01
330	100.3	0.15	-1.62	-0.007	10.8	0.15	331.3		-0.6	-0.0028	0.30	0.00
430	99.0		-1.63	-0.005	8.89		281.7		-0.8	-0.0025	0.35	
530	95.9		-1.66	-0.004	7.28		240.3		-0.9	-0.0022	0.40	
630	93.3		-1.69	-0.003	5.96		206.5		-1.1	-0.0021	0.45	
730	91.1		-1.72	-0.003	4.88		178.8		-1.2	-0.0020	0.51	
830	89.2		-1.74	-0.002	4.00		156.1		-1.4	-0.0019	0.57	
930	87.5		-1.76	-0.002	3.27		137.5		-1.5	-0.0018	0.64	
1030	85.9		-1.77	-0.002	2.68		122.3		-1.6	-0.0018	0.70	
1130	84.6		-1.79	-0.002	2.19		109.9		-1.7	-0.0017	0.77	
1230	83.3		-1.81	-0.002	1.80		99.7		-1.8	-0.0016	0.84	
1330	82.1		-1.82	-0.001	1.47		91.3		-1.9	-0.0016	0.90	
1440	77.5		-1.88	-0.001	1.25		85.8		-2.0	-0.0015	0.90	

Table 3.4. Non-nitrate redox species. Standard deviations for species analyzed with the ion chromatograph ($[NO_2^-N]$, $[SO_4^{2-}]$) and TOC Analyzer (DOC) were calculated from 2-4 laboratory replicates. Summer test samples for $[NH_4^+ N]$ (collected in separate Nalgene (HDPE) bottles and analyzed using wet chemistry methods) were field-sampled in duplicate; single laboratory analyses of duplicate samples were used to calculate standard deviation for summer ammonium. Iron also was analyzed using a wet chemistry method; there were neither field nor laboratory iron replicates.

21-Oct-04

Time (min)	$[NO_2^-N]$ (uM)	SD	$[NH_4^+N]$ (uM)	SD	$[SO_4^{2-}]$ (uM)	SD	$[Fe^{2+}]$ (uM)	$[Fe_{tot}]$ (uM)	DOC (uM)	SD
0										
30										
40	0.21	0.03	4.7		13.6	0.13	16.9	18.5	47.4	0.9
60	0.13				13.7					
90	0.18	0.01	6.1		13.4		40.2	50.5	37.1	0.8
100										
110	0.18				15.6					
120	0.20	0.02	5.9		13.4	0.06	37.6	48.4	37.4	0.8
130										
140										
150										
160	0.20	0.04	6.5		13.7	0.08	36.9	44.0	46.7	1.0
170										
180										
190										
200	0.19	0.02	5.9		13.3	0.19	35.8	38.0	44.0	0.4
220										
230	0.17		6.0		13.4	0.04	40.2	43.3	45.0	0.1
240										
250	0.19		5.6		13.3	0.01	33.9	39.1	39.1	0.4
260										
270										
280	0.21		5.9		13.8	0.07	36.7	39.1	39.4	0.8
290										
300							38.3	40.5		
310	0.18				13.4					
320	0.15				13.2	0.17				
340	0.18	0.02	5.8		13.3	0.02	36.2	37.6	37.6	0.4
370	0.19	0.01	6.0		13.4	0.11	37.3	47.5	41.0	0.4

Table 3.4 (continued)

21-Oct-04

Time (min)	$[NO_2^-N]$ (uM)	SD	$[NH_4^+N]$ (uM)	SD	$[SO_4^{2-}]$ (uM)	SD	$[Fe^{2+}]$ (uM)	$[Fe_{tot}]$ (uM)	DOC (uM)	SD
0										
30										
40	0.21	0.03	4.7		13.6	0.13	16.9	18.5	47.4	0.9
60	0.13				13.7					
90	0.18	0.01	6.1		13.4		40.2	50.5	37.1	0.8
100										
110	0.18				15.6					
120	0.20	0.02	5.9		13.4	0.06	37.6	48.4	37.4	0.8
130										
140										
150										
160	0.20	0.04	6.5		13.7	0.08	36.9	44.0	46.7	1.0
170										
180										
190										
200	0.19	0.02	5.9		13.3	0.19	35.8	38.0	44.0	0.4
220										
230	0.17		6.0		13.4	0.04	40.2	43.3	45.0	0.1
240										
250	0.19		5.6		13.3	0.01	33.9	39.1	39.1	0.4
260										
270										
280	0.21		5.9		13.8	0.07	36.7	39.1	39.4	0.8
290										
300							38.3	40.5		
310	0.18				13.4					
320	0.15				13.2	0.17				
340	0.18	0.02	5.8		13.3	0.02	36.2	37.6	37.6	0.4
370	0.19	0.01	6.0		13.4	0.11	37.3	47.5	41.0	0.4

Table 3.4 (continued)

21-Oct-04

Time (min)	$[NO_2^-$ N] (uM)	SD	$[NH_4^+$N] (uM)	SD	$[SO_4^{2-}]$ (uM)	SD	$[Fe^{2+}]$ (uM)	$[Fe_{tot}]$ (uM)	DOC (uM)	SD
0										
30										
40	0.21	0.03	4.7		13.6	0.13	16.9	18.5	47.4	0.9
60	0.13				13.7					
90	0.18	0.01	6.1		13.4		40.2	50.5	37.1	0.8
100										
110	0.18				15.6					
120	0.20	0.02	5.9		13.4	0.06	37.6	48.4	37.4	0.8
130										
140										
150										
160	0.20	0.04	6.5		13.7	0.08	36.9	44.0	46.7	1.0
170										
180										
190										
200	0.19	0.02	5.9		13.3	0.19	35.8	38.0	44.0	0.4
220										
230	0.17		6.0		13.4	0.04	40.2	43.3	45.0	0.1
240										
250	0.19		5.6		13.3	0.01	33.9	39.1	39.1	0.4
260										
270										
280	0.21		5.9		13.8	0.07	36.7	39.1	39.4	0.8
290										
300							38.3	40.5		
310	0.18				13.4					
320	0.15				13.2	0.17				
340	0.18	0.02	5.8		13.3	0.02	36.2	37.6	37.6	0.4
370	0.19	0.01	6.0		13.4	0.11	37.3	47.5	41.0	0.4

Table 3.4 (continued)

17-Aug-04
Protected Stream, Station 4

Time (min)	[NO_2^- N] (uM)	SD	[NH_4^+N] (uM)	SD	[SO_4^{2}] (uM)	SD	[Fe^{2+}] (uM)	[Fe_{tot}] (uM)	[DOC] (uM)	SD
0			0.65		11.9		8.5	11.2	45.1	2.7
30			1.14		11.7				57.8	0.9
60			0.56		11.9				42.2	1.9
90	0.17	0.04	0.66	0.04	11.8	0.35			27.5	3.3
100	0.14		0.61		11.6		10.1	13.9		
110			0.85		11.2				38.8	0.8
120	0.14		0.57		11.1				43.7	2.4
130	0.14		0.75		11.5	0.03	4.2	5.7	35.5	1.5
140	0.14		0.69		11.5				38.5	1.5
150			1.02		11.3				32.8	1.0
160	0.13	0.01	0.53	0.14	11.7	0.09	4.5	7.7	24.0	3.0
170					11.4					
180	0.11		0.49		11.9				32.6	3.7
190	0.12		0.41	0.03	11.9	0.35	9.4	18.4	25.2	3.9
200			0.35	0.02	11.6				25.0	2.7
220	0.21		0.35	0.02	11.4	0.45	4.6	11.7		
230	0.13		0.37		12.0				28.7	2.5
240	0.18		0.44		11.9					
250	0.17	0.01	0.44	0.02	11.9	0.10	4.1	6.5	21.0	3.4
270	0.16		0.33		11.9	0.04			25.0	1.5
280	0.15				12.0	0.02	3.1	4.6	24.4	1.0
300	0.13	0.01	0.35	0.03	12.0	0.07			24.7	1.1
330	0.15	0.00	0.59	0.18	12.0	0.01				
1440			1.15		17.8	0.12			47.9	1.8

Table 3.4 (continued)

17-Aug-04
Runoff Stream, Station 3

Time (min)	$[NO_2^-$ N] (uM)	SD	$[NH_4^+$N] (uM)	SD	$[SO_4^{2}]$ (uM)	SD	$[Fe^{2+}]$ (uM)	$[Fe_{tot}]$ (uM)	DOC (uM)	SD
0	0.23		0.80		14.3				130.6	1.0
30	0.15		0.71		13.9				133.8	2.0
60	0.30				14.2				111.4	1.2
90	0.74	0.10	0.82	0.08	14.4	0.23	44.3	49.9	101.3	2.3
110	0.92		0.81		14.8				104.6	2.9
120	1.04	0.05	0.84	0.10	15.2	0.13	38.9	46.0	106.1	11.4
140	1.16		0.81		16.2		40.5	55.9	100.6	2.1
150	1.13		0.81		16.4				96.5	2.6
170	1.09		0.89		17.5				105.8	1.6
180	1.05	0.10	0.94	0.27	17.4	0.06	31.6	40.0	95.6	16.6
190	1.15	0.02	1.02		17.2	0.30			95.7	3.2
200	1.00	0.01	0.99		17.0	0.13			94.3	1.7
210	0.90	0.05	0.98	0.02	19.0	0.17	39.7	51.1	101.1	4.8
220	0.81	0.05	0.99		18.5	0.09			100.9	3.0
230	0.77		1.00		19.6				112.0	1.6
240	0.72	0.03	1.07	0.26	19.9	0.54	24.9	31.9	108.1	8.0
250	0.65		0.84		20.2				96.4	6.4
270			0.82	0.15	20.5		28.5	33.6	102.3	1.7
280	0.49		0.78		20.4				99.7	2.8
300	0.50	0.04	0.85	0.04	20.4	0.29			103.0	5.8
330	0.45	0.03	0.93		20.2	0.03			106.1	5.4
1440	0.30		1.39		21.3					

Table 3.5. Dissolved gases. Gas sample jars were analyzed twice on the gas chromatograph. Water temperature at the time of gas headspace withdrawal was estimated based on stream and final (post-analysis) sample water temperatures. Results for each GC peak area also were calculated at +/- 2°C of the initial estimated temperature, for a total of 3 temperatures per each of two GC injects. The 6 results per sample were used to calculate standard deviation.

21-Oct-04
Protected Stream, Station 4

Time (min)	[N_2O^- -N] (uM)	SD	[CO_2] (uM)	SD	[CH_4] (uM)	SD	[H_2] (nM)	SD
40	0.149	0.013	962.2	126.0	9.165412837	2.120237184	0.14	
90	0.159	0.006	1136.7	78.9	23.49880173	3.0270499	0.62	
120	0.177	0.008	1171.9	60.8	23.19768532	2.185796395	0.75	
160	0.160	0.011	937.1	102.7	14.68028303	2.930143744	0.48	
200	0.167	0.002	923.7	26.3	16.9010832	0.011696026	1.57	0.08
230	0.192	0.006	1083.4	13.6	20.64613532	0.925650062	0.49	0.43
250	0.206	0.001	1128.4	14.0	18.74260065	0.262363253	0.61	0.15
280	0.206	0.000	1078.0	10.9	21.01384944	0.292661095	0.68	0.03
340	0.201	0.001	1052.2	19.3	19.8695833	0.24289734	0.66	0.09
370	0.200	0.002	1025.5	36.0	19.26173083	0.402519848	0.92	0.20

8-Feb-05
Protected Stream, Station 4

Time (min)	[N_2O^- -N] (uM)	SD	[CO_2] (uM)	SD	[CH_4] (uM)	SD	[H_2] (nM)	SD
60	0.168	0.003	432.0	0.2	1.880267108	0.044511539	0.21	0.03
90	0.166	0.001	405.2	0.9	1.647703818	0.037459805	0.27	0.14
110	0.163	0.008	401.5	32.5	1.440931434	0.147454107	0.51	0.30
140	0.168	0.005	422.8	8.1	1.220688973	0.055966258	0.14	0.11
170	0.174	0.002	419.0	3.7	1.476727722	0.015999774	0.43	0.00
200	0.166	0.006	385.2	18.4	1.631669813	0.155674217	0.33	0.21
220	0.171	0.000	387.1	1.7	2.0790147	0.023142782	0.26	0.20
240	0.167	0.005	336.2	8.8	0.664907936	0.044266974	0.52	0.61
270	0.164	0.002	356.4	6.7	0.77339114	0.021486225	0.56	0.32
300	0.169	0.003	394.5	5.4	1.013789335	0.057327975	0.71	0.32
360	0.176	0.002	478.4	7.4	1.19165827	0.044612361	0.48	0.33

Table 3.5 (continued)

17-Aug-05

Protected Stream, Station 4

Time (min)	[N_2O^- -N] (uM)	SD	[CO_2] (uM)	SD	[CH_4] (uM)	SD	[H_2] (nM)	SD
70	0.226	0.012	512.6	31.6	0.832	0.10	1.69	1.00
100	0.255	0.012	556.1	23.0	1.268	0.01	1.00	0.06
130	0.261	0.014	497.6	24.4	1.137	0.02	0.54	0.00
185	0.357	0.013	504.5	18.5	0.528	0.01	1.40	0.02
215	0.333	0.013	453.7	17.1	0.488	0.01	5.40	0.11
285	0.361	0.014	473.8	6.6	0.275	0.00	1.12	0.07

Runoff Stream, Station 3

Time (min)	[N_2O^- -N] (uM)	SD	[CO_2] (uM)	SD	[CH_4] (uM)	SD	[H_2] (nM)	SD
70	0.222	0.015	621.3	54.4	34.269	0.88	0.35	0.00
90	0.782	0.034	788.8	30.1	16.181	0.63	1.43	0.40
120	1.896	0.073	790.4	30.5	24.523	0.36	1.36	0.01
180	3.958	0.158	802.6	30.6	20.155	0.32	1.14	0.09
200	4.127	0.151	806.6	29.7	13.782	0.12	1.33	0.01
280	2.889	0.108	964.3	15.9	27.379	0.26	1.06	0.05

Table 3.6 Calculated loads and masses, and chloride concentrations. Stations 3 and 4, summer test. Based on day-of-experiment average [Cl-] in each stream and discharge at Station 1 (Table 3.1), calculated discharge at Station 4 (Protected Stream) was 40.5 L/min and at Station 3 (Runoff Stream) was 8.5 L/min. Loads are the product of calculated discharge at Stations 3 and 4 using Eq. 3.9 – 3.12, and N and Br^- concentrations (Table 3.3). Mass recovered was calculated from the area under the load vs. time curve, and total mass recovered is the sum of incremental masses.

Protected Stream, Station 4

Time (min)	Br- Loads (mmol/ min)	SD	Br- Mass (mmol)	SD	$NO3^-$ - N Loads (mmol/ min)	SD	$NO3^-$ - N Mass (mmol)	SD	fBr- Loads (mmol/ min)	SD	fBr- Mass (mmol)	SD	[Cl-] (uM)	SD
0	0				9.2	0.3			9.2	0.50			207.6	
30	0		0		9.0	0.1	2.6		9.2	0.45	0		208.9	
60	0		0		9.2	0.3	3.2	0.3	9.2	0.47	0		203.0	5.4
90	0.324	0.012	4.9		15.3	0.4	91.6	1.7	17.5	0.36	124.5	2.0	208.2	0.9
100	0.524		4.2		19.7		83.0		22.6		108.7		210.1	
110	0.573	0.023	5.5	0.81	21.1	0.5	112.0	3.4	23.9	0.63	140.7	3.4	204.5	
120	0.557	0.020	5.7	0.75	20.7	0.3	117.3	3.4	23.5	0.57	144.9	3.8	207.7	
130	0.499	0.017	5.3	0.73	19.3	0.8	108.5	3.3	22.0	0.49	135.4	3.7	212.1	5.8
140	0.435	0.014	4.7	0.68	18.1	0.3	95.5	3.1	20.3	0.41	119.7	3.5	209.7	
150	0.366	0.005	4.0	0.63	16.6	0.5	81.8	2.9	18.6	0.24	102.7	3.2	207.2	
160	0.335	0.006	3.5	0.59	15.9	0.4	70.8	2.7	17.8	0.25	89.9	3.0	210.5	0.9
170	0.294	0.006	3.1	0.56	15.1	0.2	63.5	2.5	16.7	0.24	80.6	2.8	215.2	
180	0.257	0.006	2.8	0.53	14.4	0.2	55.8	2.4	15.8	0.24	70.6	2.7	209.9	
190	0.233	0.005	2.5	0.50	13.7	0.5	48.6	3.4	15.2	0.21	62.9	3.7	207.8	1.6
200	0.224	0.008	2.3	0.48	13.7	0.3	44.9	2.1	14.9	0.26	58.7	2.4	216.4	
220	0.183	0.007	4.1	0.45	12.4	0.4	77.0	3.1	13.9	0.24	104.4	3.4	197.5	7.7
230	0.177	0.002	1.8	0.42	12.7	0.2	33.8	1.8	13.7	0.17	46.1	2.2	205.9	
240	0.166		1.7		12.2		32.9		13.4		44.0			
250	0.158	0.003	1.6	0.40	11.7	0.4	27.9	1.7	13.2	0.17	41.5	2.0	210.1	0.1
270	0.143	0.002	3.0	0.39	11.4	0.5	47.7	1.5	12.8	0.15	77.2	2.0	209.3	
280	0.137	0.002	1.4	0.37	11.0	0.1	20.3	1.4	12.7	0.15	35.9	1.9	210.3	
300	0.125	0.002	2.6	0.36	11.2	0.4	38.1	1.4	12.4	0.15	67.3	3.1	210.1	0.0
330	0.115	0.003	3.6	0.35	11.0	0.4	57.0	1.4	12.1	0.16	92.2	1.8	210.6	0.2
430	0.077		9.6		10.7		168.9		11.2		246.3			
530	0.053		6.5		10.6		151.3		10.6		167.9			
630	0.037		4.5		10.5		140.7		10.1		115.9			
730	0.026		3.1		10.4		130.2		9.8		80.1			
830	0.018		2.2		10.3		119.7		9.6		55.3			

Table 3.6 (continued)

Time (min)	Br- Loads (mmol/min)	SD	Br- Mass (mmol)	SD	NO3- -N Loads (mmol/min)	SD	NO3- -N Mass (mmol)	SD	fBr- Loads (mmol/min)	SD	fBr- Mass (mmol)	SD	[Cl-] (mmol)	SD
930	0.012		1.5		10.2		109.4		9.5		38.2			
1030	0.008		1.0		10.1		99.2		9.4		26.4			
1130	0.006		0.7		10.0		89.0		9.3		18.2			
1230	0.004		0.5		9.9		79.0		9.3		12.6			
1330	0.003		0.3		9.8		69.1		9.3		8.7			
1440	0.002	0.011	0.3	0.0	10.5	0.2	108.0	0.1	9.2	0.30	6.8		209.0	4.0
mass recovered			98.4	9.0			2578.1	43.6			2524.5	50.8		
mass injected			107.3				2751.7				2751.7			
% recovered			91.7				93.7				91.7			
Runoff Stream, Station 3														
0	0				0.5				0.5				399.1	
30	0		0		0.4		0.1		0.5		0		393.5	
60	0.058		0.9		1.8		20.4		1.9		22.4		401.1	
90	0.184	0.01	3.6	0.3	4.3	0.3	40.8	2.4	5.2	0.2	93.1	2.7	394.6	3.1
110	0.185		3.7		4.2		75.2		5.2		94.6		397.0	
120	0.182	0.01	1.8	0.4	4.0	0.4	36.5	1.9	5.1	0.2	47.0	2.2	394.4	3.3
140	0.169		3.5		3.6		67.6		4.8		89.9		398.5	
150	0.160		1.6		3.4		30.5		4.6		42.2		392.3	
170	0.148		3.1		3.0		54.7		4.3		79.1		398.2	
180	0.135	0.01	1.4	0.4	2.7	0.4	23.7	1.5	3.9	0.1	36.4	1.9	390.9	7.9
190	0.124	0.00	1.3	0.4	2.3	0.4	20.3	1.4	3.6	0.1	33.3	1.8	385.6	3.1
200	0.111	0.00	1.2	0.3	2.0	0.3	16.8	1.3	3.3	0.1	30.2	1.7	382.7	2.2
210	0.125	0.00	1.2	0.4	2.2	0.4	16.4	1.3	3.7	0.1	33.9	1.7	395.8	3.1
220	0.115	0.00	1.2	0.3	1.9	0.3	16.3	1.3	3.4	0.1	30.9	1.8	396.3	2.2
230	0.119		1.2		2.0		15.2		3.5		30.0		399.4	
240	0.114	0.00	1.2	0.3	1.8	0.3	14.6	1.2	3.4	0.1	29.9	1.7	399.8	1.4
250	0.113		1.1		1.8		13.6		3.3		29.1		395.7	
270	0.106		2.2		1.5		24.2		3.2		56.3		397.0	

Table 3.6 (continued)

Time (min)	Br- Loads (mmol/ min)	SD	Br- Mass (mmol)	SD	NO3- -N Loads (mmol/ min)	SD	NO3- -N Mass (mmol)	SD	fBr- Loads (mmol/ min)	SD	fBr- Mass (mmol)	SD	[Cl-] (mmol)	SD
280	0.104		1.1		1.5		10.5		3.1		27.0		396.4	
300	0.098	0.00	2.0	0.3	1.1	0.3	16.5	0.9	3.0	0.1	51.8	1.6	398.8	2.0
330	0.091		2.8	0.3	0.8	0.3	15.5	0.7	2.8	0.1	72.8	1.6	398.3	1.7
430	0.075		8.3		0.8		38.7		2.4		212.6			
530	0.061		6.8		0.8		36.9		2.0		174.4			
630	0.050		5.6		0.8		34.5		1.7		142.8			
730	0.041		4.6		0.8		32.5		1.5		116.9			
830	0.034		3.7		0.7		30.7		1.3		95.7			
930	0.028		3.1		0.7		29.2		1.2		78.4			
1030	0.023		2.5		0.7		27.8		1.0		64.2			
1130	0.018		2.0		0.7		26.6		0.9		52.5			
1230	0.015		1.7		0.7		25.5		0.8		43.0			
1330	0.012		1.4		0.7		24.4		0.8		35.2			
1440	0.011		1.3		0.7		24.2		0.7		32.3		410.5	
mass recovered			77.0	3.5			860.4	14.0			1978.0	18.8		
mass injected			107.3				2751.7				2751.7			
% recovered			71.8				31.3				71.9			

Table 3.7. Calculation of tracer mass and removal efficiency, Protected Stream, Summer Test. The left column is the percent of total nitrate N mass (tracer + background, which was the area under the Nitrate-N load vs. Time) removed between Station 8 and Station 4. “Low end” is the ratio between actual background nitrate N loads. “high end” Station 4 load was calculated from Station 8 concentration and Station 4 Q. On 25-Mar-04, 28% of tracer + background nitrate N was lost between Stations 8 and 4. However, between 19% (actual) and 30% (if there were no N removal processes between Stations 8 and 4) would have been removed from the wetland. For most Protected Stream experiments, addition of tracer spike does not cause a large disproportionately large increase in N removal rates.

		background N removed in Protected Stream		
		low end	high end	
Date	% tracer+ BG St. 4 / St.8 mmol	% BG St.4/St.8 (actual) mmol/min	% BG St.4/St.8 (if no N lost between SpW2 & St. 4) mmol/min	
25-Mar-04	28	19	30	% removed
21-Oct-04	60	53	61	% removed
08-Feb-05	16	-8	10	% removed
17-Aug-05	33	11	37	% removed

Table 3.8. Electron balance for [NO_3^- N] loss through NO_2^- N and N_2O to N_2. Measured values of [NO_3^- N], [NO_2^- N], [N_2O –N], [SO_4^{2-}] and [CO_2] at specific times show that S^- and C_{org} provided more than enough electrons for denitrification to N_2. [SO_4^{2-}] and [CO_2] were chosen as a first approximation because these species reflect oxidation of a pool of reduced solids and concentrations increase conspicuously during the Summer, Runoff Stream test. Unaccounted for electrons may be due to partitioning of N_2O and CO_2 to the atmosphere, and to the presence of other reductants such as ferrous iron. Concentrations enclosed in boxes correspond to times when sulfate concentration varied the greatest with changing N Recovery (Figure 3.11).

					[NO_3^--N]$_t$ lost from tracer plume relative to [Br^-]$_t$		**[NO_2^--N]$_t$ relative to [NO_2^- -N]$_0$**	**1 umol e- accepted per umol NO_2 -N gained as [NO_3^- -N] -->[NO_2^--N]**		
	from Table 3.3		from Table 3.3			from Table 3.4				[corrected] from Table 3.5
	N Recovery	1 - Recovery	[NO_3^- -N]			[NO_2^--N]		e^- (umol) accepted		[N_2O -N]
	(fract N remain)	(fract. N lost)		[NO_3^--N] (uM)	[NO_3^--N]$_{conserve}$ - [NO_3^- -N]$_{actual}$		[NO2--N]$_t$ - [NO_2^- -N]$_0$	ıs NO_3^- -N --> NO_2^- -N	tracer [NO_3^--N]$_t$	
Time (min)	[NO_3^- - N]$_t$/f[Br]$_t$		[NO_3^- -N] (uM)	if N conservative	(uM)	[NO_2^--N] (uM)	(uM)	[e^-] (umol)	remaining	[N_2O -N] (uM)
0	1	0	53.6	53.6	0.0	0.29	0.00	0.00	0.00	
30	0.99	0.01	53.1	53.6	0.5	0.15	-0.13	-0.13	0.66	
60	0.93	0.07	215.5	230.2	14.7	0.30	0.01	0.01	14.68	
70										0.22
90	0.82	0.18	506.4	595.4	89.0	0.74	0.45	0.45	88.55	0.78
110	0.80	0.20	494.8	593.3	98.5	0.92	0.64	0.64	97.86	
120	0.79	0.21	480.7	581.2	100.6	1.04	0.75	0.75	99.82	1.90
140	0.76	0.24	430.2	534.5	104.3	1.16	0.87	0.87	103.43	
150	0.74	0.26	401.9	505.9	103.9	1.13	0.85	0.85	103.07	
170	0.70	0.30	355.8	461.3	105.5	1.09	0.80	0.80	104.73	
180	0.68	0.32	315.3	417.6	102.3	1.05	0.77	0.77	101.57	3.96
190	0.63	0.37	274.7	375.0	100.3	1.15	0.86	0.86	99.46	
200	0.59	0.41	232.9	328.0	95.1	1.00	0.72	0.72	94.37	4.13
210	0.61	0.39	263.9	368.1	104.2	0.90	0.62	0.62	103.58	
220	0.57	0.43	231.7	330.9	99.2	0.81	0.52	0.52	98.68	
230	0.57	0.43	236.3	338.4	102.2	0.77	0.49	0.49	101.66	
240	0.55	0.45	219.1	318.8	99.7	0.72	0.44	0.44	99.22	
250	0.53	0.47	211.0	310.1	99.2	0.65	0.36	0.36	98.79	
270	0.49	0.51	183.6	278.1	94.5					
280	0.47	0.53	173.6	265.8	92.2	0.49	0.21	0.21	91.98	2.89
300	0.37	0.63	129.9	212.0	82.1	0.50	0.22	0.22	81.90	
330	0.30	0.70	100.3	170.3	69.9	0.45	0.16	0.16	69.77	

Table 3.8 (continued)

$[N_2O\ \text{-N}]_t$ relative to $[N_2O\ \text{-N}]_0$	**4 umol e- accepted per umol N_2O -N gained as $[NO_3^-\ \text{-N}]$ -->$[N_2O\ \text{-N}]$**		From Table 3.4		**assume 7 umol e^- donated by S to e acceptor(s) to produce 1 umol SO_4^{2-}**	minimum umol e lost by NO_3^- -N to NO_2^- -N and N_2O^- -N	S electrons donated and not accounted for	From Table 3.5		**assume 4 umol e^- donated by C_{org} to e acceptor(s) to produce 1 umol CO_2**
	e^- (umol) accepted as NO_3^- -N --> N_2O -N	tracer $[NO_3^-\text{-N}]_t$				at tracer times=t				
$d[N_2O\ \text{-N}]$ (uM)	$[e^-]$ (umol)	remaining	$[SO_4^{2-}]$ (uM)	$[SO_4^{2-}]_t - [SO_2^-]_0$ (uM)	$[e^-]$ (umol)	$[e^-]$ (umol)	$[e^-]$ (umol)	$[CO_2]$ (uM)	$[CO_2]_t - [CO_2]_0$ (uM)	$[e^-]$ (umol)
			13.9							
			13.9	0.0	0					
			14.2	0.3	2.1					
0.00	0.00							621.3	0.0	
0.56	2.24	86.3	14.4	0.5	3.7	2.7	1.0	788.8	167.5	669.9
			14.8	1.0	6.8					
1.67	6.70	93.1	15.2	1.3	9.1	7.5	1.6	790.4	169.1	676.3
			16.2	2.4	16.5					
			16.4	2.5	17.5					
			17.5	3.6	25.1					
3.74	14.95	86.6	17.4	3.5	24.5	15.7	8.8	802.6	181.3	725.0
			17.2	3.4	23.6					
3.91	15.62	78.8	18.0	4.1	28.8	16.3	12.5	806.6	185.3	741.2
			19.0	5.2	36.1					
			18.5	4.6	32.5					
			19.6	5.7	40.2					
			19.9	6.1	42.4					
			20.2	6.3	44.3					
			20.5	6.6	46.3					
2.67	10.67	81.3	20.4	6.6	46.0	10.9	35.1	964.3	343.0	1372.0
			20.4	6.5	45.7					
			20.2	6.3	44.4					

Table 3.8
(continued)

Table 3.8 (continued)

minimum umol e lost by NO_3^- -N to NO_2^- -N and N_2O^- -N at tracer times=t [e^-] (umol)	C_{org} electrons donated and not accounted for [e^-] (umol)	$S^- + C_{org}$ electrons donated and not accounted for	Time (min)	(carried from previous column) tracer [NO_3^--N]$_t$ still remaining	**assume complete denitrification** **$2NO_2^-$ N + $10e^-$ = N_2** [N2] (uM)	e^- required [e^-] (umol)	$S^- + C_{org}$ electrons donated and not accounted for [e^-] (umol)
			0				
			30				
			60				
			70				
2.7	667.2	668.2	90	86.3	43.15	431.54	236.7
			110				
7.5	668.8	670.4	120	93.1	46.56	465.60	204.8
			140				
			150				
			170				
15.7	709.3	718.1	180	86.6	43.31	433.14	285.0
			190				
16.3	724.9	737.3	200	78.8	39.38	393.77	343.6
			210				
			220				
			230				
			240				
			250				
			270				
10.9	1361.2	1396.3	280	81.3	40.65	406.53	989.8
			300				
			330				

Map of Field Area

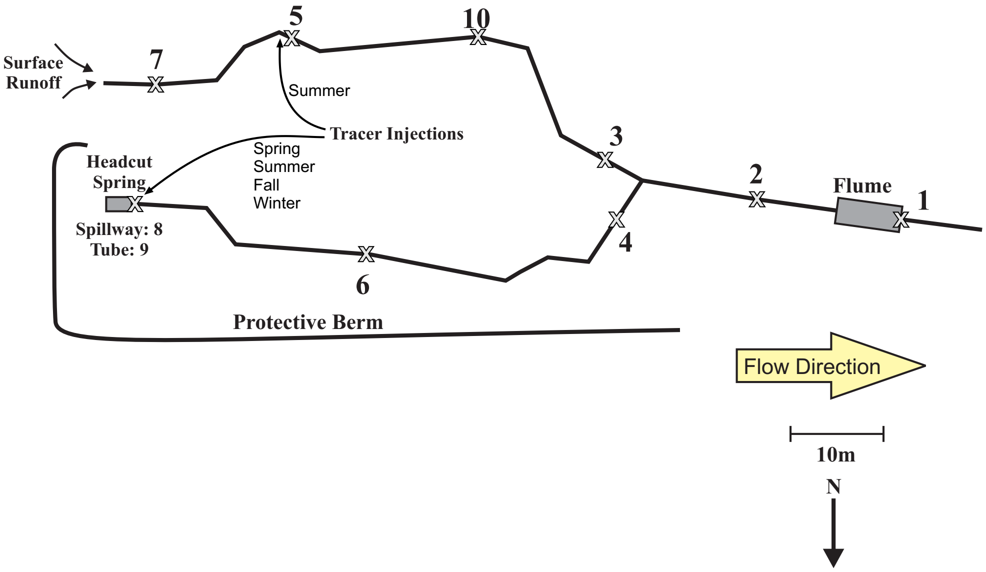

Figure 3.1. Schematic map of field area. The Protected Stream (north side) tracer was injected 1 meter downstream of Station 8, the headcut-spring flume and upstream samples were collected approximately 2m downstream of the point of injection. Stations 6 and 4 were the midstream and downstream sampling locations in the Protected Stream. Runoff Stream (south side, summer experiment only), tracer was injected about 2m upstream of Station 5; upstream samples were collected at Station 5. Station 10 was the midstream and Station 3 the downstream sampling locations in the Runoff Stream. Note that the map is oriented with the North arrow pointing down so that flow is left-to-right, corresponding to the direction of plume evolution in the concentration vs. time graphs.

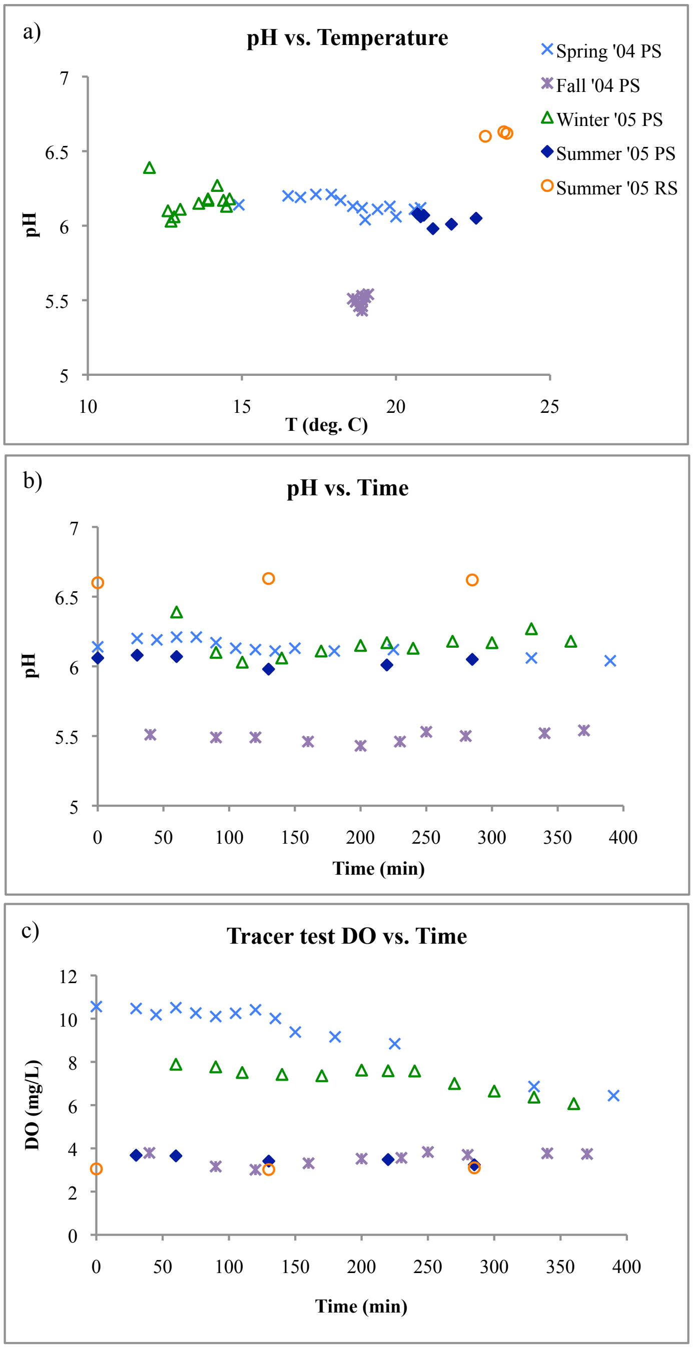

Figure 3.2. pH, Temperature and Dissolved Oxygen. Temperature increases during the Spring, Winter and Summer Protected Stream tests did not influence pH (top plot). The Fall Protected Stream and Summer Runoff Stream showed very little variation in Temperature (there were only 3 data points for the Summer Runoff Stream). pH decreased somewhat after initial value (middle plot) during the Summer, Spring and Winter Protected Stream tests. Summer Runoff Stream pH was about 6.5, and fall Protected Stream 5.5, compared to pH values of about 6 during the other Protected Stream experiments. Dissolved O_2 initially was highest in the Spring and decreased after about 100 minutes. Water temperature during the Spring test increased from 14.9 to 20.8 (Table 3.2), the greatest T difference for any of the tests.

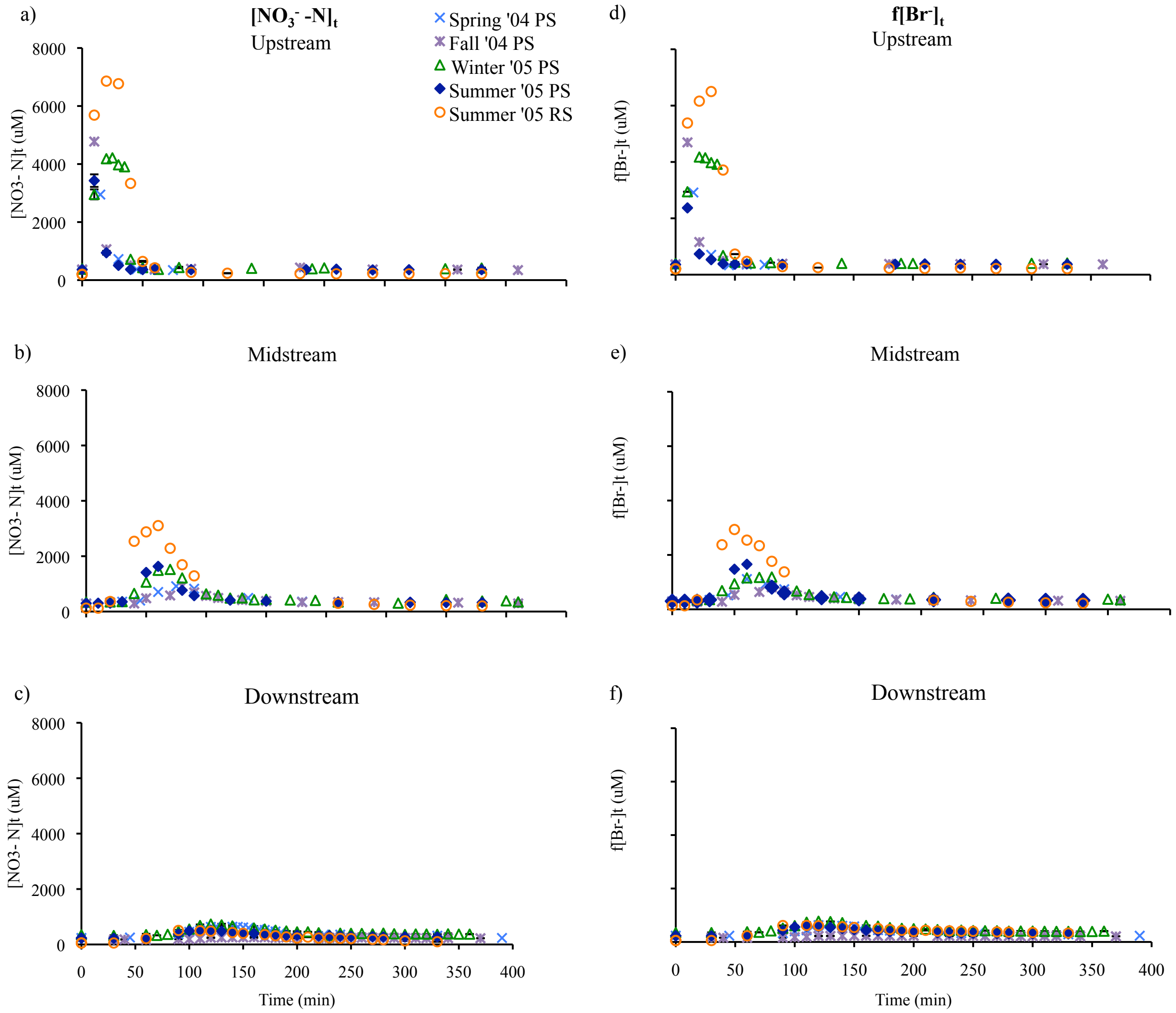

Figure 3.3. Tracer breakthrough curves. Distance between the point of injection was 58m in the Protected Stream and 52m in the Runoff Stream (summer test only). The limbs of the $[NO_3^- -N]_t$ and f[Br-]t (Table 3.3) breakthrough curves became progressively wider at mid- and downstream locations, with an increasingly steeper rising than falling limb, likely due to longitudinal dispersion.

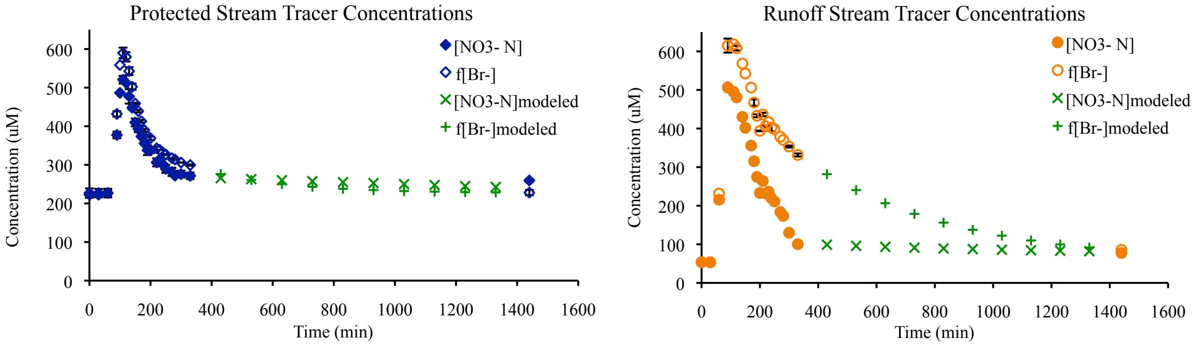

Figure 3.4. Summer downstream breakthrough curves. Data from Table 3.3, plotted on a different scale than in Figure 3.2, show higher background [NO_3^- -N] in the Protected Stream than in the Runoff Stream at the upstream sampling locations (about 2m downstream of the points of injection). In addition, [NO_3^- -N] and f[Br^-] are similar in the Protected Stream whereas the difference in concentrations becomes increasingly pronounced in the Runoff Stream, especially after peak tracer concentration. Estimated concentrations ([NO_3^- -N]$_{modeled}$ and f[Br-] between t=330min and t=1440min were calculated using natural rate of decay equations 3.13 – 3.18 (see Methodology, Data Analysis).

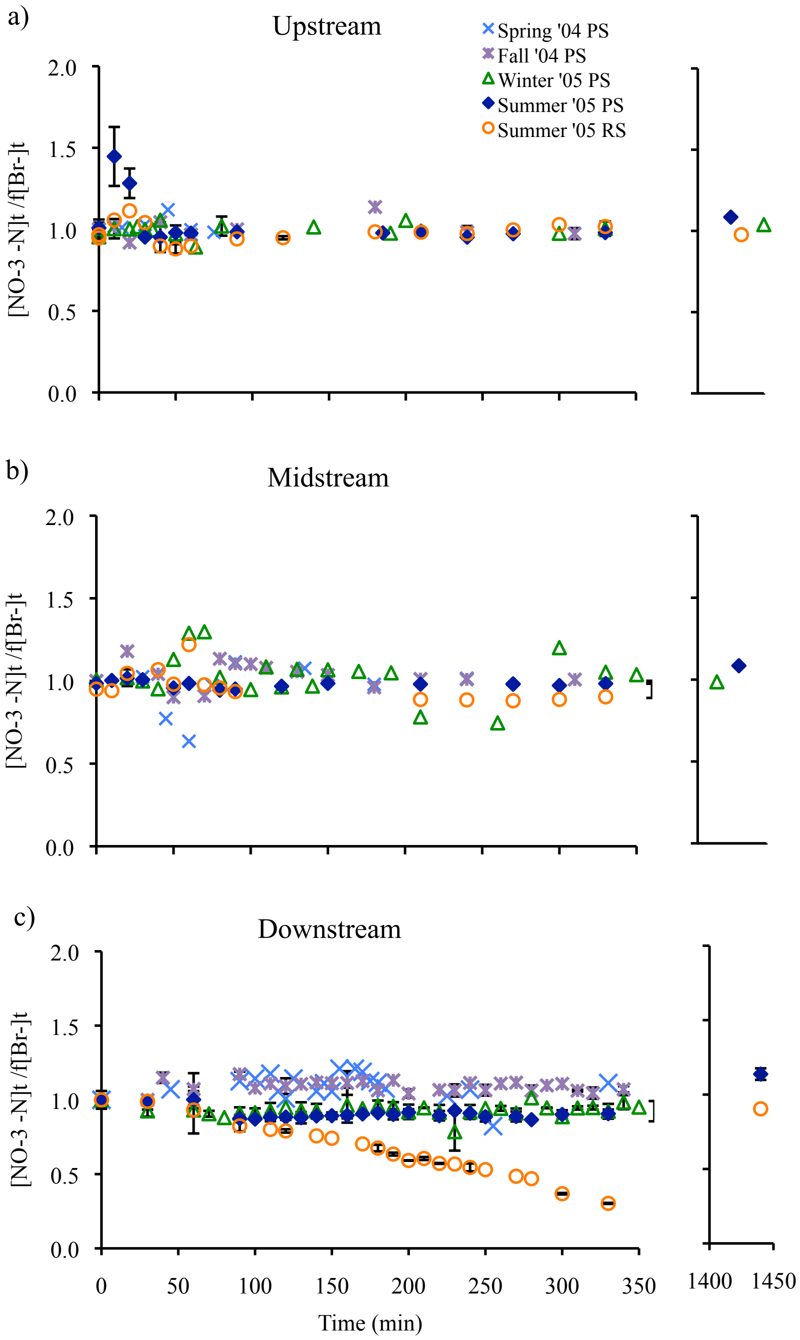

Figure 3.5. N Recovery. Nitrate-N and bromide concentration data (Table 3.3) were used to calculate N Recovery: [NO$^{-}_{3}$ -N]$_{t}$ /f[Br-]t,). At the up- and midstream sampling locations, Recovery fluctuates around unity, with more scatter when the tracer plume moved through each location. Downstream, N Recovery in the Protected Stream dipped to 0.87 at t=100min and gradually increased to 0.91 at t=330min and 1.1 the next morning at t=1440min. In contrast, Runoff Stream N Recovery decreases sharply after t=60min, to a minimum of 0.30 at t=330min. Runoff Stream N Recovery was 0.90 at t=1440min.

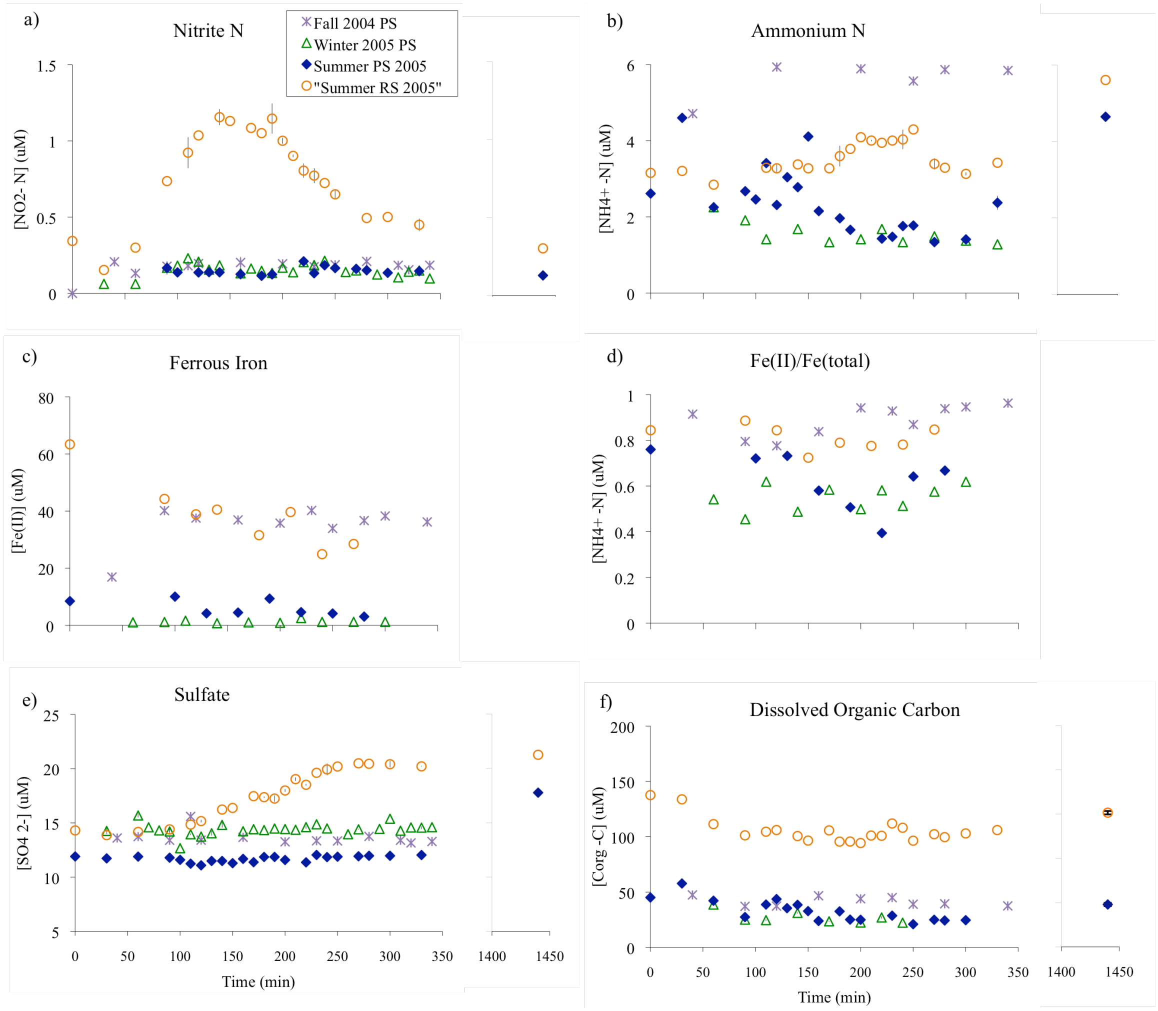

Figure 3.6. Downstream chemically reduced N species and lower-potential redox species. Graphed data from Table 3.4 show: a) significant rise and fall in Runoff Stream (RS) [NO_2^- -N] corresponding to arrival of tracer breakthrough curve, with stable [NO_2^- -N] in the Protected Stream (PS); b) highest [NH_4^+ -N] in fall PS and lowest in winter PS; highest c) [Fe^{2+}] and d) [Fe^{2+}]:[Fe_{total}] in summer PS and fall RS; e) increasing [SO_4^{2-}] in the Runoff Stream only and f) 2.5- to 3-fold higher concentration and apparent dip and recovery of [DOC] in the Runoff Stream.

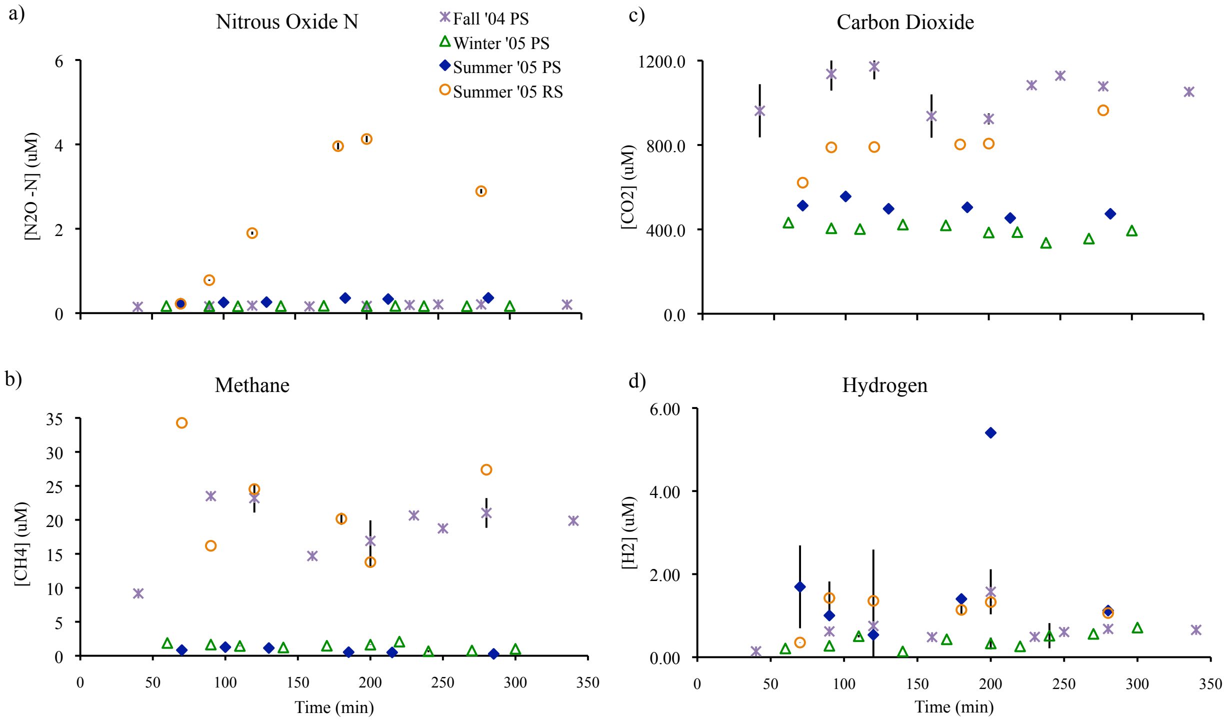

Figure 3.7. Downstream dissolved gases. Data from Table 3.5 show: a) same initial concentration and subsequent sharp increase in Runoff Stream dissolved [N_2O -N]; b) Dissolved [CO_2] was highest in the fall and lowest in winter Protected Stream, and increased in the Runoff Stream during the summer test; c) Higher Runoff Stream [CH_4] and d) somewhat higher summer PS and RS [H_2].

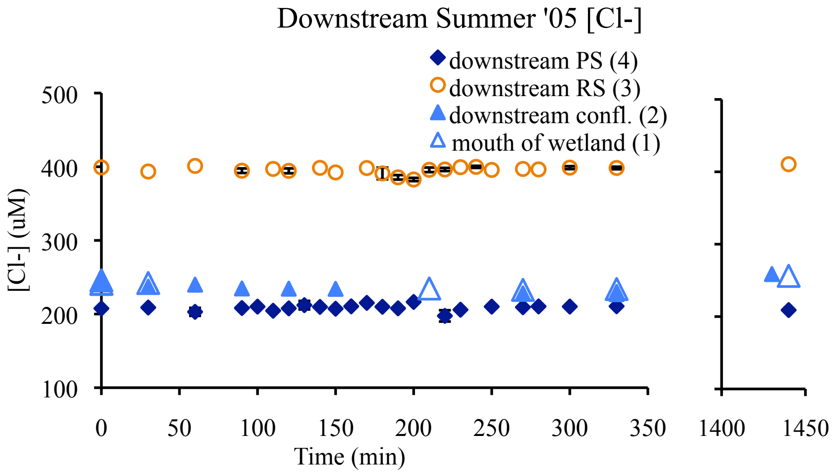

Figure 3.8. Downstream summer chloride. Background [Cl$^-$] (Table 3.3) was consistently twice as high during the tracer experiment, as it was for most of the two-year study period. Chloride concentrations at Station 2 (downstream of the confluence) and Station 1 (at the mouth of the wetland) were consistent with each other through time. This condition indicated that it was appropriate to include average [Cl$^-$] at Station 1, where discharge was measured at the flume spillway, in the conservation of mass balance equations that were used to calculate discharge at Stations 4 (40.5 mL/min) and 3 (8.5 mL/min).

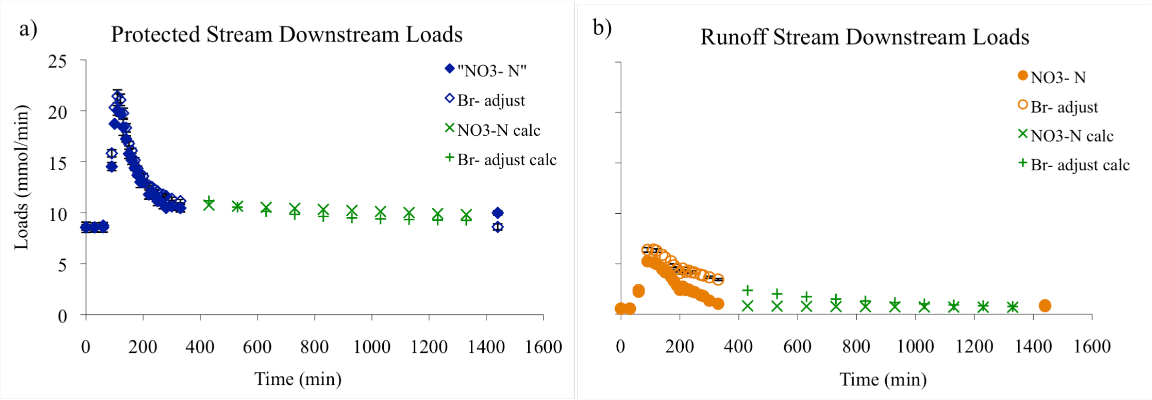

Figure 3.9. Downstream summer tracer loads. Loads (Table 3.3) are the products of concentrations (Table 3.3) and calculated discharge at Stations 3 (8.5 mL/min) and 4 (40.5 mL/min), respectively, for the Runoff Stream and Protected Stream.

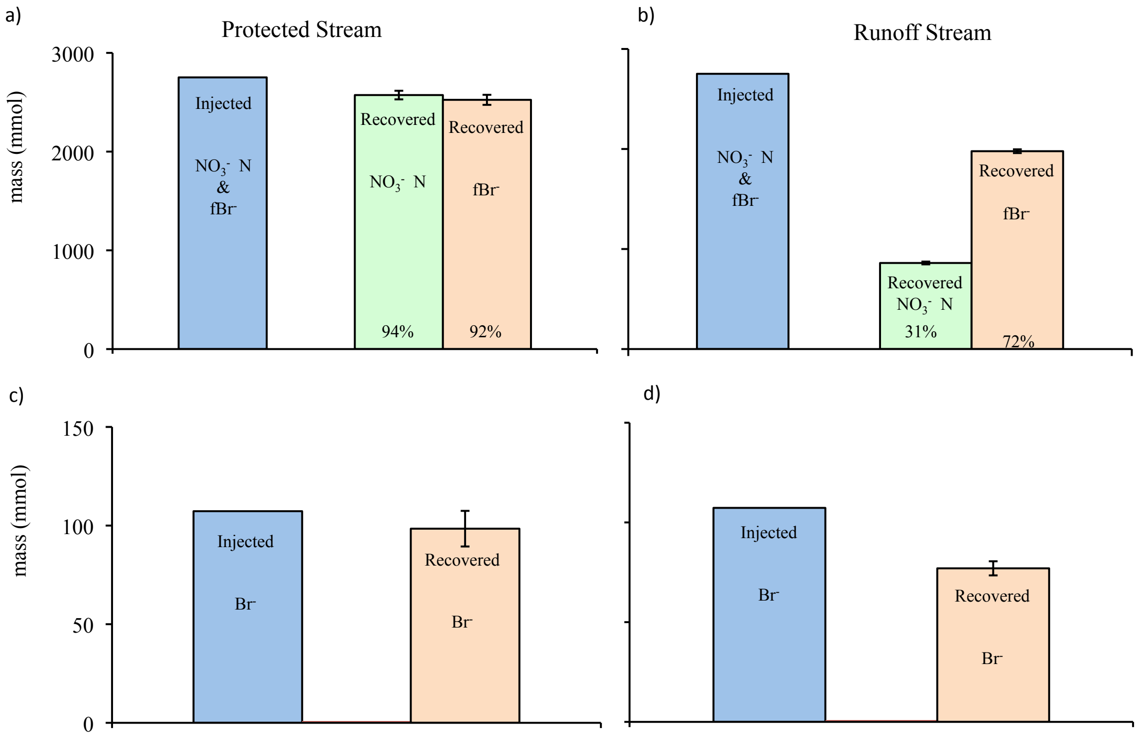

Figure 3.10. Injected and recovered summer tracer mass. Total downstream mass recovered (Table 3.3) was determined geometrically, in increments of each successive data point, as the area under the measured and modeled load vs. time curves (Figure 3.6) and above background of 8.6 mmol/min at Station 4 (Protected Stream) and 0.0mmol/min at Station 3 (Runoff Stream).

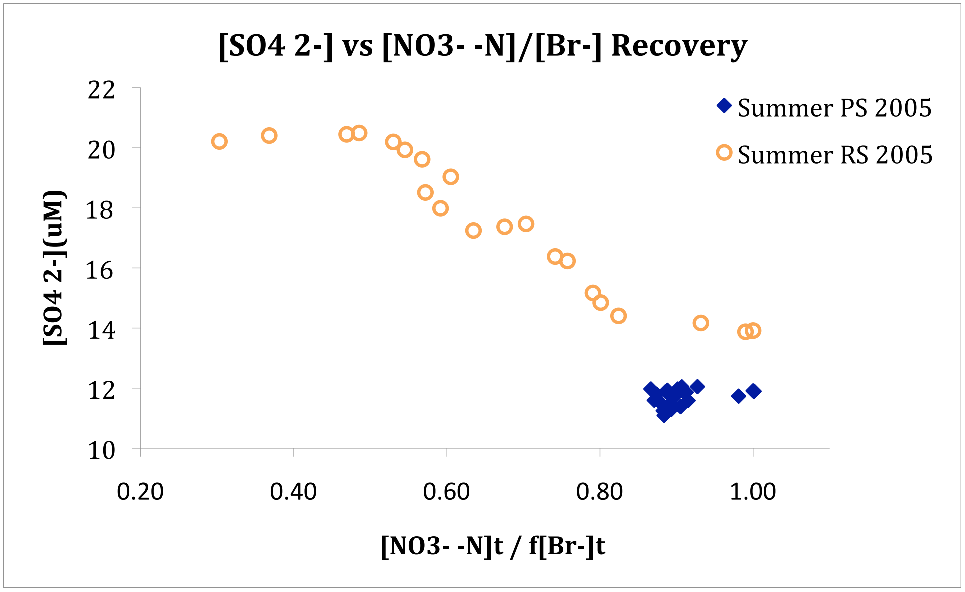

Figure 3.11. Summer [SO_4^{2-}] vs. N Recovery. Summer Runoff Stream [SO_4^{2-}] increases from 14uM to 20uM as N Recovery values of 0.8 to 0.5, indicating that a process other than S^- oxidation accounts for apparent N loss below Recovery = 0.5. An abundant, low potential reductant such as C_{org} may account for decreasing [NO_3^- N] relative to [Br^-] below this threshold. Protected Stream [SO_4^{2-}] and N Recovery are not correlated.

References

Aravena, R. and W.D. Robertson (1998) Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic plume. Ground Water 36(6):975-982.

Bastviken, S.K., P.G. Eriksson, I. Martins, J.M. Neto, L. Leonardson and K. Tonderski (2003) Wetlands and aquatic processes: Potential nitrification and denitrification on different surfaces in a constructed treatment wetland. J. Environ. Qual. 32:2414-2420.

Beaulieu, J.J., C.P. Arango, and J.L. Tank (2009) The effects of season and agriculture on nitrous oxide production in headwater streams. J. Environ. Qual. 38:637-646.

Bennet, C.A. and N.L. Franklin (1954) Statistical Analysis in Chemistry and the Chemical Industry. John Wiley & Sons, New York, 724 p.

Beristain-Cardoso, R., A-C. Texier, R. Sierra-Álvarez, E. Razo-Flores, J.A. Field, J. Gómez (2009) Effect of initial sulfide concentration on sulfide and phenol oxidation under denitrifying conditions. Chemosphere 74:200-205.

Botter, G., N.B. Basu, S. Zanardo, P.S.C. Rao, and A. Rinaldo (2010) Stochastic modeling of nutrient losses in streams: Interactions of climatic, hydrologic, and biogeochemical controls. Water Resources Research 46(W08509), 14p.

Burns, D.A. amd L. Nguyen (2002) Nitrate movement and removal along a shallow groundwater flow path in a riparian wetland within a sheep-grazed pastoral catchment: Results of a tracer study. New Zealand Journal of Marine and Freshwater Research 36: 371-385.

Clesceri, L., A Greenberg and A. Eaton, 1998. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, New York.

Cooper, A.B. (1994) Coupling wetland treatment to land treatment: An innovative method for nitrogen stripping? Water Science and Technology 29: 141-149.

Edwards, R.T. (1998) The Hyporheic Zone. *In* Naiman, R.J. and R.E. Bilby, eds. River Ecology and Management: Lessons from the Pacific Coastal Ecoregion. Springer –Verlag, 705p.

Ferguson, S.J. (1994) Denitrification and its control. Antonie van Leeuwenhoek 66:89-110.

Faure, Gunter (1998) Principles and Applications of Geochemistry, Second Edition. Prentice Hall, 600p.

Endale, D.M., J.W. Washington, and L. Samarkina (2003) Role of iron-rich Georgia soils in controlling nitrate contamination of ground water. Proceedings of the 2003 Georgia Water Resources Conference, held April 23-24, 2003 at the University of Georgia. Karen J. Hatcher, editor, Institute of Ecology, The University of Georgia, Athens, Georgia.

Ernstsen, V. (1996) Reduction of nitrate by Fe^{2+} in clay minerals. Clays and Clay Minerals 44(5):599-608.

Ferguson, S.J. (1994) Denitrification and its control. Antonie van Leeuwenhoek 66:89-110.

Field, M.S. (2002) Efficient hydrologic tracer-test design for tracer-mass estimation and sample-collection frequency, 2. Experimental Results. Environmental Geology 42: 839-850.

Galloway, J.N., A.R. Townsend, J.W. Erisman, M. Bekunda, Z. Cai, J.R. Freney, L.A. Martinelli, S.P. Seitzinger, M.A. Sutton (2008) Transformation of the nitrogen cycle: Recent trends, questions and potential solutions. Science 320:889-892.

Georgia Forestry Commission (2011) Fire Weather System Data from 1200 Hog Mountain Road, at USDA, ARS: http://weather.gfc.state.ga.us/climate/climate.aspx

Holmer, M. and P. Storkholm (2001) Sulphate reduction and sulphate cycling in lake sediments: a review. Freshwater Biology 46:431-451.

Howarth, R.W., E.W. Boyer, W.J. Pabich and J.N. Galloway (2002) Nitrogen use in the United States from 1961-2000 and potential future trends. Ambio 31(2):88-96.

Inwood, S.E., J.L. Tank, and M.J. Bernot (2007) Factors controlling sediment denitrification in Midwestern streams of varying land use. Microbial Ecology 53:247-258.

Jonsson, K., H. Johansson, A. Wörman (2003) Hyporheic exchange of reactive and conservative solutes in streams – tracer methodology and model interpretation. Journal of Hydrology 278:153-171.

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

Jorgensen, C.J., O.S. Jacobsen, B. Elberling, and J. Aamand (2009) Microbial oxidation of pyrite coupled to nitrate reduction in anoxic groundwater sediment. Environ. Sci. Technol. 43(13):4851-4857.

Kadlec, R.H. (2010) Nitrate dynamics in event-driven wetlands. Ecological Engineering 36:503-516.

Kaplan, W.A. and S.C. Wofsy (1985) The biogeochemistry of nitrous oxide: a review. Advances in Aquatic Microbiology, Vol. 3: 181-206.

Kappor, A., (1997) Nitrate removal from drinkingw water – review. Jour. Environmental Engineering 123(4).

Kellman, L. and C. Hillaire-Marcel (1998) Nitrate cycling in streams: using natural abundances of NO_3^- - delta^{15}N to measure *in-situ* denitrification. Biogeochemistry 43: 273-292.

Kilpatrick, F.A. and E.D. Cobb (1985) Measurement of discharge using tracers: Techniques of water-resources investigations of the United States Geological Survey Book 3, Chapter A16.

Kirchner, J.W., X. Feng, C. Neal (2001) Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations. Journal of Hydrology 254:82-101.

Korom, S. (1992) Natural denitrification in the saturated zone: A review. Water Resources Research 28(6):1657-1668.

Laverman, A.M., J.A. Garnier, E.M. Mounier, C.L. Roose-Amsaleg (2010) Nitrous oxide production kinetics during nitrate reduction in river sediments. Water Research 44:1753-1764.

Lin, A.Y.-C., J.F. Debroux, J.A. Cunningham, M. Reinhard (2003) Comparison of rhodamine WT and bromide in the determination of hydraulic characteristics of constructed wetlands. Ecological Engineering 20: 75-88.

Madigan, M.T., J.M. Martinko and J. Parker (2003) Brock Biology of Microorganisms, Tenth Edition. Prentice Hall, 1005 p.

Maître, V., A.-C. Cosandey, E. Desagher, A. Parriaux (2003) Effectiveness of groundwater nitrate removal in a river riparian area: the importance of hydrogeological conditions. Journal of Hydrology 278:76-93.

Manson, J.R. (2000) Predicting stream transient storage zone characteristics from tracer data. Water Resources Research 36(2): 629-631. Marine Science Today (2009).

Martin, J.L., S.C. McCutcheon and R.W. Schottman (1999) Hydrodynamics and Transport for Water Quality Monitoring. CRC Press, 795p.

Mayer B., E.W. Boyer, C. Goodale, N.A. Jawarski, N. Van Breemen, R.W. Howarth, S. Seitsinger, G. Billen, K. Lajtha, K. Nadelhoffer, D. Van Dam, L.J. Heitling, M. Nosal, K. Paustian (2002) Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints. Biogeochemistry 57/58: 171-197.

Meile, C., W.P. Porubsky, R.L. Walker, and K. Payne (2010) Natural attenuation of nitrogen loadings from septic effluents: Spatial and environmental controls. Water Research 44:1399-1408.

Mitsch, W.J., J.W. Day, L. Zhang, and R.R. Lane (2005) Nitrate-nitrogen retention in wetlands in the Mississippi River Basin. Ecological Engineering 24:267-278.

Molénat, J. and Gascuel-Odoux, C. (2002) Modelling flow and nitrate transport in groundwater for the prediction of water travel times and of consequences of land use evolution on water quality. Hydrological Processes 16: 479-492.

Muckler, J.F. (2010) Nitrogen transformations in the vadose zone of a small zero-order piedmont watershed in Watkinsvile, Georgia. Master of Science Thesis, University of Georgia Department of Geology, 135p.

Nangia, V., P.H. Gowda, and D.J. Mulla (2010) Effects of changes in N-fertilizer management on water quality trends at the watershed scale. Agricultural Water Management:97:1855-1860.

Ocampo, C.J., C.E. Oldham, and M. Sivapalan (2006) Nitrate attenuation in agricultural catchments: Shifting balances between transport and reaction. Water Resources Research 42, WO1408: 16 p.

Ostrom, N.E., L.O. Hedin, J.C. von Fischer, and G.P. Robertson (2002) Nitrogen transformations and NO_3^- removal at a soil-stream interface: A stable isotope approach. Ecological Applications 12(4): 1027-1043.

Peterson, B.J., W.M. Wolheim, P.J. Mulholland, J.R. Webster, J.L. Meyer, J.L. Tank, E. Marti, W.B. Bowden, H.M. Valett, A.E. Hershey, W.H. McDowell, W.K. Dodds, S.K. Hamilton, S. Gregory, D.D. Morrall (2001) Control of nitrogen export from watersheds by headwater streams. Science 292: 86-90.

Poor, C., and J.J. McDonnell (2007) The effects of land use on stream nitrate dynamics. J. Hydrology 332:54-68.

Ribolzi, O., P. Andrieux, V. Valles, R. Bouzigues, T. Bariac, M. Voltz (2000) Contribution of groundwater and overland flows to storm flow generation in a cultivated Mediterranean catchment. Quantification by natural chemical tracing. Journal of Hydrology 233:241-257.

Rivera-Monroy, V.H., P. Lenaker, R.R. Twilley, R.D. Delaune, C.W. Lindau, W. Nuttle, E. Habib, R.W. Fulweiler, E. Castañeda-Moya (2010) Denitrification in coastal Louisiana: A spatial assessment and research needs. Journal of Sea Research 63: 157-172.

Rose, A.W., H.E. Hawkes, J.S. Webb (1979) Geochemistry in Mineral Exploration. Academic Press, 323p.

Rutherford, J.C. (1994) River Mixing. John Wiley, New York. 362p.

Rutherford, J.C. and M.L. Nguyen (2004) Nitrate removal in riparian welands: Interactions between surface flow and soils. Journal of Environmental Quality 33: 1133-1143.

Schroer, K.L., D.M. Endale, C.L. Tebes-Stevens, J.W. Washington, and V. Nzengung (2007) Concentrations and estimated loads of nitrogen contributed by two adjacent wetland streams with different flow-source terms in Watkinsville, GA. Proceedings of the 2007 Georgia Water resources Conference, held March 27-29, 2007, at the University of Georgia. 4p.

Seaman, J. C., P.M. Bertsch, S.F. Korom and W.P. Miller (1996) Physicochemical controls on nonconservative anioin migration in coarse-textured alluvial sediments. Ground Water 34(5):778-783.

Seo, D.C., and R.D. DeLaune (2010) Fungal and bacterial mediated denitrification in wetlands: Influence of sediment redox condition. Water Research 44: 2441-2450.

Silvennoinen, H., A. Liikanen, J. Torssonen, C. Florian Stange, and P.J. Martikainen (2008) Denitrification and nitrous oxide effluxes in boreal, eutrophic river sediments under increasing nitrate load: a laboratory microcosm study. Biogeochemistry 91:105-116.

Smith, M.S.. and J.M. Tiedje (1979) Phases of denitrification following oxygen depletion in soil. Soil Biol. Biochem. 11:261-267.

Solecki, J. (2010) Studies of phosphate anion sorption using the soil samples. J. Radioanal. Nucl. Chem. 284: 623-627.

Matheson, F.E. and J.P. Sukias (2010) Nitrate removal processes in a constructed wetland treating drainage from a dairy pasture. Ecological Engineering 36:1260-1265.

Thieu, V., G. Billen, and J. Garnier (2009) Nutirent transfer in three contrasting NW European watersheds: the Seine, Somme and Scheldt rivers: a comparitive application of the Seneque/Riverstrahler model. Water Research 43(6):1740-1754.

Triska, F.J., V.C. Kennedy, R.J. Avanzino, G.W. Zellweger, and K.E. Bencala (1989) Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes. Ecology 70(6): 1893-1905.

Triska, F. J., Pringle, C.M., Zellweger, G.W., Duff, J.H., and Avanzino, R.J. (1993) Dissolved inorganic nitrogen composition, transformation, retention and transport in naturally phosphate-rich and phosphate-poor environments. Canadian Journal of Fisheries and Aquatic Science 50: 665-675.

UNEP (2010) UNEP Year Book: New Science and Developments in our Changing Environment 2010. United Nations Environmental Programme. 66p.

USEPA (2009) Natural Water Quality Inventory: Report: to Congress, 2004 Reporting Cycle. Office of Water EPA-841-R-08-001, 37p.

Valett, H.M., J.A. Morrice, C.N. Dahm, and M.E. Campana (1996) Parent lithology, surface-groundwater exchange, and nitrate retention in headwater streams. Limnology and Oceanography 41(2): 333-345.

van Groenigen, J.W., P.J. Kuikman, W.J.M. de Groot, and G.L. Velthof (2005) Nitrous oxide emission from urine-treated soil as influenced by urine composition and soil physical conditions. Soil Biology and Biochemistry 37:463-473.

Verchot, L.V., E.C. Franklin and J.W. Gilliam (1997) Nitrogen cycling in piedmont vegetaded filter zones: I. Surface Soil Processes. Journal of Environmental Quality 26: 327-336.

Viollier, E., P.W. Inglett, K. Hunter, A.N. Roychoudhury and P. Van Cappellen (2000) The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. Applied Geochemistry 15: 785-790.

Wagner, B.J. and J.W. Harvey (1997) Experimental design for estimating parameters of rate-limited mass transfer: Analysis of stream tracer studies. Water Resources Research 33:1731-1741.

Washington, J.W., D.M. Endale, L.P. Samarkina and K.E. Chappell (2004) Kinetic control of oxidation state at thermodynamically buffered potentials in subsurface waters. Geochimica et Cosmochimica Acta 68, 4831-4842.

CHAPTER 4

CONTROLS ON WETLAND NITRATE REMOVAL AS INFERRED BY A TWO-YEAR SAMPLING STUDY IN TWO ADJACENT WETLAND STREAMS WITH DIFFERENT GEOCHEMISTRY AND FLOW-SOURCE TERMS IN THE GEORGIA PEIDMONT[1]

---

[1] Schroer, K.L., J.W. Washington, D. Endale, R. Thomas and V. Nzengung. To be submitted to *Environmental Science and Technology*

Abstract

A small wetland has been modified to study the effect of different flow-source terms on N cycling. Two adjacent shallow streams flow through a small wetland draining a cattle pasture. Surface runoff is prevented from flowing to the Protected Stream by a man-made earthen berm, and there is a flowing spring at its headcut. The adjacent Runoff Stream (14m apart at headcut) accepts water and soil runoff from the up-gradient pasture. Based on a two year, approximately monthly sampling study, higher Runoff Stream concentrations of organic C, ammonium, methane, and hydrogen indicated reducing conditions relative to the Protected Stream. In addition, higher Runoff Stream concentrations of nitrite and nitrous oxide, and lower downstream concentrations of nitrate, were evidence of enhanced denitrification in the Runoff Stream. Samples were collected ~monthly for two years at 8-10 sampling stations and samples were analyzed for the above parameters using field probes, laboratory instruments and wet chemistry methods. The Pearson's R test was used to test for linear correlations, and results between were highlighted for all parameters at 0.95 and 0.99 confidence intervals. Statistically significant positive and negative coefficients were investigated, in conjunction with tracer test results, to further constrain controls on wetland nitrate removal processes based on inter-seasonal, inter-stream and intra-stream comparisons. Organic carbon was the main electron donor in both streams. Sulfide may be an important secondary reductant. Temperature exerted control on stream redox processes, indicated by moderate to strong increases in [NO_3^- -N] , [$H_2CO_3^*$], [DOC], [Fe^{2+}] and [Fe^{3+}] above 18-20°C . Stream baseflow exerted less control than baseflow-plus-runoff on the wetland's capacity to remove nitrate N. These results constrain processes that influence the efficiency of wetland streams to remove nitrate N from agricultural sources.

Introduction

The increase in littoral, estuarine and lacustrine dead zones, and human health issues such as blue baby syndrome, cause rising concerns about sources of reactive nitrogen (N), in particular from agricultural sources. The areas of some dead zones, such as the one in the Gulf of Mexico, are quite large (seasonally as large as 21,000 km^2) (Rivera-Monroy et al., 2010), and averaging 15,500 km^2 between 2004 - 2009 (Marine Science Today, 2009). Environmental and human health problems attributed to reactive N increasingly are recognized as critical issues of national and international scope. In the most recent bi-annual water quality report to Congress, states cite nutrients such as nitrate among the highest priority pollutants in streams, lakes, ponds, reservoirs, bays and estuaries (USEPA, 2009).

Many process-level controls on N cycling have been difficult to constrain due to the complexity of the N cycle and its interaction with other biogeochemical cycles and hydrological processes. These include 1) lack of tools for estimating how watershed-scale conditions (e.g., local soils, climate) and changes therein influence nitrate concentrations (Poor and McDonnell, 2007; Kaushal et al., 2010; Yang and Jin, 2010); 2) difficulties in quantifying nitrate export from wetlands and headwater streams due to poor understanding of N cycling processes across spatial and temporal scales (Ocampo et al., 2006); 3) factors that limit nitrate removal in wetlands (Bastviken et al., 2009); and 4) the effects of temperatures below 20 deg. C on denitrification (Elefsiniotis and Li, 2006).

Background

Nitrogen Cycle

Nitrogen exists in a total of 9, but commonly 7, oxidation states (Figure 4.1) from –3 to +5 (Whitten and Gailey ,1981; Zumdahl, 2000). Major N compounds in the environment include nitrate (NO_3^-, +5), nitrogen dioxide gas (NO_2, +4), nitrite (NO_2^-, +3), nitric oxide gas (NO, +2), and nitrous oxide gas (N_2O, +1). Nitrogen in ammonia gas (NH_3) and ammonium ion (NH_4^+) are in the –3 oxidation state, and organic N (R- NH_2) is generally -3 as well (Madigan et al., 2003, Stumm and Morgan, 1996). Elemental (valence state = 0) nitrogen is in the form of dinitrogen (N_2), which is a gas at atmospheric pressures. N_2 gas comprises about 78% of the atmosphere (Fetter, 1992) and requires much energy (22 kcal/mol, Groffman, 2000) to break the triple N_2 bond. Reactions that break the strong N_2 bond, called "fixing" the nitrogen, produce the bioavailable and/or much more chemically reactive nitrogen species.

Redox Environment

Stumm and Morgan (1996) report a classic, biologically-mediated reduction sequence in ground waters in which oxygen and then nitrate (high potential oxidants) are the initial electron acceptors from lower-potential species, followed by iron and sulfate reduction and methanogenesis. In this scenario, the higher potential species are reduced first because the greater differences in redox potential between reduced electron donors and oxidized electron acceptors yield more energy and thus more efficient microbial growth (Tiedje et al., 1981). Some case studies (e.g., Puckett et al., 2002) have reported this sequence along ground water flow paths. However, caution must be used in making assumptions about any strict ordering in the sequence of redox reactions. For example, dissolved O_2 often reacts relatively slowly with some reductants because of kinetic limitations. Consequently, reduced species such as Fe^{2+} often are in solution with dissolved oxygen, reflecting nonequilibrium (McBride, 1994). The "local partial equilibrium" (LPE) approach recognizes that products of slow fermentative degradation of organic matter become reactants in relatively rapid secondary and tertiary redox reactions. In the LPE approach, the segregation in many natural settings of electron acceptors into distinct zones (e.g., O_2 -reducing, NO_3^- -reducing, Fe^{3+} -reducing) reflects equilibrium between two or more redox pairs in each zone rather than as a net energy yield of all redox species in the system (Postma and Jakobsen, 1996). Washington et al. (2004) further demonstrated that a bimodal clustering of redox potentials (calculated from activities of redox-sensitive species in water samples) exists in settings where there are sources both of high-potential oxidants (dissolved O_2, NO_3^-) and low potential reductants (C_{org}). In general, species of dissolved reactive N are very sensitive to shifts in redox environment (McClain et al., 1994).

Redox reactions often result in products that are in a different phase than reactants due to precipitation/dissolution reactions and the production of gases. For example, sulfate reduction in ground water, with organic C as the electron donor, results in precipitation of amorphous and mineral iron sulfide (e.g., mackinawite, pyrite) solids. Many redox reactions thus are limited in their reversibility due to insoluble or volatile end products and/or changing pH as the redox environment changes (Correll, 1997).

Materials and Methods

Study Area Description

At the USDA-ARS, J. Phil Campbell Sr. Natural Resource Conservation Center in Watkinsville, Georgia, two adjacent streams (14m apart at headcut) in a wetland depression provide drainage for an upland pasture for beef cattle. One of the streams is protected from surface run-off by a man-made berm and has a flowing spring at its head-cut (Figure 4.2). The other stream was not protected from runoff and did not have a conspicuous spring. Both streams received base flow from ground water. Chemical species distribution was very different in the two adjacent streams due to the partly different flow-source terms. During a two-year, approximately monthly, dry weather sampling program, discharge from the spring varied from about 7 to 31 L/min, with an average of 23 L/min. Average in-stream concentrations of relatively oxidized species such as NO_3^-, Fe^{3+} and O_2 were consistently higher in the Protected, spring-fed stream than in the Runoff Stream. Concentrations of some chemically reduced species such as dissolved organic C, CH_4, NO_2^-, NH_4^+, and Fe^{2+} often were two- to five-times higher in the runoff stream, depending on location along the flow path. The field site is in the Oconee River Watershed, Southern Piedmont Physiographic Province between the Southern Appalachian Mountains and the Georgia Coastal Plain. Local soil type is Cecil and Pacolet series, clayey, koalinitic, thermic, Typic Kanhapludult. A saprolite layer, <8 to >21 meters depth and developed on the Athens Gneiss, which also forms an unconfined aquifer through which shallow ground water flows to the wetland (Washington et al, 2004). The research area (Figure 3.1) is a small (92m long, 40m wide) vegetated depression at the base of USDA's Watershed 2, which is about 10ha. Most of this area is in cow pasture and vegetated buffer around the wetland. A small portion of the watershed draining to the wetland was in rotating crop (e.g., cotton, sorghum, pearl millet, barley, clover, rye (D. Endale, pers. comm.)). The cropped area was slightly below grade, inhibiting most surface runoff toward the wetland. However, the wetland likely was hydrologically connected to a portion of the cropped area via shallow ground water flow through the saprolite and/or underlying fractured bedrock. During the study period (2003-2005), the upgradient pasture was fertilized once or twice per year at a rate of 57-114 kgN/ha (Muckler, 2010). At varying intervals, averaging about one week in every six, 80-100 cows were rotated into the pasture immediately up-gradient and beyond the catchment of the study wetland. Cattle waste is high both in N and available organic C (van Groenigen et al., 2004). Local climate is seasonally variable with hot, humid summers and cool winters with frequent sub-freezing temperatures at night. The study period, 2003-2005 had annual rainfalls of 52, 48 and 61 cm, respectively (Georgia Forestry Commission, 2011), which were the rainiest years between 1998 and 2008. Vegetation in the depression includes both forest (e.g., oak, privet) and wetland species (e.g., duckweed, other prevalent grasses, and willow).

Study Design and Laboratory Analysis

Surface water samples were collected approximately monthly at 10 sampling stations (Figure 4.2) in each of the two adjacent wetland streams. Samples were analyzed in the laboratory for NO_3^-, Br^-, Cl^-, SO_4^{--}(Dionex Anion IC with a specific-conductivity dectector (SpCD) for September-December 2003 samplings; Metrohm Peak dual-channel (cation/anion) Ion Chromatograph (SpCD) from January 2004 – September 2005) dissolved NO_2^- (Diazotization, Hach DR 2010 Spectrophotometer), NH_4^+ (Phenate method (Washington et al., 2004 after Clesceri et al., 1998)) urea (Urease-phenate/spectrophotometer) (Washington et al., 2004); dissolved gases (N_2O, H_2 CH_4, CO_2) (Agilent 6890 Gas Chromatograph (ECD/TCD, Washington et al., 2004); Fe (II, III and total) (Ferrozine/spectrophotometer (Washington et al., 2004, after Viollier et al., 2000); and dissolved organic carbon (DOC) (Shimadzu 5050A Total Organic Carbon Analyzer).

Discharge Calculations

Discharge was measured directly using a bucket and stopwatch at flumes at Stations 8 (head-cut spring) and 1 (mouth of wetland). The wetland streams are too slow and shallow to accurately measure velocity during each sampling round. Thus, discharges at Stations 3 and 4 were calculated using the steady-state conservation-of-mass equations for fluid and a conservative solute. The continuity equation for conservation of mass of an incompressible fluid is given by (Triska et al., 1989):

$$Q_1 = Q_3 + Q_4 \tag{4.1}$$

$$Q_1 [Cl^-]_1 = Q_3[Cl^-]_3 + Q_4 [Cl^-]_4 \tag{4.2}$$

where Q_1 was measured in the field and $[Cl^-]_1$, $[Cl^-]_3$ and $[Cl^-]_4$ were quantified in the laboratory using ion chromatography. Combination and rearrangement of terms in Eq 3.11 provides estimates of the discharge in the two wetland streams at the time of data collection (Schroer et al., 2007):

$$Q_3 = Q_1 (([Cl^-]_1 - [Cl^-]_4) / ([Cl^-]_3 - [Cl^-]_4)) \tag{4.3}$$

$$Q_4 = Q_1 - Q_3 \tag{4.4}$$

Chloride concentrations are conservative along the streams and are consistently two times higher in the Runoff (Station 3) than in the Protected Stream (Station 4). For each sampling date, Eq 4.3 was solved using the measured discharge at Station 1 and measured $[Cl^-]$ at Stations 1, 3, and 4. The discharge at Station 4 was then calculated using Eq. 4.1.

Statistical Analysis

Stream parameter pairs were tested for Pearson's R using MS Excel for all dates on a station-by-station basis (i.e., inter-seasonal, intra-sampling-station). In comparisons between any two parameters, there were dates when one or both parameters were not measured at a particular sampling station. A sensitivity test ensured that Excel ignores unpaired data points. Degrees of freedom for each parameter pair were calculated as the minimum (where there was a difference between pairs) number of samples minus 2. Two confidence intervals, 0.05 and 0.01, were highlighted among the results (School of Psychology, University of New England).

Pearson's R correlation coefficients measure degree of linearity between parameters (Helsel and Hirsch, 2002) and have been used constrain water quality (e.g., Francy et al., 2005) and physical/hydrlogical water basin characteristics (e.g., Paybins, 2008). Coefficient signs (postitive or negatitive) indicate whether two parameters both increase (positive), or one parameter increases while the other decreases (negative). The absolute value of the coeffiecient indicates the strength of the correlation. The Pearson's R test does not detect trough-shaped relationships, where a scatter plot between two variables doubles back on itself. Also, Pearson's R is not as sensitive as other tests (e.g., Spearman's rho) for identifying exponential relationships between pairs (Helsel and Hirsch, 2002).

Results

Discharge (Q) (Table 4.1, Figure 4.3) at the headcut spring (Station 8) was about 30 L/min at the beginning of the project period in September, 2003, decreased a low of 7 L/min in July 2004, and increased to about 30L/min in the summer of 2005. On sampling dates when Q at Station 8 was highest (e.g., 31L/min on 14 June 2005), Q at Station 1 (the flume spillway at the mouth of the wetland) was almost twice as high (59L/min). The lowest ratios between Station 1 and Station 8 Q correlated with the lowest overall Q measurements at both stations. During the project period there was about a 4-fold variation in Station 8 Q and a 5-fold variation in Station 1 Q. Average Station 8 Q was 22.8 (+/- 7.2) and average Station 1 Q was 38.3 (+/- 13.7)

Discharges at Stations 3 (downstream, Runoff Stream) and 4 (downstream, Protected Stream) (Table 4.1) were calculated using Equations 4.1 – 4.4. Average Q was 13.5L/min (+/- 7.9) at Station 3 and 26.4L/min (+/- 8.2) at Station 4. Station 4 Q was, on average, 14% greater than Q measured upstream at the headcut spring (Station 8). Average measured Q at Station 1, the mouth of the wetland, was 32% higher than calculated Station 4 Q and 68% higher than calculated Station 3 Q.

Summer temperature (T) (Table 4.1, Figure 4.3) maxima were about 21°C in the Protected Stream and 23°C in the Runoff Stream, with lower downstream T in the Runoff (4-9° C) than the Protected (10-11°C) Stream. In both streams, T decreased along the flow path in winter and increased slightly downstream during the summer. Average Protected Stream T was 18.2° C (+/- 2.9) at Station 8; 18.2° C (+/- 3.3) at Station 6; and 17.3° C (+/- 3.8) at Station 4. Average Runoff Stream T was 17.4° C

(+/- 4.1) at Station 7; 16.8° C (+/- 4.8) at Station 5; 18.2° C (+/- 6.1) at Station 10; and 15.9° C (+/- 6.0) at Station 3.

Protected Stream dissolved oxygen (DO) concentrations (Table 4.1, Figure 4.3) exhibited a strong seasonal trend and decreased from along the flow path for most sampling dates; exceptions to this trend were in December through March of both winter seasons. Runoff Stream DO generally increased along the flow path during the winter months and generally decreased along the flow path during summer. Average Protected Stream [DO] was 7.6mg/L (+/-0.8) at Station 8; 5.8 mg/L (+/- 2.1) at Station 6; and 5.5 mg/L (+/- 2.5) at Station 4. Average Runoff Stream [DO] was 5.0 mg/L (+/- 2.3) at Station 7; 3.4mg/L (+/- 1.6) at Station 5; 5.4mg/L (+/- 3.8) at Station 10; and 5.0mg/L (+/- 2.4) at Station 3.

pH fluctuated in both streams, with highest values in winter and spring and lowest in summer fall. Protected Stream pH increased along the flow path, whereas Runoff Stream pH changed little along the flow path on most dates. Average Protected Stream pH was 4.9 (+/- 0.3) at Station 8; 5.7 (+/- 0.2) at Station 6 and 6.0 (+/- 0.2) at Station 4. Average Runoff Stream pH was 5.9 (+/- 0.4) at Station 7; 6.1 (+/- 0.2) at Station 5; 6.4 (+/- 0.1) at Station 10; and 6.4 (+/- 0.3) at Station 3).

Protected Stream SpC (Table 4.1, Figure 4.3) values changed very little along the flow path on most sampling dates: average values were 82.7μS/cm (+/- 6.82) at Station 8; 80.3μS/cm (+/- 7.3) at Station 6; and 80.2μS/cm (+/- 7.2) at Station 4. Runoff Stream SpC was about twice as high as in the Protected Stream and Runoff Stream values decreased from up- to downstream, a trend that was most pronounced during the winter months. Average Runoff Stream SpC was 140.9μS/cm (+/- 18.5) at Station 7; 118.4μS/cm (+/- 13.2) at Station 10; and 114.5μS/cm (+/- 10.7) at Station 3.

Alkalinity (Table 4.1, Figure 4.3) was below detection in most Protected Stream samples except in four consecutive Station 4 samples during the spring and summer of 2004, ranging from 11-24 mgCaCO$_3$/L. In contrast, alkalinity often was well above detection in the Runoff Stream, where alkalinity was highest in summer and fall and generally increased along the flow path. Average Runoff Stream values were highly variable: 3.34mgCaCO$_3$/L (+/- 6.95) at Station 7; 10.78mgCaCO$_3$/L (+/- 9.13) at Station 5; 14.83mgCaCO$_3$/L (+/- 3.54) at Station 10; and 13.72mgCaCO$_3$/L (+/- 12.6) at Station 3.

NO_3^- -N concentrations (Table 4.2, Figure 4.4) were highest in winter, lowest in summer, and decreased along the flow path in both streams, often with a more pronounced decrease in the Runoff Stream. Average Protected Stream [NO_3^- -N] was 4.9mg/L (+/- 0.) at Station 9; 5.6mg/L (+/- 1.4) at Station 8; 4.4mg/L (+/- 1.1) at Station 6; and 3.5mg/L (+/- 1.4) at Station 4. Average Runoff Stream [NO_3^- -N] was 6.5mg/L (+/-2.7) at Station 7; 2.7mg/L (+/- 0.8) at Station 5; 2.1mg/L (+/- 0.5) at Station 10; and 0.9mg/L (+/- 0.1) at Station 3.

On most sampling dates, [NO_2^- -N] (Table 4.2, Figure 4.5) was about 2-3 times more concentrated in the Runoff than in the Protected Stream. Seasonal summer highs and winter lows are evident in the Protected up- (Station 7) and mid-(Station 5) stream locations. Seasonal trends are weak or absent at Station 3 in the Runoff Stream and all stations in the Protected Stream. Average Protected Stream [NO_2^- -N] 0.005mg/L (+/- 0.002) at Station 8; 0.004mg/L (+/- 0.001) at Station 6; and 0.004mg/L (+/- 0.002) at Station 4. Average Runoff Stream [NO_2^- -N] was higher: 0.010 (+/- 0.005 at Station 7; 0.008mg/L (+/- 0.006) at Station 5; 0.008mg/L (+/-0.003) at Station 10; and 0.006mg/L (+/- 0.002) at Station 3.

Protected Stream [NH_4^+ -N] (Table 4.2, Figure 4.5) increased along the flow path, whereas Runoff Stream [NH_4^+ -N] was usually highest at midstream Station 5. Average Protected Stream [NH_4^+ -N] was 0.03mg/L (+/- 0.02) at Stations 8 and 6, and 0.04mg/L (+/- 02) at Station 4. Average Runoff Stream [NH_4^+ -N] was 0.09mg/L (+/- 0.07) at Station 7; 0.21mg/L (+/- 0.10) at Station 5; 0.15mg/L (+/- 0.12) at Station 10; and 0.16mg/L (+/- 0.06) at Station 3. Thus, Runoff Stream [NH_4^+ -N] was 2-5 times more concentrated.

In both streams, Sulfate (Table 4.2, Figure 4.5) concentrations were highest in winter and spring and lowest in summer and fall. Protected Stream [SO_4^{2-}] often varied by as little as 0.05mg/L along the flow path; concentrations decreased slightly (by ~0.2mg/L) along the Protected Stream flow path during summer and increased (by ~0.6mg/L) during winter. In contrast, Runoff Stream [SO_4^{2-}] decreased along the flow path on most sampling dates, from a 0.5mg/L decrease between Stations 7 and 3 during winter to a 2.5mg/L decrease in June. Average Protected Stream [SO_4^{2-}] was 1.5mg/L (+/- 0.8) at Station 8; 1.4mg/L (+/- 0.3) at Station 6; and 1.3mg/L (+/- 0.4) at Station 4. Average Runoff Stream [SO_4^{2-}] was 3.3mg/L (+/- 0.7) at Station 7; 2.5mg/L (+/- 0.4) at Station 5; 2.5mg/L (+/- 0.7) at Station 10; and 1.9mg/L (+/- 0.7) at Station 3.

Ferrous and total iron concentrations (Table 4.3, Figure 4.5) increased along the flow path in both streams. The highest concentrations were at Station 4 (downstream) in the Protected Stream and at Stations 3 (downstream) or 10 (midstream) in the Runoff Stream. In the Protected Stream, average [Fe^{2+}]/[Fe_{total}] was 0.13/0.44mg/L (+/- 0.10/0.47) at Station 8; 0.23/0.48mg/L (+/- 0.14/0.22) at Station 6; and 0.90/1.28mg/L (+/- 1.02/1.14) at Station 4. Runoff Stream average [Fe^{2+}]/[Fe_{total}] was 0.33/0.71mg/L (+/- 0.32/0.67) at Station 7; 1.67/2.31mg/L (+/- 0.78/0.81) at Station 5; 0.93/1.84mg/L (+/- 0.85/1.22) at Station 10; and 1.61/2.11mg/L (+/- 1.30/1.63) at Station 3. Ferrous iron was 60-75% total iron; higher ratios of ferrous to total iron were observed at higher temperatures.

Dissolved organic carbon concentrations (Table 4.3, Figure 4.7) were 2-5 times higher in the Runoff than the Protected Stream, and increased along the flow paths of both streams. [DOC] exhibited seasonal trends, with highest concentrations in summer and lowest in winter. Average Protected Stream [DOC] was 0.40mg/L (+/- 0.43) at Station 8; 0.96mg/L (+/- 0.21) at Station 6; and 1.44mg/L (+/- 0.38) at Station 4. Average Runoff Stream [DOC] was 1.21mg/L (+/-0.45) at Station 7; 2.99mg/L (+/- 1.25) at Station 5; 3.18mg/L (+/- 1.53) at Station 10; and 4.28mg/L (+/- 2.33) at Station 3.

Chloride (Table 4.3, Figure 4.8 (ratios)) remained fairly consistent along the stream flow path on a given date. Average Protected Stream [Cl^-] was 7.4mg/L (+/- 1.9) at Station 8; 7.6mg/L (+/- 2.0) at Station 6; and 7.7mg/L (+/- 1.8) at Station 4. Average Runoff Stream [Cl^-] was 13.3mg/L (+/- 4.1) at Station 7; 14.5mg/L (+/- 4.7) at Station 5; 15.7mg/L (+/- 5.8) at Station 10; and 15.7mg/L (+/- 4.0) at Station 3. Downstream of the confluence, average [Cl^-] was 8.8mg/L (+/- 2.6) at Station 2 and 10.0mg/L (+/- 2.8) at Station 1.

N_2O –N (Table 4.2, Figure 4.4) concentrations decreased along the flow paths in both streams; and concentrations were about twice as high in the Runoff Stream. Concentrations fluctuated on different sampling dates but did not exhibit a seasonal trend. Average Protected Stream [N_2O –N] was 6.8μg/L (+/- 2.2) at Station 9; 5.1μg/L (+/- 1.2) at Station 8; 2.9μg/L (+/- 0.6) at Station 6; and 2.4μg/L (+/- 0.9) at Station 4. Average Runoff Stream [N_2O –N] was 8.6μg/L (+/- 1.7) at Station 7; 4.4μg/L (+/- 1.4) at Station 5; 2.5μg/L (+/- 1.0) at Station 10; and 1.4μg/L (+/- 0.9) at Station 3. In the Runoff Stream, gas sampling at Station 7 did not commence until December of 2004, due to the limited number of gas sampling bottles at the beginning of the project period. Also, the stream was dry for all three sampling stations in the Runoff Stream in July 2004, and was dry in September 2004 at Station 3.

Protected Stream dissolved Carbon Dioxide ($CO_{2(aq)}$) (Table 4.4 , Figure 4.6) is reported as $H_2CO_3^*$, which represents [$CO_{2(aq)}$] + [H_2CO_3] (Snoeyink and Jenkins 1980). In the Protected Stream, both [$H_2CO_3^*$] and [N_2O] decreased along the flow path. At the upstream locations especially, winter $H_2CO_3^*$ concentrations were lower than adjacent fall and spring values. Average Protected Stream [$H_2CO_3^*$] was 4.0mg/L (+/- 1.3) at Station 8; 1.8mg/L (+/- 0.7) at Station 6; and 1.7mg/L (+/- 1.1) at Station 4. In the Runoff Stream, upstream [$H_2CO_3^*$] was lower than in the Protected Stream, and there was not a consistent trend along the flow path. Average Runoff Stream [$H_2CO_3^*$] was 2.6mg/L (+/- 1.1) at Station 7; 2.6mg/L (+/- 0.7) at Station 5; 1.9mg/L (+/- 1.0) at Station 10; and 2.0mg/L (+/- 1.4) at Station 3.

Dissolved Methane (Table 4.4 , Figure 4.6) often was below detection in the Protected Stream. In the Runoff Stream, highest [CH_4] was 2- to 10 times greater than the highest concentrations in the Protected Stream, with the highest Runoff Stream concentrations measured at the mid- and downstream stations. Average Protected Stream [CH_4] was 1.1μg/L (+/- 1.0) at Station 8; 2.0μg/L (+/- 1.0) at Station 6; and 27.1μg/L (+/- 22.7) at Station 4. Average Runoff Stream [CH_4] was 42.1μg/L (+/- 24.9) at Station 7; 342.0μg/L (+/- 344.0) at Station 5; 71.1μg/L (+/- 80.3) at Station 10; and 92.3μg/L (+/- 98.5) at Station 3.

Dissolved Hydrogen gas was highly variable in both streams. Average Protected Stream [H_2] was 0.72ng/L (+/- 0.64) at Station 8; 0.71ng/L (+/- 0.47) at Station 6; and 0.79ng/L (+/- 0.70) at Station 4. Average Runoff Stream [H_2] was 0.99 g/L (+/- 0.82) at Station 7; 2.7ng/L (+/- 6.4) at Station 5; 0.69ng/L (+/- 0.87) at Station 10; and 1.0ng/L (+/- 0.80) at Station 3.

Pearson's R coefficients (Table 4.5) show significant positive correlations between [NO_3^- -N] and Station 3 calculated discharge, especially in the Protected Stream, and between [SO_4^-] and Station 3 calculated discharge in both streams. Temperature was negatively correlated with [NO_3^- -N] (downstream stations) and [SO_4^-] (all stations except Station 7). Temperature was strongly correlated with [$H_2CO_3^*$] in the Protected Stream and downstream in the Runoff Stream. Temperature was also correlated with DOC at stations in both streams. Dissolved oxygen [DO] percent saturation was positively correlated with both [NO_3^- -N] and [SO_4^-] at the downstream sampling stations of both streams and downstream of the confluence. [NO_3^- -N] and [SO_4^-] exhibited a significant positive correlation with each other in the Protected Stream, Station 3 of the Runoff Stream and downstream of the confluence.

[NO_3^- -N] was negatively correlated with [Fe^{2+}], [$H_2CO_3^*$] and [DOC] at the downstream stations of both streams and downstream of the confluence. [NH_4^+ -N] correlated positively with [$H_2CO_3^*$] at Stations 5, 10 and 3 in the Runoff Stream and Station 6 in the Protected Stream. [SO_4^-] and [$H_2CO_3^*$] were negatively correlated at the downstream stations in both streams and Station 5 in the Runoff Stream. [SO_4^-] and [DOC] also were negatively correlated at downstream stations. There were significant positive correlations between [Fe^{2+}] and [$H_2CO_3^*$] and between [CH_4] and [DOC], especially at downstream stations. [$H_2CO_3^*$] and [DOC] were positively correlated at Station 4 in the Runoff Stream, Stations 10 and 3 in the Protected Stream, and downstream of the confluence.

For most sampling dates, calculated nitrate loads (Figure 4.8, from data in Tables 4.1, 4.2 and 4.3) in the Protected Stream were about 30 mg/min lower or at the downstream location (Station 4) than at the spring (Station 8). Calculated loads at Station 4 were 3 to 18 times higher than at Station 3. Average Protected Stream loads are 135.5mg/min (+/- 60.3) at measured at Station (measured) and

90.5mg/min (+/- 53.6) calculated at Station 4. Average Runoff Stream load is 17.9 (+/- 17.0) calculated at Station 3. Station 4 NO_3^- -N Loads were 33% lower than Station 8 loads.

[NO_3^- -N] versus T (Table 4.5, Figure 4.9) for all stations exhibited a T maximum that increased as a straight line with increasing T except for winter maximum temperatures at Station 8, the headcut spring. [NO_3^- -N] decreased with increasing temperature at several of the wetland stations; b) [NO_3^- -N] exhibited 0.95 or greater confidence intervals for Pearson's R coefficients at Stations 4 in the Protected Stream, 10 and 3 in the Runoff Stream and Stations 2 and 1. [NO_3^- -N] remained fairly constant at T greater than 19°C at Runoff Stream Stations 3 and 10, although there were only 6 data points at Station 10; c) [NO_2^- -N] versus T for all Stations exhibited boomerang- and crescent-shaped zones, with a positive increase in [NO_2^- -N] between ~17-19°C; d) Pearson's R coefficients for [NO_2^- -N] were significant at 0.95 confidence or higher only at Stations 6 (Protected) and 7 (Runoff); Station 7 [NO_2^- -N] increases at about 17°C, and concentrations are scattered at higher T; e) [SO_4^{2-}] versus T for all stations displayed as a random scatter plot; f)) [SO_4^{2-}] decreased with T at Protected Stream Stations 8 and 4 and at Protected Stream Stations 5, 10 and 3.

Dissolved [$H_2CO_3^*$] and [DOC] [Fe^{2+}] and [Fe^{3+}] versus T scatter plots (Figures 4.10 and 4.11) exhibited a crescent-shaped envelope for stations with significant correlations. Concentrations remained fairly constant with incrased T to 18-20° C, above which there was greater increase in concentration with increasing T, especially at Runoff Stream stations.

[NO_3^- -N]/discharge correlations (Table 4.5, Figure 4.12) were significant for all Protected Stream stations, Station 3 in the Runoff Stream, and Stations 2 and 1 downstream of the confluence. The most significant correlations between [NO_3^- -N] and discharge at any of the four stations where discharge was measured (Stations 8 and 1) or calculated (Stations 3 and 4) were at Station 3, which is in the Runoff Stream. Figure 4.11 shows increasing [NO_3^- -N] by about 100uM for each station between 4 and 8mL/min, little or no change in concentration between 8 and 21mL/min, and increasing [NO_3^- -N] by about 120uM at $Q > 21$mL/min.

Significant [NO_3^- -N]/[SO_4^{2-}] correlations Table 4.5, Figure 4.13) show relatively distinct segregation between stations, each sloping toward the lowest [NO_3^- -N] (2-6uM) at [SO_4^{2-}] between 7-12uM. At any given [SO_4^{2-}] between 10-18uM, Station 3 (Runoff Stream) [NO_3^- -N] concentrations are lowest, and [NO_3^- -N] increased successively at Stations 1 and 2 (downstream of confluence), 4, 6 and 8 (Runoff Stream).

Discussion

The highest Protected Stream [N_2O] at Station 9 (tygon tube inserted into the saprolite aquifer) indicates that reducing conditions are present in the saprolite. Aquifer solids trap gaseous reactions products such as N_2O. Wetland [N_2O] were two orders of magnitude lower than [NO_3^- -N] because the wetland streams are open systems gas exsolves to the atmosphere. N_2O generated in wetlands also can be entrapped in sediments and/or in plant aerenchyma (low-resistance channels and cavities in plants that allow exchange of gases at the root zone) (Matheson and Sukias, 2010).

There are many processes that control concentration of dissolved iron and distribution between [Fe^{2+}] and [Fe^{2+}] in aquifers and streams. Endale et al. (2003) determined that denitrification in the saprolite aquifer at the current study site was coupled to $Fe(OH)_3$ production. This results in the chemical reduction of nitrate, oxidation of ferrous iron, and precipitation of ferric iron as relatively insoluble oxides and oxyhydroxides. A net reaction is (Ernstsen, 1996):

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow N_2 + 10FeOOH + 18H^+ \qquad (4.5)$$

Organic ligands such as siderophores (excreted by bacteria) contribute to dissolution of iron solids. The complexes may sorb to clay minerals, generally as pH increases, where the iron remains bioavailable but does not significantly increase dissolved iron concentration (Siebner-Freibach et al., 2004). Dissolved Fe^{3+} can be chemically reduction to Fe^{2+}, which can be facilitated by solar energy during the day (McKnight and Duren, 2004). Ultimately, processes that control Fe^{2+} oxidation to Fe^{3+} may exert a primary control on [Fe^{2+}] in solution (McKnight and Duren, 2004). Finally, ferrous iron often is in solution with dissolved oxygen due to kinetic limitations of Fe^{2+} oxidation (McBride, 1994).

Reduced sulfur species (e.g., amorphous iron monosulfides, mackinawite and pyrite) are a source of sulfate from lake bottom sediments when electron acceptors such as nitrate are present (Holmer and Storkholm, 2001). In aerobic conditions, denitrification with sulfide as the electron donor is facilitated by lithoautotrophic bacteria as (Beristain-Cardoso, 2009; Sher et al., 2008):

$$5H_2S + 8NO_3^- \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O + 2H^+ \qquad (4.6)$$

This reaction consumes alkalinity equivalent to 20mg $CaCO_3$/mole of H_2S (2 meq alkalinity lost per 5 moles of H_2S (van Rijn et al., 2006).

Sulfate concentrations decreased along the flow path for many sampling dates in the Protected Stream and all sampling dates in the Runoff Stream. Also [SO_4^2] exhibited significant positive correlations with discharge and [NO_3^- -N], which argue against sulfate production coupled with nitrate reduction. However, sulfide may be an important secondary reductant. Also, there was an increase in Protected Stream Station 4 (downstream) [SO_4^{2-}] on several winter sampling dates. During the summer tracer test (Chapter 3), [SO_4^{2-}] remained stable at about 14 uM with decreasing Runoff Stream [N]/[fBr^-] Recovery from 1.0 to 0.8, then increased to 20uM Recovery decreased to about 0.5, and remained at 20uM as Recovery decreased to 0.3. The threshold changes in slope may also indicate rapid secondary oxidation of sulfide. Sulfide consumption was not measured directly but inferred only by sulfate production, which may not represent all sulfide oxidation.

Temperature exerted control on stream redox processes. [NO_3^- -N] decreased with increasing temperature at Stations 4 in the Protected Stream, 10 and 3 in the Runoff Stream and Stations 2 and 1. [NO_3^- -N] remained fairly constant at T greater than 19°C at Runoff Stream Stations 3 and 10, although there were only 6 data points at Station 10. [NO_2^- -N] versus T for all Stations exhibited boomerang- and crescent-shaped zones, with a positive increase in [NO_2^- -N] between ~17-19°C. Pearson's R coefficients for [NO_2^- -N] were significant at 0.95 confidences or higher only at Stations 6 and 7 Station. Both [$H_2CO_3^*$] and [DOC] versus T relationships exhibited a crescent-shaped relationship with an increase in concentration slope with increasing T above 18-20° C. [Fe^{2+}] for stations the yielded significant (0.95

confidence or greater) Pearson's R coefficients had concentrations between 0-40μM at 5-20°C, above which [Fe^{2+}] increased to 60-100μM. [Fe^{2+}] and [Fe^{3+}] both increased 3-4 fold above temperatures higher than 19°C at Stations for which Pearson's R correlation coefficients were 0.95 or greater. Elefsiniotis and Li (2006) determined that a temperature increase between 10 and 20 degrees C resulted in a greater increase in dentrification and carbon consumption rate than a change from 20 to 30 decrees C. When temperature is held constant, dentrification rates increase with increasing nitrate and/or organic C concentration, and also depend on the specific type of organic C (Elefsiniotis and Li, 2006).

Stream baseflow exerted less control than baseflow-plus-runoff on a wetland's capacity to remove nitrate N. This is related to the control of residence time on N Removal tested in Chapter 3. At several sampling stations (8,6,4,3,2,1), [NO_3^- -N] increases with increasing baseflow (represented by Station 3 Q) between about 3-7 L/min, remains relatively constant to 20L/min, and increases at baseflow Q greater than 20L/min. In contrast, [NO_3^- -N] increases with increasing discharge at Station 1 (representing baseflow plus runoff) between ~10 and 45-50 L/min, above which [NO_3^- -N] decreases with increasing Station 1 Q. Thus, there is a wide range (between 7-20L/min) within which increases in baseflow Q have no effect on [NO_3^- -N]. However, baseflow plus runoff Q cause a continual increase in [NO_3^- -N] to a critical threshold (~45L/min), above which [NO_3^- -N] decreases with higher Q, likely due to dilution. Runoff Stream Station 3consistently delivered smaller loads of nitrate than Station 4 (Protected Stream). Flow in the Protected Stream is dominated by the perennial spring. However, sedimentation in the Runoff Stream and saturated riparian soils allow for some stream water to be transported through the organic rich sediments as through-flow. This allows for intimate contact between the nitrate contaminated water and the organic rich sediment leading to slow discharge and more residence time for a higher rate of denitrification. Thus, the lower Q at Station 4 facilitates removal processes caused by longer residence times, yielding even smaller loads than the lower discharge.

Conclusions

Runoff Stream Station 3 NO_3^- -N loads were consistently one-third or less those at Station 4 during the two-year project period. Organic carbon was the main electron donor in both streams.

However, sulfide may be an important secondary reductant. Temperatures exerted control on stream redox processes, indicated by moderate to strong increases in [NO_3^- -N] , [$H_2CO_3^*$], [DOC], [Fe^{2+}] and [Fe^{3+}] above 18-20°C . Stream baseflow exerted less control than baseflow-plus-runoff on the wetland's capacity to remove nitrate N.

Results of this study will help modelers by establishing discharge, load, temperature, and multiple redox-species concentration relationships at small spatial scales and short residence times. These in turn will constrain processes that affect the efficiency of wetland streams to remove nitrate N from agricultural sources.

Table 4.1. Field parameters.

Protected Stream

	Q		pH	T		DO		SpC	Alkalinity (CaCO3 eq)	
Station 9	L/mn	SD	SU	deg C	SD	mg/L	uM	uS/cm	mg/L	uM
23-Jun-04			4.76	18.90	0.12	7.27	227.20	73.40	BDL	
27-Jul-04			4.95	20.50	0.15	6.30	196.88	71.80	BDL	
15-Sep-04			4.64	20.80	0.12	6.22	194.38	78.70	BDL	
1-Dec-04			5.17	17.35	0.22	6.73	210.32	96.30	BDL	
17-Feb-05			5.33	12.75	0.35	7.18	224.4	94.00	BDL	
15-Mar-05			5.23	13.40	0.26	7.50	234.4	88.00	BDL	
10-May-05			5.16	15.40	0.10	7.51	234.7	72.00	BDL	
14-Jun-05			5.14	17.70	0.26	5.66	176.9	86.60	BDL	
27-Jul-05			4.94	20.57	0.55	4.96	155.0	87.40	BDL	
21-Sep-05			5.02	21.10	0.44	5.88	183.8	83.30	BDL	
Station 8										
4-Sep-03	29.0	0.77	4.93	20.80	0.00	6.85	214.1	81.60	BDL	
10-Sep-03	28.4	0.77	4.42	20.83	0.05	6.67	208.4	80.50	BDL	
10-Sep-03	27.6	0.69	4.56	20.70	0.14	7.24	226.3	79.40	BDL	
17-Sep-03	25.8		4.51	20.63	0.05	6.84	213.8	78.60	BDL	
1-Oct-03	27.7	0.71	4.54	20.23	0.05	7.18	224.4	81.10	BDL	
1-Oct-03	27.5	0.75	4.90	20.27	0.05	7.81	244.1	80.20	BDL	
22-Oct-03	22.1	0.58	5.14	19.27	0.05	8.00	250.0	83.50	BDL	
20-Nov-03	25.9	0.76	5.11	18.03	0.05	7.61	237.8	89.50	BDL	
16-Dec-03	22.6	0.57	4.70	15.53	0.05	8.69	271.6	88.10	BDL	
8-Jan-04	19.3	0.48							BDL	
10-Feb-04	25.7	0.71	5.20	12.23	0.06	8.74	273.1	90.80	BDL	
25-Mar-04	22.3	0.60							BDL	
6-May-04	14.3	0.37	5.29	15.47	0.06	8.64	270.0	75.20	BDL	
27-May-04	11.0	0.28							BDL	
23-Jun-04	10.0	0.34	4.71	18.90	0.00	7.77	242.8	74.10	BDL	
27-Jul-04	7.1		4.89	20.53	0.06	6.72	210.0	72.00	BDL	
15-Sep-04	8.7	0.22	4.64	20.83	0.06	6.89	215.3	84.20	BDL	
21-Oct-04	13.9	0.44							BDL	
1-Dec-04	23.3	0.58	5.26	17.57	0.06	7.48	233.8	95.10	BDL	
8-Feb-05	27.7	1.02							BDL	
17-Feb-05	27.5	0.78	5.35	12.97	0.21	8.51	265.9	93.00	BDL	
15-Mar-05	28.6	0.79	5.22	13.23	0.23	8.91	278.4	89.40	BDL	

Table 4.1 (continued)

	Q		pH	T		DO		SpC	Alkalinity (CaCO3 eq)	
Station 8	L/mn	SD	SU	deg C	SD	mg/L	uM	uS/cm	mg/L	uM
10-May-05	30.4	0.93	5.14	15.13	0.12	8.00	250.0	70.30	BDL	
14-Jun-05	31.3	0.79	5.15	17.50	0.20	7.03	219.7	87.30	BDL	
27-Jul-05	29.4	0.74	4.90	20.30	0.61	6.66	208.1	84.50	BDL	
17-Aug-05	28.4	0.81							BDL	
21-Sep-05	21.5	0.68	5.02	21.03	0.49	6.62	206.9	78.70	BDL	
Station 6										
4-Sep-03			5.75	22.13	0.05	4.75	148.4	79.20	BDL	
10-Sep-03			5.45	20.30	0.00	4.26	133.1	76.40	BDL	
10-Sep-03			5.42	21.30	0.00	4.85	151.6	77.30	BDL	
17-Sep-03			5.42	19.93	0.05	4.57	142.8	74.40	BDL	
1-Oct-03			5.41	18.10	0.08	4.91	153.4	75.60	BDL	
1-Oct-03			5.67	19.97	0.05	4.87	152.2	77.80	BDL	
22-Oct-03			5.78	18.03	0.05	5.30	165.6	81.40	BDL	
20-Nov-03			5.50	16.67	0.05	4.91	153.4	90.50	BDL	
16-Dec-03			5.26	12.87	0.05	6.50	203.1	86.70	BDL	
10-Feb-04			5.89	11.73	0.06	10.57	330.3	88.90	BDL	
6-May-04			6.00	21.27	0.06	7.59	237.2	71.00	BDL	
23-Jun-04			5.68	20.43	0.06	4.27	133.4	72.70	BDL	
27-Jul-04			5.80	21.17	0.06	3.59	112.2	71.40	BDL	
15-Sep-04			5.66	20.10	0.00	4.07	127.2	66.60	BDL	
1-Dec-04			5.75	15.03	0.06	5.37	167.8	93.60	BDL	
17-Feb-05			6.08	11.60	0.20	9.72	303.8	90.50	BDL	
15-Mar-05			5.88	14.53	0.15	10.77	336.6	86.80	BDL	
10-May-05			5.66	16.57	0.29	6.50	203.1	82.50	BDL	
14-Jun-05			5.78	18.47	0.21	5.29	165.3	84.30	BDL	
27-Jul-05			5.59	21.13	0.58	4.30	134.4	81.20	BDL	
21-Sep-05			5.81	21.27	0.55	4.40	137.5	76.90	BDL	
Station 4										
4-Sep-03			6.20	21.27	0.05	5.11	159.7	81.00	BDL	
10-Sep-03			5.68	19.87	0.05	4.68	146.3	72.20	BDL	
10-Sep-03			6.15	21.27	0.05	4.44	138.8	73.70	BDL	
17-Sep-03			5.74	19.47	0.05	4.49	140.3	71.00	11.0	109.9
1-Oct-03			5.62	16.70	0.08	5.19	162.2	70.70	BDL	
1-Oct-03			6.05	19.37	0.05	4.82	150.6	74.20	BDL	
22-Oct-03			6.13	16.90	0.00	6.06	189.4	78.80	BDL	
20-Nov-03			5.72	14.87	0.05	5.67	177.2	91.20	BDL	
16-Dec-03			5.61	10.03	0.05	8.45	264.1	88.10	BDL	
8-Jan-04	22.83	0.85								
10-Feb-04	25.26	1.23	6.29	10.23	0.06	10.32	322.5	89.20	BDL	
25-Mar-04			6.14	14.9		10.56		80.4		
6-May-04	15.58	0.70	6.32	18.80	0.10	5.61	175.3	71.70	11.0	109.9
23-Jun-04	11.69	3.33	5.82	20.83	0.06	2.48	77.5	72.10	14.5	144.9

Table 4.1 (continued)

Station 4 continued	Q L/mn	 SD	pH SU	T deg C	 SD	DO mg/L	 uM	SpC uS/cm	Alkalinity (CaCO3 eq) mg/L	 uM
27-Jul-04			6.08	21.53	0.46	1.09	34.1	89.30	24.0	239.8
15-Sep-04			5.80	19.97	0.06	1.84	57.5	79.80	17.0	169.9
21-Oct-04	18.74	0.67	5.51	18.6		3.79	82.1			
1-Dec-04	26.82	1.39	6.02	13.43	0.06	4.94	154.4	89.90	BDL	
8-Feb-05			6.39	12		7.89		89.9		
17-Feb-05	25.15	1.57	6.21	10.73	0.15	7.96	248.8	87.80	BDL	
15-Mar-05	31.38	2.51	6.09	13.60	0.10	9.63	300.9	84.20	BDL	
10-May-05	36.45	1.28	5.97	16.43	0.15	5.30	165.6	80.10	BDL	
14-Jun-05	36.97	2.05	6.15	18.80	0.26	4.24	132.5	86.50	BDL	
27-Jul-05	39.11	3.41	5.91	21.50	0.61	3.79	118.4	79.00	BDL	
17-Aug-05	27.43	0.87	6.08	20.7				70.9		
21-Sep-05	25.52	5.83	6.13	20.87	0.46	3.68	115.0	73.80	BDL	
Runoff Stream										
Station 7										
4-Sep-03			5.49	21.57	0.05	2.67	83.4	155.80	BDL	
10-Sep-03			5.19	20.17	0.05	4.16	130.0	150.40	BDL	
10-Sep-03			5.58	20.83	0.05	2.97	92.8	153.60	BDL	
17-Sep-03			5.38	19.70	0.00	3.65	114.1	147.80	BDL	
1-Oct-03			5.47	17.23	0.12	3.48	108.8	151.10	BDL	
1-Oct-03			5.79	18.83	0.05	4.21	131.6	161.00	BDL	
22-Oct-03			5.96	17.03	0.05	4.18	130.6	163.50	BDL	
20-Nov-03			5.95	15.60	0.00	4.05	126.6	167.80	BDL	
16-Dec-03			5.39	10.83	0.05	4.33	135.3	153.60	BDL	
10-Feb-04			6.04	9.23	0.06	5.59	174.7	143.40	BDL	
6-May-04			6.40	18.33	0.12	5.21	162.8	130.00	22.0	219.8
23-Jun-04			6.22	21.90	0.00	6.44	201.3	136.80	16.5	164.9
27-Jul-04	dry									
15-Sep-04			5.98	19.40	0.00	4.39	137.2	135.10	15.0	149.9
1-Dec-04			5.82	12.37	0.06	2.90	90.6	144.60	10.0	99.9
17-Feb-05			6.23	10.50	0.20	7.37	230.3	130.10	BDL	
15-Mar-05			6.17	13.83	0.23	13.22	413.1	124.60	BDL	
10-May-05			5.88	16.53	0.12	5.02	156.9	89.60	BDL	
14-Jun-05			7.00	20.43	0.32	4.31	134.7	126.20	BDL	
27-Jul-05			5.99	23.03	0.67	5.86	183.1	128.50	BDL	
21-Sep-05			6.10	21.47	0.47	5.43	169.7	124.70	BDL	
Station 5										
4-Sep-03			6.20	22.07	0.05	1.97	61.6	126.00	BDL	
10-Sep-03			5.74	19.30	0.00	1.71	53.4	113.20	BDL	
10-Sep-03			6.62	21.07	0.05	2.01	62.8	118.90	BDL	

Table 4.1 (continued)

									Alkalinity	
Station 5	Q		pH		T		DO	SpC	(CaCO3 eq)	
continued	L/mn	SD	SU	deg C	SD	mg/L	uM	uS/cm	mg/L	uM
17-Sep-03			5.74	19.30	0.00	1.36	42.5	113.20	18.0	179.8
1-Oct-03			5.81	14.73	0.05	2.93	91.6	107.60	BDL	
1-Oct-03			6.22	17.50	0.08	2.27	70.9	113.70	15.0	149.9
22-Oct-03			6.28	15.47	0.05	2.57	80.3	119.30	11.5	114.9
20-Nov-03			5.89	13.50	0.00	2.60	81.3	134.20	BDL	
16-Dec-03			5.98	7.80	0.08	5.30	165.6	124.10	BDL	
10-Feb-04			6.26	8.40	0.10	5.35	167.2	121.90	BDL	
6-May-04			6.39	19.70	0.10	1.98	61.9	123.60	25.0	249.8
23-Jun-04			6.07	22.80	0.00	3.51	109.7	134.70	27.0	269.8
27-Jul-04	dry									
15-Sep-04			5.99	19.57	0.06	2.05	64.1	126.10	22.0	219.8
1-Dec-04			5.96	11.27	0.06	3.71	115.9	126.40	16.0	159.9
17-Feb-05			6.37	9.70	0.17	6.55	204.7	115.70	10.0	99.9
15-Mar-05			6.36	13.17	0.15	6.07	189.7	112.10	10.0	99.9
10-May-05			6.22	17.50	0.10	4.30	134.4	85.20	15.0	149.9
14-Jun-05			6.33	21.77	0.38	4.06	126.9	121.60	15.0	149.9
27-Jul-05			6.04	20.93	0.06	5.24	163.8	127.30	16.0	159.9
21-Sep-05			6.18	21.27	0.55	2.73	85.3	114.70	15.0	149.9
Station 10										
17-Feb-05			6.54	9.23	0.15	9.20	287.5	116.10	11.0	109.9
15-Mar-05			6.54	12.33	0.23	10.69	334.1	110.60	10.0	99.9
10-May-05			6.28	18.90	0.35	4.24	132.5	103.00	15.0	149.9
14-Jun-05			6.45	22.73	0.40	3.44	107.5	122.40	18.0	179.8
27-Jul-05			6.32	24.73	0.67	4.26	133.1	116.80	17.0	169.9
21-Sep-05			6.33	21.27	0.46	0.64	20.0	141.70	18.0	179.8
Station 3										
4-Sep-03			6.62	22.33	0.05	4.43	138.4	119.20	BDL	
10-Sep-03			6.10	19.27	0.05	3.68	115.0	109.40	BDL	
10-Sep-03				20.57	0.05	3.59	112.2	112.90	BDL	
17-Sep-03			6.32	18.80	0.00	3.65	114.1	106.50	32.0	319.7
1-Oct-03			5.68	13.73	0.05	5.15	160.9	94.50	BDL	
1-Oct-03			6.59	16.00	0.08	5.19	162.2	95.80	17.0	169.9
22-Oct-03			6.71	13.97	0.05	5.43	169.7	110.35	20.0	199.8
20-Nov-03			6.15	11.63	0.05	4.92	153.8	117.50	BDL	
16-Dec-03			6.02	4.50	0.00	10.35	323.4	110.50	BDL	
8-Jan-04	11.06	0.32								
10-Feb-04	23.25	0.59	6.54	6.80	0.10	9.54	298.1	119.30	BDL	
6-May-04			6.59	18.40	0.17	4.18	130.6	108.70	27.0	269.8
23-Jun-04	5.175	0.14	6.01	22.83	0.06	1.04	32.5	142.20	35.0	349.7
27-Jul-04	4.264	0.15								
15-Sep-04	dry									

Table 4.1 (continued)

Station 3	Q		pH	T		DO		SpC	Alkalinity (CaCO3 eq)	
continued	L/mn	SD	SU	deg C	SD	mg/L	uM	uS/cm	mg/L	uM
21-Oct-04	7.176	0.18								
1-Dec-04	22.05	0.68	6.37	10.20	0.00	5.20	162.5	115.20	15.50	154.9
17-Feb-05	25.45	0.68	6.45	8.57	0.15	7.30	228.1	112.50	10.00	99.91
15-Mar-05	20.76	0.63	6.50	10.23	0.12	8.00	250.0	114.30	11.20	111.9
10-May-05	12.93	0.50	6.46	17.07	0.12	4.93	154.1	114.90	14.00	139.9
14-Jun-05	21.79	1.19	6.60	22.50	0.44	2.46	76.9	128.60	23.00	229.8
27-Jul-05	8.747	0.56	6.38	24.93	0.67	3.23	100.9	123.90	26.00	259.8
17-Aug-05	7.272	0.18								
21-Sep-05	5.522	0.17	6.32	20.40	0.44	2.30	71.9	119.80	30.00	299.7
Combined Channel										
Station 2										
4-Sep-03			6.44	21.67	0.05	4.26	133.1	104.00	BDL	
10-Sep-03			6.08	19.53	0.05	4.69	146.6	81.40	BDL	
10-Sep-03			6.06	21.13	0.05	4.94	154.4	82.00	BDL	
17-Sep-03			6.02	19.00	0.00	4.87	152.2	85.50	14.0	139.9
1-Oct-03			5.95	15.47	0.05	6.22	194.4	78.40	12.5	124.9
1-Oct-03			6.40	18.33	0.05	5.51	172.2	80.20	10.5	104.9
22-Oct-03			6.42	15.77	0.05	6.06	189.4	89.50	10.5	104.9
20-Nov-03			5.99	13.33	0.05	5.86	183.1	99.20	BDL	
16-Dec-03			5.60	7.67	0.05	8.48	265.0	111.80	BDL	
10-Feb-04			6.47	8.23	0.06	9.51	297.2	98.30	BDL	
6-May-04			6.43	17.00	0.10	4.85	151.6	85.20	13.0	129.9
23-Jun-04			5.90	21.20	0.00	2.04	63.8	83.10	20.0	199.8
27-Jul-04			6.11	22.43	0.06	0.87	27.2	102.40	27.0	269.8
15-Sep-04			5.98	19.83	0.06	2.23	69.7	77.70	18.0	179.8
1-Dec-04			6.40	12.20	0.00	5.38	168.1	97.90	15.5	154.9
17-Feb-05			6.49	9.90	0.10	8.35	260.9	93.60	BDL	
15-Mar-05			6.27	11.17	0.06	7.00	218.8	99.20	BDL	
10-May-05			6.23	16.23	0.06	5.65	176.6	93.50	11.5	114.9
14-Jun-05			6.29	19.47	0.21	4.13	129.1	93.30	13.0	129.9
27-Jul-05			6.05	22.03	0.67	3.50	109.4	92.80	14.0	139.9
21-Sep-05			6.09	20.60	0.44	2.96	92.5	86.10	15.0	149.9
Station 1										
4-Sep-03	55.0	1.50	6.45	21.80	0.00	6.75	210.9	97.70	BDL	
10-Sep-03	43.2	1.15	6.02	19.37	0.05	7.36	230.0	88.10	BDL	
10-Sep-03	35.1	0.96	6.02	21.50	0.00	7.58	236.9	88.90	BDL	
17-Sep-03	38.3		6.18	18.67	0.05	7.59	237.2	84.10	19.0	189.8
1-Oct-03	47.0	1.35	5.59	15.13	0.05	7.93	247.8	84.90	21.0	209.8
1-Oct-03	40.2	1.13	6.37	18.57	0.05	8.08	252.5	87.90	11.5	114.9
22-Oct-03	36.8		6.30	15.27	0.05	8.45	264.1	98.90	15.5	154.9
20-Nov-03	48.5	1.21	5.93	12.97	0.05	7.69	240.3	109.00	BDL	
16-Dec-03	43.1	1.44	5.19	6.97	0.05	11.28	352.5	104.40	BDL	

Table 4.1 (continued)

Station 1	Q		pH	T		DO		SpC	Alkalinity (CaCO3 eq)	
(continued)	L/mn	SD	SU	deg C	SD	mg/L	uM	uS/cm	mg/L	uM
10-Feb-04	48.5	1.23	6.47	7.70	0.00	10.14	316.9	106.10	BDL	
6-May-04	20.8	0.52	6.59	17.53	0.12	7.54	235.6	90.90	16.2	161.9
23-Jun-04	16.0	0.50	6.13	22.13	0.06	5.68	177.5	112.10	33.0	329.7
27-Jul-04	11.0		6.32	22.83	0.06	5.15	160.9	114.30	30.0	299.7
15-Sep-04	11.7	0.76	6.14	19.70	0.00	6.46	201.9	121.90	32.0	319.7
21-Oct-04	25.9	0.67								
1-Dec-04	48.9	1.39	6.36	11.50	0.00	8.14	254.4	85.00	16.0	159.9
8-Feb-05	52.3									
17-Feb-05	50.6	1.32	6.70	9.53	0.12	9.28	290.0	96.70	BDL	
15-Mar-05	52.1	1.31	6.38	10.73	0.06	10.82	338.1	93.50	BDL	
10-May-05	49.4	1.27	6.35	16.33	0.06	7.15	223.4	92.00	12.5	124.9
14-Jun-05	58.8	1.90	6.42	19.90	0.17	5.61	175.3	98.80	20.0	199.8
27-Jul-05	47.9	3.08	6.23	22.33	0.67	5.83	182.2	94.80	16.0	159.9
21-Sep-05	31.0	0.78	6.40	20.60	0.44	5.82	181.9	80.70	15.0	149.9

Table 4.2. Nitrogen ions and sulfate.

Protected Stream

	$[NO_3^-]$				$[NO_2^-]$				$[NH_4^+]$				$[SO_4^{2-}]$			
Station 9	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
23-Jun-04	3.79	0.01	270.5	0.6	0.005	1.1E-03	0.34	0.076	0.013	2.9E-03	0.92	0.20	0.96	5.2E-03	10.0	0.05
27-Jul-04	3.37	0.55	240.7	39.6	0.003	2.1E-03	0.21	0.151	0.016	6.0E-03	1.14	0.43	0.91	1.4E-01	9.5	1.49
15-Sep-04	4.73	0.01	337.5	0.4	0.005	5.3E-04	0.32	0.038	0.025	4.2E-03	1.75	0.30	1.01	3.2E-03	10.5	0.03
1-Dec-04	5.41		386.3		0.004	0.0E+00	0.29	0.000	0.026	7.0E-03	1.85	0.50	1.10		11.5	0.00
17-Feb-05	6.84	0.00	488.5	0.2	0.003	4.8E-04	0.24	0.034	0.013	3.6E-03	0.96	0.26	1.64	1.1E-02	17.0	0.12
15-Mar-05	4.91	0.01	350.4	0.5	0.005	0.0E+00	0.36	0.000	0.023	7.4E-03	1.63	0.53	1.51	8.9E-03	15.7	0.09
10-May-05	4.69	0.00	334.9	0.2	0.006	7.1E-04	0.39	0.050	0.021	6.6E-04	1.50	0.05	1.56	1.1E-02	16.3	0.12
14-Jun-05	5.27	0.03	376.0	2.0	0.005	5.3E-04	0.32	0.038	0.089	5.6E-03	6.35	0.40				
27-Jul-05	5.07	0.03	361.9	2.1	0.005	0.0E+00	0.36	0.000	0.018	2.0E-03	1.27	0.14	1.85		19.2	
21-Sep-05	4.75	0.00	338.8	0.2	0.005	4.8E-04	0.34	0.034	0.023	2.9E-03	1.62	0.21	1.63	9.8E-03	17.0	0.10
Station 8																
4-Sep-03	6.86	0.07	489.8	5.0	0.006	1.6E-03	0.39	0.114								
10-Sep-03	7.16	0.27	511.2	19.2	0.004	0.0E+00	0.29	0.000								
10-Sep-03	6.35	0.25	453.4	18.2	0.004	0.0E+00	0.29	0.000								
17-Sep-03					0.004	0.0E+00	0.29	0.000	0.052	0.0E+00	3.68	0.00				
1-Oct-03	7.52	1.06	536.9	75.7	0.003	0.0E+00	0.21	0.000								
1-Oct-03	7.34	0.27	524.0	19.2	0.004	0.0E+00	0.29	0.000								
22-Oct-03	5.09	0.01	363.4	0.7	0.004	4.2E-04	0.27	0.030	0.021	1.1E-03	1.52	0.08				
20-Nov-03	9.97	0.06	711.4	4.6	0.012	5.3E-04	0.82	0.038	0.067	2.3E-02	4.79	1.64				
16-Dec-03	5.19	0.00	370.5	0.0	0.004	5.2E-04	0.31	0.037	0.021	1.7E-03	1.52	0.12				
8-Jan-04	4.60		328.2		0.004	0.0E+00	0.29	0.000					1.87		19.5	
10-Feb-04	7.04	0.12	502.3	8.2	0.007	0.0E+00	0.50	0.000	0.044	1.8E-03	3.17	0.13	4.09		42.6	

Table 4.2 (continued)

Station 8	$[NO_3^-]$				$[NO_2^-]$				$[NH_4^+]$				$[SO_4^{2-}]$			
(continued)	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
25-Mar-04	4.67		333.3		(tracer test)											
6-May-04	3.91	0.01	278.9	0.5		9.2E-04	0.00	0.066	0.020	9.1E-04	1.45	0.07	0.90	2.0E-04	9.3	0.00
23-Jun-04	3.80	0.01	271.5	1.0	0.004	9.9E-04	0.28	0.071	0.019	3.7E-03	1.39	0.27	1.01	9.0E-03	10.5	0.09
27-Jul-04	3.89	0.01	277.5	0.4	0.005	5.3E-04	0.32	0.038	0.013	3.4E-03	0.92	0.25	1.06	8.6E-03	11.1	0.09
15-Sep-04	4.68	0.00	333.9	0.0	0.004	0.0E+00	0.29	0.000	0.021	5.2E-03	1.51	0.37	1.01		10.5	0.00
21-Oct-04	5.14		367.1		(tracer test)								1.38	0.0E+00	14.3	
1-Dec-04	5.38	0.01	383.9	0.4	0.004	0.0E+00	0.29	0.000	0.018	3.4E-03	1.29	0.24	1.11	2.0E-02	11.5	0.21
8-Feb-05	5.45		389.0		0.001		0.09						1.31	1.8E-01	13.6	1.85
17-Feb-05	6.83	0.04	487.4	2.8	0.004	0.0E+00	0.29	0.000	0.019	7.4E-03	1.39	0.53	1.62	1.3E-02	16.9	0.14
15-Mar-05	5.08	0.00	362.6	-0.4	0.005	0.0E+00	0.36	0.000	0.019	5.2E-04	1.33	0.04	1.62	1.1E-02	16.9	0.12
10-May-05	4.72	0.01	336.9	0.6	0.004	2.8E-04	0.30	0.020	0.025	5.6E-03	1.79	0.40	1.60	7.8E-03	16.7	0.08
14-Jun-05	5.29	0.01	377.6	0.5	0.004	3.2E-04	0.29	0.023	0.086	7.0E-03	6.14	0.50				
27-Jul-05	4.92	0.00	351.4	0.2	0.005	4.2E-04	0.34	0.030	0.017	2.9E-03	1.19	0.21	1.73		18.1	
17-Aug-05	5.07		362.2	1.9	(tracer test)		0.09						1.35		14.0	
21-Sep-05	4.55	0.01	324.9	0.5	0.006	5.3E-04	0.39	0.038	0.022	2.0E-03	1.60	0.14	1.41	1.5E-02	14.6	0.16
Station 6																
4-Sep-03	6.04	0.05	431.2	3.6	0.006	3.5E-04	0.42	0.025								
10-Sep-03	5.43		387.7		0.004	0.0E+00	0.29	0.000								
10-Sep-03	5.61	0.14	400.5	10.1	0.004	0.0E+00	0.29	0.000								
17-Sep-03	4.30	0.00	307.0	0.0	0.004	0.0E+00	0.29	0.000	0.042	0.0E+00	2.96	0.00				
1-Oct-03	6.01	0.03	429.1	2.0	0.004	0.0E+00	0.29	0.000								
1-Oct-03	6.60	0.18	471.2	13.1	0.004	0.0E+00	0.29	0.000								
22-Oct-03	4.36	0.00	311.3	0.0	0.004	4.8E-04	0.31	0.034	0.028	1.4E-03	2.00	0.10				
20-Nov-03	4.91	0.00	350.5	0.0	0.003	1.2E-03	0.22	0.085	0.032	2.3E-02	2.26	1.63				
16-Dec-03					0.004	5.3E-04	0.25	0.038	0.022	1.2E-03	1.55	0.09				
8-Jan-04	4.02		286.7		0.004	3.2E-04	0.29	0.023					1.52		15.8	
10-Feb-04	4.99	0.02	356.3	1.4	0.004	0.0E+00	0.29	0.000	0.007	2.3E-03	0.52	0.16	1.69		17.6	
25-Mar-04	4.12		294.0		(tracer test)											
6-May-04	2.99	0.00	213.8	0.3	0.004	0.0E+00	0.29	0.000	0.029	4.8E-03	2.08	0.34	0.91	9.6E-03	9.5	0.10
23-Jun-04	2.45	0.01	175.0	0.9	0.004	0.0E+00	0.29	0.000	0.034	3.6E-03	2.44	0.26	0.98	1.4E-03	10.2	0.01

Table 4.2 (continued)

Station 6	[NO_3^-]				[NO_2^-]				[NH_4^+]				[SO_4^{2-}]			
(continued)	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
27-Jul-04	2.02	0.03	144.3	1.9	0.004	5.7E-04	0.28	0.041	0.016	1.6E-03	1.12	0.12	1.02	1.6E-03	10.6	0.02
15-Sep-04	2.83	0.04	202.3	2.9	0.004	0.0E+00	0.29	0.000	0.026	4.4E-03	1.88	0.31	1.13	1.1E-02	11.8	0.11
21-Oct-04	3.90		278.4		(tracer test)								1.35		14.0	
1-Dec-04	4.52	0.03	323.0	1.8	0.004	7.1E-04	0.25	0.050	0.029	2.3E-03	2.04	0.17	1.55	5.6E-03	16.1	0.06
8-Feb-05	4.77		340.4		(tracer test)								1.32		13.7	
17-Feb-05	5.97	0.00	426.4	-0.2	0.004	4.2E-04	0.27	0.030	0.017	3.4E-03	1.22	0.24	1.79	6.1E-03	18.6	0.06
15-Mar-05	4.47	0.01	319.5	0.6	0.004	0.0E+00	0.29	0.000	0.023	4.1E-03	1.62	0.30	1.71	3.8E-03	17.8	0.04
10-May-05	4.17	0.01	298.1	0.7	0.005	7.1E-04	0.32	0.050	0.039	4.5E-03	2.77	0.32	1.66	3.3E-03	17.3	0.03
14-Jun-05	4.47	0.01	319.2	0.5	0.005	3.2E-04	0.35	0.023	0.100	4.0E-03	7.10	0.28				
27-Jul-05	4.07	0.01	290.4	0.8	0.005	0.0E+00	0.36	0.000	0.039	3.1E-03	2.81	0.22	1.75	8.2E-03	18.3	0.09
17-Aug-05	4.14		295.8		(tracer test)								1.12		11.6	
21-Sep-05	3.61	0.18	257.8	13.0	0.006	5.3E-04	0.39	0.038	0.026	1.8E-03	1.83	0.13	1.44	5.7E-02	15.0	0.59
Station 4																
4-Sep-03	4.92	0.09	351.3	6.4	0.004	3.5E-04	0.29	0.025								
10-Sep-03	4.42	0.27	315.6	19.2	0.004	5.2E-04	0.31	0.037								
10-Sep-03	4.48	0.10	319.8	7.1	0.004	0.0E+00	0.29	0.000								
17-Sep-03		0.00		0.0	0.007	0.0E+00	0.50	0.000	0.044	0.0E+00	3.14	0.00				
1-Oct-03	4.94	0.18	352.7	13.1	0.004	5.2E-04	0.31	0.037								
1-Oct-03	5.17	0.31	369.1	22.2	0.004	0.0E+00	0.29	0.000								
22-Oct-03	3.48	0.00	248.5	0.0	0.003	8.2E-04	0.19	0.059	0.033	2.6E-03	2.39	0.19				
20-Nov-03	4.07	0.00	290.2	0.4	0.004	1.3E-03	0.31	0.096	0.055	2.3E-02	3.89	1.62				
16-Dec-03	4.16	0.01	296.6	1.1	0.003	3.2E-04	0.21	0.023	0.050	4.1E-03	3.54	0.29				
8-Jan-04	3.63		259.3		0.003	0.0E+00	0.21	0.000					1.59		16.5	
10-Feb-04	4.47	0.02	318.8	1.8	0.003	5.3E-04	0.18	0.038	0.028	4.9E-03	1.98	0.35				
25-Mar-04	3.28		233.8		(tracer test)											
6-May-04	2.18	0.02	155.8	1.2	0.003	5.3E-04	0.18	0.038	0.047	4.1E-03	3.34	0.29	0.85	6.4E-03	8.9	0.07
23-Jun-04	0.71	0.00	50.8	-0.4	0.005	5.3E-04	0.32	0.038	0.038	3.5E-03	2.74	0.25	0.82	2.2E-03	8.6	0.02
27-Jul-04	0.03	0.00	1.8	-0.3	0.002	5.3E-04	0.11	0.038	0.035	6.7E-03	2.47	0.48	0.70	3.4E-02	7.3	0.35
15-Sep-04	0.31	0.00	22.2	0.1	0.005	0.0E+00	0.36	0.000	0.054	5.6E-03	3.89	0.40	1.02	9.1E-03	10.7	0.10
21-Oct-04	2.21		157.7		0.000	3.6E-04	0.00	0.025	0.066		4.71		1.41	0.0E+00	14.7	

Table 4.2 (continued)

Station 4	$[NO_3^-]$				$[NO_2^-]$				$[NH_4^+]$				$[SO_4^{2-}]$			
(continued)	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
1-Dec-04	3.65	0.01	260.5	0.9	0.004	7.1E-04	0.25	0.050	0.053	3.3E-03	3.75	0.23	1.74	1.8E-02	18.1	0.18
8-Feb-05	4.89		349.2	4.5	0.001		0.06		0.032		2.25		1.39		14.5	
17-Feb-05	5.26	0.01	375.8	0.9	0.004	0.0E+00	0.29	0.000	0.028	5.2E-03	2.03	0.37	1.56	4.1E-01	16.2	4.29
15-Mar-05	3.97	0.02	283.7	1.3	0.004	0.0E+00	0.29	0.000	0.025	6.9E-04	1.78	0.05	1.75	6.3E-03	18.3	0.07
10-May-05	3.52	0.01	251.3	1.1	0.006	7.1E-04	0.39	0.050	0.028	9.5E-04	1.97	0.07	1.61	1.1E-02	16.8	0.11
14-Jun-05	3.54	0.00	252.6	0.0	0.005	3.2E-04	0.35	0.023	0.110	1.8E-03	7.85	0.13				
27-Jul-05	3.07	0.00	219.1	0.1	0.005	7.1E-04	0.32	0.050	0.024	4.9E-03	1.68	0.35	1.70		17.7	
17-Aug-05	3.24		231.1		0.002		0.14		0.032		2.25		1.14		11.9	
21-Sep-05	2.83	0.00	202.2	0.0	0.005	4.2E-04	0.34	0.030	0.022	1.5E-03	1.60	0.11	1.43	5.9E-03	14.9	0.06
Runoff Stream																
Station 7																
4-Sep-03	10.07	0.54	718.9	38.6	0.017	0.0E+00	1.21	0.000								
10-Sep-03	11.56	0.58	825.3	41.4	0.013	0.0E+00	0.93	0.000								
10-Sep-03	10.28	0.83	733.9	59.6	0.018	0.0E+00	1.29	0.000								
17-Sep-03	9.18	0.00	655.4	0.0	0.009	7.4E-04	0.67	0.053	0.055	0.0E+00	3.89	0.00				
1-Oct-03	9.29	0.08	663.3	6.1	0.011	4.5E-04	0.77	0.032								
1-Oct-03	10.52	0.16	751.1	11.1	0.010	5.2E-04	0.74	0.037								
22-Oct-03	8.22	0.00	586.9	0.0	0.015	9.7E-04	1.04	0.069	0.072	4.6E-04	5.16	0.03				
20-Nov-03	5.54	0.04	395.2	2.5	0.005	5.3E-04	0.32	0.038	0.023	2.3E-02	1.62	1.67				
16-Dec-03	0.00	0.00	0.0	0.0	0.009	5.3E-04	0.61	0.038	0.055	3.3E-03	3.89	0.23				
8-Jan-04	5.56	0.03	397.1	2.2	0.009	0.0E+00	0.64	0.000					3.17	6.7E-02	33.0	0.70
10-Feb-04	5.48	0.00	390.9	0.4	0.004	4.8E-04	0.26	0.034	0.004	2.0E-03	0.26	0.14	1.48	1.7E-02	15.4	0.18
6-May-04	3.60	0.01	257.3	0.7	0.021	0.0E+00	1.50	0.000	0.211	3.9E-03	15.08	0.28	3.53	2.9E-02	36.7	0.30
23-Jun-04	3.76	0.01	268.7	0.9	0.014	0.0E+00	1.01	0.000	0.169	5.9E-02	12.10	4.18	3.20	1.3E-02	33.3	0.14
15-Sep-04	3.76	0.00	268.6	-0.3	0.015	0.0E+00	1.04	0.000	0.137	4.4E-03	9.80	0.32	2.91	1.9E-02	30.3	0.20
1-Dec-04	6.09	0.00	434.7	0.0	0.008	0.0E+00	0.57	0.000	0.075	8.4E-03	5.36	0.60	3.07		32.0	
17-Feb-05	3.50		250.2		0.005	0.0E+00	0.34	0.000	0.062	5.6E-03	4.42	0.40	3.73		38.8	
15-Mar-05	5.12	0.01	365.6	0.5	0.004	0.0E+00	0.29	0.000	0.037	1.6E-02	2.64	1.12	3.81	9.0E-03	39.7	0.09
10-May-05	4.38	0.00	312.8	-0.3	0.008	1.4E-03	0.57	0.101	0.091	1.4E-03	6.48	0.10	4.03	5.5E-02	41.9	0.57
14-Jun-05	4.23	0.00	302.2	0.0	0.006	0.0E+00	0.43	0.000	0.230	4.8E-03	16.42	0.35				
27-Jul-05	5.15	0.01	367.4	0.6	0.008	0.0E+00	0.57	0.000	0.065	8.4E-03	4.66	0.60	4.02		41.8	
21-Sep-05	4.86	0.00	347.2	0.0	0.006	0.0E+00	0.43	0.000	0.043	2.2E-03	3.09	0.16	3.27	3.5E-02	34.1	0.37

Table 4.2 (continued)

Station 7	$[NO_3^-]$				$[NO_2^-]$				$[NH_4^+]$				$[SO_4^{2-}]$			
(continued)	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
4-Sep-03	3.66	0.29	261.3	20.7	0.001		0.04									
10-Sep-03	3.82	0.30	272.7	21.2	0.011	1.4E-03	0.79	0.101								
10-Sep-03	4.01	0.28	286.3	20.2	0.012	0.0E+00	0.86	0.000								
17-Sep-03					0.009	8.9E-04	0.66	0.063	0.156	0.0E+00	11.14	0.00				
1-Oct-03	3.64	0.21	259.9	15.1	0.008	5.3E-04	0.54	0.038								
1-Oct-03	3.70	0.07	264.2	5.0	0.009	5.2E-04	0.67	0.037								
22-Oct-03	2.67	0.02	190.6	1.4	0.009	0.0E+00	0.64	0.000	0.140	4.6E-04	10.00	0.03				
20-Nov-03	2.78	0.00	198.1	-0.4	0.007	5.3E-04	0.46	0.038	0.272	2.2E-02	19.41	1.57				
16-Dec-03					0.008	5.3E-04	0.54	0.038	0.132	5.4E-02	9.45	3.84				
8-Jan-04	2.94		209.6		0.005	5.3E-04	0.32	0.038					2.64	9.3E-02	27.5	0.97
10-Feb-04	2.85	0.05	203.5	3.6	0.004	0.0E+00	0.29	0.000	0.135	5.2E-02	9.64	3.74	3.23		33.6	
6-May-04	1.20	0.03	86.0	2.1	0.016	5.3E-04	1.11	0.038	0.362	5.6E-03	25.86	0.40	2.32	2.0E-02	24.2	0.21
23-Jun-04	1.77	0.10	126.6	7.4	0.012	2.1E-03	0.86	0.151	0.392	2.8E-03	28.01	0.20	2.07	3.7E-03	21.6	0.04
27-Jul-04	dry															
15-Sep-04	1.33	0.01	95.2	0.4	0.031	1.6E-03	2.18	0.113	0.154	3.5E-02	10.97	2.50	2.01	2.2E-03	21.0	0.02
1-Dec-04	2.74	0.00	195.8	-0.1	0.002	0.0E+00	0.14	0.000	0.159	1.7E-03	11.39	0.12	2.42	1.7E-02	25.2	0.17
17-Feb-05	1.79		127.6		0.003	0.0E+00	0.21	0.000	0.131	3.9E-03	9.35	0.28	3.08		32.1	
15-Mar-05	2.70	0.02	192.8	1.7	0.003	7.1E-04	0.18	0.050	0.094	2.6E-03	6.73	0.19	2.76	3.8E-02	28.8	0.39
10-May-05	2.11	0.01	150.5	0.5	0.008	7.1E-04	0.54	0.050	0.243	1.4E-03	17.34	0.10	2.73	9.1E-03	28.5	0.09
14-Jun-05	2.05	0.00	146.6	0.2	0.005	0.0E+00	0.36	0.000	0.371	1.5E-02	26.49	1.06				
27-Jul-05	2.65	0.01	189.0	0.4	0.008	7.1E-04	0.54	0.050	0.204	5.0E-03	14.55	0.35	2.82		29.3	
17-Aug-05	2.65		189.1		(tracer test)								1.94	4.2E-02	20.2	0.44
21-Sep-05	2.81	0.00	200.4	0.0	0.008	0.0E+00	0.54	0.000	0.210	2.7E-03	14.99	0.19	2.15	5.9E-03	22.4	0.06
Station 10																
17-Feb-05	3.03	0.03	216.5	2.3	0.006	0.0E+00	0.43	0.000	0.064	6.6E-03	4.57	0.47	3.14	4.3E-03	32.7	0.05
15-Mar-05	2.47	0.01	176.1	0.4	0.004	1.4E-03	0.29	0.101	0.046	8.6E-03	3.26	0.62	3.09	2.0E-03	32.1	0.02
10-May-05	1.67	0.01	119.2	0.7	0.013	7.1E-04	0.89	0.050	0.229	3.0E-03	16.31	0.21	2.63	1.9E-02	27.3	0.20
14-Jun-05	1.60	0.00	114.0	0.3	0.008	0.0E+00	0.57	0.000	0.353	1.2E-02	25.20	0.86				
27-Jul-05	2.09	0.00	149.1	0.0	0.011	5.7E-04	0.81	0.040	0.117	3.1E-03	8.37	0.22	2.25		23.4	
17-Aug-05	1.73		123.3		(tracer test)								1.54		16.0	
21-Sep-05	2.21	0.01	157.5	0.7	0.008	5.3E-04	0.54	0.038	0.081	3.1E-03	5.79	0.22				

Table 4.2 (continued)

	$[NO_3^-]$				$[NO_2^-]$				$[NH_4^+]$				$[SO_4^{2-}]$			
Station 3	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
4-Sep-03	0.71	0.00	50.7	0.0	0.009	5.3E-04	0.61	0.038								
10-Sep-03	0.52	0.01	37.1	1.0	0.005	1.5E-03	0.38	0.108								
10-Sep-03	0.11	0.03	7.9	2.0	0.006	0.0E+00	0.43	0.000								
17-Sep-03	0.15	0.01	10.4	0.4	0.004	8.9E-04	0.30	0.063	0.131	0.0E+00	9.32	0.00				
1-Oct-03	1.17	0.03	83.5	2.0	0.008	0.0E+00	0.57	0.000								
1-Oct-03	0.32	0.10	22.8	7.1	0.008	0.0E+00	0.57	0.000								
22-Oct-03	0.21	0.00	15.0	0.0	0.007	5.3E-04	0.46	0.038	0.126	4.4E-04	8.96	0.03				
20-Nov-03	0.70	0.00	50.0	0.0	0.006	0.0E+00	0.43	0.000	0.132	2.2E-02	9.45	1.56				
16-Dec-03	1.63	0.01	116.0	1.1	0.008	3.2E-04	0.56	0.023	0.063	2.5E-03	4.49	0.18				
8-Jan-04	2.19		156.1		0.007	5.3E-04	0.46	0.038					2.53		26.3	
10-Feb-04	2.34	0.02	167.1	1.4	0.007	4.2E-04	0.51	0.030	0.049	2.4E-03	3.52	0.17				
25-Mar-04	0.74		53.1		(tracer test)											
6-May-04	0.08	0.01	5.7	0.4	0.002	5.2E-04	0.17	0.037	0.050	9.1E-04	3.58	0.07	1.17	1.0E-03	12.1	0.01
23-Jun-04	0.03	0.00	1.8	0.1	0.004	1.2E-03	0.28	0.085	0.264	3.3E-03	18.84	0.24	0.65	3.5E-03	6.7	0.04
27-Jul-04	dry															
21-Oct-04					(tracer test)								1.58		16.5	
1-Dec-04	0.55	0.00	39.1	0.0	0.002	7.1E-04	0.11	0.050	0.120	2.7E-03	8.56	0.19	2.25		23.4	
17-Feb-05	1.96	0.02	140.3	1.4	0.003	5.3E-04	0.18	0.038	0.074	1.2E-02	5.25	0.88	2.70		28.1	
15-Mar-05	1.91	0.01	136.3	0.6	0.003	1.4E-03	0.21	0.101	0.065	6.9E-04	4.64	0.05	2.99	6.9E-03	31.1	0.07
10-May-05	1.42	0.02	101.6	1.4	0.010	0.0E+00	0.71	0.000	0.058	3.3E-03	4.18	0.23	2.50	2.1E-02	26.1	0.22
14-Jun-05	0.86	0.00	61.4	0.1	0.007	5.3E-04	0.46	0.038	0.184	8.3E-03	13.10	0.59				
27-Jul-05	0.73	0.01	52.0	0.6	0.005	7.1E-04	0.32	0.050	0.080	4.9E-03	5.75	0.35	1.79		18.7	
17-Aug-05	0.74		53.1		(tracer test)								1.36	2.7E-02	14.1	0.28
21-Sep-05	1.03	0.00	73.4	0.1	0.003	5.3E-04	0.18	0.038	0.065	1.0E-02	4.61	0.71	1.76	1.9E-02	18.3	0.20
Combined Channel																
Station 2																
4-Sep-03	3.50	0.03	249.9	2.1	0.003	3.5E-04	0.21	0.025								
10-Sep-03	3.47	0.03	247.7	2.0	0.003	2.3E-03	0.21	0.164								
10-Sep-03	3.37	0.17	240.6	12.1	0.005	4.6E-04	0.34	0.033								
17-Sep-03	2.50	0.03	178.5	2.1	0.004	5.3E-04	0.25	0.038	0.085	0.0E+00	6.03	0.00				

Table 4.2 (continued)

Station 2	$[NO_3^-]$				$[NO_2^-]$				$[NH_4^+]$				$[SO_4^{2-}]$			
(continued)	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
1-Oct-03	3.93	0.17	280.6	12.1	0.002	6.7E-04	0.16	0.048								
1-Oct-03	4.17	0.14	297.7	10.1	0.004	6.7E-04	0.31	0.048								
22-Oct-03	2.53	0.08	180.3	5.4	0.004	5.2E-04	0.31	0.037	0.046	8.1E-03	3.27	0.58				
20-Nov-03	3.05	0.05	217.8	3.6	0.005	0.0E+00	0.36	0.000	0.097	2.4E-02	6.94	1.69				
16-Dec-03	3.35	0.00	239.2	0.0	0.003	4.2E-04	0.23	0.030	0.082	3.1E-03	5.88	0.22				
8-Jan-04	3.24	0.07	231.6	4.9	0.004	5.3E-04	0.25	0.038					1.80	5.4E-02	18.7	0.57
10-Feb-04	3.80	0.01	271.3	0.7	0.004	4.2E-04	0.27	0.030	0.085	2.6E-02	6.05	1.82				
25-Mar-04	2.58		184.5		(tracer test)											
6-May-04	1.60	0.01	114.4	0.4	0.002	5.2E-04	0.17	0.037	0.147	1.2E-02	10.52	0.89	0.84	1.2E-02	8.7	0.12
23-Jun-04	0.45	0.01	32.5	1.0	0.004	5.2E-04	0.31	0.037	0.086	1.4E-02	6.10	0.97	0.82	3.6E-03	8.5	0.04
27-Jul-04	0.01	0.00	0.6	0.2	0.003	1.6E-03	0.18	0.113	0.119	2.1E-03	8.47	0.15	0.79	1.5E-04	8.2	0.00
15-Sep-04	0.09	0.00	6.5	0.1	0.004	5.3E-04	0.25	0.038	0.099	1.2E-02	7.03	0.82	0.93	5.6E-03	9.7	0.06
21-Oct-04	0.73		52.0		0.000		0.00						1.44		15.0	
1-Dec-04	2.44	0.14	174.5	9.9	0.001	0.0E+00	0.07	0.000	0.173	3.2E-02	12.32	2.30	2.05	1.0E-01	21.3	1.06
8-Feb-05	3.02		215.3		(tracer test)								2.09		21.8	
17-Feb-05	4.18	0.03	298.1	2.4	0.003	0.0E+00	0.21	0.000	0.057	2.9E-03	4.08	0.21	1.55	6.8E-04	16.2	0.01
15-Mar-05	2.98	0.17	212.4	12.1	0.003	7.1E-04	0.18	0.050	0.102	1.3E-02	7.27	0.95	2.15	3.7E-02	22.4	0.39
10-May-05	2.75	0.00	196.1	0.2	0.004	1.4E-03	0.29	0.101	0.081	4.2E-03	5.77	0.30	1.79	7.8E-03	18.7	0.08
14-Jun-05	2.68	0.00	191.7	0.2	0.006	7.0E-04	0.46	0.050	0.147	4.2E-03	10.46	0.30				
27-Jul-05	2.44	0.00	174.3	0.0	0.005	0.0E+00	0.36	0.000	0.104	2.8E-03	7.41	0.20	1.64		17.1	
17-Aug-05	2.03		145.0		(tracer test)								0.99		10.3	
21-Sep-05	2.29	0.00	163.7	0.2	0.005	5.3E-04	0.32	0.038	0.076	2.5E-03	5.39	0.18	1.37	7.5E-03	14.3	0.08
Station 1																
4-Sep-03	2.15	0.14	153.5	10.0												
10-Sep-03	3.47	0.06	247.7	4.0	0.002	0.0E+00	0.14	0.000								
10-Sep-03	3.34	0.01	238.5	1.0	0.004	1.1E-03	0.29	0.076								
17-Sep-03					0.005	5.3E-04	0.32	0.038	0.086	0.0E+00	6.10	0.00				
1-Oct-03	3.57	0.34	254.9	24.2	0.004	5.3E-04	0.25	0.038								
1-Oct-03	3.84	0.30	274.2	21.2	0.005	0.0E+00	0.36	0.000								
22-Oct-03	2.30	0.02	163.8	1.1	0.003	0.0E+00	0.21	0.000	0.113	6.9E-04	8.05	0.05				
20-Nov-03	2.74	0.01	195.6	0.7	0.004	0.0E+00	0.29	0.000	0.265	2.1E-02	18.93	1.52				
16-Dec-03	2.85	0.08	203.5	5.7	0.003	5.3E-04	0.18	0.038	0.177	9.4E-03	12.61	0.67				

Table 4.2 (continued)

Station 1	$[NO_3^-]$				$[NO_2^-]$				$[NH_4^+]$				$[SO_4^{2-}]$			
(continued)	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
8-Jan-04	2.84		203.1		0.003	0.0E+00	0.21	0.000					1.82		18.9	
10-Feb-04	3.42	0.00	244.2	0.0	0.003	4.8E-04	0.24	0.034	0.173	1.1E-02	12.33	0.75	2.36		24.5	
25-Mar-04	2.78		198.4		(tracer test)											
6-May-04	1.47	0.01	105.0	0.9	0.002	0.0E+00	0.14	0.000	0.144	3.9E-03	10.25	0.28	0.83	1.1E-02	8.6	0.11
23-Jun-04	0.18	0.00	13.1	0.1	0.002	2.1E-03	0.14	0.151	0.275	3.5E-03	19.63	0.25	0.62	1.3E-02	6.5	0.14
27-Jul-04	0.03	0.03	2.2	2.4	0.003	2.6E-03	0.18	0.188	0.202	1.8E-02	14.44	1.29	0.92	1.6E-02	9.6	0.16
15-Sep-04	0.00	0.00	0.0	0.1	0.000	0.0E+00	0.00	0.000	0.162	5.4E-03	11.58	0.39	0.57	3.7E-03	6.0	0.04
21-Oct-04	1.11		79.2		(tracer test)								1.46		15.2	
1-Dec-04	1.96	0.01	140.2	0.6	0.004	7.1E-04	0.25	0.050	0.118	6.9E-03	8.46	0.49	2.11	9.7E-03	21.9	0.10
8-Feb-05	3.02		215.3		(tracer test)								2.09	8.2E-03	21.7	0.09
17-Feb-05	3.38	0.00	241.3	0.3	0.004	0.0E+00	0.28	0.000	0.073	1.1E-03	5.24	0.08	2.16	3.1E-01	22.5	3.25
15-Mar-05	2.78	0.03	198.2	2.1	0.004	0.0E+00	0.29	0.000	0.054	8.5E-03	3.86	0.60	2.16	2.9E-02	22.5	0.30
10-May-05	2.51	0.00	178.9	-0.3	0.005	2.8E-04	0.37	0.020	0.067	2.9E-03	4.80	0.20	1.75	3.9E-03	18.2	0.04
14-Jun-05	1.91	0.07	136.1	4.7	0.007	7.0E-04	0.47	0.050	0.198	4.2E-03	14.10	0.30				
27-Jul-05	2.14	0.00	152.7	0.3	0.006	7.1E-04	0.39	0.050	0.134	3.3E-01	9.57	23.42				
17-Aug-05	1.69		120.4		(tracer test)											
21-Sep-05	1.86	0.01	133.0	0.4	0.005	0.0E+00	0.36	0.000	0.032	3.2E-03	2.28	0.23	1.28	6.5E-03	13.3	0.07

Table 4.3. Dissolved iron, organic carbon and chloride.

Protected Stream

	$[Fe_2^+]$				$[Fe_{total}]$				[DOC]				$[Cl^-]$			
Station 9	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
23-Jun-04	0.27	0.24	4.86	4.23	0.31	0.25	5.48	4.49	0.10	0.03	2.94	0.95	6.85	0.01	193.33	0.31
27-Jul-04	0.04	0.04	0.73	0.66	0.07	0.07	1.33	1.31	0.19	0.18	5.53	5.33	5.45	1.40	153.66	39.51
15-Sep-04	0.13	0.00	2.36	0.01	0.58	0.01	10.46	0.13	0.61	0.14	17.91	4.15	6.94	0.02	195.74	0.52
1-Dec-04	0.40	0.21	7.10	3.69	0.61	0.01	10.99	0.12	0.14				7.49	0.04	211.37	0.99
17-Feb-05	0.09	0.00	1.67	0.07	0.63	0.09	11.29	1.54	0.26	0.03	7.56	0.77	2.43	0.01	68.54	0.35
15-Mar-05	0.08	0.04	1.50	0.70	0.43	0.19	7.65	3.34					9.43	0.04	265.85	1.27
10-May-05	0.10	0.03	1.85	0.54	0.25	0.08	4.47	1.35	0.64	0.18	18.92	5.38	8.42	0.09	237.41	2.41
14-Jun-05	0.08	0.03	1.43	0.45	1.12	0.16	20.03	2.84	0.11	0.09	3.27	2.64	8.95	0.05	252.58	1.35
27-Jul-05	0.20	0.00	3.66	0.06	0.49	0.00	8.79	0.01					8.77	0.07	247.50	1.95
21-Sep-05	0.10	0.04	1.79	0.69	0.18	0.00	3.25	0.06					6.63	0.02	187.04	0.46
Station 8																
17-Sep-03	0.05	0.01	0.95	0.15	0.61	0.20	10.96	3.55								
22-Oct-03	0.09	0.08	1.60	1.41	0.23	0.13	4.14	2.41	0.42	0.06	12.43	1.68				
20-Nov-03	0.19	0.04	3.38	0.76	0.26	0.02	4.63	0.33	1.56	0.57	45.78	16.86				
16-Dec-03	0.26	0.06	4.57	1.05	0.35	0.05	6.32	0.86	0.35	0.05	10.42	1.60				
8-Jan-04													6.79		191.47	
10-Feb-04	0.10	0.01	1.76	0.09	0.16	0.01	2.88	0.24	0.97	0.14	28.34	4.11	9.93		280.05	2.37
6-May-04	0.01	0.01	0.12	0.15	0.02	0.14	0.33	0.01	0.09	0.05	2.64	1.57	7.40	0.05	208.67	1.37
23-Jun-04	0.27	0.07	4.85	1.29	0.49	0.20	8.70	3.57	0.13	0.00	3.82	0.06	7.01	0.00	197.83	0.05
27-Jul-04	0.01	0.00	0.26	0.03	0.04	0.02	0.68	0.30	0.50	0.38	14.64	11.29	6.56	0.02	185.04	0.50
15-Sep-04	0.34	0.07	6.12	1.19	1.08	0.27	19.36	4.75	0.53	0.10	15.67	2.88	6.91		194.88	0.00
1-Dec-04	0.04	0.03	0.72	0.60	0.08	0.03	1.37	0.60	0.15	0.02	4.49	0.60	7.47		210.79	0.00
17-Feb-05	0.12	0.03	2.20	0.57	0.57	0.01	10.22	0.18	0.27	0.02	7.83	0.48	2.42	0.02	68.14	0.50
15-Mar-05	0.06	0.01	1.07	0.18	0.26	0.15	4.63	2.70					9.44	0.00	266.20	0.01

Table 4.3 (continued)

	$[Fe_2^+]$				$[Fe_{total}]$				[DOC]				$[Cl^-]$			
Station 8	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
10-May-05	0.12	0.01	2.17	0.24	0.26	0.06	4.59	1.04	0.21	0.01	6.02	0.29	8.36	0.04	235.86	1.20
14-Jun-05	0.08	0.03	1.48	0.51	0.60	0.62	10.79	11.07	0.07	0.10	2.13	3.01	9.00	0.01	253.89	0.35
27-Jul-05	0.26	0.01	4.64	0.17	1.87	1.10	33.55	19.74	0.00	0.00			8.48	0.00	239.27	0.05
21-Sep-05	0.09	0.01	1.68	0.16	0.18	0.00	3.17	0.02					6.27	0.02	176.93	0.64
Station 6																
17-Sep-03	0.07	0.04	1.23	0.67	0.49	0.47	8.72	8.46	0.84		24.66	0.00				
22-Oct-03	0.10	0.02	1.82	0.39	0.35	0.01	6.28	0.14	0.75	0.01	21.98	0.44				
20-Nov-03	0.34	0.13	6.17	2.33	0.48	0.14	8.53	2.52	1.20	0.01	35.15	0.33				
16-Dec-03	0.46	0.12	8.21	2.11	0.61	0.13	10.91	2.32	0.91	0.12	26.71	3.64				
8-Jan-04													7.20		202.95	
10-Feb-04	0.26	0.09	4.71	1.65	0.46	0.08	8.27	1.43	0.47	0.05	13.86	1.54	10.47		295.41	
6-May-04	0.10	0.00	1.87	0.00	0.15	0.00	2.68	0.00	0.99	0.02	28.96	0.73	7.71	0.05	217.56	1.34
23-Jun-04	0.28	0.17	5.08	2.98	0.42	0.27	7.55	4.79	0.92	0.01	26.91	0.38	7.30	0.00	206.02	0.06
27-Jul-04	0.10	0.04	1.71	0.64	0.13	0.04	2.33	0.69	1.17	0.03	34.48	0.98	6.83	0.00	192.77	0.01
15-Sep-04	0.17	0.20	2.98	3.52	0.26	0.27	4.59	4.76	1.11	0.05	32.49	1.33	6.94	0.02	195.74	0.52
1-Dec-04	0.26	0.22	4.69	3.91	0.34	0.27	6.00	4.80	0.94		27.55	0.00	7.80	0.05	220.09	1.49
17-Feb-05	0.19	0.04	3.36	0.74	0.70	0.01	12.52	0.20	0.74	0.01	21.86	0.19	2.54	0.01	71.69	0.14
15-Mar-05	0.36	0.27	6.48	4.80	0.70	0.45	12.45	8.12	1.27	0.06	37.16	1.90	9.91	0.03	279.45	0.83
10-May-05	0.11	0.00	2.03	0.04	0.27	0.06	4.82	0.99	1.16	0.49	34.03	14.41	8.90	0.20	250.93	5.66
14-Jun-05	0.17	0.04	3.00	0.70	0.79	0.27	14.21	4.77	0.97	0.24	28.54	7.02	9.13	0.01	257.64	0.28
27-Jul-05	0.15	0.00	2.77	0.04	0.79	0.18	14.13	3.24	0.93	0.10	27.16	2.91	8.61	0.02	242.99	0.52
21-Sep-05	0.52	0.15	9.23	2.75	0.77	0.14	13.83	2.42					6.00	0.51	169.25	14.46
Station 4																
17-Sep-03	0.16	0.05	2.84	0.92	0.36	0.18	6.48	3.27								
22-Oct-03	0.26	0.04	4.57	0.63	0.42	0.08	7.56	1.49	1.21	0.13	35.65	3.78				
20-Nov-03	0.70	0.06	12.54	1.00	0.93	0.18	16.74	3.20	1.52	0.03	44.62	0.85				
16-Dec-03	1.01	0.23	18.02	4.19	1.10	0.26	19.65	4.65	1.42	0.07	41.56	1.97				
8-Jan-04													7.32		206.50	
10-Feb-04	0.89	0.14	15.89	2.46	1.01	0.20			0.84	0.15	24.64	4.44	10.47		295.41	

Table 4.3 (continued)

	[Fe$_2^+$]				[Fe$_{total}$]				[DOC]				[Cl$^-$]			
Station 4	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
6-May-04	0.89	0.41	15.89	7.43	1.07	0.42			1.26	0.03	37.13	0.81	7.68	0.00	216.75	0.04
23-Jun-04	0.98	0.33	17.48	5.96	1.33	0.63	23.82	11.37	1.78	0.11	52.12	3.09	7.41	0.01	209.00	0.37
27-Jul-04	4.82	0.37	86.36	6.56	5.17	0.44	92.56	7.86	2.31	0.13	67.81	3.84	6.97	0.22	196.74	6.19
15-Sep-04	1.54	0.56	27.49	10.04	1.94	0.19	34.79	3.45	1.83	0.13	53.81	3.75	6.94	0.02	195.74	0.52
21-Oct-04	0.94		16.916		1.03		18.49		1.62	0.03	47.567	0.91	7.51		211.88	
1-Dec-04	0.74	0.02	13.25	0.36	0.90	0.04	16.05	0.65	1.30	0.06	38.27	1.73	7.84	0.06	221.25	1.80
8-Feb-05	0.06		1.05		0.11		1.93		1.32		38.729		8.76		247.10	
17-Feb-05	0.89	0.21	15.94	3.68	1.38	0.29	24.75	5.19	0.92	0.02	26.97	0.52	2.53	0.00	71.44	0.07
15-Mar-05	0.31	0.05	5.51	0.83	0.77	0.37	13.87	6.65					9.92	0.09	279.83	2.40
10-May-05	0.25	0.02	4.55	0.33	0.49	0.04	8.86	0.68	1.35	0.12	39.54	3.47	8.78	0.26	247.53	7.22
14-Jun-05	0.66	0.27	11.91	4.77	1.91	0.42	34.14	7.60	1.83	0.32	53.78	9.49	9.11	0.02	257.04	0.42
27-Jul-05	1.12	0.75	19.99	13.48	2.86	1.58	51.20	28.35	1.05	0.38	30.82	11.07	8.62	0.00	243.06	0.08
17-Aug-05	0.47		8.48		0.62		11.15		1.54	0.09	45.141	2.67	7.09		200.11	
21-Sep-05	0.51	0.66	9.12	11.88	0.89	1.10	16.01	19.76					6.33	0.01	178.68	0.30
Runoff Stream																
Station 7																
17-Sep-03	0.10	0.14	1.72	2.43	0.67	0.93	11.93	16.69	1.34		39.23					
22-Oct-03	0.09	0.03	1.59	0.53	0.22	0.03	3.98	0.61	1.54	0.05	45.22	1.58				
20-Nov-03	0.09	0.04	1.55	0.76	0.24	0.03	4.30	0.46	0.63	0.07	18.38	1.91				
16-Dec-03	0.12	0.12	2.19	2.14	0.16	0.14	2.85	2.51	1.13	0.04	33.09	1.32				
8-Jan-04													12.42	0.14	350.35	4.01
10-Feb-04	0.18	0.11	3.18	1.99	0.26	0.16			0.22	0.01	6.51	0.38	16.43		463.50	
25-Mar-04																
6-May-04	1.26	0.46	22.58	8.28	0.26	0.16			1.35	0.05	39.52	1.44	15.16	0.01	427.75	0.31
27-May-04																
23-Jun-04	0.64	0.03	11.49	0.47	0.86	0.01	15.34	0.10	1.44	0.04	42.26	1.17	14.95	0.06	421.76	1.82
27-Jul-04																
15-Sep-04	0.29	0.00	5.24	0.05	1.09	0.25	19.58	4.53	1.95	0.07	57.38	2.20	6.94	0.02	195.74	0.52
21-Oct-04																
1-Dec-04	0.69	0.03	12.31	0.56	0.78	0.03	13.95	0.61	1.36		39.89	0.00	12.06		340.18	0.00

Table 4.3 (continued)

	[Fe$_2^+$]				[Fe$_{total}$]				[DOC]				[Cl$^-$]			
Station 7	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
17-Feb-05	0.18	0.11	3.26	1.92	0.43	0.35	7.64	6.27	1.00		29.27	0.00	3.92	0.77	110.45	21.68
15-Mar-05	0.15	0.06	2.70	1.15	0.62	0.23	11.17	4.09	1.44	0.19	42.27	5.71	15.72	0.03	443.29	0.72
10-May-05	0.17	0.10	2.97	1.80	0.28	0.16	5.08	2.90	1.36	0.16	40.01	4.84	15.38	0.03	433.72	0.78
14-Jun-05	0.29	0.02	5.17	0.30	1.40	0.07	25.11	1.24	1.51	0.26	44.40	7.64	17.25	0.07	486.59	1.91
27-Jul-05	0.42	0.01	7.49	0.17	2.76	0.90	49.49	16.18	0.67	0.22	19.63	6.50	16.96	0.02	478.38	0.53
21-Sep-05	0.29	0.06	5.12	1.00	0.57	0.26	10.17	4.72					12.28	0.02	346.28	0.53
Station 5																
17-Sep-03	1.36	0.13	24.36	2.39	1.89	0.47	33.80	8.45								
22-Oct-03	1.21	0.02	21.65	0.33	1.55	0.17	27.77	3.04	2.11	0.20	62.09	6.00				
20-Nov-03	0.86	0.14	15.45	2.56	1.55	0.22	27.71	3.98	2.35	0.11	69.00	3.16				
16-Dec-03	2.01	0.07	36.02	1.23	2.76	0.18	49.38	3.22	2.19	0.12	64.41	3.53				
8-Jan-04													13.33	0.25	375.97	7.02
10-Feb-04	1.69	0.08	30.18	1.44	1.82	0.09			1.12	0.04	32.78	1.07	19.31		544.78	
6-May-04	3.31	0.01	59.26	0.09	3.65	0.09			3.37	0.12	99.08	3.60	16.16	0.19	455.71	5.26
23-Jun-04	2.62	0.25	46.83	4.49	2.98	0.22	53.33	3.90	2.99	0.02	87.83	0.45	14.53	0.05	409.95	1.39
15-Sep-04	0.27	0.06	4.87	1.11	0.94	0.24	16.78	4.25	3.34	0.21	98.05	6.26	6.94	0.02	195.74	0.52
1-Dec-04	1.44	0.13	25.78	2.26	2.31	0.29	41.35	5.16	2.32	0.01	68.14	0.24	14.03	0.27	395.83	7.63
17-Feb-05	1.09	0.00	19.59	0.09	1.48	0.29	26.59	5.13	2.16		63.39	0.00	4.61	0.26	130.07	7.36
15-Mar-05	1.16	0.07	20.77	1.19	1.60	0.22	28.60	3.91					18.44	0.29	520.06	8.11
10-May-05	2.08	0.02	37.17	0.33	2.38	0.16	42.64	2.92	3.54	0.37	103.81	10.90	17.68	0.08	498.81	2.19
14-Jun-05	2.52	0.12	45.20	2.17	4.04	0.57	72.38	10.28	4.90	0.51	143.92	14.84	18.80	0.01	530.30	0.14
27-Jul-05	1.32	0.10	23.59	1.81	2.90	0.46	52.01	8.19	5.53	3.57	162.31	104.89	17.79	0.01	501.74	0.30
21-Sep-05	2.12	0.63	37.96	11.28	2.74	0.60	49.08	10.68					12.55	0.01	354.09	0.37
Station 10																
17-Feb-05	0.35	0.09	6.28	1.56	1.25	0.37	22.40	6.71	2.36	0.16	69.29	4.65	5.39	0.09	152.00	2.41
15-Mar-05	0.27	0.00	4.80	0.05	0.74	0.23	13.18	4.13	1.87	0.26	54.98	7.68	20.74	0.29	584.88	8.05
10-May-05	1.55	0.48	27.74	8.57	3.43	2.79	61.45	50.03	4.20	0.13	123.38	3.86	18.46	0.08	520.69	2.27
14-Jun-05	2.36	0.20	42.23	3.56	3.24	0.12	57.93	2.20	5.35	0.02	157.19	0.56	19.20	0.10	541.67	2.90
27-Jul-05	0.64	0.00	11.49	0.00	1.73	0.01	30.94	0.11	2.09	0.00	61.32	0.01	17.85	0.00	503.58	0.08
21-Sep-05	0.38	0.09	6.89	1.53	0.65	0.18	11.59	3.17					12.53	0.07	353.33	1.98

Table 4.3 (continued)

	[Fe$_2$$^+$]				[Fe$_{total}$]				[DOC]				[Cl$^-$]			
Station 3	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
17-Sep-03	1.46	0.09	26.12	1.67	1.96	0.52	35.09	9.33	4.41		129.40	0.00				
22-Oct-03	0.59	0.04	10.53	0.79	0.83	0.05	14.80	0.85	3.94	0.14	115.78	4.11				
20-Nov-03	0.29	0.09	5.23	1.60	0.58	0.45	10.33	8.02	3.29	0.11	96.45	3.36				
16-Dec-03	0.20	0.02	3.54	0.42	0.30	0.02	5.40	0.42	2.26	0.32	66.37	9.48				
8-Jan-04													14.47		408.11	
10-Feb-04	0.25	0.07	4.46	1.17	0.38	0.02	6.80	0.37	1.71	0.30	50.18	8.81	20.22		570.20	
6-May-04	1.15	0.02	20.52	0.36	1.33	0.13	23.88	2.36	5.11	0.02	150.15	0.59	16.05	0.02	452.84	0.46
23-Jun-04	2.56	0.02	45.82	0.42	3.12	0.09	55.81	1.55	6.50	0.16	190.91	4.61	14.45	0.12	407.70	3.30
21-Oct-04													14.78		416.97	
1-Dec-04	0.95	0.10	17.05	1.82	1.17	0.07	20.89	1.22	3.36		98.63	0.00	15.67		442.13	0.00
17-Feb-05	0.87	0.01	15.56	0.18	1.28	0.08	22.84	1.40	2.48	0.11	72.89	3.18	5.23	0.03	147.40	0.85
15-Mar-05	1.28	0.23	22.85	4.20	1.80	0.20	32.16	3.54	1.33	0.02	39.00	0.58	20.62	0.08	581.64	2.14
10-May-05	0.82	0.05	14.68	0.85	1.05	0.04	18.77	0.66	4.16	0.15	122.23	4.36	18.76	0.01	529.20	0.14
14-Jun-05	3.27	0.27	58.52	4.76	4.49	0.48	80.40	8.66	6.84	0.08	200.97	2.30	19.31	0.03	544.77	0.78
27-Jul-05	2.82	0.63	50.56	11.27	4.50	1.55	80.66	27.80	10.08	3.09	296.07	90.79	17.72	0.05	499.76	1.46
17-Aug-05	3.54		63.36		4.19		75.04		4.45	0.03	130.62	1.00	13.99		394.56	
21-Sep-05	4.12	0.06	73.72	1.10	4.72	0.38	84.52	6.83					12.69	0.20	357.89	5.77
Combined Channel																
Station 2																
17-Sep-03	3.18	0.42	56.88	7.43	3.981	1.04723	71.275	18.75	2.33		68.27	0.00				
22-Oct-03	1.07	0.08	19.15	1.41	1.285	0.13152	23.009	2.355	2.28	0.05	66.83	1.49				
20-Nov-03	0.57	0.09	10.12	1.55	0.986	0.10621	17.653	1.902	2.18	0.34	64.14	9.86				
16-Dec-03	1.14	0.08	20.43	1.49	1.339	0.22627	23.976	4.052	1.83	0.16	53.73	4.65				
8-Jan-04													8.72	0.17	245.97	4.71
10-Feb-04	1.05	0.24	18.75	4.33	1.233	0.14249	22.079	2.551	1.09	0.12	31.90	3.47				
6-May-04	1.26	0.46	22.58	8.28	1.622		29.036	0	2.08	0.14	61.01	4.05	9.19	0.22	259.28	6.11
23-Jun-04	0.70	0.11	12.56	1.96	1.039	0.19684	18.6	3.525	2.66	0.06	78.15	1.67	7.80	0.01	219.92	0.22
27-Jul-04	5.27	0.59	94.28	10.52	6.088	1.01696	109.01	18.21	3.44	0.11	101.13	3.17	7.17	0.14	202.31	4.01
15-Sep-04	2.38	0.00	42.59	0.06	3.384	0.00129	60.593	0.023	2.49	0.40	73.22	11.88	6.94	0.02	195.74	0.52
1-Dec-04	1.76	0.19	31.50	3.39	1.879	0.21511	33.639	3.852	2.15	0.19	63.13	5.51	10.24	0.45	288.75	12.72

Table 4.3 (continued)

	$[Fe_2^{+}]$				$[Fe_{total}]$				[DOC]				$[Cl^{-}]$			
Station 2	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD	mg/L	SD	uM	SD
17-Feb-05	0.66	0.19	11.77	3.47	0.908	0.33564	16.259	6.01	1.43	0.12	41.93	3.53	3.11	0.03	87.67	0.92
15-Mar-05	1.46	1.09	26.11	19.52	1.839	1.34987	32.935	24.17	1.14	0.08	33.54	2.29	12.99	0.15	366.53	4.14
10-May-05	1.77	0.11	31.71	1.99	1.952	0.15952	34.959	2.856	2.20	0.02	64.70	0.73	11.10	0.08	313.21	2.12
14-Jun-05	1.34	0.04	24.03	0.67	2.856	0.22233	51.137	3.981	2.40	0.37	70.50	10.92	10.88	0.04	306.96	1.06
27-Jul-05	2.12	0.24	38.02	4.25	3.901	0.33943	69.854	6.078	1.56	0.14	45.83	3.99	10.24	0.04	288.75	1.08
21-Sep-05	1.93	0.04	34.57	0.64	2.2	0.10723	39.386	1.92					7.45	0.01	210.08	0.15
Station 1																
17-Sep-03	1.23	0.01	21.98	0.19	1.48	0.08	26.45	1.44								
22-Oct-03	1.68	0.07	30.07	1.28	2.19	1.25	39.29	22.35	2.58	0.54	75.78	15.82				
20-Nov-03	1.30	0.18	23.21	3.22	1.60	0.07	28.65	1.29	2.82	0.05	82.83	1.41				
16-Dec-03	1.70	0.07	30.47	1.20	1.99	0.07	35.66	1.25	2.40	0.38	70.39	11.02				
8-Jan-04													9.65	0.14	272.27	4.07
10-Feb-04	1.11	0.06	19.89	1.02	1.26	0.10	22.57	1.81	1.18	0.13	34.69	3.72	15.14		427.11	
6-May-04	1.80	0.39	32.26	7.06	2.30	0.62	41.26	11.03	2.66	0.27	78.00	7.96	9.77	0.08	275.62	2.14
23-Jun-04	4.58	0.22	82.07	3.86	5.05	0.45	90.40	8.10	4.32	0.29	126.82	8.62	9.29	0.12	262.11	3.48
27-Jul-04	5.50	0.17	98.57	2.96	6.21	0.24	111.17	4.32	3.96	0.27	116.28	7.89	8.33	0.03	234.84	0.83
15-Sep-04	5.90	0.02	105.65	0.44	7.31	0.10	130.81	1.88	4.54	0.16	133.36	4.72	6.94	0.02	195.74	0.52
21-Oct-04													9.52		268.66	
1-Dec-04	1.09	0.50	19.56	8.99	1.42	0.86	25.36	15.32	2.52	0.21	74.10	6.15	11.38	0.10	320.91	2.77
8-Feb-05													11.63		328.17	
17-Feb-05	0.57	0.10	10.22	1.84	1.01	0.36	18.08	6.42	1.53		44.92	0.00	3.89	0.01	109.65	0.14
15-Mar-05	0.39	0.01	7.04	0.27	0.64	0.02	11.44	0.44					14.18	0.20	400.03	5.70
10-May-05	0.77	0.12	13.84	2.23	0.98	0.23	17.61	4.09	2.25	0.09	66.01	2.53	11.39	0.04	321.28	1.20
14-Jun-05	0.93	0.11	16.65	1.90	1.95	0.09	34.85	1.63	3.48	0.64	102.22	18.83	12.90	0.57	363.73	16.07
27-Jul-05	0.63	0.10	11.32	1.71	1.27	0.38	22.78	6.83	1.86	0.60	54.55	17.65	10.28	0.03	289.97	0.98
17-Aug-05													8.54		240.85	
21-Sep-05	0.42	0.08	7.61	1.49	0.69	0.01	12.41	0.20					7.46	0.02	210.56	0.53

Table 4.4 Dissolved gases.

Protected Stream

	$[N_2O]$				$[H_2CO_3^*]$				$[CH_4]$				$[H_2]$			
Station 9	ugN/L	SD	uM	SD	mg/L	SD	uM	SD	ug/L	SD	uM	SD	ng/L	SD	uM	SD
23-Jun-04	3.87	0.01	1.4E-01	3.7E-04	1.4	0.77	22.2	12.5	unst.		unst.	0.14	0.80	0.44	0.40	0.22
27-Jul-04	4.34	0.07	1.6E-01	2.4E-03	4.6	0.05	73.4	0.8	BDL		BDL		1.09	0.14	0.54	0.07
1-Dec-04	5.54	0.25	2.0E-01	8.8E-03	4.7	0.31	76.1	5.1	82.2	5.60	5.13	0.35	0.94	0.39	0.46	0.19
10-May-05	7.01	0.38	2.5E-01	1.4E-02	5.2	0.31	84.1	5.0	BDL		BDL		0.39	0.12	0.20	0.06
14-Jun-05	8.84	0.13	3.2E-01	4.5E-03	6.3	0.11	100.9	1.8	BDL		BDL		0.27	0.23	0.14	0.11
27-Jul-05	8.96	0.46	3.2E-01	1.6E-02	7.3	0.32	117.8	5.1	BDL		BDL		2.56	0.33	1.27	0.17
21-Sep-05	8.78	0.08	3.1E-01	2.9E-03	6.4	0.14	103.3	2.3	BDL		BDL		0.49	0.00	0.24	0.00
Station 8																
17-Sep-03	4.15	0.14	1.5E-01	5.1E-03	3.8	0.03	60.9	0.5	0.8	0.42	0.05	0.03	0.33	0.19	0.67	0.37
22-Oct-03	3.08	0.07	1.1E-01	2.7E-03	1.8	0.10	28.4	1.6	0.9	0.00	0.05	0.02	0.33	0.08	0.66	0.17
20-Nov-03	3.45	0.01	1.2E-01	2.0E-04	2.7	0.31	43.2	5.0	2.2	0.24	0.14	0.02	0.31	0.02	0.63	0.03
16-Dec-03	5.32	0.03	1.9E-01	1.2E-03	2.4	0.19	38.9	3.0	1.9	2.68	0.12	0.17	BDL		BDL	
10-Feb-04	6.44	0.17	2.3E-01	6.2E-03	3.2	1.15	51.2	18.5	3.4	0.65	0.21	0.04	1.14	0.97	2.30	1.95
6-May-04	3.98	0.08	1.4E-01	2.7E-03		(TCD not working: no CO2, CH4 or H2 analyses)										
23-Jun-04	3.13	0.32	1.1E-01	1.1E-02	3.5		56.2	0.0	unst.		unst.		BDL		BDL	
27-Jul-04	3.61	0.01	1.3E-01	3.4E-04	3.8	0.03	61.7	0.5	BDL		BDL		0.23	0.01	0.46	0.02
15-Sep-04	6.01	0.07	2.1E-01	2.5E-03	5.1	0.12	82.9	2.0	0.8	0.07	0.05	0.00	0.35	0.14	0.71	0.28
1-Dec-04	4.60	0.11	1.6E-01	4.1E-03	3.8	0.14	61.5	2.2	1.3	0.09	0.08	0.01	0.22	0.13	0.45	0.27
17-Feb-05	5.88	0.11	2.1E-01	3.9E-03	3.7	0.15	59.1	2.4	BDL		BDL		0.15	0.06	0.31	0.11
15-Mar-05	5.60	0.15	2.0E-01	5.2E-03	4.2	0.22	68.1	3.5	0.4	0.02	0.02	0.00	0.31	0.02	0.62	0.04
10-May-05	6.20	0.08	2.2E-01	3.0E-03	4.5	0.01	72.4	0.2	BDL		BDL		0.34	0.09	0.68	0.18
14-Jun-05	8.03	0.20	2.9E-01	7.0E-03	5.7	0.00	91.2	0.1	1.2	0.12	0.08	0.01	0.20	0.13	0.40	0.26
27-Jul-05	6.77	0.80	2.4E-01	2.9E-02	6.4	0.10	103.8	1.7	1.3	0.60	0.08	0.04	1.02	0.01	2.06	0.03
21-Sep-05	5.74	0.02	2.0E-01	7.4E-04	5.5	0.04	88.5	0.6	BDL		BDL		0.42	0.12	0.84	0.25

Table 4.4 (continued)

	$[N_2O]$				$[H_2CO_3^*]$				$[CH_4]$				$[H_2]$			
Station 6	ugN/L	SD	uM	SD	mg/L	SD	uM	SD	ug/L	SD	uM	SD	ng/L	SD	uM	SD
17-Sep-03	2.38	0.09	8.5E-02	3.4E-03	1.4	0.02	22.8	0.3	2.6	0.23	0.16	0.01	0.26	0.05	0.52	0.10
22-Oct-03	1.98	0.12	7.1E-02	4.2E-03	0.9	0.02	13.8	0.3	3.0	1.49	0.19	0.09	0.60	0.11	1.21	0.21
20-Nov-03	2.55	0.01	9.1E-02	2.2E-04	1.2	0.09	18.6	1.5	3.1	1.48	0.19	0.09	0.40	0.07	0.81	0.14
16-Dec-03	3.25	0.01	1.2E-01	3.3E-04	1.1	0.19	18.5	3.1	1.8	2.55	0.11	0.16	0.37	0.75	0.74	1.51
10-Feb-04	2.65	0.12	9.4E-02	4.2E-03	0.9	0.18	14.7	2.8	3.0	1.73	0.18	0.11	0.39	0.16	0.79	0.31
6-May-04	2.77	0.01	9.9E-02	1.8E-04		(TCD not working: no CO2, CH4 or H2 analyses)										
23-Jun-04	2.29	0.14	8.2E-02	4.9E-03	2.2		35.7		unst.		unst.		BDL		BDL	
27-Jul-04	3.37	0.02	1.2E-01	5.7E-04	1.9	0.00	30.9	0.0	BDL		BDL		0.35	0.07	0.71	0.15
15-Sep-04	2.81	0.01	1.0E-01	2.6E-04	1.9	0.00	31.2	0.0	1.3	0.15	0.08	0.01	0.41	0.51	0.83	1.03
1-Dec-04	2.94	0.01	1.1E-01	5.0E-04	2.2	0.07	35.7	1.2	1.1	0.30	0.07	0.02	0.40	0.05	0.81	0.10
17-Feb-05	3.14	0.06	1.1E-01	2.0E-03	1.2	0.06	19.1	1.0	0.3	0.04	0.02	0.00	0.20	0.01	0.41	0.02
15-Mar-05	3.17	0.10	1.1E-01	3.4E-03	1.2	0.05	19.1	0.8	0.8	0.11	0.05	0.01	0.18	0.01	0.37	0.02
10-May-05	3.52	0.11	1.3E-01	3.9E-03	2.7	0.03	43.4	0.4	0.7	0.06	0.04	0.00	0.28	0.01	0.57	0.01
14-Jun-05	3.62	0.03	1.3E-01	1.1E-03	2.7	0.02	43.6	0.3	3.2	0.30	0.20	0.02	0.23	0.04	0.47	0.08
27-Jul-05	4.14	0.08	1.5E-01	3.0E-03	3.1	0.03	50.7	0.5	2.5	0.15	0.16	0.01	1.03	0.05	2.07	0.10
21-Sep-05	2.54	0.08	9.1E-02	2.8E-03	2.1	0.04	34.2	0.6	2.9	0.27	0.18	0.02	0.15	0.13	0.30	0.26
Station 4																
17-Sep-03	2.23	0.07	8.0E-02	2.6E-03	1.0	0.02	16.5	0.4	16.6	0.79	1.04	0.05	0.84	0.02	1.70	0.04
22-Oct-03	1.77	0.11	6.3E-02	4.0E-03	0.7	0.03	10.8	0.5	17.3	0.72	1.08	0.05	0.53	0.16	1.06	0.32
20-Nov-03	1.97	0.01	7.0E-02	1.9E-04	0.8	0.02	13.3	0.3	31.8	6.49	1.98	0.41	0.26	0.05	0.52	0.09
16-Dec-03	2.18	0.07	7.8E-02	2.5E-03	0.9	0.00	15.0	0.0	36.6	0.50	2.29	0.03	BDL		BDL	
10-Feb-04	1.89	0.00	6.7E-02	1.5E-04	0.8	0.07	13.4	1.0	39.0	5.08	2.43	0.32	0.31	0.09	0.62	0.17
6-May-04	1.60	0.08	5.7E-02	3.0E-03		(TCD not working: no CO2, CH4 or H2 analyses)										
23-Jun-04	3.40	0.03	1.2E-01	1.1E-03	1.7	1.67	27.5	26.9	unst.		unst.		BDL		BDL	
27-Jul-04	0.64	0.00	2.3E-02	1.2E-04	4.8	0.06	78.0	0.9	BDL		BDL		0.36	0.08	0.73	0.17
15-Sep-04	4.15	0.06	1.5E-01	2.1E-03	3.3	0.04	54.0	0.6	63.1	2.95	3.94	0.18	0.33	0.30	0.66	0.61
21-Oct-04	2.09	0.26	7.5E-02	9.4E-03	2.1	0.26	33.4	4.3	59.4	10.11	3.70	0.63	1.44	1.84	2.91	3.71
1-Dec-04	1.50	0.04	5.4E-02	1.4E-03	1.6	0.05	26.5	0.8	9.5	0.30	0.59	0.02	0.25	0.00	0.50	0.00
8-Feb-05	2.36	0.07	8.4E-02	2.3E-03	1.0	0.00	15.3	0.0	17.0	0.30	1.06	0.02	0.21	0.03	0.42	0.06
17-Feb-05	1.81	0.03	6.5E-02	1.1E-03	0.9	0.07	14.8	1.2	11.7	0.18	0.73	0.01	0.28	0.02	0.56	0.03
15-Mar-05	1.82	0.04	6.5E-02	1.4E-03	0.9	0.06	15.3	1.0	20.5	0.04	1.28	0.00	0.40	0.13	0.80	0.27

Table 4.4 (continued)

	$[N_2O]$				$[H_2CO_3^*]$				$[CH_4]$				$[H_2]$			
Station 4	ugN/L	SD	uM	SD	mg/L	SD	uM	SD	ug/L	SD	uM	SD	ng/L	SD	uM	SD
10-May-05	2.73	0.14	9.7E-02	5.0E-03	1.7	0.59	27.0	9.5	2.4	0.48	0.15	0.03	0.33	0.18	0.67	0.37
14-Jun-05	3.30	0.06	1.2E-01	2.0E-03	2.7	0.03	42.9	0.4	79.0	0.65	4.93	0.04	0.14	0.04	0.28	0.08
27-Jul-05	3.99	0.09	1.4E-01	3.2E-03	2.2	0.04	35.5	0.7	13.4	0.27	0.83	0.02	0.86	0.44	1.72	0.89
17-Aug-05	3.16	0.16	1.1E-01	5.8E-03	1.1	0.07	17.9	1.1	9.7	0.84	0.61	0.05	0.35	0.00	0.71	0.01
21-Sep-05	2.21	0.04	7.9E-02	1.5E-03	1.8	0.02	29.6	0.3	6.1	0.09	0.38	0.01	0.15	0.08	0.30	0.15
Runoff Stream																
Station 7																
1-Dec-04	10.97	0.10	3.9E-01	3.7E-03	4.6	0.06	73.7	0.9	90.7	2.86	5.66	0.18	0.60	0.31	1.21	0.62
17-Feb-05	8.76	0.02	3.1E-01	6.5E-04	2.4	0.10	38.5	1.6	40.4	1.43	2.52	0.09	0.15	0.09	0.31	0.18
15-Mar-05	8.85	0.17	3.2E-01	6.0E-03	1.5	0.06	24.7	1.0	21.0	0.20	1.31	0.01	0.19	0.04	0.38	0.09
10-May-05	9.11	0.17	3.3E-01	6.0E-03	3.1	1.09	49.9	17.6	29.3	8.68	1.82	0.54	0.61	0.70	1.22	1.41
27-Jul-05	8.64	0.46	3.1E-01	1.6E-02	2.1	0.04	34.4	0.6	31.6	1.24	1.97	0.08	1.21	0.23	2.43	0.45
21-Sep-05	5.55	0.03	2.0E-01	1.1E-03	2.0	0.02	32.1	0.3	39.6	0.09	2.47	0.01	0.19	0.05	0.39	0.11
Station 5																
22-Oct-03	3.71	0.34	1.3E-01	1.2E-02	1.8	0.00	29.4	0.04	119.9	0.16	7.48	0.01	0.38	0.02	0.77	0.04
20-Nov-03	6.69	0.10	2.4E-01	3.6E-03	2.4	0.48	39.3	7.7	933.4	240.33	58.22	14.99	0.33	0.18	0.67	0.37
16-Dec-03	5.69	0.34	2.0E-01	1.2E-02	2.0	0.06	32.8	1.0	1113.9	66.29	69.48	4.13	BDL		BDL	
10-Feb-04	6.67	0.02	2.4E-01	8.6E-04	2.5	1.14	40.9	18.4	526.9	138.69	32.86	8.65	11.36	2.30	22.90	4.64
15-Sep-04	5.98	0.01	2.1E-01	5.3E-04	2.9	0.05	47.4	0.7	45.5	3.20	2.84	0.20	0.63	0.58	1.26	1.18
1-Dec-04	4.46	0.11	1.6E-01	4.1E-03	3.8	0.21	62.0	3.5	167.7	0.12	10.46	0.01	0.66	0.08	1.33	0.15
17-Feb-05	2.85	0.12	1.0E-01	4.4E-03	1.9	0.15	31.2	2.4	298.7	28.66	18.63	1.79	0.27	0.09	0.55	0.18
15-Mar-05	2.54	0.11	9.1E-02	3.8E-03	1.5	0.16	23.8	2.6	89.3	2.04	5.57	0.13	0.27	0.09	0.55	0.18
10-May-05	3.94	0.03	1.4E-01	1.1E-03	3.2	0.01	51.1	0.1	139.3	1.78	8.69	0.11	0.15	0.06	0.30	0.12
14-Jun-05	3.69	0.04	1.3E-01	1.4E-03	3.6	0.03	57.4	0.5	214.5	1.28	13.38	0.08	0.25	0.10	0.51	0.20
27-Jul-05	3.47	0.12	1.2E-01	4.4E-03	2.6	0.03	41.4	0.4	184.1	1.62	11.48	0.10	1.36	0.11	2.74	0.22
21-Sep-05	3.70	0.09	1.3E-01	3.2E-03	3.2	0.01	51.1	0.2	270.3	1.28	16.86	0.08	0.27	0.04	0.55	0.08

Table 4.4 (continued)

	[N_2O]				[$H_2CO_3^*$]				[CH_4]				[H_2]			
Station 10	ugN/L	SD	uM	SD	mg/L	SD	uM	SD	ug/L	SD	uM	SD	ng/L	SD	uM	SD
17-Feb-05	1.52	0.07	5.4E-02	2.4E-03	1.0	0.03	16.1	0.5	0.02	0.00	24.12	0.31	0.09	0.04	0.18	0.08
15-Mar-05	1.38	0.03	4.9E-02	1.0E-03	0.6	0.03	9.4	0.4	0.01	0.00	17.52	0.06	0.37	0.08	0.75	0.17
10-May-05	2.78		9.9E-02		2.8		45.5		0.05	0.00	485.64		0.26		0.13	
14-Jun-05	3.02	0.03	1.1E-01	1.1E-03	3.0	0.02	47.8	0.4	0.05	0.00	211.69	0.00	0.15	0.05	0.30	0.10
27-Jul-05	2.41	0.04	8.6E-02	1.5E-03	1.8	0.04	29.3	0.6	0.03	0.00	42.92	0.18	1.20	0.00		
21-Sep-05	3.75	0.00	1.3E-01	1.4E-04	2.3	0.02	36.7	0.3	0.04	0.00	59.26	0.58	0.11	0.04	0.23	0.09
Station 3																
17-Sep-03	1.24	0.06	4.4E-02	2.0E-03	1.8	0.09	29.6	1.4	370.9	29.74	23.13	1.85	0.63	0.03	0.31	0.02
22-Oct-03	0.43	0.03	1.5E-02	1.0E-03	0.7	0.06	11.7	0.9	38.7	6.65	2.42	0.41	1.08	0.35	0.54	0.17
20-Nov-03	1.90	0.11	6.8E-02	3.9E-03	0.9	0.05	13.8	0.8	42.2	5.23	2.63	0.33	1.72	0.01	0.85	0.01
16-Dec-03	1.77	0.12	6.3E-02	4.4E-03	0.6	0.03	9.1	0.4	6.9	1.73	0.43	0.11	1.50	2.71	0.74	1.34
10-Feb-04	2.27	0.15	8.1E-02	5.3E-03	0.9	0.20	15.1	3.3	23.0	5.46	1.43	0.34	1.04	0.52	0.52	0.26
6-May-04	0.13	0.05	4.6E-03	1.7E-03		(TCD not working: no CO2, CH4 or H2 analyses)										
23-Jun-04	0.06	0.04	2.2E-03	1.4E-03	5.5		88.0		unst.		unst.		BDL		BDL	
1-Dec-04	1.62	0.03	5.8E-02	9.4E-04	1.8	0.16	29.0	2.6	40.3	2.95	2.52	0.18	3.12	1.82	1.55	0.90
17-Feb-05	0.76		2.7E-02		1.2		19.9		45.3		2.82		0.53		0.26	
15-Mar-05	0.68	0.00	2.4E-02	3.8E-05	1.1	0.13	17.3	2.2	67.3	1.76	4.20	0.11	1.12	0.12	0.56	0.06
10-May-05	1.02	0.06	3.6E-02	2.3E-03	2.0	0.08	32.5	1.2	34.2	0.62	2.14	0.04	0.40	0.02	0.20	0.01
14-Jun-05	1.89	0.10	6.8E-02	3.5E-03	3.1	0.04	49.2	0.6	130.3	0.66	8.13	0.04	0.31	0.03	0.15	0.01
27-Jul-05	2.94	0.61	1.0E-01	2.2E-02	2.8	0.01	44.8	0.2	110.1	2.22	6.87	0.14	1.53	0.47	0.76	0.23
17-Aug-05	3.10	0.22	1.1E-01	7.7E-03	1.3	0.11	21.4	1.8	94.1	2.24	5.87	0.14	0.71	0.01	0.35	0.00
21-Sep-05	1.17	0.11	0.042	4.1E-03	4.0	0.07	63.8	1.1	196.0	2.85	12.23	0.18	0.28	0.00	0.14	0.00
Combined Channel																
Station 2																
17-Sep-03	1.22	0.24	4.4E-02	8.7E-03	1.2	0.23	18.8	3.7	18.7	5.26	299.39	84.38	1.73	0.12	0.86	0.06
22-Oct-03	1.22	0.07	4.3E-02	2.3E-03	0.7	0.14	11.4	2.3	1.7	0.38	27.23	6.04	0.70	0.05	0.35	0.03
20-Nov-03	1.50	0.10	5.4E-02	3.5E-03	1.0	0.04	16.2	0.6	3.4	0.00	55.15	0.02	1.75	0.10	0.87	0.05
16-Dec-03	1.60	0.51	5.7E-02	1.8E-02	0.6	0.17	10.4	2.7	13.1	4.23	209.94	67.84	2.69	1.33	1.33	0.66
10-Feb-04	1.69	0.08	6.0E-02	2.9E-03	0.9	0.34	13.8	5.5	6.1	0.58	98.34	9.24	2.17	0.72	1.08	0.35
6-May-04	1.58	0.06	5.6E-02	2.1E-03		(TCD not working: no CO2, CH4 or H2 analyses)										

Table 4.4 (continued)

Station 2			$[N_2O]$				$[H_2CO_3^*]$				$[CH_4]$				$[H_2]$	
(continued)	ugN/L	SD	uM	SD	mg/L	SD	uM	SD	ug/L	SD	uM	SD	ng/L	SD	uM	SD
23-Jun-04	1.62	0.12	5.8E-02	4.2E-03			57.5		unst.		unst.		BDL		BDL	
27-Jul-04	0.11	0.01	3.8E-03	4.2E-04	4.3	0.03	69.8	0.5	BDL		BDL		0.49	0.21	0.24	0.11
15-Sep-04	0.86	0.10	3.1E-02	3.6E-03	2.5	0.28	40.8	4.4	9.4	0.48	150.98	7.62	0.90	1.28	0.45	0.63
1-Dec-04	1.48	0.09	5.3E-02	3.0E-03	1.9	0.10	30.1	1.7	3.9	0.20	62.33	3.20	0.86	0.30	0.42	0.15
17-Feb-05	1.37	0.10	4.9E-02	3.5E-03	1.2	0.08	19.8	1.4	3.7	0.13	59.47	2.12	0.61	0.15	0.30	0.08
15-Mar-05	1.42	0.06	5.1E-02	2.0E-03	1.6	0.11	26.1	1.7	10.7	0.57	172.12	9.08	0.54	0.01	0.27	0.01
10-May-05	1.94	0.17	6.9E-02	6.2E-03	2.5	0.05	40.5	0.8	7.0	0.21	112.69	3.32	0.54	0.19	0.27	0.10
14-Jun-05	2.68	0.00	9.6E-02	1.4E-04	3.0	0.08	48.3	1.3	7.9	0.12	126.91	1.96	0.44	0.05	0.22	0.03
27-Jul-05	3.78	0.24	1.3E-01	8.5E-03	3.1	0.11	50.8	1.7	unst.		unst.		2.75	0.42	1.36	0.21
21-Sep-05	2.34	0.06	8.4E-02	2.2E-03	3.1	0.01	50.3	0.2	11.4	0.18	182.16	2.93	BDL		BDL	
Station 1																
17-Sep-03	0.80	0.02	2.8E-02	7.5E-04	0.9	0.00	14.4	0.0	6.6	0.24	106.32	3.89	3.34	0.70	1.65	0.35
22-Oct-03	0.81	0.06	2.9E-02	2.1E-03	0.8	0.02	12.5	0.3	9.1	0.43	146.41	6.83	1.13	0.02	0.56	0.01
20-Nov-03	1.17	0.12	4.2E-02	4.4E-03	0.9	0.04	15.1	0.7	17.3	0.52	276.87	8.31	3.36	0.66	1.67	0.33
16-Dec-03	1.39	0.40	5.0E-02	1.4E-02	0.6	0.08	10.0	1.3	15.0	1.72	241.07	27.60	1.87	1.63	0.93	0.81
10-Feb-04	1.44	0.11	5.1E-02	3.8E-03	1.0	0.52	16.2	8.4	15.4	7.59	247.67	121.63	1.46	0.83	0.72	0.41
6-May-04	0.87	0.06	3.1E-02	2.0E-03		(TCD not working: no CO2, CH4 or H2 analyses)										
23-Jun-04	0.63	0.02	2.3E-02	7.4E-04	1.8	2.21	29.2	35.7	unst.		unst.		BDL		BDL	
27-Jul-04	0.15	0.01	5.4E-03	3.4E-04	3.6	0.06	57.4	1.0	BDL		BDL		0.52	0.24	0.26	0.12
15-Sep-04	0.08	0.03	2.7E-03	9.2E-04	2.8	0.19	44.8	3.0	9.6	0.24	153.95	3.87	0.54	0.20	0.27	0.10
1-Dec-04	1.26	0.04	4.5E-02	1.5E-03	1.4	0.14	21.9	2.2	2.2	0.05	35.38	0.81	1.40	0.04	0.69	0.02
17-Feb-05	1.05	0.12	3.8E-02	4.3E-03	0.9	0.03	13.9	0.4	2.6	0.09	42.08	1.44	0.53	0.14	0.27	0.07
15-Mar-05	1.04	0.12	3.7E-02	4.2E-03	0.8	0.03	13.4	0.5	1.4	0.08	21.77	1.26	0.50	0.08	0.25	0.04
14-Jun-05	1.99	0.06	7.1E-02	2.2E-03	2.6	0.10	42.2	1.6	2.0	0.02	32.77	0.35	0.38	0.22	0.19	0.11
27-Jul-05	1.72	0.60	6.1E-02	2.1E-02	1.5	0.01	23.4	0.2	unst.		unst.		2.79	1.55	1.38	0.77
21-Sep-05	1.70	0.01	6.1E-02	2.5E-04	1.8	0.02	29.2	0.3	1.3	0.03	21.09	0.42	BDL		BDL	

Table 4.5. Pearson's R correlation coefficients. Stream parameter pairs were tested for Pearson's R using MS Excel for all dates on a station-by-station basis and results highlighted at two confidence intervals: 0.05 and 0.01. All positive correlations (0.05 or better) are shaded green and enclosed by line borders; negative correlations are blue. Correlations with coefficients in the 0.01 confidence interval are in bold font. Degrees of freedom (df = n-2, where n is the smaller number in a given pair) are to the right of each coefficient. Protected Stream values are on the left of the table, with flow direction from Station 8 (upstream), to 6 and 4 (downstream) from left to right. The upstream station in the Runoff Stream (Station 7) is on the far right, with flow direction from right to left. Note that Station 2 appears twice to represent its position between Station 1, at the mouth of the flume, and Stations 3 in the Runoff Stream and 4 in the Protected Stream.

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
Q8/Q4					**0.920**	11														
Q8/Q3													0.588	11						
Q8/Q1									**0.919**	25										
Q8/T	-0.19	19	-0.278	19	-0.246	23	-0.245	19	-0.256	19	-0.245	19	-0.034	17	0.064	4	-0.161	18	-0.112	18
Q8/[DO]	0.06	19	0.267	19	0.482	19	0.555	18	0.324	19	0.555	18	0.207	17	0.323	4	0.259	18	0.008	18
Q8/DO%	-0.10	19	0.251	19	0.541	19	**0.672**	18	0.387	19	**0.672**	18	0.316	17	0.440	4	0.080	18	-0.044	18
Q8/pH	0.113	19	-0.176	19	0.182	19	0.240	18	0.006	19	0.240	18	0.175	16	0.113	4	0.083	18	-0.166	18
Q8/SpC	0.354	19	**0.581**	19	0.032	19	0.127	18	**-0.596**	19	0.127	18	-0.316	17	-0.785	4	-0.455	18	-0.022	18
Q8/[NO_3^- N]	0.522	22	**0.774**	23	**0.858**	22	**0.822**	23	**0.777**	23	**0.822**	23	0.234	19	-0.388	5	**0.560**	17	0.415	17
Q8/[NO_2^- N]	0.073	22	0.235	20	0.311	22	0.332	21	**0.738**	19	0.332	21	0.389	19	0.304	4	**-0.671**	19	-0.423	19
Q8/[N_2O]	0.538	16	0.340	16	0.120	17	0.593	14	**0.797**	13	0.593	14	0.604	13	-0.379	4	-0.439	10	0.332	4
Q8/[NH_4^+ N]	0.439	14	0.352	14	-0.053	16	-0.102	14	-0.411	14	-0.102	14	-0.364	12	0.593	4	-0.256	13	-0.392	13
Q8/[SO_4^{2-}]	0.400	13	**0.747**	13	**0.771**	12	**0.713**	12	**0.872**	11	**0.713**	12	0.660	9	-0.195	3	0.582	10	0.272	9
Q8/[Fe^{2+}]	-0.177	14	0.105	14	**-0.630**	17	-0.401	14	**-0.902**	14	-0.401	14	0.021	13	0.623	4	-0.103	13	-0.496	13
Q8/[Fe^{3+}]	0.222	14	**0.662**	14	0.279	17	0.076	14	-0.420	14	0.076	14	0.350	13	0.647	4	0.321	13	0.250	13
Q8/[$H_2CO_3^*$]	0.139	13	0.033	13	**-0.615**	16	-0.459	13	-0.619	12	-0.459	13	-0.516	12	0.164	4	-0.059	10	-0.270	4
Q8/[CH_4^+]	0.009	8	0.062	13	-0.414	16	-0.080	12	-0.225	12	-0.080	12	0.004	12	0.413	4	0.053	10	-0.608	4
Q8/[DOC]	0.095	10	-0.162	13	-0.589	14	**-0.642**	13	**-0.723**	11	**-0.642**	13	-0.060	12	0.849	3	0.171	10	-0.439	11
Q8/[H_2]	0.293	13	0.194	13	-0.070	16	0.302	13	0.402	12	0.302	13	0.106	12	0.224	4	0.043	10	0.368	4

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
Q4/Q3													0.407	11						
Q4/Q1									**0.844**	11										
Q4/T	0.044	11	-0.125	11	-0.053	11	0.042	11	0.012	11	0.042	11	0.091	11	0.632	4	-0.027	11	0.048	11
Q4/[DO]	-0.359	11	-0.045	11	0.174	11	0.118	11	-0.040	11	0.118	11	0.127	11	-0.188	4	0.438	11	0.023	11
Q4/DO%	-0.647	11	-0.088	11	0.094	11	0.197	11	-0.060	11	0.197	11	0.217	11	-0.034	4	-0.090	11	0.016	11
Q4/pH	0.135	11	-0.394	11	0.133	11	0.032	11	-0.087	11	0.032	11	0.450	11	-0.421	4	-0.028	11	0.007	11
Q4/SpC	0.232	11	0.462	11	0.408	11	0.596	11	-0.287	11	0.596	11	-0.171	11	-0.478	4	-0.468	11	-0.466	11
Q4/[NO$_3^-$ N]	0.274	11	0.487	11	0.530	11	0.502	11	0.474	11	0.502	11	0.270	11	-0.558	5	0.378	11	0.311	11
Q4/[NO$_2^-$ N]]	0.147	11	0.456	11	0.490	11	0.446	11	**0.899**	11	0.446	11	0.408	11	0.648	4	-0.496	11	-0.608	11
Q4[N$_2$O]	**0.856**	11	**0.878**	11	0.365	11	0.608	11	**0.807**	11	0.608	11	0.591	11	0.092	4	-0.307	10	0.177	4
Q4/[NH$_4^+$ N]	0.336	11	0.425	11	0.050	11	0.041	11	-0.395	11	0.041	11	-0.300	11	0.616	4	-0.339	11	-0.238	11
Q4/[SO$_4^{2-}$]	0.225	11	**0.740**	11	**0.760**	11	0.638	11	**0.712**	11	0.638	11	0.597	9	-0.098	3	0.413	10	0.358	9
Q4/[Fe^{2+}]	0.020	11	-0.187	11	-0.386	11	0.625	11	**-0.727**	11	0.625	11	0.111	11	0.614	4	-0.476	11	-0.595	11
Q4/[Fe^{3+}]	0.541	11	0.637	11	0.625	11	0.571	11	0.236	11	0.571	11	0.544	11	0.582	4	0.608	11	0.615	11
Q4/[H$_2$CO$_3^*$]	0.683	11	0.437	11	0.254	11	-0.003	11	0.129	11	-0.003	11	-0.405	11	0.454	4	0.129	10	-0.159	4
Q4/[CH$_4^+$]	-0.110	8	0.136	11	-0.064	11	0.238	11	-0.345	11	0.238	11	0.123	11	0.453	4	-0.547	10	-0.463	4
Q4/[DOC]	0.024	10	0.271	11	-0.170	11	-0.250	11	-0.357	11	-0.250	11	0.206	11	0.410	3	0.542	10	-0.112	12
Q4/[H$_2$]	0.356	11	0.608	11	0.014	11	0.414	11	0.547	11	0.414	11	0.194	11	0.565	4	-0.343	9	0.781	4
Q3/Q1									**0.833**	11										
Q3/T	-0.656	11	**-0.887**	11	**-0.856**	11	**-0.787**	11	**-0.795**	11	**-0.787**	11	**-0.744**	11	-0.689	4	**-0.791**	11	**-0.791**	11
Q3/[DO]	0.363	11	0.611	11	**0.705**	11	**0.775**	11	0.654	11	**0.775**	11	**0.715**	11	0.740	4	**0.690**	11	0.145	11
Q3/DO%	-0.035	11	0.494	11	0.635	11	**0.771**	11	0.536	11	**0.771**	11	0.672	11	0.719	4	0.623	11	-0.046	11
Q3/pH	0.656	11	0.380	11	0.410	11	**0.700**	11	0.454	11	**0.700**	11	0.492	11	0.862	4	0.263	11	0.090	11
Q3/SpC	**0.826**	11	**0.921**	11	**0.960**	11	**0.849**	11	0.079	11	**0.849**	11	-0.312	11	-0.422	4	-0.132	11	0.195	11
Q3/[NO$_3^-$ N]	**0.798**	11	**0.850**	11	**0.824**	11	**0.762**	11	**0.713**	11	**0.762**	11	**0.584**	11	0.459	5	0.168	11	0.236	11
Q3/[NO$_2^-$ N]	0.222	11	-0.412	11	0.191	11	0.005	11	0.261	11	0.005	11	0.057	11	-0.554	4	**-0.819**	11	-0.682	11

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
Q3/[N_2O]	0.477	11	0.220	11	-0.375	11	-0.301	11	0.204	11	-0.301	11	0.096	11	-0.686	4	0.164	10	0.674	4
Q3/[NH_4^+ N]	0.372	11	0.013	11	0.168	11	0.071	11	-0.167	11	0.071	11	-0.170	11	0.122	4	-0.581	11	-0.323	11
Q3/[SO_4^{2-}]	0.493	11	**0.722**	11	0.666	11	**0.718**	11	**0.911**	11	**0.718**	11	**0.807**	9	0.905	3	**0.750**	10	-0.279	9
Q3/[Fe^{2+}]	-0.368	11	-0.098	11	-0.127	11	-0.252	11	-0.471	11	-0.252	11	-0.555	11	0.164	4	-0.608	11	-0.515	11
Q3/[Fe^{3+}]	-0.093	11	0.298	11	0.068	11	-0.082	11	-0.024	11	-0.082	11	-0.172	11	0.006	4	0.014	11	-0.112	11
Q3/[$H_2CO_3^*$]	-0.388	11	-0.550	11	-0.347	11	**-0.830**	11	-0.370	11	**-0.830**	11	-0.667	11	-0.385	4	-0.209	10	0.301	4
Q3/[CH_4^+]	0.323	8	-0.316	11	0.195	11	-0.657	11	0.299	11	-0.657	11	-0.623	11	0.157	4	0.252	10	0.321	4
Q3/[DOC]	0.415	10	-0.284	11	-0.430	11	-0.501	11	-0.489	11	-0.501	11	-0.581	11	0.082	3	-0.428	10	-0.210	11
Q3/[H_2]	0.021	11	-0.039	11	-0.260	11	0.154	11	0.087	10	0.154	11	0.361	11	-0.380	4	0.276	10	-0.393	4
Q1/T	-0.357	19	-0.474	19	-0.485	23	-0.431	19	-0.440	19	-0.431	19	-0.275	17	-0.179	4	-0.370	18	-0.339	18
Q1/[DO]	0.173	19	0.379	19	**0.567**	19	**0.629**	18	0.406	19	**0.629**	18	0.394	17	0.514	4	0.444	18	0.066	18
Q1/DO%	-0.080	19	0.333	19	**0.638**	19	**0.690**	18	0.352	19	**0.690**	18	0.454	17	0.596	4	0.279	18	-0.022	18
Q1/pH	0.299	19	-0.054	19	0.179	19	0.292	18	0.018	19	0.292	18	0.173	16	0.466	4	0.027	18	-0.033	18
Q1/SpC	**0.555**	19	**0.765**	19	0.361	19	0.374	18	0.018	19	0.374	18	-0.132	17	-0.676	4	-0.266	18	-0.010	18
Q1/[NO_3^- N]	**0.528**	22	**0.731**	23	**0.841**	22	0.799	23	0.718	23	0.799	23	0.440	19	0.040	5	0.405	17	0.210	17
Q1/[NO_2^- N]	0.133	22	0.172	20	0.209	22	0.201	21	**0.678**	19	0.201	21	0.316	19	-0.053	4	**-0.803**	19	**-0.559**	19
Q1/[N_2O]	0.517	16	0.347	16	-0.010	17	0.510	14	**0.776**	13	0.510	14	0.446	13	-0.530	4	-0.300	10	0.828	4
Q1/[NH_4^+ N]	0.453	14	0.321	14	0.072	16	0.007	14	-0.280	14	0.007	14	-0.278	12	0.508	4	-0.267	13	-0.377	13
Q1/[SO_4^{2-}]	0.454	13	**0.837**	13	**0.862**	12	**0.878**	12	**0.942**	11	**0.878**	12	**0.844**	9	0.928	3	**0.768**	10	0.142	9
Q1/[Fe^{2+}]	-0.173	14	0.172	14	-0.563	17	-0.459	14	**-0.853**	14	-0.459	14	-0.250	13	0.543	4	-0.126	13	-0.456	13
Q1/[Fe^{3+}]	0.121	14	0.581	14	0.247	17	0.009	14	-0.404	14	0.009	14	0.198	13	0.386	4	0.325	13	0.147	13
Q1/[$H_2CO_3^*$]	0.030	13	-0.039	13	**-0.595**	16	-0.509	13	-0.602	12	-0.509	13	-0.552	12	-0.034	4	-0.037	10	0.188	4
Q1/[CH_4^+]	0.193	8	-0.005	13	-0.210	16	-0.255	12	-0.137	12	-0.255	12	-0.373	12	0.414	4	0.174	10	-0.023	4
Q1/[DOC]	0.122	10	-0.177	13	-0.588	14	**-0.652**	13	**-0.705**	11	**-0.652**	13	-0.209	12	0.678	3	0.036	10	-0.466	11
Q1/[H_2]	0.222	13	0.159	13	-0.125	16	0.310	13	0.344	12	0.310	13	0.363	12	0.043	4	0.102	10	0.193	4

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
T/[DO]	**-0.874**	19	**-0.758**	19	**-0.804**	19	**-0.888**	18	**-0.892**	19	**-0.888**	18	**-0.900**	17	-0.835	4	**-0.591**	18	-0.259	18
T/DO%	-0.464	19	**-0.642**	19	**-0.745**	19	**-0.779**	18	**-0.646**	19	**-0.779**	18	**-0.824**	17	-0.742	4	-0.531	18	-0.065	18
T/pH	**-0.671**	19	-0.172	19	-0.127	19	-0.118	18	0.177	19	-0.118	18	0.107	16	-0.754	4	0.065	18	-0.002	18
T/SpC	-0.430	19	**-0.782**	19	**-0.649**	19	-0.461	18	-0.008	19	-0.461	18	0.360	17	0.334	4	0.046	18	-0.033	18
T/[NO_3^- N]	0.003	19	-0.287	19	-0.467	22	-0.471	19	-0.481	19	-0.471	19	**-0.641**	17	-0.786	4	0.001	17	0.256	17
T/[NO_2^- N]	-0.161	19	0.478	19	0.214	22	0.310	19	0.059	19	0.310	19	-0.019	17	0.662	4	0.358	18	0.507	18
T/[N_2O]	-0.277	16	-0.052	16	0.374	17	0.153	14	-0.230	13	0.153	14	-0.050	13	0.758	4	-0.311	10	-0.594	4
T/[NH_4^+ N]	-0.021	14	0.300	14	0.101	16	0.147	14	0.153	14	0.147	14	0.444	12	0.528	4	**0.645**	13	0.492	13
T/[SO_4^{2-}]	-0.550	13	**-0.691**	13	-0.562	12	**-0.667**	12	**-0.912**	11	**-0.667**	12	**-0.746**	9	**-0.991**	3	**-0.740**	10	0.406	9
T/[Fe^{2+}]	0.223	14	-0.302	14	0.305	17	0.536	14	0.451	14	0.536	14	**0.793**	13	0.479	4	0.323	13	0.250	13
T/[Fe^{3+}]	0.333	14	-0.051	14	0.358	17	0.607	14	0.505	14	0.607	14	**0.702**	13	0.137	4	0.327	13	0.560	13
T/[$H_2CO_3^*$]	0.294	13	0.563	13	**0.594**	16	**0.811**	13	**0.705**	12	**0.811**	13	**0.789**	12	0.738	4	0.439	10	-0.367	4
T/[CH_4^+]	-0.222	8	0.413	13	0.079	16	0.273	12	-0.384	12	0.273	12	0.583	12	0.524	4	-0.542	10	-0.345	4
T/[DOC]	0.003	10	0.365	13	0.602	14	**0.696**	13	0.668	11	**0.696**	13	**0.904**	12	0.454	3	**0.781**	10	0.392	11
T/[H_2]	-0.089	13	0.140	13	0.294	16	-0.346	13	-0.169	12	-0.346	13	-0.449	12	0.450	4	-0.364	10	0.543	4
[DO]/DO%	**0.834**	19	**0.985**	19	**0.985**	19	**0.974**	18	**0.908**	19	**0.974**	18	**0.978**	17	**0.988**	4	**0.674**	18	**0.979**	18
[DO]/pH	0.538	19	0.522	19	0.364	19	0.231	18	-0.245	19	0.231	18	0.057	16	0.795	4	0.268	18	0.389	18
[DO]/SpC	0.311	19	0.537	19	0.352	19	0.328	18	-0.105	19	0.328	18	-0.365	17	-0.599	4	-0.079	18	-0.433	18
[DO]/[NO_3^- N]	-0.001	19	0.211	19	**0.607**	19	**0.771**	18	**0.605**	19	**0.771**	18	**0.738**	17	0.642	4	-0.294	17	-0.458	17
[DO]/[NO_2^- N]	0.080	19	-0.203	19	-0.125	19	-0.147	18	-0.103	19	-0.147	18	0.208	17	-0.583	4	-0.460	18	-0.412	18
[DO]/[N_2O]	-0.067	16	0.052	16	-0.285	17	0.047	14	0.134	13	0.047	14	0.181	13	**-0.979**	4	-0.374	10	-0.138	4
[DO]/[NH_4^+ N]	-0.156	14	-0.323	14	-0.284	16	-0.279	14	-0.247	14	-0.279	14	-0.606	12	-0.443	4	-0.341	13	-0.169	13
[DO]/[SO_4^{2-}]	0.389	13	0.519	13	0.578	12	**0.699**	12	**0.823**	11	**0.699**	12	**0.878**	9	0.903	3	**0.860**	10	0.286	9
[DO]/[Fe^{2+}]	-0.127	14	0.152	14	-0.486	17	-0.582	14	-0.418	14	-0.582	14	**-0.745**	13	-0.394	4	-0.072	13	-0.095	13
[DO]/[Fe^{3+}]	-0.454	14	0.115	14	-0.233	17	-0.484	14	-0.508	14	-0.484	14	-0.515	13	-0.052	4	0.088	13	0.066	13

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
[DO]/[$H_2CO_3^*$]	-0.588	13	-0.503	13	**-0.760**	16	**-0.861**	13	**-0.762**	12	**-0.861**	13	**-0.818**	12	-0.834	4	-0.424	10	-0.742	4
[DO]/[CH_4^+]	0.230	8	-0.404	13	-0.264	16	-0.215	12	0.325	12	-0.215	12	-0.585	12	-0.483	4	0.099	10	-0.659	4
[DO]/[DOC]	-0.007	10	-0.294	13	**-0.778**	14	**-0.806**	13	-0.655	11	**-0.806**	13	**-0.782**	12	-0.699	3	-0.068	10	-0.007	11
[DO]/[H_2]	-0.074	13	-0.200	13	-0.257	16	0.432	13	0.177	12	0.432	13	0.343	12	-0.007	4	0.232	10	-0.420	4
DO%/pH	0.231	19	**0.562**	19	0.225	19	0.274	18	-0.177	19	0.274	18	0.152	16	0.744	4	0.366	18	0.415	18
DO%/SpC	0.074	19	0.443	19	0.264	19	0.214	18	-0.259	19	0.214	18	-0.455	17	-0.672	4	-0.229	18	-0.467	18
DO%/[NO_3^- N]	0.019	19	0.177	19	**0.700**	19	**0.854**	18	**0.676**	19	**0.854**	18	**0.700**	17	0.544	4	-0.298	17	-0.458	17
DO%/[NO_2^- N]	-0.029	19	-0.143	19	-0.108	19	-0.091	18	-0.096	19	-0.091	18	0.276	17	-0.499	4	-0.369	18	-0.333	18
DO%/[N_2O]	-0.451	16	0.045	16	-0.323	17	0.118	14	0.020	13	0.118	14	0.184	13	**-0.984**	4	-0.200	10	-0.243	4
DO%/[NH_4^+ N]	-0.289	14	-0.284	14	-0.189	16	-0.280	14	-0.370	14	-0.280	14	**-0.683**	12	-0.368	4	-0.123	13	-0.065	13
DO%/[SO_4^{2-}]	0.084	13	0.436	13	0.632	12	**0.708**	12	**0.701**	11	**0.708**	12	**0.870**	9	0.834	3	0.378	10	0.377	9
DO%/[Fe^{2+}]	-0.006	14	0.098	14	-0.521	17	-0.599	14	-0.407	14	-0.599	14	**-0.755**	13	-0.319	4	0.131	13	-0.027	13
DO%/[Fe^{3+}]	-0.499	14	0.106	14	-0.194	17	-0.435	14	-0.455	14	-0.435	14	-0.475	13	0.020	4	-0.371	13	0.184	13
DO%/[$H_2CO_3^*$]	**-0.803**	13	-0.466	13	**-0.759**	16	**-0.881**	13	**-0.784**	12	**-0.881**	13	**-0.864**	12	-0.789	4	-0.219	10	-0.819	4
DO%/[CH_4^+]	0.188	8	-0.392	13	-0.122	16	-0.206	12	0.191	12	-0.206	12	-0.581	12	-0.431	4	0.087	10	-0.730	4
DO%/[DOC]	-0.007	10	-0.238	13	**-0.823**	14	**-0.805**	13	-0.638	11	**-0.805**	13	**-0.750**	12	-0.743	3	-0.482	10	0.064	11
DO%/[H_2]	-0.265	13	-0.201	13	-0.014	16	0.428	13	0.188	12	0.428	13	0.344	12	0.102	4	0.105	10	-0.325	4
pH/SpC	0.372	19	0.136	19	0.229	19	0.028	18	-0.105	19	0.028	18	0.089	16	-0.115	4	-0.077	18	-0.454	18
pH/[NO_3^- N]	-0.086	19	-0.214	19	0.180	19	0.262	18	-0.157	19	0.262	18	-0.012	16	0.641	4	-0.143	17	**-0.791**	17
pH/[NO_2^- N]	0.273	19	0.217	19	-0.191	19	-0.137	18	0.239	19	-0.137	18	-0.048	16	-0.877	4	-0.118	18	-0.228	18
pH/[N_2O]	0.172	16	-0.031	16	-0.241	17	-0.022	14	-0.005	13	-0.022	14	-0.096	13	-0.723	4	-0.629	10	-0.509	4
pH/[NH_4^+ N]	0.033	14	-0.144	14	-0.266	16	0.156	14	-0.383	14	0.156	14	-0.336	12	-0.266	4	0.121	13	0.635	13
pH/[SO_4^{2-}]	0.292	13	0.065	13	-0.015	12	0.433	12	0.535	11	0.433	12	0.568	9	0.879	3	0.478	10	0.109	9
pH/[Fe^{2+}]	-0.532	14	-0.194	14	-0.053	17	-0.160	14	-0.178	14	-0.160	14	-0.031	13	-0.236	4	0.370	13	0.332	13

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
pH/[Fe^{3+}]	-0.323	14	0.053	14	0.034	17	-0.185	14	0.052	14	-0.185	14	0.074	13	-0.462	4	-0.208	13	0.200	13
pH/[$H_2CO_3^*$]	-0.064	13	-0.060	13	-0.090	16	-0.156	13	0.204	12	-0.156	13	-0.307	12	-0.695	4	-0.295	10	-0.796	4
pH/[CH_4^+]	-0.026	8	-0.264	13	-0.302	16	-0.605	12	-0.609	12	-0.605	12	-0.053	12	-0.115	4	-0.454	10	-0.559	4
pH/[DOC]	-0.019	10	-0.171	13	-0.334	14	-0.302	13	-0.175	11	-0.302	13	-0.021	12	-0.301	3	0.027	10	0.125	11
pH/[H_2]	0.154	13	-0.220	13	-0.408	16	-0.325	13	-0.383	12	-0.325	13	-0.054	12	-0.272	4	0.155	10	-0.602	4
SpC/[NO_3^- N]	0.424	19	0.451	19	0.106	19	0.112	18	-0.594	19	0.112	18	-0.024	17	0.059	4	-0.152	17	**0.640**	17
SpC/[NO_2^- N]	0.307	19	-0.222	19	-0.356	19	-0.147	18	-0.523	19	-0.147	18	-0.232	17	-0.239	4	0.121	18	0.232	18
SpC/[N_2O]	0.302	16	0.176	16	-0.376	17	-0.054	14	-0.533	13	-0.054	14	0.065	13	0.637	4	0.441	10	0.193	4
SpC/[NH_4^+ N]	0.227	14	-0.021	14	0.198	16	0.085	14	**0.730**	14	0.085	14	**0.700**	12	-0.119	4	0.231	13	-0.283	13
SpC/[SO_4^{2-}]	0.385	13	**0.837**	13	0.358	12	0.531	12	-0.477	11	0.531	12	-0.624	9	-0.018	3	-0.322	10	-0.608	9
SpC/[Fe^{2+}]	0.083	14	0.353	14	0.252	17	0.020	14	**0.775**	14	0.020	14	0.564	13	-0.172	4	-0.070	13	-0.159	13
SpC/[Fe^{3+}]	0.094	14	0.248	14	-0.025	17	-0.195	14	0.537	14	-0.195	14	0.475	13	-0.728	4	0.292	13	-0.188	13
SpC/[$H_2CO_3^*$]	-0.156	13	-0.272	13	0.056	16	-0.289	13	0.435	12	-0.289	13	**0.818**	12	0.178	4	-0.037	10	0.194	4
SpC/[CH_4^+]	0.456	8	-0.124	13	0.300	16	-0.113	12	0.651	12	-0.113	12	-0.122	12	0.222	4	0.374	10	0.605	4
SpC/[DOC]	0.295	10	-0.222	13	-0.050	14	-0.228	13	0.615	11	-0.228	13	0.514	12	0.149	3	-0.057	10	-0.215	11
SpC/[H_2]	0.146	13	0.089	13	-0.309	16	0.428	13	-0.158	12	0.428	13	-0.344	12	-0.137	4	0.115	10	-0.025	4
[NO_3^- N]/[NO_2^- N]	**0.557**	22	0.035	20	0.112	22	0.199	21	0.411	19	0.199	21	0.166	19	-0.638	4	-0.386	17	0.331	17
[NO_3^- N]/[N_2O]	0.008	16	0.056	16	-0.178	17	0.355	14	0.640	13	0.355	14	0.224	13	-0.644	4	0.041	10	0.336	4
[NO_3^- N]/[NH_4^+ N]	0.564	14	0.049	14	-0.113	16	-0.265	14	-0.382	14	-0.265	14	-0.576	12	-0.818	4	-0.447	13	-0.455	13
[NO_3^- N]/[SO_4^{2-}]	**0.695**	13	**0.791**	13	**0.768**	12	**0.738**	12	**0.907**	11	**0.738**	12	**0.877**	9	0.736	3	0.291	10	-0.288	9
[NO_3^- N]/[Fe^{2+}]	0.080	14	0.140	14	**-0.641**	17	-0.558	14	**-0.865**	14	-0.558	14	-0.290	13	-0.808	4	-0.287	13	-0.405	13
[NO_3^- N]/[Fe^{3+}]	-0.085	14	0.513	14	-0.046	17	-0.272	14	-0.639	14	-0.272	14	-0.168	13	-0.429	4	0.126	13	-0.043	13
[NO_3^- N]/[$H_2CO_3^*$]	-0.351	13	-0.375	13	**-0.797**	16	**-0.724**	13	-0.825	12	**-0.724**	13	-0.438	12	-0.861	4	-0.119	10	0.440	4

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
[NO$_3^-$ N]/[CH$_4^+$]	0.523	8	-0.125	13	-0.407	16	-0.205	12	0.188	12	-0.205	12	-0.491	12	-0.799	4	0.381	10	0.556	4
[NO$_3^-$ N]/[DOC]	0.816	10	-0.390	13	**-0.750**	14	**-0.780**	13	**-0.907**	11	**-0.780**	13	-0.567	12	-0.760	3	-0.245	10	-0.051	11
[NO$_3^-$ N]/[H$_2$]	0.193	13	0.099	13	-0.127	16	0.385	13	0.422	12	0.385	13	-0.022	12	-0.062	4	0.300	10	0.378	4
[NO$_2^-$ N]/[N$_2$O]	-0.127	16	0.257	16	0.389	17	0.565	14	**0.807**	13	0.565	14	0.282	13	0.464	4	0.355	10	0.317	4
[NO$_2^-$ N]/[NH$_4^+$ N]	0.463	14	0.398	14	0.042	16	-0.290	14	-0.323	14	-0.290	14	-0.067	12	0.452	4	0.161	13	0.622	13
[NO$_2^-$ N]/[SO$_4^{2-}$]	0.655	13	0.187	13	0.239	12	-0.151	12	0.648	11	-0.151	12	0.208	9	-0.854	3	-0.653	10	0.111	9
[NO$_2^-$ N]/[Fe^{2+}]	0.101	14	-0.006	14	-0.270	17	-0.260	14	**-0.754**	14	-0.260	14	-0.334	13	0.433	4	-0.143	13	**0.660**	13
[NO$_2^-$ N]/[Fe^{3+}]	-0.184	14	0.497	14	0.362	17	0.494	14	-0.308	14	0.494	14	-0.122	13	0.780	4	-0.079	13	-0.100	13
[NO$_2^-$ N]/[H$_2$CO$_3^*$]	-0.230	13	0.574	13	-0.061	16	0.152	13	-0.177	12	0.152	13	-0.287	12	0.690	4	0.104	10	0.645	4
[NO$_2^-$ N]/[CH$_4^+$]	0.536	8	0.279	13	-0.125	16	-0.035	12	-0.441	12	-0.035	12	-0.306	12	0.249	4	-0.198	10	0.420	4
[NO$_2^-$ N]/[DOC]	**0.935**	10	-0.098	13	-0.056	14	0.050	13	-0.453	11	0.050	13	-0.051	12	0.356	3	0.185	10	0.535	11
[NO$_2^-$ N]/[H$_2$]	0.263	13	0.127	13	-0.217	16	0.047	13	0.222	12	0.047	13	-0.211	12	0.353	4	-0.134	10	0.790	4
[N$_2$O]/[NH$_4^+$ N]	0.276	14	0.302	14	0.174	16	0.082	14	-0.184	13	0.082	14	-0.209	12	0.452	4	0.044	10	0.555	4
[N$_2$O]/[SO$_4^{2-}$]	0.545	13	0.466	13	0.043	12	0.368	12	0.662	11	0.368	12	0.017	9	-0.815	3	-0.098	10	0.009	4
[N$_2$O]/[Fe^{2+}]	0.142	14	-0.111	14	-0.299	17	-0.363	14	**-0.811**	13	-0.363	14	0.249	13	0.409	4	-0.210	10	0.462	4
[N$_2$O]/[Fe^{3+}]	0.456	14	0.422	14	0.525	17	0.463	14	-0.324	14	0.463	14	0.440	13	-0.026	4	-0.175	10	-0.064	4
[N$_2$O]/[H$_2$CO$_3^*$]	**0.686**	13	0.606	13	0.072	16	0.126	13	-0.348	12	0.126	13	-0.252	12	0.831	4	0.145	10	0.680	4
[N$_2$O]/[CH$_4^+$]	-0.026	8	-0.309	13	0.321	16	0.025	12	-0.180	12	0.025	12	-0.027	12	0.520	4	0.616	10	0.509	4
[N$_2$O]/[DOC]	-0.194	10	0.310	13	0.038	14	-0.437	13	-0.603	11	-0.437	13	0.218	12	0.837	3	-0.471	10	0.457	4
[N$_2$O]/[H$_2$]	0.389	13	0.376	13	-0.009	16	0.295	13	0.158	12	0.295	13	0.317	12	-0.159	4	0.474	10	0.317	4

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
[NH$_4^+$ N]/[SO$_4^{2-}$]	**0.891**	13	-0.081	13	-0.260	12	0.045	12	-0.538	11	0.045	12	-0.605	9	-0.562	3	-0.521	10	0.246	9
[NH$_4^+$ N]/[Fe^{2+}]	-0.094	14	-0.226	14	0.002	16	0.205	14	0.539	14	0.205	14	0.319	12	**0.998**	4	**0.700**	13	0.620	13
[NH$_4^+$ N]/[Fe^{3+}]	0.010	14	0.535	14	0.190	16	0.276	14	0.289	14	0.276	14	0.244	12	0.461	4	0.205	13	0.139	13
[NH$_4^+$ N]/[H$_2$CO$_3^*$]	0.042	13	0.545	13	0.258	16	0.361	13	0.308	12	0.361	13	0.608	12	0.830	4	0.597	10	0.707	4
[NH$_4^+$ N]/[CH$_4^+$]	0.382	8	0.333	13	**0.813**	16	-0.024	12	**0.726**	12	-0.024	12	0.315	12	**0.985**	4	0.035	10	0.326	4
[NH$_4^+$ N]/[DOC]	0.374	10	0.166	13	0.436	14	0.216	13	0.552	11	0.216	13	0.403	12	**0.973**	3	0.483	10	0.584	11
[NH$_4^+$ N]/[H$_2$]	0.048	13	-0.039	13	0.036	16	-0.039	13	0.123	12	-0.039	13	-0.228	12	-0.192	4	-0.213	10	0.497	4
[SO$_4^{2-}$]/[Fe^{2+}]	-0.072	13	0.230	13	-0.578	12	-0.301	12	**-0.782**	11	-0.301	12	-0.520	9	-0.483	3	-0.198	10	0.075	9
[SO$_4^{2-}$]/[Fe^{3+}]	-0.020	13	**0.707**	13	0.293	12	-0.183	12	-0.672	11	-0.183	12	-0.136	9	-0.508	3	-0.095	10	0.340	9
[SO$_4^{2-}$]/[H$_2$CO$_3^*$]	-0.272	13	-0.139	13	-0.618	12	**-0.723**	12	**-0.802**	11	**-0.723**	12	**-0.768**	9	-0.667	3	-0.534	10	-0.506	4
[SO$_4^{2-}$]/[CH$_4^+$]	**0.810**	8	-0.090	13	-0.511	12	-0.258	12	-0.043	11	-0.258	12	-0.594	9	-0.954	3	0.623	10	-0.799	4
[SO$_4^{2-}$]/[DOC]	**0.794**	10	-0.280	13	**-0.732**	12	**-0.706**	12	**-0.898**	11	**-0.706**	12	-0.595	9	-0.210	3	-0.281	10	0.382	9
[SO$_4^{2-}$]/[H$_2$]	**0.777**	13	0.335	13	0.244	12	0.250	12	0.642	11	0.250	12	0.302	9	-0.772	3	0.544	10	0.348	4
[Fe^{2+}]/[Fe$_3{}^+$]	0.481	14	-0.128	14	0.088	17	0.359	14	0.610	14	0.359	14	**0.692**	13	0.484	4	-0.036	13	-0.036	13
[Fe^{2+}]/[H$_2$CO$_3^*$]	0.128	13	-0.206	13	**0.826**	16	0.536	13	**0.692**	12	0.536	13	**0.689**	12	0.807	4	0.368	10	0.737	4
[Fe^{2+}]/[CH$_4^+$]	0.163	8	0.063	13	0.513	16	**0.725**	12	0.312	12	**0.725**	12	0.472	12	**0.982**	4	0.139	10	0.876	4
[Fe^{2+}]/[DOC]	0.193	10	0.086	13	0.621	14	0.586	13	**0.841**	11	0.586	13	**0.704**	12	**0.983**	3	0.202	10	0.171	11
[Fe^{2+}]/[H$_2$]	0.006	13	-0.304	13	-0.015	16	-0.071	13	-0.315	12	-0.071	13	-0.440	12	-0.221	4	0.061	10	0.473	4
[Fe^{3+}]/[H$_2$CO$_3^*$]	**0.646**	13	0.264	13	0.317	16	0.472	13	**0.719**	12	0.472	13	0.454	12	0.437	4	0.406	10	-0.349	4
[Fe^{3+}]/[CH$_4^+$]	-0.097	8	0.172	13	0.174	16	0.304	12	-0.114	12	0.304	12	0.330	12	0.203	4	-0.056	10	-0.303	4
[Fe^{3+}]/[DOC]	-0.183	10	-0.240	13	-0.014	14	0.187	13	0.675	11	0.187	13	**0.814**	12	0.414	3	**0.768**	10	-0.067	11
[Fe^{3+}]/[H$_2$]	0.427	13	0.253	13	0.100	16	0.227	13	-0.308	12	0.227	13	-0.181	12	0.072	4	-0.325	10	0.784	4

Table 4.5 (continued)

	Protected Stream						Downstream of Confluence						Runoff Stream							
	St. 8	df	St. 6	df	St. 4	df	St. 2	df	St. 1	df	St. 2	df	St. 3	df	St. 10	df	St. 5	df	St. 7	df
$[H_2CO_3^*]/[CH_4^+]$	-0.342	8	-0.038	13	0.544	16	0.127	12	-0.301	12	0.127	12	0.497	12	0.845	4	-0.235	10	0.880	4
$[H_2CO_3^*]/[DOC]$	-0.389	10	0.315	13	**0.764**	14	0.604	13	**0.739**	11	0.604	13	**0.677**	12	0.894	3	0.387	10	0.298	4
$[H_2CO_3^*]/[H_2]$	0.310	13	0.203	13	0.070	16	-0.466	13	-0.466	12	-0.466	13	-0.465	12	-0.178	4	-0.020	10	0.232	4
$[CH_4^+]/[DOC]$	0.631	8	-0.321	13	0.619	14	0.062	12	-0.133	11	0.062	12	0.325	12	**0.988**	3	-0.404	10	0.181	4
$[CH_4^+]/[H_2]$	0.481	8	0.262	13	0.116	16	0.243	12	0.612	12	0.243	12	-0.367	12	-0.255	4	0.128	10	0.080	4
$[DOC]/[H_2]$	0.483	10	-0.123	13	-0.076	14	-0.435	13	-0.479	11	-0.435	13	-0.180	12	-0.492	3	-0.414	10	-0.606	4

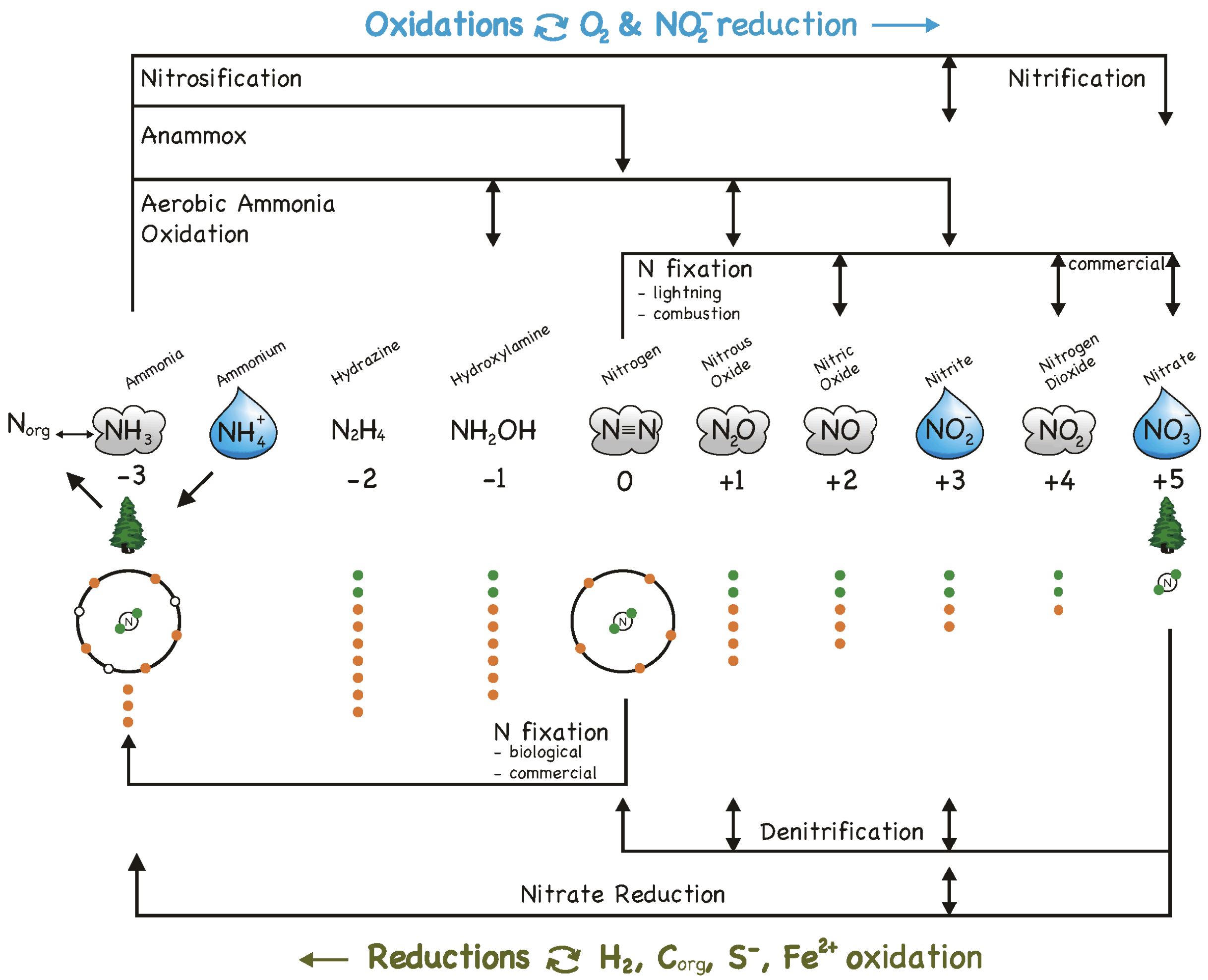

Figure 4.1. Nitrogen cycle. The valence states for N (-3 - +5) are listed under each species, with the most reduced N species on the left and becoming progressively more oxidized toward the right. Cloud symbols are gases at earth surface pressure and water droplets are aqueous ions. Major oxidation pathways are indicated by arrows in the top half of the diagram and major reduction pathways are on the bottom half. Inner shell electrons are indicated by green dots and outer shell by orange dots. End-member species, NH_3/NH_4^+ (-3) and NO_3^-, each with full outer electron shells, are favored by plants.

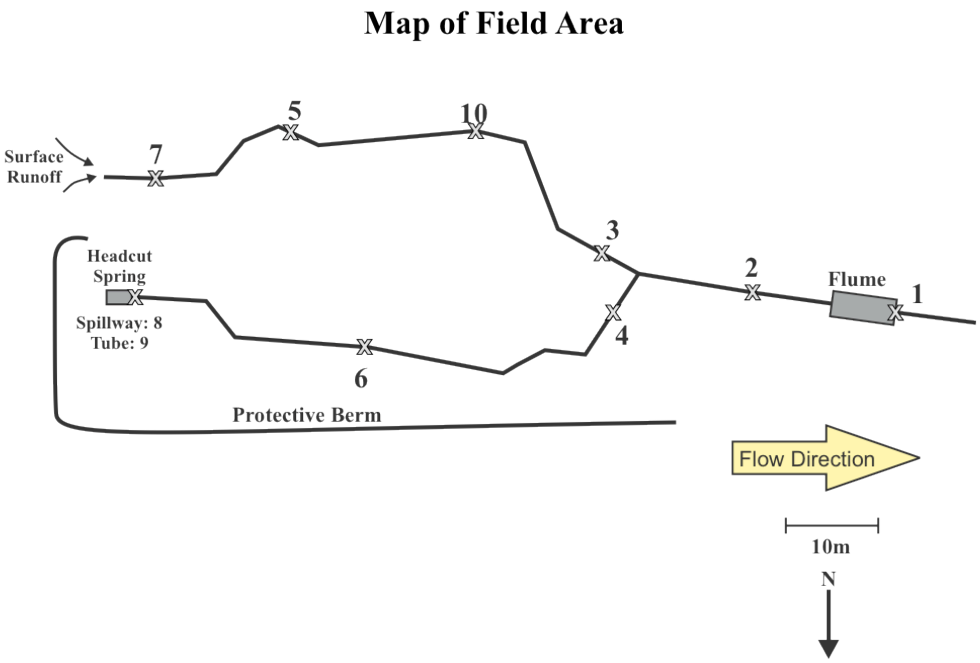

Figure 4.2. Schematic map of field area. A man-made earthen berm prevents runoff from entering the Protected Stream (Stations 9 (tygon tubing inserted in the saprolite aquifer), 8 (spillway of a flume built into the headcut spring) 6 and 4. During rainfall events, runoff enters the Runoff Stream (Stations 7, 5, 10 and 3). Station 2 is downstream of the confluence and Station 1 is the spillway of a large H-flume at the mouth of the wetland. Note that the North arrow is pointing south so that direction of flow is consistent with concentration versus time graphs in the tracer injection tests (Chapter 3).

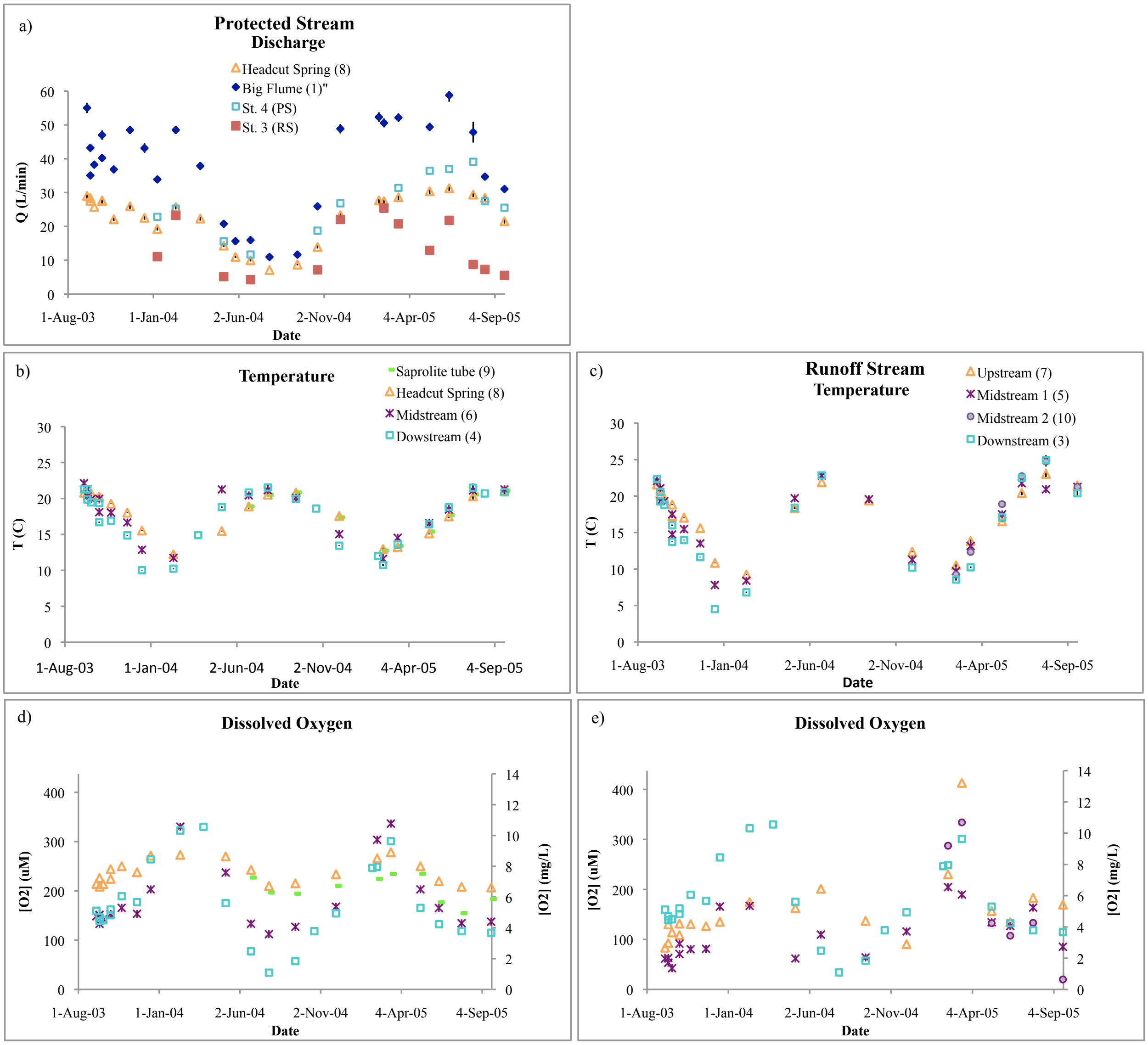

Figure 4.3. Field parameters. a) Discharge was more variable at the mouth of the wetland (Station 1) than at the headcut spring (Stations 8 and 9), reflecting a greater response in Runoff Stream discharge during rainfall events; b) and c) Water temperature were less variable in the Protected Stream due to ground water emerging at the headcut spring (Stations 9 and 8); d) Protected Stream DO was highest in winter and lowest in summer, when decrease along the flow path was greatest and T was highest; e) Runoff Stream DO also varied seasonally. Runoff Stream midstream Stations 5 and 10 often had lowest DO.

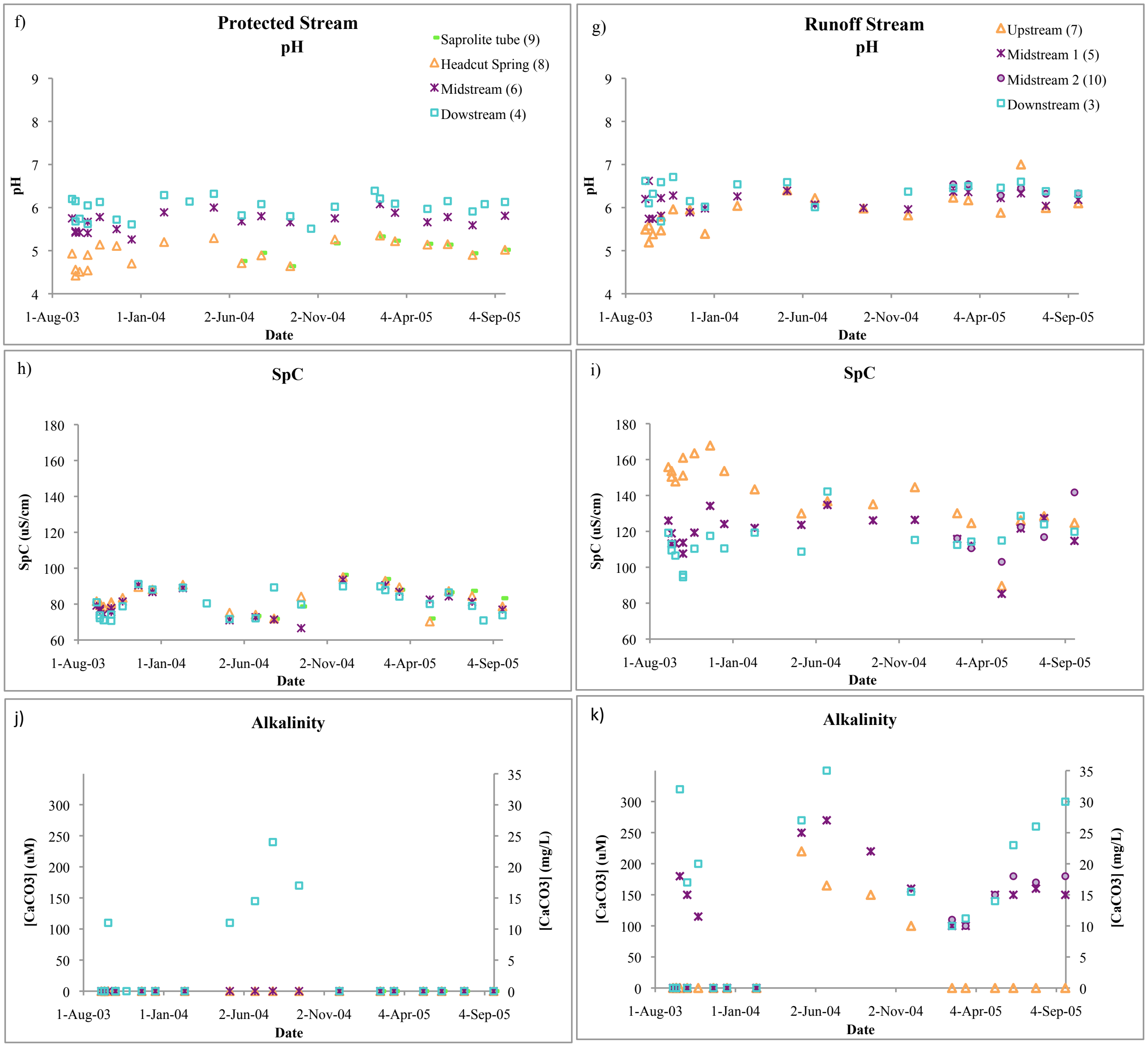

Figure 4.3. Field parameters (continued). f) Protected Stream pH increased by 0.8-0.9 (up to 2) pH units along the flow path; g) Runoff Stream pH also was highest at the downstream location on most sampling dates, but Runoff Stream pH range was usually less than 0.5 pH on a given sampling date; h) Protected Stream SpC was much lower than i) Runoff Stream SpC, which was ~1.5 times higher and exhibited more a wider range and generally decreased along the flow path; j) Protected Stream alkalinity was occasionally measured at the downstream location, whereas alkalinity was frequently between 100-250uM in the Runoff Stream, with highest concentrations at the mid- (Station 5) or downstream (Station 3) locations.

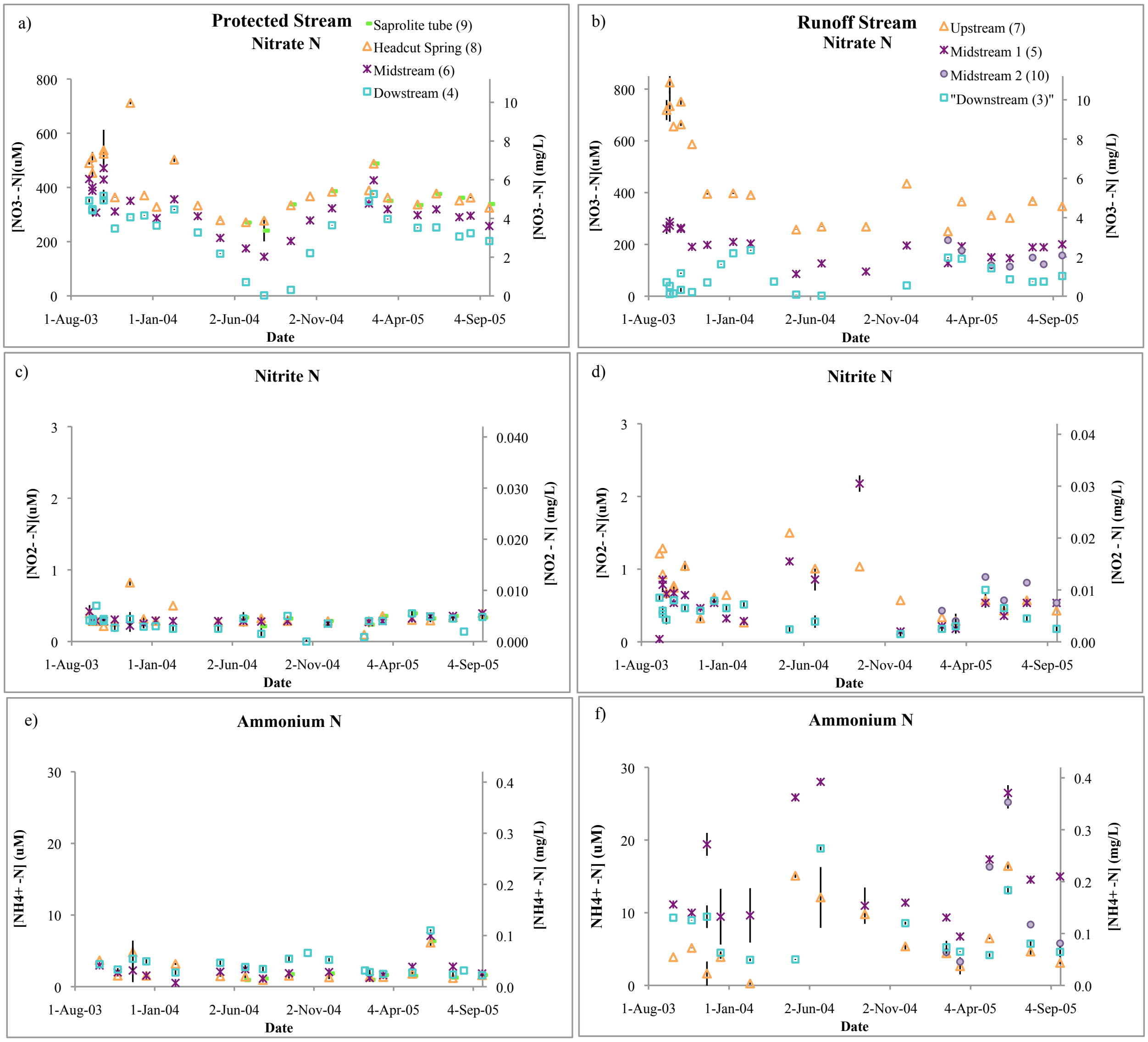

Figure 4.4. Nitrogen ions. a) Protected Stream [NO_3^- -N] was highest in summer, lowest in winter and decreased along the flow path; b) Runoff Stream [NO_3^- -N] exhibited similar seasonal and flow path trends, except that downstream [NO_3^- -N] was lower, reflecting a greater concentration loss along the flow path; c) Protected Stream [NO_2^- -N] exhibited very little variation along the flow path or with time; d) maximum Runoff Stream mid- and upstream [NO_2^- -N] were 3-10 times more higher than Protected Stream concentrations; e) Protected Stream [NH_4^+ -N] was highest in summer in fall, and increased along the flow path; f) Runoff Stream [NH_4^+ -N] exhibited much greater variation, with highest concentrations usually at midstream Station 5.

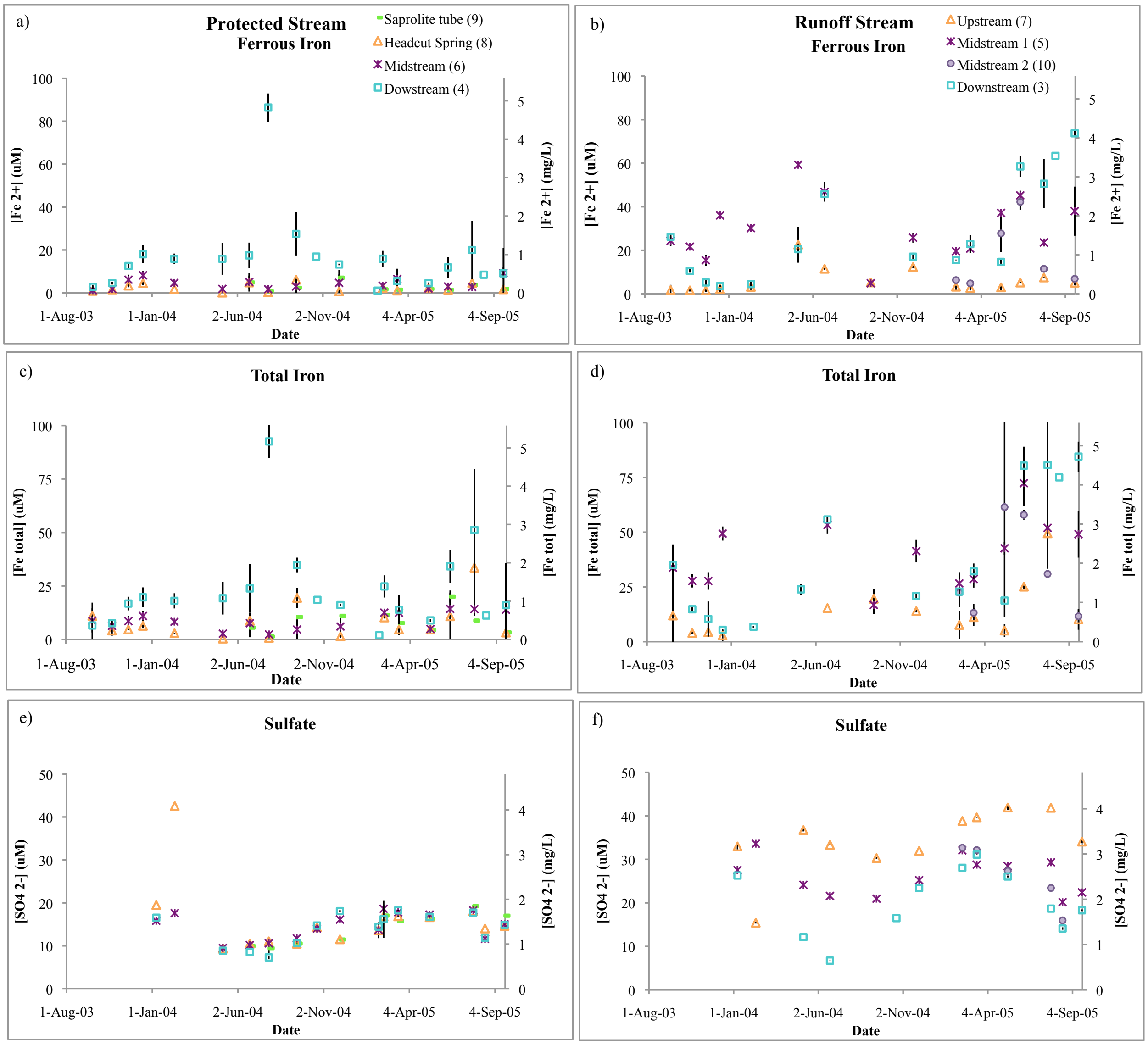

Figure 4.5. Iron and sulfate. Duplicate dissolved iron samples show a high degree of variability. a) Protected Stream [Fe^{2+}] increased along the flow path and b) Runoff Stream [Fe^{2+}] also was highest at mid- and downstream locations; c) and d) [Fe_{total}] is dominated by [Fe^{2+}]; e) Protected Stream [SO_4^{2-}] was lowest in summer and highest in winter. Concentrations varied little along the flow path but decreased along the flow path in summer and increased in winter. Maximum concentrations were ~2mg/L; f) Runoff Stream [SO_4^{2-}] decreased along the flow path by up to 75% in summer and about 28% in winter, with maximum upstream concentrations of ~4mg/L.

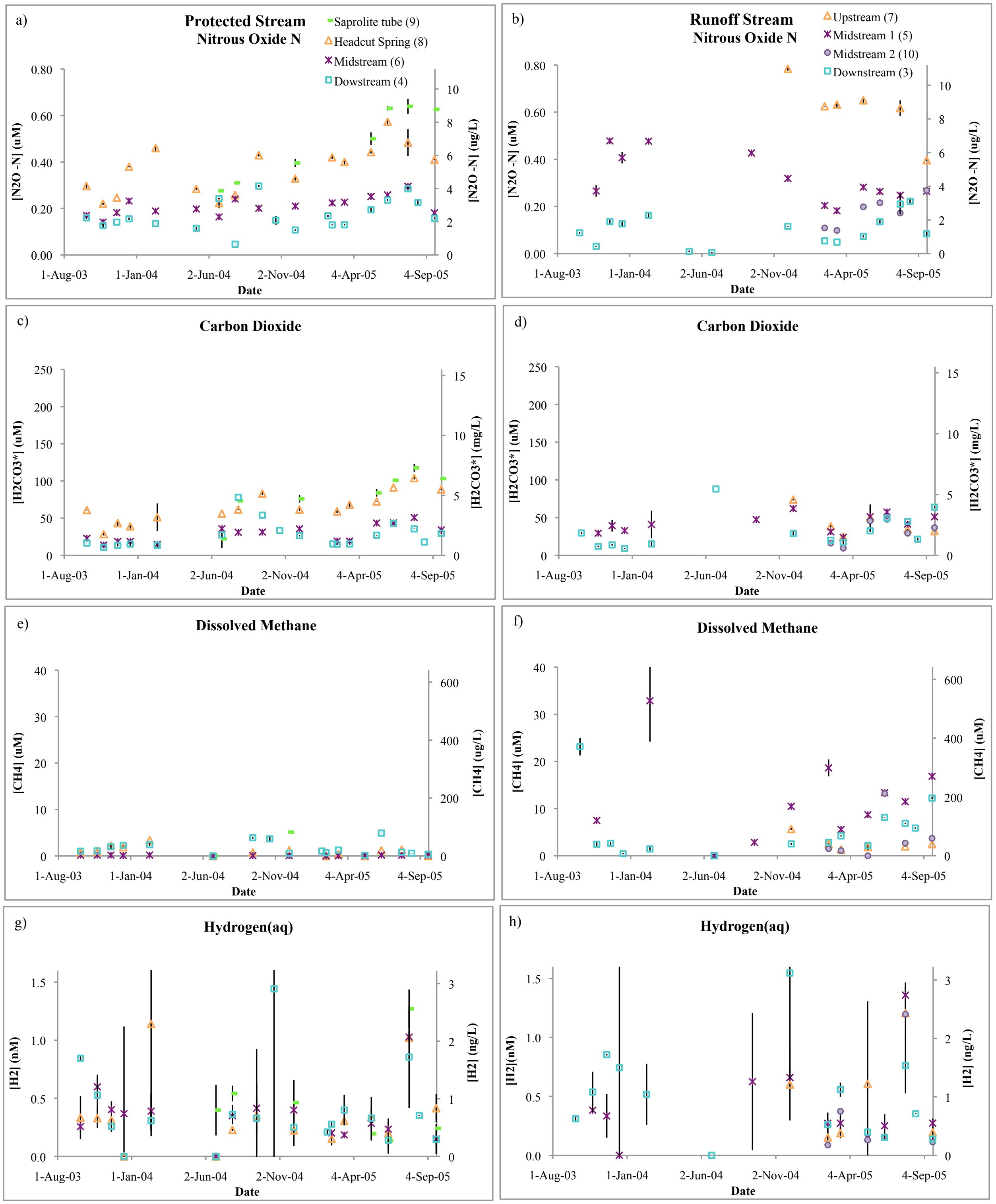

Figure 4.6. Dissolved gases. a) and b) [N_2O] decreased along the flow path in both streams, but was often twice as concentrated at midstream and half as concentrated at downstream locations in the Runoff Stream; c) Protected Stream [$H_2CO_3^*$] decreased by 2-8 fold along the flow path; d) Runoff Stream [$H_2CO_3^*$] remained fairly constant; e) Protected Stream [CH_4] increased downstream; often 4-5 times higher in f) the Runoff Stream; g) and h) [H_2] was <2nM and highly variable in both wetland streams.

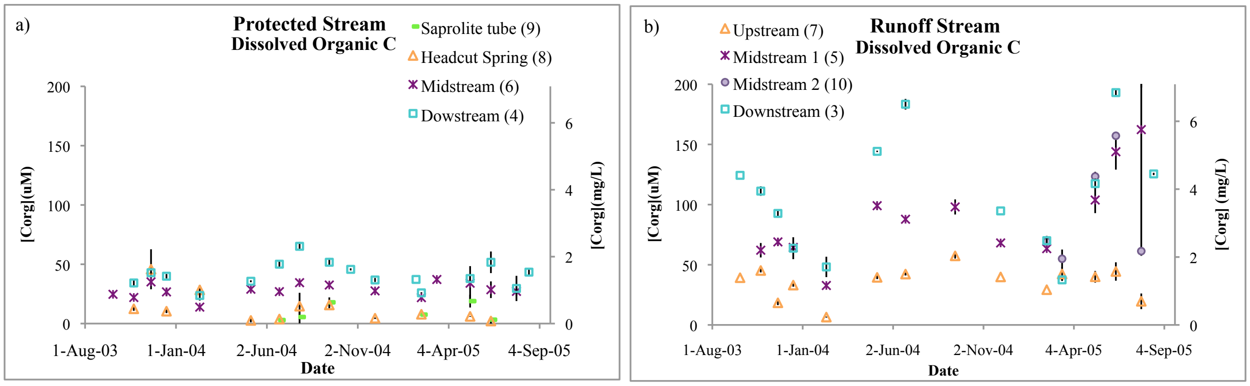

Figure 4.7. Dissolved organic carbon. a) DOC concentrations increased from up stream to downstream in both streams; b) Mid- and downstream concentrations in Runoff Stream were 2-5 times higher than in the Protected Stream.

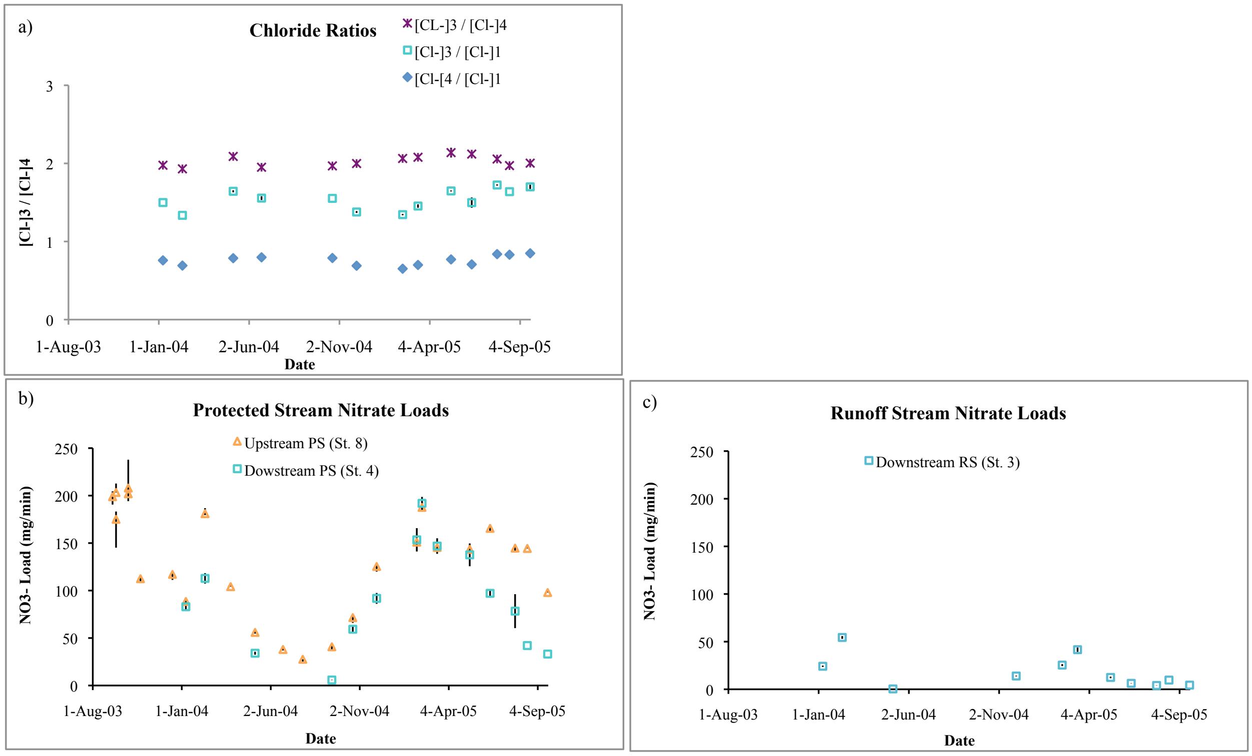

Figure 4.8. Chloride concentration ratios and calculated downstream nitrate loads. Loads were calculated using equations (Eq. 4.1 – 4.4). a) $[Cl^{-}]_3/[Cl^{-}]_4$ was about 2 throughout the 2-year project period; b) Station 4 NO_3^- -N Loads were 33% lower than Station 8, whereas Station 4 Q was14% greater than Station 8 Q; c) Lower nitrate loads: lower discharge during dry weather and concomitant longer residence times in organic rich sediment, contributing to hydrologic storage.

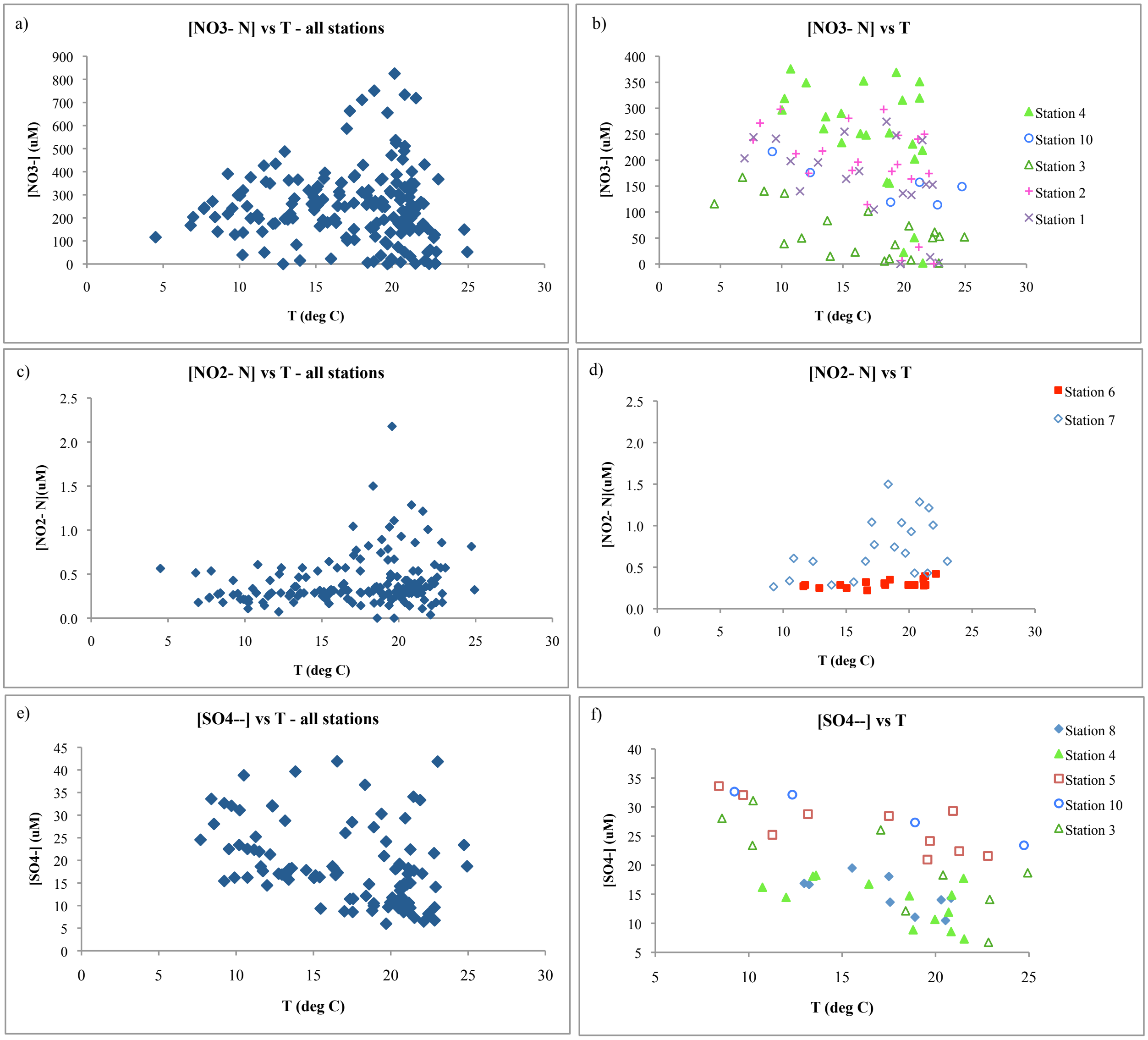

Figure 4.9. Dissolved nitrate, nitrite and sulfate versus temperature. a) [NO_3^- -N] versus T for all stations exhibited a T maximum that increased as a straight line with increasing T except for winter maximum temperatures at Station 8, the headcut spring. [NO_3^- -N] decreased with increasing temperature at several of the wetland stations; b) [NO_3^- -N] exhibited 0.95 or greater confidence intervals for Pearson's R coefficients at Stations 4 in the Protected Stream, 10 and 3 in the Runoff Stream and Stations 2 and 1. [NO_3^- -N] remained fairly constant at T greater than 19°C at Runoff Stream Stations 3 and 10, although there were only 6 data points at Station 10; c) [NO_2^- -N] versus T for all Stations exhibited boomerang- and crescent-shaped zones, with a positive increase in [NO_2^- -N] between ~17-19°C; d) Pearson's R coefficients for [NO_2^- -N] were significant at 0.95 confidence or higher only at Stations 6 (Protected) and 7 (Runoff); Station 7 [NO_2^- -N] increases at about 17°C, and concentrations are scattered at higher T; e) [SO_4^{2-}] versus T for all stations displayed as a random scatter plot; f)) [SO_4^{2-}] decreased with T at Protected Stream Stations 8 and 4 and at Protected Stream Stations 5, 10 and 3.

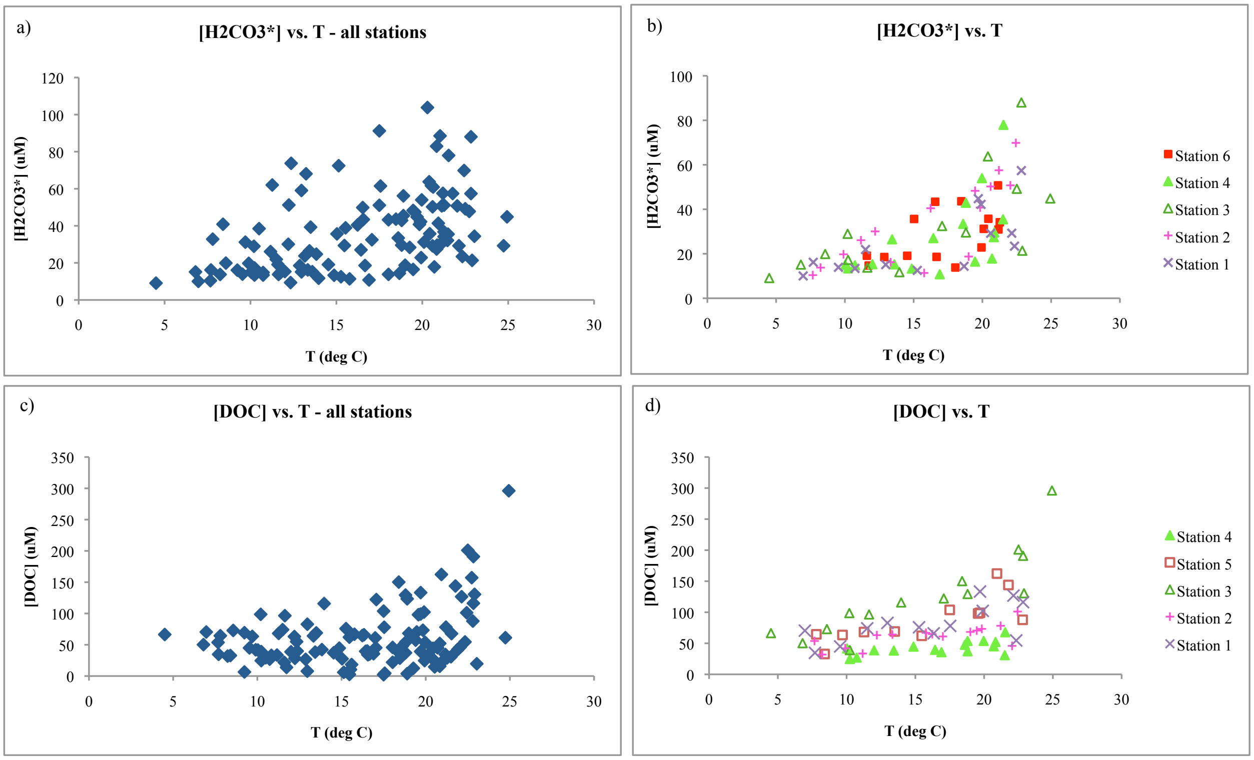

Figure 4.10. Dissolved carbon dioxide and organic carbon versus temperature. a) [$H_2CO_3^*$] versus T for all stations; b) at sampling stations with Pearson's R coefficients of 0.95 or greater confidence intervals were in the Protected Stream Stations 6 and 4, Runoff Streat Station 3, and Stations 2 and 1; c) [DOC] versus T for all stations and d) [DOC] versus T correlations were significant for Protected Stream Station 4, Runoff Stream Stations 5 and 3, and Stations 2 and 1. Both [$H_2CO_3^*$] and [DOC] versus T relationships exhibited a crescent-shaped relationship with an increase in concentration slope with increasing T above 18-20° C.

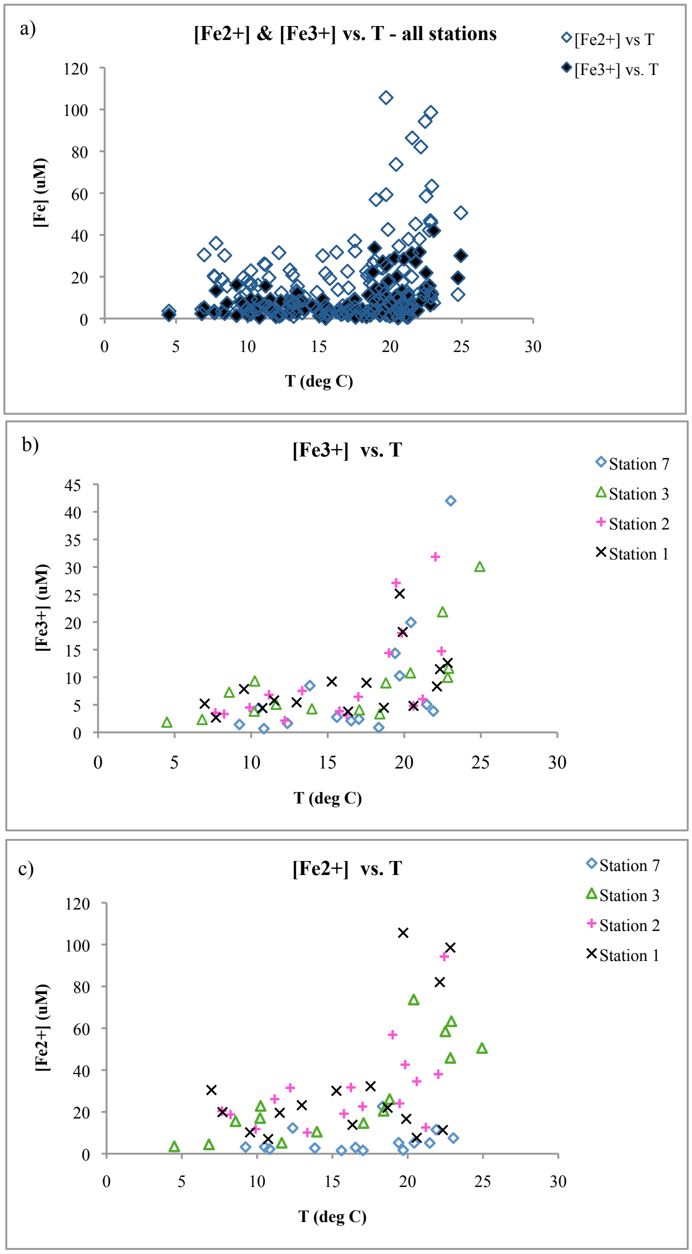

Figure 4.11. Dissolved iron versus temperature. $[Fe^{2+}]$ and $[Fe_{total}]$ were measured; $[Fe^{3+}] = [Fe_{total}] - [Fe^{2+}]$. a) Data for all stations: $[Fe^{2+}]$ was the dominant species in the wetland streams; b) $[Fe^{2+}]$ for stations the yielded significant (0.95 confidence or greater) Pearson's R coefficients had concentrations between 0-40µM between 5-20°C, above which $[Fe^{2+}]$ increased to 60-100µM. b) and c) $[Fe^{2+}]$ and $[Fe^{3+}]$ both increased 3-4 fold above temperatures higher than 19°C at Stations for which Pearson's R correlation coefficients were 0.95 or greater.

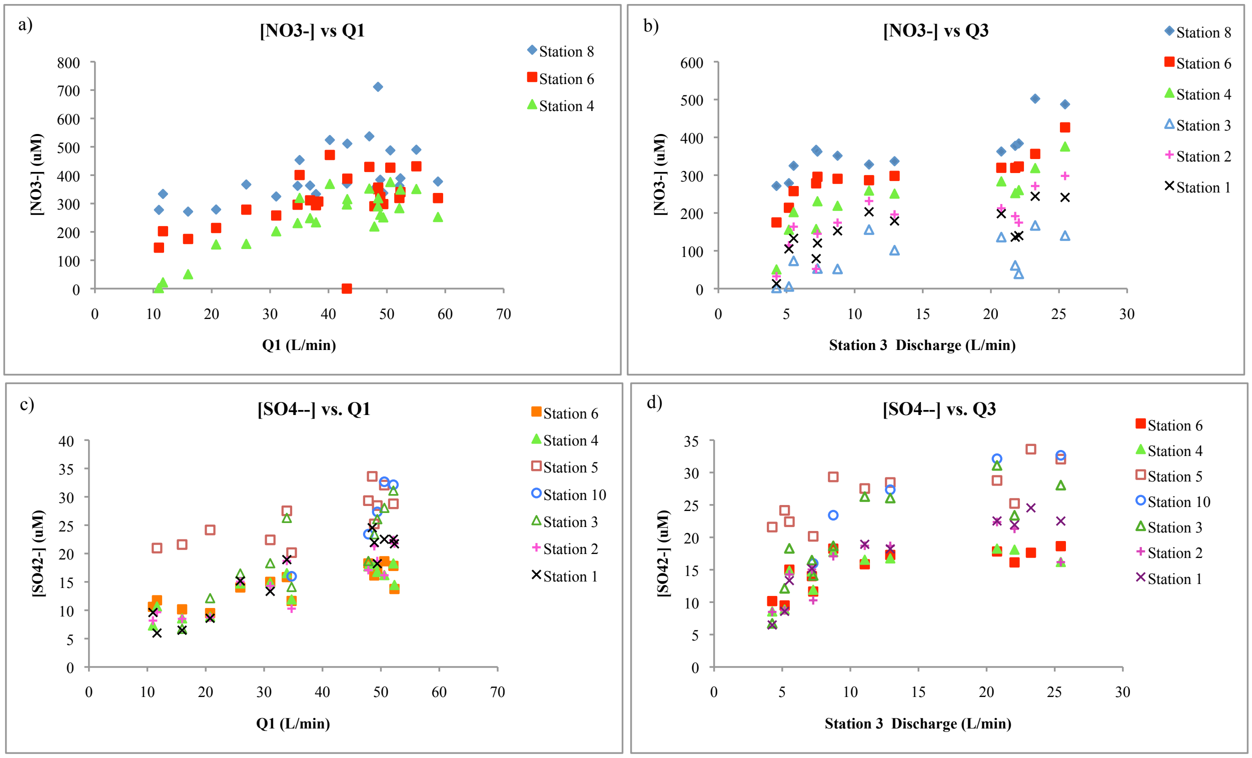

Figure 4.12. Nitrate and Sulfate versus discharge. Station 1 discharge represented the sum of base flow and runoff, minus storage, leaving the wetland. Station 3 Q provided an approximate measure of ground water discharge through the stream bed. Stations plotted exhibited significant Pearson's R correlations. a) [NO_3^- -N] increases with increasing discharge at Station 1, the mouth of the wetland, between ~10 and 45-50 L/min, above which [NO_3^- -N] decreases with increasing Station 1 Q. b) [NO_3^- -N] increases with increasing Station 3 Q between about 3-7 L/min, remains relatively constant to 20L/min, and increases at Station 3 Q greater than 20L/min. c) [SO_4^{2-}] also increases with increasing Station 1 Q. d) [SO_4^{2-}] generally increases with increasing Station 3 Q but there is more scatter; the rate [SO_4^{2-}] increases did not change at Q3 above 20L/min

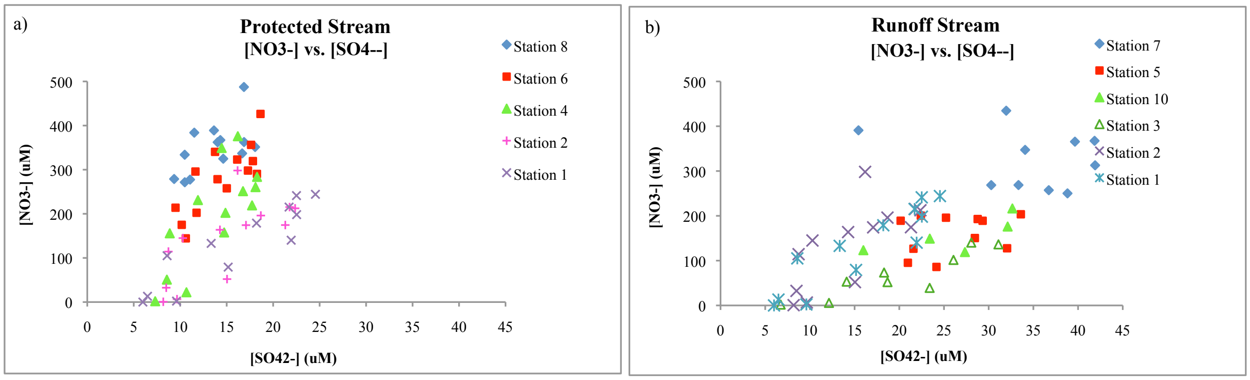

Figure 4.13. Nitrate versus sulfate. a) Protected Stream [SO_4^{2-}] increased along the flow path at [NO_3^- -N] between about 280 and 330μM. b) Runoff Stream [SO_4^{2-}] decreased or exhibited the same concentration range for all [NO_3^- -N].

References

Bastviken, S.K., P.G. Eriksson, I. Martins, J.M. Neto, L. Leonardson and K. Tonderski (2003) Wetlands and aquatic processes: Potential nitrification and denitrification on different surfaces in a constructed treatment wetland. J. Environ. Qual. 32:2414-2420.

Beristain-Cardoso, R., A-C. Texier, R. Sierra-Álvarez, E. Razo-Flores, J.A. Field, J. Gómez (2009) Effect of initial sulfide concentration on sulfide and phenol oxidation under denitrifying conditions. Chemosphere 74:200-205.

Clesceri, L., A. Greenberg and A. Eaton (1998) Standard methods for the examination of water and wastewater. American Public Health Association, New York.

Correll, D.L. (1997) Buffer zones and water quality protection: general principles. Pgs 7-20 in Buffer Zones: Their Processes and Potential in Water Protection – The Proceedings of the International Conference on Buffer Zones, September 1996. Haycock, N.E., T.P. Burt, K.W.T. Goulding, and G. Pinay (eds). Quest Environmental, Herfordshire, UK.

Elefsiniotis, P. and D. Li, (2006) The effect of temperature and carbon source on denitrification using volatile fatty acids. Biochemical Engineering Journal 28:148-155.

Endale, D.M., J.W. Washington, and L. Samarkina (2003) Role of iron-rich Georgia soils in controlling nitrate contamination of ground water. Proceedings of the 2003 Georgia Water Resources Conference, held April 23-24, 2003 at the University of Georgia. Karen J. Hatcher, editor, Institute of Ecology, The University of Georgia, Athens, Georgia.

Ernstsen, V. (1996) Reduction of nitrate by Fe^{2+} in clay minerals. Clays and Clay Minerals 44(5):599-608.

Fetter, C.W. (1992) Contaminant Hydrology. Macmillan Publishing Company.

Francy, D.S., P. Struffolino, A.M.G. Brady, and D.F. Dwyer (2005) A spatial, multivariable approach for identifying proximate sources of Escherichia coli to Maumee Bay, Lake Erie, Ohio. U.S. Geological Survey Open-File Report 2005-1386, 24 p.

Georgia Forestry Commission (2011) Fire Weather System Data from 1200 Hog Mountain Road, at USDA, ARS: http://weather.gfc.state.ga.us/climate/climate.aspx

Helsel, D.R. and R.M. Hirsch (2002) Statistical Methods in Water Resources Techniques of Water Resources Investigations, Book 4, Chapter A3. U.S. Geological Survey. 522 p.

Holmer, M. and P. Storkholm (2001) Sulphate reduction and sulphate cycling in lake sediments: a review. Freshwater Biology 46:431-451.

Kaushal, S.S., M.L. Pace, P.M. Groffman, L.E. Band, K.T. Belt, P.M. Mayer, and C. Welty (2010) Land use and climate variability amplify contaminant pulses. Eos 91(25):221.

Marine Science Today (2009)
http://marinesciencetoday.com/2009/08/05/gulf-of-mexico-dead-zone-smaller-than-predicted-but-deeper/

Madigan, M.T., J.M. Martinko and J. Parker (2003) Brock Biology of Microorganisms, Tenth Edition. Prentice Hall, 1005 p.

McBride, M.B. (1994) Environmental Chemistry of Soils. Oxford University Press, 406p.

McKnight, D.M. and S.M. Durem (2004) Biogeochemical processes controlling midday ferrous iron maxima in stream waters affected by acid rock drainage. Applied Geochimstry 19:1075-1084.

McClain, M.E., J.E. Richey and T.P. Pimentel (1994) Groundwater nitrogen dynamics at the terrestrial-lotic interface of a small catchment in the Central Amazon Basin. Biogeochemistry 27: 113-127.

Muckler, J.F. (2010) Nitrogen transformations in the vadose zone of a small zero-order piedmont watershed in Watkinsvile, Georgia. Master of Science Thesis, University of Georgia Department of Geology, 135p.

Nielsen, L.P., N. Risgaard-Petersen, H. Fossing, P.B. Christensen and M. Sayama (2010) Electric currents couple spatially separated biogeochemical processes in marine sediment. Nature 463:1071-1074.

Ocampo, C.J., C.E. Oldham, and M. Sivapalan (2006) Nitrate attenuation in agricultural catchments: Shifting balances between transport and reaction. Water Resources Research 42, WO1408: 16 p.

Paybins, K.S (2008) Basin characteristics for selected streamflow-gaging stations in and near West Virginia. U.S. Geological Survey Open-File Report 2008-1087, 9 p.

Poor, C., and J.J. McDonnell (2007) The effects of land use on stream nitrate dynamics. J. Hydrology 332:54-68.

Postma, D. and R. Jakobsen (1996) Redox zonation: Equilibrium constraints on the Fe(III)/SO_4^{-3} reduction interface. Geochimica et Cosmichimica Acta 60(17) 3169-3175.

Puckett, L.J., T.K. Cowdery, P.B. McMahon, L.H. Tornes, and J.D. Stoner (2002) Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system, Water Resour. Res. 38:1-20.

Rivera-Monroy, V.H., P. Lenaker, R.R. Twilley, R.D. Delaune, C.W. Lindau, W. Nuttle, E. Habib, R.W. Fulweiler, E. Castañeda-Moya (2010) Denitrification in coastal Louisiana: A spatial assessment and research needs. Journal of Sea Research 63: 157-172.

School of Psychology, University of New England
http://www.une.edu.au/WebStat/unit_materials/c6_common_statistical_tests/test_signif_pearson.html

Schroer, K.L., D.M. Endale, C.L. Tebes-Stevens, J.W. Washington, and V. Nzengung (2007) Concentrations and estimated loads of nitrogen contributed by two adjacent wetland streams with different flow-source terms in Watkinsville, GA. Proceedings of the 2007 Georgia Water resources Conference, held March 27-29, 2007, at the University of Georgia. 4p.

Sher, Y., K. Schneider, C.U. Scwermer, and J. van Rijn (2008). Sulfide-induced nitrate reduction in the sludge of an anaerobic digester of a zero-discharge recirculating mariculture system. Water Research 42: 4386-4392.

Siebner-Freibach, H., Y. Hadar and Y. Chen (2004). Interaction of iron chelating agents with clay minerals. Soil Sci. Soc. Am. J. 68:470-480.

Snoeyink, V.L. and D. Jenkins (1980) Water Chemistry. John Wiley & Sons, 463p.

Stumm, W. and J.J. Morgan (1996) Aquatic chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd Edition. John Wiley and Sons, Inc.

Tiedje, J. M., J. Sorensen and Y.-Y.L. Chang (1981) Assimilatory and dissimilatory nitrate reduction: Perspectives and methodology for simultaneous measurement of several nitrogen cycle processes. Ecol. Bull. (Stockholm) 33: 331-342.

Triska, F.J., V.C. Kennedy, R.J. Avanzino, G.W. Zellweger, and K.E. Bencala (1989) Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes. Ecology 70(6): 1893-1905.

USEPA (2009) Natural Water Quality Inventory: Report: to Congress, 2004 Reporting Cycle. Office of Water EPA-841-R-08-001, 37p.

van Groenigen, J.W., P.J. Kuikman, W.J.M. de Groot, and G.L. Velthof (2005) Nitrous oxide emission from urine-treated soil as influenced by urine composition and soil physical conditions. Soil Biology and Biochemistry 37:463-473.

van Rijn, J., Y. Tal, and H.J. Schreier (2006) Denitrification in recirculating systems. Agricultural Engineering 34: 364-376.

Viollier, E., P.W. Inglett, K. Hunter, A.N. Roychoudhury and P. Van Cappellen (2000) The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. Applied Geochemistry 15: 785-790.

Washington, J.W., D.M. Endale, L.P. Samarkina and K.E. Chappell (2004) Kinetic control of oxidation state at thermodynamically buffered potentials in subsurface waters. Geochimica et Cosmochimica Acta 68, 4831-4842.

Washington, J.W., R.C. Thomas, D.M. Endale, K.L. Schroer, and L.P. Samarkina (2006) Groundwater N speciation and redox control of organic N mineralization by O_2 reduction to H_2O_2. Geochimica et Cosmochimica Acta 70:3533-3548.

Whitten, K.W. and K.D. Gailey (1981) General Chemistry. Saunders College Publishing, 621 pgs.
Yang, X. and W. Jin (2010) GIS-based spatial regression and prediction of water quality in river networks: A case study in Iowa. J. Environ. Management 91:1943-1951.

Zumdahl, S.S. and S.A. Zumdahl (2000) Chemistry. Houghton Mifflin Company, 1143p.

CHAPTER 5

CONCLUSIONS

A two-year sampling program was conducted to elucidate controls on nitrate N removal and retention in two small wetland streams that drain portions of a 10ha cattle pasture and crop field. Cow manure and synthetic fertilizer were the main sources of nitrate N to the wetland.

The field site was at USDA's J. Phil Campbell Sr. Natural Resource Conservation Center (Watkinsville, GA) in the Oconee River Watershed, Southern Piedmont Physiographic Province between the Southern Appalachian Mountains and the Georgia Coastal Plain. Climate was hot and humid in summer, cool and frequently sub-freezing in winter, and had average annual rainfalls of 54cm during the project period. Vegetation included both forest (e.g., oak, privet) and wetland species (e.g., duckweed and willow). The field site and surrounding area was underlain by a metamorphic rock formation, the Athens Gneiss. A layer of saprolite was formed on the gneiss 8~21 meters below ground, and served as an unconfined aquifer through which shallow ground water flowed to the wetland. A clayey soil was developed on the saprolite.

The wetland had been modified to serve as an outdoor laboratory. A man-made earthen berm prevented surface runoff from entering the Protected Stream, which was dredged to facilitate channelized flow. The adjacent Runoff Stream received surface runoff from the pasture. The Protected Stream had a perennial spring flowing from its headcut; the Runoff Stream did not. The Protected Stream is 63 meters long from the headcut spring to its confluence with the Runoff Stream. The more meandering Runoff Stream is 70 meters long, and the two streams are 14m apart at headcut The entire wetland and riparian buffer zone was about 92m long and 40m wide.

Accumulation of cow manure was anecdotally observed in the Runoff Stream, whereas seasonal accumulations of other sources of organic C (e.g., fallen leaves and dormant vegetation) were observed in both streams.

Four seasonal tracer injection tests (Chapter 3) were conducted to evaluate wetland stream response to a pulse of high but realistic concentration of [NO_3^- -N] (50mg/L at the point of mixing). Mixed nitrate and bromide tracer were pumped at a steady rate for 30 minutes into the Protected Stream during the spring, fall, winter and summer tracer tests, and simultaneously into both streams during the summer test. Downstream samples were collected during the rise, plateau and fall of the tracer breakthrough curves and analyzed for field parameters (DO, SpC, pH, T and discharge); reduced N ions ([NO_2^- -N], [NH_4^+ -N]); [Br^-]; [Fe^{2+}]; [Fe_{total}]; [SO_4^{2-}]; [DOC]; [Cl^-]; and dissolved gases [N_2O], [$H_2CO_3^*$], [CH_4] and [H_2]. Tracer [NO_3^- -N]/[Br^-] recovery indicated if nitrate N behaved conservatively with respect to bromide. Total tracer mass recoveries, electron mass balances, and stream N removal efficiencies (with/without tracer) were also calculated. These field experiments tested the hypothesis that residence time exerts a primary control on nitrate removal.

Samples were collected ~monthly for two years at 8-10 sampling stations and samples were analyzed for the above parameters using field probes, laboratory instruments and wet chemistry methods. The Pearson's R test was used to test for linear correlations, and results between were highlighted for all parameters at 0.95 and 0.99 confidence intervals. Statistically significant positive and negative coefficients were investigated, in conjunction with tracer test results, to further constrain controls on wetland nitrate removal processes based on inter-seasonal, inter-stream and intra-stream comparisons.

Summary of Findings

Chapter 3 - Tracer Tests

Residence time exerted a primary control on N removal processes during the tracer tests.

Thirty-one per cent of Runoff Stream tracer NO_3^- -N mass was recovered after 24 hours compared to 72% bromide mass recovery. Thus, about 28% of tracer bromide and 41% (72-31%) of summer Runoff Stream NO_3^- -N mass were retained in the wetland. Nintety-four per cent of the Protected Stream tracer NO_3^- -N and 92% of tracer bromide were recovered. Runoff Stream Station 3 NO_3^- -N loads were consistently one-third or less those at Station 4 during the two-year project period.

Denitrification and/or nitrate reduction to ammonia was an important tracer N removal process during the Runoff Stream summer tracer test and Protected Stream fall test. The 30% of tracer NO_3^- -N that was neither stored nor recovered was chemically reduced or removed by other wetland removal processes such as plant uptake. Increased concentrations of NO_3^- -N reduction products ($[NO_2^-$ -N], $[N_2O]$) and increased concentrations in oxidized species of possible reductants ($[SO_4^{2-}]$, $[H_2CO_3^*]$) reflected dentrification. Electron mass balance indicated that there were more than enough electrons donated by sulfide and organic C to reduce NO_3^- -N lost from the tracer plume to N_2; however, this does not take kinetic controls into consideration. Plant uptake was not measured but may have accounted for some of the nitrate N removed during the summer test.

Fall tracer $[NH_4^+$ -N] is 5 times higher, $[H_2CO_3^*]$ 2-3 times higher, [DOC] 1.5-2 times higher and $[CH_4]$ 10-30 times higher than either summer or winter Protected Stream values. This suggests that some NO_3^- -N may have been reduced to ammonia. Peak $[NO_3^-$ -N] was attained 10-30 minutes later at Station 6 and 35-60 minutes later at Station 4 during the fall than during the spring, winter or summer Protected Stream tests, indicating that leaf litter caused both increased residence time and more reducing conditions in the fall than during the other Protected Stream tests.

Addition of tracer spike did not cause a disproportionately large increase in N removal rates from the Protected Stream. Protected Stream tracer NO_3^- -N mass (tracer + background, which was the total area under the NO_3^- -N load vs. Time) was compared to background "low end" (percent increase between Stations 8 and 4 using actual background nitrate N loads) and "high end" (percent increase between Station and 8 and Station 4 if Station 4 load was calculated using Station 8 background concentrations). For example, during the spring tracer test, 28% of tracer-plus-background NO_3^- -N was lost between Stations 8 and 4. However, between 19% (actual background loads) and 30% (if there had been no removal processes between Stations 8 and 4) background NO_3^- -N would have been removed from the wetland. Only the winter stream Protected Stream test yielded a greater % loss in tracer mass than the background "low end" and "high end" ranges.

Organic carbon was the main electron donor in both streams. Electron mass balance calculations indicated that reducing equivalents available from organic C to reduce nitrate N were 2 orders of magnitude higher than reducing equivalents that would be available via sulfide oxidation to sulfate.

Chapter 4 - Monthly Sampling

Organic carbon was the main electron donor in both streams. Chapter 4 supported this finding by showing that there were approximately equimolar concentrations of $[H_2CO_3^*]$, a product of organic C oxidation, in both streams. Several mid- and downstream sampling locations exhibited significant (0.95 - 0.99) negative Pearson's R coefficients between $[NO_3^-$ -N] and $[H_2CO_3^*]$. Finally, $[SO_4^{2-}]$ decreased along the stream flow paths on many sampling dates.

Some $[SO_4^{2}]$ in the wetland streams may be due to sorptive exchange on iron hydroxides in stream-bottom sediments. Sulfate concentrations decreased along the flow path for many sampling dates in the Protected Stream and all sampling dates in the Runoff Stream. Also, sulfate exhibited significant positive correlations with discharge and $[NO_3^-$ -N]. Thus, sulfate production did not correlate with $[NO_3^-$ -N] reduction.

However, sulfide may be an important secondary reductant. Sulfide consumption was not measured directly but inferred only by sulfate production, which may not represent all sulfide oxidation. There was an increase in Protected Stream Station 4 (downstream) $[SO_4^{2-}]$ on several winter sampling dates. During the summer tracer test, $[SO_4^{2-}]$ remained stable at about 14 uM with decreasing Runoff Stream [N]/$[fBr^-]$ Recovery from 1.0 to 0.8, then increased to 20uM Recovery decreased to about 0.5, and remained at 20uM as Recovery decreased to 0.3. The threshold changes in slope may also indicate rapid secondary oxidation of sulfide.

Temperature exerts control on stream redox processes. $[NO_3^-$ -N] decreased with increasing temperature at Stations 4 in the Protected Stream, 10 and 3 in the Runoff Stream and Stations 2 and 1. $[NO_3^-$ -N] remained fairly constant at T greater than 19°C at Runoff Stream Stations 3 and 10. $[NO_2^-$ -N] versus T for all Stations exhibited boomerang- and crescent-shaped zones, with a positive increase in [NO_2^- -N] between ~17-19°C. Pearson's R coefficients for [NO_2^- -N] were significant at 0.95 confidences or higher only at Stations 6 and 7 Station. Both [$H_2CO_3^*$] and [DOC] versus T relationships exhibited a crescent-shaped relationship with an increase in concentration slope with increasing T above 18-20° C. [Fe^{2+}] for stations the yielded significant (0.95 confidence or greater) Pearson's R coefficients had concentrations between 0-40μM at 5-20°C, above which [Fe^{2+}] increased to 60-100μM. [Fe^{2+}] and [Fe^{3+}] both increased 3-4 fold at temperatures higher than 19°C at Stations for which Pearson's R correlation coefficients were 0.95 or greater.

Stream baseflow exerts less control than baseflow-plus-runoff on a wetland's capacity to remove nitrate N. This is related to the control of residence time on N Removal tested in Chapter 3. At several sampling stations (8,6,4,3,2,1), [NO_3^- -N] increases with increasing baseflow (represented by Station 3 Q) between about 3-7 L/min, remains relatively constant to 20L/min, and increases at baseflow Q greater than 20L/min. In contrast, [NO_3^- -N] increases with increasing discharge at Station 1 (representing baseflow plus runoff) between ~10 and 45-50 L/min, above which [NO_3^- -N] decreases with increasing Station 1 Q. Thus, there is a wide range (between 7-20L/min) within which increases in baseflow Q have no effect on [NO_3^- -N]. However, baseflow plus runoff Q cause a continual increase in [NO_3^- -N] to a critical threshold (~45L/min), above which [NO_3^- -N] decreases with higher Q, likely due to dilution. However, sedimentation in the Runoff Stream and saturated riparian soils allow for some stream water to be transported through the organic rich sediments as through-flow. This allows for intimate contact between the nitrate contaminated water and the organic rich sediment leading to slow discharge and more residence time for a higher rate of denitrification. Thus, the lower Q at Station 4 facilitates removal processes caused by longer residence times, yielding even smaller loads than the lower discharge.

In summary, residence time exerted a primary control on N removal processes in the wetland streams. Denitrification and/or nitrate reduction to ammonia were important tracer N removal process during the Runoff Stream summer tracer test and Protected Stream fall test. Addition of tracer spike did not cause a disproportionately large increase in N removal rates from the Protected Stream. Organic carbon was the main electron donor in both streams. Sulfide may be an important secondary reductant. Temperature exerted control on stream redox processes, indicated by moderate to strong increases in [NO_3^- -N] , [$H_2CO_3^*$], [DOC], [Fe^{2+}] and [Fe^{3+}] above 18-20°C . Stream baseflow exerted less control than baseflow-plus-runoff on the wetland's capacity to remove nitrate N. These results constrain processes that affect nitrate N removal efficiency in agricultural wetland streams.