

# 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

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[1] A combination of chemical and dissolved gas analyses, chlorofluorocarbon age dating, and hydrologic measurements were used to determine the degree to which biogeochemical processes in a riparian wetland were responsible for removing  $\text{NO}_3^-$  from groundwaters discharging to the Otter Tail River in west central Minnesota. An analysis of river chemistry and flow data revealed that  $\text{NO}_3^-$  concentrations in the river increased in the lower half of the 8.3 km study reach as the result of groundwater discharge to the river. Groundwater head measurements along a study transect through the riparian wetland revealed a zone of groundwater discharge extending out under the river. On the basis of combined chemical, dissolved gas, age date, and hydrologic results, it was determined that water chemistry under the riparian wetland was controlled largely by upgradient groundwaters that followed flow paths up to 16 m deep and discharged under the wetland, creating a pattern of progressively older, more chemically reduced, low  $\text{NO}_3^-$  water the farther one progressed from the edge of the wetland toward the river. These findings pose challenges for researchers investigating biogeochemical processes in riparian buffer zones because the progressively older groundwaters entered the aquifer in earlier years when less  $\text{NO}_3^-$  fertilizer was being used.  $\text{NO}_3^-$  concentrations originally present in the groundwater had also decreased in the upgradient aquifer as a result of denitrification and progressively stronger reducing conditions there. The resulting pattern of decreasing  $\text{NO}_3^-$  concentrations across the riparian zone may be incorrectly interpreted as evidence of denitrification losses there instead of in the upgradient aquifer. Consequently, it is important to understand the hydrogeologic setting and age structure of the groundwaters being sampled in order to avoid misinterpreting biogeochemical processes in riparian zones. *INDEX TERMS:* 1831 Hydrology: Groundwater quality; 1871 Hydrology: Surface water quality; 1890 Hydrology: Wetlands; *KEYWORDS:* riparian zone, redox, nitrate, denitrification, flow path, chlorofluorocarbon

## 1. Introduction

[2] Over the last two decades, there has been growing interest in the use of riparian buffer zones along river corridors to mitigate the effects of nonpoint-source pollution on water quality [Hill, 1996]. Most early interest in riparian buffer zones focused on their ability to trap sediment and sediment-borne contaminants [Young *et al.*, 1980; Dillaha *et al.*, 1989; Vought *et al.*, 1994], while recent interest has shifted to their ability to remove contaminants from groundwater before it enters surface water bodies [Groffman *et al.*, 1992; Haycock *et al.*, 1993; Gilliam, 1994; Jansson *et al.*, 1994; Hill, 1996]. The ability of riparian buffer zones to remove pollutants, particularly nitrate ( $\text{NO}_3^-$ ), from groundwater is related primarily to the presence of reducing

conditions in the organic-rich, saturated sediments that commonly occur in riparian buffer zones. Nitrate removal in riparian buffer zones is important because (1) it poses human and ecosystem health risks [Mueller *et al.*, 1995], (2) it is the most common nonpoint-source pollutant [Mueller *et al.*, 1995], and (3) it is mobile in ground and surface water [Mueller *et al.*, 1995]. Under reducing conditions nitrate can be converted to  $\text{N}_2\text{O}$  and then  $\text{N}_2$  gas by the microbially mediated process of denitrification [Korom, 1992]:



Studies of denitrification potential in riparian buffer zones increase our understanding of factors controlling this process and may allow us to predict when, where, and how riparian buffer zones will be effective nonpoint-source pollution controls.

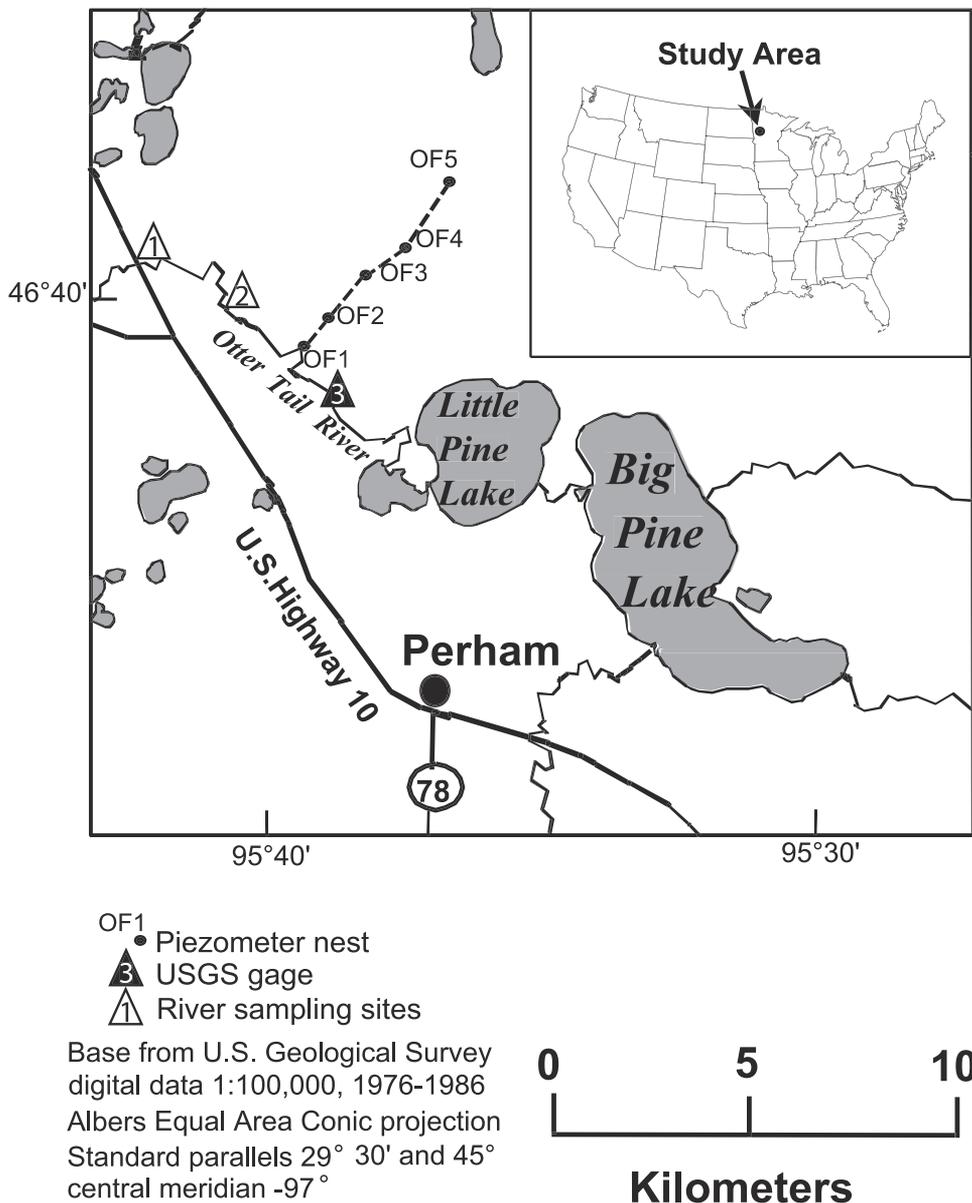
[3] Assuming  $\text{NO}_3^-$  is present, there are three basic requirements for denitrification: (1) a microbial denitrifier population, (2) low concentration of dissolved oxygen ( $\text{O}_2$ ), and (3) a readily available source of C or a reduced inorganic species such as  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , or  $\text{S}^{2-}$  to serve as

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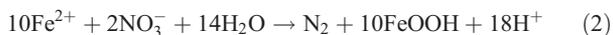
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**Figure 1.** Location of the study area north of the Otter Tail River along with the upgradient aquifer transect.

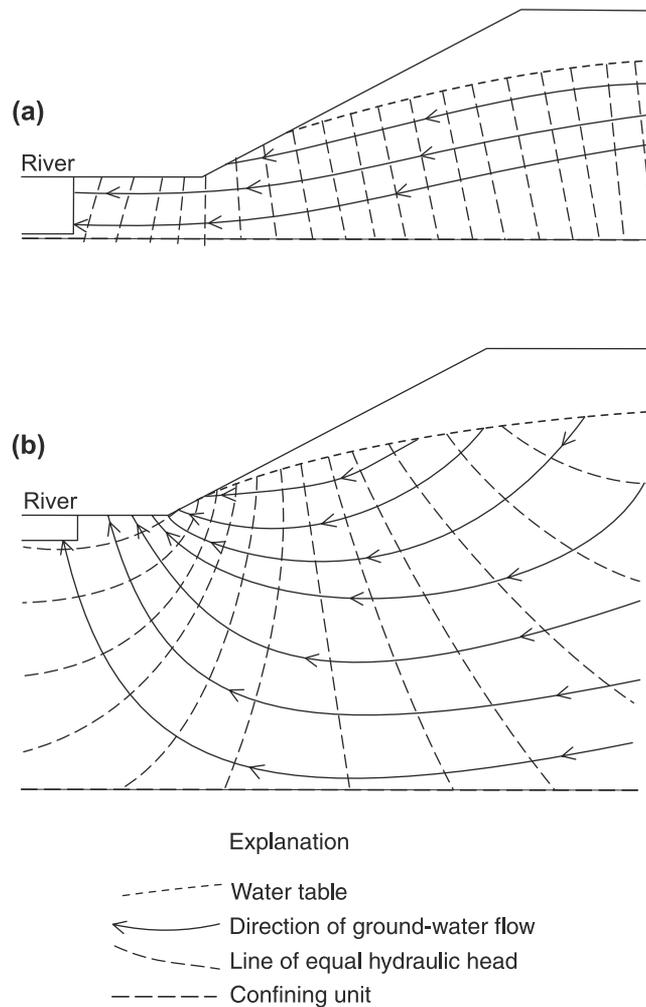
an electron donor [Tiedje *et al.*, 1982; Postma *et al.*, 1991; Korom, 1992] following a reaction of the form:



In reactions (1) and (2),  $\text{NO}_3^-$  is converted to  $\text{N}_2$  gas. Under most conditions, this  $\text{N}_2$  gas will remain in solution until the groundwater discharges to a surface water body and equilibrates with the atmosphere [Heaton and Vogel, 1981; Blicher-Mathiesen *et al.*, 1998]. By measuring this excess  $\text{N}_2$ , it is possible to reconstruct, in effect, the amount of  $\text{NO}_3^-$  originally present in the groundwater [Heaton and Vogel, 1981; Vogel *et al.*, 1981; Wilson *et al.*, 1990; Smith *et al.*, 1991; Bohlke and Denver, 1995; Blicher-Mathiesen *et al.*, 1998; Modica *et al.*, 1998]. Most studies of  $\text{NO}_3^-$  removal by riparian zones have inferred denitrification losses based on measurements of the decrease in  $\text{NO}_3^-$

concentrations at several locations across the riparian zone, but few if any studies have measured nitrogen gas phases to verify that conclusion. Even fewer riparian zone studies have conducted a complete, simultaneous analysis of the various nitrogen species coupled with an analysis of the controlling hydrogeologic and biogeochemical processes involved, leaving many questions unanswered with respect to the true fate of  $\text{NO}_3^-$ .

[4] Hill [1996] provided a critical review of the current state of our knowledge concerning  $\text{NO}_3^-$  retention by riparian buffer zones. He concluded that previous research had failed to adequately consider hydrogeologic controls on biogeochemical processes and had been conducted in similar settings, making it difficult to extrapolate findings to other areas. These conclusions seem particularly relevant in light of recent studies that have shown that groundwater may flow under riparian zones and discharge to streams



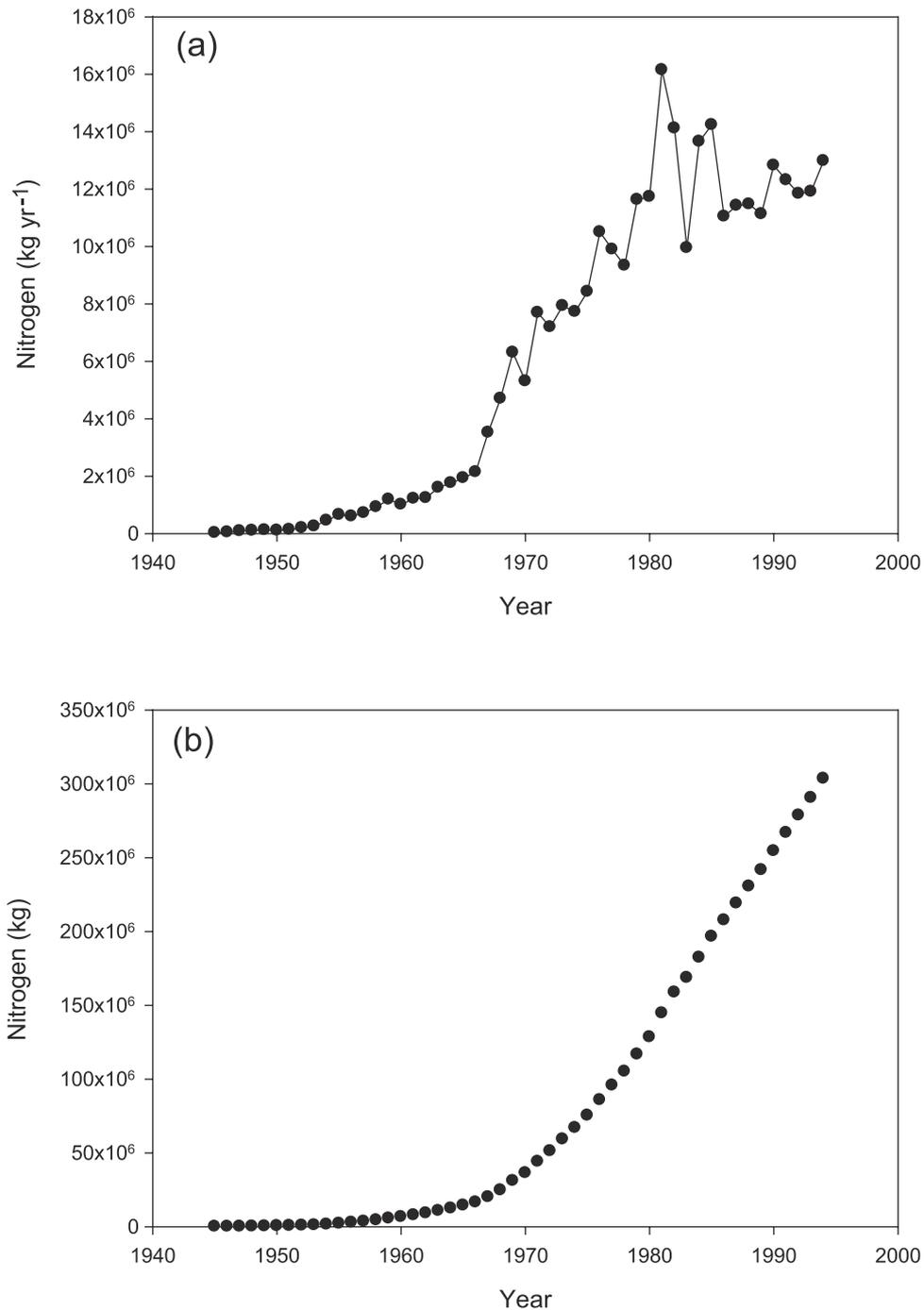
**Figure 2.** Conceptual flow systems showing (a) shallow horizontal and (b) deep parabolic flow paths [after Patton and Hendron, 1974].

without undergoing denitrification [Bohlke and Denver, 1995; Burt *et al.*, 1999], or may take many decades to transit groundwater flow paths before discharging to surface waters [Modica *et al.*, 1997, 1998].

[5] In this paper, we examine the hydrogeologic and biogeochemical controls on the evolution of water chemistry at a site in west central Minnesota. Previous work in the area examined nitrogen cycling in the 212 km<sup>2</sup> agroecosystem [Puckett *et al.*, 1999] and hydrogeologic and biogeochemical processes controlling the transport and fate of nitrogen in an upland portion of the aquifer [Puckett and Cowdery, 2002]. The Puckett and Cowdery [2002] study demonstrated a pattern of decreasing NO<sub>3</sub><sup>-</sup> concentrations with both increasing depth and groundwater age along a representative 5 km flow system transect, and their modeling results predicted that groundwater from deep in the aquifer should discharge at the terminus of the flow system in the riparian zone adjacent to the Otter Tail River.

[6] The study reported here focused on the hydrogeology and biogeochemistry of the riparian zone where the original 5 km transect intersected the Otter Tail River (Figure 1). Examination of historical water quality data for the Otter Tail River indicated that in spite of the large amounts of nitrogen entering the Otter Tail watershed [Puckett *et al.*, 1999], little

was being discharged in the river and almost none of that was in the form of NO<sub>3</sub><sup>-</sup>. Our primary hypothesis in this study, therefore, was that denitrification was taking place in the riparian buffer zone, preventing NO<sub>3</sub><sup>-</sup> contamination of the Otter Tail River. Within the context of this hypothesis, we evaluated the commonly reported occurrence that groundwater flowing horizontally through the riparian zone as shown in Figure 2a, passes through progressively stronger redox environments, resulting in the loss of NO<sub>3</sub><sup>-</sup> through denitrification. Denitrification losses, inferred by measuring changes in NO<sub>3</sub><sup>-</sup> concentration at various points across the riparian zone, are frequently offered as evidence of this process. However, this approach has drawbacks since it is possible that by sampling along a transect through the riparian zone, investigators are merely observing a series of discharging groundwaters of progressively greater age and stronger redox state, containing less NO<sub>3</sub><sup>-</sup>. This pattern of decreasing NO<sub>3</sub><sup>-</sup> concentration may occur because less fertilizer was applied in earlier years when the water originally recharged and (or) because denitrification occurred in the upgradient aquifer. Consequently, we also considered the alternative hypothesis that groundwater from deeper and progressively more reduced portions of the upgradient aquifer were discharging in the riparian zone as shown in



**Figure 3.** Nitrogen application in commercial fertilizer in Otter Tail County since 1945 (a) on an annual basis and (b) cumulative inputs during the same period.

Figure 2b, thereby creating the appearance of  $\text{NO}_3^-$  loss in the riparian zone.

[7] Although the chemistry of groundwater sampled along the riparian transect may appear similar in each scenario, the two different flow paths should result in distinctively different patterns of water age with the deepest and longest flow paths shown in Figure 2b resulting in groundwater ages up to several decades older. Therefore one important criterion for evaluating these two hypotheses would be that there should be no significant horizontal age gradient across the riparian zone if groundwater is moving horizontally as shown in

Figure 2a, whereas there should be a gradient of increasing age across the riparian zone if groundwater is discharging vertically as shown in Figure 2b.

## 2. Study Area

[8] This study was conducted in Otter Tail County in west central Minnesota, United States (Figure 1) in a 36 km<sup>2</sup> subunit of the Otter Tail outwash aquifer north of the Otter Tail River near Perham. The Otter Tail outwash aquifer consists mostly of fine to coarse, fairly well sorted sand,

but also contains some gravel and silt-clay lenses. Aquifer thickness is generally about 18 m but may be over 30 m in places [Reeder, 1972]. It was deposited by meandering debris-laden streams flowing from the disintegrating margin of the Des Moines glacial lobe sometime between 14,000 and 12,000 years BP [Wright, 1972]. After the outwash sands were deposited, stagnant ice blocks within the aquifer melted, forming the abundant lakes and wetland depressions common throughout the area [Goldstein, 1985].

[9] Recharge to the aquifer occurs over much of its area from snowmelt and rainfall and was estimated at  $17.7 \text{ cm yr}^{-1}$  on the basis of a steady state groundwater model developed for the aquifer [Cowdery, 1997; Puckett et al., 1999]. Groundwater flow is generally from the higher elevations of the moraines on the west, north, and east sides of the aquifer toward the Otter Tail River-chain of lakes in the center of the aquifer. Wetlands, lakes and streams are in hydraulic connection with the groundwater. Water loss from the aquifer is through discharge to the Otter Tail River, lakes, wetlands, pumping from wells, and through evapotranspiration.

[10] Climate of the West Central Minnesota climate division has been described as subhumid continental and annual average temperature and precipitation in the area during the 30 year period from 1961 to 1990 was  $5.6^\circ\text{C}$  and 68 cm, respectively [Stoner et al., 1993]. Open water evaporation in the study area exceeds precipitation by about  $10 \text{ cm yr}^{-1}$  [Winter and Woo, 1990]. Historically, the portion of the area up gradient of the study transect was prairie, surrounded by hardwood and conifer forests on the morainal uplands: however, at the time of the study, approximately 73% of the land was cropland.

[11] Fertilizer nitrogen use for agricultural purposes in Otter Tail County (Figure 3a) increased from about 28 metric tons in 1945 to about 13000 metric tons in 1994 (J. Fletcher, West Virginia University, written communication, 1996). A major step change in the application rate occurred about 1967 and the rate of increase has been virtually linear since about 1970 (Figure 3b). More than half of the total amount of nitrogen used during the 1945–1994 period has been applied since 1982.

[12] Samples for this study were collected at a point on the Otter Tail River (Figures 1 and 4a) at an elevation of about 407 m. Here the river is about 48 m wide, 1 m deep, and is bordered to the north by a 40 m wide wetland and a 46 m wide forest buffer zone. The forest buffer zone comprises various oak, ash, and poplar species (*Quercus*, *Fraxinus*, and *Populus*) with scattered spruce and fir (*Picea* and *Abies*). Vegetation in the wetland is dominated by common reed (*Phragmites australis* [Cav.] Tin. Ex Steudel), cattail (*Typha latifolia* L.), wild rice (*Zizania aquatica* L.), jewelweed (*Impatiens capensis* Meerb.), cyperus (*Cyperus strigosus* L.), orchardgrass (*Dactylis glomerata* L.), and scattered grasses and sedges. The wetland soil consists of a layer of peat up to 2 m thick, underlain by sand and gravel deposits of the aquifer. Springs and seeps in the forest and wetland suggest the presence of a groundwater discharge zone.

### 3. Materials and Methods

#### 3.1. Water Sample Collection and Analysis

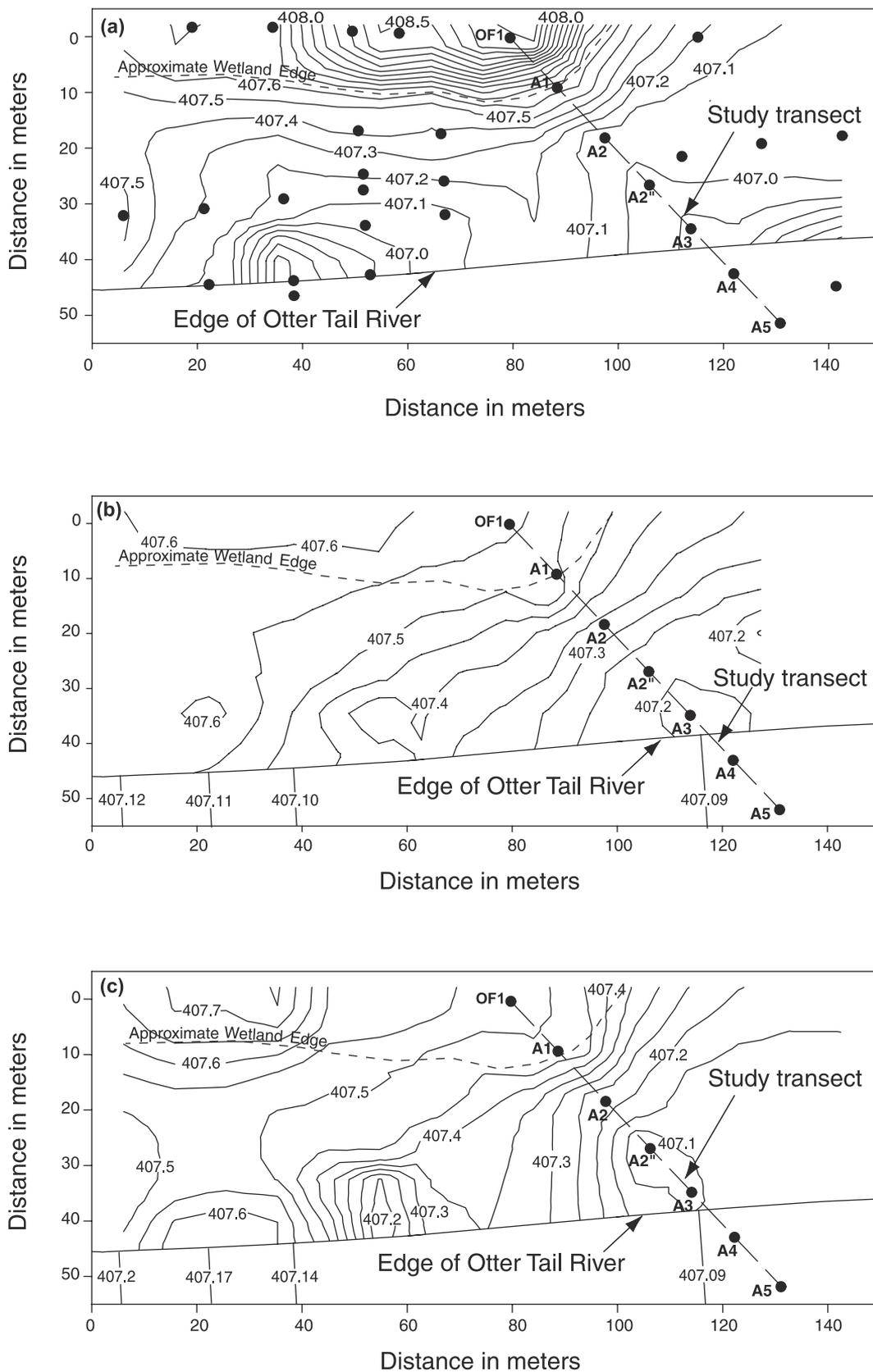
[13] Otter Tail River samples were collected approximately monthly at a gaging station about 1 km downstream

of the intersection of the study transect and the river (Figure 1). Additional stream samples were collected and flow was measured at 1–2 upstream sites shown in Figure 1 during February 1994, June 1994, August 1994, and August 1995, to test for changes in discharge and chemistry that may have occurred as a result of groundwater discharge to the intervening 8.3 km reach. Samples were collected in multiple vertical sections using a depth-integrating sampler [Tornes et al., 1997]. Water levels at the gaging station were recorded hourly and converted to discharge with a calibrated rating curve, and individual flow measurements elsewhere were made with a current meter [Buchanan and Somers, 1969]. Total nitrogen (calculated as the sum of total Kjeldahl nitrogen, nitrate, and nitrite) fluxes were calculated using the minimum variance unbiased estimator method [Cohn et al., 1989; Tornes et al., 1997].

[14] Groundwater samples were collected from the aquifer at site OF1 (Figures 1 and 4) at the terminus of the upland transect described by Puckett and Cowdery [2002]. Site OF1 consisted of a nest of 5 permanent piezometers, installed at depths ranging between 3 and 13.5 m below land surface, and made of 5 cm inside diameter, polyvinyl chloride (PVC) pipe with slotted PVC screens 0.76 m long; the exceptions being the shallowest and deepest piezometers at this location, which were 1.5 m long.

[15] Groundwater samples were also collected along a transect that extended from piezometer nest OF1 through the wetland and into the Otter Tail River at sites A1–A5 (Figure 4) using minipiezometers [Winter et al., 1988]. Minipiezometers were constructed of a 0.6 cm diameter, 2 m long stainless steel tube having a 2.54 cm long screen and 2.0 cm diameter tip, nested in a 2.0 cm diameter stainless steel sleeve. The minipiezometer was inserted into the sediment to the desired depth, and the outer sleeve was pulled back to expose the screened interval during sampling. Initially, during preliminary sampling and site selection in June 1994, minipiezometer samples were collected at approximately 6 m intervals. In later sampling, however, this interval was increased to about 12 m, after it was determined that the differences in chemistry between intermediate sites were not of sufficient magnitude to justify continued sampling. Similarly, samples were initially collected at depths just below the bottom of the peat and again at 0.5 m below it. After it was determined that there were only minor chemical differences, the shallow samples were eliminated. Samples were collected from the minipiezometers in August 1994, 1995, and 1997. Sampling was conducted in August because it is a period of stable, low stream flow when groundwater would be most likely to contribute to surface water quality and flow, and temperatures would be less likely to limit microbial activity. Locations and elevations of all sample sites were surveyed relative to the permanent piezometer nest (OF1) in the forest buffer zone to allow resampling at the same locations. Groundwater heads were measured relative to surface water using a portable manometer [Winter et al., 1988] and were referenced to the permanent piezometer nest elevation, which was established by surveying to the nearest USGS benchmark.

[16] A peristaltic pump and copper tubing with a short piece of Tygon or Viton tubing in the pumphead was used to sample minipiezometers. Permanent piezometers were sampled using a stainless steel positive displacement pump



**Figure 4.** Contour maps showing (a) land surface elevations and locations of sampling points and (b and c) groundwater and river elevations in the 40 m by 140 m study area in the riparian wetland in August 1994 and 1995, respectively. (Individual sample locations are shown as solid circles. Contour intervals are 0.1 m for land surface elevations, 0.05 m for groundwater elevations, and 0.01 m for river elevations).

with Teflon tubing; copper tubing was used for CFC and dissolved gas sampling and the Tygon or Viton tubing was pretested for CFC contamination. Water temperature, specific conductance, and dissolved oxygen ( $O_2$ ) concentration were monitored continuously prior to sample collection. When these measures stabilized, sample collection began. Samples for chemical analyses were filtered through a 0.45  $\mu\text{m}$  nitrocellulose filter (a silver filter was used for dissolved organic carbon (DOC) samples). Mercuric chloride preservative was added to nutrient samples during 1994 but afterward, no preservative was added and nutrient and DOC samples were shipped on ice the same day that they were collected to the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado for immediate analyses. Cation samples were preserved with nitric acid, major cations and silica were analyzed by inductively coupled plasma spectroscopy, anions by ion chromatography, and nutrients by colorimetric methods [Fishman and Friedman, 1989; Fishman, 1993; Wershaw et al., 1987]. Alkalinity was determined in the field by incremental titration of filtered samples [Koterba et al., 1995]. Equipment blank samples, field blank samples, replicate samples, and spiked samples showed a general lack of sampling contamination [Koterba et al., 1995; Menheer and Brigham, 1997]. Sulfide ( $S^{2-}$ ) was measured for most groundwater samples by the methylene blue method [Standard Methods, 1975]. Samples were processed immediately using a HACH 2000 portable spectrophotometer with detection limits of 0.28  $\mu\text{mol L}^{-1} S^{2-}$ . The geochemical model WATEQ as implemented in NETPATH [Plummer et al., 1994] was used for speciation and calculation of saturation indices.

[17] To gain a better understanding of the spatial distribution of  $\text{NO}_3^-$  and potential reducing conditions in the riparian buffer zone, in August 1994 and 1995 samples were collected from 30–40 separate locations within a 40 m wide by 140 m long segment of the study area paralleling the Otter Tail River (Figure 4a). At each location, land surface elevation was surveyed relative to site OF1 and groundwater head,  $O_2$ , and  $\text{NO}_3^-$  were measured at a depth of about 1 m below land surface, depending on the thickness of the peat. For these samples,  $\text{NO}_3^-$  was measured in the field by the cadmium reduction method [Standard Methods, 1975] with a HACH 2000 portable spectrophotometer having detection limits of 6.4  $\mu\text{mol L}^{-1} \text{NO}_3^-$ . The SigmaPlot program [SPSS, 1997] was used to produce contour plots of land surface elevation, groundwater heads,  $O_2$ , and  $\text{NO}_3^-$ .

[18] Dissolved gases ( $\text{N}_2$ , Ar,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $O_2$ ) were analyzed in groundwater samples by gas chromatography after extraction in headspaces of glass samplers [Busenberg et al., 1998]. Results were corrected for solubility in sample water at laboratory temperatures and have an error of  $\pm 2$ –4%. Concentrations of  $\text{N}_2$  and Ar gases dissolved in water were used to estimate the amount of nitrogen resulting from denitrification [Vogel et al., 1981; Wilson et al., 1990; Bohlke and Denver, 1995; Blicher-Mathiesen et al., 1998]. This approach required the assumption that the atmosphere and denitrification were the only sources of  $\text{N}_2$  in groundwater. However, excess air can also become trapped in recharging groundwater and can affect dissolved gas concentrations. Where excess air alone affects dissolved gas concentrations,  $\text{N}_2$  and Ar increase linearly, making it possible to estimate the amount, which typically is negligible (less than 3 cc

$\text{kg}^{-1}$ ) and often ignored in studies of this nature [Bohlke and Denver, 1995; Plummer and Busenberg, 1999]. However, we made corrections to the excess  $\text{N}_2$  estimates by subtracting the air-saturated water plus excess air concentrations from the measured concentrations. We estimated the original or reconstructed concentration of  $\text{NO}_3^-$  (prior to denitrification) as the sum of measured  $\text{NO}_3^-$  and excess  $\text{N}_2$ . We also applied the methods presented by Blicher-Mathiesen et al. [1998] to evaluate the potential for degassing of groundwater. This method involves comparing the total partial pressures of dissolved gases in each sample to the hydrostatic pressure of the groundwater at the sample depth. Where partial pressures exceed hydrostatic pressure, the potential exists for degassing.

[19] Samples for analyses of the chlorofluorocarbons  $\text{CFC}_{11}$  (CFC-11),  $\text{CF}_2\text{Cl}_2$  (CFC-12), and  $\text{C}_2\text{F}_3\text{Cl}_3$  (CFC-113) were collected for age dating groundwater using a stainless steel sampling apparatus under an ultra-pure nitrogen atmosphere and were flame sealed in 62 cc borosilicate glass ampoules, thus preventing atmospheric contamination [Busenberg and Plummer, 1992]. Five ampoules were collected at each site, three of which were used for analyses by electron capture gas chromatography with a detection limit of 0.3 picograms per kilogram of water ( $\text{pg kg}^{-1}$ ) for CFC-11 and CFC-12 and 1.0  $\text{pg kg}^{-1}$  for CFC-113 [Busenberg and Plummer, 1992]. CFC's are known to exhibit varying degrees of susceptibility to biodegradation and sorption on organic matter, with CFC12 being least affected and CFC11 and CFC113 being the most affected [Cook et al., 1995; Lovely and Woodward, 1992; Plummer and Busenberg, 1999]. Consequently, CFC12 was used in most cases for age determinations. Sample ages were assigned on the basis of comparison of CFC equilibrium partial pressures, corrected for recharge temperature, with a chronology of atmospheric partial pressures [Busenberg and Plummer, 1992]. Recharge temperatures were estimated in two ways: (1) using Ar concentrations and assuming equilibrium with the atmosphere, and (2) where Ar was not measured, on the basis of the average annual temperature [Busenberg and Plummer, 1992]. Another potential source of uncertainty arises from the fact that CFC apparent ages reflect the year in which groundwater was last in contact with unsaturated zone air, but not necessarily the year in which it fell [Cook and Solomon, 1995]. Previous modeling work at this site has shown that it can take from 0.5 to 1 year for water to percolate through the vadose zone to the water table, so any error would be negligible. These methods result in a potential uncertainty of about  $\pm 2^\circ\text{C}$ , which translates to an age uncertainty of about 1 year prior to 1970, 1–3 years for 1970–1990, and 3 years or more for waters that recharged after 1990. The increasing uncertainty in recent years results from the flattening of the CFC input function due to reductions in CFC usage. Because they typically require some degree of subjective interpretation, CFC age dates are referred to as model or apparent ages [Plummer and Busenberg, 1999].

### 3.2. Denitrification

[20] Sediment samples were collected in August 1995 for denitrification rate assays using the acetylene block method, which blocks the conversion of  $\text{N}_2\text{O}$  to  $\text{N}_2$  [Yoshinari and Knowles, 1976; Yoshinari et al., 1977] so  $\text{N}_2\text{O}$  production can be used to measure potential denitrification rates

[Klmedston *et al.*, 1988; Morris *et al.*, 1988; Fujikawa and Hendry, 1991; Bradley *et al.*, 1995]. Sample sites were selected on the basis of water quality data collected during the 1994 sampling and on field data from the August 1995  $\text{NO}_3^-$  spatial distribution study. Our hypothesis was that denitrification was carbon limited in the forest at site OF1 and the wetland edge at site A1, but not under the river at site A5. Accordingly, sediment samples were collected in the forested area near the permanent piezometer nest OF1, the wetland edge at site A1, and the bottom of the river at site A5. The sediment near site OF1 was collected from the bottom of a 1 m deep, 5 cm diameter auger hole, at the water table. Sediment from the wetland edge at site A1 was collected from a 5 cm diameter, 30 cm deep auger hole, immediately below the peat layer at site A1. River sediment was collected at a depth of about 30 cm below the bed at site A5. Samples were placed in an autoclaved large-mouth glass jar, covered with water from the sample location, shipped to the laboratory on ice, and maintained at 4°C until the incubation began.

[21] Sediments were drained to decrease background concentrations of  $\text{NO}_3^-$  and dissolved C. Known amounts of  $\text{NO}_3^-$  and C were then added to the sediments. Methodology followed that previously described by Pfenning and McMahon [1996] with the exception of the  $\text{NO}_3^-$  and C concentrations, and had a detection limit of 2  $\text{nmol L}^{-1}$   $\text{N}_2\text{O}$  with a precision of  $\pm 5\%$ . These sediments were incubated in solutions containing 375, 714, or 1785  $\mu\text{mol L}^{-1}$   $\text{NO}_3^-$  with no additional C to test whether denitrification was limited by  $\text{NO}_3^-$  alone, or 0, 125, or 375  $\mu\text{mol L}^{-1}$  C with 375  $\mu\text{mol L}^{-1}$   $\text{NO}_3^-$  added to test whether denitrification was being limited by C. These concentrations are typical for groundwater in the area [Puckett *et al.*, 1999; Puckett and Cowdery, 2002].

[22] When the experiments were completed, sediments were oven-dried and weighed and a separate aliquot of each sample was analyzed for total carbon (C) and nitrogen, using a Carlo Erba elemental analyzer. A duplicate sample was exposed to hydrochloric acid fumes to remove inorganic C, after which organic C content was measured, and inorganic C was calculated as the difference between total and organic C [Hedges and Stern, 1984]. Concentrations were normalized using sediment dry weights.

[23]  $\text{N}_2\text{O}$  production was analyzed by linear regression of the time series data using a nonparametric, multifactor rank transformation test [Helsel and Hirsch, 1992] to test for significant differences ( $\alpha = 0.05$ ) in  $\text{N}_2\text{O}$  production rates among sites, and treatments. This procedure was carried out by ranking the  $\text{N}_2\text{O}$  production rates and performing an analysis of variance (ANOVA) on the ranks. This method approximates a nonparametric ANOVA on medians and is more robust than ANOVA on data not normally distributed or simply log-transformed. Where significant differences were determined, Tukey's HSD multiple comparison test was used to determine significant differences among the sites [Helsel and Hirsch, 1992].

## 4. Results

### 4.1. Surface Water

#### 4.1.1. Hydrology

[24] Mean daily flow during 1 October 1993 to 30 September 1994 was 5.0  $\text{m}^3 \text{s}^{-1}$  and ranged from 2.3 to

**Table 1.** Changes in Discharge and Chemistry at Two to Three Points on the 8.3 km Study Reach of the Otter Tail River<sup>a</sup>

Date	Site 1	Site 2	Upstream Net Change	Site 3	Downstream Net Change	Total Change
February 1994						
Discharge	2.1	–	–	2.5	0.4	0.4
June 1994						
Discharge	5.0	5.0	0	5.0	0	0
August 1994						
Discharge	2.6	2.8	0.2	3.0	0.2	0.4
$\text{NO}_3^-$	0	0	0	5.1	5.1	5.1
$\text{Cl}^-$	81.7	90.1	8.4	95.8	5.7	14.1
August 1995						
Discharge	2.1	2.1	0	1.9	–0.2	–0.2
$\text{NO}_3^-$	10	9.3	–0.7	12.1	2.8	2.1
$\text{Cl}^-$	87.3	90.1	2.8	98.6	8.5	11.3

<sup>a</sup> Site 1 is the farthest upstream site, and site 3 is the gage site shown in Figure 1. Discharge units are  $\text{m}^3 \text{s}^{-1}$ , and  $\text{NO}_3^-$  and  $\text{Cl}^-$  are in  $\mu\text{mol L}^{-1}$ . Values reported as "0" were less than the detection limit.

18.4  $\text{m}^3 \text{s}^{-1}$ . Typically, flows were largest during the spring quarter (April–June) as a result of snowmelt and runoff, and during the fall quarter (October–December) following leaf fall. Flows were lowest in the winter quarter (January–March) and during the summer (July–September), with the exception of August 1993, which coincided with an unusually wet summer throughout the region [Tornes *et al.*, 1997].

[25] Comparisons of flow at 2–3 points on the river during February 1994, June 1994, August 1994 and August 1995 (Table 1) revealed that flow increased through the 8.3 km study reach by as much as 20% during February 1994 and by 14% during late August 1994. It is interesting to note that the August 1994 increase of 0.4  $\text{m}^3 \text{s}^{-1}$  was almost as great as the 0.42  $\text{m}^3 \text{s}^{-1}$  value recorded in February 1994. The August sampling was on the last day of the month at the end of the growing season, when evapotranspiration losses may have been greatly reduced. The increases in flow during what were typically low-flow periods are what would be expected for a river that gains flow from groundwater discharge. Therefore it would appear that average groundwater discharge within the 8.3 km long reach is about 0.4  $\text{m}^3 \text{s}^{-1}$ . Flow through the same reach was constant in June 1994 but decreased by 9.2% (0.2  $\text{m}^3 \text{s}^{-1}$ ) in early August 1995. Assuming that the groundwater contribution of 0.4  $\text{m}^3 \text{s}^{-1}$  is relatively constant, this suggests a net loss of about 0.4  $\text{m}^3 \text{s}^{-1}$  in June 1994 and 0.6  $\text{m}^3 \text{s}^{-1}$  in August 1995.

#### 4.1.2. Water chemistry

[26] Nutrient concentrations in the river (Table 2) were small in spite of the intense agricultural inputs in fertilizer reported by Puckett *et al.* [1999]. Concentrations of  $\text{NO}_3^-$  were small and in a third of samples were below the reporting limit (3.6  $\mu\text{mol L}^{-1}$ ). The largest concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  typically occurred during the winter months, when biological uptake would have been lowest, whereas the concentrations were smallest during the summer, when biological uptake would have been most intense. Comparisons of  $\text{NO}_3^-$  and  $\text{Cl}^-$  concentrations at 3 points on the river during August 1994 and August 1995 revealed that concentrations of both constituents typically increased through the study reach (Table 1). On both sampling dates, concentrations of  $\text{NO}_3^-$  increased only in the lower segment of the reach whereas concentrations of  $\text{Cl}^-$  increased

**Table 2.** Concentrations of Selected Constituents in the Otter Tail River Between 8 February 1993 and 2 August 1995<sup>a</sup>

Constituent	Median	Range
pH	7.9	7.3–8.4
O <sub>2</sub>	246.9	68.8–393.8
HCO <sub>3</sub> <sup>-</sup>	3696	3229–4802
Ca <sup>2+</sup>	1048	923–1322
Mg <sup>2+</sup>	863.7	740.3–1111
Na <sup>+</sup>	200.1	156.6–282.8
K <sup>+</sup>	56.3	30.7–76.7
SiO <sub>2</sub>	233.0	124.8–316.2
Fe <sup>2+</sup>	1.68	0.32–3.2
Mn <sup>2+</sup>	0.96	0.29–2.4
Cl <sup>-</sup>	90.3	62.1–141.1
SO <sub>4</sub> <sup>2-</sup>	27.1	10.4–44.8
PO <sub>4</sub> <sup>3-</sup>	0.2	0–1.0
DP	0.2	0–1.0
TP	1.0	0.20–1.9
NO <sub>3</sub> <sup>-</sup>	5.0	0–46.4
NH <sub>4</sub> <sup>+</sup>	2.1	0.5–15.0
DKN	35.7	28.6–57.1
TKN	46.4	28.6–64.3
DOC	675.0	566.7–1000

<sup>a</sup> All concentrations are in  $\mu\text{mol L}^{-1}$  with the exception of pH, which is in standard units; DKN and TKN are reported as  $\mu\text{mol L}^{-1}$  N; dissolved organic carbon (DOC) is reported as  $\mu\text{mol L}^{-1}$  C; sample depths are in meters. DKN, dissolved Kjeldahl nitrogen; TKN, total Kjeldahl nitrogen. Values reported as “0” were less than the detection limit.

throughout the entire reach, indicating that evaporation alone was not responsible for the increase in concentration and that groundwater discharges were contributing NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> to the stream.

[27] Most nitrogen in the river was present in the organic form; typically about 86% of nitrogen was organic. Furthermore, about 77% of total organic nitrogen (TKN) was in a dissolved form (DKN). Concentrations of all forms of organic nitrogen were smallest during the growing season and largest in the winter months, probably due to decomposition of plant matter from the previous growing season. Total nitrogen fluxes were 127.5 Mg N in 1994. The largest fluxes of total nitrogen occurred during the spring (40.1 Mg N) and fall (39.9 Mg N) high-flow quarters with about 31% being transported in each. The winter (27.9 Mg N) and summer (19.7 Mg N) quarters accounted for about 22 and 16% of the annual flux, respectively.

[28] Like many rivers in western Minnesota, Otter Tail River chemistry (Table 2) is dominated by Ca<sup>2+</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> [Tornes *et al.*, 1997]. Glacial deposits in the area have been shown to contain calcite and dolomite, which controls the evolution of water chemistry [Berndt, 1987; Puckett and Cowdery, 2002; Tucillo *et al.*, 1999]. As a consequence, pH and concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> are about what would be expected for waters near equilibrium with calcite and dolomite, and saturation indices calculated in WATEQ were 0.3 and 0.4, respectively. Concentrations of Na<sup>+</sup> and K<sup>+</sup> on the other hand were small, accounting for less than 6% of total cations on an equivalent basis, and Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and SiO<sub>2</sub> concentrations were similarly small. There was virtually no difference between dissolved phosphorus and orthophosphate indicating that orthophosphate was the dominant dissolved form; however, their concentrations were small relative to total phosphorus, indicating that most phosphorus probably was associated with organic matter or suspended sediment. Dissolved Fe<sup>2+</sup>

and Mn<sup>2+</sup> were minor constituents, which is to be expected in waters that are typically well oxygenated. Dissolved organic carbon (DOC) concentrations were large, probably as a result of the wetlands along the river and in the lakes through which it flows.

## 4.2. Groundwater

### 4.2.1. Hydrology

[29] Water levels in the permanent piezometers OF1S, OF1A, OF1B, and OF1C were all consistently within a few centimeters of each other (medians were 407.54 m in August 1995 and 407.75 m in August 1997). Water levels in the deepest piezometer (OF1D) however were as much as 1.9 m greater than the other piezometers at the site (408.65 m in August 1995 and 409.66 m in August 1997), probably as a result of a thin silt layer immediately above it, indicating a strong upward flow potential in the deepest part of the aquifer adjacent to the river.

[30] Observations made along the riparian wetland study transect (A1-A5) revealed groundwater seepage in the vicinity of site A2, and minipiezometer head measurements were as much as 50 cm higher relative to surface water, decreasing toward the river (Figures 4b and 4c). Groundwater heads at other sites throughout the wetland (Figures 4b and 4c) were variable and ranged as much as 50 cm higher relative to surface water in one area near the river. There were also seepage areas at various locations along the wetland edge and springs were noted in the forested buffer zone. In general, these results indicate an area of potential groundwater discharge along the axis of the transect and across the wetland extending out under the river.

[31] Given reported hydraulic conductivities for the aquifer materials of 30.5–73.2 m d<sup>-1</sup>, average porosity of 0.25–0.3 [Cowdery, 1997; Puckett and Cowdery, 2002], and the measured heads and water levels, it is possible to estimate the average velocity of pore waters beneath the wetland. Gradients between piezometers OF1 and A4 ranged from 0.0042–0.026 resulting in estimated average velocities of 0.4–7.6 m d<sup>-1</sup>. At these velocities and assuming horizontal flow, it would take from 7–128 days with a median of 29 days, for water flowing under the wetland to traverse the 55.2 m from the permanent piezometer nest at OF1 to the outer edge of the wetland at A4.

### 4.2.2. Dissolved gases

[32] With the exception of site OF1S, O<sub>2</sub> concentrations (Tables 3 and 4) decreased with increasing age, depth, and distance along the wetland transect, suggesting that oxygen was being consumed within the system, presumably to oxidize organic carbon. Waters older than about 8 years, although not completely anoxic, were extremely hypoxic (O<sub>2</sub> < 16  $\mu\text{mol L}^{-1}$ ).

[33] Concentrations of N<sub>2</sub> (Table 4 and Figure 5) ranged from near equilibrium with the atmosphere (682  $\mu\text{mol L}^{-1}$  at 5.6°C) to 958  $\mu\text{mol L}^{-1}$  with a median of 842  $\mu\text{mol L}^{-1}$ . Ar concentrations ranged from 15.0 to 18.9  $\mu\text{mol L}^{-1}$ . Excess air estimates ranged from 0.6 to 1.41 cc kg<sup>-1</sup> with a median of 1.06 cc kg<sup>-1</sup>. Concentrations of both N<sub>2</sub> and excess N<sub>2</sub> were lower in OF1S and A1, then increased with depth and distance along the transect before decreasing again. Excess N<sub>2</sub> concentrations were as large as 284  $\mu\text{mol L}^{-1}$ , equivalent to 568  $\mu\text{mol L}^{-1}$  NO<sub>3</sub><sup>-</sup> assuming the excess N<sub>2</sub> was derived from denitrification.

**Table 3.** Median Concentrations of Major Ions in Samples Collected Between 1994 and 1997<sup>a</sup>

Site	Depth	pH	O <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SiO <sub>2</sub>	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Org-N	DOC
OF1S	3.35	7.16	9.4	5343	2495	1172	100.1	35.8	416.0	0	0.4	479.6	249.8	0.6	928.3	0.7	6.4	149.9
OF1A	5.19	7.43	43.8	4796	2196	946.0	87.0	38.4	366.1	0	0	423.2	333.1	0.6	628.4	0.6	6.5	91.6
OF1B	6.54	7.36	17.2	4605	2221	946.0	82.7	40.9	366.1	0	1.5	371.0	327.9	0.6	609.9	1.0	6.0	108.2
OF1C	9.97	7.22	2.3	5446	1946	863.7	139.2	40.9	432.6	50.7	11.3	162.2	84.3	1.3	0	20.5	4.2	199.8
OF1D	13.11	7.55	3.1	6058	1971	863.7	200.1	42.2	432.6	79.7	3.7	45.1	10.4	5.1	0	45.7	7.9	262.3
A1	1.0	7.34	101.1	4932	2495	1111	87.0	37.1	416.0	0	0	564.2	301.9	1.1	1249.6	1.8	5.3	104.1
A2	1.45	7.50	15.6	4720	2183	946.0	80.5	33.2	366.1	0	0	338.5	333.1	0.5	531.6	1.4	5.7	104.1
A2''	1.3	7.41	8.9	4739	2146	884.3	80.5	38.4	357.8	3.1	5.9	270.8	312.3	0.9	43.7	7.5	0	124.9
A3	1.0	7.31	1.8	5449	2146	884.3	84.8	42.2	549.1	55.5	7.6	310.3	244.6	1.4	0	11.1	3.2	154.3
A4	1.0	7.25	6.3	5655	2046	863.7	82.7	43.5	582.4	58.0	5.6	259.5	66.1	4.4	0	34.7	4.6	183.2
A5	0.5	7.06	10.2	6517	2171	822.6	113.1	51.1	865.3	131.2	7.5	172.1	0.5	2.7	0	194.6	27.3	283.1
River	-	7.99	246.9	3696	1048	864.0	200.1	56.3	233.0	1.68	0.9	90.3	27.1	0.2	5.0	2.1	44.3	675.0

<sup>a</sup> All concentrations are in  $\mu\text{mol L}^{-1}$  with the exception of pH, which is in standard units; organic nitrogen (Org-N) is reported as  $\mu\text{mol L}^{-1}$  N; dissolved organic carbon (DOC) is reported as  $\mu\text{mol L}^{-1}$  C; sample depths are in meters. Values reported as "0" were less than the detection limit.

[34] Sulfide (Table 4) was only detected in groundwater from sites that also had relatively small  $\text{SO}_4^{2-}$  concentrations, indicating that  $\text{SO}_4^{2-}$  reduction was occurring there. Because of the relatively large concentrations of  $\text{Fe}^{2+}$  and limited availability of  $\text{SO}_4^{2-}$  (Table 3) it is unlikely that free  $\text{S}^{2-}$  would reach even moderate concentrations due to its tendency to form metal sulfide precipitates.

[35] Concentrations of  $\text{CH}_4$  were negligible except in the deepest two piezometers at OF1 and toward the end of the wetland transect, with the largest concentrations at OF1D and A5 (Table 3). The large concentrations at A5 indicate strong reducing conditions. Concentrations of  $\text{CH}_4$  were so large at this site that we believe bubbles of gas formed, creating a space into which other gases evolved. Evidence of degassing can be seen in the low concentrations of  $\text{N}_2$  and Ar relative to other sample sites and the fact that both  $\text{N}_2$  and Ar concentrations are much less than their equilibrium concentrations. In addition, the sum of gas partial pressures equaled or exceeded hydrostatic pressure at site A5, indicating that degassing is likely to have occurred.

#### 4.2.3. CFC age dates

[36] CFC apparent ages ranged from 8 to 50 years (Table 4), displayed a pattern of increasing age with increasing depth at site OF1, and reflect the travel times from the upland recharge areas and the vertical age distribution of groundwater in the upgradient aquifer [Stoner *et al.*, 1997; Puckett and Cowdery, 2002]. Apparent ages also increased from 8 to 45 years with increasing distance along the study transect

from site A1 through A4. Because of degassing, age dating at site A5 was impossible.

[37] It is important to note that the 37 year difference in apparent ages between OF1S and A4 is inconsistent with the 7–128 day travel times estimated earlier for groundwater to travel the distance from OF1S to A4. In order for the assumption of horizontal flow to be correct, there should be no significant difference in water ages across the riparian wetland transect. In fact, the age distribution along the wetland transect was a horizontal reflection of the vertical age distribution at OF1, suggesting that groundwater of progressively greater age from the upgradient aquifer was discharging below the wetland and was the reason for the horizontal age distribution.

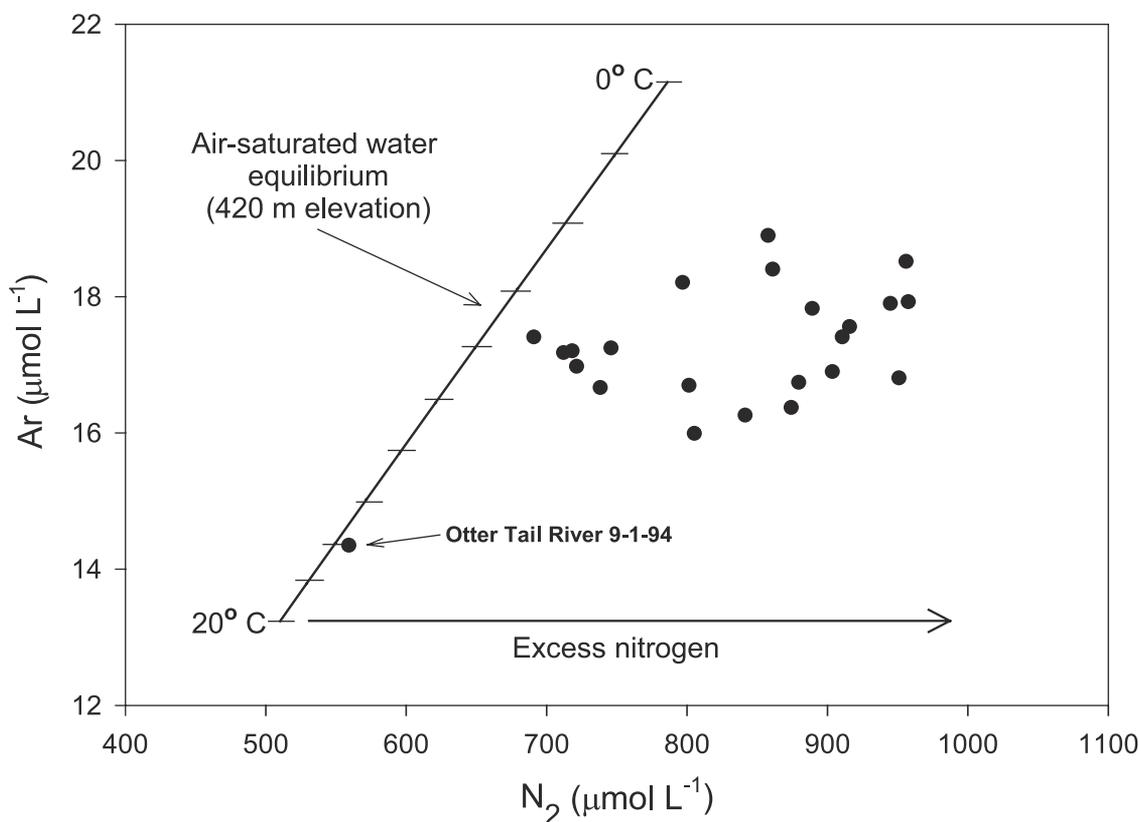
#### 4.2.4. Water chemistry

[38]  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  were the dominant dissolved species, which is consistent with what is known of the outwash mineralogy and agricultural applications. Puckett and Cowdery [2002] found that groundwater carbonate chemistry was controlled by dissolution of  $\text{CaCO}_3$  and  $\text{CaMg}(\text{CO}_3)_2$ . Interestingly, the concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  were considerably larger in groundwater than in the river but  $\text{Mg}^{2+}$  concentrations were about the same, suggesting that as groundwater discharges into the river  $\text{CaCO}_3$  may precipitate. This is further supported by the fact that groundwater generally was under saturated with  $\text{CaCO}_3$  and  $\text{CaMg}(\text{CO}_3)_2$  whereas the river was slightly over saturated with both.

**Table 4.** Median Concentrations of  $\text{S}^{2-}$ , Dissolved Gases,  $\text{NO}_3^-$ , Excess  $\text{N}_2$  ( $\text{Xs N}_2$ ), Reconstructed  $\text{NO}_3^-$  ( $\Sigma\text{NO}_3^-$ ), and CFC Apparent Ages of Samples Collected Between 1994 and 1997<sup>a</sup>

Site	$\text{S}^{2-}$	O <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	Ar	N <sub>2</sub>	Xs N <sub>2</sub>	NO <sub>3</sub> <sup>-</sup>	$\Sigma\text{NO}_3^-$	CFC Apparent Age
OF1S	0	11.5	788.6	0.1	17.2	746.3	60.3	1071.4	1192.0	8
OF1A	0	37.5	545.5	0	16.7	880.0	215.2	628.6	1059.0	22
OF1B	0	10.0	521.9	0	17.6	928.2	217.0	610.7	991.0	24
OF1C	0.78	2.3	600.8	15.5	18.2	957.3	243.5	0	487.0	46
OF1D	0.84	4.9	621.6	214.7	18.6	859.8	114.7	0	229.4	50
A1	0	87.5	690.9	0	17.2	712.6	29.5	1000.0	1059.0	8
A2	0	12.1	518.2	0	16.9	903.9	232.5	528.6	993.6	24
A2''	0	10.4	629.0	0.3	16.3	858.3	211.3	42.9	465.5	30
A3	0	2.6	865.1	11.6	16.3	803.8	155.6	0	311.2	28
A4	1.84	1.7	801.0	23.2	16.7	738.4	32.4	0	64.8	45
A5	1.00	2.2	1416.5	1010.8	10.1	340.2	-	0	-	-

<sup>a</sup> All concentrations are in  $\mu\text{mol L}^{-1}$ , and ages are in years.  $\text{NO}_3^-$  concentrations may differ from Table 3 because only samples having paired  $\text{N}_2$  gas data were included in the calculations. Values reported as "0" were less than the detection limit.



**Figure 5.** Argon and nitrogen gas concentrations in groundwater and their theoretical values assuming air-saturated water equilibrium at 420-m elevation and temperatures ranging from 0° to 20°C. Values to the right of the air-saturated water equilibrium line represent excess nitrogen concentrations. (Horizontal tick marks on the equilibrium line indicate Ar and N<sub>2</sub> equilibrium concentrations from 0° to 20°C in 2° increments).

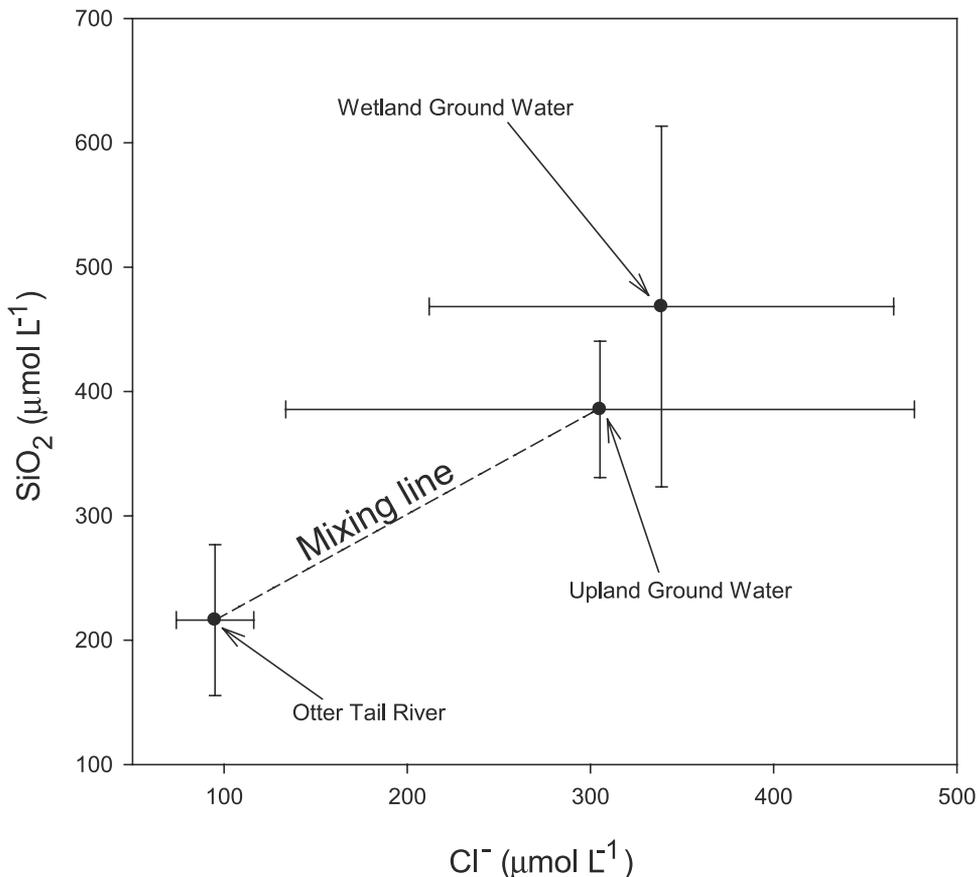
[39] SiO<sub>2</sub> concentrations were consistently larger in groundwater than in the river and accumulate as a product of silicate mineral weathering. Chloride concentrations also were larger in groundwater than in the river but tended to decrease with increasing depth and distance along the transect. Chloride occurs in fertilizer as potassium chloride (KCl) and is a common contaminant associated with agricultural areas [Anderson, 1993]. Comparisons of Cl<sup>-</sup> and SiO<sub>2</sub> concentrations in Otter Tail River water and in the groundwaters sampled under the wetland and in the adjacent upgradient aquifer (Figure 6) indicate that mixing of ground and surface waters in the riparian zone is unlikely since the wetland samples did not fall along the mixing line between the two end-members. Although concentrations of both Cl<sup>-</sup> and SiO<sub>2</sub> were significantly larger in wetland and upland groundwater than in the river, they did not differ significantly ( $\alpha = 0.05$ ) among themselves.

[40] SO<sub>4</sub><sup>2-</sup> concentrations in groundwater were much larger than in the river but tended to decrease with increasing depth at OF1 and distance along the transect from the forest to the river. There is little available sulfur in the outwash sediments; therefore, it is commonly supplied as an agricultural supplement either as gypsum (CaSO<sub>4</sub> · 2H<sub>2</sub>O) or in more recent years as ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) at rates of 28–336 kg S ha<sup>-1</sup> (D. Cooper, University of Minnesota Extension Service, oral communication, 1996). Puckett and Cowdery [2002] estimated these application

rates would result in a spatially average concentration of 495–5930 μmol SO<sub>4</sub><sup>2-</sup> L<sup>-1</sup> and therefore can easily account for the observed groundwater concentrations. The lower concentrations are associated with the oldest groundwaters, which is to be expected because less fertilizer was used at that time. Also, the older waters are more likely to have undergone some degree of SO<sub>4</sub><sup>2-</sup> reduction; a conclusion supported by the observation that S<sup>2-</sup> concentrations increased sharply in those samples in which SO<sub>4</sub><sup>2-</sup> concentrations sharply decreased.

[41] Manganese concentrations reached as much as 11 μmol L<sup>-1</sup> and typically reached a maximum where most NO<sub>3</sub><sup>-</sup> had been consumed and Fe<sup>2+</sup> was increasing. Iron concentrations displayed a large range, from below detection to as high as 131 μmol L<sup>-1</sup>. Such relatively large concentrations of dissolved iron suggests that the predominant terminal electron accepting process had changed from reduction of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, and manganese oxides to iron oxide reduction. This pattern agrees with the reported redox sequence in which manganese oxide reduction occurs at pE levels after denitrification and before iron oxide reduction [Stumm and Morgan, 1981].

[42] Concentrations of NO<sub>3</sub><sup>-</sup> behaved like O<sub>2</sub>, generally decreasing with increasing age, depth, and distance along the transect (Tables 3 and 4). This decreasing pattern suggests that once O<sub>2</sub> was limiting, NO<sub>3</sub><sup>-</sup> was utilized as the terminal electron acceptor in the oxidation of organic



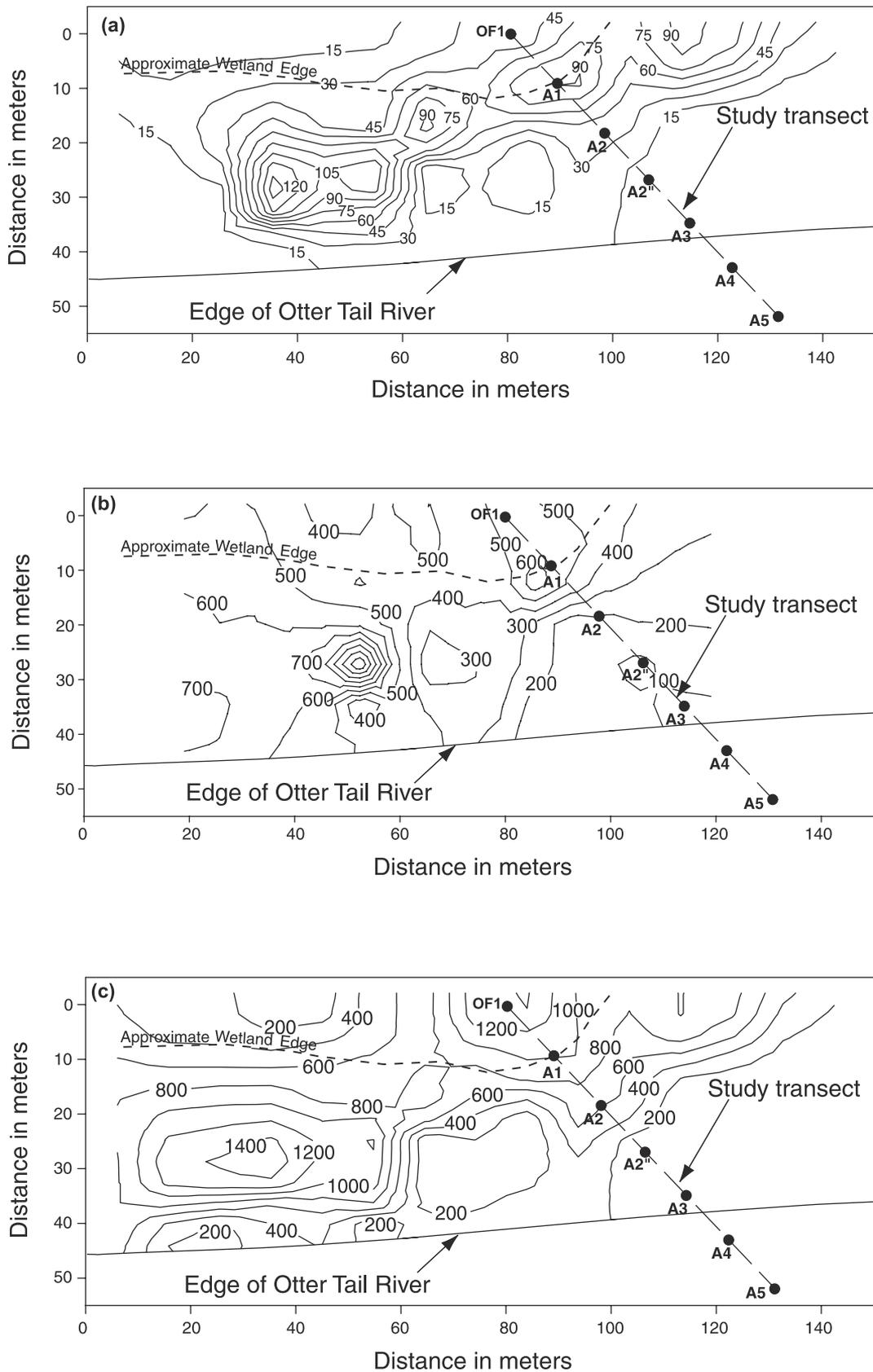
**Figure 6.** Concentrations of  $\text{Cl}^-$  and  $\text{SiO}_2$  in wetland and upgradient groundwaters and in the Otter Tail River. (Data points are averages, and error bars are 1 standard deviation).

carbon. Samples greater than about 30 years old were virtually depleted of  $\text{NO}_3^-$ .  $\text{NH}_4^+$  concentrations generally increased with increasing age, depth, and distance along the transect (Table 3). Although the exact source of  $\text{NH}_4^+$  was not determined, in other studies of sediments in similar redox environments,  $\text{NH}_4^+$  production has been traced to mineralization of nitrogen in buried organic matter and not to dissimilatory nitrate reduction [McMahon *et al.*, 1999]. Other forms of nitrogen were negligible. Excess  $\text{N}_2$  concentrations first increased and then decreased with both increasing age and depth at OF1 and increasing age and distance along the transect from A1 to A4 (Table 4). The decrease in measured  $\text{NO}_3^-$  concentrations was related primarily to removal of  $\text{NO}_3^-$  by denitrification as well as lower fertilizer use in earlier years. The more complex pattern for excess  $\text{N}_2$  occurred because in younger groundwater, as  $\text{NO}_3^-$  was being converted to  $\text{N}_2$  through denitrification, its concentration increased. The decrease in excess  $\text{N}_2$  concentrations in samples of older groundwater, however, reflected the smaller amounts of fertilizer used in the earlier years so there was less  $\text{NO}_3^-$  to convert to  $\text{N}_2$ . The distribution of the reconstructed  $\text{NO}_3^-$  concentrations calculated as the sum of measured  $\text{NO}_3^-$  and excess  $\text{N}_2$  was similar to that of measured  $\text{NO}_3^-$ . The decrease in reconstructed  $\text{NO}_3^-$  concentrations with both increasing age and depth was due to the fact that less fertilizer was applied in the earlier years when these older groundwaters recharged. About 69% (adjusted  $r^2 = 0.689$ ) of the variance in

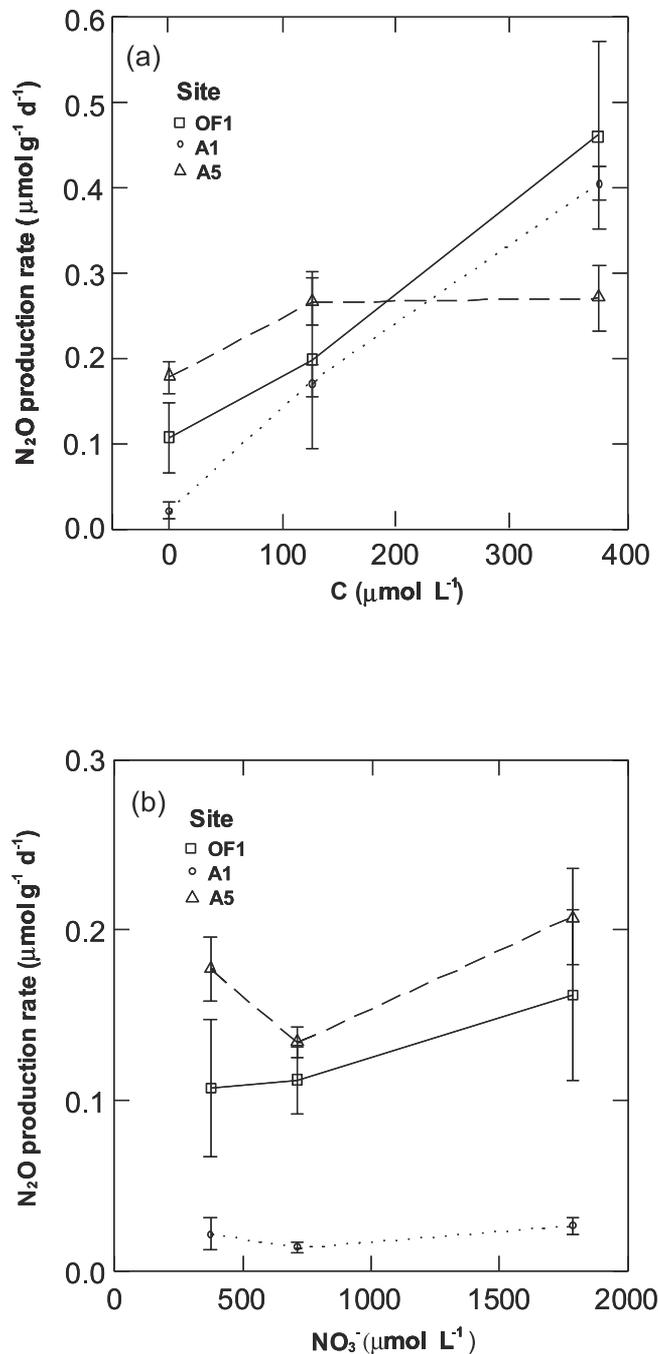
reconstructed  $\text{NO}_3^-$  concentrations was explained by the corresponding groundwater age with the remaining variation presumably due to annual variability in the amount of fertilizer applied in the past, the amount of nitrogen removed in harvested crops, volatilization and other losses prior to and during recharge.

[43] Results of the spatial distribution study revealed overlapping areas of relatively high  $\text{O}_2$  and  $\text{NO}_3^-$  concentrations (Figures 7a and 7b) that appear to be associated with groundwater highs between elevations of 407.4 and 407.55 m (Figures 4b and 4c). Examination of the heads also suggests that like the study transect (A1-A5) the generalized discharge zone actually intersects the river at an angle of about  $45^\circ$  instead of being perpendicular to it. The result is that although  $\text{O}_2$  and  $\text{NO}_3^-$  concentrations decreased toward the river,  $\text{NO}_3^-$  concentrations still exceeded  $400 \mu\text{mol L}^{-1}$  about 70 m upstream of site A3 at the edge of the river and were greater than  $200 \mu\text{mol L}^{-1}$  under the river.

[44] The presence of  $\text{NO}_3^-$  at relatively large concentrations under the river is significant in that it indicates that groundwater containing  $\text{NO}_3^-$  was able to move along flow paths, under the wetland, where little if any  $\text{NO}_3^-$  was removed. Furthermore, the spatial distribution study results demonstrate the potential heterogeneity of the riparian zone and the need to conduct these types of riparian zone studies. For example, on the basis of results of the wetland transect portion of the study from OF1 to A5 alone, it



**Figure 7.** Contour maps showing spatial distribution of (a) dissolved oxygen in August 1995 and (b and c) nitrate concentrations in the 40 m by 140 m study area in the riparian wetland in August 1994 and 1995, respectively. (Contour intervals are 15  $\mu\text{mol L}^{-1}$  for dissolved oxygen, 100  $\mu\text{mol L}^{-1}$  for nitrate in 1994, and 200  $\mu\text{mol L}^{-1}$  for nitrate in 1995).



**Figure 8.** Denitrification rates (expressed as  $\mu\text{mol N}_2\text{O g}^{-1} \text{d}^{-1}$ ) in response to (a) organic carbon amendments for sediments at OF1, A1, and A5 and (b)  $\text{NO}_3^-$  amendments for sediments at OF1, A1, and A5 with no additional organic C. (Data points are averages, and error bars are 1 standard deviation).

would be easy to incorrectly infer that all  $\text{NO}_3^-$  was removed before it reached the river. However, our results from the spatial distribution study clearly show that at some locations,  $\text{NO}_3^-$  does reach the river and explains how the downstream increase in  $\text{NO}_3^-$  observed in the Otter Tail River occurred.

#### 4.3. Denitrification

[45] Denitrification rates (expressed as  $\mu\text{mol N}_2\text{O g}^{-1} \text{d}^{-1}$ ) measured by the acetylene block incubation method gener-

ally increased with increasing organic C concentrations, especially in sediments from OF1 and A1 (Figure 8a). Site A5 sediment incubation responses (Figure 8a) were virtually the same for the 125 and 375  $\mu\text{mol L}^{-1}$  organic C amendments, indicating that organic C did not limit denitrification beneath the river. Statistically, the responses to  $\text{NO}_3^-$  additions of 375 and 714  $\mu\text{mol L}^{-1}$  with C amendments held constant, were not significantly different from one another, but were significantly less than the rates at 1785  $\mu\text{mol L}^{-1}$ . In spite of the significantly larger rates at 1785  $\mu\text{mol L}^{-1}$   $\text{NO}_3^-$ ,

**Table 5.** Organic Carbon and Nitrogen Content of the Sediments and Concentrations of DOC, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and O<sub>2</sub> in Groundwater From Each Site at the Time of Sample Collection<sup>a</sup>

	OF1	A1	A5
Organic carbon, %	0.38	0.69	1.08
Nitrogen, %	0.055	0.060	0.065
DOC, μmol C L <sup>-1</sup>	100.0	100.0	283.3
NO <sub>3</sub> <sup>-</sup> , μmol L <sup>-1</sup>	599.8	1099.7	0
NH <sub>4</sub> <sup>+</sup> , μmol L <sup>-1</sup>	1.4	1.4	150.0
O <sub>2</sub> , μmol L <sup>-1</sup>	15.6	101.3	1.6

<sup>a</sup> Values reported as "0" were less than the detection limit.

the slopes of regression lines fit through the rates for each site were all zero, indicating the response to NO<sub>3</sub><sup>-</sup> addition alone was not significant (Figure 8b).

[46] The strongest denitrification response therefore was to organic C amendment, particularly the highly linear response of forest (OF1) and wetland edge (A1) sediments (Figure 8a). This positive response to organic C and limited response to NO<sub>3</sub><sup>-</sup> indicates that denitrification is organic C limited at all sites except in river sediments at A5. The wetland edge sediments at A1, with their moderate organic C content and relatively high groundwater NO<sub>3</sub><sup>-</sup> concentration (Table 5), had the lowest overall denitrification rates in the absence of added organic carbon, but these rates were equal to or greater than rates for the forest sediments at OF1 when both organic C and NO<sub>3</sub><sup>-</sup> were added (Figures 8a and 8b).

## 5. Discussion

[47] Several studies have reported denitrification rates for sand and gravel sediments [Trudell *et al.*, 1986; Smith and Duff, 1988; Lowrance, 1992; Smith *et al.*, 1996; Aelion and Shaw, 2000; Tesoriero *et al.*, 2000]. These rates fall within a range of 0–0.44 μmol N<sub>2</sub>O g<sup>-1</sup> d<sup>-1</sup> however those reported by Smith and Duff [1988], Smith *et al.* [1996], and Lowrance [1992] were at the lower end of that range (0.001–0.007 μmol N<sub>2</sub>O g<sup>-1</sup> d<sup>-1</sup>) for aquifers in Cape Cod and south Georgia, respectively. Trudell *et al.* [1986], Aelion and Shaw [2000], and Tesoriero *et al.* [2000] covered the entire range of values (0–0.44 μmol N<sub>2</sub>O g<sup>-1</sup> d<sup>-1</sup>) for aquifers and stream sediments in southern Ontario, South Carolina and, western British Columbia, respectively. The Otter Tail results (0.012 to 0.417 μmol N<sub>2</sub>O g<sup>-1</sup> d<sup>-1</sup>) are similar to those reported by the latter group of investigators and the aquifer is similar in composition and organic carbon content to the southern Ontario site, and denitrification was carbon limited in both studies.

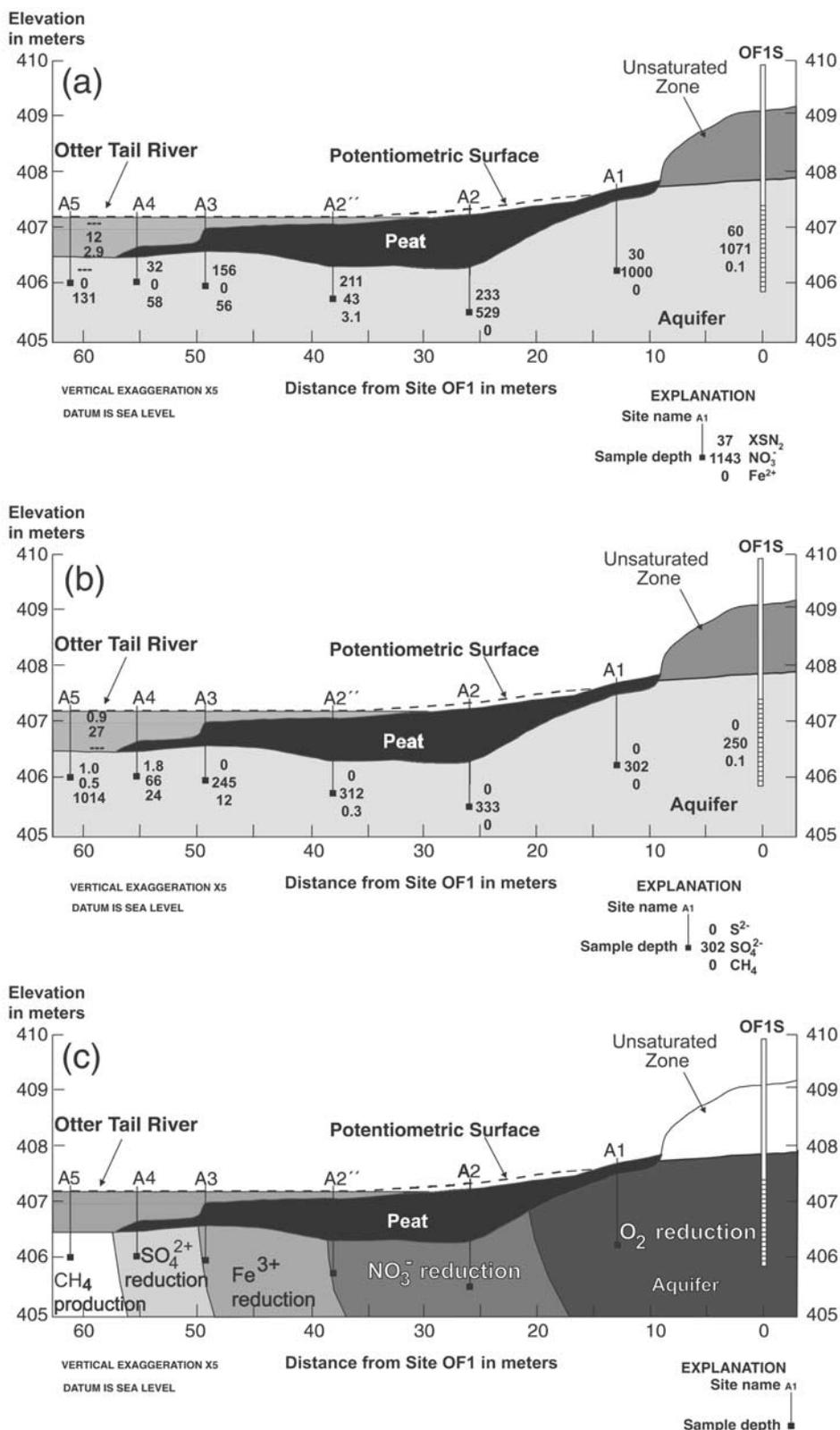
[48] Where the oxidation of organic carbon does occur, O<sub>2</sub> is thermodynamically favored over NO<sub>3</sub><sup>-</sup> as the terminal electron acceptor [Stumm and Morgan, 1981; Korom, 1992; Chapelle, 1993; Chapelle *et al.*, 1995]. When sufficient O<sub>2</sub> is consumed to limit microbial aerobic respiration, denitrification becomes the thermodynamically favored terminal electron accepting process, leading to lower NO<sub>3</sub><sup>-</sup> concentrations as well. Once most of the available NO<sub>3</sub><sup>-</sup> is consumed, bacteria utilize manganese oxides and then iron oxides as terminal electron acceptors. Under very strong reducing conditions, bacteria capable of deriving energy from sulfate reduction and methanogenesis are favored. The

net result of this evolution of water chemistry is a predictable sequence in which O<sub>2</sub> and then NO<sub>3</sub><sup>-</sup> are consumed, manganese and iron come into solution, sulfate is consumed and sulfide may come into solution, and finally methane may appear in solution [Stumm and Morgan, 1981; Korom, 1992; Chapelle, 1993; Chapelle *et al.*, 1995]. By sampling along groundwater flow paths, it may be possible to observe this sequence and thereby infer the redox state and dominant chemical processes involved.

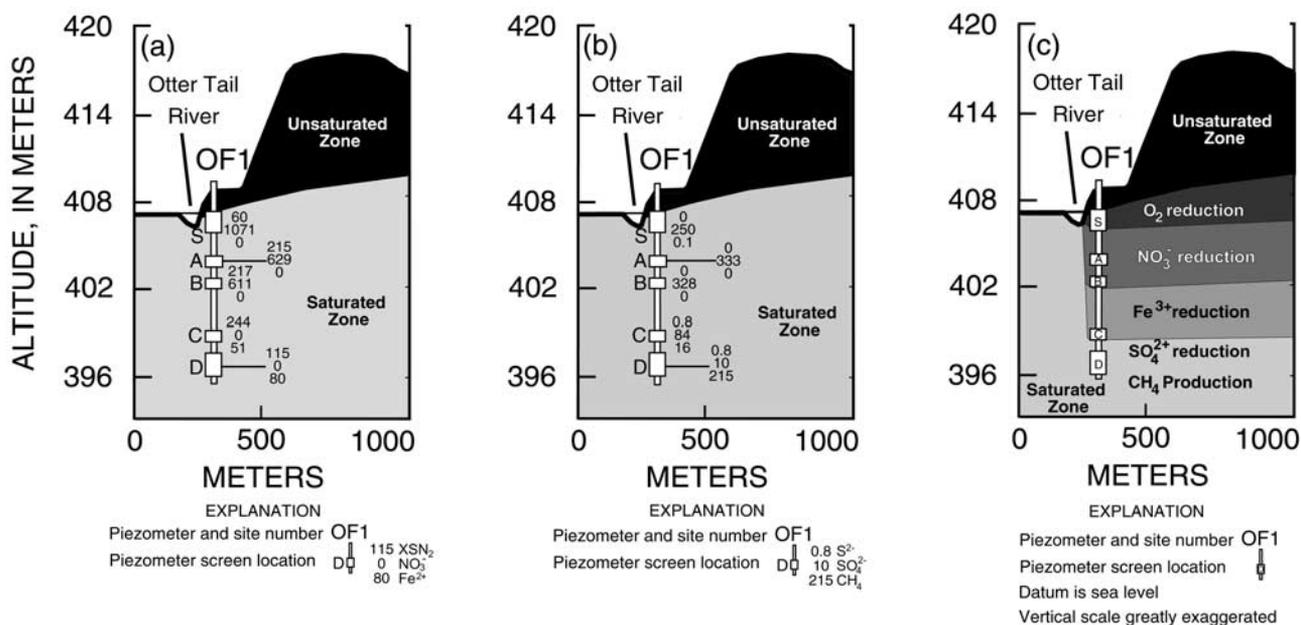
[49] The distribution of the redox sensitive constituents measured in this study suggest that as groundwater flows under the wetland peat it passes first through a zone between sites OF1 and A1 where O<sub>2</sub> was being reduced and the presence of about 30–60 μmol L<sup>-1</sup> excess N<sub>2</sub> indicated limited denitrification was occurring (Tables 3 and 4), then between A1 and A2'' where NO<sub>3</sub><sup>-</sup> was completely denitrified to N<sub>2</sub> gas (Figure 9a). Between sites A2'' and A3, Fe<sup>2+</sup> came into solution (Figure 9a) presumably as a result of iron oxide reduction, and between sites A3 and A5 there was almost complete reduction of SO<sub>4</sub><sup>2-</sup> to S<sup>2-</sup> (Figure 9b). Also between sites A3 and A5 CH<sub>4</sub> was produced as the result of methanogenesis (Figure 9b). The resulting redox sequence (Figure 9c) is similar to that conceptualized by Correll *et al.* [1992] for horizontal flow systems of the Atlantic Coastal Plain and therefore appears to support our hypothesis that NO<sub>3</sub><sup>-</sup> was being removed in the riparian buffer zone by denitrification due to the progressively stronger redox conditions under the wetland. This interpretation would assume that groundwater was flowing horizontally beneath the wetland in a manner similar to that shown in Figure 2a.

[50] Horizontal flow systems like that depicted in Figure 2a have been shown to occur in a number of studies of denitrification in riparian zones. Mengis *et al.* [1999] demonstrated denitrification in a southern Ontario riparian zone having saturated thickness of <1.5 m and a horizontal flow system over a clay till. Results of a study by Devito *et al.* [2000] demonstrated denitrification along horizontal flow paths in another riparian zone in southern Ontario having 4–6 m saturated thickness above a clay-confining layer. Several studies in the southeastern Atlantic Coastal Plain of the United States suggest that shallow flow systems of this type may be common there [Correll *et al.*, 1992; Jacobs and Gilliam, 1985; Jordan *et al.*, 1993; Lowrance, 1992; Puckett, 1999; Shedlock *et al.*, 1993]. For example, Correll *et al.* [1992] and Jordan *et al.* [1993] reported most NO<sub>3</sub><sup>-</sup> was removed from groundwater in riparian zones in Maryland having saturated thickness of <2 m and horizontal flow above a clay confining unit. Lowrance *et al.* [1984] reported similar results for a site in Georgia having saturated thickness of <1.5 m. Correll *et al.* [1992] proposed that the presence of shallow confining units was an important factor in the function of these riparian buffer zones in that groundwater was forced to remain in contact with vegetation and reducing conditions there. Although a clay lens about 30 cm thick was identified at a depth of 10.5 m at site OF1, there are no known shallow clay confining units beneath the Otter Tail riparian zone, and the underlying clay till surface is about 16 m below land surface.

[51] Although the results seem to support the hypothesis of horizontal flow, examination of the data from the piezometers at site OF1 (Figure 10) revealed a vertical



**Figure 9.** Concentrations of (a) excess N<sub>2</sub> (XS N<sub>2</sub>), NO<sub>3</sub><sup>-</sup>, and Fe<sup>2+</sup>, (b) S<sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and CH<sub>4</sub>, and (c) the redox state of groundwater along the transect from OF1S-A5. (All concentrations are μmol L<sup>-1</sup>).



**Figure 10.** Concentrations of (a) excess N<sub>2</sub> (XS N<sub>2</sub>), NO<sub>3</sub><sup>-</sup>, and Fe<sup>2+</sup>, (b) S<sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and CH<sub>4</sub>, and (c) the redox state of groundwater in the permanent piezometers at site OF1. (All concentrations are μmol L<sup>-1</sup>).

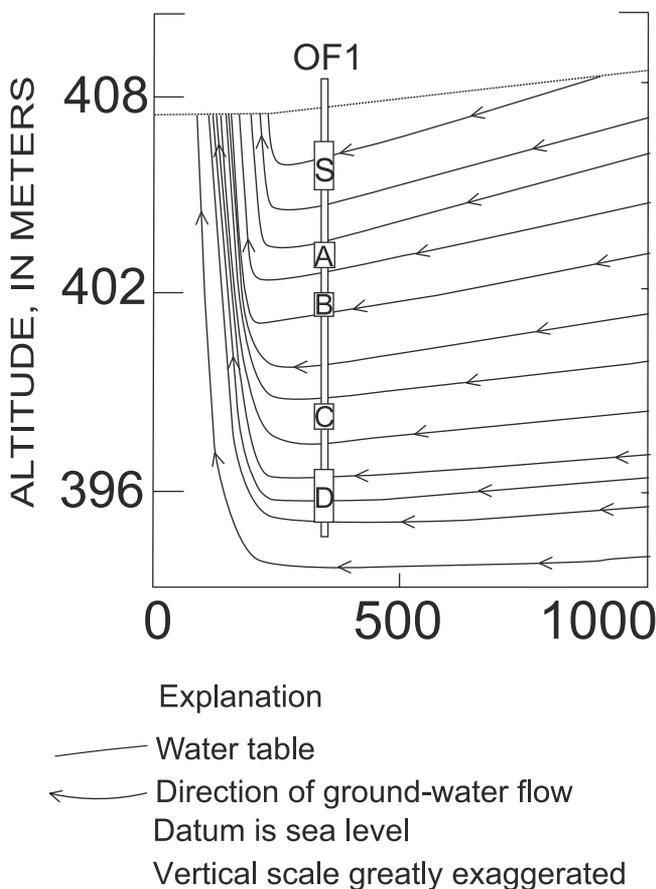
chemical sequence similar to the horizontal sequence shown in Figure 9. Groundwater in the upper portion of the aquifer at site OF1S was suboxic (<65 μmol L<sup>-1</sup> O<sub>2</sub>) (Tables 3 and 4) and the presence of about 60 μmol L<sup>-1</sup> excess N<sub>2</sub> indicates that some denitrification had taken place. At sites OF1A and OF1B, an almost total lack of O<sub>2</sub> and large amounts of excess N<sub>2</sub> indicated that this zone was dominated by denitrification. Between sites OF1B and OF1C, NO<sub>3</sub><sup>-</sup> was totally removed and reduction of iron oxides resulted in Fe<sup>2+</sup> coming into solution (Figure 10a). Also at OF1C (Figure 10b), S<sup>2-</sup> was present and SO<sub>4</sub><sup>2-</sup> concentrations decreased sharply, indicating that SO<sub>4</sub><sup>2-</sup> reduction was occurring and some CH<sub>4</sub> was present, indicating methanogenesis was beginning. Finally, at OF1D, SO<sub>4</sub><sup>2-</sup> concentrations further decreased and CH<sub>4</sub> increased indicating that methanogenesis was becoming the dominant redox process. The resulting redox sequence (Figure 10c) was previously described by Puckett and Cowdery [2002] for the upgradient aquifer and results from a combination of oxidation of organic carbon in the sediments and the relatively long (>50 year) residence time. We propose that the redox sequence shown in Figure 9c is a horizontal reflection of the vertical sequence between OF1S and OF1D (Figure 10c) and supports our alternative hypothesis that the changes in chemistry along the riparian wetland transect were the result of progressively older and more chemically reduced groundwater from the upgradient aquifer discharging under the wetland in a manner similar to that shown in Figure 2b.

[52] The similar water chemistry and redox sequences, therefore, can lead to conflicting interpretations as to which of the hydrologic flow systems are correct; however, the CFC apparent age dates and groundwater head measurements provide the most compelling evidence of which of the flow systems is most plausible. Groundwaters at site OF1

become progressively older with depth, ranging from 8 to 50 years in age (Table 4). This age distribution arises due to the differential travel times and flow path lengths from the upgradient recharge zones to the discharge zone at the river [Stoner *et al.*, 1997; Puckett and Cowdery, 2002]. The age distribution found along the wetland transect (Table 4) indicates that groundwater similar in age and chemistry to that at OF1 was discharging under the wetland and this conclusion is supported by the groundwater modeling results of Puckett and Cowdery [2002] shown in Figure 11. Head measurements along the wetland transect also provide evidence of a groundwater discharge zone there. Furthermore, the presence of a horizontal flow system is unlikely given our calculations of potential groundwater velocities, which indicated that if horizontal flow was occurring there should be no measurable differences in age along the wetland transect.

[53] The flow system shown in Figures 2b and 11 explains why the age distribution and water chemistry found at site OF1 would be repeated in the discharge zone associated with the wetland transect. As shown, shallow, younger groundwater discharges in seeps and springs at the break in slope near the edge of the wetland, and deeper, older groundwater discharges at progressively greater distances along the transect. This flow system also indicates that the presence of progressively more reduced zones along the transect are largely the result of the progressively older and more reduced groundwaters from the upgradient aquifer discharging there. Consequently, a horizontal flow system such as that shown in Figure 2a was ruled out in favor of the deeper version shown in Figure 2b.

[54] In the absence of shallow confining units, groundwater flow systems similar to those shown in Figure 2b may develop, the depth and complexity of which are determined largely by the general slope and local relief [Toth, 1963].



**Figure 11.** The groundwater flow system for the study area based on results from the Modflow/Modpath groundwater particle-tracking model presented by *Puckett and Cowdery* [2002]. Flow lines reflect the movement of particles originating at various points along the transect and do not represent equal volumes of flow.

*Bohlke and Denver* [1995] demonstrated similar flow system dynamics in their investigation of two agricultural watersheds in Atlantic Coastal Plain of Maryland. In their study, flow paths up to 20 m deep exhibited residence times of 30–50 years, and bypassed the riparian zone to discharge directly into a stream. *Modica et al.* [1998], working in similar watersheds in New Jersey with depths up to 55 m, found residence times >45 years also and groundwater discharging directly to streambeds. The results of our study indicate that saturated thickness of as little as 16 m is adequate for development of these long, deep flow systems. Depending on their configuration, these deeper flow systems may result in groundwater being discharged into both the riparian zone and streambed, or directly into streambeds alone.

## 6. Conclusions

[55] Moderately deep flow systems like that identified in this study pose several implications for the effectiveness of riparian buffer zones to remove  $\text{NO}_3^-$  and also for researchers investigating the processes involved. Such deep flow systems may allow  $\text{NO}_3^-$  in groundwater to be carried beneath riparian buffer zones and discharge unaltered into

streams. The riparian buffer zone in this study had only a minor role in preventing  $\text{NO}_3^-$  in groundwater from reaching the Otter Tail River for two reasons: (1) most  $\text{NO}_3^-$  had been removed by denitrification in the upgradient aquifer, and (2) shallow groundwater containing  $\text{NO}_3^-$  was able to move along some flow paths below the riparian zone where little  $\text{NO}_3^-$  was removed. Although we did not investigate the process, it is likely that some  $\text{NO}_3^-$  was removed from discharging groundwater as it moved upward through the peat and hyporheic zone of the streambed.

[56] Such moderately deep flow systems make it necessary for investigators to develop a complete understanding of the hydrologic flow system in the study area and the upgradient aquifer in order to be able to distinguish between biogeochemical processes that may be taking place in the riparian buffer zone and those that are controlled instead by processes in the upgradient aquifer. For example, by sampling along a discharge gradient across a riparian buffer zone like the one reported here, investigators may misinterpret decreases in  $\text{NO}_3^-$  concentrations occurring due to either increasing age or denitrification in the upgradient aquifer as evidence for denitrification in the riparian buffer zone. These conclusions are especially applicable to aquifers where a shallow confining layer is absent. More importantly, by developing an understanding of the hydrology and biogeochemistry of both the riparian and upgradient aquifer and how they interact, we can in the end develop a more accurate capability to predict when and where riparian buffer zones will be most effective in protecting water quality.

[57] As we have shown in this study, residence time and age of groundwater are important factors because fertilizer nitrogen use throughout the United States has increased 20 fold in the last 55 years. Consequently, long and deep flow systems contain older groundwaters with potentially less  $\text{NO}_3^-$  simply because less fertilizer was used when these waters entered the aquifer. In addition, long residence times may allow biogeochemical processes to remove  $\text{NO}_3^-$  even in systems where the process is carbon limited. Conversely, short and shallow flow systems have short residence times allowing less time for  $\text{NO}_3^-$  to be removed by biogeochemical processes, and greater potential for larger  $\text{NO}_3^-$  concentrations because more fertilizer may have been applied at the time of recharge. These differences in flow systems pose challenges for  $\text{NO}_3^-$  management strategies. Although shallow flow systems with short flow paths and short residence times may contain the largest  $\text{NO}_3^-$  concentrations, they will respond more quickly (on the order of a few years to a couple decades) to decreased  $\text{NO}_3^-$  inputs in the recharge area. However, deep flow systems with long flow paths and long residence times may require several decades to a century for decreases in  $\text{NO}_3^-$  input to be reflected in the discharge zone. As a compensating factor, longer residence times may provide sufficient time for slow reactions, such as the carbon-limited denitrification noted at this site, to remove  $\text{NO}_3^-$  before it is discharged to surface waters.

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