

Mechanism and rate of denitrification in an agricultural watershed:

Electron and mass balance along groundwater flow paths

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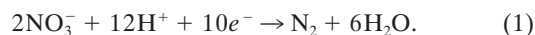
Abstract. The rate and mechanism of nitrate removal along and between groundwater flow paths were investigated using a series of well nests screened in an unconfined sand and gravel aquifer. Intensive agricultural activity in this area has resulted in nitrate concentrations in groundwater often exceeding drinking water standards. Both the extent and rate of denitrification varied depending on the groundwater flow path. While little or no denitrification occurred in much of the upland portions of the aquifer, a gradual redox gradient is observed as aerobic upland groundwater moves deeper in the aquifer. In contrast, a sharp shallow redox gradient is observed adjacent to a third-order stream as aerobic groundwater enters reduced sediments. An essentially complete loss of nitrate concurrent with increases in excess N_2 provide evidence that denitrification occurs as groundwater enters this zone. Electron and mass balance calculations suggest that iron sulfide (e.g., pyrite) oxidation is the primary source of electrons for denitrification. Denitrification rate estimates were based on mass balance calculations using nitrate and excess N_2 coupled with groundwater travel times. Travel times were determined using a groundwater flow model and were constrained by chlorofluorocarbon-based age dates. Denitrification rates were found to vary considerably between the two areas where denitrification occurs. Denitrification rates in the deep, upland portions of the aquifer were found to range from <0.01 to 0.14 mM of N per year; rates at the redoxcline along the shallow flow path range from 1.0 to 2.7 mM of N per year. Potential denitrification rates in groundwater adjacent to the stream may be much faster, with rates up to 140 mM per year based on an in situ experiment conducted in this zone.

1. Introduction

Nitrate (NO_3^-) is a widespread pollutant of shallow groundwater and often poses a serious threat to the quality of public drinking water supplies. In fact, it has been suggested that nitrate may be the most ubiquitous contaminant of groundwater in the world [Spalding and Exner, 1993]. Furthermore, groundwater containing high concentrations of nitrate discharging to streams may pose a serious threat to the stability and diversity of aquatic biota in some ecosystems [Cooper, 1993]. According to the Clean Water Action Plan [U.S. Environmental Protection Agency and U.S. Department of Agriculture, 1998], overenrichment by nutrients is the largest overall source of impairment of the nation's rivers and streams. While overlooked in many nutrient management plans, groundwater discharges of nitrate to streams may contribute the majority of the total amount of stream nitrogen [e.g., Williamson et al., 1998].

To better understand and anticipate the threat that nitrate

contamination poses to drinking water quality and streams, it is essential that the fate of this compound is better understood. Removal of nitrate from groundwater occurs primarily by either denitrification or reduction to ammonium (NH_4^+). Denitrification refers to a microbial respiratory process where nitrate is used as terminal electron acceptor and is reduced to N_2 by the following generalized half reaction:



Intermediates in this reaction may include nitrite (NO_2^-), nitric oxide (NO), and nitrous oxide (N_2O). Most denitrifying bacteria are facultative anaerobes [Firestone, 1982] and as such are capable of surviving with or without dissolved oxygen (O_2). Facultative anaerobes begin to use nitrate as an electron acceptor when O_2 becomes limited. In anaerobic environments, denitrifiers compete with organisms that dissimilate nitrate to ammonium. Unlike the end products of denitrification, ammonium can be converted back to nitrate by nitrification should groundwater enter an aerobic zone. Since both mechanisms can occur in anaerobic systems, measuring the products of these reactions is necessary to determine the dominant pathway [Tiedje, 1982].

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The high concentrations of nitrate introduced into groundwater by agricultural practices typically far exceed the reduction capacity present in dissolved species. As such, "extra" reduction capacity must be present in the sediments for appreciable amounts of nitrate reduction to occur. Organic carbon is the most common electron donor, and its role in the reduction of nitrate has been studied in both field [e.g., *Trudell et al.*, 1986; *Smith et al.*, 1991a] and laboratory experiments [e.g., *Smith and Duff*, 1988]. Reduced inorganic species may also serve as electron donors for nitrate reduction. Sulfur and to a lesser degree ferrous iron (Fe^{2+}) from iron sulfide mineral (e.g., pyrite) dissolution are the most common inorganic species suggested as possible electron donors in denitrification reactions [*Kölle et al.*, 1985; *Postma et al.*, 1991].

The ability of stream riparian zones to remove nitrate has been promoted as a way to reduce the effects of pollution from nonpoint sources [*Osbourne and Kovacic*, 1993; *Mengis et al.*, 1999]. Stream riparian zones are defined as those areas which have direct interaction between terrestrial and aquatic ecosystems with boundaries of the riparian zone extending outward to the extent of flooding [*Gregory et al.*, 1991]. The interface at the upland edge of the riparian zone is often denoted by steep chemical gradients that occur when aerobic upgradient groundwater enters the typically more reduced riparian zone. The effectiveness of stream riparian zones in reducing nitrate is thought to be dependent on the hydrogeologic setting and its effect of groundwater flow paths [*Hill*, 1996].

While there have been several studies that have examined nitrate reduction in groundwater, few have been adequately linked to flow paths. Further, few studies have examined the oxidation half reactions that accompany nitrate reduction. In this study, reactants and products of denitrification reactions are measured along shallow and deep flow paths to determine the extent, mechanism, and rates of nitrate reduction in a shallow aquifer system. A two-dimensional transient flow model was developed to determine groundwater flow paths. Potential nitrate reduction reactions and rates are evaluated by examining changes in nitrogen species as well as potential electron donors along flow paths. Nitrate consumption, N_2 gas production, and results from in situ experiments are used to provide estimates of the rate of nitrate reduction in the aquifer.

2. Methods

2.1. Hydrogeologic Setting

This study was conducted in the Abbotsford-Sumas aquifer, which is located in the Fraser-Whatcom Lowlands of southwestern British Columbia, Canada, and northern Washington State, United States of America. Much of this aquifer is overlain by intensive agricultural activities including poultry operations and raspberry production. The Abbotsford-Sumas aquifer is largely composed of glacial-fluvial coarse sands and gravels that were deposited as outwash during the Sumas Stage of the Fraser glaciation [*Armstrong*, 1981]. Dominant mineral phases for deposits composing the Abbotsford-Sumas aquifer are quartz and albite with lesser amounts of muscovite and microcline. On a regional scale, aquifers having deposits resulting from this glaciation compose the Fraser aquifer and are present beneath over 14,000 km^2 of the Puget Sound Lowland [*Vaccaro et al.*, 1998].

This study is focused on a transect from a recharge area near the Abbotsford Airport to discharge at Fishtrap Creek near the international border (Figure 1). Fishtrap Creek is a perennial

third-order stream that drains an intensive agricultural area. The riparian zone of Fishtrap Creek at the international border is dominated by uncultivated grasses and blackberries (*Rubus sp.*) in the approximately 15 m adjacent to the creek, with cultivated raspberries farther upland. Prior to the construction of dikes along this reach of Fishtrap Creek, flooding of adjacent areas was frequent and extensive given the gentle topography of the area. The Abbotsford-Sumas aquifer in this area is unconfined, with depths to groundwater typically ranging between 2 and 10 m. The Abbotsford-Sumas aquifer is underlain by the Everson Interstade, which in this area forms a confining unit composed of thick accumulations of glaciomarine clays. Soil borings taken along the southwestern end of the transect place the top of this unit approximately 20 m below the land surface.

2.2. Sample Collection and Analysis

Wells used in this study for water sampling were installed by the U.S. Geological Survey, British Columbia Ministry of the Environment, and Environment Canada. Well screens are usually less than 2 m in length. Water-quality sampling was performed as a part of the U.S. Geological Survey's National Water-Quality Assessment Program and was conducted according to protocols established for this program [*Koterba et al.*, 1995]. Submersible pumps and teflon lines were used for all water-quality sampling except for chlorofluorocarbon sampling where copper tubing was used.

Dissolved oxygen and pH were measured using electrodes placed in a flow cell chamber to minimize atmospheric interactions. Alkalinity was determined in the field by titration. Water samples for major ions and nutrients were filtered using a 0.45 μm capsule filter. Sulfate (SO_4^{2-}) was analyzed by ion chromatography. Magnesium, silica (SiO_2), iron, and manganese were analyzed using inductively coupled plasma and mass spectrometry. Nitrate, nitrite, ammonium, and bromide were analyzed using colorimetric methods. Detailed descriptions of the analytical methods for the above mentioned major ions and nutrients are provided by *Fishman and Friedman* [1989]. Dissolved organic carbon was analyzed by ultraviolet-promoted persulfate oxidation and infrared spectrometry [*Brenton and Arnett*, 1993]. All of the above analyses were conducted at the U.S. Geological Survey's National Water Quality Laboratory in Arvada, Colorado. Analyses of water samples for sulfide were made in the field using a spectrophotometer. Total inorganic carbon in groundwater was determined using water chemistry data and the geochemical program PHREEQC [*Parkhurst*, 1995]. Samples for chlorofluorocarbons (CFCs) (trichlorofluoromethane, CFC 11; dichlorodifluoromethane, CFC 12; and trichlorotrifluoroethane, CFC 113) and dissolved gases (N_2 and Ar) were collected and analyzed as described by *Busenberg and Plummer* [1992] and *Busenberg et al.* [1993], respectively.

Cores samples were taken from selected wells by driving a split-spoon sampler during well installation. Cores were analyzed for total carbon by measuring carbon dioxide production after a sample was oxidized in an induction furnace and were analyzed for inorganic carbon by measuring carbon dioxide production after treatment with hydrochloric acid and heating [*Wershaw et al.*, 1987]. Organic carbon content of core material was determined by the difference between total and inorganic carbon.

Denitrification experiments were conducted using a single-well method similar to that described by *Istok et al.* [1997] with

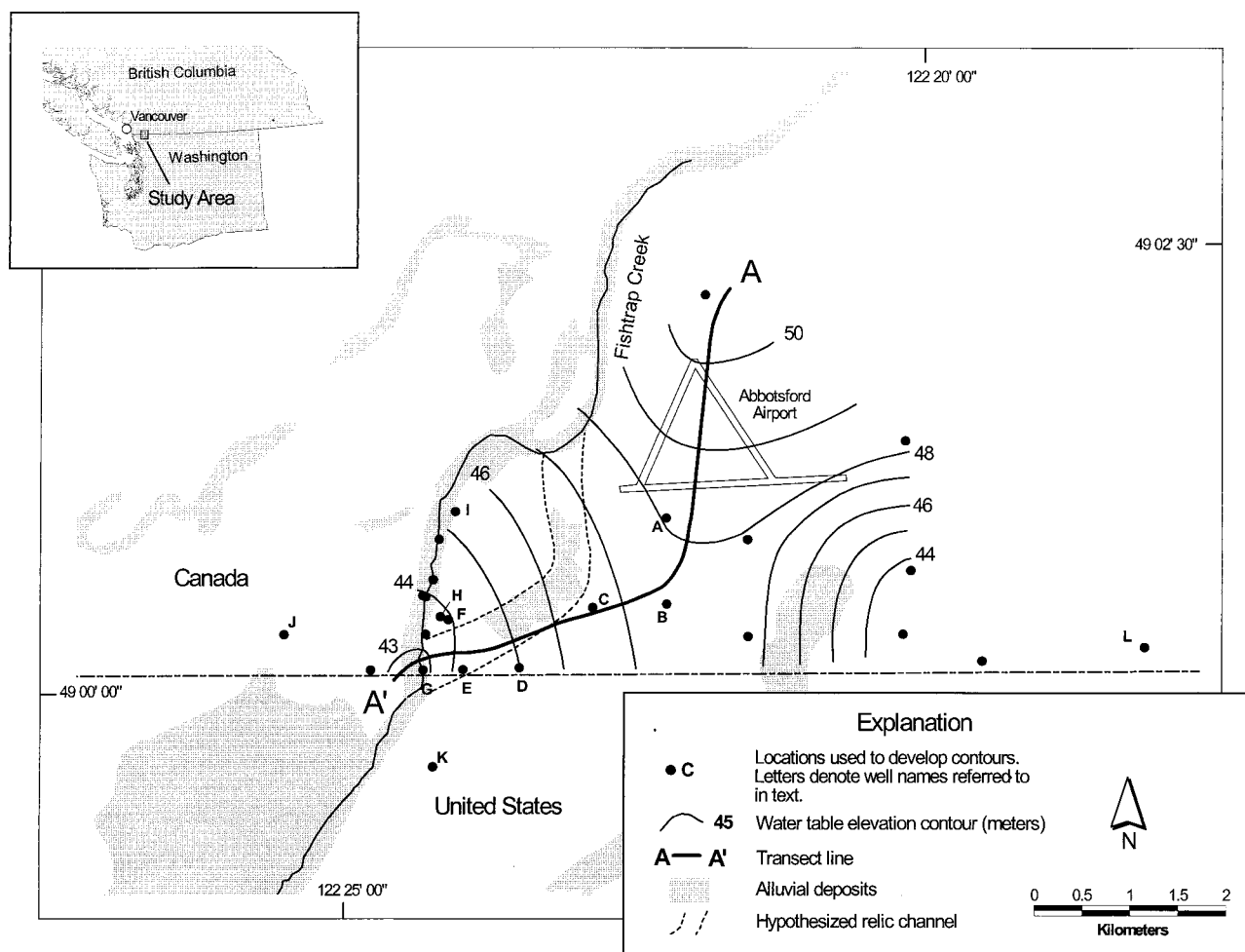


Figure 1. Water table elevation contours and well locations in the Abbotsford-Sumas aquifer in southwestern British Columbia. A-A' delineates the location of the cross-sectional flow model. Letters A through L indicate well (or well nest) locations. Alluvial deposit information is from Vacarro *et al.* [1998].

the notable exception that pumping was only conducted during sampling in this study to minimize the loss of injectate. An inflatable packer was placed just above the well screen to minimize the amount of water that must be purged prior to sampling. After purging, the injectate was prepared using a peristaltic pump to place approximately 180 L of groundwater into a gas-impermeable bag. The gas-impermeable bag was previously sparged with N_2 and contained 1 L of a concentrated N_2 -sparged solution of NaBr and KNO_3 . Gas-impermeable bags and sparging with N_2 have been used successfully to minimize the introduction of atmospheric O_2 into anaerobic groundwater [e.g., Smith *et al.*, 1991b]. KNO_3 was added to provide an initial nitrate concentration of approximately 0.4 mM for the injectate. Bromide (as NaBr) was added as a conservative tracer to correct reactant and product concentrations for dilution. The injectate had a bromide concentration of about 0.2 mM, which was well above ambient levels in groundwater (<0.004 mM). The injectate was placed back into the well by reversing the direction of flow on the peristaltic pump. Measurements of dissolved oxygen upon withdrawal and just prior to injection confirmed that insignificant amounts of O_2 (<0.013 mM) were introduced while preparing the injectate. Sampling of groundwater was initiated once all of the

injectate was pumped into the aquifer. The concentrations of dissolved oxygen, nitrate, nitrite, ammonium, and bromide were measured for all samples collected. Selected samples were also measured for iron and sulfate. All analytes were corrected for mixing with surrounding groundwater using the bromide concentration in each sample to measure the amount of injectate remaining.

2.3. Delineation of Groundwater Flow Paths

A groundwater flow model was constructed to identify wells that are generally along a flow path. A one-layer transient cross-sectional model was constructed using the groundwater flow code MODFLOW [Guiguer and Franz, 1997; McDonald and Harbaugh, 1988] to represent flow from a local groundwater high to a discharge location at Fishtrap Creek (section A-A' in Figure 1). The letter portion of well names refers to the location of the well in Figure 1; the number in the well name refers to the approximate depth of the well in meters (e.g., well C23 is a located at site C and is 23 m deep). A transient model was used because vertical gradients beneath Fishtrap Creek change from essentially zero at low-flow conditions to an upward gradient of 0.05 (0.5 m head change over 10 m vertical distance) during high flow.

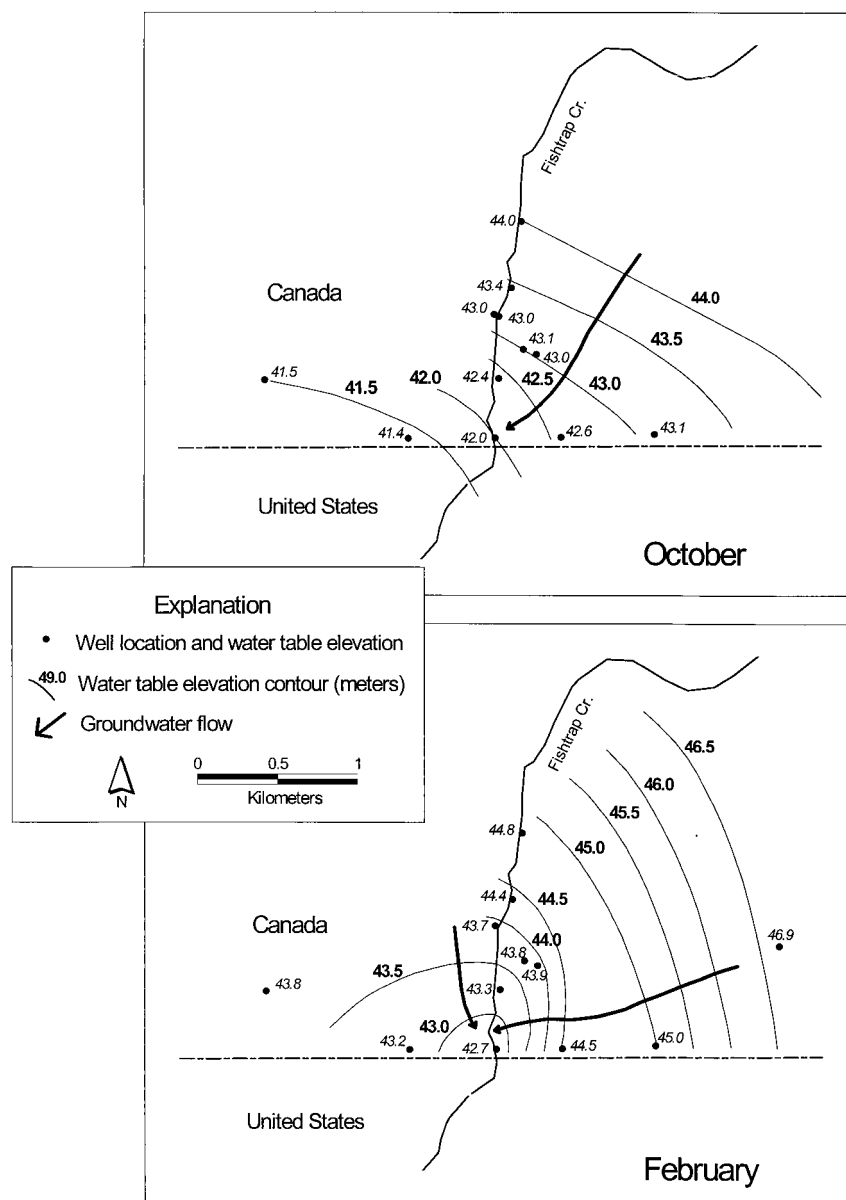


Figure 2. Water table elevation contours and flow directions in the vicinity of Fishtap Creek for October 1994 and February 1995.

No-flow boundaries were assumed for the upgradient edge of the section as well as for the bottom of the aquifer. Assuming no flow into Everson Interstade is reasonable considering the thickness (>30 m) and low hydraulic conductivity for much of this unit ($\approx 10^{-9}$ m/s [Cox and Kahle, 1999]). The boundary for the downgradient end of the section was assumed to be a constant head boundary. Head values for this boundary oscillate between 41 m during low-flow conditions and 43 m during high flow; these estimates are based upon measured water levels in the area (e.g., Figure 2). Mean annual recharge was calculated on a yearly basis from 1994 to 1996 using precipitation data and a regression equation derived by Vaccaro *et al.* [1998] for outwash-covered areas in the Puget Sound Basin. Annual recharge estimates vary from 660 to 890 mm during the calibration period of 1994 to 1996. Annual recharge was apportioned over the months of October through May according to the amount of precipitation received in each month. This

resulted in varying recharge values for each month during the recharge season and no recharge from June through September. River stage near well G (Figure 1) oscillated in the model between 41.9 m at base flow and 42.2 m during high-flow periods based on levels measured by Environment Canada.

Hydraulic conductivity values were used to calibrate the simulated heads to measured head values. A hydraulic conductivity value of 3.5×10^{-3} m/s for the Abbotsford-Sumas aquifer provided a good fit to observed data (Figure 3). This value is within the range of measured values (2.4×10^{-5} to 2.8×10^{-2} m/s) reported by Cox and Kahle [1999] and is in general agreement with their median value of 1.0×10^{-3} m/s. An anisotropy (horizontal/vertical hydraulic conductivity) value of 50 was assumed.

Both measured and simulated values for the shallow and deep wells near Fishtap Creek (G2 and G12, respectively) indicate an upward gradient is maintained for much of the year

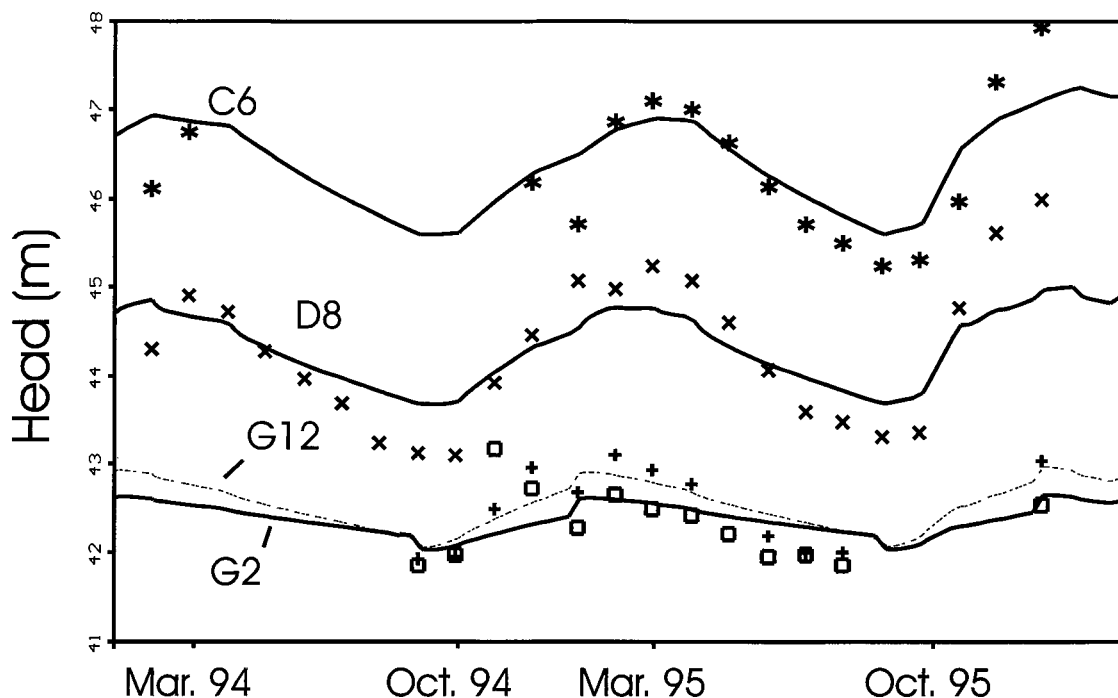


Figure 3. Hydraulic head values versus time for selected wells along transect A-A' in Figure 1. Lines are the hydraulic head values predicted by the groundwater flow model. Individual points represent water level measurements. Plus signs and dashed line refer to well G12; open squares refer to well G2.

(Figure 3). This gradient becomes smaller as low-flow conditions (October) are approached, suggesting that discharge to Fishtrap Creek has little influence on groundwater flow directions during this time. This is consistent with flow directions suggested by contouring groundwater table elevations (Figure 2). While most shallow flow paths likely discharge to Fishtrap Creek, deeper flow paths may travel beneath it (Figure 4).

3. Results and Discussion

3.1. Groundwater Chemistry

Loss of nitrate due to nitrate reduction is accompanied by changes in other redox-active species and the production of reduced forms of nitrogen. As such, an evaluation of dominant species of the major redox-active elements including oxygen,

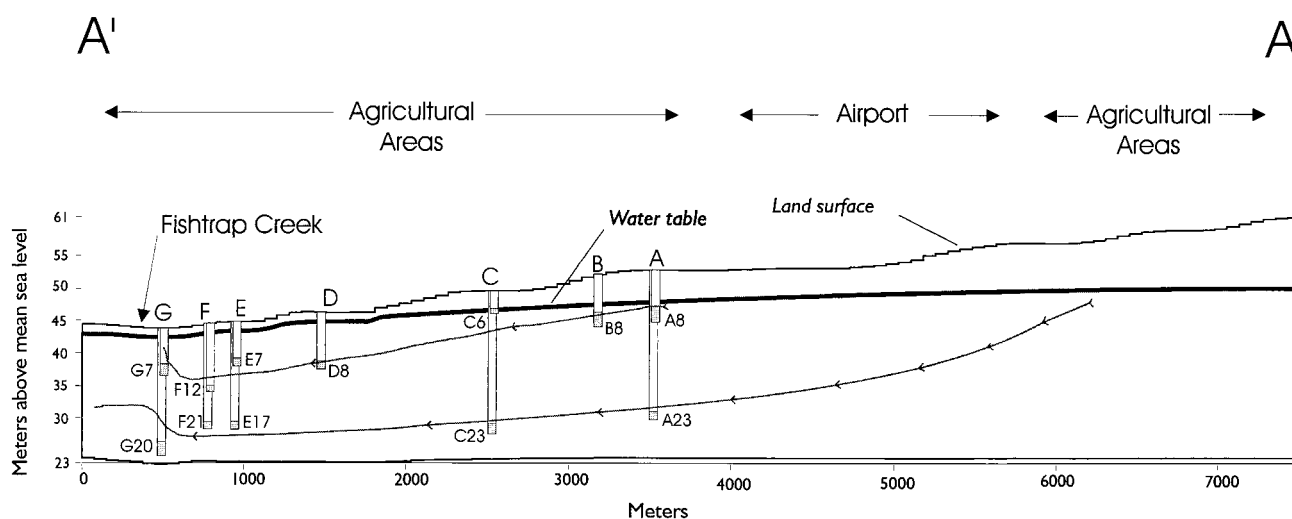


Figure 4. Shallow and deep groundwater flow paths determined by flow model. Wells along each flow path are identified. Shaded boxes indicate the approximate location of the screened interval.

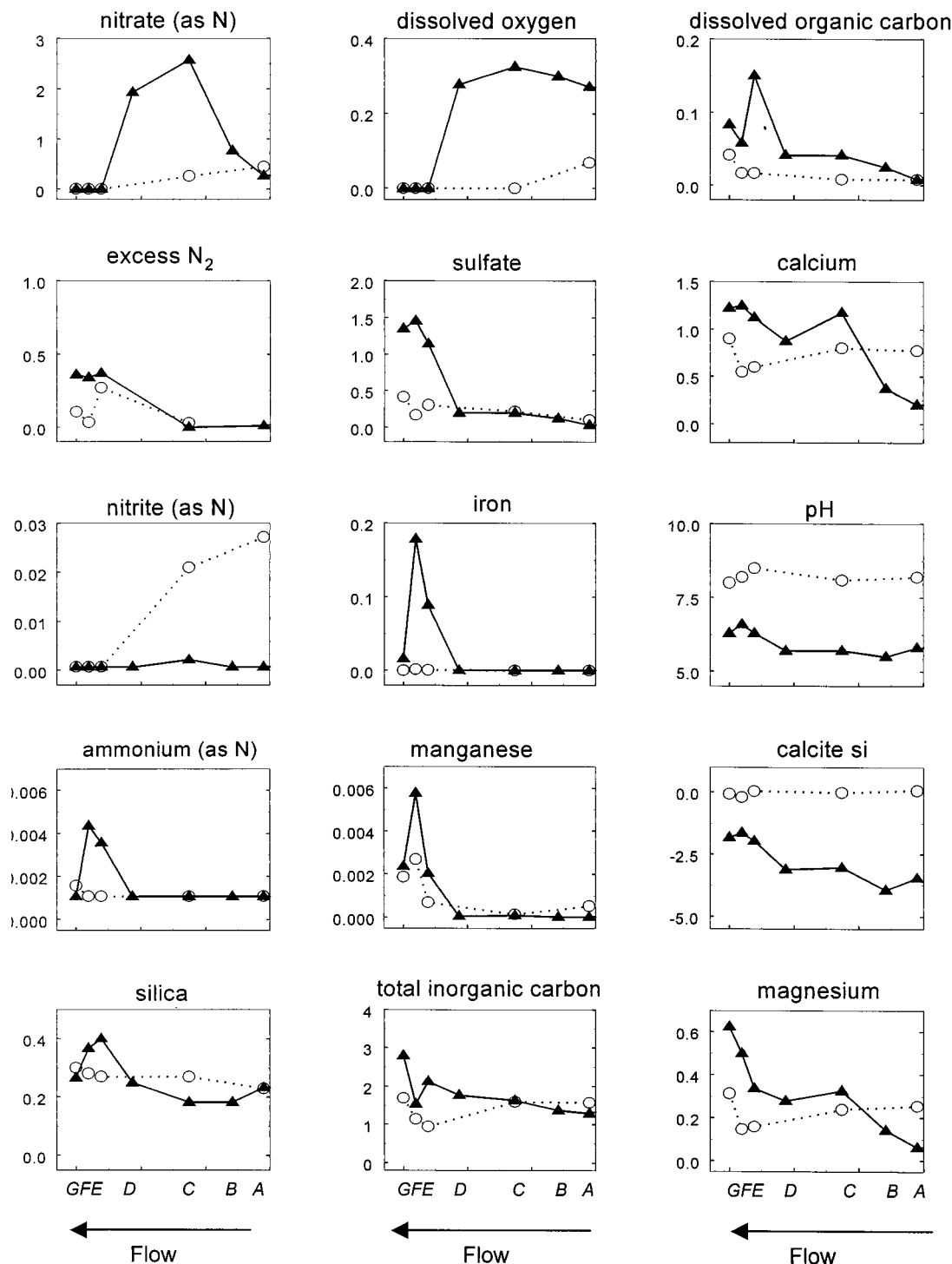


Figure 5. Concentrations of constituents in groundwater samples along shallow (triangles) and deep (circles) flow paths along transect A-A' in Figure 1. Data are for wells identified in Figure 4 with one exception: Excess N₂ data for G7 are not available; data for G12 are reported instead. Units are in millimolar except for pH (in standard units) and calcite saturation index (SI). The calcite saturation index is defined as the log of the ratio of the ion activity product and the solubility product for calcite; a value of zero for SI indicates groundwater is in equilibrium with respect to calcite.

iron, manganese, sulfur, carbon, and nitrogen can provide clues to the mechanism of nitrate removal. The shallow and deep flow paths are discussed separately to illustrate the differences between the two end-member cases for groundwater flow in this aquifer.

Nitrate concentrations above the U.S. Environmental Protection Agency maximum contaminant level of 0.7 mM are found in water from shallow wells at sites B, C, and D (Figure 5 and Table 1). As groundwater moves along the shallow flow path, an abrupt decrease in nitrate concentration is observed

Table 1. Concentrations of Selected Chemical Constituents in Groundwater

Well	Depth of Screened Interval, m	Sampling Date	pH	O ₂ , mM	SO ₄ ²⁻ , mM	Fe, μ M	NO ₃ ⁻ , mM	NO ₂ ⁻ , mM	NH ₄ ⁺ , mM	N ₂ , mM	Ar, mM
A8	4.6–7.0	Sept. 5, 1997	5.8	0.272	0.03	<0.05	0.269	<0.001	<0.002	0.757	0.0185
A23	21.0–21.9	Sept. 2, 1997	8.2	0.069	0.10	<0.05	0.453	0.027	<0.002	...	...
B8	4.6–7.0	Sept. 5, 1997	5.5	0.300	0.13	0.12	0.771	<0.001	<0.002	...	...
C6	3.7–6.1	Feb. 5, 1997	5.7	0.325	0.20	<0.05	2.571	0.002	<0.002	0.751	0.0188
C17	15.8–16.8	Sept. 4, 1997	6.9	0.103	0.13	0.06	0.492	<0.001	<0.002	...	...
C23	21.9–22.9	Sept. 4, 1997	8.1	<0.002	0.22	<0.05	0.264	0.021	<0.002	0.820	0.0191
D8	7.8–8.8	Feb. 6, 1997	5.7	0.278	0.20	0.23	1.929	<0.001	<0.002	...	...
E7	5.8–6.7	Sept. 3, 1997	6.3	<0.002	1.15	89.29	<0.004	<0.001	0.004	1.120	0.0187
E17	16.2–17.1	Sept. 3, 1997	8.5	<0.002	0.30	0.55	<0.004	<0.001	<0.002	1.073	0.0192
F12	12.1–13.0	Sept. 10, 1997	6.6	<0.002	1.46	178.57	<0.004	<0.001	0.004	1.191	0.0165
F21	18.4–19.4	Sept. 10, 1997	8.2	<0.002	0.17	1.73	<0.004	<0.001	<0.002	0.834	0.0191
G4	3.4–4.3	Nov. 14, 1997	5.8	0.003	1.35	0.34	0.099	<0.001	<0.002	...	...
G7	6.4–7.3	Feb. 6, 1997	6.3	<0.002	1.35	16.43	<0.004	<0.001	<0.002	...	...
G12	11.0–11.9	Feb. 27, 1997	...	...	...	...	...	...	...	1.202	0.0166
G20	18.0–19.5	Nov. 14, 1997	8.0	<0.002	0.42	0.18	<0.004	<0.001	<0.002	0.894	0.0190
H8	6.9–7.9	Sept. 9, 1997	5.8	0.003	0.83	1.09	1.879	0.002	<0.002	1.103	0.0183
I10	8.2–9.8	Nov. 13, 1997	6.1	0.141	1.25	0.11	0.346	<0.001	<0.002	...	...
J21	18.6–20.1	Feb. 4, 1997	6.1	0.163	0.35	<0.05	1.071	0.001	<0.002	0.719	0.0183
K7	4.6–5.5	Nov. 10, 1997	5.7	0.111	0.08	<0.05	0.713	0.002	<0.002	0.801	0.0195
K15	11.6–13.1	Nov. 10, 1997	6.0	0.024	0.32	2.12	0.621	0.003	<0.002	0.944	0.0196
K24	20.7–22.3	Nov. 10, 1997	8.3	<0.002	0.25	0.12	<0.004	0.001	0.005	0.957	0.0192
L29	25.9–27.4	Feb. 3, 1997	6.8	0.224	0.17	<0.05	1.286	0.001	0.005	0.885	0.0198

Ellipsis indicates data are not available for this constituent.

between wells D and E (Figure 5). Dissolved oxygen decreases abruptly in the same manner as nitrate. Dissolved oxygen is thermodynamically preferred as a terminal electron acceptor over nitrate such that nitrate reduction is not expected when dissolved oxygen is present. Given that relation, the reduction of dissolved oxygen and subsequently nitrate must occur along the shallow flow path in the time that it takes for groundwater to travel from well D8 to well E7. An abrupt change in redox chemistry such as this is referred to as a redoxcline. Sulfate and iron concentrations in groundwater increase markedly at the redoxcline, suggesting that sulfur- and iron-containing minerals are participants in redox or associated reactions. Manganese concentrations also increase at the redoxcline but to a much lesser extent. Both iron and manganese concentrations in groundwater subsequently decrease farther downgradient, suggesting that precipitation of minerals containing these elements occurs.

Selected water samples along the flow paths were tested for dissolved nitrogen and argon gas to estimate the amount of nitrogen derived from atmospheric sources (Table 1). Nitrogen and argon are incorporated in groundwater during recharge by air-water equilibration processes. Air bubbles can also be transported to the saturated zone resulting in concentrations of N₂ and Ar in excess of equilibrium [Heaton and Vogel, 1981]. The portion of N₂ gas that is derived from atmospheric sources (both from air-water equilibrium and excess air) can be estimated based on the N₂/Ar ratios of water samples for aerobic portions of the aquifer where N₂ from denitrification is not expected [Dunkle et al., 1993]. A line depicting concentrations N₂ and Ar for a recharge temperature of 9°C with varying amounts (up to 5 cm³/L) of excess air provides a good fit to the aerobic water data and is used to estimate the atmospheric portion of N₂ in groundwater (Figure 6). The amount of dissolved N₂ present in water samples that exceeds the atmospheric amount is assumed to be from denitrification and is termed excess N₂. Two samples with high N₂ concentrations

had unusually low Ar concentrations indicating that some degassing had occurred. An Ar concentration (0.0198 mM) consistent with large amounts of excess air was used to calculate minimum estimates of excess N₂ concentrations for these samples. Excess N₂ concentrations in groundwater along the shallow flow path range up to 0.37 mM, which is equivalent to 0.74 mM of reduced N (Figure 5).

Nitrate concentrations are typically lower in water from wells along the deeper flow path (Figure 5). Decreasing nitrate concentrations along the transect are also observed in the deeper flow path; however, nitrate concentrations in groundwater decrease more gradually along this flow path. Low dissolved oxygen concentrations along this transect allow for denitrification throughout much of this section. Nitrite is detected in upgradient wells that also contain detectable levels of nitrate. This fact suggests that nitrate reduction is ongoing at these locations in the aquifer, especially given the short-lived nature of this intermediate. Excess N₂ gas concentrations up to 0.27 mM are found in water from deeper wells in the flow path. The maximum excess N₂ value accounts for 0.54 mM of reduced nitrate, which is similar to the maximum value of nitrate (0.45 mM), found in water from wells along the deep transect. Ammonium is found at low levels throughout the deeper transect and is not a major form of reduced nitrogen.

3.2. Reactions Occurring Along the Transect

Initially, shallow groundwater is relatively dilute, as the impacts of agricultural activities are likely to be less at the shallow well at site A relative to wells farther downgradient (Figure 4). Concentrations of nitrate, calcium, and to a lesser extent magnesium increase in the shallow flow path downgradient from well A. Most of the nitrate in this aquifer is derived from the nitrification of reduced forms of N from poultry manure or ammonium-based fertilizers; nitrate-based fertilizers were not indicated as a significant source of nitrate [Wassenaar, 1995].

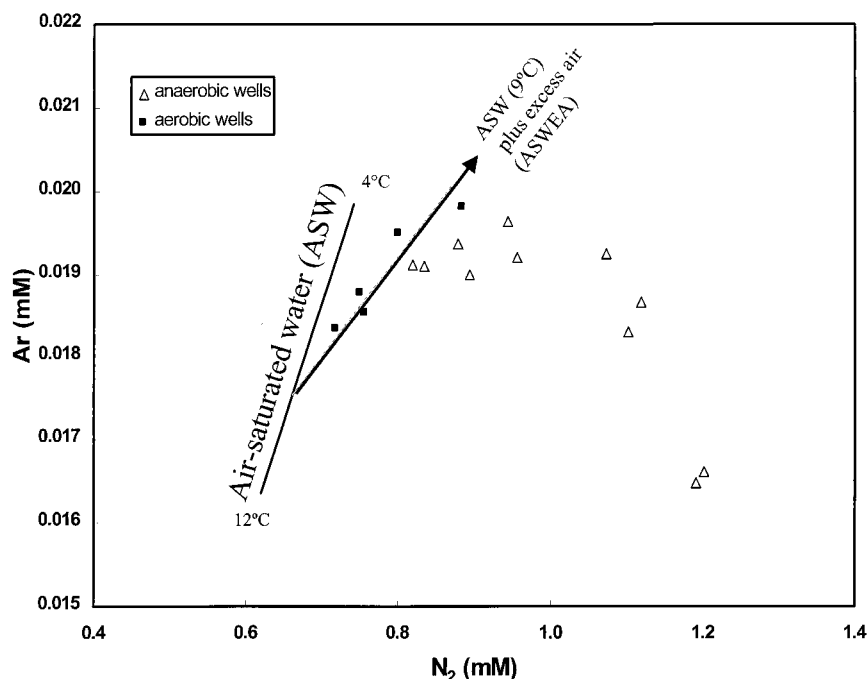
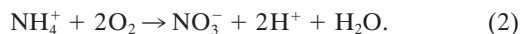


Figure 6. Data points indicate concentrations of N_2 and Ar gas in groundwater for aerobic and anaerobic samples. Air-saturated water (ASW) line indicates concentrations of N_2 and Ar derived from air-water equilibration at varying temperatures. Air-saturated water plus excess air (ASWEA) line assumes an equilibration temperature of 9°C and includes additional N_2 and Ar derived from gas bubbles transported to the saturated zone. The horizontal distance between each anaerobic data point and the ASWEA line indicates the amount of nonatmospheric N_2 . Two samples had unusually low levels of Ar, indicating that degassing has occurred.

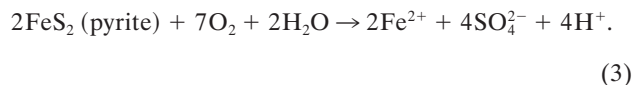
Nitrification of ammonium occurs in aerobic environments by reactions of the type:



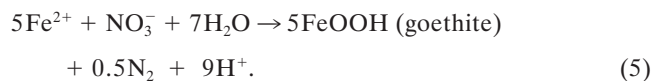
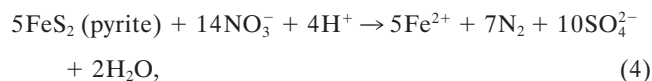
Nitrate reduction by denitrification is indicated by the dramatic increase in excess N_2 concentrations in groundwater immediately downgradient from the nitrate plume (Figures 5 and 7). Variable nitrate concentrations in upgradient aerobic waters, ranging from 0.5 to over 2.5 mM, make a strict mass balance accounting for nitrogen difficult. However, the large amounts of excess N_2 (equivalent of up to and possibly exceeding 0.74 mM NO_3^-) coupled with very little production of ammonium suggests that denitrification to N_2 is responsible for the majority of the reduced nitrate. The absence of nitrite along the shallow flow path suggests that this intermediate in the denitrification reaction pathway is quickly converted to more reduced forms. To illustrate where denitrification is occurring along the transect, the dominant terminal electron acceptor [Chapelle *et al.*, 1995] for each area of the aquifer was determined (Figure 8).

It has been concluded in a previous investigation of this area using stable isotopes of nitrate ($\delta^{18}O$ and $\delta^{15}N$) that denitrification is not occurring to a large extent in this aquifer [Wasenaar, 1995]. We concur that denitrification is not occurring over much of the aquifer; however, denitrification does occur adjacent to Fishtrap Creek as evidenced by an increase in excess N_2 concentrations coupled with a decline in nitrate levels. Because denitrification occurs quickly in this area, the nitrate-reducing zone is small (Figure 8). As a result, few, if any wells were sampled for stable isotopes from this zone in the Waasenaar study.

The sharp chemical gradients observed between D8 and E7 suggests that the riparian zone extends over 500 m to beyond well E7. While rather wide, the flat topography and seasonally high water table found here would have led to a wide flood plain prior to the construction of dikes. Furthermore, the occurrence and orientation of alluvial deposits (Figure 1) suggests that this area may include a relic channel or a filled wetland. Pyrite occurs in freshwater wetlands [Marnette *et al.*, 1993], and several lines of evidence suggest deposits of pyrite and/or other iron sulfides are present here. Increases in sulfate and iron concurrent with a loss of nitrate and dissolved oxygen across the redoxcline would be expected if iron sulfide oxidation occurred. Furthermore, the fact that several wells in the anaerobic zone contain a sulfur odor and trace levels of sulfide in water samples supports the presence of iron sulfide deposits. Pyrite is considered in the following discussion as a possible mineral phase. Suggested reactions for pyrite oxidation by dissolved oxygen include [Moses *et al.*, 1987]:



Suggested reactions where reduced forms of sulfur and iron are electron donors in denitrification reactions include [Kölle *et al.*, 1985]:



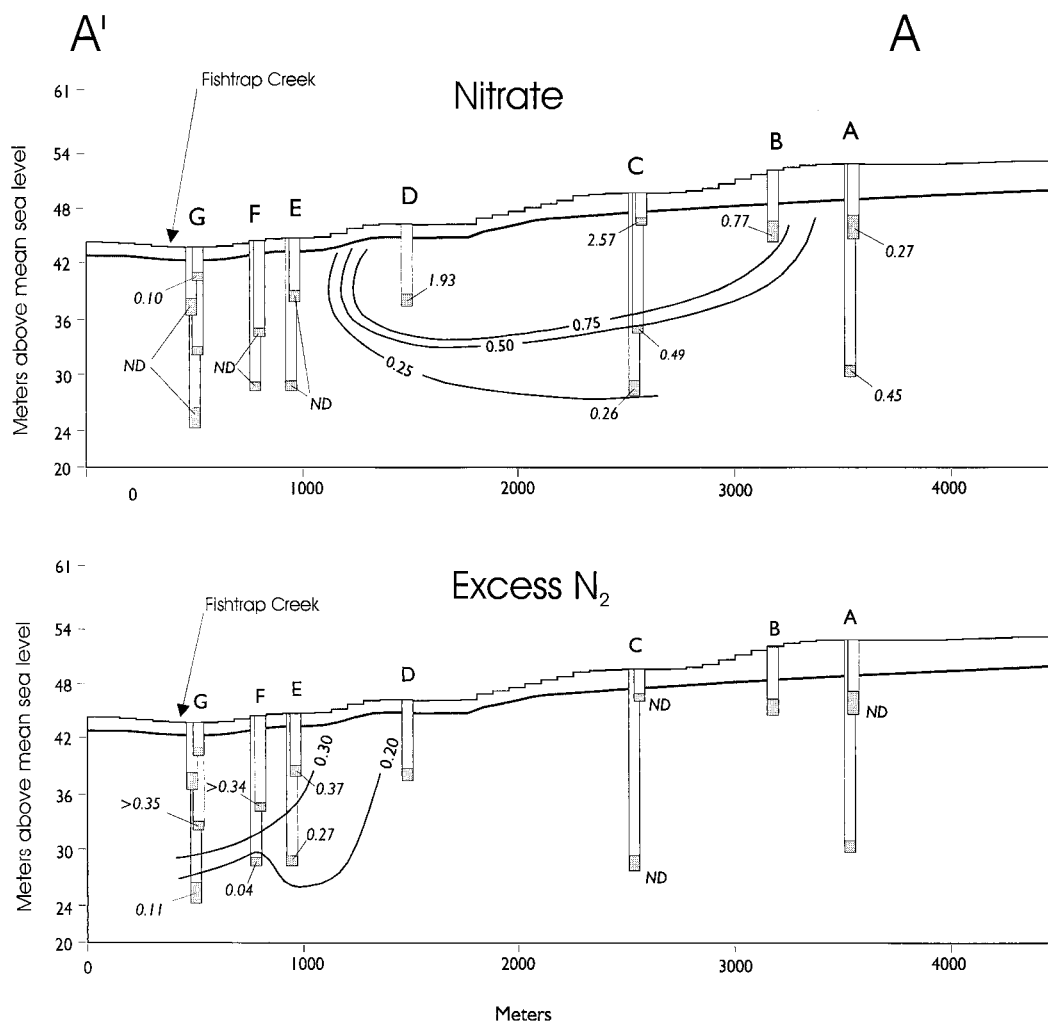
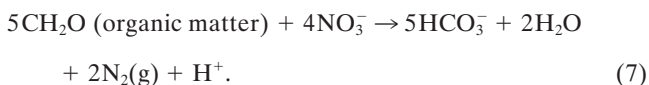
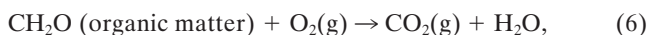


Figure 7. Contour plot of nitrate concentrations (in millimolar as N) and excess N_2 concentrations (in millimolar as N_2) in groundwater along transect A-A' in Figure 1. ND denotes nondetectable concentrations of constituent.

Reduction of dissolved oxygen and nitrate may also occur with organic carbon as an electron donor:



Naturally occurring organic matter is varied and may contain several different oxidation states [Thurman, 1985]. An average oxidation state of zero is assumed for organic carbon in the above equations and in calculations to follow.

The relative importance of organic carbon and pyrite as electron donors along the shallow flow path are examined using a method presented by Postma *et al.* [1991]. The half reactions considered include the reduction of oxygen and nitrate and the oxidation of pyrite and organic matter (Table 2). For reduction reactions, reactants are used to track changes, whereas products are used for oxidation reactions. In this way the dominant electron donors and acceptors along a flow path can be evaluated. Moreover, an assessment can be made re-

garding whether there is sufficient production of oxidized species to account for the loss of reduced species.

For this analysis, increases in total inorganic carbon (TIC) along the flow path are assumed to be from the dissolution of organic matter. Organic carbon in the solid phase is present in cores taken from this portion of the aquifer at levels ranging from 0.05 to 0.13% by weight. While only a small fraction of the solid phase, this amount of organic matter has the potential to denitrify amounts of nitrate well in excess of the amount of nitrate found in the aerobic zone of this aquifer [Trudell *et al.*, 1986]. Pyrite is modeled as a source of iron and sulfur. Pyrite oxidation comprises two parts: oxidation of sulfide to sulfate and oxidation of Fe^{2+} resulting in the formation of goethite. Goethite ($FeOOH$) is suggested as a possible sink for iron because complete pyrite oxidation produces increases in Fe^{3+} possibly resulting in oversaturation with respect to goethite.

For the shallow flow path, results of this analysis suggest that the oxidation of pyrite to sulfate is the most important electron donor for reactions occurring across the redoxcline (between wells D8 and E7 in Figure 9). Increases in the electron equiv-

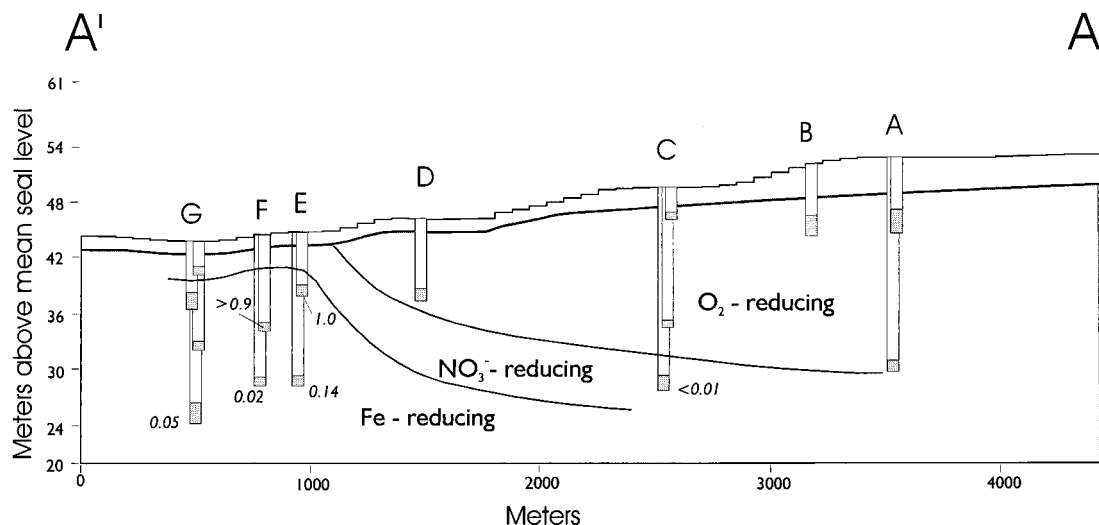


Figure 8. Dominant terminal electron acceptor and denitrification rates along transit A–A' in Figure 1. Value is the denitrification rate millimolar of N per year calculated using the concentration of excess N_2 and groundwater travel time in the anaerobic zone only.

alents for sulfate at the redoxcline are of a similar magnitude as the loss of electron equivalents of nitrate and dissolved oxygen. The production of small amounts of goethite across the redoxcline is suggested to achieve mass balance for iron. However, precipitation of goethite would cause a significant drop in pH that is not observed. Either goethite precipitation does not occur, or it is accompanied by reactions that buffer pH. Data on the mineralogy of these deposits are insufficient to evaluate possible buffering mechanisms.

Increases in TIC along the shallow flow path are not sufficient to account for much of the electron equivalents lost by nitrate and dissolved oxygen (Figure 9). This is in spite of the fact some of the increase in TIC along the shallow flow path may be due to the land application of calcite or dolomite. All water samples along the shallow flow path were undersaturated with respect to carbonates, so carbon loss due to precipitation was not likely. While not a significant source of electrons across the redoxcline, an increase in TIC as the stream is approached suggests that oxidation of organic matter may be more important in this portion of the aquifer.

Assessing the dominant redox reactions along the deeper flow path using this approach is more difficult because changes in electron equivalents are less dramatic (Figure 9). Furthermore, groundwater in this part of the aquifer is also at or near saturation with respect to calcite (Figure 5). As such, a loss of TIC from calcite precipitation may have occurred along this flow path, resulting in an underestimate of the amount of organic matter oxidation.

3.3. Reaction Rates and Groundwater Travel Times

Average rates of denitrification for the anaerobic portions of the aquifer were estimated by evaluating the loss of nitrate and the production of N_2 along groundwater flow paths. In situ experiments were also used to estimate denitrification rates where rates were expected to be fast. Slower rates of reaction make the use of in situ experiments more problematic because reagents are swept downgradient before reactions can be measured; multiple-well natural-gradient experiments minimize but do not eliminate this constraint.

Groundwater travel time estimates are required for the mass

balance methods and were determined using the groundwater flow model. Travel time estimates were constrained using age dates derived from CFC concentrations in groundwater. Concentrations of CFCs have been increasing in the atmosphere and have been successfully used to chronicle the history and fate of nitrate contamination in groundwater [Böhlke and Denver, 1995]. Selected wells along the transect were sampled for CFC 11, CFC 12, and CFC 113 (Table 3). Dissolved CFC concentrations were converted to equilibrium partial pressures for a recharge temperature of 9°C. Partial pressures were then compared to atmospheric data to determine the year that recharge water left contact with air.

In an environment where ages are well constrained by tritium data and numerical simulation, CFC 12 was found to be the most conservative CFC and to yield the most reliable groundwater ages. In contrast, CFC 11 and CFC 113 were found to significantly overestimate groundwater ages because of the degradation and sorption of these compounds [Cook *et al.*, 1995]. As such, CFC 12 age estimates were chosen as the best estimate of groundwater age for most samples. Under anaerobic conditions, even CFC 12 has been shown to degrade, albeit more slowly than CFC 11 or CFC 113 [Oster *et al.*, 1996; Goode, 1998]. Degradation of CFCs in anaerobic samples collected in this study is indicated by the presence of 24 pCi/L of tritium in the sample from well G12, where CFC-based ages would indicate little tritium. Accordingly, CFC 12 ages for anaerobic samples are considered maximum ages. When CFC 12 concentrations exceeded modern concentrations suggesting

Table 2. Half Reactions and Electron Equivalents for Redox Reactions

Half Reactions	Electron Equivalents
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	4[O_2]
$NO_3^- + 6H^+ + 5e^- \rightarrow 0.5N_2 + 3H_2O$	5[NO_3^-]
$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$	4[TIC]
$0.5FeS_2 + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 7e^-$ + 0.5 Fe^{2+}	7[SO_4^{2-}]
$Fe^{2+} + 2H_2O \rightarrow FeOOH + 3H^+ + e^-$	[0.5[SO_4^{2-}]] – [Fe^{2+}]

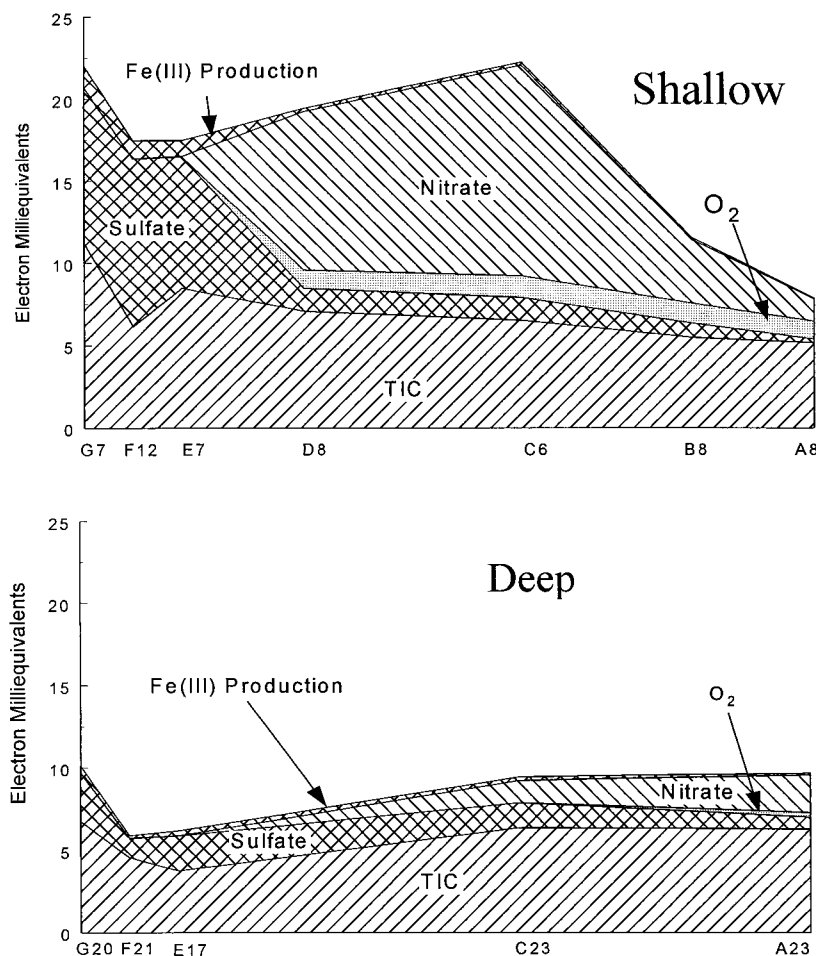


Figure 9. Cumulative distribution of electron milliequivalents for wells along the shallow and deep flow paths in Figure 4. Electron milliequivalents are millimolar concentrations multiplied by the number of electrons transferred in the half reactions shown in Table 2. Length of section is shown in 3000 m.

Table 3. Average Chlorofluorocarbon (CFC) Concentrations and Groundwater Age Estimates

Well	Sampling Date	Number ^a	CFC 11				CFC 12				CFC 113				Best Estimate of		Flow Model Age ^c , years
			pg/kg ^b	SD	Year	SD	pg/kg	SD	Year	SD	pg/kg	SD	Year	SD	Year	Age, years	
A8	Sept. 2, 1997	3	630	12	1984	0.3	768	19	C	ND	190	10	C	ND	>1984	<13	2
A23	Aug. 27, 1997	3	53	1	1963	<0.1	457	95	C	ND	68	8	1987	0.9	>1987	<10	12
C6	Aug. 27, 1997	3	634	10	1984	0.3	1141	54	C	ND	133	12	modern	ND	modern	<2	1.5
C17	Feb. 5, 1997	3	122	2	1967	0.3	228	27	1981	2.5	8	1	1971	0.9	1981	16	7.5
C23	Feb. 5, 1997	2	19	0.3	1957	0.4	110	73	1971	6.4	<1	<1	ND	ND	>1971	<26	16
D8	Feb. 6, 1997	3	605	8	1983	0.3	365	30	1994	4.6	74	6	1987	0.9	1994	3	5
E7	Aug. 27, 1997	3	<1	<1	ND	ND	180	1	1977	0.0	4	4	1968	1.8	>1977	<20	3.5
E17	Aug. 27, 1997	3	<1	<1	ND	ND	<1	<1	ND	ND	6	3	1968	3.0	ND	ND	12
G4	Nov. 4, 1997	3	90	0.4	1966	<0.1	238	7	1982	0.6	36	1	1981	0.4	>1982	<15	9
G7	Feb. 27, 1997	2	8	0.2	1954	0.4	102	6	1971	0.7	14	14	1972	8.8	>1971	<26	10
G12	Feb. 27, 1997	5	<1	<1	ND	4.9	4	4	1946	15.9	0.3	1	ND	ND	>1953 ^d	<44	12.5
G20	Nov. 4, 1997	3	9	2	1954	0.8	<1	<1	ND	ND	3	2	1965	0.7	ND	ND	22.5

Definitions are as follows: SD, standard deviation; C, contaminated; ND, not determined; and modern, water less than 2 years old.

^aThis is the number of samples used for calculating average concentration.

^bConcentration of CFC in ground water is given in picograms per kilogram.

^cFlow model age is calculated by averaging the travel times for water entering the top and bottom of the screened interval.

^dEstimated year is based on a tritium concentration of 24 pCi/L.

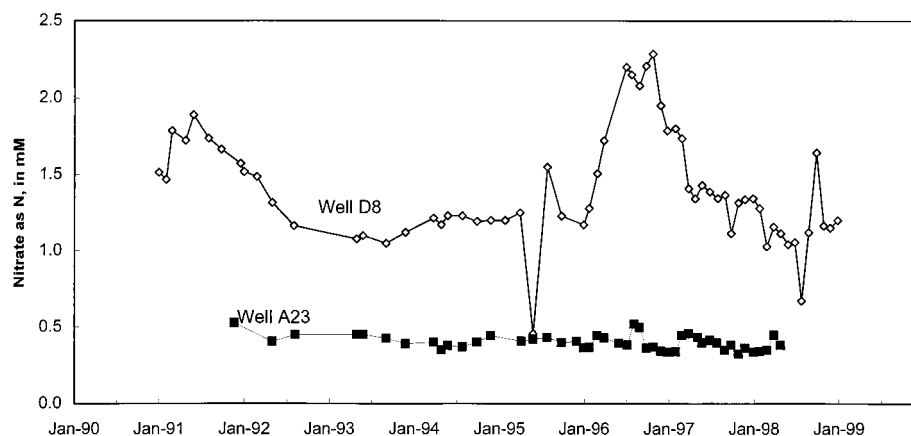


Figure 10. Nitrate concentrations in groundwater from wells A23 and D8 versus time.

that contamination has occurred, groundwater age estimates were based on CFC 11 or CFC 113 concentrations. Degradation or sorption of these compounds is indicated here by the consistently older ages provided by CFC 11 and CFC 113 than those of CFC 12. As such, these values are also presented as maximum ages.

Because of the limitations discussed above, most CFC age estimates provide only an upper bound on the age of groundwater (Table 3). Comparing flow model ages to the maximum CFC ages in these water samples suggests that actual groundwater ages might be up to 3 times older than model ages. Actual ages that are significantly younger than model ages are unlikely given the fact that the hydraulic conductivity value used in the model is in the top quartile of measured values for this aquifer. Denitrification rate calculations to follow were made based on groundwater travel times from the groundwater flow model with the recognition that rates may overestimate actual rates by as much as a factor of 3 because of uncertainties in groundwater velocities.

3.3.1. Denitrification rates along the shallow flow path.

Along the shallow flow path, profiles of the concentrations of nitrate, nitrite, and dissolved oxygen all suggest that denitrification occurs more quickly than along the deep flow path. Assuming there are no other sources or sinks of nitrate along this flow path, it is possible to calculate an average rate of denitrification in this zone using the nitrate concentrations in an upgradient and downgradient well pair and the groundwater travel time between these wells.

The groundwater travel time between D8 and E7 is estimated by the flow model to be approximately 9 months. Nitrate concentrations in groundwater from well D8 have varied from 1 to 2 mM over the 7 year period from 1991 to 1998, with no apparent trend with respect to time (Figure 10). A similar relation is observed for other shallow wells in the aerobic portion of the aquifer (not shown). Since no nitrate is present in E7 or other wells in this area, complete removal of 1–2 mM of nitrate occurred over a 9 month period, resulting in an average denitrification rate over this interval of between 1.3 and 2.7 mM of nitrate per year.

Alternatively, denitrification rates can be determined using groundwater travel times and excess N_2 concentrations [e.g., Vogel *et al.*, 1981]. While the same assumption is required regarding sources and sinks, there are no other likely sources

of excess N_2 in groundwater, and the only sink is outgassing. Where outgassing was suspected, denitrification rates are reported as minimum values. Denitrification rates up to and possibly exceeding 1.0 mM per year were calculated from excess N_2 measurements and groundwater travel times for only the portion of the flow path that is in an anaerobic environment where denitrification can occur (assumed to be from well D8 to E7, Figure 8). These estimates are in general agreement with the range in denitrification rates calculated based on nitrate loss.

Denitrification rates estimated using both nitrate loss and N_2 production are average values since the rate of denitrification is essentially zero at wells D8 and E7 because of inhibition due to the presence of dissolved oxygen and lack of nitrate, respectively. As such, reaction rates must occur more quickly at some point between wells D8 and E7. Two in situ experiments were conducted to estimate denitrification rates immediately adjacent to Fishtrap Creek and to improve estimates of denitrification across the redoxcline. The first experiment was conducted using a well which was less than 10 m east of Fishtrap Creek to estimate denitrification rates in the streamside portion of the aquifer (for landowner privacy considerations, exact well locations are not given). High denitrification rates have been observed near streams in other environments [e.g., Duff and Triska, 1990]. The well is screened between 7 and 8 m below land surface and has a depth to water which is typically less than 2 m. As described in section 2.1, the experiment was initiated by pumping approximately 180 L of groundwater mixed with NaBr and KNO_3 into the well. Bromide, nitrate, nitrite and ammonium concentrations were monitored during the course of the experiment. Nitrate concentrations decrease more quickly than bromide indicating that nitrate reduction is occurring (Figure 11). Nitrate concentrations, corrected for dilution using bromide data, indicated a loss of 0.016 mM per hour (140 mM per year, Figure 11). Essentially constant levels of ammonium during the course of this experiment are evidence that nitrate loss was primarily by denitrification and not by nitrate reduction to ammonium. Sulfate and iron concentrations increased only slightly during the experiment, suggesting that significant amounts of pyrite oxidation did not occur. This well did not contain a sulfur odor or detectable concentrations of sulfide.

To better estimate the rate at which denitrification occurs at

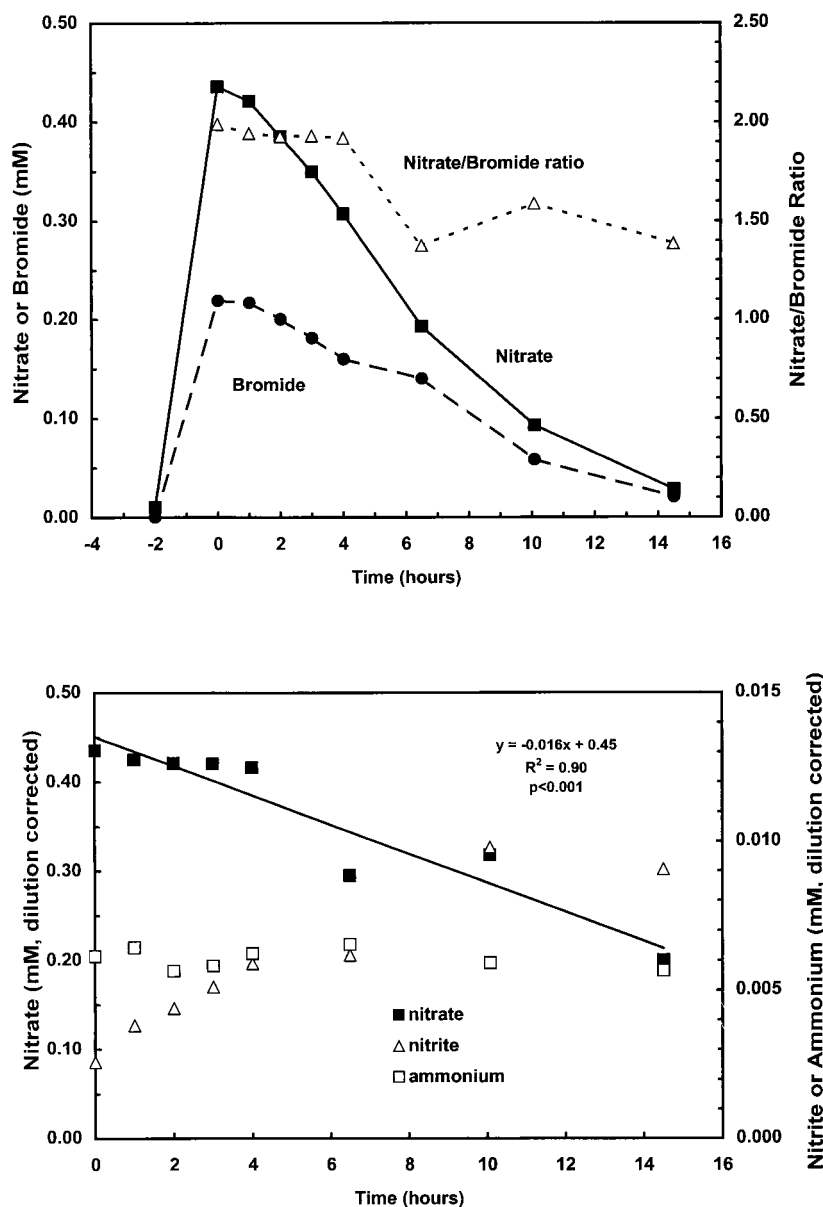


Figure 11. (top) Nitrate and bromide concentrations and nitrate/bromide ratio in groundwater during an in situ experiment conducted within 10 m of Fishtap Creek. (bottom) Nitrate, nitrite, and ammonium concentrations during the experiment which have been corrected for dilution. Line is linear regression of nitrate concentration data.

the redoxcline, an in situ denitrification experiment was conducted in this portion of the aquifer. The well used for this experiment is approximately 500 m east of Fishtap Creek and is screened between 5.8 and 6.7 m below land surface. Depth to water in this well is typically less than 3 m. The loss of nitrate was not statistically significant ($p = 0.72$), indicating that the rate of denitrification was too low (estimated to be <45 mM per year) to be measured during the duration of this experiment. In experiments of this type, reactions must take place before the groundwater-reagent mixture is swept downgradient. Unlike the well used in the first experiment, water from this well has not had detectable concentrations of nitrate for several years (if ever). Nitrate-poor sites are thought to respond much more slowly to nitrate additions [Groffman, 1994], which may explain the slower rate observed here in spite of the

strong reducing conditions found in this portion of the aquifer. Another possible explanation of slower rates in this experiment than in the streamside experiment is that a different electron donor may be dominant. The well used in the second experiment contained trace levels of sulfide and increased iron concentrations, suggesting that iron sulfides may be important electron donors in this portion of the aquifer. Increasing proportions of inorganic electron donors likely affect denitrification rates; however, their effect on rates is not well understood [Korom, 1991; Böettcher et al., 1991].

3.3.2. Denitrification rates along the deep flow path. The low levels of dissolved oxygen along the deep flow path and the presence of nitrite in the water samples from the deep wells at sites A and B suggest that denitrification is occurring in this portion of the aquifer. Farther downgradient along the deeper

flow path at well E17, excess N_2 is observed, additional evidence that denitrification occurs.

A groundwater travel time from the deep well at site A (well A23) to a location just below E17 is estimated to be 4 years from the groundwater flow model. Concentrations of nitrate in well A23 have been fairly consistent over the past 7 years at a concentration of approximately 0.4 mM (Figure 10). Complete nitrate reduction is indicated by the time groundwater reaches site E since all deep (and shallow wells for that matter) show nondetectable nitrate levels, resulting in an average denitrification rate of 0.1 mM per year for deep groundwater in this aquifer. Average denitrification rates calculated from excess N_2 measurements and groundwater travel times for only the portion of the flow path that is in an anaerobic environment where denitrification can occur (assumed to be from well A23 to E17) range from 0.02 to 0.14 mM per year (Figure 8). These rates are in general agreement with those calculated based on nitrate loss.

3.3.3. Denitrification rate comparisons. Few studies have focused on identifying aquifer-wide denitrification rates. Rates across this aquifer have markedly different rates of denitrification: Potentially fast rates occur in streamside groundwater, somewhat slower rates occur in shallow groundwater across the redoxcline, and much slower rates occur in deeper portions of the aquifer. Rates found here were converted to $\mu\text{mol cm}^{-3}$ aquifer yr^{-1} assuming a porosity of 0.3 in order to compare them to denitrification rates from other investigations.

Nitrous oxide production in sediment slurries collected from streamside (<12 m inland) cores was used to estimate potential denitrification rates adjacent to a stream in northern California [Duff and Triska, 1990]. The movement of surface water containing relatively high concentrations of dissolved oxygen into these wells resulted in aerobic conditions for many of the sites examined. Potential denitrification rates increased with increasing distance from the stream, with a maximum rate of approximately $100 \mu\text{mol cm}^{-3}$ aquifer yr^{-1} for the only sample that likely represented true groundwater. This value is of similar magnitude as the potential denitrification rate of $42 \mu\text{mol cm}^{-3}$ aquifer yr^{-1} obtained in the streamside in situ experiment conducted here. High rates in this region are facilitated by anaerobic conditions and the ample supply of electron donors (organic carbon and reduced minerals) often found in this zone.

Shallow anaerobic groundwater not immediately adjacent to streams has variable but generally lower denitrification rates. Natural gradient tracer tests (a depth to water of 5 m and a tracer test depth below water table of 4 m) yielded potential denitrification rates ranging from 0.44 to $1.1 \mu\text{mol cm}^{-3}$ aquifer yr^{-1} for a shallow sand and gravel aquifer on Cape Cod, Massachusetts [Smith et al., 1996]. Higher estimates of potential denitrification rates ($24 \mu\text{mol cm}^{-3}$ aquifer yr^{-1}) were calculated from an in situ experiment conducted 3 m below the land surface in a shallow aquifer in Ontario, Canada [Trudell et al., 1986]. The range of values estimated for the redoxcline in this aquifer ($0.3\text{--}0.8 \mu\text{mol cm}^{-3}$ aquifer yr^{-1}) is similar to that found by Smith et al. [1996]; however, higher rates would have likely been found in this study had a finer sampling grid been available. Relatively low denitrification rates were observed along the deep flow path in this study ($<0.04 \mu\text{mol cm}^{-3}$ aquifer yr^{-1}). Few studies have examined denitrification rates at significant depths below the water table (>15 m in this study); however, lower rates of denitrification might be expected as reaction rates become limited by low nitrate concentrations.

4. Conclusions

Multiple lines of evidence were used to evaluate the rate and mechanism of nitrate reduction along groundwater flow paths in a glacial outwash aquifer. The fate of nitrate varies considerably across this aquifer and illustrates the importance of adequately linking chemical changes to flow paths. While much of the aquifer has negligible nitrate reduction because of insufficient electron donors (as evidenced by the presence of dissolved oxygen), areas exist where significant denitrification occurs. Rapid and essentially complete reduction of large amounts of nitrate in a heavily contaminated aquifer occurs in shallow groundwater adjacent to a third-order stream, with average denitrification rates calculated using nitrate loss and increases in excess N_2 ranging from 1.0 to 2.7 mM per year. However, these values likely underpredict denitrification rates occurring at the redoxcline. In situ experiments conducted adjacent to the stream suggest potential denitrification rates may be as high as 140 mM per year. In deeper, anaerobic portions of the aquifer, denitrification occurs much more slowly, with rates less than 0.14 mM per year. High denitrification rates associated with the stream illustrate the importance of minimizing the use of drainage systems (e.g., tile drains) which bypass riparian zones and discharge directly to streams. Mass and electron balance calculations suggest that iron sulfide deposits and to a lesser degree organic matter are likely electron donors for denitrification reactions occurring in the riparian zone.

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