

Transport And Fate Of Nitrate In A Glacial Outwash Aquifer In Relation To Ground-Water Age, Land Use Practices and Redox Processes

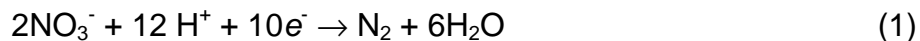
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ABSTRACT

A combination of ground-water modeling, chemical and dissolved gas analyses, and chlorofluorocarbon age dating of water was used to determine the relation between changes in agricultural practices, and NO_3^- concentrations in ground water of a glacial outwash aquifer in west-central Minnesota. The results revealed a redox zonation throughout the saturated zone with oxygen reduction near the water table, NO_3^- reduction immediately below it, and then a large zone of ferric iron reduction, with a small area of sulfate (SO_4^{2-}) reduction and methanogenesis (CH_4) near the end of the transect. Analytical and NETPATH modeling results supported the hypothesis that organic carbon served as the electron donor for the redox reactions. Denitrification rates were small, 0.005 to 0.047 $\text{mmol NO}_3^- \text{ yr}^{-1}$, and were limited by the small amounts of organic carbon, 0.01 to 1.45 percent. In spite of the organic carbon limitation, denitrification was virtually complete because residence time is sufficient to allow even slow processes to reach completion. Ground-water sample ages showed that maximum residence times were on the order of 50-70 years. Reconstructed NO_3^- concentrations, estimated from measured NO_3^- and dissolved nitrogen gas showed that NO_3^- concentrations have been increasing in the aquifer since the 1940s have been above the 714 $\mu\text{mol L}^{-1}$ maximum contaminant level at most sites since the mid- to late-1960s. This increase in NO_3^- has been accompanied by a corresponding increase in agricultural use of fertilizer, identified as the major source of NO_3^- to the aquifer.

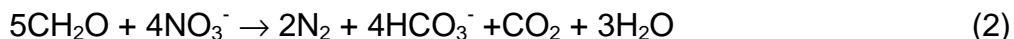
INTRODUCTION

Nitrate is recognized as the most ubiquitous contaminant of shallow aquifers (Postma et al., 1991; Spalding and Parrott, 1994). This ground-water contamination provides cause for concern because elevated concentrations of NO_3^- have been associated with human health risks (Spalding and Parrott, 1994), and when NO_3^- discharges to surface waters it may contribute to eutrophication. Consequently, there has been growing interest in processes and conditions that lead to natural remediation of NO_3^- contaminated aquifers. The primary pathway for removal of NO_3^- from ground water is denitrification, wherein nitrogen serves as the terminal electron acceptor following the general reaction:



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Bacteria that derive energy from the oxidation of a reduced species typically mediate this reaction. Organic carbon (Gillham and Cherry; 1978, Morris et al., 1988; Starr and Gillham, 1993) is a common electron donor in the heterotrophic denitrification process:



Alternatively, other reduced species such as ferrous iron in pyrite (FeS_2) and silicate minerals such as pyroxenes and amphiboles, can serve as the electron donor in the autotrophic denitrification process (Kolle et al., 1983; Strebel et al., 1985; van Beek et al., 1988; Postma et al., 1991; Bohlke and Denver, 1995):



It is significant that in all these reactions, NO_3^- is converted from a potentially harmful form to a benign form as N_2 gas. Under most conditions, the N_2 gas produced as the result of denitrification will remain in solution until the ground water discharges to a surface-water body and equilibrates with the atmosphere (Heaton and Vogel, 1981; Blicher-Mathiesen, 1998). By measuring this excess N_2 , it is possible to estimate the amount of NO_3^- originally present in the ground water (Heaton and Vogel, 1981; Vogel et al., 1981; Wilson, et al., 1990; Smith et al., 1991; Bohlke and Denver, 1995; Blicher-Mathiesen, 1998; Modica et al., 1998).

Dissolved oxygen (O_2) is thermodynamically favored over NO_3^- as the terminal electron acceptor in the oxidation of organic carbon (Stumm and Morgan, 1981; Chapelle et al., 1995). When virtually all the available O_2 is consumed, denitrification becomes the terminal electron accepting process, leading to lower NO_3^- concentrations as well. Once most of the available NO_3^- 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 will be favored. The net result of this evolution of water chemistry is a predictable sequence where O_2 and then NO_3^- are consumed, manganese and iron come into solution, sulfate is consumed and sulfide may come into solution, and finally methane may appear in solution (Chapelle et al., 1995). This predictable sequence, under some conditions, may allow determination of the redox state of the aquifer at various points along a flow path, and prediction of the fate of NO_3^- in the aquifer. Few studies have conducted a complete, simultaneous analysis of the various nitrogen species, particularly N_2 , coupled with an analysis of the redox processes involved, leaving many questions unanswered with respect to the true fate of NO_3^- .

In addition to denitrification, other factors may affect spatial and temporal patterns of NO_3^- along ground-water flow paths. For example, inputs of nitrogen in atmospheric deposition, fertilizer, and animal wastes have increased markedly over the past 5 decades (Puckett, 1995). When ground waters of increasing age are analyzed, the older waters will appear to have less NO_3^- simply because they received less at the time of recharge. Also, conditions favoring denitrification can be patchy in some environments (Addy et al., 1999; Gold et al., 1998; Jacinthe et al., 1998) making it

possible to have discordant NO_3^- concentrations in an aquifer. All of these conditions make it necessary to develop a complete understanding of both the hydrogeologic and biogeochemical processes involved in the transport and fate of NO_3^- .

Puckett et al. (1999) presented a mass-balance analysis for the Otter Tail aquifer system in west-central Minnesota and concluded that although the 212.4 km² system receives about 2000 metric tons of nitrogen each year, only 229 metric tons (11 percent) actually enters the ground-water system. Their analysis indicated that about 181 metric tons (44 percent) of the excess nitrogen leaving the root zone was removed through denitrification. Their evidence for denitrification was based on the loss of nitrate from the system in the mass-balance model as well as an analysis of the oxidation-reduction (redox) conditions in ground water sampled as part of the study. However, that analysis focused entirely on landscape and watershed processes, including the upper 2 meters of the shallow ground-water system; no information was provided on the transport and fate of nitrogen as it moved through the aquifer. Because of the potentially harmful nature of NO_3^- , it is important to understand its transport from the shallow ground-water system into deeper portions of aquifers where most drinking water well screens are located. Also, developing a complete understanding of the biogeochemical reactions involved in the transformation of NO_3^- to other forms may allow us to more accurately predict when and where drinking water supplies may be contaminated.

In this paper, we present the results of a study designed to examine the hydrogeologic and biogeochemical processes controlling the evolution of water chemistry along flow paths of a representative cross-section within the Otter Tail aquifer studied by Puckett et al. (1999). We examine the hypothesis that denitrification is responsible for the loss of NO_3^- and further that it is driven by oxidation of organic matter. We also consider the hypothesis that changes in concentrations of NO_3^- are a function of changes in agricultural practices over time and, therefore, the age of water sampled along the transect. In evaluating these hypotheses, we develop an analysis of the transport and fate of the major nitrogen species, the redox reactions involved, and the age-distribution of waters along the transect.

STUDY AREA

This study was conducted in Otter Tail County in west-central Minnesota, USA (Figure 1) in a 36 km² 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. Cowdery (1995) reported that the outwash material consisted of 21% gravel, 45% coarse sand, 27% medium sand, and 7% fine sand and silt. 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).

Recharge to the aquifer occurs over much of its area from snowmelt and rainfall and was estimated at 17.7 cm yr^{-1} on the basis of a hydrologic budget and analyses of ground-water hydrographs (Cowdery, 1997; Puckett et al., 1999). Ground-water 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 ground water. Water loss from the aquifer is through discharge to the Otter Tail River, lakes, wetlands, pumping from wells, and through evapotranspiration.

Climate of the West Central Minnesota climate division has been described as sub-humid continental and annual average temperature and precipitation in the area during the 30-year period from 1966 to 1995 was 5.6° C and 68 cm, respectively (Stoner et al., 1993). Open water evaporation in the study area exceeds precipitation by about 10 cm yr^{-1} (Winter and Woo, 1990) consequently ground-water recharge occurs primarily during spring snowmelt when potential evaporation is small. Historically the study area was prairie, surrounded by hardwood and conifer forests on the morainal uplands however, at the time of the study, approximately 73 percent of the land was cropland.

Fertilizer nitrogen use for agricultural purposes in Otter Tail County (Figure 2) increased from about 28 metric tons in 1945 to about 13000 metric tons in 1994 (Jerald Fletcher, 1996, West Virginia University, written communication). A major step change in the application rate occurred about 1967 and the rate of increase has been essentially linear since about 1970. Over half of the total amount of nitrogen used during the 1945-1994 period has been applied since 1982.

METHODS

Study Design

Piezometers were installed at 5 locations along a 5 km transect, beginning near the northeastern edge of the aquifer and ending at the Otter Tail River to the southwest (Figure 1, 3). This transect was chosen after examination of a water-table map developed from ground-water measurements made in wells in the area and from Reeder (1972). The 5 sites were chosen to provide roughly equidistant sampling points along the transect, although access limitations dictated that some sites were spaced closer than others. At three locations multiple piezometers were installed in a nest to define vertical gradients in the flow system. Screens were positioned to allow sampling of recently recharged ground water just below the water table at each site. Multiple screened intervals were positioned at 4 other depths at OF1, the most down gradient site, and at a deep and intermediate depth position at OF3, roughly at the midpoint of the transect. An additional deep screened interval was installed at site OF2 to provide more detail in that portion of the aquifer. The resulting distribution of sampling points was concentrated in the lower half of the transect where we expected the greatest age distribution and variability in ground-water concentrations due to biogeochemical evolution along longer flow paths.

Piezometers installed for the study were made of 5-cm inside-diameter, polyvinyl chloride (PVC) pipe with slotted PVC screens 1.5 meters (m) long; the exceptions being site OF3S which was 3 m long and sites OF1A, OF1B, and OF1C which were 0.76 m long. Longer screens were used in locations where extreme fluctuations in water table elevations were expected. After the PVC pipe was set, the hollow-stem auger flights were removed, allowing the aquifer formation to collapse around the screen. Piezometers were then sealed with at least 0.6 m of bentonite pellets and drill cuttings were used to fill the annulus to within 0.6 m of land surface. A 2-m long, steel protection pipe was set in concrete around the well and closed with a locking cap. Between well sites, the power auger was steam-cleaned to prevent cross-contamination. Piezometers were developed until they supplied clear water at a rate of at least 2 L min⁻¹. No water was introduced into the well except deionized water where necessary for development.

Hydrologic Modeling

The ground-water flow models MODFLOW (McDonald and Harbaugh, 1988; Harbaugh and McDonald, 1996) and MODPATH (Pollock, 1989) were used to develop a 3-dimensional steady-state flow model of the study area, delineate flow paths, and estimate ground-water travel times. A 3-layer model was constructed for a 26.7-km² portion of the study area using approximately 100 by 100 m cell dimensions. The model was based on a detailed study of the physical and hydrologic characteristics of the aquifer reported by Reeder (1972). The bottom of Layer 1 was set at 4 m below the initial water table and configured as unconfined with an average effective recharge rate (total precipitation minus losses from runoff and evapotranspiration) of 17.7 cm yr⁻¹ (Puckett et al., 1999). Layer 2 was 4 m thick and the thickness of layer 3 varied depending on the total thickness of the aquifer. Based on reported hydraulic conductivities of 0.009 m d⁻¹ for the underlying till, and 27 to 183 m d⁻¹ for the aquifer materials (Reeder, 1972), the bottom of layer 3 was designated as a no-flow boundary as were the northern, eastern, and western edges of the model area; porosity of the sand was assumed to be 0.3. Although flow may occur across the boundary at the till-sand contact, because of the great disparity in hydraulic conductivities, this component of flow was not considered to be significant. The boundary with Little Pine Lake on the southeastern corner of the area was modeled with constant head cells. The Otter Tail River on the southern side was modeled using the river option with a conductance per unit length of 300 m² d⁻¹ m⁻¹ assuming a vertical hydraulic conductivity of 6 m d⁻¹, an average width of 50 m, and a thickness of 1 m. Wetlands were modeled as drains with a conductance per unit length of 83 m³ d⁻¹ m⁻¹ assuming a vertical hydraulic conductivity of 0.5 m d⁻¹, an average width of 50 m, and a thickness of 0.3 m. Peat hydraulic conductivities used in estimating wetland conductance were based on a range of measurements reported by Siegel and Glaser (1987), Siegel (1988), and Romanowicz et al. (1993). Isotropic conditions of horizontal hydraulic conductivity and a ratio of horizontal to vertical hydraulic conductivity of 5 were assumed.

The ground-water model was calibrated by adjusting the hydraulic conductivity until horizontal hydraulic gradients and predicted water levels reasonably matched those reported in previous investigations and determined by water-level measurements in this

study (Reeder, 1972). The model-applied hydraulic conductivity of 30 m d^{-1} was at the lower end of the reported range of 27 to 183 m d^{-1} and all factors used in the simulations were within reasonable limits of measured or reported values (Reeder, 1972; Fetter, 1994). The path-line tracking option of MODPATH was used to compute ground-water travel times and delineate flow paths. When initiating particle tracking, particles were placed at the midpoint depth of each well screen (which was the point where we sampled), and the reverse tracking option was used to track the particle back to the position at the water table where it would have originated.

Sample Collection and Analysis

Sediment samples were collected using a continuous piston core barrel with a polycarbonate sleeve. Selected samples from sites 1 and 3 were sorted into bulk and $<1 \text{ }\mu\text{m}$ size fractions and analyzed for mineralogy by x-ray diffraction. Samples for these analyses were selected to provide a description of mineralogy at several points across the thickness of the aquifer at these locations. A separate aliquot of each sample was analyzed for total carbon (C), 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).

Piezometers were sampled up to 7 times during the period from April 1994 to August 1997, using a stainless steel positive displacement pump with Teflon tubing. Sampling procedures are detailed in protocols by Koterba et al. (1995) and Menheer and Brigham (1997) report the specific application of these protocols to this study. Water temperature, specific conductance, and dissolved-oxygen (O_2) concentration were continuously monitored prior to sample collection. When these measures stabilized, and at least three casing volumes of water had been extracted from the piezometer, sample collection began.

Samples were filtered through a $0.45 \text{ }\mu\text{m}$ nitrocellulose filter (a silver filter was used for dissolved organic carbon (DOC) samples. Mercuric chloride preservative was added to nutrient samples during 1994 but afterwards, no preservative was added, instead samples were shipped on ice the same day to the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado for immediate analyses; cation samples were preserved with nitric acid. Alkalinity was determined in the field by incremental titration of filtered samples. Specific conductivity, pH, temperature, and O_2 were all measured in a sealed flow-through cell attached to the sample discharge line.

Major cations and silica were analyzed by inductively-coupled plasma spectroscopy, anions by ion chromatography, nutrients by colorimetric methods (Fishman and Friedman, 1989; Fishman, 1993; Wershaw et al., 1987) and DOC by persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1992). Equipment blank samples, field blank samples, replicate samples, and spiked samples (Koterba et al., 1995; Menheer and Brigham, 1997) showed a general lack of sampling contamination.

Sulfide (S^{2-}) was measured by the methylene blue method (Standard Methods, 1975). Samples were processed immediately using a HACH 2000 portable spectrophotometer with a detection limit of $1.87 \mu\text{mol L}^{-1} S^{2-}$. The geochemical model WATEQ as implemented in NETPATH (Plummer et al., 1994) was used for speciation and calculation of saturation indices. The WATEQ output was then used in the NETPATH program (Plummer et al., 1994) to evaluate various biogeochemical reactions controlling water chemistry along the transect.

Dissolved gases (N_2 , Ar, CO_2 , CH_4 , O_2) were analyzed in ground-water 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 ± 2 -4 percent. Concentrations of 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 N_2 in ground water and the atmosphere was the only source of Ar. However, excess air can also become trapped in recharging ground water due to entrainment of air bubbles, and increase dissolved gas concentrations accordingly. This is more of a problem in arid zones where rapid recharge occurs and in fine-grained sediments, but is usually small in coarse sediments and fractures. Where excess air alone affects dissolved gas concentrations, N_2 and Ar increase linearly in a ratio defined by their relative solubilities in water and concentrations in the atmosphere, making it possible to estimate the amount of excess air, which typically is negligible (less than 3 cc kg^{-1}) and often ignored in studies of this nature (Busenberg et al., 1993; Bohlke and Denver, 1995; Plummer and Busenburg, 1999). However, we made corrections to the excess 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 NO_3^- (prior to denitrification) as the sum of measured NO_3^- and excess N_2 . Denitrification rates were calculated by dividing the excess N_2 gas by sample age.

We also applied the methods presented by Blicher-Mathiesen et al. (1998) to evaluate the potential for degassing of ground water. This method involves comparing the total partial pressures of dissolved gases in each sample to the hydrostatic pressure of the sampled piezometer. Where partial pressures exceed hydrostatic pressure the potential exists for degassing.

Samples for analyses of the chlorofluorocarbons $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), and $C_2F_3Cl_3$ (CFC-113) were collected using a stainless steel sampling apparatus under an ultra-pure nitrogen atmosphere and were flame sealed in 62 cc borosilicate glass ampoules, 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 (pg kg^{-1}) for CFC-11 and CFC-12 and 1.0 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 based on 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 based on the average annual temperature (Busenberg and Plummer, 1992). These methods result in a potential uncertainty of about 2° C which translates to an age-dating 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 and are considered a minimum age (Plummer and Busenberg, 1999).

RESULTS

Hydrogeology

Bulk fraction mineralogy (Table 1) was dominated at both sites by five minerals: quartz, plagioclase (probably albite), potassium feldspar, dolomite, and calcite. Quartz was the most abundant except at site OF3, near the contact with the underlying till where plagioclase dominated. Also, potassium feldspar was more common at site OF3 and only appeared in the sample from 12.2 m deep at site OF11. Dolomite (up to 19 percent) was usually more abundant than calcite (up to 15 percent) although, values in the 1-3 percent range for each were more common. Examination of sediments during drilling revealed that most of the sand was tinted a yellow-red color indicating the presence of iron oxide coatings. These results are also consistent with those reported by Berndt (1987) and Tuccillo et al. (1999) for outwash deposits nearby in the vicinity of Bemidji, Minnesota.

Among the <1 µm size fraction minerals, smectite (probably montmorillonite) was consistently most abundant, followed by illite and kaolinite. Chlorite appeared in samples from site 1 whereas dolomite was in all the samples and calcite was not detected in the 11.6 m deep sample from site OF3. Feldspars (probably albite and potassium feldspar) were common in all samples and hornblende may have been present in 3 samples.

Total carbon was in consistently greater abundance at site OF1, ranging from 1.11 to 3.17 percent, than at site OF3 where it ranged from 0.06 to 0.89 percent. Interestingly the peak abundance at site OF1 coincided with what had been identified during drilling as a thin black organic layer at 4.6 m in depth. Inorganic carbon abundance was similar in all samples except for the shallow sample at site OF3 where it was 0.04 percent and the black organic layer at site OF1 where it was 1.71 percent. Organic carbon abundance was variable ranging from 0.01 to 1.45 percent (median=0.15) with the

largest abundance in the black organic layer at site OF1 and the smallest in the shallow sample from site OF3.

Results of the MODFLOW/MODPATH models indicated that ground water generally flowed north to south, towards the Otter Tail River or Little Pine Lake. Predicted and observed water levels (Table 2) agreed within about 0.6 m with a root mean square error (RMS) of 0.44. Simulated flow lines and particle tracking results from the MODPATH simulation (Figure 4) indicated that travel times increased with increasing depth and distance traveled along the transect. Ground water flowing along the deepest and longest flow paths along the transect, from the northern edge of the aquifer to the Otter Tail River, can be expected to take >70 years to reach its discharge point in the area of the Otter Tail River (Figure 4). The net result is a well-stratified age distribution within the aquifer (Figure 5).

Dissolved Gases

Although the median O_2 concentration was $8 \mu\text{mol L}^{-1}$ and values as high as $225 \mu\text{mol L}^{-1}$ were measured, these were well below the equilibrium value of $373 \mu\text{mol L}^{-1}$ at 5.6°C . With the exception of site OF1S, dissolved oxygen concentrations decreased with both increasing age and depth (Table 3) suggesting that oxygen was being consumed within the system, presumably to oxidize organic carbon in the outwash sediments. With minor exceptions, samples greater than 10 years old were suboxic ($< 64 \mu\text{mol L}^{-1}$) and appeared to shift from O_2 reduction to denitrification as the terminal electron accepting process.

Concentrations of N_2 ranged from near equilibrium with the atmosphere ($682 \mu\text{mol L}^{-1}$ at 5.6°C) to $982 \mu\text{mol L}^{-1}$ with a median of $828 \mu\text{mol L}^{-1}$ and Ar concentrations ranged from 15.0 to $20.3 \mu\text{mol L}^{-1}$ (Table 3, Figure 6). The smallest excess N_2 concentrations were in waters containing the most O_2 , whereas the greatest concentrations were in water containing little or no O_2 (Table 3), suggesting that denitrification was producing the excess N_2 . Excess N_2 concentrations were as large as $394.4 \mu\text{mol L}^{-1}$; equivalent to $788.8 \mu\text{mol L}^{-1} \text{NO}_3^-$, assuming the excess N_2 was derived from denitrification. Also, excess N_2 concentrations were generally less than $100 \mu\text{mol L}^{-1}$ in the shallow portions of the aquifer near the water table, increased to the maximum $394.4 \mu\text{mol L}^{-1}$ at mid-depths, and then decreased again in the deeper, down-gradient portions of the transect (Figure 7). Denitrification rates calculated from excess N_2 gas and sample age, ranged from 0.005 to $0.047 \text{ mmol NO}_3^- \text{ L}^{-1} \text{ yr}^{-1}$.

Both S^{2-} and CH_4 concentrations were below detection or negligible in all but the deepest samples (Table 3). S^{2-} concentrations rose above the detection limit in those samples where SO_4^{2-} concentrations decreased sharply (Table 4), but even in those cases it remained below $1.0 \mu\text{mol L}^{-1}$ as would be expected given the tendency of S^{2-} to form iron sulfide precipitates. The presence of both S^{2-} and CH_4 in these deeper portions of the transect indicates the development of relatively strong reducing conditions there.

CFC Apparent Age Dates

CFC apparent ages ranged from 5 years in the shallow piezometers to >50 years at OF1D and are consistent with the modeling results, given the greater uncertainty of the post-1970 apparent ages. There was a pattern of increasing age with increasing depth along the transect (Figure 5), and a linear relationship ($r^2=0.759$) between age and depth. The CFC apparent ages and those simulated using the MODPATH model were generally in good agreement ($r^2=0.835$) although the MODPATH ages tended to be younger (Table 2).

CFC apparent ages reflect the year in which ground water was last in contact with unsaturated zone air (Cook and Solomon, 1997) and previous 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, and about 2.5 to 4.8 years for water to then reach the sampling zone of the shallow piezometers (Stoner et al., 1997; Puckett et al., 1999). Therefore, a lag of 3 to 6 years between the age of shallow samples and the year in which the precipitation fell is expected. Dissolved gas results indicated that at this site excess air was small and therefore the effects on CFC apparent-age dates were negligible (Plummer and Busenberg, 1999). CFC data for piezometers OF4S and OF3M were much older than could be explained based on model projections. The recharge areas for these sites however, are in an old outwash channel containing wetlands, factors we feel resulted in sorption of the CFC's, leading to the older apparent ages.

Major Ion Chemistry

Concentrations of NO_3^- which were as high as $1785 \mu\text{mol L}^{-1}$ with a median of $107 \mu\text{mol L}^{-1}$, behaved like O_2 , decreasing with both increasing age and depth (Table 3, Figure 8). This decreasing pattern suggested that once O_2 was depleted, NO_3^- was utilized as the terminal electron acceptor in the oxidation of organic carbon. Samples greater than 30 years old were essentially depleted of NO_3^- . Concentrations of NH_4^+ reached $50 \mu\text{mol L}^{-1}$ with a median of $2.1 \mu\text{mol L}^{-1}$. There was a general trend of increasing NH_4^+ concentration with increasing age and depth. Although the exact source of NH_4^+ was not determined, in other studies of sediments in similar redox environments, NH_4^+ production has been traced to mineralization of organic nitrogen and not to dissimilatory nitrate reduction (McMahon et al., 1999). Other forms of nitrogen were negligible.

Median DOC concentration was $158 \mu\text{mol L}^{-1}$ but ranged as high as $375 \mu\text{mol L}^{-1}$, and generally increased with depth. There are several possible explanations for the near-linear increase in DOC concentrations with depth. First, it may be due to the fact that in earlier years there may not have been sufficient terminal electron acceptors such as NO_3^- , available to support DOC oxidation. Second, DOC concentrations may have been greater in earlier years. Finally, there is the possibility that DOC concentrations increased over time due to accumulation of the more refractory by-products of organic carbon decomposition.

Iron concentrations displayed a large range, from below detection to as high as 135 $\mu\text{mol L}^{-1}$. Such relatively large concentrations of dissolved iron suggests that the predominant terminal electron accepting process had changed from reduction of O_2 , NO_3^- , and manganese oxides to iron oxide reduction. Furthermore, these concentrations are consistent with results from similar sediments nearby in Bemidji, Minnesota that contain sufficient coatings of iron oxides on quartz and feldspar grains to generate Fe^{2+} concentrations of 35000 $\mu\text{mol L}^{-1}$ if reduced simultaneously (Tuccillo et al., 1999). Manganese concentrations reached as much as 11 $\mu\text{mol L}^{-1}$ and typically peaked when most NO_3^- had been consumed and Fe^{2+} was increasing. This pattern agrees with the reported redox sequence where manganese oxide reduction occurs at pe levels after denitrification and before iron oxide reduction (Stumm and Morgan, 1981).

Ca^{2+} , Mg^{2+} , and HCO_3^- were the dominant dissolved species, which is consistent with what is known of the outwash mineralogy and agricultural applications. Farmers in the area typically apply 6.7-8.9 metric tons $\text{ha}^{-1} \text{yr}^{-1}$ of limestone containing both calcite and dolomite (Denzel Cooper, University of Minnesota Extension Service, oral communication, 1996). Infiltrating ground waters would therefore be expected to develop a carbonate signature as a result of dissolution of these carbonates. The ratio of Ca^{2+} to Mg^{2+} was approximately 2:1 which suggests dissolution of calcite and dolomite in roughly equal amounts. HCO_3^- concentrations generally increased with increasing depth in the aquifer.

Chloride (Cl^-) and sulfate (SO_4^{2-}) concentrations ranged as high as 2003 and 1103 $\mu\text{mol L}^{-1}$, respectively. Chloride commonly occurs in fertilizer as potassium chloride (KCl) and is a common contaminant associated with agricultural areas. With respect to sulfur, there is little available in the outwash sediments; therefore, it is commonly supplied as an agricultural supplement either as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or in more recent years as ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) at rates of 28-336 kg S ha^{-1} (Denzel Cooper, University of Minnesota Extension Service, oral communication, 1996). Typically, the larger amount is applied once in a 6-year rotation as a starter for alfalfa and the smaller amount is applied as a starter for corn. At the estimated ground-water recharge rate of 17.7 cm yr^{-1} (Cowdery, 1997; Puckett et al., 1999), these application rates would result in a spatially average concentration of 495-5934 $\mu\text{mol SO}_4^{2-} \text{L}^{-1}$ and therefore can easily account for the observed concentrations. The distributions of both Cl^- and SO_4^{2-} (Figure 9a, b) reflect the most intensive areas of agriculture along the transect, and the lowest concentrations are generally found in the deeper, down-gradient portions of the transect. These lower concentrations also are associated with the oldest ground waters, which is to be expected since less fertilizer was used at that time and some SO_4^{2-} reduction occurred as well.

Biogeochemical Modeling

The NETPATH model (Plummer et al., 1994) employs a reverse-reaction process that predicts the net amount of various minerals or gas phases that must enter or leave

solution in order to explain the observed changes in water chemistry between two points on a flow path. In this case, we focused on the reactions in the upper portion of the aquifer where the ground water becomes depleted in O_2 and NO_3^- accompanied by increases in HCO_3^- . We used water chemistry for the piezometers at sites OF3S and OF1B for the NETPATH runs since these sample points lie roughly along the same flow path (Figure 4).

Our focus in the model was on the reactions responsible for O_2 and NO_3^- losses, and increases in C, Ca^{2+} , and Mg^{2+} , including deducing the electron donors in the redox reactions. In addition to the calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and organic matter, that occur naturally in the soil, agricultural inputs at the site include calcite, dolomite, potassium (as KCl), nitrogen (as NO_3^- and NH_4^+), and sulfur (as $CaSO_4 \cdot 2H_2O$ or $(NH_4)_2SO_4$). Accordingly, C, Ca, Mg, K, Na, N, S, Cl and redox state were among the constraints in the model and the phases included nitrogen gas (N_2), organic matter (CH_2O), calcite, dolomite, gypsum ($CaSO_4 \cdot 2H_2O$), and potassium chloride (KCl). We also modeled ion exchange of both K and Na with Ca and Mg. The phases were chosen on the basis of mineralogy and the saturation indices calculated in WATEQ.

Four NETPATH models (Table 5) were found that fit the constraints, phases, saturation indices and mineralogy. In all the models organic matter was oxidized and N_2 left solution, small amounts of KCl and gypsum were dissolved, and Na exchanged for Ca and Mg. Calcite and/or dolomite dissolved in all of the models, and in those models where one phase or the other was not selected, K exchange for Ca or Mg balanced the reaction. Because we know that both calcite and dolomite are applied in the area, models 1 and 2 (Table 5) seem most realistic.

These results indicate that in this portion of the aquifer O_2 and NO_3^- were being reduced by oxidation of organic matter with about two thirds (66.5 percent) of the net increase in carbon being generated in the process. O_2 loss accounted for about 8 percent of the oxidation of organic carbon while NO_3^- reduction accounted for the other 92 percent. Dissolution of carbonates accounted for about a third (33.5 percent) of the net increase in carbon. The net loss of N_2 most likely was required in order to balance differences in the amount of nitrogen applied in fertilizer at the time of recharge. This was not surprising given the approximate doubling in the amount of fertilizer nitrogen applied in Otter Tail county during the 16-20 year time period between the recharge dates of the two samples (Figure 2).

DISCUSSION

Redox Processes

Analytical results (Table 3, 4) show that the upper 3-4 m (<10 years old) of the saturated zone were well below the equilibrium concentration for O_2 ($373 \mu\text{mol L}^{-1}$). However, this zone was not anoxic, indicating that it was a zone where O_2 reduction was occurring (Figure 10). Below the zone of O_2 reduction was another 3-4 m (10-20 years old) thick zone essentially depleted of O_2 , where NO_3^- reduction was occurring with essentially complete denitrification at its base. Most of the remainder of the outwash sediments comprised a zone of iron oxide reduction ranging from 20 to 50 years in age, with a small zone of SO_4^{2-} reduction and CH_4 production in the sediments containing ground water >50 years in age (Figure 10). The loss of both O_2 and NO_3^- in the shallow portions of the aquifer (Table 3, 4), accompanied by the production of large amounts of HCO_3^- (Table 4) and excess N_2 (Figure 7) indicate that oxidation of organic carbon with NO_3^- as the electron acceptor was occurring and this is supported by the NETPATH model results. At equilibrium, dissolved O_2 would be $373 \mu\text{mol L}^{-1}$ and therefore would place a demand of 1492 electron equivalents (Postma et al., 1991). The introduction of $463 \mu\text{mol NO}_3^- \text{ L}^{-1}$ (the median concentration of NO_3^- in the shallow aquifer) places an additional demand of 2315 electron equivalents. The combined electron demand is about 2.5 times that of O_2 alone, increasing the amount of C oxidized. As organic C continues to be oxidized in the shallow sediments we can expect to see the depths to which NO_3^- persists increase, however the rate of downward movement can be expected to take decades. Similar conclusions were reached by Robertson et al. (1996) for an aquifer in southern Ontario where reduced sulfur compounds served as the electron donor for autotrophic denitrification.

Together, these results indicate that the biogeochemistry of the shallow ground-water system is dominated by facultative anaerobes that initially derive energy from the oxidation of organic carbon in the sediments, and once concentrations of O_2 are limiting, switch to denitrification as the terminal electron accepting process for carbon oxidation. Deeper in the aquifer, iron-reducing bacteria become favored, followed by SO_4^{2-} reducers and then methanogens, creating the pattern depicted in Figure 10. This pattern follows the predicted redox sequence based on thermodynamics of the reactions involved and microbial energy demands (Stumm and Morgan, 1981; Chapelle, 1993; Chapelle et al., 1995).

The redox zonation has implications on the potential transport and fate of NO_3^- entering the aquifer. Specifically, NO_3^- is thermodynamically and biologically unstable below a depth of about 3-4 m below the water table. Because the denitrification process is dependent on organic C as an electron donor, the future ability of this aquifer to continue removing NO_3^- is dependent on the availability of reactive organic C. It is generally accepted that leaching from soil horizons is the primary source of dissolved organic carbon to shallow flow systems (Chapelle, 1993). Korom (1992) has stated that given the stoichiometry of equation 2, on a molar basis there must be 25 percent more dissolved organic carbon than NO_3^- , in order for denitrification to proceed to completion.

However, this assumption ignores another widely accepted fact that buried organic matter may also provide the organic carbon required for denitrification (Chapelle, 1993; Appelo and Postma, 1996). Also, because this buried organic matter often is refractory, and may limit microbial processes, its reactivity controls the extent of denitrification (Chapelle, 1993; Appelo and Postma, 1996).

Sediment organic carbon content was variable but ranged from 0.01-1.45 percent with a median of 0.15 percent. Applying an analysis similar to that of Trudell et al. (1986), and assuming a porosity of 0.3 and a particle density of 2.65 g cm^{-3} , results in an estimate of 52-7471 mmol organic C with a median of 773 mmol C, in each 3.3 L volume of sediment. Based on the stoichiometry of denitrification in equation 2, this would translate to the ability to reduce 42-5977 mmol NO_3^- in each liter of water in contact with each 3.3 L volume of sediment. Given that the maximum concentration of NO_3^- measured along the transect was $1785 \mu\text{mol L}^{-1}$, it is obvious that even the relatively small amounts of organic carbon present in the aquifer are adequate to explain the redox conditions. Grischek et al. (1998) reached similar conclusions in their study of a sand and gravel aquifer in Germany that had received organic carbon from infiltrating Elbe River waters.

At the smallest organic C concentration (0.01 percent) and the median NO_3^- concentration at the water table ($436 \mu\text{mol L}^{-1}$) all of the O_2 ($373 \mu\text{mol L}^{-1}$ assuming equilibrium with the atmosphere) and NO_3^- originally present should be consumed in the upper 2 m of the saturated zone. That this is not occurring suggests that either the organic C is not readily accessible for O_2 reduction and denitrification, or that other biological, thermodynamic, and (or) kinetic constraints exist with the result that most of the aquifer appears to be carbon limited, resulting in slow denitrification rates.

Denitrification Rates

Denitrification rates are typically measured in controlled incubations under laboratory conditions; however, these rates are typically greater than those determined by in-situ studies, or even tracer studies and all appear to overestimate nitrate losses under natural conditions. Smith et al. (1996) attempted to correct for these overestimates by injecting bromide as a tracer along with nitrate and then monitoring along the flow path for denitrification products. The rates calculated from their experiments were less than slurry and soil core incubations done with the same material but were of the same order of magnitude. Other in-situ studies (Trudell et al., 1986; Gillham et al., 1990; Tesoriero et al., 2000) typically have produced rates an order of magnitude greater than those of Smith et al. (1996). Another method is to measure the production of excess N_2 or N_2O gas generated from denitrification and estimate a denitrification rate based on sample age (Vogel et al., 1981; Smith et al., 1996; Tesoriero et al., 2000). Rates based on the excess N_2 method may be an order of magnitude lower than those based on tracer tests.

Denitrification rates based on excess N_2 gas and sample age measured in this study, ranged from 0.005 to $0.047 \text{ mmol NO}_3^- \text{ L}^{-1} \text{ yr}^{-1}$. These rates are orders of magnitude

lower than what has typically been measured in laboratory and in-situ incubations (Table 6) but are comparable to those from other field-based studies in sand and gravel aquifers (Bohlke and Denver, 1995; Smith et al., 1996; Tesoriero et al., 2000). The slowest denitrification rates (Table 6) were from Vogel et al. (1981), who reported a loss of 1.5 mmol NO_3^- over a period of about 14000 years for a carbon limited system in the Kalahari Desert. Rates reported by Tesoriero et al. (2000) overlap those reported here and were dependent on both carbon and pyrite weathering providing Fe^{2+} as the electron donor. The somewhat faster rates reported by Smith et al. (1996) were measured in an aquifer contaminated with treated sewage, but denitrification was still carbon limited. These studies indicate that rates measured under field conditions are generally much lower than either laboratory or isolated in-situ incubations and we theorize that they reflect the natural variability of conditions favorable for denitrification. Because there are no additions or modifications to the natural system (other than well installation and sampling) these rates may come closest to actual denitrification rates. Rates derived in this manner therefore are likely better measures of natural denitrification rates and would provide more accurate predictions of NO_3^- transport and fate.

Age and Land-Use Relations

The distribution of the reconstructed concentrations (Figure 11) and ground-water age dates (Figure 5) clearly show that NO_3^- has been increasing in the study area since the 1940s, and concentrations have nearly doubled in some portions of the aquifer since the mid-1960s. Most importantly, since the late 1960's, reconstructed NO_3^- concentrations at many sites have been near or exceeded the maximum contaminant level (MCL) of $714 \mu\text{mol NO}_3^- \text{ L}^{-1}$ ($10 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$) set by the U.S. Environmental Protection Agency (1996). Puckett et al. (1999) showed that most of the nitrogen reaching the water table in the study area originated as fertilizer, and this increase in NO_3^- concentrations over time corresponds to a similar increase in the use of fertilizer nitrogen in the study area, particularly after the late-1960s (Figure 2). These results support our hypothesis that changes in concentrations of NO_3^- are a function of changes in agricultural practices over time and, therefore the age of water sampled along the transect.

Although limited, there is growing evidence that increased fertilizer use since the 1960s has led to aquifer contamination. Bohlke and Denver (1995) reported a similar increase in NO_3^- in ground water in sandy unconsolidated sediments of the Atlantic Coastal Plain of Maryland beginning in the late 1960s or early 1970s. Johnston et al. (1998) noted an increase from $<178 \mu\text{mol NO}_3^- \text{ L}^{-1}$ to more than $714 \mu\text{mol NO}_3^- \text{ L}^{-1}$ since 1970 in a sand and gravel outwash aquifer in southern Ontario, Canada. However, because Johnston et al. (1998) did not measure dissolved N_2 in the deeper, older ground water; it is impossible to definitively say whether or not the lower concentrations there were due to lower fertilizer usage in earlier years or were the result of denitrification. It is significant that in both these studies, widespread NO_3^- contamination of the aquifers has occurred, and in the Maryland study area, NO_3^- -contaminated ground water was discharged to

streams. On the other hand, in the Otter Tail aquifer denitrification has removed most NO_3^- in all but the upper few meters of the saturated zone.

CONCLUSIONS

The results of this study demonstrate the importance of developing a complete understanding of the hydrogeologic and biogeochemical processes involved when evaluating the fate of ground-water contaminants. Age-dating techniques combined with sampling along flow paths, allow us to develop a chronology of the change in contaminant concentrations over time and to relate those changes to historical changes in land-use and management practices. Because residence times on the order of 50 years or more are not unusual, there may be adequate time in many aquifers for even slow biogeochemical process to modify original contaminant concentrations. These modifications require us to monitor not only the original contaminant concentrations but the breakdown products as well in order to understand the processes involved. The final result however, is a more comprehensive appreciation of the biogeochemical processes involved than could be gained from a one- or two-dimensional sampling approach. More studies are required in order to document the spatial extent of the role of denitrification in removing NO_3^- from contaminated aquifers; it is likely however that many other aquifers in settings similar to the Otter Tail aquifer contain sufficient organic carbon to support denitrification and natural bioremediation.

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Table 1. Bulk and <1 µm fraction mineralogy of sediment samples collected at various depths from sites 1 and 3.

Site	Depth (m)	Location	Bulk fraction †	<1 µm fraction	Total C (%)	Organic C (%)	Inorganic C (%)
OF1	1.5	Top OF1S	qtz, plag, cal.	NA	1.49	0.74	0.76
OF1	3.0	Bottom OF1S	qtz, plag, cal., dol.	NA	1.19	0.3	0.89
OF1	4.6	Thin organic layer	qtz, plag, dol., cal.	smect., illite, kaol., chlor., dol., cal., feld., horn., qtz.	3.17	1.45	1.71
OF1	12.2	Top OF1D	qtz, plag, kspar, dol., cal.	smect., illite, kaol., chlor., dol., cal., feld., horn., qtz.	1.11	0.21	0.9
OF3	1.5	Unsat. Zone	qtz, kspar, plag, dol., cal.	smect., illite, kaol., chlor., dol., cal., feld., horn., qtz.	0.06	0.02	0.05
OF3	6.1	OF3S	qtz, kspar, plag, dol., cal.	NA	0.84	0.04	0.8
OF3	11.6	Top clay lens below OF3M	qtz, plag, kspar, dol., cal.	smect., illite, kaol., chlor., dol., cal., feld., horn., qtz.	0.89	0.09	0.81
OF3	18.3	OF3D	plag, qtz, dol., cal.	NA	0.89	0.01	0.88

† qtz=quartz; plag=plagioclase; kspar=potassium feldspar; cal.=calcite; dol.=dolomite; smect.=smectite; kaol=kaolinite;
chlor=chlorite; feld=feldspar; horn.=hornblend

Table 2. Observed and predicted water levels (in meters) and ages (in years) in the Otter Tail transect piezometers based on the MODFLOW/MODPATH simulation, August 1995 measurements, and CFC apparent ages.

Site	Observed Water Level August 1995	Predicted Water Level	CFC Apparent Age	Predicted Age
OF1S	407.5	408.1	8-11	4-8
OF1A	407.6	408.1	22	13-14
OF1B	407.5	408.1	24-25	18-19
OF1C	407.6	408.1	46-47	29-43
OF1D	408.7	408.1	>50	45-53
OF2S	409.9	410.0	†	2
OF2D	409.5	410.0	†	38-43
OF3S	413.4	413.0	5-8	3
OF3M	413.4	413.0	37	14-15
OF3D	412.9	413.0	47-48	39-45
OF4S	416.0	416.2	23	2-4
OF5S	418.9	418.5	5-8	1-2

† no data available

Table 3. Median concentrations of S^{2-} , dissolved gases, NO_3^- , excess N_2 ($Xs\ N_2$), reconstructed NO_3^- (ΣNO_3^-), and CFC-based apparent ages of samples collected during 1994, 1995, and 1997. [All concentrations are $\mu\text{mol L}^{-1}$ and ages are in years. NO_3^- concentrations may differ from Table 4 because only samples having paired N_2 gas data were included in the calculations.]

Site	S^{2-}	O_2	CO_2	CH_4	Ar	N_2	$Xs\ N_2$	NO_3^-	ΣNO_3^-	CFC Apparent Age
OF1S	0	11.5	788.6	0.1	17.2	746.3	97.7	1071.4	1266.8	8-11
OF1A	0	37.5	545.5	0.0	16.7	880.0	249.0	628.6	1126.5	22
OF1B	0	10.0	521.9	0.0	17.6	928.2	265.4	610.7	1141.4	24-25
OF1C	0.78	2.3	600.8	15.5	18.2	957.3	274.6	0	549.2	46-47
OF1D	0.84	4.9	621.6	214.7	18.6	859.8	162.2	0	324.4	>50
OF2D	0.5	6.3	493.2	2.2	18.1	982.1	302.3	0	604.6	†
OF3S	0	145.3	250.0	0	18.7	747.9	48.9	564.3	662.2	5-8
OF3M	0	0	634.6	0.3	15.1	967.4	394.4	4.3	793.15	37
OF3D	0.9	0	570.0	25.1	16.8	980.2	345.9	5.1	696.9	47-48
OF5S	0	181.3	1045.5	0	20.3	813.2	88.4	95.7	272.4	5-8

† no data available

Table 4. Median concentrations of major-ions in samples collected during 1994, 1995, and 1997. [All concentrations are $\mu\text{mol L}^{-1}$ with the exception of pH which is in standard units; organic nitrogen (Org-N) is reported as NH_4^+ .]

Site	T °C	pH	O ₂	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe ²⁺	Mn ²⁺	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻	NH ₄ ⁺	Org-N	DOC
OF1S	11.8	7.16	9.4	5343	2495	1172	100.1	35.8	0.1	0.4	479.6	249.8	0.6	928.3	0.7	6.4	149.9
OF 1A	8.8	7.43	43.8	4796	2196	946.0	87.0	38.4	0.0	0.0	423.2	333.1	0.6	628.4	0.6	6.5	91.6
OF1B	9.0	7.36	17.2	4605	2221	946.0	82.7	40.9	0.0	1.5	371.0	327.9	0.6	609.9	1.0	6.0	108.2
OF1C	10.2	7.22	2.3	5446	1946	863.7	139.2	40.9	50.7	11.3	162.2	84.3	1.3	1.8	20.5	4.2	199.8
OF1D	9.4	7.55	3.1	6058	1971	863.7	200.1	42.2	79.7	3.7	45.1	10.4	5.1	1.8	45.7	7.9	262.3
OF2S	10.2	7.43	112.5	4736	2021	863.7	82.7	30.7	1.1	0.0	338.5	291.5	0.2	292.8	0.7	6.4	91.6
OF2D	10.4	7.55	0.2	6316	2033	843.2	71.8	33.2	44.8	3.8	141.1	197.8	0.6	3.6	9.3	12.1	183.2
OF3S	10.5	7.05	140.6	2016	1372	575.8	89.2	43.5	0.3	0.0	203.1	177.0	3.2	1285	1.4	5.7	116.6
OF3M	9.4	7.24	1.6	5849	2495	1111	78.3	40.9	73.4	6.7	592.4	374.8	0.3	1.8	12.2	5.3	233.1
OF3D	9.2	7.36	2.3	5960	2246	987.1	82.7	40.9	64.5	4.7	366.7	177.0	0.2	1.8	24.7	7.4	258.1
OF4S	9.5	7.37	5.5	4848	2869	1357	506.8	89.5	0.2	0.5	1664	983.7	1.4	340.1	1.0	13.3	166.5
OF5S	8.9	7.23	192.2	5892	2071	1064	169.7	168.8	0.7	0.0	204.5	89.5	0.2	167.8	1.0	15.4	233.1

Table 5. Biogeochemical reactions determined from the NETPATH modeling process. Reaction coefficients represent the amount in $\mu\text{mol L}^{-1}$ of phases entering (positive values) or leaving (negative values) solution.

Phases	Models			
	1	2	3	4
CH ₂ O	1510	1510	1510	1510
CaCO ₃	357	259	759	†
CaMg(CO ₃) ₂	201	250	†	379
N ₂	-350	-350	-350	-350
CaSO ₄ •2H ₂ O	23	23	23	23
KCl	88	88	88	88
Ca/K Exchange	†	-49	201	-179
Mg/K Exchange	-49	†	-250	130
Ca+Mg/Na Exchange	-17	-17	-17	-17

† Phase not included in the model

Table 6. Denitrification rates from studies of various sand and gravel aquifers. Methods included slurry incubations, in-situ studies, excess N₂ analyses, and tracer tests.

Studies	Method	Denitrification rate mmol NO ₃ ⁻ L ⁻¹ yr ⁻¹	
		Minimum	Maximum
Vogel et al. (1981)	Excess N ₂ and Tritium age dates	NA	0.0001
Trudell et al. (1986)	In-situ study	4.88	81.3
Gillham et al. (1990)	In-situ study	15.0	87.6
Bohlke and Denver (1995) †	Excess N ₂ and CFC age dates	0.001	0.01
Smith et al. (1996)	Tracer study	0.13	0.31
	Slurry incubation	0.53	1.23
	Soil core incubation	0.69	1.61
	Soil core incubation	1.38	3.22
Tesoriero et al. (2000)	Excess N ₂ and CFC age dates	0.01	0.14
	Excess N ₂ and CFC age dates	1.3	2.7
	In-situ study	NA	140
Puckett et al. (2002)	Slurry incubation	0.99	34.46
This study	Excess N ₂ and CFC age dates	0.005	0.047

† Rates calculated from data provided by Bohlke and Denver

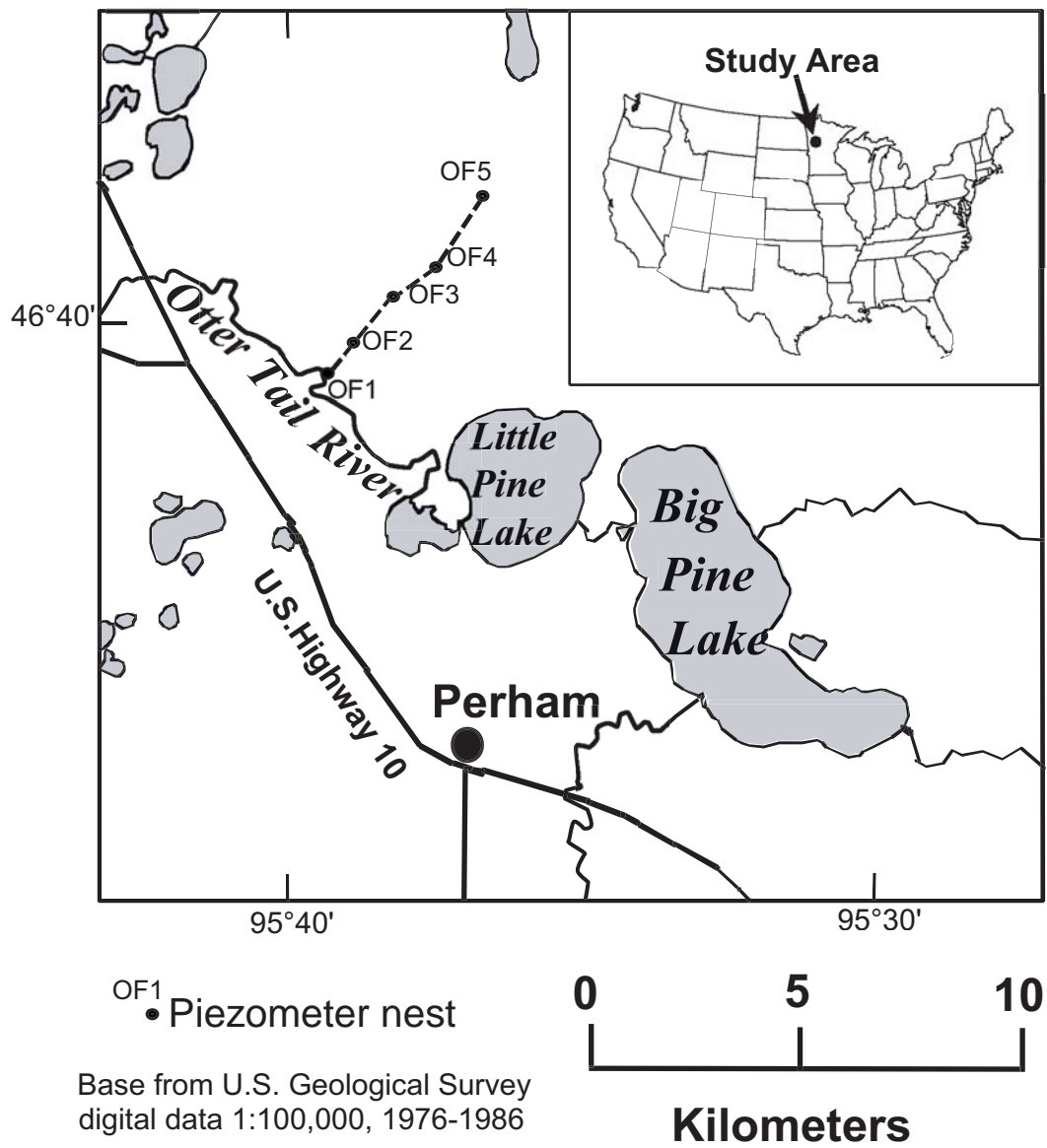


Figure 1. Location of the study area north of the Otter Tail River.

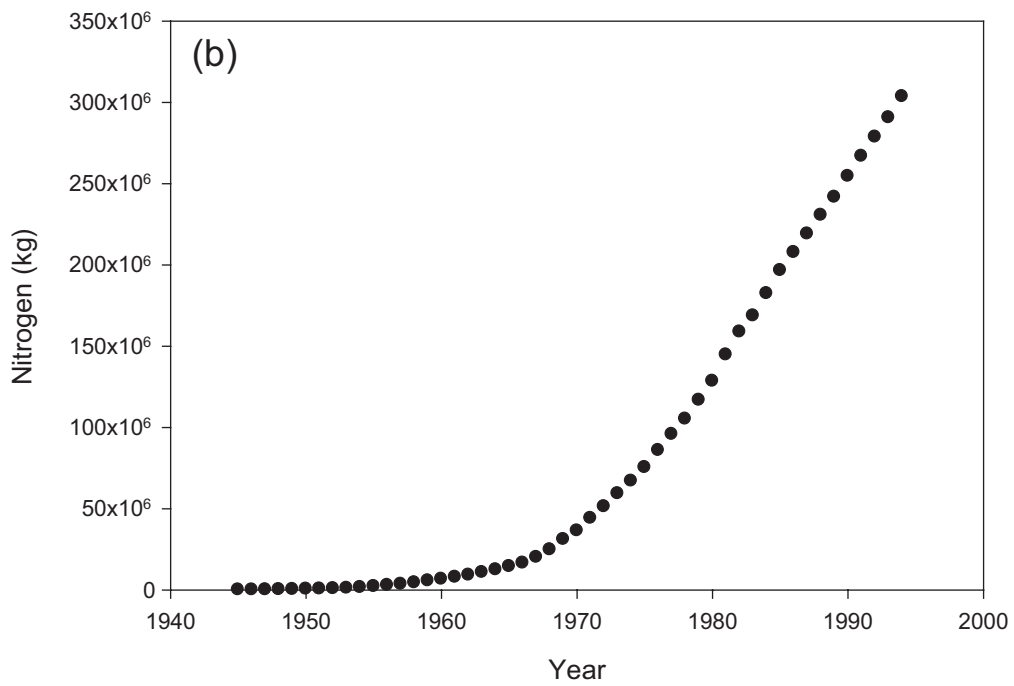
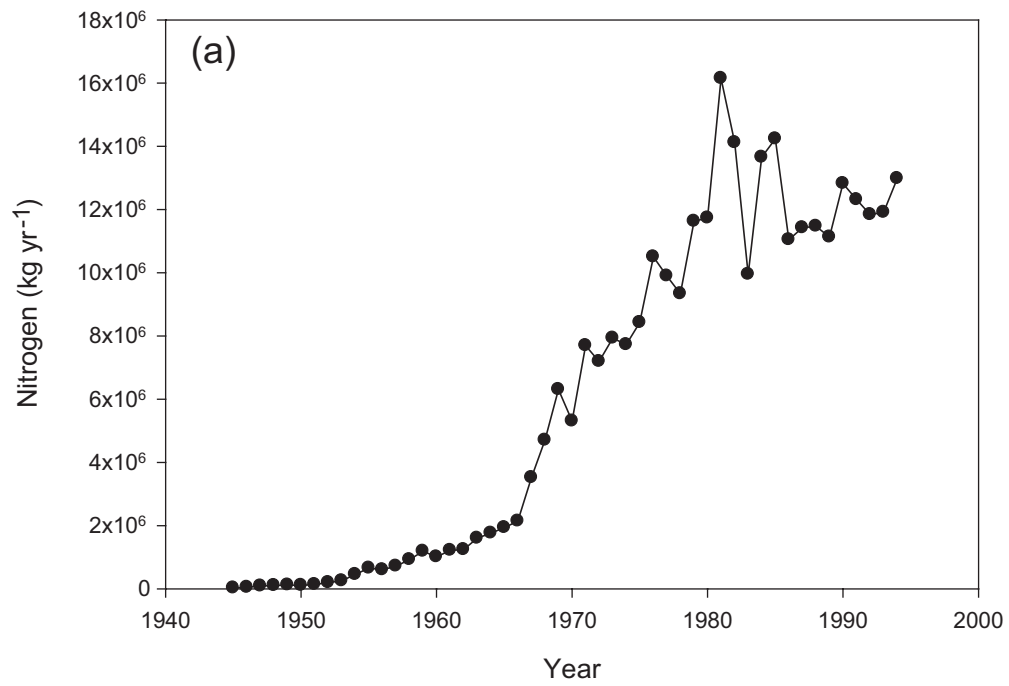


Figure 2. (a) Annual fertilizer nitrogen applications in Otter Tail county since 1945, and (b) cumulative nitrogen applications during the same period.

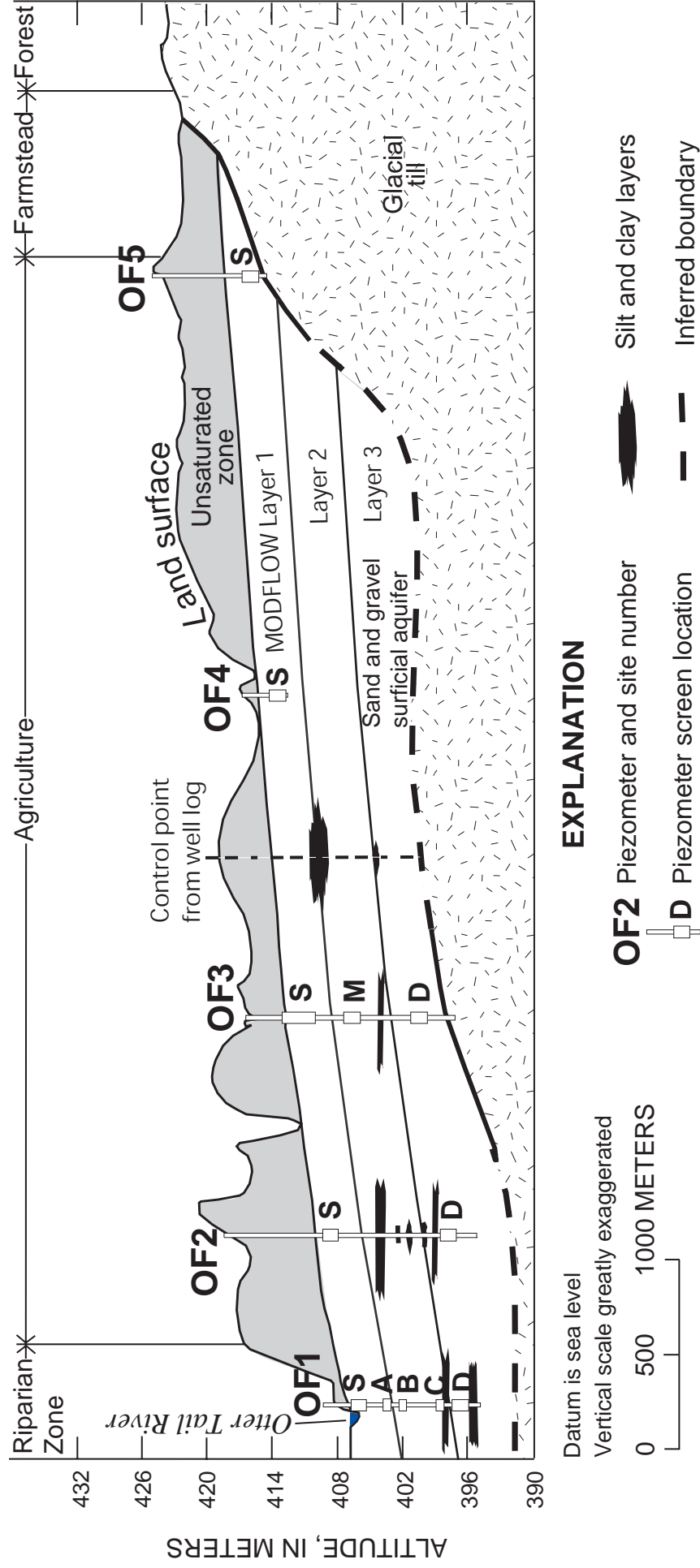


Figure 3. Cross-section of the study transect showing land use, piezometer nest locations, screened intervals, and known stratigraphy.

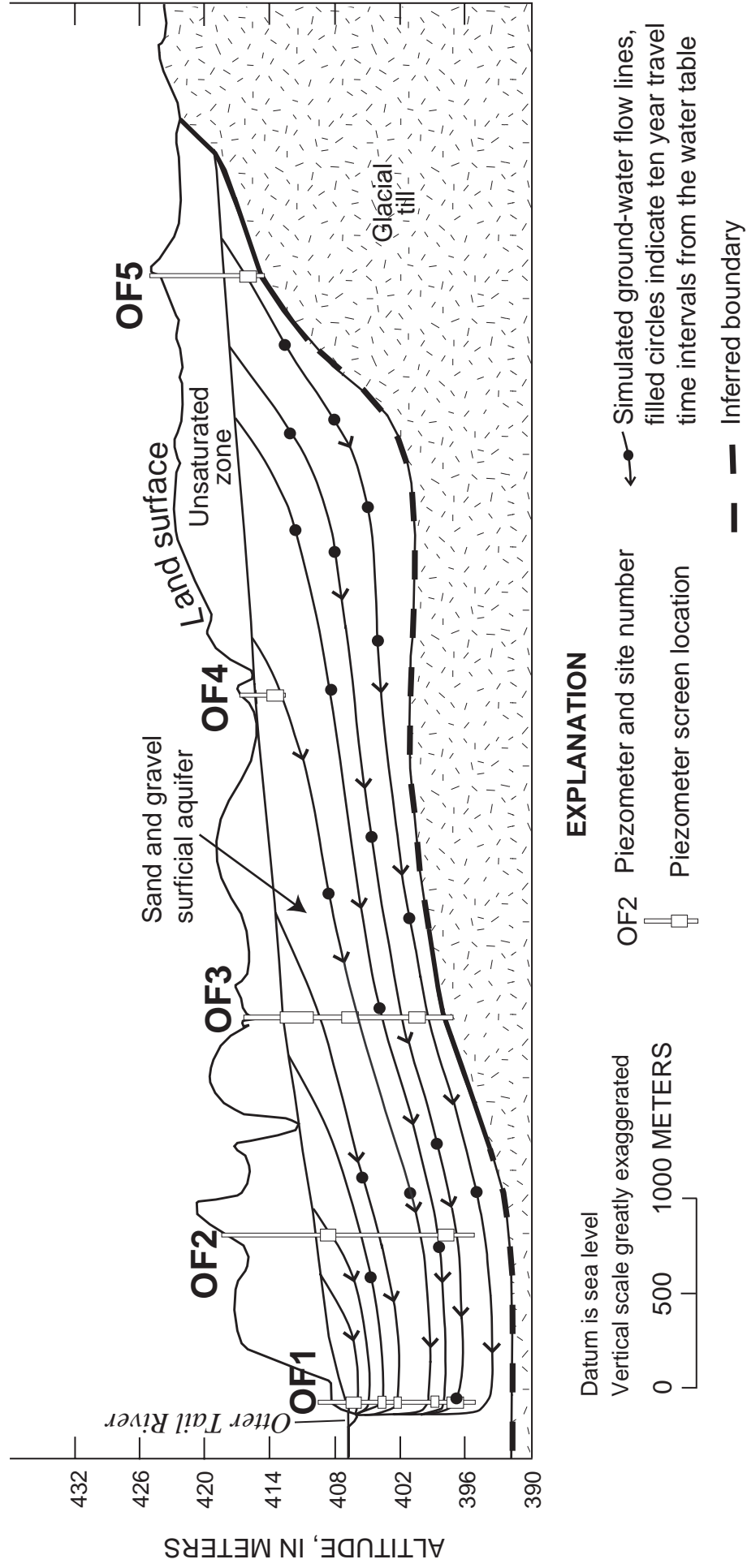


Figure 4. Ground-water flow lines and travel times along the study transect based on the MODFLOW/MODPATH simulation.

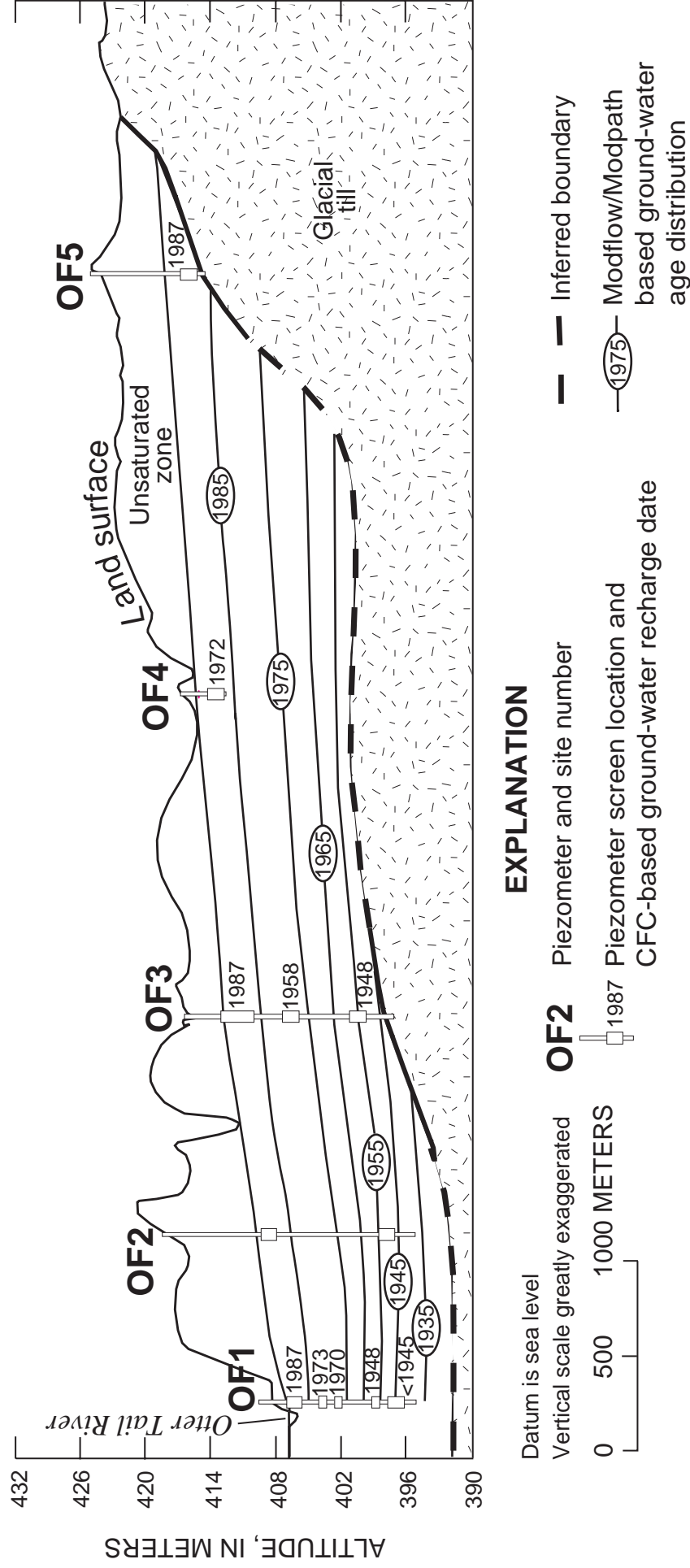


Figure 5. Apparent ground-water recharge dates as determined from chlorofluorocarbon (CFC) concentrations measured in ground-water samples and generalized age distribution along the transect based on the MODFLOW/MODPATH simulation.

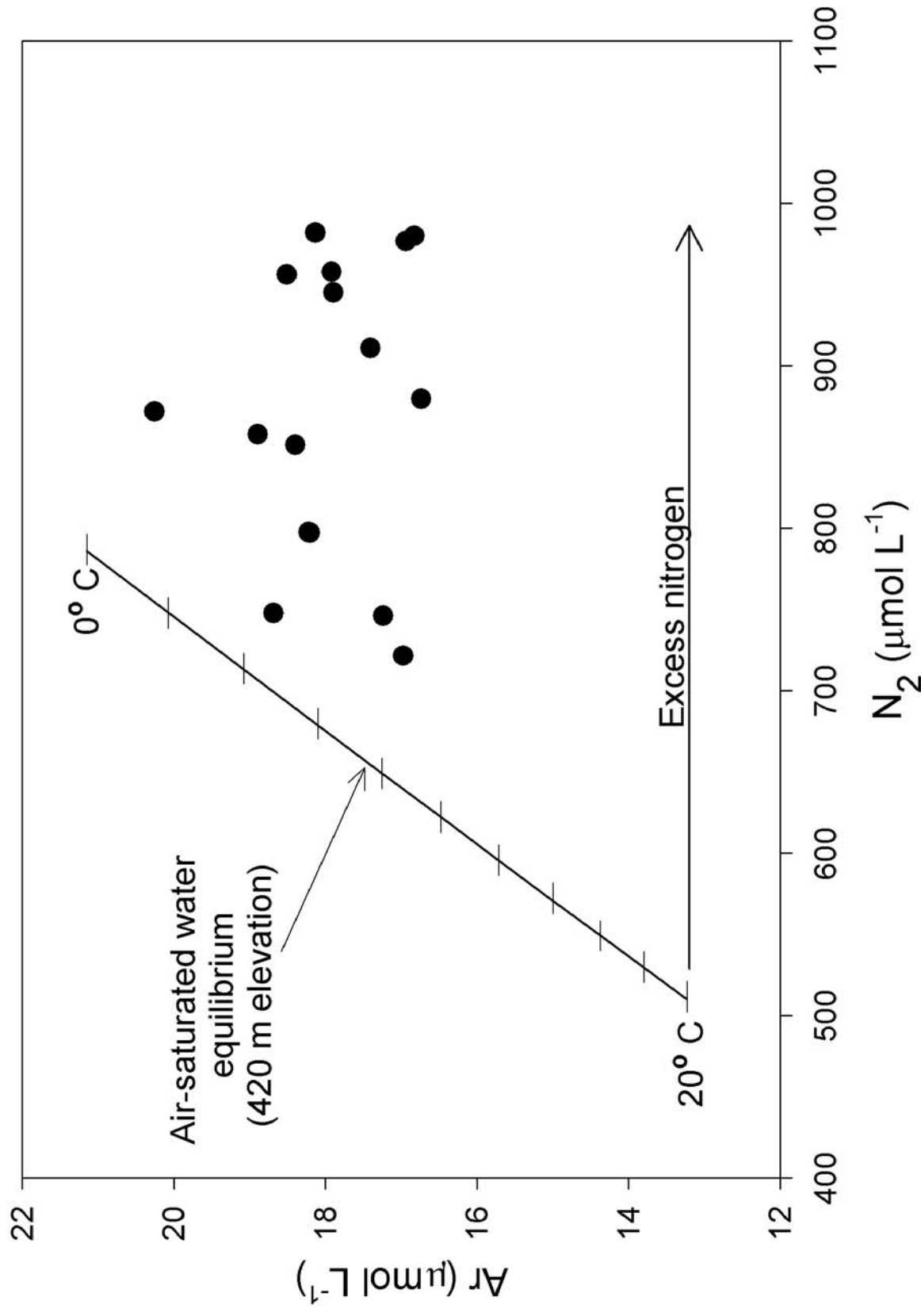


Figure 6. Argon and nitrogen gas concentrations for samples collected during 1994, 1995, and 1997 and their theoretical values. Values to the right of the air-saturated water equilibrium line represent excess nitrogen concentrations. Horizontal tick marks on the equilibrium line indicate Ar and N₂ equilibrium concentrations from 0° to 20° C in 2° increments.

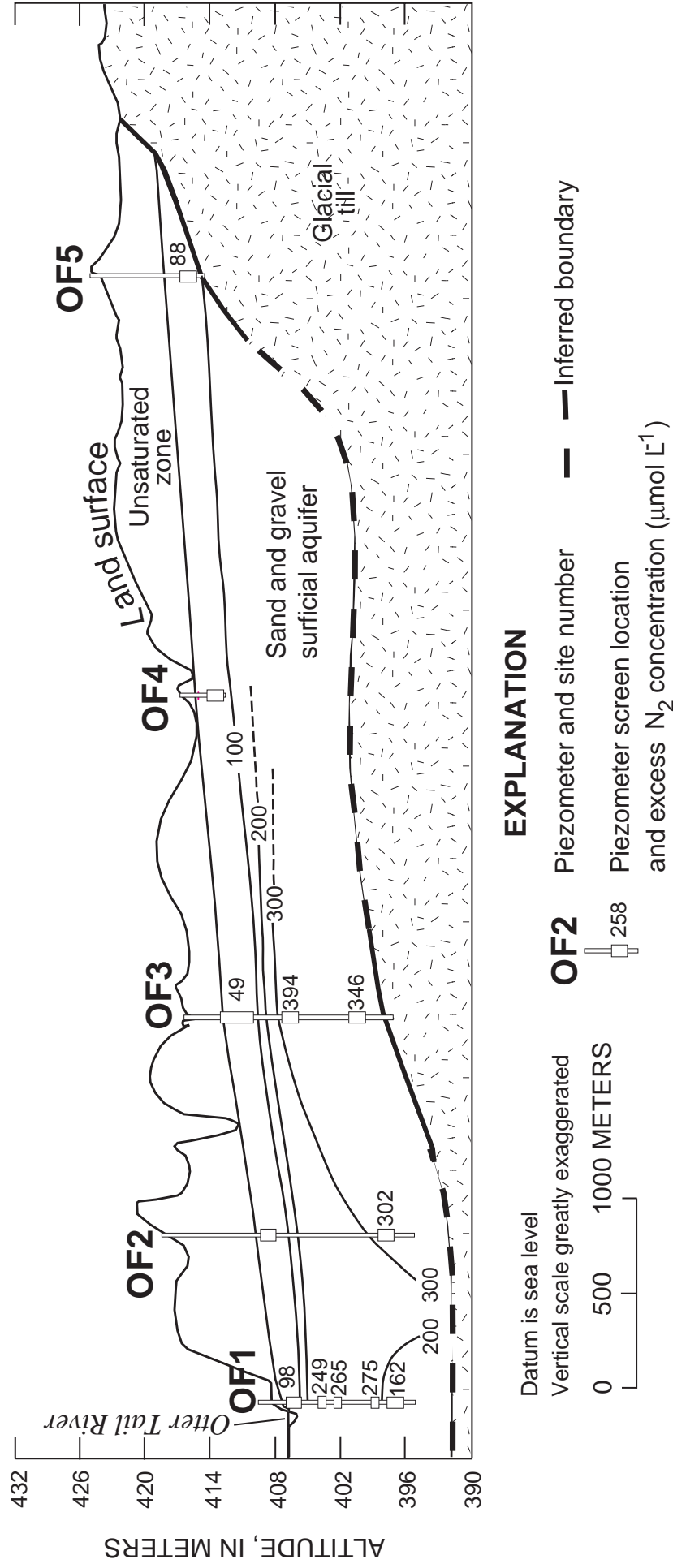


Figure 7. Distribution of excess nitrogen along the transect.

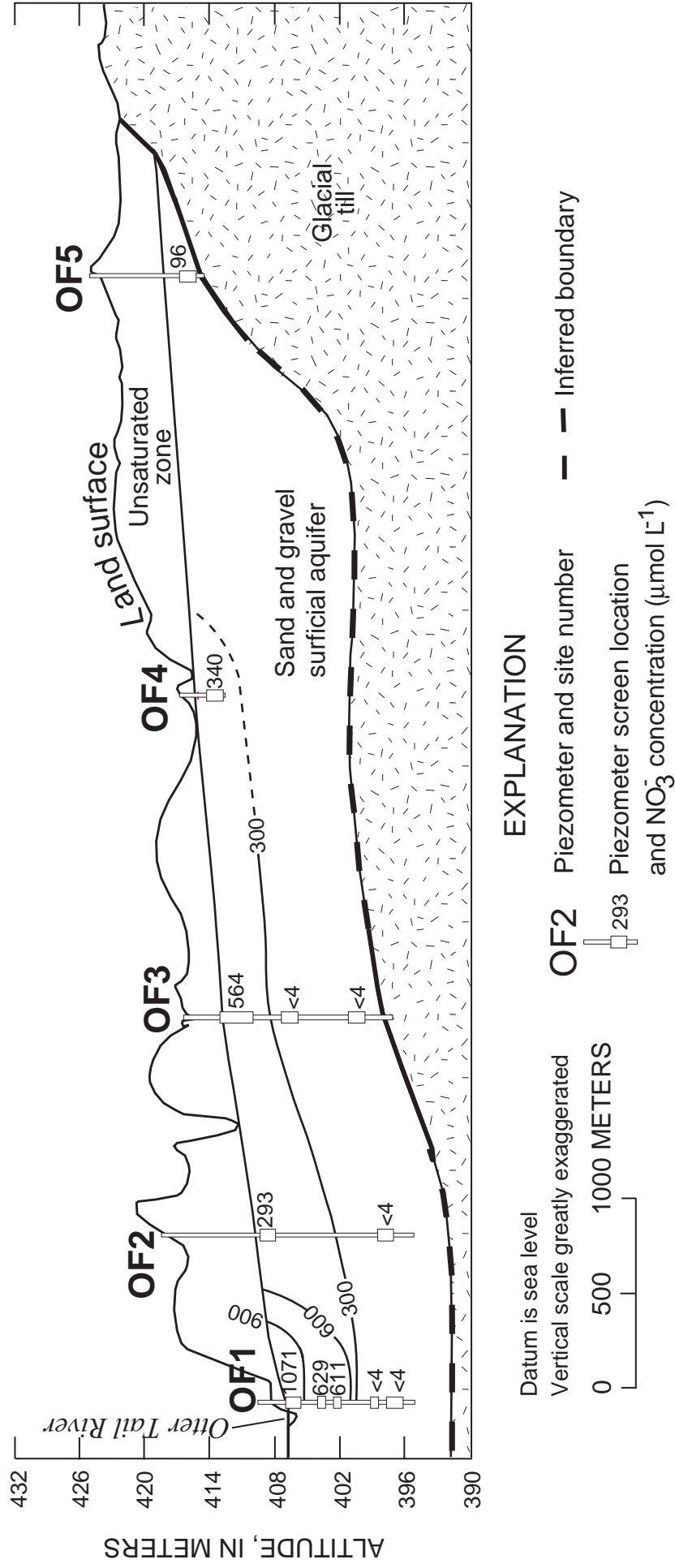


Figure 8. Concentrations of NO_3^- along the transect.

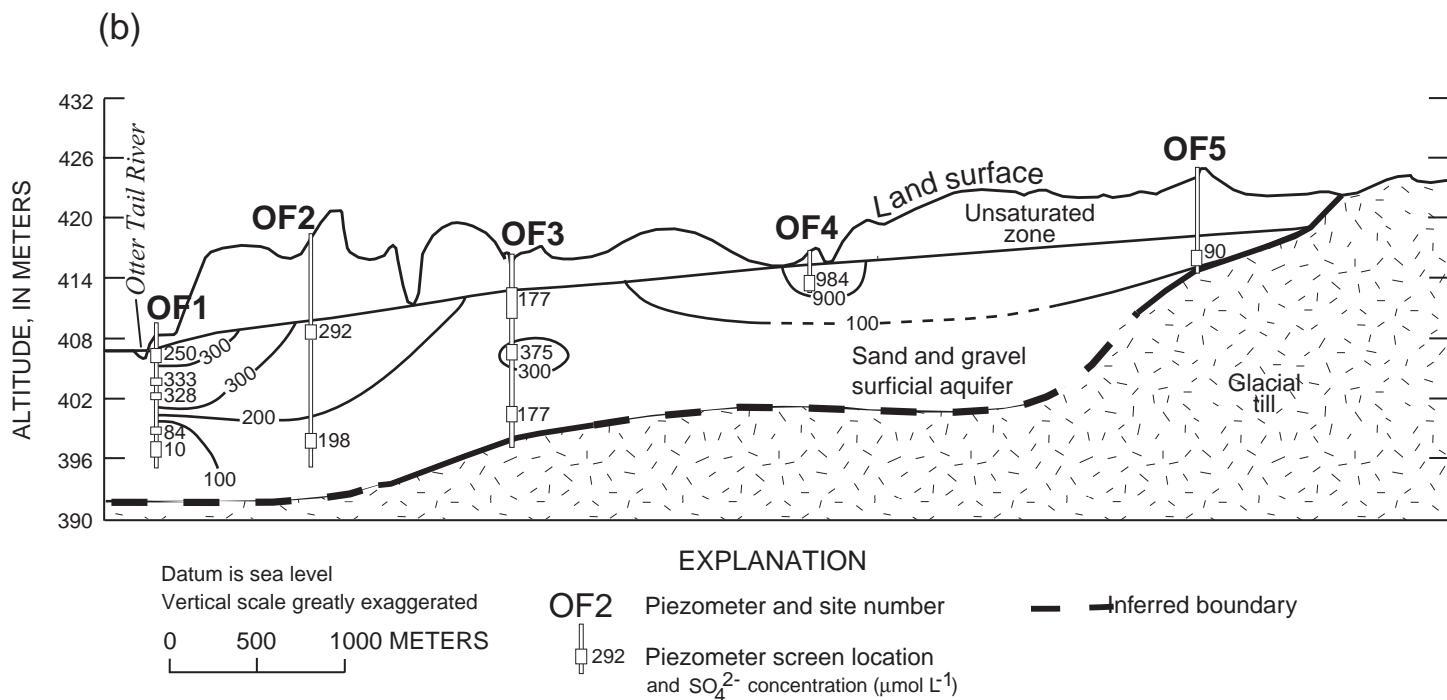
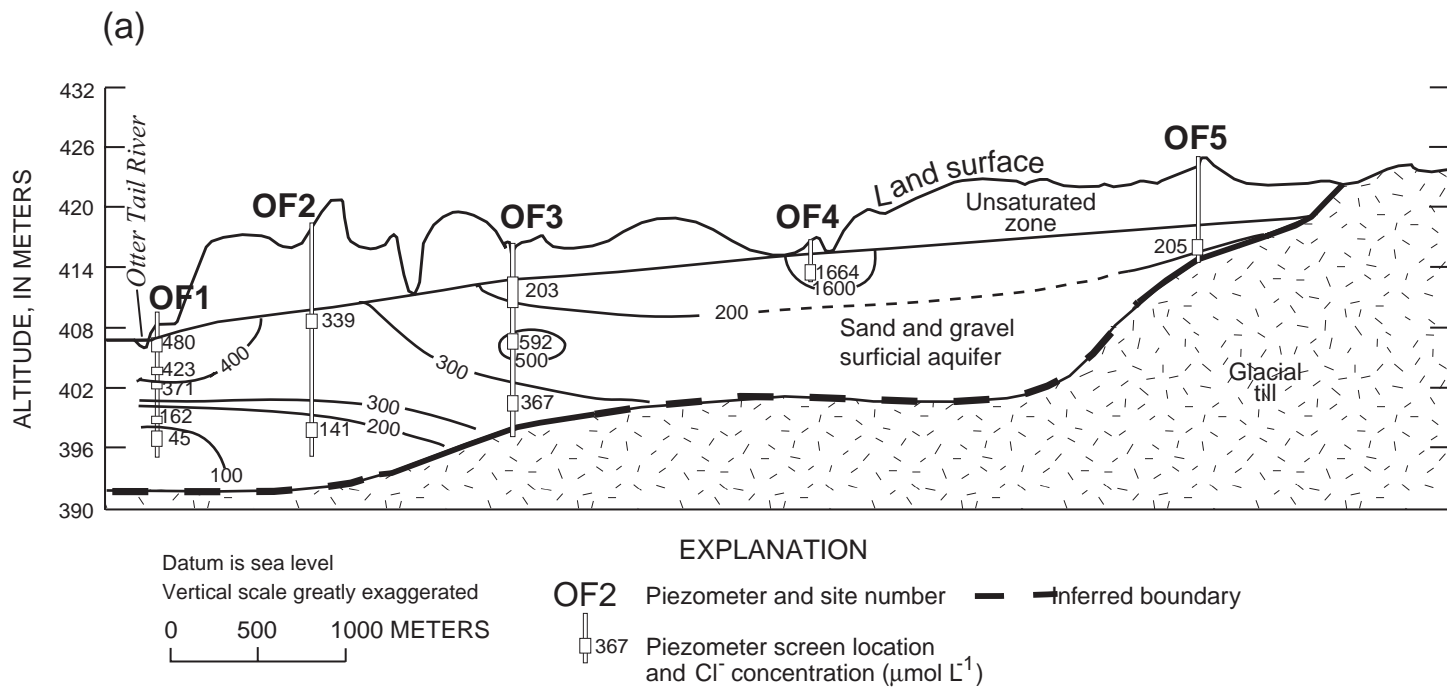


Figure 9. Distribution of (a) Cl^- and (b) SO_4^{2-} along the transect.

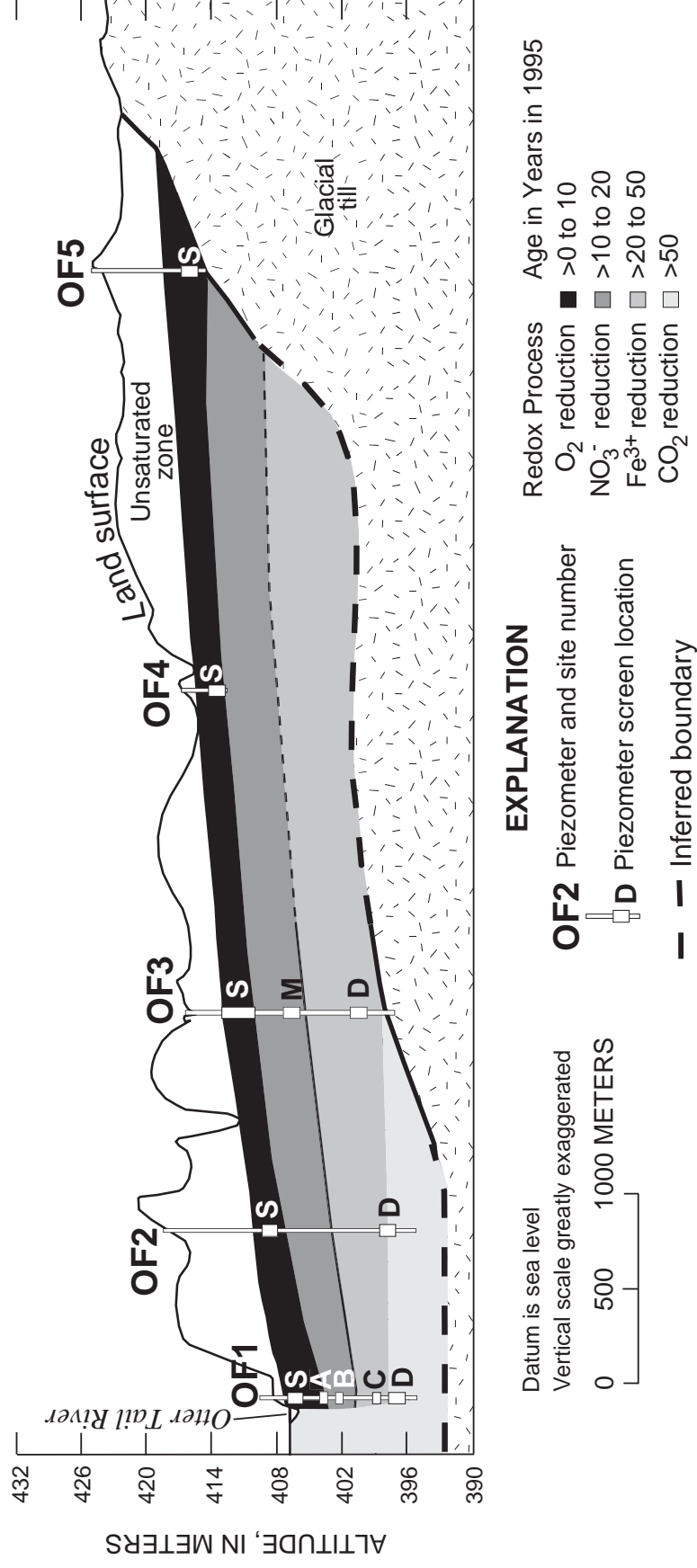


Figure 10. The generalized redox state of the aquifer along the transect.

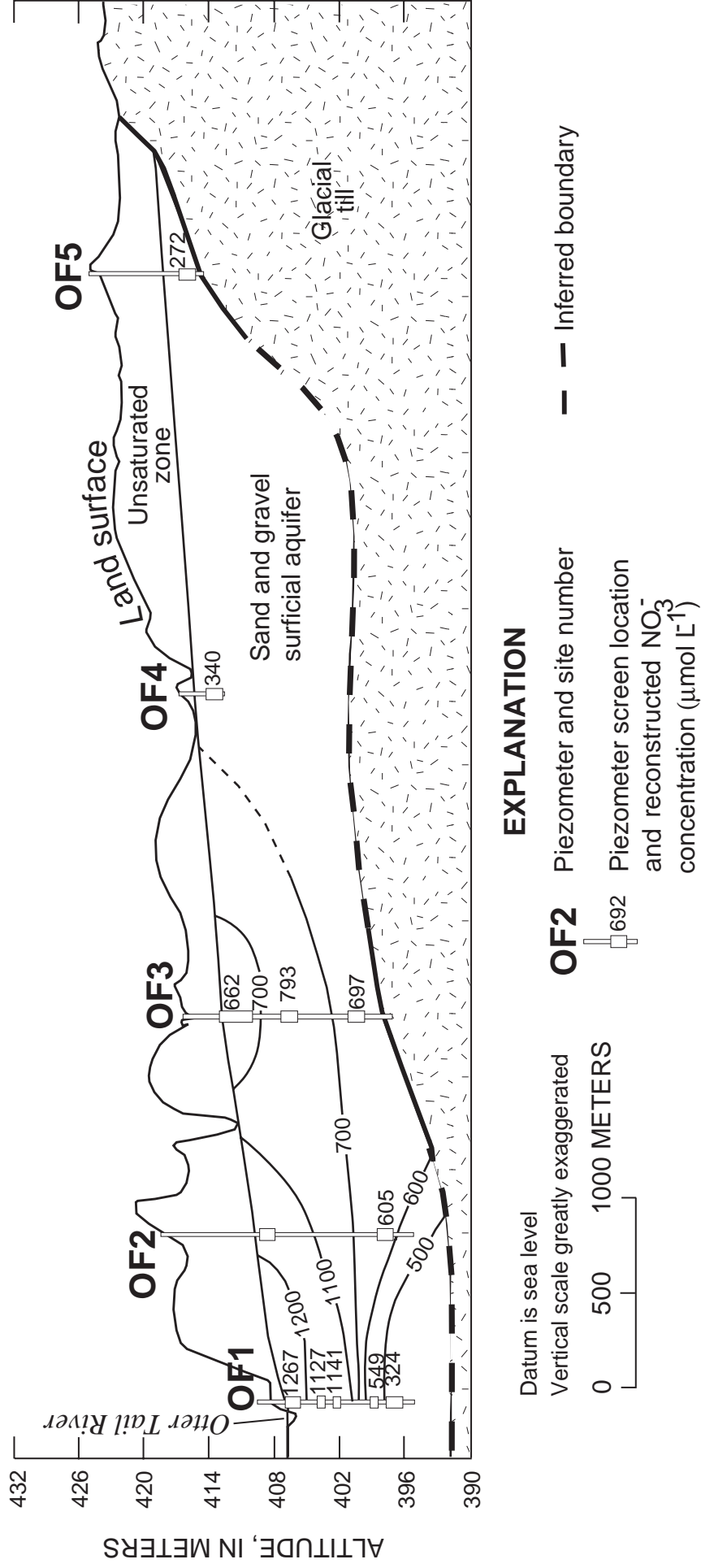


Figure 11. Distribution of reconstructed (original) concentrations of NO_3^- calculated as the sum of excess N_2 and NO_3^- measured along the transect.