T-3408

MIGRATION AND TRANSFORMATIONS OF AMMONIUM AND NITRATE IN A SEWAGE-CONTAMINATED AQUIFER AT CAPE COD, MASSACHUSETTS

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science of Geochemistry.

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ABSTRACT

This thesis investigates the fate of ammonium and nitrate in a sewage-contaminated aquifer at Cape Cod, Massachusetts. Rapid-infiltration disposal of secondary effluent into a permeable sand and gravel aquifer over a 53 year period has resulted in a plume of contaminated groundwater that is more than 3350 m long, 1000 m wide, and 50 m thick. Ammonium is the predominant nitrogen species near the sewage infiltration beds but is depleted or absent farther than 1,830 meters from the beds. Conversely, nitrate is the predominant species of inorganic nitrogen from 1,830 m to the toe of the plume. Such ammonium-nitrate distributions suggest that ammonium is being transformed to nitrate by nitrification or that rates of transport differ for ammonium and nitrate due to ammonium sorption.

Nitrification rates measured in material collected from the aquifer suggest that nitrification could account for all ammonium consumption in the sewage plume as long as oxygen is present. The nitrogen budget in the plume, however, indicates that ammonium attenuation cannot be attributed entirely to nitrification.

Evidence for ammonium sorption and cation exchange was obtained from laboratory and field experiments. A laboratory sediment-extraction experiment indicated that a significant fraction of the total ammonium is sorbed on aquifer solids and batch experiments showed that ammonium sorption at the site can be described by a Freundlich isotherm equation. Divergent tracer tests conducted at the site provide direct evidence

that cation exchange is largely responsible for differential rates of transport for ammonium and nitrate in the aquifer. Tracer-test results specifically indicate that ammonium and also potassium are displacing native aquifer cations; field evidence shows this effect as higher concentrations of calcium, magnesium, and sodium are evident downgradient of the ammonium and potassium front in the sewage plume.

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ACKNOWLEDGEMENTS

I would like to dedicate this work to my children, Josh and Chris, whose love and understanding made completion of this study possible. Many thanks are due to my thesis advisor, Dr. Dave Updegraff for enlightening me on the finer details of geomicrobiology, assisting in the laboratory and in the field, and generally encouraging me in this research effort. My sincere thanks to Dr. Mike Thurman, who has been an indefatigable source of information, guidance, and moral support. I would also like to thank my other thesis committee members, Dr. Don Macalady and Dr. Tom Zamis for their guidance during the course of this study. A special thanks to Dr. Richard Smith for his assistance in the laboratory and in the field and also his careful reviewing of this thesis. Also to Larry Barber for our long discussions on geochemistry and Pinki Barber for technical assistance in completing this thesis. I am particularly grateful to my parents, Perry and Esther, who have encouraged me to think, be persistent, and do the best I possibly can in life's endeavors. Thanks to Linda Lindgren for her generosity and belief in me and to Carol Bowles who gave me moral support throughout the course of this project.

I would like to acknowledge with great appreciation the funding of this research in its entirety to the U.S. Geological Survey, Water Resources Division, National Research Program. Special thanks is due to Denis LeBlanc of the U.S. Geological Survey in New England for his technical assistance in the field.

INTRODUCTION

Contamination of groundwater by inorganic nitrogen is recognized as a major environmental problem (Behnke, 1975). Since techniques for collection of groundwater samples have improved in the past decade, incidents of groundwater contamination by inorganic nitrogen are being reported with increasing frequency (Barcelona and Naymik, 1984; Burden, 1982; Capone and Bautista, 1985; Egboka, 1984; Eisen and Anderson, 1979; Flipse and Bonner, 1985; Gromly and Spalding, 1979; Hendry et al., 1984; Hill, 1982; Jacks and Sharma, 1983; Katz et al., 1980; Kreitler et al., 1978; Porter, 1980; Robertson, 1979; Saffigna and Keeney, 1977; Silver and Fielden, 1980; Spalding et al., 1978; Spalding et al., 1982; and Super et al., 1981).

Particular attention has been directed to contamination of groundwater by nitrate (NO_3^-) because: 1) NO_3^- is the most common contaminant identified in groundwater (Behnke, 1975); 2) infants ingesting excessive concentrations of NO_3^- (greater that 10 milligrams per liter as nitrogen; 10 mg N /L) or nitrite (NO_2^-) (greater than 1 mg N/L) risk contracting "blue baby disease" or methemoglobinemia (Behnke, 1975); and 3) the presence of NO_3^- in drinking water has been linked to stomach cancer (Jensen, 1982). There is also evidence that the presence of ammonium (NH_4^+) and ammonia (NH_3) in groundwater can pose health problems (Denne et al., 1984; Messer et al., 1984).

Nitrogen speciation in contaminated groundwater is critical in the assessment of contamination problems and the occurrences and concentrations of various inorganic nitrogen species are largely determined by the geochemistry and geomicrobiology of the aquifer. Yet, few case studies treat the fate and transport of inorganic nitrogen under the influence of known hydrogeologic, chemical, and biological constraints. With this in mind, this research was initiated to develop an understanding of the processes that control the transport and speciation of NH_4^+ and NO_3^- in contaminated groundwater.

The site selected for this study is Otis Air Base (OAB), at Cape Cod, Massachusetts. This site is the location of a groundwater contaminant plume generated by the rapid-infiltration land disposal of secondary sewage effluent. The OAB site was selected for several reasons: 1) the extent of the contamination is well-delineated and characterized by the U.S. Geological Survey (LeBlanc, 1984a); 2) the plume contains high concentrations of NH_4^+ (up to 13 mg N/L) and NO_3^- (up to 14 mg N/L); 3) the hydrogeology of the plume is well-characterized; and (4) many coastal communities, like the OAB site, dispose of their wastewater by rapid infiltration.

This investigation is part of a multidisciplinary research program by the U.S. Geological Survey involving hydrologists, organic and inorganic geochemists, transport modellers, and microbiologists. The goal of this study is to provide data on the occurrence, distribution, geochemistry, and geomicrobiology of inorganic nitrogen compounds in the contaminated groundwater. These data combined with other research efforts will provide a comprehensive evaluation of the contamination problem.

The first section of the thesis summarizes the problem of nitrogen contamination in groundwater. The sources of nitrogen contamination are briefly reviewed with special attention directed to nitrogen contamination resulting from land disposal of wastewater. General considerations concerning hydrogeology, geochemistry, and microbiology of nitrogen-contaminated groundwater are also discussed.

Section II describes the study site for the field investigation. The site location, cultural setting, and the network of monitoring wells are described. Also, pertinent hydrogeologic, geochemical, and microbiological information concerning the site is presented, with reference to previous studies conducted at this location.

Section III describes the research model used to answer the fundamental question about mechanisms affecting transport and attenuation of NH_4^+ and NO_3^- in contaminated groundwater. The section also includes discussion of background, rationale, and experimental methods.

Section IV presents details on laboratory and field methods. Equipment, chemical reagents, and procedures used for sample collection, preservation, and analytical methods are described. Included in this section are descriptions of chemical, microbiological, and field tracer-test procedures.

Results are discussed in Section V. Part A concerns results of groundwater sampling studies designed to determine contaminant patterns for NH_4^+, NO_3^-, and other pertinent chemical and microbiological parameters at the field site. Parts B and C discuss the results of nitrification studies and sorption studies respectively. Part D presents the results of field tracer studies. The thesis is concluded in Section VI with a summary of results and conclusions.

I. NITROGEN CONTAMINATION IN GROUNDWATER: AN OVERVIEW

A. SOURCES OF NITROGEN IN GROUNDWATER

There are numerous diverse sources of nitrogen contamination in groundwater (Egboka, 1984). Substantial increases in nitrogen compounds in a groundwater system may reflect pollution from point sources such as feedlots, barnyards, manure, waste lagoons, septic systems, and land-disposed sewage effluent. Nitrogen contamination can also occur from a distributed source such as precipitation and mineralization of nitrogen in soil organic matter. These point and non-point sources can be classified into five general mechanisms for introducing nitrogen into groundwater (Feth, 1966): 1) atmospheric precipitation into ground and surface waters; 2) leaching of nitrogen inherent in the soil; 3) agricultural sources of nitrogen compounds other than those inherent in the soil, such as fertilizers and barnyard and silo effluents; 4) geologic sources other than the soil including cave deposits, caliche deposits, and playa deposits; and 5) waste disposal practices.

Land disposal of wastewater, especially sewage wastes, is a well-known source of nitrogen in groundwater. Each year, 2×10^{10} cubic meters (m^3; 5×10^6 million gallons per day, MGD) of municipal wastewater is discharged to the environment with an estimated 2.9×10^9 m^3 (7×10^5 MGD) of this amount discharged to the land (Johnson, 1979). Contaminants in municipal wastewater reach groundwater by three direct pathways: 1) leakage from the treatment plant during processing; 2) leakage from collecting sewers; and 3) land disposal of the treatment plant effluent (Miller, 1980).

Presently, land is used either for primary wastewater effluent or more frequently for tertiary treatment. Land treatment methods can be classified into the following categories: irrigation, overland flow, and rapid infiltration. These land treatment methods differ in efficiency, purpose, and degree of pollution abatement. Irrigation is very effective in the removal of nutrients because these compounds are used for plant uptake. Overland flow is used in clay or loamy soils and is very effective for decreasing the biological oxygen demand (BOD), suspended solids, and heavy metals, but is only moderately efficient in nutrient removal.

Wastewater disposal by rapid infiltration is more efficient than other land treatment methods in terms of acreage required per wastewater volume and is, therefore, frequently the method of choice (Idelovitch and Michail, 1984; Mathews et al., 1982). Rapid infiltration is used in coarse-grained sediments and, therefore, has been developed for groundwater recharge. The degree of nitrogen removal varies from 30 to 90% depending on the type of soil, infiltration rates, and other management techniques (Mathews et al., 1982). It is necessary to evaluate the effectiveness of rapid infiltration in removing nitrogen by examining the quality of groundwater resulting from this type of land treatment. The field site used for this study is an aquifer that has been contaminated with nitrogen and other contaminants due to rapid-infiltration land-disposal of secondary-treated wastewater. The site is described in detail in section II.

B. HYDROGEOLOGY OF NITROGEN-CONTAMINATED GROUNDWATER

Hydrogeologic investigations provide insight into the physical factors that influence the subsurface migration of dissolved contaminants when they are introduced into groundwater. Under ideal conditions of homogeneity, contaminants introduced into the aquifer will be transported in the direction of groundwater flow resulting in an elliptical plume having well-defined boundaries (Freeze and Cherry, 1979). Aquifers, however, can exhibit significantly different fluid mechanics due to the hydraulic properties of the flow system resulting in non-ideal behavior for pollutant transport. Detailed accounts of the hydrogeologic properties that affect contaminant distribution in groundwater are discussed by Freeze and Cherry (1979) and Pye et al. (1983).

C. GEOCHEMISTRY OF NITROGEN-CONTAMINATED GROUNDWATER

In natural waters nitrogen often forms compounds by bonding to 2, 3, or 4 adjacent atoms. Examples of dissolved nitrogen compounds found in natural waters are: dissolved nitrogen gas (N_2), NH_3, NH_4^+, NO_2^-, NO_3^-, nitroxyl (HNO), hydroxylamine (NH_2OH), as well as organic nitrogen. In general, the predominant inorganic nitrogen species in sewage-contaminated groundwater are NH_3 or NH_4^+ and NO_3^- (Behnke, 1975).

NO_3^- is very soluble in water and is a chemically stable compound in aerated groundwater (Behnke, 1975; Feth, 1966). It is generally not sorbed or ion exchanged in the subsurface because most soils and sediments have low anion exchange capacity (Fenchel and Blackburn, 1979). Although the concentration of NO_3^- can be reduced by biological processes, in oxidized waters this form of nitrogen can be persistent in groundwater for extended periods and can migrate large distances from input areas (Freeze and Cherry, 1979).

NH_3 is highly soluble in water (approximately 525 g of NH_3 will dissolve in 1 liter of water at 20°C) (Behnke, 1975). NH_3 and water form NH_4^+ and hydroxide ions (OH^-) according to the following reaction:

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \quad \text{(Eq. 1)}$$

The pH and temperature are critical factors in determining which nitrogen species, NH_3 or NH_4^+, will predominate in solution. Within the temperature range of most groundwaters NH_3 is in greater abundance at high pH's (greater than pH of 9), while ionic NH_4^+ is the predominate species at pH's lower than 9. NH_3 ionization is also a function of ionic strength, however, the errors resulting from using ionization fractions that are uncorrected for ionic strength are small (15-20%) and in the range of error that is frequently incurred in pH measurements (Messer et al., 1984).

This speciation has important ramifications for nitrogen transport in groundwater. Soil studies have demonstrated that NH_3 is volatilized in alkaline soils and NH_4^+ tends to be sorbed or ion exchanged on negatively charged soil particles (Allison, 1966). NH_4^+ is a potentially reactive constituent of many contaminated groundwater systems since a portion of the dissolved NH_4^+ that is transported by the groundwater flow can be transferred to the aquifer solids as a result of sorption (a term used for both adsorptive and ion-exchange reactions; Grove and Stollenwerk, 1984). The partitioning of NH_4^+ between the liquid and solid phases in a porous medium can be determined in laboratory batch and column experiments or in field tracer test studies.

Sorption reactions are commonly described by a two-ordinate graph (termed a sorption isotherm) where sorbed mass of contaminant per unit mass of solids is plotted against the concentration of contaminant in solution. The isotherms can have a variety of shapes (Vermeulen, 1973). If the isotherm is shaped convex-upward and has an increasing slope with decreasing concentrations, it is termed a favorable isotherm. Conversely, an unfavorable isotherm is shaped concave downward indicating a decreasing slope with decreasing concentrations. When an isotherm is linear the slope is termed the distribution coefficient.

Sorption reactions can also be described by using the mass-action ion-exchange, Langmuir, or Freundlich adsorption equations, assuming sorption processes are equilibrium controlled (Grove and Stollenwerk, 1984). Sorption equilibrium constants (obtained from the solution of the equations mentioned above) and distribution coefficients (obtained from linear sorption isotherms) have been applied in groundwater contaminant models to estimate the rate of transport of retarded constituents such as NH_4^+ (Grove and Rubin, 1977; Reardon, 1981).

D. MICROBIOLOGY OF NITROGEN-CONTAMINATED GROUNDWATER

The occurrence and concentration of various nitrogen species that occur in groundwater are largely determined by the microbial nitrogen cycle. The cycle involves an eight electron shift between the most oxidized form (NO_3^-) and the most reduced form (NH_4^+). Nitrogen has an unusual number of oxidation states that allows it to be cycled through many chemical transformations; it can combine with hydrogen, oxygen, and other atoms to form a great variety of biological compounds. The limits imposed on nitrogen metabolism by the pH and oxidation reduction potential (Eh) of the natural environment are given by Baas Becking et al. (1960).

The bulk of nitrogen in land-disposed domestic wastewaters is in the form of NH_3 or NH_4^+ depending on the pH of the water (Behnke, 1975). NH_4^+ (or NH_3) is produced in the wastewater because it contains proteins and protein derivatives, such as purines and pyrimidines, which when hydrolyzed or catabolized by bacteria produce NH_4^+ as an end product (Fenchel and Blackburn, 1979; Feth, 1966; Painter, 1970). When this wastewater or treated wastewater is disposed of on land, it can percolate through permeable sediment to the groundwater. During migration through the unsaturated zone and saturated zone the following can occur: 1) it can be transported in the direction of regional groundwater flow; 2) the rate of transport can be affected by sorption; 3) it can be removed from the groundwater system by volatilization; 4) it can be re-incorporated into cellular mass by bacterial assimilative processes; or 5) it can be oxidized to NO_2^- and NO_3^- in the presence of oxygen and autotrophic bacteria by nitritrification (Barcelona and Naymik, 1984; Behnke, 1975; Feth, 1966; Whitelaw and Rees, 1980).

The presence and activity of these nitrifying bacteria in groundwater results in toxic end products (NO_3^- and NO_2^-). Since sediments and soils are generally lacking in anion exchange capacity (Fenchel and Blackburn, 1979), there is a tendency of NO_3^- to be transported through the aquifer to increasingly oxygen-deficient zones where denitrification can occur in the presence of organic matter and denitrifying bacteria (Behnke, 1975; Feth, 1966; Whitelaw and Edwards, 1980; Whitelaw and Rees, 1980).

Autotrophic bacteria are primarily responsible for nitrification, although some heterotrophs, both bacteria and fungi, can oxidize NH_4^+ (Painter, 1970). Heterotrophic bacterial nitrification is significant because it can result in a transient accumulation of $HONH_2$ (Verstraete and Alexander, 1973). The occurrence of heterotrophic nitrification has been demonstrated in soils and other natural ecosystems (Ishaque and Cornfield, 1976; Schimel et al., 1984).

Autotrophic nitrifying bacteria have an absolute requirement for three substrates: CO_2, oxygen (O_2), and NH_4^+ (or NO_2^-). In most environments it is unlikely that CO_2 is limiting; usually either O_2 or NH_4^+ are deficient relative to CO_2 (Fenchel and Blackburn, 1979). Nitrifying bacteria can survive for long periods in an anoxic environment, although they cannot grow (Hattori et. al, 1978; Painter, 1970) and activity can occur at oxygen concentrations as low as 0.1 mg/L (Carlucci and McNally, 1969). The other limiting nutrient is

NH_4^+; it is a requirement that nitrifying bacteria be in a region where NH_4^+ is available. Since NH_4^+ binds to negatively-charged soil particles it may not be available to nitrifying bacteria, although workers have demonstrated that nitrification occurs at these sites (Fenchel and Blackburn, 1979).

The autotrophic oxidation of NH_4^+ occurs in two steps. The first step is the oxidation of NH_4^+ to NO_2^- and is carried out primarily by species of Nitrosomonas (Fenchel and Blackburn, 1979):

$$NH_4^+ \longrightarrow NH_2OH \longrightarrow ? \longrightarrow NO_2^- \quad \Delta G' = -66\text{kcal} \quad \text{(Eq. 2)} .$$

The $\Delta G'$ is defined here as the change in standard free energy for 1 mol of NH_4^+ reactant converted to 1 mol of NO_2^- product at pH 7, 25° C, and 1 atmosphere. The biochemistry of this process is not completely understood although NH_2OH is a well-established intermediary (Wallace and Nicholas, 1969). Furthermore, it has been demonstrated that nitrous oxide (N_2O) is produced during the oxidation of NH_4^+ to NH_2OH, and its production under some circumstances may be considerable (Ritchie and Nicholas, 1972). Members of the genus Nitrobacter complete the two-electron oxidation of nitrite to nitrate (Fenchel and Blackburn, 1979):

$$NO_2^- + 0.5\ O_2 \longrightarrow NO_3^- \quad \Delta G' = -17.5\ \text{kcal} \quad \text{(Eq. 3)}$$

No intermediates are involved in this oxidation. A detailed explanation of the biochemical pathways and intermediates involved in autotrophic nitrification can be found in Painter (1970), Steinmuller and Bock (1977), Wallace and Nicholas (1969) and Wood et al. (1981).

II. SITE DESCRIPTION

A. LOCATION AND CULTURAL SETTING

The OAB site is located approximately 128 km southeast of Boston on a broad glacial outwash plain of Pleistocene age that slopes southward to Nantucket Sound (Figure 1). The study area extends approximately 25 km^2 south of the OAB sewage treatment plant and is bounded by Coonamessett and Johns ponds to the west and east respectively. This area includes 2 golf courses, a wildlife management area, and recreational ponds. A detailed explanation of the physical and cultural setting of the study area is presented by LeBlanc (1984a).

Otis Air Base has been a military reservation since 1936 and housed as many as 70,000 troops during World War II. Between 1948 and 1973 the base was utilized by the U.S. Air Force. Since 1973 the Massachusetts Air National Guard and the U.S. Coast Guard have operated the base. Although the study area is predominantly rural, the number of private homes in the area has increased during the last two decades. Many of these residences rely entirely on groundwater from shallow, small diameter wells for their drinking water.

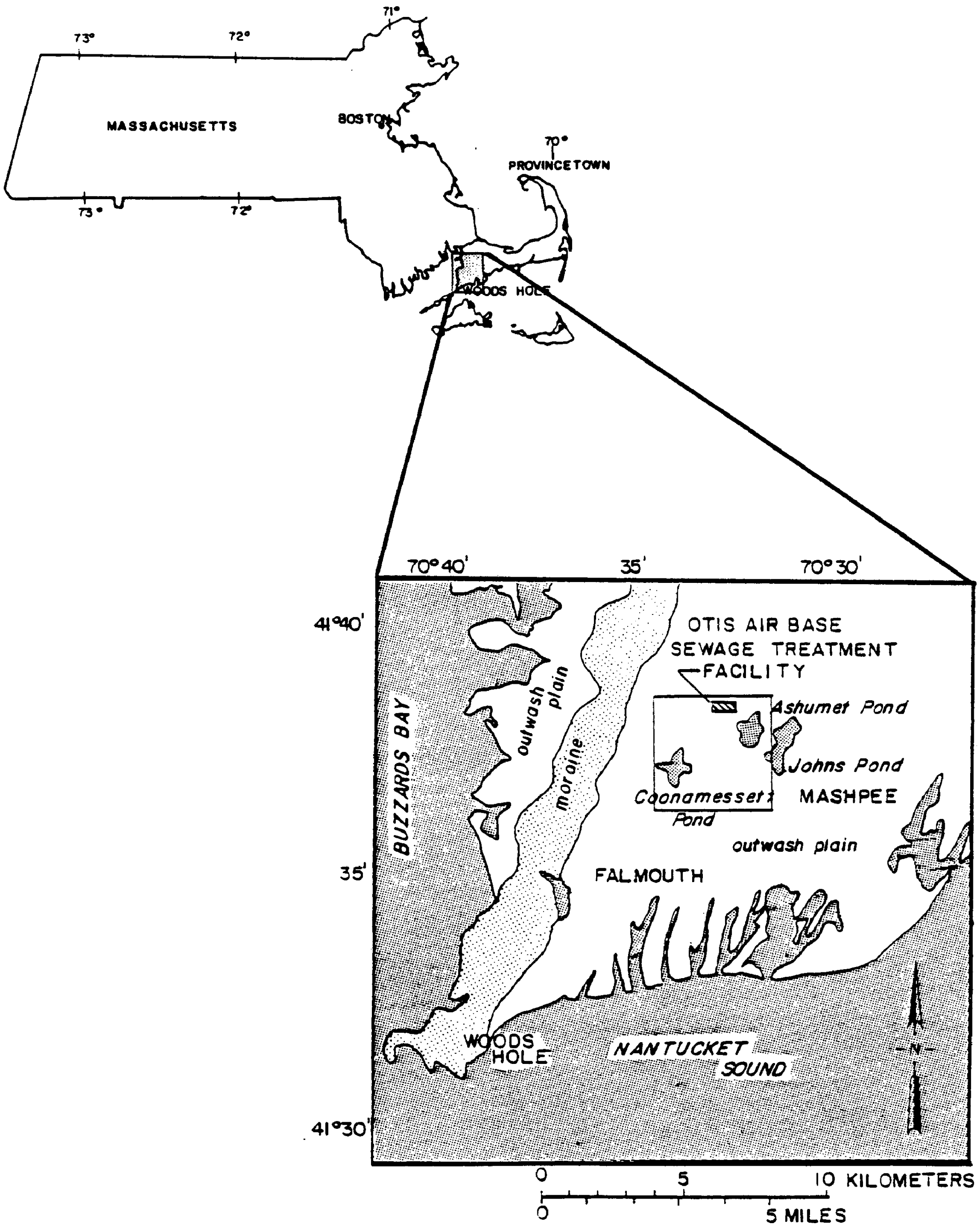


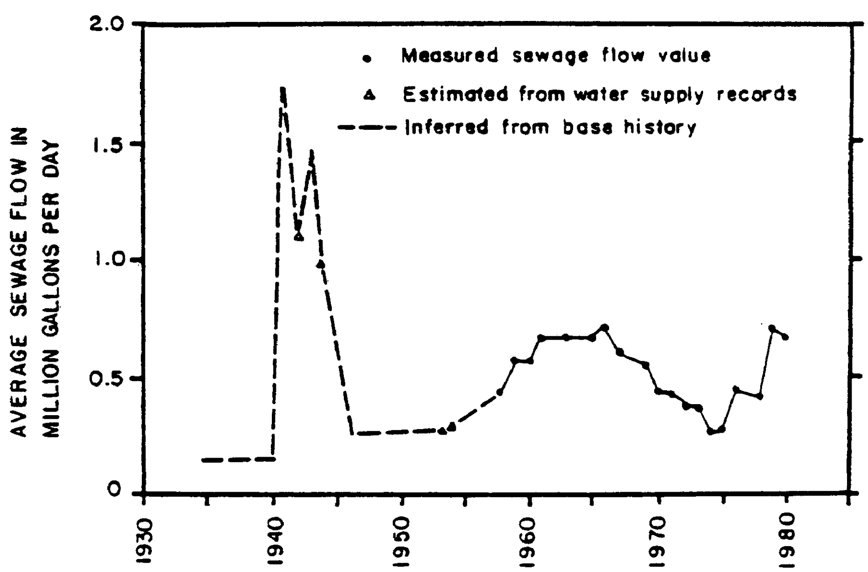
Figure 1. Study area location map.

B. THE OTIS AIR BASE SEWAGE-TREATMENT FACILITY

The OAB sewage-treatment facility provides secondary treatment to sewage generated from the base. Between 1936 and 1941 a small treatment plant with 4 acres of sand beds served the base. The present treatment plant was constructed in 1941 at the same site as the original plant. Primary treatment of the sewage consists of a comminutor with a bar screen, an aerated grease-removal unit, and anaerobic digestion in Imhoff tanks. For secondary treatment the sewage is aerobically digested in trickling filters and then sent to secondary settling tanks. Details of the plant and treatment process can be found in Kerfoot et al. (1975).

The treated sewage is discharged to 24 one-half-acre sand infiltration beds. Each bed was designed to be loaded with an average of 500 m^3/d (1.25×10^8 gallons/d) of treated sewage. The treated sewage then infiltrates the ground and percolates through the unsaturated zone to the water table, which is located about 6.6 m below land surface. The beds have not all been actively used and historical records on usage and loading rates were not available.

The OAB treatment facility was designed to treat an average of 12,000 m^3/d (3 MGD) and a maximum of 24,000 m^3 (6 MGD) of wastewater. The daily volume of sewage treated at the plant from 1936 through 1980 is shown is Figure 2. Since records of the volume of sewage treated at the plant are available for only part of this 45-year period, sewage flows for the remainder of the period were estimated from water-supply pumpage records and the history of base populations. The volume of



(after LeBlanc, 1984a)

Figure 2. Estimated volume of sewage treated between 1936 and 1980.

effluent discharged was greatest during World II between 1941-1944 (5600 m^3; 0.14 MGD). Post World War II effluent volumes have decreased and have been less than the designed capacity of the plant, therefore, treated effluent has been recycled to maintain operation efficiency. A total of 3.2×10^7 m^3 (8 billion gallons) of sewage was treated at the OAB facility from 1936 through 1980. Although the composition of the effluent at the OAB site has probably varied during the 51 years of base operation, few chemical data are available prior to 1974 to confirm this.

Sludge from the plant is dried on sludge-drying beds south of the plant and then transported to the OAB landfill located 4 km northwest of the treatment facility. Since sludge may have been stored or buried at the plant in the past, it is another potential source of contamination.

C. THE OAB GROUNDWATER MONITORING NETWORK

The U.S. Geological Survey has installed an extensive network of monitoring wells at the OAB site. These wells were initially installed to collect water-level and inorganic water-quality data. Figure 3 is a planar view of the site showing the location of the monitoring wells. Figure 4 is an index of the cross-section along the transect line AA′ shown in Figure 3. This cross section is used for presentation of chemical and physical data in the following sections. Each well has a unique identification number consisting of five or six digits. The first three numbers identify the location of the well (shown in Figure 3) and the following digits indicate the depth in feet to the bottom of the screened interval below land surface.

Two methods were used to install the wells at the study site: 1) a hollow stem auger, and 2) a pound and wash method. All wells installed after 1980 were 5.1 centimeters (cm) in diameter allowing sampling by a submersible pump. A peristaltic pump was used to sample wells with diameters less than 5.1 cm. All wells sampled had a 1.2 m screened interval with 0.1 millimeter (mm) slots. A detailed explanation of well construction at the OAB site is presented in Barber (1985). General considerations of well-casing material and well installation methods are presented in Scalf et al. (1981).

Many of the OAB monitoring wells are screened at only one depth. These wells do not provide vertical resolution of the contaminant plume and may not be screened within the contaminated portion of the aquifer. Vertical profiles of the plume were obtained using a number of well

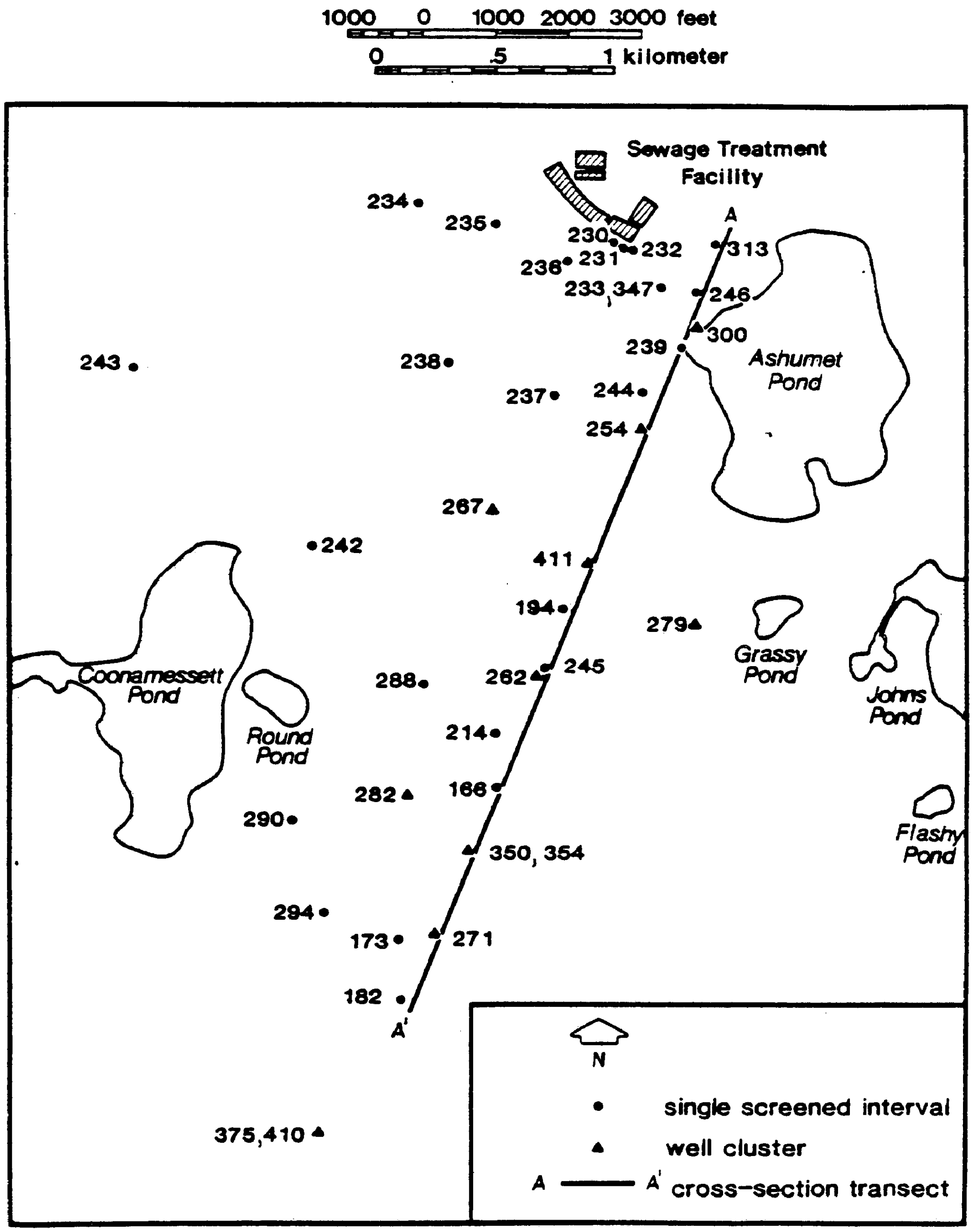


Figure 3. Index map showing the location of monitoring wells. Transect AA' used for cross-section shown in Figure 4.

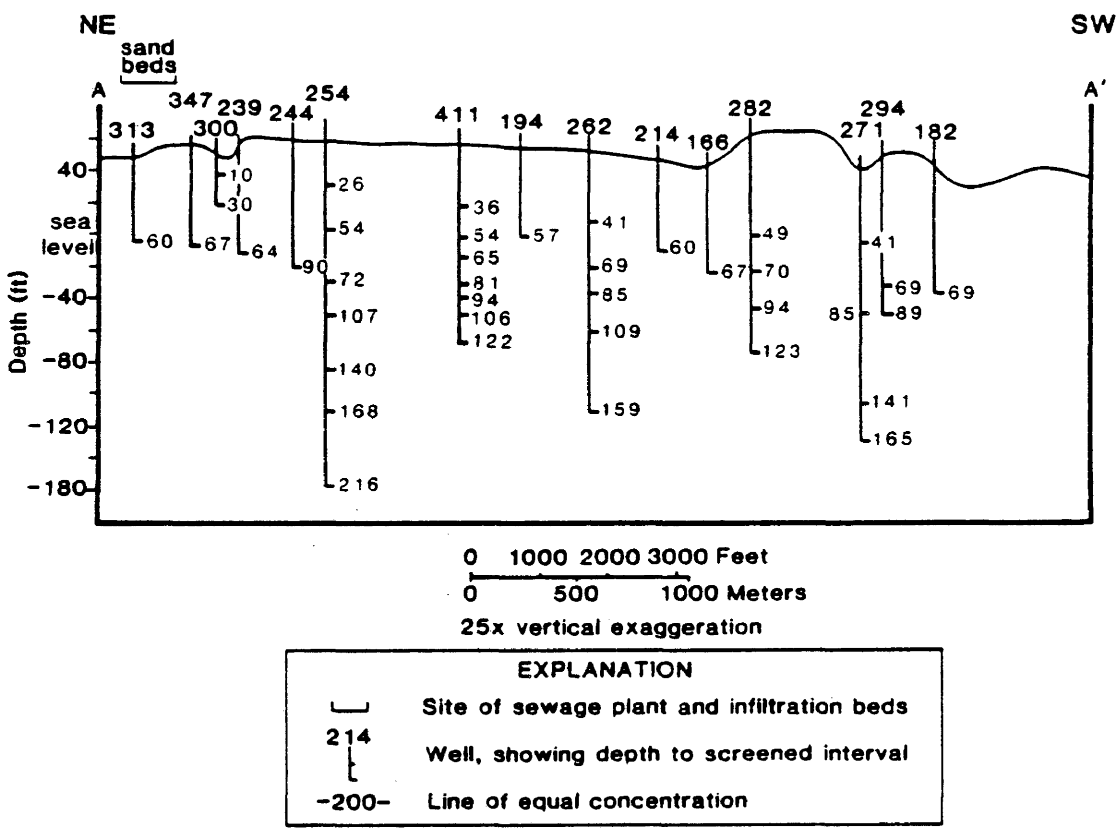


Figure 4. Index cross-section showing depth to screened interval below land surface in feet. Transect line AA' shown in Figure 3.

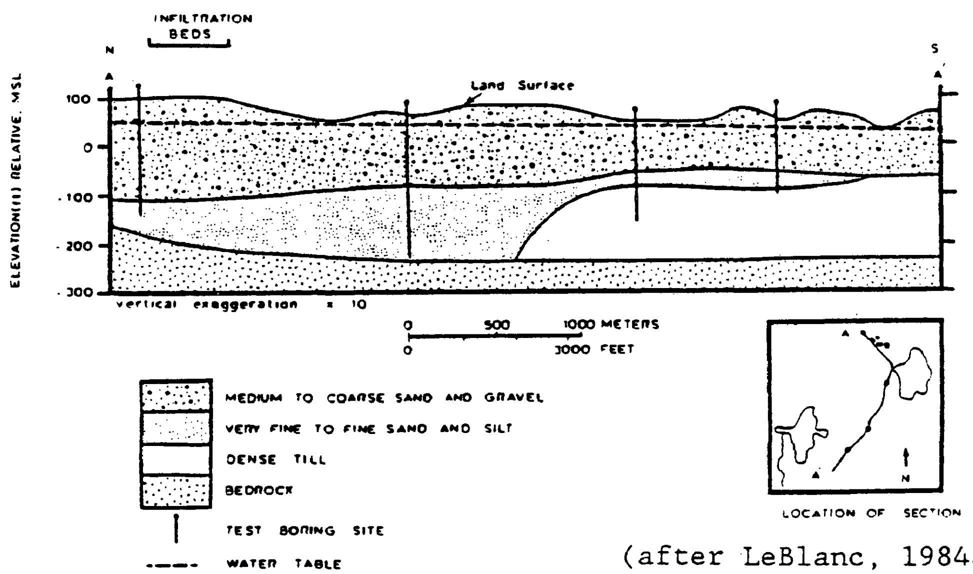
clusters consisting of wells screened at different depths. Well clusters are shown as triangles in Figure 3, and as a series of vertical wells in Figure 4. Well cluster FSW 347 contains a multilevel point sampler that is used to collect water at narrow depth intervals of about 0.6 m (Cherry et al., 1983). This device consists of bundles of polyethylene tubes that extend down a PVC pipe that is 3 cm in diameter. Each tube extends through a hole in the PVC pipe and is screened to a specific depth with nylon mesh. Water was obtained from the multilevel well using a peristaltic pump.

D. HYDROGEOLOGY OF THE STUDY SITE

The aquifer that is recharged by the OAB effluent is composed of Pleistocene glacial deposits of sand, gravel, silt, and clay that overlie crystalline bedrock (Figure 5). Lithologic and stratigraphic features were determined from samples collected from test borings at the wells shown in the cross section, supplemented by data from additional test holes (LeBlanc, 1984a).

The top 27 to 42 m of the aquifer consists of well-sorted medium to very coarse sand and some gravel. To the north sand and gravel outwash overlies fine to very fine sand and some silt. In the south half of the study area, the outwash overlies fine to very fine sand and silt and dense sandy till containing lenses of silt, sand, clay, and gravel. These unconsolidated sediments overlie crystalline bedrock that slopes from west to east (Oldale, 1976). A detailed explanation of the geology of the site can be found in Barber (1985). Although on a large scale the aquifer exhibits homogeneous behavior, there is considerable small-scale heterogeneity due to stratigraphic variability (LeBlanc, personal communication).

The aquifer is recharged primarily by precipitation and inflow from adjacent parts of the aquifer (primarily across the northern boundary of the study area). Surface runoff is negligible because of the permeable sandy sediments. Seasonal variations in aquifer recharge cause the water table altitude to fluctuate 0.3 to 1 meter per year (m/yr). The annual recharge to the aquifer has been estimated to be 53 cm, which is about 45 percent of the average annual precipitation. Using flow-net



(after LeBlanc, 1984a)

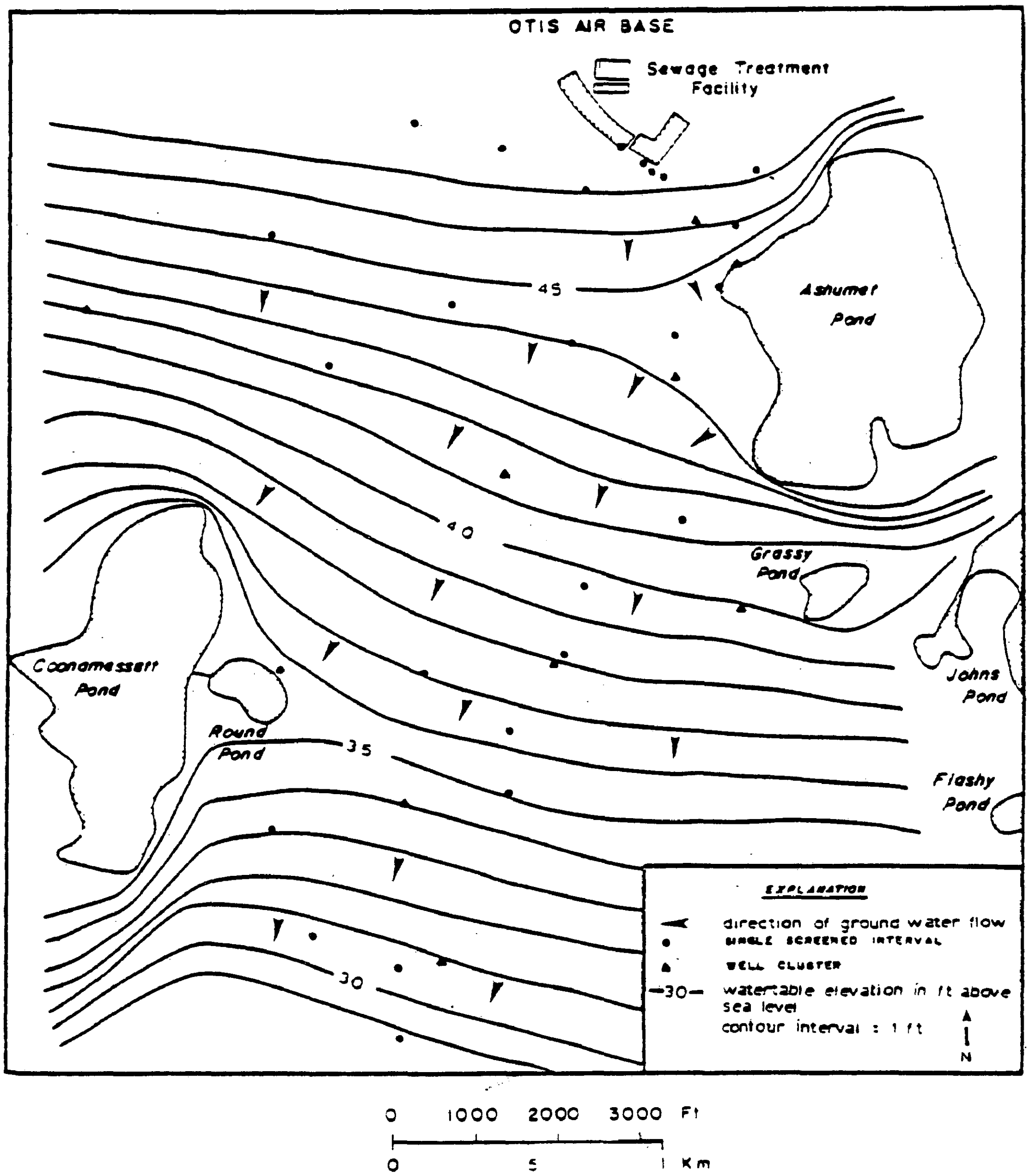
Figure 5. Hydrogeologic cross-section through the study area.

analysis, the rate of inflow across the northern boundary of the study area was estimated to be 1250 to 2000 m^3/d (LeBlanc, 1984a).

Groundwater in the aquifer occurs under unconfined water table conditions. The potentiometric surface slopes to the south-southwest at 1.5 meters per kilometer (m/km) (Figure 6). The direction of groundwater flow is generally south-southwest as inferred from the potentiometric surface. Flow patterns are distorted near the large ponds.

The groundwater flow velocity through the sand and gravel portion of the aquifer is estimated to be 0.3 m/d (LeBlanc 1984b). The groundwater flow velocity in fine sand and silt is lower than in coarse sand and gravel because the hydraulic conductivity is considerably lower. Field chemical analyses suggest that the plume is present in high permeablity sand and gravel and the less permeable silt. The crystalline bedrock has a very low hydraulic conductivity compared to that of the overlying unconsolidated sediments, therefore, it is assumed to be the bottom of the groundwater flow system.

Most groundwater flows across the southern boundary of the study area and is ultimately discharged to streams, ponds, and wetlands in southern Falmouth and ultimately to Nantucket Sound (LeBlanc, 1984a). Net discharge through wells is small because most water is returned to the aquifer by onsite sewage effluent recharge and by return flows from irrigation. Water lost to evapotranspiration is probably negligible because the water table is more than 3m below the land surface within most of the study area.



(after LeBlanc, 1984a)

Figure 6. Potentiometric map of study area showing depth to watertable and direction of groundwater flow.

E. GEOCHEMISTRY OF THE STUDY SITE

Between 1978 and 1985 water-quality samples were collected from the OAB monitoring network and analyzed for a variety of inorganic and organic constituents. This effort delineated a well-defined zone of contamination originating from the disposal of wastewater in the rapid-infiltration beds. LeBlanc (1984a) and Thurman et al. (1984b) present detailed accounts of the distribution and concentration of inorganic constituents in the groundwater. LeBlanc (1984a) assayed the groundwater for inorganic constituents and physical properties including specific conductance, temperature, boron, chloride (Cl^-), sodium (Na^+), orthophosphate (PO_4^{-3}), NH_4^+, NO_3^-, and dissolved oxygen (DO). Specific conductance (SC) and boron (B) have been used to delineate the extent of the contaminant plume at this study site (Barber, 1985; LeBlanc, 1984a).

Organic solute distribution in the plume has been delineated using four components: 1) dissolved organic carbon (DOC), 2) dissolved organic carbon fractionation (DOC_f; Malcolm et al., 1977), 3) detergents as methylene blue active substances (MBAS), and 4) volatile organic compounds. Barber et al. (1985), LeBlanc (1984a), and Thurman et al. (1986) discuss details on the detergent distributions in the groundwater. The DOC data is presented by Barber (1985) and Thurman et al. (1984b). Barber (1985) discusses DOC_f data at the OAB site. Details concerning the volatile organic plume are presented in Barber (1985) and Thurman et al. (1984b). Specific organic compound identification in the plume was conducted by Barber (1985).

F. MICROBIOLOGY OF THE OAB SITE

In comparison to the hydrogeologic and geochemical investigations that have been conducted at the OAB study site, very little was done to characterize the microbiology of the site until 1983. Between 1983 and 1985 the OAB site was sampled for microbiological parameters. Harvey et al. (1984) determined bacterial abundance, distribution, and heterotrophic uptake in sewage-contaminated and uncontaminated groundwater and in sediment-cores collected from two sites: 1) a site located 210 m from the contaminant source and 2) a site located 2930 m from the source. Smith and Duff (1984b) conducted a study on denitrifying activity in aquifer solids and in contaminated and uncontaminated groundwater using the acetylene block technique (Balderston et al., 1976; Knowles, 1982).

III. RESEARCH MODEL

The specific objective of this research is to evaluate the roles of nitrification and sorption in determining the fate of NH_4^+ and NO_3^- in groundwater. This section has been included: 1) to provide a review of previous nitrification and sorption studies conducted in contaminated and uncontaminated ecosystems; 2) to explain how this study differs from these previous investigations; and 3) to discuss the experimental approaches used to evaluate the significance of these two mechanisms in the nitrogen-contaminated groundwater at the field site.

A. NITRIFICATION INVESTIGATION: RATIONALE AND APPROACH

The occurrence of nitrification in aerated soils is well-documented in the soils literature (Allison, 1966; Ardakani and McLaren, 1977; Behnke, 1975; Cho, 1971; Feth, 1966; Ishaque and Cornfield, 1976; Misra et al., 1974; Misra et al., 1978; Preul and Schroepfer, 1968; Reneau, 1975; Schimel et al., 1984; Verstreate and Alexander, 1973). Furthermore, nitrifying activity has been demonstrated in marine and lake sediments (Cavari, 1977; Chen et al., 1972; Hall, 1982; Hansen et al., 1981; Hattori et al., 1978; Kuznetsov, 1968; Mevel and Chamroux, 1981; Vanderborght and Billen, 1975; Vincent and Downes, 1981). Yet, there have been few definitive studies concerning nitrification in subsurface groundwater systems (Fenchel and Blackburn, 1979). Evidence suggests that specific microbial activities similar to those in aerated or water-logged soils are occurring in groundwater. These activities include sulfate reduction (Dockins et al., 1980), nitrate reduction (Whitelaw and Rees, 1980; Whitelaw and Edwards, 1980), and nitrification (Barcelona and Naymik, 1984; Whitelaw and Rees, 1980). However, evidence supporting the presence of nitrifying bacteria in the subsurface is sparse and evidence substantiating their activity and effect on groundwater chemistry is nonexistent. Hence, this study was undertaken to determine whether nitrification was occurring at the study site and to what extent it affects the nitrogen chemistry of the groundwater.

Three approaches were employed at the OAB site to evaluate the occurrence and extent of nitrification: 1) identification of probable zones of nitrifying activity that are defined by substrates or products; 2) determination of the presence of nitrifying organisms in the aquifer material; and 3) measurements of nitrifying activity on samples from the aquifer. It was thought that zones in the aquifer containing nitrification products, substrates, and nitrifying bacteria are likely areas for nitrification to occur.

Groundwater samples from the contaminated aquifer were assayed for NH_4^+, NO_3^-, NO_2^-, and dissolved oxygen (DO). Potential nitrification zones were identified by aquifer zones containing nitrification substrates (NH_4^+ or NO_2^- and DO) and nitrification products (NO_2^- or NO_3^-).

Aquifer samples were assayed for nitrifying bacteria since the presence of these bacteria can serve as an indicator of nitrification potential. Bacteria are capable of existing for long periods of time in a dormant state if a critical substrate is missing (Stevenson, 1978).

Only those microorganisms that are favored by the local and temporary environment reproduce and their growth ceases when their environment becomes unfavorable. However, if only a few cells of a specific type of microorganism persist, a new burst of growth can occur when conditions once again become favorable for their development.

In terrestrial studies involving fertilizer nitrogen and occasionally in marine systems and lakes, the substrate concentrations are high and sufficient product is generated to measure in situ nitrification activity by the routine chemical monitoring of various pools of combined nitrogen (Cavari, 1977; Hansen et al., 1981). In pristine groundwater systems this mass- balance approach would probably not be applicable since bacterial substrate concentrations are low and, therefore, microbial growth and activities are probably low (Olson et al., 1981). However, it was hypothesized that higher rates of nitrification would occur in an NH_4^+-contaminated aquifer than in pristine groundwaters, therefore, a mass balance approach was applied at the study site to measure nitrifying activity.

B. AMMONIUM SORPTION INVESTIGATION: RATIONALE AND APPROACH

There are many studies in the soil science literature documenting sorption and ion exchange of NH_4^+ on soil clay particles (Allison, 1966; Ardakani and McLaren, 1977; Elprince et al., 1980; Misra et al., 1974; Preul and Schroepfer, 1968). In fact, NH_4^+ will generally displace other monovalent cations occupying clay sorption sites (Behnke, 1975).

Investigations of contaminated aquifers containing a high percentage of clay have indicated the importance of cation exchange in attenuating cationic contaminants. A study by Roberts et al. (1978b) showed evidence that cation exchange involving NH_4^+, sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) was affecting groundwater chemistry in an alluvial aquifer. In the same aquifer Valocchi et al. (1981) used a hydrogeological transport model and laboratory-determined ion exchange selectivity coefficients to simulate the transport of potassium (K^+), NH_4^+, Na^+, Ca^{2+}, and Mg^{2+}. A study by Ragone and Vecchioli (1975) also indicated that cation exchange was significant in determining groundwater chemistry in a clay-containing sand and gravel aquifer.

The aquifer at the OAB site is composed primarily of glaciofluvial sand and gravel and has a low percentage of clay. The influence of sorption and cation exchange in such aquifers has often been ignored because the aquifer solids have frequently been found to have low cation exchange capacities (Reardon, 1981; Sudicky et al., 1983). However, two recent field studies involving in situ natural-gradient tracer tests in a sand and gravel aquifer containing a low percentage of clay have shown that consideration of cation exchange processes can account for a significant portion of the observed temporal and spatial variability in groundwater chemistry (Dance and Reardon, 1983; Nicholson et al., 1983). These studies also showed that K^+ was preferred over Ca^{2+} and Mg^{2+} in these exchange reactions; NH_4^+ cation exchange, however, was not investigated in these studies. Based on the results of these groundwater studies, it was thought that NH_4^+ sorption and cation exchange could significantly affect the rate of NH_4^+ transport in the groundwater at the study site.

The following methods were used to evaluate sorption of NH_4^+ between the solid and the solution phases in the groundwater system at the study site: 1) a chemical survey of the ground-water, 2) laboratory sorption studies, and 3) <u>in situ</u> field tracer tests.

Groundwater was assayed to determine contaminant patterns at the site. Attenuation of NH_4^+ relative to a conservative contaminant can provide evidence that sorption on aquifer solids is occurring. However, since the processes affecting nitrogen chemistry and biology are frequently exceedingly complex, there may be other factors besides sorption affecting the distribution of NH_4^+. Therefore, other types of approaches must also be employed.

Laboratory batch studies were conducted to determine the NH_4^+ sorption isotherm. For data from these experiments to be applied with confidence in the analysis of field situations, laboratory column studies or field tracer tests should be conducted. Therefore, an <u>in situ</u> field tracer test was conducted to determine the effect of sorption on the rate of ammonium transport.

IV. MATERIALS AND METHODS

The equipment, chemical reagents, and procedures used for sample collection and sample analysis are described in the following pages. This section is divided as follows: 1) sample collection, 2) analytical methods, 3) microbiological methods, 4) laboratory sorption experiments, and 5) field transport study techniques.

A. SAMPLE COLLECTION

Water samples were collected from wells in place at the OAB site (see section II). These wells are constructed of polyvinylchloride (PVC) and vary from 3.2 cm to 5.1 cm in diameter. For wells with a casing diameter of 5.1 cm, water samples were collected by a stainless steel, positive displacement (helical rotor), submersible pump (Model SP81, Keck Geophysical Instruments, Okemos, Michigan). Well cluster FSW 347 contains a multilevel point sampler that is used to collect water at narrow depth intervals of about 0.6 m (Cherry et al., 1983). This device consists of bundles of polyethylene tubes that extend down a PVC pipe (3.8 cm outside diameter; O.D.). Each tube extends through a hole in the PVC pipe and is screened to a specific depth with nylon mesh.

Wells with a casing diameter of less than 5.1 cm were initially evacuated by a gasoline powered, centrifugal-suction pump. After evacuation, water samples were collected using a peristaltic pump (Model 760, Geotech Environmental Equipment, Denver, Colorado.) All wells were pumped until a minumum of three casing volumes of water were evacuated prior to sample collection.

Aquifer sediment was collected with a truck-mounted drilling rig equipped with hollow-stem augers. The auger was advanced to a desired depth and a split-spoon corer was pounded down into virgin aquifer material beneath the bottom of the auger. Cores were taken at selected depths and transferred into widemouth acid-washed jars; cores for microbiological analyses were transferred into sterile widemouth jars.

B. SAMPLE PRESERVATION AND CHEMICAL ANALYTICAL METHODS

A summary of sample preservation methods is given in Table 1. Specific conductance, pH, and temperature were measured at the time of groundwater collection. Dissolved oxygen (DO) was measured at the time of collection or was fixed using the Winkler method (American Public Health Association, 1981). All samples collected for analyses other than specific conductance, pH, and DO were filtered in the field through a 0.45 micron Nucleopore or Gelman membrane filter.

Analytical techniques are summarized in Table 2. Specific conductance (SC) was measured with a digital meter (Extch Company. Model 440, Waltham, Massachusetts) and values were corrected for the temperature of the groundwater (mean temperature is $10^{o}C$). The pH was measured with an Orion Model 81-55 and 81-56 Ross combination glass electrode and an Orion Ionalyzer Model 901 pH meter. Dissolved oxygen was measured with a oxygen meter (Yellow Springs Instrument Company) or the Winkler method (American Public Health Association, 1981). Samples for inorganic nitrogen were analyzed in the field, or preserved for later analysis and shipped to the U.S. Geological Survey Water Quality Laboratory in Arvada, Colorado. Samples for NH_4^+ analyses were preserved with sulfuric acid (H_2SO_4). NO_3^- and NO_2^- samples were preserved by freezing at $0^{o}C$. Samples for cation analyses were preserved in the field by acidification with nitric acid. Samples for anion analyses were unacidified and frozen at $0^{o}C$ until analysis.

Colorimetric methods were employed to analyze dissolved nitrogen species. These analyses are automated by an autoanalyzer system

Table 1. Summary of perservation methods for the analyzed chemical species.

Chemical Species	Method of Preservation
Ammonium	-0.2 ml concentrated sulfuric acid per 60 ml -plastic bottle -storage at 4 degrees C
Nitrate, Nitrite	-plastic bottle -storage at 0 degrees C
Sodium, Potassium Calcium, Magnesium	-0.2 ml concentrated nitric acid per 60 ml -plastic bottle -storage at 4 degrees C
Chloride, Bromide Sulfate	-plastic bottle -storage at 0 degrees C
Dissolved Oxygen	-analyzed at time of collection or fixed by Winkler method (A.P.H.A., 1981)

Table 2. Summary of methods used for chemical analyses.

Parameter	Method of Analysis	Lower Limit of Detection	Reference
Dissolved Ammonium	automatic, colorimetric, salicylate-hypochlorite	0.01 mg N/L	Skougstad et al. (1979)
Total Ammonium	KCl sediment extraction and automatic, colorimetric, salicylate hypochlorite	0.01 mg N/L	Bremner and Keeney (1966), and Skougstad et al. (1979)
Nitrate + Nitrite	automatic, colorimetric, cadmium reduction-diazotization	0.03 mg N/L	Skougstad et al. (1979)
Nitrite	automatic, colorimetric-diazotizatization	0.01 mg N/L	Skougstad et al. (1979)
Calcium	atomic absorption spectroscopy	0.10 mg/L	Skougstad et al. (1979)
Magnesium	atomic absorption spectroscopy	0.10 mg/L	Skougstad et al. (1979)
Sodium	atomic absorption spectroscopy	0.10 mg/L	Skougstad et al. (1979)
Potassium	atomic absorption spectroscopy	0.10 mg/L	Skougstad et al. (1979)
Bromide	ion chromatography	0.10 mg/L	Small et al. (1979)

Table 2. Summary of methods used for chemical analyses (continued).

Parameter	Method of Analysis	Lower Limit of Detection	Reference
Chloride	ion chromatography	0.10 mg/L	Small et al. (1979)
Sulfate	ion chromatography	0.05 mg/L	Small et al. (1979)
Dissolved Oxygen	electrode or Winkler method	0.10 mg/L	A.P.H.A. (1981)
pH	electrode	0.01 units	

(Technicon Instruments Corporation, Tarrytown, New York) according to the methods employed by the U.S. Geological Survey National Water Quality Laboratory in Arvada, Colorado (Skougstad et al., 1979). Samples were analyzed for NO_3^- using the cadmium-reduction method (American Public Health Association, 1981). Briefly, in this analysis NO_3^- is reduced to NO_2^- in the presence of cadmium. NO_2^- is then diazotized with sulfanilamide and coupled with N-(1 naphthyl)-ethylenediamine to form a dye the concentration of which is measured colorimetrically at 540 nm. Correction for any NO_2^- present in the sample is made by analyzing without the cadmium-reduction step. Peak areas were obtained using an integrator (Hewlett Packard Company, Model 3392A, Avondale, Pennsylvania). Integrated peak areas versus concentration were plotted to obtain the standard calibration curve.

Dissolved NH_4^+ was analyzed by a method in which inorganic NH_4^+ reacts with sodium salicylate and sodium nitroferricyanide in an alkaline medium to form a colored compound. The absorbance of this compound is directly proportional to the NH_4^+ concentration. Integrated peak areas were used to determine the standard calibration curve.

The concentration of NH_4^+ sorbed on the sediment was analyzed using a sediment extraction method modified from that of Bowden (1984) and Bremner and Keeney (1966). Sediment material was slurried in a 2 M KCl solution in a 500 ml nalgene bottle (head space volume was 250 ml). The bottle was then placed horizontally on a shaker and shaken for 2 h at ambient temperature (22 to 24°C). Subsamples were removed at the end of this extraction period, filtered, and analyzed for dissolved NH_4^+ using the method described above.

The concentrations of dissolved calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+) were assayed by atomic absorption spectroscopy (Perkin Elmer Company, Model 305B, Norwalk, Connecticut). The method used for the analyses was modified from the method described in Analytical Methods for Atomic Absorption Spectrophotometry (1973). Water samples and standards were diluted with lanthanum/cesium reagent, which was prepared from La_2O_3 and CsCl, to inhibit chemical interferences. The instrument was calibrated using a reagent blank and standards. Ca^{2+} was assayed at a visible wavelength of 422.7 nm, Mg^{2+} at 285.2 nm ultraviolet (UV) wavelength, Na^+ at 589.0 nm visible wavelength, and K^+ at 766.5 nm visible wavelength.

Dissolved bromide (Br^-), sulfate (SO_4^{2-}), and chloride (Cl^-) were measured by ion chromatography (Dionex Company, Model 14, Sunneyvale, California), using a carbonate-bicarbonate eluent (0.003 $\underline{M}$ $NaHCO_3$, 0.0024 $\underline{M}$ Na_2CO_3) (Small et al., 1975). Samples and standards were diluted with eluent in order to avoid the occurrence of a negative peak in the chromatogram.

Precision and accuracy were assessed for NH_4^+, NO_3^-, major cation, and anion analytical techniques using standard reference samples. For the nitrogen analyses, EPA standard reference samples containing high and low concentrations of NH_4^+ and NO_3^- were assayed. For anion and cation analyses, U.S. Geological Survey standard reference samples were assayed. In all cases, the standard reference samples were run in triplicate.

The results, summarized in Tables 3 and 4, demonstrate the accuracy and precision of these analyses with differences between laboratory values and documented values being generally comparable to the documented standard deviation for the method (values differed from quoted values by 5 percent or less).

Table 3. Evaluation of analytical methods for cations and anions. Brackets enclose standard deviation.

Chemical	Documented Value (mg/L)	Laboratory Result (mg/L)	Standard Reference Sample I.D. #
Ca^{2+}	26 [1.5]	26 [1.0]	U. S. G. S.[a] #90
Mg^{2+}	3.6 [0.2]	3.6 [0.1]	U. S. G. S. #82
Na^{+}	5.9 [0.3]	5.6 [0.1]	U. S. G. S. #90
K^{+}	2.2 [0.2]	2.1 [0.0]	U. S. G. S. #90
SO_4^{2-}	28 [1.8]	28 [1.5]	U. S. G. S. #82
Cl^{-}	4.2 [0.6]	4.2 [0.2]	U. S. G. S. #90
Br^{-}	0.3 [0.03]	0.3 [0.04]	U. S. G. S. #90

a. Standards were obtained from the U.S. Geological Survey, Water Quality Laboratory, Arvada, Colorado.

Table 4. Evaluation of analytical methods for ammonium and nitrate. Brackets enclose standard deviation (continued).

Chemical Species	Documented Value (mg N/L)	Laboratory Result (mg N/L)	Standard Reference Sample I.D. #
NH_4^+	1.90 [0.11]	1.90 [0.02]	E. P. A. # WP284 [a]
NH_4^+	0.28 [0.02]	0.26 [0.01]	E. P. A. # WP284
NO_3^-	1.43 [0.07]	1.43 [0.01]	E. P. A. # WP284
NO_3^-	0.14 [0.02]	0.15 [0.01]	E. P. A. # WP284

a. Standard reference samples were obtained from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

C. MICROBIOLOGICAL ASSAYS

This section explains techniques used to enumerate viable bacteria and to measure nitrifying activity at the study site. Bacteria were enumerated using plate-count techniques and MPN statistical probability dilution counts were conducted for coliform and nitrifying bacteria. Mass-balance incubation techniques were employed to determine nitrifying activity.

i. Enumeration of Viable Bacteria

Plate counts were conducted on nutrient agar and dilute soil-extract agar (DSEA) media using the pour-plate method (Wilson et al., 1983). DSEA media was prepared by autoclaving 500 g of sandy-loam surface soil obtained from the OAB site in 500 ml of distilled water for 1 hour (h) at 121°C. The resulting extract was filtered, diluted tenfold with distilled water, and amended with 1.5 percent Bactoagar (Difco Laboratories, Detroit Michigan). Nutrient agar media was prepared from nutrient agar powder (Difco Laboratories, Detroit Michigan). Both nutrient agar and DSEA media were sterilized by autoclaving at 121°C for 20 minutes.

Volumes of 1.0 ml, 0.1 ml, and 0.01 ml water samples were added to pour plates containing nutrient agar or DSEA. These plates were incubated for one week at 22° to 24°C. After the incubation period the number of colonies that grew in the agar media were counted. Because of the existence of aggregates of cells, several cells may form one colony, therefore, results are given in colony-forming units per milliliter (CFU/ml) instead of total bacteria/ml.

Coliform bacteria were determined using the total-coliform most-probable-number (MPN) presumptive test (American Public Health Association, 1981). Confirmational tests were not performed. The presumptive test was conducted by inoculating a series of tubes containing lauryl tryptose broth media with graduated quantities of water sample. Three replicates were conducted for each dilution. Sterile fermentation tubes (10 ml test tubes) were aseptically placed in an inverted position in the tubes containing the media and samples. The inoculated tubes were incubated at 35^{o}C. After 24 h the tubes were gently skaken and examamined for gas trapped in the inverted fermentation tubes. If no gas was observed, this step was repeated at the end of 48 h (observed formation of gas within 48 h constitutes a positive presumptive test). Using MPN statistical analysis, estimates of numbers of coliform bacteria can be obtained from the number of positive tubes in each three tube series.

The MPN dilution method was modified to determine the NH_4^+-oxidizing bacteria (American Public Health Association, 1981). The medium used was that described by Soriano and Walker (1968). A series of tubes containing 9 ml of media was inoculated with graduated quantities (1.0 ml, 0.1 ml and 0.01 ml) of the water-sediment slurries prepared for the nitrification incubations at the initiation of the incubation period. Three replicate tubes were used for each slurry dilution.

Inoculated MPN tubes were incubated at ambient temperature (22 to 24^{o}C) and examined periodically by spot tests (Strickland and Parsons, 1972) for the presence of NO_2^-, or NO_3^-, if the NO_2^- test was negative. Inoculated MPN tubes were examined after four weeks of incubation. Incubation was continued until no new positive tubes appeared over a two-week period. The total incubation period was nine weeks. Numbers of NH_4^+-oxidizing bacteria were estimated from the number of positive tubes using MPN statistical analysis.

ii. Nitrification Assay

Water and core material for the nitrification assays were collected from two sites; well cluster FSW 262 and FSW 347. FSW 262 is located 2030 m downgradient from the sand beds and FSW 347 is 210 m from the infiltration beds. The preliminary nitrification study was conducted in October 1984 followed by other nitrification studies in May 1985.

For the preliminary nitrification experiment, water samples and cores were collected at FSW 262, stored on ice, and shipped to the U.S. Geological Survey Water Quality Laboratory in Arvada, Colorado where nitrification assays were initiated. For all other nitrification experiments, nitrification assays were initiated on the same day the samples were collected.

Nitrifying activity was assayed by modifying incubation techniques employed by Cavari (1977), Mevel and Chamrous (1981), and Schell (1974) and monitoring changes in the concentrations of dissolved NO_2^-, NO_3^-, and NH_4^+ as a function of time. The experiments were carried out by placing 150 ml of ground water collected from a screened well in a sterile 500 ml nalgene bottle. To the container was added 150 g of core material obtained from the depth of the well screen. The core material was transferred from the collection vessel by loading into a sterile cutoff 50 cubic centimeter (cc) polypropylene syringe (Becton-Dickinson, Rutherford, New Jersey) and extruding the core material into the incubation container to form a slurry. The container was capped and placed horizontally on a shaker to maintain a well-oxygenated system (head- space volume was 300 ml) and subsamples were taken periodically. Subsamples were removed with a sterile graduated pipet, vacuum-filtered through a Gelman Metricel membrane filter (0.45 um pore size), and assayed immediately for dissolved NO_2^-, NO_3^-, and NH_4^+. Killed controls were prepared by autoclaving the slurried incubation mixture for one hour at a temperature of 121°C on two consecutive days.

For the preliminary experiment at the location of well FSW 262, four screened depths were assayed for nitrifying activity. At only one depth (21 m) was the <u>in situ</u> NH_4^+ concentration greater than 0.19 mg N/L, therefore, incubations from the other three depths were amended to a final NH_4^+ concentration of 2 mg N/L. Triplicates of each sample were incubated for three weeks at 10°C, which is the mean groundwater temperature.

Incubations were repeated in the field at well FSW 262 at the 21 m depth, for five replicate unamended slurries. In this case, incubations were conducted for eleven days at ambient temperature (22° to 24°C).

At well FSW 347, eight screened depths were assayed for nitrification within an interval of 6 to 10 m below the land surface. _In situ_ concentrations of NH_4^+ were low (less than 1 mg N/L) for five of the eight depths sampled, thus, incubation slurrries from these five depths were amended to a final NH_4^+ concentration of 1 mg N/L. The three depths containing concentrations of NH_4^+ greater than 1 mg N/L were unamended. Five replicates were prepared for each depth and incubated at ambient temperature (25°C) for a period of eleven days.

D. LABORATORY SORPTION EXPERIMENTS

This section discusses experimental procedure for a laboratory batch experiment designed to determine the NH_4^+ sorption isotherm on aquifer solids collected from the study site. In this experiment core material was mixed with known concentrations of dissolved NH_4^+ in a batch reactor and sorbed NH_4^+ was calculated from the decrease in concentration of dissolved NH_4^+ (Schweich and Sardin, 1981). Core material for these experiments was collected at the OAB site at well FSW 393-37 from a depth interval of 10 to 11.3 m below land surface. The core was chilled to 4^oC and shipped to the U.S. Geological Survey Water Quality Laboratory in Arvada, Colorado.

The batch experiment was initiated within five days of sample collection. The core was divided into 100 g portions of sediment. Half of the 100 g portion was used to determine moisture content and the other half was weighed into a 250 ml polyethylene bottle to be used for the batch experiment. To determine the moisture content the core segments were dried in an oven overnight at a temperature of 100^oC. The moisture content was calculated from the weight difference between the moist and dried sample.

NH_4^+ standards of 25, 10, 2.5, 1.0, 0.5, and 0.25 mg N/L consisted of ammonium chloride (NH_4Cl) and laboratory-simulated groundwater (Table 5). The standards (80 ml) were added to the bottles containing 50g of wet sediment (sediment-water ratio of 2:1). In order to ascertain whether sorption was occurring on the surface of the plastic container, blanks were prepared by adding 100 ml of the NH_4^+ standard to plastic

Table 5. Composition of native and simulated ground water.

Chemical Species	Simulated Ground Water (mM)	Native Ground Water (mM)
NH_4^+	0.000	0.000
Ca^{2+}	0.027	0.027
Mg^{2+}	0.042	0.042
Na^+	0.247	0.248
K^+	0.032	0.032
Cl^-	0.235	0.236
SO_4^{2-}	0.076	0.076
HCO_3^-	0.031	0.031
NO_3^-	0.000	0.000
NO_2^-	0.000	0.000

bottles containing no sediment. The assay was conducted in triplicate for each NH_4^+ concentration and for the blank.

The bottles were placed horizontally on a shaker and shaken slowly at ambient temperature (22 to 24^{o}C) to allow the sediment to equilibrate with the NH_4^+ solution. After 1, 3, 5, and 7 h, aliquots from each bottle were filtered through a 0.45 micron filter (Gelman GN-6), and assayed for dissolved NH_4^+. The results of this experiment were plotted as the concentration of sorbed NH_4^+ (ug N/cm^3) versus the dissolved NH_4^+ concentration (ug N/ml) to obtain the sorption isotherm.

E. FIELD DIVERGENT TRACER TEST METHODS

Two field transport studies were conducted in October 1985 and May 1986. These tests were designed and instrumented by Steve Garabedian (U.S. Geological Survey, Boston Massachusets). Both transport studies were run as forced advection or divergent tracer tests. The location of the divergent-tracer-test site is a pristine area to the west of the contaminant plume (well FSW 393).

The divergent-tracer-test site consists of an injection well which is screened over a depth interval from 10.0 to 11.3 m below land surface and monitoring wells containing multilevel sampling devices. The monitoring wells are located at radial distances of 1.5 m, 3.0 m, and 6.1 m from the injection well. For the initial tracer test conducted in 1985, the test consisted of: 1) collecting 200 L of groundwater from one of the existing wells proximal to the test site; 2) dissolving 375 g of ammonium bromide (NH_4Br) in the 200 L of water; and 3) reinjecting the groundwater containing the NH_4Br into the injection well. The well located 1.5 m from the injection well was used to monitor the tracer pulse. The 1986 tracer test was similar to the initial test except the tracer solution contained 60 g of potassium nitrate (KNO_3) as well as 375 grams of NH_4Br. The injection well was used to introduce the tracer solution pulse into the shallow water-table zone. The tracer solution was pumped into the well at a rate of 95 l/m, and the duration of the tracer-solution injection was five minutes. For a two hour period prior to tracer injection and throughout the remainder of the tracer test, groundwater from a nearby well was pumped into the injection well at 95 l/m.

The monitoring well was sampled at two depths (10 and 11.3 m below land surface) and samples assayed for Br^- and NH_4^+ in the field. Br^- concentration was determined using an Orion combination specific ion electrode and an Orion Model 407A Ionalyzer meter, and dissolved NH_4^+ was measured with the same instrument using an Orion gas-permeable electrode (Orion Research Incorporated, Cambridge, Massachusetts). These measurements were repeated in the laboratory using the methods listed in Table 2. For the 1985 tracer test, water samples from the monitoring wells were assayed for Br^-, dissolved NH_4^+, and the major cations and anions; for the 1986 tracer test, samples were measured for Br^-, dissolved NH_4^+, NO_3^-, and major cations and anions. Results were plotted in concentration units or percent of concentration of injectate (C/C_o) versus time. Peak areas were obtained using the "cut and weigh" method.

V. RESULTS AND DISCUSSION

A. CONTAMINANT PATTERNS

This section describes the results of field investigations that were conducted on the groundwater at the OAB site in 1983 and 1985. At the beginning of the 1983 field season, 66 observation wells were in place at the OAB site. Groundwater samples were collected from 56 of these wells and assayed for bacteria and inorganic chemical constituents in order to determine: 1) the distribution of inorganic solutes in the contaminant plume; and 2) the role played by microorganisms in the fate of sewage contaminants introduced into the groundwater. The groundwater was resampled in 1985 for inorganic chemical constituents. Interpretations of the chemical and microbiological data obtained from these studies were the basis of further investigations concerning the processes affecting inorganic nitrogen at the OAB site.

i. Specific Conductance

Specific conductance (SC) is a measure of the ability of water to conduct an electrical current and is related to the total concentration of dissolved ionic species in the water. As the ion concentration increases the conductance of the solution also increases (Hem, 1970). The SC of treated sewage is higher than uncontaminated groundwater because the concentration of dissolved ionic solids in water is increased when water is used for domestic purposes. Hence, SC data can be used to delineate the lateral and vertical extent of the contaminant plume originating from the land-disposal of sewage effluent from the OAB treatment plant (Hem, 1970).

Figure 7 is a cross-sectional map view along the transect shown in Figure 3 for SC data obtained in 1983. There is sufficient contrast in the SC of the effluent (400 $umho/cm^2$), the SC of the native groundwater (51 $umho/cm^2$), and the contaminated water (100 to 400 $umho/cm^2$) to readily define a plume that extends more than 3350 m downgradient from the sewage-infiltration beds, is 910 to 1520 m wide, and 30 to 50 m thick vertically. The longitudinal axis of the plume is oriented in the direction of regional groundwater flow. The toe of the plume is not precisely defined due to lack of appropriate wells in this region (Barber, 1985). The area of highest specific conductance is immediately adjacent to the sand beds and the specific conductance generally decreases with increasing distance from the beds. In general, the plume is being displaced vertically downward with increasing distance from the infiltration beds by recharge from precipitation (LeBlanc, 1984a).

The distribution of SC in 1985 corresponds well with the 1983 distribution (Figure 8). It is likely that the plume of contaminated groundwater was transported further downgradient from the infiltration beds from 1983 to 1985, however, the distance of migration in this two-year period is probably not detectable due to lack of appropriate wells at the plume front.

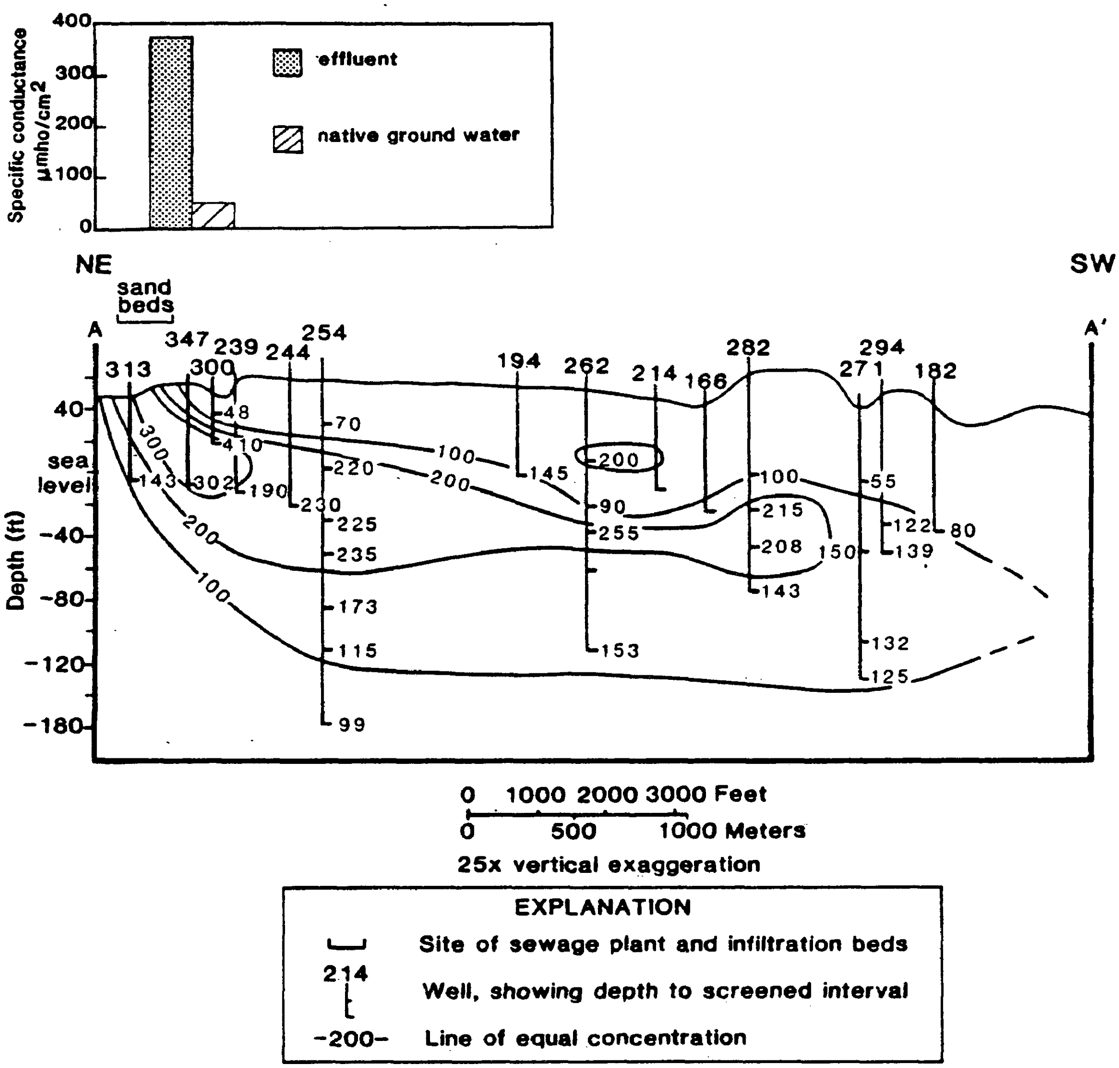


Figure 7. Distribution of specific conductance (umho/cm^2) in 1983; cross-section. Histogram comparing specific conductance in the sewage effluent and the native groundwater.

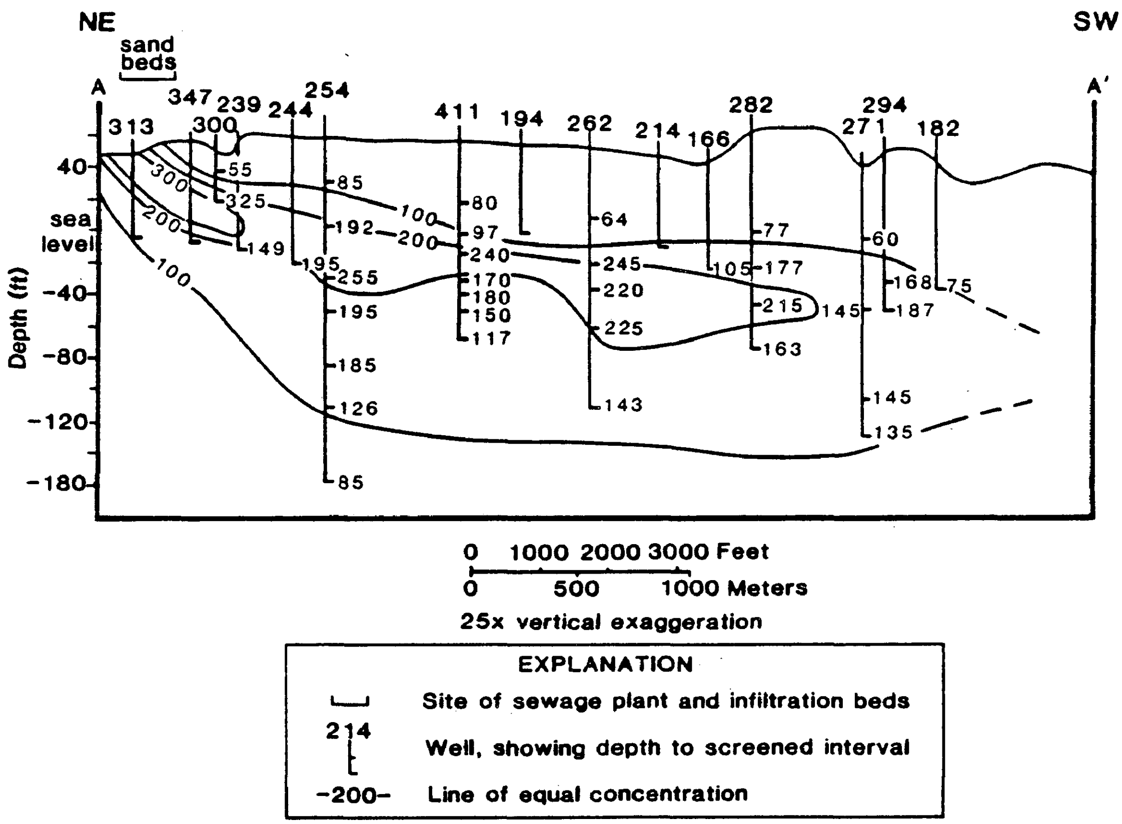


Figure 8. Distribution of specific conductance (umho/cm^2) in 1985; cross-section.

ii. Dissolved Oxygen

LeBlanc (1984a) measured dissolved oxygen (DO) in the plume in 1979-1980 and reported that within 1520 m of the infiltration beds only an upper boundary (about 8 m thick) along the top of the plume is oxygenated and below this boundary anaerobic conditions prevail (Figure 9). Anoxic conditions near the beds could be due to high chemical oxygen demand (COD) and biological oxygen demand (BOD) in this zone created by the introduction of effluent containing high concentrations of dissolved organic carbon (DOC; 12 mg/L) (Thurman, 1984b).

From 2030 m downgradient from the infiltration beds to the toe of the plume (about 3350 m downgradient), DO is found in the center of the plume. Although this zone contains relatively high DOC concentrations (as great as 4 mg/L), it has been demonstrated that 50 percent of this DOC is composed of nonbiodegradeable detergents (Thurman et al., 1986). Hence, the presence of DO in this zone could be due to insufficient oxygen demand.

The DO data from the 1983 sampling study are not included in this discussion because the data are questionable due to mechanical problems with the DO meter. The DO distribution for 1985 is similar to the 1979-1980 DO distribution (Figure 10; values of 0.1 mg/L or less do not indicate detectable DO since the detection limit for the assay is 0.1 mg/L).

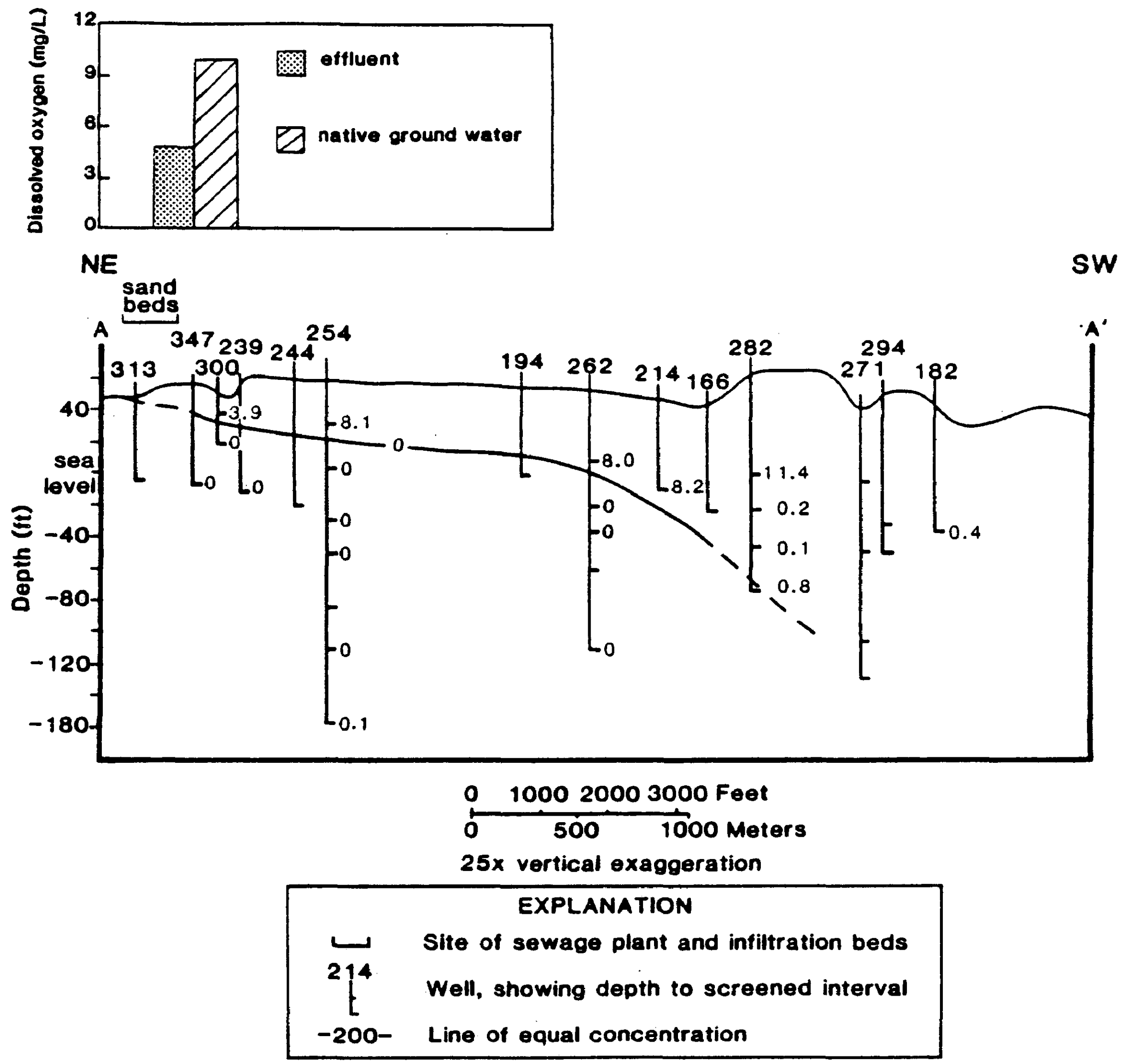


Figure 9. Distribution of dissolved oxygen (mg/L) in 1979-1980; cross-section. Histogram comparing dissolved oxygen concentrations in the sewage effluent and the native groundwater.

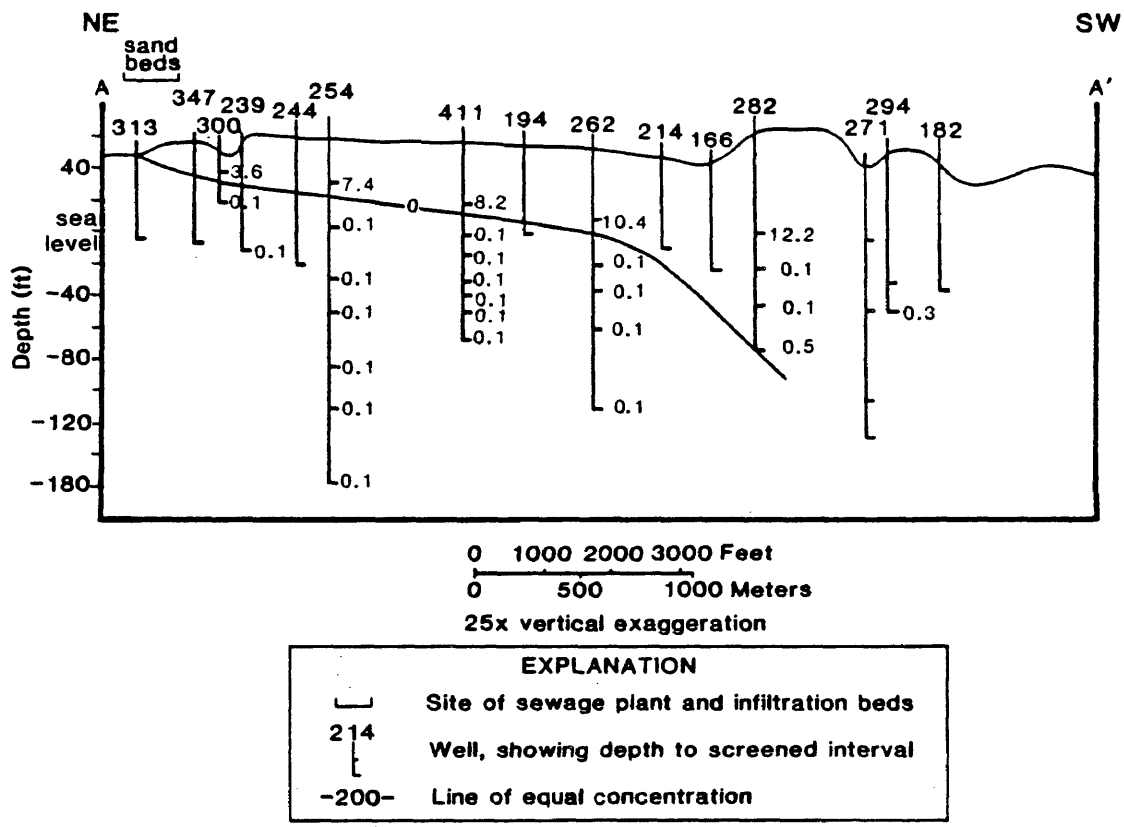


Figure 10. Distribution of dissolved oxygen (mg/L) in 1985; cross-section.

iii. Ground Water pH Measurements

Figure 11 depicts the distribution of pH in 1983. The pH of the groundwater ranges from 4.7 to 6.9 and is higher in the center of the contaminant plume (6.2 to 6.9) than along the upper vertical boundary of the plume (4.9 to 6.0). Nitrification is one possible explanation for these pH distributions because the nitrification process increases the proton concentration and is more likely to occur where dissolved oxygen is present. Also, groundwater recharge by acid rain could be lowering pH in the shallow part of the aquifer.

The 1985 pH distribution in the contaminant plume is consistent with the 1983 distribution with lower pH's (5.3 to 5.9) along the upper vertical boundary of the contaminant plume and higher pH's (6.1 to 7.4) in center of the plume (Figure 12).

iv. Nitrate

The predominant inorganic nitrogen species derived from sewage are NH_4^+ and NO_3^-. The effluent from the OAB treatment facility is compared with effluents from other secondary treatment plants in Table 6 (Bouwer et al., 1974; Olson et al., 1980). The sewage effluent originating from the OAB treatment plant has a lower NH_4^+ concentration (6.4 mg N/L) and a higher NO_3^- concentration (12 mg N/L) than the other effluents. This is probably a result of the recycling procedure used on the sewage effluent at the OAB treatment plant allowing for oxidation of NH_4^+ and organic nitrogen to NO_3^-.

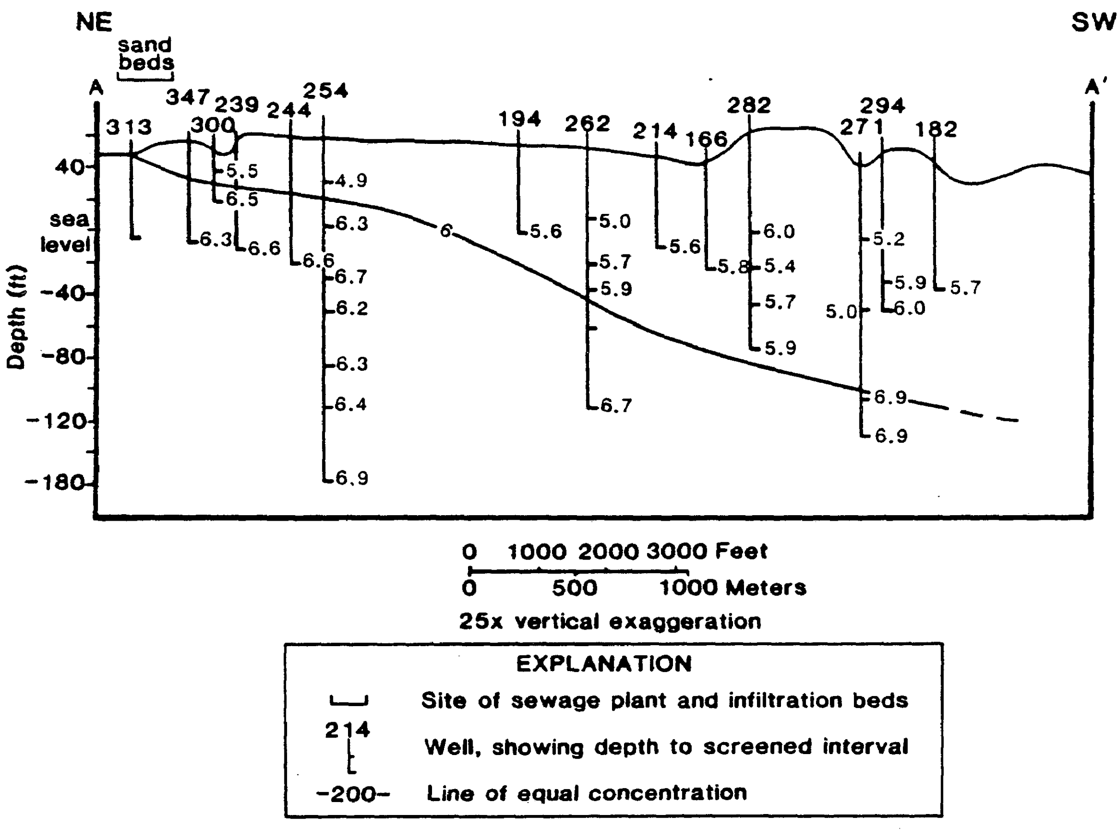


Figure 11. Distribution of pH in 1983; cross-section.

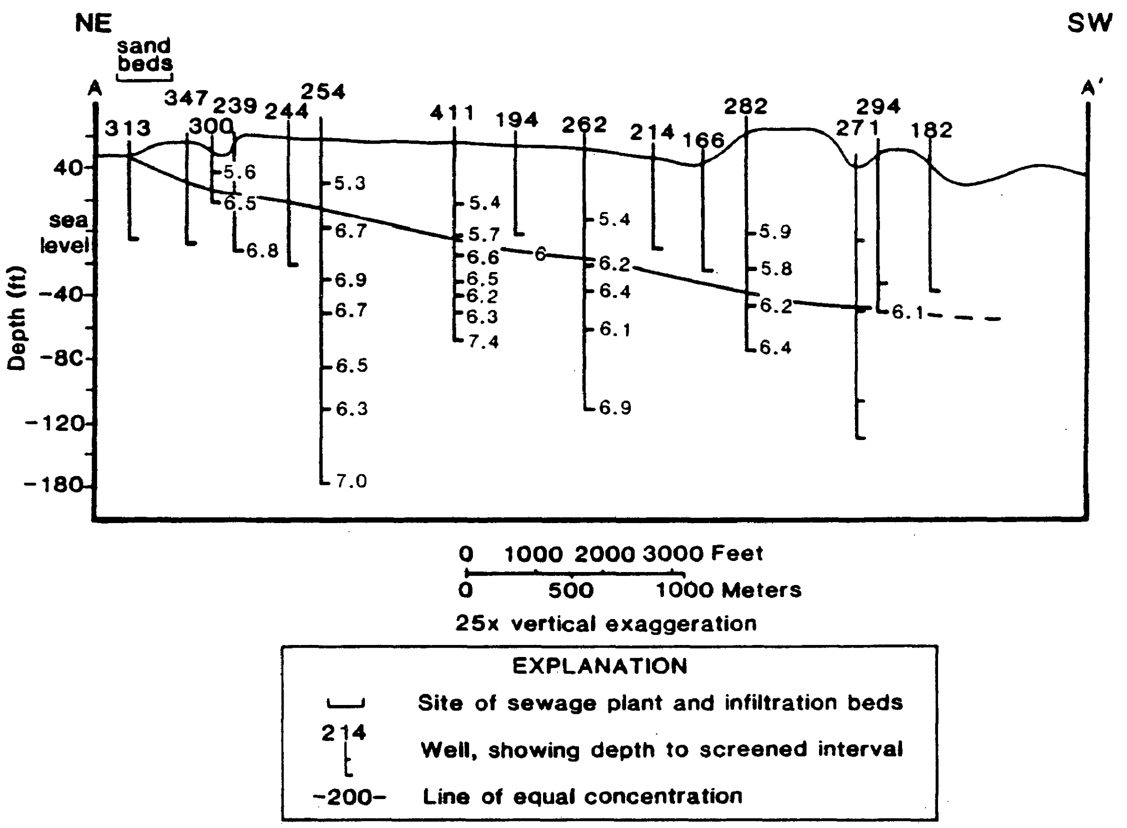


Figure 12. Distribution of pH in 1985; cross-section.

Table 6. Composition of Otis Treatment Plant secondary effluent. Effluents from two other locations are given for comparison. Concentrations in mg/L except for specific conductance (umho/cm^2) and pH.

Constituent	OAB Site	I Arizona	II California
pH	5.9	7.6	7.3
Sp. Cond.	394.0	--	1790.0
Alkalinity	3.0	381.0	446.0
Nitrite as N	0.5	0.3	--
Nitrate as N	12.0	2.0	0.4
Ammonium as N	6.4	40.0	25.0
Orthophosphate as P	7.0	15.0	10.0
Calcium	13.0	82.0	54.0
Magnesium	6.0	36.0	64.0
Potassium	9.0	8.0	13.0
Sodium	43.0	200.0	262.0
Chloride	34.0	213.0	284.0
Fluoride	0.2	4.1	0.7
Sulfate	34.0	107.0	213.0
TOC	19.0	213.0	248.0
MBAS	0.4	--	--
Boron	0.5	0.8	1.4

TOC = Total Organic Carbon
MBAS = Detergents as Methylene Blue Active Substances
I. = after Bouwer et al., 1974
II. = after Olson et al., 1980

The 1983 NO_3^- distribution at the OAB site is shown in cross-section in Figure 13. The NO_3^- concentration in the sewage effluent is 12 mg N/L while the native ground water contains 0.2 mg N/L. The concentration of NO_3^- within 300 m of the beds is as high as 14 mg N/L, which is greater than the NO_3^- concentration in the effluent (12 mg N/L). However, the NO_3^- concentrations drop off very sharply further downgradient, with concentrations of about 1 to 2 mg N/L throughout most of the contaminant plume. Furthermore, there is a zone of depleted NO_3^- (less than 1 mg N/L) in the center of the plume, which extends from the infiltration beds to about 1700 m downflow from the beds. These results indicate that there is a NO_3^- sink in the aquifer, which may be a result of bacterially-mediated reactions such as assimilative nitrate reduction, denitrification, and dissimilatory nitrate reduction. Studies conducted by Smith and Duff (1984b) have demonstrated that denitrification is occurring in the aquifer solids at the OAB site.

In spite of low concentrations of NO_3^- throughout most of the groundwater system in 1983, the NO_3^- plume is still recognizable with concentrations greater than 1 mg N/L. The extent of the NO_3^- plume coincides with the extent of the contaminant plume as indicated by specific conductance. The distribution of NO_3^- in 1985 is consistent with the 1983 distribution (Figure 14).

v. Ammonium

The NH_4^+ concentration in the sewage effluent is 6.4 mg N/L and no NH_4^+ is detected in the native groundwater. The result of the sewage

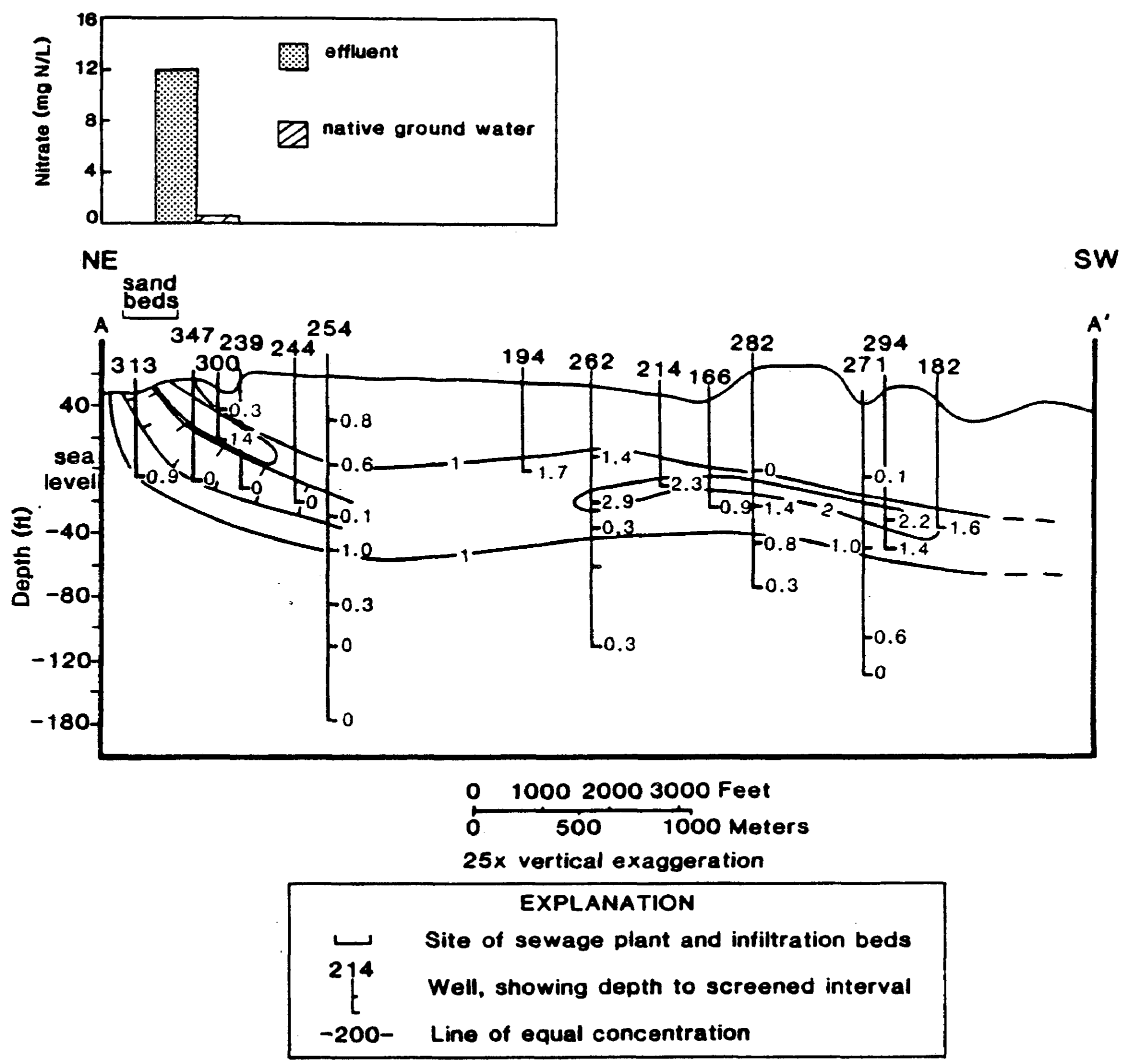


Figure 13. Distribution of nitrate (mg N/L) in 1983; cross-section. Histogram comparing nitrate concentrations in the sewage effluent and the native groundwater.

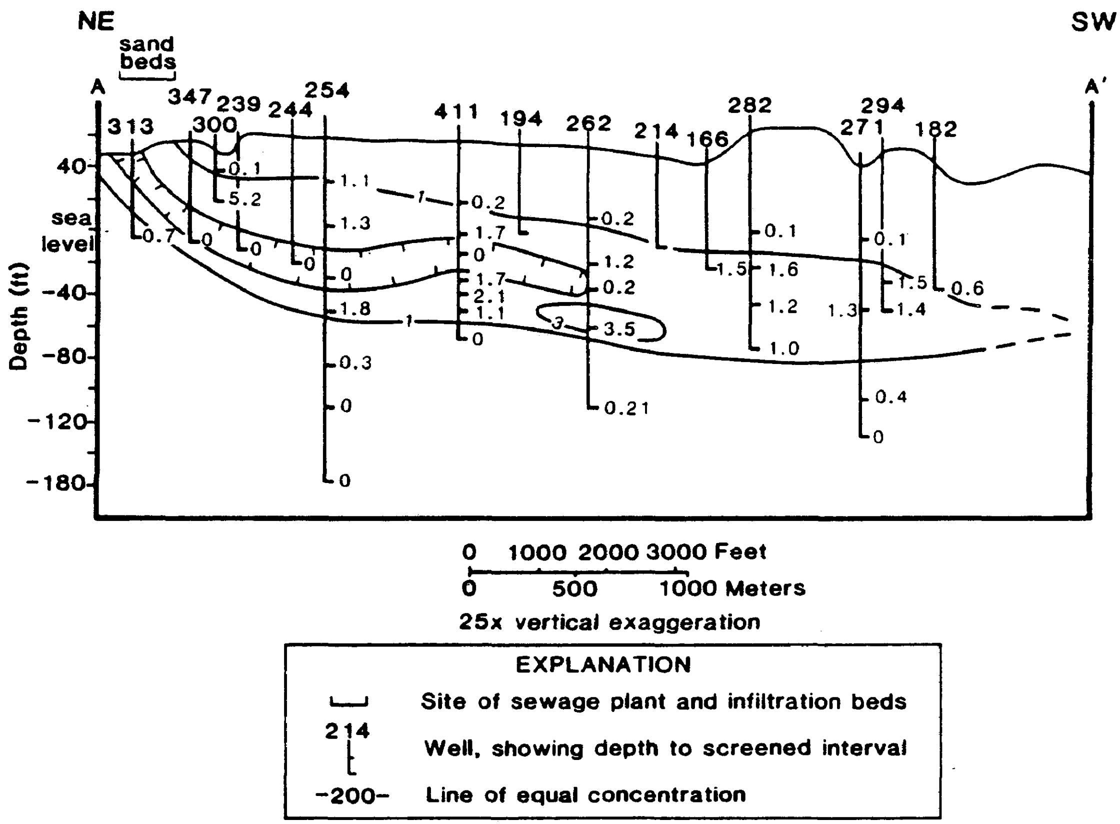


Figure 14. Distribution of nitrate (mg N/L) in 1985-1986; cross-section.

contamination is a plume of NH_4^+-containing groundwater that ranges from 2 to 10.7 mg N/L (Figure 15). NH_4^+ concentrations exceeding 10 mg N/L are detected within 300 m downgradient from the sand beds . This zone contains NH_4^+ concentrations that are higher than the sewage effluent concentration. The source of this NH_4^+ could be: 1) NH_4^+ in the sewage effluent; 2) NH_4^+ derived from dissolved organic nitrogen (DON) or particulate organic nitrogen (PON) present in the sewage effluent; and 3) NH_4^+ derived from the biological reduction of NO_3^- in the effluent by dissimilatory nitrate reduction.

Beyond 1830 m from the beds NH_4^+ is depleted or absent. The same trend for NH_4^+ was observed when the groundwater was resampled in 1985 (Figure 16). Assuming a constant source, these results indicate that NH_4^+ is being removed upgradient of 1830 m or the transport of NH_4^+ is affected by additional factors. Potential non-biological geochemical processes that could cause this attenuation of NH_4^+ are dilution, volatilization, and sorption. Assuming a constant source, SC data indicates that dilution is not entirely responsible for the decrease in NH_4^+ between the sand beds and 1830 m downgradient from the beds. Likewise, the pH of the groundwater at the OAB site ranges between 4.0 and 7.1 and, therefore, volatilization is probably not an important process at this site (Behnke, 1975). However, within this pH range NH_4^+ can be sorbed onto aquifer solids if they possess cation binding sites.

It is known that clays readily undergo cation exchange with NH_4^+ (Allison, 1966; Ardakani and McLaren, 1977). It is also well-established that the surface of most silicate minerals become negatively charged at

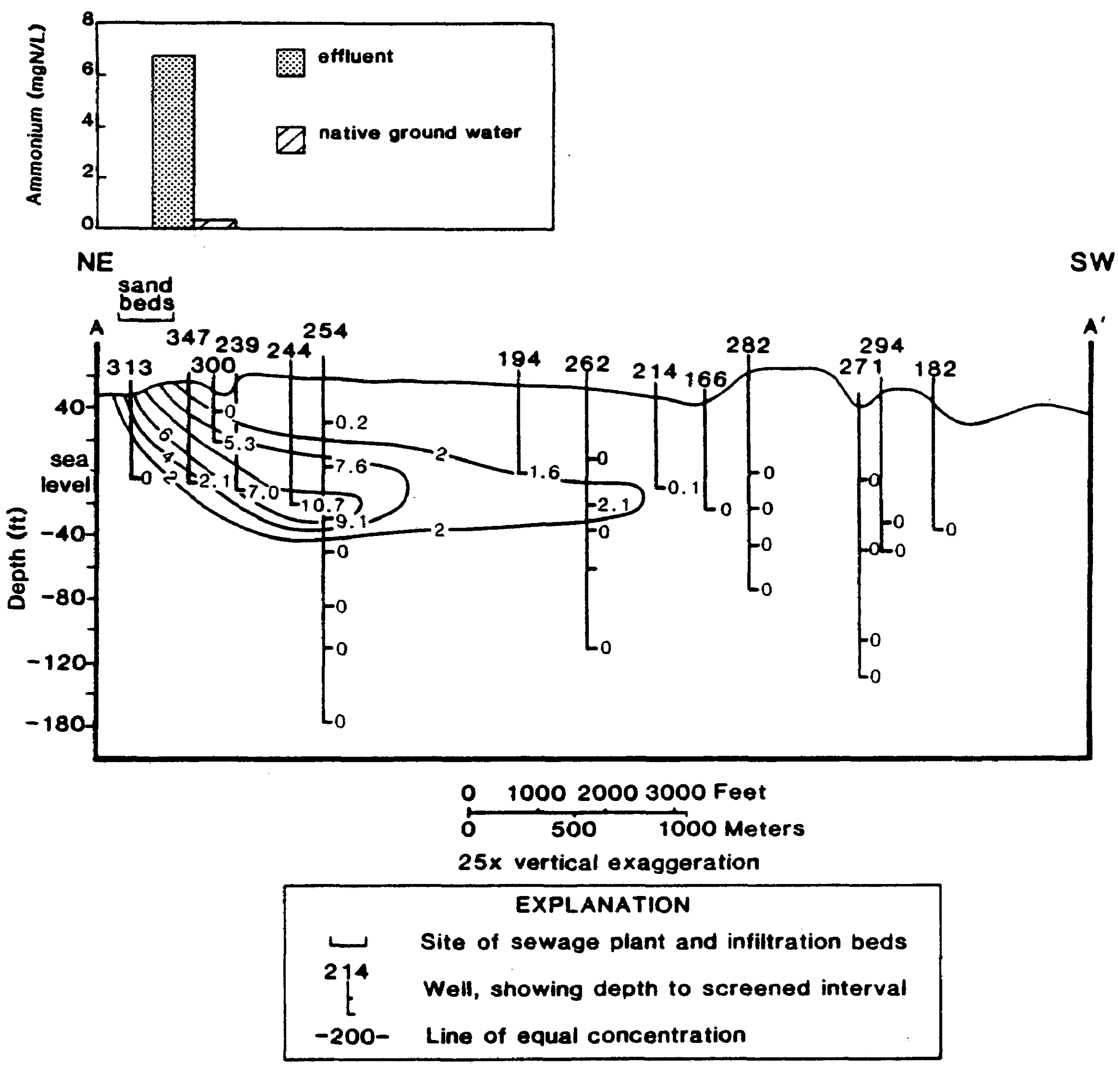


Figure 15. Distribution of ammonium (mg N/L) in 1983; cross-section. Histogram comparing ammonium concentrations in the sewage effluent and the native groundwater.

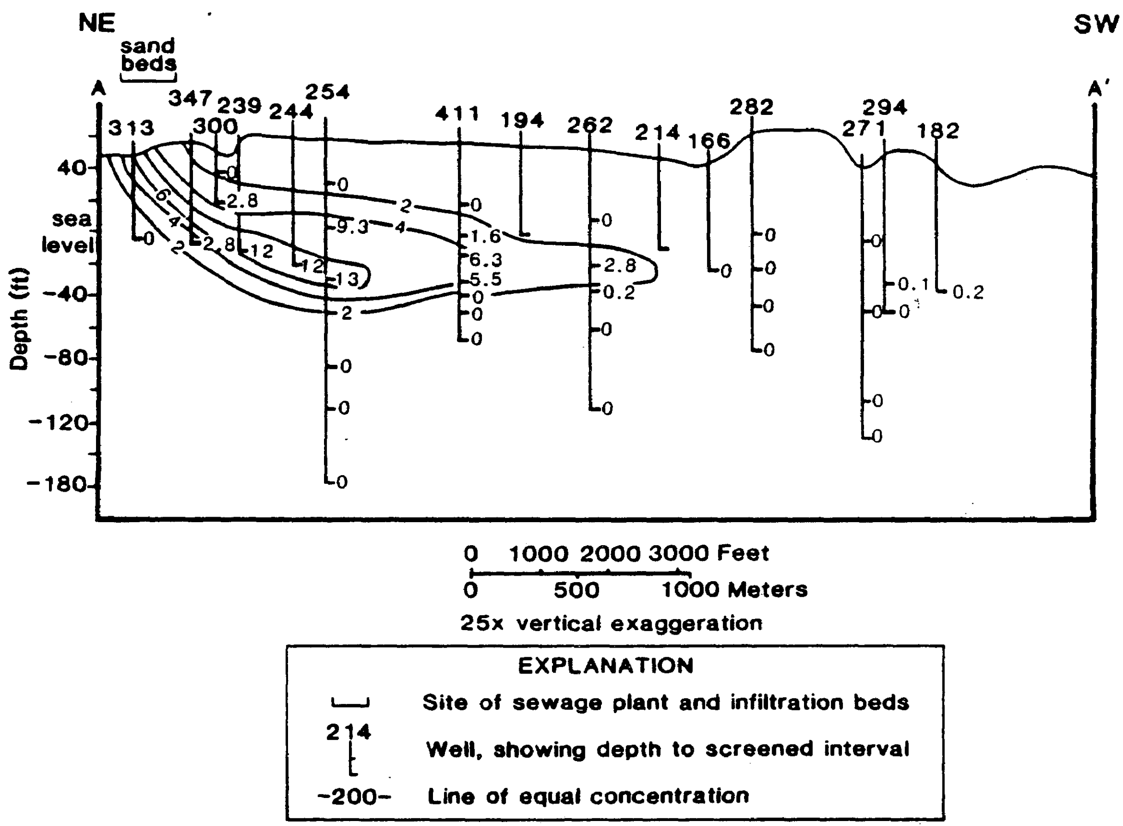


Figure 16. Distribution of ammonium (mg N/L) in 1985-1986; cross-section.

pH's greater than 2 and, therefore, can act as a weak cation exchanger (Stumm and Morgan, 1981). Although the aquifer material at the study site contains less than 1% clay, the sediment is composed primarily of sand-size grains of quartz and feldspar, the surface of which would be negatively charged at the pH of the groundwater providing cation binding sites for NH_4^+ (Barber, 1985). Hence, sorption is a likely process affecting the rate of NH_4^+ transport at the OAB site.

Biochemical processes such as incorporation into biomass and nitrification would remove NH_4^+ from the groundwater system and, therefore, could also account for the removal of NH_4^+ upgradient of 1830 m (Barcelona and Naymik, 1984; Whitelaw and Rees, 1980). In the center of the plume within 1830 m of the sand beds, most of the nitrogen is in the form of NH_4^+. Relatively high NO_3^- concentrations (greater than 2 mg N/L) and depleted or absent NH_4^+ concentrations (less than 3 mg N/L) are found from 1830 to 2030 m downflow from the source. NO_3^- but no NH_4^+ is present beyond 2440 m downgradient from the sand beds. Since at 2030 m from the source of contamination there is dissolved oxygen present in the center of the plume, which corresponds to decreases in NH_4^+ and increases in NO_3^-, it appears that nitrification may be a mechanism of NH_4^+ removal in the aquifer.

vi. Major Cations

The extent and pattern of the K^+ plume in 1983 and 1985 (Figures 17 and 18) differs from SC and follows the same trends as the NH_4^+ plume.

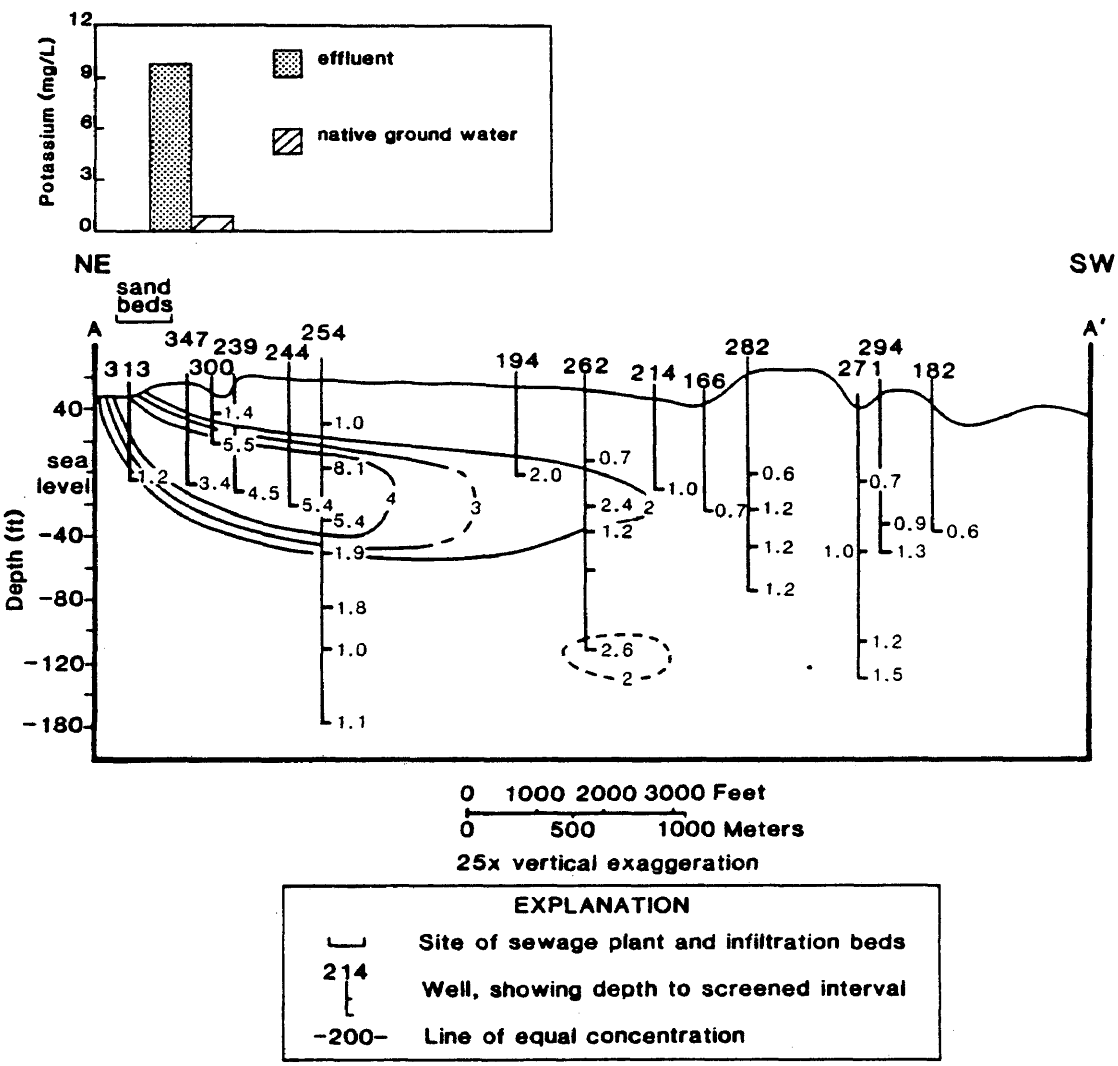


Figure 17. Distribution of potassium (mg/L) in 1983; cross-section. Histogram comparing potassium concentrations in the sewage effluent and the native groundwater.

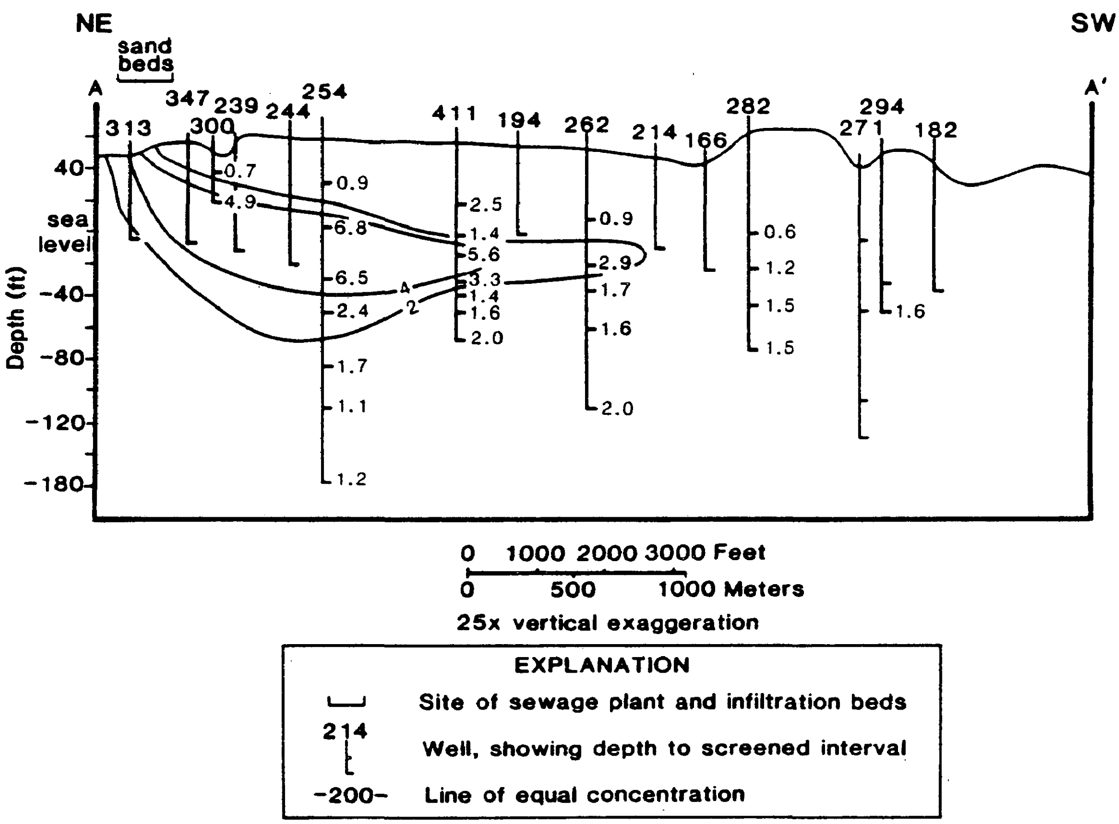


Figure 18. Distribution of potassium (mg/L) in 1985; cross-section.

K^+ concentrations are highest near the infiltration beds (5.4 to 8.1 mg/L in 1983; 6.2 to 6.8 mg/L in 1985) and show abrupt decreases in the vertical and horizontal directions. Thus, since there are no obvious geochemical or biological processes that could remove K^+ from the groundwater, the attenuation of K^+ is probably due to a retarded rate of transport. One potential process that could affect K^+ transport is sorption on aquifer solids. Furthermore, K^+ is known to be quite similar to NH_4^+ in its ion exchange characteristics (Preul and Schroepfer, 1968; Stevenson, 1962).

In 1983 and 1985 the zones of high Ca^{2+} (greater than 4 mg/L), Mg^{2+} (greater than 3 mg/L), and Na^+ (greater than 10 mg/L) correspond to the zone of high SC (Figures 19 to 24). However, unlike SC, concentrations of Mg^{2+}, Ca^{2+}, and Na^+ do not show a trend of decreasing concentration with distance from the infiltration beds suggesting that there is a source of these cations in the aquifer. Since the fronts of the Ca^{2+}, Mg^{2+}, and Na^+ plumes extend further downgradient than the NH_4^+ and K^+ fronts, NH_4^+ and K^+ may be displacing Ca^{2+}, Mg^{2+}, and Na^+ from cation exchange sites on the aquifer solids.

vii. <u>Bacterial Plate Counts</u>

Bacterial counts were conducted on two types of agar: 1) nutrient agar which is a rich organic medium; and 2) dilute soil extract agar (DSEA), which is derived from aquifer material and has lower levels of organic nutrients. In general, DSEA medium yielded higher cell counts

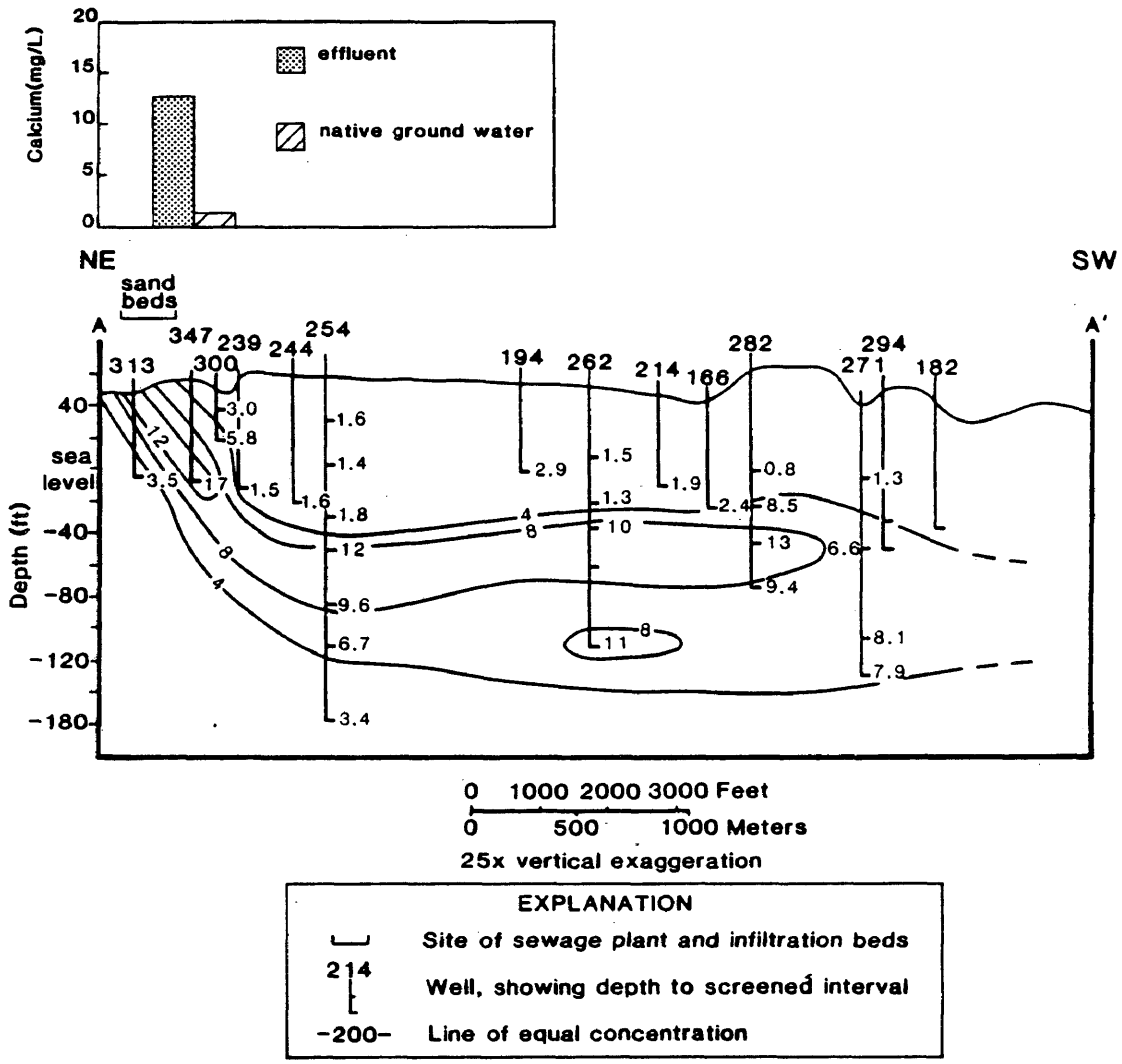


Figure 19. Distribution of calcium (mg/L) in 1983; cross-section. Histogram comparing calcium concentrations in the sewage effluent and in the native groundwater.

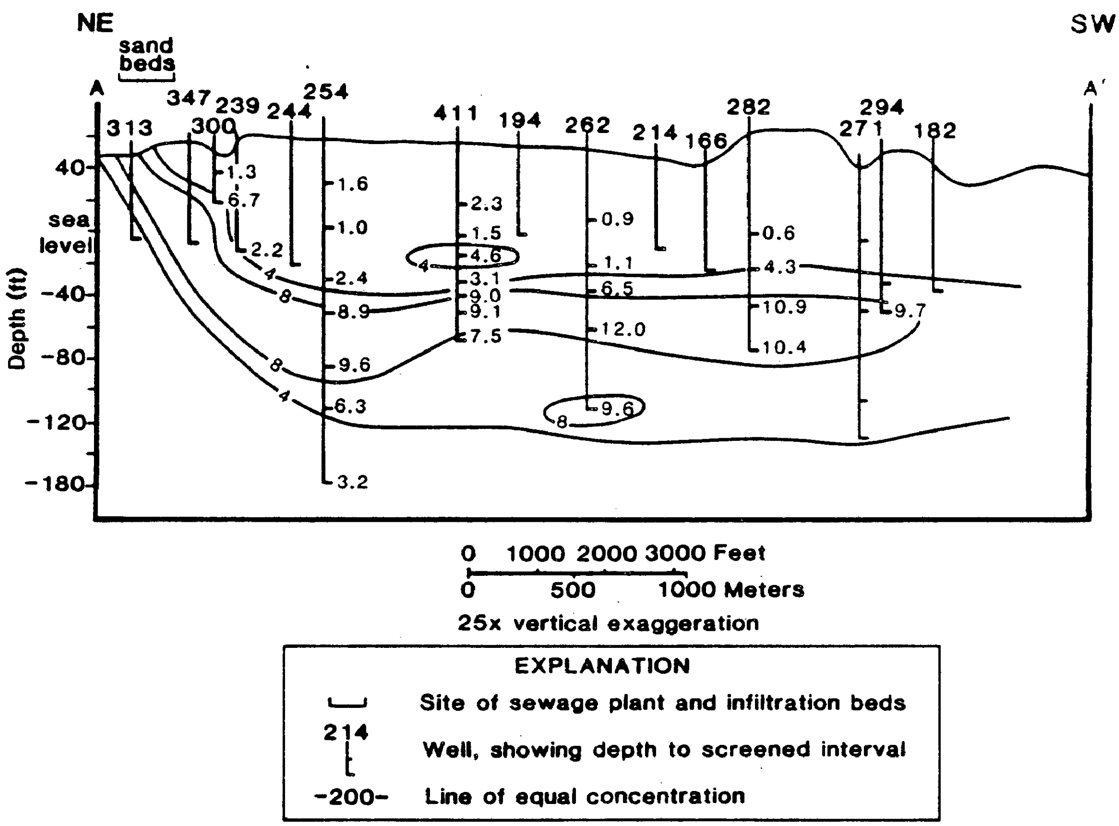


Figure 20. Distribution of calcium (mg/L) in 1985; cross-section.

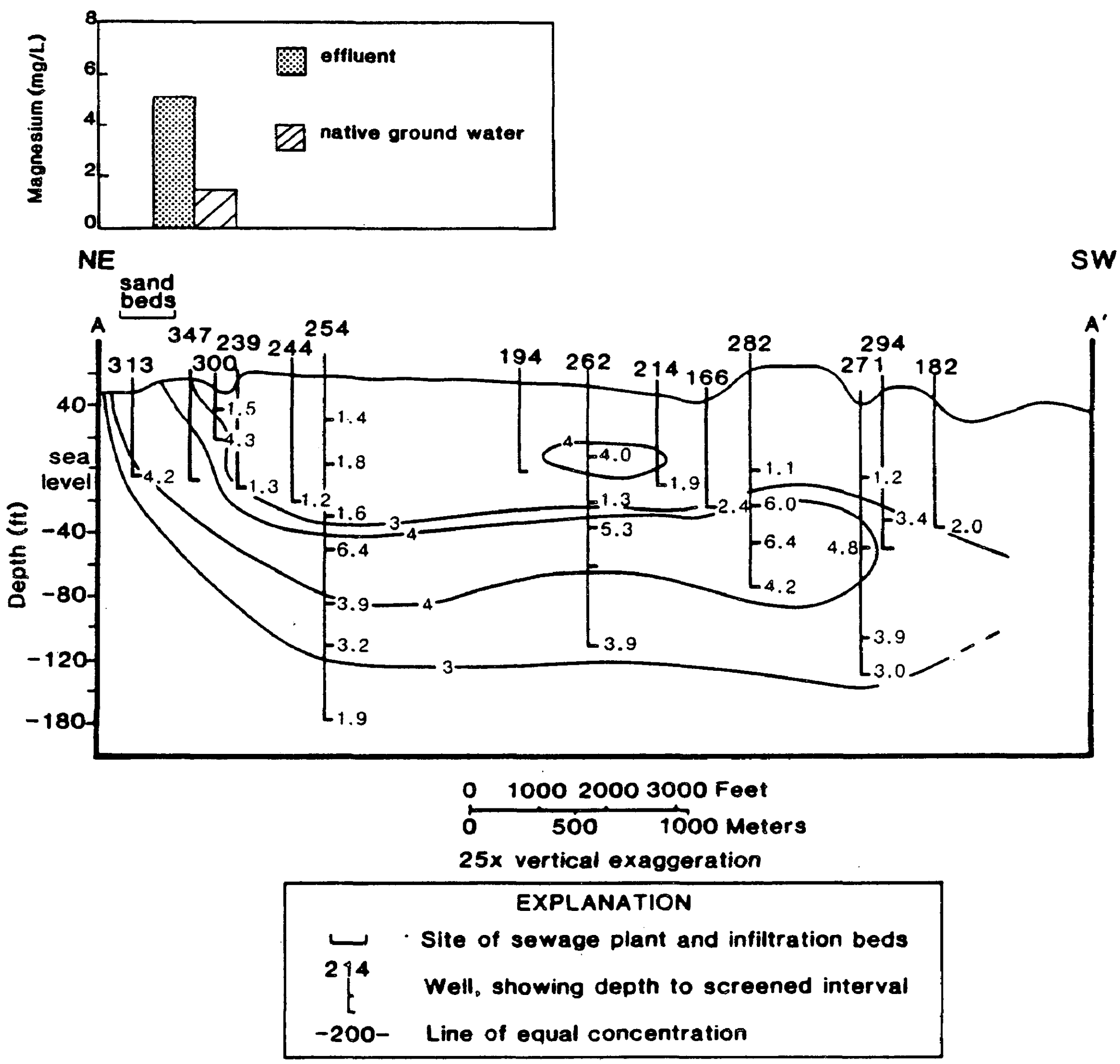


Figure 21. Distribution of magnesium (mg/L) in 1983; cross-section. Histogram comparing magnesium concentrations in the sewage effluent and native groundwater.

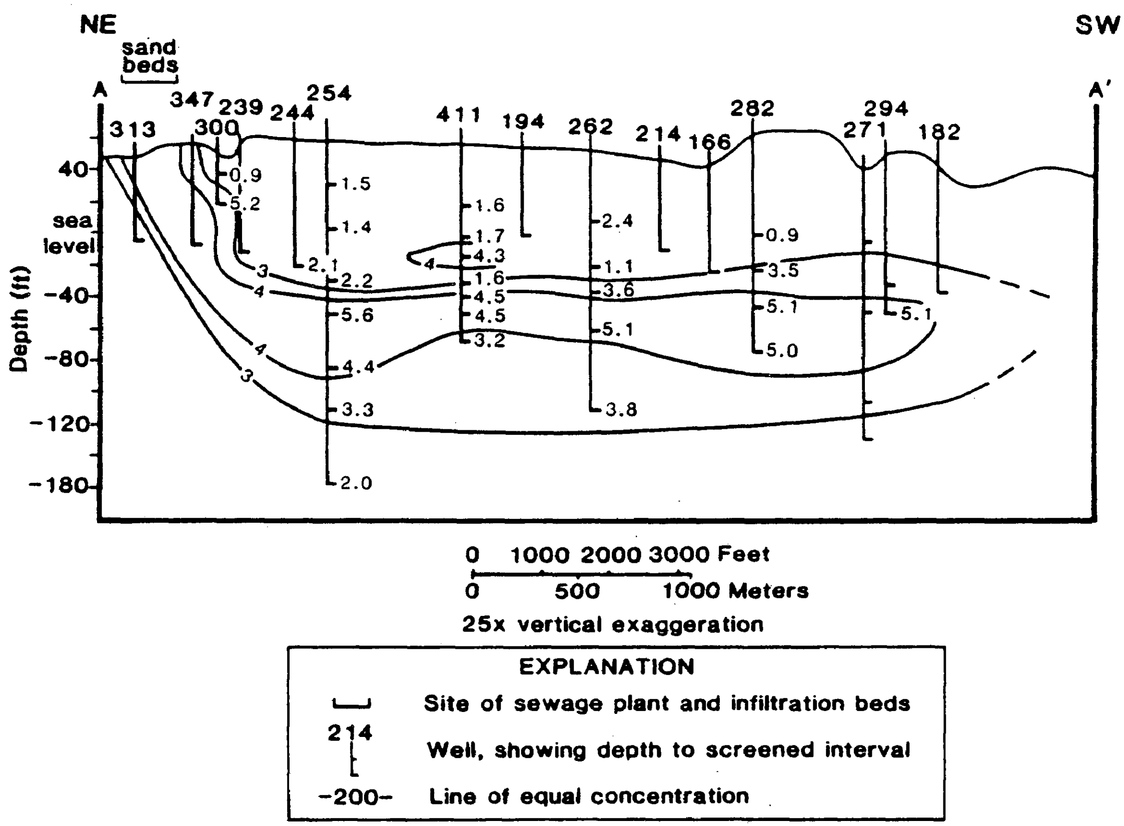


Figure 22. Distribution of magnesium (mg/L) in 1985; cross-section.

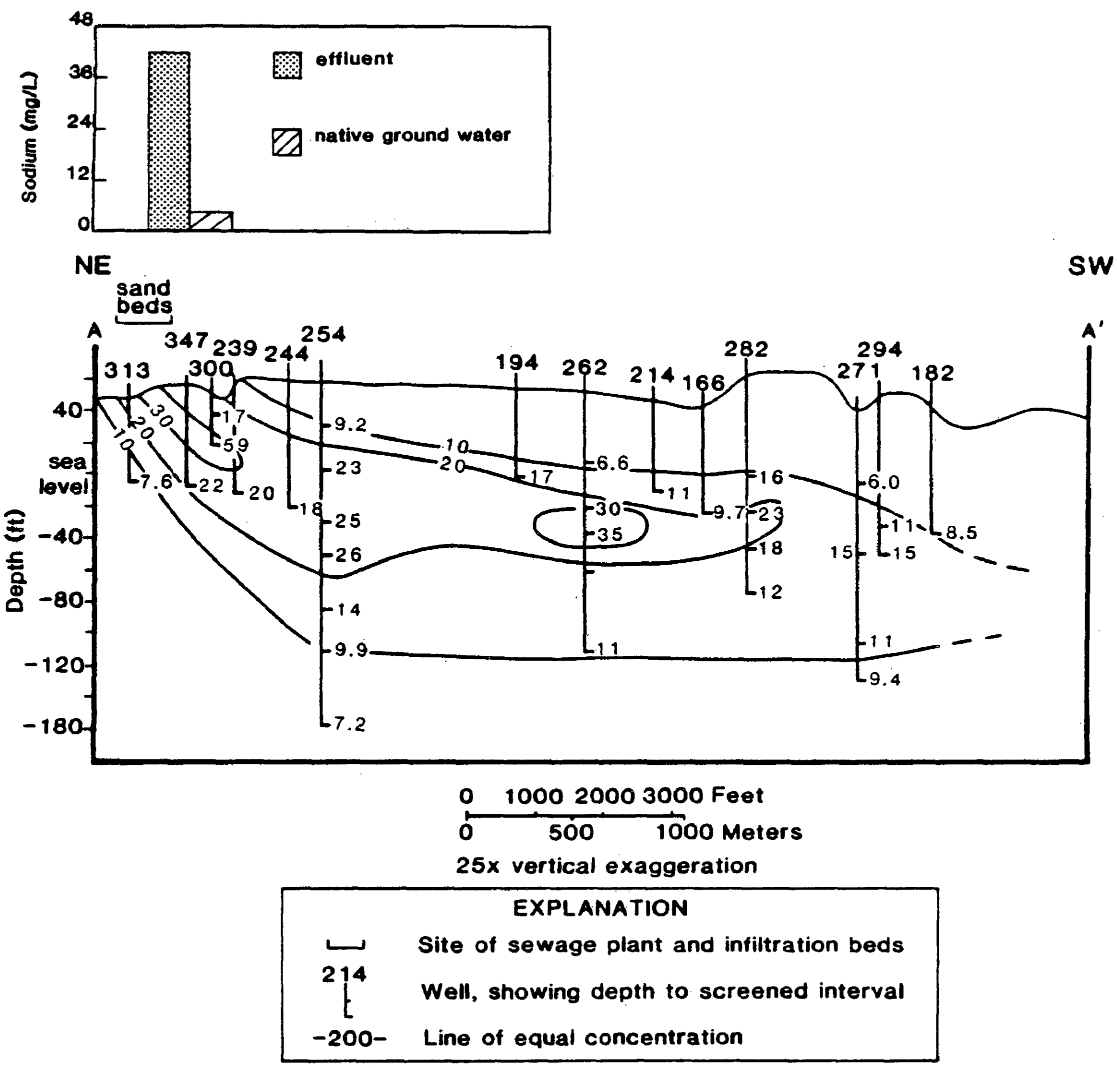


Figure 23. Distribution of sodium (mg/L) in 1983; cross-section. Histogram comparing sodium concentrations in the sewage effluent and native groundwater.

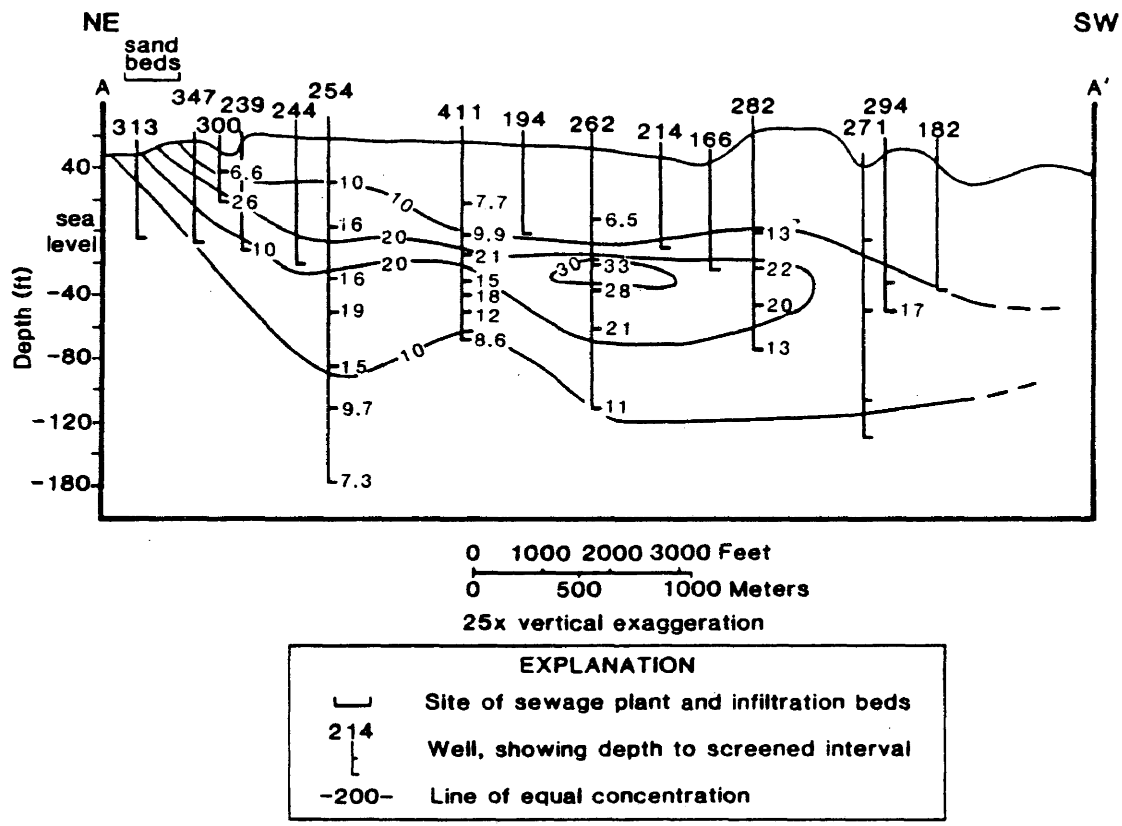


Figure 24. Distribution of sodium (mg/L) in 1985; cross-section.

and smaller colonies than nutrient agar. Similar results have been found in other aquifer systems (Ghiorse and Balkwill, 1985; Wilson et al., 1983). In a groundwater system where organisms are adapted to oligotrophic conditions, it is not surprising that DSEA is the preferred medium.

The plate counts for free-living bacteria on nutrient agar and DSEA give similar spatial profiles of the plume (Figures 25 and 26). The areas of elevated plate counts (greater than 4000 colony forming units in DSEA, CFU/ml; greater than 2000 CFU/ml in nutrient agar) extends at least 3350 m downgradient from the sand beds. In general, the highest plate counts are found 300 to 910 m from the contaminant source and decrease with distance from the infiltration beds. These profiles indicate that the number of free-living bacteria vary with distance from the contaminant source and correlate with specific conductance. This result is consistent with total bacterial counts conducted at the study site by Harvey et al. (1984).

viii. Coliform Bacteria

No coliform bacteria were detected in the groundwater, except in wells FSW 254-107 and FSW 262-85 (Table 7). Neither of these wells were in the vicinity of the sand beds; therefore, coliforms from the sewage effluent at the OAB treatment plant do not appear to be transported through the groundwater system. The reason coliform bacteria were

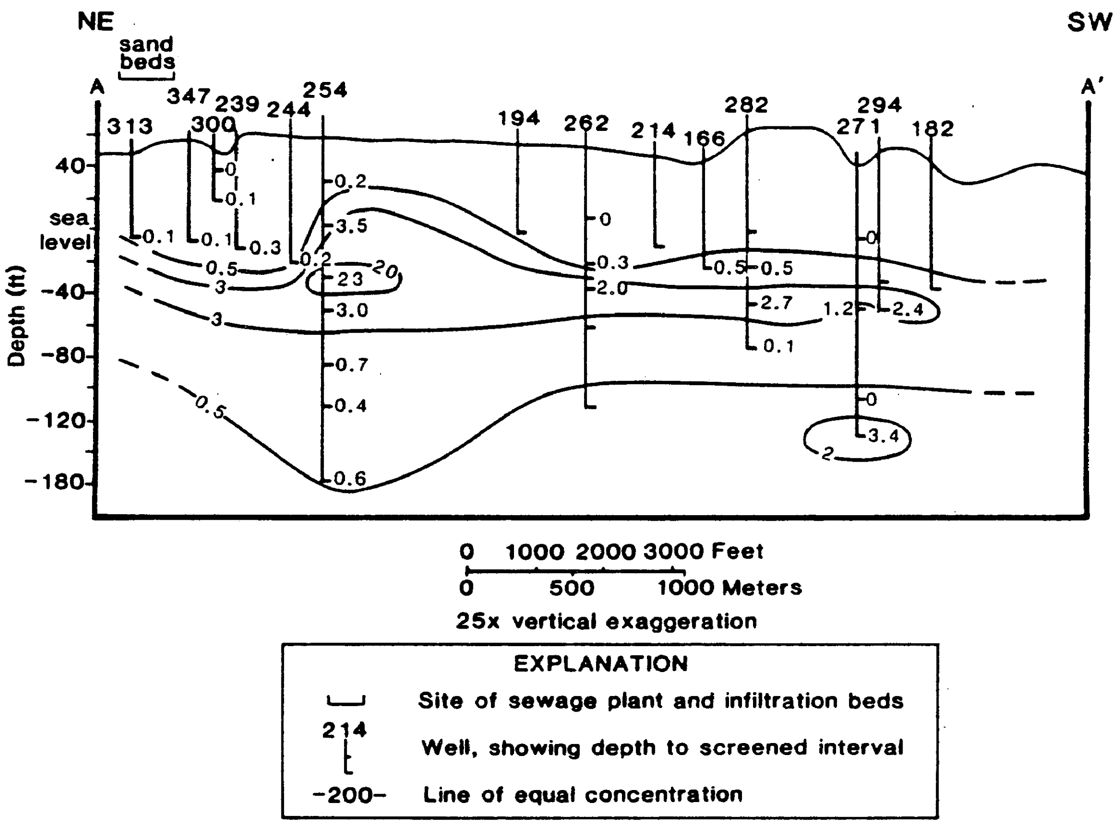


Figure 25. Distribution of nutrient-agar plate-count bacteria (CFU/ul) in 1983; cross-section.

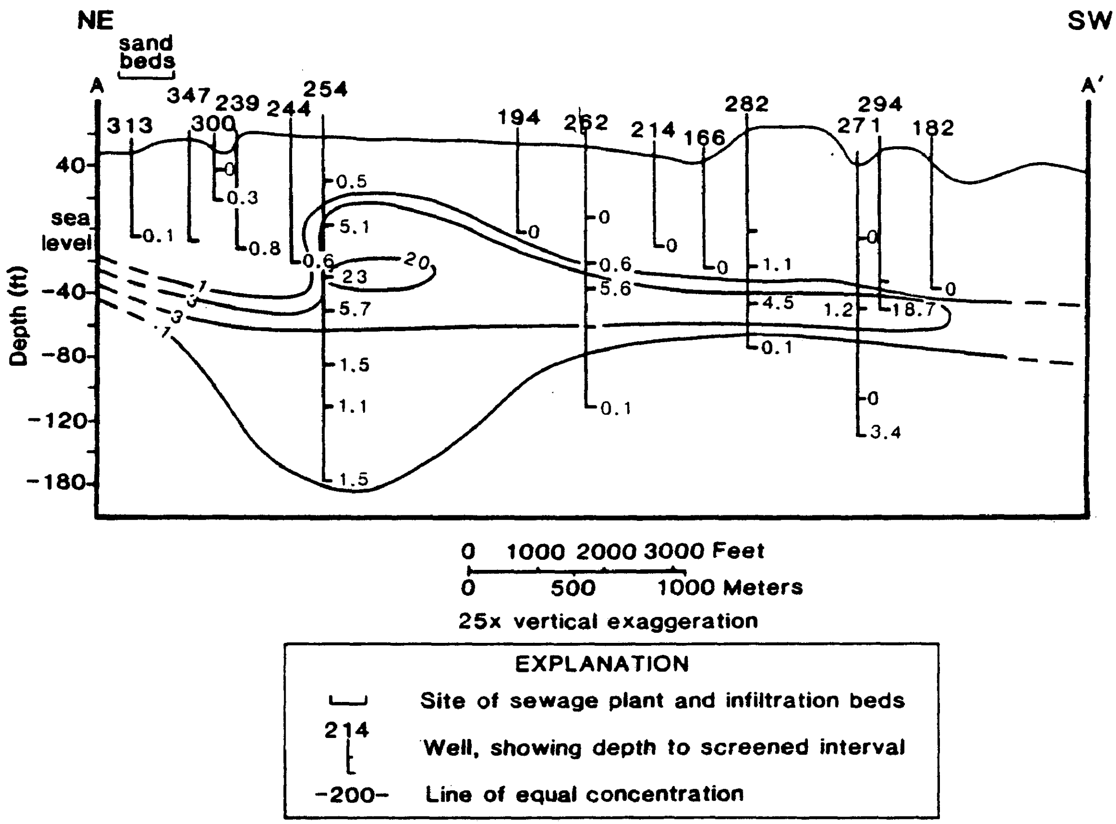


Figure 26. Distribution of dilute-soil-extract-agar plate-count bacteria (CFU/ul) in 1983; cross-section.

Table 7. Summary of results for MPN presumptive coliform test. Specific conductance values are given to indicate contaminated and uncontaminated zones.

Distance to Contaminant Source (m)	Depth from Land Surface (m)	Ground-water Spec. Cond. (umho/cm^2)	MPN Coliform
210	20	302	0*
900	8	70	0
900	16	220	0
900	22	225	0
900	33	235	0
900	43	175	0
900	51	115	0
900	66	59	0
1830	13	90	0
1830	21	200	0
1830	26	255	+*
1830	33	--	0
1830	49	125	0

*0 = negative presumptive test
*+ = positive presumptive test

detected in two of the wells is unknown since there is no obvious source of coliforms (such as septic tanks) in the vicinity of these wells.

B. NITRIFICATION STUDIES

This section presents the results of a study designed to obtain direct evidence that nitrification is occurring at the OAB site. Groundwater and core material were collected and assayed for nitrifying activity and nitrifying bacteria. Aquifer material was assayed from two sites: 1) the site at well FSW 262, which is 2030 m downflow from the infiltration beds; and 2) the site of well FSW 347, which is 210 m from the beds.

i. Preliminary Nitrification Study at Well FSW 262

The specific conductance of groundwater collected from the 21 m and 26 m depths at FSW 262 are 220 and 245 umho/cm^2 respectively (Table 8). These values compared to the specific conductance of the sewage effluent (390 umho/cm^2) and the uncontaminated groundwater (53 umho/cm^2) clearly indicate that this well series is within the zone of contamination. The shallowest and deepest wells in this series are located on the upper and lower vertical boundaries of the contaminant plume. Furthermore, the NO_3^-, NH_4^+, and DO distributions, discussed in the previous section, suggest that nitrification is occurring at this site.

Groundwater was obtained from four screened depths in this well series and cores of solid aquifer material were collected from depths adjacent to the screened wells. Water from each depth was added to the respective solid material from that depth to form slurries, which were

Table 8. Comparison of chemistry of ground water collected from well series FSW 262 and FSW 347, sewage effluent, and uncontaminated ground water from well FSW 242.

Sample Location or well #	Depth (m)	Sp. Conc (umho/cm^2)	DO (mg/L)	$[NO_3^-]$ (mg N/L)	$[NO_2^-]$ (mg N/L)	$[NH_4^+]$ (mg N/L)
Sewage Effluent I	0	394	5.0	12.0	0.50	6.4
FSW 347	5.6	42	5.2	0.1	0.01	0.03
FSW 347	6.2	68	5.0	1.0	0.01	0.03
FSW 347	6.7	128	3.2	3.5	0.01	0.03
FSW 347	7.3	220	0.3	8.5	0.01	1.13
FSW 347	7.9	350	0.4	15.0	0.01	2.42
FSW 347	8.5	385	--	15.9	0.01	1.09
FSW 347	9.1	340	0.4	12.9	0.01	0.02
FSW 347	9.7	340	--	10.6	0.02	0.06
FSW 347	10.2	330	0.3	9.6	0.03	0.27
FSW 347	10.8	330	--	3.5	0.01	3.24
FSW 347	11.4	335	0.3	3.1	0.01	3.67
FSW 347	12.0	330	--	1.0	0.01	3.20
FSW 347	12.6	335	0.3	0	0.01	3.36
FSW 347	13.1	335	--	0	0.01	3.96
FSW 347	13.7	325	0.3	0	0.01	4.14
FSW 262	12.5	64	9.2	0.7	0	0
FSW 262	21.0	245	0.5	1.2	0	2.84
FSW 262	25.9	220	0.3	0.2	0	0.19
FSW 262	48.5	143	0.5	0.2	0	0
FSW 242	23.5	53	11.3	0.1	0	0

I. = after LeBlanc (1984a)

assayed for nitrifying bacteria and nitrifying activity. To measure nitrifying activity, slurries were incubated and monitored for substrates and products of nitrification (NH_4^+, NO_2^-, and NO_3^-); slurries containing low NH_4^+ concentrations (less than 1 mg N/L) were amended with NH_4^+. Slurries were also examined for the presence of nitrifying bacteria using MPN dilution counts for NH_4^+-oxidizing bacteria.

The concentration of NH_4^+ after three weeks was lower than the initial concentration in all incubated sediment slurries; the rate of NH_4^+ loss was slightly higher for the shallowest well (Table 9). Nitrite was not detectable during the course of the incubation. At only two depths was there any detectable NO_3^- produced in the slurries (12.5 and 21 m below land surface). At the 21 m depth the amount of NO_3^- produced (0.5 mg N/L) is roughly equivalent to the amount of NH_4^+ lost from the aqueous phase (0.4 mg N/L) indicating that nitrification is responsible for 80% of the NH_4^+ loss. However, from the point of view of the nitrogen budget this may not be a fair comparison since total NH_4^+ (sorbed and dissolved) was not determined for this preliminary experiment.

Nitrifying bacteria are present at two depths at this site: 1) the 21 m depth where there is measurable nitrifying activity (i.e., NO_3^- was produced during incubation); and 2) the 26 m depth where no NO_3^- was produced during incubation even though slurries from this depth were amended with NH_4^+ (Table 9). This suggests that although nitrifying bacteria are present at the 26 m depth they are in an inactive form.

Table 9. Results of preliminary nitrification assays at well series FSW 262 (for samples incubated for 3 weeks at 10 degrees C), and MPN dilution counts for ammonium-oxidizing bacteria.

Depth Below Land Surface (m)	$[NH_4^+]$ Consumed (mg N/L)	$[NO_3^-]$ Produced (mg N/L)	$[NO_2^-]$ Produced (mg N/L)	MPN Nitrifying Bacteria (bacteria/100 ml)
12.5	0.7	0.1	0	0
21.0	0.4	0.5	0	150
25.9	0.5	0	0	150
48.5	0.5	0	0	0

ii. Further Nitrification Studies at Well FSW 262

Based on the preliminary results at well FSW 262, the assay for nitrifying activity was repeated on unamended slurries taken from the 21 m depth. Three factors distinguish this experiment from the preliminary experiment: 1) sediment slurries were prepared from freshly-collected core and water samples in the field; 2) slurries were incubated for shorter periods of time and were monitored every two to three days; and 3) both dissolved and sorbed NH_4^+ constituents were determined. The purpose of using fresh aquifer material and a shorter incubation period is to obtain a direct measure of activity.

The time course study for the incubated sediment slurries and the killed control is presented for dissolved NH_4^+ and NO_3^- in Figure 27. Five replicate slurries were incubated and the standard deviation for these samples is represented by error bars. Differences in initial NH_4^+ and NO_3^- concentrations between the killed control and the slurries is due to the autoclaving process used for the killed control. During the course of the incubation there was a linear decrease in NH_4^+ and a non-linear production of NO_3^- in the slurries; whereas, there was no significant loss of NH_4^+ or production of NO_3^- in the killed control. These results indicate that there is biologically-mediated NH_4^+ consumption at this site. The NO_3^- concentration in the incubated slurries increased during the first 4 days by 0.22 mg N/L and remained constant or decreased for the remainder of the experiment indicating that nitrification occurred during the first 2-4 days of the incubation. After 4 days NH_4^+ concentrations continued to decrease in the incubated

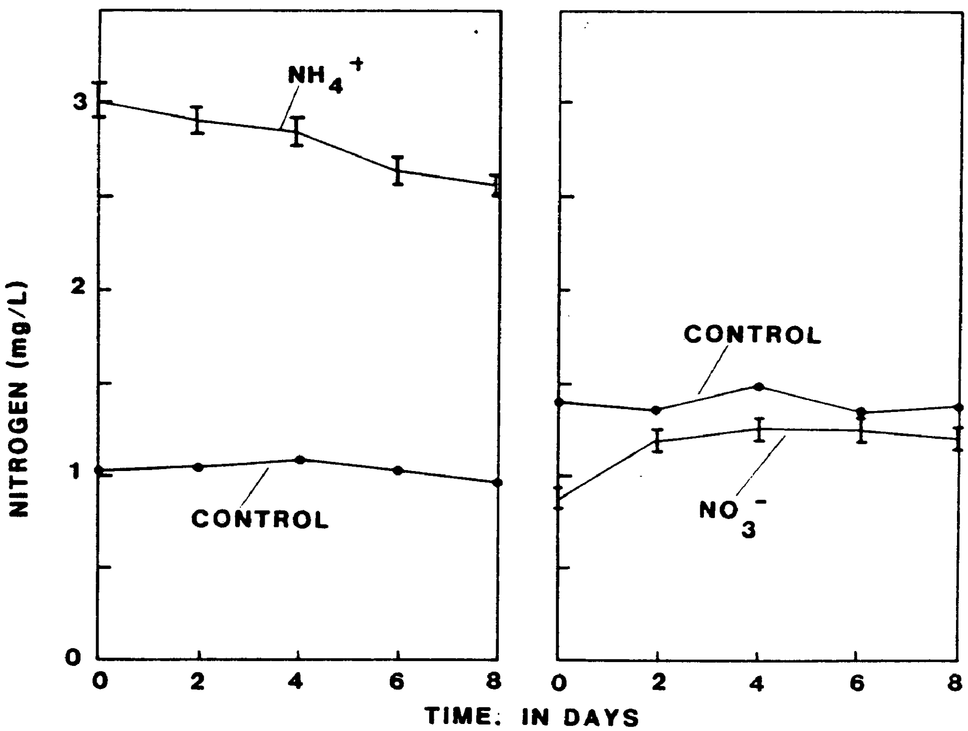


Figure 27. Time course study showing dissolved ammonium and nitrate concentrations during eight days of incubation; well FSW 262-69. Error bars represent standard deviation for five replicate sediment-water slurries.

slurries but not in the killed control suggesting that another mechanism of NH_4^+ loss is occurring. This mechanism could be incorporation of NH_4^+ into microbial biomass.

The total NH_4^+ (sorbed + dissolved) lost in the incubated slurries due to biological processes is 0.82 mg N/L (Table 10). The mean rate of total microbial NH_4^+ consumption is 81 ng N/(cm^3 of fresh aquifer material)/d. Literature values for biological NH_4^+ consumption are significantly higher than the rates measured in this experiment. Using isotope dilution techniques Blackburn (1980) measured a mean rate of NH_4^+ consumption in the top 2 cm of marine sediment of 570 ng/(cm^3 of fresh sediment material)/d. Bowden (1984) using the same technique measured a mean rate of NH_4^+ consumption in the top several centimeters of marsh sediments of 2156 ng/(cm^3 of fresh sediment)/d.

Comparing the value of total NH_4^+ consumption during the incubation period (0.82 mg N/L) to the NO_3^- production during the same period (0.12 mg N/L), only 15 percent of the NH_4^+ loss can be attributed to nitrification (Table 10). The rate of nitrification calculated for the first 4 days of incubation is 0.03 mg N/L/d. This rate, however, may not be representative of rates of nitrifying activity in the aquifer since incubation conditions, such as high dissolved oxygen, differ from the aquifer conditions (0.5 mg/L oxygen) possibly favoring the growth of heterotrophic organisms over autotrophic organisms.

Since NH_4^+ consumption and nitrification rates are relatively low in this portion of the plume, it does not appear to be a zone of high biological NH_4^+ consumption or of high nitrifying activity. However, due

Table 10. Results of nitrification assays at wells FSW 262 and FSW 347 at the OAB site. Rates of ammonium consumption in other ecosystems are given for comparison. Brackets enclose standard deviation.

Well Number	Depth Below Land Surface (m)	Total NH_4^+ Conc. Consumed (mg N/L)	Aqueous NO_3^- Conc. Produced (mg N/L)	Rate of NH_4^+ Consumption (ng/cm^3 of aquifer material/d)*
FSW 262	21.0	0.82 [0.03]	0.12 [0.01]	80.9
FSW 347	6.2	0.68 [0.04]	0.04 [0.02]	70.0
FSW 347	6.7	0.71 [0.02]	0.11 [0.02]	79.0
FSW 347	7.3	0.83 [0.04]	0.09 [0.08]	87.0
FSW 347	7.9	0.82 [0.02]	0.24 [0.08]	69.0
FSW 347	8.5	0.62 [0.03]	0.20 [0.21]	63.6
FSW 347	9.1	0.68 [0.03]	0	71.8
FSW 347	9.7	0.77 [0.02]	0	90.0
FSW 347	10.1	0.79 [0.03]	0.55 [0.09]	82.7
Marsh Sediment I				2156.0
Marine Sediment II				570.0

* = Determined from porosity data and measured NH_4^+ consumption in core samples taken adjacent to screens of sampled wells.
I. = after Bowden, 1984
II. = after Blackburn, 1980

to long groundwater residence times even very low rates of microbial activity could account for large decreases in NH_4^+ concentrations over time and distance. Since the groundwater velocity is 0.3 m/d (LeBlanc, 1984b), it takes approximately 30 years for groundwater to travel the length of the plume. In this length of time 335 mg N/L of NH_4^+ could be converted to nitrate, assuming the rate of nitrification is 0.03 mg N/L/d; therefore, nitrification could account for all NH_4^+ consumption in the plume. However, mass balance evidence in the sewage plume indicates that NO_3^- concentrations cannot account for all the NH_4^+ removal (see section IV, part A). One possible reason for this is that a large part of the plume is anaerobic; therefore, oxygen is probably a limiting nutrient in the nitrification process.

iii. Near-Bed Nitrification Study at Well FSW 347

In addition to well site FSW 262, a near-bed site located 210 m from the source of contamination (well FSW 347) was assayed for nitrification. The depth profiles for specific conductance and dissolved oxygen for the groundwater samples collected from well cluster FSW 347 are presented in Table 8. The specific conductance is 220 umho/cm^2 or greater, with the exceptions of the three shallowest wells, indicating that this well cluster is within the zone of contamination. The shallowest wells represent the upper periphery of the zone of contamination, which is diluted by recharge from precipitation (LeBlanc, 1984a). The oxygen profile is exactly the inverse of specific conductance indicating high oxygen demand, either biological or chemical, in the core of the plume. Except for the three shallowest depths, the concentrations of dissolved oxygen are low (0.38 mg/L or less). However, nitrifying bacteria are very slow growing microaerophilic organisms, which allows them to grow at oxygen concentrations as low as 0.1 mg/L (Carlucci and McNally, 1969). The NO_3^- concentrations at several depths (from 8 to 9 m) are higher than the NO_3^- concentration in the sewage effluent (12.0 mg N/L). One explanation for this difference is that the additional NO_3^- is produced within the aquifer between the infiltration beds and well FSW 347. Dissolved NH_4^+ is also present throughout the well series although at very low concentrations in several of the wells. Since NO_3^-, NH_4^+, and oxygen are present within the zone of contamination, it was hypothesized that nitrification is occurring at this location.

Eight depths at this location (from 6.2 m to 10.1 m) were assayed for nitrifying activity and bacteria using techniques similar to those used at FSW 262. Total (sorbed + dissolved) NH_4^+ concentrations decreased in slurries from all depths during the course of the incubation period (Table 10). The values of total NH_4^+ consumption during the entire incubation period ranged from 0.68 to 0.83 mg N/L similar to the value obtained at well FSW 262-69. Incubated slurries from six of the depths produced detectable NO_3^- during the course of the incubation. No substantial NO_2^- was produced during the course of the experiment.

Greater numbers of NH_4^+-oxidizing bacteria were detected at FSW 347 than at FSW 262 (Table 11). The highest number of NH_4^+-oxidizing bacteria occur at the 10.1 m depth at FSW 347, which is the depth at which NO_3^- production is the highest. This depth (10 m) may denote the beginning of a zone of high nitrifying activity although this is unknown because no samples were assayed below this depth.

The mean rates of NH_4^+ consumption due to biological processes for this near-bed site range from 63.6 to 90.0 ng N/(cm^3 of aquifer material)/d (Table 10). The percent of total NH_4^+ removal that can be attributed to nitrification at this location ranges from 9% (at the 6 m depth) to 63% (at the 10 m depth). Although the rates of microbial NH_4^+ consumption at the near-bed site are similar to the rate measured at FSW 262-69, data on NO_3^- production and nitrifying bacteria indicate that higher rates of nitrifying activity may be occurring at the near-bed site.

Table 11. Results of MPN dilution counts for nitrifying bacteria at well series FSW 347.

Well Number	Depth Below Land Surface (m)	MPN Nitrifying Bacteria (Bacteria/100 ml)
FSW 347	6.2	700
FSW 347	6.7	700
FSW 347	7.3	700
FSW 347	7.9	1100
FSW 347	8.5	700
FSW 347	9.1	400
FSW 347	9.7	5900
FSW 347	10.3	13150

C. LABORATORY SORPTION STUDIES

The laboratory sorption experiments were conducted: 1) to obtain direct evidence that NH_4^+ is sorbed on aquifer solids; and 2) to evaluate the NH_4^+ sorption isotherm.

i. Total Ammonium Assays

Total NH_4^+ assays conducted for the nitrification studies show that a significant fraction of the total NH_4^+ is sorbed on aquifer solids (Table 12). Aquifer solids for this study were collected in the contaminant plume from a near-bed site (210 m downflow from the infiltration beds) and a site further downgradient (2030 m downflow from the beds). The ratio of sorbed NH_4^+ to aqueous NH_4^+ ranges from 0.59 ml/cm^3 of dry aquifer solids to 1.08 ml/cm^3 of dry aquifer solids and is greater at the near-bed site than the downgradient site. Results presented in the following section suggest that these ratio differences are probably a function of the concentration of dissolved NH_4^+.

ii. Ammonium Isotherm Study

To obtain the NH_4^+ sorption isotherm, various concentrations of dissolved NH_4^+ were allowed to react with solid aquifer material in a batch reactor. Samples were assayed for dissolved NH_4^+ at several time intervals to determine the equilibration period (Table 13). After the sorption reaction reached equilibrium (1 hour), sorption per dry weight of aquifer solids was calculated from the resulting decrease in the

Table 12. Results of total ammonium assays at well FSW 262-69 and well series FSW 347. Brackets enclose standard deviation.

Well Number	Depth Below Land Surface (m)	NH_4^+ Conc. in Aqueous Phase (ug/ml)	NH_4^+ Conc. in Solid Phase (ug/cm^3)	Ratio of Sorbed NH_4^+ Conc. to Aqueous NH_4^+ Conc. (ml/cm^3)
FSW 262	21.0	2.46 [0.09]	1.45 [0.12]	0.59
FSW 347	6.2	0.22 [0.04]	0.18 [0.06]	0.82
FSW 347	6.7	0.21 [0.02]	0.20 [0.02]	0.95
FSW 347	7.3	0.53 [0.03]	0.46 [0.05]	0.87
FSW 347	7.9	1.41 [0.05]	0.85 [0.06]	0.60
FSW 347	8.5	0.41 [0.05]	0.35 [0.05]	0.85
FSW 347	9.1	0.26 [0.03]	0.23 [0.03]	0.88
FSW 347	9.7	0.26 [0.03]	0.28 [0.06]	1.08
FSW 347	10.1	0.36 [0.03]	0.31 [0.04]	0.89

Table 13. Summary of results of sorption kinetic experiments for NH_4^+. Brackets enclose standard deviation.

Equilibration Time (h)	Initial Concentration of Dissolved NH_4^+ (mg N/L)	Concentration of Dissolved NH_4^+ after Equilibration (mg N/L)
1	1.0	0.51 [0.02]
3	1.0	0.48 [0.02]
5	1.0	0.48 [0.02]
7	1.0	0.48 [0.02]

dissolved NH_4^+ concentration. This experiment was conducted on a sediment core collected at FSW 393 from 10 to 11.3 m below land surface. This location is the site of the divergent tracer tests and is a pristine area located to the west of the contamination plume.

The results of the batch experiment are represented in a plot of dissolved NH_4^+ concentrations versus sorbed NH_4^+ concentrations (sorption isotherm) (Figure 28). These results indicate that NH_4^+ sorption on aquifer solids follows a non-linear Freundlich sorption equation (Helfferich, 1962):

$$S = K_f C^b \quad \text{(Eq. 4)}$$

where S represents sorption in ug of NH_4^+ per dry weight of sediment, C is the concentration of NH_4^+ in the solution when equilibrium is reached, K_f is the Freundlich sorption equilibrium coefficient, and b is the Freundlich exponent. In this case K_f is equal to 0.70 ml/cm^3 and b is equal to 0.80. The isotherm has a changing slope that increases with decreasing concentrations of dissolved NH_4^+ indicating that the extent of NH_4^+ partitioning along the flow path in the sewage plume changes as a function of dissolved NH_4^+.

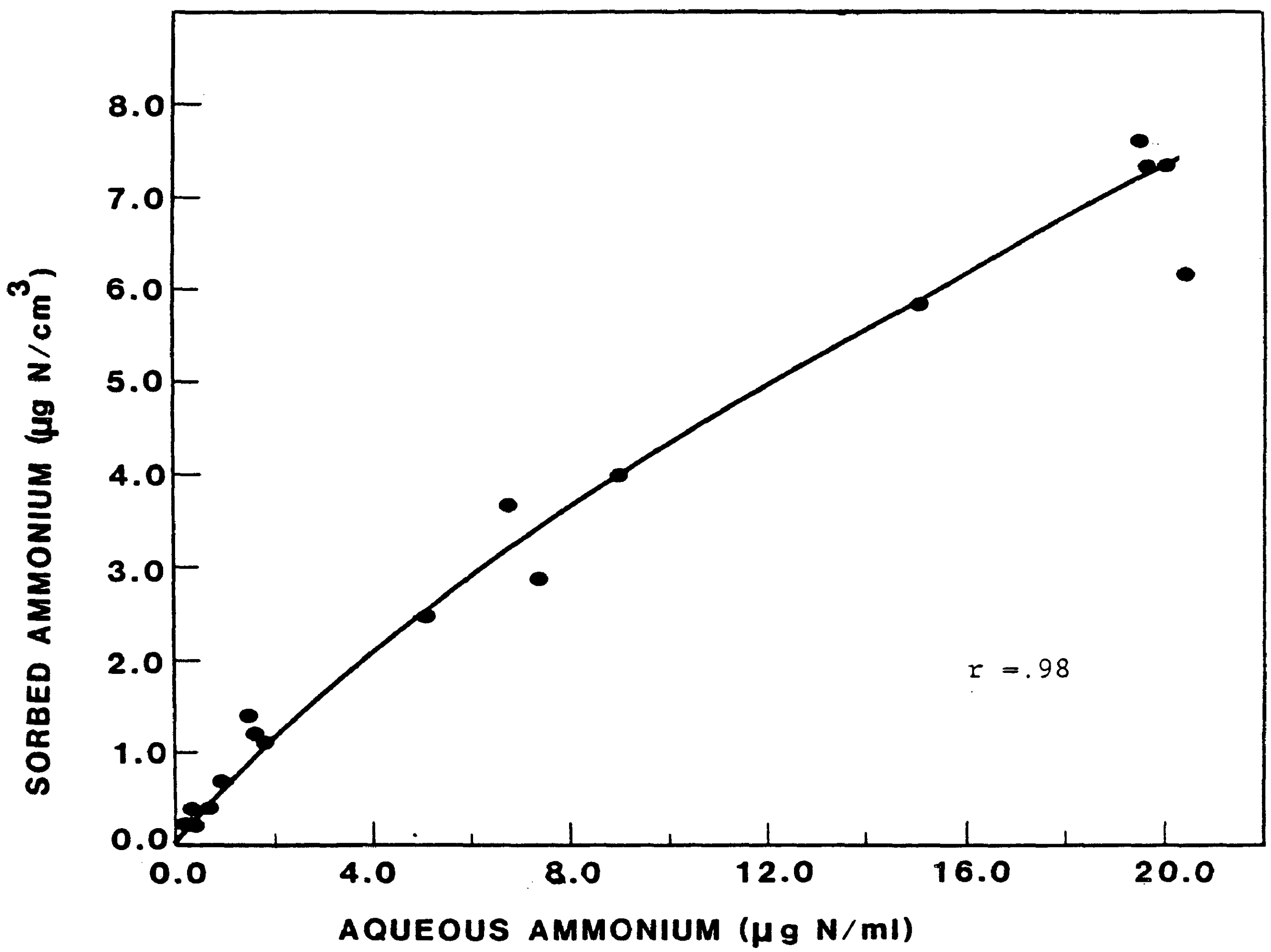


Figure 28. Ammonium sorption isotherm for aquifer material collected at well FSW 393 at a depth interval of 10 to 11.3 m below land surface.

D. FIELD TRANSPORT STUDIES

Two divergent tracer tests were conducted at the OAB site in 1985 and 1986. The objectives of these tests were to obtain *in situ* evidence of NH_4^+ cation exchange and to investigate relative transport differences for NH_4^+ and NO_3^-.

In these experiments a radially divergent flow field was formed by continuous injection of native groundwater obtained from a nearby well into a well with a 1.4 m long screen (Figure 29). The injection rate was about 95 l/min. Tracers were added as a pulse into the injection well and monitored as they moved with the radial flow past a multilevel sampling device located 1.5 m from the injection well. The tracers were monitored at two depths opposite the top and bottom of the injection zone. The tracers injected in the 1985 tracer test were Br^- and NH_4^+ (Table 14). Tracers for the 1986 test included Br^-, NH_4^+, NO_3^-, and K^+. Groundwater was also monitored for major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+). These data are graphically represented on plots of percent of concentration of injectate or microequivalents per liter (ueq/l) versus time.

i. Defining the Hydrogeology: Observed Bromide Tracer Patterns

An ideal conservative tracer for groundwater studies should correctly depict velocity variations due to hydrogeologic parameters without altering the transmission of the liquid-porous medium system (Sudicky et al., 1983). A further prerequisite for the tracer is that

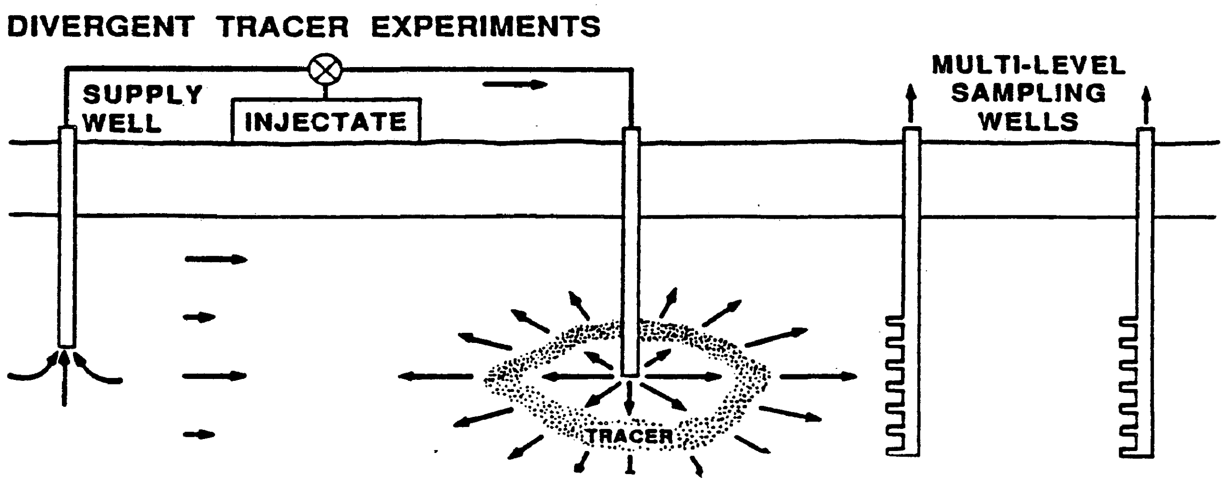


Figure 29. Schematic diagram showing operation of divergent tracer test experiment. After Harvey, 1987.

Table 14. Chemistry of native ground water at the site of well FSW 393, and injectate water, in the 1985 and 1986 divergent tracer tests. Concentrations are given in mg/L except for nitrogen species (mg N/L).

Chemical Species	Concentration in Native Ground Water	Concentration in 1985 Injectate Water	Concentration in 1986 Injectate Water
NH_4^+	0.04	268.30	265.30
NO_3^-	0	0	43.00
Ca^{2+}	1.23	1.28	0.30
Mg^{2+}	1.00	1.17	1.10
Na^+	5.40	6.60	5.80
K^+	1.08	1.18	117.00
Br^-	0.02	1531.00	1490.00
Cl^-	7.73	8.37	9.11
SO_4^{2-}	6.08	7.28	8.40

it should not be retained on the solid phase by sorption or ion exchange to the extent that it would cause a significant retardation of the migrating front. Also, it should not be attenuated by geochemical or biological processes. Br^- was selected as a conservative tracer to use in this experiment because it meets the above criteria. Additionally, Br^- can be monitored in the field by specific ion electrode and background levels at the site are low.

It is evident from the arrival times of the Br^- pulse that the two monitored zones have distinctly different Br^- migration rates (Figure 30). It took twice as long for the peak concentration of the Br^- pulse to arrive at the monitored depth that is opposite the top of the injection zone (the low velocity zone) than the depth opposite the bottom of the injection zone (the high velocity zone). This result is probably due to hydraulic conductivity variations within the aquifer.

The injection of Br^- tracer was repeated at the same concentration for the 1986 tracer test. The results of the second tracer test are consistent with the first tracer test and confirm that the two monitored zones have different groundwater velocities as defined by Br^- (Figure 31).

ii. Ammonium Transport

In comparison to Br^- the transport of NH_4^+ in the 1985 tracer test was significantly retarded in the low velocity zone (Figure 32). Except for the slight tailing of the NH_4^+ peak there is little evidence of

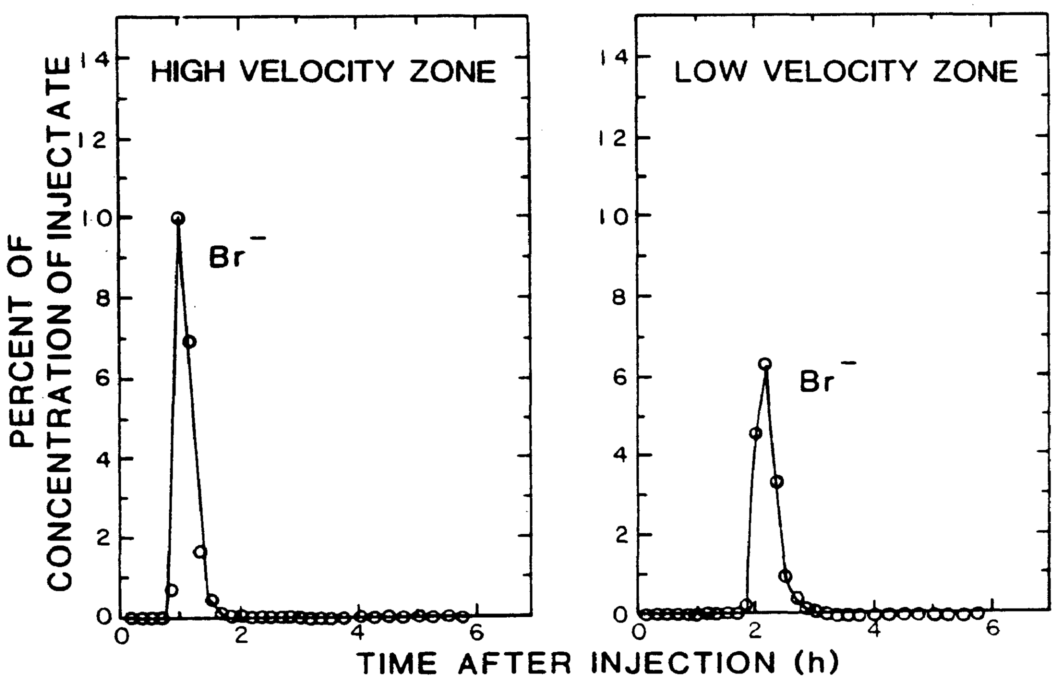


Figure 30. Time course plots for bromide during the 1985 divergent tracer test at well FSW 393. Samples collected 1.5 m from injection well, at 10 m and 11.3 m below the land surface.

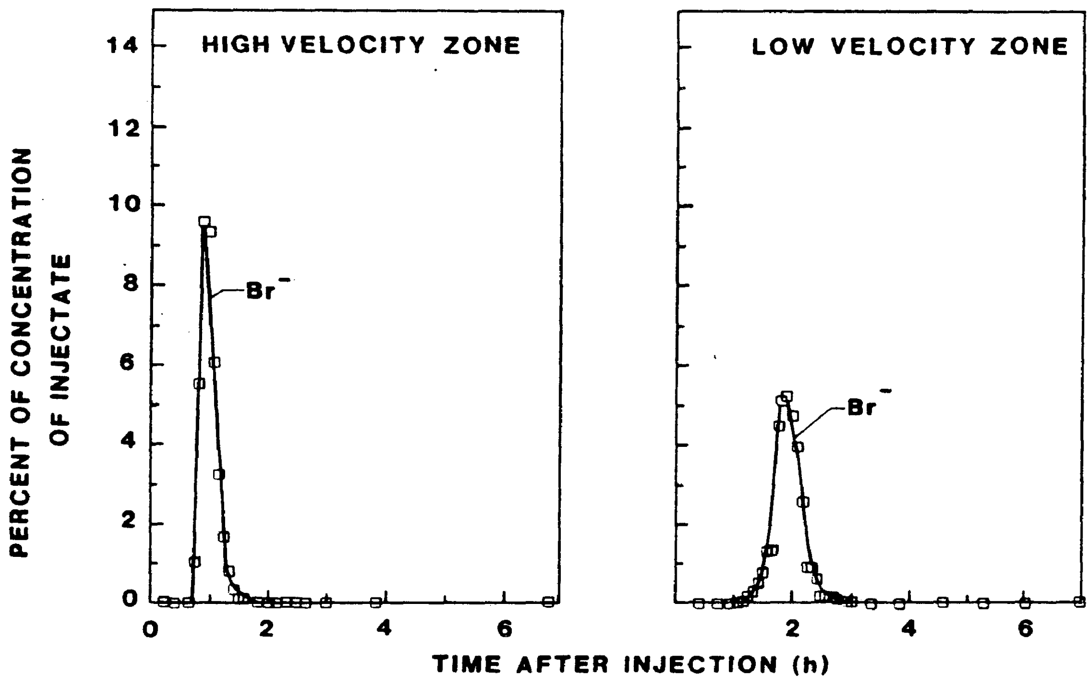


Figure 31. Time course plots for bromide during the 1986 divergent tracer test at well FSW 393. Samples collected at 1.5 m from the injection well at 10 m and 11.3 m below land surface.

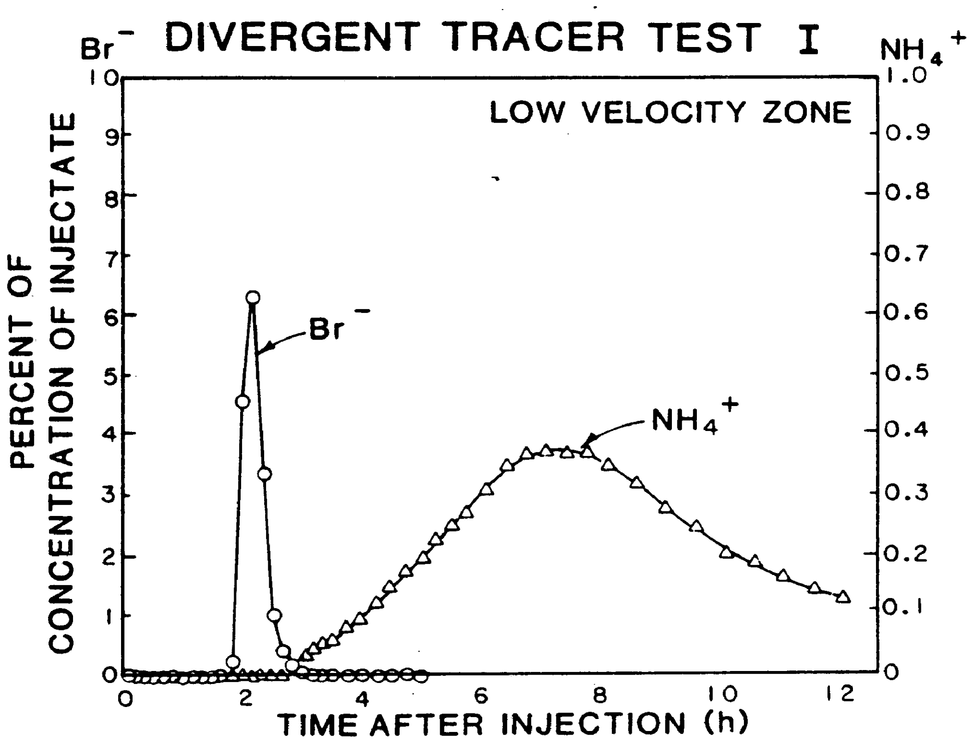


Figure 32. Time course plots for bromide and ammonium during the 1985 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 10 m below land surface.

retardation in the high velocity zone (Figure 33). The NH_4^+ results for the 1986 test are consistent with the 1985 tracer test demonstrating retardation only in the low velocity zone (Figures 34 and 35).

The difference in NH_4^+ retention time in the high and low velocity zones may be due to several factors. Kinetics may be a factor in the high velocity zone where there is less time for the tracer to interact with aquifer solids. Also, the low velocity zone is likely to have a greater sorption capacity as a result of more surface area, different mineralogy, etc.

iii. <u>Nitrate Transport</u>

The 1985 tracer test confirmed that the NH_4^+ transport rate is retarded in the aquifer, however, there are two predominant forms of inorganic nitrogen present in the sewage-contaminant plume, NH_4^+ and NO_3^-. One of the purposes for conducting the second tracer test in 1986 was to investigate the <u>in situ</u> transport of injected NO_3^- and NH_4^+ relative to the conservative Br^- tracer.

The NO_3^- and Br^- results in the low velocity zone are shown in Figure 36. The pulse of injected NO_3^- arrived simultaneously with injected Br^- in this zone. Furthermore, peak heights and peak areas for these two species are similar (less than 9% difference). Therefore, unlike NH_4^+, NO_3^- transport is not retarded. Figure 37 compares the results for NO_3^- and NH_4^+ in the low velocity zone. The arrival time of the peak of the NH_4^+ pulse is significantly retarded relative to the

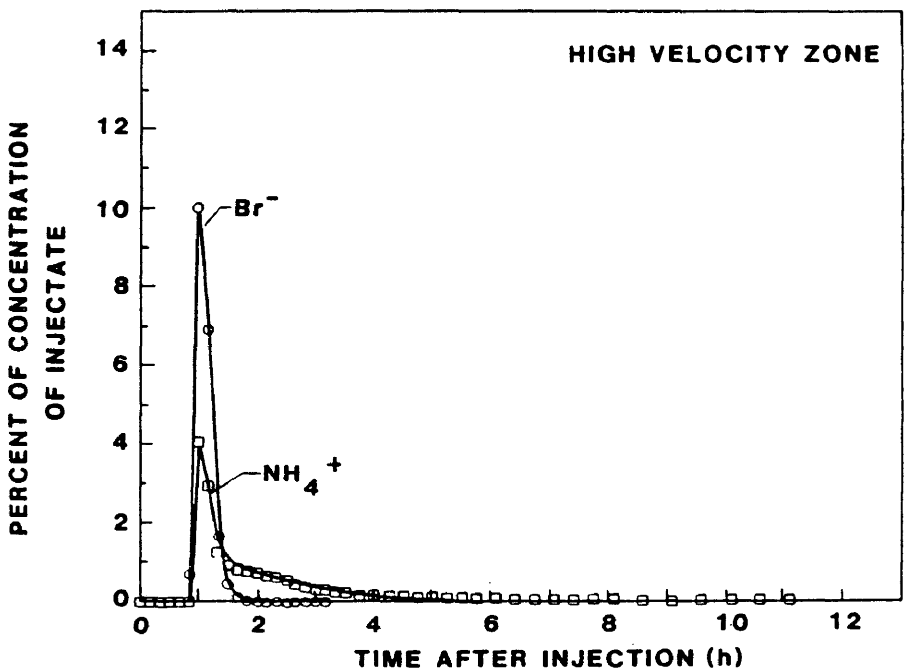


Figure 33. Time course plots for bromide and ammonium during the 1985 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 11.3 m below land surface.

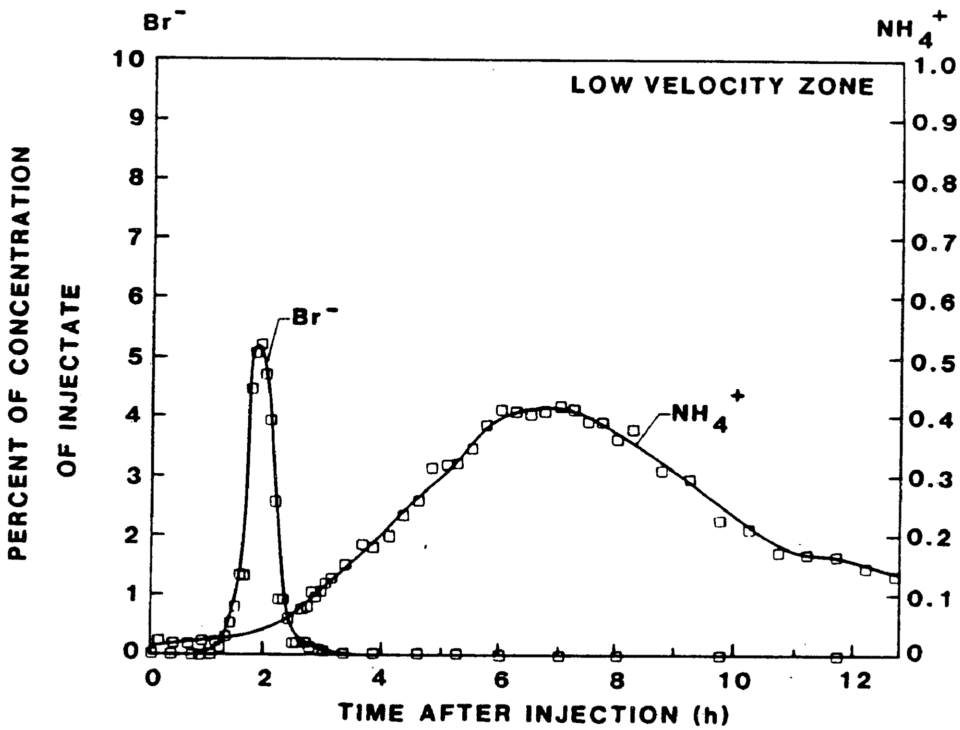


Figure 34. Time course plots for bromide and ammonium during the 1986 divergent tracer test at FSW 393. Sample collected 1.5 m from the injection well at 10 m below land surface.

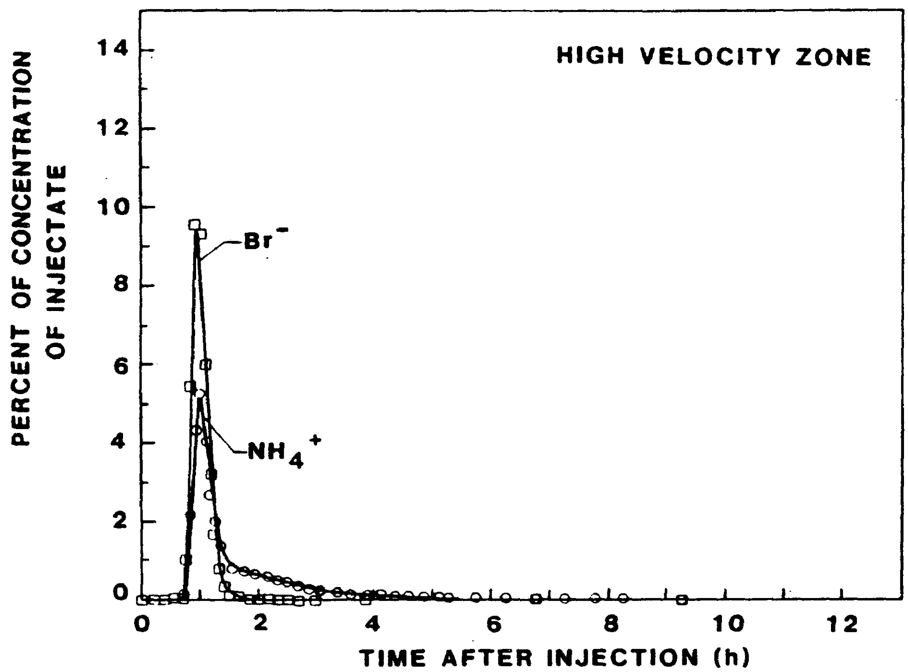


Figure 35. Time course plots for bromide and ammonium during the 1986 divergent tracer test at FSW 393. Sample collected 1.5 m from the injection well at 11.0 m below land surface.

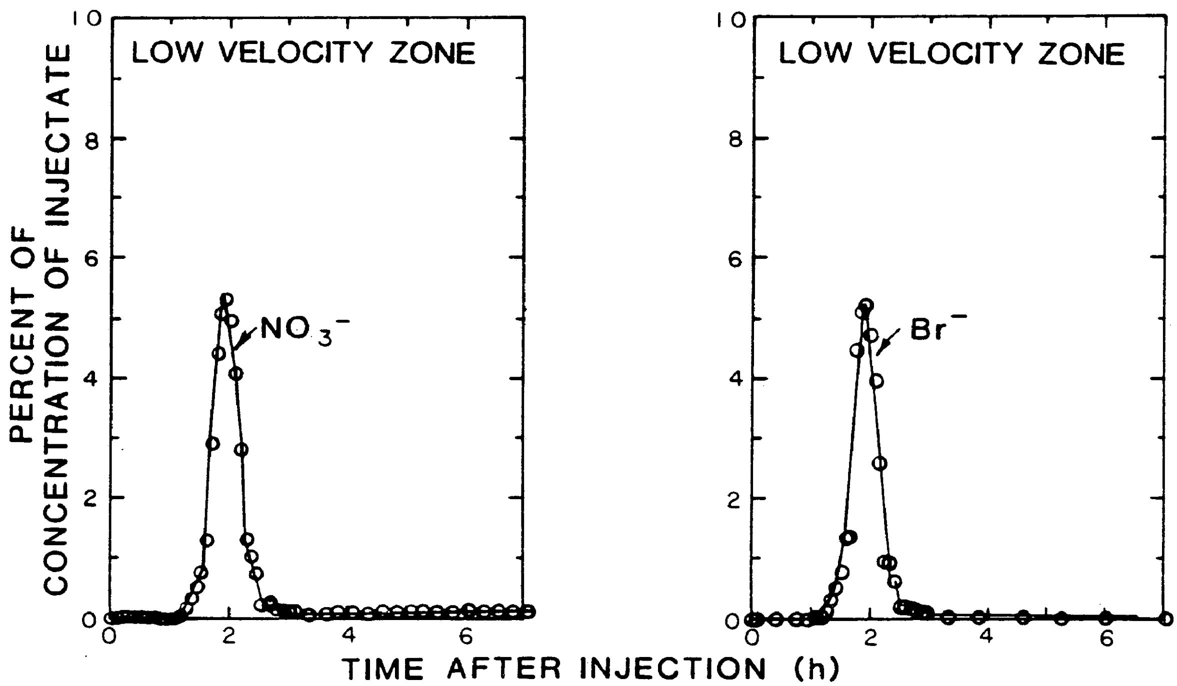


Figure 36. Time course plots for nitrate and bromide during the 1986 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 10.0 m below land surface.

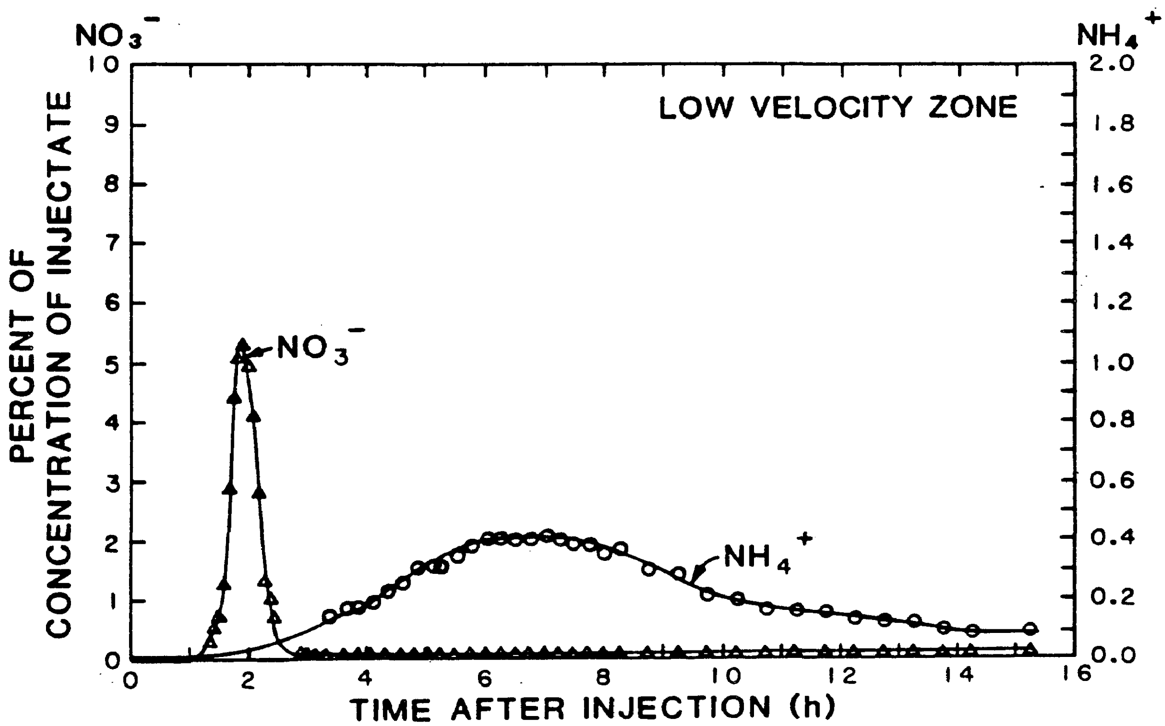


Figure 37. Time course plots for ammonium and nitrate during the 1986 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 10.0 m below land surface.

arrival time of the peak of the NO_3^- pulse illustrating the differential rates of transport for NH_4^+ and NO_3^- in the aquifer.

iv. Evidence of Cation Exchange

Results from the 1985 tracer test show that a pulse of non-injected cations arrived simultaneously with the Br^- peak in the low velocity zone where NH_4^+ was significantly retarded (Figure 38). On the basis of ueq/l, this cation peak was composed of 57.5% Mg^{2+}, 24% Ca^{2+}, 15.8% Na^+, and 2.7% K^+. Since these cations were not injected, the cation pulse was probably caused by displacement of sorbed aquifer cations by the NH_4^+ tracer.

Unlike the sewage plume where there is a continuous source of NH_4^+, NH_4^+ was injected as a pulse in the divergent tracer tests. If cation exchange was occurring during the tracer tests, cations in the native groundwater should have displaced sorbed NH_4^+ tracer. Tracer test evidence for Ca^{2+} and Mg^{2+} shows this effect (Figures 39 and 40). Ca^{2+} and Mg^{2+} concentrations decrease below injectate concentrations following the composite cation peak that eluted with Br^-. After Ca^{2+} and Mg^{2+} concentrations decreased they slowly increased back toward injectate concentrations forming negative peaks, which occurred simultaneously with the elution of the retarded NH_4^+ peak. These results indicate that Ca^{2+} and Mg^{2+} displaced the sorbed NH_4^+ tracer. Na^+ is probably also involved in this ion exchange process because it

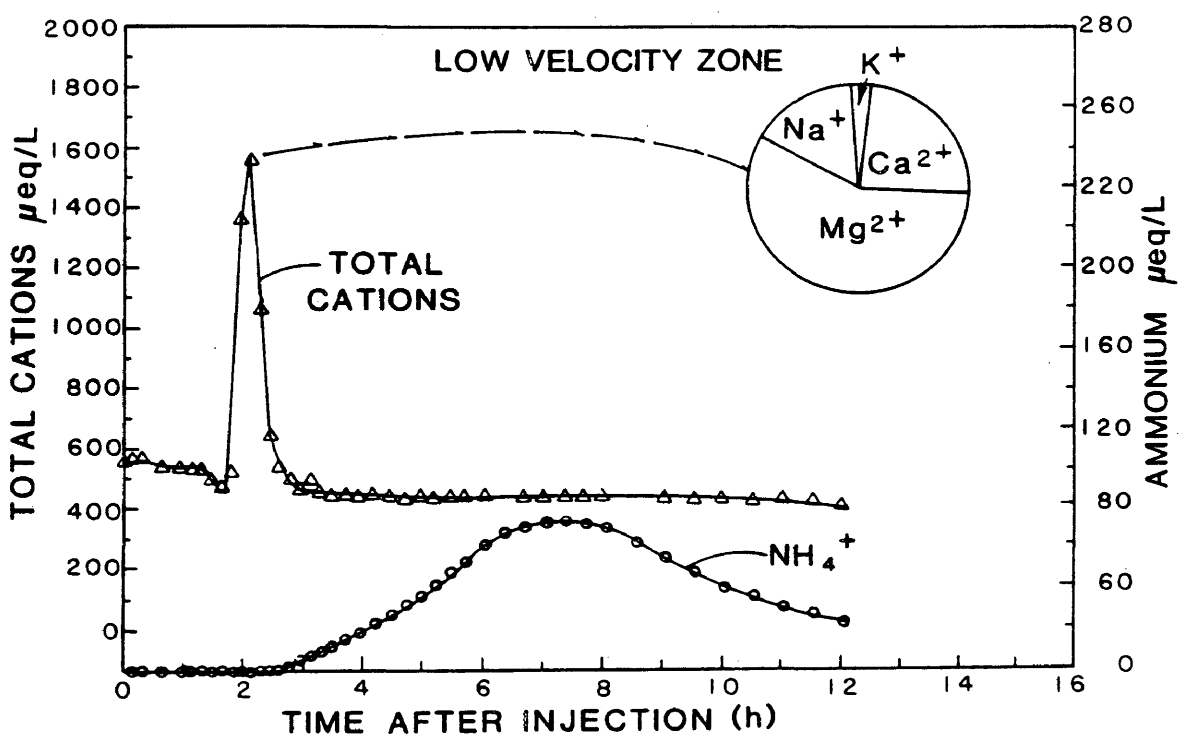


Figure 38. Time course plot for the sum of the cations (magnesium, calcium, sodium, potassium, and ammonium) compared to a plot for ammonium alone during the 1985 divergent tracer test at well FSW 393. Sample collected 1.5 m from the injection well at 10 m below land surface.

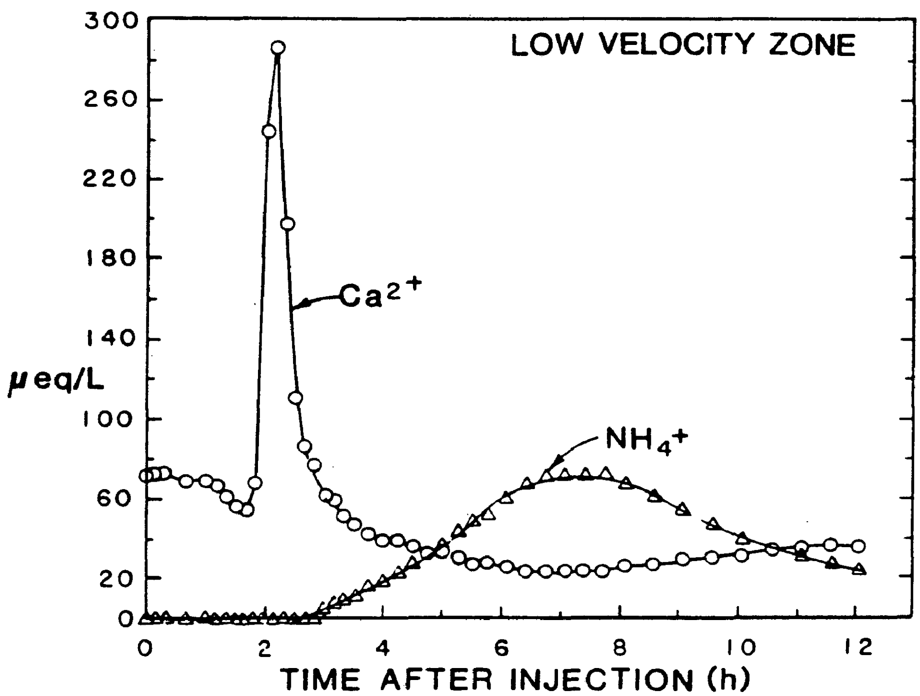


Figure 39. Time course plots for calcium and ammonium during the 1985 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 10.0 m below land surface.

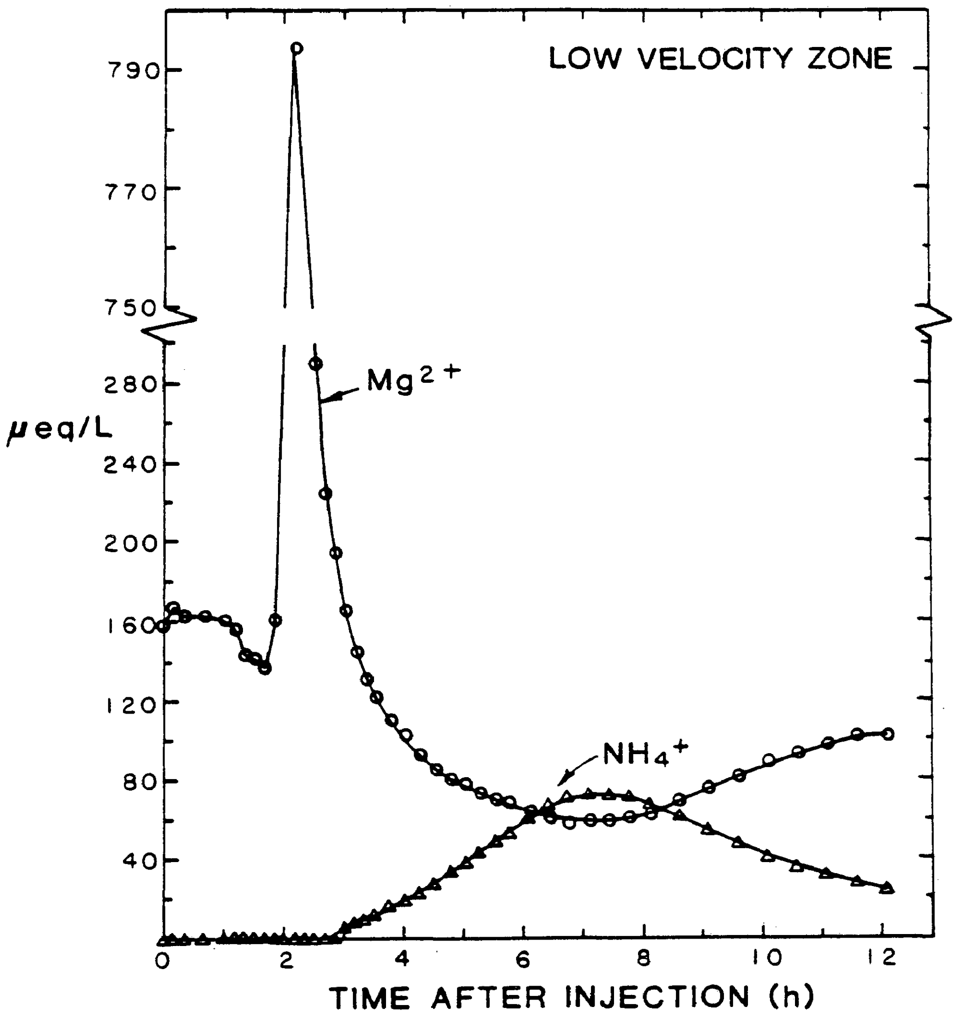


Figure 40. Time course plots for magnesium and ammonium during the 1985 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 10.0 m below land surface.

showed a similar but smaller negative peak after elution of the composite cation peak (Figure 41).

The behavior of K^+ in the low velocity zone was different from the other cations because there is no indication of a negative K^+ peak following the composite cation peak that coeluted with Br^- (Figure 42). There is, however, a subtle indication of a positive K^+ peak that occurred simultaneously with the retarded NH_4^+ peak. Furthermore, the combined areas of the Ca^{2+} and Mg^{2+} negative peaks are equivalent (within 10 %) to the combined areas of the retarded NH_4^+ and the K^+ peaks in the low velocity zone (Figure 43). This result provides equivalent balance evidence that NH_4^+ displaces sorbed aquifer cations and also suggests that K^+ is competing with NH_4^+ for cation exchange sites.

In order to evaluate K^+ behavior in the low velocity zone, both K^+ and NH_4^+ tracer were injected in the second (1986) tracer test. Results of this test show that a cation pulse again coeluted with Br^- in the low velocity zone (Figure 44). The arrival times and integrated peak areas for the cations that coeluted with Br^- are comparable for the 1985 and 1986 tracer tests (their areas differ by less than 7%). When the aquifer material is in contact with the native groundwater, equilibrium dictates that the ratio and mass of cations sorbed on the aquifer solids remains constant, provided the water chemistry does not fluctuate. Hence, cation equivalent balance for the 1985 and 1986 tracer tracer studies provides further evidence that the source of the cation

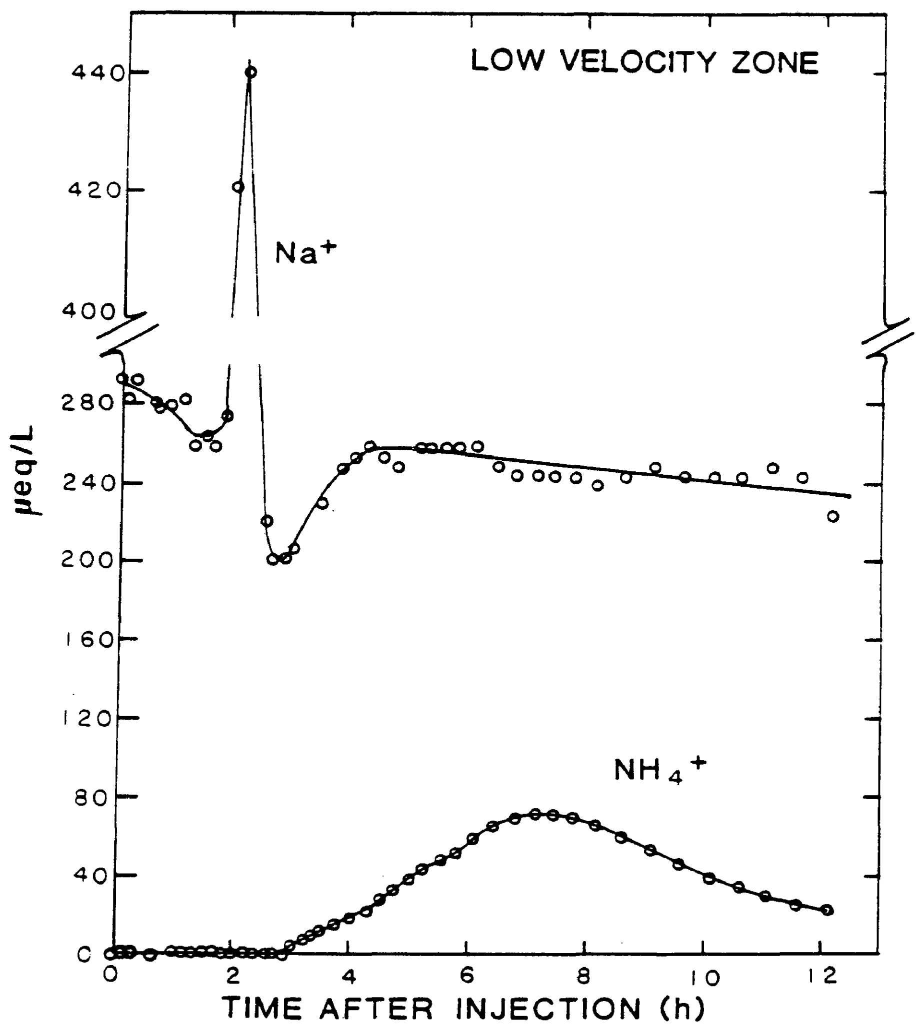


Figure 41. Time course plots for sodium and ammonium during the 1985 divergent tracer test at well FSW 393. Sample collected 1.5 m from the injection well at 10.0 m below land surface.

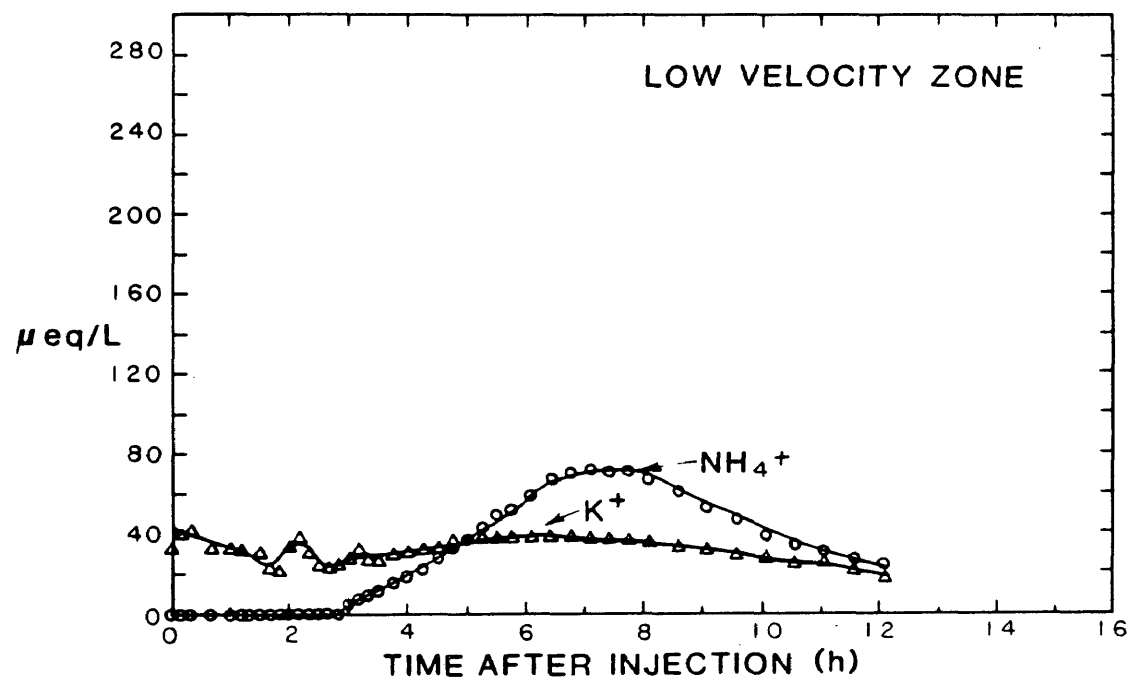


Figure 42. Time course plots for potassium and ammonium during the 1985 divergent tracer test at well FSW 393. Sample collected 1.5 m from the injection well at 10.0 m below land surface.

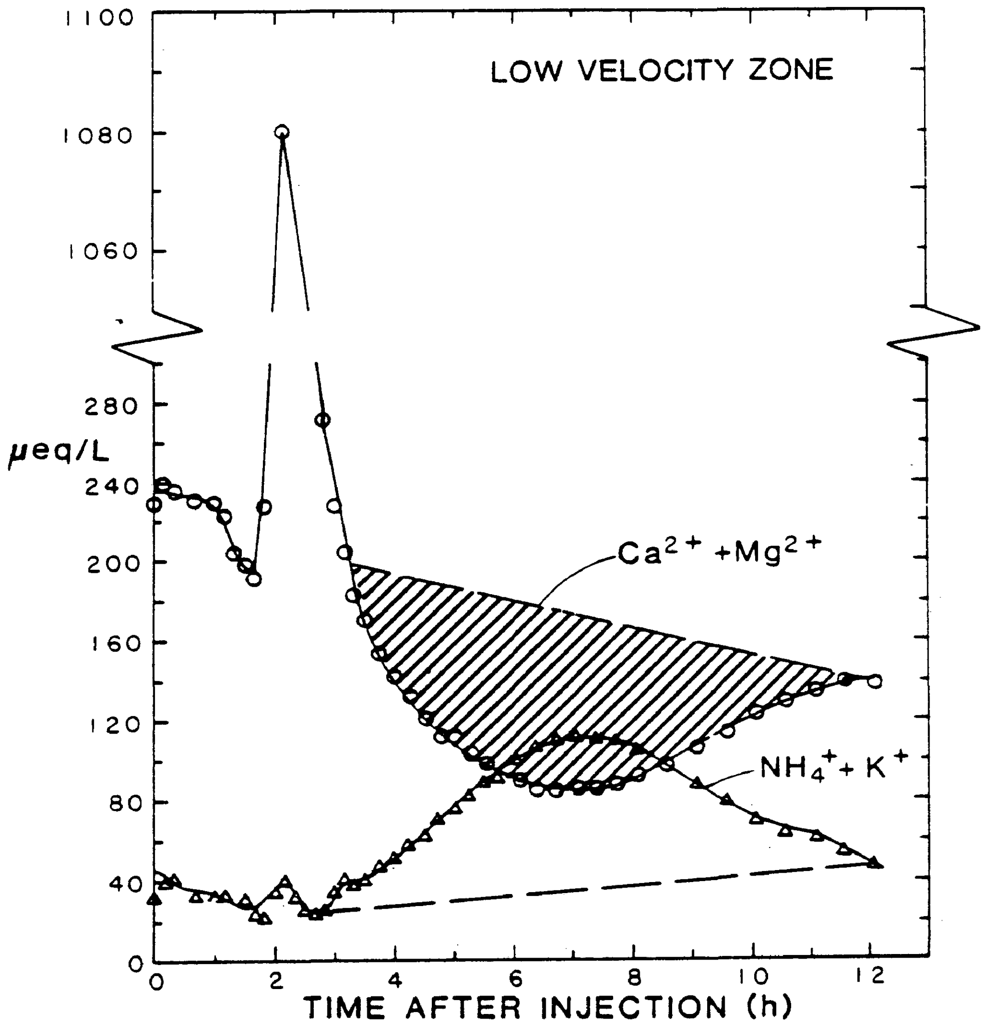


Figure 43. Time course plots comparing combined areas for ammonium and potassium peaks to combined areas for calcium and magnesium inverse peaks during the 1985 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 10.0 m below land surface.

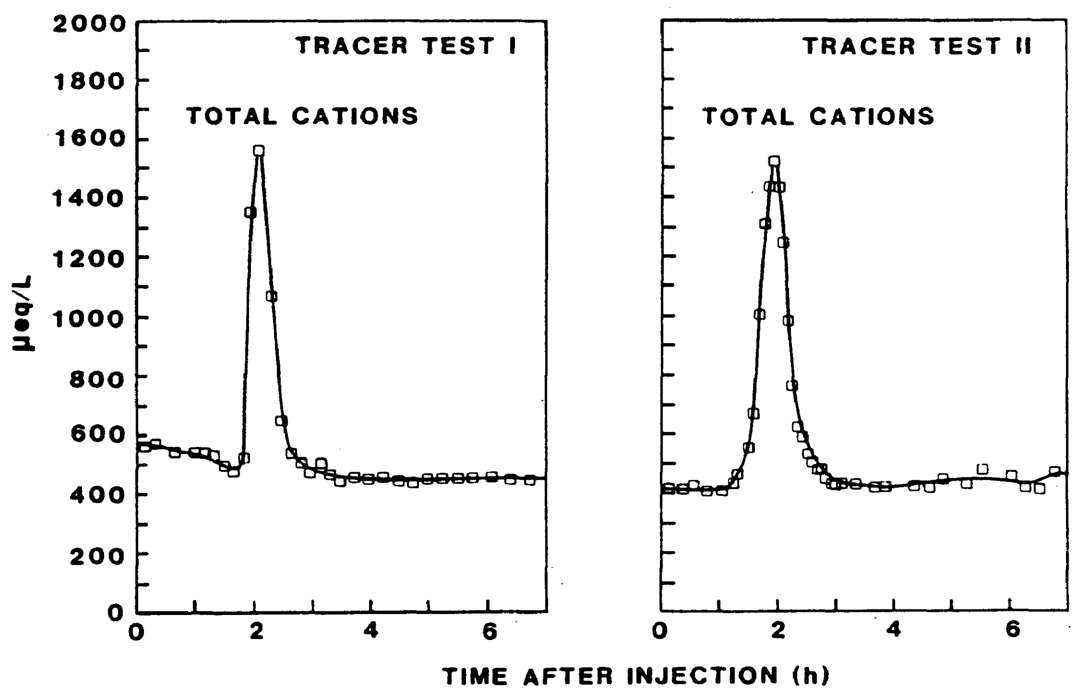


Figure 44. Time course plots for sum of the cations during the 1985 and 1986 divergent tracer tests at well FSW 393. Samples collected 1.5 m from the injection well at 10.0 m below land surface.

pulse in these tracer tests is native-aquifer cations that have undergone an ion exchange process with tracer cations.

The K^+ results from the 1986 test show that the pulse of injected K^+ eluted with the pulse of injected NH_4^+ (Figure 45). This result indicates that the K^+ transport rate is retarded in the aquifer and K^+ is competing with NH_4^+ for cation exchange sites on the aquifer solids.

v. Accuracy of Analytical Methods

The mass of the cations that coeluted with the Br^- tracer was contrasted with the mass of major anions (Br^-, Cl^-, and SO_4^{2-}) across this same peak in the low velocity zone for the 1985 tracer test (Figure 46). These results show that the cation and anion peak areas are equivalent (within 7%), thus, there is ion equivalent balance indicating that the chemical measurements conducted for the tracer-test samples were accurate.

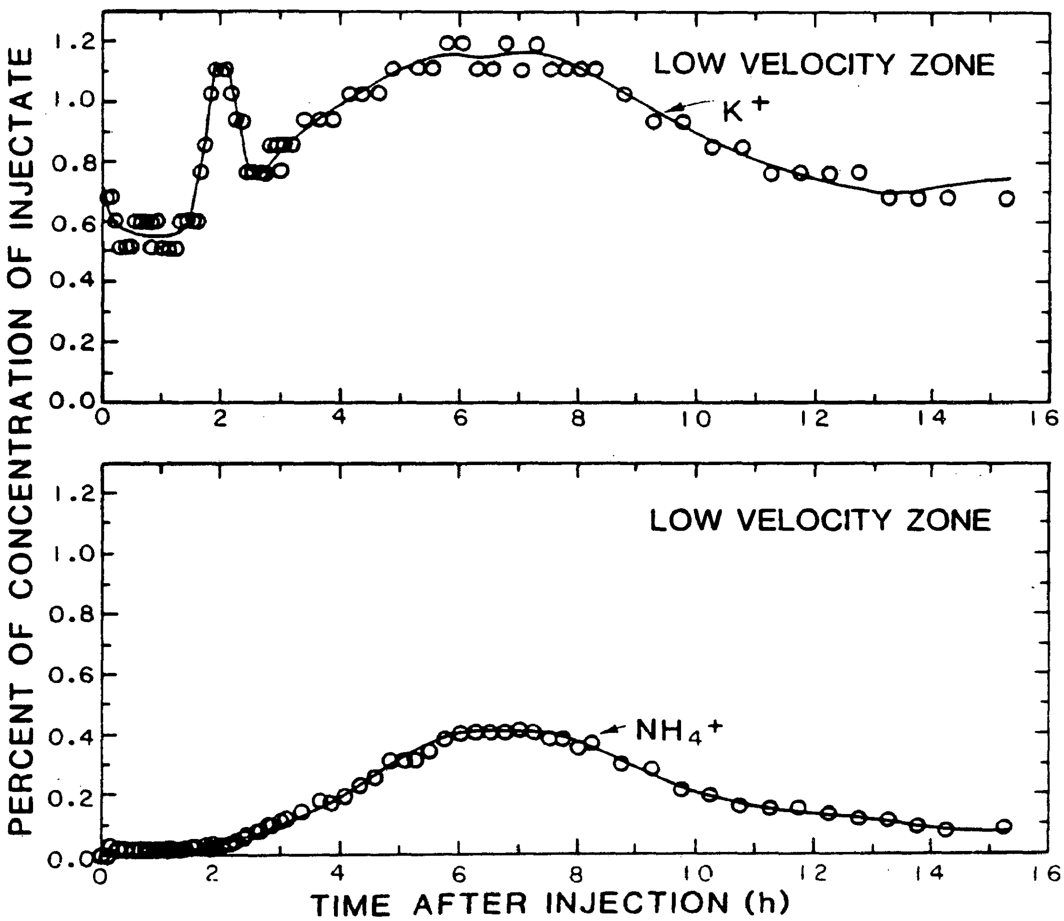


Figure 45. Time course plots for potasssium and ammonium during the 1986 divergent tracer test at well FSW 393. Sample collected at 1.5 m from the injection well at 10.0 m below land surface.

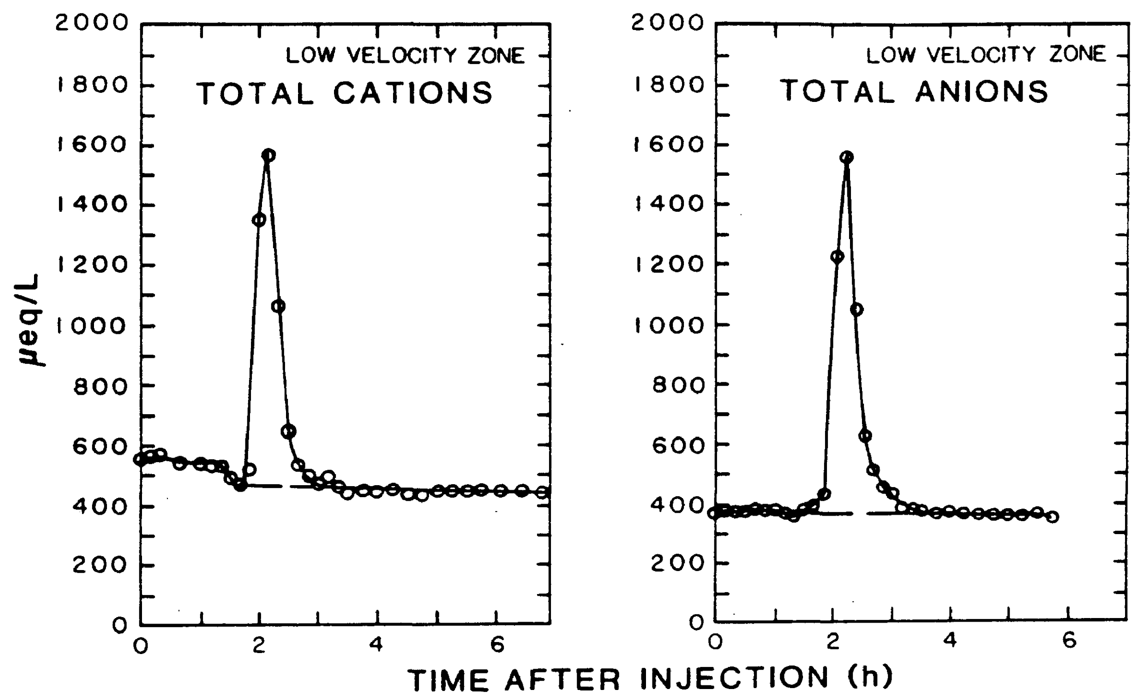


Figure 46. Time course plots for the sum of the anions and the sum of the cations during the 1985 divergent tracer test at well FSW 393. Sample collected 1.5 m from the injection well at 10.0 m below land surface.

VI. SUMMARY AND CONCLUSIONS

A. SUMMARY OF RESULTS

The subject investigated in this study is the fate and transport of NH_4^+ and NO_3^- in groundwater. Otis Air Base at Cape Cod, Massachusetts was selected as the field site for this study since the groundwater at this location is extensively contaminated with nitrogen due to the rapid-infiltration land disposal of secondary-treated sewage. The objective of this study was to test the following hypotheses in the contaminated groundwater at the site: 1) NH_4^+ is attenuated in the subsurface relative to NO_3^-; 2) nitrification is occurring and plays a role in NH_4^+ attenuation; and 3) the coarse-grained aquifer sediments affect the rate of NH_4^+ transport through the process of sorption and cation exchange.

A three-pronged approach was used to investigate these hypotheses: 1) the distributions of NH_4^+, NO_3^-, and various other chemical and microbiological parameters at the site were determined; 2) nitrification assays were conducted on aquifer solids and groundwater; and 3) NH_4^+ sorption on aquifer solids was evaluated using laboratory and field experiments.

The distribution of specific conductance at the site indicates that the contaminant plume extends at least 3350 m downgradient from the sewage-infiltration sand beds. Contaminant patterns indicate that there are two nitrogen-containing zones: one in which NH_4^+ is the predominant species and one in which NO_3^- predominates. The zone of groundwater that is contaminanted with NO_3^- extends to the toe of the plume; NH_4^+ is present in high concentrations within 1830 m of the beds but is depleted or absent from 1830 m to the toe of the plume. These results indicate that NH_4^+ is attenuated relative to NO_3^-.

The zone where NH_4^+ is depleted or absent is adjacent to an elevated NO_3^- zone suggesting that nitrification is occcurring at the site. The distribution of plate-count bacteria correspond to the contaminant plume as delineated by specific conductance indicating that there is a positive response of subsurface bacteria to the contaminant source. Therefore, microbiological processes may be important at this site. Results of nitrification assays indicate that nitrifying bacteria are present and that there is measurable nitrifying activity. Although the rates of microbial NH_4^+ consumption are low compared to rates measured in other ecosystems, these activities could affect the groundwater chemistry over time and distance due to long groundwater residence time. NH_4^+ and NO_3^- mass balance evidence in the plume indicate that NH_4^+ attenuation cannot be entirely due to nitrification; this result may be due to limited concentrations of dissolved oxygen in the plume.

Sediment-extraction experiments conducted on aquifer solids collected from the OAB site indicate that a significant fraction of the total NH_4^+ is sorbed on the aquifer solids. The NH_4^+ sorption isotherm obtained from a laboratory batch study followed a non-linear Freundlich sorption equation. This result indicates that the partitioning of NH_4^+ on aquifer solids in the contaminant plume can be simulated by a non-linear sorption isotherm, in which the distribution of NH_4^+ between solids and solution is a function of NH_4^+ concentrations in the groundwater; the concentration of NH_4^+ sorbed decreases with increasing concentrations of dissolved NH_4^+.

Two divergent tracer tests were conducted in the field. Results from the first tracer test demonstrate that: 1) the rate of NH_4^+ transport is retarded; 2) NH_4^+ displaces other cations (primarily Ca^{2+} and Mg^{2+}). The results of the second tracer test indicate that: 1) there are differential rates of transport of NH_4^+ and NO_3^- in the aquifer; and 2) K^+ is competing with NH_4^+ for cation exchange sites on aquifer solids. Tracer test results are consistent with cation distributions in the sewage plume.

B. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

A conceptual model depicting the factors that control the behavior of NH_4^+ and NO_3^- in the sewage-contaminated groundwater system at the study site is illustrated in Figure 47. NH_4^+ and NO_3^- are moved downgradient from the source of contamination by advective and dispersive transport processses. As these two species are transported downgradient, NH_4^+ is converted to NO_3^- by nitrifying bacteria if dissolved oxygen is present. Other types of bacteria are also utilizing NH_4^+ at the site, although the precise mechanism for this activity was not determined in this study. Although biological processes play a role in NH_4^+ attenuation at the study site, the observed NH_4^+-NO_3^- distributions in the contaminant plume plume are not entirely due to these mechanisms. Potential topics for future research in this subject area include: 1) determination of the types of bacteria (sorbed bacteria or free-living bacteria) predominantly responsible for the observed nitrification at the site; and 2) determination whether sorbed and/or dissolved NH_4^+ is utilized for this activity.

NH_4^+ that does not undergo nitrification is subject to sorption by aquifer solids (Figure 47). Conversely, NO_3^- is not being significantly sorbed by aquifer solids. The NH_4^+ sorption process results in differential transport rates for NH_4^+ and NO_3^- in the aquifer; NH_4^+ transport is retarded and NO_3^- is transported with conservative constituents unless it is exposed to an anoxic zone where it may be biologically reduced.

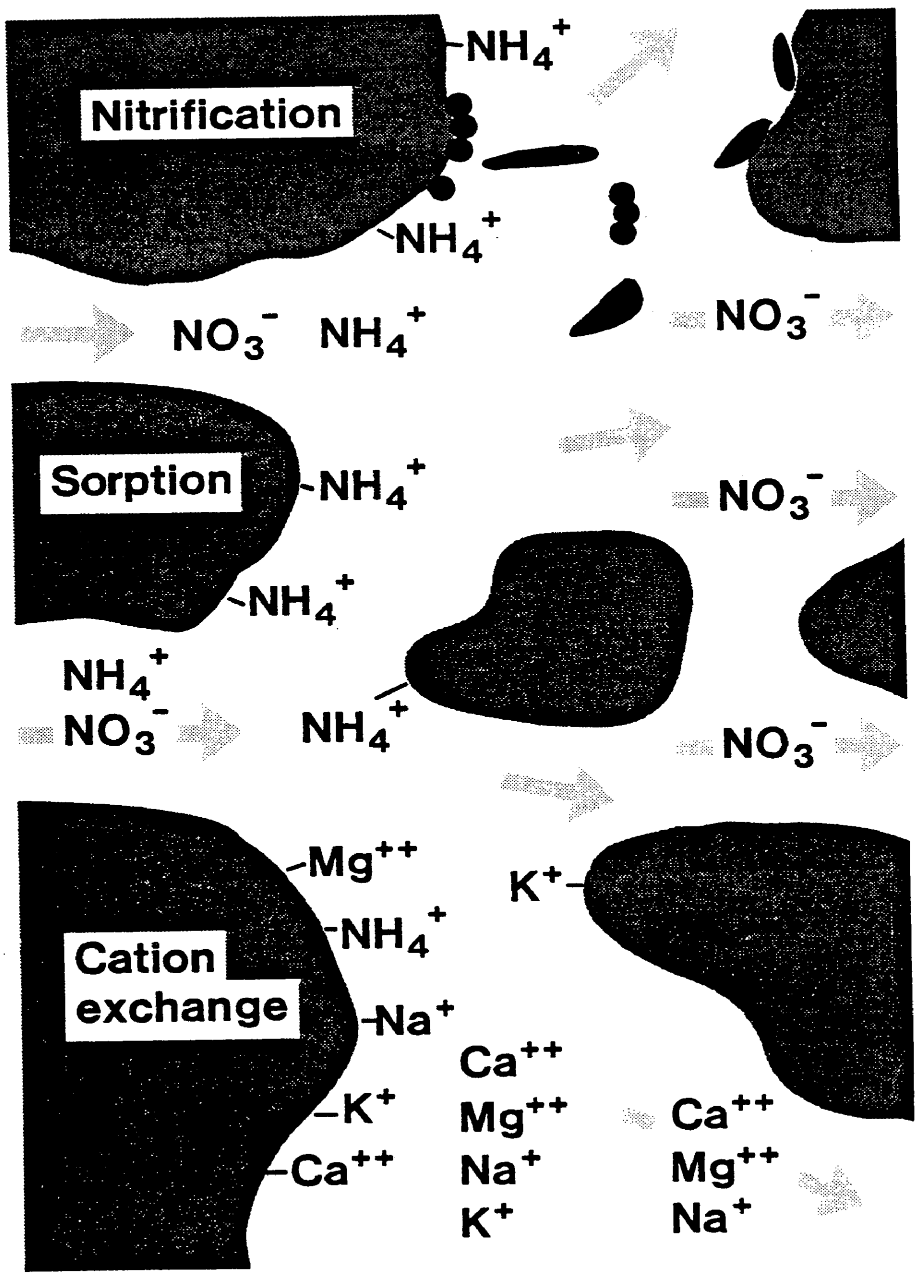


Figure 47. Conceptual model depicting factors affecting migration of NH_4^+ and NO_3^- in the groundwater at the OAB site.

NH_4^+ displaces native Ca^{2+}, Mg^{2+}, and Na^+ from cation-exchange sites on aquifer solids resulting in a zone of high Ca^{2+}, Mg^{2+}, and Na^+ downgradient from the NH_4^+ front in the contaminant plume (Figure 47). K^+ is competing with NH_4^+ for cation-exchange sites; therefore K^+ transport is retarded to the same extent as NH_4^+. Hence, cation exchange processes are significant in determining the distribution of cations in the groundwater contaminant plume at the study site. There are many examples in the literature invoking NH_4^+ cation exchange on clay sites but the aquifer solids at the OAB site are composed primarily of sand and gravel with a very low percentage of clay; an important subject for future research efforts is to determine what types of cation-exchange sites are involved in this process. Furthermore, a future study could involve computer modelling, using Freundlich sorption or ion exchange parameters, to simulate NH_4^+ transport in the groundwater at the OAB site or in a similar nitrogen-contaminated groundwater site.

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